

August 16, 2013

Mr. Steven F. Nightingale, P.E. Manager, Permit Section Illinois Environmental Protection Agency Bureau of Land 1021 North Grand Avenue East Springfield, Illinois 62794

Subject: Air Sparging and Soil Vapor Extraction Pilot Test – East 4th Street and Chaffer Street Roxana, Illinois 119115002 – Madison County Equilon Enterprises LLC d/b/a Shell Oil Products US Log No. B-43-CA-50

Dear Mr. Nightingale:

On behalf of Shell Oil Products US, URS Corporation is submitting the enclosed work plan for your review. This work plan includes a report of the results of the Rapid Optical Screening Tools (ROST) assessment conducted in accordance with the ROST Assessment Plan, approved by the IEPA on June 19, 2013.

If you have any questions during your review, please contact Kevin Dyer, SOPUS Principal Program Manager, at <u>kevin.dyer@shell.com</u> (618/288-7237), or Bob Billman at bob.billman@urs.com (314/743-4108).

Sincerely,

URS Corporation, on behalf of Shell Oil Products US

~ Canow

John Carrow Senior Geologist

Robert Bith

Robert B. Billman Senior Project Manager

Enclosures: Work Plan – Air Sparging and Soil Vapor Extraction Pilot Test – East 4th Street and Chaffer Street (original plus 2 copies)

cc: Kevin Dyer, SOPUS Amy Boley, IEPA, Springfield Jim Moore, IEPA, Collinsville Roxana Public Library Marty Reynolds, Village of Roxana

1001 Highland Plaza Drive West, Suite 300 St. Louis, MO 63110 Phone: 314.429.0100 Fax: 314.429.0462



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ILLINOIS EPA RCRA CORRECTIVE ACTION CERTIFICATION

This certification must accompany any document submitted to Illinois EPA in accordance with the corrective action requirements set forth in a facility's RCRA permit. The original and two copies of all documents submitted must be provided.

1.0 Facility Identification

Name	Equilon Er	nterprises LLC d/b/a Shell Oil Products US	County	Madison	
Street	Address	900 South Central Ave.	Site No.	(IEPA)	1191150002
City	Roxana, Illir	nois 62084	Site No.	(USEPA)	ILD 080 012 305

3.0 Operator Information

2.0 Owner Information

Name Not	Applicable	Name Equilon Enterprises LLC d/b/a Shell Oil Products US	
Mail Address		Mail Address 17 Junction Drive, PMB #399	
City		City Glen Carbon	
State	Zip Code	State IL Zip Code 62034	
Contact Name		Contact Name Kevin Dyer	
Contact Title		Contact Title Principal Program Manager	
Phone		Phone 618-288-7237	

4.0 Type of Submission (check applicable item and provide requested information, as applicable)

RFI Phase I Workplan/Report	IEPA Permit Log No. B-43R
RFI Phase II Workplan/Report	Date of Last IEPA Letter on Project June 19, 2013
CMP Report;	Log No. of Last IEPA Letter on Project B-43R - CA-50
X Other (describe): Does t	his submittal include groundwater information: X Yes No
Air Sparging & Soil Vapor Extraction Pilot Test-4th	St. & Chaffer St.
Date of Submittal 8-16-13	

5.0 Description of Submittal: (briefly describe what is being submitted and its purpose)

Air Sparging and Soil Vapor Extraction Pilot Test Work Plan - East 4th Street and Chaffer Street located in the Village of Roxana

6.0 Documents Submitted (identify all documents in submittal, including cover letter; give dates of all documents)

Cover Letter, RCRA Corrective Action Certification and Air Sparging and Soil Vapor Extraction Pilot Test Work Plan, dated August 16, 2013

7.0 Certification Statement

(This statement is part of the overall certification being provided by the owner/operator, professional and laboratory in Items 7.1, 7.2 and 7.3 below). The activities described in the subject submittals have been carried out in accordance with procedures approved by Illinois EPA. I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

IEPA RCRA Corrective Action Certification

For: Equilon Enterprises LLC d/b/a Shell Oil Products US

Date of Submission: 8-16-13

7.1 Owner/Operator Certification

7.2

(Must be completed for all submittals. Certification and signature requirements are set forth in 35 IAC 702.126.) All submittals pertaining to the corrective action requirements set forth in a RCRA Permit must be signed by the person designated below (or by a duly authorized representative of that person):

- 1. For a Corporation, by a principal executive officer of at least the level of vice president.
- 2. For a Partnership or Sole Proprietorship, by a general partner or the proprietor, respectively.
- 3. For a Governmental Entity, by either a principal executive officer or a ranking elected official.

A person is a duly authorized representative only if:

- 1. the authorization is made in writing by a person described above; and
- 2. the written authorization is provided with this submittal (a copy of a previously submitted authorization can be used).

Owner Signature:	Date:
Title:	
Operator Signature: Jum Edge	Date: 8/14/13
Title: Principal Program Manager	
Professional Certification (if necessary)	

Work carried out in this submittal or the regulations may also be subject to other laws governing professional services, such as the Illinois Professional Land Surveyor Act of 1989, the Professional Engineering Practice Act of 1989, the Professional Geologist Licensing Act, and the Structural Engineering Licensing Act of 1989. No one is relieved from compliance with these laws and the regulations adopted pursuant to these laws. All work that falls within the scope and definitions of these laws must be performed in compliance with them. The Illinois EPA may refer any discovered

violation of these laws to the appropriate regulating authority. Any person who knowingly makes a false, fictitious, or fraudulent material statement, orally or in writing, to the Illinois EPA commits a Class 4 felony. A second or subsequent offense after conviction is a Class 3 felony. (415 ILCS 5/44 (6)) 1

	a/16/13
Professional's Signature:	Date: 8/13/1 J
Professional's Name Robert B. Billman	PROFESSIONAL
Address URS Corporation, 1001 Highlands Plaza Drive West	Rrofessional's Seal:
City St. Louis	18
State MO Zip Code 63110	ROBERT B BILLMAN
Phone 314-743-4108	196-000646
Laboratory Certification (if necessary)	
The sample collection, handling, preservation, preparation	and analysis efforts for which this laborat

7.3

tory was responsible were carried out in accordance with procedures approved by Illinois EPA.

Name of Laboratory		
	Date:	
Signature of Laboratory Responsible Officer		
Mailing Address of Laboratory		
Address		
City	Name and Title of Laboratory Responsible Officer	
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JM:bjh\RCRA-CORRECTIVE-ACTION-CERTIFICATION-FORM.DOC

WORK PLAN

AIR SPARGING AND SOIL VAPOR EXTRACTION PILOT TEST – EAST 4TH STREET AND CHAFFER STREET

ROXANA, ILLINOIS

Prepared for

Shell Oil Products US 17 Junction Drive PMB #399 Glen Carbon, IL 62034

August 2013

URS Corporation 1001 Highlands Plaza Drive West, Suite 300 St. Louis, MO 63110 314.429.0100 Project #21562850

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URS Corporation (URS), on behalf of SOPUS, designed an SVE system, *Conceptual*\ *Final Design Report* (SOPUS 2011) along the west fence line area of the Wood River Refinery (WRR) **Figure 1**. The system was constructed in the Fall of 2011 and became operational in January 2012. The SVE system utilizes 34 extraction wells (25 wells at the WRR site, 3 wells in the Village, and 6 wells at the Public Works site) plumbed through six independently valve lines or legs. The piping leads to the treatment equipment, which consists of a vapor extraction blower, two vapor liquid separators (VLS') with associated aboveground storage tanks (ASTs), a regenerative thermal oxidizer (RTO), and a control room. Additional information is available in the *SVE System Construction Completion Report*, dated May 30, 2012 (SOPUS 2012) and the *SVE System Construction Completion Report* Addendum, dated February 14, 2013.

This Air Sparging and Soil Vapor Extraction (AS/SVE) Pilot Test Work Plan is being prepared to evaluate the viability of adding air sparging (AS) to enhance the performance of the existing SVE system in the vicinity of East 4th Street and Chaffer Street. The pilot test will be performed on properties owned by SOPUS, west of the intersection of Fourth Street and Chaffer Street, as shown on **Figure 2**¹.

¹ SOPUS purchased the properties at 147, 147 and 150 E. 4th Street, and removed the structures in November and December 2012.



