Minnesota Pollution Control Agency

August 26, 2002

Tony Nuzzo
US Steel Corporation
Project Manager
600 Grant St.
Pittsburgh, PA. 15219-2749

RE: Approval of LIF (Laser Induced Fluorescence) Investigation Report, U.S. Steel Duluth
    Works Site, Duluth, MN

Dear Mr. Nuzzo:

The Minnesota Pollution Control Agency (MPCA) staff assigned to the US Steel Duluth
Works (USS) Site have reviewed the above captioned work plan dated July 24, 2002, and
submitted on the behalf of U.S. Steel by URS, Inc. The LIF investigation is a supplement to
the Former Duluth Works Sediment Characterization and Risk Assessment Work Plan, 2000.

MPCA staff approves the data presented in the LIF Investigation Report. We thought the
field methods discussion and report presentation were effective. However, some of the data
interpretation methods presented for examining the LIF results are not representative of
contaminant levels, specifically the averaging of LIF values over one-foot increments. The
MPCA suggests that there are several methods of examining the data that will provide useful
information when determining extent and magnitude of pollutants. In order to advance the
commenting process, we have provided the attached technical memo from Andrew Streitz that
outlines the examination of maximum LIF readings. MPCA staff would like USS to consider
LIF maximum readings when selecting the next phase of sediment sampling locations.

MPCA staff does not accept the ground water discussion at the end of the LIF Investigation
Report, Section 5.5.2. *Preservation of Fine-scale Heterogeneous LIF Response.* The goal of
this study was to determine extent and magnitude of the pollutants. Defining groundwater
characteristics using LIF response is not an acceptable methodology. MPCA will comment
on the Hydrogeological Groundwater Investigation report in regards to groundwater
characteristics at the site.

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In a July meeting, the MPCA and USS discussed having a meeting to propose sediment sampling locations. Due to scheduling conflicts, the meeting has been tentatively scheduled for September in coordination with a public meeting (last two weeks of September). To move this process along, MPCA staff suggests USS submit purposed sediment sampling locations in advance of the meeting in order to have a working meeting to discuss details. The goal of the meeting would be to finalize sediment sampling locations in order to work towards completion of the Former Duluth Works Sediment Characterization and Risk Assessment Work Plan and commence field sampling this winter.
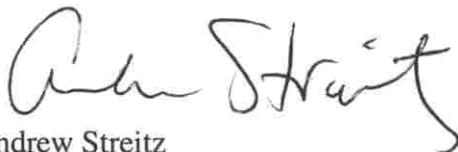
Your cooperation is appreciated.

If you have any questions or comments, please contact Susan Johnson at (218) 725-7762 or Andrew Streitz at (218) 723-4929.

Sincerely,

Susan Johnson
Project Leader
Northern Response and Assessment Unit
Majors and Remediation Division

Andrew Streitz
Technical Analyst
Northern Response and Assessment Unit
Majors and Remediation Division

SJ:AS:pp

Enclosure

Cc: Dean Stockwell, URS, Inc.
    Margaret Zak, USS Corp.
    Anne Moore, MPCA, Duluth

FORMER DULUTH WORKS
LIF INVESTIGATION REPORT

Prepared for
U.S. Steel
600 Grant Street
Pittsburgh, PA 15219-2749

July 24, 2002

URS Corporation

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Tables, Figures, and Appendices

Tables

Figures

Appendices

Executive Summary

A laser-induced fluorescence (LIF) study of native and non-native sediments in the St. Louis River, Duluth, Minnesota, was conducted to identify the horizontal and vertical extent and relative magnitude of chemicals in sediments associated with historical activity at the United States Steel (USS) Duluth Works Site. A total of 189 sample locations were investigated in the Unnamed Creek and Wire Mill Basin Areas of Interest (AOIs). Depth-to-sediment measurements at each location established a site bathymetry consistent with previous studies and charts. The location of LIF borings and Geoprobe sediment core borings at 13 nodes within the 200 foot sample grid demonstrated that an elevated LIF response was primarily associated with two sediment types: non-native sediments (e.g. coal tar with polyaromatic hydrocarbons (PAHs)) and native peat. The material in each sediment that fluoresced (PAHs in the coal tar and organic acids in the peat) produced resolvable waveform signals that could be identified and separated within each raw LIF response.

The consistency of the LIF results with the established conceptual model of the Site supports the utility of the LIF technique in delineating the AOIs. The "coal tar" and "peat" signals are typically distinct, except for a few locations where impacted peat layers were identified (in some cases with sediment core evidence). The resolved "coal tar" LIF response can be contoured at each AOI with magnitude decreasing as the distance from the shore increases. The highest LIF responses are in areas adjacent to the presumed source areas (Wire Mill Pond and the mouth of Unnamed Creek). The thickness of "surface-down" low LIF response layers, presumed to generally be native cover sediments, increases as distance from shore increases, with thickness contours that roughly parallel the shoreline. Elevated raw LIF responses at lower depths (greater than seven feet) and at the margins of the AOIs were generally related to native peat sediments.

Comparison of the LIF responses in each of the AOIs suggest that the relative magnitude of PAHs associated with non-native sediments is higher in the Wire Mill Basin AOI. The Wire Mill Basin AOI also displays a larger areal extent, although the Unnamed Creek AOI displays deeper "coal tar" sediments (greater than 12 feet, compared with less than six feet deep in Wire Mill Basin AOI). Most of the AOIs are covered with a layer of low-LIF "cover" material that ranges from 0.5 to more than two feet in thickness. In locations where sediment cores document non-native sediments at the surface, a low and relatively "flat" LIF response in the upper 0.5 to 1.5 foot interval is interpreted to represent equilibration and PAH release to the environment through bioturbation and exchange with surface water.

Collection and laboratory analysis of sediment samples suggests that the LIF response is generally a good proxy indicator for elevated metal concentrations at the Site. Correlation of LIF response and PAH concentration will be assessed during the magnitude and extent and risk assessment sampling. LIF may be less reliable as an indicator when non-native sediment is at the sediment surface, since the PAHs responsible for the LIF response are more mobile than metals. In these areas, the LIF technique may suggest lower metals concentrations than what is actually present. The lack of good correlation at two locations was attributable to the difficulty in assigning cored sediment depths when incomplete recovery was obtained.

The LIF results can also be used to qualitatively evaluate the magnitude of vertical fluid flow through the native and non-native river sediments, even though this was not an established study goal. In almost all of the samples, the boundaries between low-LIF zones and elevated LIF

zones are sharp and distinct. Within the elevated LIF zones associated with coal tar, the fluorescence versus depth (FVD) plots display high peaks and valleys, with variations of more than 50% of total signal response occurring over a few tenths of inches. This strong heterogeneity in the LIF response within the non-native sediments, and the sharp divide between high and low-LIF intervals is consistent with an environment in which there is relatively little exchange of material between adjacent layers, suggesting vertical fluid flow.

The success of the LIF technique in bounding the relative magnitude and extent of non-native sediments in the AOIs will allow each of the sample locations to be categorized based on relative risk. The LIF technique will also allow portions of the Site to be eliminated from further consideration, once a correlation has been established between LIF response and PAH concentrations. It is recommended that the relative magnitude of LIF response in the upper two feet of sediments, the thickness of non-native sediment layers within the upper two feet of sediments, and the amount of cover sediments (indicated by low-LIF response from surface-down) be used to group each of the sample locations into low, medium and high risk groups for the purposes of a focused risk-based analytical and toxicological investigation at a limited (18 to 24) number of sample stations. It is further recommended that the documented extent of chemicals in sediments be confirmed by additional limited collection and analysis of sediment samples from the margins of each AOI.

1.0   Introduction

1.1. LOCATION

The United States Steel Corporation (USS) Duluth Works Site (Site) is located in Sections 34 and 35, T49N, R15W, and Sections 2 and 3, T48N, R15W in the southern portion of the city of Duluth in St. Louis County, Minnesota. The Site location is shown in Figures 1 and 2. The Site is adjacent to the St. Louis River, which discharges into Lake Superior approximately three miles downstream of the Site. A small stream, referred to as the Unnamed Creek, flows through the northern portion of the Site and discharges to the St. Louis River. The Site is bounded by Morgan Park to the north, the St. Louis River (also called Spirit Lake) to the east, and Duluth Missabe and Iron Range Railroad property to the west and south. The two Areas of Interest (AOIs) that have not been closed at the Site are near-shore sediments located within the St. Louis River due east of the mouth of the Unnamed Creek and Wire Mill Pond locations (Figure 2).

The Site is comprised of approximately 600 acres. USS built the former steel-making facility in 1907 which consisted of a fully integrated steel manufacturing plant with coke production, iron and steel making, casting, primary rolling and roughing, hot and cold finishing, and galvanizing. The operation closed in 1979.

1.2   TOPOGRAPHY

A U.S. Geological Survey topographic map (USGS – West Duluth, 1954 - Photorevised 1969 - Figure 1) indicates that the Site elevation ranges from 600 to 670 (National Geodetic Vertical Datum of 1929) feet above mean sea level (amsl). The majority of the Site is fairly flat, and sits on a bluff above the St. Louis River (Spirit Lake) and the Unnamed Creek. Surface storm water at the Site drains to the Unnamed Creek and to the St. Louis River. The Unnamed Creek flows in a northeasterly direction.

1.3   HYDROGEOLOGIC SETTING

The Site is underlain by two distinct Quaternary hydrogeologic units (Barr 1984). The majority of the Site, located on the bluff, rests on thick lacustrine silt and clay deposits associated with Glacial Lake Duluth (USGS 1979, MGS 1982). In contrast, thinner layers of reworked glacial sediments underlie the Unnamed Creek, St. Louis River and their associated banks. This distinct stratigraphy is the result of a period of low lake levels (approximately 400 feet MSL) in the ancestral Lake Superior. This led to the creation of deeply incised canyons through which the Unnamed Creek and St. Louis River flowed as they discharged to the lake. As lake levels subsequently rose to current surface elevations, approximately 200 feet of reworked glacial sediments were deposited under and along the Unnamed Creek and St. Louis River.

The bedrock geology of the Site consists of the Duluth Complex; a complex of early Precambrian rocks that include multiple intrusions of gabbroic anorthosite, troctolite, gabbro, anorthosite   and   felsic   rocks   (Sims   1970).

Fill material encountered during subsurface investigations at the Site consists of sand, clay, gravel, cinders, fragments, and other materials. The characteristics and depth of the fill material vary throughout the Site. While fill depths are restricted to a few feet over most of the Site, portions of the bluff area south of Unnamed Creek have been historically extended with 30 to 40 foot layers of fill.

The native sediments present beneath the fill material consist of red-brown clay underlain, and at times interbedded, with a fine to medium sand (Barr 1986). The clay unit depth varies from 2 to 48 feet beneath the ground surface (dependent on thickness of fill), and the thickness ranges from 2 to 32 feet. Beneath the clay unit are deposits of sand and gravel. Groundwater is generally found at 27 to 31 feet below the ground surface.

