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Residual Saturation, Fire/Explosion Hazard and Hydrophobicity Methodology and Results
PTAC - GREEN ZONE SUBSOIL GUIDELINE PROJECT

Prepared by

ALBERTA INNOVATES – TECHNOLOGY FUTURES (AITF)

Bonnie Drozdowski, Bob Faught, and Dani Degenhardt

For

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1.0 INTRODUCTION

This PTAC project had two main objectives. The first, which was executed by Millennium EMS Solutions Ltd. was to investigate how far the roots of Alberta Green Zone trees penetrate into the ground, and hence identify a depth below which the ecological direct contact pathway may not be a primary concern. The second, and the subject of this document was to provide scientific evidence to support the management limits that may be appropriate at remote forested Green Zone sites on public land for non-mobile petroleum hydrocarbons (i.e., fractions F2 and F3) in soil.

Management limits currently exist for petroleum hydrocarbon (PHC) fractions F1 to F4. These management limits were calculated based on a range of considerations including: free phase formation, vapour exposure of workers in trenches, fire/explosion hazard, effects on buried infrastructure, aesthetics, and technological factors. These considerations were primarily developed with urban settings in mind.

Some of the considerations noted above are relevant to a remote Green Zone setting, and others are much less so. The Technical Steering Committee for this project agreed at their January 16, 2012 teleconference that the primary considerations of concern relevant to developing green zone management limits for F2, F3, and F4 were:

- Free phase formation;
- Fire/explosion hazard;
- Hydrophobicity; and,
- Upward migration.

These considerations include some from the existing management limits (free phase formation and fire/explosion hazard) and some new considerations (hydrophobicity and upward migration). The main objective of this study was to evaluate hydrophobicity, flammability and residual NAPL saturation of coarse and fine grained soil.

To determine residual saturation, the difference between free NAPL (non-aqueous phase liquid) and mobile NAPL must be quantified. Mobile NAPL was defined as being continuous in the pore space and flows under a pressure gradient or gravitational force. Residual NAPL was defined as immobile, non-water entrapped NAPL that does not drain from the pore spaces and is conceptualized as being either continuous or discontinuous (White et al., 2004). Below the residual saturation, NAPL becomes discontinuous and is immobilized by capillary forces (Mercer and Cohen 1990, Brost and DeVaull 2000). Residual NAPL concentrations in soil depend on NAPL properties including liquid density, surface tension and viscosity and soil properties such as porosity, organic carbon fraction, moisture content, relative permeability, moisture wetting history and soil heterogeneity (Brost and DeVaull 2000). Residual NAPL concentration in soil decreases with increasing particle size and is reduced at higher moisture contents (Brost and DeVaull 2000).

2.0 METHODOLOGY

The methods for this experimental approach were modified from White et al., (2004). The experiment was set up with the following variables:

- 2 soil types – coarse and fine grained soil
- 2 moisture contents – air dry and field capacity (saturated and drained for 24 to 48 hours)
- 2 hydrocarbon fractions – F2 (>nC10 to nC16) and F3 (>nC16 to nC34)

The overall experimental approach was:

1) Each of the coarse and fine textured soils were prepared – air dried, ground, screened to a uniform, homogenous size (2 mm) and homogenized by cone and quarter method (Schumacher et al., 1990).
2) The respective columns were packed to the specified bulk density (coarse textured soil ~ 1.3 g/cm^3 and fine textured soil ~1.4 g/cm^3).
3) Saturated 6 columns for each soil type with water by injecting water from the bottom of the column and applying a hydraulic pressure head to ensure the soil was entirely saturated from the bottom to the top. Once saturated, the soil was allowed to freely drain for a period of 24 to 48 hours until a field capacity moisture content was achieved. Graduated cylinders were used to measure the volume of liquid transferred into the soil.
4) Saturated wet soils with the appropriate PHC fractions
    a. 3 columns saturated with F2 PHC and 3 columns saturated with F3 PHC for each soil type in August 2012
    b. 6 columns saturated with F2 PHC and 6 columns saturated with F3 PHC for the fine soil type and 6 columns saturated with F2 PHC and 3 columns saturated with F3 PHC for the coarse textured soil in November 2012
5) Saturated 6 air dried columns with appropriate hydrocarbons.
    a. 3 columns saturated with F2 PHC and 3 columns saturated with F3 PHC for each soil type in August 2012
6) Calculated residual saturation by determining the amount of PHC required to saturate the soil material, and the amount of PHC collected after the soil had drained for 7 to 21 days. The difference was assumed to be the amount of PHC held by capillary tension in the soil and therefore considered residual saturation. This value was confirmed through sample analysis and the following calculation (for air dried columns) (Brost and DeVaull 2000):

$$C_{res} = (1.05 * \theta_T * P_o/P_s - 0.15) * 10^6 \text{ mg/kg}$$

Where:

C_{res} = residual NAPL concentration in soil (mg residual/kg soil)
θ_T = soil porosity (cm^3 void/cm^3 soil)
P_o = density of NAPL (g residual/cm^3 residual
P_s = bulk density of dry soil (g soil/ cm^3 soil)

7) Obtained soil samples from the top 15 cm of the columns and bottom 15 cm of the column and sent for PHC F1 to F4 analysis to EXOVA, an external accredited laboratory.

Upon completion of the initial experiment in August 2012 it was determined that the field capacity moisture content better represented reasonable worst case field conditions and the experiment was re-ran with 6 replicates for each of the treatments in November 2012:

- coarse and fine grained soil at field capacity
- F2 and F3 PHC

The methodology was slightly modified from White et al. (2004) during the second experiment in that all the columns had the F2 and F3 hydrocarbons added from the top off the column similar to the second experiment performed by White et al. (2004) and all columns were allowed to drain for 21 days after the addition of hydrocarbon.