The subsurface conditions underlying the pilot test area generally consist of two primary strata, a layer of silty clay that grade out to sandy clay that is approximately seven feet thick, underlain by silty sands and fine to medium grain sands to the depths explored in the area (approximately 70 feet below ground surface (bgs)). There are relatively thin discontinuous intervals of finer-grained material (e.g., silts and clays) between approximately 22 to 24 feet bgs and 35 to 40 feet bgs (based on existing CPT/ROST-8). On January 31, 2013, URS (on behalf of SOPUS) submitted a plan to collect additional subsurface information at the subject properties. The scope of work included Cone Penetration Testing (CPT) and Laser Induced Fluorescence (e.g., Rapid Optical Screening Tool (ROSTTM)) to provide continuous vertical characterization of stratigraphy and petroleum hydrocarbon distribution (SOPUS 2013). This information is summarized in this work plan and has been integrated with previously collected data to refine the conceptual model and design for possible application of air sparge at these properties.

CPT/ROST Procedures

ROSTTM and CPT borings were advanced to obtain additional information on the potential presence of residual hydrocarbons in the subsurface and to help characterize the geology of the pilot test area. FUGRO Consultants, Inc. (Fugro), under contract with URS advanced 12 CPT Borings (ROST-31 through ROST-42) beneath the three parcels during May 2013. The probes were completed to depths ranging from approximately 70 to 72 feet bgs.

The field investigation was performed in accordance with the ROST Assessment Plan submitted to the IEPA on January 31, 2013. In addition, applicable URS standard operating procedures, and SOPUS' protocols were followed. The CPT/ROST investigation was conducted between May 6 and May 10.

The following firms supported URS on this field work:

- FUGRO Consultants, Inc. of Houston, Texas CPT and ROSTTM probing services.
- Roberts Environmental Drilling Inc. (REDI), of Millstadt, Illinois borehole clearing

Figure 3 shows the CPT/ROST investigation locations.

Health and Safety during the field activities was governed by the Health and Safety Plan prepared for the *Rapid Optical Screening Tool Assessment 146, 147 and 150 E. 4th Street Roxana, Illinois, January 31, 2013.*

Field activities for this investigation were conducted on SOPUS owned property. Prior to the start of work, investigation locations were marked in the field (e.g., spray paint, stakes). A utility locate was arranged using Illinois' Joint Utility Locating Information for Excavators (JULIE)



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service. All utilities were documented to have been disconnected at the main lines in the streets and alleys prior to entering the properties. As a precaution, URS contracted REDI to clear proposed investigation areas for potential subsurface utilities by utilizing ground penetrating radar and electromagnetic utility locating equipment. Borehole clearance activities using an air knife and vacuum truck were not required. IEPA personnel visited the site during this scope of work to observe and document the field activities.

CPT probes were completed in accordance with ASTM D-5778-07 by hydraulically pushing a cone, equipped with a pore pressure transducer, through the soil at a rate of 2 cm/sec. The cone has a tip cross sectional area of 15 cm^2 and a friction sleeve area of 200 cm². Measurements of resistance to penetration, sleeve friction and pore pressure were recorded once per second during advancement of each boring. These measurements provided soil property data, which were converted to a stratigraphic profile for each boring. The report for the CPT probes including CPT logs, and additional information on this technology are presented in **Appendix A**.

The ROSTTM technology was advanced at the same time as the CPT technology. ROSTTM utilizes a laser-induced fluorescence sensor, which consists of a small diameter sapphire window mounted flush with the side of a CPT probe. The down-hole ROSTTM sensor uses the standard CPT technology described above. As the ROSTTM sensor is advanced, the laser transmits pulses of light to the sensor through a fiber optic cable connected to the sapphire window. The pulsed light causes petroleum hydrocarbons in the soil to fluoresce, and the fluorescence signal travels through a second cable to a detection system in the CPT rig. Relative concentration and a spectral product fingerprint are presented continuously in real-time. Since fluorescence intensity is proportional to petroleum hydrocarbon concentration, ROSTTM technology can effectively delineate the extent of affected soils. A reference solution was placed on the sapphire window prior to each location as a quality control check to make sure the system's performance was within specification and to allow for normalization of the data from the various test locations (e.g., laser power, operating conditions, etc.). Refer to the report in **Appendix A** for additional information.

Upon completion, each probe hole was backfilled with granular bentonite poured from the surface or with high solids bentonite grout via the tremmie method. Locations of CPT/ROST probes were measured from surveyed landmarks and the figures presented in this work plan are approximate. The locations and elevations will be surveyed after the wells are installed for the pilot test.

During the ROSTTM/CPT activities, equipment was decontaminated by wiping down the cone and rods with alconox and distilled water soaked paper towels. Other than paper towels and



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gloves that were managed as municipal waste, no investigation-derived waste (IDW) (e.g., purge water, soil cuttings, etc.) was produced during these activities.

Summary of CPT/ROST Findings

The CPT logs and results of the ROSTTM probes (in % fluorescence) are provided in **Appendix A** with additional information on this technology. Soils encountered in the CPT probe holes consisted of clay and silt fill material, reworked native soil to a depth of approximately 7 to 8 feet. This material transitioned into silty sand and sand. A thin layer of clay and/or silt was encountered at about 20 feet bgs in a few of the northern CPT locations (ROST 32, 34, 35, 36). This is similar to observations of previous investigations performed north of the alley and near third street. Additional thin silty layers were encountered between 30 and 40 feet bgs in seven of the twelve CPT locations. Groundwater was encountered between 40 and 45 feet bgs, based on pore pressure readings in the Cone. This is consistent with groundwater levels observed in nearby monitoring wells.

ROST response is measured in percent fluorescence. Ten of the twelve ROST locations had maximum fluorescence ranging from 3% to 10%, which indicate minor amounts of residual hydrocarbon. Four locations had maximum fluorescence greater than 10%. ROST 32 had 84% maximum fluorescence at 31 feet bgs. This did not correlate with fine grained layers or perched water. ROST 37 had 79% at a depth of 39 feet bgs. The higher fluorescence at ROST 37 was approximately two feet below a silty or clayey silt layer. Groundwater was encountered in this borehole at approximately 42 feet bgs.

CPT and ROST data were input into Environmental Visualization System (EVS) software. EVS builds three-dimensional visualization of the soils based on the CPT data and the estimate of the residual hydrocarbon distribution based on ROST responses above 2 % fluorescence. A model of the 2% fluorescence was used to show residual hydrocarbon concentrations beneath the water table. This information was used for locating the Air Sparging (AS), Soil Vapor Extraction (SVE), Vapor Monitoring Points (VMPs), and Observation Wells (OWs) for the pilot test. Oblique and profile views of the EVS models are presented on **Figures 4** and **5**.



There are currently three SVE wells in the proposed pilot test area, SVE-3, SVE-4, and SVE-25. SVE-3 and SVE-4 are screened from 5 feet to 10 feet bgs. SVE-25 is screened from 10 feet to 25 feet bgs. These wells are located in 4th Street, just west of the intersection of 4th and Chaffer St (**Figure 3**). Wells SVE 25 and SVE-3 (modified as described below) will be operated individually and then together in order to assess the most effective removal of sparge air and soil vapors.

This section describes the planned pilot test protocols.

Air Sparging, Soil Vapor Extraction, Vapor Monitoring Points, and Observation Wells

The following wells and monitoring points will be installed for this test:

- Air Sparging Well AS-1
- Vapor Monitoring Point (VMP) VMP-56
- Observation Wells OW-1, OW-2, and OW-3.

In addition, the existing soil vapor extraction well SVE-3 will be over drilled and modified with a deeper (30-40 feet bgs) screen interval. The rationale for this planned modification is based on screening results from nearby VMP wells that show only minor concentrations of petroleum hydrocarbon vapors at the shallower depths. The soil vapor extraction well SVE-4, which has a screen interval of 5-10 feet bgs and the shallow sample port of the newly installed VMP-56 will be used to monitor soil vapors in the shallow vadose zone during the pilot test. If soil vapor extraction is required at the shallow depths during the test, SVE 4 can also be opened. The proposed approximate locations of the AS well, SVE wells, VMP, and observation wells are provided on **Figure 3** and shown schematically on **Figure 6**.

Prior to installing the AS well, soil samples will be continuously collected using a direct-push or hollow-stem auger rig to evaluate the lithology for the entire depth of the boring. Up to three soil samples will be collected from the boring for analysis of VOCs. Samples will be collected from intervals exhibiting the greatest apparent impact based on field observations. The AS well will be constructed of 2-inch diameter PVC with 2 feet of 0.010-inch slotted well screen. A granular filter pack will extend to approximately 1-foot above the top of the screen followed by a fine sand seal. A three foot thick bentonite chip seal will be installed immediately above the sand pack and the remaining annular space will be filled with a cement bentonite grout to approximately 3feet bgs. The termination of the bentonite grout at 3 feet bgs is so that the AS well can be attached to underground piping should AS be added to the remediation system in the future. The base of the screen for the AS well will be set at a depth of approximately 52 feet bgs. The depth of the AS well is based on the observations at ROST 37.