Groundwater in the lacustrine deposits beneath the Site discharges to the St. Louis River. Groundwater monitoring wells installed from previous investigations in the main upland area are screened above river level, which is very nearly the same as the level of Lake Superior, normally 601 feet above mean sea level (amsl). These wells show the water table at elevations of 620 to 625 feet within 1,000 feet of the riverbank, with the water table sloping steeply toward the river (Geraghty and Miller, 1995). Seeps have been noted along the lower portion of the embankment near the river. These seeps are likely produced by a thick clay layer that impedes shallow groundwater flow towards the St. Louis River.

1.4. PREVIOUS INVESTIGATIONS

The lateral extent of non-native sediments data has previously been obtained from a bathymetric survey of the AOIs conducted in the Spring of 2000 (see Section 2.2 of the Work Plan) and a previous remedial investigation (Barr Engineering, December 1986). The sediment data collected in 2000 indicated that a layer of non-native sediment approximately two feet thick occurs up to 1,400 feet east of the mouth of Unnamed Creek and up to 1,000 feet east of the mouth of the Wire Mill Pond (Figures 3 and 4).

As noted in the Work Plan, the sources of non-native sediments in the two AOIs were different as follows:

- In the Unnamed Creek AOI, non-native sediments are assumed to have been derived from coking operation wastes.

- In the Wire Mill Pond AOI, non-native sediments were discharged from the Wire Mill area via an 84 inch diameter combined stormwater and process wastewater sewer. No clearly defined source material has been identified.

2.0   Scope of Work

2.1   RATIONALE FOR A LIF INVESTIGATION

On March 5, 2002, URS submitted to the Minnesota Pollution Control Agency (MPCA) the Former Duluth Works Sediment Characterization and Risk Assessment Work Plan – LIF Sampling and Analysis Plan Supplement (Supplement). This Supplement incorporated comments from a February 25, 2002 conference call between the MPCA, URS and USS. This Supplement was an amendment to the Project Approach and the Sampling and Analysis Plan presented in the draft Former Duluth Works Sediment Characterization and Risk Assessment Work Plan dated September 29, 2000 (Work Plan). This Supplement described a MPCA proposed approach that uses laser-induced fluorescence (LIF) as a screening tool to delineate the extent of chemicals in sediments at the Site. The MPCA approved the Supplement with conditional amendments on March 11, 2002.

Use of the LIF screening technology changes the key objectives of the Project Approach and the Sampling and Analysis Plan portions of the Work Plan. The LIF approach more thoroughly delineates the horizontal and vertical extent of non-native sediment chemicals in the AOIs than the nature and extent sampling proposed in the Work Plan. By implementing this approach, it was expected that a reduction of nature and extent/risk assessment sampling requirements could be made from the 65 locations indicated in the Work Plan to approximately 18 to 24 locations.

2.2   INVESTIGATION TASKS

The Scope of Services outlined within the MPCA-approved Supplement included the following tasks:

- Completion of a Site-Specific Health and Safety Plan;

- Construction of a GIS-surveyed grid of 210 LIF sampling points within the 2 AOIs;

- Advancement of a LIF sensor into the sediment at each sampling point to a minimum of two feet beyond no LIF response, with an anticipated maximum depth of ten feet;

- Completion of 20 Geoprobe™ sediment borings, and field characterization of retrieved sediments;

- Collection of one to two samples from each Geoprobe™ boring for laboratory analysis of Resource Conservation and Recovery Act (RCRA) metal concentrations; and,

- Completion of this report, including:

  ➢ Plotting and graphical presentation of sediment boring data by location relative to the St. Louis River and surrounding topography;

  ➢ Geoprobe™ boring and LIF logs;

  ➢ Analysis of the correlation between RCRA metals and LIF response;

> ➢ Potential revision to the Site conceptual model based on the newly obtained data; and,

> ➢ Identification of criteria that should be used to identify sample locations with similar levels of potential risk.

2.3   DEVIATIONS FROM SCOPE OF SERVICES

The approved scope of work included 20 Geoprobe borings and a sampling grid of 210 node points. Field conditions, safety issues associated with ice thickness, and the task of extending LIF traverses until background levels were obtained led to deviations from the approved scope of work.

The LIF investigation was conducted using a Geoprobe drill rig that was mounted on either a two-ton truck or a skid-steer vehicle that weighed approximately 500 pounds. The weight difference was important; while the truck rig required a minimum of 24 inches of ice, the skid-steer could work on thinner ice (down to ten inches thick). The truck was used for as many sampling locations as possible, since it was much faster to operate (top speed of the skid-steer was 1.5 mph). However, ice conditions only permitted truck use for 14 of the sample points, less than what was anticipated. This reduced the number of borings performed each day.

The total time available for field work was also limited by safe ice limitations. The start of Spring thaw, particularly noted in the last few days, significantly thinned the ice in the shallow estuary areas; the skid-steer rig partially broke through the ice a few hundred feet from shore on the last day of sampling.

A total of 189 LIF borings were completed. Some of the locations sampled were outside of the established nodal grid, following the work plan task of extending traverse lines until background LIF levels were reached. Metals samples were collected from 13 boring locations, rather than the 20 identified in the work plan. Facing time constraints, additional LIF borings were made rather than collecting additional metals samples at fewer LIF sample locations.

Field decisions on drilling locations and sample collection were made with approval in the field from the MPCA, whose staff were on Site during a good portion of the field program. Based on the results obtained, it is our opinion that the deviations from the established scope of work did not adversely affect the sampling program, limit the usefulness of the data obtained, or require remobilization to finish the grid next year.

3.0   Methods

3.1   BORING PLACEMENT

LIF boring locations were selected based on a 200-foot by 200-foot grid overlaying the AOIs and a 400-foot by 400-foot grid overlaying the area between the AOIs. A total of 210 nodes were originally identified within this grid. During the course of the field investigation, additional data points were added that were outside this grid for delineation purposes, and several nodes within the Unnamed Creek portion of the grid were not sampled, due to time constraints and/or unsafe ice. Figure 5 displays the grid and identifies those node points that were sampled. Figure 5 also plots the locations of the cross-section previously prepared (Figures 3 and 4). Table 1 contains the Universal Transverse Mercator (UTM) locations for each LIF boring location. Global positioning system (GPS) satellite equipment was used to place each boring within two meters of the described field location. Each boring location was flagged at the start of the field investigation. The location of borings added to the sample grid during the field investigation was identified within two meters of accuracy with use of a measured tape and triangulation (i.e. locating a point along intersecting grid diagonals) and were resurveyed with GPS as time and equipment allowed.

3.2   LIF BORING INSTALLATION

LIF borings were completed on ice, using either a truck-mounted or track-mounted, skidsteer-driven Geoprobe™ operated by Dakota Technologies, Inc. (DTI). At each LIF boring location, a power auger was used to bore an eight-inch diameter hole through the ice. The ice depth, depth to sediments and firmness of the sediments was measured for each boring (Table 1). The LIF sensor was then pushed into the sediment to a minimum of two feet beyond no LIF response (above background). DTI's Operating Procedures for LIF analysis is contained in Appendix A.

3.3   GEOPROBE™ BORING INSTALLATION

Geoprobe™ borings were completed at selected LIF boring locations to correlate LIF response with sediment type and to collect sediment samples to be analyzed for RCRA metals. The Supplement called for sediment borings at ten locations with low LIF response (probable native sediment) and ten locations with high LIF response (probable non-native sediment). The sampling plan and data collection methods are provided in the Supplement, and summarized below.

Sediment cores were retrieved in four-foot long acetate sleeves by the Geoprobe™, and processed on the ice surface. The sleeves were cut lengthwise along opposite sides using a utility knife, without cutting significantly into the sediment core itself. Once the liner wall was cut and removed, a tape measure was extended beside the core, starting at the top end. Digital photographs of the core were taken with a small label to identify the core.

3.4.   SEDIMENT SAMPLING

Six-inch long sample intervals were marked. Sediment samples from a specific interval were collected with a clean, stainless steel spoon or spatula. A representative sample was placed in the proper analytical container, labeled, and preserved on ice. A chain of custody form was completed and included with each batch of samples submitted to the laboratory for analysis of the eight Resource Conservation and Recovery Act (RCRA) total metals and percent solids. The chain of custody form contained the sample identification, sample container type and number, date and time of sample collection, sample matrix type, and date and time of change in sample custodian. A copy of the completed chain of custody form(s) was included with each analytical laboratory data report. Investigation derived waste (IDW) generated from the Geoprobe™ sampling process was containerized in a 55-gallon steel drum. IDW from the LIF process consisted of wipes used to clean the shock-protected optical cylinder.

3.5   LIF SIGNAL RESOLUTION

DTI provided URS with color printouts of the fluorescence versus depth (FVD) plots in the field. Once field work was completed, a full set of FVD plots was provided electronically. URS compiled the boring log information collected at the 13 locations where sediments were retrieved, and identified locations and depth intervals where non-native sediments were observed. DTI used this compiled sediment information to facilitate resolution of the raw LIF response into the component constituents. The methods used in resolving the signal are provided in the DTI Report (Appendix A).

4.0   Results

4.1   SITE BATHYMETRY

The depth to sediment information (Table 1) was used to create a bathymetric map of the area of investigation. Figure 6 displays the interpolated sediment depths, and compares these results with published topographic information and the latest Electronic Navigation Chart (ENC) data from the National Oceanic and Atmospheric Administration (NOAA).

There is generally good agreement between the bathymetric data sets.   The interpolated bathymetric map displays an area of relatively deep water north of the Wire Mill Basin and immediately east of the former water station. This area was reportedly dredged as a water intake area during historic Site operations. Deeper water in the southeastern and northern portion of the Site appear to correspond with the active river channel and historic dredged channel, respectively. Areas with relatively shallow water are located east of the Wire Mill Pond and mouth of the Unnamed Creek. There is also a shallow zone approximately 1,000 feet east of the Wire Mill Pond that may correspond to a sand bar location.

The simple interpolation methods produced false sediment depths along the shoreline; the railroad tracks, for example, are present and above the river surface. However, it is also noted that the USGS topographic map incorrectly displays the shoreline in the Unnamed Creek Area; all of the LIF data points were collected on river ice, even though the topographic map suggests that some were taken on dry land.

4.2   LIF FIELD DATA

A LIF profile was developed at 189 boring locations across the Site. LIF probe depths ranged from eight to 20 feet within sediments (i.e. not including water depths). LIF measurements were obtained at approximately 0.1 foot intervals; more than 20,000 data points were obtained from the boring locations.

A FVD plot for each sample location is provided in Appendix B. Each FVD plot displayed on the second of two plots for each location shows the total fluorescence intensity (TVI) at a given depth and displays discrete colors to readily represent the waveform shapes that are associated with the fluorescence.

4.3   GEOPROBE™ BORINGS

Geoprobe™ borings were completed at 13 locations, with boring depths ranging from four to 20 feet beneath sediment surface (bss).   Detailed boring logs are provided in Appendix C. A representative digital photograph of a portion of the sediment core from Sample Location G-6 is provided in Figure 7.