2.1 F2 and F3 PHC Distillation

Appropriate PHC contaminants were obtained by the Fuels and Lubricants Laboratory at Alberta Innovates - Technology Futures by separating the various fractions of oil within a mixture of various crude oils by distillation (ASTM D2892). The distillation was at atmospheric pressure and was gradually heated to a boiler temperature of 273°C. The second distillation was at reduced pressure of 99.2 mm Hg to an AET (Atmospheric Equivalent Temperature) of 287°C. The final distillation to obtain the F3 fraction was a vacuum distillation to reach 481°C (atmospheric equivalent) (ASTM D5236). The following fractions were collected from the distillation:

Fraction #1: nC6 to nC10 (Initial Boiling Point (IBP) -174°C)
Fraction #2: >nC10 to nC16 (IBP -174°C-287°C)
Fraction #3: >nC16 to nC34 (IBP -287°C-481°C)
Fraction #4: nC35+ (IBP -481°C+)

Density measurements (ASTM D4052 or D5002) of the F2 and F3 fractions were used to obtain a proper mass balance and to quantify the amount of contaminant required for each soil and concentration:
F2 = 823.6 kg/m^3 @ 15°C (Calculated at 20°C = 820.1 kg/m^3)
F3 = 868.8 kg/m^3 @ 30°C

This methodology ensured there was no interference from other PHC fractions in the soil. The F2 and F3 PHC fractions were sent to EXOVA for mass fraction characterization by GC-FID (gas chromatogram flame ionized detector) and the chromatogram for each fraction is provided in Table 1 and Appendix A. The data indicate 96.4 % of the mass fraction of the F2 PHC products used in the experiments was within the defined F2 fraction and 94.5% of the F3 PHC product used in the experiments was within the defined F3 fraction. Sudan IV red dye (Fisher Scientific) was added to the F2 and F3 fractions at a concentration of 0.1 g/L to allow visual tracking of the fractions during saturation.

Table 1. Mass balance of F2 and F3 products used in experiments.

PHC Fraction	Carbon	Product		
		F2 - 2011	F2- 2012	F3-2012
F2	C11	0.168	0.175	<0.0001
	C12	0.137	0.146	<0.0001
	C13	0.154	0.148	<0.0001
	C14	0.202	0.193	0.0002
	C15	0.18	0.178	0.0008
	C16	0.123	0.124	0.014
Total within F2 Fraction		**96.4%**	**96.4%**	**1.5%**
F3	C17	0.0363	0.0343	0.066
	C18	0.0008	0.0005	0.0914
	C19	<0.0001	<0.0001	0.0835
	C20	<0.0001	<0.0001	0.076
	C21	<0.0001	<0.0001	0.0695
	C22	<0.0001	<0.0001	0.0656
	C23	<0.0001	<0.0001	0.0503
	C24	<0.0001	<0.0001	0.0646
	C25	<0.0001	<0.0001	0.0577
	C26	<0.0001	<0.0001	0.0486
	C27	<0.0001	<0.0001	0.056
	C28	<0.0001	<0.0001	0.0185
	C29	<0.0001	<0.0001	0.071
	C30	<0.0001	<0.0001	0.041
	C31	<0.0001	<0.0001	0.026
	C32	<0.0001	<0.0001	0.0314
	C33	<0.0001	<0.0001	0.0181
	C34	<0.0001	<0.0001	0.0097
Total within F3 Fraction		**3.7%**	**3.5%**	**94.5%**

2.2 Soil

Representative fine (Gleyed Grey Luvisol) and coarse (Orthic Dystric Brunisol) textured bulk soil samples were collected in the Cold Lake/Bonnyville area of Alberta on July 29, 2012. Samples were transferred to a drying room at 40^{o}C and mixed regularly.

When samples reached constant weights, the coarse textured bulk samples were passed through a 2 mm sieve to avoid clumping and achieve particle size consistency to prevent preferential flow within the columns. The samples were then homogenized using the cone and quartering method to ensure consistency of soil properties. The fine textured bulk samples first had the large clumps reduced with a soil chipmunker and were then ground to 2 mm and homogenized using the cone and quartering method (Schumacher et al. 1990) (Plate 1).

Plate 1. Cone and quartering and sieving of bulk coarse textured soil samples prior to column preparation.

Three representative grab samples of the fine and coarse textured soils were submitted to EXOVA for basic salinity, 75 µm sieve, Total C, particle size distribution by hydrometer and Alberta Tier 1 particle size confirmation.

2.3 Column Preparation

Soil column experiments were conducted using 1000 mL glass graduated cylinders equipped with an attached bottom valve used for saturating and draining procedures. To prevent soil from moving out of the column during saturation and draining a filter was constructed at the bottom of column. The filter consisted of a glass wool layer, a 5 cm layer of glass beads, another layer of glass wool covered by a 1 mm mesh screen on top (Plate 2).

Plate 2. Glass beads, glass wool and 1 mm screen used as a filter in the bottom of each soil column.

The cylinders were filled with a known volume of coarse or fine soil using a funnel attached to tubing which was gradually moved upwards during filling to maintain soil contact and ensure even particle size distribution through the soil column. After each 75 grams of soil addition, the cylinder was tapped 10 times to eliminate voids and avoid differential flow during saturation and draining.

The soil bulk density achieved was determined from the weight of soil added to achieve a 30 cm height in the column (Plate 3).

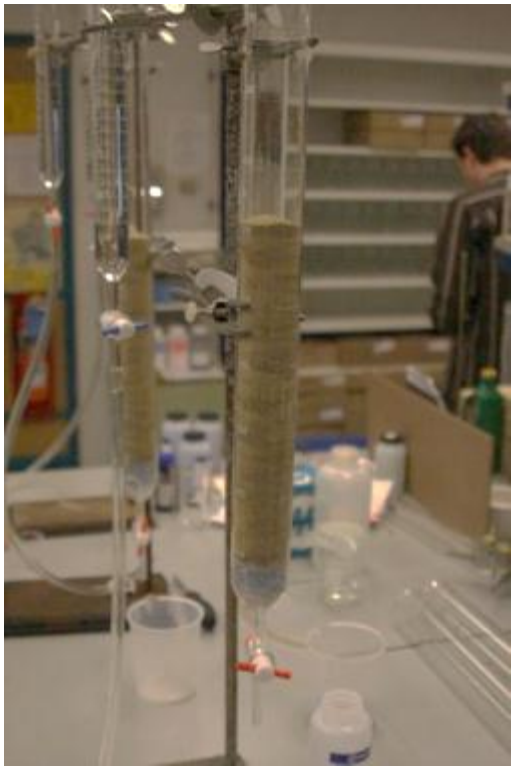

Plate 3. Soil added to achieve a 30 cm column.

2.4 Soil Moisture Content

In August 2012, three replicates of coarse and fine grained columns were saturated with water and allowed to drain to field capacity (24 to 48 hours). Water saturation was achieved through the addition of water from the bottom of the column. A 250 ml graduated cylinder with attached tubing was assembled next to the soil column at a higher level to achieve an appropriate hydraulic head. Water flowed from the 250 ml cylinder to the soil column until the wetting front reached the top of the soil and the soil was completely saturated (Plate 4). The amount of water required to reach saturation was recorded when free water appeared at the top of the soil column. The columns were then allowed to drain for 24 to 48 hours and the amount of water collected was recorded.

