DES Waste Management Division 29 Hazen Drive; PO Box 95 Concord, NH 03302-0095

RESULTS OF LASER INDUCED FLUORESCENCE SURVEY Westboro Roundhouse 26 Railroad Avenue West Lebanon, New Hampshire 03784

> NHDES Site #: 199210036 Project Type: LAST Project Numbers: 3990

Prepared For: New Hampshire Department of Transportation 7 Hazen Drive, P.O. Box 483 Concord, NH 03302-0483 Phone Number (603) 271-6370 RP Contact Name: Mr. Dale O'Connell, P.G. RP Contact Email: do'connell@dot.state.nh.us



Prepared By: Stantec Consulting Services, Inc. 5 Dartmouth Drive, Suite 101 Auburn, NH 03032 Phone Number: (603) 669-8672 Contact Name: David Allwine, P.G. Contact Email: dave.allwine@stantec.com

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Mr. Worthen Muzzey, P.G. New Hampshire Department of Environmental Services 29 Hazen Drive, P.O. Box 95 Concord, NH 03302-0095

Reference: Results of Laser Induced Fluorescence Survey Former Westboro Roundhouse, West Lebanon, NH NHDES Site #199210036, LAST Project #3990

Dear Mr. Muzzey:

Stantec Consulting Services Inc. (Stantec) is pleased to submit the results of a laser induced fluorescence (LIF) survey conducted at the above-referenced property (the "Site"). This report is submitted on behalf of the New Hampshire Department of Transportation (NHDOT) in accordance with a Work Scope Authorization (WSA) approved by the New Hampshire Department of Environmental Services (NHDES) on June 19, 2012. The Site location and pertinent site features are shown in Figure 1: Site Location Map and Figure 2: Site Plan, respectively (attached).

BACKGROUND

The Site is a historic rail yard located along the east side of the Connecticut River at its confluence with the White River. The Site was in active use from 1848 through the late 1970s. After an approximate 20-year hiatus, rail service was restored at the Site through an agreement between NHDOT and the Claremont Concord Rail Company, which currently uses a portion of the property for rail storage.

The Site encompasses the entire former Westboro rail yard including both the former Tidewater Oil site and the former Purcell Oil facility. Results from previous investigations and remedial actions indicated that the sources of petroleum impacts at the Site were surface releases at the former fuel platform north of the Sand House located on the Site adjacent to the Roundhouse building, potential releases from the northwestern end of the Roundhouse, and a release of petroleum from aboveground storage tanks (ASTs) in the Tidewater Oil portion of the Site (a.k.a. "North Yard"). Releases in the vicinity of the Roundhouse are the subject of this report. The releases in the northern portion of the Site (North Yard area) are not addressed.

On December 9, 1974, oil was observed floating on the surface of the Connecticut River approximately 10 feet from the river's east bank, which forms the western boundary of the Site. Immediate response actions were taken by B&M, the property owner at the time the release was identified, to remove the oil and attempt to determine the source of the seep. A containment boom and absorbent pillows were used to capture floating product. In an attempt to determine the source of the seep, B&M excavated several test pits and trenches along the riverbank. Black, oil-

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saturated soil was encountered at a depth of approximately 20 feet from the top of the riverbank. A large trench (approximately 75 feet in length) was excavated to a depth of 23 feet below ground surface (bgs) on the lower river terrace parallel to a City of Lebanon sewer line. No petroleum-impacted soils were identified in this trench.

In January of 1975, B&M constructed a containment system consisting of a trench excavated in the riverbank parallel to the river. A clay berm was then constructed to contain the oil leaching from the bank into the trench and prevent it from entering the river. An oil recovery system was also constructed using the trench and clay berm. According to a pre-construction design schematic drawing drafted by B&M in 1974, the system consisted of a 2-foot diameter perforated pipe installed horizontally at a depth of approximately 15 bgs. The horizontal pipe was connected to an 8-foot diameter, corrugated steel recovery well.

During the construction of the containment and recovery system, 29 soil borings were advanced throughout the Site to investigate the source of the oil seeping from the riverbank and to delineate the horizontal extent of petroleum-impacted soil at the Site. According to test boring logs dated January 1975, petroleum-impacted soil was observed in 15 of the 29 soil borings at depths ranging from 1.5 to 30 feet bgs. The investigation determined that oil was distributed generally in the area surrounding the fuel platform north of the Sand House and along the river; however, the sketch showing boring locations did not provide adequate location control to correlate exactly with other data. The fueling platform was supplied by a 300,000-gallon AST located in the central portion of the Westboro Yard (to the north of the Roundhouse area).

In 1992, an oil sheen was again reported on the Connecticut River adjacent to the Site. The NHDES) arrived on-site on November 13, 1992 and confirmed the report. The observed release of a regulated substance prompted the NHDES to issue a request for a Site Investigation to B&M. In response, ERM-New England, Inc. (ERM) advanced multiple soil borings and installed monitoring wells to update soil conditions and evaluate site groundwater. The eight monitoring wells were identified as ERM-1 through ERM-7 and ERM-9. Petroleum-impacted soil, as evidenced by elevated photoionization detector (PID) readings, petroleum odor, and black staining, was encountered in borings for wells ERM-1, ERM-3, ERM-5, and ERM-6. Several volatile organic compounds (VOCs) were detected in groundwater samples from these wells. The highest VOCs concentrations were detected in the groundwater sample from ERM-6, located adjacent to the former fuel platform. Light non-aqueous phase liquid (LNAPL) petroleum was detected in wells ERM-5 and ERM-6 at thicknesses of 0.04 feet and 0.61 feet, respectively. LNAPL sampled from ERM-6 was identified as No. 2 fuel oil by EPA Method 8100M fingerprinting analysis.

In March 1994, ERM returned to the Site, at the request of the NHDES, to conduct an Additional Site Investigation. The investigation included the excavation of eight test pits (TP-1 through TP-8), collection of groundwater samples from existing monitoring wells, collection of surface water samples from the Connecticut River, and assessment of the recoverability of LNAPL at the Site. During the excavation of test pit TP-3, a clay pipe was identified at a depth of 5.5 feet bgs. The

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pipe was also identified in test pits TP-4 through TP-7. According to the ERM report, the pipe location corresponded to a sewer line identified on a Right-Of-Way and Track Map drawn by B&M, dated October 31, 1930. Petroleum-impacted soil was encountered at approximately 6 feet bgs in test pits TP-1 through TP-5.

After the NHDOT's purchase of the Site in 1999, Jacques Whitford Company, Inc. (now Stantec) conducted additional subsurface investigations at the Site. On August 16 and 17, 2000 and September 14 and 15, 2000, Jacques Whitford directed the excavation of 10 test pits (identified as TP-9 through TP-19) to determine the source of the petroleum seeping into the Connecticut River. Test pits were excavated by Moulton Construction, Inc. (Moulton) of West Lebanon, New Hampshire. Test pits TP-9 through TP-12 and TP-14 were excavated along the eastern bank of the river with the focus on the area that appeared to be the source of the most upstream portion of the seep, as seen during the sediment inspection activities and during previous site visits made by Jacques Whitford and the NHDES. Test pits TP-13 and TP-15 through TP-18 were installed to trace the petroleum-impacted soil upgradient and attempt to determine the source area location. The horizontal portion of the oil recovery system previously installed by B&M was discovered during the excavation of TP-14. Test pit TP-19 was installed adjacent to the corrugated steel recovery well to confirm the location of the horizontal corrugated pipe identified during the installation of test pit TP-14 (described in detail below). Petroleum-related compounds (VOCs, polynuclear aromatic hydrocarbons [PAHs], and total petroleum hydrocarbons [TPH]) were detected in all of the soil samples submitted for laboratory analysis. However, none of the compounds were detected above the most stringent NHDES soil standards in force at the time. The petroleum detected in two of the soil samples (TP-16 and TP-17) was identified as No. 2 fuel oil/diesel fuel by EPA Method 8100M fingerprinting analysis.

During the installation of test pit TP-14, the excavator uncovered a 10-inch diameter, steel corrugated pipe. The pipe was encountered at a depth of approximately 11 feet below the top of the riverbank and was oriented north to south. A layer of crushed stone approximately 2 to 4 inches thick surrounded the pipe. Once the pipe was uncovered, water and LNAPL began flowing into the excavation. Jacques Whitford directed the excavation of test pit TP-16 topographically upgradient of TP-14 and east of the City of Lebanon sewer line to determine if the source of the LNAPL was coming from the direction of the Roundhouse. Groundwater was encountered during the excavation of test pit TP-16 at a depth of approximately 19 feet bgs. No sheen was observed on the groundwater and no LNAPL was encountered in test pit TP-16.

