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The Reduction of Petroleum Hydrocarbons In Soil Under Saline Conditions Using Ultrasound

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Outline

- Research Background
- Introduction to Sonochemistry
- Objectives
- Methodology
- Results
- Conclusions
- Questions

Research Background

- **Hydrocarbon and Salt Contamination**

Two of the most common soil contaminants found at oil and gas extraction sites are petroleum hydrocarbons (PHCs) and salts generated from spilled diesel, crude, condensate, or produced water brine

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

High concentrations of salt from brine spills may amplify the challenges of soil remediation by reducing the solubility and bioavailability for remediation

Research Background

- **What is ultrasound?**

Sound with a frequency higher than that to which the human ear can hear (usually above 20 kHz)

Power ultrasound (high intensity) which carries high energy sound waves with frequency between 20 and 100 kHz has been applied in many environmental scientific studies: surface cleaning, emulsification, disinfection, etc.

Cavitation effect of ultrasonic waves transforms sonic energy into intense localized temperature (hot spots) and pressure (microstreaming) which generate two primary effects of ultrasound.

Research Background

- **Chemical Effect: Destruction (Degradation)**

The destruction of contaminants is completed by the direct oxidation under the high temperature and pressure environments created by sonic cavitation

Long-chain or aromatic hydrocarbons with complex structure can be broken down into fragments and simple hydrocarbons with higher solubilities and bioavailability

Research Background

- **Physical Effect: Desorption (Separation)**

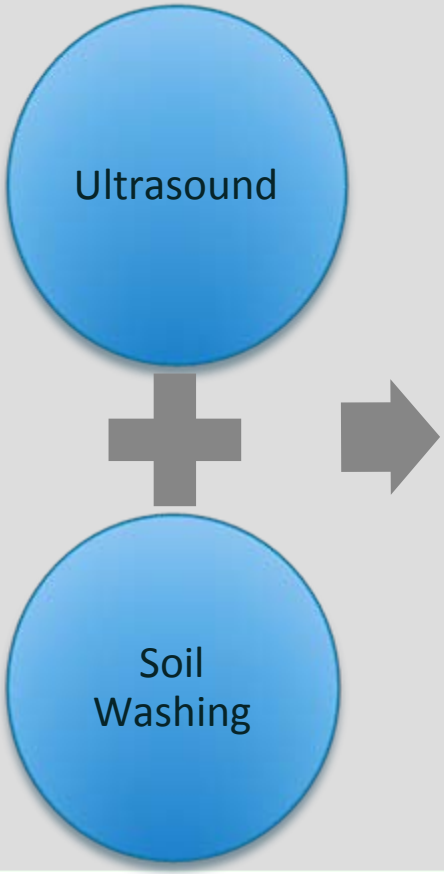
Desorption of contaminants from soil particles is completed by breaking the physical bonds between the adsorbate and adsorbent

Ultrasonic cavitation cleans the surface of the aggregates of solid particles and also reaches the areas of the interface in the contaminant/soil system which is inaccessible in other separation methods

The cavitation waves (microstreaming) can break up the aggregates of solid particles and increase turbulence and transportation of contaminants in the medium

Research Background

- **Enhancement of Ultrasonic Soil Washing**



Two primary mechanisms for ultrasonic enhanced soil washing: Degradation and Desorption