In November 2012, 12 fine grained columns and 9 coarse grained columns were saturated with water the same way as described above and allowed to drain to field capacity to prepare additional replicates to repeat the experiment.

Plate 4. Water saturation of columns by hydraulic head.

2.5 Residual Saturation

2.5.1 F2 PHC Fraction – August 2012

Saturation of the soil columns with the F2 PHC fraction was achieved in August 2012 by adding Sudan IV dyed F2 PHC from the bottom of the column to prevent air locks. The dye allowed for visual tracking of the F2 fraction as it moved through the column and confirmation of the formation of free phase F2 on the surface. The F2 saturation point for each soil and moisture content was determined as the amount added to achieve visual presence of free phase F2 PHC at the soil column surface (Plates 5 and 6). Saturation was achieved in a matter of hours for both soil types under dry conditions.

Plate 5. Saturation of the Columns with Sudan IV Dyed F2 Fraction in August 2012.

Plate 6. Free phase F2 PHC on the surface of a coarse grained replicate.

After hydrocarbon saturation was achieved the tubing supplying the F2 PHC was removed and the F2 freely drained into a beaker. The dry coarse and fine grained F2 PHC saturated columns were allowed to drain for 7 days (Table 2) (White et al. 2004), after which the residual content of the F2 PHC fraction was

evaluated by physically sampling and analyzing the F2 PHC concentration in the soil. The columns were sampled by inverting the column and selectively collecting the 0-15 cm and 15-30 cm depths (Plate 7). Each depth was homogenized individually, packed into 250 ml glass jars and sent to EXOVA for Alberta Tier 1 PHC analysis.

Table 2. Method of hydrocarbon saturation and # of column drainage days in August 2012 trial.

PHC	Moisture Content	Replicate	Coarse Soil		Fine Soil	
			Hydrocarbon Addition*	# days drained	Hydrocarbon Addition*	# days drained
F2	Dry	1	Bottom	7	Bottom	7
		2	Bottom	7	Bottom	7
		3	Bottom	7	Bottom	7
F2	FC	1	Bottom	8	Top	30
		2	Bottom	8	Top	30
		3	Bottom	8	Top	30
F3	Dry	1	Top	8	Top	19
		2	Top	25	Top	24
		3	Top	8	Top	19
F3	FC	1	Top	25	Top	15
		2	Top	8	Top	15
		3	Top	8	Top	15

**Hydrocarbon addition either from the top or bottom of the soil column as in the first and second experiments described in White et al. (2004).*

Plate 7. Collecting samples for residual F2 PHC analysis.

The wet coarse textured columns were treated similarly and were saturated from the bottom of the column with F2 PHC until free phase hydrocarbons formed on the surface. The columns (3 replicates) were then allowed to drain freely for 7 days (Table 2).

There were difficulties saturating the wet fine textured columns with F2 PHC. The hydrocarbon material would not infiltrate the soil from the bottom regardless of the hydraulic head, therefore the hydrocarbon was applied to the top of the column and allowed to saturate the wet fine textured soil by gravity. It took nearly 7 days for the hydrocarbons to reach the bottom of the 30 cm column. Once visual confirmation of saturation was confirmed, free hydrocarbon was removed from the top of the columns and the columns

were allowed to drain. Given the time required to saturate the columns, additional time was allocated for drainage (Table 2).

2.5.2 F3 PHC Fraction – August 2012

The high viscosity and wax content of the F3 PHC fraction obstructed the saturation of the soil using the hydraulic head pressure method, therefore F3 PHC was added to the top of the soil column and saturation was achieved using gravitational force similar to the second experiment conducted by White et al. (2004) (Plate 8). Difficulties with saturation of the coarse and fine wet soils with F3 PHC included solid wax buildup at the top of the soil column and restricted flow. Solid wax formation at the top and bottom of the column was liquefied with a stream of hot air or heating coil to remove the waxy buildup (Plate 9). In the event of flow restriction a small suction was applied to the outlet valve of the column. Saturation of the F3 fraction was determined when the first amount of F3 appeared at the cylinder outlet valve. Displaced water remaining in the column was collected.

It was determined that 7 days may not be sufficient to adequately drain the entire 30 cm column therefore one replicate from each of the dry and wet coarse textured columns saturated with F3 PHC were left to drain for longer (Table 2). The fine textured soils also required additional time to reach F3 saturation; therefore all columns were allowed to drain for a longer time period (Table 2). The third replicate in the fine wet F3 PHC treatment was compromised during sampling and contaminated with free F3 PHC, therefore was not submitted for analysis.

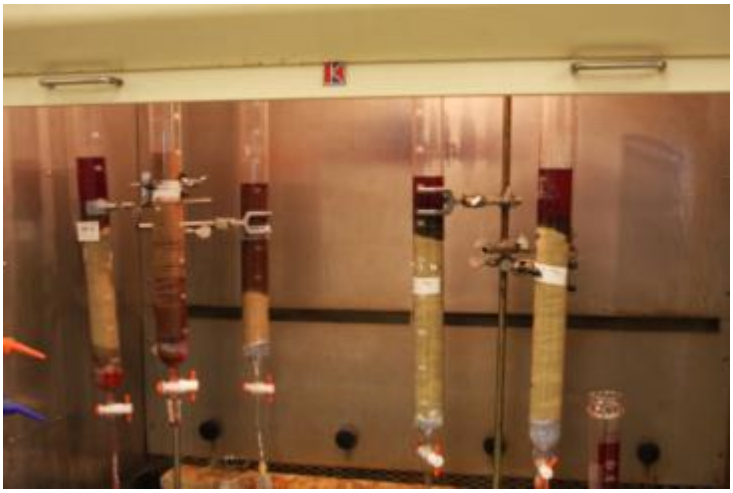

Plate 8. Saturating dry coarse and fine textured columns with F3 PHC using gravity method.

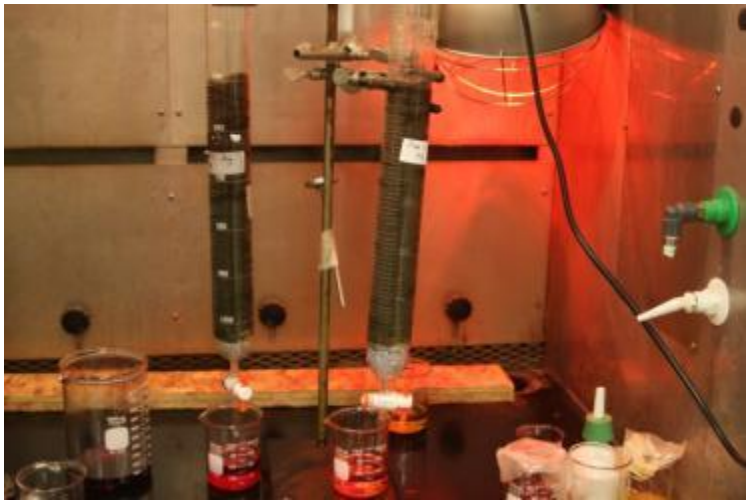

Plate 9. F3 Fraction wax buildup and heat lamp for liquefying solids.