Well SVE-3R will be modified with the screen installed below the depth at which SVE-25 is screened in order to target vapor removal from the lower vadose zone. This SVE well will be modified by using a hollow-stem auger to over drill SVE 3, remove the casing, screen, and sand pack. The hollow stem auger will be used drill to a depth of approximately 40 feet bgs. The SVE well will consist of 4-inch diameter PVC with a granular filter pack that will extend to approximately 2 feet above the top of a 10-foot long, 0.010-inch slotted screen. The screen interval will be placed above and below fine grained soil observed at approximately 38 feet in ROST 37. The actual screen interval will be based on observations and the soil encountered in the bore hole for the well. A 2- foot thick bentonite chip seal will be installed immediately above the sand pack and the remaining annular space will be filled with a cement bentonite grout to within one foot of the floor of the vault. The well will be completed at the floor of the vault with one-foot of concrete The SVE line going to the RTO vapor treatment equipment will be reconnected upon completion of the well.

An additional VMP will be installed to monitor the vacuum at various depths throughout the pilot test. VMP-56 will be installed northwest of SVE-3R and SVE- 25. The VMP will have three, 6-inch long stainless steel well screens (ports). The individual ports will be set at a depth of approximately 10 feet bgs, 25 feet bgs, , and 40 feet bgs. The VMP will be constructed following previously approved procedures. The actual depths may be adjusted in the field based on observations and soil encountered.

Observation wells OW-1, OW-2, and OW-3 will be installed to serve as groundwater observation points during the pilot test. The groundwater observation wells will be installed using a direct-push or hollow-stem auger rig. Each observation well will consist of a 2-inch diameter schedule 40 PVC casing with 10 feet of 2-inch diameter 0.010-inch schedule 40 PVC slotted well screen from approximately 41 to 51 feet bgs. The granular filter pack will extend to approximately 1-foot above the top of the screen. A 2-foot thick bentonite chip seal will be installed immediately above the sand pack and the remaining annular space will be filled with a cement bentonite grout to the ground surface and completed at the surface with a flush-mounted protective cover. The screen will be installed with approximately 9 feet of screen below the water table and 1 foot above it.

Soil Vapor Extraction Wells

The existing SVE wells SVE-25 and modified well SVE-3R will be utilized during the pilot test.



Vapor Monitoring Points

Existing VMPs in the area (e.g., VMP-43, VMP-31) and proposed VMP-56 will be used during the pilot test.

Air Sparging and Observation Well Sampling

Prior to and approximately a week after the pilot test, groundwater samples will be collected from the observation wells and well MW-17, which is located in Chaffer Street. Groundwater samples will be collected in accordance with URS/SOPUS approved standard operating procedures.

AS/SVE Pilot Test Equipment

Test equipment used during the pilot test will be rented from a qualified vendor and include the following:

- A compressor capable of at least 100 cfm at 50 psi with an oil coalescing filter.
- VMP wellhead connections that allow for vacuum and pressure monitoring.
- Observation well head connections that allow for vacuum, pressure, and water level monitoring.
- Magnehelic vacuum gauges for vacuum, pressure, and air flow monitoring.
- Flow meters to measure air flow rates.
- A helium tracer system with a helium injector pump equipped with a flowmeter, pressure gauge, and metering valve.
- Miscellaneous ancillary equipment including but not limited to health and safety monitoring equipment, water level meters, air sampling and monitoring equipment, helium monitoring equipment, and flow meters.

Pre-AS/SVE Pilot Test

A preliminary helium tracer test will be performed in the newly installed VMP-56 and the modified SVE-3R prior to the actual pilot test. This will provide data on air flow pathways for the SVE portion of the test. The test will be completed by filling tedlar bags with 5 ml of helium and injecting the contents of each into the 25 and 40 foot bgs ports of the VMP. SVE 25 will be operated in soil vapor extraction mode and the extracted soil vapor sampled for helium. SVE 3R will be operated and extracted vapor will be similarly sampled for helium. The helium detector will be connected to the sample port on the SVE wells through a pump in order to overcome back pressure in the SVE line.



The existing SVE system will provide vacuum to the extraction wells and will be used for vapor recovery and treatment. It is anticipated that the current SVE system will be able to handle the vapor concentrations expected during the test. Additional wells on the blue line of the SVE System will be closed in order target the vacuum for AS/SVE pilot test area Wells, SVE- 4, 10, 11, and 12 will be closed for the duration of the test. Wells SVE-3R and 25 will be closed when not in use for the test. An optional AS/SVE trailer, that would include an appropriately sized air sparge compressor, a vacuum blower, and vapor liquid separator, may be used during the pilot test to assure constant vacuum rates. If the AS/SVE trailer is used, it will be connected to the existing SVE system. Therefore, no vapor treatment equipment will be used on the AS/SVE trailer.

Baseline vacuum readings will be recorded for the SVE, VMP and OW wells prior to beginning the test. SVE flow rate will be measured with an in line pitot tube and recorded. Static baseline groundwater elevations in OW wells will also be recorded.

SVE Pilot Test Procedures

Day 1 of the pilot test will consist of SVE operation only. SVE-3R, and SVE-25, will be used for soil vapor extraction. Testing will proceed from deep to shallow SVE wells.

The test will begin by running the unit at approximately 10 inches of water (IN-H₂O). The vacuum will be increased in approximately 10-inch increments (e.g., 10", 20", 30", etc.). It is anticipated that there will be three to four steps but the applied vacuum is subject to change in order to evaluate the flow processes within the vadose zone. Each step will be operated for approximately $\frac{1}{2}$ hour or until a point where the vacuum in the surrounding observation wells and VMPs equalize. Vacuum measurements will be collected at the extraction well, each observation well, and nearby VMPs. Once the testing is completed at SVE-3R, the same step process will be conducted at SVE-25.

Upon completion of the individual tests the SVE wells will be operated simultaneously. The operating format will be similar as described in the previous paragraph.

Based on the results of the preliminary helium tracer test performed in the VMP well and the SVE only portion of the test it will be determined, whether SVE-3R and/or SVE-25 will be used for soil vapor extraction during the combined AS/SVE portion of the pilot test. The results of the SVE only portion of the test will also be used to determine the optimum wellhead vacuum and air flow rate that the SVE system will be set at during the combined AS/SVE portion of the test.



Data Collection

Measurements will be documented on the Pilot Test Field Data Forms provided in **Appendix B**. The vacuum readings in the surrounding observation wells are expected to stabilize within the first ¹/₂ hour of each increase in well head vacuum. Data will be collected prior to initiation of the test, 15 and 30 minutes after each step increase followed by every 30 minutes thereafter. Prior to shutting down the system at the end of Day 1, a Tedlar bag sample and summa canister sample will be collected from the SVE system in the configuration that will be used during the AS portion of the test to determine VOC concentrations. Air analytical results will be utilized to determine mass removal rates. Additionally, vapor samples will be collected in tedlar bags from a sample port throughout the pilot test and monitored utilizing a photoionization detector (PID).

AS/SVE Pilot Test Procedures

On Day 2 of the pilot test, AS-1 will be operated at a low air flow rate of approximately 1 cfm to 3 cfm. The actual air flow rate will be determined based on field observations. AS-1 and SVE-3R and/or SVE-25 will run simultaneously for this pilot test. Calculations for the minimum breakout and maximum air pressure allowable at the air sparging well AS-1 are included in **Appendix B**.

The air flow rate for the AS compressor on Day 3 for the pilot test will be initiated at 5 cfm followed by an increase to 10 cfm. Based on URS' experience, it is anticipated that each step of the test will be operated for approximately four to five hours as this is typically the range in which the mounding subsides and pseudo equilibrium is achieved in fine to medium grained sands. These air flow rates may be altered based on the response of the aquifer. If the maximum allowable injection pressure is exceeded for the AS compressor at any time, the compressor will be shut down manually.

Data Collection

On Day 2 or Day 3, depending on selection of the optimum AS and SVE flow, a helium tracer will be incorporated into the air stream of the AS compressor. Two valve sample ports will be installed on the SVE line. The first port will be used for injection of helium to establish the maximum recoverable helium as a baseline. The second port will be used for helium recovery. A flow and pressure gauge will be used to meter helium injection rates. A helium detector will be used in the SVE influent line to measure recovery. The maximum helium recovery will be calculated. The injection rates will be adjusted to achieve a 1 to 2% v/v concentration. Helium injection in the AS well will begin after vacuum readings in OW-1, OW-2 and OW-3 have stabilized. During the helium tracer the SVE influent air stream will be monitored continuously.



