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Removal of Organic and Inorganic Contaminants from Oil Sands Tailings using Carbon Based Adsorbents and Native Sediment

by

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Dedication

“You can’t outgear friendship” – Cole MacIver

Abstract

The extraction and refinement of oil sands bitumen produces substantial quantities of liquid tailings and solid coke. Tailings contain metals and naphthenic acids, which require remediation before mine closure. Adsorption is a potential remediation technique which may reuse stockpiled petroleum coke. This thesis investigates the adsorption of contaminants on sediment, petroleum coke and biochar. The determination of naphthenic acid concentration using ESI-FTICR-MS was also explored. Results suggest limited adsorption of naphthenic acids on sediment occurred, while petroleum coke and biochar removed elevated concentrations of naphthenic acids and metals. Pretreating petroleum coke by acid washing increased its ability to adsorb contaminants by removing surface bound impurities. Electrospray ionization was a strong semi-qualitative tool for naphthenic acid measurement, but deviated significantly from other methods for quantitative measurement. In summary, the adsorption of oil sands contaminants is feasible using carbonaceous adsorbents. Metal release was limited when pretreated petroleum coke and biochar was used.

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List of Abbreviations

BET: Brunauer-Emmett-Teller

DIC: Dissolved Inorganic Carbon

DOC: Dissolved Organic Carbon

ESI-FTICR-MS: Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

ESP: Exchangeable Sodium Percentages

ESR: Exchangeable Sodium Ratio

FT-IR: Fourier Transform Infrared

GC-FID: Gas Chromatography Flame Ionization Detector

GC-MS: Gas Chromatography Mass Spectrometry

HCl: Hydrochloric Acid

Metals:

- Al: Aluminium
- As: Arsenic
- Ba: Barium
- Cd: Cadmium
- Cr: Chromium
- Cu: Copper
- Fe: Iron
- Mo: Molybdenum
- Mn: Manganese
- Ni: Nickel
- Pb: Lead
- Se: Selenium
- Sr: Strontium
- Ti: Titanium
- V: Vanadium
- Zn: Zinc

N_2: Nitrogen

OSPW: Oil Sands Process Water

PAH: Polycyclic Aromatic Hydrocarbons

STP: South Tailings Pond

Chapter 1 - Introduction

The Canadian Oil Sands, located in northern Alberta, are the epicentre for oil production in Western Canada. The oil sands are a bituminous mixture consisting of approximately 80% sand, 10% water and clay, and 10% bitumen – a viscous oil that must be refined into synthetic crude oil (Government of Canada, 2013). The industry is located in three distinct regions of Alberta: The Athabasca region (44,000 km^2), the Cold Lake region (22,000 km^2) and the Peace River region (8,000 km^2; Oil Sands Discovery Centre, 2008). Of the three, only the Athabasca region has surface minable reserves – oil sand located to a depth of 75m or less (Government of Alberta, 2013). From its 170 billion barrel reserve, the operations produce over 1.6 million barrels of synthetic crude oil per day from both its truck and shovel and Steam Assisted Gravity Drainage (SAGD) operations (Government of Alberta, 2013). The ease of accessibility of the surface mining and the production of tailings has placed the emphasis on the Athabasca region (Government of Alberta – Alberta Energy, 2013).

Typical mining activities generate a wet waste stream of tailings material, and a dry waste rock stream which are managed over the long term (Lottermoser, 2010). Waste materials in oil sands production consist of a dry sand fraction and wet clay-rich tailings. The industry adheres to a “zero-discharge” policy, inhibiting the release of any tailings into the receiving environment. Current estimations suggest the oil sands in Alberta will produce 3.7 million barrels per day by 2021 (Government of Alberta – Alberta Energy, 2013). It is therefore necessary to construct long term storage facilities for containment and subsequent management of oil sands tailings (Small, 2011).

The most economically feasible method for tailings management is through the use of engineered tailings impoundments (Lottermoser, 2010). In the oil sands, these impoundments are typically constructed utilizing separated sand for dyke construction. The tailings stream is deposited as a slurry through end-of-pipe discharge, meaning settling and consolidation occurs in the ponds (Allen, 2008). The large percentage of fines in the tailings (roughly 30%), unaided, would take decades before consolidating (Suncor, 2013).

The wet tailings stream contains primarily process water (subsequently deemed OSPW); water used in the Clark hot water extraction process (Allen, 2008). Tailings also contain non-recoverable bitumen, sand, fine clays and inorganic and organic contaminants (Allen, 2008). Residual contaminants in the OSPW from oil sands separation and upgrading results in both high concentrations of dissolved salts (Allen, 2008) and, of larger concern, naphthenic acids, BTEX and polycyclic aromatic hydrocarbons (PAH's) (Small, 2011; Allen, 2008; Holowenko et al. 2002). The organic contaminants may be toxic to downstream receptors, and present a concern should they migrate from containment facilities over time (Holden et al., 2011). Such migration may be occurring at one of Suncor's facilities, the South Tailings Pond (STP; Holden et al. 2011).

The South Tailings Pond is a relatively new, 23 km^2 tailings containment facility, and the first to be built on a pre-existing subsurface sand channel. The sand channel formed due to the flow of meltwater during glacial recession and subsequent deposition of sands and gravels in the eroded channel (Holden et al., 2011). The channel has a relatively high hydraulic conductivity compared to the surrounding material, and therefore may serve as a preferential flow path for OSPW (Holden et al., 2011). Holden et al. (2009) provides specific detail on the subsurface geology present under the South Tailings Pond. Briefly, the pond overlies a thin Muskeg deposit (1-2m), Pleistocene glacial till (8-15m) and the Wood Creek Sand Channel. Areas of the South Tailings Pond are in direct contact with the underlying sand channel, and Holden et al. (2009) suggests that this contact may alter the geochemistry of the area. It is therefore necessary to monitor the adsorption or desorption of contaminants with the sediment to determine the natural equilibrium in the subsurface.

Oil sands tailings contain a variety of inorganic and organic compounds. Due to its high toxicity to aquatic organisms, naphthenic acids have been identified as a principle organic contaminant of concern (Allen, 2008). They are a group of cyclic and aliphatic carboxylic acids found naturally in the ore deposit, but are released and concentrated during the bitumen extraction (Allen, 2008). The classic naphthenic formula, $C_nH_{2n+z}O_2$ is the industry standard used to characterize the compounds (Mohammed et al. 2008). Continuous reuse of water has concentrated organic contaminants such that process efficiency may be hampered (Mohammed et al., 2008). Recent work has suggested that the classic naphthenic acid formula is obsolete (Barrow et al. 2009, Han et al. 2009, Grewer et al. 2010, Zhao et al. 2012). Studies have shown that mono and di-oxide naphthenic acids, $C_nH_{2n+z}O_3$ and $C_nH_{2n+z}O_4$, exist in both Suncor and Syncrude tailings water, comprising of over 50% of the detectable naphthenic acid compounds (Grewer et al, 2010). These compounds, initially suggested by Lee (1940), can be deemed “oxy-naphthenic acids” (Grewer et al. 2010).

Holden et al. (2011) further suggests that the migration of OSPW through the subsurface may release trace metals. Groundwater quality concerns include both contaminants found in the tailings (notably naphthenic acids and dissolved salts) as well as trace metals. Due to the potential for water contamination, groundwater may require contaminant remediation.

An effective treatment strategy that is economically feasible should involve simultaneous passive contaminant removal, such as a groundwater barrier. Permeable barriers are physical media through which groundwater must pass, adsorbing contaminants as the flow permeates. Innovative barrier adsorption technologies, such as an acid washed activated coke or biochar barrier, provides industry by-product use for the removal of such contaminants. Adsorption is the physical process in which a compound enters the pore-space of an adsorbent and resides on its outer surface (Martin-Gullón and Menéndez-Diaz, 2006). Adsorption is governed by van der Walls forces; weak bonds formed by the fluctuating polarity created as ions within an atom rotate (Gregg and Sing, 1982). The process attracts ions which ‘stick’ to a compound (Small, 2011), forming a complex that may desorb under specific conditions. A common organic adsorbent is granular activated carbon (GAC), which can remove organic contaminants such as naphthenic acids, BTEX, and polycyclic aromatic hydrocarbons from solution (Small et al., 2012; Martin-Gullón and Menéndez-Diaz, 2006; VanOsdell et al., 1996; Clark, 1987). However, studies from Small (2012) have shown delayed coke, a by-product of the bitumen extraction process (Fedorak and Coy, 2006), can be used to remove naphthenic acids and some trace metals. Coke may therefore be a viable alternative to other granular carbons, as an industry waste product is used to remediate contaminants in the subsurface (Small, 2011). Small et al. (2012) further indicated that, while trace metals may be adsorbed, some elements such as Al, Mo, and V are also released from the coke. Acid washing of the coke prior to activation may inhibit desorption of trace metals (Small et al., 2012).

Coke is created in the coking process, after the oil is separated from the sand. The process occurs in refinement, where the bitumen is thermally treated to remove volatiles, ash and particles, creating a lighter crude and granular carbon material. The coke is recovered from the process (approximately 22% for Suncor) and stockpiled on site where it remains in disuse (Etsell and Jang, 2006). Between Suncor Energy Inc. and Syncrude Canada Ltd., approximately 5 million tonnes of coke are produced annually (Fedorak and Coy, 2006). Such industry by-products will not generate revenue and are considered mining waste (Lottermoser, 2010). It is therefore theoretically feasible to utilize this waste as a physical medium through which adsorption may occur.

Biochar is an emerging technology that is currently used for the enhancement of soil productivity (Lehmann and Joseph, 2009). Biochar is produced by thermally decomposing organic material at a relatively low temperature (<700°C) and low oxygen content (Lehmann and Joseph, 2009). As the organic material is heated, impurities in the carbon structure are released, while larger, more resilient carbon chains remain. This differs from conventional pyrolysis in that remaining ash has been exposed to abundant oxygen, fully volatilizing the structure and leaving mainly magnesium and calcium (Lehmann and Joseph, 2009). In addition to improving soil productivity, biochar can be used to filter soil water, and its application may be extended to inorganic and organic contaminant removal. It is feasible that biochar may remove oil sands contaminants while limiting the release of inorganic and organic contaminants.

1.1 Research Objectives

The goal of this research is to develop an *in situ* remediation plan for the simultaneous removal of metals and organics, specifically naphthenic acids, within the Wood Creek Sand Channel underlying the South Tailings Pond using adsorptive materials. Materials selected will include delayed coke and biochar. The goal will be accomplished through key objectives:

1. Determine oil sands naphthenic acids adsorption or release from surficial sediment.
    - 1a. Compare oil sands naphthenic acids concentrations measured using ESI-FTICR-MS, GC-FID and FT-IR.
2. Determine the trace metal and naphthenic acid removal efficiency of acid washed delayed (activated and non-activated) coke.
3. Assess the functionality of a natural adsorbent, biochar, for the removal of trace metals and naphthenic acids.

These objectives will be completed through the use of 48 h batch tests. First, mixing of OSPW and sediment underlying Suncor's South Tailings Pond will be used to determine the natural fate of oil sands contaminants. Testing on delayed coke will determine if acid washing reduces trace metal release from solution, and if the medium is feasible for oil sands naphthenic acid and trace metal removal. Finally, a similar test will be conducted on biochar, determining if organic residue may be used to adsorb contaminants. Trace metal measurements will be accomplished through the analysis using inductively coupled plasma mass spectrometry (ICP-MS). Analysis of oil sands naphthenic acids will include Fourier transform infra-red spectrometry (FT-IR) and ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FTICR-MS). Successful adsorption will involve the removal of trace metals below current provincial and federal guidelines and oil sands naphthenic acid removal below detection limits.

This research is relevant because it assesses the feasibility of two adsorbents (delayed coke and biochar) for the simultaneous removal of oil sands naphthenic acids and trace metals. These materials are readily available within the industry, and may be implemented economically for the removal of contaminants. Adsorbents may also be added to large scale treatment operations to further assist removal of contaminants.

1.2 Thesis Outline

This thesis consists of a detailed literature review and summarization of background information related to the oil sands and its contaminants, provided in Chapter 2. Chapter 3 focuses on the batch experiments using OSPW and sediment cores comparing removal or release of contaminants with varying ratios of sediment:OSPW. A detailed analysis of naphthenic acid compounds using ESI-FTICR-MS and technique comparison with GC-FID and FT-IR is also reported in this Chapter. Chapter 4 details the adsorption of trace metals and oil sands naphthenic acids on acid washed (activated and non-activated) delayed coke. Chapter 5 addresses the adsorption with biochar, providing background to the genesis of the material and its' industrial application as an adsorbent. Conclusions and the relevance to engineering of this research is provided in Chapter 6.

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Chapter 2 - A Review of Mining Activities, Contaminant Identification and Remediation Strategies

2.1 Mining Activities

The oil sands in Northern Alberta are estimated to contain 174 billion barrels of bitumen (Allen, 2008). A zero-discharge policy currently enforced in the industry has necessitated the long term storage of wastes produced (Holden et al, 2011; Small et al., 2012). Consequently, tailings are placed in engineered containment facilities (tailings ponds) where sediment separates from OSPW. Settling of fine clay particles without any additives requires extensive time (Suncor, 2013), thereby necessitating treatment of current impounded wastes.

The tailings ponds reside over the surficial geological deposits predominant in the area: thin muskeg and a glacial till layer, providing a relatively impermeable base through which pond water may not migrate (Holden et al., 2011). Beneath lies the Wood Creek Sand Channel, a pre-glacial sand channel through which groundwater migrates. Suncor's South Tailings Pond (STP) resides over areas of thin (<5m) or absent glacial till (Holden et al., 2011). The underlying till may not sufficiently inhibit OSPW in the tailings pond from migrating to the sand channel (Holden et al., 2011). Abolfazlzadehdoshanbehbazari et al. (2013) identified seepage through the till at a rate of 0.9 m per two years (measuring ^{2}H and ^{18}O tracers). It is therefore possible that contaminant migration from the containment facility to an underlying aquifer may be occurring.

The possibility of contaminant migration into local groundwater has necessitated an investigation into a remediation technology for simultaneous removal of inorganic (metals) and organic (naphthenic acids) contaminants. Current technologies are refined for classes of contaminants; inorganic contaminant removal is carried out using zero valent iron (Blowes et al, 1998), adsorbents (Small et al., 2012), stabilization, or co-precipitation (Bailey et al., 1999). Organic contaminant removal can be done using industry by-products (Shawwa et al., 2001) or oxidation (Gamal El-Din et al., 2011). Some studies (Herman et al., 1993; Headley et al., 2008) have also explored the use of augmented bioremediation for the removal of naphthenic acids.

Yet, to date, there is limited research concerning the simultaneous contaminant removal of both naphthenic acids and metals from OSPW. Given the high cost of remediation activities (Bailey et al., 1999), an economically feasible treatment system of tailings water should use relatively available materials, be inexpensive to operate, and provide combined contaminant removal.

2.2 Contaminant Identification

Within the context of oil sands tailings, the identified compounds of concern are naphthenic acids, PAHs, phenols, metals and salts (Allen, 2008). This section will provide an overview on two of the mentioned contaminants: naphthenic acids and metals.

2.2.1 Naphthenic Acids

Naphthenic acids are a group of naturally occurring carboxylic acids found in crude oil with the general formula $C_nH_{(2n+z)}O_2$, where *n* indicates the carbon number and *z* the hydrogen deficiency (indicating the number of cyclic rings in a series [Han et al., 2009; Grewer et al., 2010; Zhao et al., 2010]). The acids are released during the Clark hot water extraction process, further enhanced by elevated pH levels common in oil sands processing (Holowenko et al., 2002). Bitumen extraction releases naphthenic acids into solution, which tend to accumulate as OSPW is recycled (Allen, 2008). Increasing concentrations of naphthenic acids can influence the extraction chemistry (reducing extraction efficiency) and corrode extraction equipment (Mohammed et al., 2008). This presents a potentially large cost for oil sands operators. Naphthenic acids are also toxic to humans and aquatic organisms (Clemente and Fedorak, 2005), necessitating an increased characterization and understanding of their fate in the environment.

The complexity and variety of naphthenic acids has made accurate characterization difficult. With a large range of carbon numbers (n=5 to 30), isotopes, and the presence of sodium dimers, physical and chemical properties may vary widely (Clemente and Fedorak, 2005). Therefore, the properties and fate of naphthenic acids in the environment is difficult to predict. Whitby (2010) and Small (2011) report that phenols, pyrroles and thiophenes may exist in the OSPW, further increasing the difficulty in accurate measurement of naphthenic acids, as these organics may interfere, or be falsely identified. Whitby (2010) shows several examples of naphthenic acid structure in Figure 2-1.

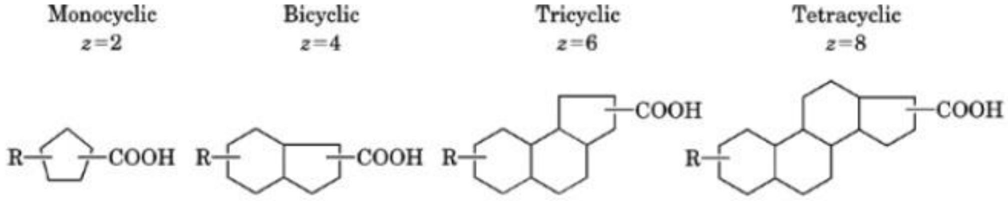


Figure 2-1: Varying naphthenic acid structures found naturally in Athabasca oil sands OSPW (Figure taken directly from Whitby 2010).

Holowenko et al. (2002) further report that the majority of naphthenic acids found in the Athabasca oil sands bearing the generic formula $C_nH_{(2n+z)}O_2$ are midweight (C12-C19) acids. Increasing complexity (carbon numbers) increases the molecular weight, and subsequently changes the chemical and physical properties, requiring remedial efforts to focus on a broad spectrum of compounds (Gamal El-Din et al., 2011).

Studies on oil sands tailings have found that the organic fraction of contaminants are the major contributing factor to toxicity (Scarlett et al., 2012; Rogers et al., 2002; Clemente and Fedorak, 2005). In neutral-alkaline environments, such as those present in OSPW, naphthenic acids are soluble and readily available for uptake by plants, bacteria, rats and fish (Clemente and Fedorak, 2005). Toxicity assays are often measured using the killoff of *vibrio fischeri*, a luminescence bacterium (Clemente and Fedorak, 2005). These bacteria emit a luminescence measured using a luminescence detector. After 5 and 15 minutes, a 20% luminescence inhibitory concentration is measured, providing a rough estimation of toxicity. The luminescence inhibition at 5 minutes is largely caused by organic compounds, while longer (15 minute) luminescence inhibition is usually associated with heavy metal toxicity (ASTM, 2009a). This is due to the relatively rapid availability of organic compounds in solution when compared to metals.

In one study, Rogers et al., (2002) used rats to determine acute and subchronic toxicity of naphthenic acids. Results indicated that, when male rats were exposed to a single dose of naphthenic acids (300 mg/kg body weight), significant liver damage occurred (Rogers et al, 2002). Subchronic intake of naphthenic acids was measured on female rats, with daily doses (0.6 mg/kg, 6 mg/kg, and 60 mg/kg body weight) occurring over 90 days. Female rats experienced an increase in liver, kidneys and brain weight, while 17% experienced seizures (Rogers et al., 2002). This study indicated the liver and kidneys as a likely target for naphthenic acids. Dokholyan and Magomedov (1984) studied the effect of naphthenic acids on various fish species (salmon, sturgeon, kutum and roach fingerling). The study found 50% mortality rates after 10 days of exposure in 2 month old salmon (25 mg/L), kutum and roach fingerlings (50 mg/L), 2 year old sturgeon (50 mg/L) and roach fingerlings (75 mg/L; Dokholyan and Magomedov, 1984). In general, toxicity of naphthenic acids is attributed to lower molecular weight naphthenic compounds (Holowenko et al., 2002). Biodegradation of naphthenic acids was also shown to significantly reduce toxicity as lower molecular weight naphthenic acids were preferentially removed (Clemente et al., 2004).

Measuring naphthenic acids is conventionally done using FT-IR at 1706 and 1743 nm^{-1} (Jivraj et al., 1995). Due to its relative ease in sample measurement and preparation, low cost, and limited training required, FT-IR is the industry standard for naphthenic acids measurement.. However, FT-IR cannot differentiate between individual naphthenic acids, limiting its use in studies requiring an understanding of specific compounds and their degradation. FT-IR measurements may also be skewed by organic compounds with molecular weights similar to that of naphthenic acids, as their response could be a similar wavelength (Holowenko et al. 2002). Mass spectrometry techniques can be used to accurately characterize individual naphthenic acid compounds. This enables mechanisms associated with removal to be understood in greater detail. These techniques usually have fewer false positives, leading to more accurate measurements (Holowenko et al. 2002).

The diversity of naphthenic acid structures presents further challenges in understanding their fate in the environment. Monocyclic naphthenic acids, for example, are a lighter molecular weight and are therefore more likely to be soluble in water, biodegradable, and have a higher volatility (Janfada, 2007). The detection of a relatively high percentage of C_{22}+ clusters using GC-MS has been attributed to aged tailings and varying ore body composition (Holowenko et al., 2002). These varying attributes pose a remediation challenge as many strategies are often contaminant specific and cannot accommodate the range of molecular properties inherent in naphthenic acids.

The toxicity and complexity of naphthenic acids has necessitated further work into the identification and characterization of these compounds (Grewer et al., 2010). Recent work (Han et al., 2009; Grewer et al., 2010; Zhao et al., 2010) suggests that the classical naphthenic acid formula ($C_nH_{(2n+z)}O_2$) should be updated to include mono and di-oxide naphthenic acids ($C_nH_{(2n+z)}O_x$ with *x* values ranging from 3-4). Grewer et al., (2010) further showed that in Albanian, Syncrude and Suncor samples, mono and di-oxide naphthenic acids with an oxygen number (*x*) of 3-5 comprised of over 50% of the detectable naphthenic acid concentration. These samples were measured using electrospray ionization fourier tranforms ion cyclotron resonance mass spectrometry (ESI-FTICR-MS). Electrospray ionization is beneficial amongst mass spectrometry techniques, as it can overcome fragmentation of macromolecules (Zhao et al., 2012). Fragmentation occurs when a large ionization potential splits molecules prior to analysis, thereby inhibiting the measurement of a 'true' concentration (Zhao et al., 2012). Electrospray can operate at a lower ionization potential, limiting this fragmentation. Martin et al., (2008) suggest that mass spectrometry techniques provide a powerful analysis tool for the detection of individual naphthenic acid compounds. This work, however, stipulates that these methods may still provide false positives. ESI MS, in particular, can misrepresent derivatized hydroxyl naphthenic acids as classical acids. Therefore these methods should be used for semi quantitative purposes only (Martin et al., 2008).

2.2.2 Metals

Mining activities often produce metal wastes, which may contaminate freshwater sources (Bulut and Tez, 2007). Several studies (Allen, 2008; Holden et al., 2011; Kasperski, 1992) have identified metals the OSPW in the Northern Alberta oil sands. Studies identified Al, As, Fe, Mo, Mn (Allen, 2008; Kasperski, 1992; Holden et al., 2011) as priority metals, while Allen (2008a) and Kasperski (1992) added Cd, Cr, Cu, Pb, Ti, V, and Zn. Holden et al., (2011) further showed that, when OSPW was mixed with the underlying sediment, bound metals were released into solution. The US EPA (2009) has categorized the following metals as priority pollutants: As, Cd, Cr, Cu, Ni, Pb, and Zn. These metals are non-biodegradable, and may lead to adverse toxicological effects on organisms such as humans and fish (Bailey et al. 1999). Less attention, when compared with organic contaminants, has been given to the remediation of metals present in OSPW (Mahdavi et al., 2012). Exceeding surface water quality guidelines in OSPW were Cr, Cu, Pb, Ni and Zn (Allen, 2008b). Mahdavi et al. (2012) focused on the removal of the aforementioned metals and Mn, Zn, Sr, As, Mo and Ba. In elevated concentrations, these metals are shown to be toxic to both aquatic and human life (Febrianto et al., 2009). One study (Gamal El-Din et al., 2011) considered an OSPW pre-treatment using Syncrude coke prior to naphthenic acid ozonation. However this study did not consider heavy metal remediation.

Predicting the metal speciation related to the oil sands is critical for understanding which metals are of concern in OSPW, and further aid in remediation efforts. As the Alberta oil sands tailings are alkaline, many metals are likely to remain in non-toxic, insoluble forms (Essington, 2003). A redox ladder and subsequent construction of pE-pH diagrams can be used to determine the speciation of metals based on redox conditions and pH (Essington, 2003). The ladder demonstrates which species of metal will be dominant at a given pH, and is constructed using the reduction half reactions for a given reaction. Equation 2.1 displays a general reduction half reaction (where m and p are the number of moles of oxidized species [A] and reduced species [B] respectfully, and n and q are the number of moles of protons and water respectively; Essington, 2003).

$$mA_{oxidant} + nH^{+} + e^{-} \rightarrow pB_{reduced} + qH_2O$$

Equation 2-1

The generic half reaction (Equation 2-1) can be rearranged to determine the equilibrium constant. The constant, K, is defined as the ratio of reaction products to reactants (Essington, 2003). Rearranged, and solved for the unit electron (e^-), yields Equation 2-2.

$$e^{-} = \frac{(A_{reduced})^{p}}{(A_{oxidized})^{m}(H^{+})^{n}(K_R)}$$

Equation 2-2

Finally, applying the logarithm of Equation 2-2 yield Equation 2-3 (where $pE = \log(e^{-})$ and $pH = \log(H^{+})$). This equation is used at varying pH values to calculate a pE value. These varying pH and pE values can be plotted, producing a figure similar to Figure 2-2.

$$pE = log(K_R) + log\left(\frac{(A_{oxidized})^{m}}{(A_{reduced})^{p}}\right) - n(pH)$$

Equation 2-3

Applying conditions on temperature and natural gas constant lead to the development from Equation 2-3 to the Nernst Equation (Equation 2-4).

$$E_H = {E_H}^{o} - \frac{0.059}{n}\log\left(\frac{(A_{reduced})}{(A_{oxidized})(H^{+})^{m}}\right)$$

Equation 2-4

Where $E_H = \frac{RTln(10)}{F} * pe$, F = Faradays constant (96484.56 Cmol^{-1}), R = Natural Gas Constant (8.314 J/K*mole) and T = Temperature (298.15K).

Diagrams tend to be constructed using Nernst equation (Equation 2-4) rather than equation 2-3, however the former will be used due to the elimination of standardized temperature and gas constant. An example diagram of Se is constructed using this process (Figure 2-2).

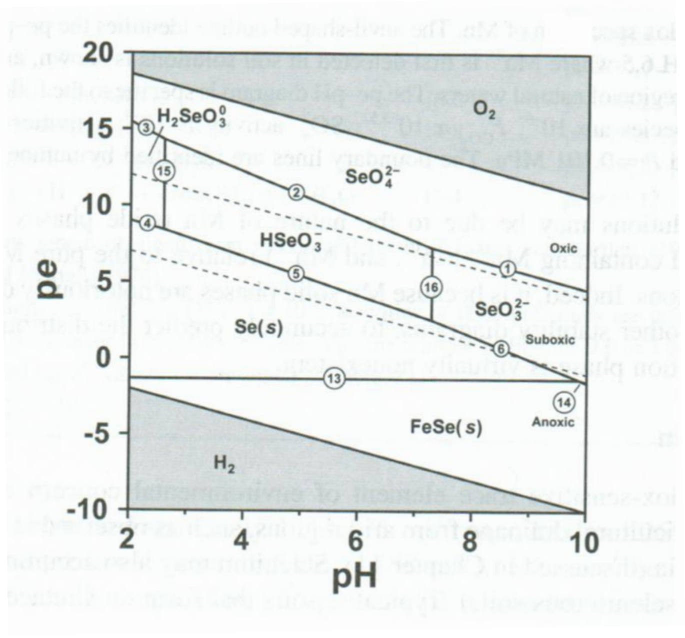


Figure 2-2: Speciation of Se in water with the following conditions: activities of 10^{-6}, Fe^{2+} activity of 10^{-6}, activity for H_2O and solids are 1.0, T=25°C and P=0.101 MPa. Illustrated are boundary lines for O2 and H2, and oxic, suboxic and anoxic conditions. Figure taken directly from Essington (2003).

Figure 2-2 demonstrates that in anoxic conditions, Se is largely present as Se(s) or FeSe(s). This indicates that in strictly anoxic conditions, selenium may not be a concern, as it is predominantly in solid form. However, in oxic conditions (such as aerobic tailings), Se is present as selenite (Se(VI)), a dissolvable ionic form of Se. Both selenate (Se(IV)) and selenite are toxic in low concentrations to aquatic organisms (Goldberg et al., 2006), and given the relatively slow transformation rates, both species often coexist in aerobic environments. Tailings ponds largely contain anaerobic areas (Clemente and Fedorak, 2005), therefore the existence of Se, from Figure 2-2, is predicted to be an insoluble complex, likely bound to the fine fraction of particles settling within the tailings ponds. From pe-ph diagrams, it is possible to predict the individual speciation of each metal present in the oil sands tailings ponds. This will be explored in Section 2.3.2.2.

2.3 Remediation of Oil Sands Contaminants

Remediation of OSPW contaminants, including naphthenic acids and metals, is largely limited to oil sands naphthenic acids (Mahdavi et al., 2012), and there is limited focus on the removal of metals from OSPW. To date, no combined removal investigation of metals and naphthenic acids has been extensively investigated. Naphthenic acid removal has seen a focus on oxidation methods, specifically using ozone (Scott et al., 2008; Garcia-Garcia et al., 2011; Gamel El-Din et al., 2011), biological treatment (Clemente et al., 2004; Toor et al., 2013; Mahdavi et al. 2012), and physical adsorption processes (Gamal El-Din et al., 2011; Small et al., 2012). While oxidation is advantageous for its relatively short timeframe required for remediation (US EPA, 2004), passive adsorption using available by-products provides a cheaper alternative (Zhang et al., 2005)

Remediation options for metals in aqueous solutions are extensive, and can be classified into chemical, biological or physical (Hashim et al., 2011). Technologies identified by Bailey et al. (1999) include chemical precipitation, ion exchange, adsorption and membrane filtration. Regardless, technologies for groundwater remediation operate based on contact optimization for treatment results. In the case of the oil sands, contaminants are present in a surface water body, allowing contact optimization between OSPW and treatment media (Hashim et al., 2011). Studies on the removal of OSPW heavy metal contaminants have focused on biological uptake (Mahdavi et al., 2012; Lourie et al., 2010) or physical removal (Small et al., 2012; Sarkar, 2013; Janfada, 2007). Both methods present advantages and disadvantages. Biological remediation of metals, for example, can cater to a variety of conditions and effectively remove a breadth of contaminants (Eccles, 1999). Lourie et al. (2010) describe how a biological system may be more effective for metals at low concentrations. They can also be used without the production of a secondary waste stream (Lourie et al., 2010). However, in the case of the oil sands, a readily available, high carbon adsorbent exists. Though previous work on petroleum coke has shown a tendency for metal release (Small et al., 2012; Janfada 2007), the ability to passively remediate a large portion of contaminants presents a large advantage. Chemical precipitation of metals is difficult in OSPW, as the water is a complex system and contains a variety of contaminants (ITRC, 2013).

Aqueous metal removal technologies are often limited due to their expense (Lourie et al., 2010; ITRC, 2013). Passive remediation technologies, such as permeable reactive barriers, provide a means to remediate metals in a more cost effective manner (US EPA, 1998) by providing a barrier through which contaminated water may pass and decontaminate as it does (US EPA, 1998, US EPA, 2001). Ideally, these technologies operate in a pre-existing channel through which the contaminated water flows and can be easily accessed for upkeep (US EPA, 1998). Blowes et al. (1998) suggested that metals, including As, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Se, and V can be treated using passive barrier technologies. Typical adsorption media for these barriers are carbon based materials (Small et al., 2012; Kurniawan et al., 2006) or zero valent iron (if a reactive barrier is desired [US EPA, 1998]).

Current reclamation efforts from Suncor Energy Inc. and Syncrude Canada Ltd. are focused on large scale tailings consolidation and trafficable surface creation. Suncor Energy Inc. for example are implementing their Tailings Reduction Operations (TRO™), where a polymer is added to the tailings to encourage coagulation and eliminate water from pores (Suncor, 2013). Both Suncor Energy Inc. and Syncrude Canada Ltd. are utilizing petroleum coke in their remediation efforts. Suncor Energy Ltd. are field testing a ‘coke capping’ (Suncor, 2013) method, where ponds are capped with petroleum coke to provide a trafficable surface. Syncrude Canada Ltd. are using their coke for tailings toxicity reduction, demonstrated recently in a small aquarium. Tailings water was filtered through their coke by-product and used in an aquarium, demonstrating toxicity reduction of their water (Syncrude, 2013a). Further work, including composite tailings and centrifuging, focus on removing water from the tailings to produce a higher solids fraction material. Finally, Syncrude Canada Ltd. is developing and testing constructed wetlands for treatment of their tailings waste (Syncrude, 2013b).

2.3.1 Adsorption

An increase in global industrial mining production has necessitated the removal of pollutants from a growing volume of waste. Current technologies for metal and organic removal are expensive and ineffective at low concentrations (Kurniawan et al., 2006). Low cost adsorbents are a growing area of interest, as they may be implemented in an economic manner. Using by-products from agricultural waste, for example, provides a means through which to reuse a waste product for the remediation of organic and inorganic contaminants (Kurniawan et al., 2006). Barrier-based remediation technologies depend on a materials adsorption capacity (US EPA, 1998). In order to manage uptake of organic and inorganic contaminants, the processes surrounding adsorption must be adequately interpreted and understood.

Adsorption is a process in which a substance in liquid phase is transferred to an adsorbent solid phase, and is bound to the surface of the adsorbent by physical or chemical forces (Kurniawan et al., 2006). Van der Walls forces, weak bonds formed by fluctuating polarity as an atoms ion cloud rotates, create temporary polar charges on compounds (Gregg and Sing, 1982). When these polar compounds attract to an adsorbent, polarity fluctuations bind the compound tothe surface (Small, 2011), leading to physical adsorption. Specific conditions may encourage the adsorption or desorption of compounds.

The structure and chemical properties of carbon adsorbents depends on their source (Martin-Gullón and Menéndez-Diaz, 2006). The governing property is the surface availability for adsorbates to contact, measured as pore surface area. Pore classification can be done following Martin-Gullón and Menéndez-Diaz (2006), with macropores having a width >50 nm, mesopore width 2<width<50 nm and micropore <2nm. Heteroatoms, or non-carbon based compounds, can be present on the surface of the granular material, limiting adsorption processes by occupying the space. Heteroatoms may also cause physical and chemical reactions to occur, which may promote or discourage desorption (Gregg and Sing, 1982).

Optimal adsorption occurs when an adsorbent has a large specific surface area; that is, a large surface area-to-volume ratio. This high SA:V ratio is required as the primary factor for adsorption is the formation of physical and/or chemical bonds with the adsorbent, and this requires contact between adsorbate and adsorbent (Martin-Gullón and Menéndez-Diaz, 2006). Batch tests providing continuous contact between adsorbate and adsorbent such that equilibrium can be obtained in 24 hrs (ASTM, 2009a). Granular materials are often selected as adsorbents due to their scattered structure and presence of voids (Martin-Gullón and Menéndez-Diaz, 2006). Granular activated carbon, for example, can remove organic contaminants such as naphthenic acids, BTEX, and polycyclic aromatic hydrocarbons from solution (Small et al., 2012; Martin-Gullón and Menéndez-Diaz, 2006; VanOsdell et al., 1996; Clark, 1987).

2.3.1.1 Brunauer-Emmett-Teller Model

The adsorption capacity of a material can be measured using various parameters (I_2 adsorption, methylene blue adsorption; ASTM, 2011; Hang and Brindley, 1999). The Brunauer-Emmett-Teller (BET) equation is the most common for specific surface area measurements of carbon adsorbents (Martin-Gullón and Menéndez-Diaz, 2006). The BET isotherm is produced by the adsorption of N_2 at 77 K or CO_2 at 273 K. Both gases can be used in conjunction to enhance data (Martin-Gullón and Menéndez-Diaz, 2006). The theory assumes uniform energy is required for adsorption, by assuming monolayer formation on the adsorption sites. N_2 is assumed to penetrate larger pores in the structure, while CO_2 can effectively measure micropores of approximately 10^{-9}m width (Choma et al. 1991). Diffusion of gasses into the pores is assumed to not occur, though this may not be the case with low temperature (77K) N_2, as it may have insufficient kinetic energy to penetrate the micropores (Martin-Gullón and Menéndez-Diaz, 2006). Martin-Gullón and Menéndez-Diaz (2006) measure the BET adsorption using Equation 2-5 and Equation 2-6:

$$\frac{\frac{p}{p^o}}{n(p^o - p)} = \frac{1}{nC} + \frac{C-1}{n_m C}\frac{p}{p^o}$$

Equation 2-5

$$C = \exp\left(\frac{q_1 - q_L}{RT}\right)$$

Equation 2-6

From these equations, the monolayer capacity (n_m in mmol/g) can be calculated assuming $(p/p^o)/(n(p^o\text{-}p))$ and (p/p^o) are linear (Martin-Gullón and Menéndez-Diaz, 2006). Studies (Martin-Gullón and Menéndez-Diaz, 2006; Bansal and Goyal, 2005) have shown that the applicability to porous carbon structures is limited, as linearity is only achieved consistently through a partial pressure (p/p^o) of 0.05 to 0.3. Despite the limited operational ranges, activated carbons can still be measured successfully using BET, with results ranging from 500-1500 m^2/g (Small, 2011; Martin-Gullón and Menéndez-Diaz, 2006).