2.5.3 F2 and F3 PHC Fraction – November 2012

Due to high variability in the trial conducted in August, and the refinements in methodology that were developed during this trial, it was determined that additional replication was desirable to increase the confidence in the evaluation, therefore another experiment was initiated in November 2012. The methodology differed from the August 2012 trial in that all PHCs were added from the top of the soil column and the columns were allowed to drain for 21 days. The detailed methods were as follows:

1) 12 fine textured columns were packed to a bulk density of ~1.4 g/cm^{3}and 9 coarse textured columns were packed to a bulk density of ~ 1.3 g/cm^3.
2) Saturated all columns with water by injecting water from the bottom of the column and applying a hydraulic pressure head to ensure the soil was entirely saturated from the bottom to the top. Once saturated, the soil was allowed to freely drain for a period of 24 to 48 hours until a field capacity moisture content was achieved. Graduated cylinders were used to measure the volume of liquid transferred into the soil.
3) Added appropriate Sudan IV dyed PHC fractions to the columns:
    a. 6 fine textured columns saturated with 100 ml F2 PHC
    b. 6 coarse textured columns saturated with 100 ml F2 PHC
    c. 6 fine textured columns saturated with 100 ml F3 PHC
    d. 3 coarse textured columns saturated with 100 ml F3 PHC (coarse soil was only replicated three times for confirmatory experimentation because it was known from the hydrophobicity analysis that the management limits would be limited by the concentration at which the soil became hydrophobic as opposed to residual saturation).
4) Samples drained for 21 days and the amount of PHC recovered from individual columns was recorded for mass balance quantifications (Table 3).
5) Obtained soil samples from the top 15 cm of the columns and bottom 15 cm of the column and sent for PHC F1 to F4 analysis to EXOVA, an external accredited laboratory.

6) EXOVA analyzed each sample (2 depths for each soil column) in triplicate to provide data for statistical analysis of lab and sample variance (i.e., both depths within individual columns had three samples prepped and analyzed).

Difficulties encountered in August with restricted flow and wax build up in the F3 PHC columns were not an issue during the November trial. All columns drained well resulting in approximately 54 to 71 ml of recovered F3 PHC from the columns. There was a wax buildup at the top of the F3 PHC columns however it was removed prior to sampling.

Table 3. Method of hydrocarbon saturation and # of column drainage days in October 2012 trial.

PHC	Moisture Content	Replicate	Coarse Soil		Fine Soil	
			Hydrocarbon Addition*	# days drained	Hydrocarbon Addition*	# days drained
F2	FC	1	Top	21	Top	21
		2	Top	21	Top	21
		3	Top	21	Top	21
		4	Top	21	Top	21
		5	Top	21	Top	21
		6	Top	21	Top	21
F3	FC	1	Top	21	Top	21
		2	Top	21	Top	21
		3	Top	21	Top	21
		4	-	-	Top	21
		5	-	-	Top	21
		6	-	-	Top	21

**Hydrocarbon addition either from the top of the soil column as in the second experiments described in White et al. (2004).*

2.6 Hydrophobicity

The Molarity of Ethanol Droplet (MED) test was used to assess soil hydrophobicity (King 1981). A total of 31 ethanol solutions were prepared to include all 0.2 M increments from 0.0 to 6.0 M concentrations (Plate 10).

The following series of 10 concentrations plus control was initially prepared with dry soil in August 2012 for F2 and F3 PHC fractions: 0, 125, 250, 500, 1,000, 2,000, 4,000, 8,000, 16,000, 32,000, 64,000 mg/kg for each soil type. The samples were prepared from a stock of the highest concentration, diluted with clean dry soil to achieve the targeted concentration (Plate 10).

The rationale for this series was that the factor of 2 between each concentration allowed for reasonable precision in the determination of the critical effect, the low end is below the current Tier 1 guideline for all PHC fractions, and the upper end extends into the range where F2 is known to separate from a fine grained soil (based on observations in a PTAC ecotoxicity study (Tindal, Personal Communication, 2012)).

A second hydrophobicity test was conducted in December 2012 to narrow down the concentration which coarse and fine textured soils were affected by F3 PHC. An additional 7 to 10 concentrations were evaluated for each dry soil type between the concentrations where hydrophobicity was noted in August. The materials were evaluated with a 0.0 M ethanol solution (i.e., water) to determine the lowest concentration of F3 contamination which caused any amount of hydrophobicity (i.e., prevented the water droplet from entering the soil within 10 seconds) as per the MED test.

A second stock of dry coarse and fine grained materials were contaminated to 64,000 mg F3 PHC/kg to determine if there would be any differences between age of contaminants, to increase the confidence in the measurements and to narrow down the range of concentrations. It was determined that the nature of the test was too subjective to narrow the range to a specific concentration therefore the evaluation was completed when there was a good degree of confidence in the range.

Plate 10. Preparation of ethanol solutions and contaminated soils for hydrophobicity testing.

2.7 Flammability and Explosion Hazard

A simple flammability test was performed on the contaminated soil by applying a flame directly to the soil surface for 3-5 seconds. Flammability tests were also performed on the liquid F2 and F3 fractions (Plate 11).

Plate 11. Flammability test on contaminated soils and F2 and F3 liquid fractions.

2.8 Hydrocarbon Remobilization

There were concerns that some of the residual hydrocarbons could remobilize if the soil were flooded, therefore one of each of the F2 PHC and F3 PHC fine texture columns (replicate 6 and replicate 4, respectively) were retained from the November 2012 trial and used for a remobilization trial. A coarse F2 PHC column was also set up for the trial, however no column was prepared for the coarse F3 PHC given that it had been determined that management limit was not going to be established based on residual saturation and would be considerably lower based on hydrophobicity analysis and pose very limited risk to remobilization.

The columns were flooded through the addition of water from the bottom of the column. A 250 ml graduated cylinder with attached tubing was assembled next to the soil column at a higher level to achieve an appropriate hydraulic head. Water flowed from the 250 ml cylinder to the soil column until the wetting front reached the top of the soil and the soil was completely saturated (Plate 12). The water was allowed to surpass the surface of the soil by approximately 5 cm (Plate 13). Sudan IV was added to the surface of the water to enable easier visual detection of hydrocarbons. The columns were allowed to sit for 12 hours for the particles to settle and the surface of the water was visually assessed for hydrocarbons which had been remobilized and replaced by water in the soil columns.