4.4 SEDIMENT CHEMISTRY

A total of 21 sediment samples (including one duplicate) were collected from 13 sample locations. Seven borings that displayed both low LIF and high LIF responses were sampled within both of these response zones. Laboratory analytical results for the eight RCRA total metals and percent solids are provided in Appendix D; a summary of results for each of the samples is provided in Table 2.

In addition to the analytical results, Table 2 presents the field description of each sediment type sampled and also provides information about the total LIF response associated with each of the intervals sampled. Two responses are provided; the highest "coal tar" LIF response for a data point within the depth interval and the average response for all data points within the depth interval.

4.5 REFINED LIF RESULTS

Changes in the color assigned to LIF responses in the FVD plots (Appendix B) over depth may qualitatively indicate different types of fluorescing material. That different types of material may be responsible for the LIF response is also suggested by waveform plots provided at distinct depths. These plots are generated by LIF probe software protocols that can be used to distinguish chemicals producing different waveform patterns. For example, many of the waveforms plotted distinct peaks at three of the four collectors (2, 3 and 4), with the peak at channel 3 higher than the channel 2 peak, which is higher in turn than the channel 4 peak. DTI field personnel indicated that this pattern was similar to the waveform generated when a sample of coal tar was used to test the potential applicability of the technique for the Site. In contrast, a waveform pattern in which the channel 2 peak was nearly as great or greater than the channel 3 peak was also observed at the Site.

DTI, using the methods described in Appendix A, refined the raw total LIF response into six distinct components:

- Three "coal tar" signals;
- Two "peat" signals; and,
- A "background" signal.

The identification of these signals as either "coal tar" or "peat" does not indicate what is fluorescing - these are the signals most often encountered in peat and coal tar zones as identified from sediment cores.

Appendix B displays the resolved LIF responses for each of the 189 boring locations, as well as the distinct waveforms associated with each of the "coal tar" and "peat" signals. These plots were provided directly from DTI.

Given the interest in determining the magnitude and extent of chemicals associated with non-native sediments, it was elected to simplify data presentation by presenting the sum of the three "coal tar" signals and the sum of the two "peat" signals rather than presenting the five distinct signals separately.

Figures provided in Appendix E display plots of fluorescence versus depth for summed "coal tar" and "peat" signals in their correct relative position within the sample grid. The depictions on these 13 individual figures are combined into a single PowerPoint figure provided in Appendix F. Note that within each plot, depth increases along the x-axis, rather than down the y-axis. This rotation in view emphasizes a correlation between sample locations in the same column, parallel to stream flow direction. Red lines at the two-foot depth intervals have been added to facilitate correlation between adjacent sheets and to provide a reference point for visually assessing depth within the sediment column. Appendix F also contains an Excel database containing all of the raw and refined LIF results (more than 20,000 data points) on a CD-ROM disk. This CD-ROM disk also contains the original data files provided by DTI, as well as the JPEG files depicting each FVD plot.

Figure 8 contours the highest summed coal tar LIF response obtained at each sample station, while Figure 9 contours the correlative depth at which this high response was recorded. Given the emphasis in the Work Plan on the upper two feet of the sediment column, Figure 10 contours the highest coal tar LIF response within the zero to two-foot interval at each station.

Figures 11.1 through 11.10 plot the summed coal tar LIF response in one-foot increments to a depth of ten feet. While some LIF borings were advanced to greater sediment depths, there are too few data points to warrant contouring beyond ten feet bss, and the significance of LIF response beyond this depth is, from a risk standpoint, low.

Figure 12 contours the shallowest depth at which a summed coal tar LIF response greater than 0.3% was recorded. This measurement roughly approximates the thickness of a low-LIF cover layer within the two AOIs. Twenty-nine sample locations were not included in this contoured plot because they did not display a summed coal tar LIF response greater than 0.3% in any portion of its sediment column.

5.0   Discussion

5.1   CORRELATION OF REFINED LIF RESPONSE WITH THE PHYSICAL ENVIRONMENT

The correlation of sediment type with LIF response supports the identification of distinct waveforms by DTI, and permits identification of the horizontal and vertical limits of non-native sediments by tracking the summed coal tar response, rather than the total LIF response. The relative consistency between the FVD plots of neighboring sample locations, particularly in the Wire Mill Basin AOI, also lends confidence to the correlation of LIF response and stratigraphy at locations where sediment cores were not retrieved.

5.1.1 Distinguishing between native peat and non-native sediments

One of the main goals of the LIF investigation was to delineate the horizontal and vertical extent of non-native sediments within each of the AOIs. LIF had been successfully used at other sites to distinguish areas of impacted and non-impacted sediments, and preliminary testing by DTI had shown that a coal tar sample from the Site returned an 18% response.

The LIF technique readily identifies petroleum hydrocarbons. The LIF response in coal tar is attributed to the presence of napthalene and other PAHs. However, it has been shown that native sediments, like peat, also fluoresce. Given the presence of peat layers and other organic matter logged in borings across the Site (in particular, the piezometers installed on-shore adjacent to the two AOIs), there was interest in whether any coal tar-related material could be distinguished, using LIF techniques, from native sediments that have not been influenced or associated with the Site.

A comparison of the LIF response for the various "coal tar" and "peat" waveforms with correlative sediments retrieved in the Geoprobe borings demonstrates excellent correlation between LIF response and sediment type. For example, Figure 13 combines the boring log for location J-48 with the FVD results for summed coal tar and peat signals. The sediment core displayed non-native sediments (black silt with a petroleum sheen and odor) from 0 to 3.3 feet, and fibrous organic matter free of sheen or odor (peat) from 4 to 8 feet bss. The associated LIF plot displays separated coal tar and peat response that exactly match the sediment core. A similar sediment stratigraphy and correlated LIF response is displayed at G-6 (Figure 7).

5.1.2 Identification of native sediments affected by Site operations

The identification of native sediments that have been potentially affected by Site operations is facilitated by the resolution of the total LIF response into separate responses from material associated with coal tar and peat. This study documented the existence of coal tar and peat material at sample locations F-12, L-6, and L-8. Descriptions of F-12 and L-6 are provided below.

5.1.2.1. Sample Location F-12

Boring location F-12 is located just off the shoreline, approximately 600 feet north and downstream from the mouth of the Wire Mill Pond. At this location, a 4.5-foot layer of fine grained, well-sorted brown sand overlies a 3.0-foot thick interval of petroleum-stained material. This interval apparently contains non-native material and is a mixture of thin layers of peat, black sand and black silt. The two distinct peat intervals that were identified at this location were 0.5 feet and 0.35 feet thick; the thicker interval contained fibrous organic material, while the thinner interval contained mollusk shells. The thinner interval is underlain by a brown sandy silt with some organic material.

Two sediment samples were collected from location F-12. Sample F-12a was collected from the well-sorted sand between two and three feet bss, while sample F-12b was collected from the petroleum-stained zone, between 6.5 and 7.0 feet. The sediment in this interval was black sandy silt and black silty sand. As shown in Table 2, sample F-12b, from the zone of petroleum-stained sediments, has distinctly higher chromium, lead, mercury and zinc concentrations, and a lower percentage of solids. Sample F-12a displays, in contrast, metals concentrations that are relatively low.

The LIF response obtained at this sampling location is shown in Figure 14. The total LIF response, the sum of the three coal tar responses and the sum of the two peat responses are plotted against depth. The LIF response correlates almost perfectly with the boring log, an observation particularly noteworthy given the 77% recovery in the eight feet of sediment core. A total response of less than 1% is logged from 0 to 5 feet bss and from 7.5 to 12 feet bss (the LIF was advanced four feet further than the sediment core). This correlates well with the 4.5 feet of well-sorted sand on top and the brown sandy silt logged below the area of petroleum staining. Within the area of sediment staining (5.5 to 7.25 feet) the LIF response is elevated, with a total signal greater than 10% at 6.1 feet. This total response, however, is the sum of both coal tar and peat responses. The peat signal reaches a maximum at six feet depth, exactly at the midpoint of the logged 0.5-foot layer of petroleum-stained black fibrous organics (peat). While the peat and coal tar signals track over most of the interval, the match is not perfect. At 7.1 feet the coal tar signal displays a minor peak with a value of 3.55%; at that same interval, the peat signal is close to zero. This correlates well with a black silty sand layer logged between 6.7 and 7.2 feet.

5.1.2.2. Sample Location L-6

At sample location L-6, non-native sediment was logged from the top of sediments to 1.4 feet, overlying a 0.9-foot thick peat layer. A petroleum sheen was logged from 1.15 to 1.95 feet, an interval that overlaps the boundary between non-native sediment and peat. The correlative LIF response over this interval displays distinct coal tar and peat peaks with overlapping shoulders; the coal tar peak is highest at 1.35 feet, while the peat peak is highest at 1.91 feet. The overlapping shoulder of coal tar in the upper portion of the peat layer corresponds with the petroleum sheen. It is possible that material associated with the non-native sediments migrated into the upper portion of the peat layer. If so, the absence of a coal tar LIF response or petroleum sheen across the entire peat layer suggests that the downward migration of this material was limited.

5.1.3   Identification of Potential False Positives

Two sample locations (F-66 and O-50) displayed elevated LIF responses that could not be correlated with the retrieved sediments. In both instances, however, there was poor recovery (less than 1.5 feet of sediment from a four foot core), and extremely soft sediments, which hampers the preparation of accurate boring logs. In all other sediment core locations, an elevated LIF response over more than a few tenths of a foot was always associated with non-native sediments in the sediment core. Thus, the lack of correlation in these two sample locations is believed to be due to the inability to accurately identify the interval represented by the partial core that was retrieved.

There are also several locations at the margins of each AOI (e.g. G-0, P-16, U-30) where the covariance of relatively small (i.e. less than 1%) peat and coal tar signals over identifiable depth intervals (i.e. more than 0.5 feet) is observed. At these locations, the peat signal is typically greater by a factor of two or more. It may be that these locations are not associated with coal tar or are influenced by coal tar material, and that the coal tar signal reflects the limitations of the LIF signal resolution technique.   If true, these locations represent false positives.   The confirmation of sediment types and their associated risk will be considered in the next phase of data gathering.

5.1.4   Identification of Potential False Negatives

Petroleum sheens and odors were noted in portions of nine of the 13 sediment core locations. Every instance of petroleum staining or sheens or petroleum odor correlates with an elevated coal tar LIF response. In this case, a definite correlation can be made between LIF response and these visual and olfactory indications of a non-native sediment; there were no "false negatives" with respect to these signs.

In some of the sample locations, a discrete sediment unit that displayed petroleum sheens or staining only did so over a portion of its depth interval. In these instances, the LIF response tracked more closely with the petroleum staining and smell than with physical sediment characteristics.   Sediment sampling and PAH analysis of discrete portions of this type of sediment will be conducted during the risk-analysis portion of the project to evaluate whether the LIF response and associated visual signs are correlated with all or some portion of the chemical constituents associated with the non-native sediments. Two possible explanations for these observations are provided in Sections 5.1.6 and 5.1.7.

