

FINAL REPORT

Direct Push Optical Screening Tool for High-Resolution, Real-Time Mapping of Chlorinated Solvent DNAPL Architecture

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14. ABSTRACT Chlorinated solvents are among the most common organic contaminants detected in groundwater at Department of Defense (DoD) sites. The sources of these contaminants are often historical releases of dense nonaqueous phase liquids (DNAPL). Unfortunately, chlorinated solvent DNAPL source zones are difficult to locate using conventional subsurface characterization technologies. Laser-induced fluorescence (LIF) tools are currently available for real-time, high-resolution mapping of petroleum hydrocarbon and coal tar-based NAPL source zones. The objective of this project is to demonstrate a new optical screening tool, that extends the LIF technology to chlorinated solvent DNAPLs.					
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Executive Summary

This report describes field testing of a new direct push optical screening tool for high-resolution three-dimensional subsurface mapping of chlorinated solvent dense nonaqueous phase liquids (DNAPLs) in unlithified sediments. The new tool, a laser induced fluorescence (LIF) technology referred to as “DyeLIF™,” was developed and validated during this ESTCP project and is now commercially available from Dakota Technologies, Inc. (Dakota)

[\[http://www.dakotatechnologies.com/services/dyelif\]](http://www.dakotatechnologies.com/services/dyelif).

The DyeLIF tool is a new site characterization technology that – for the first time – facilitates rapid, cost-effective 3-dimensional (3-D) delineation of residual chlorinated solvent DNAPL in the subsurface (**Figure ES-1** below). This type of high-resolution source characterization can identify previously unknown residual DNAPL, thereby optimizing source zone excavation or in situ treatment programs. In particular, high-resolution characterization using DyeLIF can dramatically reduce cumulative remediation costs and improve remediation performance by targeting excavation or treatment on the most impacted areas that convey mass to potential receptors. Similarly, a site investigations program using DyeLIF can also quickly determine that residual DNAPL is not present in the subsurface at a particular site. That knowledge can also be very valuable for risk evaluations and scoping of remediation systems.

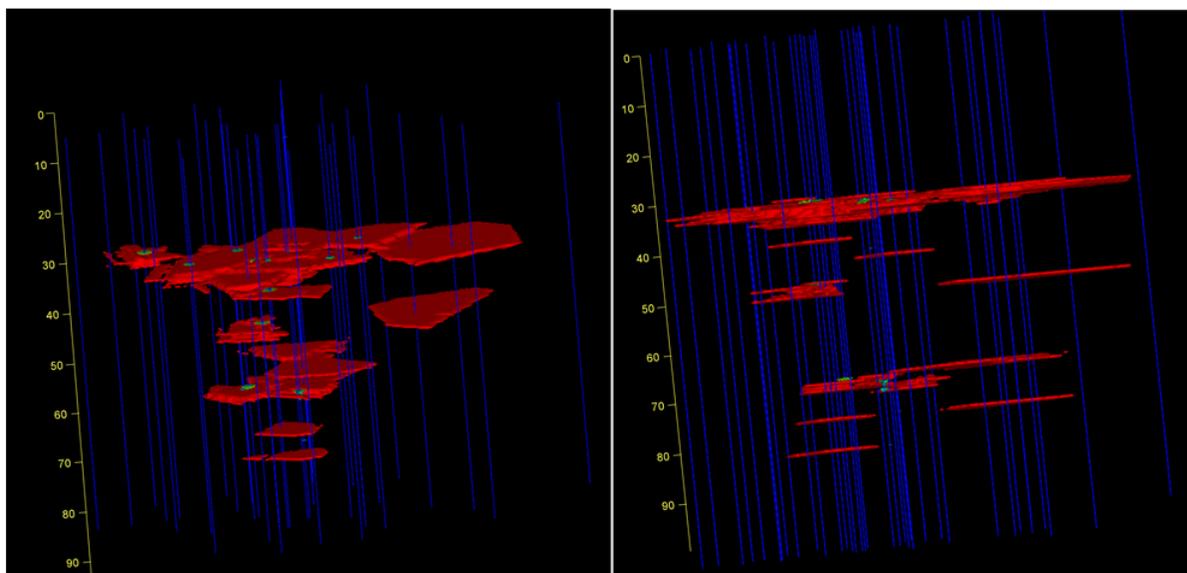


Figure ES-1. Three-dimensional graphical depictions of the DNAPL source zone at demonstration site. This site assessment, performed in only four days using DyeLIF, provides the most detailed delineation of subsurface DNAPL ever made at a non-research field site.

In addition to yielding information on the subsurface DNAPL distribution, the recording of dye solution flow rate and injection back-pressure provides high-resolution information on the lithology and hydraulic conductivity of the soil, similar to other profiling tools such as the Geoprobe HPT™ (Hydraulic Profiling Tool) and Waterloo APS™ (Advanced Profiling System).

The DyeLIF system was field tested at a Formerly Used Defense (FUD) facility in Massachusetts in fall 2013 (Geoprobe® delivery) and again in March 2014 (CPT delivery). The primary field demonstration completed in 2013 included two components: one week of DyeLIF probing and a

second week of follow-on soil coring using research-quality direct push (DP) soil coring methods. To minimize biases resulting from the heterogeneous distribution of DNAPL in the subsurface, replicate samples for various types of testing were collected from the same depth interval from within the same soil core. At each sampling interval, four sub-cores were collected: one sub-core was analyzed with “tabletop” DyeLIF;¹ one sample was field preserved in methanol for subsequent laboratory analysis; one was collected for moisture content analysis, and a fourth sub-core underwent a dye “shake test” using a visual hydrophobic dye (Oil-Red-O). PID readings were also collected at each depth interval.

Several performance objectives were established in the project demonstration work plan – and all were met or exceeded. The performance objective for chemical analysis was 70% consistency between positive DyeLIF responses and samples when DNAPL saturations were greater than 5%. The demonstration results showed 100% consistency between chemical analysis and DyeLIF for saturations greater than 1.9% (35 of 35 samples), and 95% consistency for estimated saturations greater than 0.5% (40 of 42 samples).

The performance objective for the dye shake tests was 70% consistency between a positive DyeLIF response and a positive colorimetric response with the dye shake test when the DNAPL saturation was estimated to be above 5%. For the dye shake tests, the demonstration results showed 100% consistency between DyeLIF and the shake tests at saturations as low as 1.3% percent (37 of 37 samples). There was 98% consistency between DyeLIF and dye shake tests above 0.5% saturation (41 of 42 samples). Therefore, the performance objective for dye shake tests was also exceeded.

The hammering and stress of percussive drilling over the one week drilling program allowed the project team to evaluate the durability of the DyeLIF tool. A performance objective of 90% uptime was specified in the work plan for the field demonstration. 100% uptime was achieved during the field demonstration.

A performance objective was also established for the average linear feet of drilling production achieved per day. A performance goal of 150 feet per day was proposed in the work plan. The production rate for the week of DyeLIF probing averaged over 400 feet of probing per day, greatly exceeding the 150 feet per day goal. The production rate, coupled with the extremely fine vertical resolution of DyeLIF (~ one data point per 0.5 centimeter probed), results in an extremely high data acquisition rate for the DyeLIF tool. Using a typical LIF production rate average of 334 feet probed per day,² the number of data points generated per day would be greater than 20,000. Considering the excellent correlation between DyeLIF and colorimetric dye shake tests, one day of DyeLIF probing is essentially equivalent to conducting 20,000 colorimetric dye shake tests, something that would take several months of expensive soil coring and detailed sub-coring to complete.

No drag-down of DNAPL was observed in the DyeLIF logs. This is consistent with the thousands of LIF probes advanced in NAPL sources by Dakota Technologies. The absence of drag-down in this project or other LIF NAPL investigations is primarily because CPT and other DP tools displace 100% of the volume of the DP probe, creating a seal against the DP rods and

¹ “Tabletop” DyeLIF utilized the DyeLIF technology placed on a bench at the ground surface; see discussion in main report for more information about this method.

² Dakota Technologies has maintained a running average production rate for its TarGOST LIF tool over many years and dozens of sites probed. That average is 334 feet per day.

tooling as they are being advanced. This can be contrasted with soil borings, where the soil is physically removed from the subsurface, thereby increasing the potential for vertical migration of DNAPL.

A detailed cost comparison of high-resolution soil sampling and DyeLIF is included in Section 7.3 of this report. Not only are the number of data points per day far higher with DyeLIF, but the costs per data point are dramatically lower than analysis of soil samples retrieved from the subsurface. For the cost analysis in Section 7.3 it is assumed that a closed-piston, large-diameter soil sampler (e.g. Geoprobe MC7) would be used to provide greater core recovery and enough sample volume to collect multiple samples at each depth interval. It is assumed that photoionization detector (PID) screening would be completed every 0.167 feet (~5 centimeters) and that 25% of the PID locations (75 total samples) would undergo dye shake tests and be analyzed with an onsite laboratory. Due to the higher production rate and higher vertical resolution of the DyeLIF, the costs per data point are significantly lower. The costs per data point for DyeLIF, dye shake test, and onsite laboratory are \$0.40, \$58.67, and \$98.67 per data point, respectively.

Another cost that is important to consider is the benefit that DyeLIF could have on remediation costs and performance. More accurate mapping of DNAPL source zones allows for more targeted and focused source zone remediation, particularly if in-situ remedial options such as chemical oxidation, in-situ bioremediation or thermal treatment are selected. In many cases, delineation of residual DNAPL with DyeLIF may show that the extent of DNAPL is actually much smaller than previously thought. Thus, targeted aggressive remediation may be feasible and cost effective, even when it had been previously been ruled out based on assumptions of NAPL nature and extent made using conventional methods.

The authors of this report believe that the new DyeLIF technology will be a “game-changer” for characterizing DNAPL sites in the U.S. and around the world. There are many examples where source zone remediation has been performed, only to learn later that only a portion of the residual DNAPL was removed or treated. In response, many remediation system designers now err on the side of conservatism and overdesign source zone remediation systems. The additional and ongoing costs of ineffective and overly conservative source zone remediation are staggering. EPA estimates that \$209B is needed to fully remediate hazardous waste sites in the U.S. (USEPA, 2004). An expert panel with the National Research Council (NRC) considers that figure an underestimate of the actual costs that will be incurred, partially because the distribution of the sources of the contamination remains undefined (NRC, 2013). The NRC authors stress that improved long-term management of hazardous waste sites requires a much better understanding of the spatial distribution of the contaminants in the subsurface, which can be obtained by the application of emerging diagnostic tools (e.g., DyeLIF). Thus, development and application of the new DyeLIF technology to quickly and fully delineate subsurface DNAPL in three dimensions will likely be a game-changing new site assessment technology that will lead to much more focused and effective source zone remediation programs. The cost savings achieved via better delineation of the remediation targets will likely be measured in billions of dollars.

A key attribute of DyeLIF is its ability to delineate residual NAPL without false-positives caused by high concentrations of dissolved or sorbed VOC mass. The Membrane Interface Probe (MIP) detects hydrophobic VOCs in all phases, including residual NAPL, dissolved, sorbed, and vapor phase. Thus, MIP results can overstate the volume of the subsurface that actually contains residual DNAPL. This was the case at the demonstration site where high MIP responses and

groundwater concentrations 100 feet downgradient of the DNAPL source zone could lead some to falsely conclude that the extent of residual DNAPL was larger than it really is (**Figure ES-2**).