Plate 12. Water saturation of Fine F2 and F3 PHC and Coarse F2 PHC columns after the residual saturation trial.

Plate 13. Over saturation of water in Fine F3 PHC remobilization trial

3.0 RESULTS

3.1 Soils

Basic soil physical and chemical analyses were completed for the coarse and fine textured soils and are provided in Tables 4 and 5. Analyses confirmed the appropriate texture and inorganic properties of the soils for use in the residual saturation experiments.

Table 4. Texture and classification of soils used in residual saturation column experiment.

Soil Type	Texture	Sand	Silt	Clay	Wet Sieve	Texture
		2mm-50µm	50µm-2µm	>2µm	75µm sieve	
		% by weight			% retained by weight	
Fine	Loam	30	48	22	19.8	Fine
Coarse	Sand	97	<0.1	3	95.8	Coarse

Table 5. Properties of soils used in residual saturation column experiment.

Soil Type	pH	EC (dS/m)	SAR	Total Carbon %	Dry Bulk Density‡	Water Holding Capacity		
						FC*	WP±	AWHC
					(g/cm^3)	Volumetric %		
Fine	7.5	1.63	0.5	0.46	1.26	28.4	12.2	16.2
Coarse	6.6	0.08	0.4	<0.05	1.48	4.3	1.4	2.9

‡*Dry Bulk density targeted in the soil columns*

**FC – Field capacity – determined with pressure plate analysis at 33 kPa for fine textured soil and 10 kPa for coarse textured soil*

± *WP – Wilting point – determined with pressure plate analysis at 1500 kPa*

3.2 Moisture Contents

The saturation and field capacity were determined for the wet columns evaluated in August 2012 (data not reported). The amount of water required to saturate the columns was measured and compared to the amount of water collected after the columns freely drained for 24 to 48 hours. Field capacity was calculated from the difference. Additional columns were prepared in November 2012 and the volumetric water content in each column was recorded prior to hydrocarbon addition (Tables 6 to 9).

Table 6. Volumetric water content of fine textured soil columns prior to F2 PHC addition in November 2012.

Soil	Replicate	Volumetric Water Content cm^3 water/cm^3 soil	
		Saturation	Field Capacity
Fine (F2)	1	0.46	0.40
	2	0.46	0.39
	3	0.48	0.42
	4	0.48	0.39
	5	0.44	0.31
	6	0.48	0.39
	Average (StDev)	**0.47 (0.02)**	**0.38 (0.14)**

Table 7. Volumetric water content of fine textured soil columns prior to F3 PHC addition in November 2012.

Soil	Replicate	Volumetric Water Content cm^3 water/cm^3 soil	
		Saturation	Field Capacity
Fine (F3)	1	0.47	0.38
	2	0.48	0.40
	3	0.50	0.39
	4	0.44	0.35
	5	0.44	0.35
	6	0.44	0.35
	Average (StDev)	**0.46 (0.03)**	**0.37 (0.02)**

Table 8. Volumetric water content of coarse textured soil columns prior to F2 PHC addition in November 2012.

Soil	Replicate	Volumetric Water Content cm^3 water/cm^3 soil	
		Saturation	Field Capacity
Coarse (F2)	1	0.40	0.34
	2	0.39	0.32
	3	0.40	0.32
	4	0.38	0.32
	5	0.40	0.34
	6	0.40	0.32
	Average (StDev)	**0.39 (0.01)**	**0.33 (0.01)**

Table 9. Volumetric water content of coarse textured soil columns prior to F3 PHC addition in November 2012.

Soil	Replicate	Volumetric Water Content cm^3 water/cm^3 soil	
		Saturation	Field Capacity
Coarse (F3)	1	0.39	0.32
	2	0.41	0.32
	3	0.39	0.32
	Average (StDev)	**0.39 (0.01)**	**0.32 (0.004)**

3.3 F2 PHC Fraction

Results are presented from analytical analysis as opposed to the quantified mass balance of hydrocarbons within the soil columns due to increased confidence in the results. Accuracy was difficult to obtain with mass balance quantifications as a result of the volume of hydrocarbon retained within the glass beads/filter at the bottom of the column and volatilization losses during drainage. Results of analysis ran by Exova for the August 2012 trial on the coarse and fine F2 PHC residual saturation columns are presented in Tables 10 and 11, respectively. Given the variability in the coarse 0-15 cm depth, there were some uncertainties in the reported data and Exova was contacted in October to re-extract and analyze the coarse replicate 3 for the 0-15 cm depth (1,510 mg/kg). The results were exactly the same after the second extraction (1,510 mg/kg).

The air dry soil for both the coarse and fine textured materials was able to retain more F2 PHC than the wetter soil and the fine textured soil retained more than the coarse. The dry soil results for both hydrocarbon fractions are comparable with those reported by Brost and DeVaull (2000) for dry soils of similar texture and NAPLs, and the calculated values obtained by the equation outlined in Section 2.0 above (Table 12). It was speculated that the 0-15 cm depth better represented residual saturation given that the hydrocarbon first drained from the 0-15 cm depth into the 15-30 cm depth and then out of the column. If there were any restrictions of hydrocarbon movement within column then the 15-30 cm depth

would likely be over saturated. The standard deviations were high among replicates therefore an additional experiment with more replicates initially at field capacity moisture content was conducted to increase the confidence in the reported values.

The experiment was set up again in November 2012 with one moisture content (Field Capacity) and six replicates. The F2 PHC (coarse soil – Table 13; fine soil – Table 14) was added from the top and the columns drained for 21 days. Five of the six replicate samples were sent to Exova for analysis and were extracted and analyzed in triplicate to better understand the variability associated with the samples and analytical analysis.

Table 10. F2 PHC residual saturation for coarse textured soil at field capacity and air dry moisture contents measured at 0-15 and 15-30 cm depths in August 2012.

Soil	Replicate	Sample Depth	Residual F2 (C10-C16) PHC Concentration (mg/kg)	
			Dry	**Field Capacity**
Coarse	1	0-15	33,800	8,900
	2		42,300	13,400
	3		22,400	1,510*
	Average (StDev)		**32,833 (9,985)**	**11,150 (3,182)**
Coarse	1	15-30	125,000	13,600
	2		114,000	16,100
	3		60,500	12,600
	Average (StDev)		**99,833 (34,504)**	**14,100 (1,803)**

**Confirmed by second analysis performed by Exova in October 2012*

Table 11. F2 PHC residual saturation for fine textured soil at field capacity and air dry moisture contents measured at 0-15 and 15-30 cm depths in August 2012.