Test pit TP-19 was excavated adjacent to the corrugated steel recovery well to confirm the identification of the 10-inch diameter, steel corrugated pipe encountered during the excavation of test pit TP-14. A vacuum truck was mobilized to the Site in the event LNAPL entered the excavation as occurred in test pit TP-14. Petroleum-impacted soil, as indicated by an elevated PID reading (125 parts per million or ppm) and strong petroleum odor, was encountered from approximately 5 feet bgs to 14 feet bgs, the maximum excavation depth of test pit TP-19. No LNAPL was encountered. The corrugated steel pipe was not encountered during the excavation.

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According to the schematic drawing of the recovery system by B&M, dated July 16, 1975, the horizontal portion of the system was located at a depth of approximately 15 feet bgs. Due to collapsing excavation walls increasing the test pit area and encroachment upon the sewer line to the east, the excavator was unable to reach a depth of 15 feet bgs.

The general stratigraphy observed during the 2000 test pit investigation consisted of an upper layer of fill or rip-rap extending to depths ranging from 0.5 to 1.5 feet bgs, followed by a thick (from 10 to 17 feet) layer of light brown fine sand with trace amounts of silt and clay. In the test pits where a petroleum odor was observed (all test pits with the exception of TP-15), there was a distinct color change in the sand layer from light brown to gray at depths ranging from 10 feet bgs in test pits TP-9 through TP-10 to 17 feet bgs in test pit TP-13. The change in color was accompanied by an increase in moisture content, the presence of a petroleum odor, and increased PID readings ranging from 36.5 to 202 ppm.

Jacques Whitford concluded that the source of the petroleum contamination along the Connecticut River was apparently the outlet of a former pipe leading from the former fuel platform at the Site west to the river. Spillage during fueling would have been conveyed down the pipe to the edge of the river. Because of the expected influence of stream flow and the fluctuation of water levels, the contamination was believed to have been "dragged" southward in and along the river, while being smeared between high and low groundwater levels.

As a part of additional assessment activities in October 2005, Jacques Whitford was on site to advance soil borings along the bank of the Connecticut River via a manual Geoprobe® unit and/or stainless steel hand auger. A total of 24 locations were advanced along the riverbank between the top of the riverbank and the edge of the river. In November 2005, Stantec installed seven well points (designated WP-1 through WP-7) in select borings advanced in October 2005. Widespread soil and groundwater impacts including measurable LNAPL were observed in the riverbank area. In addition to measurable LNAPL in locations JW-5 and WP-6, exceedences of applicable NHDES standards were observed in soil and groundwater samples collected from several of the sample locations along the river bank. Soil data indicated an area of highest impacts centered in the vicinity of borings TB-118, TB-119, and TB-110 located on the upper portion of the river bank. The majority of soil impacts appeared to be limited to this general area and, consistent with historical observations of soil impacts, appeared to be limited to approximately 10 to 20 feet below grade. This area generally coincided with the approximate area of the former B&M clay berm and recovery trench. Modifications to the riverbank in this area may have influenced the observed elevated impacts in this area. Soil data from the eastern investigation area did indicate a gap between impacts in the fuel platform area and impacts along the riverbank. These data supported the interpretation of the former drainage pipe outlet as the likely original source of impacts to the river and riverbank. The data also suggested a potential secondary source for riverbank impacts along the northwestern end of the former Roundhouse. It was conjectured that the possible secondary source area could have been partially related to or had been exacerbated by modifications to the riverbank during installation of the former recovery trench and clay berm.

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Since 2005, LNAPL has been consistently detected in monitoring well JW-5 and well point WP-6. Until 2010, passive LNAPL recovery was conducted using absorbent wicks installed in monitoring wells. LNAPL has also been removed using bailers and/or a peristaltic pump during groundwater sampling events. To date, approximately 11 gallons of LNAPL have been recovered by these methods. Groundwater monitoring at the Site is ongoing in accordance with Groundwater Management Permit (GMP) #GWP-199210036-L-001 issued January 30, 2008, revised March 10, 2010 and October 13, 2011.

In a cover letter to the October 13, 2011 GMP revision, the NHDES requested additional subsurface investigation on the riverbank in the vicinity of points JW-5 and WP-6 with the intent of further delineating the extent of free product and the migration of free product in this area. In addition to the free product delineation activities, NHDES requested repair of a monitoring well (later determined to be monitoring well MW-3) located in the drive for the Eagle Leaf Concrete facility, which is situated approximately 1,000 feet north of the Roundhouse structure. After subsequent discussions with NHDES, it was determined that additional unused wells should be decommissioned concurrent with well repair activities.

The work requested by the NHDES in October 2011 was completed between December 2011 and January 2012 and was summarized in a *Report on Additional Free Product Delineation and Monitoring Well Repair and Decommissioning* dated April 24, 2012. The work included the advancement of six test pits along the riverbank slope to depths ranging between 11 and 14 feet below grade. Recovery wells were installed in four of the six test pits. Results of this investigation were generally consistent with the findings of previous free product investigations completed at the Site and evidence of petroleum impacts were identified in all six of the completed test pits. However, contaminant concentrations above SRS were detected only in test pits TP-3 and TP-4, which were located north-northeast of well point WP-6 and southwest of JW-5 (both being wells that consistently contain LNAPL). Laboratory analysis identified the petroleum contamination as No. 2 fuel oil.

While the December 2011 test pit data served to enhance the understanding of subsurface contaminant distribution at the Site, it did not provide conclusive information regarding the source of the petroleum contamination. Therefore, following submittal of the April 2012 report, the NHDES requested that Stantec submit a WSA for an LIF survey at the Site to provide additional information on the source of petroleum impacts.

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WORK PERFORMED

Utility Clearance and Health and Safety Plan

Stantec updated the existing health and safety plan (HASP) used for field investigations at the Site in accordance with 29 CFR 1910.120. Stantec also contacted the local utility clearance service, DigSafe, as well as the Lebanon Department of Public Works, to clear utilities prior to the initiation of subsurface work.

LIF/UVOST[®] Survey

On June 26 and 27, 2012, a total of 27 boreholes (designated LIF01 to LIF27) were completed at the Site as part of the Laser Induced Fluorescence/Ultraviolet Optical Screening Tool (LIF/UVOST[®]) survey. Stantec retained the services of Columbia Technologies (Columbia) of Baltimore, Maryland to conduct the LIF/UVOST[®] survey. The purpose of the survey was to delineate the vertical and horizontal extent of residual free-phase petroleum in the Site's subsurface. To achieve this goal, down-hole sensors provided by Columbia were advanced into the subsurface using Geoprobe® direct push drill rigs operated by Geosearch, Inc. (Geosearch) of Fitchburg, Massachusetts. Data were obtained continuously as the probe was advanced to below the water table (the zone expected to be most impacted by LNAPL which, due to its density of less than 1.0, floats on the capillary fringe (for all practical purposes, the water table surface at this site). Subsurface data were relayed in real time back to monitoring instrumentation contained in a separate vehicle, where it was processed. After processing, log sheets for each completed borehole were uploaded to a password-protected website, where they were subsequently accessed and downloaded. The log sheets are provided in Columbia's Subsurface Characterization Using Laser Induced Fluorescence (LIF) Technology report (attached). The Columbia report also provides more in-depth description of the LIF/UVOST[®] equipment and its operation during the survey.

The borehole locations were selected by Stantec's on-site representative. The survey began by advancing boreholes as close as possible to monitoring well JW-5 and well point WP-6, where LNAPL has been consistently detected, in order to establish the baseline fluorescence characteristics for LNAPL at the Site. It should be noted that due to the locations of JW-5 and WP-6 on a steep riverbank, the baseline borings were advanced along the flat river terrace located immediately east (uphill) of JW-5 and WP-6. Additional borings were then advanced along the access road on the west side of the Roundhouse building, in the area to the north of the Roundhouse and west of former fueling platform, and to the east of the platform. Boring locations are depicted on Figure 2.

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RESULTS

Magnitude and Distribution of Oil Impacts

As discussed in Columbia's *Subsurface Characterization Using Laser Induced Fluorescence (LIF) Technology* report (attached), the total fluorescence intensity recorded at each interval during advancement of the LIF boring is compared to a reference emitter (RE) standard. Note that the RE standard is a specially designed petroleum mixture created by Dakota Technologies, the designers of the LIF/UVOST[®] equipment, and is not representative of a particular petroleum product. In general, a higher total fluorescence intensity (measured as a percentage of the RE standard [%RE]) recorded in the LIF boring corresponds with higher concentrations of PAHs in the subsurface. A summary of the highest total fluorescence intensities measured in each boring is provided in Table 1 (attached). A visual 2-dimensional (2-D) depiction of detected intensities is provided as Figure 2 in the attached Columbia report.