Limitations of this model revolve around the inherent assumptions, rather than the understanding of individual parameters (Bansal and Goyal, 2005), since BET theory assumes uniform adsorption energy at the monolayer. However, as Bansal and Goyal (2005) remark, porous and non-porous structures alike will adsorb a finite amount, and not a limitless amount as the model suggests. The model further suggests that any adsorption past the first layer occurs at a coordination number of 12, releasing full heat of liquefaction (Bansal and Goyal, 2005). This may hold in uniformly layered adsorption, however, as Figure 2-3 demonstrates, adsorption may not occur in a uniform sequence.

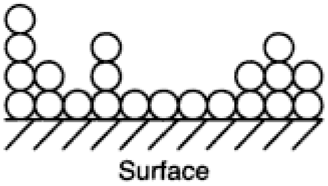


Figure 2-3: Adsorption of gaseous molecules onto a surface. This demonstrates non-uniform layering as adsorption occurs, thereby decreasing coordination numbers (from 12) and providing a limitation to the BET model (Figure taken directly from Bansal and Goyal, 2005).

The non-uniformity of adsorption layers means that, with a space against molecules on a given layer, a coordination number of 12 is not achieved (Bansal and Goyal, 2005).

2.3.1.2 Adsorption of Oil Sands Contaminants

Early work in mine waste reclamation involved the identification and reclamation of organic contaminants (Sigworth and Smith, 1972).While these are a large concern in the oil sands, metals also lead to toxicity within the tailings ponds (Mahdavi et al., 2012). Some early work in metal removal from water was undertaken by Sigworth and Smith (1972). They identified multiple metals (Ni, Pb, V, Sb, As, Sn, and others) in relatively elevated concentrations in drinking water. The study identified Ni, Pb and V to have ‘fairly good adsorbability (Sigworth and Smith, 1972)’ onto the carbon adsorbent (Sigworth and Smith, 1972). However V’s adsorption was limited at neutral pH. Other metals relevent to OSPW metal, but not included in this study are Cu, Mn, Mo, Zn and Se.

The sorption of organic compounds, specifically non-polar ionisable compounds such as naphthenic acids, is dependent upon several factors including pKa and the equilibrium constant of the adsorbate, pH of the system, water solubility and organic content (f_{oc}; Delle Site, 2001; Fetter, 1999). These parameters vary greatly in the field (Bachu et al., 1993). Fluctuations in pH, for example, will change the surface activity and cation exchange capacity (Delle Site, 2001). Changes in these parameters promote the uptake and release of compounds, depending on their property. Nodwell (2011), for example, found that commercial naphthenic acids presented hydrophobic adsorption onto mineral surfaces and reaction vessels at pH 3, due to the insolubility of these organic compounds in low pH solutions. At neutral to alkaline pH (8.0), copper complexes were formed, leading to a reduction in naphthenic acid concentration (Nodwell, 2011). Janfada (2007) further noticed preferential adsorption for mid-to-high range molecular weight naphthenic acids. Naphthenic acids with a carbon number 5-14 were less adsorbed. These lighter molecular weight compounds tend to be more soluble and therefore mobile (Bedient et al., 1997). This presents an issue for groundwater remediation as the contaminants are more mobile and available to environmental receptors (Janfada, 2007). It can be stipulated that complex mixtures of OSPW and adsorbents may display a multitude of sorption mechanisms; whether it is preferential sorption on an adsorbent (Janfada, 2007) or the interaction of inorganic salts with naphthenic acids, creating insoluble metallo-organic complexes (Nodwell, 2011).

Studies from Small et al. (2012) and Sarkar (2013) have shown delayed coke, a by-product of the bitumen extraction process (Fedorak and Coy, 2006), can be used to remove naphthenic acids and some trace metals. Coke may therefore be a viable alternative to GAC, as an industry waste product for the remediation of contaminants in the subsurface.

2.3.2 Oil Sands Coke

Bitumen is mainly composed of four fractions: saturates, aromatics, resins and asphaltenes. Asphaltenes, high weight, non-volatile carbon matter, are produced in high concentrations (>50% by weight) during the upgrading process from bitumen (Puttaswamy, 2011; Gray, 2002). During upgrading, asphaltenes are only partially thermally decomposed. The high molecular weight fraction (n-heptane and cyclohexane) polymerize to form a solid, carbonaceous product. The process of bitumen upgrading frequently produces a waste product termed coke (Speight, 1986).

A process diagram for the production of coke is provided in Figure 2-4. Information is compiled from US EPA (2008), Jankowski et al. (1991), and Small (2011).

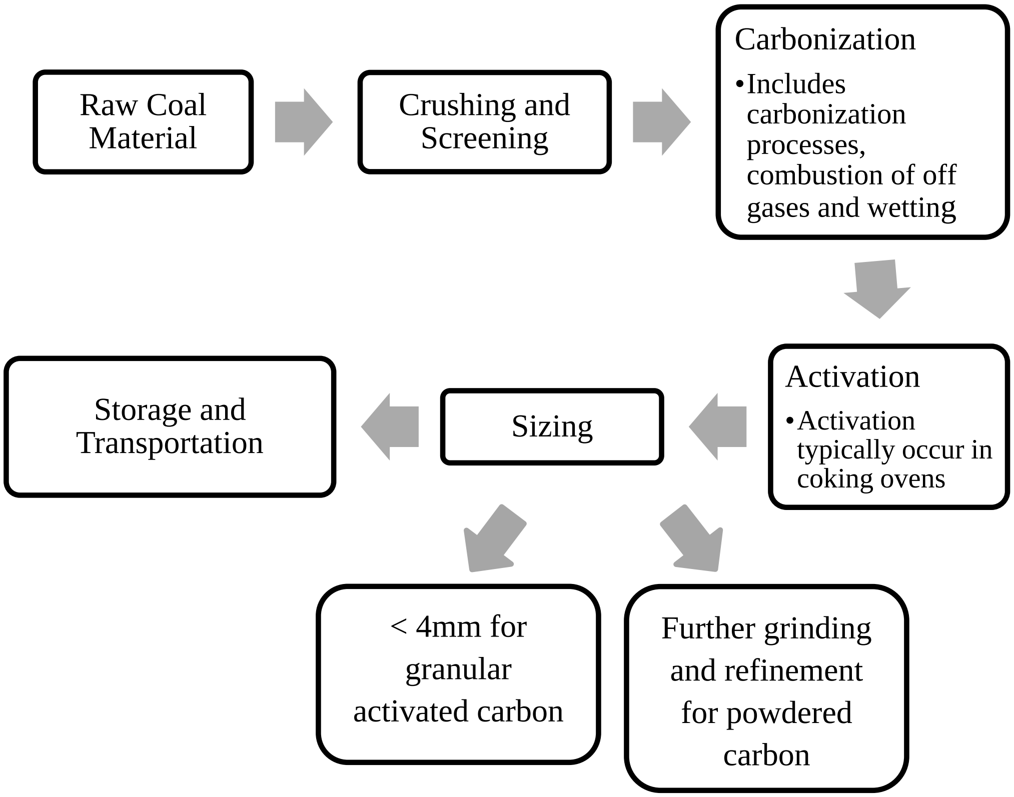


Figure 2-4: Process flow diagram for the creation of activated carbons. Information taken from US EPA 2008, Jankowsky et al., 1991 and Small, 2011.

The primary objective of coking is to remove impurities from bitumen, breaking down the heavier hydrocarbons and producing a lighter crude oil. The heavier fraction is highly carbonaceous, but can concentrate with other impurities found within the bitumen (Puttaswamy, 2011). These impurities include sulphur, mineral matter and some metals (chiefly Ni and V; Puttaswamy, 2011).

Northern Alberta oil sands coking is accomplished using two different methods, producing a delayed coke (Suncor Energy Inc.) and fluid coke (Syncrude Canada Ltd.). Fluid coke is produced when oils are sprayed onto hot coke particles through steam injection (Small et al., 2012; Onder and Bagdoyan, 1994). The result is an instantaneous conversion from liquid oil to solid coke via thermal cracking (Scott and Fedorak, 2004), with an off stream of lighter crude produced. This process allows for the recycling of coke, however much is still stockpiled and remains an industrial waste (Fedorak and Coy, 2006). Delayed coke is produced by rapid heating of oil in a furnace at optimal thermal cracking temperature and pressure (Onder and Bagdoyan, 1994). Prior to separation of liquid and solids, coke is transferred to a coking drum, and the remaining solids are present as delayed coke (Scott and Fedorak, 2004; Small, 2011). Due to its processing, delayed coke exhibits more of a sponge-like structure, whereas fluid coke displays a more uniform, spherical shape (Fedorak and Coy, 2006).

Scanning electron microscopy is a particle viewing tool in which a rough, solid sample can be examined in detail (Wells, 2001). An image is formed when an electron beam returns an excitation response based on the material surface. For oil sands coke, the imaging provides a tool to examine surface porosity before and after activation, as depicted in Figure 2-5 (Chen and Hashisho, 2012).

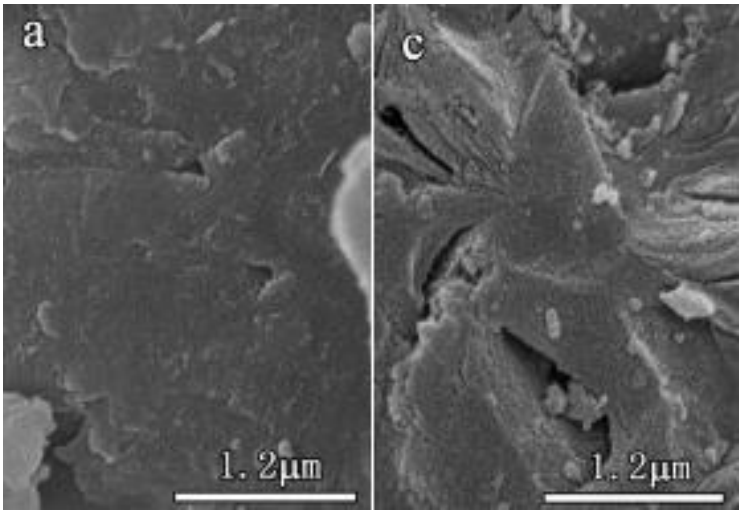


Figure 2-5: Scanning electron microscopy (SEM) image of raw (a) and activated (c) delayed coke. Coke was activated using microwave heating combined with KOH and humidified nitrogen. Activation is further discussed in Section 2.3.2.1. Images taken from Chen and Hashisho (2012).

The surface of activated delayed coke (Figure 2-5c) is dominated by a limited number of large cracks. The structure of delayed coke allows for these deep cavities to form, granting access to meso and micropores (Chen and Hashisho, 2012). In contrast, layering within fluid coke provides a structure with a larger number of fractures, but shallower cavities (Figure 2-6).

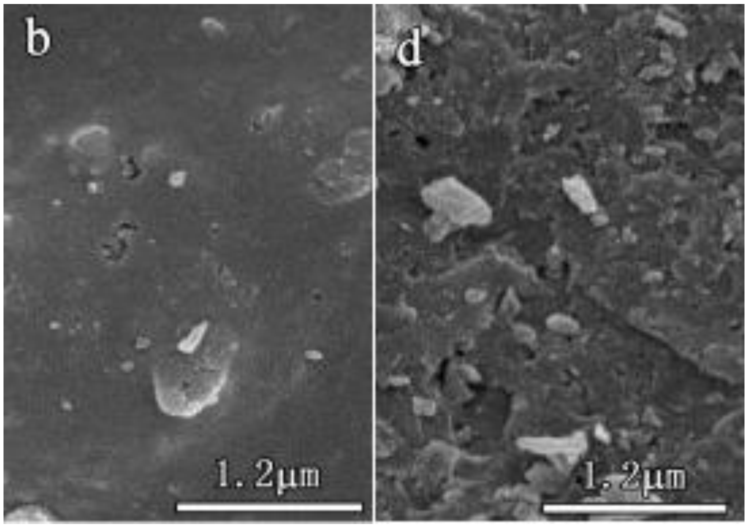


Figure 2-6: Scanning electron microscopy (SEM) image of raw (b) and activated (d) fluid coke. Coke was activated using microwave heating combined with KOH and humidified nitrogen. Activation is further discussed in Section 2.3.2.1. Images taken from Chen and Hashisho (2012).

Elementally, the composition of both cokes is similar due to the proximity of each ore body to another (Furminsky, 1999). Both have relatively high fixed carbon (~85%) and sulphur (~5%) percentages, however fluid coke has a surface area of approximately half. This is due to the layered structure produced during the formation of fluid coke, allowing limited access to meso and micropores (Chen and Hashisho, 2012). Coke composition is summarized in Table 2-1.

Table 2-1: Elemental composition of oil sands delayed and fluid coke. Values (except otherwise marked) are from Furminsky (1998).

		Delayed Coke	Fluid Coke
Proximate Analysis	Ash (%)	3.6	4.8
	Volatile Matter (%)	12.4	5.0
	Fixed Carbon (%)	84.0	90.0
	Moisture (%)	-	0.25
Ultimate Analysis	Carbon (%)	84.2	83.7
	Hydrogen (%)	3.8	1.8
	Nitrogen (%)	1.5	2.0
	Sulphur (%)	5.8	5.5
	Oxygen (%)	1.1	0.9
	Surface Area (m^2/g)	5.1	2.7[1]

[1] Values obtained from Small et al. (2012).

Coke is currently being considered as a remediation medium due to its large onsite volume, which is currently considered a waste product. Between Suncor Energy Inc. and Syncrude Canada Ltd., approximately 5 million tonnes of coke are produced annually (Fedorak and Coy, 2006). Since it currently has limited use (Small et al., 2012), it is feasible to utilize this waste as a physical medium for remediation.

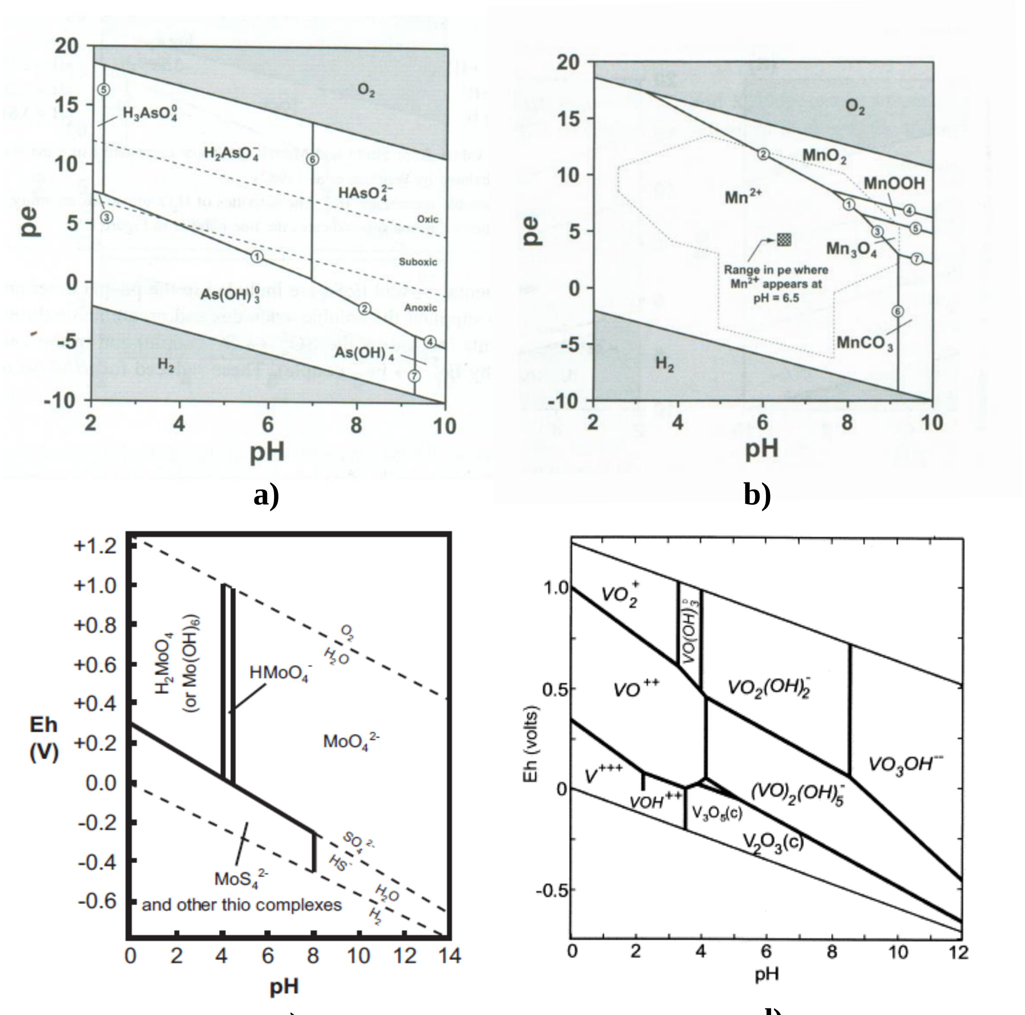
2.3.2.1 Activation of Coke

Carbonaceous materials can be enhanced by increasing pore size and interparticulate surface area via activation (Figure 2-5 and Figure 2-6; Bansal and Goyal, 2005). This can be accomplished chemically or physically. While chemical activation can produce higher yields at a lower pyrolysis temperature (Lillo-Ródenas et al., 2003), it also can be corrosive to materials used in the process and creates an additional waste stream (Teng and Lin, 1998). Within the context of the Alberta oil sands, physical activation is relatively advantageous, as many of the required infrastructure is currently available and additional waste stream production is limited (Small et al., 2012). Physical activation of coke occurs in two main steps: carbonation and activation. Carbonation occurs via pyrolysis at temperatures below 800°C, where non-carbon impurities are volatilized (Bansal and Goyal, 2005). The volatilization of non-carbon elements such at oxygen, nitrogen, hydrogen and sulphur reduces material in the porespace, allowing the carbon material to rearrange itself into irregular sheets. The irregularity promotes the uptake of compounds when used as an adsorbent (Bansal and Goyal, 2005; Bansal et al., 1998). Activation, occurring physically or chemically, involves primarily the enhancement of surface area.

2.3.2.2 Acid Washing of Coke

Small (2011) suggested that, to reduce the impact of metal release from its surface, coke should be acid washed prior to use as an adsorbent. Puttaswamy (2011) identified Ni and V as the toxic components of coke metal release. Small et al. (2012) further indicated that, while trace metals such as Mn, Cu, and Pb may be adsorbed, some elements such as Al, Mo, and V are also released. Acid washing of the coke prior to activation may inhibit desorption of trace metals (Small et al., 2012). A low pH encourages the release of metals, dissolving them in solution and increasing their mobility (Essington, 2003). Therefore, a pre-treatment of coke using an acid solution can purify the carbonaceous material, allowing enhanced adsorption to occur over a non-acid washed coke.

Marsden and House (2006) suggest that, given its widespread industrial application, hydrochloric acid be used. The low pH promotes the dissolution of metals into solution (of interest are Al, As, Pb, Mn, Mo, Se, V). Dissolving these metals removes those that were not in the carbonation sequence of activation. Several figures (Figure 2-7a, b, c, and d) demonstrate the speciation of metals related to tailings ponds, including As (Figure 2-7a), Mn (Figure 2-7b), Mo (Figure 2-7c), Se (Figure 2-2), and V (Figure 2-7d).



a)

b)

c)

d)

Figure 2-7: Speciation of a) As b) Mn c) Mo and d) V in water. Conditions for the production of the diagrams were the following: a) and b) had an Fe^{2+} activity of 10^{-6}, activity for H_2O and solids are 1.0, T=25°C and P=0.101 MPa (taken directly from Essington, 2003); c) had a total Mo activity of 10^{-6} and total S activity of 10^{-4} (taken directly from Anbar, 2004); and d) had an activity of 10^{-5} (taken directly from Peacock and Sherman, 2004).

From Figure 2-7a, As is present in ionic form in most conditions. However, in acidic soils, As exists in conjunction with Fe(III), while Ca arsenates form in neutral to alkaline soils (Essington, 2003). The more toxic form of As, As(III), exists in anoxic conditions, which are present in tailings ponds anaerobic zone. The measurement of acidity (pH) can be conjoined with pK_a, a measurement of the equilibrium constant of an acid-base reaction. A larger pK_a value indicates favourability towards the forward reaction, meaning a stronger acid (Petrucci et al., 2007). A relatively high pK_a value (9.29; Essington, 2003) indicates that adsorption will increase as pH increases. In an alkaline environment such as the oil sands tailings ponds, adsorption is likely to be favourable (Essington, 2003).

The distribution of Mn (Figure 2-7b) is largely dominated by Mn(II) in acidic and neutral environments. While Mn in an essential nutrient for humans, toxic effects may also occur at higher concentrations (US EPA, 2007). Mn solid phases are difficult to predict, as they are naturally disordered (Essington, 2003). However, in suboxic-anoxic condition in tailings ponds, it is likely speciation of solid Mn (Mn(VI)) and soluble Mn (Mn(II)) may exist, and therefore adsorption of these compounds is a concern for tailings remediation.

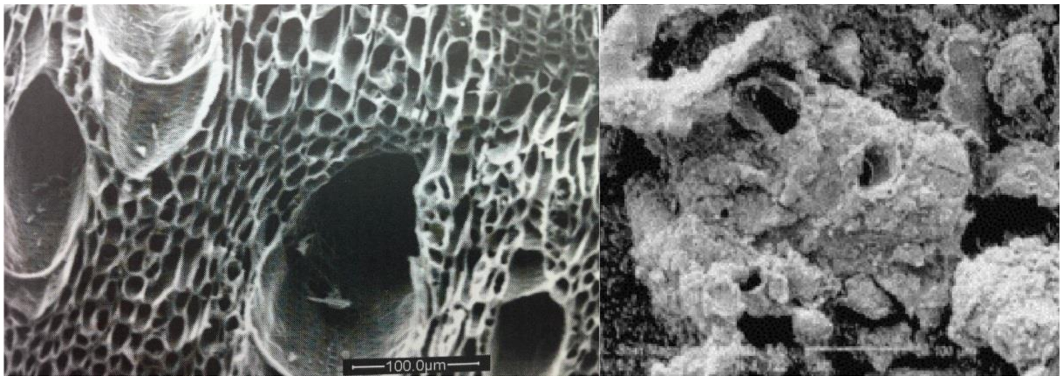
Mo (Figure 2-7c) will be present as Mo(VI) and sulphate bearing Mo compounds, as the environment is largely anoxic and suboxic in alkaline conditions. Barceloux (1999) reports limited toxicity from Mo in this state, and therefore adsorption in aerobic tailings water can be limited. However, in groundwater and deep in the tailings ponds (anoxic conditions), Mo reacts with sulphur present in solution, encouraging the formation of HS^- (assuming a system bearing SO_4 exists; Barceloux, 1999). Such conditions are likely present in the tailings ponds, and therefore necessitate the removal of Mo.

V, according to Peacock and Sherman (2004), is readily adsorbed at neutral pH (Figure 2-7d) through ligand exchange. At low pH, the formation of VO_2^+ is encouraged, contributing to an increase in aqueous V concentration. Acid washing at a pH<4 in suboxic or oxic conditions is therefore sufficient to dissolve V into solution, despite electrostatic repulsion present from the positive surface (Peacock and Sherman, 2004).

Acid washing introduces a low pH solution to the metals bound on the surface and within the pores. This solution will mobilize metals bound to coke, dissolving them in solution and eliminating them from the porespace and surface of the material.

2.3.3 Biochar

Charcoal can trace its usage back 30,000 years, when early cave sketches were made from a charcoal based carbon product (Harris, 1999). Not until the Ancient Egyptians used carbon for water purification purposes was the technology used in different means (Marsh et al., 1997). The earliest studies of charcoal as an adsorbent are from the 18th century by Carl Wilhelm Scheele. Scheele identified the uptake of vapours using charcoal, and subsequent release when material was cooled (Harris, 1999). Work using charcoal did not progress until 1914, when the use of poison gas as a weapon during in WWI necessitated protection for soldiers (Hall and King, 1988). They found that gas masks filled with wood charcoal adsorbents successfully the mitigated effects of chlorine gas (Hall and King, 1988). Since then, a variety of terms have been used to describe charcoal functionalities; amongst them are char, agrichar, biochar, activated carbon, and black C (Lehmann and Joseph, 2009). Only recently has the term ‘biochar’ been used as a product whose purpose is to improve soil quality (Lehmann and Joseph, 2009). The term began to be recognized under its current definition after work from Kishimoto and Sugiura (1985). It is produced when organic biomass is thermally decomposed at low temperature (<700°C) in the absence of oxygen (Lehmann and Joseph, 2009). It differs from charcoal in its intention of usage; that is, the intent of biochar is to improve soil productivity, carbon storage, or filtration of water (Lehmann and Joseph, 2009). Chemically, biochar is difficult to define. Preston and Schmidt (2006) demonstrate a black carbon continuum that suggests, as a biomass is heated, several stages of carbon-based structures. Biochar is the result of heading to a non-volatilized state, or, from Preston and Schmidt (2006), is a combustion residue. Specifically, biochar is produced from potentially any organic biomass under varying heating conditions. This results in a large variation of structure (including poresize and interlayer organization) and functionality (Lehmann and Joseph, 2009). Common between the varieties of biochar, however, is the elevated carbon content composed mainly of aromatic, carbon based rings. Biochar is also advantageous when compared with petroleum coke, as it contains significantly less sulphur (Chen, 2010; Beesley et al., 2011).



a) b)

Figure 2-8: Scanning electron microscopy (SEM) image of a) wood-derived biochar and b) activated petroleum coke. Both display the formation of macro and micropores, with biochar displaying a more uniform layering when compared with petroleum coke. Images taken directly from a) Lehmann and Joseph (2009) and b) Lee and Choi (2000).

Much like activated carbon, biochar shows an increase in surface area (calculated using the BET model) with increasing pyrolysis temperature. At times, biochar can experience pore clogging from volatiles present in the structure, however this has limited effect on the ultimate porosity of the material (Ghania et al., 2013).

Compiled values from various sources of literature (Ghani et al., 2013; Zhao et al., 2013; Tsai et al., 2012; Mašek et al., 2013; Spokas et al., 2011; Table 2-2) demonstrate the variability of sources of biochar. Organic manure and waste (including paper, bone dregs and shrimp hull) display lower percentages of fixed carbon when compared with plant derived biochars (12.6%-20.6%; Zhao et al. 2013). However, those same low carbon content biochars have equal potential for carbon sequestration, ranging from 21.1% to 47.1%. This indicates that, while fixed carbon provides a means through which to classify biochars, it does not accurately indicate its potential for adsorption (Zhao et al., 2013; Ghania et al., 2013). Sawdust-derived biochar presented the highest surface area (203 m^2/g; Zhao et al., 2013), while wheat-straw derived biochar had the highest affinity for cation adsorption (95.5 cmol/kg; Zhao et al., 2013).

Table 2-2: Elemental composition and physical properties of biochars including manure-derived, sawdust-derived, willow-derived and wheat straw-derived biochars.

		Manure-Derived Biochar	**Sawdust Derived Biochar**	**Willow-Derived Biochar**	**Wheat Straw-Derived Biochar**
Pyrolysis Conditions	**Temperature (ºC)**	500	500-850[6]	350-500[6]	500
Proximate Analysis	**Fixed Carbon (%)**	40.2[2]	72.0[2]	49.9[3,4]	63.7[2]
	Volatile Matter (%)	49.8[1]	51.39[2]	21.6[3,4]	17.6[2]
	Ash (%)	45.8±0.7[1]	22.67[2]	0.8[3]	18.0[2]
	Moisture (%)	4.4±0.2[1]	Nm	9.10[3]	Nm
Ultimate Analysis	**Carbon (%)**	41.8±0.2[1]	53.4[5]	48.29[3]	45.34[3,4]
	Hydrogen (%)	1.0±0.0[1]	6.7[5]	6.01[3]	5.97[3,4]
	Nitrogen (%)	2.6±0.0[1]	3.1[5]	1.04[3]	0.41[3,4]
	Oxygen (%)	18.4±0.1[1]	36.8[5]	Nm	Nm
	Surface Area (m^2/g)	47.4[2]	203[2]	Nm	33.2[2]
	Cation Exchange Capacity (cmol/kg)	82.8[2]	41.7[5]	Nm	95.5[2]
	pH	10.5[2]	10.5[2]	Nm	10.2[3]

Nm: not measured. [1]Values from Tsai et al., 2012. [2]Values from Zhao et al., 2013. [3]Values from Mašek et al., 2013. [4] Values measured at 350°C. [5]Values from Ghania et al. 2013. [6]Range of temperature from studies.

The studies are in agreement that the primary factors involved in adsorption are pyrolysis conditions (Zhao et al., 2013; Ghania et al., 2013; Mašek et al., 2013). Mašek et al. (2013) concluded that, despite a lower temperature, rapid pyrolysis obtained the same surface areas than slower pyrolysis at elevated temperatures. Ghania et al. (2013) determined that, with temperatures increasing from 450-

600°C, the BET surface area increased. Past this point, a reduction in surface area occurred, likely due to the presence of impurities clogging pores (Ghania et al., 2013). Further evidence was observed by Tsai et al., (2012), who noticed increasing pore properties with temperature, but decreasing nitrogen and oxygen content. This was due to the volatilization of nitrogen and oxygen bearing compounds in the manure biochar (Tsai et al., 2012).

Biochar has been shown to operate as an effective soil conditioner, increasing cation exchange capacity, pH, and water retention (Uchimiya et al., 2010). As a soil conditioner, work suggests that it functions at a higher capacity than traditional fertilizer (Lehmann and Joseph, 2009); in part due to a higher charge density, which improves nutrient retention (Liang et al., 2006). Steiner et al., (2007) report that metal uptake and minimal nutrient release can also occur, further increasing soil quality. The majority of research (Sneath et al., 2013; Beesley et al., 2011; Fellet et al., 2011; Uchimiya et al., 2011) has focused on the use of biochar as a soil conditioner, and measured the results related to metal mobility and plant revegetation. Sneath et al., (2013) investigated biochar in conjunction with iron shavings for heavy metal removal, and found that biochar increases pH, increasing As mobility. The uptake to plants, as a result, was increased as well. Fellet et al., (2011) investigated mine waste remediation using biochar and determined that biochar increases water retention in soils. Higher water retention in soil allows for longer contact time between root and water, which allows for ameriorated plant uptake of nutrients. This increases the effectiveness of phytoremediation. A study conducted by Bailey et al. (1999) removed typical mining related metals (Cd, Cr, and Pb) through the use of low cost, natural materials. The use of natural materials as adsorbents is therefore feasible. This was further encouraged by Beesley et al. (2011), who concluded that natural materials such as biochar are a good candidate for environmental remediation.

Natural materials such as biochar present a reasonable alternative to contaminant remediation using adsorbents, as little material preparation is required (Bailey et al., 1999). However, some issues associated with natural materials include phenol release (Vázquez et al., 1994) and water discoloration (Bailey et al., 1999). Specifically, Bailey et al. (1999) noticed discoloration due to phenolic compounds in tannin rich materials such as bark. Vázquez et al. (1994) suggested acidified formaldehyde to remove these compounds. Chemical pretreatments of natural materials can limit these adverse effects; however subsequent waste streams may be formed (Vázquez et al. 1994).The advantage of biochar is that thermal preparation of the material eliminates impurities through volatilization, limiting the release of organic compounds such as phenols and discoloration agents (Ghania et al., 2013).

Despite the research on characterization of biochar and feasibility studies of biochar as an adsorbent, there lacks research on biochar as a potential adsorbent for oil sands contaminants, specifically those found in Northern Alberta. In addition, the use of biochar solely as an adsorbent and without consideration to plant growth has been sparsely investigated.

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Chapter 3 - The Adsorption of Naphthenic Acids onto Glacial Till and Wood Creek Sand Channel Sand Underlying the South Tailings Pond

3.1 Introduction

Canada's oil sands, with a proven reserve of 170 billion barrels, are the world's third largest behind Saudi Arabia (264.5 billion barrels) and Venezuela (211.2 billion barrels; Government of Alberta, 2013). Current production of approximately 1.7 million barrels per day is divided equally amongst *in situ* mining and truck-and-shovel operations (Government of Alberta, 2013). Surface mining, conducted solely in the Athabasca Region, creates a wet and dry waste stream and necessitates the construction of tailings retainment structures. Water withdrawal concerns have encouraged the recycling of process water to the extent of process impairment due to water quality (Allen, 2008). The extensive water reuse has also concentrated contaminants to toxic levels (Fedorak and Coy, 2006).

The tailings ponds are primarily built on the underlying clay-till, which provides a reasonable barrier through which tailings water will not rapidly migrate (Holden et al., 2011). However, one pond, Suncor's South Tailings Pond, is built on an area with thin or absent till. Approximately 50% of this tailings containment facility is built upon a glaciofluvial outwash channel, the Wood Creek Sand Channel. This presents a channel through which contaminants may migrate into receiving water bodies (Holden et al., 2011). In a seepage study, Abolfazlzadehdoshanbehbazari et al. (2013) suggested a rate of 0.9 m over the two year trial period, measuring the movement of ^{2}H and ^{18}O tracers.

The tailings contaminants of concern are mainly metals, salts and organic compounds that have been concentrated through continuous water reuse (Allen, 2008). Naphthenic acids have been the focus of oil sands organic contaminant research due to their complexity, toxicity to aquatic organisms and potential to migrate through aqueous systems. Studies have focused on the detection of the compounds (Grewer et al., 2010; Han et al., 2010; Martin et al., 2008), while others study the toxicological effects (Fedorak and Coy, 2006) and remediation (Small et al., 2012; Gamal El-Din et al., 2011). Yet there remains a knowledge gap in the fate of naphthenic acids as they migrate below the tailings ponds.

Furthering current work on the enhanced data resolution of naphthenic acids can also be undertaken in conjunction.

Understanding the subsurface migration of naphthenic acids presents a challenge, as geochemistry and geostratigraphy can vary highly (Janfada, 2007). This can limit the strength of batch tests, as they use a limited amount of material, Therefore, sorption tests apply only to the individual sediment, as each case may present unique soil characteristics. Naphthenic acid concentration in OSPW can be monitored as it is mixed with subsurface till and sand to determine if there is significant sorption or desorption. The response will indicate whether, as OSPW migrates through the subsurface, significant changes in naphthenic acid concentration will occur. These changes in concentration will be measured using GC-FID primarily. However, more detailed analysis of naphthenic acids can indicate whether preferential adsorption is occurring (observed by Janfada, 2007). Measurement using ESI-FTICR-MS can provide the resolution necessary to determine any preferential adsorption. It is necessary to continue previous work on ESI-FTICR-MS (Grewer et al., 2010) for oil sands remediation purposes. The enhanced data resolution of naphthenic acid detection relies on the sensitivity of the instrument. A machine such as the ultrahigh resolution electrospray ionization fourier transform ion cyclotron resonance mass spectrometer can identify individual naphthenic acid compounds, with the potential to include isotopes and sodium dimers (Grewer et al., 2010).

The objectives of this study are to:

1. Determine if any naphthenic acid adsorption is occurring when sediment underlying Suncor Energy Inc.’s STP is mixed with OSPW.
2. Compare the measurement of naphthenic acids using ESI-FTICR-MS, GC-FID and FT-IR.

This work will provide further understanding in the fate of naphthenic acids in the natural environment as well as an increased understanding of the distribution of compounds within OSPW.

3.2 Procedure

3.2.1 Adsorption media preparation

Core sampling was completed by SDS Drilling at Suncor Energy Ltd.’s STP using a 1503 Nodwell SONIC Drill Rig. Lexan casing enclosed the samples as the drill was operating, limiting the interaction between sediment and air. Further capping and sealing occurred when samples were shipped. Cores were frozen after being drilled, shipped frozen, and stored frozen prior to use in this study. Two core samples were selected for the adsorption bench scale experiment. The first, Core 4D, was taken at a depth of 38.1 meters below ground level while the second, core 4B, was 60.96 meters below ground level.

The American Society for Testing and Materials (ASTM) procedure for batch type adsorption experiments suggests durations of 24 h (ASTM 2008). To ensure equilibrium was achieved at that time, three ratios of sediment:OSPW were selected and shaken at 12 5rpm for 48 h. The sediment:OSPW ratios selected were 1:10, 1:12 and 1:15 (weight:volume) as suggested by ASTM (2008), Chang and Wang (2002), and Barone et al. (1992). Samples achieved equilibrium after 48 hours, after which limited naphthenic acid concentration change was observed. The average ratio, 1:12, was selected for use.

Frozen core samples were thawed and dried at 110°C for 24 h. Approximately 42 g of dried sediment was placed in a 1L glass Corning Pyrex Erlenmeyer flask (Fisher Scientific, Waltham, Massachusetts, USA) mixed with 500 mL of OSPW and shaken at 125 rpm for 48 h. During shaking, samples were capped with aluminium foil and remained aerobic at room temperature. Sample times were 3 h, 6 h, 12 h, 24 h and 48 h to obtain a time distribution of naphthenic acid concentration. Negative and positive controls, OSPW without sediment and sediment with deionized water respectively, were done in tandem. Once taken, samples were centrifuged at 3750 rpm for 20 minutes and filtered through 0.45 µm nylon filters.