While DyeLIF is the preferable technology for delineation of residual DNAPL, MIP and groundwater profiling tools are useful to detect dissolved phase CVOCs, which DyeLIF cannot do. Transects of MIP and groundwater profiling tools are recommended technologies for delineating dissolved phase CVOC plumes. Together, DyeLIF and MIP/groundwater profiling tools constitute a set of synergistic technologies for thorough, high-resolution characterization of DNAPL source zones and dissolved plumes.

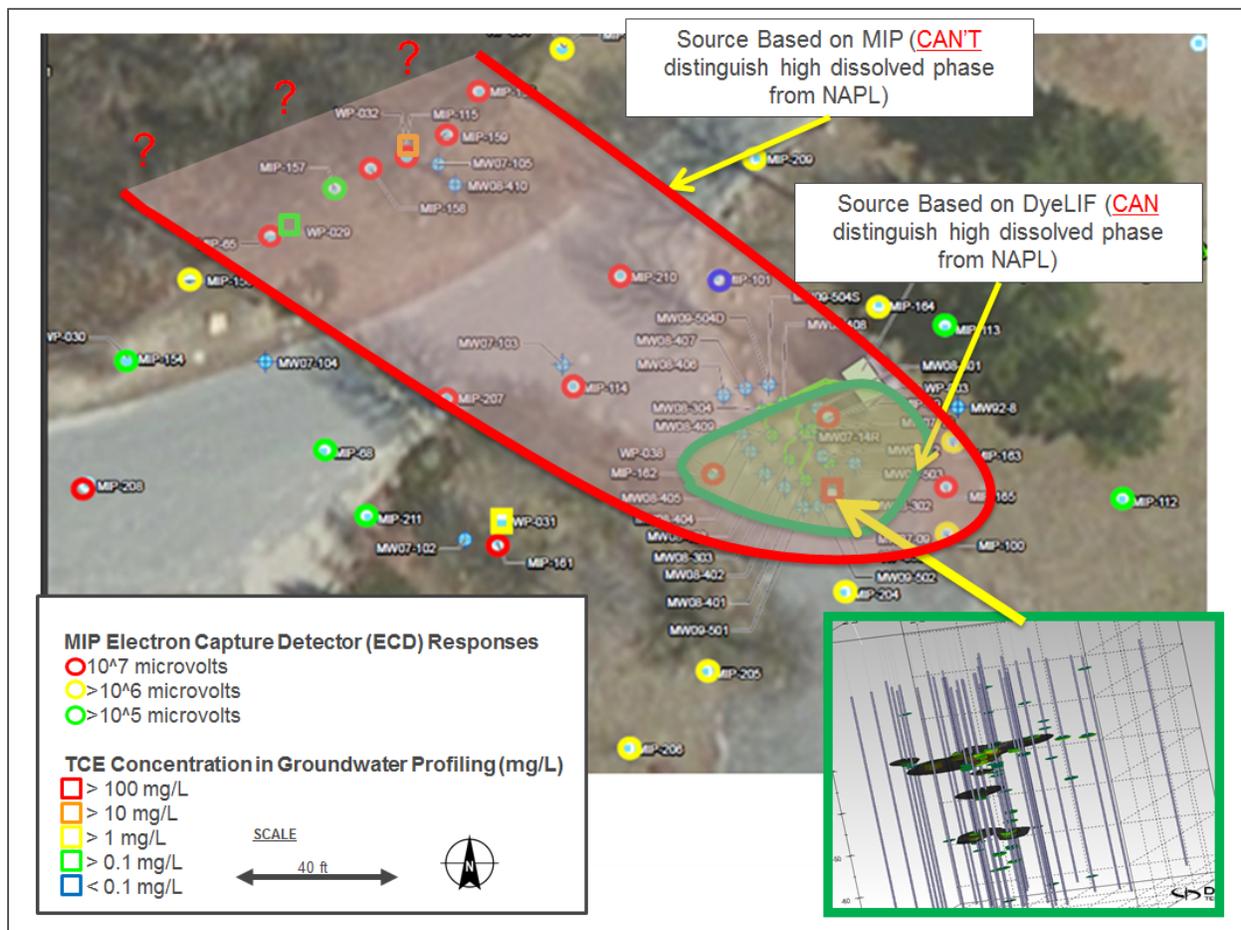


Figure ES-2. Groundwater and MIP sampling results in the demonstration area. These results illustrate the challenge of delineating a DNAPL source zone with high-resolution characterization tools that cannot distinguish between high-concentration dissolved-phase contamination and DNAPL. DyeLIF detects only separate-phase NAPLs, which is advantageous for source zone assessments.

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Acronym List

ADA	Advanced Data Analysis
bgs	below ground surface
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
cm	centimeter
CPT	Cone Penetrometer Testing
Dakota	Dakota Technologies
DNAPL	Dense Nonaqueous Phase Liquid
DP	Direct Push
DSITMS	Direct Sampling Ion Trap Mass Spectrometer
DyeLIF™	Dye-Enhanced Laser-Induced Fluorescence
ECD	Electron Capture Detector
HPT	Hydraulic Profiling Tool
HRSC	High Resolution Site Characterization
LIF	Laser Induced Fluorescence
MGP	Manufactured Gas Plant
MIP	Membrane Interface Probe
mL	milliliter
mm	millimeter
NAPL	Nonaqueous Phase Liquid
NNLS	non-negative least squares regression
PAH	Polycyclic Aromatic Hydrocarbon
RE	Reference Emitter
sec	second
TarGOST	Tar-specific Green Optical Screening Tool
UVOST	Ultra Violet Optical Screening Tool
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compound

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1.0 INTRODUCTION

This report describes field testing of a new direct push optical screening tool for high-resolution subsurface mapping of chlorinated solvent dense nonaqueous phase liquids (DNAPLs) in unlithified sediments. The new tool, referred to as “DyeLIF”, was developed and validated during this ESTCP project and is now commercially available from Dakota Technologies, Inc. (Dakota) [<http://www.dakotatechnologies.com/services/dyelif>].

1.1 BACKGROUND

Chlorinated solvents are among the most common organic contaminants detected in groundwater at Department of Defense sites. The sources of these dissolved contaminants are often historical releases of DNAPLs. The distribution of residual DNAPL is typically complex due to small-scale variations in soil permeability (Kueper et al., 1993) and to the ‘aging’ of the DNAPL source zones during the years to decades since the initial DNAPL releases occurred. During that time, dissolution accentuates the heterogeneous distribution of chlorinated solvent DNAPLs, making it even more difficult to locate the residual DNAPL (Guilbeault et al., 2005; Parker et al., 2003).

Until development of the new DyeLIF technology, no field methods have existed for rapidly delineating subsurface DNAPL in three dimensions. Kueper and Davies reviewed various approaches for characterizing DNAPL source zones (Kueper and Davies, 2009; Kueper and Davies, 2014). Those approaches are described in **Table 1** below. Lacking a single diagnostic technology, Kueper and Davies suggested a “multiple lines of evidence” approach where visual observation of DNAPL (e.g. in monitoring wells) or chemical concentrations above a threshold DNAPL saturation (e.g., 5% of saturation) are considered evidence of a “Confirmed/Probable” DNAPL source zone. Other lines of evidence listed in **Table 1** are considered evidence of a “potential” DNAPL source zone. Other authors have provided similar reviews and comparisons of different DNAPL characterization approaches and methods (Cohen et al., 1992; Griffin and Watson, 2002; Kram et al., 2001).

Several of the methods listed in **Table 1** require the collection of soil cores and subsequent subsampling for field screening (e.g. dye shake test) or fixed laboratory analysis. A primary challenge associated with these approaches is that DNAPL often occurs in thin layers (e.g., centimeter [cm] scale) such that high resolution (i.e., closely spaced) vertical sampling is required in order to have a high probability of identifying DNAPL (Parker et al., 2003). Parker et

al. (2003) recommend vertical sampling intervals of no more than 5 cm combined with careful examination of fine scale lithologic contacts and more intensive sampling near interfaces with fine-grained layers in order to have a high probability of identifying these thin DNAPL intervals. Dye shake tests work well with this type of high-resolution vertical sampling as they are relatively simple to complete and are effective down to DNAPL saturations on the order of 1% (Cohen et al., 1992; Parker et al., 2003).

The use of onsite mobile laboratories with high throughput sampling methods has also made high-resolution soil sampling and analysis more feasible, allowing modifications to the sampling program “on the fly” as results become available.

Table 1. Summary of DNAPL Source Zone Characterization Approaches (from Kueper and Davies, 2009)

METHOD	DESCRIPTION
“Confirmed/Probable” Lines of Evidence	
Visual Observation in Groundwater or Sediment Samples	DNAPL observed in a monitoring well using interface probe or bailer, etc. or direct observation in pumped groundwater samples or core sediment samples. The authors note that suspected DNAPL in soil cores should be confirmed with laboratory testing.
Chemical Concentrations in Soil Above Threshold DNAPL Saturation	Soil samples collected from soil cores and submitted for laboratory analysis. Equilibrium partitioning calculations are used to estimate the amount of contaminant in the aqueous, vapor, and sorbed phases. The remaining mass is assumed to be DNAPL and converted to an estimated saturation. Estimated DNAPL saturations above 5% are considered strong evidence that DNAPL is present.
“Potential” Lines of Evidence	
Chemical Concentrations in Soil Above Partitioning Threshold	Equilibrium partitioning calculations are used to estimate the maximum amount of contaminant that could exist in the aqueous, sorbed, and vapor phases. Soil concentrations above this estimated partitioning threshold would indicate potential DNAPL.
Site Use/History	The authors note that past experience has shown that DNAPLs are frequently associated with specific industrial practices and waste handling processes.
Vapor Concentrations	The authors discuss vapor-phase concentrations and the distribution of the vapor-phase plume as useful for deciding where to collect additional data. The authors caution against the use of vapor-phase data alone to evaluate if DNAPL is potentially present since it is focused on the capillary fringe and vadose zone only and would not be expected to identify DNAPL present well below the water table.
Hydrophobic Dye Testing on Soil Core Samples	Hydrophobic dyes, such as Oil-Red-O, that partition into the DNAPL and trigger a colorimetric response. Dye shake tests where a small amount of dye is placed into a sample jar with soil and water and shaken is a common field test method for DNAPL source zone investigations that is easy to use and effective down to DNAPL saturations of 1 % (Cohen et al., 1992).
Groundwater Methods	Several groundwater-based methods are described, including the “1% rule” where groundwater concentrations in excess of 1% of the effective solubility of the DNAPL indicate the potential presence of DNAPL. The other groundwater-based methods are related to temporal (e.g. plume persistence) and spatial trends (e.g. increasing concentration with depth) of the dissolved phase plume.
Other Methods	The other methods discussed include Laser Induced Fluorescence, Membrane Interface Probe, partitioning tracer tests, and other methods in this section.