During the June 2012 LIF survey, the highest total fluorescence intensities (greater than 90%RE) were recorded in borings LIF01, LIF02, LIF08, LIF12, LIF14, LIF18, LIF23, and LIF25. Borings LIF14 and LIF25 were located to the west of the northern end of the former fueling platform (located northeast of the Roundhouse). Additional borings to the north (LIF26), east (LIF24), south (LIF13), and west (LIF15 and LIF16) of these two borings exhibited significantly lower total fluorescence intensities. These data suggest that the subsurface contamination detected in borings LIF14 and LIF25 is likely localized.

Conversely, borings LIF23, LIF12, LIF18, LIF08, LIF02, and LIF01 form a northeast to southwest trending line leading from near the southern end of the former fueling platform (LIF23) to the vicinity of WP-6 (LIF01). This pattern of elevated total fluorescence intensities is consistent with the southwesterly direction of groundwater flow historically calculated at the Site.

An additional cluster of borings that also had elevated total fluorescence intensities, but with %RE readings lower than those noted above (ranging from approximately 40%RE to 80%RE), was detected at LIF04, LIF05, LIF07, LF09, and LIF20. These borings were located in lateral (cross-gradient) positions on the north and south sides of the line of greatest total fluorescence intensities described above. The observed decrease in fluorescence intensity in cross-gradient directions may represent the natural diffusion/dispersion of oil from high to low concentrations in a porous media, which would naturally result in decreasing petroleum concentrations as you move perpendicularly (cross-gradient) from the main impacted zone.

In the remaining borings, the highest total fluorescence intensities were at approximately 25%RE or lower. Furthermore, in borings LIF26, LIF27, LIF11, and LIF06, which represent the northernmost, easternmost, southernmost, and northwestern-most borings of the investigation area, respectively, maximum total fluorescence intensities were only marginally elevated above background.

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As noted above, a 2-D representation of the LIF/UVOST[®] survey data from the Site produces a generally northeast to southwest trending band of elevated fluorescence intensities from LIF23 (upgradient) to LIF01/LIF02 (downgradient). Moving north and south (cross-gradient) from this zone results in decreasing fluorescence intensities. When accounting for depth, the detections of elevated fluorescence intensities generally appeared to correspond with the depth of the water table when compared to historical water levels measured in wells closest to the borings. The depths at which elevated fluorescence intensities were detected ranged from approximately 5 to 30 feet below ground surface. The greatest thicknesses of elevated fluorescence intensities were detected in borings LIF01, LIF02, LIF04, LIF05, LIF08, LIF12, LIF18, and LIF23. In these locations, elevated fluorescence intensities were detected in soil horizons with thicknesses ranging up to approximately 10 feet. These data likely represent the presence of elevated PAH concentrations in the smear zone of Site's water table. The 3-dimensional (3-D) nature of the contaminant distribution is shown on Figures 3 and 4 in the attached Columbia report.

In a Dakota Technologies presentation entitled Direct Push Site Characterization of NAPL with Laser-Induced Fluorescence (LIF), given in Tampa, Florida on January 16, 2008, Travis Martin and Randy St. Germain explain that the total fluorescence (as %RE) has a semi-linear relationship with TPH concentrations. As noted above, the highest total fluorescence intensities were detected at LIF01, LIF02, LIF08, LIF12, LIF14, LIF18, LIF23, and LIF25. The maximum total fluorescence intensities recorded in these borings ranged from 91.7 %RE at LIF01 to 161.1 %RE at LIF14. Based on a graph included in the January 2008 Dakota Technologies presentation (see page 30 of the attached copy of the referenced PowerPoint presentation), these total fluorescence intensities correspond to TPH concentrations of approximately 5,000 ppm to 9,000 ppm (assuming the product is diesel, as noted below). These estimated TPH concentrations are fairly consistent with TPH concentrations detected in samples collected for laboratory analysis from test borings TB-101 to TB-123 during Jacques Whitford's 2005 pre-remedial investigation. For instance, the maximum total fluorescence recorded in LIF08 (111.4 %RE), which was encountered at approximately 26 feet below ground surface, corresponds to a TPH concentration of approximately 5,500 ppm; the TPH concentration detected in a soil sample collected for laboratory analysis from TB-111 (20 to 25 feet below ground surface), located approximately 30 feet east of LIF08, was 4,430 ppm.

Petroleum Identification

In addition to recording the total fluorescence intensity detected during boring advancement, the LIF survey equipment also records the fluorescence intensity of each of four specific wavelengths (350, 400, 450, and 500 nanometers [nm]). Since different petroleum products fluoresce with different intensities at different wavelengths (lighter products tend to fluoresce with greater intensity at shorter wavelengths while heavier products tend to fluoresce with greater intensity at longer wavelengths), the LIF data can be utilized to identify different types of petroleum products. As shown on the LIF logs in their report, Columbia projects the intensity and duration of fluorescence for each of the four wavelengths fluoresced at the depth of maximum total fluorescence intensity in an area graph. In the area graph, the height for each wavelength area is based on its intensity of

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fluorescence while the width of the wavelength area is based on the duration of fluorescence. Intensity (Y-axis) on the area graphs is measured in microvolts (μ V) while duration (X-axis) is a constant 320 nanoseconds. Each wavelength area is also designated with its own color: blue for 350 nm, green for 400 nm, orange for 450 nm, and red for 500 nm. By blending the wavelength designated colors, weighted by each wavelength's areal extent (determined by fluorescence intensity and duration), a colorimetric scale for the detected petroleum product is created. In this colorimetric scale, lighter petroleum products are depicted with green to blue colorations (corresponding to greater fluorescent intensity at shorter wavelengths) while heavier petroleum products are depicted with yellow to orange/red colorations (corresponding to greater fluorescent intensity at longer wavelengths). This colorimetric scale is used to shade the total fluorescent intensity versus depth graphs contained in Columbia's LIF/UVOST[®] logs. A fingerprint of the detected petroleum product can be discerned by looking at the color depicted in the total fluorescent intensity versus depth graphs in combination with the pattern of the associated wavelength area graph.

The majority of the petroleum product detected during the LIF/UVOST[®] survey completed at the Site resulted in a generally green to yellow-green coloration in the total fluorescent intensity versus depth graphs. The coloration in these graphs was generally similar for most of the borings where elevated fluorescent intensities were detected. Notable exceptions to this generality include boring LIF12, where a more blue-green color is depicted at the shallower depths (approximately 5 to 7 feet below ground surface). However, this coloration is depicted with relatively low total fluorescent intensity (approximately 5 to 10%RE), whereas the depth where the greatest total fluorescent intensity was detected (depth of approximately 11 feet below ground surface and intensity of approximately 155%RE) is depicted with a more green coloration. Therefore, while it appears that a relatively low concentration of a different petroleum composition was detected in this boring, the greatest concentration of petroleum appears to be of a makeup similar to that detected in other borings. Conversely, a more yellow-green to orange colorations appear to represent relatively minor detections of a product with a makeup different from the primary petroleum product detected at the Site.

The area graphs depicting the duration and intensity of the four specific wavelengths (350 nm, 400 nm, 450 nm, and 500 nm) also show a generally similar pattern across the Site. In general, the 400 nm wavelength fluoresced with greatest intensity (up to approximately 150 μ V) while the 500 nm wavelength fluoresced with the least intensity. The 350 nm and 450 nm wavelengths generally fluoresced at fairly similar intensities. When compared to standards provided in the Columbia report, the patterns on the wavelength area graphs and coloration on the total fluorescent intensity versus depth graphs for the product detected at the Site appears to most closely resemble the standard called "Diesel 1995". Although fluorescence intensity detected from the product at the Site was lower than the intensity of the diesel standard (maximum intensities of each wavelength at the Site were approximately half the intensity each wavelength of the diesel standard), the intensity is dependent upon PAH concentrations. Therefore, the lower fluorescence intensity detected at the

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Site reflects the fact that PAH concentrations at the Site were lower than the PAH concentrations of the diesel standard, which was developed from sand saturated with product.