A similar test was done anaerobically to determine if the presence of oxygen altered the distribution of naphthenic acids. 16 g of sediment was mixed with 200 mL of OSPW in a 500 mL Corning Pyrex Erlenmeyer flask (Fisher Scientific, Waltham, Massachusetts, USA). OSPW was purged with nitrogen and sealed in an anaerobic chamber using thread seal tape, a rubber stop and duct tape. The anaerobic chamber provides positive pressure at 5% CO_2, 5% H_2 and balanced with N_2. An indicator was mixed and kept in the chamber to ensure conditions remained anaerobic. Sample frequency and controls remained constant.

3.2.2 Naphthenic acid extraction

Extraction of the naphthenic acid compounds was done using dichloromethane as a solvent. Samples were mixed with 1M NaOH until a pH of >10 was achieved. This ensures acid extractable naphthenic acids remain in solution while any other organic compounds that dissolve in methylene chloride are removed. Approximately 5 mL of dichloromethane was added to 20 mL of sample and shaken. As the solution settles, organic compounds dissolve in the solvent. Dichloromethane was then transferred to a waste vial and discarded. The process was repeated twice to ensure full removal of organic compounds. Samples were then acidified with 0.25M HCl (Sigma Aldrich co., St. Louis, MO, USA) to a pH of <2. Acid extractable naphthenic acids are then dissolved in dichloromethane, which was transferred to a 40 mL glass vial (Sigma Aldrich co., St. Louis, MO, USA) to dry. The process was again repeated twice, ensuring all naphthenic acids were dissolved in dichloromethane. Once samples were dry, 1mL of dichloromethane was added, mixed, and transferred to a 2 mL target DP vials (National Scientific, Rockwood, Tennessee, USA). The transfer was repeated twice to ensure all naphthenic acids were transferred.

3.2.3 Comparison study

The development of an enhanced measurement technique for naphthenic acids was undertaken following the recommendation from Grewer et al. (2010). Briefly, it was suggested that using ultrahigh resolution Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (ESI-FTICR-MS) could identify individual naphthenic acid compounds with the general formula $C_nH_{(2n+z)}O_x$ (with carbon number [*n*] values ranging from 5-33, saturation [*z*] from 0 to -12 and oxygen number [*x*] from 2-5). This method was further refined to include sodium dimers and carbon isotopes. To determine the precision of the data analysis, a comparison study was done. 10 mL OSPW was extracted (as detailed in Section 3.2.2) and measured using FT-IR, GC-FID and ESI-FTICR-MS.

3.2.4 Analysis

Analysis of OSPW was done using FT-IR, GC-FID and ESI-FTICR-MS. Extraction procedures were identical for each method, while the analysis will be described in detail.

3.2.4.1 Laboratory Analysis of Sediments

Samples analyzed for CEC, exchangeable cations and pH followed the procedure introduced by McKeague (1978). Samples were mixed with NH_4Ac and shaken. The principle is to measure the uptake of NH_4Ac to represent the total potential uptake of cations of a sediment. This can have errors in sediments with gypsum or lime, as elevated Ca^{2+} concentrations may interfere with adsorption. This will lead to higher than expected Ca^{2+} values and a smaller CEC. Exchangeable cations are measured by digesting soil and subsequent analytical measurements. The pH was measured using a 1:2 soil water ratio, wherein soil is mixed with distilled water and pH in the solution is measured.

Particle size distribution was measured following Carter and Gregorich (2008). Briefly, samples are sieved through 10, 20, 40, 100 and 200 sieve number mesh to obtain the coarse fraction particle size distribution. Hydrometer testing provides results on the fine fraction, where the remaining sediment from sieving is mixed in slurry and placed in a hydrometer. The hydrometer depth is correlated to a diameter of particle size using a known soil density.

C and N percentages were measured following Ulery and Drees (2008). Samples for nitrogen and carbon measurements are over dried and stored in a desiccator until use. Thermogravimetric analysis was done to measure the ratio of nitrogen and carbon in sample, measured a thermobalance. Available nitrogen and carbon is measured in a similar manner, however samples are first mixed with water to remove excess carbon and nitrogen that is not readily available for reaction (Pansu and Gautheyrou, 2006).

3.2.4.2 Fourier Transform Infrared Spectrometry

Comparison study samples were analyzed using a Fourier Transform Infrared (FT-IR) Spectrometer. Approximately 5g of dichloromethane was added to dried samples and transferred to an FT-IR cell (0.1 mm pathlength KBr cell, International Crystal Laboratories, Garfield, New Jersey, USA). The FT-IR will pass an infrared light through a 3mm thick sample, and measure the change in adsorbance. Jivraj et al. (1995) identified the adsorbences of 1743 nm^{-1} and 1706 nm^{-1} as oil sands naphthenic acids. Calibration was done using Merichem model naphthenic acids at 6 different concentrations. The calibration curve is provided in Appendix A.

3.2.4.3 GC-FID

48 h batch sorption test samples were analysed for naphthenic acids using a gas chromatographer equipped with a flame ionization detector. Standards were prepared using 1000 mg/L heptadodecanoic acid. Three standard concentrations were used to create the calibration curve: 10 mg/L, 25 mg/L and 50 mg/L. This standard curve, as well as one produced with Merichem model naphthenic acids, is provided in Appendix A. 25 µL of *N*-*tert*-Butyldimethylsilyl-*N*-methyltrifluoroacetamide (MTBSTFA) were added to each sample, as well as the standards, as a derivitizing agent. Samples were then transferred to a 60ºC glass oven for 20 minutes. Samples were analyzed within 48 hrs to ensure accurate values were measured. A calibration curve is provided in Appendix A.

The following parameters were used in the measurement of naphthenic acids using an Agilent 7890A GC System (Agilent Technologies, Santa Clara, California, USA). The splitless inlet temperature was 300ºC at 30 psi, with a septum purge flow of 5 mL/min. The column used was an Agilent J&W GC column (DB-5MS UI). The program was as follows: initial temperature of 50ºC, holding for 2 minutes. The ramp was 30ºC/min to a temperature of 320ºC, holding for 5 minutes and running for 16 minutes. The detector was a flame ionization detector at 350ºC with an H_2 flow at 40 mL/min, an air flow of 450 mL/min and an He flow of 25 mL/min.

3.2.4.4 Ultrahigh Resolution Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (ESI-FTICR-MS)

Select samples were analyzed using an ultrahigh resolution electrospray ionization fourier transform ion cyclotron resonance mass spectrometer (Bruker 9.4 T Apex-Qe FTICR mass spectrometer, Bruker Daltonics, Billerica, Massachusetts, USA). Analysis was done in the University of Alberta Chemistry Department, following the procedure outlined by Grewer et al. (2010). Samples preparation involved the dilution of approximately 10 mg of naphthenic acids using 3:1 methanol:toluene to a final concentration of 0.001 to 0.002 mg/mL (Grewer et al. 2010). Sample was introduced with an Apollo II MTP source at a flow rate was 2 µL/min with an external hexapole collision cell accumulation time of 10 s. Samples were injected into the ion cyclotron resonance stage using a side-kick trap. Time domain data sets (4 million points) were summed (16 acquisitions) to enhance signal-to-noise. Calibration was done using a mixture of C_{17} and C_{26} saturated carboxylic acids.

3.3 Results and Discussion

3.3.1 Sediment and Naphthenic Acid Concentration Analysis

Samples were sent to a commercial laboratory (Exova Canada Inc., Mississauga, ON, Canada) for soil classification, including grain size distribution, TOC, TIC, exchangeable ions, soil pH and CEC. Raw data can be found in Appendix A. A summary of information is provided in Table 3-1.

Table 3-1: Properties of sediment used in a batch sorption experiment including organic and inorganic carbon, cation concentration, cation exchange capacity and grain size classification.

Property	Soil 4B	Soil 4D	Nominal Detection Limit
Organic Carbon (%)	0.28	1.66	0.05
Inorganic Carbon (%)	0.12	0.61	0.05
Na^+ (mg/kg)	58	29	20
Ca^{2+} (mg/kg)	1190	3020	10
Mg^{2+} (mg/kg)	44	205	5
K^+ (mg/kg)	27	99	20
Cation Exchange Capacity (meq/100g)	<4	8	4
Sand (%)	93.4	57.4	0.1
Silt (%)	2.4	25.8	0.1
Clay (%)	4.2	16.8	0.1
Moisture (%)	10.8	11.2	0.1
pH	8.2	8.0	-

The soils presented have elevated Ca^{2+} concentrations when compared with other cations in solution. Calculating the exchangeable sodium percentage (ESP) is valuable in determining if the soil is sodic or normal. From Essington (2003), the ESP can be calculated using Equation 3-1.

$$ESP = 100 * \frac{ESR}{(1 + ESR)}$$

Equation 3-1

Where ESR = exchangeable sodium ratio. The ESR can be calculated using Equation 3-2 or Equation 3-3.

$$ESR = \frac{[NaX]}{[CEC - NaX]}$$

Equation 3-2

$$ESR = \frac{[NaX]}{[(Ca + Mg)X * 0.5]}$$

Equation 3-3

Where NaX is the concentration of Na (in units of mmol$_c$/kg) and (Ca+Mg)X is the concentration of Ca and Mg (in units of mmol$_c$/kg). A value in mmol$_c$/kg is the charge equivalence of an ion, meaning that Ca^{2+}, for example, will have an effective concentration of half, due to the charge. This is demonstrated in Equation 3-4.

$$[Ca^{2+}]\left(\frac{mg}{kg}\right) = \frac{[Ca^{2+}]}{\frac{40.08 g/mol}{2\ Charges}} = \frac{[Ca^{2+}]}{20.04\ mol_c} = [Ca^{2+}]\left(\frac{mmol_c}{kg}\right)$$

Equation 3-4

Where $[Ca^{2+}]$ is the concentration of Ca^{2+} ions in sediment. Using Equation 3.2 and 3.1 for Soil 4D and 3.3 and 3.1 for Soil 4B, the ESP can be calculated. These values are presented in Table 3-2.

Table 3-2: Summarized values of ESR, ESP and CEC calculated using Equation 3-2, Equation 3-3, and Equation 3-4. Values presented are an approximation of soil sodicity.

Parameter	Soil 4B	Soil 4D
Na^+ (mmol$_c$/kg)	58	29
Ca^{2+} (mmol$_c$/kg)	1190	3020
Mg^{2+} (mmol$_c$/kg)	44	205
K^+ (mmol$_c$/kg)	27	99
ESR (unitless)	8E-2	2E-1
ESP (unitless)	7	2
CEC (meq/kg)	57[1]	80
CEC (meq/100g)	6[1]	8

[1] Back calculated using Equation 3.2

A soil with an ESP>15 is generally defined as sodic (USSLS, 1954). A more updated definition stipulates that a soil with an ESR>0.1 can be deemed sodic (Essington, 2003). Given the conditions of the soil, the former definition is more accurate. Despite high Ca^{2+} concentrations, the number of sites occupied by Na^{+} remains low. The low sodicity also means that migration of water through the subsurface will not be hindered to an extensive degree. A sodic soil will produce an overlap in double diffuse layers, which promotes repulsion between particles. These active repulsion forces will inhibit water entry, thereby reducing the hydraulic conductivity (Essington, 2003). This reduction in hydraulic conductivity is not as dominant in Ca^{2+} rich soils, as the double diffuse layers tend to remain smaller, allowing the passage of water through the soil lattice. This, in turn, allows for a more elevated hydraulic conductivity (Essington, 2003). Figure 3-1 demonstrates the relationship between hydraulic conductivity and observed ESP.

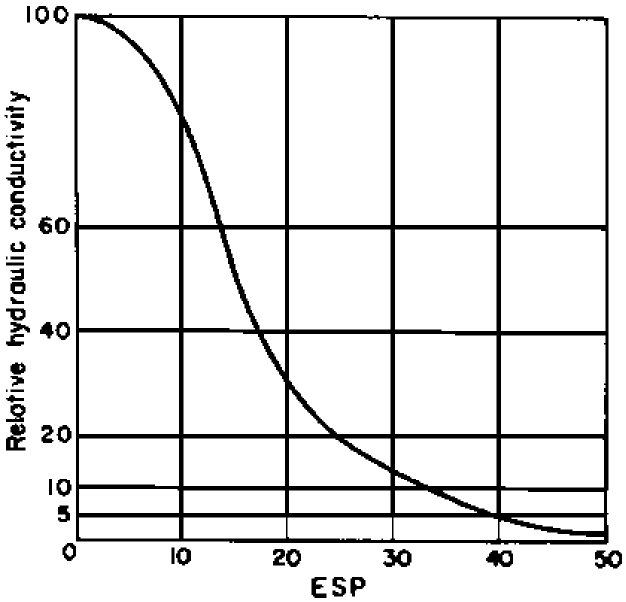


Figure 3-1: Relationship between relative hydraulic conductivity and ESP. A slow decrease is observed initially (<10 ESP), after which a decreasing conductivity is observed (10<ESP<40). Elevated ESP values (>40) do not decrease the conductivity rapidly. Figure taken directly from Abrol et al., 1988.

With relatively low ESP values, we can expect limited hydraulic conductivity inhibition from soil sodicity.

Naphthenic acid concentrations were also measured in the soils. The initial concentration of naphthenic acids was an average of 3.23 mg/L (from triplicate initial samples of 3.56, 3.04 and 3.08 mg/L). Concentrations of naphthenic acids fluctuated from initial (3.23 mg/L) to 4.47 mg/L. Final concentrations were 4.33, 4.26 and 3.22 mg/L for 1:12 aerobic clay, 1:12 aerobic sand and 1:12 anaerobic sand respectfully. Samples were analyzed at 0 h, 3 h, 6 h, 12 h, 24 h and 48 h, and are displayed in Figure 3-2.

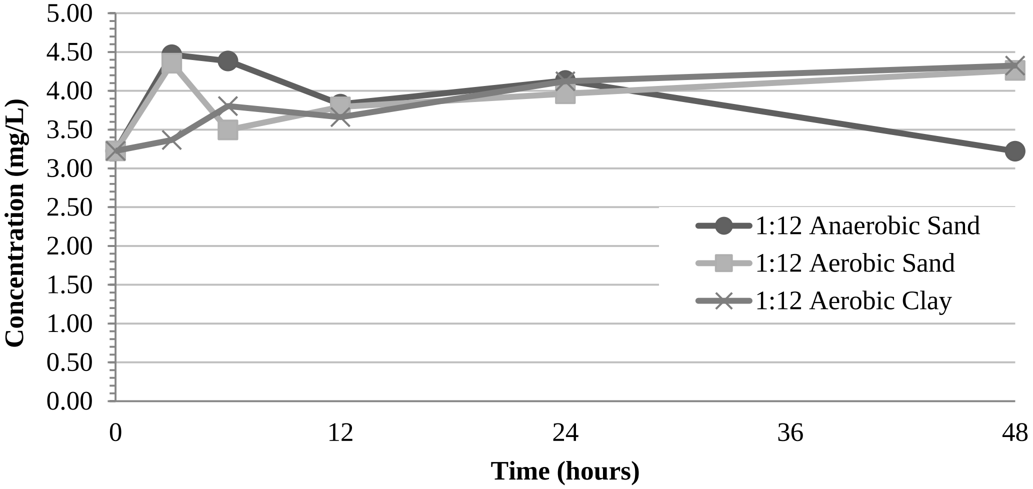


Figure 3-2: Naphthenic acid concentration fluctuation from OSPW mixed with native sediment (depth of 38.1 m for 1:12 Aerobic Clay and 60.96 m for 1:12 Aerobic Sand and "1:12 Anaerobic Sand") for the duration of the 48 h batch test.

The results are consistent with Peng et al. (2002) who found a very low adsorption isotherm (limited adsorption) occurring in local sediment using model naphthenic acids. In their study, two soils were used from Syncrude Canada Ltd., the properties of which are summarized in Table 3-3. Also provided are the related properties of soil 4B and 4D used in the batch sorption experiment.

Table 3-3: A comparison of values obtained by Peng et al. (2002) and sediment used in a 48 h batch sorption test. Significant differences in Ca^{2+}, K^{+}, and cation exchange capacity were observed.

Property	Soil No. 1	Soil No. 2	Soil 4B	Soil 4D
Organic Carbon (%)	1.6	2.7	0.28	1.66
Inorganic Carbon (%)	0.23	0.26	0.12	0.61
Na (mg/kg)	64[1]	107[1]	58	29
Ca (mg/kg)	98[1]	177[1]	1190	3020
Mg (mg/kg)	16[1]	37[1]	44	205
K (mg/kg)	3[1]	4[1]	27	99
Cation Exchange Capacity (meq/100g)	16.2	19.4	<4	8
pH	7.7	7.7	8.2	8.0

[1] Reported in µg/g.

Consistent with Peng et al. (2002), little adsorption was observed. Both materials had relatively low organic and inorganic carbon (Essington, 2003). In general, a decrease in soil organic matter leads to a smaller cation exchange capacity, as organic matter has a high affinity for adsorption (Brady and Weil, 2007). Cation exchange capacity is also governed by cation selectivity, or the lyotropic series (Leberman, 1991). The series stipulates that the greater the valence of a cation, and the smaller the hydrated radius, the greater the adsorption (Brady and Weil, 2007). In general, the selectivity can be seen as:

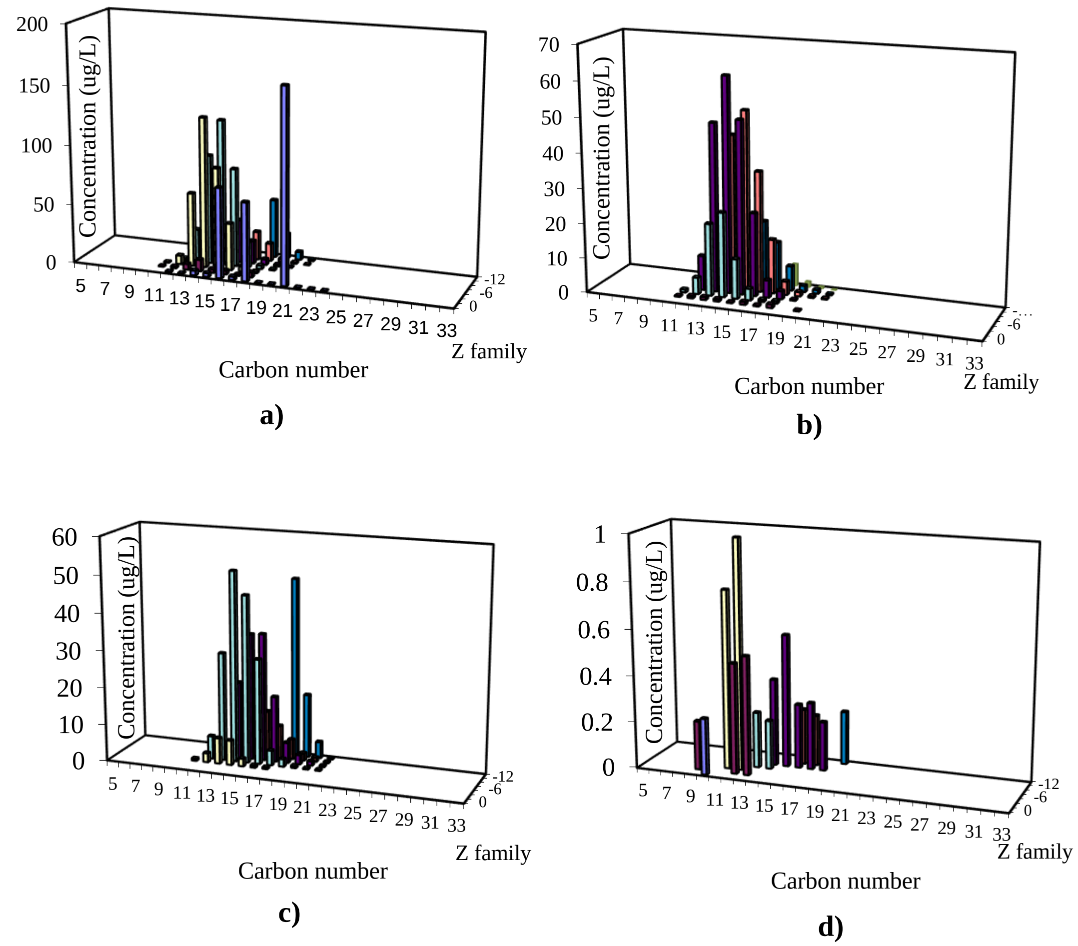
$$Al^{3+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Cs^{+} > K^{+} = {NH_4}^{+} > Na^{+} > Li^{+}$$

Equation 3-5

From Equation 3-5, an aluminum ion in solution will preferentially adsorb over any cation present with a smaller hydrated radius and valence. With an increase in cation concentration bound to the surface of soils 4B and 4D, it is expected that less adsorption will occur. The soils prepared in this study have: 1) a smaller fraction of organics (leading to a smaller cation exchange capacity [Brady and Weil, 2007]), 2) a larger concentration of cations that may interfere with adsorption processes (Leberman, 1991; Brady and Weil, 2007), resulting in 3) a smaller cation exchange capacity and therefore a smaller potential for naphthenic acid adsorption (Brady and Weil, 2007). Cation exchange capacities are consistent with those found by Holden (2012) who used similar sediments in his study. It is undetermined whether fluctuations in naphthenic acid concentration were the result of adsorption/desorption reactions caused by porewater contact (Martin-Gullón and Menéndez-Diaz, 2006), naphthenic acid adsorption onto inorganic minerals, with subsequent inorganic metal hydroxide formation (Nodwell, 2011), or simply natural fluctuations caused by machine sensitivity. To accompany these results and determine if fluctuations are consistent between measurement techniques, 1:12 anaerobic clay was analyzed using ESI-FTICR-MS. The measurement technique has a higher resolution, allowing for more accurate measurements of naphthenic acids concentration.

3.3.2 OSPW Analysis Using Ultrahigh Resolution ESI-FTICR-MS

A spreadsheet was developed to measure individual components present in naphthenic acids. Using a carboxylic standard (Carbon number 21), response intensity can be correlated properly to those of naphthenic acids bearing a similar structure. Included in that analysis are all naphthenic acids bearing the general formula $C_nH_{(2n+z)}O_x$, where n is carbon number, z is the degree of saturation (a negative value meaning unsaturated) and x is the oxygen number. The n values range from 5-33, z values range from 0 to -12 (intervals of 2) and x values range from 2-5. Also included in the analysis are sodium dimers and isotopes. Initial OSPW samples were analyzed using ESI-FTICR-MS spreadsheet, and are displayed in Figure 3-3. Figure 3-3 a), Figure 3-3 b), Figure 3-3 c) and Figure 3-3 d) are representative of naphthenic acids bearing the formula $C_nH_{(2n+z)}O_2$, $C_nH_{(2n+z)}O_3$, $C_nH_{(2n+z)}O_4$ and $C_nH_{(2n+z)}O_5$ respectfully. Further output, including C^{13} isotopes and sodium dimer concentrations are presented in Figure 3-4.



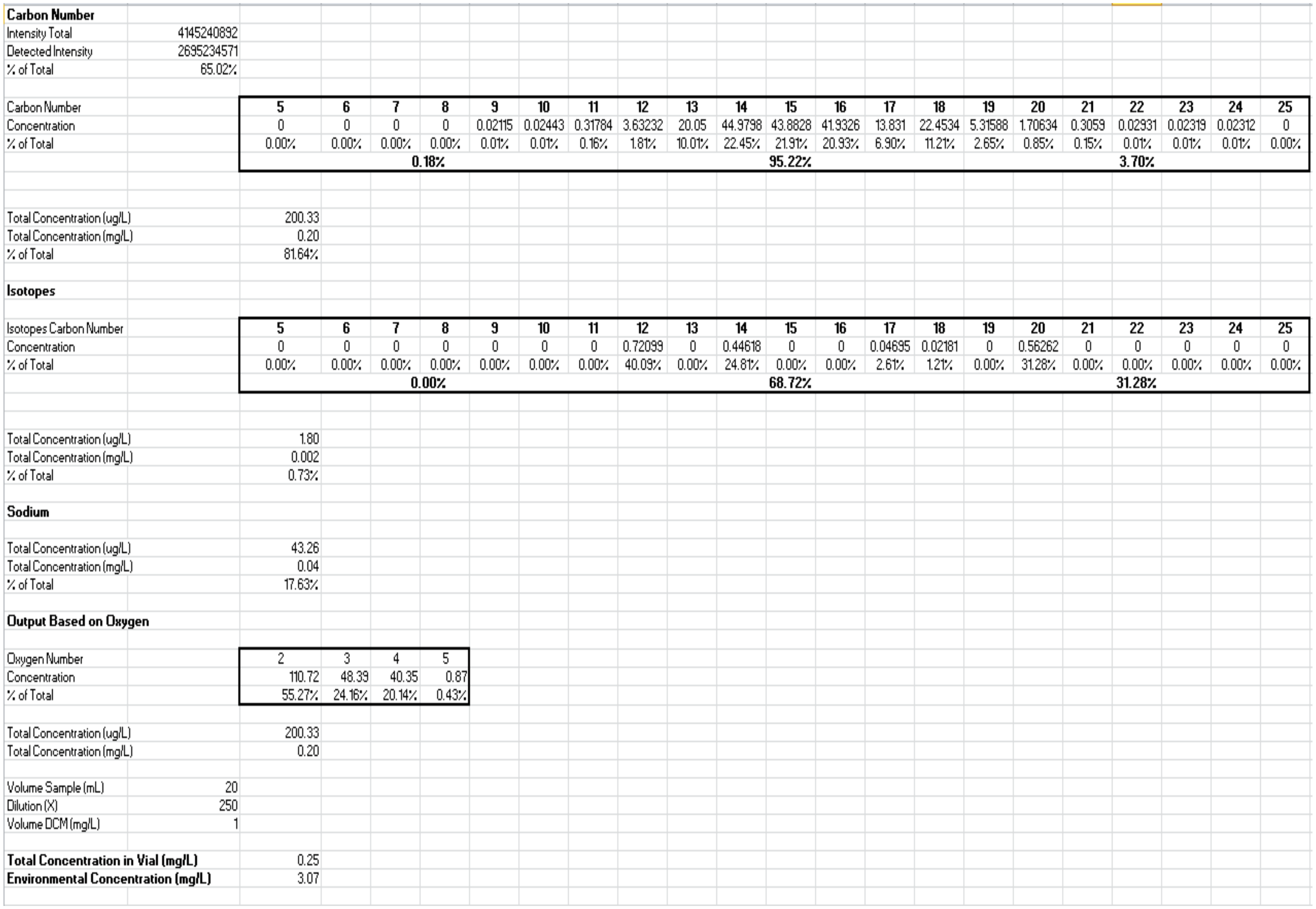
a)

b)

c)

d)

Figure 3-3: ESI-FTICR-MS data for the initial OSPW characterization. Charts represent naphthenic acids in the generic formula $C_nH_{(2n+z)}O_x$, with a) $C_nH_{(2n+z)}O_2$, b) $C_nH_{(2n+z)}O_3$, c) $C_nH_{(2n+z)}O_4$ and d) $C_nH_{(2n+z)}O_5$.



Carbon Number

Intensity Total	4145240892
Detected Intensity	2695234571
% of Total	65.02%

Carbon Number	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Concentration	0	0	0	0	0.02115	0.02443	0.31784	3.63232	20.05	44.9798	43.8828	41.9326	13.831	22.4534	5.31588	1.70634	0.3059	0.02931	0.02319	0.02312	0
% of Total	0.00%	0.00%	0.00%	0.00%	0.01%	0.01%	0.16%	1.81%	10.01%	22.45%	21.91%	20.93%	6.90%	11.21%	2.65%	0.85%	0.15%	0.01%	0.01%	0.01%	0.00%
	0.18%							**95.22%**							**3.70%**						

Total Concentration (ug/L)	200.33
Total Concentration (mg/L)	0.20
% of Total	81.64%

Isotopes

Isotopes Carbon Number	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Concentration	0	0	0	0	0	0	0	0.72099	0	0.44618	0	0	0.04695	0.02181	0	0.56262	0	0	0	0	0
% of Total	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	40.09%	0.00%	24.81%	0.00%	0.00%	2.61%	1.21%	0.00%	31.28%	0.00%	0.00%	0.00%	0.00%	0.00%
	0.00%							**68.72%**							**31.28%**						

Total Concentration (ug/L)	1.80
Total Concentration (mg/L)	0.002
% of Total	0.73%

Sodium

Total Concentration (ug/L)	43.26
Total Concentration (mg/L)	0.04
% of Total	17.63%

Output Based on Oxygen

Oxygen Number	2	3	4	5
Concentration	110.72	48.39	40.35	0.87
% of Total	55.27%	24.16%	20.14%	0.43%

Total Concentration (ug/L)	200.33
Total Concentration (mg/L)	0.20

Volume Sample (mL)	20
Dilution (X)	250
Volume DCM (mg/L)	1

Total Concentration in Vial (mg/L)	0.25
Environmental Concentration (mg/L)	3.07

Figure 3-4: Spreadsheet output for the characterization of naphthenic acids in OSPW. Carbon number provides an output based on carbon number *n*, while isotope output is solely the concentration of C^{13} isotopes based on concentration, and sodium output presents the concentration of sodium dimers (excluding values obtained from the O_2 series).

Figure 3-4 is a complete output from the characterization of the first 1:12 anaerobic clay sample. The total concentration is 3.07 mg/L, of which 81.6 % (0.25 mg/L) is $C_nH_{(2n+z)}O_x$. Isotope concentrations represent 0.7% (0.002 mg/L) while 17.6% (0.04 mg/L) are sodium dimers. Sodium dimer values exclude $C_nH_{(2n+z)}O_2$, as a sodium molecule cannot attach itself to a carboxylic acid and remain in a negative state, required for the analysis.

Within the detected naphthenic acids (0.20 mg/L), 55.3% (0.11 mg/L) are “classical” naphthenic acids bearing the formula $C_nH_{(2n+z)}O_2$, while the remaining 44.73% (0.09 mg/L) are from $C_nH_{(2n+z)}O_3$, and $C_nH_{(2n+z)}O_4$. $C_nH_{(2n+z)}O_5$ showed no detectable concentration. The predominance of naphthenic acids, based on carbon number, is between C_{12} to C_{18}, with 95.2% (0.19 mg/L). Therefore, most naphthenic acids present in this sample of OSPW are midrange molecular weight compounds.

Several finding were in close agreement with Grewer et al. (2010), namely the detection of only ~30% of intensities being attributed to naphthenic acids. The remaining 70% are detected intensities that do not correspond to the classic or oxy-naphthenic acid formula (Grewer et al., 2010). Grewer et al. (2010) also found that aged water sources consistently contained the largest percentage of peaks attributed to “classical” naphthenic acids. However, the sum of the oxy-naphthenic acid (O_3 to O_5) concentration consistently exceeded the classic formula. This indicates that the source of tailings in the present study is relatively fresh when compared with aged samples acquired by Grewer et al. (2010) (Han et al., 2009). Furthermore, the presence of oxidized naphthenic acids indicates biodegradation is occurring (Han et al., 2009). Over time, the dominance of classic naphthenic acids increased (from 55.3% to 62.2%). This increase could enhance results from Janfada (2007), who observed preferential adsorption in the mid-high weight range naphthenic acids (C14-C37). It is likely that preferential adsorption/desorption of heavier molecular weight naphthenic acids is more active in samples than lower weight classic naphthenic acids.

Concentrations were calculated using ESI-FTICR-MS for 1:12 anaerobic clay. A limited fluctuation was also observed and presented in Figure 3-5. This observed fluctuation was also observed in the analysis of naphthenic acids using GC-FID. The difference in concentration can be attributed to the machine sensitivity between ESI-FTICR-MS and GC-FID.

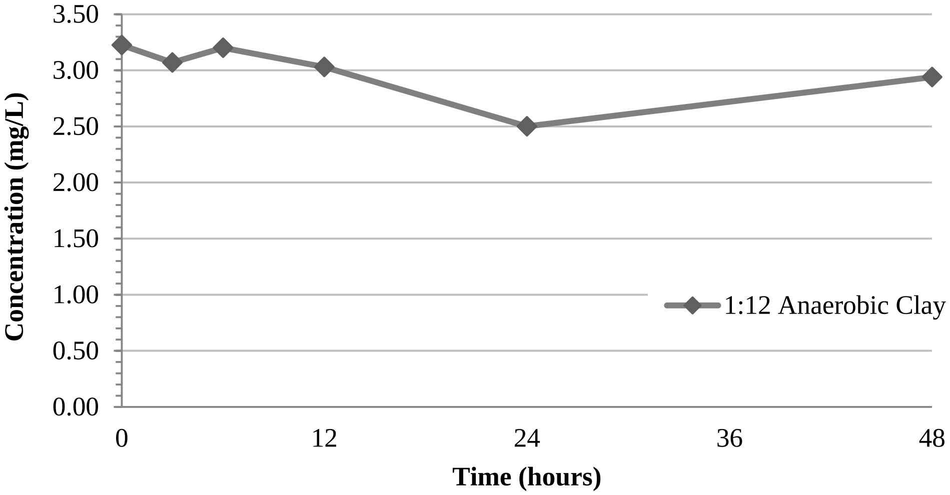


Figure 3-5: Concentration profile for naphthenic acids analyzed using ESI-FTICR-MS. Total concentration, the summation of $C_nH_{(2n+z)}O_2$, $C_nH_{(2n+z)}O_3$, $C_nH_{(2n+z)}O_4$, and $C_nH_{(2n+z)}O_5$, all C^{13} isotopes, and sodium dimers, is presented. Initial concentration from GC-FID data.

The limited adsorption of naphthenic acids is due to the physical properties, specifically the hydrophobicity, of the compounds. As molecular weight increases, naphthenic acids tend to become more hydrophobic (Nodwell, 2011). Non-polar, hydrophobic compounds lack the strength to readily form weak bonds with adsorbents, limiting their uptake (Nodwell, 2011). Small (2011) also suggests that the dissociation of naphthenic acids are highly influenced by pH. In neutral-to-alkaline conditions (a pH of ~9 in this study), naphthenic acids tend to remain in solution, further limiting the adsorption on natural sediment. Finally, naphthenic acids may be a force in asphaltene disintegration, though within OSPW this influence may be minimal (Brandal, 2005).

Results presented are consistent with trends observed by measurement using GC-FID. The fluctuation between concentrations measured using ESI-FTICR-MS was, at its maximum (between sample 2 and 4) 22%, while measurement using GC-FID fluctuated between 0.3% (1:12 Anaerobic Sand) and 30% (1:12 Aerobic Clay).

Separate samples were also analyzed to determine the variability between concentrations observed by ESI-FTICR-MS, GC-FID and FT-IR. This analysis will determine the average discrepancy between samples measured using the various techniques. These values are presented in Table 3-4.

Table 3-4: OSPW naphthenic acid concentration determined using GC-FID, FT-IR and ESI-FTICR-MS.

Naphthenic Acid Source	GC-FID (mg/L)	FT-IR (mg/L)	ESI-FTICR-MS (mg/L)
Horizon	60.8	118.4	10.3
STP	40.5	96.3	16.9
Pond 2/3	31.9	75.9	2.9
WIP	29.2	68.6	12.4

The results indicate a high variability between FT-IR, GC-FID and ESI-FTICR-MS. Though the analysis was done with GC-MS, a similar discrepancy between FT-IR was observed by Grewer et al. (2010). Normalization of data provides a means by which data can be meaningfully represented. This is presented in Table 3-5.

Table 3-5: Normalized (to FT-IR) OSPW naphthenic acid concentration determined using FT-IR, GC-FID and ESI-FTICR-MS. Average discrepancy between samples is also presented.

Naphthenic Acid Source	GC-FID (mg/L)	FT-IR (mg/L)	ESI-FTICR-MS (mg/L)
Horizon	0.51	1	0.09
STP	0.42	1	0.18
Pond 2/3	0.42	1	0.04
WIP	0.43	1	0.18
Average	0.45	1	0.12

Normalizing data to the highest detected concentration (FT-IR in every case) shows a larger consistency between GC-FID and FT-IR than ESI-FTICR-MS and FT-IR. The average relative concentration between GC-FID and FT-IR was 0.45 (45% of the concentration of FT-IR) while ESI-FTICR-MS was 0.12.

While it is currently the industry standard for naphthenic acid measurement (Zhao et al., 2012), FT-IR may often overestimate concentrations (Grewer et al., 2010; Yen et al., 2004). Scott et al. (2008) further report that this overestimation may be more pronounced in surface water. The primary reason for the overestimation is lack of sensitivity between measuring classic and non-classical naphthenic acids, as well as any additional organics that may adsorb at the same wavelength (Zhao et al., 2012).

Limited work is presented for the analysis of naphthenic acids using GC-FID. One study (Jones et al., 2001) used GC-MS and GC-FID to measure the acids in crude oil. The study stipulates that GC-FID can be advantageous when measuring the absolute carboxylic acid content. Since samples are combusted, the FID provides a reasonable measurement of non-ionisable compounds (ASTM, 2011), though lacks the sensitivity to measure individual naphthenic acids. Compounds with a similar weight and ionization potential may be detected as a naphthenic acid as well (Zhao et al., 2012).