Helium in the SVE piping will be plotted over time starting with the initial injection in the AS well and ending after non-detectable helium readings have been observed for 30 minutes. Helium tracer procedures will follow those presented in the guidance *SVE Recovery-Helium Tracer Testing Guidance (Quick Ref)* developed by Shell.

The following data will be collected every 15 minutes for the first 30 minutes of each step increase followed by every 30 minutes, if applicable:

- Pressure/vacuum and helium readings at the wellheads of the SVE, AS, VMPs and observation wells.
- Groundwater elevations during pilot study operation.
- Air flow rate, including the air flow stream temperature and pressure at the location of the air flow rate measurement to accurately convert the rate to standard temperature and pressure.
- Visual observations.
- Dissolved oxygen in groundwater.
- Volume of groundwater recovered during the pilot test.

Soil vapor samples (stainless steel (summa) canisters) will be collected at the end of each day from the SVE well used.

Water may be recovered during the pilot test either as liquid water or condensate. Recovered water will be removed from the vapor stream in the SVE system knockout tank and storage tank, and managed in accordance with current protocols for the SVE system.

Activities associated with pilot testing will be conducted as described in this plan, and in accordance with procedures previously used for Roxana/West Fence Line investigations, and URS Standard Operating Procedures (SOPs)/guidelines and SOPUS guidelines.

Health and Safety

Health and Safety during the pilot tests and investigation activities will be governed by a health and safety plan developed for this work.

Prior to beginning site work and at the start of work each day, a daily safety meeting will be held. The purpose of this meeting is to discuss the day's planned activities and to address any potential health and safety concerns. As a part of the daily safety meeting, job safety analyses (JSAs) will be reviewed to address task specific safety concerns.



URS field personnel will be wearing U.S. Environmental Protection Agency (USEPA) modified Level D personal protective equipment (PPE), which include a hard hat, steel-toed boots, safety glasses, etc.

A photoionization detector (PID) with a 10.6 electron volt (eV) lamp, combustible gas indicator (CGI), and a benzene-specific compound air monitor will be used during the field activities to monitor air quality. Field instruments will be calibrated prior to use each day in accordance with the manufacturer's specifications.

Decontamination

Field personnel and equipment will incorporate decontamination procedures to ensure the health and safety of those present, to maintain sample integrity, and to minimize cross contamination. Sampling equipment (e.g., groundwater pump) will be decontaminated prior to the collection of each analytical sample, between sample locations, and prior to leaving the investigation site by washing with LiquiNox[®] and a distilled water rinse. Interface probes will be decontaminated using isopropyl alcohol. Personnel and small equipment decontamination will be performed at the sample locations.

Investigation Derived Waste

Investigative derived waste (IDW), such as soil cuttings, purge water and decontamination water generated during groundwater sampling activities will be collected, stored and disposed of in accordance with applicable regulations. Soil cuttings will be stored in a covered container (e.g. cubic yard box) and appropriately staged prior to disposal. Expendable materials (e.g., disposable sampling equipment such as gloves and tubing) will be collected in trash bags and disposed as municipal waste.

Decontamination fluids and purge water from air sparging, observation, and monitoring wells located at the each of the pilot test sites will be staged in 55-gallon steel drums for proper disposal. Characterization sampling will be performed, if necessary.



Groundwater Gauging and Sampling

AS and observation well samples will be collected via low-flow groundwater purging and previously approved sampling procedures. Prior to groundwater monitoring well sampling, the initial water level will be measured and recorded on field forms. AS and observation wells will be purged and sampled using a stainless steel submersible pump with designated polyethylene tubing². Groundwater samples will be collected for analysis of VOCs via USEPA Method 8260B. Samples will be collected in laboratory-supplied containers and labeled in the field. Sample information will be recorded on a chain of custody (COC) form at the time of collection. The sample identification data (ID) format is "well ID-ROX-date". Upon collection and labeling, sample containers will be immediately placed inside an iced cooler, packed in such a way as to help prevent breakage and maintain inside temperature at or below 4°C. The samples will then be delivered via overnight courier, under the proper COC documentation, to Accutest Laboratories in Marlborough, Massachusetts.

Soil Vapor Sampling

Soil vapor samples will be collected using tedlar bags and stainless steel (summa) canisters using similar procedures used for sample collection with the SVE system. The tedlar bag samples will be screened for petroleum hydrocarbons using a flame ionization detector (FID)/photo ionization detector (PID). The summa canister samples will be analyzed for the USEPA method TO-15 VOCs and ASTM-D-1946 constituents established for the project. The samples will be delivered under COC documentation to Eurofins/Air Toxics Laboratory in Folsom, California.

Permitting

The air sparge well is considered to be a Class V Injection well under the IEPA's Underground Injection Control (UIC) program. URS will prepare the necessary notification and well inventory for submittal.

² Designated tubing is stored in a sealed bag designated for the particular well between sampling events.



SECTIONFOUR

The Pilot Test process is expected to take approximately five months. A project schedule is shown below.

The information derived from the pilot test will be incorporated into a report for submittal to IEPA. The report will include a summary of the pilot test procedures and results.

SCHEDULE





SECTIONFIVE

- Illinois Environmental Protection Agency (IEPA). November 15, 2010. Letter of work plan approval with conditions. Sent to URS Corporation.
- Shell Oil Products US. September 20, 2010. *Vapor Intrusion Investigation Work Plan*. Prepared by URS Corporation.
- Shell Oil Products US. December 31, 2010. *Soil Vapor Extraction Pilot Test Work Plan.* Prepared by URS Corporation.
- Shell Oil Products US. June 10, 2011. *Conceptual/Final Design Report*. Prepared by URS Corporation.
- Shell Oil Products US. May 30, 2012. *SVE System Construction Completion Report*. Prepared by URS Corporation.
- Shell Oil Products US. January 31, 2013. *ROST Assessment Plan*. Prepared by URS Corporation.
- Shell Oil Products US. February 13, 2013.SVE System Construction Completion Report Addendum. Prepared by URS Corporation.







DSGN. BY: djd CHKD. BY: wmp















FUGRO CONSULTANTS, INC.



Date: May 31, 2012 Report Number 04.19130025 6105 Rookin Road Houston, Texas 77074 Tel: 713-346-4000 Fax: 713-346-4002

URS Corporation 1001 Highlands Plaza Drive West St. Louis, MO 63110

Attention: Mr. Bob Billman

REPORT FOR PIEZOCONE PENETRATION TESTING, RAPID OPTICAL SCREENING TOOL (CPT/ROST™) TESTING AND RELATED SERVICES ROXANA, ILLINOIS

Dear Mr. Billman:

Fugro Consultants (Fugro) is pleased to present this data report for Cone Penetration (CPT) and Rapid Optical Screening Tool (ROST[™]) testing at the above-referenced site. CPT/ROST[™] provided continuous characterization of stratigraphy and petroleum hydrocarbon distribution at the testing locations. A description of the CPT and ROST[™] technologies and a discussion of general ROST[™] data interpretation follow. CPT and ROST[™] logs and electronic data CD are included as attachments. The final data has been reviewed and has undergone the appropriate QA/QC process.

Cone Penetration Testing

CPT was performed simultaneously with each ROST[™] sounding and yielded real-time stratigraphic data. CPT is a proven method for rapidly evaluating the physical characteristics of unconsolidated soils. It is based on the resistance to penetration of an electronically instrumented cone, which is continuously advanced into the subsurface. In accordance with ASTM Standard D5778-07, the cone was advanced at a rate of two centimeters per second with the driving force provided by hydraulic rams.

The CPT cone used at this site had an apex angle of 60 degrees with a base area of 15 square centimeters (cm^2), and friction sleeve with a surface area of 200 cm². The standard geotechnical sensors within the cone measure tip resistance and sleeve friction in tons per square foot (TSF). The combined data from the tip resistance and sleeve friction form the basis of the soil classification (e.g., sand, silt, clay, etc.).

Soil stratigraphy was identified using Robertson et al. Campanella's 1986 Soil Behavior Chart. Please note that because of the empirical nature of the soil behavior chart, the soil identification should be verified locally. Some soils, such as glacial till, cemented soils and calcareous soils are outside the scope of these soil behavior charts."



ROST[™] Testing

Fugro Consultants' ROSTTM Laser-Induced Fluorescence system was used for this investigation to screen soils for petroleum hydrocarbon materials containing aromatic hydrocarbon constituents. The system consists of a tunable laser mounted in the CPT truck that is connected to a down-hole sensor. The down-hole sensor consists of a small diameter sapphire window mounted flush with the side of the cone penetrometer probe.

The laser and associated equipment transmit 50 pulses of light per second to the sensor through a fiber optic cable. The wavelength of the pulsed excitation light is tunable and can be set to wavelengths of 266 nanometers (nm) or to wavelengths between 280 and 300 nm. An excitation wavelength of 290 nm was used for each test during this project.