DISCUSSION

The LIF/UVOST[®] survey data produce a distinct band of elevated fluorescence intensities/PAH concentrations in the Site's subsurface extending from LIF23 southwest to LIF02. These data are consistent with the source of contamination being a release of diesel off the southern end of the former fueling platform. Over time, the diesel likely migrated downward into the subsurface and to the southwest following the local groundwater flow gradient. Downgradient of the fuel platform, concentrations in cross-gradient directions to the north and south from the main impacted zone decrease.

These data appear to be inconsistent with historical groundwater analytical data collected from monitoring wells ERM-5, JW-3, and ERM-1 (REP). Although these wells appear to be located within the main impacted zone identified during the LIF/UVOST[®] survey, groundwater samples collected from the wells have generally not contained significantly elevated contaminant concentrations. Furthermore, LNAPL has not historically been detected in these three wells.

One explanation for this inconsistency could be the relatively low solubility of PAHs, coupled with the possibility that the detected contamination is bound within the soil matrix and does not exist as LNAPL. This inference is fairly consistent with historical soil analytical data collected from test borings TB-110, TB-111, and TB-113, which were installed in the general vicinities of LIF/UVOST[®] borings LIF02, LIF08, and LIF18 (in the main impacted zone) in 2005. Elevated VOC, TPH, and/or PAH concentrations were detected in soil samples collected from the three test borings at their time of installation, but the lack of LNAPL impacts in nearby wells suggested the presence of contaminated, though not necessarily fully oil-saturated, soils at the Site. However, the distribution of fully oil-saturated soils at the Site may be heterogeneous, so it is possible that areas of LNAPL are present within the main band of contamination, but are not present where monitoring wells were installed.

One other inconsistency is how the LIF/UVOST[®] data compares to actual locations in which LNAPL has been detected. LNAPL has been regularly detected in monitoring well JW-5 and well point WP-6. Although elevated fluorescence intensities were detected in the LIF/UVOST[®] borings advanced closest to JW-5 and WP-6 (LIF04 and LIF01, respectively), the maximum detected fluorescence intensities in LIF04 and LIF01 were not the highest intensities detected at the Site and were not higher than intensities detected further to the east and closer to the source area. No LNAPL has been detected in wells JW-2 or ERM-5, which are the wells located closest to the LIF/UVOST[®] borings with the highest maximum fluorescence intensities detected at the Site (LIF14 and LIF12). These data suggest that the elevated fluorescence intensities detected at the Site may not necessarily correspond with the presence of LNAPL.

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As previously noted, LNAPL continues to be detected in monitoring well JW-5 and well point WP-6, which are located on the banks of the Connecticut River within approximately 50 feet of the normal river channel. Past observations during sampling events suggest that JW-6 may be within the river channel during times of high flooding. Periodic water level fluctuations in the river, coupled with the presence of the clay berm installed parallel to the Connecticut River as part of an oil containment system in 1975, likely contribute to the on-going detection of LNAPL in the noted wells. High water in the river could cause a temporary reversal in groundwater flow towards the river, thereby causing LNAPL migration in the area to slow or stop. Although the exact location of the clay berm is not known, it is possible that it is impeding horizontal flow of LNAPL towards the Connecticut River and causing it to pool along the riverbank in the vicinities of JW-5 and WP-6.

CONCLUSIONS

Stantec has completed an LIF/UVOST[®] survey at the former Westboro Roundhouse property to investigate the source of LNAPL detected in monitoring well JW-5 and well point WP-6. Based on the results of this survey, Stantec concludes the following:

- Elevated PAH concentrations as inferred by elevated fluorescence intensities were detected in a line running roughly northeast to southwest from near the southern end of the former fueling platform to near WP-6. The depths of elevated fluorescence intensities generally appeared to correspond with the groundwater table smear zone based on water levels historically measured in nearby monitoring wells. Downgradient of the fuel platform, crossgradient fluorescence intensities to the north and south of the main impacted zone decreased. The extent of elevated PAH concentrations appears to have been delineated during the LIF/UVOST[®] survey.
- Inferred concentrations of PAHs in the main impacted zone appear to be in the 5,000-9,000 ppm range, which is consistent with prior sampling results in the area. Fingerprinting of the detected petroleum product by the LIF/UVOST[®] equipment suggests it is diesel.
- Historical soil and groundwater sampling data, as well as the newly collected LIF/UVOST[®] data, suggest that PAH levels detected in the main impacted zone are not reflective of LNAPL in the subsurface; rather, the data suggest that the subsurface PAHs are bound to the soil matrix and do not exist in high enough concentrations currently to manifest as LNAPL. Due to subsurface heterogeneities, this may not apply to all areas of the main impacted zone.
- The LIF/UVOST[®] survey results indicate that the likely source of LNAPL in JW-5 and WP-6 is a historical release of diesel in the vicinity of the former fueling platform located northeast of the Roundhouse building. Although the data do not suggest that significant LNAPL exists in the area between the suspected source area (fuel platform) and the riverbank where LNAPL is regularly observed in JW-5 and WP-6, periodic water level fluctuations in the river,

November 8, 2012 Results of Laser Induced Fluorescence Survey Page 12 of 13

Reference: Results of Laser Induced Fluorescence Survey Former Westboro Roundhouse, West Lebanon, NH DES Site #199210036, Project #3990

coupled with the presence of the clay berm installed parallel to the Connecticut River as part of an oil containment system in 1975, likely contribute to the on-going detection of LNAPL in the noted wells.

RECOMMENDATIONS

Based on the LIF/UVOST[®] survey, the contaminant mass appears to extend from the source area near the former fueling platform to the river. Given the depth of the contaminant mass (up to 30 feet below ground surface), it is unlikely that excavation of the contaminant soil would be a feasible remedial alternative. Furthermore, since contaminant concentrations in Roundhouse monitoring wells have mostly exhibited stable to decreasing trends, the value of remediating such a large volume of impacted soil would be low.

However, along the riverbank, well point WP-7 contained naphthalene at its highest recorded concentration for the well point during the November 2011 sampling event. In addition, free product thickness was measured at record or near-record highs in monitoring well JW-5 and well point WP-6 during the May 2011 sampling event. Removal of residual LNAPL from the area could address both issues. Therefore, Stantec recommends the following:

 Conduct passive recovery of LNAPL from the monitoring points in which it is detected using adsorbent socks on a bimonthly basis (May, July, September and November). To be cost effective, NAPL recovery visits in May and November could be coordinated with the GMP sampling normally scheduled for those months.

November 8, 2012 Results of Laser Induced Fluorescence Survey Page 13 of 13

Reference: Results of Laser Induced Fluorescence Survey Former Westboro Roundhouse, West Lebanon, NH DES Site #199210036, Project #3990

If you have any questions, comments, or require additional information, please do not hesitate to contact the undersigned at 603-206-7553.

Respectfully,

STANTEC CONSULTING SERVICES INC.

Abigail P. Bline Project Scientist Tel: (603) 206-7554 Fax: (603) 669-7636 abigail.bline @stantec.com

Attachments

c. Dale O'Connell, NHDOT file

and a alline

David A. Allwine, P.G. Senior Associate Tel: (603) 206-7553 Fax: (603) 669-7636 Dave.Allwine@stantec.com

Table 1Maximum Recorded Total Fluorescence IntensitiesWestboro Roundhouse

West Lebanon, NH

Boring ID	Maximum Total Fluorescence Intensity (%RE)	Depth of Maximum Signal (feet below ground surface)	
LIF14	161.1	12.9	
LIF12	155.1	11.02	
LIF02	134.0	11.02	
LIF25	130.0	8.12	
LIF23	119.6	11.67	
LIF08	111.4	26.83	
LIF18	109.5	14.95	
LIF01	91.7	6.87	
LIF05	78.6	20.17	
LIF07	61.8	16.03	
LIF04	61.3	10.42	
LIF09	53.6	24	
LIF20	43.7	13.86	
LIF10	25.9	22.86	
LIF19	23.2	0	
LIF16	23.1	12.8	
LIF03	21.3	15.95	
LIF15	20.1	7.52	
LIF13	13.1	8.28	
LIF24	9.4	5.98	
LIF22	8.2	13.11	
LIF06	2.1	0.05	
LIF11	1.4	0.25	
LIF21	1.2	0.22	
LIF17	1.0	0.06	
LIF27	1.0	6.98	
LIF26	0.8	0	

Notes:

1. %RE = percent of the reference emitter standard





SmartData Solutions®



Subsurface Characterization Using Laser Induced Fluorescence (LIF) Technology Westboro Roundhouse 27 Railroad Avenue West Lebanon, New Hampshire

PREPARED FOR

Stantec Wellington Business Park 5 Dartmouth Drive, Suite 101 Auburn, New Hampshire 03032

July 16, 2012

PREPARED BY

COLUMBIA Technologies, LLC

1448 South Rolling Road Baltimore, Maryland 21227 410-536-9911 www.columbiatechnologies.com

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FIGURES

Figure 1	Sitemap	and L	Locations
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Figure 2 ... Plan View, LIF Response > 25%RE and 50%RE

Figure 3 Oblique View Looking Northeast, LIF Response > 25%RE and 50%RE

Figure 4 ... Transect View Looking North, LIF Response > 25%RE and 50%RE

Figure 5 ... Transect View Looking East, LIF Response > 25%RE and 50%RE

APPENDICES

Appendix A: LIF/UVOST[®] Logs

Appendix B: UVOST Response to Various Random Products Saturated on Wet Sand

Introduction

Stantec (Stantec) contracted **COLUMBIA Technologies, LLC (COLUMBIA)** to conduct an investigation of subsurface contamination at the Westboro Roundhouse site, located in West Lebanon, New Hampshire. This investigation involved delineating the depth and horizontal extent of free product and residual petroleum contamination using Laser Induced Fluorescence/Ultraviolet Optical Screening Tool (LIF/UVOST[®]) technology.