ESI-FTICR-MS may carry limitations in its measurement from hydroxylated naphthenic acid measurement and elevated salt concentrations. The former may be an issue when samples are derivatized (Zhao et al., 2012). During the derivatization, carboxyl and hydroxyl function groups present on the naphthenic acids may both derivatize. This will cause error in measurement, as more samples are misrepresented and therefore measured incorrectly (Zhao et al., 2012). Wang and Kasperski (2010) also demonstrated interference from waters having elevated salt concentrations, such as those present in oil sands tailings. Elevated salt concentrations provide a large flux of ions to the machine, which may potentially block the electrospray probe (Wang and Kasperski, 2010).

Regardless of technique, most methods can only be considered semi-quantitative (Zhao et al., 2012). This is due to issues of naphthenic acid impurity and complexity when selecting a calibration standard. In most cases, model compound standards are used to correlate the response with oil sands naphthenic acids response. However the chemical composition and predominance in oil sands acids vary highly (Zhao et al., 2012). Therefore, a correlation between the calibration standard and oil sands naphthenic acids may not be accurate, thereby promoting the use of data as a semi-quantitative tool. Using machines that do not use model standards may eliminate this issue, however there is a lack of certainty if the standards used produce similar responses as naphthenic acids (Zhao et al., 2012).

3.4 Conclusions and Recommendations

In this study, the partitioning of naphthenic acids in local sediment underlying Suncor Ltd’s STP was examined. Part of the data was analyzed using ESI-FTICR-MS, and a novel output was produced to include the concentration of isomers and sodium dimers within OSPW.

Sediment analysis indicated that, underlying the STP, there exists a layer of larger clay fraction sediment and one of sand. These results are consistent with Holden (2012), who summarized the site geology. The fractions correspond to the layer of clay-till and Wood Creek Sand Channel under the STP.

Results from a 48 h batch sorption test indicate that little fluctuation in naphthenic acid concentration occurs when OSPW is mixed with sediment. This was due to the low cation exchange capacity and cation saturation of sediment. Specifically, high Ca^{2+} and Na^{+} values present within OSPW limit available receptors for adsorption.

Enhanced naphthenic acid data using ESI-FTICR-MS also confirmed results from Grewer et al. (2010), who showed that mono and dioxy-naphthenic acids compose approximately 50% of the total detected concentrations. Further data analysis reveals a small (0.14%) concentration of isomers present in the OSPW, and small (~2%) concentration of sodium dimers. Limitations of ESI-FTICR-MS include the inability to accurately identify individual sodium dimers and misdetection of other organic compounds responding in a similar fashion as samples.

Future work related to the adsorption of naphthenic acids onto sediment should enhance the soil characterization and provide a correlation to physical soil properties, such as an adsorption isotherm and adsorption parameters. These could be small values, however their determination could assist further in understand the fate of naphthenic acids within the sediment. Work on naphthenic acid characterization using ESI-FTICR-MS should include nitrogen and sulphur compounds. With the introduction of a sulphur and nitrogen bearing carboxylic acid standard, intensities can correlate to those compounds in the sample. It is possible to identify these nitrogen and sulphur bearing components with isotopes.

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Chapter 4 - Oil Sands Tailings Metal Removal Using Granular Delayed Coke

4.1 Introduction

The combined oil production between all operating companies in the Northern Alberta oil sands is approximately 1.7 million barrels per day. The upgrading process involves cracking the bitumen, creating lighter oil and a carbonaceous by-product, coke. Collectively, the oil sands companies predict over a billion m^3 of coke will be produced over the lifetime of their operations (Small et al., 2012a). The volume of coke presents a lifelong legacy for mining companies. Therefore, studies in coke management strategies, including its reuse as an adsorbent, are necessary to reduce the legacy of the operations.

Upgrading of bitumen occurs after bitumen has been separated from the sand in the hot water extraction process. In the Athabasca oil sands, two coking technologies are used: delayed and fluid coking (Chen and Hashisho, 2012). Delayed coking is a process where, once heated, coke particles are transferred to a drum, allowing separation to occur (Scott and Fedorak, 2004). Fluid cokes are produced at marginally higher temperatures, where thin layers of oil are sprayed on existing hot coke particles in a fluid coking drum (Scott and Fedorak, 2004). Both cokes exhibit similar compositions (Fedorak and Coy, 2006), however delayed coke tends to have more of a ‘sponge-like’ structure, while fluid cokes are more spherical and layered.

Impurities within both streams of coke, including metals (Small et al., 2012b) and high sulphur content (Lee and Choi, 2010) have limited the use of coke as a fuel source (Lee and Choi, 2010). Therefore, much of the oil sands coke is stockpiled (Chen and Hashisho, 2012). The high carbon content and availability of the coke has produced research interest using the by-product for contaminant remediation. One study in particular examined the activation of fluid and delayed coke and their potential for naphthenic acid removal (Small et al., 2012b). An issue within this study was the release of metals, in particular, V. Work from Puttaswamy (2011) has identified leaching of Al, Fe, Mn, Ni, Ti, and V. Delayed and fluid coke have been identified as potential contaminant adsorbents if impurities could be removed prior to use (Small, 2011).

The objective of this study will be to demonstrate the effectiveness of delayed coke, prepared in different conditions, at simultaneously removing metals and naphthenic acids from solution. In a previous study (Small et al., 2012b), delayed coke had successfully removed naphthenic acids from OSPW. The performance of the coke is expected to be similar; therefore this study will focus on the removal of metals. Groundwater beneath Suncor's STP was selected for use, as the contaminant concentrations reflect those that would be present when large scale remediation efforts are considered. Measuring the performance of coke under various preparation methods will be accomplished by:

1. Preparing coke with the following conditions: Raw coke stream of acid and non-acid washed delayed coke (75-150 µm, 0.8-2 mm), activated coke stream of acid and non-acid washed coke (75-150 µm).
2. Measure initial and final naphthenic acid concentration from 48 h batch sorption test to confirm coke functionality from Small et al. (2012).
3. Measure heavy metal concentration over the 48 h batch sorption test to determine if metal release or uptake is occurring.

This work will enhance existing studies on petroleum coke by adding a pre-treatment step to remove loosely bound surface contaminants. This will determine whether petroleum coke, once cleaned, can be used to remediate oil sands contaminants.

4.2 Procedure

4.2.1 Activation and Acid Washing of Delayed Coke

Delayed coke, obtained from Suncor Energy Ltd, was ground and sieved to 75-150 µm and 0.8-2 mm grain size. Crushing of coke, and further sieving to 75-150 µm necessitates additional material handling. Much of the coke could be sieved to 0.8-2 mm without grinding. A study using a 0.8-2 mm grain size is therefore merited, as limited additional material handling is required.

Preparation and activation of delayed coke was done using the procedure outlined by Small et al. (2012a). The coke was thermally activated using a muffle bed furnace, in which 20 g of coke was placed in a quartz reactor. Small et al. (2012a) determined the optimized conditions for activation of coke: 6 h activation time, 0.5 mL H_2O stream and 900°C under carbon dioxide. The furnace was initially purged of oxygen using $N_{2(g)}$ and heated to 900°C. At this point, activation began, and the system was heated with CO_2 and steam. Steam was injected using a 50 mL syringe pump, with tubing into the system wrapped in 150°C heat tape (Omega Engineering Inc. Stamford, Connecticut, USA). This ensured that steam did not condense prior to entering the furnace.

Delayed coke was acid washed to remove metals from the surface. Puttaswamy (2011) in particular noticed the loosely bound nature of V to coke, resulting in release upon contact with solution. The acid molarity was first optimized by testing 0.25M, 0.5M and 1M hydrochloric acid solution. All cases has a pH <2 and presented extensive metal release. A larger solution of 0.25M acid was prepared, and samples of delayed coke were washed. A mixture of coke and acid was washed on a shaker table for 24 h, and flushed with 1.5 L of deionized water. This process was repeated 2 times, after which delayed coke samples were dried in an oven at 110°C for 24 h.

4.2.2 Adsorption of Metals and Naphthenic Acids

Samples of raw and activated coke were prepared following the recommendations of Small et al. (2012b). The work suggests that the optimal dosage of coke for the treatment of trace metals and naphthenic acids are 5 g/L and 300 g/L for activated and raw coke respectively (Small et al., 2012a). Groundwater was sampled from Suncor Energy Ltd. in 2012 and stored in a sealed container at 4°C until use. Groundwater was selected for its increased concentration of trace metals relative to OSPW. Samples were taken June 2012, with a small volume taken from the more contaminated nest 2G, and more volume from nest 2A. Sample preparation is summarized in Table 4-1, with a target mass for activated coke of 0.625 g and 37.5 g for raw coke for 125 mL of groundwater.

Table 4-1: Masses of delayed coke with various preparation methods used for a 48 h batch sorption tests.

Sample	Mass Coke Added (g)	Volume of groundwater (mL)
Activated Coke (75-150 µm) 1	0.620	125
Activated Coke (75-150 µm) 2	0.623	125
Activated Coke + Acid Wash (75-150 µm) 1	0.626	125
Activated Coke + Acid Wash (75-150 µm) 2	0.622	125
Raw Coke (75-150 µm) 1	37.57	125
Raw Coke (75-150 µm) 2	37.58	125
Raw Coke + Acid Wash (75-150 µm) 1	37.49	125
Raw Coke + Acid Wash (75-150 µm) 2	37.79	125
Raw Coke (0.8-2 mm) 1	37.51	125
Raw Coke (0.8-2 mm) 2	37.52	125
2mm Raw Coke + Acid Wash (0.8-2 mm) 1	37.48	125
2mm Raw Coke + Acid Wash (0.8-2 mm) 2	37.48	125

Samples were mixed with groundwater in a 250 mL beaker and shaken for 48 h. Initial and final samples were taken for naphthenic acid and trace metal analysis, while samples at 3 h, 6 h, 12 h and 24 h were taken exclusively for trace metal analysis.

4.2.3 Analysis

Initial and final samples were taken for naphthenic acid analysis. Extraction and measurement was done as described in Chapter 3, Section 3.2.2.

4.2.3.1 ICP-MS

Samples for trace metal analysis were done using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), the current industry standard for trace metal analysis. Samples were prepared first by filtering 10 mL through a 0.45 µm nylon filter. Samples were then diluted 20X and 25X, for non-acid washed and acid washed experimentation respectfully. 250 µL of internal standard solution was added to each sample, then diluted to 50 mL using trace metal grade 1% $HNO_{3(aq)}$ (Sigma Aldrich co., St. Louis, MO, USA). 5 standards were prepared using stock solutions. The following volumes of elemental solutions were added to create a 0.2 µg/L, 2 µg/L, 10 µg/L, 50 µg/L and 100 µg/L: 1 µL of B, P and Mo, 10 µL of B, P and Mo, 50 µL of B, P, Mo and Si, 250 µL of B, P, Mo and Si and 500 µL of B, P, Mo and Si respectfully. A sixth standard was prepared containing 200 µg/L Al, 500 µg/L Si and 500 µg/L Fe, K, Ca, Na, and Mg. Prior to sampling, daily performance checks and optimization were passed.

4.2.3.2 Surface Area and Pore Size Distribution

Samples for surface area analysis were done using nitrogen adsorption isotherms. Preparation involved first drying samples at 100ºC to assist in the degassing process and weighed to ensure analysis was done in the optimal range (between 10-20 m^2 of surface area). The samples were transferred to the sample vessel (6 mm outer diameter Quantachrome large bulb, Quantachrome Instruments, Boynton Beach, Florida, USA) and degassed for a minimum of 5 hours at 250ºC. The degassing process removes any volatiles and moisture present in the sample. Upon degassing, samples were backfilled with helium. Analysis on a Quantrachrome Autosorb 1MP (Quantachrome Instruments, Boynton Beach, Florida, USA) was done under liquid nitrogen (77.3K). A 40 point adsorption-desorption curve was produced to determine pore size distribution and BET surface area.

4.2.4 Statistical Analysis on Duplicate Samples

Chapters 4 and 5 provide statistical analysis on duplicate samples. The procedure for analysis is outlined by Synek (2008). The standard deviation from paired data can be calculated using Equation 4-1:

$$s = \sqrt{\frac{\sum (x_i' - x_i'')^2}{2m}}$$

Equation 4-1

Where 'm' number of samples analyzed, 'x_i'' and 'x_i''' are paired results and 's' is the standard deviation.

4.3 Results and Discussion

4.3.1 Initial Conditions

Groundwater from nests 2G (more contaminated) and 2A (less contaminated) was analyzed for metals and naphthenic acids (Table 4-2). The metal data presented represents the average of duplicate samples. The following metals from nest 2A exceeded groundwater guidelines: Al (144.7 µg/L), Cu (21.6 µg/L), Mn (393.0 µg/L), while groundwater from nest 2G exceeded in As (32.4 µg/L), Cu (35.4 µg/L), Mn (609.1 µg/L), Se (137.5 µg/L), and V (64.4 µg/L). A complete list of metals is provided in Appendix B.

Table 4-2: Initial groundwater conditions used in a 48 h batch sorption test with oil sands petroleum coke.

Variable	Groundwater guidelines[1] (µg/L)	Initial Groundwater Concentration Nest 2A	Initial Groundwater Concentration Nest 2G
pH	-	7.59	7.48
Naphthenic Acids (mg/L)[3]	-	1.12	1.29
Al (µg/L)	100	144.7	90.3±1.9
As (µg/L)	5	0.0±0.0	32.4±0.4
Cd (µg/L)	0.097	0.0±0.0	0.0±0.0
Cu (µg/L)	4	21.6±0.6	35.4±0.4
Mn (µg/L)	200[2]	393.0±2.5	609.1±0.8
Mo (µg/L)	73	8.2±0.0	5.9±0.0
Ni (µg/L)	150	29.1±0.1	13.6±0.4
Pb (µg/L)	200	12.5±0.1	0.0±0.0
Se (µg/L)	1	0.0±0.0	137.5±2.2
V (µg/L)	6[4]	0.0±0.0	64.4±1.0

[1]Guidelines from CCME (2006). [2]Values from Alberta Environment (1999). [3]Measured using GC-FID (methodology detailed in Section 3.2.4.3). [4]Guidelines from Government of British Columbia (2006)

4.3.2 Surface Area and Pore Size Distribution

All delayed coke used were analyzed using a Quantachrome Autosorb-1 (Quantachrome Instruments, Boynton Beach, Florida, USA). The BET surface areas for 75-150 µm raw coke were 1.9 and 1.8 m^2/g (for non-acid washed and acid washed respectfully), and 248.4 and 267.4 m^2/g for non-acid washed and acid washed activated coke (respectfully). 0.8-2 mm coke, in both cases, did not measure any pores. This was due to the lack of micropores and mesopores, and a surface area below that of the machines measurement ability using N_2. Both 75-150 µm raw cokes (non-acid washed and acid washed) had larger mesopore volumes than micropores (0.009 cm^3/g compared to 0.005 cm^3/g, respectfully, for both cokes). Activation significantly increased the surface area, increasing the

BET surface area from 1.9 to 248.4. 75-150 µm raw and activated non-acid washed coke (respectfully).

Table 4-3: Surface area determined using BET method, pore size distribution and total pore volume of granular delayed coke prepared under various conditions.

Sample	BET Surface Area (m^2/g)	Pore Volume (cm^3/g) Micropores	Mesopores	Macropores	Total Pores
0.8-2 mm Raw Coke	Nd	Nd	Nd	Nd	Nd
0.8-2 mm Acid Washed Raw Coke	Nd	Nd	Nd	Nd	Nd
75-150 µm Raw Coke	1.9	0.005	0.009	-	0.014
75-150 µm Acid Washed Raw Coke	1.8	0.005	0.009	-	0.014
75-150 µm Activated Coke	248.4	0.073	0.005	0.009	0.087
75-150 µm Acid Washed Activated Coke	267.4	0.09	0.023	-	0.113

Nd (Non Detect): Samples below detection limit

The increase in surface area between raw and activated coke is due to the formation of micropores resulting from activation. This is apparent from the increase in micropore volume (0.005 to 0.073 cm^3/g for 75-150 µm raw and activated non-acid washed coke, respectfully). These results agree with Small et al. (2012a) and Wu et al. (2005), both of whom demonstrated an increase in pore volume and distribution of pores upon activation.

The effects of acid washing were clearly demonstrated in the activated samples. Several studies (Wang and Lu, 1998; Moreno-Castilla et al., 1998) used HCl to pre-treat activated carbon. Their results indicated limited fluctuation in BET surface area, but an increase in micropore volumes. Wang and Lu (1998) in particular demonstrated narrower micropore widths, but larger total micropore volumes, produced from the removal of mineral matter. Further studies using nitric acid, urea (Stavropoulos et al., 2008), and phosphoric acid (Jagtoyen et al., 1993) demonstrated decreases in surface area when samples were treated. These results were attributed to surface reaction produced from the acid treatment. Stavropoulos et al. (2008), for example, found nitric acid produced oxygen functional groups on the surface of the carbon, limiting the adsorption area. The study also found nitric acid to have an erosive effect on the carbon, which decreased the surface area available for reaction (Stavropoulos et al., 2008). Jagtoyen et al. (1993) found that, when coal was treated with phosphoric acid, the surface area decreased (ashless basis). This was attributed to the dissolution of ash, which had previously been considered to have a negligible porosity (Jagtoyen et al., 1993).

4.3.3 Comparison of Trace Metal Removal between Non-Acid Washed Coke

A batch adsorption test was done using non-acid washed coke with 3 conditions: 0.8-2 mm raw coke, 75-150 µm raw coke, and 75-150 µm activated coke. Uptake of Al (74%), Mn (98%), Ni (8%), and Pb (57%) occurred when nest 2A groundwater was mixed with 0.8-2 mm raw coke for 48 hrs. Samples released Cu (63%), Mo (351%), and V. The limited adsorption and release of compounds is likely due to the smaller surface area to volume ratio than 75-150 µm coke (raw and activated). The 75-150 µm raw coke removed Mn (79%) and Pb (100%), with release of Al (10532%), Cu (22%), Mo (4303%), Ni (0%) and V occurring. The relatively large release of metals is due to an increased surface area-to-volume ratio without any prior cleaning of the coke (Small et al., 2012b). Activated 75-

150 µm coke had uptake of Mn (96%) only, while release of Al (18%), As, Cu (117%), Mo (2026%), Ni (54%), Pb (195%) and V occurred.

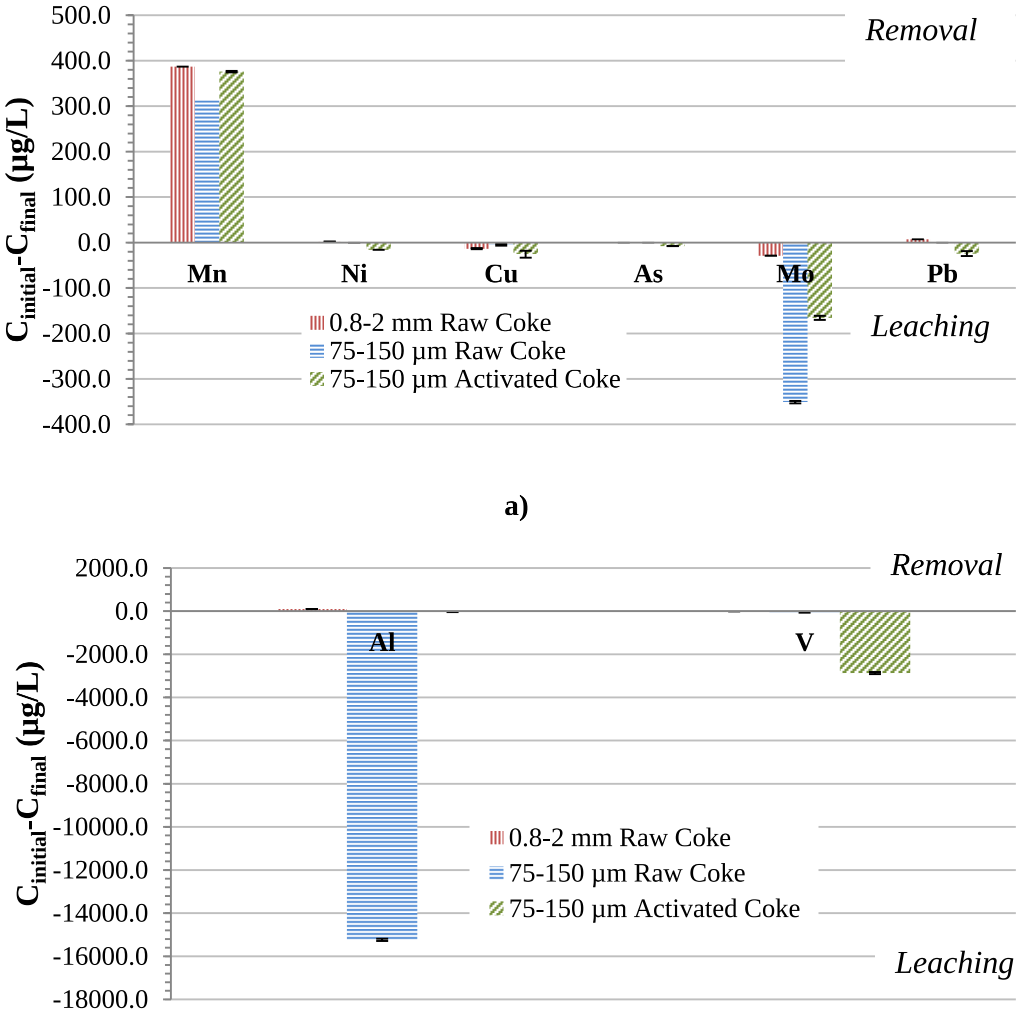
Table 4-4: Comparison of 0.8-2 mm raw coke, 75-150 µm raw coke and 75-150 µm activated coke for trace metal uptake or release. Values represent duplicate samples. A negative percentage indicates a release (increase in final concentration) of compounds.

	0.8-2 mm Raw Coke		**75-150 µm Raw Coke**		**75-150 µm Activated Coke**	
Analyte	**C_{final} (µg/L)**	**Removal (%)**	**C_{final} (µg/L)**	**Removal (%)**	**C_{final} (µg/L)**	**Removal (%)**
Al	38.0±1.5	74%	15381.2±53.4	-10532%	170±18.0	-18%
As	0.0±0.0	-	0.0±0.0	-	7.8±0.1	Release[1]
Cd	0.0±0.0	-	0.0±0.0	-	0.0±0.0	-
Cu	35.1±1.2	-63%	26.4±1.9	-22%	46.9±7.5	-117%
Mn	6.0±0.0	98%	80.7	79%	17.0±1.6	96%
Mo	36.8±0.2	-351 %	359.3±2.5	-4303%	173.5±4.5	-2026%
Ni	26.8±0.2	8%	29.2±0.3	0%	44.9±0.1	-54%
Pb	7.1±0.0	57%	0.0±0.0	100%	36.7±5.4	-195%
Se	0.0±0.0	-	0.0±0.0	-	0.0±0.0	-
V	13.2±0.1	Release[1]	67.8±0.7	Release[1]	2861.7±51.2	Release[1]

[1]"Release" indicates a change in concentration from an initial concentration of 0.

Compounds released are consistent with results from Small (2011) and Puttaswamy (2011). Puttaswamy (2011) further noted that at alkaline conditions, elevated V concentrations are the main source of toxicity. Activated coke showed consistently higher release (with Al and Mo as exceptions) of metals, likely due to the enhanced pore volume over 0.8-2 mm and 75-150 µm raw cokes. Consistent with Puttaswamy (2011), V was rapidly released from solution (>1.0 mg/L in first 3 hrs). This is due to the loosely bound nature of V to the coke surface and is therefore readily released upon contact with water. Contrary to these studies (Puttaswamy, 2011; Small, 2011), Al was released in high concentration, sometimes exceeding that of V. The particular body could have abundant aluminosilicate clay particles, encouraging the release of loosely bound Al once the coking process was complete (Puttaswamy, 2011). Though not in elevated concentrations compared to V, Small (2011) also observed Al release greater than Ni, Mo, Mn, Cu and Pb.

A comparison is provided in Figure 4-1a) and b), which shows the removal or leaching of compounds from samples. Activated coke appears to be most active, release more compounds and in higher concentration with the exception of Mo and Al. Uptake of Mn was similar to that of 0.8-2 mm coke.



a)

b)

Figure 4-1: Concentration change of a) metals and b) Al and V when groundwater is mixed with 0.8-2 mm raw coke, 75-150 µm raw coke and 75-150 µm activated coke. Values are averages of duplicate samples.

Samples intermittently exceeded guidelines for groundwater quality. 0.8-2 mm raw coke exceeded guidelines for Cu, 75-150 µm raw coke exceeded for Al, and Mo, and 0.75-150 µm activated coke exceeded for Al, As, Cu, and Mo.

The results presented agree with similar studies that have used petroleum coke (Small et al., 2012b; Janfada, 2007). As Ruthven (2008) suggests, a greater surface area will lead to enhanced adsorption. This is due to the largely non-polar surface area of the coke as well as the individual characteristics of the metals. From Ruthven (2008), it is likely that physical adsorption, specifically Van der

Waals forces, is the dominant mechanism of adsorption. It is possible that surface oxidation of the coke is occurring, stimulating the release and uptake of metals (Ruthven, 2008). The release of V, Mo, and Al suggest that the bonds holding them are weak, as the release is occurring without any the addition of significant energy.

4.3.4 Comparison of Trace Metal Removal Between Acid Washed Coke

A similar test to that found in section 4.3.3 was undertaken; however coke was cleaned prior to use. It was suggested by Small (2011) that an acid wash solution be used to remove metals that were previously released in solution. Prior to acid washing, varying molarity of HCl was tested to determine if release occurred and if increasing molarity promoted greater release. All pH values were below 2, and similar metal release was observed in all cases. Therefore, a 0.25M solution was selected.

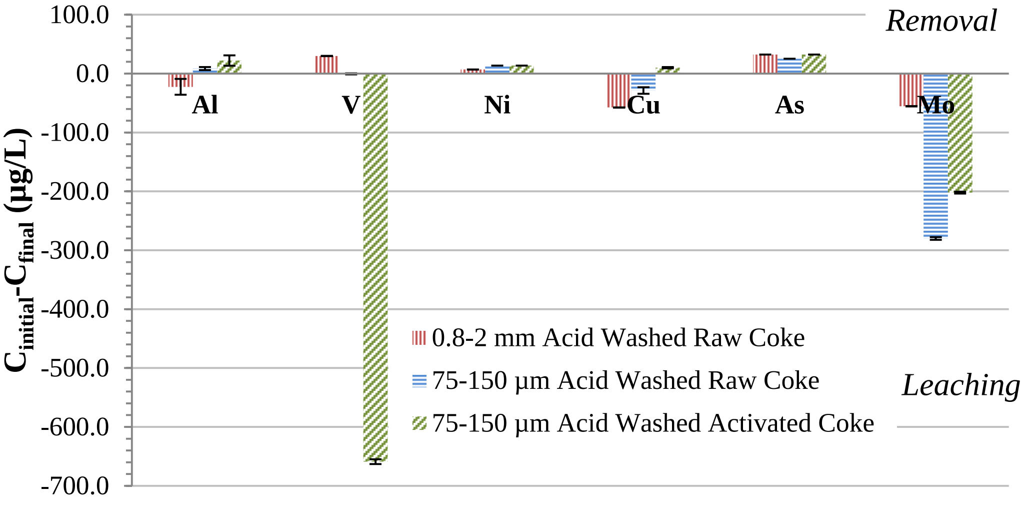
Acid washed coke was used in 48 h batch tests with metal adsorption results provided in Table 4-5. 0.8-2 mm raw acid washed coke reduced the concentration of As (100%), Mn (99%), Ni (52%), Se (95%), and V (46%), while Al (25%), Cu (162%) and Mo (937%) release was observed. The 75-150 µm coke showed uptake in Al (9%), As (78%), Mn (100%), Ni (100%) and Se (98%), while Cu (81%) and Mo (4726%) release occurred. Activation of coke yielded consistently greater uptake when compared with raw coke, with Al (25%), As (100%), Cu (28%), Mn (100%), Ni (100%) and Se (100%) being removed. Mo (3411%) and V (1023%) were released into solution.

Table 4-5: Comparison of 0.8-2 mm raw acid washed coke, 75-150 µm raw acid washed coke and 75-150 µm activated acid washed coke for trace metal uptake or release. Values represent duplicate samples. A negative percentage indicates a release (increase in final concentration) of compounds.

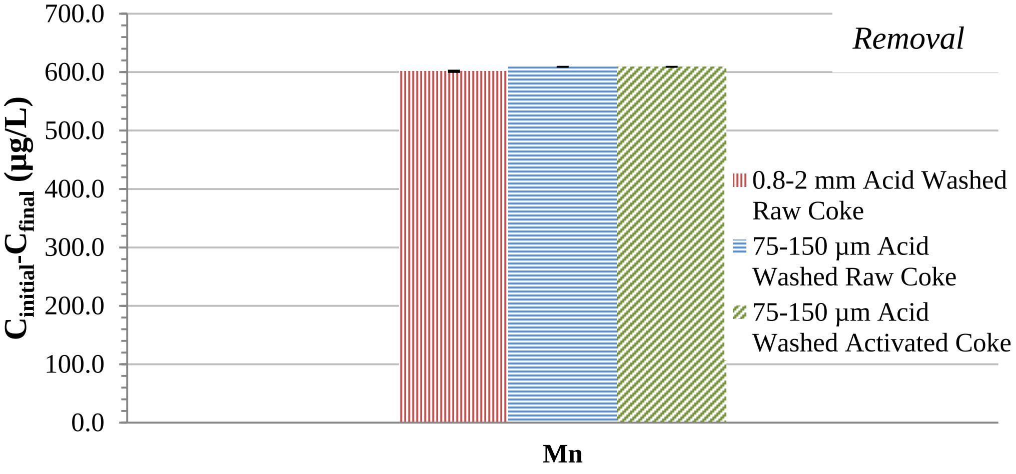
	0.8-2 mm Acid Washed Raw Coke		75-150 µm Acid Washed Raw Coke		75-150 µm Acid Washed Activated Coke	
Analyte	C_{final} (µg/L)	Removal (%)	C_{final} (µg/L)	Removal (%)	C_{final} (µg/L)	Removal (%)
Al	112.8±13.5	-25%	81.7±2.6	9%	68.2±8.9	25%
As	0.0±0.0	100%	7.2±0.0	78%	0±0.0	100%
Cd	0.0±0.0	-	0.0±0.0	-	0.0±0.0	-
Cu	92.9±0.1	-162%	64.0±5.6	-81%	25.4±1.0	28%
Mn	7.7±1.0	99%	0±0.0	100%	0±0.0	100%
Mo	61.4±0.4	-937%	286.0±2.4	-4726%	208.0±1.7	-3411%
Ni	6.6±0.1	52%	0±0.0	100%	0±0.0	100%
Pb	0.0±0.0	-	0.0±0.0	-	0.0±0.0	-
Se	6.7±0.9	95%	6.5±0.1	98%	0±0.0	100%
V	34.5±0.2	46%	64.8±0.9	-1%	723.4±4.2	-1023%

V was again released in the highest concentrations for activated acid washed coke (75-150 µm). The apparent release of V from activated coke and uptake from raw coke is likely due to the acid washing process. Since V is loosely bound to the coke, it is likely that acid washing properly cleaned the raw cokes, but could not penetrate their micropores. With activated coke, contact with micro and mesopores likely occurred, requiring more solution to dissolve V and remove from the coke (Puttaswamy, 2011). Mo release, despite a high percentage, was consistent with Small (2011).

Table 4-5 provides a visual comparison between each acid washed coke. Again, the activated coke appears to remove and release more metals than the non-activated acid washed coke with the exception of Mo. 100% removal was observed with As, Mn, Ni and Se, while only V and Mo were released from the lattice of the coke.



a)



b)

Figure 4-2: Concentration change of a) metals and b) Mn when groundwater is mixed with 0.8-2 mm acid washed raw coke, 75-150 µm acid washed raw coke and 75-150 µm acid washed activated coke. Values are averages of duplicate samples.

In this instance, a comparison can be drawn between each coke after having prepared them in an acid wash solution. Several key features are demonstrated in the data: increased removal of Cu and Al, and increased release of V and Mo with acid washing. Comparison between acid washing and non-acid washing is provided in Section 4.3.5.

The process of acid washing between samples follows trends observed with non-acid washing. Specifically, as petroleum coke is handled to produce a larger surface area-to-volume ratio, more desorption or adsorption is occurring. In a study on weathered Syncrude Canada Ltd. coke, Squires (2005) noted the release of Al, Mn, Ni, and V. The process of acid washing will mobilize metals from the surface of the adsorbent, ideally releasing them into solution (Arwidsson et al., 2010). However, any metals remaining in solution when samples are dried will resorb onto the adsorbent. In this study, it is likely that the acid wash mobilized from the pores and rebound them loosely to the coke surface. This allowed for the release of elevated concentrations of these compounds into OSPW (Arwidsson et al., 2010).

4.3.5 Comparison Between Acid Wash and Non-Acid Wash

The efficiency of acid washing can be determined when comparing the performance of coke versus the acid washed equivalent. In Table 4-6, 0.8-2 mm non-acid washed and acid washed raw coke are compared. Both had similar metals released (Cu, Mo), however acid washed coke appeared to release a larger amount (162% release of Cu compared to 63% and 938% release compared to 351%) than non-acid washed coke. Further washing of coke would allow for more contact time between the acid and the micro and macropores, promoting further metal release (Delle Site, 2001).

Table 4-6: A comparison of trace metal removal percentage between non-acid washed and acid washed 0.8-2 mm coke. Values are averages of duplicate samples.

Analyte	0.8-2 mm Non-Acid Washed Raw Coke Removal (%)	0.8-2 mm Acid Washed Raw Coke Removal (%)
Al	74%	-25%
As	-	100%
Cd	-	-
Cu	-63%	-162%
Mn	98%	99%
Mo	-351%	-937%
Ni	8%	52%
Pb	57%	-
Se	-	95%
V	-	46%

Figure 4-3 a) and b) demonstrate the removal trends of the various 0.8-2 mm coke preparation methods. Final concentrations for Cu (C_{final}=35.1 µg/L) for 0.8-2 mm raw coke exceeded groundwater criteria while 0.8-2 mm acid washed raw coke exceeded for Cu (C_{final}=92.9 µg/L) and Se (C_{final}=6.7 µg/L).

a)

b)

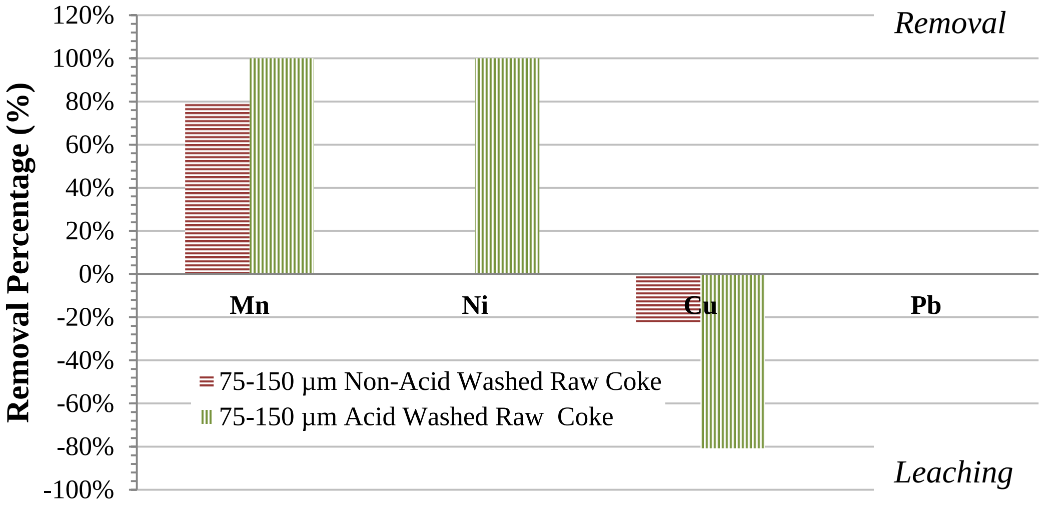
Figure 4-3: Removal percentage of a) metals and b) Mo when groundwater is mixed with 0.8-2 mm non-acid washed and acid washed raw coke. Values are averages of duplicate samples.

A similar comparison is provided in Table 4-7, where removal percentages from groundwater for 75-150 μm non-acid washed and acid washed raw coke are provided. From Table 4-7, the opposite trend seen with 0.8-2 mm coke is observed. In this case, acid washing has promoted the uptake of metals, but similar to previous trends, has encouraged further release. Pre-treatment by acid washing promoted the uptake of Al, As, Mn, Ni, and Se and increased the release of Cu, and Mo.