5.1.5   Metals Concentration

A secondary goal of this study was to determine whether there was a correlation between elevated LIF response and elevated metals concentrations in sediments. The "coal tar" displays an elevated LIF response due to the presence of PAHs, but since coal tar also often displays elevated metals concentrations relative to native sediments it was possible that LIF could serve as a proxy indicator for elevated metals.

Table 2 displays metals concentrations and associated LIF response (both raw and sum of coal tar signals). The relationship between metals concentrations and the highest and average LIF response recorded in the correlative sediment interval was examined. The results suggest that average coal tar LIF response more closely correlates with metals concentrations. There appears

to be a good correlation when average LIF response is plotted against individual metals (Figure 15); for example arsenic (15a), copper (15b), lead (15c) and mercury (15d).

The three sample groups identified in Figure 15 display a correlation of metals and LIF response that is consistent with the conceptual Site model. Native sediments have low coal-tar LIF responses and low metals concentrations, and plot as a group near each graph's origin. Non-native sediments that display a petroleum sheen or staining generally display the highest LIF response and highest concentrations for a given metal. Between these two groups are non-native sediments that lack a petroleum sheen. The values for this group's plots are intermediate. The metals concentrations of non-native sediments without staining are higher than native sediments, but lower than correlative values for petroleum-stained non-native sediments. This suggests a direct correlation between petroleum staining and both LIF response and metals concentrations.

5.1.6   Non-native sediment in contact with surface water

As noted above, a few samples of non-native sediment near the sediment surface displayed low LIF responses and lower metals concentrations relative to material at lower depth within the same sediment unit. Sample location D-56 provides the best example of this observation. A black silt was identified from the top of sediments to a depth of 3.3 feet. A coal tar odor was noted from 1.5 to 3.35 feet (i.e. the base of the black silt). The underlying sediment was a gray clayey sand that lacked an odor. Two samples of the black silt were collected for metals analysis: D-56a (zero to 0.5 feet) and D-56b (2.5 to 3.0 feet). D-56b was within the interval that displayed a petroleum odor.

The metals concentrations from D-56a and D-56b are both elevated, as shown in Table 2. The percentage of solids in these samples also inversely correlates; samples with elevated metals concentrations (relative to naturally-occurring concentrations) have percent solids that ranged from 40 to 50%, while native sediments are all greater than 50% solids.

Based on the sediment characteristics and the elevated metal concentrations, it is reasonable to assume that these samples came from the same unit of non-native sediment. However, the LIF response within this unit is stratified in a manner that tracks with the coal tar odor. The 14 LIF observations between zero and 1.5 feet have an average summed coal tar response of 0.32%, while the average LIF response for the 22 observations within the interval with a coal tar odor was 1.1%. The difference is even greater when the LIF interval is narrowed to the intervals sampled for metals; 0.01% from zero to 0.5 feet, and 2.8% from 2.5 to 3.0 feet.

It appears that material within the upper portion of this layer of non-native sediment does not contain the constituents that generate the coal tar LIF response and also displays lower metals concentrations. A possible explanation for this observation is bioturbation and loss of chemicals to the environment. This would not be surprising; the relative mobility of petroleum-related compounds when compared to metals is well-documented, and attributed to the higher solubility and degradation rates of petrochemical constituents. The mechanism for PAH mobility in the upper margins of a non-native sediment at the river bottom is also readily identifiable. As noted by Riebe (1988), "Bioturbation, the normal life-cycle activities of benthic organisms, leads to mixing and redistribution of contaminants and sediments in the upper layer. The chemical migration rate within the bioturbated zone is typically much faster than in other portions of a cap."

(Reible, 1998. Guidance for Subaqueous Capping of Contaminated Sediments: Appendix B: Model for Chemical Containment by a Cap.)

5.1.7 Potential transfer of "Coal Tar" chemicals to native sediments

While bioturbation and equilibration with river water might explain the lack of elevated LIF response and lower metals concentrations in the upper portions of non-native sediment, this mechanism cannot readily explain the presence of a "coal tar" LIF response in what appear to be native sediments. For example, at sample location L-6, described in Section 5.1.2.2, an elevated coal tar LIF response was observed in the upper portion of a peat layer that underlies non-native sediment. A petroleum sheen was also observed in this portion of the peat. Given the continuity of this petroleum-stained peat with the rest of the peat layer, it is not likely that the petroleum-stained peat was "deposited" during Site operations (unless it was generated near shore, and displaced and deposited by a storm event). More likely, the peat unit was in place within the river sediments and the chemicals were secondarily introduced. Given the observation of petroleum sheen, this material may have been PAH-bearing fluid that displaced porewater in the native sediments. Alternatively, the agent could have been fine-grained non-native sediment material that was mixed or otherwise co-mingled with the upper peat layer.

Possible support for this concept comes from the comparison of the sediment core results obtained in 2000 (Figures 3 and 4) with the LIF results. Figure 16 compares the LIF response obtained at sample locations on or near the Figure 4 cross-section of the Wire Mill Basin with the stratigraphy interpreted from the 2000 sediment core and bathymetry study. There is relatively good agreement between the two studies, with this notable exception; the zones of elevated coal tar LIF response extend to greater depths than the observed base of non-native sediments. This difference ranges from 0.5 to two feet. In contrast, the thickness of native oversediment layers and the top of the non-native sediment correlate well between the two studies.

5.2 EXTENT OF NON-NATIVE SEDIMENTS

5.2.1 Wire Mill Basin AOI

The coal tar LIF response in sample locations within the Wire Mill Basin indicates a single, relatively uniform layer of non-native sediments that is approximately 1,400 feet wide and 2,000 feet long at greatest extent (i.e. row 12 and column I, respectively). This layer of non-native sediments appears to be oval in shape, with a northeast-southwest orientation. The thickness of this layer gradually decreases from three to four feet thick nearest shore to less than two feet at its lateral extent. The depth of the elevated coal tar LIF response zone increases as distance from shore increases. This observation is supported by Figure 9, which contours the depth at which the maximum coal tar LIF response was recorded.

The consistency in the size, shape and depth of the elevated coal tar LIF response within this area of non-native sediments suggests a common depositional process over a fixed period of time. These features are consistent with the conceptual Site model presented in the Work Plan.

The upstream, or southern extent of non-native sediments is depicted in the FVD plots along rows 0 and 2 of the sample grid. At sample locations such as F-2, H-2 and J-2, the "coal tar" and

"peat" signals roughly co-vary, with the peat signal greater than the coal tar signal. The close tracking of the two summed signals at locations such as H-2 could represent an exact match in fluorescence response (e.g. PAH-impacted peat), but is more likely an artifact of the signal resolution process.

At location L-2, a sediment core contained a brown silt from zero to two feet, and sand from two to four feet. The brown silt unit contained a clam shell and lacked any visual or olfactory evidence of chemicals in sediments. The metals concentrations within the two to 2.5-foot interval were low, and representative of native sediment. While the LIF response suggested both "peat" and "coal tar" in the upper few inches of the sediment, neither were observed in the core.

The strong difference in FVD plots between these locations and sample locations immediately to the north are consistent with an upstream edge of non-native sediments bounded by these locations. This "upstream" edge moves to the north and downstream as the distance to shore increases, to become the lateral edge of non-native sediments at locations K-4, M-6, O-8 and O-10.

The downstream extent of non-native sediments within the Wire Mill Basin is, based on the observational data, approximately 1,600 feet downstream from the Wire Mill Pond, and 2,000 feet from the upstream extent. Borings I-22, J-22, K-22 and M-22 display zones of elevated coal tar LIF response that are consistent with adjacent borings upstream while the correlative borings I-26, K-26 and M-26, located downstream, do not.

Other borings within the intermediate area between the Wire Mill Basin and Unnamed Creek AOIs display somewhat anomalous readings that are not consistent with those observed in either AOI. At sample locations in the area bounded by E-30, G-38, I-32 and K-30, the thickness of the zone with elevated coal tar LIF response is often greater, and displays peak values at greater depths. For example, the high LIF reading at G-38 occurs at eight feet; a sharp peak was recorded at six feet depth in E-30. In addition, there is relatively poorer correlation between adjacent points.

5.2.2   Unnamed Creek AOI

The extent of non-native sediments within the Unnamed Creek AOI is represented by low coal tar LIF response in sample locations C-62, H-58, and L-50. The southern bound of non-native sediments is the constructed spit of land adjacent to the mouth of Unnamed Creek. This fan-shaped area is consistent with the Site conceptual model of deposition of non-native sediments transported by stream flow. The area of non-native sediments is approximately 1,600 feet long and 1,800 feet wide.

The total LIF response measured in sample locations to the north and east of this zone appears, once resolved, to be primarily the response of peat. This peat signal occurs either alone, without a "coal tar" response (e.g. H-68, K-66) or over the same depth intervals with a small "coal tar" signal, as was seen in upstream locations at the Wire Mill Basin AOI.

The Unnamed Creek depth intervals with elevated coal tar LIF response are much greater than what is observed at the Wire Mill Basin AOI, particularly in the southwest.

While most of the non-native sediments are located within the upper four feet of the Wire Mill Basin AOI, most non-native sediments are located at depths greater than four feet in this part of the Unnamed Creek AOI (bounded by B-50, D-52, G-48 and F-42). In addition, the apparent thickness of non-native sediment zones is greater in this portion of the Unnamed Creek AOI, with four to five feet thickness more common than the two foot thickness most apparent in the Wire Mill Basin AOI.

The differences in non-native sediment depths and layer thickness may reflect the differences in sources and depositional histories identified in the Work Plan. While these differences are worth noting, they should not affect the evaluation of risk associated with non-native sediments, which is based on bioavailability within the upper two feet (or less) of surface sediments.

5.3   MAGNITUDE OF NON-NATIVE SEDIMENTS

A sample of coal tar associated with the Site was examined by DTI in the lab for its florescence response prior to field investigations. An 18% total response was achieved under these controlled conditions with a "pure" sample. The elevated LIF response associated with coal tar obtained in the field was consistently less than this response, ranging from zero to 11.48 percent (L-12, 2.92 feet).

5.3.1   Wire Mill Basin AOI

Elevated coal tar LIF responses in the Wire Mill Basin AOI can be contoured in a "bulls-eye" concentration distribution, with highest concentrations observed in the center (e.g. L-12 and K-14). Figure 8 plots the highest concentration, regardless of depth, and Figures 11.1 through 11.10 all display this concentration gradient. The highest values of 10.5% (K-14) and 11.5% (L-12) were recorded at greater than two foot depth within the sediments. In fact, more than half (109 of 189) of the high coal tar LIF responses at individual sample locations were recorded at depths greater than two feet.

Figure 10, which contours the coal tar LIF response within the upper two feet of each sample location, shows the same type of "bulls-eye" concentration distribution, but with lower concentrations and a center that is farther to the southwest. This is consistent with the Site bathymetry and the figures in Appendix E that show a "layer" of elevated coal tar LIF that occurs at greater depth intervals from southwest to northeast.