Soil washing improves the transportation and removal of contaminants in solution

Objectives

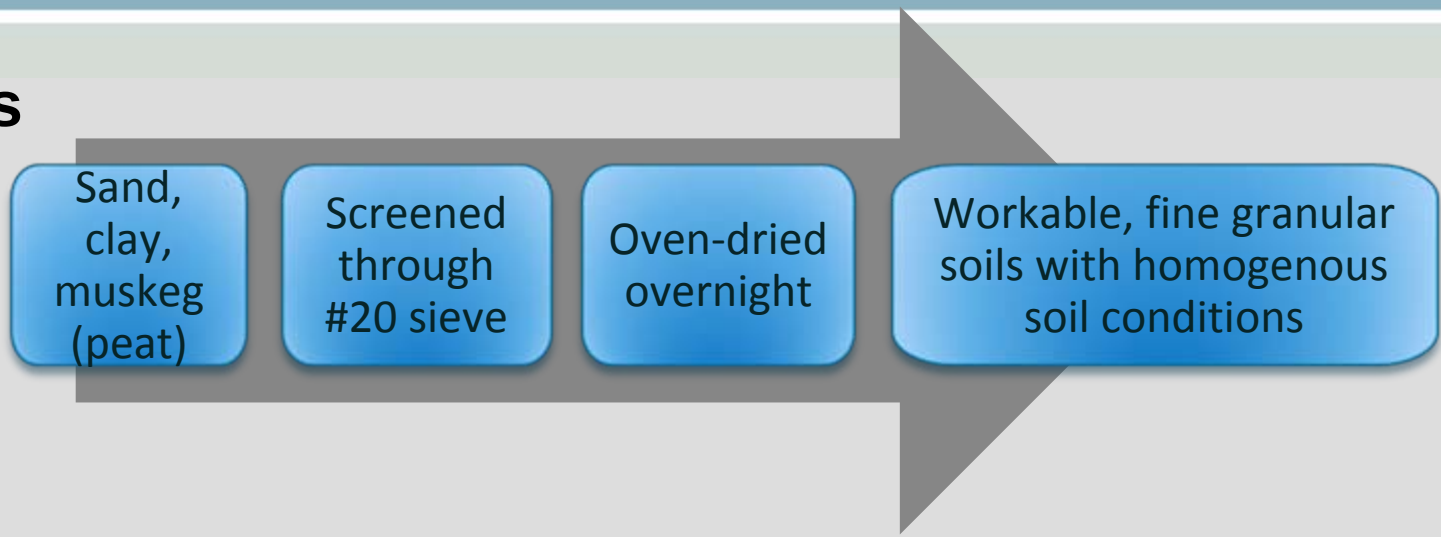
- To research the effect of soil properties and salinity on the adsorption/desorption of oil using an ultrasonic soil flushing treatment
- To evaluate the ability of ultrasonic treatment as a useful technique to enhance remediation of salt and hydrocarbon contaminated soils

Methodology

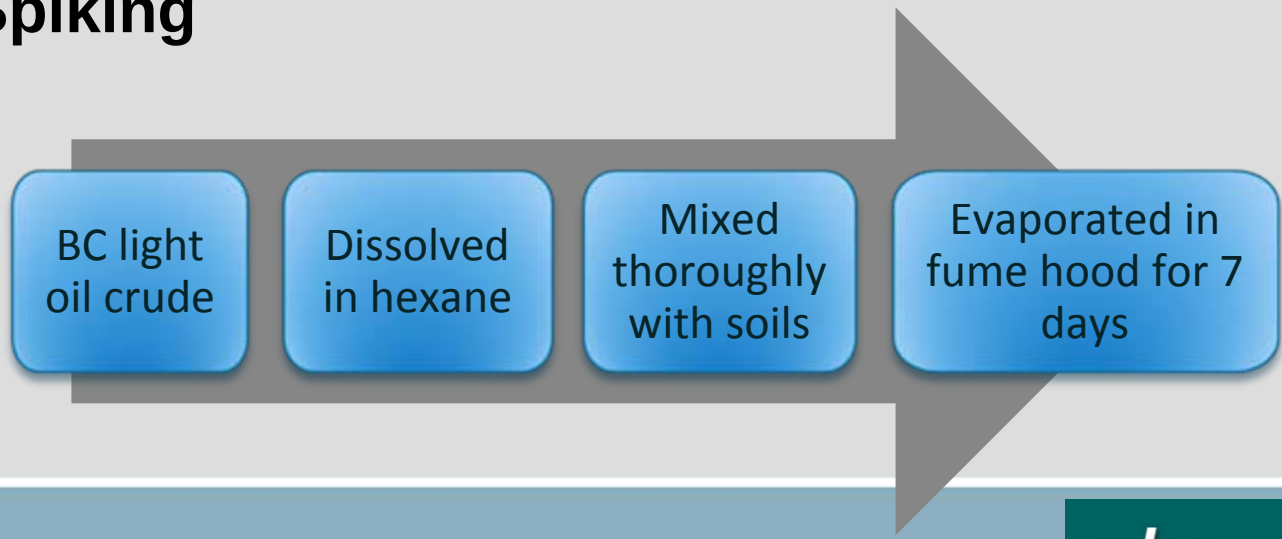
- Materials
- Experimental Design
- Sample Extraction and Analysis