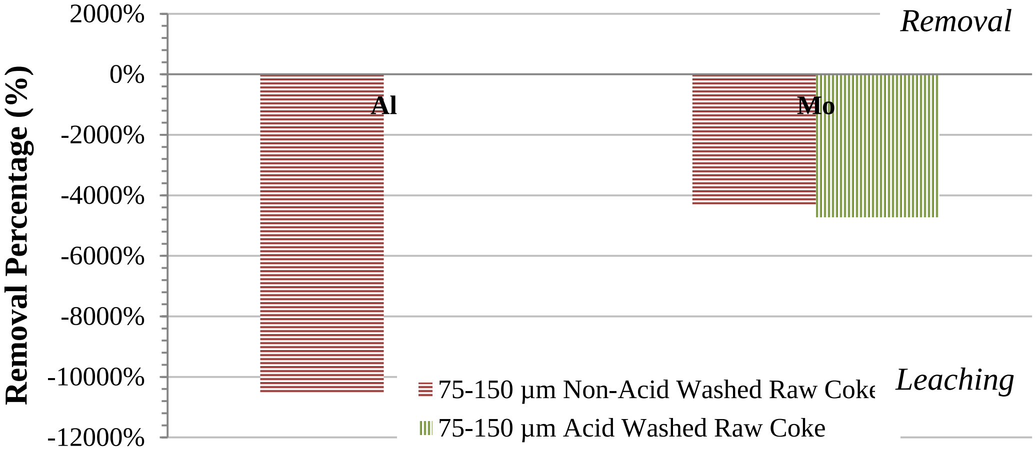
Table 4-7: A comparison of trace metal removal percentage between non-acid washed and acid washed 75-150 µm raw coke. Values are averages of duplicate samples.

Analyte	75-150 µm Non-Acid Washed Raw Coke Removal (%)	75-150 µm Acid Washed Raw Coke Removal (%)
Al	-10352%	9%
As	-	78%
Cd	-	-
Cu	-22%	-81%
Mn	79%	100%
Mo	-4303%	-4726%
Ni	0%	100%
Pb	100%	-
Se	-	98%
V	-	-1%

The comparison is shown in Figure 4-4, where greater removal and release is consistently observed by acid washed raw coke. As the exception, Al showed release for non-acid washed coke and uptake for acid washed coke. This is due to the removal of surface Al by the acid washing process.



a)



b)

Figure 4-4: Removal percentage of a) metals and b) Mo when groundwater is mixed with 75-150 mm non-acid washed and acid washed raw coke. Values are averages of duplicate samples.

Finally, a comparison between the performance of non-acid washed and acid washed activated coke is considered. From Table 4-8, acid washed coke saw uptake in Al (25%), As (100%), Cu (28%), Mn (100%), Ni (100%), and Se (100%), whereas non-acid washed coke had uptake in Mn (96%) only. Non-acid washed coke released Al (18%), Cu (117%), Ni (54%), Pb (195%) and V. Both samples of activated coke released Mo (2026% and 3411% release for non-acid washed and acid washed respectfully) and V (release and 1023% for non-acid washed and acid washed respectfully). In this case, the acid washing pre-treatment removed contaminants bound to the surface of the coke, allowing for an increase in uptake when compared with non-acid washing. These results are consistent with the trend observed from Small et al. (2012b).

Table 4-8: A comparison of trace metal removal percentage between non-acid washed and acid washed 75-150 µm activated coke. Values are averages of duplicate samples.

Analyte	75-150 µm Non-Acid Washed Activated Coke Removal (%)	75-150 µm Acid Washed Activated Coke Removal (%)
Al	-18%	25%
As	-	100%
Cd	-	-
Cu	-117%	28%
Mn	96%	100%
Mo	-2026%	-341%
Ni	-54%	100%
Pb	-195%	-
Se	-	100%
V	Release	-1023%

Again, graphical representation of the removal percentages clearly demonstrates the effectiveness of the acid washing procedure. Figure 4-5a) and b) display the removal percentages of each activated coke, with the acid washed activated coke consistently demonstrating larger removal percentages, and limited V release.

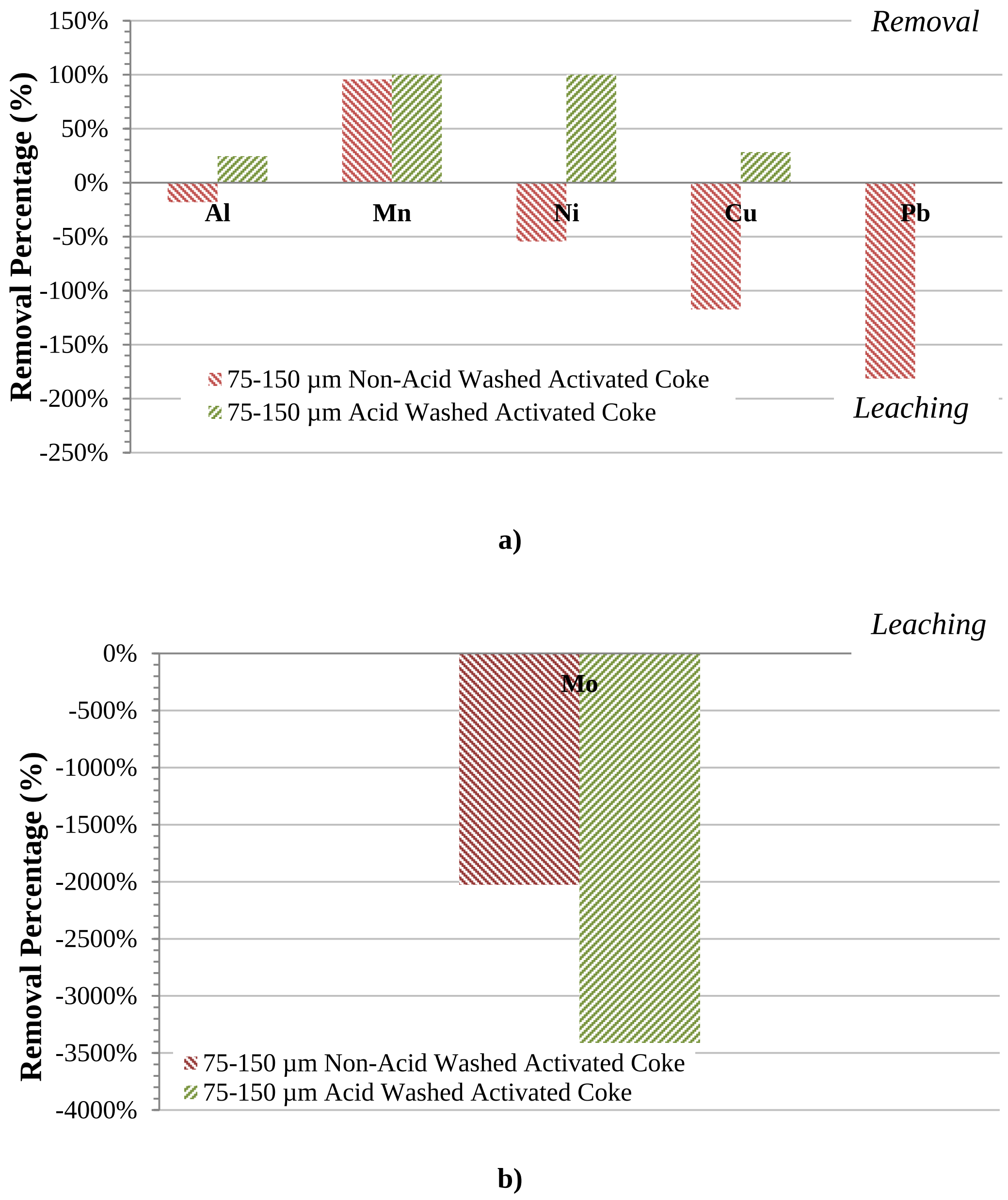


Figure 4-5: Removal percentage of a) metals and b) Mo when groundwater is mixed with 75-150 mm non-acid washed and acid washed raw coke. Values are averages of duplicate samples.

Performance comparison between all samples is provided in Table 4-9. Removal percentages are presented, with green highlighted cells representing final concentrations below groundwater guidelines and red cells representing final concentrations above groundwater guidelines. All samples consistently exceeded groundwater quality guidelines for Cu (maximum limit of 4 µg/L [CCME, 2006]), while achieving successful removal of Mn, Ni and Pb. Acid washing appears to remove Al, as no acid washed samples exceeded guidelines. Release of Mo occurred in each sample, with the higher surface area-to-volume ratios in 75-150 µm coke releasing more. The release caused those values to exceed groundwater guidelines (73 µg/L). Finally, Se, which was only present in groundwater well 2G, was successfully removed by 75-150 µm acid washed activated coke. While still removing a high percentage, both 0.8-2 mm and 75-150 µm acid washed raw coke exceeded groundwater guidelines for Se (1 µg/L). Criteria for V in water was compiled from Government of British Columbia (2006). All non-acid washed coke samples released V, while removal only occurred for 0.8-2 mm acid washed raw coke. All samples exceeded those suggested guidelines.

Table 4-9: A comparison of trace metal removal percentage between coke with various sized (0.8-2 mm and 75-150 µm) and prepared (raw, activated, non-acid washed and acid washed) coke. Values are averages of duplicate samples.

	Non-Acid Washed Coke Removal (%)			Acid Washed Coke Removal (%)		
Analyte	**0.8-2 mm Non-Acid Washed Raw Coke**	**75-150 µm Non-Acid Washed Raw Coke**	**75-150 µm Non-Acid Washed Activated Coke**	**0.8-2 mm Acid Washed Raw Coke**	**75-150 µm Acid Washed Raw Coke**	**75-150 µm Acid Washed Activated Coke**
Al	74%	-10532%	-18%	-25%	9%	25%
As	-	-	Release	100%	78%	100%
Cd	-	-	-	-	-	-
Cu	-63%	-22%	-117%	-162%	-81%	28%
Mn	98%	79%	96%	99%	100%	100%
Mo	-351%	-4303%	-2026%	-937%	-4726%	-3411%
Ni	8%	0%	-54%	52%	100%	100%
Pb	57%	100%	-195%	-	-	-
Se	-	-	-	95%	98%	100%
V	Release	Release	Release	46%	-1%	-1023%

The results indicate that an acid washing pre-treatment releases metals into solution, allowing coke to remove more contaminants. These results are consistent with Ityokumbul (1994) who showed that an acid washing pre-treatment reduced ash content within coke, thereby increasing the carbon ratio. Work from Arwidsson et al. (2010) also agrees with the results, as acid washing removed surface bound metals and released them into solution. Some metals were successfully removed using deionized water; however some resorb loosely onto the surface and were released when mixed with OSPW. The elemental concentration of coke also showed significant reduction in V, Ni, Na, Fe and Ca (Ityokumbul, 1994). Similar results were observed, however the acid washing process was not sufficient to fully dissolve V. Instead, V was likely released from the coke and bound lightly to the surface (Janfada, 2007). V uptake was observed for the larger grain size (0.8-2 mm raw coke), as the acid washing solution unlikely penetrated deep within the grains.

Ruthven (2008) emphasizes the importance of surface contact for physical adsorption. While, given the complexity of OSPW, it is possible that oxidation reaction are occurring forming chemical bonds, physical bonding is likely to be dominant (Dubinin, 1989; Ruthven, 2008). This is confirmed in this study, as greater adsorption/release is consistently observed in samples treated with a smaller grain size (75-150 µm) and activation.

Despite all samples measuring concentrations below groundwater guidelines, Ni was released by coke without any pre-treatment, while uptake was observed by the acid washing pre-treatment. Small et al. (2012b) observed similar releases, but noted that Ni may form precipitates in alkaline environments. The release of bound Ni through the acid washing process likely allowed to these complexes to form rapidly, as the Ni is more readily available after washing (Ityokumbul, 1994). The formation of these complexes promoted the precipitation of Ni onto the coke surface (Small et al., 2012b). Puttaswamy (2011) indicated that Ni and V are sources of toxicity (Ni in acidic conditions), and successful removal of Ni would lead to a decrease in apparent toxicity. With full Ni removal, a decrease in toxicity is likely to have occurred. V yet remains a source of toxicity, and its removal should be considered for toxicity reduction.

Removal of metals at low concentrations (<100ppm) is usually expensive or ineffective (Doan et al., 2008). While removal of metals is occurring, this study cannot confirm the mechanism for removal. This is due to the complexity of OSPW; the presence of multiple metals, cations, anions and organic compounds lends to a variety of removal mechanisms (Nodwell, 2011). Limitations arise with the measurement of metals in samples with elevated salt concentration. In a report, the Government of Australia (2012) highlight issues low and normal resolution ICP-MS. The salinity of samples can interfere with the sensor, providing false positives. It is likely that, given the saline nature of OSPW, this interference is occurring. While an overestimation of concentration is likely occurring, the trends in removal remain valid.

Consideration should also be given to the additional waste stream created by the acid washing process. Removed metals from coke will require additional on-site storage. While the total volume requiring storage may be less, the waste is now contaminated with metals and is highly acidic.

4.3.6 Naphthenic Acid Removal

Final naphthenic acid concentrations were also measured in this study. The initial naphthenic acid concentration for groundwater mixed with non-acid washed coke was 1.12 mg/L and 1.29 mg/L for acid washed coke. Final concentrations, summarized in Table 4-10, for non-acid washed coke were 0.50, 0.31 and 0.12 mg/L for 0.8-2mm raw coke, 75-150 µm raw coke and 75-150 µm activated coke respectively. These correspond to removal percentages of 56%, 73% and 89%. The average removal percentage for non-acid washed coke was 72%. Acid washed coke had greater removal percentages in all cases. Final concentrations were 0.22, 0.20 and 0.04 mg/L for 0.8-2 mm raw coke, 75-150 µm raw coke and 75-150 µm activated coke respectively. These correspond to removal percentages of 83%, 84% and 97%. Combined, the removal percentage for acid washed coke was 88%.

Table 4-10: Naphthenic acid removal using various coke preparations including non-acid washed 0.8-2 mm raw coke, 75-150 µm raw coke and 75-150 µm activated coke and acid washed 75-150 µm raw coke and 75-150 µm activated coke.

Coke Condition		Final Naphthenic Acid Concentration (mg/L)	Removal (%)	Average Removal (%)
Non-Acid Washed Coke	0.8-2 mm Raw Coke	0.50	56%	72%
	75-150 µm Raw Coke	0.31	73%	
	75-150 µm Activated Coke	0.12	89%	
Acid Washed Coke	0.8-2 mm Raw Coke	0.22	83%	88%
	75-150 µm Raw Coke	0.20	84%	
	75-150 µm Activated Coke	0.04	97%	

Comparing removal percentages for cokes of the same grain size yields a 27% increase for 0.8-2 mm raw coke (from 56% for non-acid washed to 83% for acid washed), an 11% increase for 75-150 µm Raw Coke (from 73% for non-acid washed to 84% for acid washed) and an 8% increase for 75-150 for activated coke (from 89% for non-acid washed to 97% for acid washed). Again, the increase in removal percentage is attributed to acid washing pre-treatment. The cleansing of the surface increases the available surface bonding sites, allowing for more adsorption (Janfada, 2007).

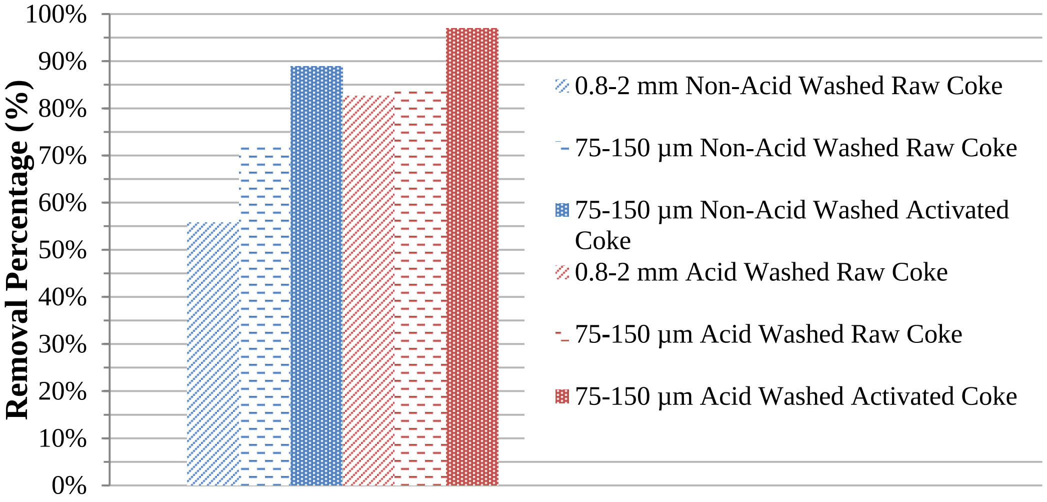


Figure 4-6: Visual comparison of naphthenic acid removal percentage (%) for various coke preparation methods. Blue values indicated non-acid washed coke while red is coke pretreated with an acid wash.

Naphthenic acid concentration reduction occurred over the entire range of coke preparation, from the least removed (56% for 0.8-2 mm non-acid washed raw coke) to the most (97% for 75-150 µm acid washed activated coke). Results agree with previous studies (Small et al., 2012b), with activated coke removing more naphthenic acids than raw coke. Ityokumbul (1994) found that acid washing coke lowered the ash and sulphur content, increasing the carbon percentage in the material. Further stipulations from Small et al. (2012a) suggest a higher carbon dose will lead to more adsorption. Therefore, the acid washing process should remove a higher percentage of organic naphthenic acids and metals. Generally, this was confirmed in this study, with increased heavy metal removal (and release) from acid washed coke than non-acid washed. Further, each size of coke showed increased adsorption as it was acid washed.

4.4 Conclusions and Recommendations

The removal of naphthenic acids and metals using delayed petroleum coke was analyzed in this study. Delayed coke, prepared at different grain sizes (0.8-2 mm and 75-150 µm), preparation methods (raw and activated), and pre-treatments (acid washed and non-acid washed) was used in a 48 h batch sorption test to determine the removal efficiency of select metals (Al, As, Cd, Cu, Mn, Mo, Ni, Pb, Se, V) and naphthenic acids.

Comparisons between the following conditions were compiled: acid washed and non-acid washed coke, sizes of coke (0.8-2mm and 75-150 µm) and activation (raw coke and activated coke). In general, a smaller grain size (75-150 µm) coke removed more metals than 0.8-2 mm coke due to the larger surface area of the smaller sized coke. A larger surface area provides more receptors upon which metal ions can adsorb, increasing the total uptake of metals. Activating coke also tended to adsorb more metals, and, in both the acid washing and non-acid washed case, adsorbed more naphthenic acids. A similar study conducted by Small et al. (2012b) concluded that activation of coke increased the specific surface area, thereby increasing the effectiveness for contaminant removal. Finally, acid washing showed a moderate tendency to improve adsorption. This is due to impurity removal both on the surface of the coke and in the pores. The BET surface area showed a moderate increase (from 248.4-267.4 m^2/g for 75-150 µm non-acid washed and acid washed activated coke respectfully), with micropore development being the most predominant (0.073 to 0.09 cm^3/g respectfully).

Future work using coke should compare cleaning techniques on activated and non-activated coke. Acid washing using HCl was done in this study, however base flushing of coke could also be done to remove any organic contaminants bound to the surface that may not be removed by acid. Various acids could also be examined to determine the most efficient removal process.

4.5 References

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Chapter 5 - Adsorption of Metals and Naphthenic Acids using Biochar

5.1 Introduction

The term ‘biochar’ has recently been developed for soil enhancement using pyrolized biomass (Lehmann and Joseph, 2009). The organic biomass is thermally decomposed under limited oxygen conditions, producing a high carbon content material. Work with biochar, and the term itself, originates from Kishimoto and Sugiura (1985). The two began examining pyrolized agricultural by-products for the enhancement of soil water retention and nutrient uptake. Since then, biochar has been seen as a relatively pure and inert substance effective at nutrient uptake (Lehmann and Joseph, 2009). However, limited work (Sneath et al., 2013; Fellet et al., 2011) has examined biochar beyond the scope of soil enhancement.

Since the pyrolysis of organic matter produces biochar, it can be derived from any organic based product. As a result, there are a variety of biochars available. Zhao et al. (2013) highlight the many sources, including manure, sawdust, wood, wheat, bone dregs, shells and weeds. Common between biochar is the relatively high purity and low cost (Ghania et al., 2013). Beesley et al. (2011) summarized properties of biochar and determined it is a viable candidate for environmental remediation.

The aim of this study is to determine the effectiveness of OSPW treatment using willow and wheat-straw derived biochars. OSPW treatment includes: the removal of naphthenic acids, metals, phenols, and PAH’s. Effectiveness will be measured by Microtox™ toxicity testing and comparing aqueous concentrations of metals, phenols, and PAH’s against surface water guidelines. The following tasks were undertaken to complete the objective:

1. Initial characterization of OSPW measuring metals, naphthenic acids, PAHs, phenols, DOC/DIC, and Microtoxicity.
2. Mixing of OSPW with wheat and willow derived biochar in a 48 h batch sorption test.

Limited work has been undertaken using biochar as an adsorbent for contaminant remediation. An investigation in naphthenic acid removal by Iranmanesh (2013) is one of the earlier investigations in this field. This work provides an analysis of the combined removal of oil sands metals and naphthenic acids using biochar.

5.2 Procedure

5.2.1 Metal and Naphthenic Acid Adsorption

Two types of Biochar samples were obtained from Dr. Derek MacKenzie (University of Alberta Department of Renewable Resources):: willow derived and wheat straw derived biochar (Subsequently referred to as willow and wheat biochar). Willow biochar is produced from the pyrolysis of willow trees, while wheat biochar is derived from wheat straw remaining after agricultural use.

Prior to experimentation, three ratios were selected to determine optimal conditions for trace metal and naphthenic acid removal. 2 g, 5 g, 8 g and 20 g were selected and mixed with 250 mL of OSPW. These masses represent a range between the optimal masses found for activated and raw coke. Given the purity of the biochar, its performance was expected to be comparable to activated coke, yet its unaltered physical structure suggested an adsorption affinity between that of activated and raw coke. After mixing the masses with OSPW and shaking for 48 hours, ICP-MS and GC-FID samples were collected and analyzed. Deionized water was almost mixed with samples to determine the release of trace metals, phenols and PAHs. These samples were analyzed due to organic adsorbents tendency for phenol and PAH release (Vázquez et al., 1994). No release of organic compounds was observed, and therefore was not tested further.

A mass of 20 g was selected based on its trace metal uptake performance and naphthenic acid removal. Duplicate samples of 20 g were prepared for willow and wheat biochar. Initial and final samples were taken for DOC/DIC, microtoxicity, naphthenic acids and trace metals. Samples taken at 3 h, 6 h, 12 h, 24 h, and 48 h were analyzed for trace metals and naphthenic acids. All samples were done in duplicates, with masses of 19.976 g and 19.952 g in 250 mL of OSPW for willow biochar and 20.041 g and 20.022 g in 250 mL OSPW for wheat biochar.

5.2.2 Analysis

Analysis of naphthenic acids and trace metals were done following the procedure outlined in section 3.2.2 and 3.2.4.3 respectfully.

5.2.2.1 Surface Area Analysis

Surface area was analyzed using a Quantachrome Autosorb 1-MP. The methodology is described in Section 4.2.3.2.

5.2.2.1 DOC and DIC

Preparation for DOC and DIC analysis involved filtering 25 mL of sample through a 0.45 µm filter and transferring to a 20 mL glass EPA vial (Fisher Scientific, Waltham, Massachusetts, USA). Samples were capped without headspace to ensure no interaction occurred with the atmosphere, which may alter the pH and chemistry. Samples were analyzed using a Shimadzu TOC-5000A (Shimadzu Corporation, Kyoto, Japan) for DOC and DIC. Filtration through a 0.45 µm filter allowed the assumption that DOC readings were entirely aqueous (Small, 2011).

5.2.2.2 Microtoxicity

Microtox™ samples were done using a Model 500 Analyzer (AZUR Environmental Corporation, Fairfax, California) using a modified 9 point dilution ASTM method. The method measures the 20% mortality (EC_{20}) of the reagent, *Vibrio fischeri,* at 5 minutes and 15 minutes. Luminescence analysis was done using the Microtox™ Omni Software (AZUR Environmental Corporation, Fairfax, California). Samples were completed within 3 hours of rehydrating luminescence bacteria.

5.2.3 PAHs and Phenols

The analysis for PAHs and phenols by Maxxam Analytical Laboratories (Edmonton, Alberta, Canada) was done following EPA 3510C/8270D for PAHs and AENV 154 for phenols.

For PAHs, separation of the organic fraction was done using dichloromethane in a process similar to naphthenic acid extraction. Dichloromethane is mixed with the sample and allowed to separate, dissolving the PAHs in solution (US EPA, 1996). The pH is adjusted and repeated, however in this case, both dichloromethane solutions are combined after extraction (US EPA, 1996). This method was altered by Maxxam Analytical Laboratories, however specific information was not available. Gas chromatography must produce acceptable calibration for each PAH of interest (US EPA, 2007).

The recommended measurement technique (from US EPA, 2007) for PAH’s is using gas chromatography mass spectrometer. US EPA (2007) suggests an ion trap mass spectrometer with axial modulation be used. The recommended column is a J&W Scientific DB5 or comparable (US EPA, 2007). Samples are recorded as benzo[a]pyrene equivalency.

Phenolic compounds are measured based on ASTM (2012). Briefly, phenolic compounds are dissolved at alkaline conditions and produce a colour. This colour is measured using an absorbance at 460 nm (ASTM, 2012).

5.3 Results and Discussion

5.3.1 Biochar Characterization

Biochar used in this study was produced by Alberta Innovates Technology Futures (Edmonton, Alberta, Canada). Biochar was produced through a partial pyrolysis/combustion process, where samples were exposed to 800°C under air. Biochar was then discharged from the furnace and quenched with water to 50°C. Analysis of the biochar is provided in Table 3-1. Further information was not available from Alberta Innovates. Surface area analysis results are also provided in Table 3-1. The preparation and analysis information is provided in Section 4.2.3.2.

Table 5-1: Analysis results of biochar produced from Alberta Innovates Technology Futures. Missing values were not reported by Alberta Innovates.

Parameter	Wheat Biochar	Willow Biochar
Volatiles (%)	5.0	18.0
Ash (%)	18.5	9.8
Fixed Carbon (%)	76.5	72.2
pH	9.7	Nm
EC (mS/cm)	1.2	Nm
Carbon (%)	65.6	Nm
Nitrogen (%)	1.1	Nm
Hydrogen (%)	2.6	Nm
Sulphur (%)	0.1	Nm
Oxygen (%)	12.2	Nm
BET Surface Area (m^2/g)	80	155.0
Micropore Volume (cm^3/g)	0.0169	0.018
Mesopore Volume (cm^3/g)	0.001	0.003
Macropore Volume (cm^3/g)	0.005	0.005
Total Volume (cm^3/g)	0.023	0.026

Nm: not measured.

Fixed carbon contents of both biochars are less than typical delayed coke produced from oil sands mining (Furminsky, 1998). A larger ash content (%) and smaller amount of volatiles (%) are present as well. The production of ash is common in organic based carbons produced through pyrolysis (Lehmann and Joseph, 2009). The decreased volatile composition is due to the relative lack of impurities present within biochar when compared with delayed coke. Micropore volumes were also relatively low when compared with activated coke. This may limit the ability for biochar to remove metals that would penetrate micropores.

5.3.2 Initial OSPW Characterization

Initial OSPW samples were analyzed for dissolved carbon, phenols, PAHs, naphthenic acids and trace metals. Initial dissolved organic and inorganic carbon concentrations were 56.0 and 161.5 mg/L respectfully. Samples were sent to a commercial lab (Maxxam Analytical Laboratories, Edmonton, Alberta, Canada) for phenol and PAH analysis. Samples reported concentrations below the detection limits for both phenols (0.002 mg/L) and PAHs (ranging from 0.0075 to 0.2 µg/L).

Naphthenic acid extraction and analysis, detailed in Chapter 3 Section 3.2.2 and 3.2.4.3, ranged from a concentration of 3.60 to 4.17 mg/L. Initial samples remain near the minimal concentration of 2.5 to 5 mg/L suggested by literature for toxicity to aquatic organisms (Clemente and Fedorak, 2005). Dissolved organic and inorganic carbon ranged from 55.7 to 56.4 mg/L and from 161.0 to 161.9 mg/L respectively. Detected metals ranged from 10.8 µg/L (Ni) to 296.2 µg/L (Mo), with no Pb and Cd detected. Values of Al (145.1 µg/L), As (38.2 µg/L), Mo (296.2 µg/L), and Se (124.6 µg/L) exceed suggested guidelines for surface water quality guidelines for the protection of aquatic organisms (CCME, 2006) are presented in Table 5-2.

Table 5-2: Initial characterization of dissolved organic and inorganic carbon, phenols, PAHs, naphthenic acids and surface water quality government regulated metals. Values represent an average of duplicate samples.

Parameter		Concentration Limit (µg/L)[1]			Concentration Limit (µg/L)[1]
DOC (mg/L)	56.0	4000	**Cu (µg/L)**	52.5±0.6	4
DIC (mg/L)	161.5		**Mn (µg/L)**	24.7±0.2	200
Phenols (µg/L)	13		**Mo (µg/L)**	296.2±2.2	73
PAHs (mg/L)	Nd.		**Ni (µg/L)**	10.8±0.3	200
Naphthenic Acids (mg/L)	3.89		**Pb (µg/L)**	0.0±0.0	200
Al (µg/L)	145.1±1.7	100	**Se (µg/L)**	124.6±2.1	1
As (µg/L)	38.2±0.2	5	**V (µg/L)**	72.3±2.4	-
Cd (µg/L)	0.0±0.0	0.097			

[1] Concentration limit for the protection of aquatic organisms (CCME, 2006)
Nd (Non Detect): samples below detection limit

5.3.3 DOC, DIC, Phenols, and PAH’s

Duplicate samples were measured for dissolved organic and inorganic carbon, PAHs and phenol concentrations. The reported detection limit for phenols was 0.002 mg/L a range from 0.0075 to 0.2 µg/L for PAHs. A complete list of detection limits for PAH analysis is provided in Appendix C. These values are summarized in Table 5-3.

Table 5-3: Final dissolved organic and inorganic carbon, PAHs, and phenol concentrations in both Wheat and Willow biochar batch-type sorption experiment.

Sample	DOC (mg/L)	DIC (mg/L)	PAH’s (mg/L)	Phenols (mg/L)
Initial OSPW	56.0	161.5	Nd[1]	0.013
Wheat Final	37.8	211.16	Nd[1]	Nd[2]
Willow Final	33.8	283.3	Nd[1]	Nd[2]
Sample	**DOC Removal (%)**	**DIC Removal (%)**	**PAH Removal (%)**	**Phenol Removal (%)**
Wheat Final	32	-32	-	100
Willow Final	40	-70	-	100

[1] Nd (Non Detect): Samples not detected at a detection limit from 0.0075 to 0.2 µg/L

[2] Nd (Non Detect): Sample detection limit of 0.002 mg/L

DOC removal from OSPW is consistent with removal studies using similar carbon adsorbents. This removal is likely attributed to a decrease in naphthenic acid, PAH, and phenol concentration. DIC increase depends often on the source of biochar. The production and pyrolysis of biochars can, at times, encourage nutrient release in the form of DOC or DIC, depending on the source (Lehmann and Joseph, 2009). Most notably, Iranmanesh (2013) observed increased inorganic carbon in waters after treatment using biochar. In the study, it was speculated that carbon dioxide used in the pyrolysis of the biochar can loosely bind to the surface upon completion. When mixed with an aqueous solution, some carbon can dissolve, forming bicarbonate and carbonate complexes (Iranmanesh, 2013). Increased DOC was attributed to the potential release of volatiles from the biochar. In the study, DOC had increased while naphthenic acid concentration was decreased (Iranmanesh, 2013). The deviation in this study (a decrease in DOC was observed) can be attributed to the variation in biochar source. Lehmann (2007) suggests further the use of biochar as a slow nutrient release soil amendment, where carbon can be slowly delivered to plants when required. Similar scenarios have been observed from laboratory produced biochars, where oxidation promoted the release of dissolved carbon (Zimmerman, 2010). Since the sources and production techniques are highly varied, it is difficult to predict whether inorganic and organic carbon will release or not (Lehmann and Joseph, 2009).

5.3.4 Metal Removal

Duplicate samples were conducted with wheat and willow biochar to determine the removal percentages of government monitored metals. Control samples of biochar and deionized water were also measured to determine if any metal release was occurring. Final concentrations and removal percentages are presented in Table 5-4. Willow and wheat biochar, when mixed with deionized water, released Al (45.56 and 4.28 µg/L respectfully) and Cu (15.56 and 23.46 µg/L respectfully), while willow also released Mo (11.34 µg/L). While removal percentages were elevated (average removal of 66% and 73% for willow and wheat biochar respectfully), the following trace metal concentrations exceeded the surface water guidelines for the protection of aquatic life: Willow and wheat As (11.5 and 11.6 µg/L respectfully), Cu (48.4 and 126.4 µg/L respectfully), Mo (297.5 and 244.3 µg/L respectfully) and Se (31.0 and 9.4 µg/L respectfully).

Table 5-4: Final concentrations of monitored trace metals after mixing OSPW with willow and wheat biochar for 48 h. Control samples demonstrate trace metal release from biochar.

Analyte	Control Samples		Willow Biochar		Wheat Biochar	
	Willow Biochar C_{final} (µg/L)	Wheat Biochar C_{final} (µg/L)	C_{final} (µg/L)	Removal (%)	C_{final} (µg/L)	Removal (%)
Al	45.6	4.3	12.6	91%	0.0±0.0	100%
As	0	0	11.5±0.1	70%	11.6±0.2	70%
Cd	0	0	-	-	-	-
Cu	15.6	23.5	48.4±5.8	8%	33.7	36%
Mn	0	0	0.0±0.0	100%	0.0±0.0	100%
Mo	11.3	0	297.5±2.0	0%	244.3±1.3	18%
Ni	0	0	0.0±0.0	100%	0±0.0	100%
Pb	0	0	-	-	-	-
Se	0	0	31.0±0.0	92%	9.4±0.5	92%
V	0	0	25.9±0.6	64%	24.3±0.0	66%

Both biochars released minimal metals when mixed with deionized water. Metals bound on the biochar after pyrolysis are dependent on the source, as evident with Al release in particular. Metals released are likely a result of uptake from soil and incomplete volatilization of compounds during pyrolysis (Lehmann and Joseph, 2009). A visual comparison of willow and wheat biochar removal of metals is presented in Figure 5-1. A removal percentage across all samples was 69%. Both biochars had similar fixed carbon percentages (76.5 and 72.2 for wheat and willow biochar respectively). While no information on ultimate composition was available for willow biochar, it is expected that they are similarly composed. Both biochars were able to remove metals from OSPW, with no metal release occurring by either adsorbent (Figure 5-1).

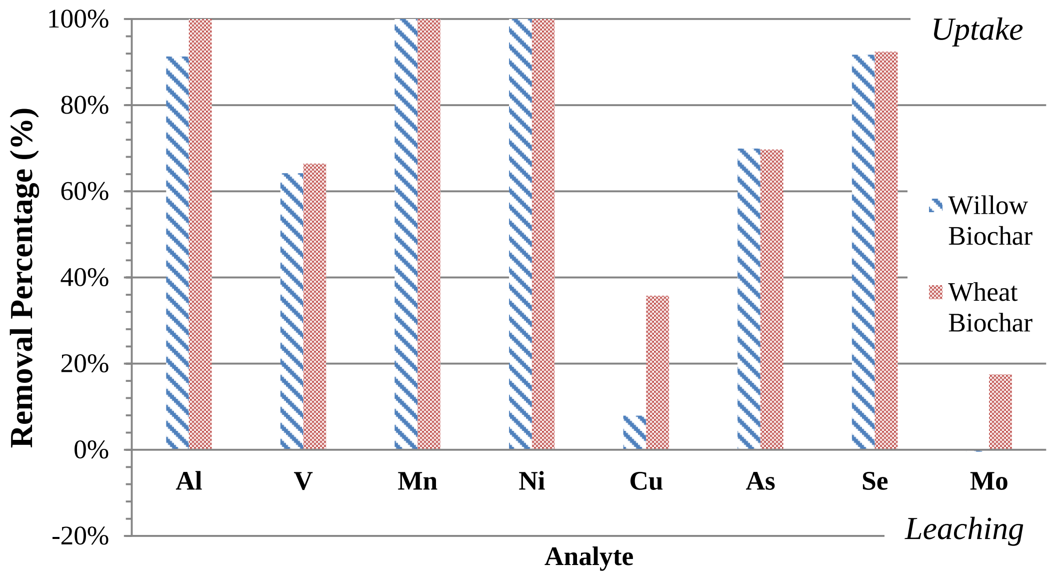


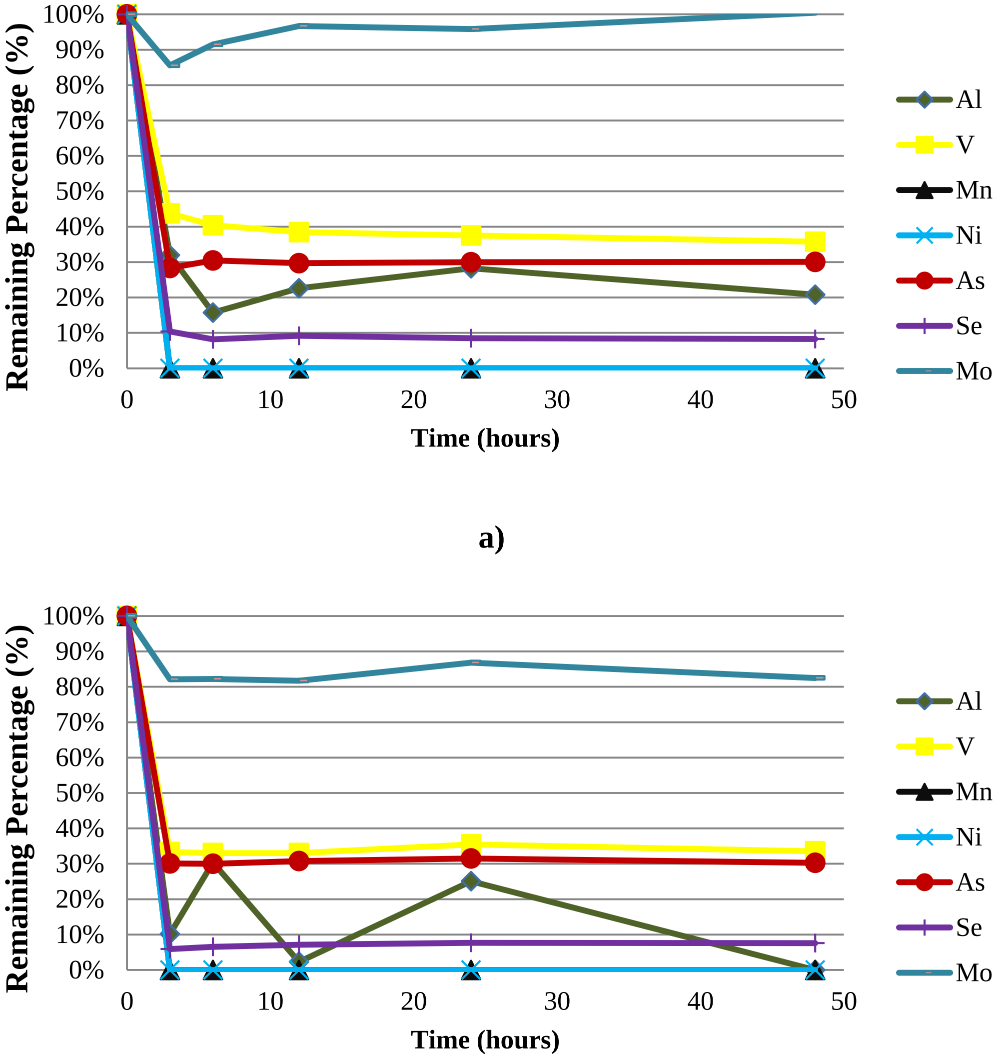
Figure 5-1: Removal percentages of metals from OSPW using willow and wheat biochar. Removal percentages represent an average of duplicates.

