Final Report

Ultrasonic Enhanced Remediation of Salt- and Hydrocarbon-Contaminated Soils

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EXECUTIVE SUMMARY

Two of the most common soil contaminants found at oil and gas extraction sites are petroleum hydrocarbons (PHCs) and salts generated from spilled crude, condensate, or produced water brine. Soil contaminated by these two pollutants is a major concern facing the oil and gas industry and may lead to a number of adverse impacts on the environment, human health, and local economy. The remediation of mixed soil contaminants of PHCs and salts is a particularly difficult challenge due to the complex interactions between contaminants and soil. Crude oil spilled at oil and gas drilling sites contains compounds that are resistant to degradation and adsorb strongly to soils containing high fractions of clay and organic matter. The adsorption and persistence of these contaminants remains a challenge for the development of successful remediation techniques. The addition of high salt concentrations from brine spills may amplify the challenges of soil remediation at these sites by reducing the solubility and bioavailability of organic compounds for remediation. The combined effects of pollutant desorption, destruction, and removal seen in ultrasonic remediation research may be applied to problems of mixed salt and hydrocarbon contamination while providing information about the interaction between contaminants and soil.

The main objective of this project is then to evaluate the ability of ultrasonic process as a useful technique to enhance the remediation effectiveness for treating salt- and hydrocarbon-contaminated soils, including (a) to show difference in the levels of salt and hydrocarbon contamination in test soil from the application of ultrasonic remediation technology, and (b) to explore the impacts of mixed salt and hydrocarbon contamination on the success of applied ultrasonic remediation technology. The research experiments in this project were divided into two parts. The first part is related to ultrasonic remediation experiments. In this part, the experiments were designed using an ultrasonic probe reactor and vacuum filtration system to treat three different soils contaminated with crude oil. Additional treatments were completed with the addition of dissolved sodium chloride salt to explore the influence of salinity on treatment results. The objectives of these experiments are to investigate the interactions of mixed salt and hydrocarbon contamination on the soil surface and to examine the effectiveness of ultrasonic treatments as a remediation tool for the reduction of hydrocarbon concentrations in soil. The second part is related to ultrasonic enhanced soil washing treatment experiments. In this part, a reactor was designed and built for enhanced treatment

combining both ultrasonic treatment technique and soil washing technique. Four factors (i.e. initial PHC concentration, salinity, ultrasonic treatment duration, and soil washing flow rate) were examined by conducting a group of full factorial experiments. The objectives of the study in this part are to investigate the optimal conditions of ultrasonic enhanced soil washing and examine the enhancement of TPH reduction as compared to the process of only using ultrasonic treatment.

Results from the first-part experiments illustrated that the TPH reduction was significantly different among the three soil types. The highest TPH reduction was obtained in sand (approximately 80 to 90%), as compared to that in clay (approximately 5 to 12%) and muskeg (approximately 30 to 40%). Physical soil properties such as surface area and grain size appeared to explain the greatest differences in TPH reduction between soil types and the results suggested that the dominant mechanism of crude oil sorption to the three soils was physical adsorption. Moreover, the application of ultrasonic treatment statistically increased the reduction of TPH when compared against the control. The highest improvement of TPH reduction due to ultrasound was observed in sand (around 50%), while other two improvements were approximately 5 to 7 % in clay and 30 to 40% in muskeg. These observations and results suggest that ultrasonic desorption and subsequent filtration was the dominant mechanism for TPH reduction in the experiment and the ultrasonic treatment was most effective on granular soil. The duration of ultrasonic treatment was found with no significant effect on TPH reduction as the maximum TPH reductions were reached within 2 minutes of treatments. According to the experimental results, the influence of salt on TPH reduction was significant for all soils. The reduction of TPH in sand was clearly impacted negatively by the addition of salt. In ultrasonic treated sand, TPH reduction was approximately 30% when salt was added and approximately 90% in no-salt treatments representing a changing in TPH reduction of approximately 60%. Under saline conditions in sand, ultrasonic treatment appeared to have no effect on TPH reduction as compared to the control. The effects of salinity on the clay and muskeg treatments were less pronounced. Only a small negative effect was observed in muskeg treatments with salt and a small positive effect was observed in clay.

Results from the 2nd-part experiments indicated that the TPH reduction efficiency was significantly enhanced by combing soil washing and ultrasonic techniques. The TPH reduction by using ultrasonic enhanced soil washing process was between 93.7% and 99.1 %. The best results of 99.1% reduction was achieved with initial contamination of 2.0% crude, no added salt, 10 minutes

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of ultrasonic treatment and a 0.7 cm^3/s soil washing velocity. TPH reduction rate of treating sand highly contaminated by salt (0.8 M), with 0.5% crude, 10 minute of ultrasonic treatment and 1.3 cm^3/s soil washing velocity was high as well (around 96%). On the contrary, the results from traditional ultrasonic treatment indicated a TPH reduction rate ranging from 35.1% to 87.4% for no-salt-added group experiments, and a TPH reduction ranging from 18.8% to 25.7% for salt-added experiments. It is thus obvious that the TPH reduction efficiency from ultrasonic enhanced soil washing process was much higher and the enhancement was significant. The results of variance analysis proved that the soil washing flow rate had significant impact on TPH reduction while the other three (i.e. initial PHC concentration, salinity, ultrasonic treatment duration) had insignificant effects on TPH reduction. The negative effect of salinity on TPH reduction using only ultrasound was eliminated by the strong positive effect on improving transportation of pollutants by using soil washing technique. Salts existing in the contaminated sand were kept being flushed out of the system during the process which led to a decreasing salinity. Thus the inhibition effect on TPH reduction was not observed even when the salinity in the soil was as high as 0.8 M, and the effect of decreasing the solubility of crude oil was also reduced. The results also observed obvious shifts of contaminant compositions after ultrasonic enhanced soil washing, and it is concluded that both desorption and destruction of TPH (i.e. from complex long-chain organic compounds to smaller and more volatile compounds) were responsible for the high TPH removal efficiency through the ultrasonic enhanced soil washing process.

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LIST OF ABBREVIATIONS

ANOVA   Analysis of variance

BC MOF   British Columbia Ministry of Forests

CCME   Canadian Council of Ministers of the Environment

CEC   Cation exchange capacity

EC   Electrical conductivity

EPA   Environmental Protection Agency

ESP   Exchangeable sodium percentage

DCM   Dichloromethane

GC   Gas chromatograph

GC-FID   Gas chromatography – flame ionization detector

K_d Distribution coefficient

MDL   Method Detection Limit

PAH   Polycyclic aromatic hydrocarbon

PCBs   Polychlorinated biphenyls

PHC   Petroleum hydrocarbon

SAR   Sodium adsorption ratio

SD   Standard deviation

TPH   Total petroleum hydrocarbons

1. INTRODUCTION

Soil contamination by petroleum hydrocarbons (PHCs) and salts is a major concern facing the oil and gas industry. Upon completion of extraction activities and removal of facilities, many oil and gas lease sites may be left with varying degrees of soil contamination. Such contaminated sites pose a risk to the environment and to human health and remain a source of long term liability to the oil and gas industry both legally and financially (Kirchmann and Ewnetu 1998).

The remediation of mixed soil contaminants of PHCs and salts is a particularly difficult challenge due to the complex interactions between contaminants and soil. The adsorption of pollutants to soil is a problem for most remedial techniques and the residual concentrations of adsorbed pollutants may persist for long periods of time. The problems associated with adsorption are dependent on two main factors: the properties of the contaminants and the properties of the soil. Crude oil spilled at oil and gas drilling sites contains compounds that are resistant to degradation and adsorb strongly to soils containing high fractions of clay and organic matter. The adsorption and persistence of these contaminants remains a challenge for the development of successful remediation techniques (Talley 2006). The addition of high salt concentrations from brine spills may amplify the challenges of soil remediation at these sites by reducing the solubility and bioavailability of organic compounds for remediation (Schwarzenbach 2003). The efficiency of common remediation techniques such as bioremediation using hydrocarbon degrading bacteria or plants are significantly hindered from the presence of high salt concentrations in soil (Cook et al 2002). Soil structure degradation from salt impacts further reduces the viability of bioremediation by limiting the infiltration of water and oxygen (Carty et al. 1997).

Remediation techniques for hydrocarbon contamination have been researched extensively; however, further research is needed to understand the issues of combined salt and hydrocarbon contamination and requires a detailed review of the complex interactions between soil and pollutants. Ultrasound used for desorption and treatment of organic pollutants is a method that appears to be very promising. It has the potential to overcome the attraction between pollutants and the adsorbent and facilitate transportation of pollutants away from the adsorbing surface (Brietbach and Bathen 2001). The process utilizes physical forces generated by an acoustic wave and does not rely on the addition of chemical agents. Several researchers have demonstrated the degradation of

persistent organic pollutants in soil using ultrasound. Experiments by Zhang and Hua (2000) and Cheung et al. (1991) showed ultrasound to be a viable technique for degrading pollutants or mixtures of pollutants in complex systems. When combined with soil flushing techniques, Kim and Wang (2003) observed that the rate of contaminant extraction increased under ultrasonic treatments. Feng and Aldrich (2000) used a similar ultrasonic soil flushing treatment for diesel contaminated soil and described the treatment as an effective method of contaminant removal. Additionally, salt impacts are shown to be effectively treated by flushing soil with water to remove soluble salts adsorbed to soil and would benefit from the improved agitation and transportation associated with ultrasound (Franzen 2003, Chung and Kamon 2005). The combined effects of pollutant desorption, destruction, and removal seen in ultrasonic remediation research may be applied to problems of mixed salt and hydrocarbon contamination while providing information about the interaction between contaminants and soil.

The main objective of this project is then to evaluate the ability of ultrasonic process as a useful technique to enhance the remediation effectiveness for treating salt- and hydrocarbon-contaminated soils. In detail, the objectives include (a) to show difference in the levels of salt and hydrocarbon contamination in test soil from the application of ultrasonic remediation technology, and (b) to explore the impacts of mixed salt and hydrocarbon contamination on the success of applied ultrasonic remediation technology.

2. LITERATURE REVIEW

2.1 Soil Properties and Adsorption

Soils at oilfields in western Canada typically consist of dense, poorly drained clay (Arocena and Rutherford 2005). In addition, water and organics accumulate in depressions known as peat bogs or muskeg and form a deposit of organic soil common in these areas. The soil properties of clay and muskeg are important for understanding the fate of hydrocarbon and salt spills at oilfield sites by controlling the degree of impacts, adsorption, and migration of pollutants in the environment.

Surface area is a primary factor controlling soil processes and function. As surface area increases, the propensity for aggregation, adsorption capacity, biological activity, and chemical exchange between particle surfaces increases (Brady and Weil 1996). Soils containing higher fractions of clay are more chemically active than coarser textured soils (i.e., sand) and have a cation exchange capacity (CEC) of two to nine times higher (per unit mass) than that of soils of other classes (Brady and Weil 1996). Organic matter is even more chemically active than clay and has a CEC of two to thirty times as much as clay minerals (Brady and Weil 1996).

2.1.1 Clay Soils

Clay in temperate regions is most commonly distinguished by the silicate clay group known as phyllosilicates and is distinguished by alternating crystalline sheets of silicon oxide tetrahedrons and aluminum or magnesium hydroxide octahedrons (Tan 1993). The arrangement of these sheets provides basis for further classification of the silicate clay as 1:1 or 2:1 configurations of silicon oxide to aluminum/magnesium hydroxide sheets (Sposito 1989). The layers of 1:1 clays are held together by tightly bound oxygen atoms and the intermicellar space between units is held together by hydrogen bonds (Tan 1993, Brady and Weil 1996). These clays, represented by kaolinite and halloysite have characteristically lower particle surface charge, CEC, plasticity, and adsorption capacity (Tan 1993). The 2:1 layer clays are split into 2 classes: expanding and non-expanding due to the bonding between layers (Tan 1993). Like 1:1 layer clays, the non-expanding 2:1 clay layers are held together tightly. Some examples of expanding 2:1 layer clays are montmorillonite (smectite)

and vermiculite (Brady and Weil 1996). Montmorillonite clays are the most abundant in the 2:1 clay group and are able to adsorb moisture and swell due to the weak bonding between units (Brady and Weil 1996). The relative surface area of montmorillonite versus kaolinite is much higher and, as a result, montmorillonite has a higher CEC, plasticity, and adsorption capacity (Tan 1993).

Clay particles often display a net negative surface charge due to the substitution of cations within the crystal clay structure (Brady and Weil 1996). This is called isomorphic substitution and occurs when an ion is replaced by another ion of similar size but different valency (Tan 1993). For example, the substitution of aluminum ions (Al^{3+}) in a clay structure by magnesium (Mg^{2+}) is common and the loss of the positive charge is represented by a net negative charge on the particle surface (Brady and Weil 1996).

Clay particles with a negative surface charge attract cations in solution that accumulate at the surface of the particle (Tan 1993). The exchange sites are taken up by a monolayer of cations followed by a swarm of cations that decreases in density with distance from the particle surface (Tan 1993). Several chemical and mathematical models such as the diffuse double layer model have been developed to explain cation responses and adsorption to negative particle surfaces (Yong et al. 1992).

2.1.2 Organic Matter

The non-living organic fraction of soil is made up of various stages of decomposing biological materials or biomass. This fraction can be split into two groups: materials that still resemble the original source, and fully decomposed materials (Tan 1993). The latter group is of greater importance to the discussion of soil chemistry. The degradation of organic matter generates byproducts such as carbohydrates, amino acids, proteins, lipids, nucleic acids, and lignins (Tan 1993). These decomposition products may be used by plants to stimulate growth or enter the metabolic pathways of soil organisms (Brady and Weil 1996). The end products of degradation are complex polymeric compounds called humus (Tan 1993). Humus accounts for 60-80% of organic matter in soil (Brady and Weil 1996). The humic substances are considered colloids like clay particles because of their small size, insolubility in water, and high relative surface area. Humus and clay colloids together are responsible for much of the chemical and biological activity in soil

including the adsorption of contaminants (Tan 1993).

2.1.3 Partitioning and Adsorption

Determining the fate of contaminants in the subsurface requires an understanding of contaminant distribution among soil and soil water. Residual oil contamination at oilfield sites typically consists of nonionic, nonvolatile, and largely nonpolar hydrocarbons (Salloum 1999). The fate of these hydrocarbons in soil can be described as either a partitioning process (entropy driven) or adsorption process (enthalpy driven) (Schwarzenbach 2003). That is, the distribution of the organic compounds into aqueous solution or to soil organic matter at equilibrium and the adsorption of organic compounds to soil mineral surfaces. The factors most important to the fate of organic compounds are the properties of the contaminant (polarity, charge, and reactivity), the properties of the soil (organic content, surface charge, and functional groups), and the properties of water (salinity or ionic strength).

Water is a unique polar solvent and has characteristically small molecules that bind to each other with relatively strong hydrogen bonds (Schwarzenbach 2003). The large nonpolar hydrocarbon molecules disrupt the bonding among water molecules and are naturally hydrophobic. At equilibrium, limited amounts of water and hydrocarbons dissolve into each other at the interface of the two liquids. The interaction between soil water and organic pollutants has a large influence on the fate of contaminants in soil; therefore, the water content of the soil (soil moisture) is an important factor determining the distribution of organic contaminants.

In saturated conditions, researchers have shown that the uptake of organic compounds is linearly related to the natural organic matter content of the soil and is described as the partitioning of the compound between the aqueous phase and the organic phase of the sorbent (Karickhoff 1979, Chiou 1979, Schwarzenbach 2003). This distribution is expressed empirically using the following equation:

$$K_d = \frac{C_s}{C_c} \qquad\qquad [2\text{-}1]$$

where K_d is the distribution coefficient, C_s is the concentration of a chemical on the solid phase, and C_c is the concentration of the chemical left in solution at equilibrium (Schwarzenbach 2003). The distribution coefficient K_d is a ratio of concentrations of organic compounds in the sorbed phase and in aqueous phase. In practice, concentrations C_s and C_c are often expressed in units mg/kg and mg/L and, as such, K_d can be expressed in corresponding units (L/kg or ml/g) (Schwarzenbach 2003). Essentially, the distribution coefficient is a ratio of the distribution of a chemical between two phases. Assuming that the distribution of organic compounds is proportional to the fraction of organic matter in the soil, the distribution coefficient (K_d) can be normalized for organic carbon content. The normalized distribution coefficient due to organic carbon content (K_{oc}) is useful for comparing geological samples and is calculated by the following equation:

$$K_{oc} = \frac{K_d}{f_{oc}} \qquad\qquad [2\text{-}2]$$

where f_{oc} is the fraction of organic carbon within the sorbent soil sample (Karickhoff 1979).

It has been observed that the presence of dissolved solids within aqueous solution decreases the solubility of organic compounds and therefore interferes with the distribution of those compounds between the aqueous phase and the solid phase (Scharzenbach 2003). To compensate for the effect of salinity, the normalized partitioning coefficient can be described with the following equation:

$$K_{oc,salt} = \left(K_{oc}\right)\left(10^{+K^s[salt]}\right) \qquad\qquad [2\text{-}3]$$

where K^s is the salting constant expressed as L/mol for that compound and [salt] is the concentration of salt in the solution expressed as mol/L (Scharzenbach 2003).

It is understood that the fraction of organic carbon present in soil is important to organic compound uptake, however, it is also recognized that other factors exist that are significant to contaminant adsorption. Most soils contain only a small fraction of organic matter (2-3%) compared to the mineral content of the soil (Mingelgrin 1983). In saturated conditions, the polar surfaces of mineral clays create relatively strong dipole interactions with water molecules. Organic compounds

must compete with water for binding sites to mineral clays. In contrast, when soil is dry, organic compounds of all polarities are attracted to inorganic surfaces (Chiou 1979, Schwarzenbach 2003). Adsorption in these conditions occurs by physical forces of attraction generated by dipolar electron distributions of molecules called Van der Waal forces. Ionic forms of organic compounds may also be attracted to clay surfaces due to electrostatic forces of attraction based on their electrical charge (Hasset and Banwart 1989, Schwarzenbach 2003). Specific organic compounds containing suitable chemical functional groups may adsorb by chemical adsorption (i.e., covalent bonding) at the strongest available adsorption sites on the surface. These sites are characterized by reactive functional groups frequently located at the edges of the clay lattice or to organic matter (Yong et al. 1992, Lowell et al. 2004).

The process of organic pollutant uptake by soil in the natural environment is complicated and depends on a large number of factors and binding processes. Assuming that since oil contaminants found at oilfield sites are largely nonpolar and nonionic, the amount of electrostatic adsorption would likely be small. Similarly, it is assumed that the number of compounds in crude oil capable of chemically binding to suitable reactive sites on soil particles would also be small (Senesi 1993). Ignoring the contributions of adsorption by electrostatic and chemical forces, the distribution coefficient (L/kg) of organic compounds may be rewritten as:

$$K_d = \frac{(C_{oc})(f_{oc})(\Phi_w) + (C_{min})(A_{surf})(\Phi_a)}{C_c}$$ [2-4]

where C_{oc} is the concentration of sorbate associated to organic matter (mol/kg); f_{oc} is the fraction of organic carbon in the soil (kg/kg); C_{min} is the concentration of sorbate associated with the mineral surface (mol $\cdot$ kg^{-1}/m^2); A_{surf} is the specific surface area of the particle surface (m^2); and C_c is the concentration of uncharged chemical contaminant in solution (mol/L) (Scharzenbach 2003). Since the proportion of partitioning to organic carbon is related to soil moisture, the partitioning term is multiplied by the soil moisture content (Φ_w) or fraction of pore space occupied by water (%) (Scharzenbach 2003). The proportion of adsorption to mineral surfaces is related to the dryness of the soil and thus the adsorption term is multiplied by the fraction of air in micropores (Φ_a) (Scharzenbach 2003).

2.1.4 Models for Adsorption

There are several models that have been developed to describe the process of adsorption by relating the curve of adsorbent concentrations over a range of pressure at a fixed temperature (Tan 1993). This is called an adsorption isotherm and is described by the Langmuir equation and the Brunauer, Emmet, and Teller (BET) equation (Tan 1993). These models were developed to relate the concentration of adsorbate molecules required to cover the surface of a solid material (Lowell et al. 2004).

The Langmuir equation was derived in 1918 from observations of water evaporation and condensation on a solid substrate (Adamson 1990). The equation uses the energy of adsorption to determine the amount of adsorbent gas required to create a monolayer on the surface (Sposito 1984). The equation is as follows:

$$\frac{W}{W_m} = \frac{C(P/P_0)}{1 + C(P/P_0)}$$ [2-5]

where W and W_m are the weights of adsorbate and monolayer, respectively, P is the equilibrium vapour pressure, P_0 is the saturation vapour pressure, and C is a constant associated with adsorption energy (Lowell et al. 2004). This model has some limitations and assumes only a monolayer of adsorption occurring.

The BET equation improves upon the Langmuir equation by extending the approach to include multilayer adsorption and is the most popular method of calculating specific surface area of granular solids (Tan 1993, Lowell et al. 2004). The equation using the same variables as the Langmuir equation is rearranged as follows (Tan 1993, Lowell et al. 2004):

$$\frac{P}{W(P_0 - P)} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(\frac{P}{P_0}\right)$$ [2-6]

The weight of the monolayer W_m is calculated by the slope and intercept of the isotherm line

(Lowell et al. 2004). The surface area can then be calculated by using the cross-sectional area of the adsorbate molecule with the following equation:

$$S_t = \frac{W_m N (A_{cs})}{M}$$

[2-7]

where S_t is the total surface area of the sample, N is Avogadro's number, A_{cs} is the cross-sectional area of the adsorbate molecule, and M is the molecular weight of the adsorbate (Lowell et al. 2004).

The use of adsorption isotherms and calculation of surface area can be tools for characterization of adsorptive properties of granular solid materials. An understanding of the properties of soils and adsorption is consequential to the activity and fate of organic pollutants in the environment (Hassett and Banwart 1989). Remediation of contaminated soil by biological, chemical, or physical methods are limited by the adsorption of organic compounds to soil and a fundamental understanding of contaminant-soil interactions is imperative to improve current remedial techniques (Salloum 1999).

2.2 Remediation of Contaminated Oilfield Sites

As described in previous sections, soil contamination has detrimental effects on environmental systems and soil remediation is the process of mitigating and minimizing the effects by reducing contamination levels. The remediation of contaminated sites is conducted for a number of reasons, including landowner claims, lease agreements, government regulations, long-term liability, company policy, and resource protection (Carty et al. 1997). Generally, the goal of soil remediation is to reduce contaminant concentrations to regulated levels that do not inhibit soil functions.

2.2.1 Remediation of Salt Impacted Soils

Salt contamination in soil can be characterized using several analytical methods. The concentration of total dissolved salts dissolved in soil water can be estimated by the measurement of electrical conductivity (EC) in deciSiemens per meter (dS/m) (Carty et al. 1997). Measurement of EC can be completed in the field or in the laboratory and when compared against the EC of normal soil (< 4 dS/m) it can provide an indication of concentrations of dissolved salts in the soil water by the increased electrical conductance. Other measurements of salinity are described by the

concentrations of cations such as sodium (Na^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}) and their exchange between the soil particle and solution. The cation exchange capacity (CEC) of soil is measured by the sum of exchangeable cations expressed as centimoles of positive charge per kilogram of soil (cmol/kg) (Brady and Weil 1996). Salt contamination in soil is often attributed to sodium chloride (NaCl). The degree of the exchange complex of a soil particle that is saturated by sodium is called the exchangeable sodium percentage (ESP) and is represented by the following equation (Brady and Weil 1996):

$$ESP = \frac{exchangeable\quad sodium(cmol_c/kg)}{cation\quad exchange\quad capacity(cmol_c/kg)} \times 100\% \qquad [2\text{-}8]$$

Another measurement based on the competitive ratio between sodium, calcium and magnesium cations for adsorption is called the sodium adsorption ratio (SAR) and is represented by the following equation (Brady and Weil 1996):

$$SAR = \frac{\left[Na^+\right]}{\left[1/2\left(\left[Ca^{2+}\right]+\left[Mg^{2+}\right]\right)\right]^{1/2}} \qquad [2\text{-}9]$$

where [Na^+], [Ca^{2+}], and [Mg^{2+}] in soil solution is expressed as mmol charge per litre (Brady and Weil 1996).

Currently the most common methods for remediating salt impacted soils are: drainage systems, soil amendments, and salt tolerant crops (i.e., phytoremediation) (Knox and Sabatini 2000). Drainage is used to leach soluble salts from soils into controlled canals and waterways (Franzen 2003). Soil amendments such as chemical additives and bulking agents are used to replace sodium at the soil surface with an alternative source of cations (eg. calcium from gypsum) or to improve infiltration of water into the soil (Qadir et al 1998, Franzen 2003). Reclamation of salt impacted soil may be completed by planting salt tolerant plants to repair soil structure damage done by salts (Carty et al. 1997). Usually a combination of drainage, amendments, and phytoremediation methods are used for site remediation. For example, Sublette et al. (2005) investigated the reduction of salt

and hydrocarbon contamination by various tilling methods using several bulking agents. The use of tillage and bulking agents increased the macropores and corresponded to an improvement of soil structure, increased hydraulic conductivity, and increased leaching of salts (Sublette et al. 2005).