Methodology

- **Soils**

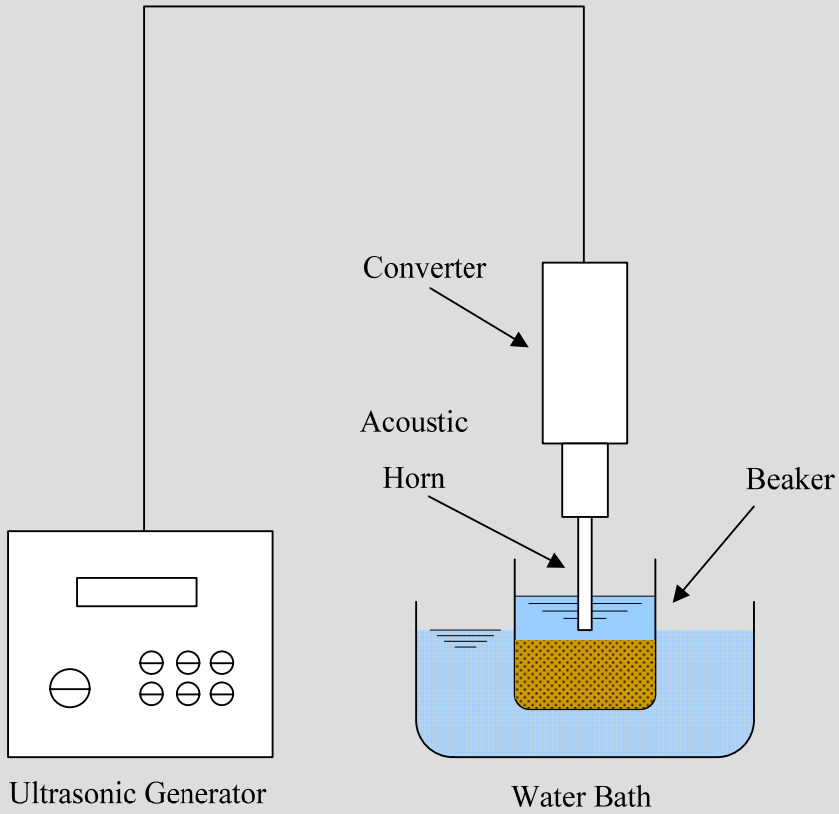


- **Oil Spiking**



Experimental Design

- **Ultrasonic Treatment**



Experimental Design

- Ultrasonic Treatment Design

Factors	Level Descriptions
Soil Type	sand, clay, muskeg
Salinity	no salt, salt added (0.27 M)
Ultrasonic Treatment Time	control (0 min) , 2 min, 5 min, 10 min, 20 min, 40 min

TPH Extraction and Analysis

Vacuum Filtration; Mechanical Shaking Extraction	Silica Gel Clean-up	Rotary Evaporation	GC-FID Analysis of TPH

Results

- **Soil Characterization Results**

Sample Name	Chemical Analysis		Salinity Parameters				
	Total Carbon	Total Nitrogen	Conductivity	Sodium (Na+)	CEC	ESP	SAR
	(%)	(%)	(ds/m)	(cmol/kg)	(cmol/kg)		
Sand	0.06	0.002	1.2	0.007	0.08	8.4	2.6
Clay	1.29	0.079	26.2	0.166	18.55	0.9	3.9
Muskeg	48.06	0.981	9.9	0.482	49.49	1	7.1