Despite high removal percentages, final metal concentrations still exceeded surface water quality guidelines. Both willow and wheat biochar exceeded guidelines in As, Cu, Mo, Se, and V. Work related to oil sands contaminant removal using biochar as an adsorbent suggested that biochar, when physically activated under carbon dioxide, produced large meso and micropore surface areas (Iranmanesh, 2013). Further stipulation from Iranmanesh (2013) suggests the production of biochar by pyrolysis yields increase micropores. These micropores may be more favorable for metal adsorption, as a larger surface area can be produced (Iranmanesh, 2013).

Table 5-5: Final concentrations of a 48h batch sorption test using willow and wheat biochar. Values in red cells represent those which exceed surface quality guidelines while green represents those under guidelines. Values represent an average of duplicates.

Analyte	Willow Biochar C_{final} (µg/L)	Wheat Biochar C_{final} (µg/L)
Al	12.6	0.0±0.0
As	11.5±0.1	11.6±0.2
Cd	0.0±0.0	0.0±0.0
Cu	48.4±5.8	33.7
Mn	0.0±0.0	0.0±0.0
Mo	297.5±2.0	244.3±1.3
Ni	0.0±0.0	0.0±0.0
Pb	0.0±0.0	0.0±0.0
Se	31.0±0.0	9.4±0.5
V	25.9±0.6	24.3±0.0

Figure 5-2 a) and b) demonstrate the remaining percentage of each trace metal in solution over the duration of the 48h batch test. The figures suggest that over 80% of trace metal removal occurs between 0 and 3 hrs with limited removal between 3 and 48 hrs. Both willow and wheat biochars display the same rapid decrease in trace metal concentration.



a)

b)

Figure 5-2: The adsorption of Government of Alberta monitored trace metals over the duration of the 48h batch test. Samples tested were a) willow biochar and b) wheat biochar.

These results are consistent with previous studies (Ho et al., 1996; Argun et al., 2007; Kwon et al., 2010), with rapid adsorption occurring within the first 3 hours. Adsorption capacities are elevated due to the purity of biochar (Lehmann and Joseph, 2010) and the elevated pH of the system (Jang et al., 2005). In their study, Jang et al. (2005) saw increased adsorption with a pH increase from 5 to 6. This was attributed to the increased formation of larger complexes that can successfully bind to the adsorbent (Jang et al., 2005). Ho et al. (2002) also found that preferential adsorption occurred with various metal ions, attributed mainly to ionic radius and specific surface area. This also agrees with theories introduced by Essington (2003). Despite the complexity of the system, adsorption occurred unhindered by ionic interference from other metals. The interference, discussed by Jang et al. (2005) and Kwon et al. (2010), reduces the total removal of other metals. Specifically, interference from Cu and Pb can reduce the adsorption of Zn and Cd. This did not occur in this study, as both Cu and Zn had elevated removal percentages (93% and 94% respectfully for willow biochar). The effective removal of Cu and Zn is due to the availability of adsorption sites on the biochar (Lehmann and Joseph, 2009). Small et al. (2012) showed that an optimal dosage of coke promotes the largest contaminant uptake. It is likely that metals in relatively low concentrations are able to adsorb without interfering with each other.

5.3.5 Naphthenic Acid Removal

Duplicate samples were analyzed for naphthenic acids. The initial concentration of naphthenic acids in was 3.60 and 4.17 mg/L. Final concentrations were 0.92 and 0.81 mg/L for willow biochar and 1.86 and 0.00 mg/L for wheat biochar. The average final concentrations and removal percentages are displayed in Table 5-6.

Table 5-6: Naphthenic acid concentration reduction by adsorption with wheat and willow biochar. Values are averages of two samples.

Sample ID	Total Concentration (mg/L)	Removal (%)
Initial OSPW	3.89	-
Willow Final	0.87	76%
Wheat Final	0.93	74%

Clemente and Fedorak (2005) suggest that a concentration of 2.5-5 mg/L of naphthenic acids is potentially toxic to aquatic organisms. While biochar presented moderate removal percentages, the final concentrations are below the suggested toxicity to aquatic organisms. As suggested by the American Society for Testing Methods (ASTM, 2009), a 24 h batch time is feasible for the study, as little decrease in concentration occurs after. Figure 5-3 displays the concentrations over the duration of the experiment. Approximately 50% of detectable naphthenic acids are removed in the first 3 h, while a decrease of a further 25% occurs by 24 hours.

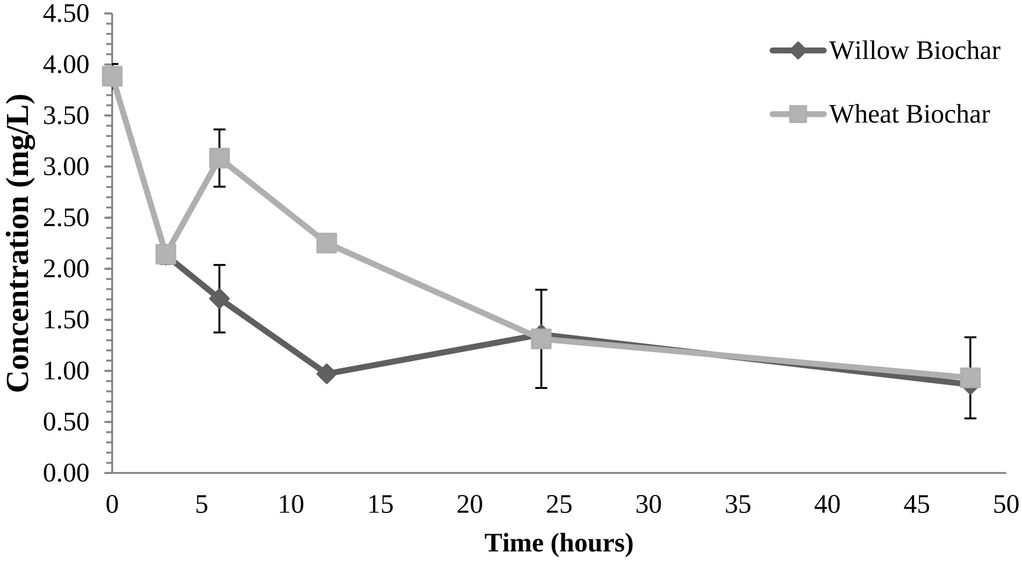


Figure 5-3: Adsorption of naphthenic acids onto willow and wheat biochar over a 48 h batch test. Concentrations displayed are an average of 2 samples. Error bars represent ± one standard deviation.

Limited work has been done regarding the adsorption of naphthenic acids by biochar. One study in particular by Iranmanesh (2013) report the removal of naphthenic acids from activated carbons produced under a variety of activation parameters. However, total carbon concentrations increased when biochar was used. It was suggested that naphthenic acid removal was occurring with biochar, but the release of loosely bound organic carbon was also occurring (Iranmanesh, 2013). The interaction between carbon material and carbon dioxide during pyrolysis and activation may also react with water during the experiment, producing carbonate compounds that may be measured as organic carbon (Iranmanesh, 2013). Such phenomena have been inconsistently observed, with parameters fluctuating based on the study. Beesley et al. (2010), for example, observed an increase in DOC while Gaskin et al. (2008) suggested leaching of organic carbon may depend on the source. In the case of willow and wheat biochar, limited DOC release occurred, with naphthenic acid removal dominating the uptake (~75%). When comparing DOC removal percentages (~35% between willow and wheat biochar), it can be suggested that the naphthenic acid fraction of organics within the OSPW is not the only source. DOC release from biochar may be occurring, however the release is less than the removal of phenols and naphthenic acids, and is therefore unquantifiable.

5.3.6 Microtox™ Toxicity Testing

Microtox™ toxicity samples were done to determine the mortality of *Vibrio fischeri* reagent bacteria. Microtox™ measures the change in luminescent output by *Vibrio fischeri* after being exposed to varying concentrations of sample. Initial OSPW samples had a 20% luminescence inhibitory concentration (IC_{20}) of 36.73% and 21.47% for 5 minutes and 15 minutes respectively. 5 minute samples are associated with organic compounds predominant in the water sample while 15 minute sample mortality is caused by metals (ASTM, 2009).

A 9 point dilution method was used to determine the toxicity of samples. In this method, a control was provided with a 9 point series 1:2 dilution of sample, meaning concentrations of sample range from 100% to 0.2%. The potential detoxification can be assessed through the comparison of initial and post-treatment samples (ASTM, 2009). From Table 5-7, treatment of water using willow and wheat biochar increased toxicity, reducing the concentration of sample required to produce an inhibition from 36.7% to 15.7% and 17.7% respectfully. This indicates an increase in sample toxicity, as a bacterial inhibition was observed at a smaller concentration of sample. Small (2011) notes a similar toxicological response. While naphthenic acids were removed in this study, other organics not measured may have been released. This release could contribute to the toxicity. A 15 minute increase in toxicity was observed, consistent with incomplete metal removal. It is likely that biochar removed non-toxic components of metals while a concentrated component remained. This would result in an increased sample toxicity.

Table 5-7: IC_{20} values for initial OSPW and final OSPW treated with willow and wheat biochar.

Sample	IC_{20} – 5 minutes (%)	IC_{20} – 15 minutes (%)
Initial OSPW	36.7%	21.5%
Biochar Willow	15.7%	16.0%
Biochar Wheat	17.7%	11.4%

Remaining naphthenic acids in solution may have contributed to components of toxicity Verbeek et al. (1993). The increase in toxicity attributed to both organic and inorganic compounds is likely due to the change in available metals and organics for bacterial uptake. For instance, Parent et al. (1996) noted that biological response to a given metal depends on the activity of the free ion. Since ICP-MS samples are acidified prior to measurement, a measurement of free ion adsorption was not undertaken. It is therefore possible that limited free ion adsorption occurred, which may result in an increased toxicity (Parent et al., 1996). The influence of elevated salts in solution may also contribute to a toxicological response (ASTM, 2009). Finally, organic compounds that were not tested may have leached into solution, causing an increase in toxicity.

5.4 Conclusion and Recommendations

The treatment of OSPW, focusing on the removal of metals, naphthenic acids, DOC, DIC, phenols, PAH's and toxicity, using two biochars (willow and wheat) was examined in this study. Both biochars were mixed with OSPW in a 48 h batch sorption test.

Results indicate a tendency to adsorb phenols, naphthenic acids and metals, with little release occurring. Phenol concentrations were decreased to below detection limits from 0.013 mg/L, while naphthenic acid concentration was reduced below 1 mg/L by both biochars. Willow and wheat biochar removed 66% and 73% (respectfully) of select metals of importance in this study. Despite the removal, As, Cu, Mo, and Se still exceeded surface water quality guidelines. This was due to the elevated metal concentrations and smaller micropore surface area present for contaminant adsorption.

Initial toxicity testing determined an initial IC_{20} of 36.7% and 21.5% for 5 minute and 15 minute inhibition (respectfully). This was reduced to 15.7% 5 minute inhibition and 16.0% 15 minute inhibition for willow biochar and 17.7% 5 minute inhibition and 11.4% 15 minute inhibition for wheat biochar. The reduction in toxicity is consistent with organic (naphthenic acids and phenols) and heavy metal concentration reduction, corresponding to a reduction in 5 and 15 minute inhibitory concentration respectfully.

Investigations into the use of biochar as an oil sands remediation tool should alter the physical structure of the biochar, specifically to increase the surface area-to-volume ratio. A full suite of physical and chemical characterization of biochar will also assist in correlating removal efficiencies with its structure and composition. Optimization of the biochar dosage may lead to its use on a larger scale within the oil sands.

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Chapter 6 - Conclusions and Recommendations for Future Work

6.1 Summary of Research

The projected expansion of Alberta's oil sands has sparked the need for contaminant management within the large volume of tailings. Investigations on the use of petroleum coke, and industry by-product, have focused largely on naphthenic acid removal. Relatively little attention has been given to metals present in the tailings. The remediation of both inorganic and organic contaminants is technically feasible using carbon-based adsorbents, including petroleum coke. Further analysis on the economic viability and performance on a large scale using these products is merited. A large scale experiment may determine if the mass of material required is operationally viable for industrial use.

This research has demonstrated the removal of naphthenic acids and metals from solution using petroleum coke and biochar. The source of tailings was from Suncor Energy Ltd.'s South Tailings Pond. The research presented is divided into 4 main components:

1. The fate of naphthenic acids as OSPW is mixed with glacial till and sand channel material underlying the STP (Section 6.2).
2. The analysis of naphthenic acids using ESI FTICR MS (Section 6.3).
3. The removal of naphthenic acids and metals from groundwater using delayed coke, an industry by-product of Suncor Energy Ltd.'s upgrading process (Section 6.4).
4. The use of biochar, a carbonaceous product produced from the pyrolysis of organic waste, for DOC, DIC, naphthenic acids, metals, PAH's, phenols and toxicity removal (Section 6.5).

6.2 Naphthenic Acid Migration Through Subsurface

OSPW from Suncor Energy Ltd was mixed with two types of sediment underlying the South Tailings Pond: glacial till and Wood Creek Sand Channel sand in order to simulate the migration of OSPW into the groundwater. The objective was to determine whether naphthenic acids adsorb of desorb as OSPW migrates through the subsurface. The two soils investigated were found in the underlying clay-till (Soil 4D sampled at 38.1 meters below ground level) and sand channel (Soil 4B sampled at 61.0 meters below ground level).

Both the low carbon content and cation exchange capacity indicated unfavorable conditions for adsorption. This was confirmed in the 48 h batch sorption study, done anaerobically and aerobically. The following conclusions were drawn from the experiment:

1. Concentrations of naphthenic acids fluctuated minimally (a maximum difference between initial and final concentrations observed for GC FID was 34%).
2. There was no difference between the adsorption behavior of naphthenic acids when experimental conditions were anaerobic or aerobic. Therefore, no competitive anaerobic reactions are occurring that may promote or discourage sorption of naphthenic acids.
3. Overall, both measurement techniques agreed that limited change in naphthenic acid concentration is occurring in solution. Therefore, naphthenic acids may be migrating with limited retardation through the underlying sediment and into the Wood Creek Sand Channel.

6.3 Enhanced Naphthenic Acids Measurement using ESI-FTICR-MS

Naphthenic acids were measured using negative ionization electrospray. While other analysis techniques such as high-pressure liquid chromatography/high-resolution mass spectrometry (HPLC/HRMS) can significantly limit false positives, electrospray ionization may also be used to provide significant data resolution on naphthenic acid measurement.

This study compared a sample of OSPW with published data on the structure and predominance of classical naphthenic acids ($C_nH_{(2n+z)}O_2$) in a sample containing oxy-naphthenic acids ($C_nH_{(2n+z)}O_x$). Outputs of individual classes of naphthenic acids ($C_nH_{(2n+z)}O_2$, $C_nH_{(2n+z)}O_3$, $C_nH_{(2n+z)}O_4$ and $C_nH_{(2n+z)}O_5$), as well as C^{13}

isotopes and sodium dimer concentrations were provided. Within the context of this study, the following conclusions were made:

1. ESI FTICR MS can be used to approximate the concentration of classical and oxy-naphthenic acids ($C_nH_{(2n+z)}O_2$, $C_nH_{(2n+z)}O_3$, $C_nH_{(2n+z)}O_4$ and $C_nH_{(2n+z)}O_5$), as well as C^{13} isotopes and sodium dimers.
2. ESI FTICR MS can be used in greater confidence for the distribution of the former parameters within a sample.
3. There is a large difference between the concentrations of samples measured using FT IR, GC FID, and ESI FTICR MS. The latter averaged a measured concentration of 12% when compared to that measured using FT IR.

6.4 Removal of Metals and Naphthenic Acids using Non-Acid Washed and Acid Washed Delayed Coke

Delayed coke from Suncor Energy Ltd. upgrading process was used to remove metals and naphthenic acids from groundwater. There exist surface bound metals on delayed coke that are deposited during the upgrading process. These metals tend to leach when delayed coke is used as an adsorbent. To inhibit this from occurring, an acid washing pre-treatment using 0.25M HCl was done to clean the outer surface, micropores and mesopores. The general results indicate greater adsorption with an acid washing pre-treatment. Specifically, the following trends were observed:

1. As surface area-to-volume ratio was increased (from 0.8-2 mm raw coke to 75-150 µm activated coke), there was a tendency for a more metal uptake and release to occur. It is likely the activation of coke enhanced pore surface area, allowing more contaminants to leach into solution.
2. Acid washing the coke showed a decrease in metal release and an increase in removal. In this case, a higher surface area-to-volume ratio generally increased uptake (or enhanced release in the case of Mo). The acid washing process removed metals bound primarily to the outer surface of the coke, with limited removal within the pores.

3. Naphthenic acid removal increased (from 56% to 89% and 83% to 97% for non-acid washed and acid washed coke respectfully) as the surface area-to-volume ratio increased (0.8-2 mm raw coke to 75-150 μm activated coke). There was also an increase in naphthenic acid removal between non-acid washed coke and acid washed coke. The acid washing process therefore promotes the adsorption of naphthenic acids from OSPW.

6.5 Removal of OSPW Contaminants using Wheat Straw and Willow Biochar

The final study done in this research was the introduction of biochar to the removal of oil sands contaminants. Biochar has previously had little research into its use as an adsorbent for contaminant removal, with much work focusing on its use as a soil conditioner. This work presents early use of biochar in oil sands contaminant remediation. From the findings, the following conclusions were made:

1. DOC and DIC concentrations were decreased and increased (respectfully), owing to the removal of phenols and naphthenic acids for DOC removal and the leaching of natural inorganic carbon material for DIC increase. Phenols were removed by both wheat and willow biochar. The preparation of biochar, and lack of impurities deposited as it is produced, allows for high contaminant uptake, despite a smaller surface area.
2. Metal uptake was observed in almost every instance (the exception being a 0% change in Mo for willow biochar). An average metal (Al, As, Cd, Cu, Mn, Mo, Ni, Pb, Se, and V) uptake was 66% and 73% for willow and wheat biochar respectfully. Several metals (As, Cu, Mo, and Se) still exceeded surface water quality guidelines, owing to the unaltered poresize of the biochar.
3. Naphthenic acids concentration was reduced below 1 mg/L by both willow and wheat biochar. Limited surface impurities and alkaline conditions favorable for naphthenic acid uptake encouraged the removal of acids.

4. Both toxicities were reduced by willow and wheat biochar, from 36.7% inhibition to 15.7% and 17% respectfully [5 minutes], and from 21.5% to 16.0% and 11.4% respectfully [15 minutes]). This toxicity reduction is consistent with the removal of organics (tend to contribute to 5 minute inhibitory toxicity) and metals (contribute to 15 minute inhibitory toxicity).

This study demonstrated that biochar, a product of the pyrolysis of organic materials, can be used to successfully remove contaminants related to oil sands mining operations.

6.6 Recommendation for Future Work

An investigation into the removal of inorganic and organic contaminants from oil sands tailings was undertaken in this study. The materials tested were clay-till and sand, both found naturally underlying a tailings pond, delayed petroleum coke and biochar. The enhanced measurement of naphthenic acids using ESI-FTICR-MS was also investigated. Studies that wish to enhance the results found in this research should focus on one of 3 main areas.

1. The use of ESI FTICR MS can be further enhanced to include a variety of naphthenic acid compounds. Work can expand the list of detected species, and include a sulphur and nitrogen bearing naphthenic acid standard. Using this, sulphur and nitrogen bearing naphthenic acids can be quantified and qualified within OSPW. Nitrogen isotopes can also be included in this analysis.
2. Further pre-treatment steps to clean delayed coke can be investigated for full removal of contaminants bound to the surface or within coke. It is likely that pore clogging is occurring when samples are acid washed, limiting the uptake and enhancing the release of contaminants in activated coke. A more rigorous acid washing, or other treatment options, should be investigated.
3. The expanded use of biochar can be investigated within the context of the oil sands operations in Alberta. Thus far, willow and wheat biochar have

shown contaminant removal, but not below surface water quality guidelines (for metals). The physical properties of the biochar source, in this study, were unaltered. Alteration of the biochar should be investigated, as simply crushing the biochar may improve removal percentages immensely.

Future work in these areas can further develop our understanding of oil sands contaminants, and may provide a viable means through which to reuse industry by-products for the treatment of tailings from the operations. The expansion of biochar in Alberta also provides an avenue through which agricultural waste may be reused to assist in soil conditioning and contaminant removal.

Chapter 7 - Appendices

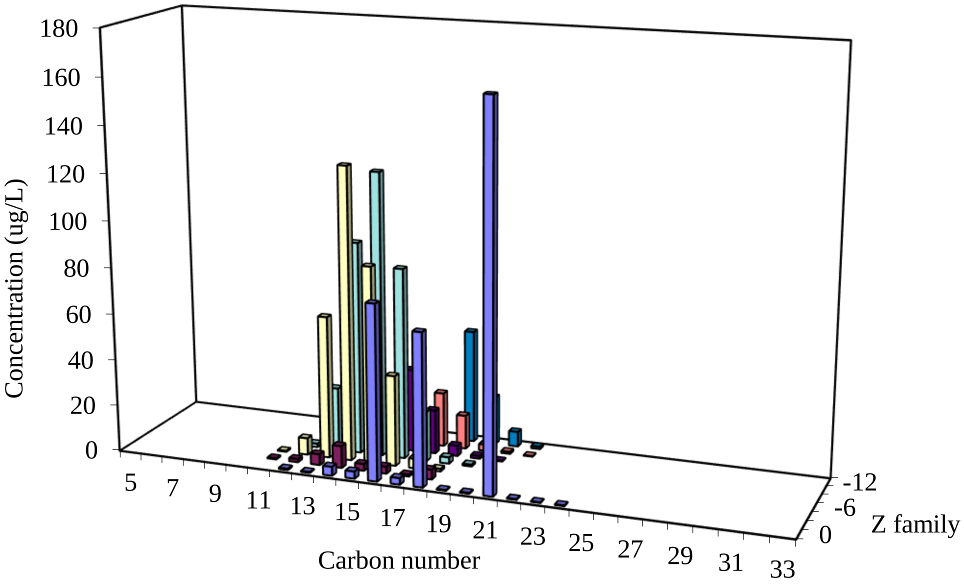
Appendix A: Commercial Laboratory Data, Compiled ESI-FTICR-MS Analysis for 1:12 Anaerobic Clay, FT-IR and GC-FID Calibration.

Appendix A summarizes data from Maxxam Commercial Laboratories (Maxxam Analytics, Edmonton, Alberta, Canada), as well as ESI-FTICR-MS analysis. Presented in Figure 7-1 through 10 are the results for samples 1 through 5 of 1:12 anaerobic clay. Finally, the calibration for FT-IR and GC-FID are provided (Figure 7-11 through 13).

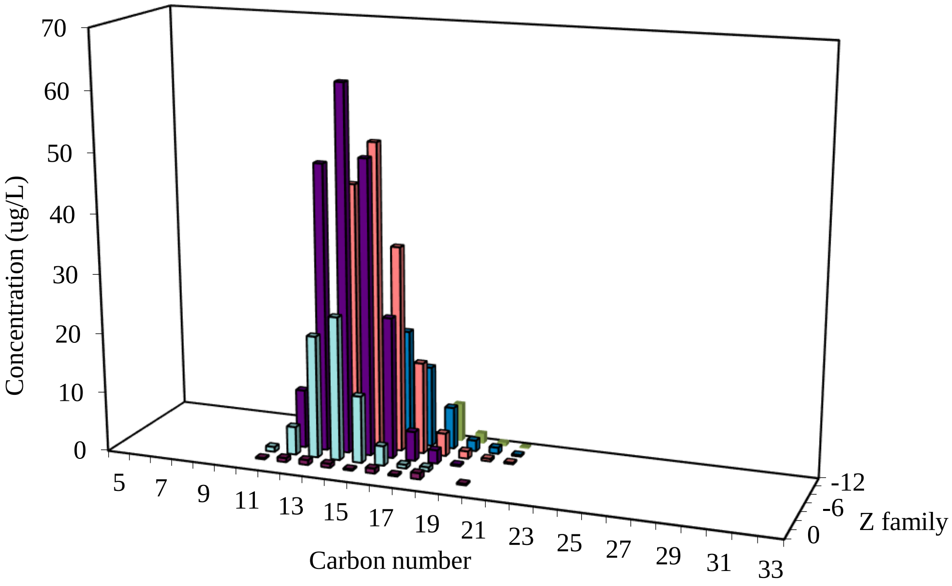
Table 7-1: Sediment Analysis of Soils 4D and 4B. Analysis completed by Maxxam Analytics (Maxxam Analytics, Edmonton, Alberta, Canada).

		Sample ID		
		Soil 4D	Soil 4B	
Property	**Units**	**Result**	**Result**	**Detection Limit**
Calcium	mg/kg	3020	1190	10
Magnesium	mg/kg	205	44	5
Potassium	mg/kg	99	27	20
Sodium	mg/kg	29	58	20
Base Saturation	%	200	>200	1
Calcium	meq/100g	15.1	5.9	0.05
Magnesium	meq/100g	1.7	0.4	0.04
Potassium	meq/100g	0.25	0.07	0.05
Sodium	meq/100g	0.1	0.2	0.05
Exchangeable Sodium	%	2	>6	p0.2
TEC	meq/100g	17	7	2
Cation Exchange Capacity	meq/100g	8	<4	4
Carbon - Total Inorganic	% dry weight	0.61	0.12	0.05
Carbon - Total Organic	% dry weight	1.66	0.28	0.05
Physical and Aggregate Properties				
Moisture	%	11.2	10.8	0.1
Texture		Sandy Loam	Sand	
Sand	% by weight	57.4	93.4	0.1
Silt	% by weight	25.8	2.4	0.1
Clay	% by weight	16.8	4.2	0.1
Bulk Density	kg/L	1.97	1.61	
Wet Bulk Density	kg/L	2.22	1.81	
Soil Acidity				
pH	pH	8	8.2	

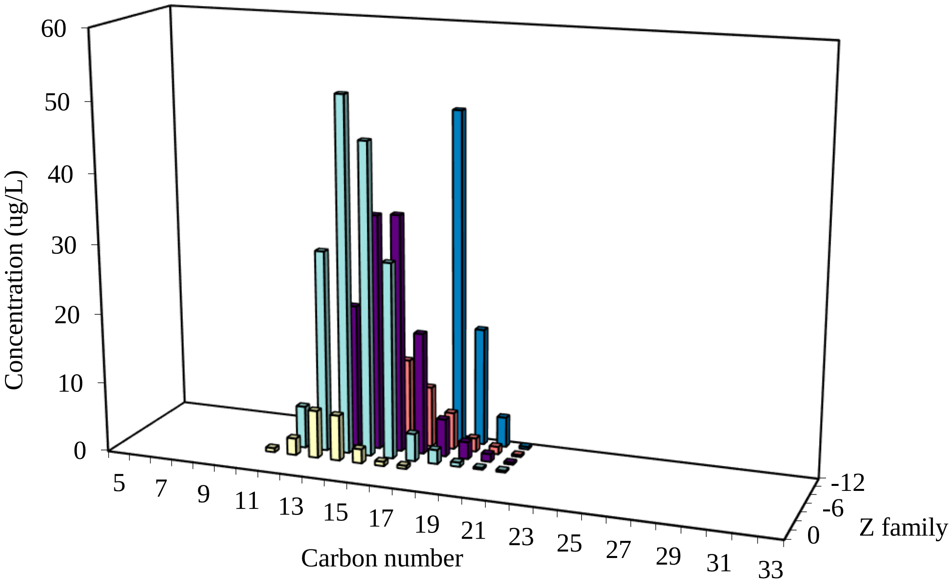
1:12 Anaerobic Clay Sample 1:



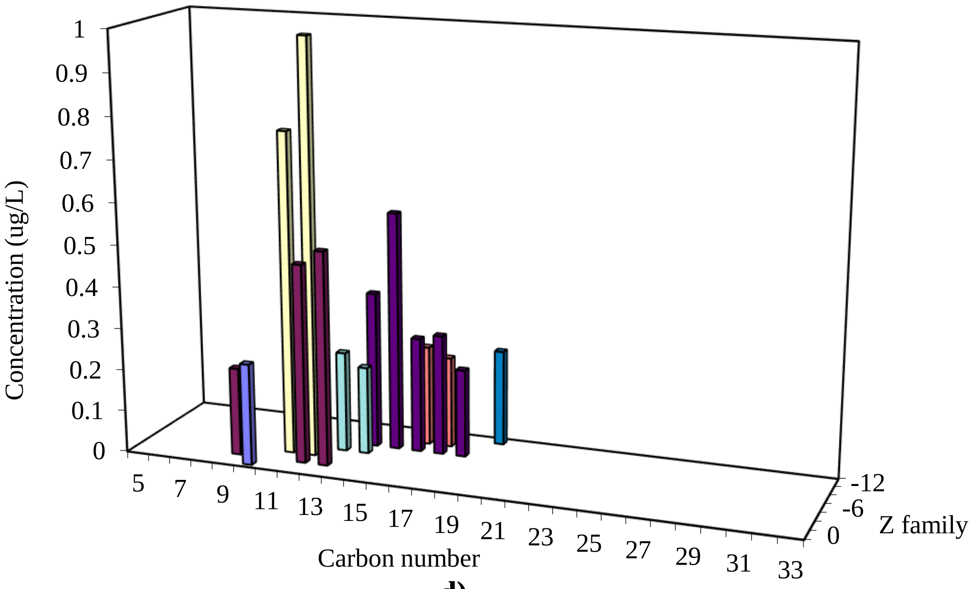
a)



b)

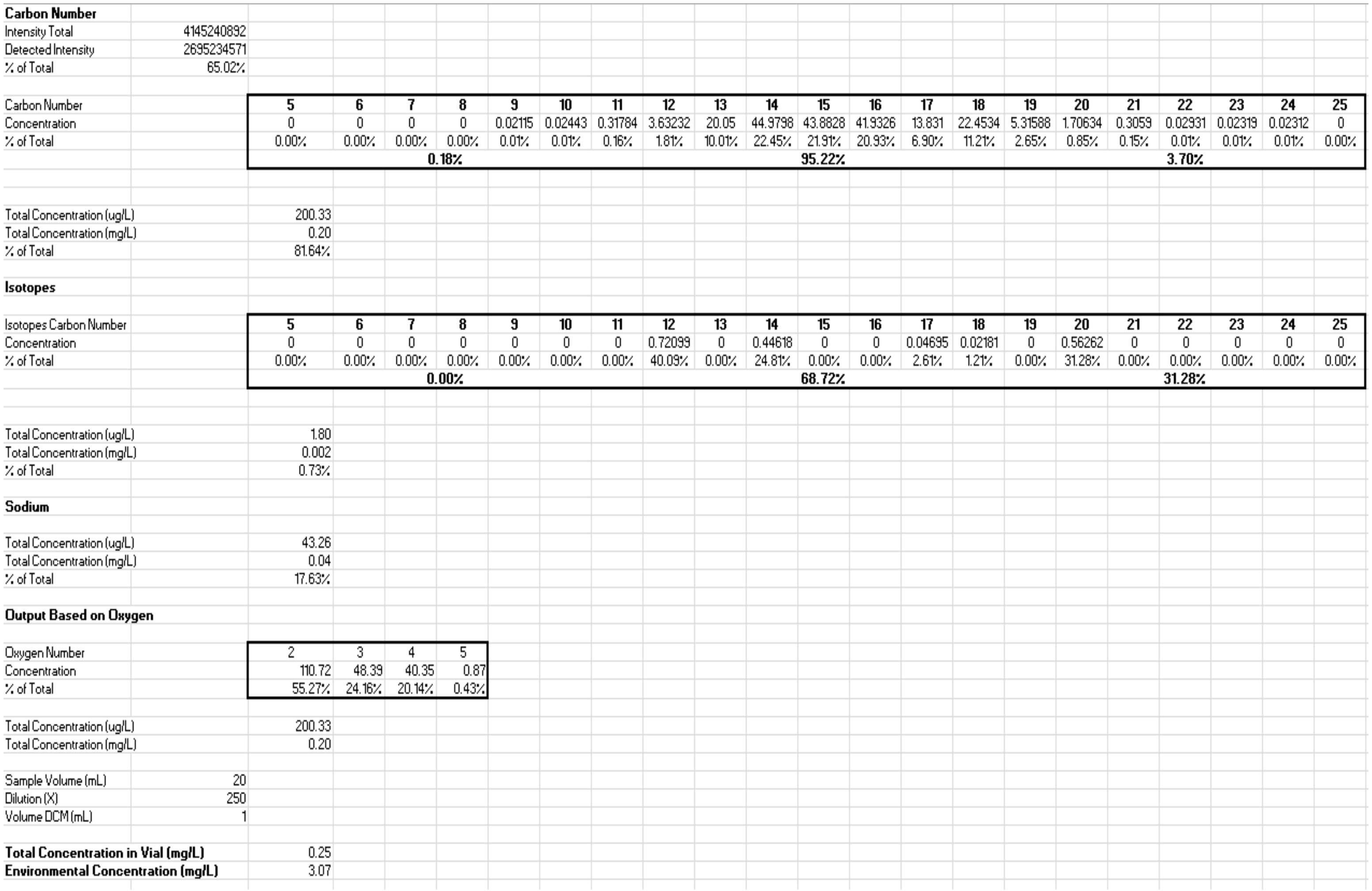


c)



d)

Figure 7-1: ESI-FTICR-MS data for sample 1 (3 h). Charts represent naphthenic acids in the generic formula $C_nH_{(2n+z)}O_x$, with a) $C_nH_{(2n+z)}O_2$, b) $C_nH_{(2n+z)}O_3$, c) $C_nH_{(2n+z)}O_4$ and d) $C_nH_{(2n+z)}O_5$.