A number of researchers have investigated the use of chemical amendments for remediating salt impacts. Knox and Sabatini (2000), and Korphage et al. (2003) used fly ash and gypsum respectively, to remove sodium from the soil particle surface. Research indicated that soil structure and vegetation visually improved from treatment; however, salt removal by these methods was limited by time (Knox and Sabatini 2000, Korphage et al. 2003). Qadir et al. (1998) implemented a multistage treatment method investigating vertical leaching, flushing events, and gypsum amendment and measured the response in crop production of rice and wheat. Research indicated that a multi-stage treatment (flushing-gypsum-flushing) generated the best results in terms of crop production (Qadir et al. 1998). The use of amendments can be an expensive method of brine spill remediation and it has been shown to require a significant amount of time and effort (Knox and Sabatini 2000, Korphage et al. 2003, Sublette et al. 2005). The application of amendment on its own is not enough to reclaim a soil and must include additional measures of irrigation and drainage for several years (Ashworth et al. 1999). Phytoremediation with salt-tolerant crops such as barley, salt grass, and wheat is an alternative method used to prevent further soil degradation (Knox and Sabatini 2000). Natural remediation by salt-tolerant plants is simple and requires less disturbance of topsoil; however, like soil amendments, the remediation process may require a long period of time compared with other methods (Carty et al. 1997).

2.2.2 Remediation of Hydrocarbon Contaminated Soils

Numerous techniques exist for remediation of hydrocarbon contamination and can be used under a variety of situations. Currently the most common treatments for hydrocarbon contamination is bioremediation, incineration, and soil vapour extraction (FRTR 1991). Due to the high cost of incineration and the conditional requirements for soil vapour extraction, the use of these techniques are limited to selected sites. Bioremediation is a more common remediation technique due to its versatility and relatively low cost (Singh and Ward 2004).

Bioremediation is described as the biological/biochemical degradation of hydrocarbon

compounds in soil by populations of carbon utilizing microorganisms (Brady and Weil 1996). The microorganisms oxidize hydrocarbon compounds to create energy (Adriano et al. 1999). In order to optimize degradation, environmental managers control certain important variables of the metabolic pathway to maximize bacterial growth (Adriano et al. 1999, Singh and Ward 2004). Laboratory studies by Dibble and Bartha (1979) demonstrated the importance of soil moisture, pH, mineral nutrients such as nitrogen and phosphorous, temperature, and aeration for controlling bioremediation of hydrocarbons in soil. To date, many experiments have investigated the effect of these factors under a variety of laboratory and field conditions. One problem observed in all hydrocarbon remediation experiments is the low bioavailability of poorly soluble residual hydrocarbons in soil. The persistence of hydrocarbon contamination from crude spills may be attributed to the high molecular weight and recalcitrance of some of the contaminant constituents (Atlas 1981, Amatya et al. 2002). The very low solubility of these recalcitrant hydrocarbon fractions translates to poor availability for metabolism by microorganisms and often residual hydrocarbons remain for long periods of time (Talley 2006). Due to their low solubility in water and low hydraulic conductivity, remediation of hydrocarbons in soil is a continuing challenge (Khaitan et al. 2005).

2.2.3 Challenges

There are several challenges to the remediation of mixed salt and hydrocarbon wastes at oilfield sites. The presence of salts has been shown to impede the growth of the hydrocarbon degrading bacteria responsible for bioremediation (Cook et al. 2002). This, in addition to the resistance of heavy fractions of hydrocarbons to degradation, may prolong the treatment time. Many forms of treatment for hydrocarbons are limited by the adsorption to soil colloids, especially organic matter. Research into the effects of high salt concentrations on residual hydrocarbons adsorbed to soil particles is limited. A greater understanding of this relationship is important to improve the current methods used to treat oilfield sites.

An effective remediation strategy to address the unique properties of the mixed hydrocarbon and salt contaminated waste could include integrated soil remediation technologies. Soil washing is a remediation technology that is already currently used at hydrocarbon contaminated sites. Soil washing is described as a waste reduction method of separating fine grained soil containing adsorbed hydrocarbons in soil/water slurry, thus concentrating the contamination in a smaller

volume (Griffiths 1995, Saponaro et al. 2002). Similarly, soil flushing is a method that is used to leach contamination from the soil surface into the aqueous phase of the slurry water (Bai et al. 1997). Research by Bai et al. (1997) used soil flushing supplemented by surfactants to leach and remove residual hydrocarbons. Results indicated that residual hydrocarbons were removed predominantly by mobilization and the increased solubilization of surfactants played an insignificant role in hydrocarbon removal (Bai et al. 1997). Research by Shin and Kim (2004) was completed to investigate the removal of phenanthrene and diesel by surfactant flushing on contaminated sand. Under optimal conditions significant reduction of contaminants was observed (Shin and Kim 2004). In both experiments, removal efficiency was determined to be dependent on the soil particle size and the type of surfactant (Bai et al. 1997, Shin and Kim 2004). It was postulated that treatment efficiency may be decreased for finer grained soils with smaller pore size under field conditions (Shin and Kim 2004). Therefore, it is assumed that the adsorption of hydrocarbons to fine-grained soil common at many drill sites in western Canada may pose a problem for the effectiveness of soil flushing (Kuhlman and Greenfield 1999). An enhanced form of soil flushing that removes adsorbed contaminants from the fine soil particles would be expected to increase the leaching effectiveness. The use of ultrasound is a technique with potential for improving contaminant desorption.

2.3 Ultrasonic Soil Treatment

2.3.1 Sonochemistry

Ultrasonic technology has become a valuable tool in the field of analytical chemistry. It has a wide range of potential applications and requires relatively inexpensive laboratory equipment. The different sizes and operating intensities of ultrasonic equipment can be easily adapted to suit specific research questions. Ultrasound is defined as the frequency of sound beyond the range of human hearing normally at 16 kHz (Mason 1990a). Sound waves above this range (particularly above 20 kHz) carry more acoustic energy and are capable of remarkable effects on many chemical reactions (Mason 1990b). Application of ultrasound to a material submits the substance to physical forces from intense heat and pressure.

Ultrasound is commonly used for medical diagnosis, materials testing, and underwater ranging

(Mason 1990a). Ultrasound and its application can be divided into two categories: low intensity and high intensity. The intensity of the ultrasound is described as the power of the acoustic wave (Watt) applied to a unit area of the medium (square centimeter) (Mason 1990a). The ultrasonic intensity can also be described as the power density of the acoustic wave.

Low intensity ultrasound is used for diagnosis, scanning, and material testing by the transmission of non-destructive levels of energy through a medium in order to obtain information (Raichel 2000). Although the frequency of diagnostic ultrasound is very high (2 to 10 MHz) compared with frequencies used in chemical applications of ultrasound (20 to 100 kHz), the low intensity of power carried by the acoustic wave has a very limited effect on the applied medium and does not influence chemical reactivity (Mason 1990a). High intensity ultrasound is used to induce a permanent chemical or physical change on the target medium (Mason 1990b). High intensity ultrasound is more commonly used in analytical sonochemistry and applies sound waves with lower frequencies and higher power intensity to achieve the intended physical or chemical effect.

The application of ultrasound in analytical chemistry is derived primarily from acoustic cavitation: the formation, growth and implosive collapse of small bubbles in a liquid (Suslick 1990). Cavitation from ultrasonic irradiation is the mechanism of transferring the acoustic energy into extreme physical forces within the medium at a localized scale. Cavitation begins with the formation of micro-bubbles within the liquid from the rarefaction of the acoustic wave (Mason 1990a, Collings et al. 2006). The compression and rarefaction phases of the acoustic wave cause rapidly alternating pressures in the liquid (Collings et al. 2006). Bubbles trapped in the liquid expand and contract with the wave. The bubbles may grow with successive waves if the rate of expansion in the rarefaction phase is greater than the rate of compression during the compression phase of the cycle (Suslick 1990, Collings et al. 2006). Once the bubble reaches a critical size and can no longer adsorb sound energy to sustain it, the surrounding liquid rushes in and the cavity violently implodes (Suslick 1990). During the collapse, the vapour and gases within the bubble are rapidly compressed, releasing instantaneous heat and pressure as high as 5000 K and 1000 atm, respectively (Mason 1990a). The collapse is significantly faster than the transportation of heat and thus creates a short-lived, localized hot spot while the temperature of the system remains generally unaffected (Suslick 1990, Mason 1990b).

When ultrasonic waves are applied to a heterogeneous liquid-solid mixture there is an empirical effect on cavitation. Cavitation becomes influenced by the presence of solid particles observed by a change in the symmetry of bubble collapse (Thompson and Doraiswamy 1999). When cavitation occurs next to a particle the collapse is asymmetrically directed at the particle surface in a high-powered microjet with velocities greater than 100 m/s (Suslick 1990). When cavitation occurs away from particles, the cavitation collapse is symmetrical and the shockwave from the collapse can generate turbulence or microstreaming across solid particles (Suslick 1990, Thompson and Doraiswamy 1999). These forces are used widely for particle cleaning of solids in suspension or slurry.

2.3.2 Sonochemistry in Remediation

Ultrasound waves have valuable potential for the destruction and removal of biological and chemical contaminants in soil or water. The destruction of contaminants is completed by the direct oxidation of chemical residues or by desorption and leaching of contaminants from materials (Mason and Lorimer 2002, Mason et al. 2004).

Ultrasonic treatment can be used to target compounds that may otherwise persist in the environment and degrade highly stable contaminants such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pesticides, and other organochlorides that adsorb to the surface of soil particles (Collings et al. 2006). The use of ultrasound as a tool for degrading hazardous chemicals has the potential to become economically competitive with other degradation technologies (Hoffman et al. 1996). Hoffman et al (1996) reported ultrasonic treatment to be effective for the destruction of organic contaminants in water due to oxidation and high localized temperatures and pressures. The breakdown of hazardous compounds into intermediate products can be relatively easy to monitor. For example, Little et al. (2002) found that the ultrasonic degradation of phenanthrene created sub-products that can be observed with gas chromatograph analysis. Results indicated at temperatures of 40°C, there was an 88% reduction in phenanthrene concentrations and an increase in concentration of degradation products anthracene, naphthalene, and phenol (Little et al. 2002). One concern regarding the destruction of complex organic compounds is the generation of dangerous byproducts. According to Collings et al. (2006), the rapid destruction of persistent organic pollutants limits the production of toxic compounds such as dioxins.

Generally, the smaller fractions of hydrocarbons produced as degradation byproducts tend to have higher solubilities and are more volatile, therefore increasing their bioavailability for remedial treatments (Feng and Aldrich 2000).

Another form of ultrasonic research is the potential for ultrasonic desorption of sorbed materials to solid particles. Studies have shown that organic and inorganic adsorbates are released by asymmetric bubble collapse, facilitating the process of cleaning, destruction and extraction within aqueous solution (Lim and Okada 2005). Experiments by Lim and Okada (2005) indicated that desorbed trichloroethylene in the liquid phase can be degraded effectively by ultrasound. Desorption of organic pollutants is achieved by breaking the physical bonds between the adsorbate and adsorbent (Lim and Okada 2005). Juang et al. (2006) compared the change in adsorption isotherms for phenol to activated carbon using ultrasound. Results indicated that when ultrasound was applied, the adsorption capacity decreased and the Langmuir constant increased with ultrasonic power while lowering the number of surface sites available for adsorption (Juang et al. 2006). Mason et al. (2004) suggested that the mechanisms for ultrasonic removal of chemical contaminants are associated with the increased abrasion on particle surfaces and the improvement of solvent leaching of entrenched residual materials. The degree of contaminant removal was determined to be dependent on ultrasonic power, water flow rate, and soil particle size (Kim and Wang 2003).

Normal leaching of contaminants relies on the interaction between the solvent and particles of solid. It is thought that ultrasonic generated microstreaming, dispersion, and turbulence enhances the solvent interaction and leaching efficiency (Mason et al. 2004). A review of ultrasonic remedial technology by Breitbach and Bathen (2001) indicated that ultrasound not only promotes desorption but also enhances the transfer of pollutants and solvent through the system. Experiments by Chung and Kamon (2005) showed an increase in permeability and removal rate of contaminants in clay from electrokinetic and ultrasonic tests. Contaminant removal was considered to be influenced by the increased water saturation and flow generated by ultrasonic waves (Chung and Kamon, 2005). The mechanisms responsible for the increased flow and transport by ultrasonic energy are attested to the displacement, velocity, and acceleration of fluid particles, and the phenomena of cavitation, acoustic streaming, and interfacial instabilities (Chung and Kamon 2005).

Certain factors have been shown to influence the success of hydrocarbon removal using

ultrasound. The variables of particle size, initial hydrocarbon concentration, salinity, pH, and surfactants have significant effects on the removal of hydrocarbons from soil (Feng and Alderich 2000). The efficiency of ultrasonic soil washing decreases with decreasing particle size and with initial concentration due to adsorption. As salinity was increased the removal of hydrocarbons increased to an optimal point (0.4 Molarity [M]) after which increasing salinity reduced the efficiency of removal (Feng and Aldrich 2000). Feng and Aldrich (2000) theorized that up to a level of 0.4 M, salinity weakened electrostatic attraction of hydrocarbon and soil particles; however as concentrations rose higher than 0.4 M the electrical potential (zeta potential) between the surface and adsorbates reached a critical point where the potential is equal to zero (Tan 1993). After this point, the removal of hydrocarbons appears to decrease continually. There is no clear explanation for this phenomenon in the existing literature.

2.4 Soil Washing Treatment

2.4.1 Basic Principles of Soil Washing

Soil washing is an extraction process to remove organic and inorganic compounds from contaminated soils (U.S.EPA, 1985). It removes contaminants by dissolving the liquid, sorbed, or vapor phase or by mobilizing contaminants existing as free product in soil pores and adsorbed to the soil (Lyman, Nornan, and Reidy, 1990). The former processes are controlled by the solubilities of the contaminants and Henry's law's constants, while the latter are removed by the pressure gradient of the washing water and are controlled by the viscosity and density of the contaminants. Water or solvent is usually used to remove contaminants from soils.

The target contaminants for soil washing include semi-volatile organic compounds, petroleum and fuel residuals, heavy metals, PCBs, PAHs, and pesticides (Mbhele, 2008). Inorganic matters like soluble salts can also be washed out from contaminated soils. However, soil washing is not often used for soils with mixture of different types of contaminants. The fundamental process involved in the removal of contaminants from soil particle surfaces is the use of an extraction fluid with higher affinity for the contaminants of interest than the soil organic matter. This transfers the contaminants from the soil surface to the fluid.

The equilibrium concentration between water and a representative organic solvent, octanol, is described by the solvent/water partition coefficient K_{ow}:

$$K_{ow} = \frac{C_o}{C_w}$$

[2-10]

where C_o is the concentration of chemicals in octanol (mg/L); C_w is the chemicals in water (mg/L);

The extent of sorption of many contaminants to soil surfaces is highly correlated to the amount of organic carbon in the soil and described by an organic carbon normalized soil-water coefficient K_{oc} (Equation 2-2). Contaminants can be grouped according to the K_d values. The greater the value for K_d is, the stronger the absorption to the soil is. The K_{oc} value reflects the impact of organic matter to adsorb organic compounds out of solution. Compounds with low solubility often have higher K_{oc} values. The efficiency of solvent extraction could be directly related to the nature of the organic contaminant in terms of its K_{ow} and K_{oc} values. For highly hydrophobic compounds with large K_{ow} values (i.e., greater than 10,000), the use of organic washing solution takes advantage of the contaminant's organic-phase affinity and effectively remove contaminant from the soil organic matter. However, when the amount of organic carbon fraction of soil increases, it tents to concentrate contaminants in the soil and makes soil more difficult to wash. For contaminant with a large K_{ow} in a soil high in organic carbon, the contaminant equilibrium distribution shifts to the soil phase, so aqueous-based washing solutions become ineffective. In order to increase the efficiency of soil washing in these kind of soils, organic solvent with stronger extraction power should be used to transfer the contaminant into the organic extraction fluid.

Usually soil washing is not a single treatment process, but a combination of several techniques to successfully finish the job. Figure 2.1 illustrates modules in typical soil washing process (EPA: Guide to Conducting Treatability Studies under CERCLA, 1991). Basically there are three steps involved in any soil washing process: (1) soil preparation for removal and cleaning of oversized material and debris; (2) soil washing process to remove the contaminants, and (3) wastewater treatment in which dispersed soil and contaminant are removed from the water. Treated water can be recycled to the soil washing process.
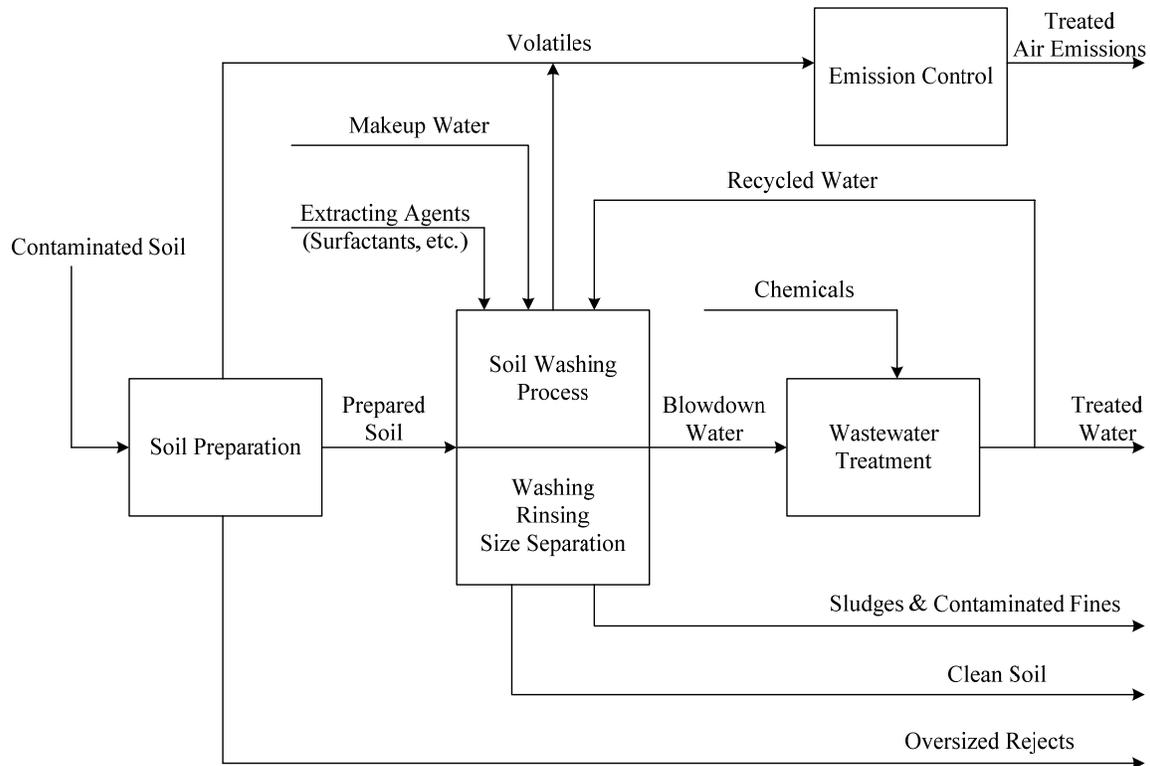
Figure 2.1 Aqueous soil washing process (From the US EPA 1990)

2.4.2 Influencing Factors of Soil Washing

Removal efficiency of contaminants from contaminated soils is highly depending on the physical and chemical characteristics of contaminants and the spatial distribution of pollutants throughout the soil. Soil washing process is also highly sensitive to site conditions. The key influencing factor is particle size (Borst, 1991). Usually the fine-grained soils are more difficult than coarser particles to be washed, because fine soil particles have large pore-surface areas for which contaminants are tended to stay adsorbed. Soil particles smaller than 0.063 mm (clay fraction) tend to be attached loosely to the coarser particles. When using the water as an extraction fluid, the physical bond was broken and the contaminants mainly stayed with the fine fraction were separated from sand and gravel factions (Anderson, 1993).

In addition to the particle size, other soil characteristics that affect wash-ability include humic content, cation exchange capacity (CEC), soil hydraulic conductivity and temperature. Contaminants partition strongly to humic matter and then make washing of high-humic-content

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soils difficult. A potential candidate soil for washing is that with at least 60% of particles greater than 0.063 mm and less than 20% of organic matter content (Hyman and Dupont, 2001). The CEC value is also very important. Better soil washing can succeed with lower CEC, especially for removal of cationic metals. Soil washing is more applicable to highly permeable soils, such as sand and gravel. Hydraulic conductivity of the soil should be at least 10^{-5} cm/sec, preferable greater than 10^{-3} cm/sec (Anderson, 1993). High silt and clay content can hinder the movement of the washing solution. The leaching fluid may not reach all contaminants in a well-compacted soil, and it may follow flow paths of least resistance (less fines and less contamination) (Eve, 1998). Temperature of the water can influence the treatment ability as well. When washing soil with aqueous solutions, heating the water usually will aid in mobilizing contaminants and therefore improve the pollutant removal efficiency (Hyman and Dupont, 2001).

2.4.3 Limitations of Soil Washing

The limitations of soil washing are basically due to a number of factors. The first one is soil particles distribution. Soil washing is not suitable for soil which contains high fraction of silt and clay. For example, high clay content may even cause adsorption of a surfactant (when used for soil washing) which makes the recovery of the solvent and surfactant difficult. The second one is related to the components of contaminants. Soil washing is not feasible when complex wastes containing many different contaminants with different solubility are involved (US EPA, 1985). Sequential washing steps using combination of different additives may be required. The last one is soil washing process itself. One of the biggest problems is the large volumes of contaminated water that require treatment before its final disposal or reuse (Lyman et al., 1990). The recovered contaminant solution can be very dilute in a large volume and, hence, difficult to treat and dispose (US EPA, 1985).

2.4.4 Soil Washing Enhanced by Ultrasonic Technique

As mentioned before, soil washing is usually not a single treatment process but integrated with several other treatments methods in order to better clean the contamination. Many scientists have been studying the application of ultrasound to soil washing technique trying to improve the pollutant removal efficiency and develop cost-effective way of treatment. Coles (1990) found that ultrasonic washing was effective for removal of organic contaminants from soil. The beaker-scale studies showed that ultrasonic cavitation could eliminate or minimize the need for surfactants in soil

washing. Kamalavathany (1997) also used an ultrasonic enhanced soil washing technique to effectively reduce the PAHs existing in the soils. The treatment process was very effective in removing PAHs from contaminated soils and the average optimum removal efficiencies during the test runs were found to be 83%.

Comparison studies were conducted for investigating the efficiencies of conventional and ultrasonic enhanced pollution extraction procedures using soil samples (granular pieces of brick) contaminated with copper oxide (Mason et al., 2004). After 30 minutes of ultrasonic enhanced soil washing treatment using a specifically designed reactor-Vibrating Tray which is shown in Figure 2.2, ultrasonic enhanced treatments illustrated a pollutant reduction of 40% while the reduction using conventional soil washing treatment was 6%.
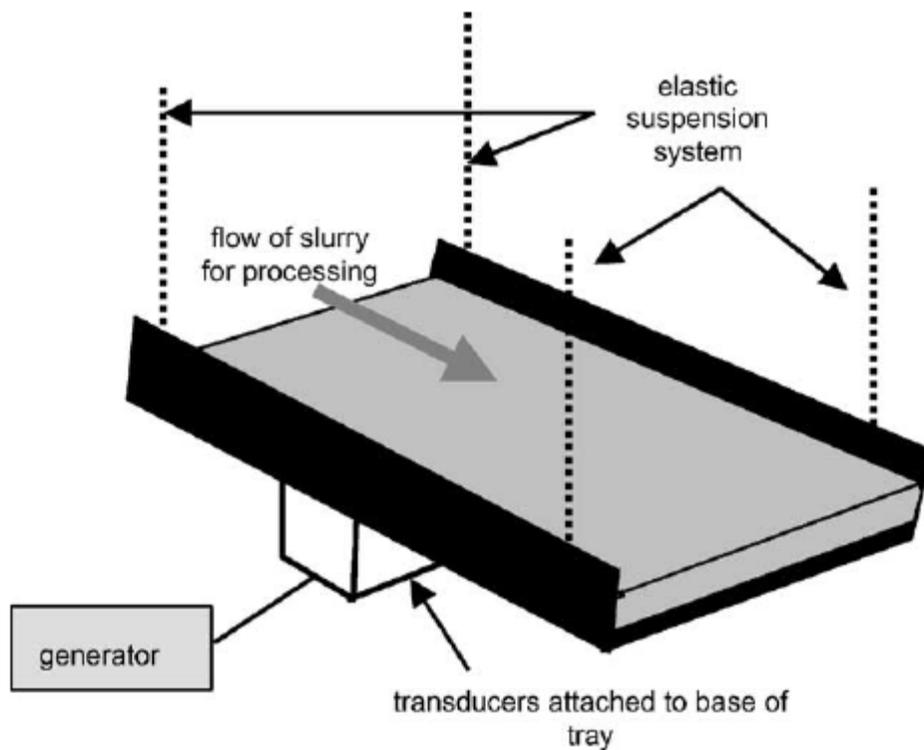
Figure 2.2 Schematic representation of the vibrating tray device used for the cleaning of contaminated soils (Mason et al., 2004)

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The mechanism of ultrasonic application is that cavities are formed by ultrasound. When these cavities implode, they generate different fluid velocity, which is capable of dispersing contaminants from the soil particles into the soil suspension by overcoming the forces binding the soil particles. The velocity perturbations occur on a microscopic scale, and are capable of dislodging contaminants from the micro-size particles in the system by overcoming the forces binding finer particles to medium-size particles.