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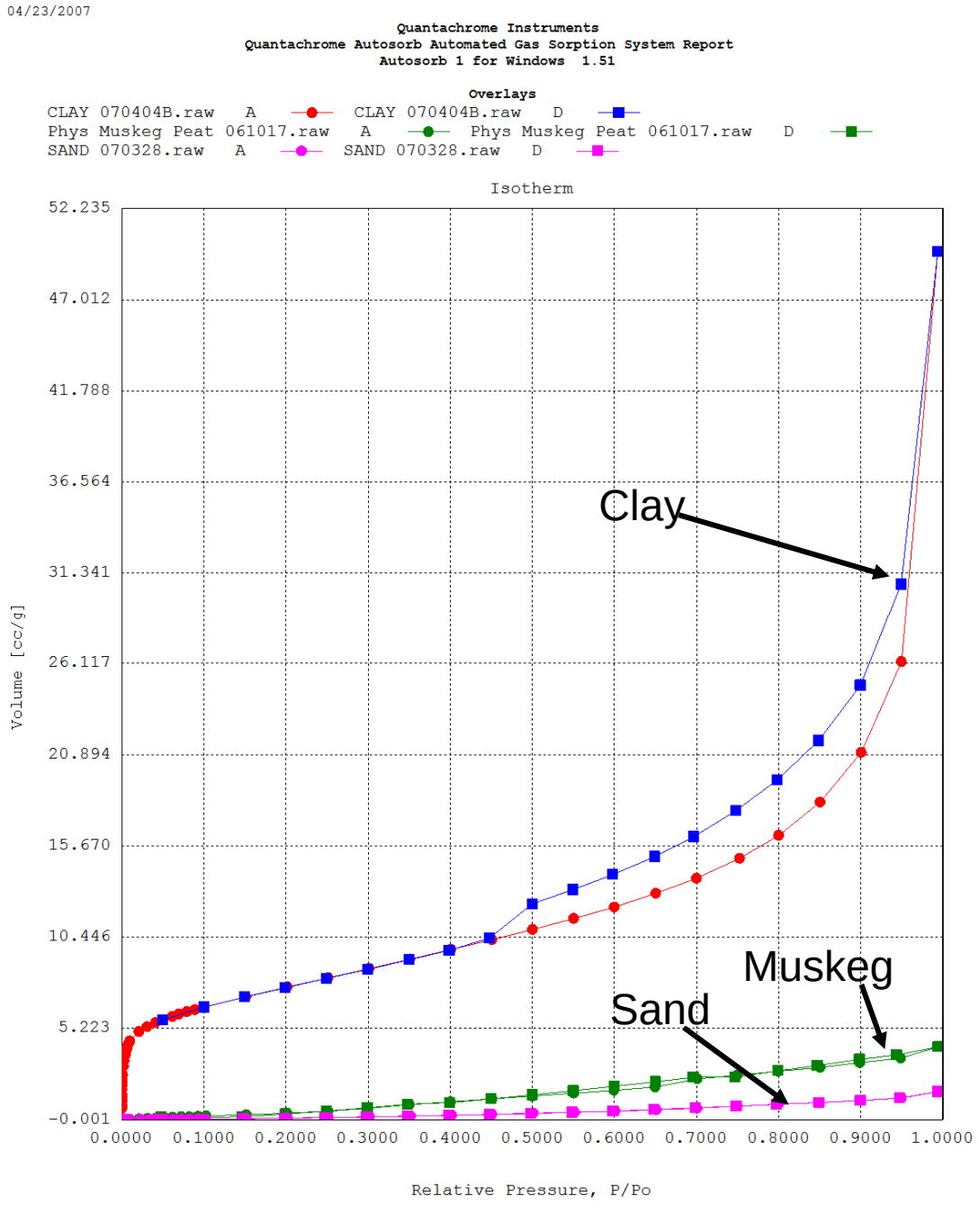
Results

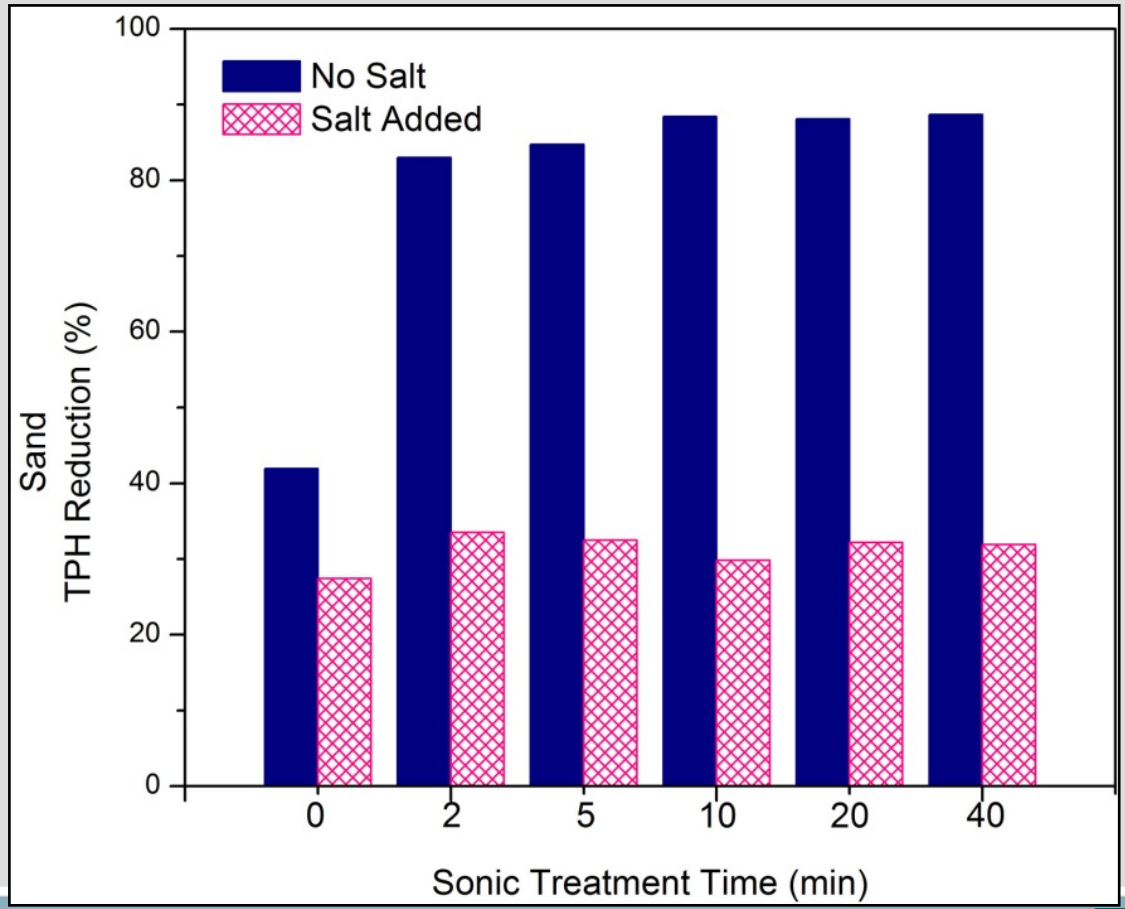
- **Adsorption Isotherms**
  - Physical Properties
    - → Particle Surface Area
    - → Total Pore Volume