While the effectiveness of simple dye shake tests and the use of onsite laboratories with high-throughput chemical analyses makes high-resolution vertical sampling more feasible, there is still a large amount of labor that is required to collect soil samples at such a high vertical resolution which limits the overall production rate (i.e., linear feet drilled and sampled per day) that can be achieved. Production rates are important in DNAPL investigations because in addition to a high degree of vertical variability, there is also a large degree of horizontal variability (Kueper et al., 1993). A small number of borings with very detailed vertical sampling is not sufficient for delineating most DNAPL source zones in three dimensions (3-D). Rather, a grid of closely spaced borings is needed at most sites. Given that DNAPL accumulates and persists at interfaces between subtle and not so subtle contrasts in permeability (resulting in complex spatial distribution horizontally and vertically), numerous sampling locations with high vertical spatial resolution are necessary, and this needs to be cost-effective. The combination of slow production rates and the need to investigate many locations to adequately define the DNAPL spatial distribution results in very high investigation costs using only continuous coring techniques with high resolution soil subsampling. Another challenge with DNAPL source delineation using soil sampling approaches is core recovery. DNAPLs preferentially migrate through more permeable soils; however, it is these cohesionless soils that are often most difficult to recover using available soil coring methods. So, even though the core barrel might be advanced through a DNAPL impacted zone, the DNAPL impacted soils may not be recovered, leading to the false assumption that DNAPL is not present. Also with poor core recovery, even if DNAPL is encountered, the exact depths and spatial distribution of the DNAPL is uncertain.

Poor core recovery coupled with the need for high-resolution vertical characterization in a large number of closely spaced borings makes downhole direct-sensing technologies attractive. The Membrane Interface Probe (MIP) is a commonly used direct push (DP) sensor used at sites where chlorinated solvents have been released. The MIP can be advanced using a Geoprobe® or CPT rig (Christy, 1996). The downhole portion of the tool consists of a heated membrane that allows volatile organic compounds (VOCs) in the soil adjacent to the membrane to volatilize and diffuse across the membrane and into a carrier gas. The carrier gas is routed to a series of aboveground detectors that provided semi-quantitative information on the concentration and type of VOCs in the vicinity of the membrane. A significant limitation of the MIP tool for nonaqueous phase liquid (NAPL) source zone investigations is that it is unable to differentiate high-concentration dissolved- and vapor-phase contamination from NAPL (McAndrews et al., 2003; Ravella et al., 2007). This limitation is particularly important when high-strength dissolved plumes exist downgradient of NAPL source zones. Because of the heterogeneity of the NAPL source zones, most of the dissolved phase contamination migrating away from the source zone is typically concentrated in a number of high-concentration but small cross-sectional-area plume 'cores' or 'local maxima' (Guilbeault et al., 2005). Those plume cores, which may only comprise 10 to 15% of the cross sectional area of the plume, commonly convey 70 to 80% of the contaminant mass flux at DNAPL sites (Guilbeault et al., 2005). Early conceptualizations of dissolved phase plumes, however, predicted that there would be significant homogenization and mixing as contaminants migrated downgradient away from the DNAPL source. Studies that have employed high-resolution characterization of the dissolved phase plume along one or more transects oriented perpendicular to the groundwater flow direction have shown however that hydrodynamic dispersion (mixing) is much less than was originally thought and high

concentration plume cores can maintain their strength and structure over relatively long travel distances (Einarson et al., 2010). The significance of this in relation to characterization of DNAPL source zones with MIP is that high-strength plumes may be misidentified as areas of residual DNAPL using technologies like MIP. Also, carryover (lingering VOCs within the sampling tubing and fittings) often creates a positive bias with MIP, particularly when penetrating DNAPL zones, which can give the impression of a much thicker and deeper NAPL zone than is actually present (Bumberger et al., 2012).

In contrast to MIP technologies, Laser Induced Fluorescence (LIF) technologies respond only to NAPL and consequently there is no chance of mistaking a high concentration dissolved plume core for a NAPL source zone. In other words, LIF is specific to NAPLs and does not respond to sorbed, dissolved, or vapor (gas) phase VOCs. This is a key advantage of LIF tools over MIP for accurate delineation of NAPL source zones. Furthermore, LIF tools also have extremely high vertical resolution (cm scale) and probing rates typically exceed 300 linear feet per day. This high vertical resolution coupled with typical probing production rates translates into tens of thousands of data points generated per day. High data production rates make LIF tools very cost effective for characterizing NAPL source zones in three dimensions, which requires a large quantity of data due to the inherent highly heterogeneous nature of most DNAPL source zones. LIF tools also provide data in real time, similar to other direct sensing equipment, which allows for the use of dynamic (adaptive) work plans where subsequent probing locations are selected in the field as new data are acquired.

The foundation of LIF technologies historically used in subsurface environmental assessments is the natural fluorescence of polycyclic aromatic hydrocarbons (PAHs) found in the NAPLs being investigated. As the probe rods are advanced into the subsurface using DP rigs (e.g., Geoprobe®, CPT) pulses of light are emitted through a small sapphire window present near the base of the probe rod. The emitted light, which is otherwise reflected (or scattered) by soil, is absorbed by PAHs such as those found in petroleum hydrocarbon and manufactured gas plant (MGP) tar NAPLs. The excited-state PAHs quickly yield fluorescence, which is transmitted to the ground surface via optical fibers in the probe rod, where it is analyzed in real-time using optical data processing equipment located in the direct push rig.

The requirement that the NAPL being investigated contain PAHs for detection has heretofore limited the usage of LIF to sites impacted by petroleum hydrocarbon fuels, creosotes, and MGP tars. The rapid, high-resolution, real-time nature of LIF technologies described above has revolutionized NAPL source zone investigations at those types of sites. However, conventional LIF tools to this point have generally not been able to detect chlorinated solvent DNAPLs because chlorinated solvents lack the polycyclic aromatic hydrocarbon (PAH) compounds responsible for the laser-induced fluorescence in coal tars and petroleum hydrocarbons.³ To extend the LIF technology to chlorinated solvent DNAPLs, a new tool, referred to as the “DyeLIF” optical screening tool, was developed and field tested, the results of which are described in this report. The primary modification made to existing LIF technology to allow for detection of chlorinated DNAPL was to add a small dye injection port beneath the sapphire window in the probe rods. As the DyeLIF probe is advanced into the subsurface, a steady stream

³ Sometimes chlorinated solvents can have a high amount of PAH containing materials solvated in them, which makes them detectable with conventional LIF technologies. There is no response of LIF to pure chlorinated solvent as they lack the aromatic ring structure that causes fluorescence.

of hydrophobic fluorescent dye is injected. If DNAPL is present adjacent to the probe rod, the dye partitions into the DNAPL, causing the solvent DNAPL to fluoresce once excited by the LIF laser. The dye therefore circumvents the requirement that the DNAPL contain naturally fluorescing PAHs. The continuous injection of an aqueous dye solution as the tool is advanced also allows for detailed vertical profiling of soil permeability.

1.2 OBJECTIVE OF THE DEMONSTRATION

The objective of the field demonstration was to provide a field-scale demonstration of the new DyeLIF tool for high-resolution subsurface mapping of chlorinated DNAPLs. The real-time, high-resolution profiles generated from the DyeLIF were then compared to profiles from high-resolution vertical soil sampling with subsequent dye shake tests and quantitative laboratory volatile organic compound (VOC) analysis.

2.0 TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

Existing, commercially-available LIF technologies such as Dakota's Ultra-Violet Optical Screening Tool (UVOST®) and the Tar-specific Green Optical Screening Tool (TarGOST®) are popular tools for real-time, high-resolution mapping of petroleum hydrocarbons, creosotes, and coal tar based NAPLs for sites with subsurface conditions amenable for direct-push probing techniques [<http://www.dakotatechnologies.com/home>]. Existing LIF technologies are described below, followed by a discussion of the new DyeLIF tool, which is the focus of this ESTCP project.

While DyeLIF is based upon these existing LIF technologies, several important system modifications were made in order to lower the detection limit (i.e., the lowest NAPL saturation that can be detected) and increase the spatial resolution of data points (currently one data point for every 0.4 to 0.5 cm probed). These improvements were made because the project team anticipates that chlorinated solvent DNAPL at many sites will have more complex architectures and be present at lower saturations and in thinner layers than MGP tar, creosote, and petroleum hydrocarbon fuels, due to higher densities, lower viscosities, and increased weathering (mass depletion) of residual chlorinated solvent DNAPL compared to those other compounds. The current, optimized version of DyeLIF is described further below and is now commercially available from Dakota [<http://www.dakotatechnologies.com/services/dyelif>].

2.1.1 Overview

Existing LIF tooling (e.g. UVOST, TarGOST) is advanced in the subsurface using CPT and percussion direct push systems such as Geoprobe® rigs [<http://geoprobe.com/>]. They consist of a light source (laser), fiber optics strung through the rod string, and optical detection and processing equipment. As the probe rods are advanced into the subsurface, short duration (1-2 nanoseconds) pulses of excitation light are emitted through a sapphire window present near the probe's tip or above the tip and sleeve sensors in the case of CPT. The laser light emitted from the window is absorbed or reflected (scattered) by soil or is absorbed by any PAHs found in the petroleum hydrocarbon, coal tar, or creosote NAPLs. These excited state PAHs quickly yield fluorescence, some of which travels back inside the probe where it is captured and transmitted back up to the ground surface via an optical fiber, where it is analyzed in real-time using detectors and data processing equipment located at the surface.

Unfortunately, the LIF tools described above do not work with chlorinated solvent DNAPLs because chlorinated solvents lack the aromatic structure responsible for fluorescence (like that of PAHs). To extend existing LIF technology to NAPLs that do not contain PAHs, a new LIF technology has been developed. The new LIF optical screening tool, referred to as DyeLIF, works by injecting an emulsion containing particles of fluorescent, hydrophobic dye through a small injection port located 22 cm below the sapphire window as the probe is advanced through the subsurface. The injected dye dissolves into the NAPL (if present) and fluoresces in the presence of a light source, allowing the same LIF tooling (lasers, optical reading and processing equipment) to be used to detect chlorinated solvent DNAPLs. This allows for chlorinated solvent DNAPL source zones to now be mapped using the same real-time, high-resolution techniques

that have historically been available only for petroleum hydrocarbon and coal tar based NAPLs. In addition, it is anticipated that the new LIF tool will also be useful for boosting the ability to detect PAH-poor petroleum hydrocarbon NAPLs such as aviation gasoline and single-ring aromatic compounds like benzene, toluene, ethylbenzene, and xylenes (BTEX).

2.1.2 DyeLIF System Design

DyeLIF is a modified version of Dakota’s TarGOST tool, which is used for creosote and MGP tar detection. A schematic of the downhole tooling for percussion direct push system deployment (e.g. Geoprobe®) is shown in **Figure 1**. The probe functions by injecting an emulsion of distilled water and particles of a proprietary hydrophobic dye through a small injection port that is situated 22 cm below the LIF sapphire window. As the probe is advanced through the subsurface, the injected emulsion deposits a film of indicator dye along the side of the probe in order to create an “interaction zone” where the dye will partition into DNAPL if it is present in the soil. Standard LIF instruments are then used to detect the fluorescence generated by the dye-labeled chlorinated solvent DNAPLs.