5.3.2   Unnamed Creek AOI

The observed total LIF responses and the summed coal tar LIF responses in the Unnamed Creek were significantly lower than values obtained in the Wire Mill Basin. The contours shown in Figure 8 are centered near the mouth of the Unnamed Creek, consistent with the Site conceptual model of chemicals in sediments. The majority of the maximum coal tar responses plotted in Figure 8 within the Unnamed Creek occur at depths greater than two feet. As a result, there is no regular distribution of concentrations depicted when the zero to two foot interval values are plotted (Figure 10). Only a handful of sample locations in the Unnamed Creek AOI display coal tar signals that are above 2% in the upper two feet.

5.4 EXTENT OF LOW-LIF COVER MATERIAL

The existence of native-sediment cover over much of the non-native sediments within the two AOIs was previously documented (see Section 2.2 of Work Plan). The data collected during this LIF study supports the presence of cover sediments.

One would predict that a LIF FVD plot at a location with a cover layer of non-impacted native sediments would display a uniformly low LIF response from the sediment surface down to the top of the non-native sediment layer. The underlying layer of non-native sediments would then be likely to display a LIF response that was both higher in intensity and more heterogeneous. The depth interval of this uniformly low LIF response zone would vary from node to node, based on the variation in cover thicknesses.

A cover layer of sediment overlying non-native material was documented in some of the sample locations with sediment cores. Sample location L-8 is a prime example; a 0.6 foot layer of yellowish brown sand overlays a 1.4-foot thick layer of petroleum-stained gray silt.

Figure 11 contours the depth at which the first coal tar LIF signal greater than 0.3% was obtained. This can be considered a rough and quick estimate of cover thickness. Figure 11 shows that the thickness of cover sediments (or other low LIF material) increases as the distance from shore increases, consistent with the Site conceptual model. Figure 16 and Figure 17 compare the LIF responses along the cross-section displayed in Figures 3 and 4. These results also suggest that sediment cover increases as distance from shore increases. Figure 17 is noteworthy in that it provides evidence of low LIF cover thickness near the shore, in an area depicted by the 2000 study as not covered with native sediments.

5.5 FLUID-SEDIMENT INTERACTIONS

5.5.1 Surface Equilibration

The recognition of a low and homogeneous LIF response in the upper portions of some non-native sediment layers suggests that a low LIF response at the river bottom may reflect a surface exposure of non-native sediments whose LIF response has been attenuated by bioturbation or equilibration with surface water.

The non-native sediments with low LIF response at the surface appear to have released much of the PAHs responsible for the LIF peaks In this sense, this upper zone may have become a low-PAH cap for underlying non-native sediments with higher PAH concentrations.

5.5.2 Preservation of Fine-scale Heterogeneous LIF Response

The LIF results can also be used to evaluate the magnitude of vertical fluid flow through the native and non-native river sediments, even though this was not an established study goal. In almost all of the samples, the boundaries between overlying low-LIF zones and underlying elevated LIF zones are sharp and distinct. Within the elevated LIF zones associated with coal tar, the fluorescence versus depth (FVD) plots display high peaks and valleys, with variations of more than 50% of total signal response occurring over a few tenths of inches. This strong heterogeneity in the LIF response within the non-native sediments, and the sharp divide between

high and low-LIF intervals is consistent with an environment in which there is relatively little upward vertical fluid flow.

6.0   Conclusions

- Depth-to-sediment measurements at each of the 189 sample locations established a Site bathymetry consistent with previous studies and charts.

- Co-location of LIF borings and Geoprobe™ sediment core borings at 13 nodes within the 200- foot sample grid demonstrated that elevated LIF response was primarily associated with two sediment types: impacted non-native sediments (e.g. coal tar) and native peat.

- The material in each sediment that fluoresced (PAHs in the coal tar and organic acids in the peat) produced resolvable waveform signals that could be identified and separated within each raw LIF response.

- The LIF results are consistent with the established conceptual model of the Site; this supports the utility of the LIF technique in delineating the AOIs.

- The "coal tar" and "peat" signals are typically distinct, except for a few locations where impacted peat layers were identified (in some cases with sediment core evidence).

- The resolved "coal tar" LIF response can be contoured at each AOI with magnitude decreasing as the distance from shore increases.

- The highest LIF responses are in areas adjacent to the presumed source areas (outfall of Wire Mill Pond and the mouth of Unnamed Creek).

- The thickness of "surface-down" low LIF response layers, presumed to generally be native cover sediments, increases as distance from shore increases, with thickness contours that roughly parallel the shoreline.

- Elevated raw LIF responses at lower depths (greater than seven feet) and at the margins of the AOIs were generally the response of native peat sediments.

- Comparison of the LIF responses in each of the AOIs suggests that the relative magnitude of PAH chemicals associated with non-native sediments is higher in the Wire Mill Basin AOI.

- The Wire Mill Basin AOI also displays a larger areal extent, although the Unnamed Creek AOI displays deeper "coal tar" sediments (greater than 12 feet, compared with less than 6 feet deep in Wire Mill Basin AOI).

- Most of the AOIs are covered with a layer of low-LIF "cover" material that ranges from 0.5 to more than two feet in thickness.

- In locations where sediment cores document non-native sediments at the surface, a low and relatively "flat" LIF response in the upper 0.5- to 1.5-foot interval is interpreted to represent equilibration and PAH release to the environment through bioturbation and exchange with surface water.

- The collection and analysis of sediment samples suggests that LIF response is generally a good proxy indicator for elevated metal concentrations at the Site. LIF is less reliable as an

indicator when non-native sediment is at the surface, since the PAHs responsible for the LIF response are lost to the environment much more readily than metals.

- The lack of good correlation between metals concentrations and LIF signal at two locations (D-66 and O-50) was attributed to the difficulty in assigning cored sediment depths when incomplete recovery was obtained.

- In almost all of the samples, the boundaries between overlying low-LIF zones and underlying elevated LIF zones are sharp and distinct. Within the elevated LIF zones associated with coal tar, the fluorescence versus depth (FVD) plots display high peaks and valleys, with variations of more than 50% of total signal response occurring over a few tenths of inches. This strong heterogeneity in the LIF response within the non-native sediments, and the sharp divide between high and low-LIF intervals is consistent with an environment in which there is relatively little vertical fluid flow.

7.0   Recommendations

The success of the LIF technique in defining the relative magnitude and extent of non-native sediments in the AOIs will allow each of the areas to be better categorized based on relative risk. It is recommended that the relative magnitude of chemicals in the upper two feet of sediments, the thickness of impacted sediment layers within the upper two feet of sediments, and the amount of cover sediments (indicated by low-LIF response from surface-down) be used to group each of the sample locations into low, medium and high risk groups for the purposes of a more focused risk-based analytical and toxicological investigation of a limited (18 to 24) number of sample stations. It is further recommended that the documented extent of chemicals in sediments be confirmed by more limited analysis of sediment samples from the margins of each AOI.

In-situ LIF System for PAH Contaminated Sediments

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Dakota Technologies, Inc. was contracted by URS Corporation (URS) to provide the instrumentation, tools, and expertise needed to remotely measure the laser-induced fluorescence (LIF) of polycyclic aromatic hydrocarbons (PAHs) in lake sediments associated with the USS Duluth Works Site (Site). The effort fell into 5 main categories.

- Measure the fluorescence of previously collected sediment samples (of varying PAH concentration) with the Rapid Optical Screening Tool (ROST). Adjust system parameters to maximize our ability to detect PAHs and distinguish them from naturally occurring interferents.
- Measure and record PAH fluorescence on sediments in real time as the probe was advanced into the sediment.
- Correlate LIF response with sediment samples taken immediately adjacent to the LIF soundings for use in validation/chemometrics analysis studies.
- Submit a report describing the technology and the data generated.

This report documents the effort and is meant to serve as a guide to understanding what was actually being measured, how it was measured, and how the data can and should be interpreted.

LIF PAH SCREENING SYSTEM DESCRIPTION

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. Our apparatus (described in the ROST System Description section) 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.
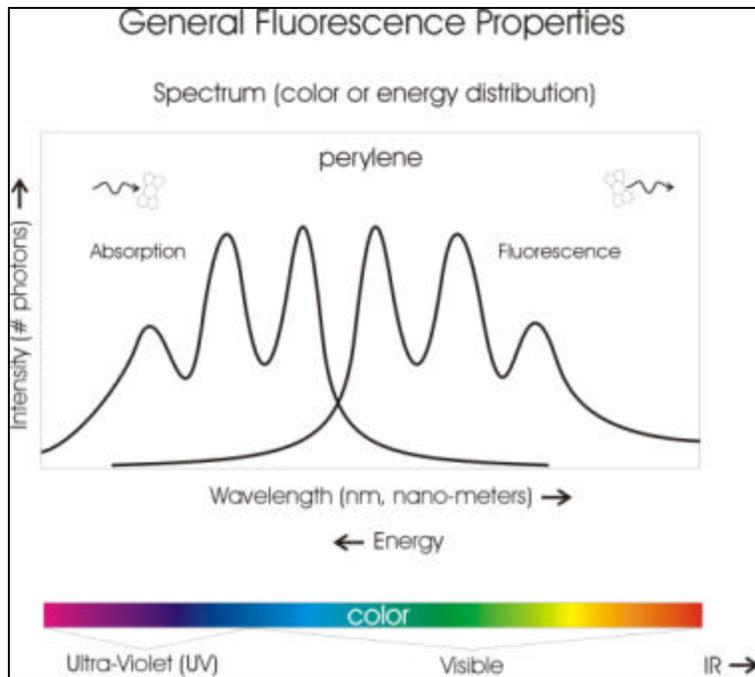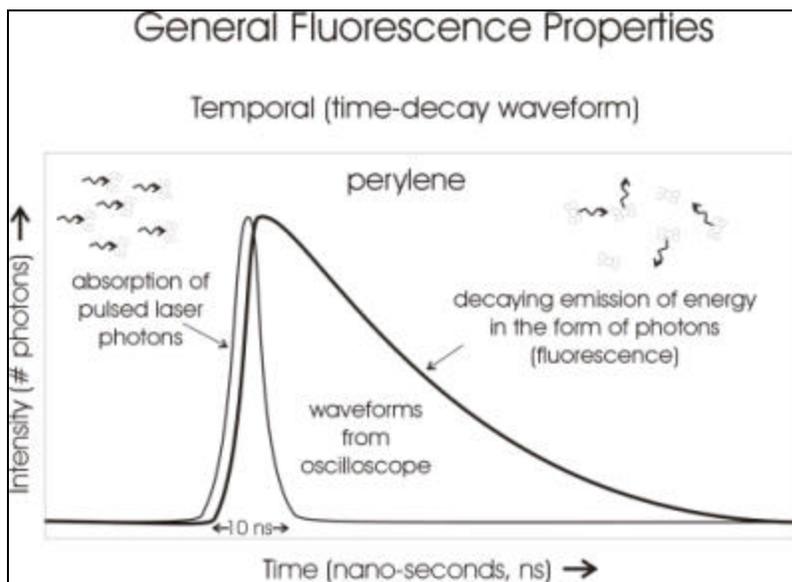
Figure 1. Spectral property of fluorescence

Figure2. 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.