The investigation was conducted on June 26, 2012 and June 27, 2012, and consisted of 27 LIF/UVOST[®] screening locations to depths ranging from 20.66 feet to 33.40 feet below ground surface (bgs). A Geoprobe[®] Direct Push Technology (DPT) drilling rig was used to advance the locations.

Objectives

The objectives of this LIF/UVOST[®] investigation were to:

- Delineate in high resolution the vertical and horizontal extent of residual and free product petroleum based contamination in the investigation area.
- Develop two-dimensional (2D) and three-dimensional (3D) graphical visualizations of the collected data to facilitate a better understanding of the contaminant distribution and the location and depths for future field activities, including sampling, well installations, and remediation remedies.

LIF/UVOST[®] Equipment Description

The LIF system utilized for this investigation is the latest generation UVOST[®] system developed by Dakota Technologies, Inc (DTI). The LIF/UVOST[®] system consists of an Excimer laser, two fiber optic cables that are pre-strung through the DPT rods, an optical detection system, a SONY ToughbookTM laptop computer, and Shock Prevention Optical Cavity (SPOC). The SPOC consists of a sapphire window and a parabolic mirror, as well as a shock absorbing gel that allows the SPOC to maintain mirror alignment under the duress of percussion during advancement.

LIF/UVOST[®] screening was performed by pushing/hammering the SPOC into the soil at the target rate of two cm/sec (0.8 inches per second). As the probe advances, the Excimer laser generates energy in the form of photons (308nm). This energy is transferred through one of the fiber optic cables at a rate of 50 pulses per second to the optical cavity, where the parabolic

mirror reflects the energy through the sapphire window. Any polycyclic aromatic hydrocarbons (PAHs) that are in contact with the sapphire window absorb this photon energy. These PAHs then emit fluorescence in order to return to their base state. A portion of this fluorescence is carried back to the optical detection system via the second fiber optic.

Once at the surface, the emitted fluorescence is measured and recorded across four specific wavelengths – 350, 400, 450, and 500 nanometers (nm). These wavelengths represent a common range of fluorescence associated with PAHs. Typically, the lighter fuels (jet fuel and gasoline) emit fluorescence at the shorter wavelengths – 350nm and 400nm, while heavier, less distilled compounds such as bunker fuel or diesel fuel emit fluorescence at the longer wavelengths – 450nm and 500nm. As the test proceeds, the total monitored fluorescence is recorded and displayed in real-time at one second intervals as a function of depth on the LIF/UVOST[®] system computer. In addition, the intensity and duration of the fluorescence at each of the four monitored wavelengths are recorded and presented in real time at one second intervals as a separate graph on the LIF/UVOST[®] system computer.

LIF/UVOST[®] System Performance Test

As a quality control check, the LIF/UVOST[®] system response is evaluated prior to and upon completion of each LIF/UVOST[®] screening location. This evaluation is completed using a Reference Emitter (RE) that consists of a blend of Non-Aqueous Phase Liquid (NAPL) and produces a consistent fluorescence response over the four wavelengths monitored by the LIF/UVOST[®] system. Collected data is then presented as a percentage of the RE. Using the same RE at each location and site allows normalization of data collected over several locations, sites or screening events. The RE standard is provided by DTI, and is the same for all LIF/UVOST[®] systems currently in operation.

In addition to obtaining a baseline RE for each location, the background reading of the LIF/UVOST[®] system is electronically recorded prior to insertion into the soil. This background reading is required to be below 0.5% of RE prior to the start of any testing. The background reading during tool advancement typically stays at or below the surface background reading – giving confidence that any increases in fluoresce are "true" readings and not fluctuations or variations in the background.

Investigation Methods

A total of 27 LIF/UVOST[®] locations were completed at the Westboro Roundhouse site. Each location was selected by Stantec's representative onsite, and the termination depth of each location was also determined by Stantec's representative onsite. Immediately upon completion of each location, the dataset is wirelessly delivered to **COLUMBIA's** remote servers for Quality Assurance/Quality Control (QA/QC) review and uploaded to a password secure website using Columbia's patented *SmartData Solutions*[®] technology. The results from each location are shown in Appendix A. Maps and 2D/3D graphics of the site have been prepared for easier visualization of the subsurface.

LIF/UVOST[®] Log Interpretation

There are three primary characteristics of fluorescence that are considered when interpreting LIF/UVOST[®] data. These characteristics are:

- 1. Fluorescence intensity how brightly does the compound fluoresce,
- 2. Wavelength what color does the compound fluoresce at, and
- 3. Duration how long does the compound fluoresce at each monitored wavelength

Individual LIF/UVOST[®] logs consist of a primary graph of total fluorescence versus depth, an information box and up to five waveform "callouts". In the primary fluorescence graph, depth is plotted on the Y axis, and the combined total fluorescence intensity of the four monitored wavelengths is plotted on the X axis. Total fluorescence intensity is presented as a percentage of the RE standard. Since various PAHs fluoresce at differing intensities, there are several compounds that fluoresce brighter than the RE standard, and therefore the total RE can exceed 100%. Total fluorescence intensity is typically proportional to concentration and responds linearly as concentration increases.

Waveform callouts are presented along the left-hand side of the primary graph. These callouts present the fluorescence intensity of each of the monitored wavelengths on the Y axis (in microvolts (uV)) and the duration of fluorescence of each wavelength on the X axis. No scale is given along the X axis, however; it is a consistent 320 nanoseconds wide. The four peaks are due to the fluorescence at the four monitored wavelengths, called channels. Each channel is assigned a color. Various NAPLs will have a unique waveform signature based on the relative

amplitude of the four channels and/or the broadening of one or more of the channels. Callouts are selected by the operator and typically correspond to peaks on the primary graph.

The fill color of the response on the primary graph is based on the relative contribution of each of the four channels' area versus the total waveform area. This allows the viewer to discern different substances at different depths based on the fill color.

See Appendix B: UVOST Response to Various Random Products Saturated on Wet Sand for the expected wavelength signature for common compounds.

Correlating LIF/UVOST® to Sampling or Laboratory Analyses

Generalized correlations between LIF/UVOST[®] and laboratory sample results can be inferred, but cannot be viewed as a linear comparison. LIF/UVOST[®] response and laboratory results are collected, analyzed and reported in different units and by different procedures, so correlation is not an exact one-to-one comparison. The LIF/UVOST[®] uses a process whereas a 2D soil surface is exposed to excitation light, and any fluorescent light emitted is analyzed at the ground surface. Soil and groundwater results involve the collection of a sample, extraction of a sub-sample at the surface, and then transporting them to a laboratory for further extraction and analysis. These processes are different by definition.

SmartData Solutions[®]

COLUMBIA's *SmartData Solutions*[®] is a patented process (U.S. Patent No, 7,058,509) that enables the rapid processing of field data into easy to understand 2D/3D visualizations, posted to a password protected website. This process includes QA/QC review, formatting and rapid visualization of the data for the project team and enables a complete check of the dataset prior to completion of fieldwork.

Delineation

The *SmartData Solutions*[®] graphics display a 3D view of the contamination plume. These plumes are calculated by extrapolating data in three dimensions between measured data points, and the plumes are only calculated within the bounds of the outermost measured points. A plume is considered to be unbounded when it extends to the bounds of those outermost measured points. A fully bounded plume will exist entirely within the confines of the outermost measured points.