By applying ultrasonic technique to soil washing, it would be able to improve the soil washing process by accomplishing the following enhancements: generating higher fluid particle shear stresses, achieving satisfactory cleaning levels, and minimizing the need for surfactants in the cleaning process. On the other hand, soil washing technique can improve ultrasonic treatment as well. One bottleneck of ultrasonic treatment is re-adsorption during and after the treatment process. Although the strong cavitation drives the contaminants to aqueous phase, the desorbed contaminants can re-adsorb on soil particles especially fines with larger surface area. By applying soil washing to ultrasonic treatment, it can increase the transportation of aqueous solution in the system and move the desorbed contaminants out of the system before re-adsorption occurs.

3. METHODS AND MATERIALS

The research experiments in this project were divided into two parts. The first part is related to Ultrasonic Remediation Experiments. In this part, the experiments were designed using an ultrasonic probe reactor and vacuum filtration system to treat three different soils contaminated with crude oil. Additional treatments were completed with the addition of dissolved sodium chloride salt to explore the influence of salinity on treatment results. The objectives of these experiments are to investigate the interactions of mixed salt and hydrocarbon contamination on the soil surface and to examine the effectiveness of ultrasonic treatments as a remediation tool for the reduction of hydrocarbon concentrations in soil. The second part is related to Ultrasonic Enhanced Soil Washing Treatment Experiments. In this part, a reactor was designed and built for enhanced treatment combining both ultrasonic treatment technique and soil washing technique. Four factors were studied by conducting a group of full factorial experiments. The objectives of the study in this part are to find out the optimum working condition of ultrasonic enhanced soil washing treatment and examine the enhancement of treating ability comparing with the results of ultrasonic treatment. A detailed description of materials and methods used to complete the experiment is provided in the following sections.

3.1 Soil

Three soils were used in the research experiments and included sand, clay, and muskeg soil. A bag of industrial quality graded sand was obtained from VWR International (Ottawa Sand – cat # 20118-003). Commercially available sand was chosen to represent coarse grained material for comparison and is commonly used for laboratory based environmental research (Fine et al. 1997, Feng and Aldrich 2000, Farmer et al. 2000). The sand was characterized by visual observation as a light brown medium grained sand.

The clay and muskeg soils were collected for the research project with the assistance of an independent petroleum development and production company operating in Fort St John, British Columbia. Un-impacted clay and muskeg soil were targeted for soil conditions commonly found at oil and gas production sites in western Canada and were collected near a former oil and gas

production site in an undisturbed area. Clay was collected from the B-horizon and was classified by visual observation as a dense grey clay unit with some silt, trace sand and gravel. Muskeg soil was collected from the A-horizon of a nearby peat bog and classified by visual observation as an organic peat containing abundant coarse organic debris (wood, rootlets, grasses, etc.). According to soil survey report No 42, "soils of Fort St. John-Dawson Creek Area" by Land Resource Research Institute (Agriculture Canada, 1985) the clay soil is most likely described as an Orthic Gray Luvisol generated by glacial morainal or lacustrotill deposits and the muskeg is classified as a Terric Mesisol generated from moderately decomposed bog peat. The clay and muskeg soils were chosen for the prevalence in drilling areas and their contrasting properties important for sorption.

The clay and muskeg soils were screened to remove coarse organic debris, homogenize soil conditions, and to remove coarse particulates (sand and gravel). The soils were dried in a laboratory oven at 60°C overnight to dry excessive moisture. The clay and muskeg were first screened with a Fisher, No. 8 sieve (2.34 mm) followed by a No. 20 sieve (0.805 mm). To assist with screening, large soil clumps were ground down using a mortar and pestle. The end result of screening was a workable, fine granular soil with homogenous soil conditions.

3.1.1 Soil Characterization

Initial characterization of the three soils was completed for physical and chemical properties. Samples of sand, clay, and muskeg were analyzed by the BC Ministry of Forests (MOF) research branch laboratory in Victoria, BC for soil texture, pH, conductivity, total carbon content, total nitrogen content, exchangeable cations, and effective CEC. Soil texture was analyzed by hydrometer, sample pH was measured using a lab pH meter and conductivity was measured with a conductivity meter by saturated paste method. Total carbon and nitrogen was measured using an elemental analyzer and exchangeable cations and effective CEC were analyzed by ICP spectrometer using a 0.1 N barium chloride extraction. ESP and SAR were calculated for each soil to assess initial salinity properties using the results for CEC and concentrations of sodium, calcium, magnesium.

3.1.2 Adsorption Characterization

Samples were analyzed for adsorption properties using the Quantachrome Autosorb-1 analyzer.

The instrument measures the quantity of gas adsorbed to a solid surface by physical van der Waals forces at equilibrium vapour pressure by static volumetric method (Quantachrome 2005). Measurement is completed at the gas critical temperature (77.35 K) using liquid nitrogen coolant in a physisorb dewer flask. Approximately 1 g of sample was placed in a 6 mm glass sample cell (part # 74028). Analysis of "physisorb micropore run" using the multi-point BET method was selected in the provided data acquisition field of the Autosorb software. Analysis was completed automatically over a 24 hour period and the adsorption isotherm was generated on the laboratory computer. Particle surface area was calculated using the slope and intercept of the adsorption isotherm and known properties of the adsorbent.

3.1.3 Crude Oil Soil Spiking

Crude oil was donated to the project by the Husky Energy light oil refinery in Prince George, BC. The crude oil is called BC light oil crude and is produced in northeastern BC and delivered via pipeline from Fort St John. The crude oil has a density of 0.8 g/ml at 15°C, 15% sulfur content and approximately 1% sediment/water content (Hughes 2005) and is refined at the Husky refinery in Prince George to produce gasoline, diesel, fuel oil, and asphalt. The salt concentration in the crude range from 16-100 pounds per thousand barrels (Hughes 2005)

Sand was spiked with concentration of 1% crude oil to sand by volume. Clay and muskeg were spiked with concentrations of 2% crude to soil by volume. The concentration mixtures were determined by trial and error and chosen to represent a high level of contamination. The volume of the total bulk soil was calculated using the bulk density. The corresponding volume of crude oil was measured out into a beaker and then diluted in hexane (Amellal et al. 2001). The hexane/crude solution was mixed thoroughly into the soil until the soil was completely saturated with hexane. The hexane was allowed to evaporate in the fume hood leaving the crude oil adsorbed evenly throughout the soil. Once the soil was dry, it was manually mixed again to assure even hydrocarbon distribution. The soil was spiked approximately 1 week before use and was stored in the fridge at 4°C. Periodic analysis of soil samples indicated that losses due to volatilization and degradation were minimal.

3.2 Ultrasonic Treatment Experimental Design

3.2.1 Ultrasonic Treatment Process

Figure 3.1 shows the entire process of ultrasonic treatment. The ultrasonic treatment experiment was completed at the Soil and Groundwater Remediation Laboratory at UNBC. Three replications were completed for each combination of treatment variables. Three variables were tested and included soil type (sand, clay, and muskeg), salinity (no salt, salt added), and sonic treatment time (control, 2 min, 5 min, 10 min, 20 min, and 40 min). Soil type classes were selected to provide a range of soil textures and to test the differences of crude oil adsorption between clay and organic matter. The "salt added" salinity class was tested to represent a soil with high salinity. Sonic treatment time was tested to observe the effect of treatment duration. The treatment class "control" illustrated the conditions completing treatment without ultrasound and was useful for comparison against other sonic treatment durations. In total there were 36 combinations of variables. Since the treatment method was destructive, only one set of analyses could be made per treatment and 36 treatments using all combinations were conducted for each replication. Table 3.1 summarizes the variable combinations for experimental design.

Table 3.1 Summary of ultrasonic treatment experimental design

Variable	Number of Classes	Class descriptions
Soil type	3	sand, clay, muskeg
Salinity	2	no salt, salt added
Treatment time	6	control, 2 min, 5 min, 10 min, 20 min, 40 min
Total number of combinations:	36	

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                    ┌─────────────────────┐
                    │        Soil         │
                    └─────────────────────┘
                               │
                               ▼
                    ┌─────────────────────┐
                    │ Sample Preparation  │
                    └─────────────────────┘
                               │
                               ▼
                    ┌─────────────────────┐
                    │ Ultrasonic Treatment│
                    └─────────────────────┘
                               │
                               ▼
              ┌─────────────────────────────────┐
              │ Residual "clean" soil and Filter Paper │
              └─────────────────────────────────┘
                               │
                               ▼
                    ┌─────────────────────┐
                    │  Shaking Extraction │
                    └─────────────────────┘
                               │
                               ▼
              ┌─────────────────────────────┐
              │  Silica Gel Column Cleanup  │
              └─────────────────────────────┘
                               │
                               ▼
              ┌─────────────────────────────┐
              │  Chemical Analysis: GC/FID  │
              └─────────────────────────────┘
                               │
                               ▼
              ┌─────────────────────────────┐
              │       Data Processing       │
              └─────────────────────────────┘
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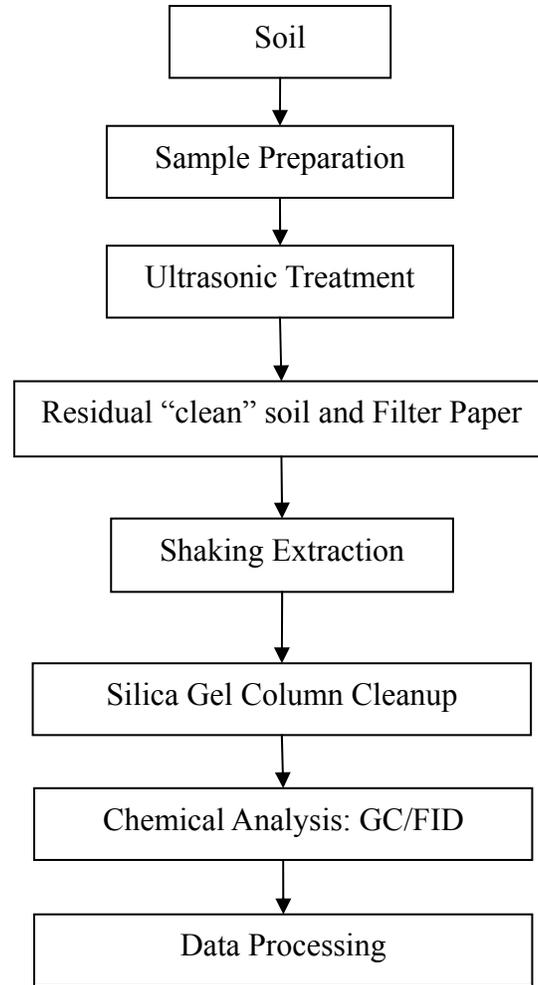
Figure 3.1 Flow chart of ultrasonic treatment process

To begin each treatment, a 30 ml volume of oven-dried soil was removed from the spiked batch. Using the bulk density of each soil the equivalent mass of 30 ml of each soil was calculated. This 30 ml volume was measured using a calibrated Denver Instrument SI-403 bench-top digital scale accurate to the milligram and corresponded to 45.9 g of sand, 35.7 g of clay, and 7.7 g of muskeg. The measured sample was placed in a 140 ml glass beaker with 50 ml of deionized water. For "salt added" treatments 0.8 g of sodium chloride was dissolved in the 50 ml of water (0.27 M sodium chloride solution) before adding to the soil (Feng and Aldrich 2000). Table 3.2 summarizes the preparation of experimental materials. The soil and water was mixed on a Fisher-Scientific magnetic stirrer for 2 minutes. After mixing the sample the stir bar was removed and rinsed with 20 ml of DI water for a total water volume of 70 ml (30 ml of DI water would be added after sonication

for a total water volume of 100 ml). The beaker containing the sample was then secured to a stand with the beaker partly submerged in a VWR circulating water bath set to 20°C. The water bath was used to maintain a constant sample temperature and prevent losses from volatilization due to heat.

Table 3.2 Summary of ultrasonic treatment experimental materials

Solid Substrate		Contaminants		Fluid Medium	
Soil	Volume	Mass [a]	Crude Oil [b]	Salt [c]	DI Water (total added)
Sand	30 ml	45.9 g	1 %	0.8 g	100 ml
Clay	30 ml	35.7 g	2 %	0.8 g	100 ml
Muskeg	30 ml	7.7 g	2%	0.8 g	100 ml

[a] Mass equivalent of 30 ml of soil.

[b] Concentration of crude oil given as volume of oil per volume of soil.

[c] For "salt added" treatment only.

3.2.2 Ultrasonic Treatment

Sonic treatment was carried out by placing the ½ inch diameter titanium sonic probe 2.5 cm into the center of the sample. The sonic probe was operated by a 20 kHz Misonix Sonicator 3000 generator set at maximum power (500-600 W output). According to Mason (1990b), the power intensity generated at the tip of the probe is equal to the electrical power of the probe divided by the surface area of the transducer tip. In this case, the power intensity of the probe used in the experiment was approximately 60 W/cm^2. The sonic treatment time was set on the digital display for the corresponding time interval. Figure 3.2 below illustrates the probe setup for each sample treatment.

Figure 3.2 Sonic probe and sample setup

3.2.3 Filtration

In order to accurately test the final concentration of TPH, it was necessary to separate and remove the water from the treated soil. After sonic treatment, the sample was removed and poured into a VWR glass filtration system that included a 250 ml glass container, a fritted glass filter, filter clamp, and a 1000 ml erlenmeyer flask. A Fisher GF/A 1.6 μm retention glass microfibre filter paper was placed between the top container and fritted glass filter and held in place with the filter clamp. The sample residue was rinsed from the beaker into the filter top with another 30 ml of DI water. Filtration was completed by vacuum filtration. Vacuum was applied by attaching the erlenmeyer to the faucet with nalgene tubing. The faucet was turned on to medium flow to start the vacuum. Figure 3.3 illustrates the apparatus setup for the filtration procedure. Once filtration was complete, the sample was transferred to a 120-ml soil jar and allowed to dry overnight.

Figure 3.3 Sample filtration apparatus setup

3.2.4 Supplemental Salinity Experiments with Sand

To elaborate upon the results generated for "no salt" and "salt added" treatments, a more extensive approach was used to explore the effect of salt concentrations on the removal of TPH. For the experiment, crude oil spiked sand from the previous experiment was used. A sample of sand (45.9 g) was measured out into a beaker. Five concentrations of sodium chloride (0, 0.02 M, 0.03 M, 0.07 M, and 0.14 M) were used to compare the effect of increasing salt on the TPH removal. The salt was measured out and dissolved in 50 ml of deionized water. Using the same methods as the previous experiment, the sample was treated with ultrasonic waves for 2 minutes and then the water was filtered using vacuum filtration. Sub-samples were collected of the treated sand for analysis of TPH concentrations.

3.3 Ultrasonic Enhanced Soil Washing Experimental Design

3.3.1 Factorial Experiment Design

Factorial experiments are designed and used in order to reduce the huge number of experiment runs and study the interactions between different factors. Four important variables including initial concentration of contaminants of petroleum hydrocarbons, salinity, ultrasonic treatment time and soil flushing rate are chosen to be the investigated factors in the experiments.

3.3.1.1 Initial Concentration of Petroleum Hydrocarbon Contaminant

The variation of the initial concentration of petroleum hydrocarbons would affect the mixture status of soil, water and oil, and may then directly affect the treatment efficiency. The change of this variable during the experiments can help understand the mechanisms of the treatment process.

3.3.1.2 Soil Salinity

According to Feng and Aldrich (2000), the removal of hydrocarbons increased to an optimal point as salinity was increased (0.4 Molarity) after which increasing salinity reduced the removal efficiency (Feng and Aldrich 2000). Thus different levels of soil salinity were used in the experiments, including 0 M (no salt), 0.4M, and 0.8M.

3.3.1.3 Ultrasonic Treatment Time

In previous researches, the maximum contaminant reduction was observed within a very short ultrasonic treatment time (5 minutes) after experiment began, indicating that the duration of ultrasonic treatment will not have a significant effect on contaminant reduction (Feng and Aldrich 2000). However, after soil washing enhancement was added to the ultrasonic treatment system, the ability of oil desorption and the oil dilution capacity of water might be increased which means the duration of ultrasonic treatment might be longer. In this project, three levels of ultrasonic treatment time will be selected (1min, 5min, 10min) to study the effect of ultrasonic treatment time on the entire soil washing system.

3.3.1.4 Soil Washing Flow Rate

Results of former studies have shown that ultrasound-enhanced soil washing treatment method can greatly improve the pollutant reduction rate. Meanwhile the soil washing can solve the problem of contaminant re-sorption and hence increase the treatment efficiency. However, according to Kim and Wang (2003), the contaminant removal decreased with increasing soil washing flow rate since for fast washing, the percolating water has less time to interact with the soil/contaminant system while the breakdown of the soil/contaminant bond is a time-dependent process. In this project, three different flow rates were selected in the experiments including 0 cm^3/s, 0.7 cm^3/s, and 1.3 cm^3/s.

3.3.1.5 Factorial Experiment Table

Table 3.3 presents the results of factorial experiment design. There were 9 experimental runs and each run was replicated for 3 times to reduce the possibility of error and to achieve reasonable statistical results. After all the experiments, statistical analyses were conducted to examine the validity of the experiments.

Table 3.3 Factorial experiment design

| Experimental Runs | Factors | | | |
	PHC Concentration	Salinity (Molarities)	Ultrasonic Treatment Time (min)	Soil Washing Velocity (cm^3/s)
1	0.5 % Crude	0	1	0
2	0.5 % Crude	0.4	5	0.7
3	0.5 % Crude	0.8	10	1.3
4	1.0 % Crude	0	5	1.3
5	1.0 % Crude	0.4	10	0 c
6	1.0 % Crude	0.8	1	0.7 c
7	2.0 % Crude	0	10	0.7 c
8	2.0 % Crude	0.4	1	1.3 c
9	2.0 % Crude	0.8	5	0

3.3.2 Ultrasonic Enhanced Soil Washing Treatment Process

Figure 3.4 illustrates the entire process of ultrasonic enhanced soil washing treatment. After the treatment, there are several other procedures including sample extractions and TPH GC-FID analysis which will be described later.

```
┌─────────────────┐
│      Soil       │
└─────────────────┘
         │
         ▼
┌─────────────────────┐
│ Sample Preparation  │
└─────────────────────┘
         │
         ▼
┌──────────────────────────────────────────────┐
│  Ultrasonic Enhanced Soil Washing Treatment   │
└──────────────────────────────────────────────┘
```

Liquid Phase (effluent): water contaminated by oil and salt

Solid Phase (residual "clean" soil): soil contaminated by oil and salt

Separation Funnel Extraction

Shaking Extraction

Silica Gel Column Cleanup

Chemical Analysis: GC/FID

Data Processing
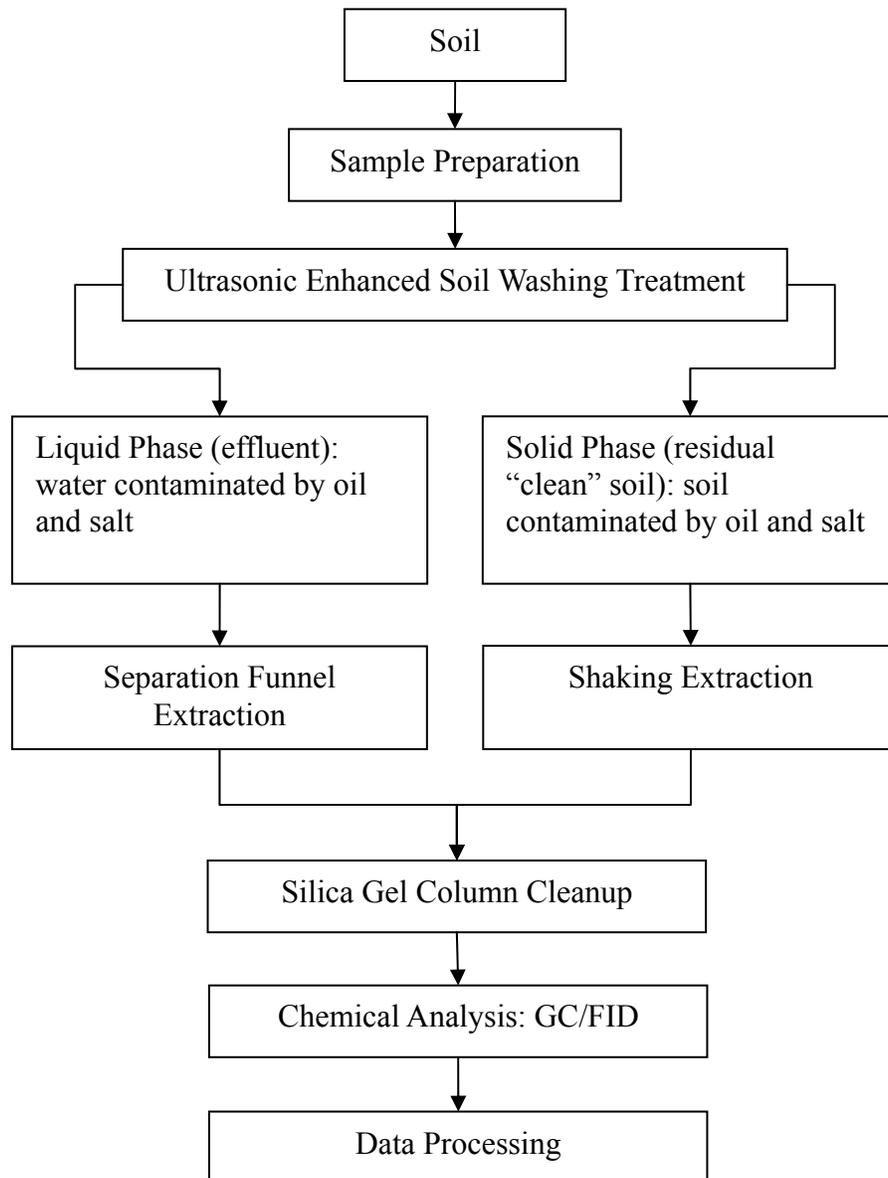
Figure 3.4 Flow chart of ultrasonic enhanced soil washing treatment process

3.3.3 Reactor Design

The ultrasonic enhanced soil washing combined two soil remediation methods in order to increase the PHC removal efficiency. Since soil washing technique can greatly increase the contaminant transportation and reduce the impact of salinity, the experimental results are expected to be better than those from using ultrasonic treatment alone.