Sample Name	Physical Properties	
	Total pore volume (mm^3/g)	Surface area (m^2/g)
Sand	0.0092	0.378
Clay	6.993	24.9
Muskeg	0.0335	2.67



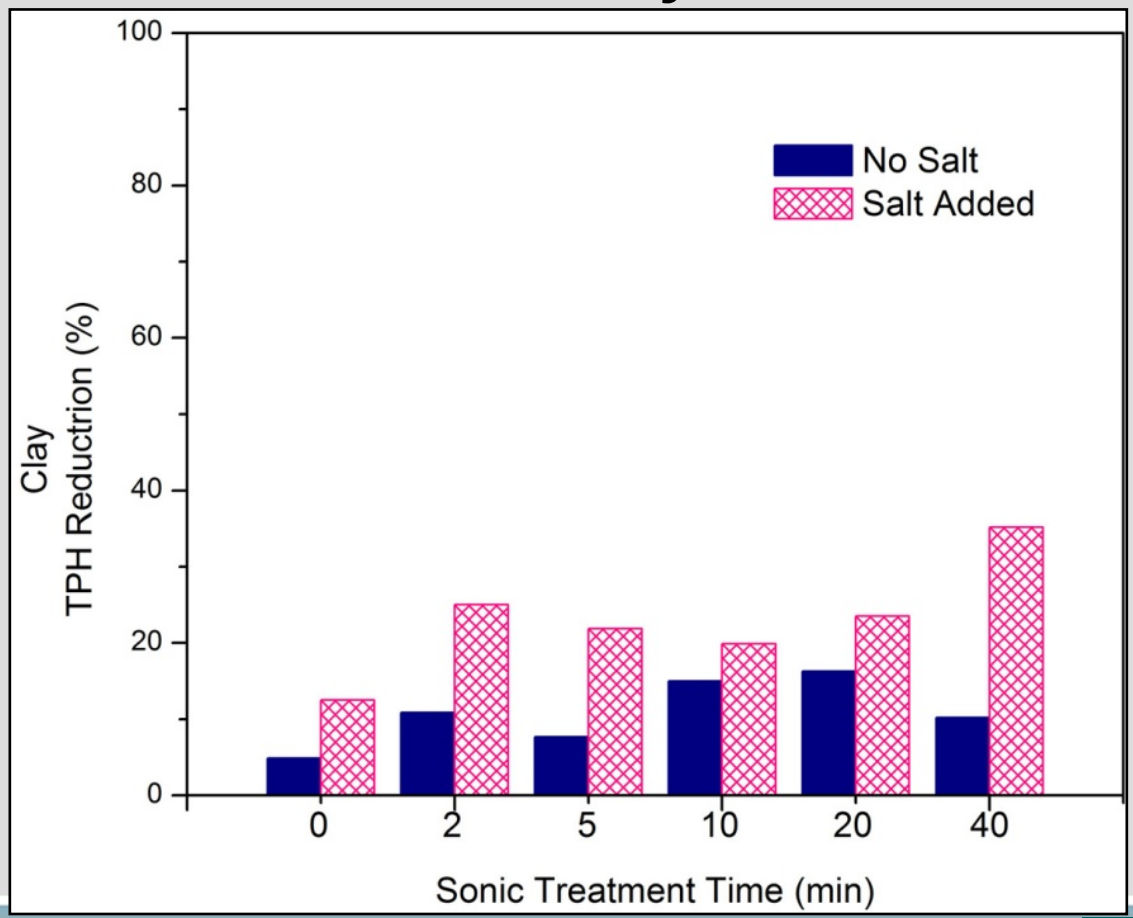
Results

- **Ultrasonic Treatment: Sand**



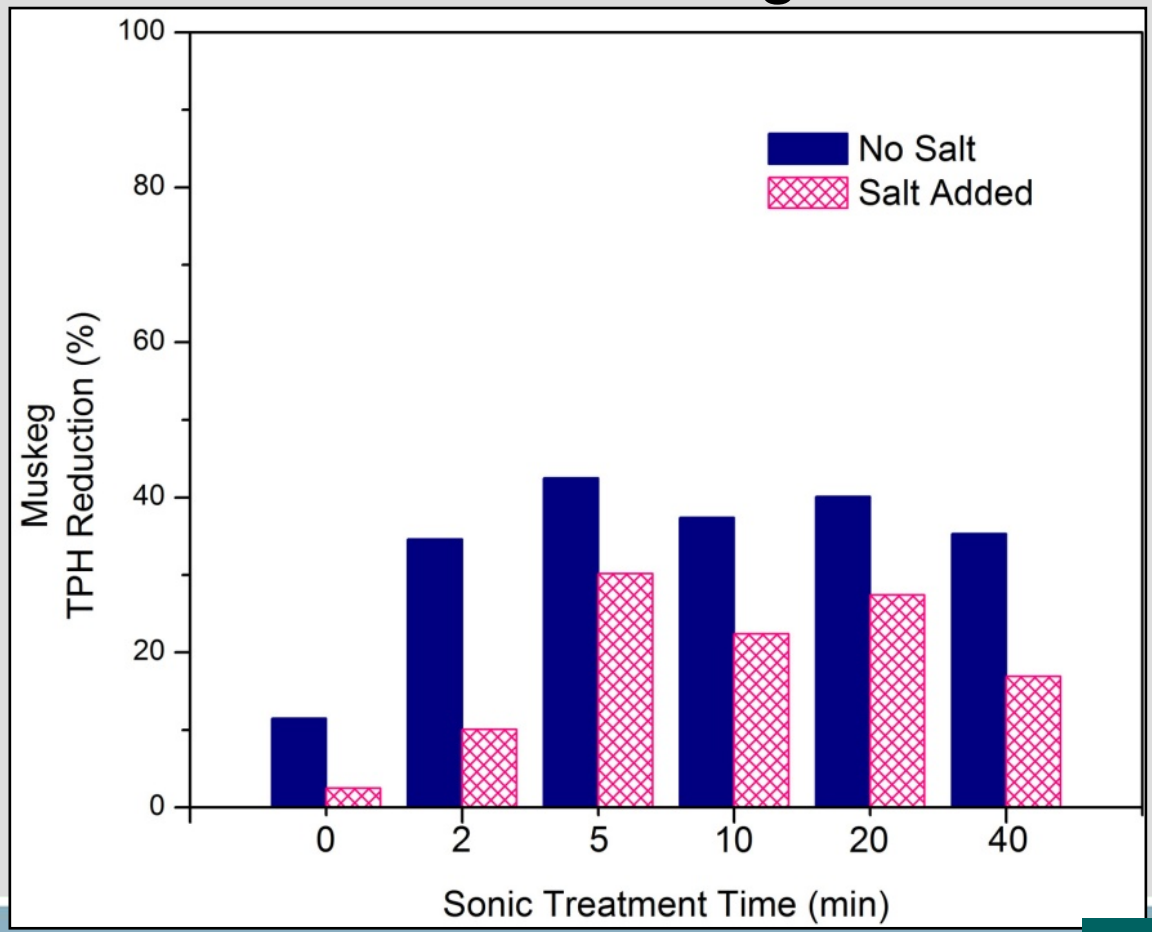
Results

- **Ultrasonic Treatment: Clay**



Results

- **Ultrasonic Treatment: Muskeg**



Results

- **Ultrasonic Treatment**

Without Salt: The peak crude oil removal from sand was reached after 2 min of treatment. Less TPH reduction was achieved from clay and muskeg.