3-Dimensional Orientation

The *SmartData Solutions*[®] graphics use a relative azimuth system to describe map orientation, as a map may not be oriented with true North at the top of the map. The relative azimuth system uses a 360° compass to describe the position *from which* the graphic is being viewed. For example, a viewer "looking east" on a North oriented map would have a relative azimuth of 270°, i.e. the viewer would be standing on the "western" 270° azimuth point looking through the center to the "east".

SmartData Solutions[®] is a registered trademark of COLUMBIA Technologies LLC. UVOST[®] is a registered trademark of Dakota Technologies Inc. Geoprobe[®] is a registered trademark of Geoprobe Systems, Inc.











APPENDIX A LIF/UVOST® Logs
























































APPENDIX B

UVOST Response to Various Random Products Saturated on Wet Sand















Direct Push Site Characterization of NAPL with Laser-Induced Fluorescence (LIF)

Travis Martin and Randy St. Germain

2008 North American Environmental Field Conference & Exposition January 16, 2008 Tampa, FL

Today's LIF Workshop

Brief History of LIF **LIF** instrumentation **Spectroscopy** Performance LIF's Pros/Cons Site Investigation Advice **Example Logs and CSMs**



■ Real-time demo of UVOST[™] and TarGOST[®]



LIF detects PAH-containing NAPLs ("source terms")

Using UV excitation...

•Gasoline (highly weathered or aviation gas fluorescence yield is very low)

Diesel
Jet (Kerosene)
Motor Oil
Cutting Fluids
Hydraulic Fluid
Crude oil

Using Visible excitation...

•Coal Tar (MGP waste) — often poor in UV due to self-quenching/intersystem crossing/photon cycling (energy transfer)

Creosote/Pentachlorophenol (wood treating) – often poor in UV due to self-quenching/intersystem crossing/photon cycling (energy transfer)

•Bunker – often poor in UV due to self-quenching/intersystem crossing/photon cycling (energy transfer)

Never/Rarely..

polychlorinated bi-phenyls (PCB)s – due to internal heavy atom effect

 chlorinated solvent DNAPL – aliphatics lack aromaticity (no ring-shapes) - but co-solvated PAHS can/do rarely respond

dissolved phase (aqueous) PAHs



Potential LIF Characterization Sites Leaking underground storage tanks •Pipelines Refineries Fueling areas Fire-training facilities Automobile service locations (hydraulic fluid, POLs) Surface spills Lagoons - waste ponds •former MGP (coal tar) and creosote (wood treating) sites



The Past vs. Present



ROST prototype circa 1991

UVOST 2008





Dakota's LIF Service Totals (3-4 field operators – part time - since 2000)

UV LIF (ROST/UVOST™)

Total production: 90,289ft (17 miles) # Logs: 2683

Visible LIF (TarGOST®)

Total production: 92,316ft (17.5 miles)

#	Logs:	369

- # Sites: 62
- # Projects: 83
- # Consultants 24

Average Feet/Day:300-500 ft/day (barge work is obviously slower)Best ever 10 hour day:767 feet (TarGOST) November, 2007



LIF Instrumentation

features a sapphire-windowed probe deployable with a wide variety of direct-push platforms

(percussion-based probes can be used when Dakota's SPOC[™] sapphire-windowed probe is employed)













LIF - a variety of direct-push platforms can be utilized to suit a wide range of site conditions














LIF Instrument Hardware Basics

(UVOST[™] shown here)







- 2. Oscilloscope
- 3. Laser
- 4. Remote Display
- 5. Emission/detection module
- 6. Breakout Box
- 7. Fiber I/O
- 8. Launch Assembly
- 9. Fiber-based Trigger
- 10. E-Deck



Fluorescence Spectroscopy

(the "mysterious magic" behind the technology)

spectroscopy = the study the interaction between light and matter

fancy quantum level physics rule the behavior

molecules first absorb light – then *might* rid themselves of that energy by emitting light aromatic (ring-shaped) molecules excel at this especially <u>poly</u>cyclic aromatic hydrocarbons (PAHs)



For details - see Joseph R. Lakowicz' "Principles of Fluorescence Spectroscopy", 3rd Edition



PAH structures – aromatic rings



PAH Structures

Pericondensed



Coronene C16H10 C24H12



Perylene C20H12



Antanthrene C22H12

Benzo[ghi]perylene



Ovalene

C22H12

C32H14

Naphthalene



Tetraphene C18H12

C10H8



Pentaphene C22H14



Chrysene C18H12



Catacondensed

Pentacene C22H14









Benzo[⊅] fluoranthene

Benzo[/]fluoranthene

Benzo[/] fluoranthene





Perylene



Benzo[a]pyrene

Anthanthrene





Benzo[الأرور]perylene

Indeno[1,2,3-cd']pyrene



Dibenz[a/#]anthracene





Coronene

Dibenzo[*ae*]pyrene







Dibenzo[a//]pyrene

Dibenzo[a/]pyrene

Dibenzo[a/]pyrene



PAH Properties fuels/oils are "soups" made up of various PAHs in an aliphatic "broth"

PAH concentrations in a crude oil and two distillate fuel oils (From Neff, 1979)								
Compound	Kuwait Crude (µg/g)	No. 2 fuel oil (µg/g)	Bunker C residual oil (µg/g)					
Naphthalene	400	4000	1000					
1-Methylnaphthalene	500	8200	2800					
2-Methylnaphthalene	700	18900	4700					
Dimethylnaphthalenes	2000	31100	12300					
Trimethylnaphthalenes	1900	18400	8800					
Fluorenes	<100	3600	2400					
Phenanthrene	26	429	482					
1-Methylphenanthrene	-	173	43					
2-Methylphenanthrene	89	7677	828					
Fluoranthene	2.9	37	240					
Pyrene	4.5	41	23					
Benz[a]anthracene	2.3	1.2	90					
Chrysene	6.9	2.2	196					
Triphenylene	2.8	1.4	31					



PAHs... prefer NAPL

Compound (C.A.S.N°)		Molecular weight	log Kow	Water solubilit y at 25°C (mg/L)	Melting point (°C)	Vapor pressure at 25 °C (mPa)
naphthalene (91-20-3)	1	128.16	3.5	31.7	80.5	11 960
acenaphthene (83-32-9)	1	154.21	4.33	3.42	95	594
fluorene (86-73-7)	1	166	4.18	1.98	116.5	94.7
phenanthrene (85-01-8)	1	178.24	4.5	1.29	101	90.7
anthracene (120-12-7)	1	178.24	4.5	0.045	216	25
pyrene (129-00-0)	1	202.26	4.9	0.135	156	91.3 x 10-6
fluoranthene (206-44-0)	1	202.26	5.1	0.26	111	1328
benz[a]anthracene (56-66-3)	1	228	5.6	0.0057	162	14.7 x 10-3
benz[a]pyrene (50-32-8)	1,	252.32	6.0	0.0038	179	0.37 x 10-6
benzo[b]fluoranthene (205-99-2)	2	252.32	6.06	0.014	168	0.13 x 10-5 to 0.133 at 20°C
benzo[j]fluoranthene (205-82-3)	2	252.32			166	
benzo[k]fluoranthene (207-08-9)	2	252.32	6.06	0.0043	217	2.8 x 10-9
indeno[1,2,3-cd]pyrene (193-39-5)	2	276	6.4	0.00053	164	1.3 x 10-5



Laser-Induced Fluorescence (LIF)

it's the poly-cyclic aromatic hydrocarbons (PAHs) found in all petroleum, oils, Iubricants (POLs) that are responsible for their innate fluorescence

emission spectrum is unique for each PAH – does not change with excitation wavelength





in fuels there is a mix of many PAHs their spectra overlap and you lose ability to identify any one PAH – just classes at best emission spectrum is still unique for each PAH BUT...

varying the excitation wavelength for PAH mixtures DOES cause a change in overall emission spectrum





UVOST emission spectra for typical fuels



308nm-excited fuel spectra





there is a 3rd dimension to fluorescence that most people don't know (or care) about it involves time over which a population of excited PAHs fluoresce Dakota's LIF systems with fast-pulsed lasers make extensive use of this property

General Fluorescence Properties Temporal (time-decay waveform) perylene photons absorption of decaying emission of energy pulsed laser in the form of photons photons (fluorescence) ntensity (# waveforms from oscilloscope <10 ns→

Time (nano-seconds, ns) \rightarrow



each mix of PAHs (along with the aliphatic solvent, oxygen concentration, matrix, etc.) yield a fairly unique wavelength/time matrix or "WTM"

all "classes" of fuels/oils have a characteristic WTM





WTMS are powerful – but they couldn't be obtained "on the move" and folks sometimes wanted them every foot or so! (back in ROST's early days – mid 90's)

so we were forced to get "clever" and design a solution... time delayed fluorescence "channels" solve this





with time delay you combine both the spectral (wavelength/color) and temporal (lifetime) fluorescence information that's being emitted by the NAPL

so for fast simultaneous quantitative and qualitative information – a multi-wavelength waveform is "tough to beat"





Colorization of UVOST Waveforms

Dakota's UVOST colorization scheme uses RGB calculations of the relative areas of the 350, 400, 450, and 500 nm channels to generate RGB fill color.





general NAPL fluorescence trends

PAH fluorescence emission generally trends with size (# rings) and degree of substitution

in general the larger the PAH – the longer its absorbance and emission wavelengths



so what effect does this have on fluorescence waveforms?