The laser light passes through the sapphire window and is absorbed by aromatic hydrocarbon molecules in contact with the window, as the probe is advanced. This addition of energy (photons) to the aromatic hydrocarbons causes them to fluoresce. A portion of the fluorescence emitted from any encountered aromatic constituents is returned through the sapphire window and conveyed by a second fiber optic cable to a detection system within the CPT rig. The emission data resulting from the pulsed laser light is averaged into one reading per one-second interval (approximately one reading per 2 cm vertical interval) and is recorded continuously. ROST[™] may be operated in single or multi-wavelength mode, depending on project objectives. For this project, ROST[™] was operated in multi-wavelength mode (MWL).

Multi-Wavelength Mode (MWL). In MWL mode, several characteristics of the emitted fluorescence are measured and recorded simultaneously at four (4) specific wavelengths (340, 390, 440, and 490 nm). These four wavelengths represent the spectrum of fluorescence typically produced by aromatic hydrocarbons ranging from light fuels through heavy contaminants such as coal tar and creosote. The recorded data is then presented as a color graph of fluorescence intensity (the combined fluorescence of all four monitored wavelengths) versus depth (FVD).

On the FVD graph, each of the four monitored wavelengths is assigned a color. These colors are combined based on the proportional fluorescence intensity of each of the individual wavelengths. The combined color is then used on the FVD graph. Changes in color on the FVD graph typically represent changes in product type. Similarly, like colors on the FVD graph typically represent the same product, regardless of the total fluorescence intensity. Changes in the total fluorescence intensity typically indicate changes in contaminant concentration, with higher fluorescence intensities representing proportionally higher concentrations when compared to lower fluorescence intensities.

In addition to the FVD graph, depth specific waveforms are presented at four (4) selected depths throughout the sounding. These waveform graphs are presented to the right of the FVD graph on each plot. In the waveform graphs, the fluorescence intensity and duration of fluorescence of each of the monitored wavelengths is represented by an individual peak, starting at 340 nm and increasing in 50 nm wavelengths as you move to the right. The intensity of each wavelength is represented by the height of the peaks, and the duration of fluorescence is represented by the width of each peak. For general interpretation purposes, lighter aromatic hydrocarbon molecules will emit fluorescence at the shorter wavelengths, and heavier, longer chained hydrocarbons will emit fluorescence at the longer wavelengths. The presented waveforms can be compared to waveforms typical of common hydrocarbon products to determine the likely product type that has been encountered. Please note that the waveforms are available at every two-centimeter interval throughout the entire sounding. Additional waveforms can be generated at any time during or after testing is complete.



REFERENCE SOLUTION: The fluorescence intensity of a reference solution placed on the sapphire window was measured immediately prior to conducting each test. This reference solution measurement serves two purposes. First, as a quality control check, the solution is used to ensure that the performance of the system is within specifications. Second, it allows for normalization of the data from different test locations for variation in laser power, operating conditions, and monitored emission wavelength. The reference solution used for this project was the standard M1 reference, which is a proprietary PHC containing solution. M1 provides consistent fluorescence response across the portion of the spectrum analyzed by ROST and therefore, allows the fluorescence data collected to be consistently normalized to intensities recorded as a percentage of M1.

LIMITATIONS OF ENVIRONMENTAL SUBSURFACE WORK

Fugro Consultants' report is based upon our observations made during fieldwork, the information provided to Fugro and the results of the ROST/CPT survey. Given the inherent limitation of environmental subsurface work, Fugro cannot guarantee that the site is free of hazardous or potentially hazardous materials or conditions or that latent or undiscovered conditions will not become evident in the future. Fugro's report was prepared in accordance with our proposal and the General Conditions agreed to between Fugro and Client and no warranties, representations, or certifications are made.

Fugro Consultants, Inc. appreciates the opportunity to be of service to your organization. Please do not hesitate to contact us if we can be of further assistance. We look forward to working with you in the future.

Sincerely, **FUGRO CONSULTANTS, INC.**

Recep Yilmaz

Senior Vice President

RY/tsp

Enclosure: - 1 CD





12 Zone Soil Behavior Chart






















Robertson et al. 1986 * Overconsolidated or Cemented









Site: Roxana, IL Client: URS Corporation

Date/Time: 5/8/2013 @ 9:17:48 AM

ROST Unit: Houston

Operator: Robert Biehle Fugro Job #: 04.1913-0025 Max fluorescence: 5.21% @ 27.18 ft Final depth BGS: 72.00 ft



Client: URS Corporation

Date/Time: 5/9/2013 @ 11:13:57 AM

ROST Unit: Houston

Operator: Robert Biehle Fugro Job #: 04.1913-0025 Max fluorescence: 84.57% @ 31.30 ft Final depth BGS: 70.02 ft



ROST-32

Site: Roxana, IL Client: URS Corporation Date/Time: 5/9/2013 @ 8:36:20 AM

ROST Unit: Houston

Operator: Robert Biehle Fugro Job #: 04.1913-0025 Max fluorescence: 4.95% @ 54.11 ft Final depth BGS: 70.04 ft



Site: Roxana, IL Client: URS Corporation Date/Time: 5/8/2013 @ 2:16:05 PM ROST Unit: Houston Operator: Robert Biehle Fugro Job #: 04.1913-0025 Max fluorescence: 3.00% @ 52.35 ft Final depth BGS: 70.08 ft



Client: URS Corporation

Date/Time: 5/8/2013 @ 10:40:00 AM

ROST Unit: Houston

Operator: Robert Biehle Fugro Job #: 04.1913-0025 Max fluorescence: 3.86% @ 37.35 ft Final depth BGS: 70.01 ft



Client: URS Corporation

Date/Time: 5/8/2013 @ 3:56:35 PM

ROST Unit: Houston

Operator: Robert Biehle Fugro Job #: 04.1913-0025 Max fluorescence: 13.58% @ 38.55 ft Final depth BGS: 70.03 ft



Client: URS Corporation

Date/Time: 5/8/2013 @ 12:08:54 PM

ROST Unit: Houston

Operator: Robert Biehle Fugro Job #: 04.1913-0025 Max fluorescence: 79.33% @ 39.27 ft Final depth BGS: 70.01 ft



Site: Roxana, IL Client: URS Corporation Date/Time: 5/10/2013 @ 8:25:56 AM

ROST Unit: Houston

Operator: Robert Biehle Fugro Job #: 04.1913-0025 Max fluorescence: 5.23% @ 52.34 ft Final depth BGS: 70.00 ft



Fugro Geosciences, Inc., 6105 Rookin, Houston, TX 77074 (713) 346-4000 www.geo.fugro.com

Site: Roxana, IL Client: URS Corporation Date/Time: 5/10/2013 @ 10:07:04 AM

ROST Unit: Houston

Operator: Robert Biehle Fugro Job #: 04.1913-0025 Max fluorescence: 6.19% @ 19.82 ft Final depth BGS: 70.02 ft



ROST-39

Site: Roxana, IL Client: URS Corporation

Date/Time: 5/9/2013 @ 2:45:15 PM

ROST Unit: Houston

Operator: Robert Biehle Fugro Job #: 04.1913-0025 Max fluorescence: 11.21% @ 18.52 ft

Final depth BGS: 70.05 ft



Client: URS Corporation

Date/Time: 5/10/2013 @ 11:35:26 AM

ROST Unit: Houston

Operator: Robert Biehle Fugro Job #: 04.1913-0025 Max fluorescence: 4.92% @ 59.52 ft Final depth BGS: 70.00 ft



Site: Roxana, IL Client: URS Corporation Date/Time: 5/9/2013 @ 1:30:41 PM ROST Unit: Houston Operator: Robert Biehle Fugro Job #: 04.1913-0025 Max fluorescence: 2.76% @ 54.71 ft Final depth BGS: 70.20 ft



ROST-42



Definitions

ROST – Rapid Optical Screening Tool

LIF - Laser-induced fluorescence

POL - petroleum, oils and lubricants

PAH - polycylic aromatic hydrocarbon

PPM - parts per million

LIF - Laser Induced Fluorescence

M1 - fluorescence reference emitter

UV - Ultraviolet (excimer wavelength - 308nm)

BGS - below ground surface

TPH - Total petroleum hydrocarbon

FVD - fluorescence vs depth data file containing full waveform data

AVD - area vs. depth file data containing abbreviated information

PST - push standard file for compatibility with previous DOS software

INFO - information file containing important notes about ROST log

JPG - Joint Photographic Experts Group image file of FVD log

Data File Information

Log Files

The *.log files are stored in Activity Logs directory that is created and maintained automatically. They contain a log of all the activity that took place each day with ROST system.