<u>Interferences</u>

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.
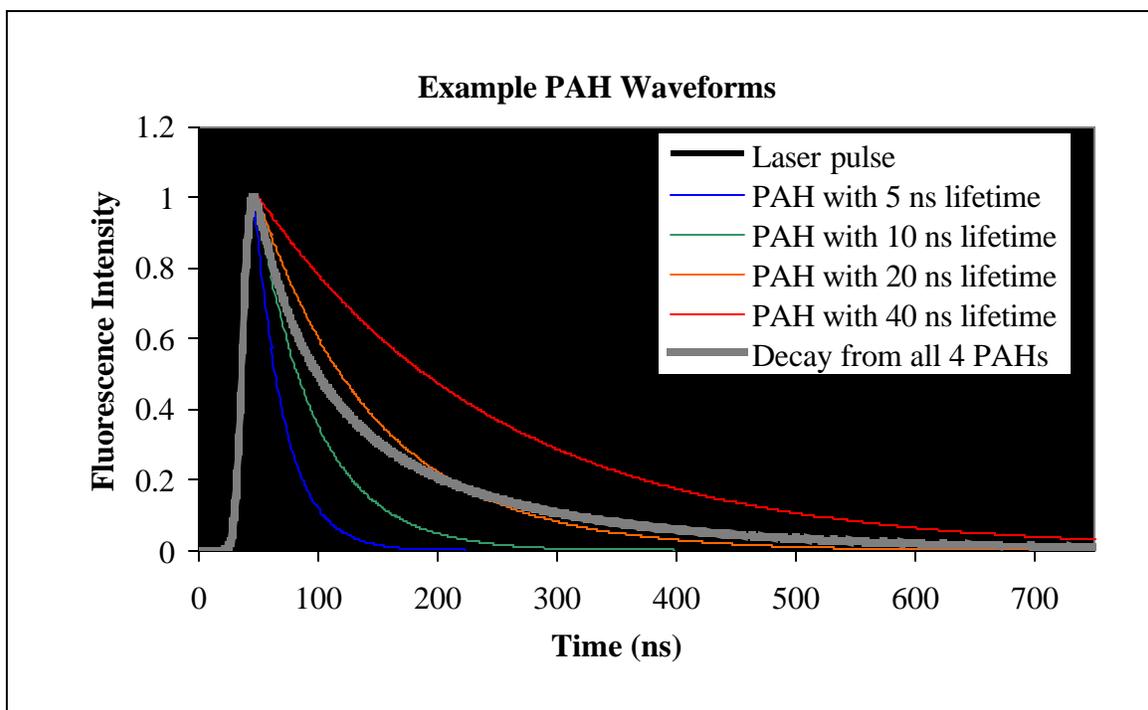

Figure 3. Temporal fluorescence examples

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.
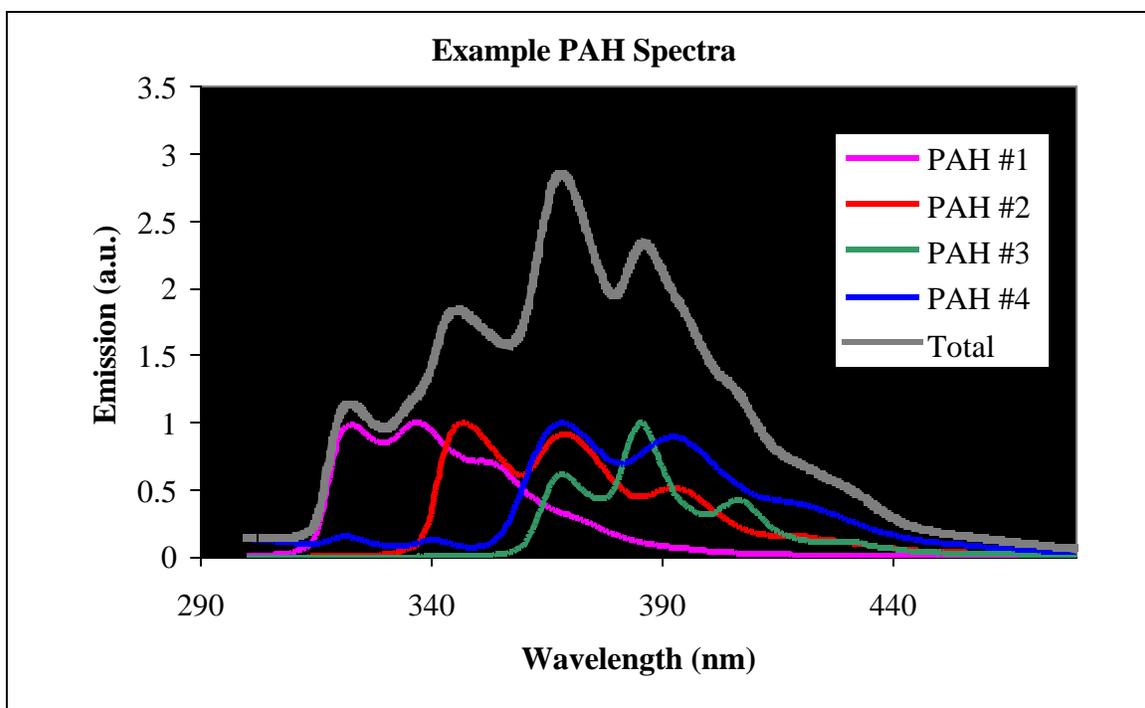
Figure 4. Spectral fluorescence examples

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 forensics.

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.
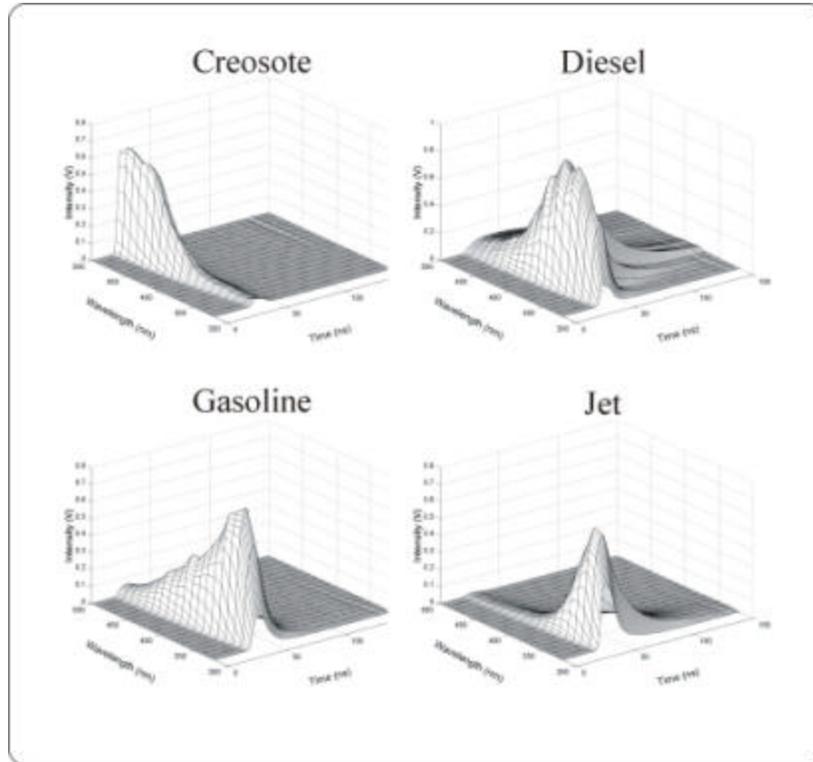

Figure 5. Example WTMs of common contaminants on sand

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.
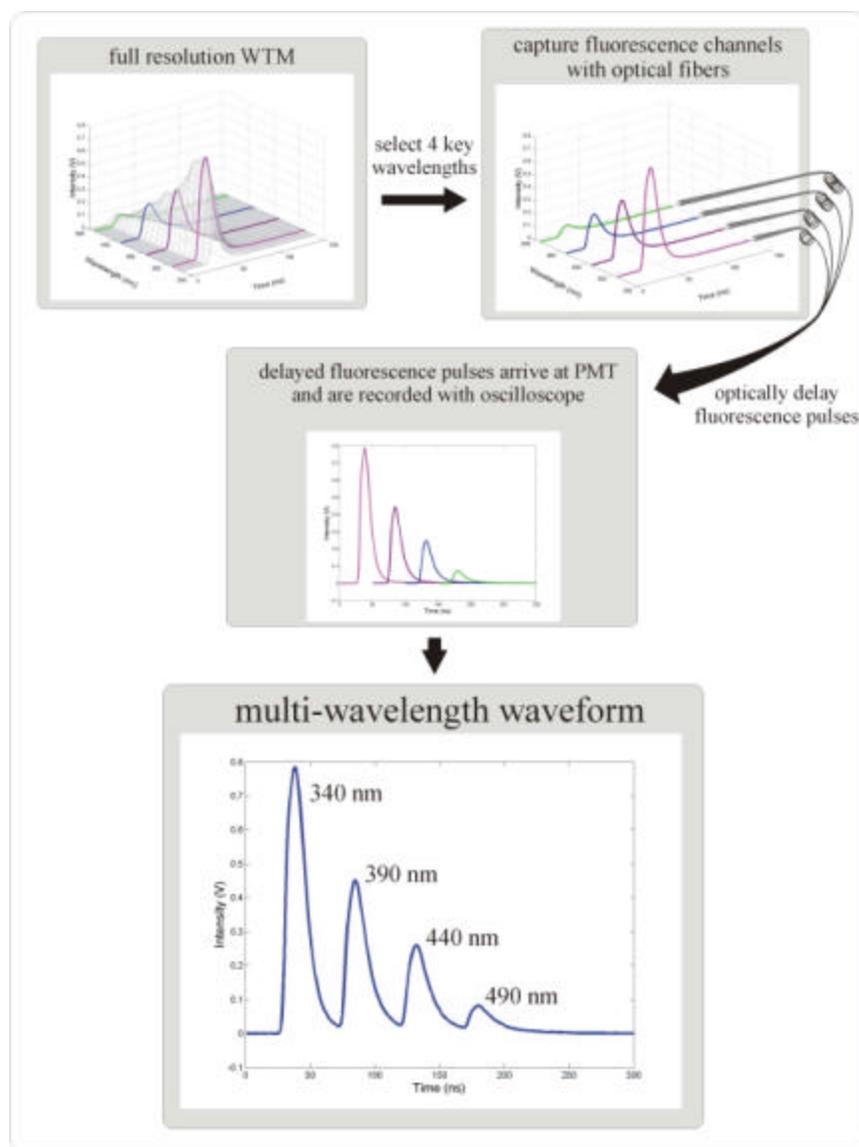
Figure 6. Multi-wavelength waveform concept