- fuels/NAPLs with predominantly smaller PAHs fluoresce in left-most channels of the waveform
- mid-range fuels/oils fluoresce "across the board" (in all 4 channels)
- "heavies" like coal tar, bunker fuels, etc. fluoresce predominantly in the right-most channels (longer wavelength) – not because they only contain large PAHs, but the large PAHs "rob" smaller PAH's absorbed energy – more about that later



UVOST Response for Various NAPLs

[wet Fisher sea sand - saturated with NAPL]



TECHNOLOGIES



UVOST Response of Various NAPLs



TECHNOLOGIES



UVOST Response of Various NAPLs





Lab study – let's examine quantitative aspect of LIF



decade series dilutions (100, 1000, 10000, 100000 ppm)







Lab studies LIF provides both "semi-quantitative" and qualitative data







more lab studies

crude oil "rollover" – note colors – energy transfer

too high RE (electronics saturation – note colors)







LIF's "semi-quantitative" performance

- typically 10-500 ppm (TRPH) limit of detection (LOD) for common petroleum fuels/oils statistically in a controlled experiment up or down from there depending on heterogeneity
- semi-linear (at least monotonic) response over several orders of magnitude on fuels/POLs
- generally speaking diesel is best behaved gasoline and kerosene can be 10-fold lower
- lab studies can "under-estimate" field LODs in downhole NAPL is mottled the sandy samples used here were mixed/equilibrated so NAPL coats all sand grains equally – this doesn't often occur in nature as one will hit globules/seams/mottling – even on very small scales (marbling/blebs) – UVOST sees these 'blebs' easier than homogeneous sheen
- note that the LOD for actual PAHs is actually lower than 10-500ppm, since PAHs often make up only fraction of fuel/oil





Dakota's Reference Emitter ("RE") (RE does NOT stand for REflectivity!!)

speaking of quantitative information ("how much NAPL?") - how does the waveform relate to the amount of NAPL?

the diagram below illustrates how the software determines fluorescence intensity as %RE - RE stands for Reference Emitter

RE is a standard Dakota-provided NAPL that you calibrate UVOST/TarGOST with prior to every sounding – think of RE as you would the tank of isobutylene used to calibrate a PID

the RE normalizes the response for laser energy changes, fiber optic cable length, detector aging, etc. – the same RE is used by all UVOST service providers worldwide

the relationship between %RE and the concentration of NAPL depends on the fuel – some simply glow brighter than others

[Note that "M1" is Dakota's former name for RE]





UVOST's semi-quantitative performance

Previous slides were results from just **one set** of randomly acquired fuels and a crude oil <u>– product "brightness" can vary, so your results may differ depending on source, age, makeup of NAPL</u>

- Gasoline is typically 32% aromatic but mostly mono-aromatics (BTEX) that UVOST "can't see" but gasoline still contains sufficient PAHs to respond to UV LIF
- Diesel is typically 38% aromatics mostly PAHs, so it "glows" nicely
- Kerosene (jet fuel) is as much as 23% aromatics nearly all naphthalenes so it does fluoresce sufficiently in UV





UVOST's qualitative performance

The fluorescence of various products are quasi "additive" – in other words, mixtures of products have waveforms that are combinations of the separate product's waveforms added together. This isn't always linear or "perfect", but waveform analysis can be used to separate the various products.

Example experiment: Mix up some 10,000 ppm kerosene and crude on sand. Log below starts out with 10,000 ppm kerosene – then 25% replacement of kerosene with crude until we reach 10,000 ppm crude oil.





Advanced Waveform Analysis



We can harvest "Basis Set" waveforms from areas we know to represent pure products.

Then do a non-negative least squares analysis on each raw waveform in the log... searching for best combination of the Basis Set waveforms to match raw waveforms – end result are logs that represent contribution of each Basis Set member.



Advanced Waveform Analysis



crude is much brighter than kerosene so it is dominating waveforms 10,000 ppm crude is "morphed" – so a bit different from 2,500 ppm crude here and you can see match isn't perfect







75% kerosene – 25% crude



Advanced Waveform Analysis

50% kerosene – 50% Crude



25% kerosene - 75% Crude



0% kerosene – 100% Crude





Advanced Waveform Analysis – Final Result

this demonstrates LIF's "additive" behavior under controlled lab conditions – site heterogeneity often limits the ability to parse out tiny amounts of product overwhelmed by other product's fluorescence this lab sample example was shown here to demonstrate analytical "power" of LIF under controlled conditions





LIF Workshop – Jan. 2008

Various Fuels Log Separation Example





Various Fuels Log Separation Example





Various Fuels Log Separation Example



examples of oxygen's affect on common fuels/NAPL

can cause 2-3 fold increase or decrease in extreme cases basic technique: bubble N/O2 mix through neat fuel in cuvette

Callouts Depth (ft) Signal (%RE) 350 400 450 500 Rate (Initi) 300 200-100-50 67.8 NHE (# 2.7) Egulibrated atr 10.0 400 200 15.0 Profilm And Con 195.5 %RE (# 11.0) W2 purged 20.0 25.0 300 30.0 200 100 29.4 35.0 63.3 MUE (s 2.5) Egulibrated Air 100 40.0 209.3 MRE (# 9.7) MI Furge 45.0 50 100 150 200 0.5 **UVOST By Dakota** Sample Data Latitude / Datum. Final depth. Site Fargo, ND 46 54.430700 N / WGS-84 41.90 ft Client Lonaltude / Fix Max signal **ABC Consulting** 096 47.753700 W / 3D 229.3 % @ 41.90 ft **Dakota Technologies. Inc.** Job Operator/Unit Date & Time: Parge. MD sP011257 4800 St. Germain/UVOST1000 2007-03-27 09:45

different product waveform? – no - O2 quenching



customer's NAPL from a well - 2005



kerosene from pump

Example Field UVOST Logs





 WI – plastic plant - plasticizer cut w/diesel fuel previously "remediated" (dug out) to 10 feet
later, free product in a well – LIF shows flawed CSM
LIF Workshop – Jan. 2008

IA – railroad yard diesel



Example Field UVOST Logs





MN – Service Station - 2 NAPLS (oil top.... gasoline bottom)



MN - bus garage No. 1 Fuel Oil

LIF Method



Desired Result





individual logs are certainly useful but even more powerful when used in concert with other site info to create Conceptual Site Model (CSM)



3D UVOST Field Data CSMs




3D UVOST Field Data CSMs





can UVOST detect BTEX?

no it can't - due to fiber optic absorbance below 280 nm UVOST would use 266nm if attenuation didn't limit us bottom line is that BTEX absorbance lies to deep in the UV to reach in practical sense this doesn't limit LIF much – UVOST "sees" gasoline's PAHs anyway





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MIP or LIF?

MIP

- Designed for VOCs including dissolved phase
- "sticky" semi-VOCs cause transfer line/carryover problems
- membrane's physical form potentially allows NAPL to hang in cracks/crevices
- difficult to find "bottom" of NAPL due to gas line carryover and resulting lag time
- logs are often less intuitive with major baseline shifts (compared to LIF logs)

LIF

- Designed specifically for NAPL delineation
- smooth/hard sapphire window is "slick" like Teflon resists carrydown
- nearly instantaneous rise/fall and 100% reversible response
- UVOST does NOT see any useful levels of response to dissolved phase
- UVOST shows intimate detail of NAPL distribution (relative to MIP)
- UVOST provides readily interpreted "spectral" information in real time
- UVOST is "blind" to halogenated hydrocarbons even hDNAPL itself
- no transfer lines to contaminate all signals up/down are light-based



can UVOST detect dissolved phase PAHs? (naphthalenes, anthracene, etc.)