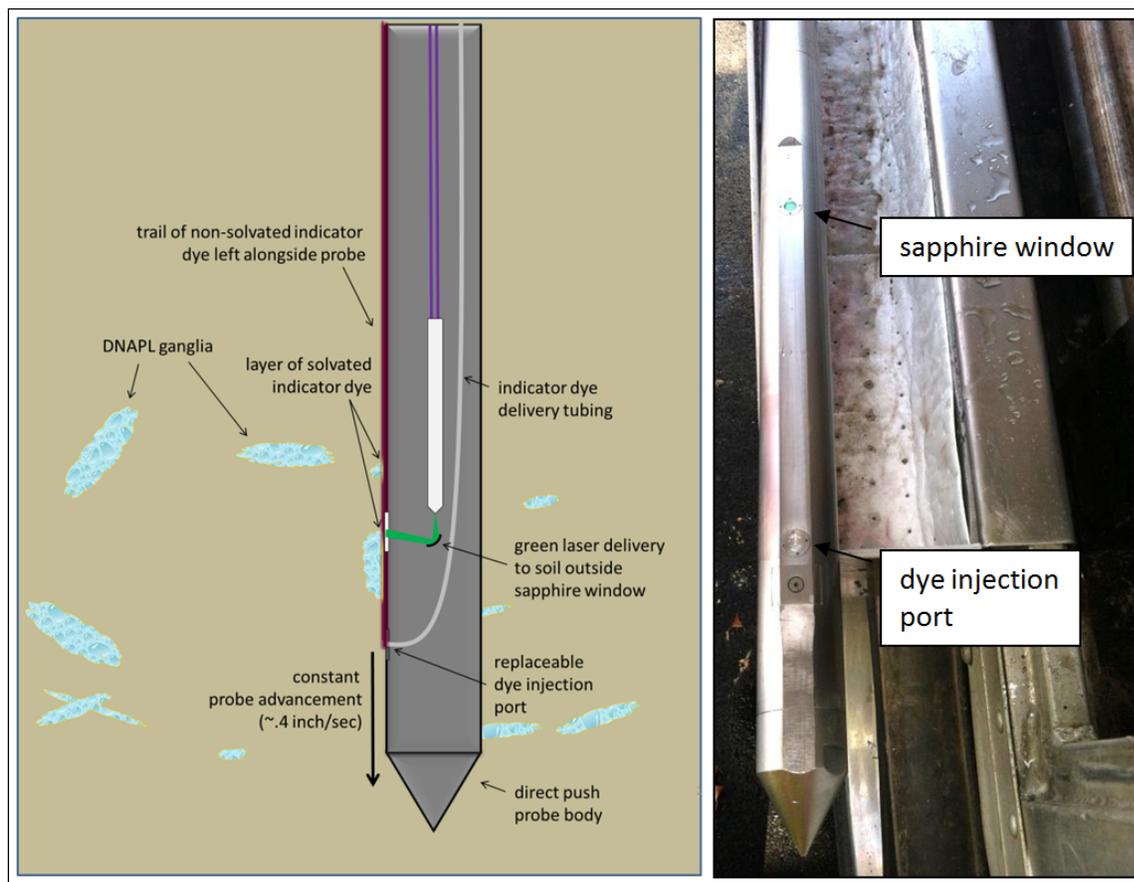


Figure 1. DyeLIF probe schematic (left) and field photo of percussion-delivered version (right).

A version of the DyeLIF that is compatible with CPT has also been developed and is shown below in **Figure 2**. The LIF detection system’s sapphire window and the injection port dimensions and their relative geometry on the CPT direct push system is nearly identical to the

percussion direct push tooling in an effort to maximize similarity between the two different delivery platforms.

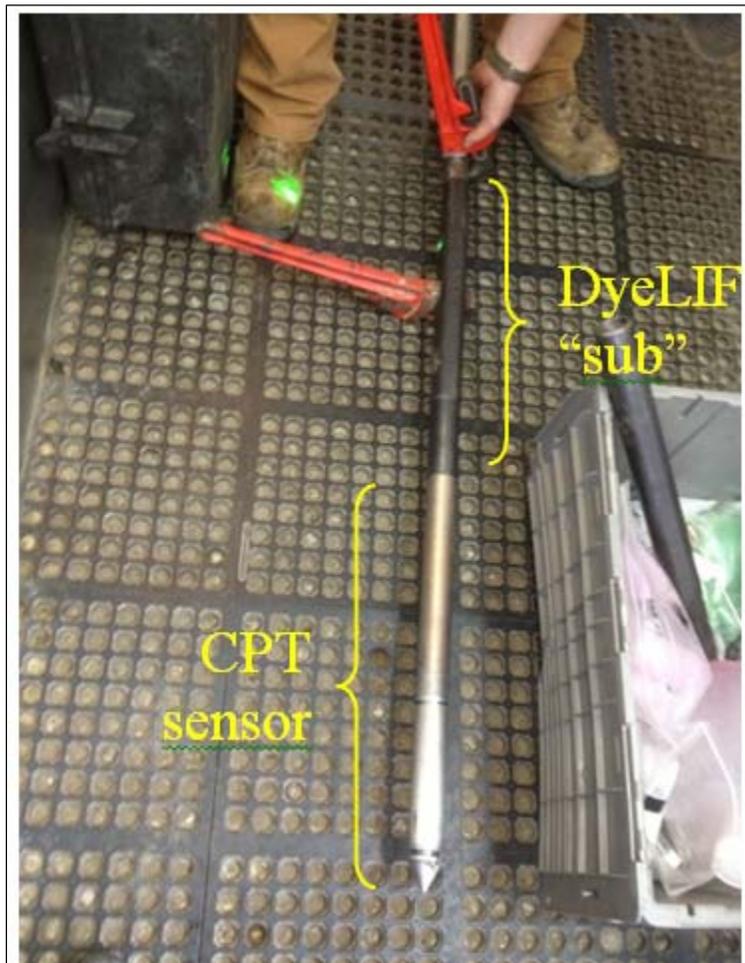


Figure 2. CPT delivered version of DyeLIF. Refer to Figure 1 schematic for additional details on DyeLIF sub.

The solvation of the dye from its emulsion into the DNAPL takes just milliseconds to occur, allowing for a continuous advancement of the DyeLIF probe as opposed to other direct sensing equipment that requires stops at specified depth intervals while measurements are taken. Penetration rates of about 1.0 cm/sec (slightly below the ASTM CPT range of 1.5-2.5 cm/sec) have been used to date in order to maximize the detection of thin cm-scale NAPL layers. Penetration rates control data density because the DyeLIF system acquires data at a fixed rate based on laser pulses, not distance. At a 1.0 cm/sec advancement rate, the average data spacing is 0.4 - 0.5 cm. We do not expect a significant change of performance at higher probe advancement speeds other than an increase in data spacing and an accompanying “averaging out” of small but potentially important responses, potentially causing non-detects in such intervals. This sub-centimeter scale resolution is preferable as previous high-resolution soil sampling of DNAPL source zones has found that DNAPL typically occurs in zones with one or more thin layers, commonly between 1 and 30 cm in thickness (Parker et al., 2003).

The dye is injected at a target flow rate of 1 milliliter per second (mL/sec), which works out to approximately 0.11 grams of dye for each meter of penetration (assuming 1 cm/sec advancement rate). These low fluid injection rates minimize the risk of displacing DNAPL ganglia away from the probe rod and outside DyeLIF's zone of optical interrogation.

In addition to yielding information on the subsurface DNAPL distribution, the dye solution injection rate and back-pressure is measured and recorded, which provides high-resolution information on the lithology and hydraulic conductivity of the soil, similar to other profiling tools such as the Geoprobe HPT™ (Hydraulic Profiling Tool) and Waterloo APS™ (Advanced Profiling System). The dye solution flow rate and back pressure are continuously monitored by pressure and flow sensors and logged by the Optical Screening Tool software that logs the fluorescence response. The resulting DyeLIF logs depict corresponding depth profiles of fluorescence response (DNAPL indicator), dye solution flow rate, and dye-solution back-pressure. Since DNAPL often pools and spreads laterally when permeability contrasts are encountered, the soil permeability information provides important supplementary information on soil type/permeability. For example, at this ESTCP project's demonstration site, a fluorescence response indicating DNAPL was present in a more permeable zone overlying a lower permeability unit or layer, consistent with conceptual models of DNAPL migration in stratified formations.

2.1.3 Dye Behavior and Waveforms

Extensive laboratory testing was completed in order to identify a dye that fluoresces poorly when suspended in water alone and efficiently when solvated in common organic solvents (e.g. trichloroethylene). A small amount of fluorescence is desirable when the dye is suspended in water as it allows the DyeLIF operator to be confident that the delivery of the dye through the injection port is being maintained. Several dyes were tested in this project. The dye judged to be most suitable is also relatively non-toxic (Rat LD50 (intraperitoneal) 4170 mg/kg) and is not a known or suspected carcinogen. Analytical testing on water left in contact with the dye for several days yielded no detectable levels of any listed VOCs or semi-VOCs. Therefore the selected dye should not face regulatory hurdles due to the minimal quantity injected (0.11 grams per meter of probe penetration), the immobility of the dye in the subsurface (it is not soluble in groundwater), and the non-toxic nature of the dye.

Example waveforms for a non-solvated (i.e., non-DNAPL) and solvated (dye solvated in DNAPL) indicator dye are shown below in **Figure 3**. The four peaks in each of the waveform plots are actually four time-series pulses of fluorescence emitted by the dye following pulsed laser excitation. The fluorescence wavelengths represented by the four peaks range in color from yellow to red. The blue, green, orange, and red peak "fill colors" used in the waveform plots correspond to actual fluorescence colors of 600 nm, 650 nm, 675 nm, and 700nm respectively.

Three waveform characteristics are of note in **Figure 3**. First, the fluorescence of the non-solvated dye is detectable but increases dramatically when solvated in DNAPL (note the scale difference for the two waveforms shown in **Figure 3**). Second, the waveform "lifetime" or the time decay of fluorescence after the excitation pulse of light has ended, increases dramatically when the indicator dye becomes solvated in DNAPL. Notice how the peaks for the non-solvated dye (left side of **Figure 3**) have much shorter lifetimes compared to the peaks for the solvated

dye (right side of **Figure 3**). Third, when the dye becomes solvated in DNAPL, the waveform becomes blue-shifted (changes to bluer color) such that the blue peak is larger than the other peaks.