The reactor used in the experiments was designed for both soil washing treatment and ultrasonic treatment. The ultrasonic enhanced soil washing treatment system consisted of two parts – a one dimensional soil washing chamber and an ultrasonic processor.
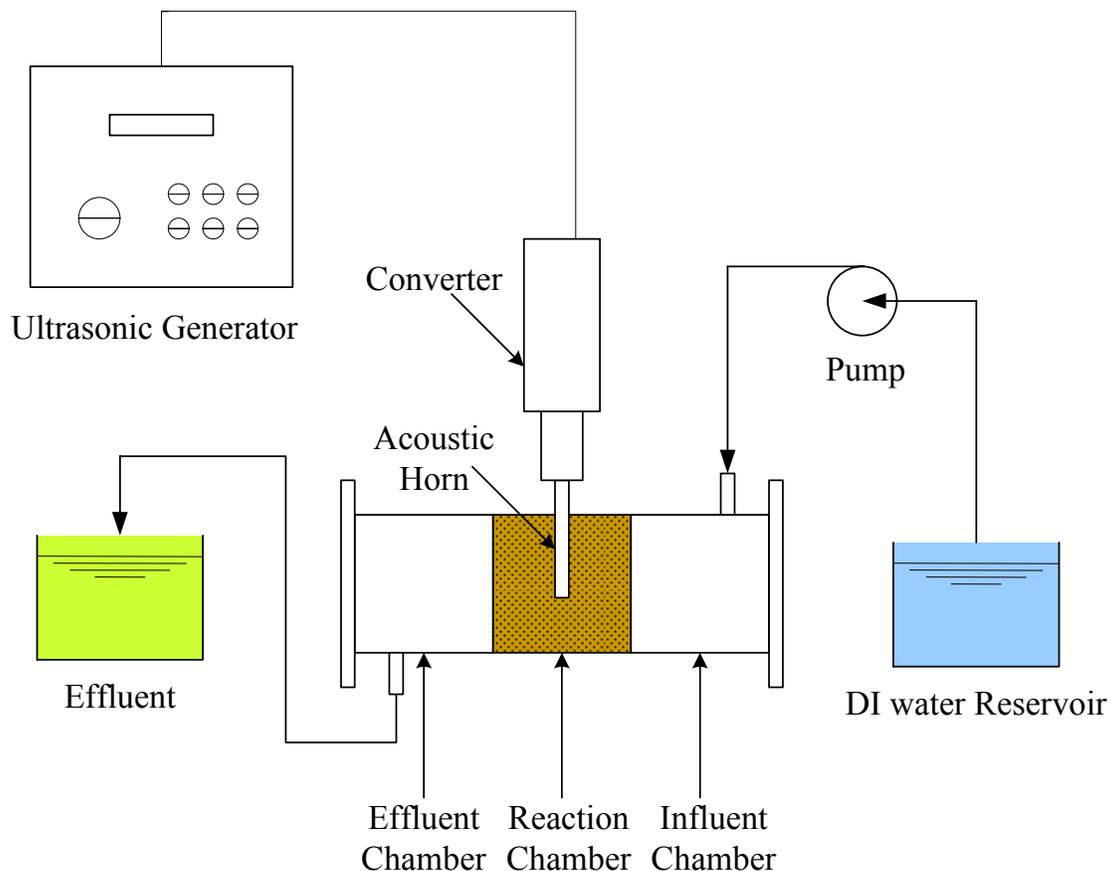
Figure 3.5 Ultrasonic enhanced soil washing treatment reactor design

The soil washing treatment chamber was made of a Plexiglas cylinder with an inside diameter of 5.0 cm and a total length of 20 cm. Figure 3.5 shows the design of the soil washing reactor. The

influent chamber was 10.0 cm long and it was connected to a reservoir of deionized water which was pumped into the reactor to flush the PHC contaminants out of the soil samples in the reaction chamber. The continuous flow pump used in the experiments was Simon Manostat Varistaltic Pump (Model No. 72-310-000) which can run from 24 to 720 rpm. The tubing used in the experiments was silicone lab tubing (4.8 mm inside diameter, Model 96400-25, Masterflex®, Cole-Parmer Instrument Co.) and it was connected to the apparatus using polyethylene-quick disconnects (Scienceware Co.). The reaction chamber was 5.0 cm long and it was the place where the soil washing treatment takes place. There is a hole with a diameter of ½ inch on the top of the reaction chamber where the ultrasonic probe was inserted for ultrasonic treatment. Between the reaction chamber and the other two chambers, woven wire mesh (stainless 120 mesh) were fitted to prevent soil loss during the flushing treatment. After certain time of treatment, the effluent with contaminants flew out of the effluent chamber which was connected to a beaker.

The ultrasonic processor used in the experiments was still the Misonix Sonicator 3000 which was composed of three components: a generator, a converter and a standard acoustic horn. The generator converted the conventional 50/60 Hz alternating current at 110 V to a 20 kHz electrical energy. The high-frequency electrical energy was fed to the converter to transform the energy to mechanical vibration. The vibration of the acoustic horn was then set at 20 kHz. The generator was set at maximum power (500-600 W output). The titanium acoustic horn was inserted with 3.75 cm into the reaction chamber from the hole and placed in the center of the soil samples. Since half of the reaction chamber was filled with soil samples, the area of the transducer tip would be approximately 5 cm^2. Thus the power intensity of the probe in the experiment was approximately 120 W/cm^2.

3.3.4 Treatment Procedure

The mixture of soil, crude oil and salt (sodium chloride) was carefully placed in the reaction chamber of the reactor. Sonic treatment was carried out by placing the ½-inch-diameter titanium sonic probe with 3.75 cm into the center of the soil specimen. The soil specimen was then saturated with DI water pumped from the DI water reservoir. Once the water level was maintained 1 cm higher than the soil specimen, the soil specimen was applied with the ultrasonic waves at 20 kHz frequency; at the same time the DI water was pumped into the reactor at a certain flow rate for soil

washing. The DI water flew from the influent chamber through the soil specimen, and then carried the contaminants from the soil specimen and eventually flew out of the effluent chamber. The effluent was collected with a beaker.

After a time period of T_{ul}, the ultrasonic treatment was stopped while the soil washing was still kept running for a certain time of T_{sw} to move all the "dirty" water into the beaker. The soil washing treatment was then followed by extractions of PHCs from the "clean" soil specimen and the effluent. The soils samples with residual crude oil were taken out of the reactor chamber and sent for soil phase extraction. The effluent collected from the outlet was extracted by using liquid-liquid extraction. Figure 3.6 shows the setup of the ultrasonic enhanced soil washing treatment.

Figure 3.6 Ultrasonic enhanced soil washing treatment system

3.4 Sample Extractions

3.4.1 Soil Extraction

Soil was sampled to investigate the reduction of TPH concentration. Before sending for GC analysis of TPH, soil extraction needs to be conducted. In this project, the soil extraction was completed using mechanical shaking method. The standard method for soil extraction is the Soxhlet method (EPA 1996, CCME 2001). However, literature shows that mechanical shaking extraction is comparable in accuracy to the Soxhlet method (Schwab et al. 1999, Siddique et al. 2006). The advantage of using mechanical shaking extraction is the ability to complete more samples at once while using less solvent.

The extraction was completed by collecting a subsample (2 g from sand, 3 g from clay, 1 g from muskeg) of each treated soil and transferring the subsample into a 40 ml glass vial. Two subsamples, or repeated measurements, were collected from each treated soil and the results were averaged to ensure the result was representative. Different masses were used between soils types to account for the different bulk densities and to improve the accuracy of subsampling. A volume of 10 ml of 1:1 hexane/acetone (CCME 2001) was added to each subsample and samples were placed in a tray on a New Brunswick Scientific C2 platform shaker at 250 rpm for 30 min. Once shaking was complete, the samples were allowed to settle and the solvent was transferred into another set of 40 ml vials with a disposable glass pipette. Another 10 ml of solvent was added to the samples and the extraction procedure was completed two more times. Following extraction, a total of 30 ml of solvent containing the extracted sample in solution was obtained. Figure 3.7 shows the how the mechanical shaking extraction works.

Figure 3.7 Mechanical shaking for soil extraction

3.4.2 Liquid-Liquid Extraction

The organic compounds existing in the effluents were extracted from water by transferring 40 ml of sample from the graduated cylinder to the separatory funnel. 10 ml of dichloromethane was then added into the separatory funnel which was sealed and shaken vigorously for 1-2 minutes with periodic venting to release excess pressure. Once shaking was completed, the organic-phase layer and water-phase layer were separated for a minimum of 10 minutes. Then the solvent extract was collected in a set of 40 ml vials with a disposable glass pipette. This extraction procedure was repeated two more times using fresh portions of solvent. The 30 ml solvent extracts were then combined in the 40 ml vials. Figure 3.8 shows the how the separatory funnel liquid – liquid extraction works.

Figure 3.8 Separatory funnel liquid – liquid extraction

3.4.3 Silica Gel Column Cleanup

The procedures for sample preparation were followed by silica gel column cleanup which included apparatus and solvents recommended by the CCME "Tier 1 Reference Method for the Canada-wide Standard of Petroleum Hydrocarbons in Soil" (CCME 2001). Extracted samples were prepared for analysis by completing a column cleanup procedure to remove moisture, particulate, and unwanted polar organic compounds. Column cleanup is a common laboratory method for improving the accuracy of analytical results by extraction (CCME 2001). Prior to completing the column, the extraction volume was reduced to approximately 2-5 ml using a Yamato RE400 rotary evaporator with the bath temperature set at 60°C. The hexane/acetone solvent was evaporated off and collected in another vessel while the extracted sample remained in the reduced volume. Pre-column evaporation to concentrate the extract is recommended by CCME (2001) to lower the

volume of acetone which can interfere with the ability of the silica gel to filter out polar organic compounds.

Figure 3.9 Silica gel cleanup of PHCs in soil

The cleanup column consisted of a 30-cm-long and 16-mm-diameter glass column plugged with glass wool (CCME 2001). For extracts from soil, approximately 6.5 cm of 70-230 mesh silica gel (Fischer S286-1 activated at 110°C for >12 hours) was placed at the column bottom followed by approximately 2.5 cm of anhydrous sodium sulfate (S415-212 dried at 400°C for 4 hours) (Hughes 2005); for extracts from liquid, approximately 4.0 cm of 70-230 mesh silica gel was placed at the bottom of the column followed by approximately 5.0 cm of anhydrous sodium sulfate. Column packing was wet using 15 ml of 1:1 hexane/DCM. The sample was carefully poured into the top of the column and then followed by another 20 ml of hexane/DCM to carry the sample through the column. The sample vial was rinsed and added to the column. The cleaned extract volume was

again reduced using the rotary evaporator to <2 ml and transferred to a 2 ml GC vial. The sample was brought to 2.0 ml with toluene. Figure 3.9 shows the operation for Silica Gel Cleanup procedure.

3.5 Hydrocarbon Analysis Using Gas Chromatograph

Samples were submitted to the Central Equipment Laboratory at UNBC for analysis of semivolatile TPH using a Varian CP-3800 Gas Chromatograph with flame ionization detector (GC-FID). A ZB-5 capillary column (Phenomenex Torrance, CA) with 15 m x 0.25 mm ID and 0.25 μm film thickness was used for the separation of the TPH extracts. Typically, 1 μL of TPH extract was injected into the GC system using a Varian CP-8400 auto-sampler. Splitless injection mode was performed on the 1079 PTV injector and after 0.7 min the split mode was activated at split ratio of 10:1. Both the injector and the detector (FID) temperatures were kept at 320°C during the analysis. The capillary column temperature was initially held at 50°C for 2 min, then ramped at 15.0°C/ min to 110°C and further increased at 10.0°C/ min to 300°C and held at 300°C for 10 min. The total run time was 35 min for each sample. The carrier gas (helium) was maintained at a constant flow rate of 1.5 mL/ min for the entire analysis and no pressure pulse was used for the injection.

For analysis of the samples from the ultrasonic treatment experiments, n-hexadecane (n-C16) at a known concentration of 1,000 ppm was used as the external standard for the calibration of the instruments and to determine the response factor for TPH. The 1,000-ppm n-C16 standard solution was used for each analysis batch for the duration of the project. The standard deviation of the response factor for the standard solution was approximately 14% and is within the range of the allowed experimental error for the method. The concentration of each TPH sample was calculated by summing up all the peak areas of the GC profile between C10 and C50 and then converted to a concentration in mg/kg (ppm) by using the response factor and bulk density of the n-C16 standard solution. The start retention time for integration at C10 was 3.40 minutes and the end time for C50 occurred at approximately 33 minutes and this marked the peak ranges for TPH.

For the analysis of samples from ultrasonic enhanced soil washing experiments, petroleum hydrocarbons were quantified by determining concentrations of CCME PHC fractions (CCME

2001). Seven straight-chain n-alkanes were used as analytical standards: decane (nC10), hexadecane (nC16), nonadecane (nC19), eicosane (nC20), tricosane (nC23), dotriacontane (nC32) and tetratriacontane (nC34). The nC19 and nC32 compounds are not required under the CCME; they were included to allow for possible comparisons with the British Columbia soil PHC standards. Five different concentrations (i.e. 10, 20, 50, 100 and 500 ppm or µg per mL) of the mixed standards were prepared in toluene. An average response factor was calculated using the response factors of the individual compounds (CCME 2001). Peak retention times were used to mark the beginning and end of the F2, F3, and F4 fractions; the chromatograms were integrated within the four fractions and the average response factor was used to determine the concentrations (CCME 2001). Figure 3.10 shows the setup for GC-FID TPH analysis procedure.

Figure 3.10 GC-FID analysis; left: analysis vials; right: GC-FID analyzer.

3.6 Quality Assurance and Quality Control (QA/QC)

To monitor the accuracy of the results, several tests were completed on different procedures and materials to ensure methods were operating as intended. All procedures were completed carefully with clean equipment. The decontamination of glassware and other materials was completed by washing with surfactant, Alconox, and hot water in approximately a 1% solution followed by a deionized water rinse. Other glassware cleaning methods were tested including a solvent/alcohol rinse, and a strong oxidizing acid bath (sodium dichromate in sulfuric acid). It was determined that with the level of analytical sensitivity associated with the GC, the Alconox washing method was sufficient to remove residuals to <5 mg/kg. Materials used in the experiment including sand, filter

papers, silica gel, sodium sulfate, toluene, hexane, acetone, and a magnetic stir bar were tested for extractable concentrations of TPH. None of the materials contained TPH concentrations greater than 3 mg/kg.

During the experiments, duplicates and blanks were analyzed to test accuracy and monitor cross contamination between samples. A repeated measurement or duplicate was conducted for every treated soil sample. Each pair of measurements was compared to test the homogeneity of the treated sample. The results of the two repeated measurements were averaged for each pair, and the average of the repeated measurements was reported in the results. Three replicates of treatments were completed to measure the accuracy of laboratory methods and the reproducibility of the experiment. The TPH concentrations of the three replicates were compared for systematic error using the average, standard deviation, and percent variation. The statistical results were used to compare against quality control standards used by the CCME laboratory methods.

According to the CCME Tier 1 laboratory procedures, the method detection limits (MDL) of semivolatile analysis for total petroleum hydrocarbon is 200 mg/kg (CCME 2001). The data quality objectives used by the CCME state that repeated analyses that contain concentrations greater than 10 times the MDL must have a % SD of less than 30% (CCME 2001). For the purposes of this project, a conservative MDL of 100 mg/kg was used for the analytical procedures. A value of 30% variability was used as an acceptable range of quality for analytical results greater than 10 times the MDL (1,000 mg/kg).

Three replicates were completed for each combination of variables. After every replication, a method blank (using uncontaminated sand sample) was run through the treatment system and then the sample was analyzed. This was completed to measure the contamination of samples by residual hydrocarbons on the experiment apparatus. Furthermore, a lab blank was analyzed for each replication and consisted of a blank GC vial of solvent to test for contamination from the analytical apparatus (GC-FID).

3.7 Reporting of Results and Statistical Analysis

Analytical results obtained from the GC-FID were tabulated. The reduction of TPH

concentrations were calculated by subtracting the final concentration from the initial concentration reported in percent reduced from initial. Graphical presentation of the data was completed using Microsoft Excel. The data was presented using a bar graph with the two salt classes presented as bars side by side for comparison.

Statistical analysis of the experimental results was completed using a univariate analysis of variance (ANOVA) test. The test was preformed with SPSS statistical software (SPSS 15.01.1 for Windows). The percent TPH reduction data was entered for the entire project as the dependent variable with salinity, and treatment time as the fixed factors. Preliminary histograms of the data identified that the data was skewed and thus a square root transformation was completed to normalize the data. A plot of the probabilities of residuals used to assess the distribution of the data indicated that the data was close to normal. The P-P plot of probabilities is presented in Figure 3.11. The results of the ANOVA test were used to determine whether the differences observed in TPH concentrations were significant with respect to the factors.
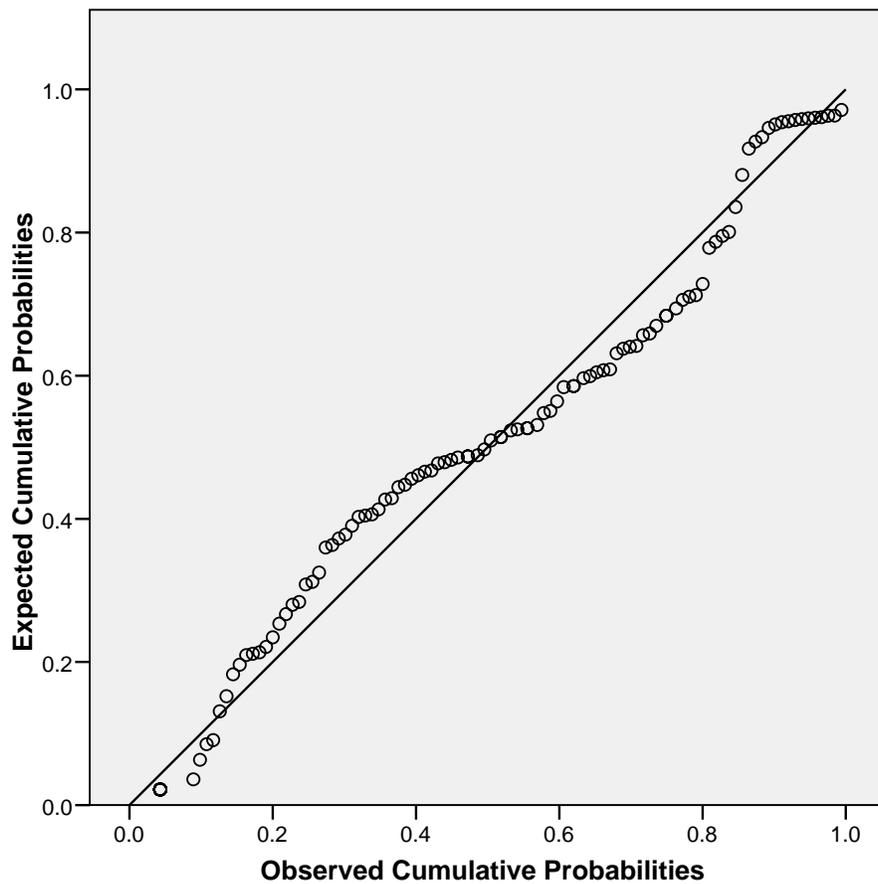
Figure 3.11 Normal P-P probability plot

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University of Northern British Columbia
Prince George, British Columbia

4. RESULTS AND ANALYSIS

4.1 Soil Physical and Chemical Properties

The results of soil characterization completed at the BC MOF laboratory in Victoria, British Columbia are summarized in Tables 4.1 and 4.2. The ESP and SAR values were calculated from the exchangeable cation concentrations and the CEC values. According to the BC MOF lab results, the organic content of the muskeg soil was too high to complete soil texture analysis. The pH of the muskeg was acidic, typical of organic soils due to the presence of organic acids. The carbon content of the muskeg accounted for nearly 50% of the sample and was approximately 37 times greater than the organic carbon content of the clay soil. The carbon content in the muskeg was similar to results obtained for an organic peat soil used in sorption experiments by Salloum (2001).

Table 4.1 Selected properties of batch soil samples

Sample Name	Texture			pH	Conductivity (ds/m)	Total Carbon (%)	Total Nitrogen (%)
	Sand	**Silt**	**Clay**				
Sand	100.0	0.0	0.0	6.91	1.2	0.06	0.002
Clay	22.2	35.7	42.1	7.38	26.2	1.29	0.079
Muskeg	n/a[a]	n/a[a]	n/a[a]	3.69	9.9	48.06	0.981

[a] Soil texture could not be completed on muskeg due to high organic content.

The EC of the clay soil was approximately 7 times greater than the conductivity of normal soil (0 to 4 dS/m) and nearly 3 times greater than the conductivity of the muskeg soil (Brady and Weil 1996). As expected, the CEC of the muskeg soil was approximately 2.5 times higher than the clay soil and approximately 600 times higher than the sand. The sodium related measurements of ESP and SAR were within normal limits (0-15 and 0-13, respectively) for all soils due to the low relative concentrations of exchangeable sodium compared with the CEC or concentrations of exchangeable calcium and magnesium (Brady and Weil 1996). The EC of clay soil was higher than expected for an unimpacted soil and may be an indication of some pre-existing salt contamination. Since the ESP and SAR for the clay soil were within normal limits, it was anticipated that the physical properties

of the clay would remain as a valuable component of the experiment for comparison to sand and muskeg.

Table 4.2 Additional properties of batch soil samples

Sample Name	Exchangeable Cations (cmol/kg)					CEC (cmol/kg)	ESP	SAR
	Al^{3+}	Ca^{2+}	Mg^{2+}	K^+	Na^+			
Sand	0.007	0.04	0.021	0.002	0.007	0.08	8.4	2.6
Clay	0.025	15.43	2.552	0.379	0.166	18.55	0.9	3.9
Muskeg	1.386	28.89	16.563	0.784	0.482	49.49	1.0	7.1

The soil physical properties were obtained from the physisorb analysis. The soil with the highest measured surface area and total pore volume was the clay soil (Table 4.3). According to the soil texture analysis, the clay soil contained a larger proportion of fine grained soil compared to the sand. The particle surface area measured for the muskeg soil was lower than expected and likely contains a larger proportion of coarse organic material still present after soil sieving and preparation techniques. The large particle size of the muskeg soil inferred by the low surface area indicates that the soil contained a lower proportion of humified material and the value of organic carbon is represented largely by coarse organic material and only a small portion of colloidal organic matter. In contrast, the organic carbon value in clay is likely represented by a high proportion of colloidal organic matter created by geological and biological weathering processes.

Table 4.3 Soil grain properties

Sample Name	Average Pore Size ($Å^a$)	Total Pore Volume (mm^3/g)	Surface Area (m^2/g)
Sand	0.9739	0.0092	0.378
Clay	11.23	6.993	24.9
Muskeg	0.5013	0.0335	2.67

[a] Angstrom unit equivalent to 10^{-8}cm

4.2 Soil Adsorption Properties

Adsorption isotherms were generated with the Quantachrome Autosorb-1 analyzer using a multi-point BET method. The method is commonly used for measuring particle properties and was used to compare the three soils. The analysis operates on the principles of physical adsorption and does not account for other sorption processes such as chemisorption or partitioning to the organic fraction of the soils. An adsorption isotherm and desorption isotherm were generated for each soil type and plotted on an overlay isotherm plot (Figure 4.1) of adsorbed nitrogen concentration (cc/g) versus relative pressure (P/P0). The shape of the clay isotherm displayed a type II form of isotherm for macroporous adsorbents with unrestricted monolayer/multilayer adsorption at the surface (Lowell et al. 2004). The inflection point of the curve (approximately 0.02 P/P0 pressure and 4.5 cc/g volume of gas) following the initial rise in adsorption indicates the point where monolayer coverage of sorbate is achieved and multilayer adsorption begins (Lowell et al. 2004). The clay exhibited a larger proportion of physical adsorption compared to the muskeg and sand. The magnitude of physisorption appeared to be correlated to the surface areas measured in Table 4.3. The muskeg and sand isotherms demonstrated nearly linear adsorption of nitrogen. Upon closer inspection, the sand isotherm was slightly convex to the pressure axis indicating the attractive adsorbate-adsorbent interactions were relatively weak (Lowell et al. 2004).

4.3 Ultrasonic Treatment Experimental Results

4.3.1 Initial Experimental Conditions

After the soil spiking procedure was completed, samples of the initial TPH concentrations were analyzed to create a baseline reference of TPH removal during treatments. Analytical results for TPH compared to the initial concentrations were reported as a percent reduction of TPH. The TPH concentrations of the initial soil samples are shown in Table 4.4. Sand spiking corresponded to 1% crude oil by volume and the clay and muskeg were spiked with 2% crude oil. Evidence of contamination was observed in each soil by color, consistency, and hydrocarbon odors.
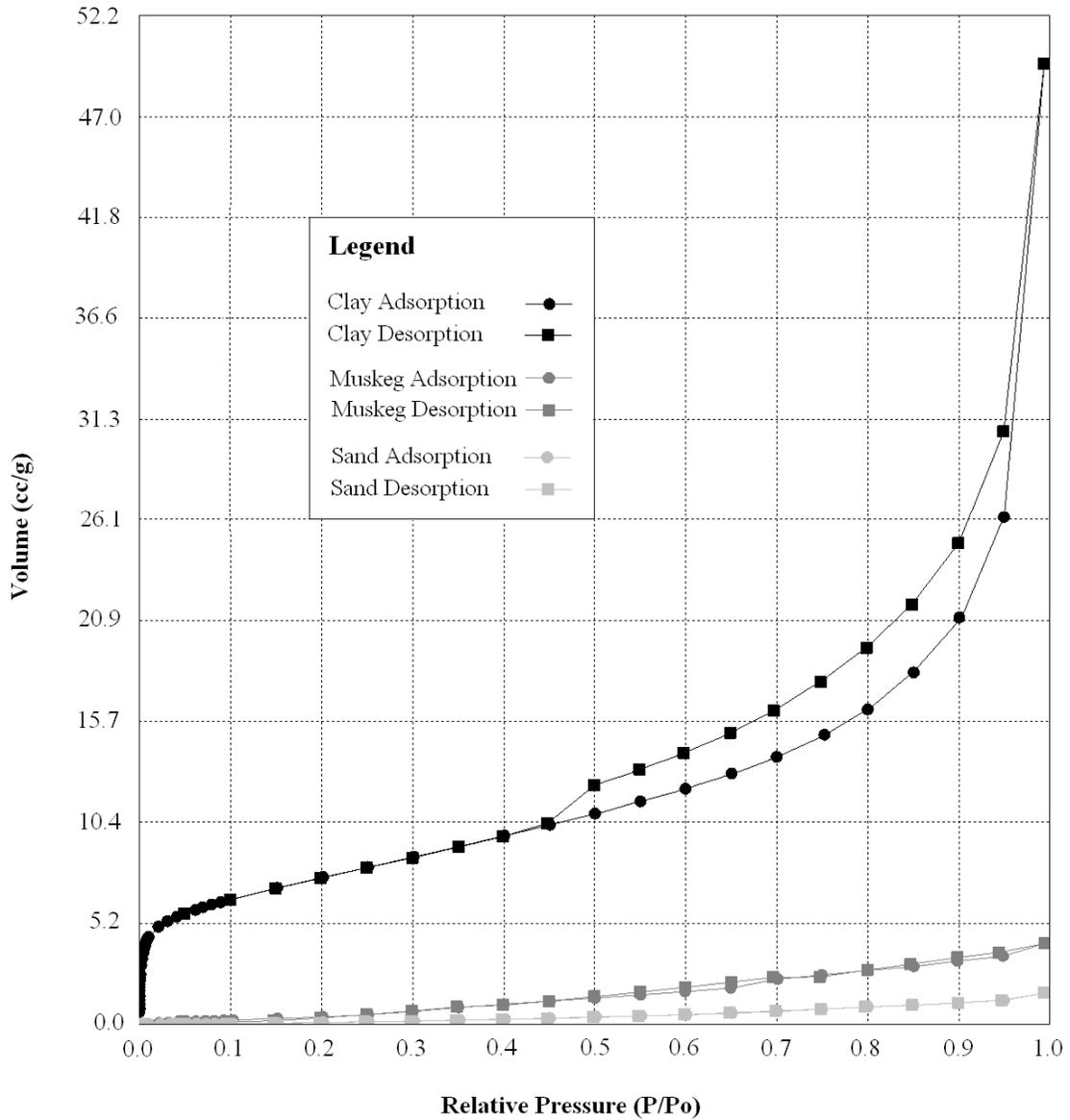
Figure 4.1 Adsorption isotherms for sand, clay, and muskeg

Table 4.4 Initial concentration of spiked soil in ultrasonic treatment

Soil Type	Initial Concentration TPH (mg/kg) Measurement number [a]						Average	Standard Deviation	% SD
	1	**2**	**3**	**4**	**5**	**6**			
Sand	2,853	3,153	4,431	3,299	2,316	2,240	3,049	801.7	26.3
Clay	7,608	7,657	9,651	9,746	7,981	8,734	8,563	967.9	11.3
Muskeg	18,201	18,845	20,427	20,076	25,611	24,308	21,245	3,017	14.2

[a] Six replicates were completed for initial TPH concentration.