Carbon Number

Intensity Total	4145240892
Detected Intensity	2695234571
% of Total	65.02%

Carbon Number	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**
Concentration	0	0	0	0	0.02115	0.02443	0.31784	3.63232	20.05	44.9798	43.8828	41.9326	13.831	22.4534	5.31588	1.70634	0.3059	0.02931	0.02319	0.02312	0
% of Total	0.00%	0.00%	0.00%	0.00%	0.01%	0.01%	0.16%	1.81%	10.01%	22.45%	21.91%	20.93%	6.90%	11.21%	2.65%	0.85%	0.15%	0.01%	0.01%	0.01%	0.00%
	0.18%							**95.22%**							**3.70%**						

Total Concentration (ug/L)	200.33
Total Concentration (mg/L)	0.20
% of Total	81.64%

Isotopes

Isotopes Carbon Number	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**
Concentration	0	0	0	0	0	0	0	0.72099	0	0.44618	0	0	0.04695	0.02181	0	0.56262	0	0	0	0	0
% of Total	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	40.09%	0.00%	24.81%	0.00%	0.00%	2.61%	1.21%	0.00%	31.28%	0.00%	0.00%	0.00%	0.00%	0.00%
	0.00%							**68.72%**							**31.28%**						

Total Concentration (ug/L)	1.80
Total Concentration (mg/L)	0.002
% of Total	0.73%

Sodium

Total Concentration (ug/L)	43.26
Total Concentration (mg/L)	0.04
% of Total	17.63%

Output Based on Oxygen

Oxygen Number	2	3	4	5
Concentration	110.72	48.39	40.35	0.87
% of Total	55.27%	24.16%	20.14%	0.43%

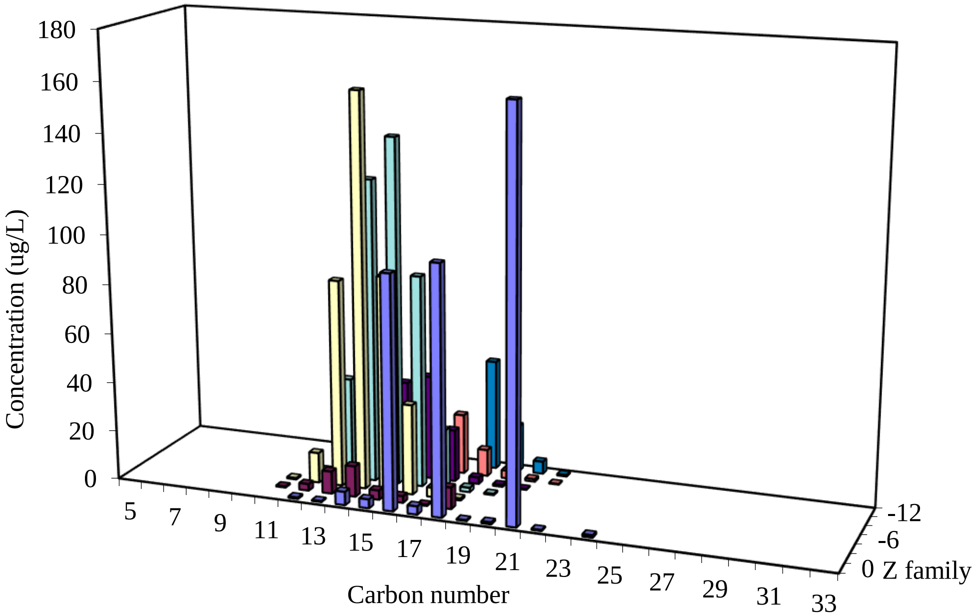
Total Concentration (ug/L)	200.33
Total Concentration (mg/L)	0.20

Sample Volume (mL)	20
Dilution (X)	250
Volume DCM (mL)	1

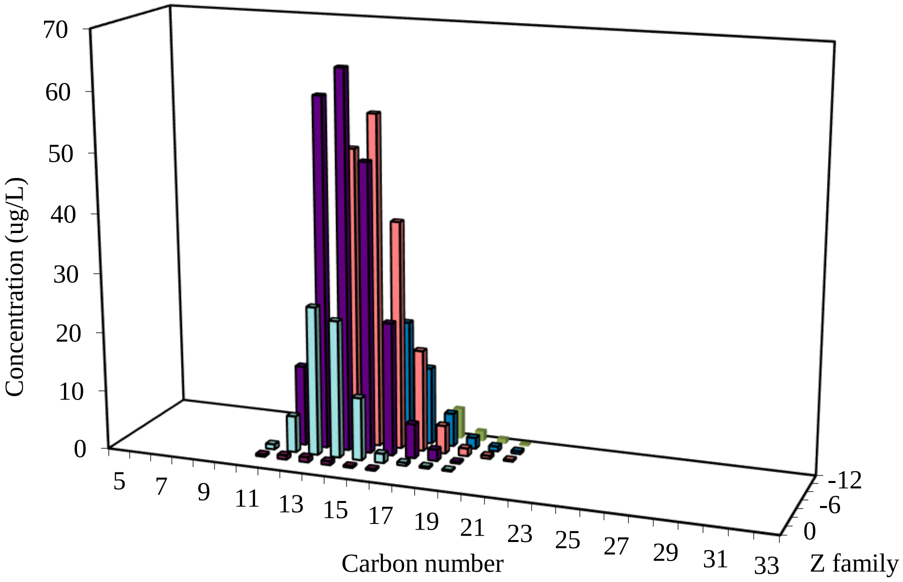
Total Concentration in Vial (mg/L)	0.25
Environmental Concentration (mg/L)	3.07

Figure 7-2: Spreadsheet output for the characterization of naphthenic acids in OSPW for sample 1 (3h). Carbon number provides an output based on carbon number n, while isotope output is solely the concentration of C13 isotopes based on concentration, and sodium output presents the concentration of sodium dimers (excluding values obtained from the O_2 series).

1:12 Anaerobic Clay Sample 2:



a)



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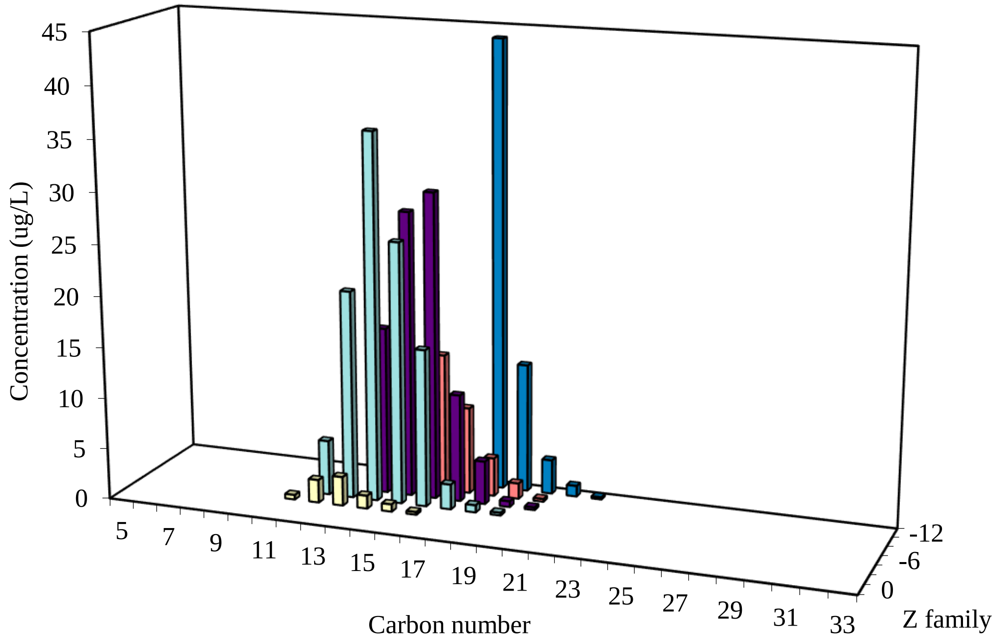
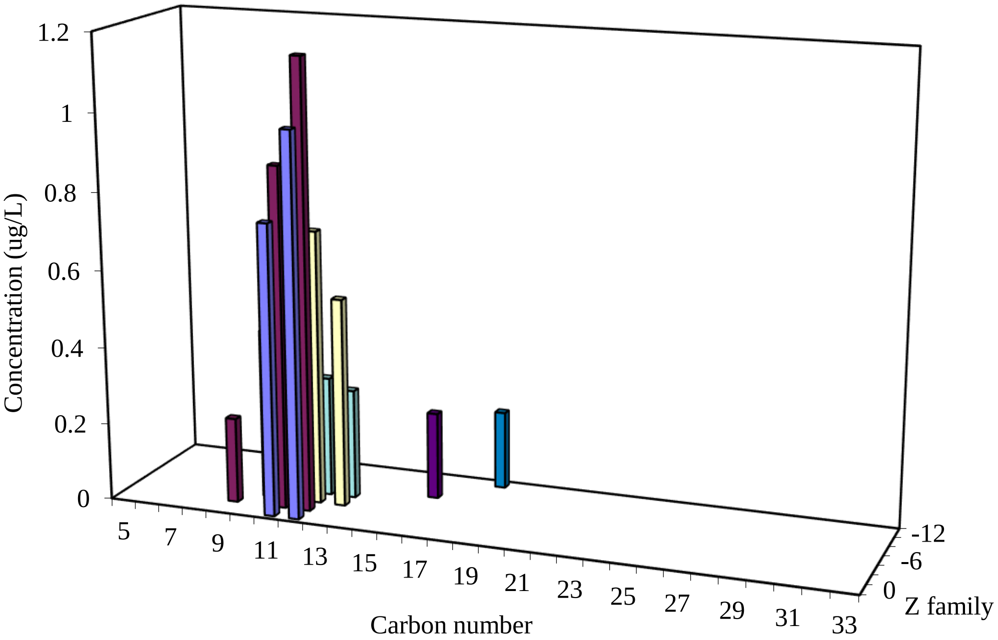
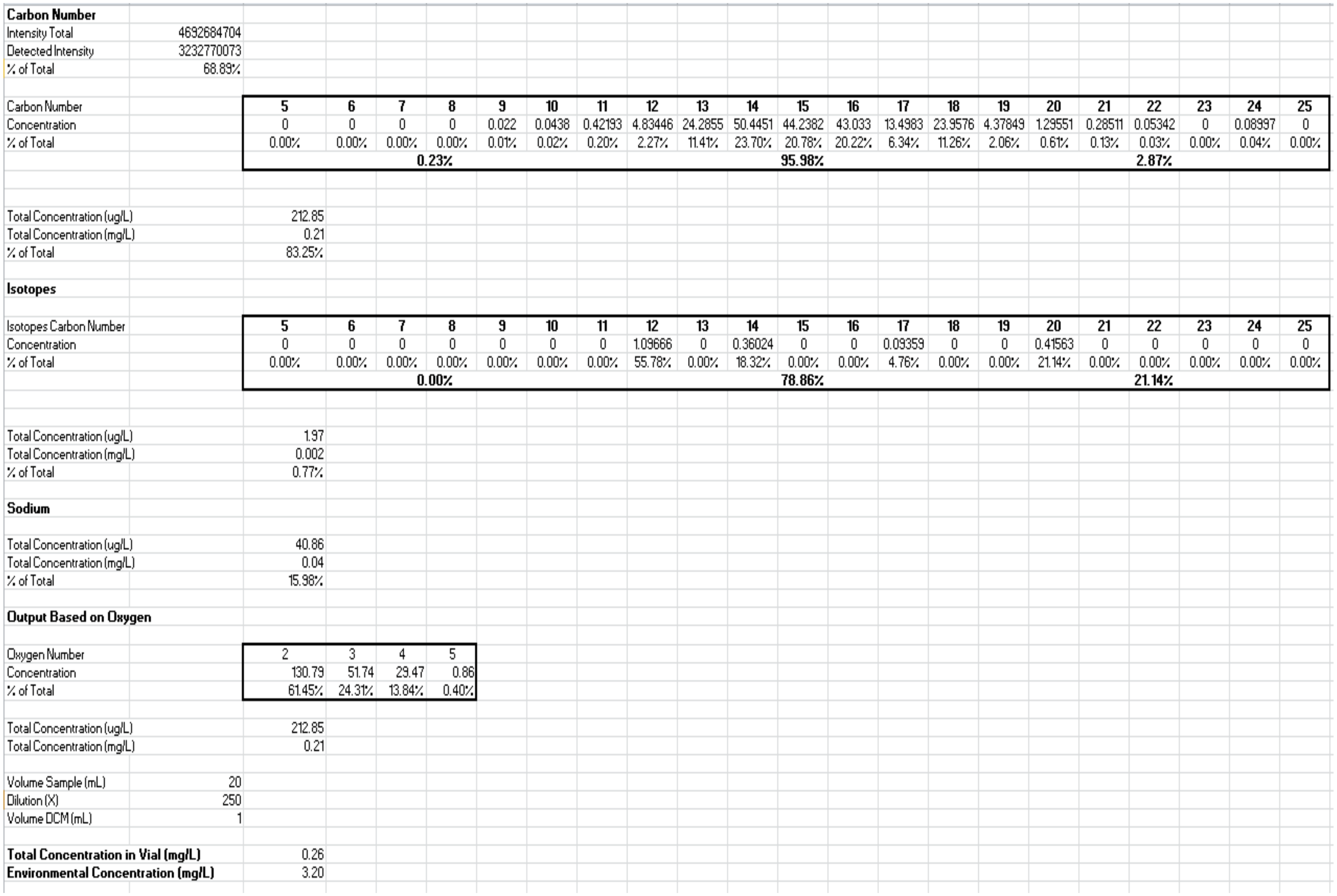


c)



d)

Figure 7-3: ESI-FTICR-MS data for sample 2 (6 h). Charts represent naphthenic acids in the generic formula $C_nH_{(2n+z)}O_x$, with a) $C_nH_{(2n+z)}O_2$, b) $C_nH_{(2n+z)}O_3$, c) $C_nH_{(2n+z)}O_4$ and d) $C_nH_{(2n+z)}O_5$.



Carbon Number

Intensity Total	4692684704
Detected Intensity	3232770073
% of Total	68.89%

Carbon Number	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Concentration	0	0	0	0	0.022	0.0438	0.42193	4.83446	24.2855	50.4451	44.2382	43.033	13.4983	23.9576	4.37849	1.29551	0.28511	0.05342	0	0.08997	0
% of Total	0.00%	0.00%	0.00%	0.00%	0.01%	0.02%	0.20%	2.27%	11.41%	23.70%	20.78%	20.22%	6.34%	11.26%	2.06%	0.61%	0.13%	0.03%	0.00%	0.04%	0.00%
				0.23%							**95.98%**							**2.87%**			

Total Concentration (ug/L)	212.85
Total Concentration (mg/L)	0.21
% of Total	83.25%

Isotopes

Isotopes Carbon Number	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Concentration	0	0	0	0	0	0	0	1.09666	0	0.36024	0	0	0.09359	0	0	0.41563	0	0	0	0	0
% of Total	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	55.78%	0.00%	18.32%	0.00%	0.00%	4.76%	0.00%	0.00%	21.14%	0.00%	0.00%	0.00%	0.00%	0.00%
				0.00%							**78.86%**							**21.14%**			

Total Concentration (ug/L)	1.97
Total Concentration (mg/L)	0.002
% of Total	0.77%

Sodium

Total Concentration (ug/L)	40.86
Total Concentration (mg/L)	0.04
% of Total	15.98%

Output Based on Oxygen

Oxygen Number	2	3	4	5
Concentration	130.79	51.74	29.47	0.86
% of Total	61.45%	24.31%	13.84%	0.40%

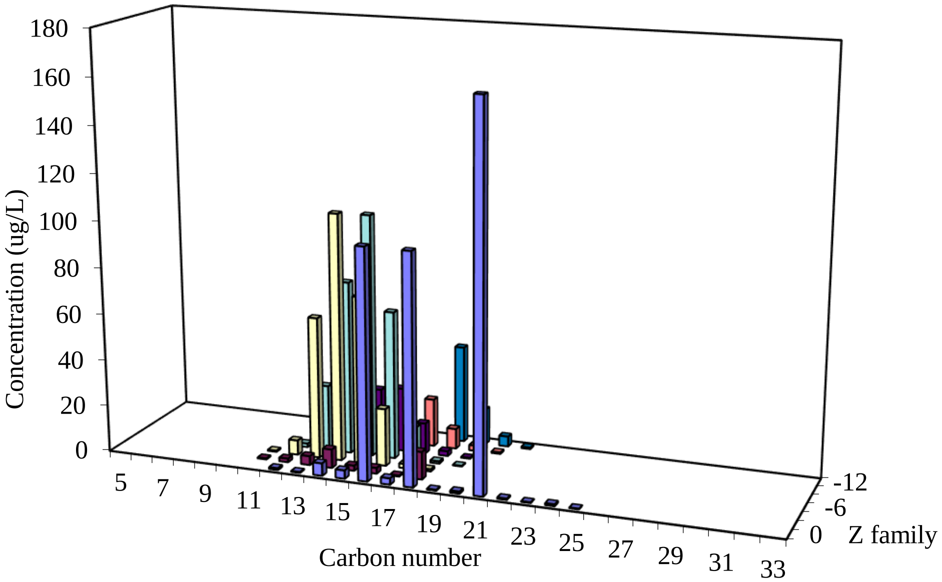
Total Concentration (ug/L)	212.85
Total Concentration (mg/L)	0.21

Volume Sample (mL)	20
Dilution (X)	250
Volume DCM (mL)	1

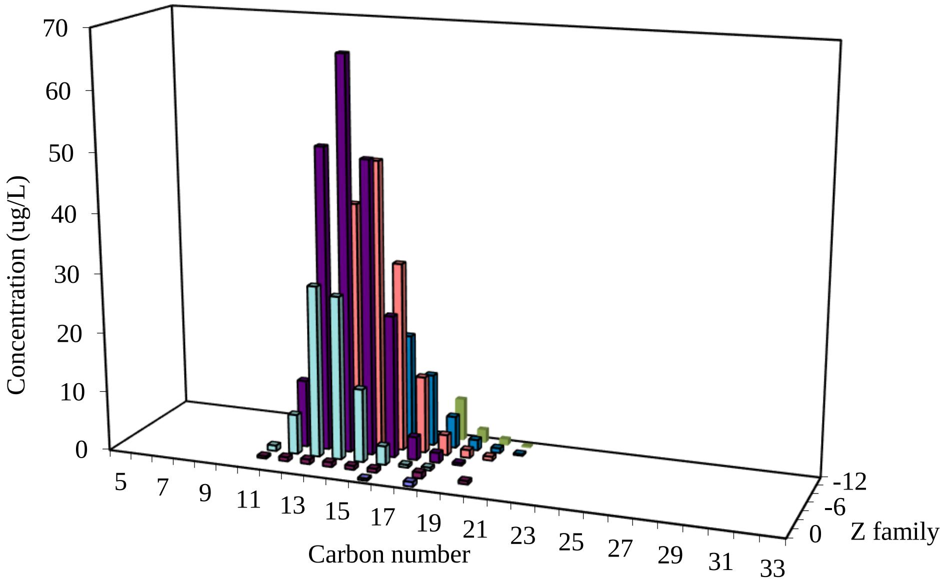
Total Concentration in Vial (mg/L)	0.26
Environmental Concentration (mg/L)	3.20

Figure 7-4: Spreadsheet output for the characterization of naphthenic acids in OSPW for sample 2 (6h). Carbon number provides an output based on carbon number n, while isotope output is solely the concentration of C13 isotopes based on concentration, and sodium output presents the concentration of sodium dimers (excluding values obtained from the O_2 series).

1:12 Anaerobic Clay Sample 3:



a)



b)

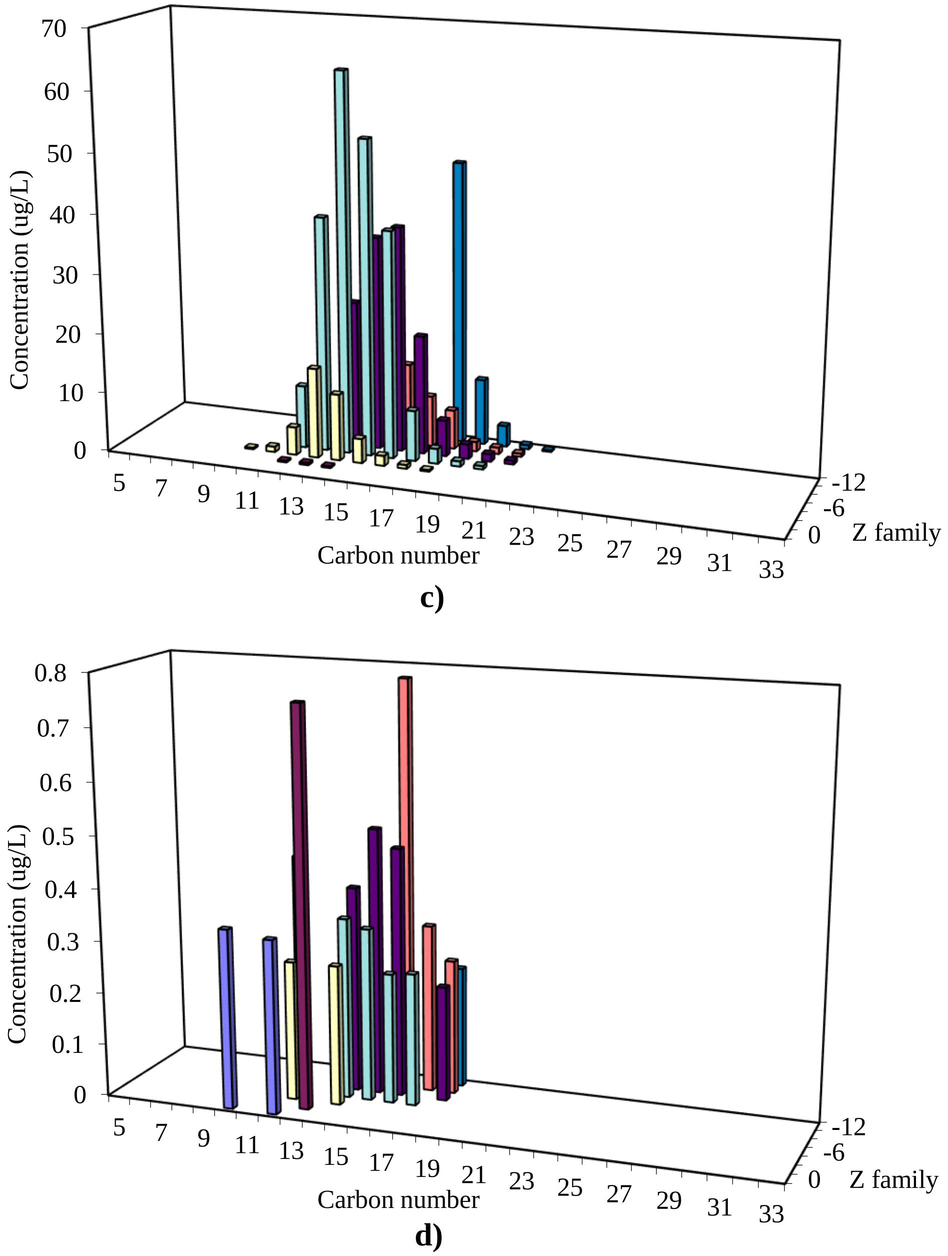
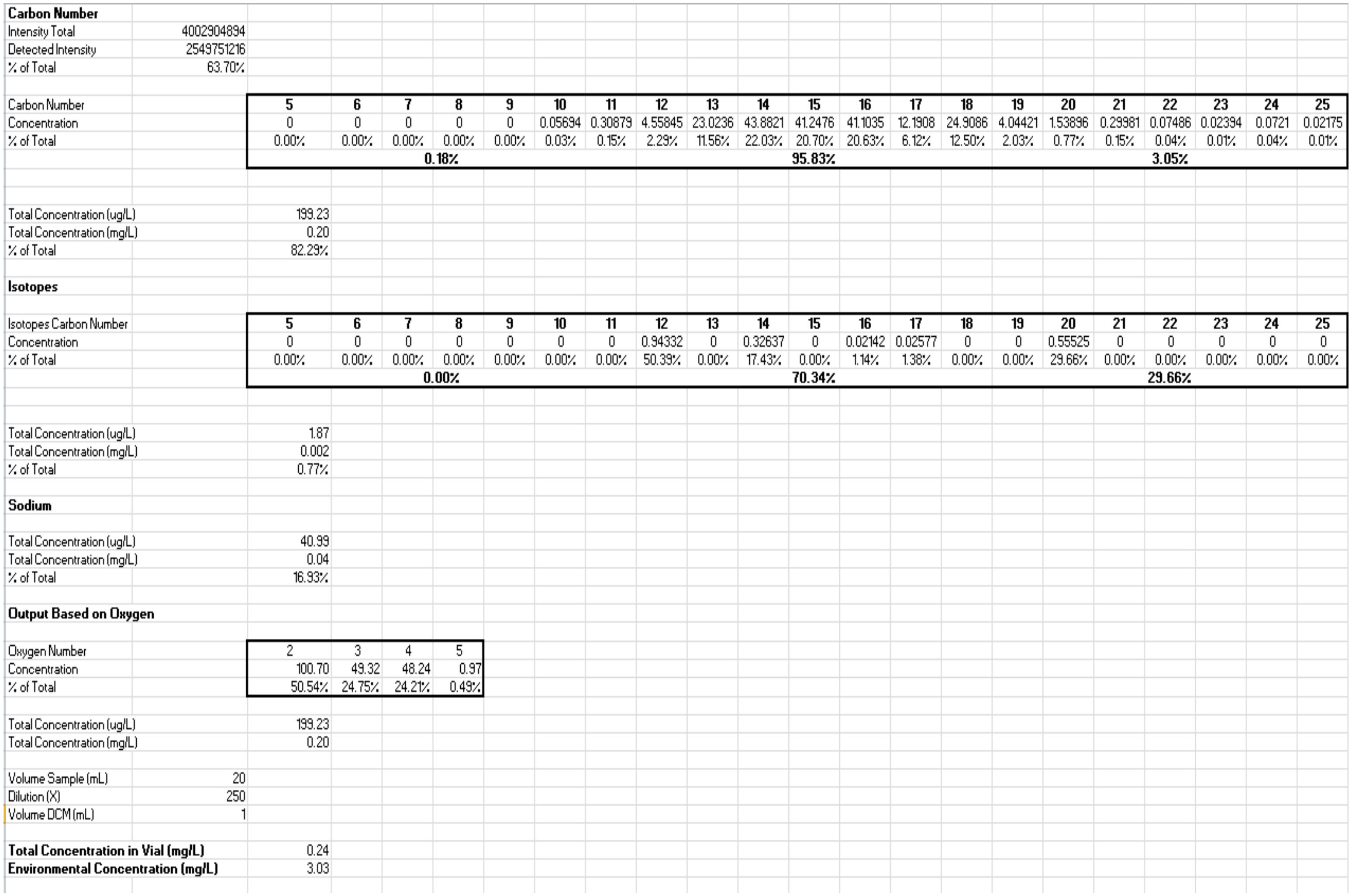


Figure 7-5: ESI-FTICR-MS data for sample 3 (12 h). Charts represent naphthenic acids in the generic formula $C_nH_{(2n+z)}O_x$, with a) $C_nH_{(2n+z)}O_2$, b) $C_nH_{(2n+z)}O_3$, c) $C_nH_{(2n+z)}O_4$ and d) $C_nH_{(2n+z)}O_5$.



Carbon Number

Intensity Total	4002904894
Detected Intensity	2549751216
% of Total	63.70%

Carbon Number	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Concentration	0	0	0	0	0	0.05694	0.30879	4.55845	23.0236	43.8821	41.2476	41.1035	12.1908	24.9086	4.04421	1.53896	0.29981	0.07486	0.02394	0.0721	0.02175
% of Total	0.00%	0.00%	0.00%	0.00%	0.00%	0.03%	0.15%	2.29%	11.56%	22.03%	20.70%	20.63%	6.12%	12.50%	2.03%	0.77%	0.15%	0.04%	0.01%	0.04%	0.01%
				0.18%							**95.83%**							**3.05%**			

Total Concentration (ug/L)	199.23
Total Concentration (mg/L)	0.20
% of Total	82.29%

Isotopes

Isotopes Carbon Number	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Concentration	0	0	0	0	0	0	0	0.94332	0	0.32637	0	0.02142	0.02577	0	0	0.55525	0	0	0	0	0
% of Total	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	50.39%	0.00%	17.43%	0.00%	1.14%	1.38%	0.00%	0.00%	29.66%	0.00%	0.00%	0.00%	0.00%	0.00%
				0.00%							**70.34%**							**29.66%**			

Total Concentration (ug/L)	1.87
Total Concentration (mg/L)	0.002
% of Total	0.77%

Sodium

Total Concentration (ug/L)	40.99
Total Concentration (mg/L)	0.04
% of Total	16.93%

Output Based on Oxygen

Oxygen Number	2	3	4	5
Concentration	100.70	49.32	48.24	0.97
% of Total	50.54%	24.75%	24.21%	0.49%

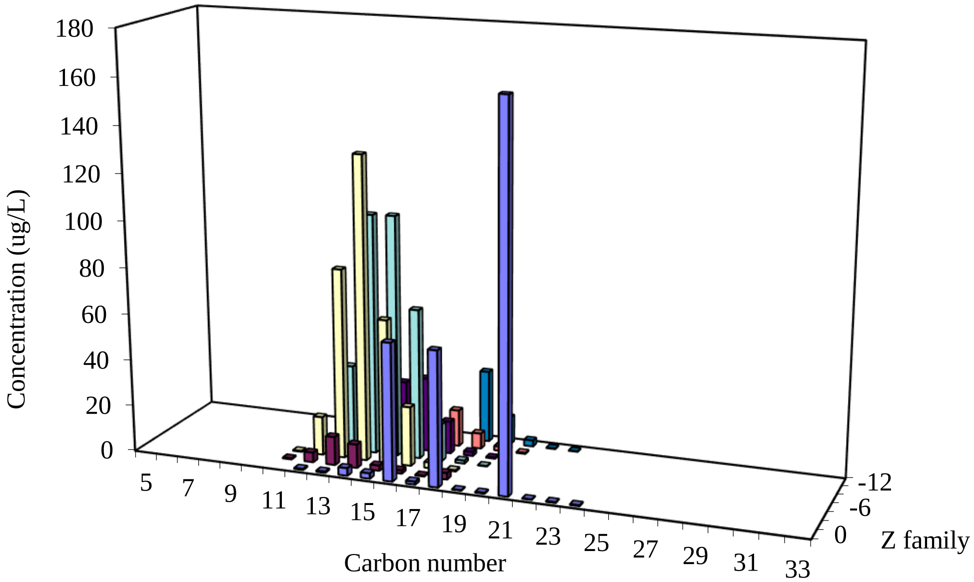
Total Concentration (ug/L)	199.23
Total Concentration (mg/L)	0.20

Volume Sample (mL)	20
Dilution (X)	250
Volume DCM (mL)	1

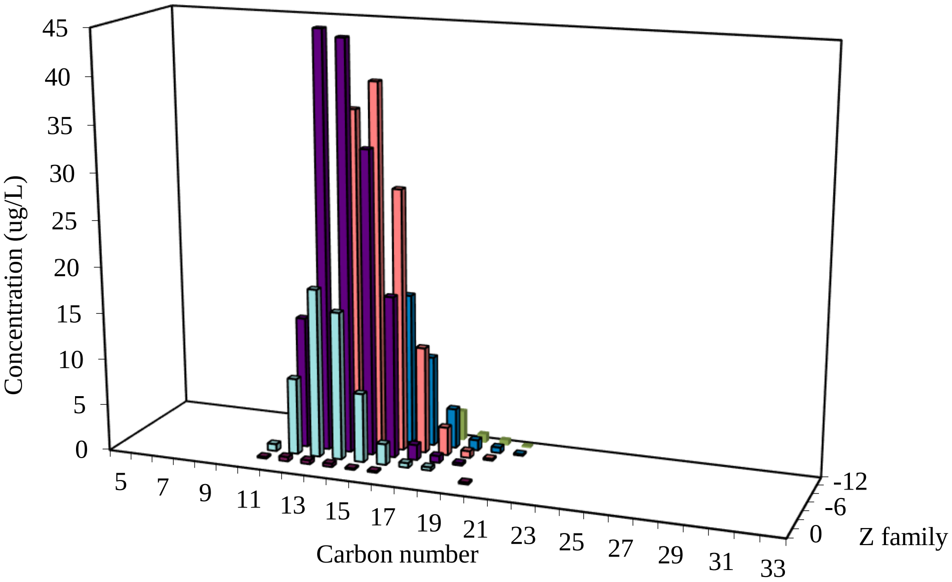
Total Concentration in Vial (mg/L)	0.24
Environmental Concentration (mg/L)	3.03

Figure 7-6: Spreadsheet output for the characterization of naphthenic acids in OSPW for sample 3 (12h). Carbon number provides an output based on carbon number n, while isotope output is solely the concentration of C13 isotopes based on concentration, and sodium output presents the concentration of sodium dimers (excluding values obtained from the O_2 series).

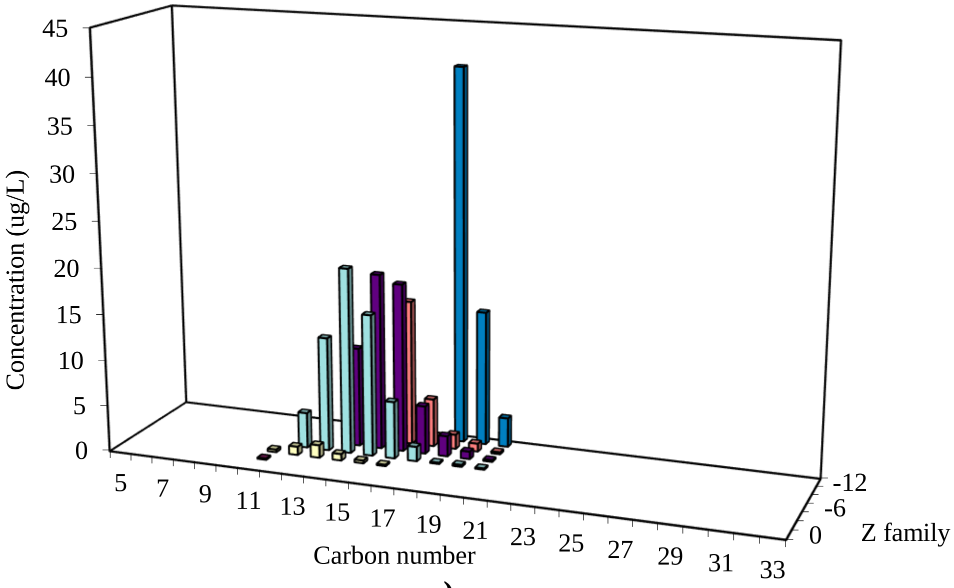
1:12 Anaerobic Clay Sample 4:



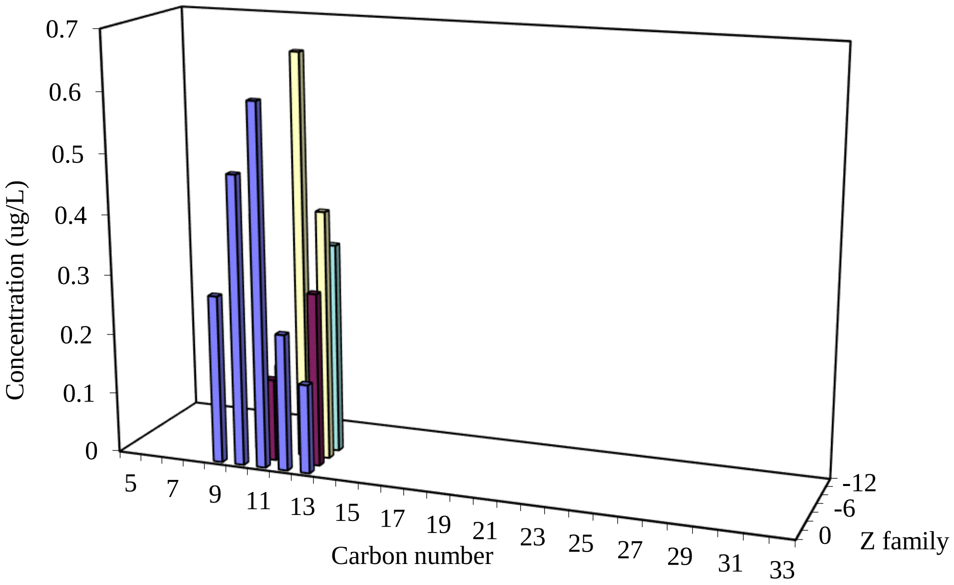
a)



b)

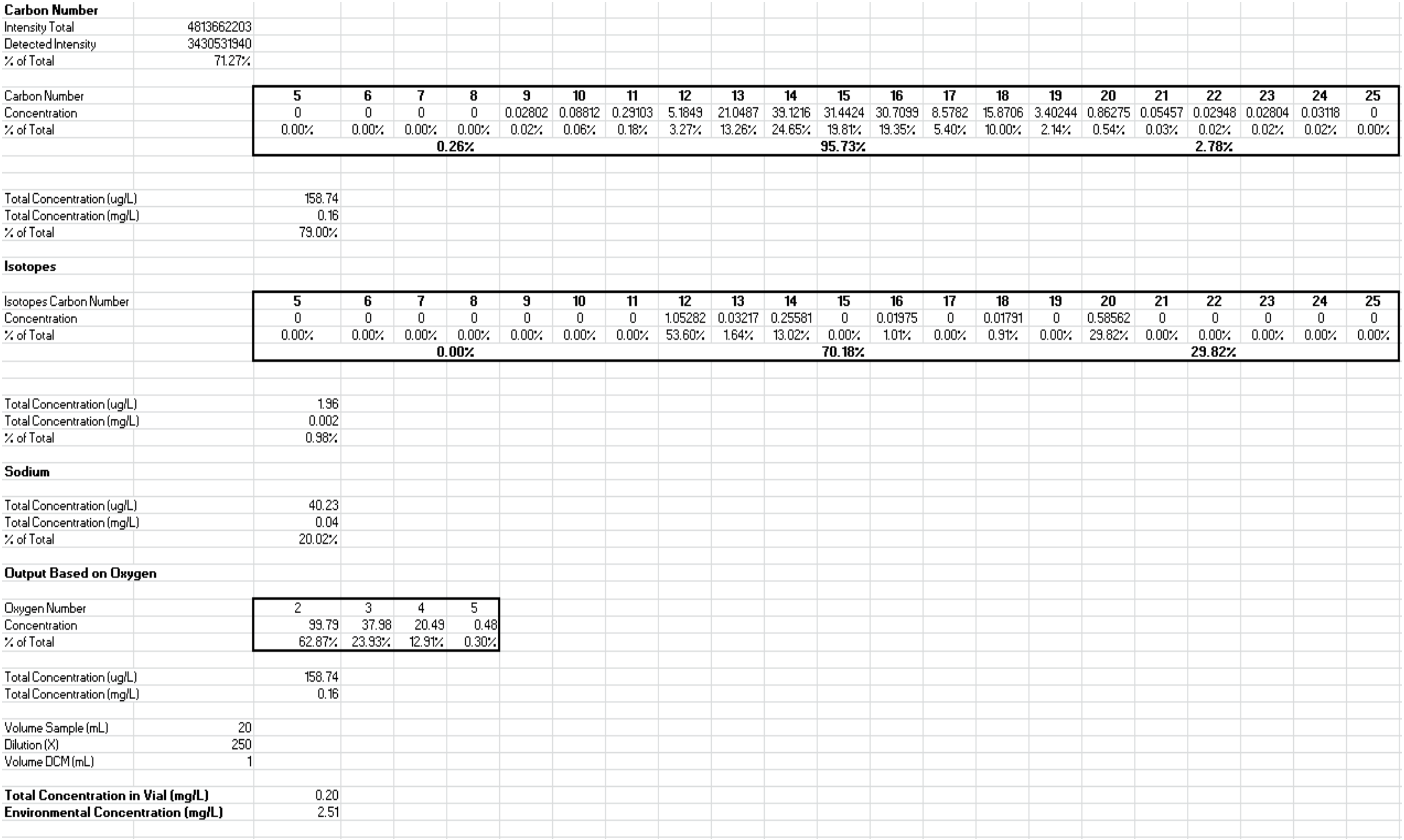


c)



d)

Figure 7-7: ESI-FTICR-MS data for sample 4 (24 h). Charts represent naphthenic acids in the generic formula $C_nH_{(2n+z)}O_x$, with a) $C_nH_{(2n+z)}O_2$, b) $C_nH_{(2n+z)}O_3$, c) $C_nH_{(2n+z)}O_4$ and d) $C_nH_{(2n+z)}O_5$.