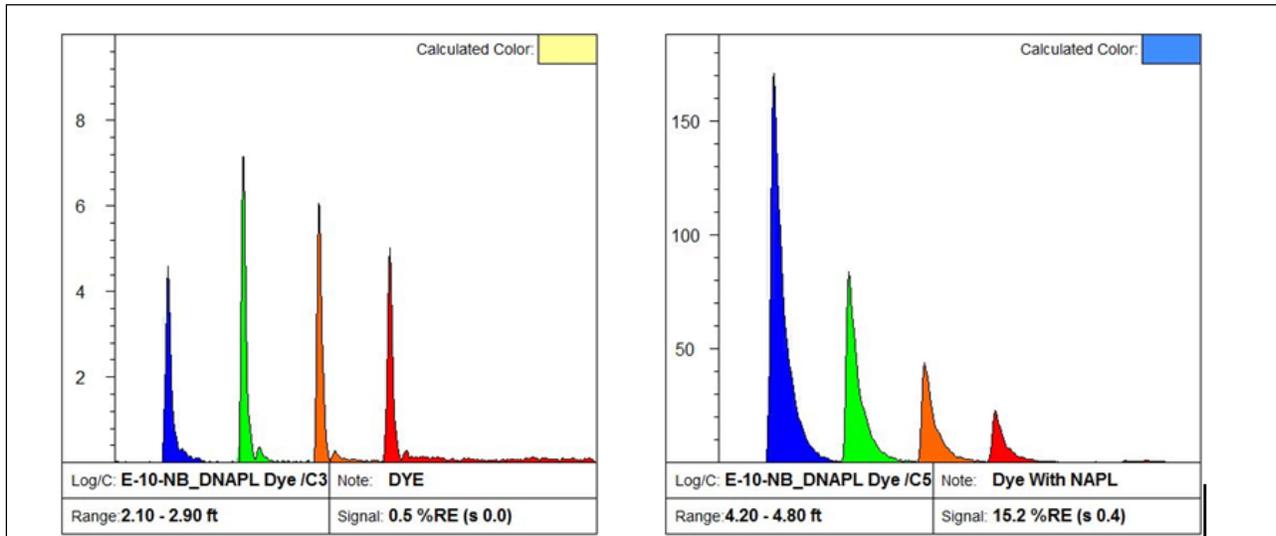


Figure 3. Indicator dye waveform in carrier water (left) and solvated in chlorinated DNAPL (right).

In order to present a single profile of fluorescence response vs. depth that can be reviewed in the field, the area under each of the four individual peaks (blue, green, orange, and red) are summed to yield a total composite fluorescence graphic. The resulting summary fluorescence vs. depth plots represent a composite of the colors of the individual peaks in the waveform plots. For example, a blue-shifted waveform where the blue peak dominates would result in a bluish color in the composite graphic. The calculated composite color for each of the waveform plots in **Figure 3** is shown in the upper right hand corner of the individual graphics. An example log from the demonstration site is shown below in **Figure 4**. Notice the larger response at approximately 35 feet with a blue-shifted composite waveform in the main graph. That peak is indicative of DNAPL.

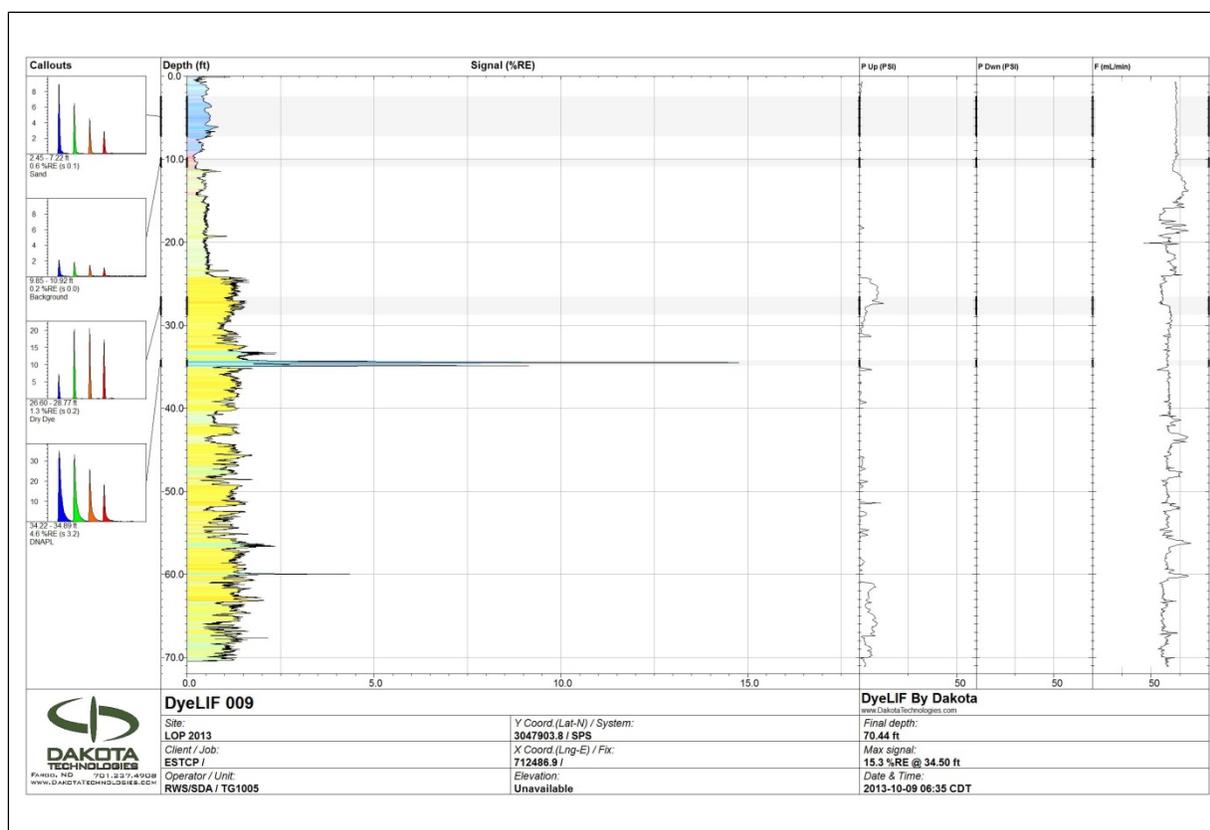


Figure 4. Example DyeLIF log depicting color coding of fluorescence response.

2.1.3 DyeLIF Calibration

Aboveground (uphole) measurements are made immediately prior to advancing each DyeLIF probe in order to be able to normalize the DyeLIF response data across the entire investigation, across prior or subsequent investigations, and for comparison with lab studies. Those uphole measurements include:

Reference Emitter (RE): The RE is a proprietary petroleum fluid that is used to calibrate the DyeLIF instrument prior to every log. Its fluorescence is well understood (it is also the RE used for UVOST) and, more importantly, stable. Measuring and recording the consistent fluorescence of this “standard” fluid serve two main functions:

- 1) **Qualitative examination of the performance of the instrument** – The shape of the RE waveform confirms that the four bands of fluorescence wavelengths previously described are being properly recorded by the instrument’s detection system. A misshapen RE waveform indicates potential problems with the detection system optics, alerting the operator that maintenance is necessary. Consistent response of all four wavelengths is necessary to obtain consistent data across a project’s duration, and on any subsequent return to a previous project site.

2) **Quantitative calibration of the instrument** – RE is used to achieve the proper signal intensity (obtained by adjusting a knob that limits the amount of laser energy delivered to the probe). An RE waveform intensity in the proper range (not too small, not too large) keeps the instrument in the optimum range for the fluorescence detector and electronics. The RE method normalizes all the downhole fluorescence data to the RE's fluorescence response by dividing the downhole fluorescence by the uphole RE fluorescence. For example, a 100% RE reading means that a measured material (in-situ) has a fluorescence intensity identical to that of RE. A 200% RE reading means a substance has a fluorescence intensity twice that of RE's fluorescence, and so forth.

RE range: RE areas (under the waveform curve) for DyeLIF typically fall between 18,000 and 25,000 picovolt-seconds (pVs). Precise RE intensity 'tuning' by adjusting the laser excitation light to achieve an exact value is unnecessary because all reported in-situ signals are normalized by converting them from pVs to a percentage (%RE) of the RE's pVs. Compared to TarGOST and UVOST RE, a more intense RE is used (factor of ten and two higher respectively). This is done in order to boost the lower detection limit of the DyeLIF. Therefore, much lower %REs can be diagnostic of DNAPL with the DyeLIF as compared to other LIF systems. The %RE values observed with DyeLIF are much lower than the %RE typically observed with UVOST and TarGOST, both of which can extend into hundreds or even thousands %RE. The need to properly interpret lower %RE responses (smaller and potentially noisy waveforms) necessitates more advanced data processing methods described later.

Background waveform: The background waveform is a pre-push measure of the optical quality of the light path (e.g. fiber optics, mirror, window, and filters) acquired immediately after cleaning of the sapphire window. Sources of signal in the background include foreign material on fiber faces, filter auto-fluorescence, mirror and window fluorescence, and reflection/scatter from worn windows. The background waveform is stored to file but is not applied to the data collected (i.e. it is not subtracted as a background) and is taken only as a general data quality measure employed by the operator to ensure there are no significant defects which may raise the system background, and make it more difficult to discern low DNAPL saturation responses. The optical path (including the fiber optics themselves) contains traces of non-contaminant fluorescing materials, which create a background signal that is unavoidable. Background RE values can vary widely (in terms of relative percent difference) from 0.1% of the RE signal to 1%. In terms of area, the values for DyeLIF should range from 0 to 20 pVs. There is no firm “go, no go” cutoff value for Background RE level. A balance must be struck between specific project conditions with the goal with DyeLIF being to obtain the highest RE-to-Background ratio as possible in order to maximize the ability to confidently detect even trace amounts of target fluorescence.

2.1.4 DyeLIF Enhanced Data Analysis

As described in Section 2.1.3, a more intense RE is used for the DyeLIF in order to boost the detection limit. This requires the identification of trace levels of DNAPL fluorescence in the presence of non-solvated dye fluorescence and other background fluorescence typically encountered in UVOST and TarGOST-type plots alone (**Figure 3**). Fortunately, as described in Section 2.1.2, the waveform lifetime (the decay of fluorescence after the excitation pulse of light has ended) increases dramatically when the indicator dye becomes solvated in DNAPL. This

unique waveform signature allows for the use of advanced data processing techniques to separate out the DNAPL waveform from other waveforms associated with non-solvated dye and background fluorescence. In other words, the non-target, background fluorescence of the unsolvated dye and other system components can be stripped from the optical signal, yielding a waveform that highlights the DNAPL, if present. The data analysis procedure and some of the new data deliverable products based on this analysis are described below in greater detail.

Dakota's proprietary Advanced Data Analysis (ADA) software (written in Matlab) allows the analyst to "harvest" waveforms from field logs (or less optimal bench-top tests) and place them in the "Basis Set". They are then assigned with recognizable names. During the field trial for example, unique waveforms associated with internal instrument background fluorescence, sand,⁴ non-solvated dye, and DNAPL made up the Basis Set. Once the Basis Set has been populated, the DyeLIF logs are individually loaded into the ADA software. The ADA software automatically compares the Basis Set waveforms to all of the log's raw waveforms (all the depths). The ADA software accomplishes this by passing each raw waveform, along with the Basis Set waveforms, to Matlab's non-negative least squares (NNLS) fitting routine [<http://www.mathworks.com/help/matlab/ref/lsqnonneg.html>]. This NNLS routine determines the proportion of each of the Basis Set waveforms that is required to optimally fit the raw waveform and returns a non-negative contribution for each Basis waveform for each depth in the log. Once the entire log of waveforms has been analyzed, the ADA software plots the original "raw" LIF log along with logs associated with each of Basis Set waveforms.