The average initial concentration of the three soils ranged from 3,049 mg/kg in sand to 19,356 mg/kg in muskeg. The differences were due to the difference in spiking concentrations (1% crude oil in sand and 2% crude oil in clay and muskeg) and the differences in bulk density. The soils were spiked on a volume basis; however, the samples for extraction were collected by mass. For example, a 1 g subsample of muskeg had a larger volume than a 1 g subsample of sand. Therefore, comparison of concentrations between soil types was completed in terms of the reduction in TPH concentration from the initial concentration and is presented as such in tables and figures throughout this thesis. Initial sample results for all three soils were all greater than 10 times the MDL and contained % SD within the acceptable variation limits.

4.3.2 Experimental Results

After ultrasonic treatments and filtering, soil samples were analyzed for final TPH concentrations. The results of TPH analysis for soil samples are presented in Table 4.5 ("no salt") and Table 4.6 ("salt added"). Three replications were completed for each combination of variables and were compared using basic descriptive statistics. The reduction of TPH from the initial concentration (see Table 4.4) is reported as percent TPH reduction in the tables.

As shown in Table 4.5, the reduction of TPH was most effective in the sandy soil. For all samples treated with ultrasound, approximately 80 to 90% reduction of TPH was observed in sand. While some TPH reduction was observed in the control sample by filtration alone (35%), ultrasonic treatment increased the reduction of TPH in sand by approximately 50% within minutes of

treatment. TPH reduction of approximately 5 to 12% was observed in clay and was notably less than sand. According to the data, the influence of ultrasonic treatment in clay only increased TPH reduction by approximately 5 to 7%. Approximately 30 to 40% TPH reduction was observed in muskeg samples. The effects of sonic in muskeg were evident and observed as a change in TPH reduction from 11.5% in the control to approximately 40% in samples treated by ultrasound. Generally, sonic treatments appeared to increase TPH reduction in all samples when compared to the control (no sonic treatment). The duration of sonic treatment did not appear to have an effect on TPH reduction. The variability among replications was within the 30% SD quality standard.

Table 4.5 TPH results – no salt added

Treatment Time	Final TPH Concentration (mg/kg)			Average	Standard Deviation	% SD	TPH Reduction (%)
	Rep1	Rep2	Rep3				
Sand							
Control	1,741	2,408	1,788	1,979	372.0	18.8	35.1
2 min	452	852	431	578	237.6	n/a[a]	81.0
5 min	492	763	306	520	230.2	n/a[a]	82.9
10 min	341	704	143	396	284.6	n/a[a]	87.0
20 min	355	558	303	405	134.9	n/a[a]	86.7
40 min	366	383	406	385	19.8	n/a[a]	87.4
Clay							
Control	5,918	10,372	8,135	8,142	2,227	27.4	4.9
2 min	7,784	7,583	7,525	7,631	136.1	1.8	10.9
5 min	7,320	7,468	8,935	7,908	892.8	11.3	7.7
10 min	6,601	7,336	7,907	7,281	654.7	9.0	15.0
20 min	6,840	7,669	7,041	7,183	432.3	6.0	16.1
40 min	6,896	7,846	8,317	7,686	724.0	9.4	10.2
Muskeg							
Control	19,193	16,303	20,924	18,807	2,335	12.4	11.5
2 min	16,138	12,506	13,017	13,887	1,966	14.2	34.6
5 min	13,026	12,596	11,006	12,209	1,064	8.7	42.5

Treatment Time	Rep1	Rep2	Rep3	Average	Standard Deviation	% SD	TPH Reduction (%)
10 min	13,515	10,798	15,556	13,289	2,387	18.0	37.4
20 min	13,797	10,431	13,938	12,722	1,985	15.6	40.1
40 min	15,499	9,406	16,311	13,739	3,774	27.4	35.3

[a] Concentration less than 10 times the MDL.

As shown in Table 4.6, the addition of salt appeared to limit the reduction of TPH from the soil samples. Generally, only approximately 20 to 30% TPH reduction was observed in samples when salt was added in solution. A small increase in TPH reduction was observed between the control and sonic treated samples in clay and muskeg. No differences were observed among the control or any treated samples within the sand group.

The variability among results observed as % SD for clay treatments was high and in some cases, close to the acceptable variability (30% SD). Even though the average TPH concentration of the three replications showed a decreasing trend from the control to samples treated by ultrasound, some of the three replication samples treated by ultrasound had measured TPH concentrations greater than the control. In each case the difference was less than 30% and may be explained by analytical and sampling variability.

Table 4.6 TPH results –salt added

Treatment Time	Final TPH Concentration (mg/kg)			Average	Standard Deviation	% SD	TPH Reduction (%)
	Rep1	Rep2	Rep3				
Sand							
Control	3,037	2,076	2,310	2,475	501.2	20.3	18.8
2 min	2,051	2,299	2,450	2,266	201.6	8.9	25.7
5 min	2,380	2,223	2,302	2,302	78.5	3.4	24.5
10 min	2,493	2,473	2,216	2,394	154.6	6.5	21.5
20 min	2,767	2,060	2,105	2,310	395.7	17.1	24.2
40 min	2,787	2,070	2,104	2,320	404.8	17.4	23.9
Clay							
Control	5,431	9,952	7,083	7,489	2,287	30.5	12.5

2 min	6,460	6,132	6,673	6,422	272.1	4.2	25.0
5 min	4,262	7,449	8,343	6,684	2,145	32.1	21.9
10 min	6,626	8,784	5,173	6,861	1,817	26.5	19.9
20 min	6,320	6,873	6,471	6,554	286.0	4.4	23.5
40 min	3,136	6,259	7,262	5,553	2,152	38.8	35.2
Muskeg							
Control	22,935	19,939	19,265	20,713	1,953	9.4	2.5
2 min	22,085	13,277	21,963	19,108	5,050	26.4	10.1
5 min	14,985	13,766	15,750	14,834	1,001	6.7	30.2
10 min	17,602	15,686	16,168	16,485	996.6	6.0	22.4
20 min	14,309	16,781	15,172	15,421	1,255	8.1	27.4
40 min	15,921	13,834	23,179	17,644	4,905	27.8	16.9

Graphical presentation of the TPH reduction results for sand, clay, and muskeg are shown in Figures 4.2, 4.3, and 4.4.
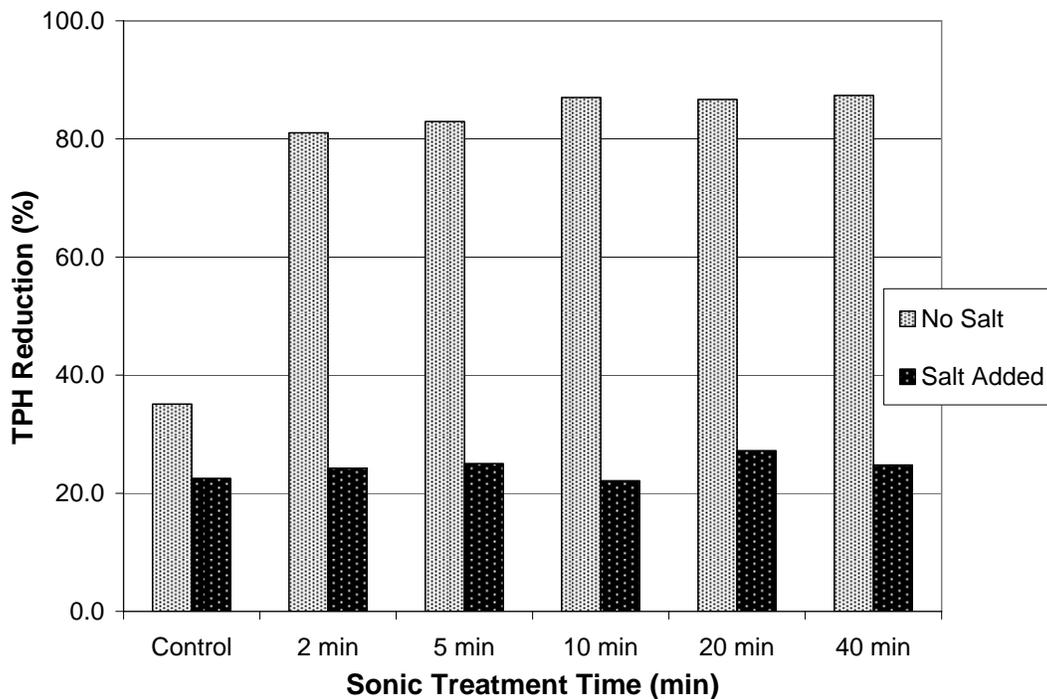
Figure 4.2 Average TPH (%) reduction versus sonic treatment time for sand soil (n=3).
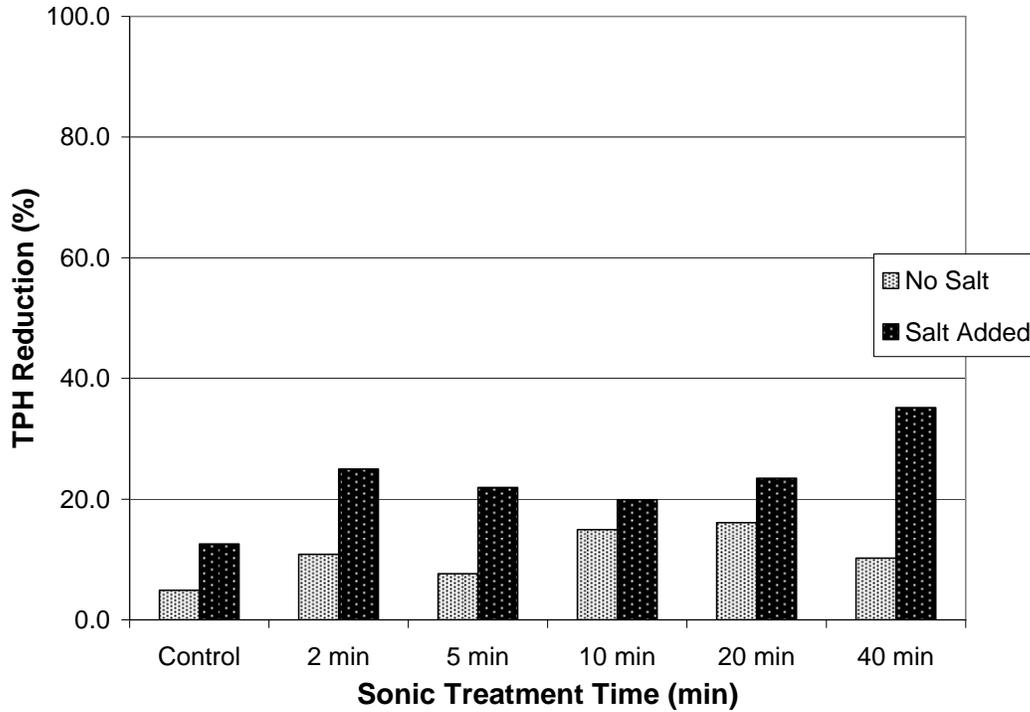
Figure 4.3 Average TPH (%) reduction versus sonic treatment time for clay soil (n=3).
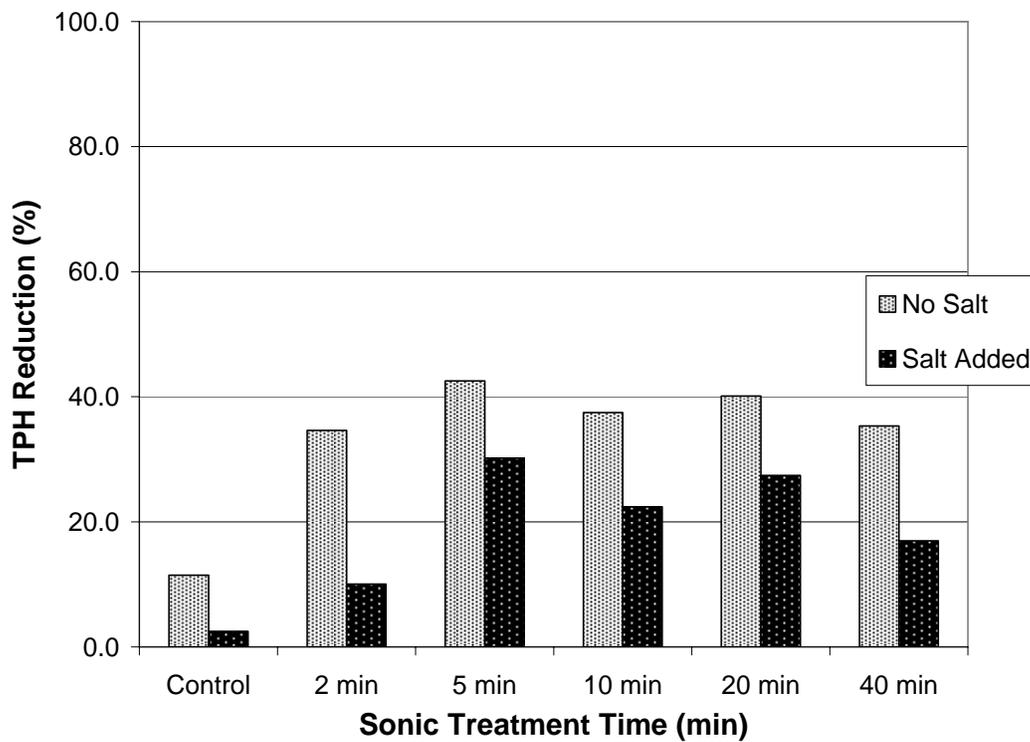
Figure 4.4 Average TPH (%) reduction versus sonic treatment time for muskeg soil (n=3).

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4.3.3 Analytical Results for the Salinity Experiment

In order to further examine the influence of salt concentration on TPH reduction, a supplemental experiment was designed to test a range of salt concentrations on the reduction of TPH in sand. The objective was to examine the trend in TPH reduction observed between the "no salt" and "salt added" treatments shown in Figure 4.2. During the salt experiment, all samples were treated with 2 minutes of sonic waves. Varying amounts of salt (0, 0.1 g, 0.2 g, 0.4 g, and 0.8 g) were dissolved in a total 100 ml of solution and added to the soil prior to treatment. The masses of salt corresponded to concentrations of 0, 0.02 mol/L, 0.03 mol/L, 0.07 mol/L, and 0.14 mol/L. The results are presented in Table 4.7 below.

Table 4.7 Analytical results – salinity experiment in sand

Salt Added (mol/L)	TPH (mg/kg)			Average	Standard Deviation	% SD	TPH Reduction (%)
	Rep1	Rep2	Rep3				
0	365	485	312	387	88.7	n/a[a]	87.3
0.02	1,629	2,189	1,438	1,752	390.6	22.9	42.5
0.03	1,868	2,368	2,312	2,182	273.6	12.5	28.3
0.07	2,194	2,521	1,972	2,229	276.5	12.4	26.8
0.14	2,186	1,975	2,045	2,069	107.6	5.2	32.1

[a] Concentration less than 10 times the MDL.

Results indicated that, even in very small amounts, salt had a large negative influence on the removal of TPH from sand. A decreasing trend of TPH reduction was observed as salt was added to a minimum TPH reduction of 26.8% observed at a concentration of 0.07 mol/L added salt. The results from Table 4.7 are presented in Figure 4.5 below.
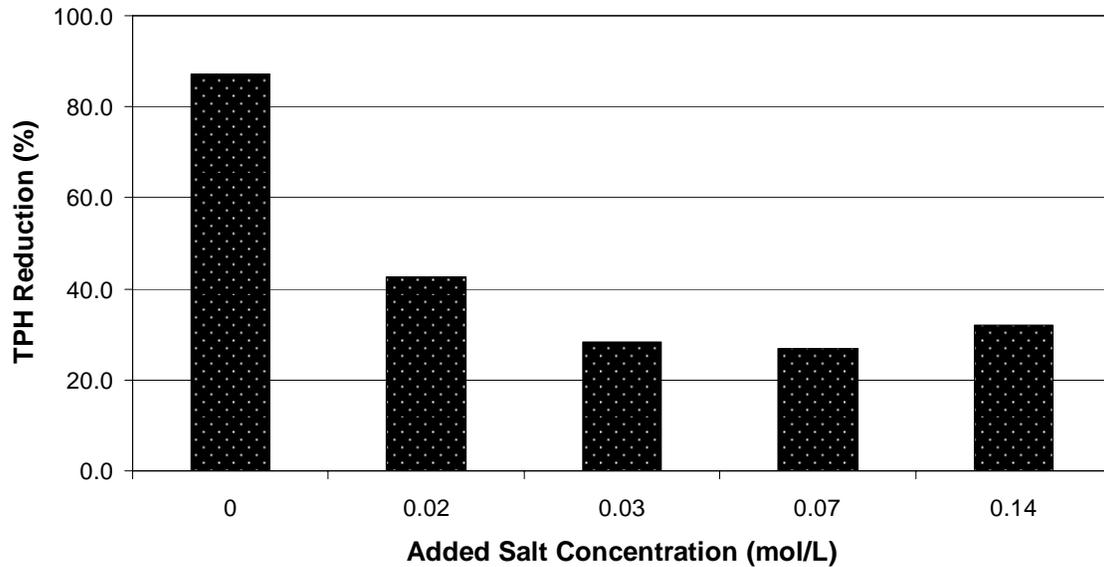
Figure 4.5 Average TPH (%) reduction versus molar concentration of sodium chloride (n=3).

4.3.4 Statistical Results

The % reduction of TPH results presented in Tables 4.5 and 4.6 were analyzed using an ANOVA to provide a statistical comparison of variable levels. Statistical analysis was used to allow confirmation of trends observed within the data. Results of statistical analysis using ANOVA including the interactions between variables are presented in Table 4.8. TPH reduction was selected as the response variable and soil type, salinity, and sonic treatment time were analyzed as the fixed factors. The significance level (alpha) for the analysis was set at 0.05 and P value results from the ANOVA analysis less than 0.05 (i.e., $P \leq 0.05$) were considered statistically significant.

According to the statistical results, the variables of soil type, salinity, and sonic time all have a significant effect on the variation in TPH reduction. The interaction of soil type and salinity also significantly explains the variation in TPH data; however, the interaction between other variable combinations was not significant. The coefficient of determination (R squared) indicates that the differences between the means of the treatment classes account for 68% of the total variation for the general linear model.

Table 4.8 Results of univariate ANOVA

Treatment	Degrees of Freedom	Mean Sum of Squares	F statistic	P value
Soil Type	2	70.329	24.152	<0.001
Salinity	1	66.428	22.813	<0.001
Sonic Time	5	12.359	4.244	0.002
Soil Type * Salinity	2	67.197	23.077	<0.001
Soil Type * Sonic Time	10	2.598	0.892	0.545
Salinity * Sonic Time	5	1.012	0.348	0.882
Soil Type * Salinity * Sonic Time	10	2.042	0.701	0.720

[a] Computed using alpha = 0.05

[b] R Squared = 0.68

The statistical results for the independent comparison between soil type variables are presented in Table 4.9. A closer look at the pair-wise comparisons for soil types indicates that TPH reduction in sand was significantly different from TPH reduction in clay and muskeg. The reduction of TPH in clay compared to muskeg was not statistically significant.

Table 4.9 Pairwise comparisons for soil type

Soil Type		Mean Difference	Standard Error	P value
Sand	Clay	7.51	0.40	<0.001
	Muskeg	3.41	0.40	<0.001
Clay	Sand	-7.51	0.40	<0.001
	Muskeg	-0.80	0.40	.087
Muskeg	Sand	-3.41	0.40	<0.001
	Clay	0.80	0.40	.087

[a] Computed using alpha = 0.05

[b] Adjusted for multiple comparisons using the Bonferroni approach.

The total results for soil type were summarized using a box plot and are presented in Figure 4.6 indicating a large variance of TPH reduction in sand ranging from a high percentage of TPH removal seen in the "no salt" treatments and a low percentage of removal when salt was added. The mean TPH reduction in clay and muskeg were noticeably lower than sand. The smaller variation around the mean in clay and muskeg suggests that there was less influence by the addition of salt on these two soils.
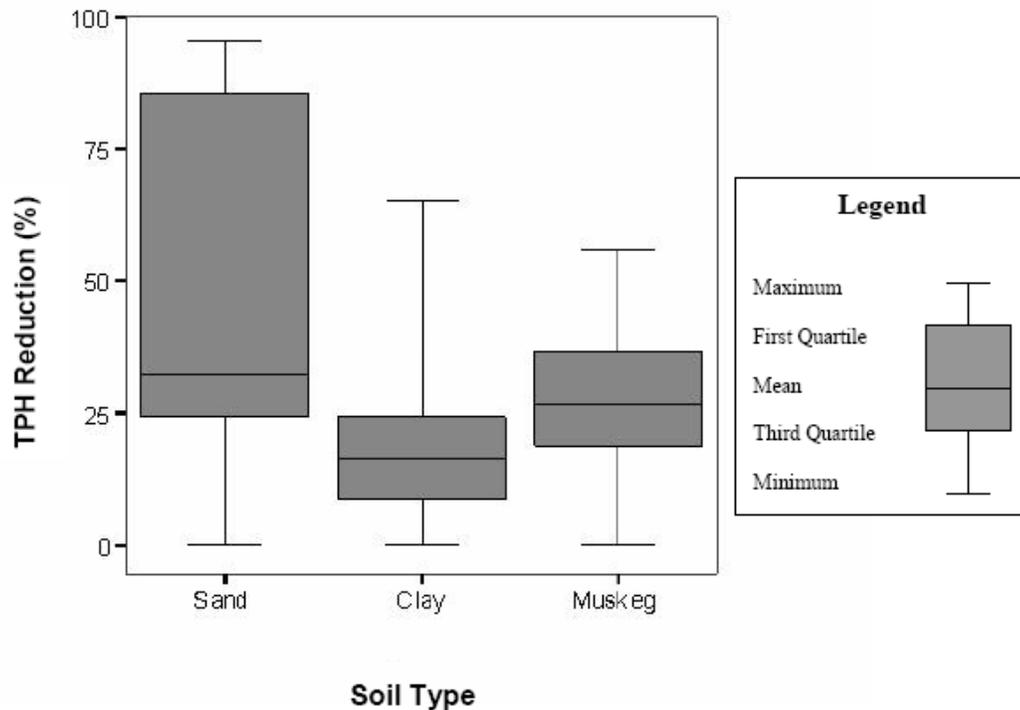
Figure 4.6 Statistical pair-wise comparison of soil type classes sand, clay, and muskeg.