NO it can't... at least not in useful conc's

the relative solubility of PAHs in water is much less than in NAPL solvent (hundreds/thousands/millions times higher solubility in NAPL than in water)

only in sandy clear pore water conditions do PAHs ever get "visible enough" to generate a detectable signal (<< 5% RE)

think of NAPL as "paint" for a visual intuitive example – the orange stained water makes dark mud – the paint itself makes orange mud – easy to see the painted mud – but impossible to see orange water after it's been made into mud

PAHs act much the same as orange dye in this example







Potential False Positives and Negatives

Previously observed positives [weak 1-3% RE, medium 3-10% RE, strong >10% RE]

sea shells (weak-medium) paper (medium-strong) peat/meadow mat (weak - medium) calcite/calcareous sands (weak-medium) asphalt (very weak) stiff/viscous tars (weak) certain soils (weak) tree roots (weak-medium) sewer lines (medium-strong) coal (very weak to none) quicklime (weak)

Previously observed negatives

extremely weathered fuels (especially gasoline) aviation gasoline (weak) coal tars (most very weak with UV) creosotes (most very weak with UV) "dry" PAHs such as aqueous phase, lamp black, purifier chips, "black mayonnaise" most chlorinated solvent NAPL (unless containing substantial PAH from degreasing) benzene, toluene, xylenes (relatively pure)



UV LIF **DOES NOT** see coal tar and creosote reliably! – why?





most coal tars and creosotes "roll over" or they simply don't fluoresce well in UV - why?

a PAH NAPLs' fluorescence spectra will sometimes "red-shift" with increasing concentration – this is due mainly to electronic energy transfer – the higher the PAH content of the NAPL, the likelier it is to morph with concentration and/or to "roll over" and lose fluorescence with increasing conc. even to the point of being non-fluorescent!

in the UV, excitation light is absorbed by smaller PAHs (they have large bandgap) – in concentrated PAH conditions this absorbed energy is readily transferred to larger molecules (small bandgap) before fluorescence can occur – continued cascading of this absorbed energy up the PAH size chain eventually results in larger PAHs emitting redder light - or "red-shifting"

each "step" along this chain is also fraught with non-radiative energy loss mechanisms – so past a point, the more and more PAHs in a NAPL the likelier it is to be "poorly behaved" in both quantitative and qualitative respects (size and shape of waveforms) – at some point photons just never get produced in appreciable amounts – majority of initially absorbed energy is simply converted to thermal energy without useful amounts of fluorescence

so to summarize - too few PAHs simply cause low signal (av gas for example), just the right amount yields nearly perfect behavior (diesel), very high PAH concentration causes morphing and roll over (crude/bunker), and getting WAY too many PAHs (coal tar) often causes very low signals and extreme rollover to the point where UVOST can be totally unreliable – small conc's of coal tar actually yield larger signals than pure coal tar – that's worst case scenario for any screening tool!



Visible Wavelength LIF Example: Tar-Specific Green Optical Screening Tool (TarGOST®)

designed <u>specifically</u> for MGP NAPL, creosotes, and pentachlorophenol (typically cut with diesel)

visible excitation defeats the energy transfer trap by "skipping over" the absorbance of the excitation source by the smaller PAHs who "love" to absorb UV

basically the visible light zips through smaller PAHs and is only absorbed by the very large PAHs which are much more likely to fluoresce due to lack of potential "neighbors" to which they can transfer the absorbed energy





TarGOST Waveforms vs. Coal Tar Concentration





Visible LIF (TarGOST)







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300

300

П

300

curve resulting from previous slide's coal tar study not all tars behave "perfectly" like this – but all are monotonic in response to concentration (no rollover) when excited with visible laser pulses





so how does TarGOST "see" tar?....

here's a conceptual view of what it looks like outside the window





so how does TarGOST "see" tar?....





Example TarGOST Field Logs





New York - done from a barge in 20+ ft. of water



Oregon 150ft – mobile NAPL at 100ft (first 30 ft were in open hole) LIF Workshop – Jan. 2008

Example TarGOST Field Logs





WI - 2 layers of MGP NAPL separation into LNAPL/DNAPL?



CA crude oil showed up better with TarGOST than UVOST

black background – for overlay on CSM software's typical black background





2D and 3D Visualization of TarGOST Data







3D Visualization of TarGOST Data



MGP NAPL pooling on clay feature (ivory color)



LIF site investigations

• NAPL can be homogeneous or heterogeneous

- conduct side by side ("sister" logs) to gauge this
- remember that LIF scans only a 3-5mm wide swath on the surface of the window/soil interface
- carryover/carrydown is nearly non-existent
- spiky log data indicates heterogeneous small scale distribution (running in veins, seams, and fractures)
- get out of "layer thought"
- start out in the "heart of it"
- bound the NAPL -- then move in and define/refine
- you'll use LIF more than you planned # holes will generally exceed expectations (due to productivity)
- #1 most common phrase "it should be clean here"
- 2nd most common phrase "there won't be any below the water table – NAPL always floats"
- 3rd most common phrase "where have you guys been all my life?"
- 4th most common phrase "what's your schedule look like?"







LIF site investigations

general tips and suggestions to conducting the site investigation

- knock out the primary locations first then fill in the "head-scratchers" and data gaps as time/budget allows
- go well below the primary affected zone 10 feet is typical – LIF often finds LNAPL well below GWS
- don't get carried away trying to interpret every log wait until the big picture starts to emerge – doing so early gets you contradicting yourself – but watch for heterogeneity's ability to make it look like "LIF was wrong"
- co-sampling answers the important/tough questions
- in-situ data is nearly always higher than ex-situ
 - O2 content (subsurface O2 can be near 0)
 - "wringing out" of NAPL
 - surface film creation (walk on the beach)
- client is in charge of locations and decisions most LIF service groups are simply data providers – LIF service providers are not able to fully interpret since they aren't privy to all the subsequent supporting data/facts like co-sampling/analysis

NAPL is sometimes VERY heterogeneous – not in 'layers'!









Data QA/QC

Dakota Technologies have spent several man-decades developing LIF systems. **IF** operated properly, and **IF** LIF's capabilities properly understood, you can be confident of the data produced. **IF** the LIF provider is disciplined they can AND SHOULD be consistently achieved. UVOST service providers are taught...

Checklist of key items that lead to quality LIF data:

- Proper RE intensity RE waveform must be certain intensity and correct shape
- Low Background levels Background waveform does not exceed 5mV and must be correct shape
- Proper penetration speed going too fast can blur/skip significant response best to error slow
- Rational and consistent callouts random or obscure callouts confuse client and clutters plots
- Elimination/control of fogging fogging will absolutely corrupt a log corrupts project data
- Proper depth encoding a dirty/bad pot or bad wiring can cause misleading depths
- Let the LIF speak for itself never oversell or over promise results set expectations and relax
- DON'T let confirmation sampling (the "gold standard") create excessive doubt if operated properly and there is/was fluorescent NAPL in front of the window, LIF will see it – heterogeneity simply happens – A LOT – one must not always conclude that LIF was wrong if poor correlation with sampling is observed – it could be heterogeneity – consider LIFing sample splits
- always have LIF provider examine non-typical NAPLs prior to considering LIF for your project



NAPL in soils - a complicated subject

- Dakota has 15 years of experience with characterizing NAPL with LIF– but publications are not something we've focused on
- plenty of anecdotal evidence but Dakota has not published any comprehensive studies in recent years
- clients WILL try to pin LIF providers down on %RE cutoff levels for "significant" contamination but co-sampling, previous studies, geology, etc. all have to be factored in when deciding on what's significant %RE and what's not and it's ultimately the consultant's job to define/defend that value

Suggested reading:

- LNAPL in Fine-Grained Soils: Conceptualization of Saturation, Distribution, Recovery, and Their Modeling, Groundwater Monitoring and Remediation 25, no. 1/Winter 2005/pages 100-112
- <u>http://www.clu-in.org/conf/tio/Inaplsbasics_121205/prez/LNAPL-Slides-10-26-05bbw.pdf</u>
- API's LNAPL FAQ Answers to Frequently Asked Questions About Managing Risk at LNAPL Sites



UVOST/TarGOST Demo

UVOST

- the "classic" fuels
- diesel response vs. concentration
- various random fuels/oils
- coal tars
- TarGOST
- coal tars



Thank you.











Fargo, ND 58102

701-237-4908

stgermain@dakotatechnologies.com



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