DyeLIF location DL-11 from the field trial serves as a good example of the ADA process because the DNAPL response is difficult to discern visually in many waveforms because its contribution is small. At other locations the DNAPL waveform is much greater in magnitude and is readily discernable in the raw waveform plots (callouts). A graphic showing the ADA setup (what the operator would see on the field laptop) is shown in **Figure 5**.

A multi-panel graphic showing the results of the ADA analysis is shown as **Figure 6**. The graphic depicts the raw waveform to the far left and the various waveforms in the Basis Set to the right (internal instrument background, non-solvated dye, sand, and DNAPL). This plot facilitates field analysis of which types of fluorescence are contributing to the overall raw fluorescence. In cases of low pore saturation DNAPL, comparing the DNAPL waveform plot to the raw data plot in **Figure 6** illustrates how it would be difficult to identify the DNAPL contaminated depths using only the raw total fluorescence LIF plot.

An additional data deliverable that was developed specifically for the DyeLIF is shown in **Figure 7** below. This graphic plots five foot depth increments (or panels) of the DNAPL waveform plot on the same printout. The expanded scale of this plot makes thin DNAPL intervals much easier to identify (e.g., compare **Figure 7** to **Figure 6**). **Figure 7** illustrates the extremely fine vertical resolution of DyeLIF, which is capable of seeing thin centimeter-scale zones of DNAPL. As described in greater detail below, one of the most exciting parts of the field trial was that these thin lenses of DNAPL quickly identified by the DyeLIF tool were confirmed

⁴ The "sand" fluorescence was most prevalent in the portion of each probe location that had been air-knived in order to ensure underground utilities were avoided. The reason for this fluorescence is unknown, but is typically observed at other field sites. It does, however, nicely illustrate how the advanced data analysis is able to separate out unique waveforms associated with different types of fluorescence.

by collecting co-located soil cores with follow on high-resolution soil sampling for both field DNAPL screening using Oil-Red-O dye shake tests and quantitative laboratory analysis.

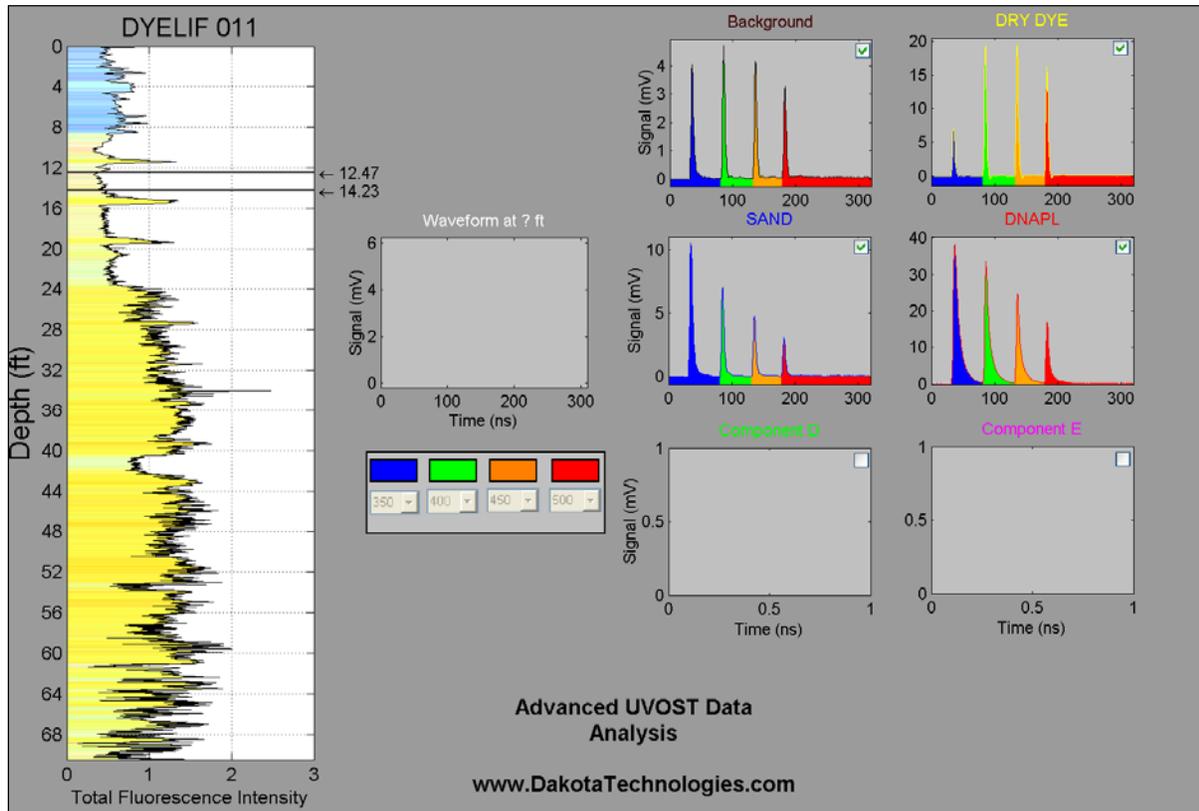


Figure 5. Setup screen for ADA analysis of DL-11.

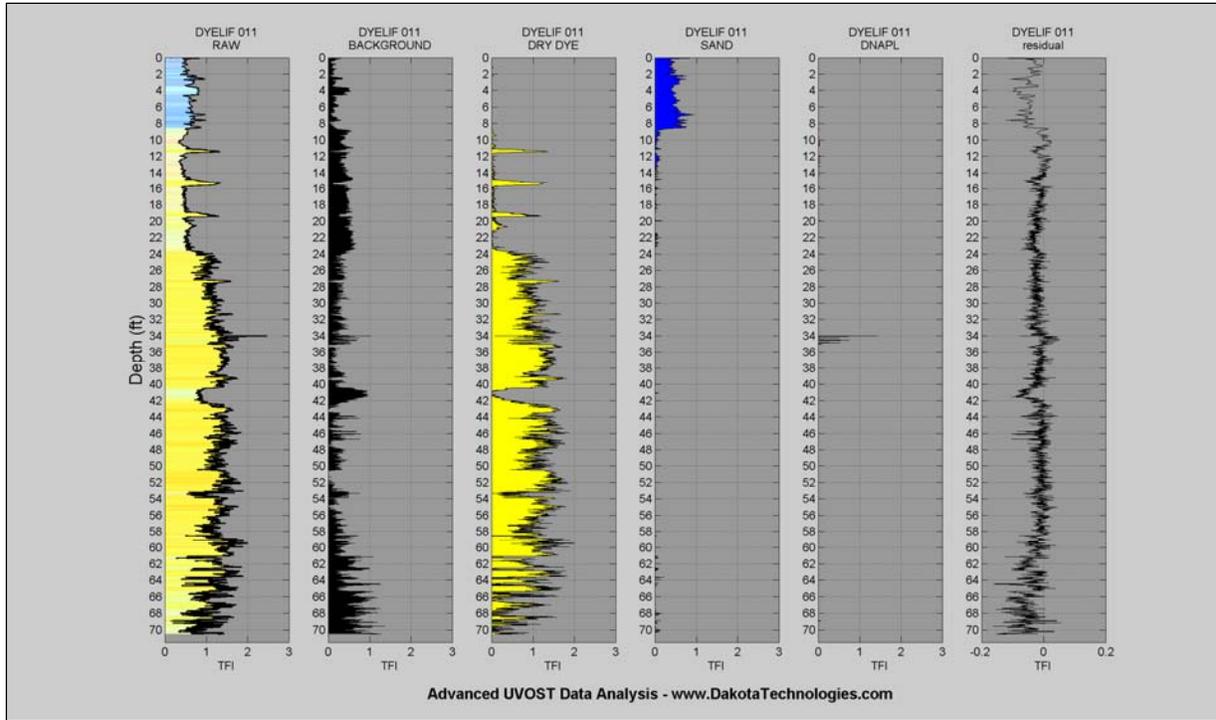


Figure 6. Strip logs showing the raw fluorescence plot along with the contributions of other waveforms in the Basis Set (instrument background, sand, non-solvated dye, DNAPL) for location DL-11.

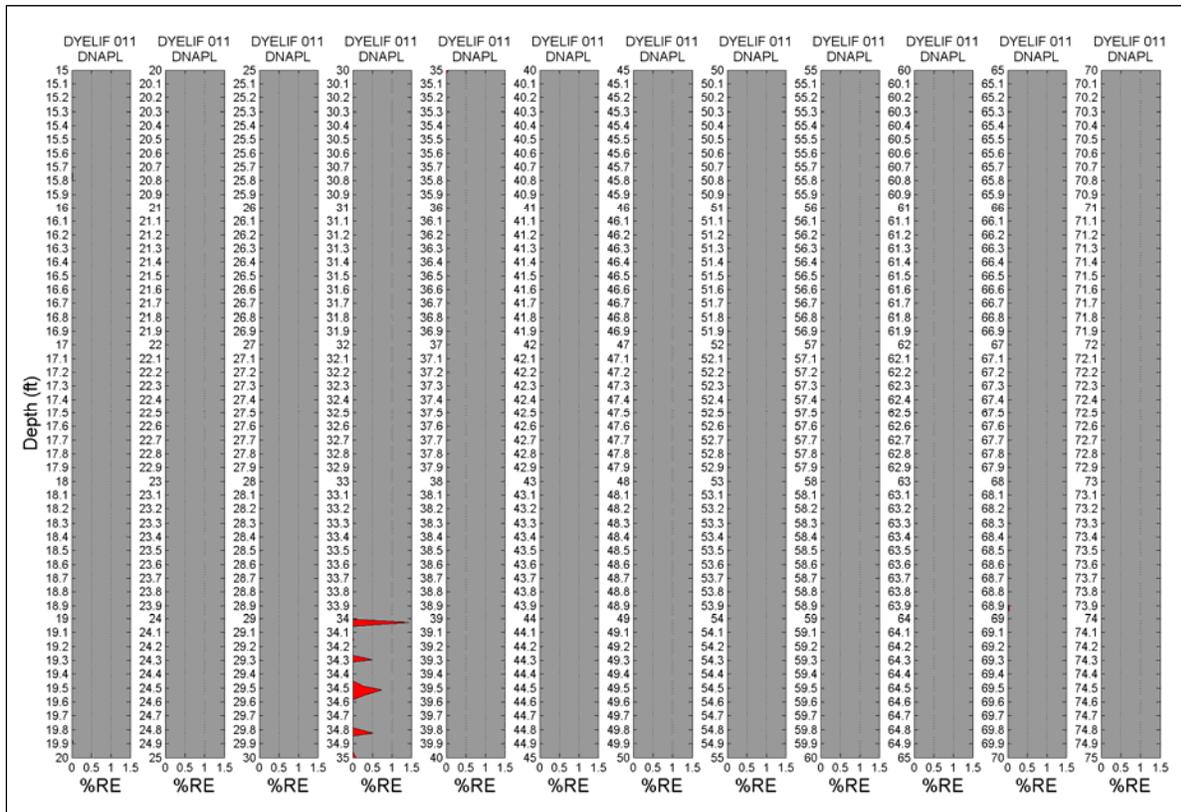


Figure 7. Multi-panel DNAPL graphic for location DL-11. Each panel corresponds to 5-feet of probing depth. This new data deliverable aids in identifying small (centimeter-scale) DNAPL zones.