The addition of salt had a significant effect on the TPH reduction. The total results for salinity are presented in Figure 4.7. There was large variation in TPH reduction for the "no salt" treatment range and was likely influenced by the large differences observed in sand. The presence of salt appears to have significantly lowered the reduction of TPH overall. The small variation around the mean for the salt added treatments indicated that the change in TPH reduction was small when salt was present for all soil types and sonic treatment classes including the control.
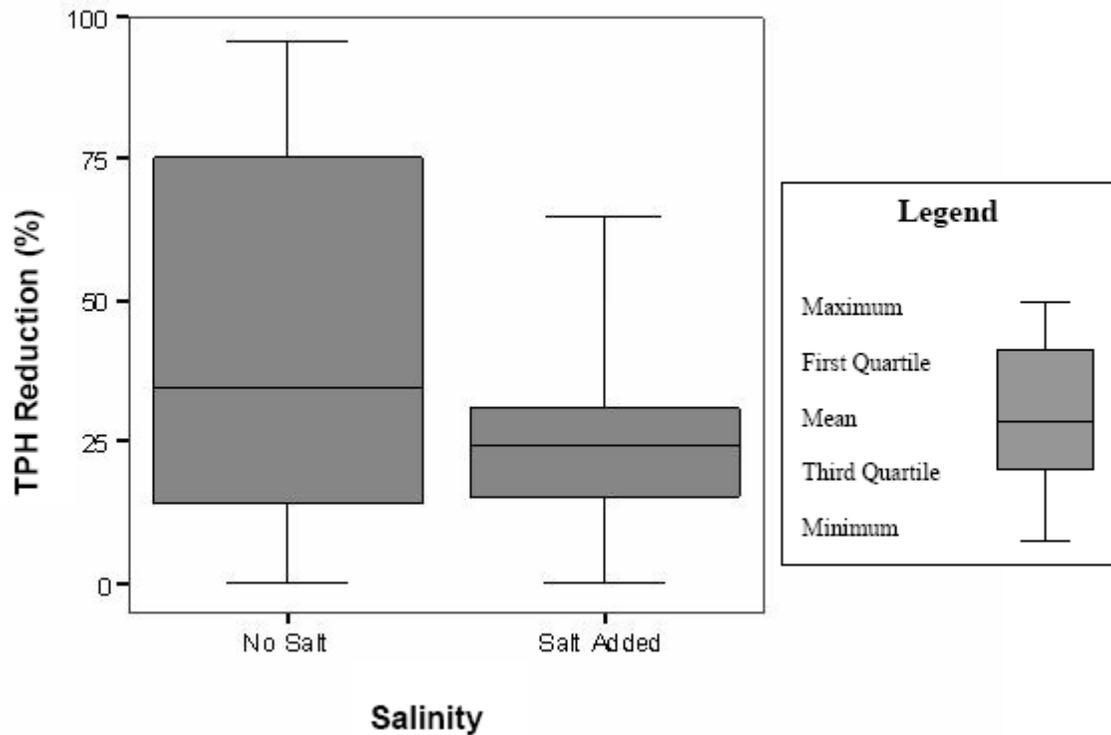
Figure 4.7 Statistical comparison of salinity classes of "no salt" and "salt added"

The results of pair-wise comparisons for the sonic time variable including the control (no sonic treatment) and the five durations of applied sonic waves are presented in Table 4.10. The effect of ultrasonic treatment on TPH reduction was significant shown by comparisons between the control and the sonic treatments for 5 min, 10 min, 20 min, and 40 min treatments. The mean TPH reduction for the control compared to 2 min of ultrasonic treatment (0.08) was only slightly above the set significance level of 0.05 (alpha). There was no significant difference or trend observed between the five duration categories of sonic treatment.

Table 4.10 Pairwise comparisons for sonic treatment times

Sonic Time		Mean Difference	Standard Error	P value
Control	2 min	-2.64	0.57	0.08
	5 min	-4.10	0.57	0.01

	10 min	-3.82	0.57	0.02
	20 min	-5.41	0.57	0.002
	40 min	-3.24	0.57	0.03
2 min	Control	2.64	0.57	0.08
	5 min	-0.16	0.57	1.00
	10 min	-0.11	0.57	1.00
	20 min	-0.49	0.57	1.00
	40 min	-0.03	0.57	1.00
5 min	Control	4.10	0.57	0.01
	2 min	0.16	0.57	1.00
	10 min	0.01	0.57	1.00
	20 min	-0.09	0.57	1.00
	40 min	0.05	0.57	1.00
10 min	Control	3.82	0.57	0.02
	2 min	0.11	0.57	1.00
	5 min	-0.01	0.57	1.00
	20 min	-0.14	0.57	1.00
	40 min	0.02	0.57	1.00
20 min	Control	5.41	0.57	0.002
	2 min	0.49	0.57	1.00
	5 min	0.09	0.57	1.00
	10 min	0.14	0.57	1.00
	40 min	0.28	0.57	1.00
40 min	Control	3.24	0.57	0.03
	2 min	0.03	0.57	1.00
	5 min	-0.05	0.57	1.00
	10 min	-0.02	0.57	1.00
	20 min	-0.28	0.57	1.00

The plot of ultrasonic treatment time (Figure 4.8) results shows significant difference of the control class from other treatment categories by the lower mean and variance. The high maximum

values observed for the 2 min, 5 min, 10 min, 20 min, and 40 min classes are represented by the high TPH reduction achieved in sand samples without salt. The maximum, minimum, and mean values for these sonic classes were reasonably similar and show no distinct trend for sonic treatment time duration on TPH reduction.
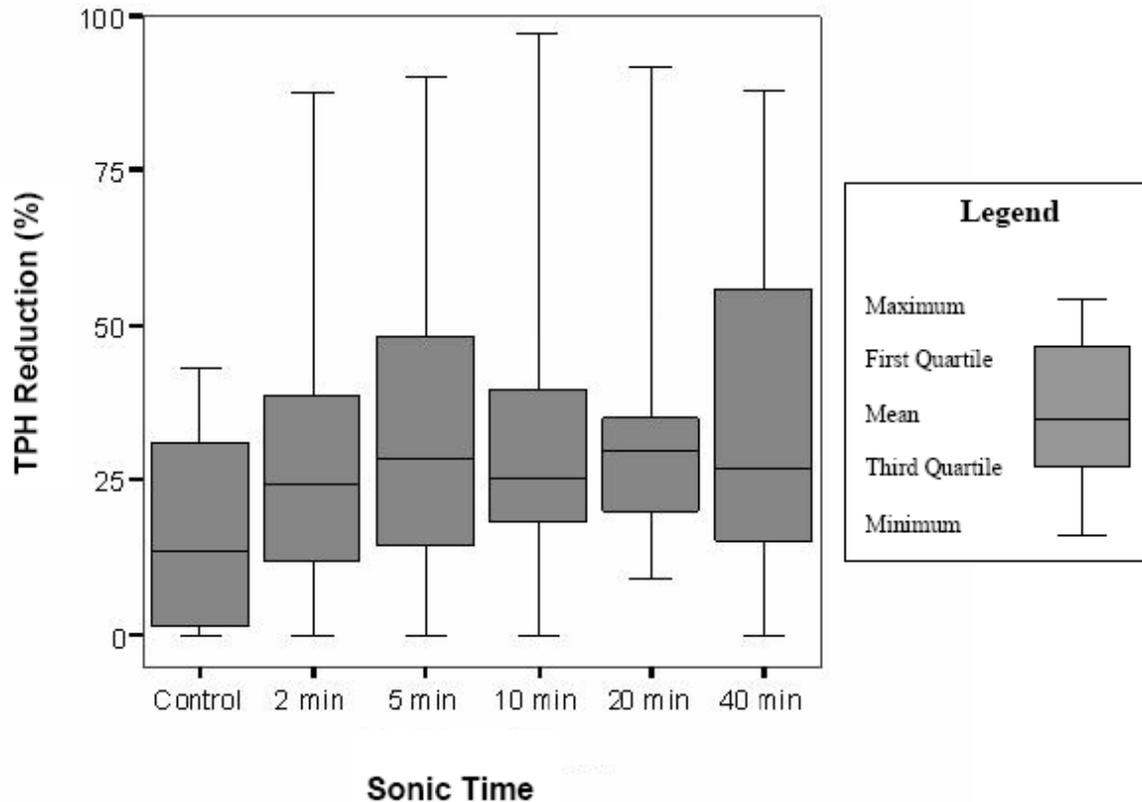
Figure 4.8 Statistical pair-wise comparison of sonic treatment time classes.

4.4 Ultrasonic Enhanced Soil Washing Experimental Results

4.4.1 Initial Experimental Conditions

The soil used in ultrasonic enhanced soil washing experiments was Ottawa sand which was the same with that used in ultrasonic treatment experiments. Pilot studies of experiments using clay and muskeg observed that the permeabilities of both soils were too low for the experiments which proved that they were not suitable for experiments using this reactor.

Contaminant concentration was one of the studying factors in this experiment. Sand was spiked again with three different contaminant concentrations: 0.5 % Crude Oil, 1.0 % Crude Oil and 2.0% Crude Oil. Each group of sand was spiked with three replicates and the fractions (F2 fraction, F3 fraction, and F4 fraction) of total petroleum hydrocarbons and TPH were analyzed. The results were shown in Table 4.11. The average TPH concentration of sand spiked with 0.5 % crude was 5693 ppm; the average TPH concentration of sand spiked with 1.0 % crude was 10,933 ppm and the average TPH concentration of sand spiked with 2.0 % crude was 27,549 ppm. Initial sample results were greater than 10 times the MDL and contained % SD within the acceptable variation limits.

Table 4.11 Initial concentration of spiked soil in ultrasonic enhanced soil washing

Experiment number		0.5 % crude	1.0 % crude	2.0 % crude
F2 fraction (mg/kg)	Rep1	158	15	26
	Rep2	145	21	26
	Rep3	151	19	28
F3 fraction (mg/kg)	Rep1	3,437	6,444	17,487
	Rep2	3,218	5,708	17,812
	Rep3	3,203	5,694	17,263
F4 fraction (mg/kg)	Rep1	2,470	5,216	10,802
	Rep2	2,308	5,179	9,507
	Rep3	1,992	4,504	9,698
TPH (mg/kg)	Rep1	6,064	11,675	28,314
	Rep2	5,670	10,907	27,344
	Rep3	5,345	10,217	26,988
Average (mg/kg)		5,693	10,933	27,549
Standard deviation		294.0	595.5	560.1
% SD		5.2	5.4	2.0

4.4.2 Experimental Results

The calculation of % reduction of PHC is described as follows:

$$\%Reduction = \frac{(C^0 - C^{'})}{C^0} \times 100 \qquad\qquad [4\text{-}1]$$

where C^0 is the initial concentration of TPH in the soil; $C^{'}$ is the final concentration of TPH in the treated soil. The results of the experiments were shown in Table 4.12. The reduction rate of PHC contaminants ranged from 35.8 % to 99.1 %.

4.4.2.1 Mass Balance

Mass losses during the experiments might happen due to volatilization. By summing up the mass of contaminants in the treated soil and effluent and comparing the results with the mass of contaminants in initial soil, the recovery rate of the treatment system were calculated and the validity of the results were verified. The results of calculation of mass balance were shown in Table 4.13. The results indicated that the recovery rate of the treatment was between 91.6 % and 97.4 % which proved that the data was valid and the experiment system was operated with high accuracy.

4.4.2.2 Influence of Initial Contaminant Concentration

From the experimental results shown in Table 4.12, it is seen that there was insignificant effect of the initial contaminant concentration on the treatment efficiency. Since the soil used in ultrasonic enhanced soil washing experiments was sand which had smaller surface area than fines, the binding between soil particle and oil was smaller than that between clay and oil. The weak bond can be easily broken by cavitation from ultrasound and then the desorbed pollutants were flushed out. On the other hand, the initial concentration of TPH in sand was not high enough due to the weak adsorption ability of sand. The resistance was not strong enough and the ultrasonic enhanced soil washing might had removed most of the contaminant in the first 2 or 3 minutes.

4.4.2.3 Influence of Salinity

The effect of salinity in sand was found not significant by examining the experimental data presented in Table 4.12. This observation was different with that from the supplemental salinity experiments for ultrasonic treatment. The transportation of pollutants might have been greatly increased due to soil washing. Thus the salt existing in the contaminated soil can be easily flushed out during the treatment process and lead to decreasing negative effect of salinity on TPH reduction.

This procedure is different from that using ultrasonic treatment in which salinity showed great inhibition effect on TPH reduction. In ultrasonic treatment, salt was kept in the beaker with no salt loss, while in the ultrasonic enhanced soil washing treatment, salt was kept decreasing during the treatment process.

4.4.2.4 Influence of Ultrasonic Treatment Time

The range of ultrasonic treatment time was 1 to 10 minutes. From the results shown in Table 4.12 it can be seen that ultrasonic treatment time had a significant effect on TPH reduction. The largest TPH reduction rate of 99.1 % was observed with a ultrasonic treatment time of 10 minutes.

4.4.2.5 Influence of Soil Washing Flow Rate

It can be easily found out that soil washing flow rate had significant effect on TPH reduction during the experiments (Table 4.12). There was obvious difference between results of experiments with soil washing and without soil washing. Results proved that soil washing had successfully increased the treatment efficiency.

4.4.3 Statistical Results

4.4.3.1 Range Analysis

The results of range analysis were listed in Table 4.14. By comparison of the change range of each studying factor, the significance order was analyzed. As compared to the former analyses of the influences of different factors, the most significant factor was soil washing velocity followed by ultrasonic treatment time and then initial PHC concentration. Salinity was found to be the less significant factor in this experiment. The optimum operation condition for each factor was analyzed as well and it is illustrated more clearly in Figure 4.9.

Table 4.12 Experimental results of ultrasonic enhanced soil washing experiments

Experimental Runs	TPH Concentration	Salinity (Molarities)	Ultrasonic Treatment Time (min)	Soil Washing Velocity (cm³/s)	Final TPH concentration (mg/kg)			Average final TPH concentration (mg/kg)	Standard Deviation	%SD	% Reduction of PHC
					Rep1	Rep2	Rep3				
1	0.5 % Crude	0	1	0	3,873	3,115	3,974	3,654	383.3	10.5	35.8
2	0.5 % Crude	0.4	5	0.7	259	307	270	278	20.5	7.4	95.1
3	0.5 % Crude	0.8	10	1.3	252	195	203	216	25.2	11.7	96.2
4	1.0 % Crude	0	5	1.3	160	115	138	137	18.4	13.4	98.7
5	1.0 % Crude	0.4	10	0	3,129	3,198	2,651	2,992	243.4	8.1	72.6
6	1.0 % Crude	0.8	1	0.7	697	713	648	686	27.7	4.0	93.7
7	2.0 % Crude	0	10	0.7	246	269	266	260	10.0	3.8	99.1
8	2.0 % Crude	0.4	1	1.3	1,982	1,661	1,359	1,667	254.6	15.3	94.0
9	2.0 % Crude	0.8	5	0	8,663	7,235	5,706	7,201	1,207.2	16.8	73.9

Table 4.13 Mass balance calculation of experimental results

Experi-mental Runs	Total Mass of TPH in treated soil (mg)				Standard Deviation	%SD	Total Mass of TPH in effluent (mg)				Standard Deviation	%SD	Total Mass in treated soil and effluent (mg)	Total Mass in initial soil (mg)	% Recovery
	Rep1	Rep2	Rep3	Average			Rep1	Rep2	Rep3	Average					
1	7,745	6,230	7,948	7,308	766.6	10.5	2,659	3,511	4,948	3,706	944.5	25.5	11,014	11,386	96.7
2	517	613	540	557	41.0	7.4	11,003	9,982	10,482	10,489	417.1	4.0	11,046	11,386	97.0
3	503	389	405	432	50.4	11.7	9,796	9,315	12,614	10,575	1455.2	13.8	11,007	11,386	96.7
4	319	229	275	274	36.5	13.3	19,685	27,955	14,941	20,860	5377.5	25.8	21,134	21,866	96.7
5	6,257	6,396	5,301	5,985	486.7	8.1	14,817	14,436	12,869	14,041	843.0	6.0	20,026	21,866	91.6
6	1,394	1,426	1,296	1,372	55.3	4.0	17,291	22,224	19,284	19,600	2026.3	10.3	20,972	21,866	95.9
7	492	537	531	520	20.3	3.9	51,251	49,884	47,059	49,398	1745.5	3.5	49,918	55,097	90.6
8	3,964	3,321	2,717	3,334	509.2	15.3	47,989	51,505	51,557	50,350	1670.0	3.3	53,684	55,097	97.4
9	17,325	14,470	11,412	14,402	1,598.1	16.8	33,813	36,186	40,692	36,897	2852.9	7.7	51,299	55,097	93.1

Table 4.14 Range analysis of the experimental results

Experimental Runs	TPH Concentration	Salinity (Molarities)	Ultrasonic Treatment Time (min)	Soil Washing Velocity (cm³/s)	% Reduction of PHC
1	0.5 % Crude	0	1	0	35.82
2	0.5 % Crude	0.4	5	0.7	95.11
3	0.5 % Crude	0.8	10	1.3	96.20
4	1.0 % Crude	0	5	1.3	98.74
5	1.0 % Crude	0.4	10	0	72.63
6	1.0 % Crude	0.8	1	0.7	93.73
7	2.0 % Crude	0	10	0.7	99.06
8	2.0 % Crude	0.4	1	1.3	93.95
9	2.0 % Crude	0.8	5	0	73.86
K_{i1}[a]	227.1	233.6	223.5	182.3	
K_{i2}	265.1	261.7	267.7	287.9	
K_{i3}	266.9	263.8	267.9	288.9	
k_{i1}[b]	75.7	77.9	74.5	60.8	
k_{i2}	88.4	87.2	89.2	96.0	
k_{i3}	89.0	87.9	89.3	96.3	
Range R_i[c]	13.24	10.06	14.80	35.53	
Order of Significance	Soil Washing Velocity > Ultrasonic Treatment Time > Initial PHC concentration > Salinity				
Optimum combination	2.0 % Crude	0.8	10	1.3	

[a] K_{ij} is the sum of the experimental results which was related to j level of the factor I;

[b] k_{ij} is the average of K_{ij};

[c] R_i is the range of the experimental result of k_i which was equal to the difference between the maximum and minimum of k_i : $R_i = \max\{kij\} - \min\{kij\}$
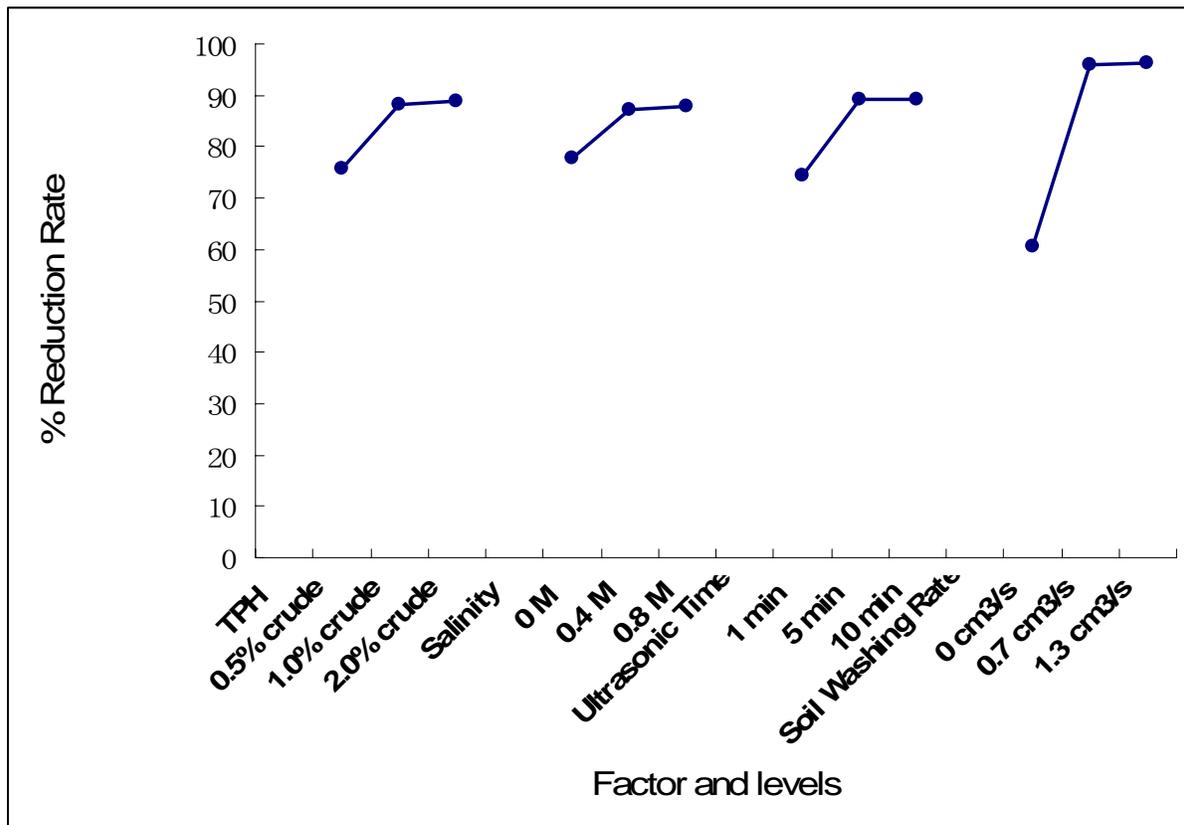
Figure 4.9 Range analysis of the experimental results

It is obvious that all of the four factors were associated with an increasing TPH reduction rate as the level of these factors increased, especially for the increment between level 1 and level 2. Though the TPH reduction rate increased from level 2 to level 3, the difference was not significant. Considering the cost-effectiveness of the treatment, the highest level might not be the optimal choice, especially for soil washing velocity and ultrasonic treatment time. Increasing ultrasonic treatment time will need more power to generate ultrasonic wave so that the cost will increase. Increasing soil washing velocity will need higher level of pumping power and more volume of water or solvent. The amount of treated water which needs further treatment for recycle or disposal might also increase. All these possibilities might lead to more expensive treatment.

4.4.3.2 Variance analysis

The % reduction TPH results in Tables 4.12 were analyzed using an ANOVA to provide a statistical comparison of variable levels. Again, TPH reduction was selected as the response variable and initial TPH concentration, salinity, ultrasonic treatment time and soil washing velocity were analyzed as the fixed factors. The significance level (alpha) for the analysis was set at 0.05 and P value results from the ANOVA analysis less than 0.05. The results were listed in Table 4.15. According to the statistical results, only soil washing velocity has significant effect on variation in TPH reduction, the other three are all not significant. The interactions between variable combinations were not significant.

Table 4.15 Results of ANOVA of ultrasonic enhanced soil washing treatment

Treatment	Degrees of Freedom	Mean Sum of Squares	F statistic	F_a (P≤0.05)
Initial TPH concentration	2	168.01	1.78	<6.94
Salinity	2	129.58	1.37	<6.94
Ultrasonic treatment time	2	218.06	2.31	<6.94
Soil washing velocity	2	1250.53	13.22	<6.94

4.4.4 Additional Experimental study

One group of additional experiments were implemented by using ultrasonic enhanced soil washing of PHC contaminated sand with a combination of 2% crude initial TPH concentration, 0.8 M of sodium chloride, 10 minute of ultrasonic treatment and 1.3 cm_3/s soil washing velocity. The purpose of this group of experiments was to more deeply understand the mechanisms of multiple remediation treatments.

The effluent from the reactor was fractionally collected with 5 different 250-ml beakers, namely B1, B2, B3, B4 and B5. The original soil (SO) with 2.0% crude and 0.8M salt, together with the treated soil (ST) were collected for soil extraction and analysis. The results of the experiments were

shown in Table 4.16 and Figure 4.10. In Figure 4.10, it can be easily found that from B1 to B5, the turbidity and chromaticity of the effluents were kept decreasing while the transparency of the effluents were increasing. This appearance was further proved by the data results in Table 4.16. The fraction of TPH in effluent B1 contained more than half of the total TPH which showed more yellowish color and more turbid. Together with effluent in B1, the effluents during the first 4 minutes contained 75.7 % of the total TPH. In the last 2 minutes, the effluent in B5 contained only 0.8 % of TPH which is almost negligible .All these results indicate that the reduction effect of ultrasonic enhanced soil washing treatment mainly took place at the beginning of the experiments. At last, after 10 minutes of treatment, the final TPH reduction rate reached 99.1%. In summary, the ultrasonic enhanced soil washing reduced most of contaminants after 4 to 5 minutes of ultrasonic soil washing treatment.

Figure 4.10 Fractional experiment results; time interval: 2min; from right to left: 1-2 min; 3-4 min; 5-6 min; 7-8 min and 9-10 min.

Table 4.16 Fractional experiment results

Fraction Number	Time Interval (min)	Mass in F2 Fraction (mg)	Mass in F3 Fraction (mg)	Mass in F4 Fraction mg	Total mass mg	Fraction percentage (%)
B1	1-2	6,689	20,181	2,793	29,663	53.8
B2	3-4	2,798	7,970	1,276	12,044	21.9
B3	5-6	1,943	5,612	856	8,411	15.3
B4	7-8n	352	782	189	1,323	2.4
B5	9-10	84	257	100	441	0.8
SO	0	52	35,040	20,004	55,097	100.0
ST	10	46	371	93	511	0.9
TPH Reduction:	99.1%					

5. DISCUSSION

5.1 Soil Discussion

It is commonly known that the interaction between soil and organic pollutants is highly dependent on soil characteristics such as grain size, surface area, soil moisture, and total carbon. Soil types used in the experiment represented a range of grain sizes and total carbon content. The results of the ultrasonic experiments demonstrated some important trends regarding soil properties and soil types.