The ROST system acquires waveforms at ~1 Hz and logs them to the hard drive continuously. As described below (see Calibration and normalization) 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.
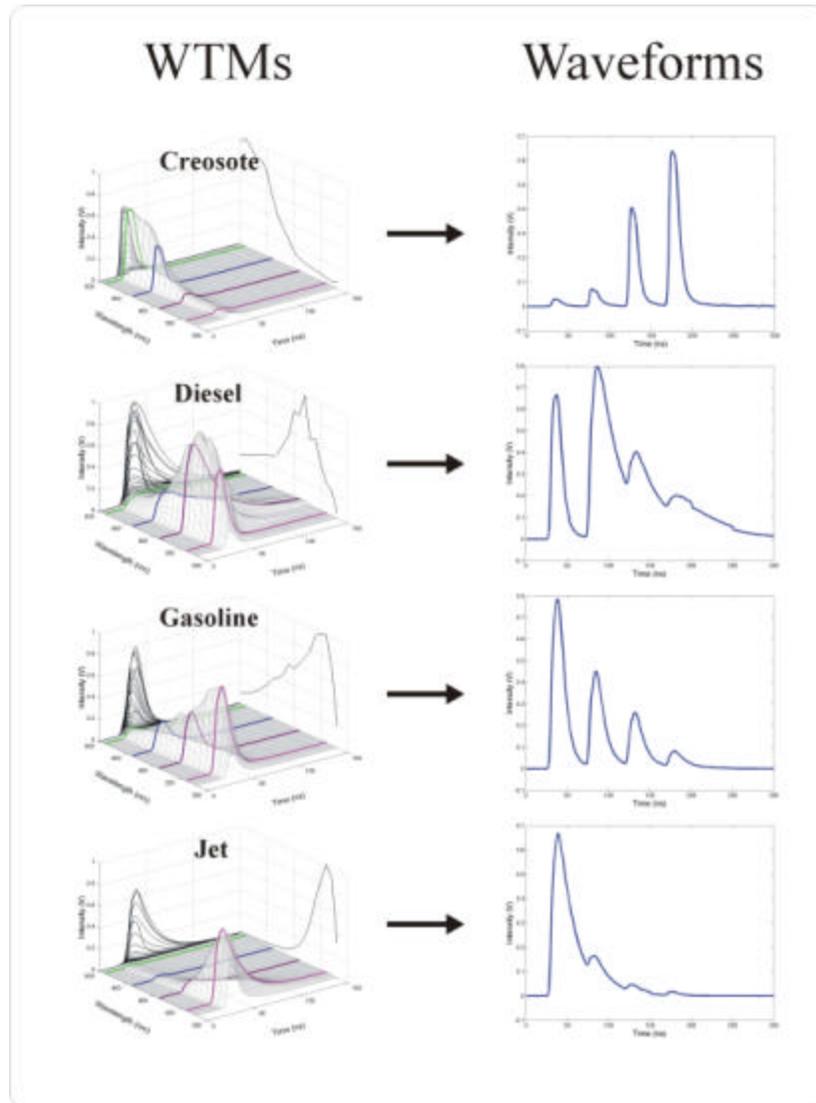
Figure 7. Waveforms of common contaminants

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.
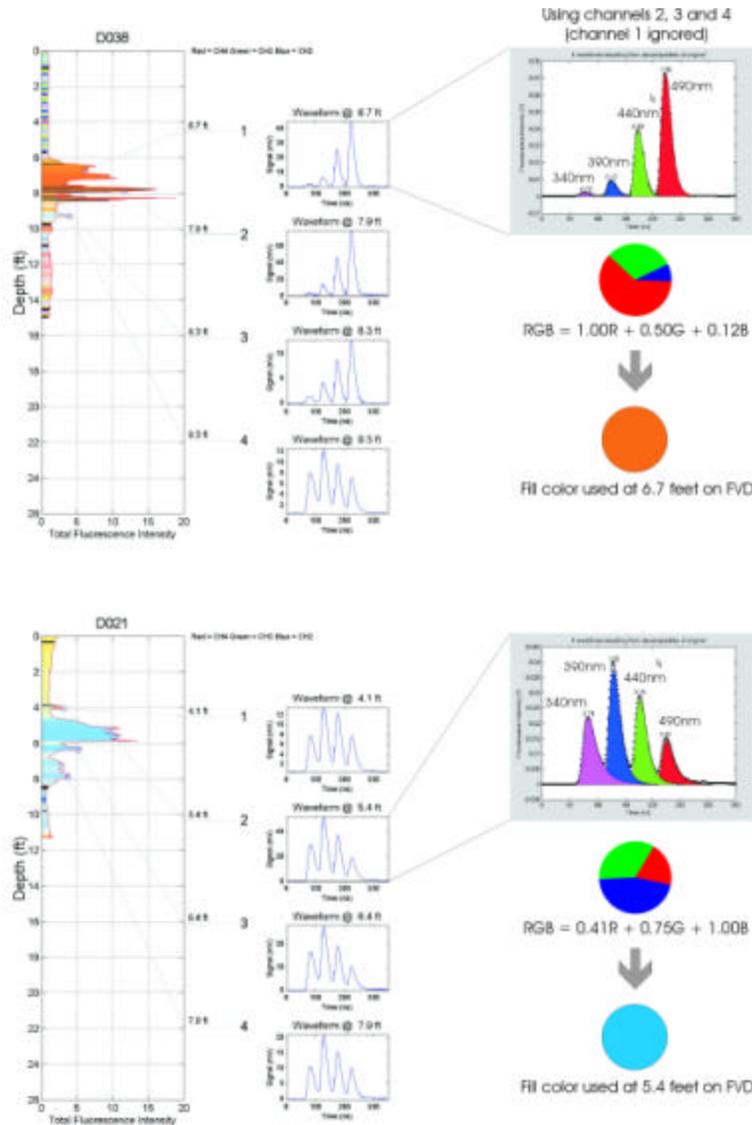

Figure 8. How color-coding is calculated

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.

ROST SYSTEM DESCRIPTION
The ROST system is contained in a ruggedized shipping container as shown in Figure 9. The system actually consists of a variety of sub-systems that are described in detail in this section.
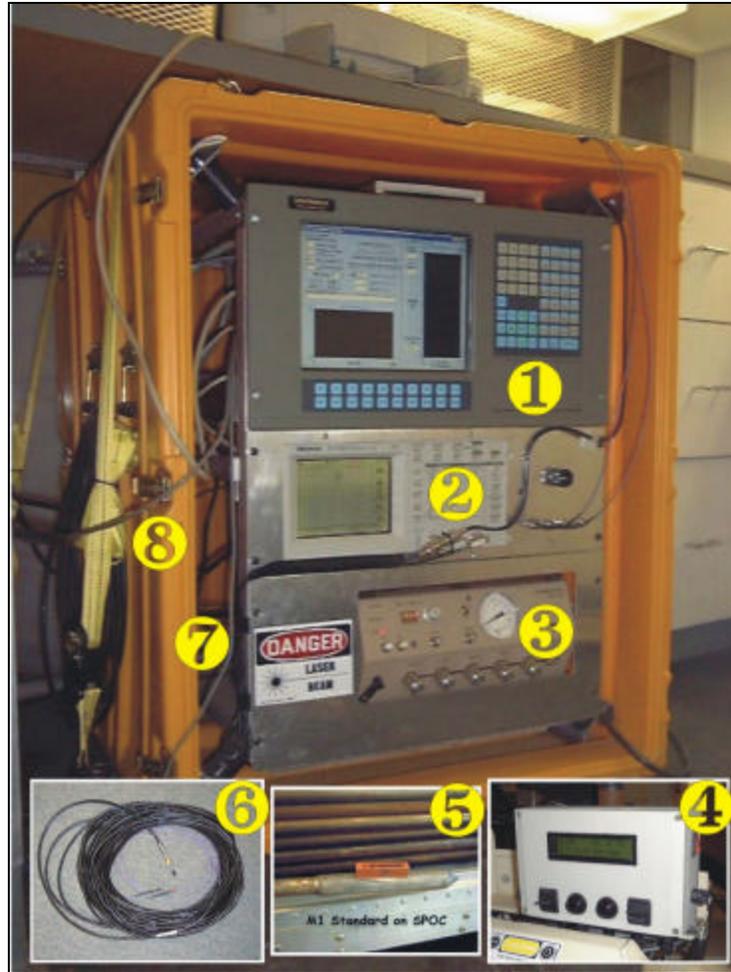
Figure 9. ROST system and key peripheral devices

Laser ⊂

The ROST system employs a pulsed XeCl excimer laser (MPB PSX-100) that generates very fast pulses of 308 nm light at 50 Hz. Each pulse measures less than 10 billionths (10 ns) of a second wide at half height. The 308 nm wavelength efficiently excites the vast majority of PAHs that are contained within the sediments being screened. A beamsplitter directs a small portion of the beam to an energy meter to monitor excitation pulse energy. A photodiode is positioned near the beamsplitter and serves as the trigger source for the time-resolved fluorescence measurement that takes place with the oscilloscope. A lens is used to launch the laser light into a fiber optic for delivery to the subsurface.

Fiber optic cable∉

The fiber optic cable consists of two 40 m silica/silica optical fibers. One fiber delivers the excitation pulse while the other serves to return a portion of the resulting fluorescence to the surface for measurement. Both silica/silica fibers with a 365 micron core-diameter and are SMA terminated at the surface. The fibers are terminated with a custom connector at the sub-surface (SPOC below). Since the fibers are readily broken if flexed or handled too aggressively, they are housed in a flexible polyurethane covered stainless

steel sheath with bend radius limiting quality that drastically reduces fiber optic failure rates.

Shock-protected optical compartment (SPOC) ∈

The fiber optics deliver and receive the light to and from a steel probe that consists of 2 threaded Geoprobe® rods (1 inch diameter) terminated with a special optics module and tip called a SPOC. DTI typically uses a Geoprobe to jackhammer the LIF probe into the sub-surface to delineate typical POL spills, such as leaking underground storage tanks. Fibers terminated into a standard optical mount would shatter or cleave instantly under the shock and vibration of the jackhammer. DTI developed and built the SPOC that employs proprietary elastomer supports, in combination with Swagelock fittings, to insure long term stability of the optical alignment along with protection against breakage. The SPOC contains a parabolic mirror that acts to turn the excitation beam 90 degrees. The beam exits the SPOC through a sapphire window that is flush-mounted on the side of the SPOC and strikes the sediment that is pressed against the window as the probe advances through the sediment. Sapphire's Moh hardness of 9 (2nd in hardness only to diamond) allows it to resist scratching or breaking under all but the most severe conditions such as jackhammering into gravels/cobbles. The laser beam illuminates several mm^2 of the sediment that is exposed to the window's surface and any resulting fluorescence (along with a substantial quantity of scattered laser light) is emitted back into the window where a portion is reflected by the parabolic mirror into the return fiber for transport to the surface.