2.2 ADVANTAGES AND LIMITATIONS OF TECHNOLOGY

As described above, the sensitivity of migrating DNAPL to small scale changes in soil permeability often leads to complex distributions of DNAPL in the subsurface (DNAPL architecture). Accurate delineation of the DNAPL location and distribution therefore necessitates collection of a large quantity of data in order to thoroughly define the DNAPL both laterally and vertically. Traditional coring based methods like soil sampling and dye shake tests may provide accurate point-scale information at relatively few locations, but are limited in terms of the amount of data that can be generated for a given investigation budget. LIF tools offer significant advantages compared to conventional approaches because they quickly provide high-resolution, real-time information about the distribution of NAPL in the subsurface. Most importantly, LIF tools produce a significantly larger amount of data for the same amount of money spent using conventional approaches. Specific advantages of the DyeLIF include:

- **High data acquisition/production rates** – A large number of data points are typically needed to adequately characterize DNAPL source zones. The DyeLIF tool produces tens of thousands of data points per day (typically greater than 20,000 data points per day) making the tool much more cost effective than conventional approaches (e.g. soil coring and sampling).
- **High vertical resolution** – High resolution, research-level soil sampling investigations of chlorinated solvent DNAPL source zones have indicated that DNAPL typically occurs in one or more very thin layers ranging in thickness from 1 to 30 cm (Parker et al., 2003). The vertical resolution of the DyeLIF is 0.4 to 0.5 cm, making it sensitive enough to detect even sub-cm thick layers of DNAPL.
- **Real-time data acquisition** – Dynamic work plans, where investigation locations are selected in the field based on real-time data acquisition, are essential for effective DNAPL investigations. Real-time data acquisition allows for DNAPL source zones to be completely delineated in a single mobilization.
- **Differentiation between NAPL and dissolved phase contamination** – As described above, MIP is capable of real-time, high-resolution mapping of subsurface VOCs but cannot differentiate between dissolved / sorbed phase contamination and DNAPL. The inability to differentiate a high strength dissolved mass from DNAPL limits the utility of the MIP tool for determining the location of DNAPL in source zones. The footprint of the presumed DNAPL source zone can appear much larger with MIP data than it actually is.

The primary limitation of the LIF technology is that it is semi-quantitative and does not provide detailed information regarding DNAPL composition and saturation as can be obtained via analysis of soils samples at a fixed laboratory. DyeLIF can, however, quickly delineate the locations of residual DNAPL in the subsurface. Selective soil sampling can then be performed, targeting specific DNAPL zones for chemical analysis.

The semi-quantitative nature of DyeLIF is similar to other High Resolution Site Characterization (HRSC) technologies like MIP. More quantitative information about a single point in space is traded for semi-quantitative information for a much larger number of data points providing much greater spatial resolution. HRSC techniques have stimulated their own increased usage as they have demonstrated just how complex most sites are, both in terms of geology and contaminant distribution. This increased understanding of system complexity has in turn led to more usage of HRSC as these technologies provide data at the spatial resolution and data production rates required to effectively characterize and remediate these sites. Trying to develop Conceptual Site Models (CSMs) from a limited monitoring well network and conventional soil sampling is simply not effective for complex chlorinated solvent sites. These sites require the use of HRSC techniques in order to develop accurate CSMs and effective remediation strategies. Selective and targeted soil sampling at key locations selected based on the HRSC dataset can provide a basis for better understanding and approximate calibration of the DyeLIF response.

3.0 PERFORMANCE OBJECTIVES

Quantitative performance objectives were based on comparisons of three different analyses of sub-cores collected from the same cores at the same depths. The three analyses were 1) quantitative analysis of soil at a fixed laboratory, 2) analysis using conventional field-based colorimetric dye “shake tests” using Oil-Red-O dye, and 3) a “tabletop” application of DyeLIF whereby the DyeLIF probe was placed horizontally on a bench and then soil sub-cores in 25 mL glass vials with the DyeLIF solution were passed in front of the sapphire window on the DyeLIF probe to measure the LIF response.

In this way, all three tests were conducted on sub-samples from the same core at the same depth interval, in order to minimize uncertainty from incomplete core recovery, spatial variability, etc. Qualitative performance objectives also included tool durability and production rates (e.g., how many linear feet can be advanced per day). The performance objectives are described in greater detail below and are summarized in **Table 2**.

3.1 PERFORMANCE OBJECTIVE: CORRELATION BETWEEN SOIL SUB-CORES

During the first week of the field demonstration, a non-uniform grid of DyeLIF probes was advanced in the suspected DNAPL source area.⁵ The DyeLIF probes were used to estimate the three dimensional distribution (architecture) of the DNAPL source area. During the second week of the field demonstration, a Geoprobe® rig was used to advance closed-piston soil samplers adjacent (within one meter) to select DyeLIF borings that had indicated DNAPL was present at a particular location. Continuous soil cores were collected across the suspected DNAPL depth interval – i.e. cores were collected beginning at a depth several feet above the suspected DNAPL area and then collecting continuously to a depth several feet below the suspected DNAPL zone. Closely spaced soil sub-samples were then collected from each soil core at a sampling interval ranging from about 0.1 to 0.5 feet, with tighter spacing in and around suspected DNAPL layers. At each sampling interval, four sub-cores were collected: one sub-core was analyzed with the tabletop DyeLIF; one sample was field-preserved in methanol for subsequent laboratory analysis; one sample was collected for moisture content analysis, and a fourth sub-core underwent a field dye “shake test” using a visual hydrophobic dye (Oil-Red-O). Photoionization detector (PID) readings were also collected at each depth interval by placing the PID tip in the center hole from core subsampling, and covering with nitrile gloved hand and reading the stabilized PID response. Additional information on field sampling procedures is included in Section 5.0.

The performance objective for chemical analysis was 70% consistency between positive DyeLIF responses and DNAPL judged to be present from chemical analysis of soil samples when laboratory results indicating DNAPL saturations greater than 5%.⁶ Similarly, the performance objective for the dye shake tests was 70% consistency between a positive DyeLIF response and a

⁵ A uniform grid was originally planned but was not possible because of temporary obstructions onsite that had to be moved. A uniform grid is recommended by the project team when feasible.

⁶ DNAPL saturations were estimated from laboratory analytical results using the software NAPLANAL. The NAPLANAL code uses equilibrium partitioning theory to estimate DNAPL saturations (Mariner, P.E., Jin, M. and Jackson, R.E., 1997. An algorithm for the estimation of NAPL saturation and composition from typical soil chemical analyses. *Groundwater Monitoring & Remediation*, 17(2): 122-129.

positive colorimetric response with the dye shake test when the DNAPL saturation was estimated to be above 5%.

The performance of the DyeLIF tool exceeded the performance objectives. There was 100% consistency between chemical analysis and DyeLIF for saturations greater than 1.9% (35 of 35 samples), and 95% consistency for estimated saturations greater than 0.5% (40 of 42 samples). For the dye shake tests there was 100% consistency between DyeLIF and the shake tests at saturations greater than 1.3% percent (37 of 37 samples),⁷ and 98% consistency between DyeLIF and dye shake tests in samples above 0.5% saturation (41 of 42 samples), based on saturation levels from the chemical analysis (the qualitative dye shake tests do not provide saturation levels).

3.2 PERFORMANCE OBJECTIVE: TOOL DURABILITY/PRODUCTION RATE

A performance objective was established for system uptime. The hammering and stress of percussive drilling over the one week drilling program allowed the project team to evaluate the durability of the DyeLIF tool. A performance objective of 90% uptime was established in the project work plan. A performance objective was also established for the average linear feet of drilling production achieved per day. A performance goal of 150 feet per day was also established in the project work plan.

A minor repair of the dye injection tubing was required that required approximately one hour to fix. 100% uptime was achieved during the field demonstration by having a second set of downhole tooling (DyeLIF sub and probe rods pre-strung with DyeLIF cables) available that could be utilized in the event that minor maintenance of the first set of downhole tooling was required. This approach is also used by most MIP contractors as a way to prevent project downtime while repairs to the MIP system are made.

The production rate for the week of DyeLIF probing averaged over 400 feet of probing per day, greatly exceeding the 150 feet per day goal. Each probe was advanced to approximately 70 feet below ground surface (bgs). The production rate was helped by a second rig on site that was performing some of the re-entry grouting. This approach limited any downtime of the DyeLIF probing rig during grouting. We estimate the production rate would have decreased approximately 20% if the DyeLIF rig also performed the re-entry grouting. Dakota Technologies has maintained a running average production rate for its TarGOST LIF tool over many years and dozens of sites probed. That average is 334 feet per day.

3.3 PERFORMANCE OBJECTIVE: NO DRAG-DOWN OF DNAPL

Some individuals new to HRSC technologies express concerns that advancing soil borings or other DP tools through DNAPL source zones may facilitate the downward migration of DNAPL as the probes are being advanced. Drag-down of contaminants can result in cross contamination and overestimates of the depth of contamination at a site. Experience with CPT and other DP

⁷ For one of the samples, both the DyeLIF test and the dye shake test indicated no DNAPL was present. Therefore the samples were consistent with each other but contradicted the lab data. This data suggests that there may have been some intra-core heterogeneity.

tools that displace 100% of the volume of the DP probe (pushing soil out to the sides), including UVOST and TarGOST, shows that there is little to no “drag-down” of DNAPL contaminants as the tools are being advanced. This is because these tools displace the soil, creating a seal against the DP rods and tooling as they are being advanced. Verification of this is straightforward with LIF because the probe tip is several inches below the sapphire window. If, after a NAPL zone has been penetrated, the response drops off rapidly (as opposed to gradually) with continued penetration, one can be confident that NAPL has not been dragged down along with the probe. Dakota has advanced thousands of LIF probes through NAPL source zones and has not experienced issues with drag-down with the exception of sticky coal tars and creosotes in soft sediments while probing in swamps or lagoons.

The other concern pertaining to potential DNAPL mobilization is any preferential vertical pathways that may remain after the probe rods have been removed. This concern is partially mitigated because, again, the soil is displaced rather than removed during advancement of the DyeLIF tool. The concern is further mitigated by appropriate grouting techniques – either retraction or reentry grouting. Discussions of grouting methods used with direct push probes are presented by USEPA (1997) and Lutenegger and DeGroot (1995). Another factor minimizing potential for drag-down is the expectation for chlorinated solvent DNAPL source zones to have ‘aged’ over the decades since releases occurred, such that the present day DNAPL distribution at many sites is generally at low residual saturation and may be largely disconnected, such that little potentially mobile DNAPL remains in the subsurface.

In addition to evaluating the DyeLIF logs, possible DNAPL mobilization was evaluated using soil cores from co-located soil borings advanced adjacent to the DyeLIF probes. The distribution of DNAPL in the soil cores was compared with that indicated in the DyeLIF probes to evaluate if vertical migration had occurred between the time the DyeLIF probe and soil borings were advanced. It is again noted that drag-down and vertical migration was considered to be highly unlikely as the DyeLIF tool displaces (as opposed to removes) soil as it is advanced and appropriate grouting procedures were used as soon as the tool was removed.