Carbon Number

Intensity Total	4813662203
Detected Intensity	3430531940
% of Total	71.27%

Carbon Number	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Concentration	0	0	0	0	0.02802	0.08812	0.29103	5.1849	21.0487	39.1216	31.4424	30.7099	8.5782	15.8706	3.40244	0.86275	0.05457	0.02948	0.02804	0.03118	0
% of Total	0.00%	0.00%	0.00%	0.00%	0.02%	0.06%	0.18%	3.27%	13.26%	24.65%	19.81%	19.35%	5.40%	10.00%	2.14%	0.54%	0.03%	0.02%	0.02%	0.02%	0.00%
	0.26%							**95.73%**							**2.78%**						

Total Concentration (ug/L)	158.74
Total Concentration (mg/L)	0.16
% of Total	79.00%

Isotopes

Isotopes Carbon Number	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Concentration	0	0	0	0	0	0	0	1.05282	0.03217	0.25581	0	0.01975	0	0.01791	0	0.58562	0	0	0	0	0
% of Total	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	53.60%	1.64%	13.02%	0.00%	1.01%	0.00%	0.91%	0.00%	29.82%	0.00%	0.00%	0.00%	0.00%	0.00%
	0.00%							**70.18%**							**29.82%**						

Total Concentration (ug/L)	1.96
Total Concentration (mg/L)	0.002
% of Total	0.98%

Sodium

Total Concentration (ug/L)	40.23
Total Concentration (mg/L)	0.04
% of Total	20.02%

Output Based on Oxygen

Oxygen Number	2	3	4	5
Concentration	99.79	37.98	20.49	0.48
% of Total	62.87%	23.93%	12.91%	0.30%

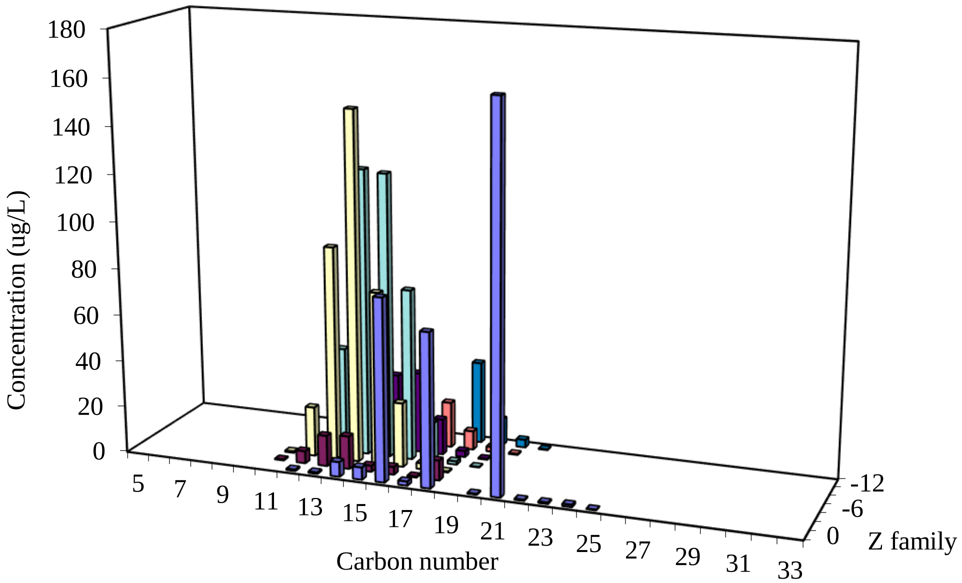
Total Concentration (ug/L)	158.74
Total Concentration (mg/L)	0.16

Volume Sample (mL)	20
Dilution (X)	250
Volume DCM (mL)	1

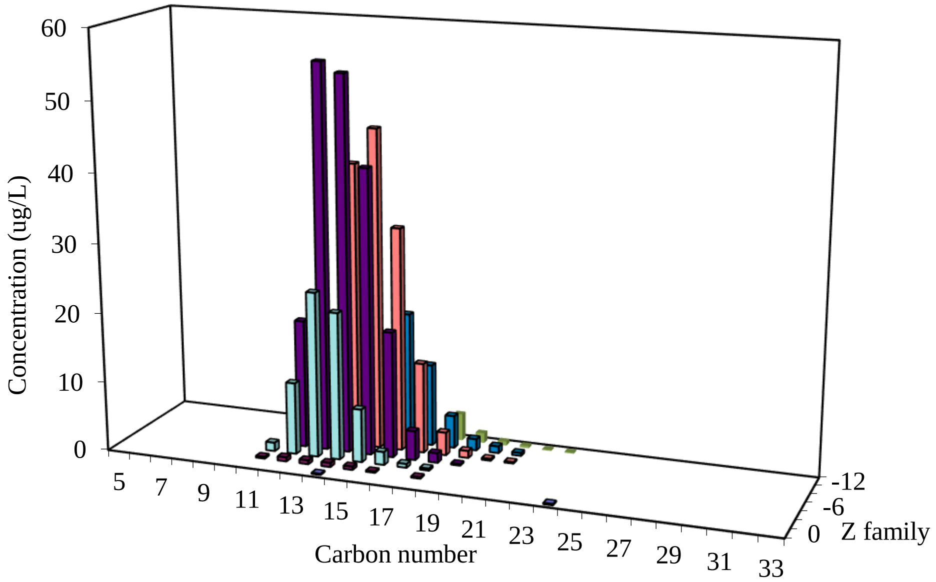
Total Concentration in Vial (mg/L)	0.20
Environmental Concentration (mg/L)	2.51

Figure 7-8: Spreadsheet output for the characterization of naphthenic acids in OSPW for sample 4 (24h). Carbon number provides an output based on carbon number n, while isotope output is solely the concentration of C13 isotopes based on concentration, and sodium output presents the concentration of sodium dimers (excluding values obtained from the O_2 series).

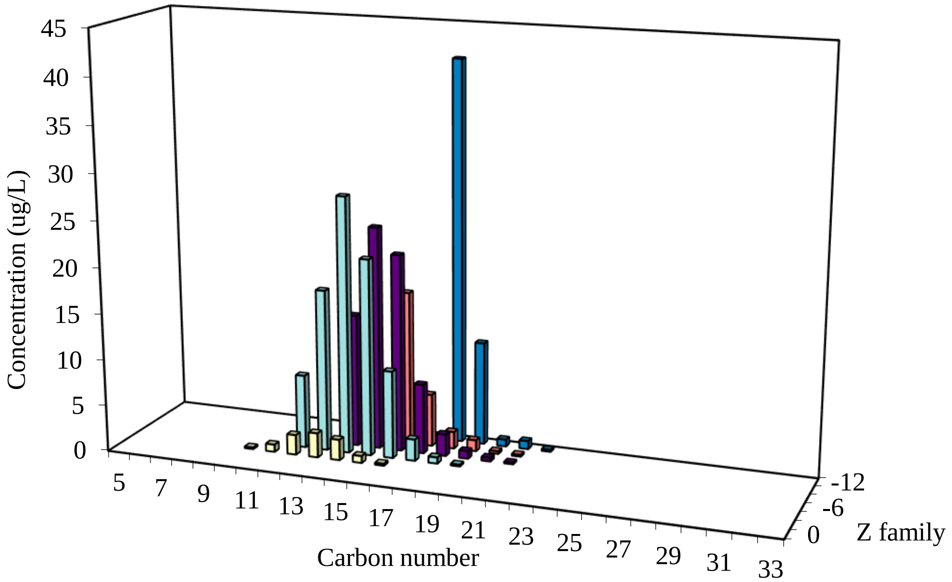
1:12 Anaerobic Clay Sample 5:



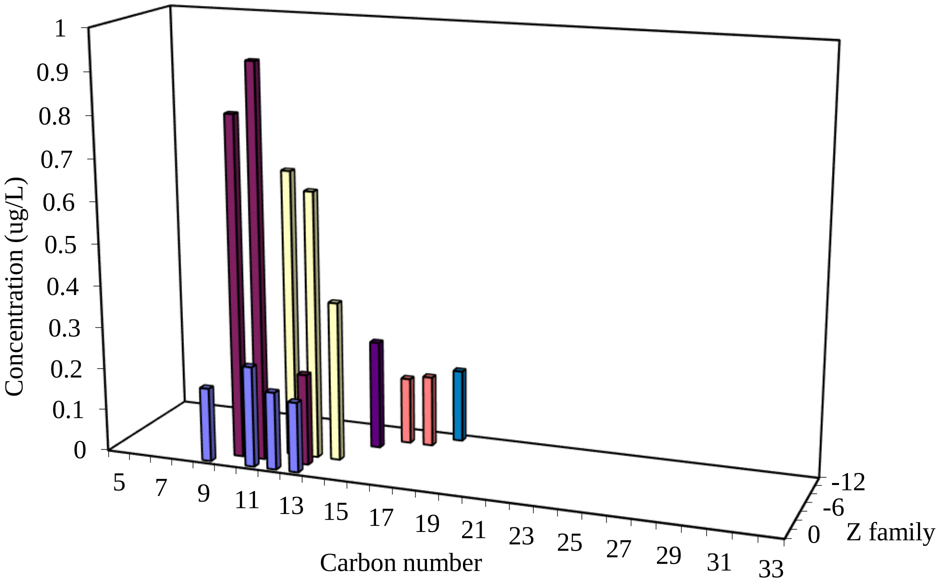
a)



b)

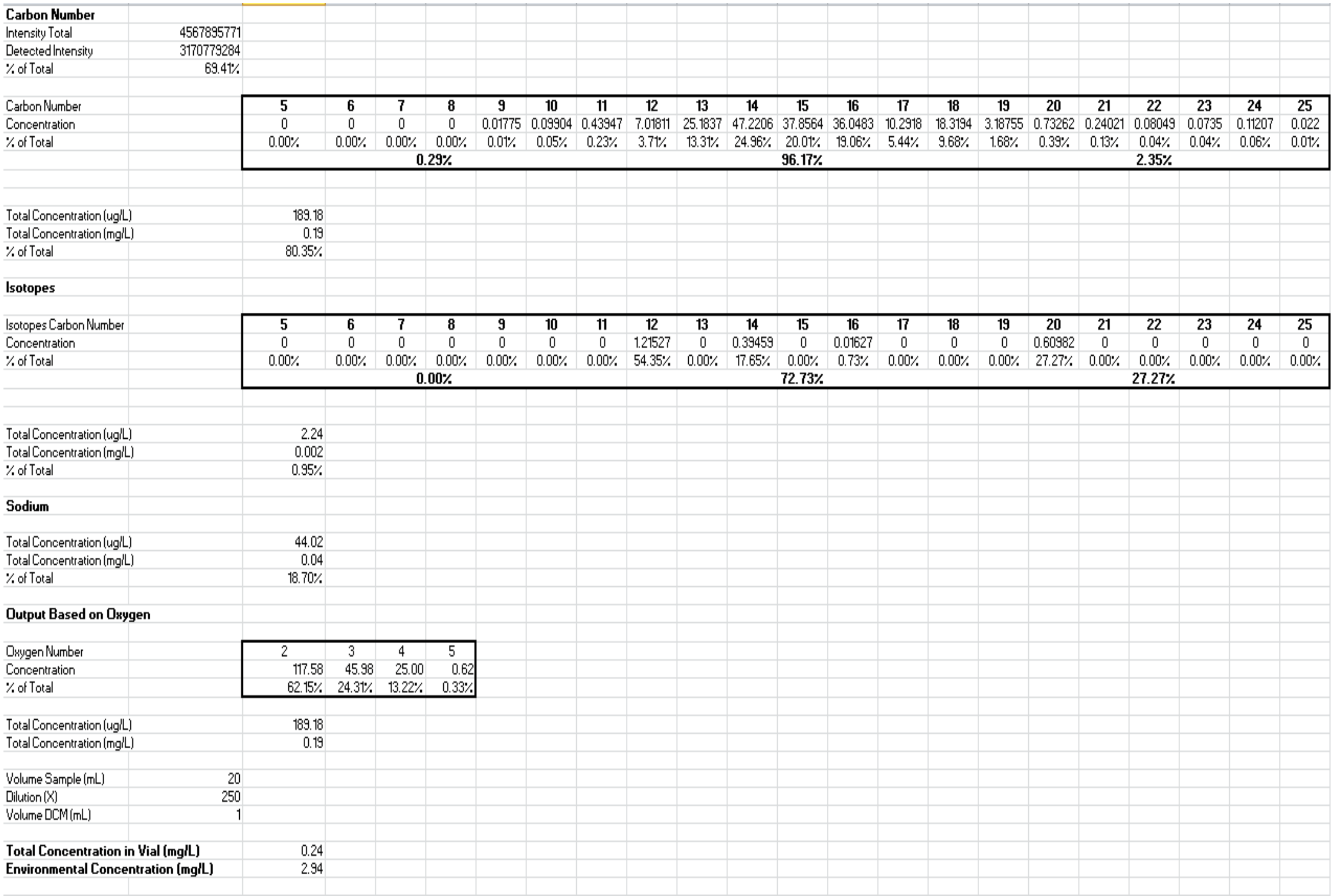


c)



d)

Figure 7-9: ESI-FTICR-MS data for sample 5 (48 h). Charts represent naphthenic acids in the generic formula $C_nH_{(2n+z)}O_x$, with a) $C_nH_{(2n+z)}O_2$, b) $C_nH_{(2n+z)}O_3$, c) $C_nH_{(2n+z)}O_4$ and d) $C_nH_{(2n+z)}O_5$.



Carbon Number

Intensity Total	4567895771
Detected Intensity	3170779284
% of Total	69.41%

Carbon Number	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Concentration	0	0	0	0	0.01775	0.09904	0.43947	7.01811	25.1837	47.2206	37.8564	36.0483	10.2918	18.3194	3.18755	0.73262	0.24021	0.08049	0.0735	0.11207	0.022
% of Total	0.00%	0.00%	0.00%	0.00%	0.01%	0.05%	0.23%	3.71%	13.31%	24.96%	20.01%	19.06%	5.44%	9.68%	1.68%	0.39%	0.13%	0.04%	0.04%	0.06%	0.01%
	0.29%							96.17%							2.35%						

Total Concentration (ug/L)	189.18
Total Concentration (mg/L)	0.19
% of Total	80.35%

Isotopes

Isotopes Carbon Number	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Concentration	0	0	0	0	0	0	0	1.21527	0	0.39459	0	0.01627	0	0	0	0.60982	0	0	0	0	0
% of Total	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	54.35%	0.00%	17.65%	0.00%	0.73%	0.00%	0.00%	0.00%	27.27%	0.00%	0.00%	0.00%	0.00%	0.00%
	0.00%							72.73%							27.27%						

Total Concentration (ug/L)	2.24
Total Concentration (mg/L)	0.002
% of Total	0.95%

Sodium

Total Concentration (ug/L)	44.02
Total Concentration (mg/L)	0.04
% of Total	18.70%

Output Based on Oxygen

Oxygen Number	2	3	4	5
Concentration	117.58	45.98	25.00	0.62
% of Total	62.15%	24.31%	13.22%	0.33%

Total Concentration (ug/L)	189.18
Total Concentration (mg/L)	0.19

Volume Sample (mL)	20
Dilution (X)	250
Volume DCM (mL)	1

Total Concentration in Vial (mg/L)	0.24
Environmental Concentration (mg/L)	2.94

Figure 7-10: Spreadsheet output for the characterization of naphthenic acids in OSPW for sample 5 (48h). Carbon number provides an output based on carbon number n, while isotope output is solely the concentration of C13 isotopes based on concentration, and sodium output presents the concentration of sodium dimers (excluding values obtained from the O_2 series).

GC-FID and FT-IR Calibration:

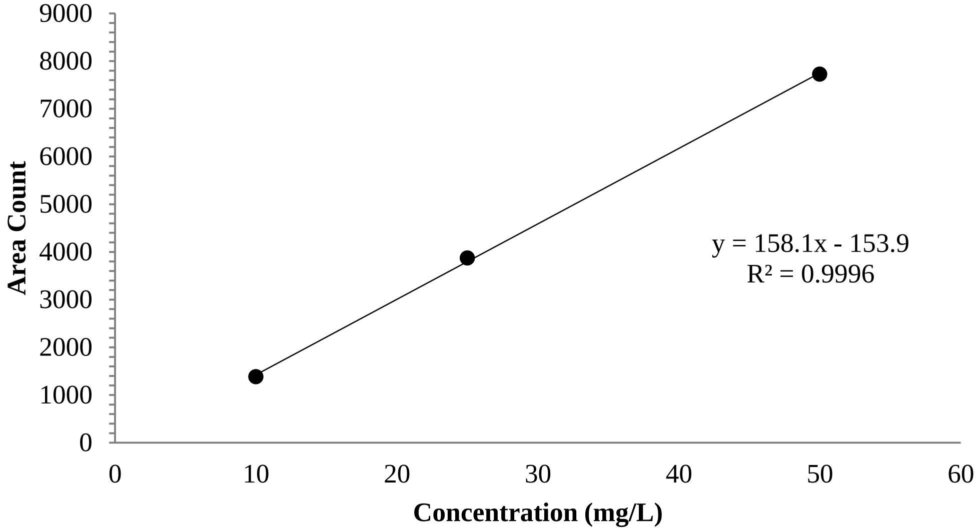


Figure 7-11: GC-FID 3-point calibration curve using Heptadodecanoic Acid at varying concentrations. Standards were 10, 25, and 50 mg/L. Calibration was used to measure naphthenic acid concentrations for sediment:OSPW study.

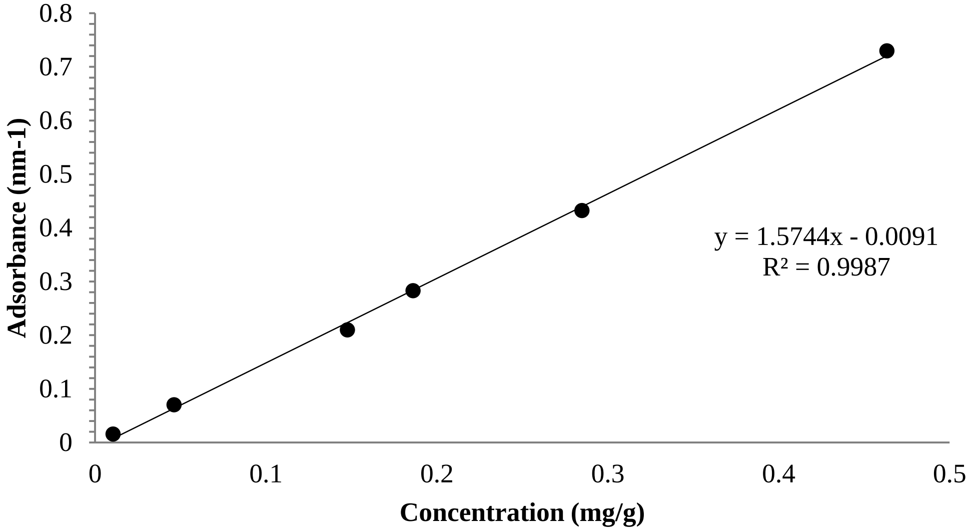


Figure 7-12: FT-IR 6-point calibration curve using Merichem naphthenic acid solution at varying concentrations. Response absorbance was measured at 1706 and 1743 nm^{-1}. Calibration was used in the comparison study between FT-IR, GC-FID and ESI-FTICR-MS.

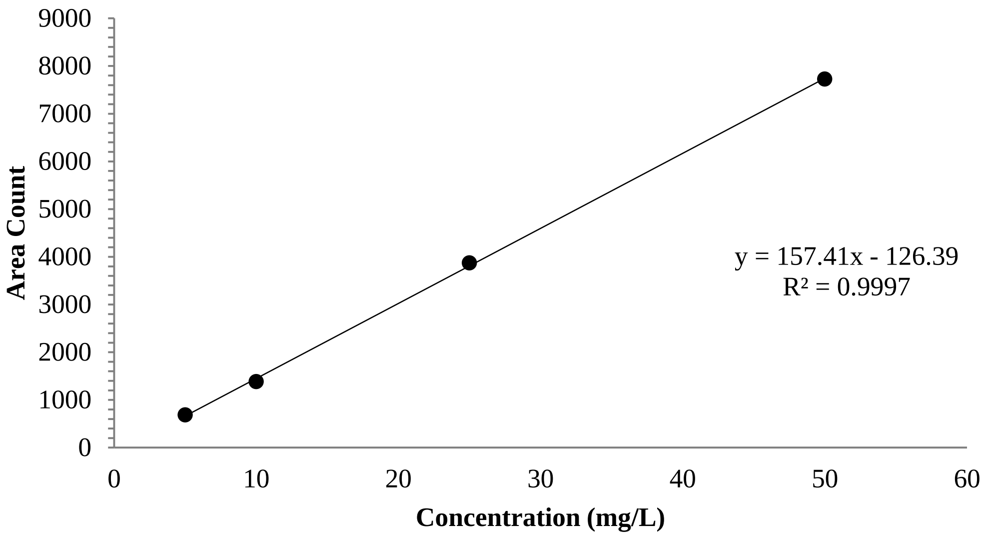


Figure 7-13: GC-FID 4-point calibration curve using Merichem naphthenic acid solution at varying concentrations. Standards were 5, 10, 25 and 50 mg/L. Calibration was used in the comparison study between FT-IR, GC-FID and ESI-FTICR-MS.

Appendix B: Summary of Metal Concentrations in Groundwater during Adsorption using Granular Delayed Coke

Table 7-2: Summary of Initial metal concentration of groundwater well 2A used in a 48 h batch sorption test.

Analyte	Initial Sample 1 Concentration (µg/L)	Initial Sample 2 Concentration (µg/L)
Al	43.4	245.9
V	0.0	0.0
Cr	20.9	22.8
Fe	0.0	0.0
Mn	383.2	402.8
Ni	29.0	29.2
Co	0.0	4.3
Cu	19.3	23.9
Zn	25.1	23.8
As	0.0	0.0
Se	0.0	0.0
Sr	327.7	337.8
Mo	8.3	8.0
Cd	0.0	0.0
Cs	676.1	678.3
Ba	207.4	215.0
Pb	12.7	12.2
U	0.0	0.0

Table 7-3: Summary of select groundwater (Well 2A) metal concentrations used in a 48 h batch sorption test with 0.8-2 mm raw coke. Values are averages of duplicate samples.

	0.8-2 mm Raw Coke				
	Sample 1 (3 h)	**Sample 2 (6 h)**	**Sample 3 (12 h)**	**Sample 4 (24 h)**	**Sample 5 (48 h)**
Al	43.0	29.2	30.0	58.1	38.0
V	5.0	5.3	4.7	9.2	13.1
Cr	19.5	18.3	17.5	17.9	15.4
Fe	0.0	0.0	0.0	0.0	0.0
Mn	28.0	7.0	6.4	6.4	5.9
Ni	31.7	30.5	29.3	28.1	26.8
Co	4.4	0.0	0.0	4.6	4.3
Cu	41.8	42.4	41.7	48.1	35.1
Zn	22.7	15.5	20.3	27.0	16.2
As	0.0	0.0	0.0	0.0	0.0
Se	0.0	0.0	0.0	0.0	0.0
Sr	258.3	221.6	194.7	146.7	100.6
Mo	11.5	12.6	13.6	26.2	36.8
Cd	0.0	0.0	0.0	0.0	0.0
Cs	669.0	667.5	662.6	675.2	680.8
Ba	106.4	80.5	60.4	35.7	21.2
Pb	5.0	5.5	5.2	5.2	5.3
U	0.0	0.0	0.0	0.0	0.0

Table 7-4: Summary of select groundwater (Well 2A) metal concentrations used in a 48 h batch sorption test with 75-150 µm raw coke. Values are averages of duplicate samples.

	75-150 µm Raw Coke				
	Sample 1 (3 h)	**Sample 2 (6 h)**	**Sample 3 (12 h)**	**Sample 4 (24 h)**	**Sample 5 (48 h)**
Al	86.2	72.1	14433.7	102.4	15381.1
V	14.2	48.1	19.3	48.2	67.7
Cr	20.2	11.9	11.4	20.0	20.4
Fe	0.0	0.0	0.0	0.0	0.0
Mn	17.8	14.6	707.4	26.0	80.6
Ni	30.6	33.7	110.3	22.1	29.2
Co	8.3	12.2	83.7	9.2	13.3
Cu	17.1	21.7	13.5	15.0	26.4
Zn	17.7	18.8	162.5	18.1	33.4
As	0.0	0.0	0.0	0.0	0.0
Se	0.0	0.0	6.7	0.0	0.0
Sr	191.1	206.4	368.9	101.9	110.7
Mo	117.9	226.6	133.2	278.3	359.2
Cd	0.0	0.0	0.0	0.0	0.0
Cs	435.1	445.5	455.6	316.9	309.1
Ba	46.7	43.2	215.6	18.3	31.7
Pb	13.9	13.2	10.7	0.0	0.0
U	0.0	0.0	0.0	0.0	0.0

Table 7-5: Summary of select groundwater (Well 2A) metal concentrations used in a 48 h batch sorption test with 75-150 µm activated coke. Values are averages of duplicate samples.

	75-150 µm Activated Coke				
	Sample 1 (3 h)	**Sample 2 (6 h)**	**Sample 3 (12 h)**	**Sample 4 (24 h)**	**Sample 5 (48 h)**
Al	126.9	187.1	106.5	6956.8	170.9
V	1823.7	2124.2	1926.9	2322.5	2861.7
Cr	20.7	20.4	18.1	20.0	21.0
Fe	0.0	0.0	0.0	0.0	0.0
Mn	216.6	187.3	37.5	236.9	17.0
Ni	53.0	55.3	46.0	53.3	44.9
Co	0.0	0.0	0.0	9.2	0.0
Cu	30.0	57.0	36.6	31.7	46.9
Zn	13.4	19.3	11.7	24.5	9.4
As	5.6	6.2	6.0	7.4	7.8
Se	0.0	0.0	0.0	0.0	0.0
Sr	324.5	313.3	203.9	138.0	94.1
Mo	144.6	160.1	144.7	159.4	173.4
Cd	0.0	0.0	0.0	0.0	0.0
Cs	674.2	658.4	673.1	690.5	671.0
Ba	130.1	126.5	53.3	40.1	22.0
Pb	61.5	63.8	37.5	33.2	36.6
U	0.0	0.0	0.0	0.0	0.0

Table 7-6: Summary of initial metal concentration of groundwater well 2G used in a 48 h batch sorption test.

Analyte	Initial Sample 1 Concentration (µg/L)	Initial Sample 2 Concentration (µg/L)
Al	83.0	97.5
V	60.4	68.4
Cr	11.2	9.1
Fe	267.3	318.2
Mn	605.9	612.3
Ni	15.2	11.9
Co	0.0	0.0
Cu	33.9	36.9
Zn	48.6	74.1
As	30.9	33.8
Se	128.7	146.1
Sr	457.0	498.7
Mo	5.9	5.8
Cd	0.0	0.0
Cs	0.0	0.0
Ba	244.9	242.6
Pb	0.0	0.0
U	0.0	0.0

Table 7-7: Summary of select groundwater (Well 2G) metal concentrations used in a 48 h batch sorption test with 0.8-2 mm acid washed raw coke. Values are averages of duplicate samples.

	0.8-2 mm Acid Washed Raw Coke				
Analyte	**Sample 1 (3 h)**	**Sample 2 (6 h)**	**Sample 3 (12 h)**	**Sample 4 (24 h)**	**Sample 5 (48 h)**
Al	77.3	92.1	96.2	112.4	112.8
V	5.9	7.1	9.3	14.0	34.4
Cr	5.2	6.3	8.5	5.9	7.0
Fe	166.2	56.5	149.7	94.2	130.6
Mn	450.1	124.5	0.0	0.0	7.7
Ni	11.1	62.7	9.1	8.2	6.5
Co	0.0	12.5	0.0	0.0	0.0
Cu	148.3	67.1	60.5	83.8	92.8
Zn	39.6	46.4	35.8	37.9	36.6
As	0.0	0.0	0.0	0.0	0.0
Se	6.4	7.5	6.2	6.4	6.6
Sr	418.3	339.0	233.3	198.6	189.6
Mo	9.1	11.8	17.3	26.9	61.4
Cd	0.0	0.0	0.0	0.0	0.0
Cs	0.0	0.0	0.0	0.0	0.0
Ba	192.5	119.9	57.1	40.6	31.7
Pb	0.0	0.0	0.0	0.0	0.0
U	0.0	0.0	0.0	0.0	0.0

Table 7-8: Summary of select groundwater (Well 2G) metal concentrations used in a 48 h batch sorption test with 75-150 µm acid washed raw coke. Values are averages of duplicate samples.

	75-150 µm Acid Washed Raw Coke				
Analyte	**Sample 1 (3 h)**	**Sample 2 (6 h)**	**Sample 3 (12 h)**	**Sample 4 (24 h)**	**Sample 5 (48 h)**
Al	58.8	53.5	49.6	51.9	68.1
V	407.8	496.1	559.4	640.0	723.4
Cr	6.5	7.6	7.5	7.2	8.5
Fe	236.4	221.5	137.1	174.2	184.5
Mn	388.0	263.4	18.7	6.4	0.0
Ni	6.3	6.9	0.0	0.0	0.0
Co	0.0	0.0	0.0	0.0	0.0
Cu	54.1	28.3	34.9	22.3	25.39
Zn	42.4	26.3	42.1	23.8	31.1
As	0.0	0.0	0.0	0.0	0.0
Se	6.0	0.0	6.9	5.5	0.0
Sr	375.3	391.0	247.8	178.5	132.9
Mo	143.9	176.3	188.9	201.9	208.0
Cd	0.0	0.0	0.0	0.0	0.0
Cs	0.0	0.0	0.0	0.0	0.0
Ba	152.7	136.9	55.2	35.2	22.4
Pb	0.0	0.0	0.0	0.0	0.0
U	0.0	0.0	0.0	0.0	0.0

Table 7-9: Summary of select groundwater (Well 2G) metal concentrations used in a 48 h batch sorption test with 75-150 µm acid washed activated coke. Values are averages of duplicate samples.

	75-150 µm Acid Washed Activated Coke				
Analyte	**Sample 1 (3 h)**	**Sample 2 (6 h)**	**Sample 3 (12 h)**	**Sample 4 (24 h)**	**Sample 5 (48 h)**
Al	58.8	53.5	49.6	51.9	68.1
V	407.8	496.1	559.4	640.0	723.4
Cr	6.5	7.6	7.5	7.2	8.5
Fe	236.4	221.5	137.1	174.2	184.5
Mn	388.0	263.4	18.7	6.4	0.0
Ni	6.3	6.9	0.0	0.0	0.0
Co	0.0	0.0	0.0	0.0	0.0
Cu	54.1	28.3	34.9	22.3	25.3
Zn	42.4	26.3	42.1	23.8	31.1
As	0.0	0.0	0.0	0.0	0.0
Se	6.0	0.0	6.9	5.5	0.0
Sr	375.3	391.0	247.8	178.5	132.9
Mo	143.9	176.3	188.9	201.9	208.0
Cd	0.0	0.0	0.0	0.0	0.0
Cs	0.0	0.0	0.0	0.0	0.0
Ba	152.7	136.9	55.2	35.2	22.4
Pb	0.0	0.0	0.0	0.0	0.0
U	0.0	0.0	0.0	0.0	0.0

Appendix C: Summary of Metal Concentration in OSPW used during Adsorption with Biochar

Table 7-10: Summary of Initial metal concentration of OSPW used in a 48 h batch sorption test.

Analyte	Initial Sample 1 Concentration (μg/L)	Initial Sample 2 Concentration (μg/L)
Al	149.2	141.1
V	66.8	77.8
Cr	6.6	0.0
Fe	137.0	32.1
Mn	25.1	24.4
Ni	10.2	11.4
Co	0.0	0.0
Cu	54.0	51.1
Zn	65.9	38.1
As	37.8	38.6
Se	119.6	129.6
Sr	313.7	314.6
Mo	301.3	291.1
Cd	0.0	0.0
Cs	0.0	0.0
Ba	87.9	88.0
Pb	0.0	0.0
U	7.7	7.4

Table 7-11: Summary of select OSPW metal concentrations used in a 48 h batch sorption test with willow biochar. Values are averages of duplicate samples.

	Willow Biochar				
Analyte	**Sample 1 (3 h)**	**Sample 2 (6 h)**	**Sample 3 (12 h)**	**Sample 4 (24 h)**	**Sample 5 (48 h)**
Al	46.4	22.8	32.8	41.0	30.2
V	31.6	29.2	27.8	27.1	25.9
Cr	3.4	5.6	5.7	6.2	5.9
Fe	158.9	164.8	89.6	96.9	75.4
Mn	0.0	0.0	0.0	0.0	0.0
Ni	0.0	0.0	0.0	0.0	0.0
Co	0.0	0.0	0.0	0.0	0.0
Cu	145.4	104.2	632.4	103.5	48.4
Zn	32.3	17.9	115.3	37.4	33.2
As	10.8	11.6	11.4	11.5	11.5
Se	12.9	10.2	11.4	10.6	10.3
Sr	71.8	93.8	61.0	53.0	49.0
Mo	253.5	271.0	286.4	283.9	297.5
Cd	0.0	0.0	0.0	0.0	0.0
Cs	0.0	0.0	0.0	0.0	0.0
Ba	17.3	17.5	16.4	12.1	12.0
Pb	0.0	0.0	0.0	0.0	0.0
U	2.7	2.9	3.1	3.0	3.1

Table 7-12: Summary of select OSPW metal concentrations used in a 48 h batch sorption test with wheat biochar. Values are averages of duplicate samples.

	Wheat Biochar				
Analyte	**Sample 1 (3 h)**	**Sample 2 (6 h)**	**Sample 3 (12 h)**	**Sample 4 (24 h)**	**Sample 5 (48 h)**
Al	14.7	44.0	3.3	36.4	0.0
V	24.1	23.9	23.9	25.7	24.3
Cr	0.0	0.0	0.0	6.4	0.0
Fe	75.7	141.8	121.0	238.9	70.6
Mn	0.0	0.0	0.0	0.0	0.0
Ni	0.0	0.0	0.0	0.0	0.0
Co	0.0	0.0	0.0	0.0	0.0
Cu	200.2	340.9	61.8	93.9	126.4
Zn	15.2	12.0	27.2	60.1	56.1
As	11.5	11.5	11.8	12.0	11.6
Se	7.4	8.1	8.9	9.6	9.4
Sr	189.4	184.3	171.6	115.9	165.3
Mo	243.2	243.5	242.0	257.1	244.3
Cd	0.0	0.0	0.0	0.0	0.0
Cs	0.0	0.0	0.0	0.0	0.0
Ba	47.9	43.9	38.5	30.4	41.0
Pb	0.0	0.0	0.0	0.0	0.0
U	6.1	5.8	5.7	2.9	5.6