FVD Files

Fluorescence vs. Depth files (*.FVD) contain the full data matrix as follows:

Row 1, Column 1 is a zero that serves as a placeholder Row 1, Column 2 to last Column is time vector in nanoseconds Row 2, Column 1 is a negative 9 serving to indicate M1 reference emitter waveform Row 2, Column 2 to last Column is the voltages of the M1 reference emitter waveform Row 3 to last Row, Column 1 is the depth of each ROST measurement Row 3 to end row, Column 2 to last Column are all the voltages of the ROST waveforms acquired at each depth

AVD Files

Area vs. Depth files (*.AVD) are an abbreviated file that is most often given to client along with INFO file. Client is typically interested in Columns 1 and 2 only. Format as follows:

Column 1 is the depth in meters or feet (look at INFO file to determine depth system)

Column 2 is total fluorescence represented as a % of M1 (to normalize data)

Column 3 is relative signal strength (area) of Channel #1 (340nm)

Column 4 is relative signal strength (area) of Channel #2 (390nm)

Column 5 is relative signal strength (area) of Channel #3 (440nm)

Column 6 is relative signal strength (area) of Channel #4 (490nm)

Column 7 is 32 bit color code number based on color scheme chosen for this test

INFO Files

The INFO files (*.INFO) are self explanatory. They contain all the information that should be stored from each test to enable printing, viewing, and analysis to take place at a later date even without having access to technician's notes. ROST software uses this to update information panel when loading previously acquired ROST logs.

PST File

The PST file (*.pst) is a legacy file. This is the M1 waveform stored as: Column 1 – Depth Column 2 – Voltage

This file is used to allow older Matlab software to view/print/analyze FVD logs.

Polycyclic Aromatic Hydrocarbon (PAH) Fluorescence Principles

Laser-induced fluorescence (LIF)

Fluorescence spectroscopy is one of the most widely applied spectroscopic techniques in use today. It is, by nature, a fast, sensitive and typically reversible process that makes it ideal for incorporation into a continuous screening technique that uses an optically transparent window as the conduit between the sensor and the analyte. Luminescence is the emission of light from any substance that returns to the ground state after being excited into an electronically excited state. If the bulk of the molecules emit their photons in less than a microsecond the emission is referred to as fluorescence. Emission that takes longer than this is called phosphorescence.

Fluorescence is typically observed in molecules that have an aromatic structure. One class of aromatics is the PAH found in quantity in typical petroleum products. The PAHs found in coal tars, creosotes and even sediments are also fluorescent, but they fluoresce much less efficiently than PAHs dissolved in more solvent-rich environments, such as the aliphatic body that makes up the bulk of fuels/petroleums. We have observed that the less solvent available, the less efficiently the PAHs fluoresce. The PAHs continue to absorb the excitation light, but there is a much higher likelihood of the PAHs finding a non-radiative mechanism with which to shed the additional energy they picked up during the absorption of the excitation photon(s). In spite of this, the PAHs in sediments can still be coaxed into fluorescing well enough to allow in-situ laser-induced fluorescence screening via a sapphire-windowed probe.

A plot of the relative distribution of the different colors (or energies) of the photons being emitted by an excited sample of PAH is called the spectrum (or spectra when referring to more than one). Figure 1 illustrates the concept of PAH absorbance and fluorescence spectra. The spectra of individual PAH species (such as naphthalene and anthracene) can contain enough structure (peaks and valleys) to be identified in simple mixtures in the lab. The fluorescence of PAHs in sediments however, is originating from such a wide variety and concentrations of PAHs and differing local environments (dissolved phase, sorbed to particles, microcrystals, etc.) that the resulting spectra are very broad and contain very little "structure" that one might use to determine which individual PAHs are responsible for the fluorescence. The spectra do shift enough to recognize that the distribution of species or environments are changing, but individual speciation is impossible.

Another property of fluorescence that can be measured is the varying amount of time it takes for the molecules to emit the photons after exposure to a pulsed excitation source, such as a laser is illustrated in Figure 2. If we use a time sensitive detector to observe the number of photons being emitted over time, we can derive more information about the nature of the fluorophores and their environment. This decay time information contained within the waveform is measured with an oscilloscope. The different PAHs and the differing environments that exist in sediments all combine to change the decay times observed. This information is readily obtained when using a pulsed source such as the laser we used in this application. ROST allows us to investigate not only what colors are being emitted, but also how long it takes for the excited population of PAHs to emit the fluorescence photons. We use a patented method of combining the photons from four regions of the emission spectrum optically collected over 20 nm wide sections of the emission spectra at 340, 390, 440, and 490 nm.



Spectral property of fluorescence



Temporal property of fluorescence

These four "channels" are delayed in time through successively longer fiber optic delay lines and eventually arrive at the detector (photomultiplier tube or PMT). The resulting oscilloscope waveform is a unique measurement of both the spectral and temporal components of the fluorescence. This allows us to simultaneously observe the spectral and temporal qualities of the fluorescence. This technique is described in detail later in this report. It is these multi-wavelength waveforms, measured continuously and stored vs. depth, that ultimately serve as our indicator of PAH concentration vs. depth in the sediment.

Interferences

Nature has co-deposited a myriad of additional fluorescent materials in sediments that will also absorb the laser light and fluoresce intensely enough to complicate the measurement of the PAH fluorescence. Example materials include minerals such as calcites and a variety of biological materials. Both living organisms and their associated breakdown products (humic and fulvic acids) fluoresce well enough to interfere with the observation of the fluorescence of the target PAHs. This fluorescence, along with scattered excitation laser light and Raman light generated throughout the optical train (fiber optics) will ultimately make it back to the detector, mixed in with true PAH fluorescence, and must be accounted for in some fashion. Throughout this document we will refer to all these sources of non-PAH emitted photons as "background" fluorescence, even though the true source might well be non-fluorescent (scatter) in nature.

Understanding ROST Fluorescence Waveforms

Spectroscopic techniques involve probing the target matrix with light and learning about the contents of that matrix by analyzing the light that is emitted or absorbed by the target matrix. For screening tools it is crucial to glean as much information from this light as one can in as little time as possible. ROST accomplishes this task in a novel fashion. The fluorescence data from ROST is deceptively simple. There is a lot more going on in a ROST waveform than one would imagine at first glance. It is actually a two-dimensional data set that contains three-dimensional fluorescence information. To complicate this, some of the information is overlapping. A full description of the multi-wavelength waveform data follows in order to give the reader an understanding of the data acquired during this study.

PAH time decay waveforms

Each type of PAH molecule (such as phenanthrene, naphthalene, or anthracene) emits fluorescence over a unique time period after being excited by a pulsed excitation source such as the laser used in ROST. The emission starts out at maximum intensity, and then decays away at a rate unique to each type of PAH. The number of rings, the bonding between them, the amount of substitution on the rings, and other structural features of the molecule determine, to a great extent, the decay rate exhibited by a particular PAH. One class of molecule, the PCBs, have a structure that would seem to fluoresce well, but the chlorine substitution on the rings causes what is referred to as the heavy-atom effect, resulting in non-radiative relaxation from the excited state and a dramatic reduction in fluorescence. In fact the reduction is so significant that PCBs are essentially non-fluorescent molecules.

The environment in which the PAH exists also has a substantial influence on the decay rate. Quenching, which refers to any process that causes a decrease in the decay time (as well as the intensity) of the fluorescence, is dependent on conditions like oxygen levels, solvent availability, solvent viscosity, and a myriad of other matrix dependent conditions. An example of this can be found with the fluorescence of PAHs in fuels (gasoline, diesel, or kerosene) vs. coal tar oil. The coal tar oil can often contain more PAHs than the fuels, but the fluorescence lifetime is much shorter and the total fluorescence of fuels is often 2 to 3 orders of magnitude more intense. If one were to dissolve coal tar in a solvent such as hexane, its fluorescence intensity would rival that of fuels because the solvent matrix is simply more suited to allow fluorescence to occur.

Figure 3 illustrates the differing decay times one might observe for 4 different PAHs, along with the time profile of the laser pulse that excited them. Now remember, these are large populations of PAHs being excited and while some begin emitting immediately, other individual PAH molecules "wait" many nanoseconds before emitting a photon. What is plotted here is a picture of the distribution of times that the PAHs are remaining in the excited state before emitting photons. Now in our case (sediments) we have many different PAHs of differing ring number and substitution levels. The bold curve in Figure 3 illustrates the fluorescence decay profile that would result if we observed the fluorescence of all four PAHs simultaneously. This is the fluorescence waveform that would result if all 4 different PAHs fluoresced with equal intensity (normalized to keep it on scale). This same concept is happening in the sediments. We are observing the sum of all the decay profiles for all the different PAHs that are absorbing and emitting photons with each pulse of the excitation laser. It should be noted that there is no predictable trend between decay rate and structure like the trend that exists between spectrum and structure as described below.