The SPOC design is watertight; a necessary attribute when probing in saturated zones such as those obviously experienced when probing sediments. Any leakage can result in evaporation of the intruding water into the air space within the SPOC. The water vapor that results can cause fogging on the interior surface of the sapphire window that has the effect of changing background levels and reducing fluorescence intensity. The moisture can also cause corrosion of the optics and hardware within the SPOC. An extra measure of humidity prevention is achieved by purging the SPOC with an inert gas immediately prior to reassembly any time it is open to the atmosphere for maintenance or adjustment.

Emission detection system ∠&∇ (hidden from view)

The collection fiber returns the entire spectrum of light ("white light") that is collected from the sediment surface. Since this is a multi-channel (multi-wavelength) detection system, we must disperse the white light. To accomplish this, the collection fiber is butt-coupled directly into an Acton SP150 imaging monochromator where a series of mirrors and a 600 groove/mm grating act to disperse the white light into a "rainbow" that can sampled (4 regions at 340, 390, 440, and 490 nm) for detection.

Before the light is dispersed by the monochromator the laser light (308 nm) must be removed and the amount of fluorescence light must be controlled. If not rejected, the relatively intense laser light that accompanies the fluorescence bounces around the interior surfaces of the monochromator and ultimately ends up in the detector. The detector does not differentiate between laser light and fluorescence, so this laser light must be filtered out. To achieve this, a cutoff long-pass filter (320 nm CFLP) is arranged

immediately inside the monochromator, rejecting the vast majority of laser light, but passing the lower energy (longer wavelength) fluorescence. Butt-coupling of the fiber to the monochromator eliminates the slits that are usually found on the entrance of a monochromator. These slits are designed to control bandpass and the amount of light that enters the monochromator to avoid saturating the detector. The ROST system employs a neutral density filter wheel for controlling light levels instead. By selecting an appropriate optical density filter the light levels can be controlled with precision. The reference emitter signal (M1 described later) was attenuated in these studies while the PAH fluorescence was passed through without filtering due to its relatively low intensity compared to standard POLs.

The fluorescence passes through the CFLP and neutral density filterwheel assembly and is ultimately dispersed into a rainbow of light on the back plate of the monochromator. The polished faces of 4 fiber optics are located on this plate and are arranged to "pick off" 4 regions of the spectrum where PAHs fluoresce with varying intensity, depending on number of rings and substitution level of the PAHs being observed. Rotating the grating allows selection of different regions, but always with 50 nm between channels because the space between fibers is not adjustable. ROST uses 340, 390, 440, and 490 nm under standard conditions and these wavelengths were used here.

At this point if all four fiber optics were of the same length and were directed into the detector (PMT), we would observe all four channels combined into a single decay curve (waveform). To achieve separation of the four channels we must time delay the photons so that they strike the detector at different times. To achieve this the fiber optics are all made 10 m longer than the next. The fibers are 2, 12, 22, and 32 m long for the 340, 390, 440, and 490 nm wavelengths, successively, delaying each channel by approximately 50 ns. These four fibers are then terminated in a single large core SMA fitting which couples to a large diameter (1500 micron) fiber optic that is .33 m in length. This large diameter fiber is taken through a relatively sharp bend that serves to "mix" the 4 fiber optic beams into one homogeneous beam. The large fiber is attached to a mount that directs the light at the photocathode of the PMT detector.

The dynode chain of the PMT is held at a –900 V bias with a high voltage power supply. This bias accelerates and multiplies the electrons that are ejected from the photocathode when the photons strike the surface. The PMT detector (Hamamatsu R928) essentially converts the pulse of photons into a pulse of electrical current. The pulse is actually a train of 4 pulses that results from each channel's photons arriving at the PMT in succession.

Oscilloscope ⊄

The pulse of electrical current is very short lived. In fact, the entire train of pulses (the waveform) arrives in less than 250 ns. A very fast device is required to accurately record the current pulse. The ROST system employs a 100 MHz Tektronix® TDS 220 digital storage oscilloscope capable of 1 billion samples per second (1 GS) to record the waveforms. A 50-ohm terminator at the input of the fluorescence channel converts the current to a voltage, allowing measurement of a voltage vs. time waveform that

represents the arrival of the photons at the PMT. A second channel of the oscilloscope is used to monitor an energy meter (a much slower measurement) before each test, to log the laser energy performance for maintenance/service tracking purposes. The fluorescence waveforms are displayed on the oscilloscope in real time and are retrieved from the oscilloscope via general-purpose interface bus (GPIB) for storage and analysis. Approximately 50 laser shots are averaged for each sampling point along the test, which ends up being equivalent to a 1 Hz waveform storage rate. At the probe advancement speed used in these studies, the vertical data density averaged 0.3 to 0.5 inches (0.8 to 1.0 cm).

Control computer ⊃

A rack-mounted industrial computer is used to control the ROST system and log the data to hard drive. The computer controls the monochromator, the oscilloscope, a differential GPS beacon, and the depth control and acquisition module (DCAM). The host computer program was written in Visual Basic 5. The software provides a real time display of the test results while the test is in progress and generates a full color picture of the log at the end of the test. The waveforms are continuously logged to the hard drive while a total FVD log is created by integrating the entire fluorescence waveform and plotting it's intensity vs. depth. The final data analysis and display was done on a separate workstation in the office.

DCAM ⊆

During an Air Force SBIR Phase II project, DTI designed and built the original DCAM. It allows a host computer to track and control the probe advancement on a Geoprobe platform. DTI built and delivered a modified version of the DCAM that monitored the gear/proximity sensor on the derrick, displayed the current depth, and communicated the results to the ROST host computer via RS-232 commands for this project. The system runs off 12 V which was supplied by the Geoprobe track rig.

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 e 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.

The DCAM monitors an optical encoder on a Geoprobe direct push probe advancement system. The DCAM's sole function is to monitor the proximity sensor, calculate the speed, direction, and distance traveled, display the result on a digital display, and make the results available to the ROST computer via RS-232 protocol.

FIELD WORK DESCRIPTION

Given the proposed use of this technique on ice, two Geoprobe direct push probe advancement systems were mobilized to the site; a standard truck mounted system and a lighter (but slower moving) skid steer vehicle. The ROST system, housed in its rugged container, was transferred to the skid-steer vehicle once most of the sample locations with sufficient ice to support the truck's weight were obtained.

DTI performed LIF and Geoprobe investigation services at the site from March X to March Y, 2002. A URS field geologist directed DTI efforts with respect to selected sample locations, boring depths and sediment core locations.

LIF WAVEFORM ANALYSIS

DTI has written software that allows us to extract information from the raw waveforms in a continuous fashion along the entire FVD log. This permits classifying certain waveform shapes as belonging to certain contaminant or naturally occurring fluorophore classes. URS's field observations and validation sampling information was used by the analyst at DTI to generate a Basis Set of waveforms that represent the general classes of waveforms observed at the site. Every data point in an FVD log has a complete waveform associated with it. The previously determined Basis Set of waveforms was applied to each of the raw waveforms using a non-negative least squares fit algorithm. An automated software system calculated the relative contributions of each class of waveform for the entire FVD log. The result of the analysis was a measure of how much tar, peat, and system/soil background is represented within the raw logs. An ASCII file and JPG image of the resulting individual component contribution logs were produced and supplied to the URS. The analysis results are valuable for understanding the distribution of the contaminants and natural interferents identified earlier during the Basis Set determination.

Brief summary of the Analysis:

1. The raw FVD ACSII data files and colorized JPG images of the plotted logs of each boring were provided to URS. URS provided detailed sediment characterizations/observations and analytical results that identified boring

locations and depth intervals that were associated with sediment types of interest (i.e. non-native "coal tar" sediments and native peat).

2. The LIF logs were loaded into the analysis software and several color-coding schemes were examined. I decided that assigning the color rendition to 440nm(Red), 390nm(Green) and 340nm(Blue) RGB color scheme gave best contrast between product types (after reviewing preview images). These were the same channels used in the field and other combinations didn't result in improved differentiation (contrast) between tars and peat.

3. I harvested (with depth cursors in software) 3 types of tar signals that I kept running across when I reviewed printouts of the logs and the spreadsheets and other documentation URS supplied us with. The tars gave consistently longer decay times (wider peaks) than the peats, but the intensity distribution in the last 3 channels seemed to shift spectrally. This could be a result of differences in oxygen content, soil type, or even tar type. Nonetheless, historical experience and URS filed observations supported the theory that all these types of waveforms were tars. I decided that if I chose tars that covered the entire range of left-right shifting, the algorithm would be able to match any tars it came across by using some combination of the 3 tars of the basis set. (see SaveTar*.* images to understand where the tar Basis Set waveforms were harvested from)

4. I harvested two peat signals that seemed to represent the two major classes of peat that I observed in the data set when reviewed against the documentation provided by URS. The peats consistently yielded very short lifetimes (very narrow peaks in time shown in waveform plots). Again, I felt that the non-negative least squares fit algorithm would be able to match all the peats found in the data set by using some combination of the two peat Basis Set waveforms. (see SavePeat*.* images to understand where the peat basis waveforms were harvested from).

5. I loaded each FVD, selected a background region (lowest signal) to use as the Background waveform of the Basis Set, and then ran the automated routine that looks at each raw waveform and attempts to fit the raw with some combination of the Basis Set. The 'Setup' names (JPGs and PNGs) represent the data just before anlaysis and the 'Result' names show the results of the analysis. The last column shows the residual between the best fit and the raw data.

Area vs. depth (.AVD) ASCII files that contain the results of the analysis were supplied to URS. The 'parsed' file contains the ASCII data of what was displayed in the 'Result" images. The columns contain Depth, Raw, TarTypeA, TarTypeB, TarTypeC, PeatA, PeatB, and residual data, respectively. The other .AVD files for each log contain the depth and fluorescence area for each basis waveform's individual contribution. Tar and peat distribution can now readily be introduced into GIS plotting programs by simply totaling the tar components or peat components vs. depth. DTI could provide this service at a nominal fee if desired. Any output data format, any combination of channels added, averaging over depth intervals (summing or averaging over 6 inch averages, correcting for water depth automatically to give elevation tagging, etc.) could be accommodated

since we have programs capable of doing these tasks for large groups of files automatically.

Overall I was pleased with the consistency of the analysis results vs. field observations. Many of the logs showed very consistent transitions between tar types and separation between tars and peats. There were some logs that showed some unique patterns and these were repeated across a number of locations. Some of the logs show a consistent "melding" of both peat and tar signals, with the distribution "oscillating" back and forth. Examples include G30, G34, and I30. I suspect that these logs might be a unique material or condition. Further validation might determine that this is co-mingled tar and peat, a new tar type, or new peat.mineral type. Re-running the data wouldn't be necessary though. If additional validation sheds insight and a certain material is identified as being responsible, the oscillatory behavior itself, or the ratio of peat/tars to each other could be used as the 'indicator' for that unique material.

Examination of the analysis results often triggers a deeper understanding of the situation. Many clients have had "eureka moments" and have re-run the data with a new modified Basis Set that substantially improved their ability to accurately graph certain contaminant distribution via GIS, etc.