Soil	Replicate	Sample Depth	Residual F2 (C10-C16) PHC Concentration (mg/kg)	
			Dry	**Field Capacity**
Fine	1	0-15	137000	9,860
	2		147000	20,400
	3		129000	15,500
	Average (StDev)		**137,666 (7,364)**	**15,253 (4,306)**
Fine	1	15-30	117,000	12,600
	2		91,700	16,900
	3		163,000	18,800
	Average (StDev)		**123,900 (29,514)**	**16,100 (2,594)**

Table 12. Calculated and measured residual saturation of coarse and fine soil for different NAPLs.

Soil and NAPL Type	Liquid Density (g/cm^3)	C_{res} (Calculated)** mg/kg	C_{res} (Measured)‡ mg/kg
Coarse F2	0.8236	107,097	22,400-125,000
Coarse F3	0.8688	121,207	40,400-158,000
Fine F2	0.8236	151,987	91,700-163,000
Fine F3	0.8688	168,560	49,500-157,000
gasoline*	0.78	3,400 to 80,000	-
diesel* (a,b)	0.94	7,700 to 34,000	-
fuel oil* (a,b)	0.94	17,000 to 50,000	-
mineral oil* (c)	0.81	20,000 to 150,000	-

** unsaturated zone fine to medium sand*

(a - Fussel et al. (1981); b - API (1980); c - Pfannkuch (1984)) in Brost and DeVuall (2000)

*** calculated based on dry soil and equation 5 in Brost and DeVuall (2000)*

‡ range observed in dry soil columns evaluated in August 2012 trial

Table 13. F2 PHC residual saturation for coarse textured soil at field capacity moisture content measured at 0-15 and 15-30 cm depths in November 2012.

Soil	Replicate	Sample Depth	Residual F2 (C10-C16) PHC Concentration (mg/kg)				
			Run 1	**Run 2**	**Run 3**	**Sample/Lab Mean***	**Sample/Lab StDev***
Coarse	1	0-15	14,800	17,200	15,200	15,733	1,286
	2		17,400	21,000	17,800	18,733	1,973
	3		15,300	17,100	14,600	15,667	1,290
	4		8,180	7,410	7,760	7,783	386
	5		14,400	15,800	16,300	15,500	985
	6		19,600	21,400	12,200	17,733	4,876
	Replicate Average (StDev)					15,192 (3,860)‡	
Coarse	1	15-30	21,000	19,500	20,600	20,367	777
	2		23,600	27,700	19,400	23,567	4,150
	3		24,100	25,300	23,800	24,400	794
	4		10,700	10,700	12,500	11,300	1,039
	5		13,100	12,200	20,100	15,133	4,325
	6		23,900	25,000	27,900	25,600	2,066
	Replicate Average (StDev)					20,061 (5,708) ‡	

**Sample/Lab Mean and StDev represent the statistics and variability reported for the triplicate analysis reported by Exova for individual replicates*

‡Replicate Average (StDev) represents the variability for all replicates at that depth in the soil column and was calculated from the Sample/Lab Mean

Table 14. F2 PHC residual saturation for fine textured soil at field capacity moisture content measured at 0-15 and 15-30 cm depths in November 2012.

Soil	Replicate	Sample Depth	Residual F2 (C10-C16) PHC Concentration (mg/kg)				
			Run 1	**Run 2**	**Run 3**	**Sample/Lab Mean***	**Sample/Lab StDev***
Fine	1	0-15	7,740	7,520	7,410	7,557	168
	2		11,800	12,400	9,050	11,083	1,786
	3		10,700	10,300	10,400	10,467	208
	4		10,400	10,600	9,980	10,327	316
	5		11,400	12,100	10,900	11,467	603
	6	water mobility experiment					
	Replicate Average (StDev)					10,180 (1,538) ‡	
Fine	1	15-30	6,990	5,990	6,790	6,590	529
	2		8,710	-	9,190	8,950	339
	3		9,900	9,800	9,880	9,860	53
	4		9,960	12,300	8,750	10,337	1,805
	5		11,300	14,000	10,800	12,033	1,721
	6	water mobility experiment					
	Replicate Average (StDev)					9,554 (2,000) ‡	

**Sample/Lab Mean and StDev represent the statistics and variability reported for the triplicate analysis reported by Exova for individual replicates*

‡Replicate Average (StDev) represents the variability for all replicates at that depth in the soil column and was calculated from the Sample/Lab Mean

3.4 F3 PHC Fraction

Results of analyses run by Exova in September 2012 on the coarse and fine F3 PHC residual saturation columns are presented in Tables 15 and 16, respectively). There were several sample results reported by Exova that created were questionable therefore Exova was contacted in October to re-extract and analyze the fine replicate 3 for the 0-15 cm depth for both moisture contents and the fine replicate 3 for the 15-30 cm depth at field capacity. The data were very different. The dry F3 Fine replicate 3 (0-15 cm) was reduced from 413,000 mg/kg to 163,000 mg/kg. The field capacity F3 fine replicate 3 (0-15 cm) was increased from 1,230 mg/kg to 29,100 mg/kg. The field capacity F3 replicate 3 (15-30 cm) was increased from non-detect (<50 mg/kg) to 6,350 mg/kg (Table 16).

Similarly to the F2 PHC trial it was determined that the air dry soil for both the coarse and fine textured materials was able to retain more F3 PHC than the wetter soil and the results were in the ranges reported by Brost and DeVaull (2000) (Table 12). Due to difficulties with saturating the wet fine soil columns with F3 PHC it was difficult to make comparisons between the fine and coarse textured soil. The standard deviations were high among replicates therefore it was determined that an additional experiment

with more replicates initially at field capacity moisture content would be conducted to increase the confidence in the reported values.

Table 15. F3 PHC residual saturation for coarse textured soil at field capacity and air dry moisture contents measured at 0-15 and 15-30 cm depths in August 2012.

Soil	Replicate	Sample Depth	Residual F3 (C16-C34) PHC Concentration (mg/kg)	
			Dry	**Field Capacity**
Coarse	1	0-15	40,400	45,300
	2		158,000	30,500
	3		44,200	28,300
	Average (StDev)		**80,867 (54,564)**	**29,400 (7,549)**
Coarse	1	15-30	80,200	69,800
	2		125,000	60,500
	3		112,000	48,400
	Average (StDev)		**105,733 (18,819)**	**54,450 (8,761)**

Table 16. F3 PHC residual saturation for fine textured soil at field capacity and air dry moisture contents measured at 0-15 and 15-30 cm depths in August 2012.