Figure 3. Temporal fluorescence examples

Of course the fluorescence decay profile observed in sediments is not made up of equal amounts of fluorescence from the various PAHs found in them. The wavelengths of light being emitted by (spectra) and the relative fluorescence yields of the different PAHs are all quite different, but the concept is still valid. The decay profile of the PAHs observed in the sediment results from the decay profiles of a mixture of different PAHs, along with fluorescence from other materials in the matrix.

PAH spectra

Let's take a look at the other property of the fluorescence emission of the same 4 example PAHs we showed at in Figure 3. This time we'll examine not the time over which they fluoresce, but instead the distribution of energies found in the photons they emit. Remember that the fluorescence emission spectrum of a pure PAH is simply a graphical representation of the energy distribution of photons that are emitted from a large population of the PAHs as they release energy that was absorbed from the excitation beam of light (in our case, a laser). Spectra of pure PAHs are typically acquired by dissolving a sample of the pure PAH in a pure solvent that does not fluoresce.

Figure 4 depicts the fluorescence emission spectra of the same 4 PAHs used in the temporal example in Figure 3. The laser wavelength is also shown in Figure 4, demonstrating the principle that fluorescence occurs at longer wavelength (lower energy) than the excitation wavelength (also known as Stokes' shift). The basic trend is toward longer wavelength emission as more rings are added or substitution increases. Naphthalene emits at around 340 nm and the spectra "red-shift" as the number of rings increase. Another general property of fluorescence is that for a pure PAH the emission spectrum remains the same irrespective of what wavelength of light is used to excite them (Kasha's rule). This is not true for mixtures however, because changing the excitation wavelength might well change which PAH are being excited and to what degree. The bold spectrum in Figure 4 is the combined spectra of all 4 PAHs. This is a simplified illustration of what generally happens if we observe the total fluorescence of a mixture of different PAHs. Any change

in the relative amounts of the differing PAHs or changes in the matrix in which they exist will cause a change in the spectrum of light actually emitted.



Figure 4. Spectral fluorescence examples

The fairly well defined structure (multiple peaks, valleys, and their various positions) of the spectra in Figure 4 suggests that perhaps one could use algorithms to extract information about the relative concentrations of the individual PAHs. While this is possible for very simple mixtures (2 to 3 PAHs) under controlled conditions, the algorithms quickly fail when many PAHs are present and interference fluorescence from humics, fulvics, and minerals is introduced. At best, one is able to use the overall shape of the total fluorescence spectrum to predict the *type* of mixture (diesel, coal tar, crude oil, etc.) and, in fact, this is routinely accomplished in environmental fluorescence for environmental fluorescence fluorescence for environmental fluorescence for environmental fluorescence for environmental fluorescence fluo

PAH multi-wavelength waveform (MWW)

The fluorescence of PAHs has both a spectral and temporal component. Real-world environmental samples typically contain at least several (if not dozens) of different PAHs along with other fluorophores, and the PAH fluorescence spectra overlap to form broad and fairly featureless spectral and temporal emission (compared to pure PAH spectra). If we were to record the temporal decay waveforms across the entire spectrum we would record what is called a wavelength-time matrix (WTM) that would describe the fluorescence emission completely. To create this we scan the emission selection monochromator from wavelength to wavelength, monitoring the pulsed emission vs. time at each wavelength with an oscilloscope.

Figure 5 contains the WTMs of diesel, jet, creosote, and gasoline on sand at several thousand ppm. The difference between the contaminants is clear and identification is straightforward. Dakota Technologies, Inc. (DTI) once employed these matrix style data sets to completely analyze the fluorescence of petroleum, oil, and lubricant (POL) contaminated soils. WTMs were (and still are) excellent for identifying/classifying the PAH fluorescence of environmental samples because of the unique information that both dimensions of PAH fluorescence exhibit when acquired in unison. While WTMs make different contaminants readily discernable from one another, they are

3-dimensional and large. Also, the screening tool must be held still while the measurement is being made. All of these qualities make WTMs unwieldy for environmental screening tools that are designed to continuously log (typically 1 Hz) the presence of PAHs vs. time or depth.



Figure 5. Example WTMs of common contaminants on sand

Because WTMs are so difficult to implement in screening mode, DTI developed (and patented) a multiple-wavelength waveform (MWW) technique that allows multi-dimensional PAH fluorescence measurements to be acquired "on the fly". Figure 6 illustrates the concept. Select regions of the spectrum are monitored for their temporal response. The responses are optically delayed and recombined, and the resulting responses converge to form one two-dimensional waveform. There is sometimes overlap between the "channels" with long decay times, and the spectral regions being monitored are fewer and farther between than WTMs, but the resulting waveform still retains a unique combination of spectral and temporal fluorescence information that makes speciation and identification of PAH mixtures possible. Figure 7 illustrates the unique waveform produced by a variety of common PAH-containing environmental contaminants.



Figure 6. Multi-wavelength waveform concept

The ROST system acquires waveforms at ~1 Hz and logs them to the hard drive continuously. As described below (see <u>Calibration and normalization</u>) the waveforms are integrated to achieve a quantitative result that is plotted vs. depth. The shape of the waveform yields information on the nature of the fluorescing material. With experience the analyst learns to look for changes or similarities in the waveform and is able to assess changes in the analyte concentration or the matrix. For instance, are the decay times for the various channels changing due to changes in the PAHs or perhaps changes in oxygen levels that affect quenching? Is the emission shifting to shorter or longer wavelengths due to changes in the amount of degradation via biological activity, weathering, or volatilization? Is the first channel (closest to the laser) getting more or less contribution from laser scatter due to improper mirror alignment? These and a myriad of other questions and answers can be gleaned from the shape of this simple, yet informative, data format.



Figure 7. Waveforms of common contaminants

FVD colorization

The waveforms that are continuously logged vs. depth with ROST contain a wealth of information, but to make this information easily interpretable in fluorescence vs. depth (FVD) log format, we need to further reduce the data to a one-dimensional data set that we can plot vs. depth. As discussed, the quantitative information is contained within the area under the waveform (total fluorescence) but how do we convert a waveform's shape into a singular entity? To accomplish this, DTI has developed and implemented a novel technique that effectively converts the shape of the waveforms into colors. These colors are then used to fill in the area under the FVD that represents the total fluorescence measured at each point in the FVD. Figure 8, derived from data from a coal tar delineation project, illustrates the technique of colorizing the FVD according to the shape of the waveforms.



Figure 8. How color-coding is calculated

The result is a data presentation technique that allows the user to assess similarities or changes in the waveform shapes vs. depth by simply observing the colors that represent the shape of each and every waveform in the data set. This technique was used on the sediment measurements made in this project, both in the lab and in the field. It should be noted that the color black indicates that the algorithm that calculates the color failed to deconvolve the waveform successfully.

The colorization technique is limited to using three of the channels as a result of the red, green, and blue (RGB) color definition which computer colorization systems typically implement. A cyan, yellow, magenta, and black colorization system (CYMK) might allow the use of all four channels and is currently being considered as a replacement for RGB. The first three channels (340, 390, and 440 nm) were used to colorize the data in this study. The 490 nm channel was used in a quantitative sense, but was ignored for the colorization. It should be noted that a strictly temporal change (where only the decay times change, not the spectrum) would not necessarily result in a

color change, since the ratios of the 3 channels used might remain constant even though the area under the waveform itself will increase or decrease.

An added benefit of this technique is that it provides insight in situations where non-linear response behavior is encountered. Many contaminants such as coal tars, heavy crudes, and creosotes do not fluoresce with concentration in a linear fashion. For instance, a 10 fold increase in PAH concentration might produce very little or no increase in total fluorescence intensity. However, a spectral or temporal shift often does continue to occur with changes in concentration due to energy transfer, photon cycling, and other phenomenon. The color of the FVD fill continues to darken or shift in color, acting as an indicator of a change in the fluorescence of the sample, alerting the analyst to a possible increase in concentration. While this technique is less than analytical it does provide the analyst with additional insight into the distribution of PAHs in the soil vs. depth. **Calibration and Normalization**

The ROST system response depends on a host of factors. These include laser energy, fiber termination quality, neutral density filter selection, parabolic mirror efficiency, and fiber length, just to name a few. To account for changes in these over time and location, a single point calibration and system check is performed. A reference emitter (coined M1) is placed on the sapphire window and the response is measured. The M1 solution is permanently stored in a quartz cuvette for convenience and the measurement takes place through the wall of the cuvette. This proprietary mix of hydrocarbons fluoresces efficiently across the entire system and serves as both an indicator of system function and as a data normalization benchmark.