With Salt: the salt limited TPH reduction and less TPH reduction was observed in sand and muskeg treatments.

The application of ultrasonic treatment appears to be more effective for treating granular soils with high hydraulic conductivity

Results

- **Statistical Results**

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
[a] Computed using alpha = 0.05				

Results of ANOVA analysis: all three variables significantly influenced TPH reduction

Only the control class significantly effected TPH reduction compared to the other classes of sonic treatment time

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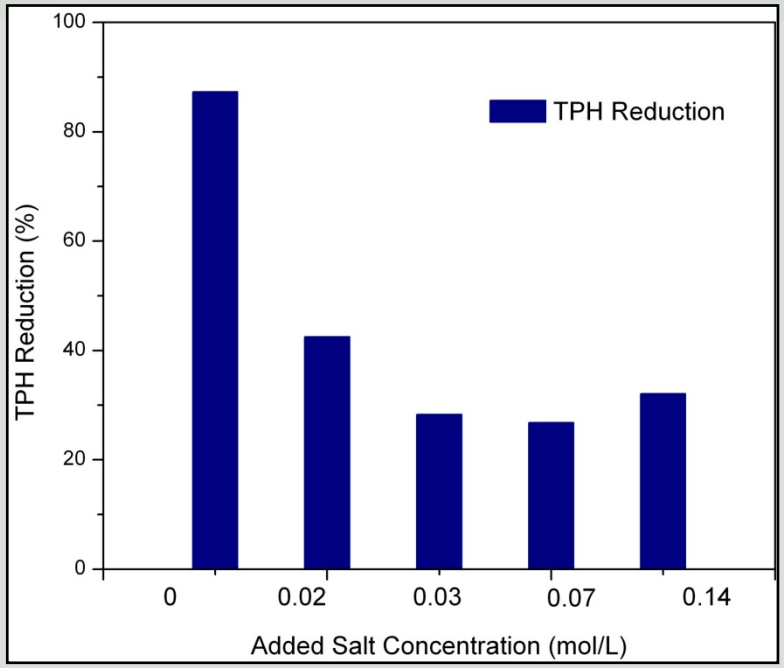
Results

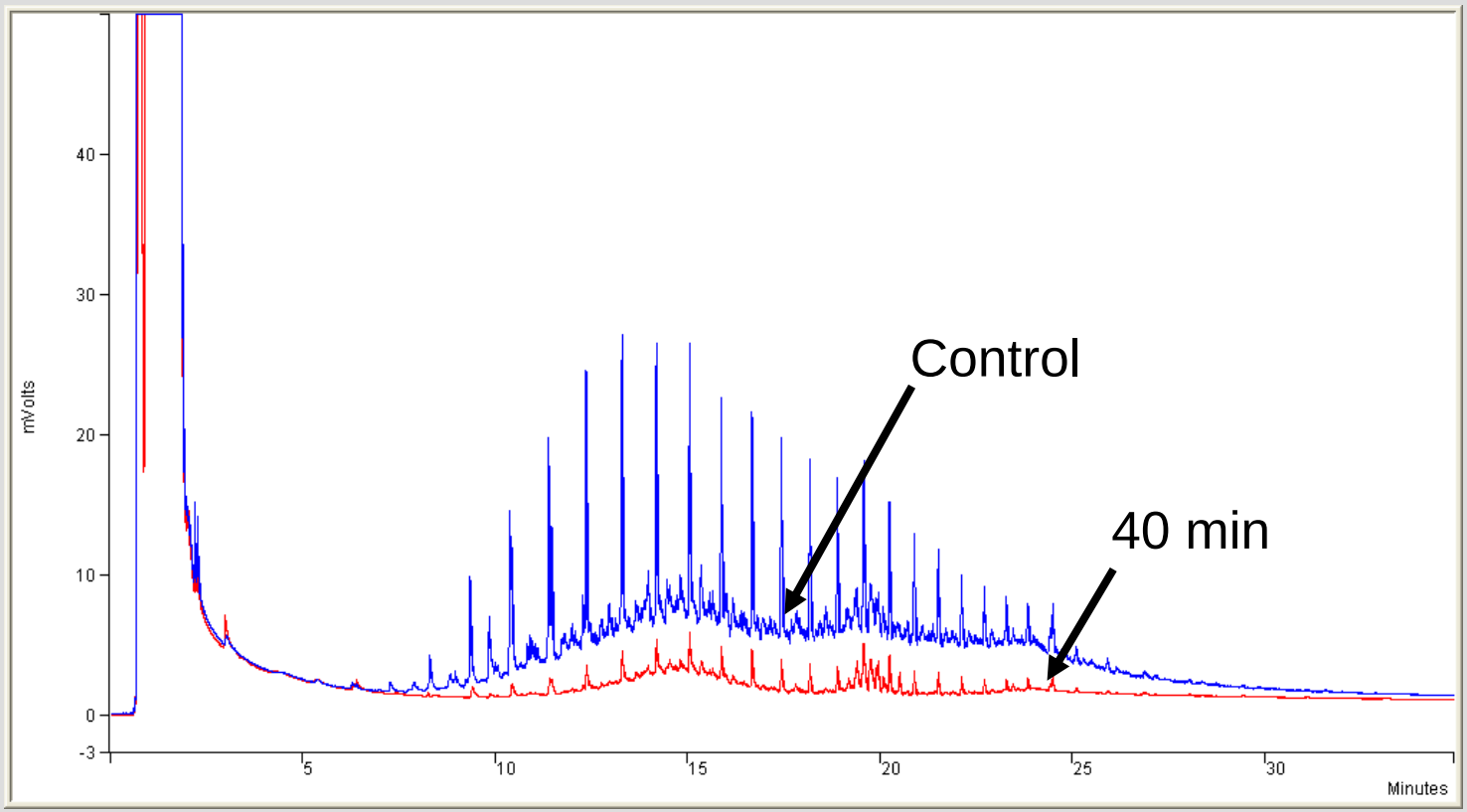
- Supplemental ultrasonic experiments
  - 2 min of ultrasonic treatment with different salt concentrations:
  - 0, 0.02, 0.03, 0.07, 0.14 mol/L