Soil	Replicate	Sample Depth	Residual F3 (C16-C34) PHC Concentration (mg/kg)	
			Dry	**Field Capacity**
Fine	1	0-15	118,000	31,500
	2		49,500	Not Available
	3		163,000*	29,100*
	Average (StDev)		**110,167 (45,666)**	**30,300 (1,200)**
Fine	1	15-30	114,000	8,660
	2		157,000	Not Available
	3		90,100	6,350*
	Average (StDev)		**120,367 (27,680)**	**7,505 (1,155)**

* *Based on second analysis performed by Exova in October 2012*

The experiment was set up again in November 2012 with field capacity moisture content using six replicates for the fine soil and three replicates for the coarse soil. Results of analyses ran by Exova in November 2012 for the F3 PHC coarse textured soil columns and fine textured soil columns are presented in Tables 17 and 18, respectively. Samples were sent to Exova for analysis and were extracted and analyzed in triplicate to better understand the variability associated with the samples and analytical analysis. Replicate 4 from the fine F3 PHC experiment was not sampled and used for a remobilization evaluation therefore the replicate average is only quantified from 5 samples.

Table 17. F3 PHC residual saturation for coarse textured soil at field capacity and air dry moisture contents measured at 0-15 and 15-30 cm depths in November 2012.

Soil	Replicate	Sample Depth	Residual F3 (C16-C34) PHC Concentration (mg/kg)				
			Run 1	**Run 2**	**Run 3**	**Sample/Lab Mean***	**Sample/Lab St.Dev***
Coarse	1	0-15	35,800	45,200	42,000	41,000	4,779
	2		39,500	35,100	52,200	42,267	8,879
	3		37,600	39,700	39,100	38,800	1,082
	Replicate Average (StDev)					40,689 (1,754)**	
Coarse	1	15-30	31,600	27,400	34,400	31,133	3,523
	2		34,800	39,100	40,100	38,000	2,816
	3		30,000	29,800	34,500	31,433	2,658
	Replicate Average (StDev)					33,522 (3,881)**	

**Sample/Lab Mean and StDev represent the statistics and variability reported for the triplicate analysis reported by Exova for individual replicates*

***Replicate Average (StDev) represents the variability for all replicates at that depth in the soil column and was calculated from the Sample/Lab Mean*

Table 18. F3 PHC residual saturation for fine textured soil at field capacity and air dry moisture contents measured at 0-15 and 15-30 cm depths in November 2012.

Soil	Replicate	Sample Depth	Residual F3 (C16-C34) PHC Concentration (mg/kg)				
			Run 1	**Run 2**	**Run 3**	**Sample/Lab Mean***	**Sample/Lab St.Dev***
Fine	1	0-15	36,300	34,200	19,800	30,100	8,982
	2		31,200	29,200	32,800	31,067	1,804
	3		39,400	37,100	47,800	41,433	5,632
	4		water mobility experiment				
	5		35,100	36,100	38,600	36,600	1,803
	6		21,100	20,400	16,800	19,433	2,307
	Replicate Average (StDev)					31,727 (8,249)**	
Fine	1	15-30	9,570	10,200	11,700	10,490	1,094
	2		20,700	20,900	20,500	20,700	200
	3		13,900	13,700	14,300	13,967	306
	4		water mobility experiment				
	5		17,100	17,100	19,900	18,033	1,617
	6		7,940	8,770	9,380	8,697	723
	Replicate Average (StDev)					14,377 (5,022)**	

**Sample/Lab Mean and StDev represent the statistics and variability reported for the triplicate analysis reported by Exova for individual replicates*

***Replicate Average (StDev) represents the variability for all replicates at that depth in the soil column and was calculated from the Sample/Lab Mean*

3.5 Hydrophobicity

The initial hydrophobicity analysis was conducted in August 2012. It was determined that no hydrophobicity was exhibited for coarse and fine textured soil contaminated with 64,000 mg/kg F2 PHC (Table 19) therefore no other hydrocarbon concentrations were evaluated for the F2 PHC fraction.

Coarse and fine textured soils exhibited severe hydrophobicity when contaminated with 64,000 mg/kg of F3 PHC, therefore a series of F3 PHC concentrations were prepared for each soil type to narrow down the threshold concentration for this effect. It was determined that the fine soil exhibited slight hydrophobicity at 32,000 mg/kg F3 PHC and coarse soil exhibited medium hydrophobicity at 8,000 mg/kg F3 PHC. Additional concentrations and replication were required to narrow down the range to a specific concentration, however due to the subjective nature of the test it was also decided to contaminate a new batch of soil and re-evaluate with multiple aged contaminated sources.

Table 19. Hydrophobicity analysis of coarse and fine textured soils contaminated with various concentrations of F2 and F3 PHCs in August 2012.

Texture	PHC Fraction	Concentration (mg/kg)	MED*	Hydrophobicity Ranking†
Fine	F2	64,000	0	None
Coarse	F2	64,000	0	None
Fine	F3	32,000	0.2	Slight
Fine	F3	64,000	5.8	Severe
Coarse	F3	8,000	1.2	Medium
Coarse	F3	16,000	5.4	Severe
Coarse	F3	32,000	6	Severe
Coarse	F3	64,000	6	Severe

**MED - Molarity of Ethanol Droplet test (Watson and Letey 1970; King 1981). Indices recorded as the molarity of lowest ethanol concentrations to penetrate completely into soil within 10 seconds.*

†*Hydrophobicity ranking - Slight (MED ≤ 1.2M); Moderate (1.2M ≤ MED ≤ 2.2M); Severe (MED > 2.2M)*

Additional hydrophobicity analysis was performed in November 2012 on the fine contaminated materials prepared in August 2012 (August stock). The analysis indicated that 11 out of 12 samples allowed water (0.0 M ethanol in the MED test) to penetrate the fine soil within 10 seconds at 40,000 mg/kg F3 PHC (Table 20). The difference between the August and November hydrophobicity analysis on the August stock could be attributed to lack of replication during the August analysis and the subjectivity of the test. Additional analysis was performed on fine contaminated materials prepared fresh in November (November stock) and indicated at 5 out of 6 samples allowed water to penetrate the fine contaminated soil within 10 seconds at 56,000 mg/kg F3 PHC. This indicated that there was an effect of the age of the contaminated material. The threshold effect concentration for hydrophobicity with F3 in fine textured soils is considered to be 40,000 mg/kg F3 PHC (Table 20).