The total fluorescence intensity (area under the waveform) of M1 serves to normalize the data from the push that immediately follows the reference emitter measurement. All the FVD logs are presented as a percentage of the signal achieved with M1. The area under every waveform in the data set is integrated, resulting in a pico-Volt-seconds unit (picoseconds * V or pVs). These values are divided by the pVs measured for M1, and the result is multiplied by 100. The result is a log with x-axis units of percent of M1. This creates a normalized data set that takes into account the entire system performance, from end to end (laser to oscilloscope). The shape of the M1 waveform acts to guide the operator in assessing proper alignment of the detection system. The relative contribution for each channel and the shape of M1 waveform is monitored for consistency to insure that the waveforms remain consistent from day to day.


MINIMUM AND MAXIMUM ALLOWABLE AIR SPARGE INJECTION PRESSURE

Project Name:	Village of Roxana					
Project Location:	Fourth Street and Chaffer Street					
By: Randy Whitesell	Date:	6/12/2013				

By: Randy Whitesell Date: 6/12/2013

To induce airflow into the formation a minimum injection pressure is required. pressure should not exceed 80% of the total overburden pressure.

Top of screen:	58.0 ft. below land surface
Minimum Pressure:	P_{min} (psig) = 0.43 * H_h Where H_h = height of water collumn above injection screen.

 $P_{min} = 6.9 psig$

To prevent secondary permeability (hydraulic fracturing), the injection pressure should not exceed 80% of the total overburden pressure.

OVERBURDEN:

Specific gravity of water:	1
Specific gravity of formation material:	2.7 (quartz sand)
Porosity:	0.2
Water column:	16.0 ft.
Soil column:	58 ft.

Water Overburden:

water column x porosity x 62.4 lbs./ft³ = water overburden (lbs./ft²)

water overburden =

Soil Overburden:

soil column x soil sp.gr. x (62.4 lbs./ft³) x (1 - porosity) = soil overburden (lbs./ft²)

200 lbs./ft²

soil overburden = 7817 lbs./ft^2

Total Overburden:

soil overburden + water overburden = total overburden (lbs./ft2)

total overburden = 8017 lbs./ft^2

 $8017 (lbs./ft^2)/(1ft^2/144 in^2) = 55.7 psig$

Maximum Pressure: P_{fracture} = 80% of total overburden

P_{fracture} = 44.5 psig

AS/SVE Pilot Test Field Data Fourth Street and Chaffer Street Site **Table 2A**: Depth to Water

		Well							
Time	(DW-1	(OW-2	(OW-3			
Baseline		-				-			
	S (feet)	ΔS (feet)	S (feet)	ΔS (feet)	S (feet)	ΔS (feet)	S (feet)	∆S (feet)	
			 						
1									

AS/SVE Pilot Test Field Data Fourth Street and Chaffer Street Site **Table 3A**: Dissolved Oxygen and Visual Observations

Time	Well											
		OW-1		OW-2			OW-3					
	DO (mg/L)	Δ DO	Bubbles	DO	Δ DO	Bubbles	DO (mg/L)	Δ DO	Bubbles	DO (mg/L)	Δ DO	Bubbles
		(mg/L)		(mg/L)	(mg/L)			(mg/L)			(mg/L)	
Baseline												

Notes:

P:\Environmental\Shell Oil Product US\SHELL OIL PRODUCTS US 2013\21562850 - ROXANA\21562850-6_AIR SPARGE\air sparge plan\Pilot Test Data Form.xls

AS/SVE Pilot Test Field Data Fourth Street and Chaffer Street Site **Table 1A**: Vacuum/ Pressure

Time	Test	SVI	E-3	SVE	-25	AS	S-1			OV	V-1	OV	V-2	O	V-3				
	1							PID (ppm)				d= f	t (SVE-3)	d= f	t (SVE-3)	d= f	t (SVE-3)		
	Duration									d- ft	(SVE-25)	d- ft	(SV/E-25)	d- ft	(SV/E-25)				
	Duration	Veeuum	Flow	Veeuum	Flow	Flow	Dragouro					d=1	(0VE 23) ft (AS-1)	d=1	(0VE 23) ft (AS-1)	d=1	(UVE 23) ft (AS-1)		
(1		(in LL O)	FIOW	(in LLO)	FIOW	FIOW	Plessure	Lie Channel	d = (7, 0, 1)		(in H O)		II (AS-1)		-				
(hrs)	(min)	$(In H_2O)$	(scfm)	$(In H_2O)$	(cfm)	(cfm)	(psi)	Unfiltered	Filtered	(111)	1 ₂ O)	(111)	1 ₂ O)	(111)	1 ₂ O)				
										Upper Screen	Lower Screen	Upper Screen	Lower Screen	Upper Screen	Lower Screen				
-																			
-																			
-																			
-																			
												T							
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Notes:



SVE Recovery- Helium Tracer Testing Guidance (Quick Ref)

Westhollow Contact:	Cristin Bruce
	3333 Hwy 6 South, Room EC-222,
	Houston, TX 77082
	Office Phone: (281) 544-7552

TEST OBJECTIVES AND SCOPE

Direct measure of the recovery efficiency of an SVE system associated with IAS

PRE-TEST CALCULATIONS

- Flow rate and total volume of tracer needed for the test (target maximum extraction concentration is 1-2% v/v if helium is used)
- For example, if you were extracting air at 20 SCFM, you would want to meter in helium at a rate of 5.6 to 11.3 LPM (which would lead to 56 ft³ of helium into the aquifer after 2 hours at the highest rate)

EQUIPMENT REQUIRED (in addition tof air injection system)

- Industrial grade (99.9 % pure) helium gas cylinder (the balloon grade may be only ~80% pure), cylinder size 049 (291ft³) or cylinder size 044 (200 ft³) (from Praxair or other gas distributor)
- Helium gas detector (i.e. Mark Products Helium Detector, detection limits 0.01% to 100%)
- Gas-tight fittings to connect lines to a) air injection well, and b) extraction air manifold
- Rotameter (i.e. Dwyer 0-10 LPM-air gauge for extraction rates of 10-30 SCFM, or a 2.5-25 LPM gauge for higher rates), valve, and pressure gauge (0 to 50 psi) for metering helium into the air injection stream
- Pressure gauge (typically reads to 60 psi)

HELIUM TEST PROCEDURE (perform this test after the ROI measurement)

- Wait until injection flow field in well-established as indicated by stable pressure transducer readings (20 minutes) also wait until SVE system has stabilized (indicated by stable vacuums in observation wells)
- Calibrate the helium detector (check for CO₂ bias, some helium detectors will give you faulty readings if there is a lot of CO₂ present)
- Record IAS and SVE flow rates
- Inject helium into a vapor extraction well line
- Measure maximum helium recovery concentration at the extraction manifold
- Adjust helium flow, if necessary, to achieve 1-2 % v/v concentration
- Inject helium into injection air manifold

• Monitor helium in extraction air manifold until stable (at least 20 minutes)

DATA

- Injection and monitoring well/bank specifics (screened intervals and positions)
- Injection pressure and flow rate vs. time
- Maximum tracer concentration in vapor extraction manifold
- Tracer concentration vs. time in vapor extraction manifold

POTENTIAL RED FLAGS DURING THE PILOT TEST

- No measurable helium in extraction air at the manifold (sufficient backpressure on the helium line?)
- Helium everywhere (Leaky system did you check all fittings for air tightness before running helium into the system? Preferential flowpaths available? Incorrectly calculated injection concentration? Measurements taken well after helium injection initiation?)

POST-TEST DATA EVALUATION

Pilot test data analysis/interpretation should yield:

A direct measure of the recovery efficiency of a soil vapor extraction system

We would like to see 80-90% recovery of our injected air to assure ourselves that we will not be liberating unwanted/ uncontrolled vapors into the subsurface.

Plot the extraction well helium levels over time. Mark on the graph the measured concentrations measured when the helium line was hooked directly to the extraction system.

DIAGRAM



ESTIMATED MATERIAL COSTS FOR TRACER TEST

- Helium cylinder : \$ 30-70
- Flowmeter : \$125
- Pressure gauge : \$ 50-100
- Helium detector (1 week rental) \$ 225
- Fittings/ tubing : \$25-100



A Mark Products Helium Detector



An example helium delivery setup

sites to see pictures of typical instrumentation:

Helium Detector: <u>http://www.ashtead-</u> <u>technology.com/Environmental/Special%20Instruments/Mark%20Products%20Helium%20Detec</u> <u>tor%20Model%209821.htm</u>

Flowmeter: http://www.nciweb.net/mini_master.htm