The application of ultrasonic treatments methods had a clear effect on the TPH reduction in sand (Table 4.5 and Figure 4.2) implying that experimental conditions in this case were well suited to the treatment. The coarse grain size and low surface area of the sand treatment allowed easier filtration of contaminants with the slurry water. Treatment results for TPH reduction were significantly less in clay than in sand (see Table 4.5). In part, the differences may be attributed to the differences in soil properties between clay and sand. It was suspected that the larger surface area and the low hydraulic conductivity of clay contributed greatly to the low TPH reduction. The larger relative surface area provided by clay particles allows for a greater total volume of crude oil adsorption. The large surface area also allows crude oil to adsorb in monolayers across particle surfaces and thus increasing the overall sorption energy. The fine grain size of clay gives it a much lower hydraulic conductivity (10^{-6} cm/s) compared to sand (10^{-2} cm/s). The slow water movement may have inhibited the removal of crude oil by filtration allowing the potential for readsorption. In sonochemistry research ultrasonic treatments have been applied to contaminated clays with mixed results. Collings et al. (2006) applied treatment with a large laboratory scale (1.5 kW) ultrasonic unit to contaminated clay soil. Treatment removed the majority of contaminants within minutes of treatment (Collings et al. 2006). Chung and Kamon (2005) used a fine clayey soil with a surface area 5.25 m^2/g (compared to 24.9 m^2/g clay in this thesis work) and observed an 81% reduction of phenanthrene using a combined electrokinetic ultrasonic treatment. Aspects of these research projects including the treatment scale and the grain size of the clay may explain the differences in results. Other researchers have observed properties of fine soils that inhibit contaminant removal. Kim and Wang (2003) observed a decrease in mobility of organic pollutants in fine soils using an

ultrasonic soil flushing method. Residual concentrations of pollutants tend to increase with increasing clay content and organic carbon (Fine et al. 1997).

Experimental results for TPH reduction in clay did not reflect results achieved by other researchers using ultrasonic treatments (Chung and Kamon 2005, Collings et al. 2006). Experimental factors such as solution equilibrium time, filtration rate, and slurry mixture can influence results (Kim and Wang 2003). Additionally, the scale of the ultrasonic reactor, ultrasonic power, and the ultrasonic intensity applied to the medium is suspected by some researchers to be related to the amount of pollutant removal (Breitbach and Bathen 2001). Due to time constraints, variables related to the scale and power of the ultrasonic system were not tested during this project. The systematic experimental factors associated with the slurry mixture and filtration, however, may partially explain the differences observed in results.

TPH reduction in muskeg was greater than observed in clay and less than in sand. The muskeg had many physical properties unique to both the clay and sand. The muskeg was lighter, less dense, and contained high organic carbon content. The particle surface area described in Tables 4.3 was relatively low for muskeg (2.67 m^2/g) and was proportionally closer to sand (0.378 m^2/g) than to clay (24.9 m^2/g). The surface area of muskeg suggested that the material was comprised of coarsely grained particles of unhumified organic matter. Limited research is available for the reduction of pollutants from muskeg or peat soils using ultrasound; however, organic pollutant sorption to soil organic matter is believed to be a very important sorption mechanism. Based on the research by Karickhoff (1981), Chiou (1989), and Salloum et al. (2001), it was suspected that the sorption of crude oil during experiments would be affected by the total organic carbon content of the soil. Evidence of increased sorption to soil organic matter was suspected to manifest in the experiment as low TPH reduction results. The results of TPH reduction in muskeg in this case do not confirm this suspicion. The muskeg soil used in the experiments contained 48.1 % organic carbon, however greater TPH reduction was achieved in muskeg than clay which contained only 1.29 % organic carbon. The organic carbon content of the muskeg was consistent with the total organic carbon of the peat soil used by Salloum et al. (2001) (48.3 %) and similar to the peat used by Fine et al. (1997) (27.8 %). Salloum (1999) described the sorption of organic pollutants as being dependent on the characteristics of the carbon material. Humified organic material that has undergone several stages of decomposition contains a larger number of colloidal organic particles to which high levels of

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sorption are attributed. The clay soil likely contains a high proportion of humified organic matter. The muskeg soil likely contained a higher proportion of unhumified coarse organic material demonstrated by the low particle surface area. The results imply that desorption and reduction of TPH from the muskeg soil was influenced more by its relatively low surface area and grain size than by its high total carbon content.

The difference observed in TPH reduction among soil types can best be explained by the sorption mechanisms and the fate of crude oil in the treatment system. The sorption of organic molecules to soil particles can be driven by physical adsorption or partitioning to soil organic carbon depending on the soil moisture conditions (Mingelgrin and Gerstl 1983, Schwarzenbach 2003). The hydrophobic interaction between organic pollutants and water is required for partitioning of organic pollutants to soil organic matter. As such, sorption in soil can be determined by three things: the moisture content of the soil, the surface area of the particle, and the total carbon content of the soil.

In natural soil systems, spills of organic pollutants are intercepted by the surface soil. Once pollutants have infiltrated into the soil, they interact with the soil minerals, organic matter, and soil moisture. In this system, soil organic matter plays a large role in the balance of distribution equilibrium by the partitioning of organic pollutants to similar organic soil carbon. The key difference of predicted interactions between soil and organic pollutants in natural soil systems and laboratory conditions was the soil moisture conditions. The fact that the laboratory soil was spiked under dry conditions may explain the majority of crude oil adsorption and desorption throughout the experiment. By adding water to the dry spiked soil immediately before treatment, the distribution of crude oil to the organic phase and aqueous phase was not allowed to reach equilibrium. The hydrophobic spiked soil further resisted mixing with water during treatment. Since the crude oil was already physically adsorbed to the soil and conditions weren't allowed to reach equilibrium, it is suspected that partitioning did not contribute significantly to the sorption of crude oil.

The muskeg and clay had larger surface areas than sand allowing crude oil to penetrate into micropores and sorb to the larger number of available adsorption sites. In the absence of water, adsorption to all three soils appeared to follow the trend of increasing surface area presented in Table 4.3. This trend is mirrored by the adsorption isotherms presented in Figure 4.1 with the clay

isotherm adsorbing the most sorbate followed by muskeg and sand. The importance of particle surface area for explaining experimental results between soils is reasonable based on the dry spiking procedure used on soils.

In summary, physical soil properties such as surface area and grain size appeared to explain the most of the results for TPH reduction differences among soil. Even though entropic sorption mechanisms such as partitioning to organic matter is an important mechanism in nature, it did not appear to explain TPH results in soils with high organic matter.

5.2 Salinity Discussion

According to the statistical results, the influence of salt on TPH reduction was significant for all soils. The reduction of TPH in sand, demonstrated in the results presented in Table 4.6 and Figure 4.2, was clearly impacted negatively by the addition of salt. In ultrasonic treated sand, TPH reduction was approximately 30 % when salt was added and approximately 90 % in no-salt treatments representing a changing in TPH reduction of approximately 60%. Under saline conditions in sand, ultrasonic treatment appeared to have no effect on TPH reduction compared to the control. The effects of salinity on the clay and muskeg treatments were less pronounced. Only a small negative effect was observed in muskeg treatments with salt and a small positive effect was observed in clay.

To understand and support these results, a review of sonochemistry literature was completed; however, limited research was found exploring the effect of salinity on ultrasonic remediation techniques for organic pollutants. One relevant research project by Feng and Aldrich (2000) examined different concentrations of potassium chloride (KCl) salt on the ultrasonic removal of diesel from fine sand. They described the influence of increasing KCl concentrations from 0 to 0.4 M as increasing diesel removal from 87 % to 88.5 % (Feng and Aldrich 2000). When KCl concentration was raised above 0.4 M, diesel reduction dropped consistently (Feng and Aldrich 2000). The change in diesel reduction discussed by Feng and Aldrich (2000) was only 1.5 % and was small compared to the 60 % change in TPH reduction observed in the thesis experiment. Feng and Aldrich (2000) interpret their results as influences of KCl concentration on the electrostatic bonding forces between the diesel and the sand particles and could reasonably account for a small

1.5 % change in diesel reduction; however, the large 60 % change in TPH reduction observed in sand results due to salt is too large to be explained by a potential change in electrostatic bonding and must be explained by other factors influencing distribution potential of the crude oil.

The results for sand with salt added were experimentally confirmed by a supplemental investigation with sand (presented in Table 4.7 and Figure 4.5). The additional results demonstrated that even a small addition of salt (0.1 g or 0.02 M) dissolved in 70 ml of water, decreased TPH reduction by 42%. The results for clay and muskeg sample analysis influenced by salt are presented in Table 4.6 and in Figures 4.3 and 4.4. The addition of salt in the clay and muskeg treatments did not have the same obvious effect as observed in sand. Salt added treatments in clay may have been influenced by the initial soil properties of the clay, specifically the EC value (Table 4.1). Even though ESP and SAR values (Table 4.2) were within the normal range for the clay soil, the high EC measured in the clay soil may indicate pre-existing salt impacts limiting the effect of salt added treatments for clay.

To understand the influence of salt observed in analytical results, a closer look at the slurry chemistry and equilibrium distribution of hydrocarbons is required. According to Schwarzenbach et al. (2003), the presence of dissolved ionic species generally leads to a decrease in aqueous solubility of organic pollutants. The empirical formula for the change in solubility of an organic compound due to the concentration of salts in solution is given by equation [2-3]. In this case, sodium chloride in aqueous solution has a salting constant of approximately 0.19 to 0.22 L/mol. The salting constant represents the difference in solubility influenced by a particular salt inferring that sodium chloride effectively induces a change in solubility for crude oil by a factor of 0.19 to 0.22.

This trend is most commonly recognized in studies of oil spills in seawater. Shiu et al. (1990) researched the solubilities of 42 different oils in distilled water and in seawater. Results in seawater (3 % NaCl) were approximately 20% less soluble than in the distilled water (Shiu et al. 1990). The solubility of the oil is dependent on the composition of the oil, temperature, water salinity, and the ratio of the volumes of water to oil that are brought into contact (Shiu et al. 1990). Larger organic molecules with higher molecular weight are more hydrophobic and have lower solubility (Schwarzenbach et al. 2003).

The reduced solubility of crude oil by added salt may help explain the results observed in this project. The reduction of TPH in the experiment is completed in part by desorption of crude oil into the aqueous phase and the separation of the solution by filtration. Sonochemistry literature suggests that ultrasonic treatment is capable of increasing the solubility and mass transport of organic compounds. In the presence of salt, the positive effects of ultrasound are countered by the negative effect of dissolved ions in the solute. The lower TPH reduction, particularly in sand, is evidence that less crude oil is removed into aqueous solution. Experimental observations of the treatment filtrations may also provide evidence of the reduced solubility of the crude oil. Filtration of treated samples was completed several times faster in samples with salt dissolved in solution than samples without salt added. The addition of salt may cause the hydrocarbon covered soil to be even more hydrophobic and thus allowing the water to be filtered more quickly. With fewer hydrocarbon molecules in solution, less hydrocarbon molecules are intercepted by the filter and the water is allowed to filter more freely.

However, in the factorial experimental results (Table 4.12, 4.14 and Figure 4.9) of using ultrasonic enhanced soil washing, salinity was shown to have no significant impacts on the TPH reduction. The negative effect of salinity on TPH reduction using only ultrasound was eliminated by the strong positive effect on improving transportation of pollutants by using soil washing technique. Salts existing in the contaminated sand were kept being flushed out from the system during the process which led to a decreasing salinity. Thus the inhibition effect on TPH reduction was not observed even the salinity in the soil was as high as 0.8 M, and the effect of decreasing the solubility of crude oil was also reduced. The results proved that removal of salinity existing in remediation system before other treatment was important for enhancing the treatment efficiency.

In summary, small amounts of salt may potentially reduce the solubility and mobility of hydrocarbons adsorbed to soil. Low solubility and low bioavailability of hydrocarbon contamination under these conditions limits the efficiency of many remediation techniques commonly used such as ex-situ bioremediation. Difficulties achieving remediation success may be compounded by soil structure issues at sites with significant salt issues. Based on the results of the experiments, salt impacts should be seriously considered when applying remediation techniques. To achieve the best results using most remediation techniques including bioremediation, it may be necessary to first address salinity problems before substantial hydrocarbon reduction can occur.

5.3 Treatment Process Discussion

The effect of ultrasonic treatment can be demonstrated by two fundamental mechanisms for pollutant removal from soil and includes: 1) the degradation and destruction of stable organic compounds and 2) desorption by particle cleaning effects and transportation with the aqueous phase induced by heterogeneous cavitation. Generally, the ultrasonic experimental results indicated that application of ultrasonic treatment compared to soil flushing alone provided a significant improvement in TPH reduction. In contrast, the duration of ultrasonic treatment did not appear to influence TPH reduction. Statistical analysis results presented in Table 4.10 and Figure 4.8 demonstrate that there was no statistical difference between the different ultrasonic treatment duration classes. This conclusion implies that samples treated with ultrasound longer do not achieve higher TPH reduction than samples treated for a shorter time. During treatment, oil is desorbed into the slurry water and generates a solution/emulsion mixture of oil and water. As treatment continues, more oil is added to the water emulsion until it reaches its maximum capacity. Equilibrium between oil re-adsorption and oil entering the solution/emulsion is quickly reached (Feng and Aldrich 2000). The trend of oil reduction is observed as high initial reduction of oil up to equilibrium followed by a steep decline in further oil reduction (Feng and Aldrich 2000). Feng and Aldrich (2000) observed peak diesel removal from sand after 5 minutes of ultrasonic treatment. In the project experiment, it appears that peak crude oil removal from sand is reached after 2 minutes of treatment.

The enhancement of ultrasonic enhanced soil washing treatment was basically designed and built on this point. As discussed before, soil washing is most helpful to increase the transportation of contaminants during the ultrasonic treatment process. The moving water or surfactant-added solvent kept dissolving the contaminants which were taken out from the soil surface and soil pores by ultrasonic wave, and carrying the contaminants out of the treatment system. Soil washing with sufficient flushing rate can flush out the contaminants before the system reaches its equilibrium between oil re-adsorption and desorption. This enhancement could make the process suitable for continuous treatment.

The enhancement can be observed by comparing the two groups of experimental results of using traditional ultrasonic treatment and ultrasonic enhanced soil washing treatment (Table 4.6 and Table 4.12). The results of ultrasonic enhanced soil washing treatment were between 93.7% and 99.1%.

The best results of 99.1% reduction was achieved with initial contamination of 2.0% crude, no added salt, 10 minutes of ultrasonic treatment and a 0.7 cm^3/s soil washing velocity. TPH reduction rate of treating sand highly contaminated by salt (0.8 M), with 0.5% crude, 10 minute of ultrasonic treatment and 1.3 cm^3/s soil washing velocity was high as well (around 96%). On the contrary, the results from traditional ultrasonic treatment indicated a TPH reduction rate ranging from 35.1% to 87.4% for no-salt-added group experiments, and a TPH reduction rate ranging from 18.8% to 25.7% for salt-added experiments. It is thus obvious that the TPH reduction efficiency from ultrasonic enhanced soil washing process was much higher and the enhancement was significant.

However, from the data range analysis of ultrasonic treatment in Table 4.14 and Figure 4.9 we can find that the increasing soil washing flow rate (i.e. from 0.7 cm^3/s to 1.3 cm^3/s) did not lead to rapid increase of TPH reduction, even though the soil washing flow rate was observed as the most influencing factor in the treatment process. This result can be explained by the mechanism of the process of breakdown of the bond between contaminant and soil. According to Kim and Wang (2003), the contaminant reduction rate decreased with increasing soil washing flow rate. They mentioned that the reason was due to the insufficient contact time during the experiments. Before the contaminant can be washed out, the contaminants existing in pore space or on surface of soil particles need to be separated from the soil phase. The breakdown of the contaminant-soil bond is a time-dependent process. When the flow rate is too high, the free contaminants might not have enough time to dissolve in the water or solvent. For slower soil washing, the percolating water has longer time to interact with the soil/contaminant system. In summary, the soil washing flow rate should be carefully chosen; if the flow rate is too slow, the transportation effect will be insufficient to carry out the contaminant timely; if the flow rate is too high, the time of interaction of water and soil/contaminant system will be insufficient to decrease the TPH reduction and result in large amount of wastewater for treatment.

5.4 TPH Degradation Discussion

According to literature, ultrasonic cavitation potentially improves the destruction and degradation of stable, persistent organic compounds and it was suspected that some level of molecular degradation would occur to compounds contained in crude oil during the experiment. The result of sonic degradation of crude oil components may be witnessed as the degradation of large

chain organic compounds into smaller, more volatile compounds.

Extractable TPH was determined in the experiment as the area under the chromatograph profile generated by the GC-FID between C10 and C50 (F2, F3 and F4). Compounds in the F4 fraction are larger, heavier molecules that are less volatile than compounds in F2 fraction. After ultrasonic treatment, a shift in the number of compounds throughout the range of TPH would be observed as a shift in the shape of the GC profile. Based on literature, it was suspected that as long chain organic molecules are degraded by treatment, an increase in short chain molecular byproducts would appear as a shift in the chromatograph curve towards the left, more volatile portion of the curve. It is recognized that the fraction of crude oil represented by the lighter more volatile compounds, including the degradation byproducts, would be more mobile, more soluble, and therefore, may be removed more easily than the heavier compounds within crude oil. The following figure (Figure 5.1) shows the shape of the GC profile for a contaminated sand sample with no ultrasonic treatment and a sand sample treated with 40 minutes of ultrasound.
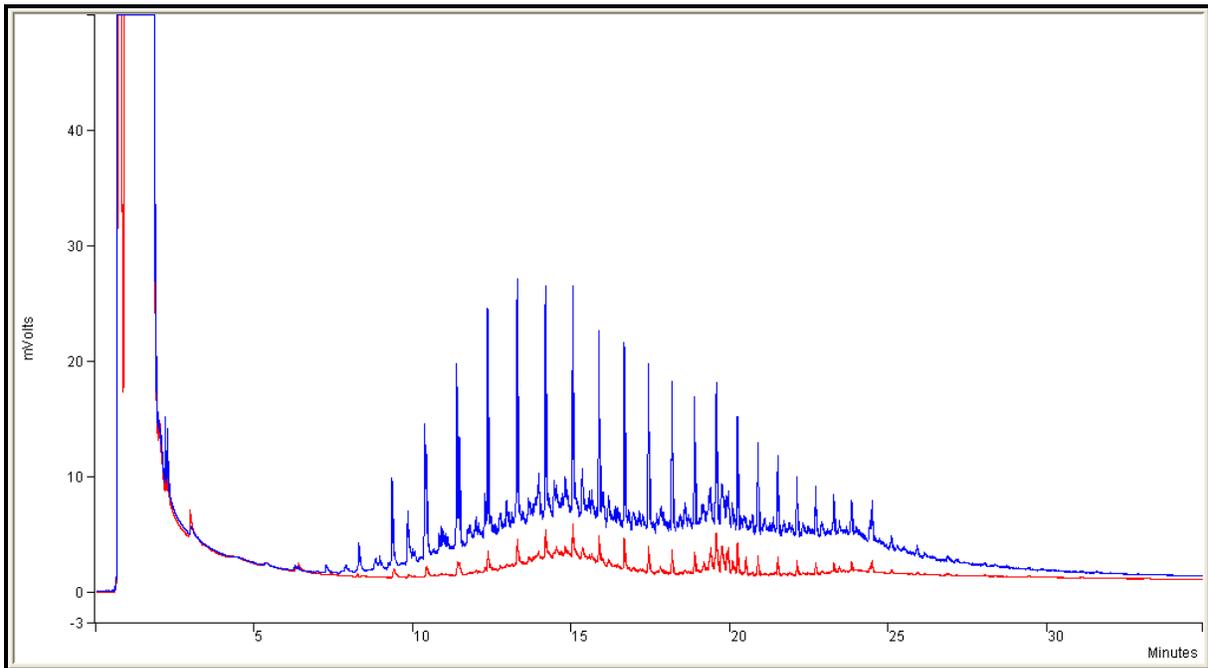
Figure 5.1 GC chromatograph for contaminated sand control with no sonic treatment (blue)
and sand with 40 minutes of ultrasonic treated with 40 minutes (red)

By the shape of the curve we can see the distribution of carbon compounds across the range of

the profile with a small rounded peak near the center. The large peak at the left of the profile represents the extraction solvent (approximately C6) and is not included in the calculation of TPH concentration. Comparing the differences in the shapes of the profile provides evidence of the influence of ultrasound on the composition of crude oil in the sample. The general shape of the two profiles displayed in Figure 5.1 is very similar. After 40 minutes of sonic treatment a clear reduction of TPH across the entire range of the profile is observed. In this case, there is no clear shift in the composition of crude oil presented by the GC chromatograph. It appeared as though ultrasonic treatment was not selectively more effective at reducing certain components of crude. In this case, it may be evidence that desorption explains more TPH reduction than ultrasonic degradation.

However, as compared to the process only using ultrasonic treatment, results of ultrasonic enhanced soil washing were different. Figure 5.2 and 5.3 illustrate the shapes of the GC profiles for two groups of sand treated with ultrasonic enhanced soil washing under different experimental conditions. Figure 5.2 was the results of experiments with no-salt-added condition while Figure 5.3 was the results of experiments with salt-added condition (0.4 M).
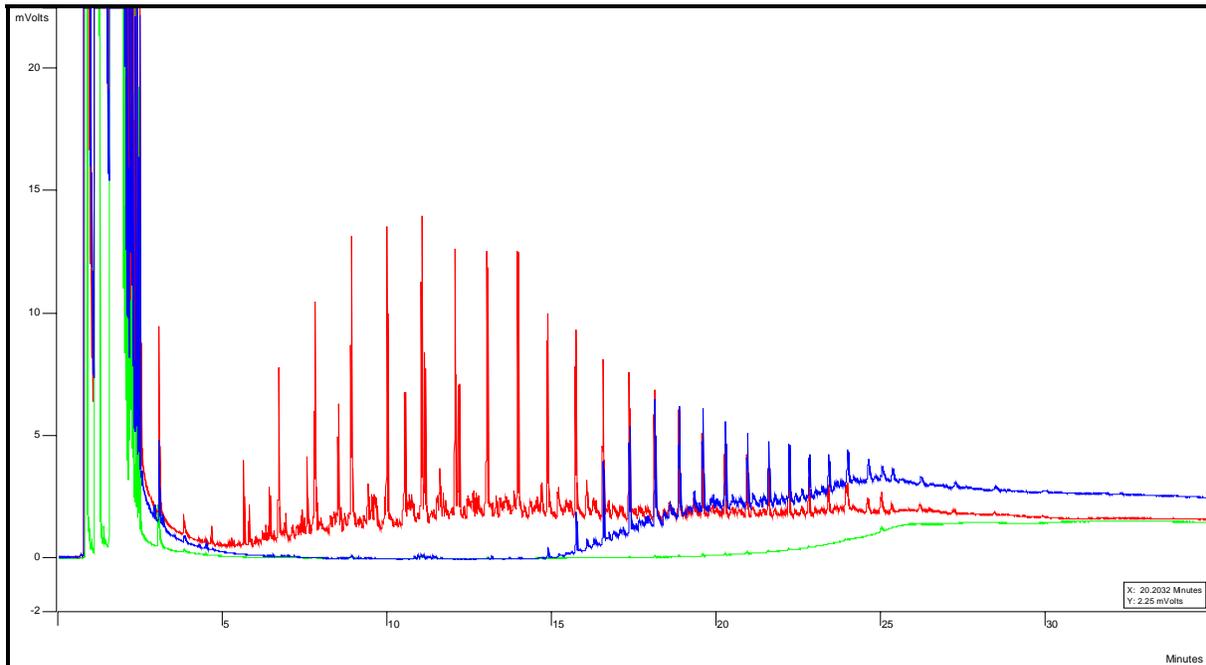
Figure 5.2 GC chromatograph of contaminants shift for result of ultrasonic enhanced soil washing treatment (a); blue: TPH in soil with no treatment; green: TPH in treated soil; red: TPH in effluent; 1.0 % crude; 0 M salinity; 5 minutes of ultrasonic treatment; 1.3 m^3/s soil washing flow rate.
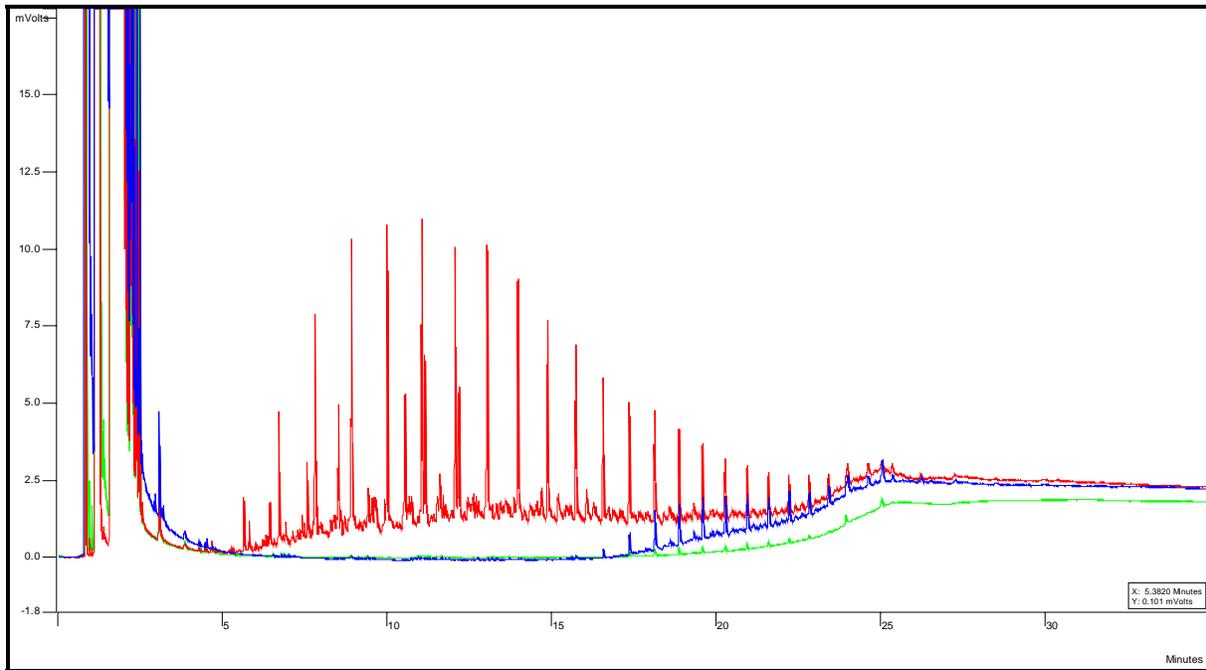
Figure 5.3 GC chromatograph of contaminants shift for result of ultrasonic enhanced soil washing treatment (b); blue: TPH in soil with no treatment; green: TPH in treated soil; red: TPH in effluent; 0.5 % crude; 0.4 M salinity; 5 minutes of ultrasonic treatment; 0.7 m^3/s soil washing flow rate.