Table 20. Hydrophobicity analysis of fine textured soils contaminated with various concentrations of F3 PHCs in December 2012.

Replicate	mg F3/kg			mg F3/kg					
	August stock*			November stock**					
	40,000	42,000	46,000	42,000	48,000	50,000	52,000	56,000	58,000
1	v	x	x	v	v	v	v	v	x
2	v	x	x	v	v	v	v	v	x
3	v	x	x	v	v	v	v	v	x
4	v	x	x	v	v	v	v	x	x
5	x	x	x	v	v	v	v	v	x
6	v	x	x	v	v	v	v	v	x
7	v	x	x	-	-	-	-	-	-
8	v	x	x	-	-	-	-	-	-
9	v	x	x	-	-	-	-	-	-
10	v	x	x	-	-	-	-	-	-
11	v	x	x	-	-	-	-	-	-
12	v	x	x	-	-	-	-	-	-

v- water droplet penetrates within 10 seconds; x- water droplet does not penetrate within 10 seconds
**original stock prepared in August 2012; ** Second stock prepared November 20, 2012*

Hydrophobicity analysis was performed in November 2012 on the coarse contaminated materials prepared in August 2012 (August stock) and freshly contaminated materials (November stock) (Table 19). The analysis indicated that 6 out of 6 samples allowed water (0.0 M ethanol in the MED test) to penetrate the coarse soil within 10 seconds at 4,000 mg/kg F3 PHC (Table 21) on the August stock and 3,500 mg/kg F3 PHC on the November stock. The difference in the contaminated materials indicates there is variability associated with the hydrophobicity of different aged contaminants. The threshold effect concentration for hydrophobicity with F3 in coarse textured soils is considered to be 4,000 mg/kg F3 PHC (Table 21).

Table 21. Hydrophobicity analysis of coarse textured soils contaminated with various concentrations of F3 PHCs in December 2012.

Replicate	mg F3/kg			mg F3/kg		
	August stock*			November stock**		
	4000	4500	5000	3500	4000	4500
1	v	x	x	v	x	x
2	v	x	x	v	x	x
3	v	x	x	v	x	x
4	v	x	x	v	x	x
5	v	x	x	v	x	x
6	v	x	x	v	x	x

v- water droplet penetrates within 10 second; x- water droplet does not penetrate within 10 seconds
**original stock made up in August 2012; ** November stock prepared November 20, 2012*

3.6 Flammability

Neither soil contaminated with F2 or F3 PHC at 64,000 mg/kg or pure F2 or F3 PHC ignited with exposure to direct flame.

Plate 14. Soil and hydrocarbon flammability test.

3.7 Hydrocarbon Remobilization

No remobilized hydrocarbons were observed for the F2 PHC fine textured column (Plate 15a). A very slight sheen was visible on the F3 PHC fine textured column, however it was not significant enough to quantify and could have easily been a result of the residual waxes from the top of the soil column (Plate 15b). There were hydrocarbons remobilized in the F2 PHC coarse textured column equivalent to approximately 4 mm (Plate 16). 4 mm of F2 PHC equates to approximately 5.8 g or 41.8% of the F2 that remained on the column after 21 days drainage (Table 22).

Table 22. Residual and remobilized F2 PHC in coarse textured soil.

Residual F2 in Soil*			Remobilized F2					% mobilized
mg F2 / kg soil	kg Soil	g F2 PHC	mm F2 PHC	mls F2 PHC / mm	mls F2 PHC	density F2$^{\pm}$ (g/ml)	g F2 PHC	
17,626	0.78	13.82	4	1.75	7.02	0.82	5.78	41.82

**Average of 6 replicates analyzed in November 2012 trial; $^{\pm}$analysis completed by AITF Fuels and Lubricants Lab*

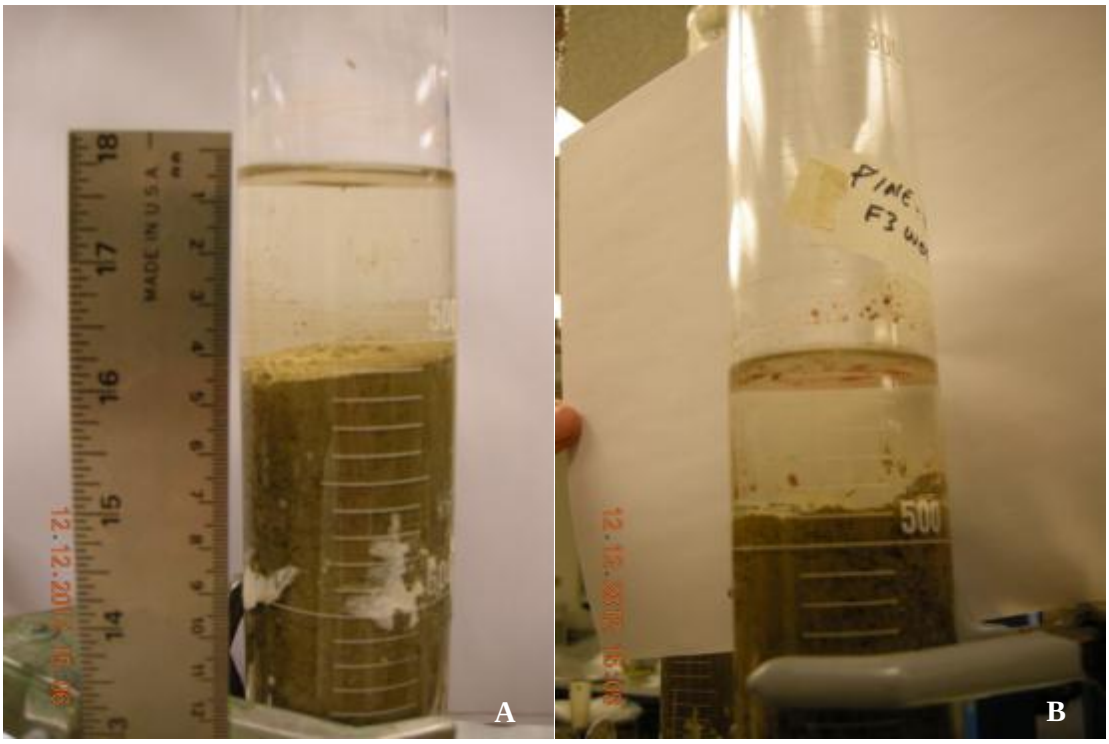

Plate 15. A) F2 PHC fine textured column and B) F3 PHC fine textured column post hydrocarbon remobilization trial.

Plate 16. F2 PHC coarse textured column post hydrocarbon remobilization trial.

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