Even in very small amount of salt (0.03M) had a strong negative influence on TPH reduction. A decreasing trend of TPH reduction was observed.

Results

- **Gas chromatograph evidence of desorption**

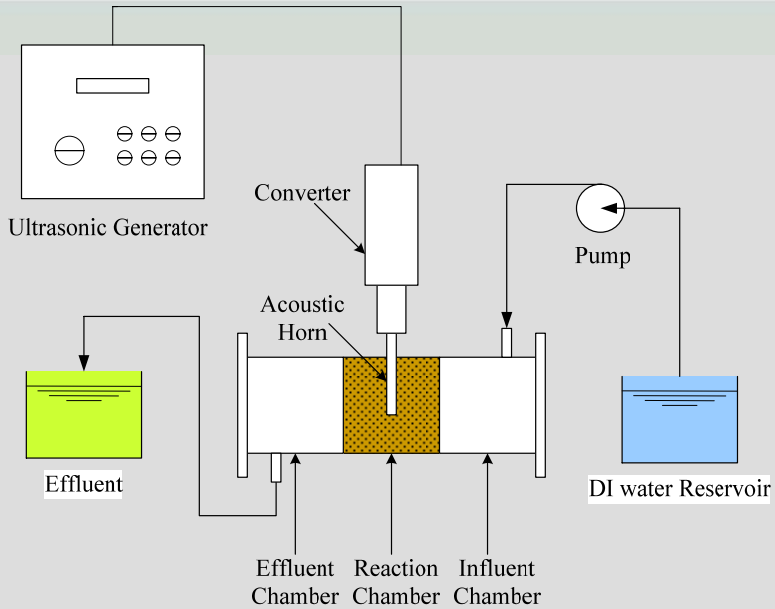


Conclusions

- The application of ultrasonic treatment significantly reduced concentrations of petroleum hydrocarbons and was most effective on granular soil free from salt impacts;
- The differences of TPH reduction between different soil types were related to soil properties such as surface area and grain size of the soils;
- The presence of salt in soil mixture greatly inhibited TPH reduction by reducing the solubility and mobility of hydrocarbons;
- The GC curve suggests that TPH reduction was best explained by desorption than degradation.

Conclusions

- **Further Research**
  - Continuous flushing/washing method



- **Challenges for Ultrasonic Remediation**
  - Operational requirements for clean water and subsequent waste water disposal
  - Costs and effort compared to alternative technologies
  - Fine grained soils and limits to soil flushing/washing

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