It is clear that there are composition shifts as shown in both Figures 5.2 and 5.3. From the blue curves we can see that the original contaminated sand basically contained F3 and F4 fractions, while little amount of F2 fraction was observed; the green curves represent the treated sand which was almost clean with less F3 and F4 fraction as compared to the original contaminated sand. Contaminants in effluents were illustrated on the graphs as well by red curves which were located at the left sides of the other two curves. The shapes of the red curves proved that there were not only F3 and F4 fractions, but also large amount of F2 fractions existing in the effluents. The reason why the total areas of the red curves are more than the total areas of the blue curves was due to the different correction factors for water and soil. In this case, obvious shifts of composition of crude oil presented by the GC chromatography can be easily observed. The shifts might be caused by the destruction of the complex long-chain organic compounds into smaller and more volatile compounds. These results proved that there were both desorption and degradation effects of ultrasound in ultrasonic enhanced soil washing treatment.

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5.5 Desorption Discussion

Results indicated that desorption is potentially an important mechanism for the reduction of TPH from soil, particularly coarser materials such as sand where physical adsorption is the principal bonding force for pollutants. The energy provided by the ultrasonic cavitation must be sufficiently strong enough to overcome the energy of adsorption and allow crude oil to be desorbed into solution. Since sand had a lower surface area, less energy was required to remove significant quantities of crude oil. According to Collings et al. (2006), ultrasonic treatment can be applied successfully to coarse and fine soils when sufficient energy is supplied. The larger surface area of muskeg and particularly clay would require greater ultrasonic energy to remove the crude oil. Once the pollutant is desorbed the problem shifts to the transportation and removal with water. The low hydraulic conductivity of fine soils may impede the transfer and removal of desorbed crude oil in the aqueous phase. Consequently, it may be reasonable to conclude that the pollutant reduction success observed in the experiment may be improved by increasing the sonic energy or by improving the transportation of aqueous solution from the treated soil. Visual evidence of desorption was observed as an accumulation of desorbed TPH in the filter paper. For example, in the sand treatment the accumulation of desorbed crude oil on the filter paper appeared as a thin layer of dark staining. Filter papers were extracted and analyzed for concentrations of TPH using similar methods for soil. Analytical results for filter papers in sand treatments are presented in Table 5.1 below.

Table 5.1 Analytical results for sand filter papers – no salt

Treatment Time	Filter paper TPH concentration (ppm/g of sample)			Average	Standard Deviation	% SD
	Rep 1	Rep 2	Rep 3			
Control	36	48	231	105	109.1	n/a[a]
2 min	890	1,068	829	929	124.3	n/a[a]
5 min	973	1,060	998	1,011	44.3	n/a[a]
10 min	1,060	1,193	1,099	1,117	68.8	6.2
20 min	1,027	903	1,006	979	66.4	n/a[a]
40 min	1,129	1,237	1,001	1,122	117.8	10.5

[a] Concentration less than 10 times the MDL.

Results show that filter papers from sand samples treated with only ultrasound intercepted a higher amount of desorbed crude oil. In contrast, analytical results for filter papers extracted from clay and muskeg treatments did not provide the same evidence for desorption. The filter papers analyzed from clay treatments all contained concentrations of TPH less than 10 ppm per gram of soil sample. The filter papers analyzed from muskeg treatments varied in TPH concentration from less than 10 ppm to as high as 500 ppm per gram of sample. No recognizable trend was observed for filter paper results from clay or muskeg treatments.

Filtration of water from clay and muskeg was very slow. If substantial quantities of crude oil were desorbed from the soil, it appears that slow filtration prevented it from being removed with filtered water. During filtration, desorbed crude oil would have sufficient time to re-adsorb to the soil before removal. Other methods of water separation such as centrifugation may have achieved better results for these fine soils.

6. CONCLUSION

6.1 Summary of Ultrasonic Remediation Experiments

The first objective of the experiments was to develop an understanding of the chemical and physical interactions between hydrocarbon contamination, dissolved salts, and the soil surface by examining the effect of salinity and soil type on desorption and removal of crude oil using ultrasonic treatments. Experimental results for the variables of soil type and salinity provided information to conclude the following:

- TPH reduction was significantly different between the three soil types and TPH reduction was the highest in sand;

- Results suggested that the dominant mechanism of crude oil sorption to the three soils was physical adsorption and partitioning of crude oil to soil organic matter did not result in stronger adsorption to soils high in total carbon (i.e., muskeg);

- Physical soil properties such as surface area and grain size appeared to explain the greatest differences in TPH reduction between soil types;

- The presence of salt in solution even in small quantities significantly lowered TPH reduction from soil and potentially reduced the solubility and mobility of crude oil adsorbed to the soil surface.

The second objective was to determine the effectiveness of ultrasonic treatment for the reduction of hydrocarbon concentrations from soil under a variety of conditions. The effectiveness of ultrasound was represented in the analytical results by the change in TPH reduction between untreated soil samples and ultrasonic treated samples. Experimental results for the variable ultrasonic treatment time provided information to conclude the following:

- Generally, the application of ultrasonic treatment statistically increased the reduction of TPH when compared against the control;

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- The duration of ultrasonic treatment (i.e., for durations tested in this experiment) did not have a significant effect on TPH reduction and therefore, peak crude oil removal under these conditions was reached within 2 minutes of treatment;

- The ultrasonic treatment of sand clearly displayed the highest TPH reduction efficiency implying that ultrasonic treatment under these conditions was most effective on granular soil free from salt impacts;

- Observations and results suggest that ultrasonic desorption and subsequent filtration was the dominant mechanism for TPH reduction in the experiment.

6.2 Summary of Ultrasonic Enhanced Soil Washing Experiments

The first objective of the experiments was to design and build a reactor suitable for ultrasonic enhanced soil washing treatment and then investigate the optimum working condition of ultrasonic enhanced soil washing through a group of factorial-designed experimental studies. Experimental results provided information to conclude the following:

- The fines (clay and silt) with large surface area and low hydraulic conductivity were not suitable for the ultrasonic enhanced soil washing treatment in the reactor which was due to the low permeability;

- The results of range analysis indicated the order of significance of four different factors as: soil washing velocity > ultrasonic treatment time > initial PHC concentration > salinity. The optimal condition for ultrasonic enhanced soil washing treatment was also observed as initial TPH concentration of 2.0% crude, 0.8 M of salinity (sodium chloride), 10 minutes of ultrasonic treatment and 1.3 cm^3/s of soil washing flow rate.

- The results of variance analysis proved that soil washing flow rate had significant impacts on TPH reduction while the other three factors (i.e. initial PHC concentration, salinity, ultrasonic treatment duration) showed insignificant effects.

- Additional experiments demonstrated that the ultrasonic enhanced soil washing removed most part of contaminants within 4 to 5 minutes of treatment.

The second objective of the experiments was to examine the enhancement of remediation capability of ultrasonic enhanced soil washing as compared with traditional ultrasonic treatment. Results for the comparisons provided information to conclude the following:

- The TPH reduction by using ultrasonic enhanced soil washing were between 93.7% and 99.1%, while the traditional ultrasonic treatment achieved TPH reduction ranging from 35.1% to 87.4% from no-salt-added experiments, and 18.8% to 25.7% from salt-added experiments. Thus the treatment efficiency by using ultrasonic enhanced soil washing process was much higher and the enhancement was significant.

- The negative effect of salinity to TPH reduction was eliminated by the effect of increasing transportation of pollutants through the soil washing technique.

- Obvious shifts of contaminant compositions after ultrasonic enhanced soil washing were observed from the GC chromatographs. The destruction of complex long-chain organic compounds into smaller and more volatile compounds was observed. The results proved that both desorption and destruction of TPH were responsible for the high TPH removal efficiency through the ultrasonic enhanced soil washing process.

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REFERENCES

Abdel-Aal, H. K., Mohamed Aggour, and M. A. Fahim. 2003. Petroleum and gas field processing. New York, NY: Marcel Dekker, Inc.

Adamson, Arthur W. 1990. Physical chemistry of surfaces. 5th ed. New York, New York: John Wiley & Sons, Inc.

Adriano, D. C., J. M. Bollag, W. T. Frankenberger Jr., and R. S. Sims, eds. 1998. Bioremediation of contaminated soils. Vol. 37. Wisconson, USA: The American Society of Agronomy, Inc.

Alberta Environment. 2001. Salt contamination assessment & remediation guidelines. Edmonton, Alberta: Alberta Environment, Environmental Sciences Division, T/606.

Amatya, P. L. Hettiaratchi, J. P. A., and R. C. Joshi. 2002. Biotreatment of flare pit waste. Journal of Canadian Petroleum Technology 41, (9): 30-36.

Amellal, N., J. M. Portal, and J. Berthelin. 2001. Effect of soil structure on the bioavailability of polycyclic aromatic hydrocarbons within aggregates of contaminated soil. Applied Geochemistry 16: 1611-1619.

Anderson, W.C. 1993. Innovative site remediation technology – soil washing / soil flushing, American Academy of Environmental Engineers, Annapolis, Maryland.

Arocena, Joselito M., and P. Michael Rutherford. 2005. Properties of hydrocarbon and salt contaminated flare pit soils in northeastern british columbia (canada). Chemosphere 60: 567-575.

Ashworth, John, Doug Keyes, and Jean-Michel Crepin. 1999. A comparison of methods for gypsum requirement of brine-contaminated soils. Canadian Journal of Soil Science 79: 449-455.

Atlas, Ronald M. 1981. Microbial degradation of petroleum hydrocarbons: An environmental perspective. Microbiological Reviews 45, (1): 180-209.

Bai, Guiyun, Mark L. Brusseau, and Raina M. Miller. 1997. Biosurfactant-enhanced removal of residual hydrocarbon from soil. Journal of Contaminant Hydrology 25: 157-170.

Borst, M., 1991. Guide to conducting treatability studies under CERCLA: soil washing interim guidance. United States Environmental Protection Agency, Office of Emergency and Remedial Response, EPA/540/2-91/020A.

Brady, Nyle C., and Ray R. Weil. 1996. The nature and properties of soils. 11th ed. Upper Saddle River, New Jersey: Prentice-Hall Inc.

Breitbach, M., and D. Bathen. 2001. Influence of ultrasound on adsorption processes. Ultrasonics Sonochemistry 8: 277-283.

Canadian Council of Ministers of the Environment (CCME). 2001. Reference method for the canada wide standard for petroleum hydrocarbons in soil - tier 1 method. Winnipeg, Manitoba: Canadian Council of Ministers of the Environment Inc., 1310.

Canadian Council of Ministers of the Environment (CCME). 2000. Canada-wide standards for petroleum hydrocarbons (PHCs) in soil: Scientific rationale - supporting technical document.

Carty, David J., Stephen M. Swetish, William F. Priebe, and Wayne Crawley. 1997. Remediation of salt-affected soils at oil and gas production facilities. Texas: American Petroleum Institute, 4663.

Chaineau, C. H., G. Rougeux, C. Yepremian, and J. Oudot. 2005. Effects of nutrient concentration on the biodegradation of crude oil and associated microbial populations in the soil. Soil Biology and Biochemistry 37: 1490-1497.

Cheung, H. Michael, Ashish Bhatnager, and Greg Jansen. 1991. Sonochemical destruction of chlorinated hydrocarbons in dilute aqueous solution. Environmental Science and Technology 25, (8): 1510-1512.

Chiou, C. T. 1989. Theoretical considerations of the partition uptake of nonionic organic compounds by soil organic matter. In Reactions and movements of organic chemicals in soils., eds. B. L. Sawhney, K. Brown. Madison WI: SSSA Special Publication 22.

Chung, Ha Ik, and Masashi Kamon. 2005. Ultrasonically enhanced electrokinetic remediation for removal of pb and phenanthrene in contaminated soils. Engineering Geology 77: 233-242.

Coles, E.T., Rubin B. and Gaire R. 1990. Removing hazardous organics from excavated soils by ultrasonic washing. Haztech International 90, Houston, Texas.

Collings, A. F., A. D. Farmer, P. B. Gwan, Sosa Pintos, A. P., and C. J. Leo. 2006. Processing contaminated soils and sediments by high power ultrasound. Minerals Engineering 19: 450-453.

Cook, S. V., A. Chu, and R. H. Goodman. 2002. Leachability and toxicity of hydrocarbons, metals and salt contamination from flare pit soil. Water, Air, and Soil Pollution 133: 297-314.

Dibble, J.T., and Bartha, R. 1979. Effect of environmental parameters on the biodegradation of oil sludge. Applied and Environmental Microbiology 37, (4): 729- 739.

Eve, R.R. 1998. Remediation of petroleum contaminated soils-biological, physical, and chemical process. CRC Press: 81-86.

Farmer, A.D., Collings, A.F. and Jameson, G..J. 2000. Effect of ultrasound on surface cleaning of silica particles. International Journal of Mineral Processing 60: 101-113.

Federal Remediation Technologies Roundtable. Remediation technologies screening matrix and reference guide, version 4.0. 1991 [cited 08/07 2007] Available from http://www.frtr.gov/matrix2/top_page.html

Feng, D. and Aldrich, C. 2000. Sonochemical treatment of simulated soil contaminated with diesel. Advances in Environmental Research 4: 103-112.

Fine, P., Graber, E.R. and Yaron, B. 1997. Soil interactions with petroleum hydrocarbons: Abiotic processes. Soil Technology 10: 133-153.

Franzen, D. 2003. Managing saline soils in north dakota. Fargo, ND: NDSU Extension Service, North Dakota State University.

Griffiths, R.A. 1995. Soil-washing technology and practice. Jounal of Hazardous Materials 40: 175-189.

Hasset, J.J. and Banwart, W.L. 1989. The sorption of nonpolar organics by soils and sediments. In Reactions and movements of organic chemicals in soils., eds. B.L. Sawhney, K.B. Madison, WI: SSSA Special Publication Number.

Hoffman, M.R., Hua, I. and Hochemer, R. 1996. Application of ultrasonic irradiation for the degradation of contaminants in water. Ultrasonics Sonochemistry 3: S163-172.

Hughes, M. 2006. The use of biosolids in the composting of a crude oil and salt contaminated clay soil. Masters of Science Dissertation., University of Northern British Columbia.

Hyman, M. and Dupont, R.R. 2001. Groundwater and soil remediation – process design and cost estimating of proven technologies. American society of civil engineers: 427-459.

Juang, R.S., Lin, S.H. and Cheng, C.H. 2006. Liquid-phase adsorption and desorption of phenol onto activated carbons with ultrasound. Ultrasonics Sonochemistry 13: 251-260.

Kamalavathany, R. 1997. Analysis and modeling of ultrasonic enhanced soil washing process. Master Thesis. New Jersey Institute of Technology, USA.

Karickhoff, S.W., Brown, D.S. and Scott, T.A. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Resources 13: 241-248.

Khaitan, S., Kalainesan, S., Erickson, L.E., Kulakow, P., Martin, S., Karthikeyan, R., Hutchinson, S.L.L., Davis, L.C.T., Illangasekare, H. and Crispin N. 2006. Remediation of sites contaminated by oil refinery opertations. Environmental Progress 25, (1): 20-31.

Kharaka, Y.K., Thordsen, J.J., Kakouros, E. and Herkelrath, W.N. 2005. Impacts of petroleum production on ground and surface waters: Results from the osage-skiatook petroleum environmental research A site, osage county, oklahoma. Environmental Geosciences 12, (2):

127-138.

Kim, Y.U., and Wang, M.C. 2003. Effect of ultrasound on oil removal from soils. Ultrasonics 41: 539-542.

Kirchmann, H. and Ewnetu, W. 1998. Biodegradation of petroleum-based oil wastes through composting. Biodegradation 9: 151-156.

Knox, R.C. and Sabatini, D.A. 2000. Reclamation of brine contaminated soil: Clearview demonstration project. University of Oklahoma: School of Civil Engineering and Environmental Science.

Korphage, M.L., Langhus, B.G. and Campbell, S. 2003. Project report: Applied phyto-remediation techniques using halophytes for oil and brine spill scars. Wichita, Kansas: Kansas Corporation Commission.

Kuhlman, M.I., and Greenfield, T.M. 1999. Simplified soil washing processes for a variety of soils. Jounal of Hazardous Materials 66: 31-45.

Land Resource Research Institute, Research Branch. 1985. Soils of Fort St. John - Dawson Creek area, British Columbia. Vancouver, BC: Agriculture Canada.

Lim, J.L. and Okada, M. 2005. Regeneration of granular activated carbon using ultrasound. Ultrasonics Sonochemistry 12: 277-282.

Little, C., Hepher, M.J. and El-Sharif, M. 2002. The sono-degradatio of phenanthrene in an aqueous environment. Ultrasonics 40: 667-674.

Lowell, S., Shields, J.E., Thomas, M.A. and Thommes, M. 2006. Characterization of porous solids and powders: Surface area, pore size and density. Netherlands: Springer.

Lyman, W.J., Noonan, D.C., and Reidy, P.j. 1990. Cleanup of petroleum contaminated soils at underground storage tanks. Pollution Technology Review, No.195. Noryes Data Corp., Park Ridge, NJ.

Mason, T.J. 2000. Large scale sonochemical processing: Aspiration and actuality. Ultrasonics Sonochemistry 7: 145-149.

Mason, T. J. 1990 (a). Critical reports on applied chemistry: Chemistry with ultrasound. Vol. 28. New York, New York: Elsevier Science Publishers Ltd.

Mason, T. J. 1990 (b). Advances in sonochemistry. Vol. 1. London, England: Jai Press Ltd.

Mason, T.J., Collings, A.F. and Sumel, A. 2004. Sonic and ultrasonic removal of chemical contaminants from soil in the laboratory and on a large scale. Ultrasonics Sonochemistry 11: 205-210.

Mason, T.J. and Lorimer, J.P. 2002. Applied sonochemistry: The uses of power ultrasound in chemistry and processing. Weinheim, Germany: Wiley-VCH.

Mbhele, P.P. 2008. Remediation of soil and water contaminated by heavy metals and hydrocarbons using silica encapsulation. Master thesis. University of the Witwatersrand. South Africa.

Mingelgrin, U. and Gerstl, Z. 1983. Reevaluation of partitioning as a mechanism of nonionic chemicals adsorption in soils. Journal of Environmental Quality 12, (1): 1-9.

Qadir, M., Qureshi, R.H. and Ahmad, N. 1998. Horizontal flushing: A promising ameliorative technology for saline-sodic and sodic soils. Soil & Tillage Research 45: 119-131.

Quantochrome. Operating manual, autosorb-1C. Boynton Beach, FL: Quantochrome Instruments.

Raichel, D.R. 2000. The science and applications of acoustics. New York, New York: Springer-Verlag New York, Inc.

Rhykerd, R.L., Weaver, R.W. and McInnes, K.J. 1995. Influence of salinity on bioremediation of oil in soil. Environmental Pollution 90: 127-130.

Salloum, M.J. 1999. Sorption of organic compounds to soil and geologic samples that vary in mineral content and diagenic properties. Doctor of Philosophy., University of Alberta.

Salloum, M.J., Dudas, M.J. and McGill, W.B. 2001. Variation of 1- naphthol sorption with organic matter fractionation: The role of physical conformation. Organic Geochemistry 32: 709-719.

Schwab, A.P., Su, J., Wetzel, S. and Banks, M.K. 1999. Extraction of petroleum hydrocarbons from soil by mechanical shaking. Environmental Science and Technology 33, (11): 1940.

Schwarzenbach, R.P., Gschwend, P.M. and Imboden, D.M. 2003. Environmental organic chemistry. 2nd ed. Hoboken, NJ: John Wiley and Sons, Inc.

Senesi, N. 1993. Organic Pollutant Migration in Soils as Affected by Soil Organic Matter. Molecular and Mechanistic Aspects. In Migration and Fate of Pollutants in Soils and Subsoils., eds. Domenico Petruzzelli, Friedrich G. Helfferich. NATO ASI Series, Vol. G 32. Springer-Verlag. Berlin.

Shin, K.H. and Kim, K.W. 2004. A biosurfactant-enhanced soil flushing for the removal of phenanthrene and diesel in sand. Environmental Geochemistry and Health 26: 5-11.

Shiu, W.Y., Bobra, M., Bobra, A.M., Maijanen, A., Suntio, L. and Mackay, D. 1990. The water solubility of crude oils and petroleum products. Oil and Chemical Pollution 7: 57-84.

Siddique, T., Rutherford, P.M., Arocena, J.M and Thring, R.W. 2006. A proposed method for rapid and economical extraction of petroleum hydrocarbons from contaminated soils. Canadian Journal of Soil Science 86: 725-728.

Singh, A. and Ward, O.P. eds. 2004. Biodegradation and bioremediation. Germany: Springer.

Sposito, Garrison. 1989. The chemistry of soils. New York, New York: Oxford University Press, Inc.

Sposito, G. 1984. The surface chemistry of soils. New York, New York: Oxford University Press, Inc.

Sublette, K.L., Moralwar, A., Ford, L., Duncan, K., Thoma, G. and Brokaw, J. 2005. Remediation of a spill of crude oil and brine without gypsum. Environmental Geosciences 12, (2): 115-125.

Suleimanov, R.R. 2005. Changed soil properties after pollution by oilfield brine at the tuimazy oilfield (republic of bashkortostan). Soil Biology 32, (5): 613-620.

Suslick, K.S. 1990. Sonochemistry. Science 247: 1439-1445.

Talley, J.W., ed. 2006. Bioremediation of recalcitrant compounds. Boca Raton, FL: Taylor & Francis Group, LLC CRC Press.

Tan, K.H. 1993. Principles of soil chemistry. 2nd ed. New York, New York: Marcel Deckker, Inc.

Thompson, L.H., and Doraiswamy, L.K. 1999. Sonochemistry: Science and engineering. Ind. Eng. Chem. Res. 38: 1215-1249.

U.S. EPA. 1985. Handbook for remedial action at waste disposal sites. Office of Solid Waste and Emergency Response, Washington, D.C. EPA/625/6-85//006.

U.S. EPA. 1990. Handbook on in situ treatment of hazardous waste-contaminated soils. Office of Solid Waste and Emergency Response, Washington, D.C. EPA/540/2-90/002.

U.S. EPA. 1996. Soxhlet extraction. United States EPA, Method 3540C.

U.S. EPA. 2000. Profile of the oil and gas extraction industry. Washington, DC: US EPA Office of Compliance Assurance, EPA/310-R-99-006.

Yong, R.N., Mohamed, A.M.O. and Warkentin, B.P. 1992. Principles of contaminant transport in soils. Netherlands: Elsevier Science Publishers.

Zhang, G., and Hua, I. 2000. Ultrasonic degradation of trichloroacteonitrile chloropicrin and bromobenzene: Design factors and matrix effects. Advances in Environmental Research 4: 211-218.