The method selected for evaluating this performance metric was a rapid drop-off in the DyeLIF signal after the tool moved through DNAPL impacted zones in all DyeLIF probes where DNAPL was identified. An example log showing this behavior is shown below in **Figure 8**. At locations where detailed coring was completed, success was defined by similar results (i.e. rapid drop-off in dye shake test) in the adjacent soil core. An example location showing the desired behavior in a co-located soil boring is shown in **Figure 8**. As expected, there was no evidence of DNAPL drag down based on the DyeLIF logs and co-located soil borings at any of the probe locations during the field demonstration.

Note in **Figure 8** that the DNAPL is perched on top of a thin silt layer, the top of which occurs at a depth of 35.0 feet. The silt layer at that depth is noted by the increase in dye solution injection backpressure as well as in the soil core from the boring advance adjacent to the DyeLIF probe.

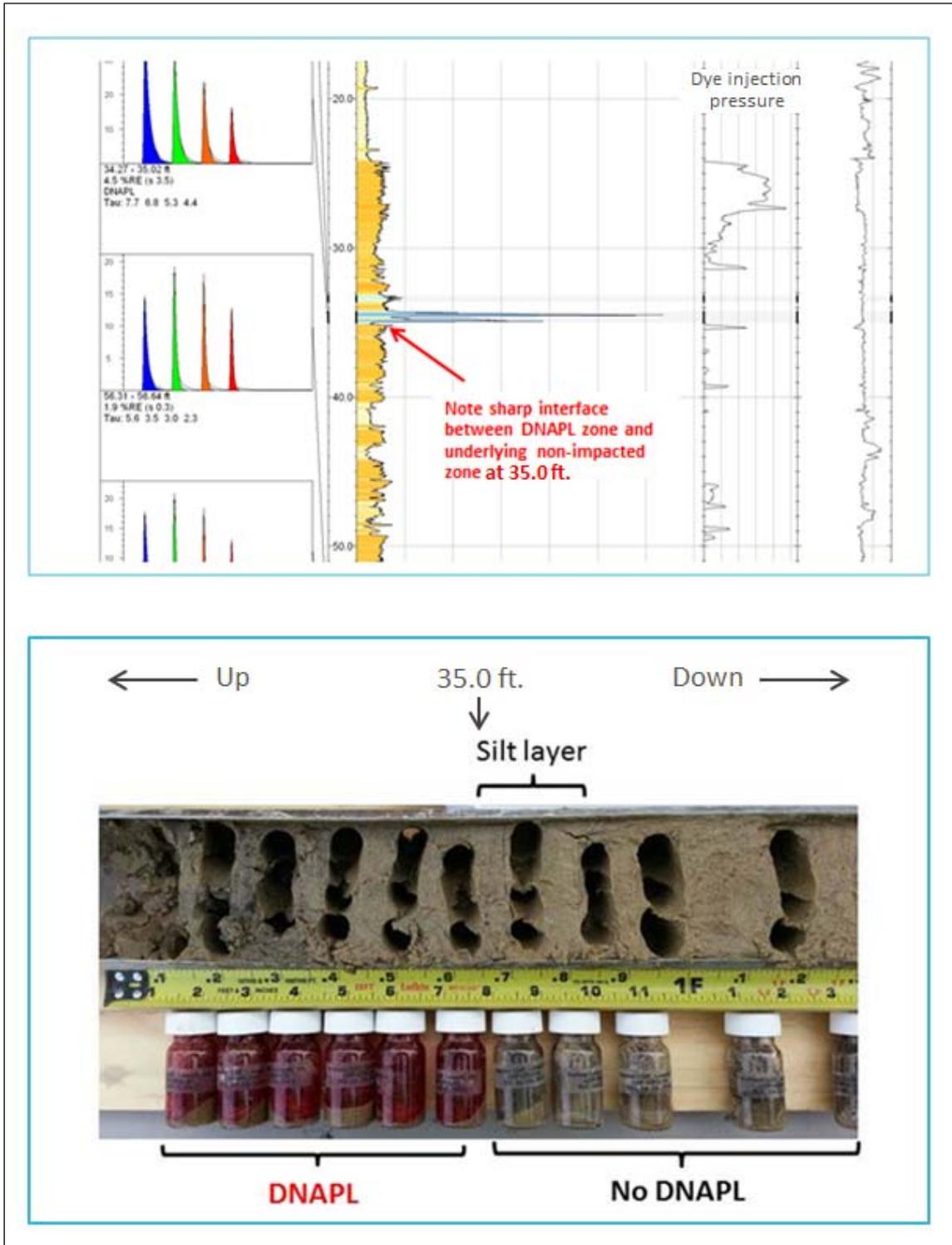


Figure 8. Example DyeLIF and soil boring logs showing no evidence of vertical DNAPL drag-down.

Table 2. Performance Objectives

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
Correlation of DyeLIF with quantitative chemical sampling.	Piston core barrels, split on their vertical axis for subcoring purposes and quantitative lab analysis.	70% consistency between DyeLIF and chemical analysis for samples above 5% DNAPL saturation. ¹	100% consistency above 1.9% saturation (n = 35). 95% consistency (40 of 42 samples) above 0.5% saturation.
Correlation of DyeLIF with qualitative dye shake tests.	Piston core barrels, split on their vertical axis for subcoring purposes. Sub-cores analyzed with dye shake test for qualitative presence/absence of DNAPL.	70% consistency between DyeLIF and dye shake test for samples above 5% DNAPL saturation. ¹	100 % consistency above 1.3% saturation (n = 37). 98% consistency (41 of 42 samples) above 0.5% saturation.
Qualitative Performance Objectives			
Durability	Week long probing event to put stress on equipment.	Greater than 90% uptime.	100% uptime by rotating two DyeLIF setups (same approach used by most MIP vendors).
Production rates	Week long probing event.	Greater than 150 feet of probing per day.	DyeLIF averaged over 400 feet of probing per day. ²
No drag-down of DNAPL	DyeLIF response signal; detailed coring used for quantitative performance objectives.	Rapid drop-off in DyeLIF signal below DNAPL layers (see Figure 2); same rapid drop-off in co-located soil core subsamples.	No evidence of drag-down or vertical mobilization in any of the DyeLIF logs or soil borings.

Notes: 1. DNAPL saturations estimated by converting chemical concentration to estimated DNAPL saturation using NAPLANAL software which is based on equilibrium partitioning theory.

2. Production rate was helped by a second rig on site that was performing re-entry grouting. This approach prevented any downtime of the DyeLIF rig during grouting. We estimate the production rate would have decreased approximately 25% if the DyeLIF rig performed the re-entry grouting.

4.0 DEMONSTRATION SITE DESCRIPTION

4.1 SITE LOCATION AND HISTORY

The site is a former ordinance plant located in Lowell, MA (Site). The area where the demonstration occurred was an active DNAPL recovery area that constitutes only a small portion of the overall Site (see inset map in **Figure 9**). DNAPL recovery in the demonstration area has been ongoing since February 2007. A series of recovery wells were installed in the demonstration area between 2007 to 2009. The nature of historical operations responsible for the DNAPL releases is unknown.

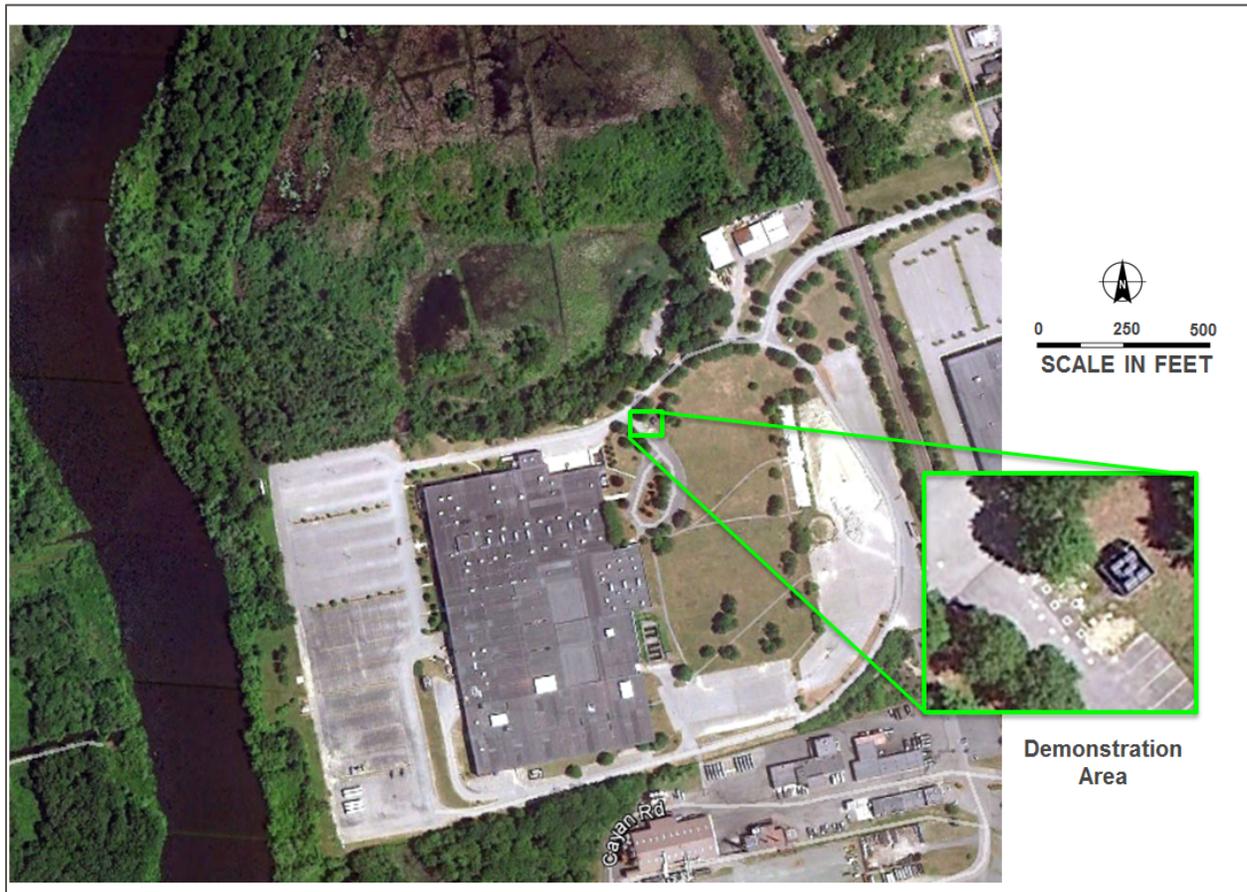


Figure 9. Demonstration area.

4.2 SITE GEOLOGY/HYDROGEOLOGY

Site documents indicate localized geology in the demonstration area can be generally classified as stratified layers of fine sand and silt with few clay layers. A silt layer was penetrated consistently at a depth of about 45 feet bgs, which is consistent with other areas of the larger Site (GZA, 2011). Groundwater was encountered at a depth of approximately 20 feet bgs in the demonstration area. Based on potentiometric surface maps, groundwater flow in the vicinity of

the demonstration area is to the northwest (GZA, 2011). In other portions of the Site, groundwater flow is more westerly, towards a river located west of the Site. A cross-section through the demonstration area, including positions of the well-screens used for DNAPL recovery, is shown in **Figure 10**.

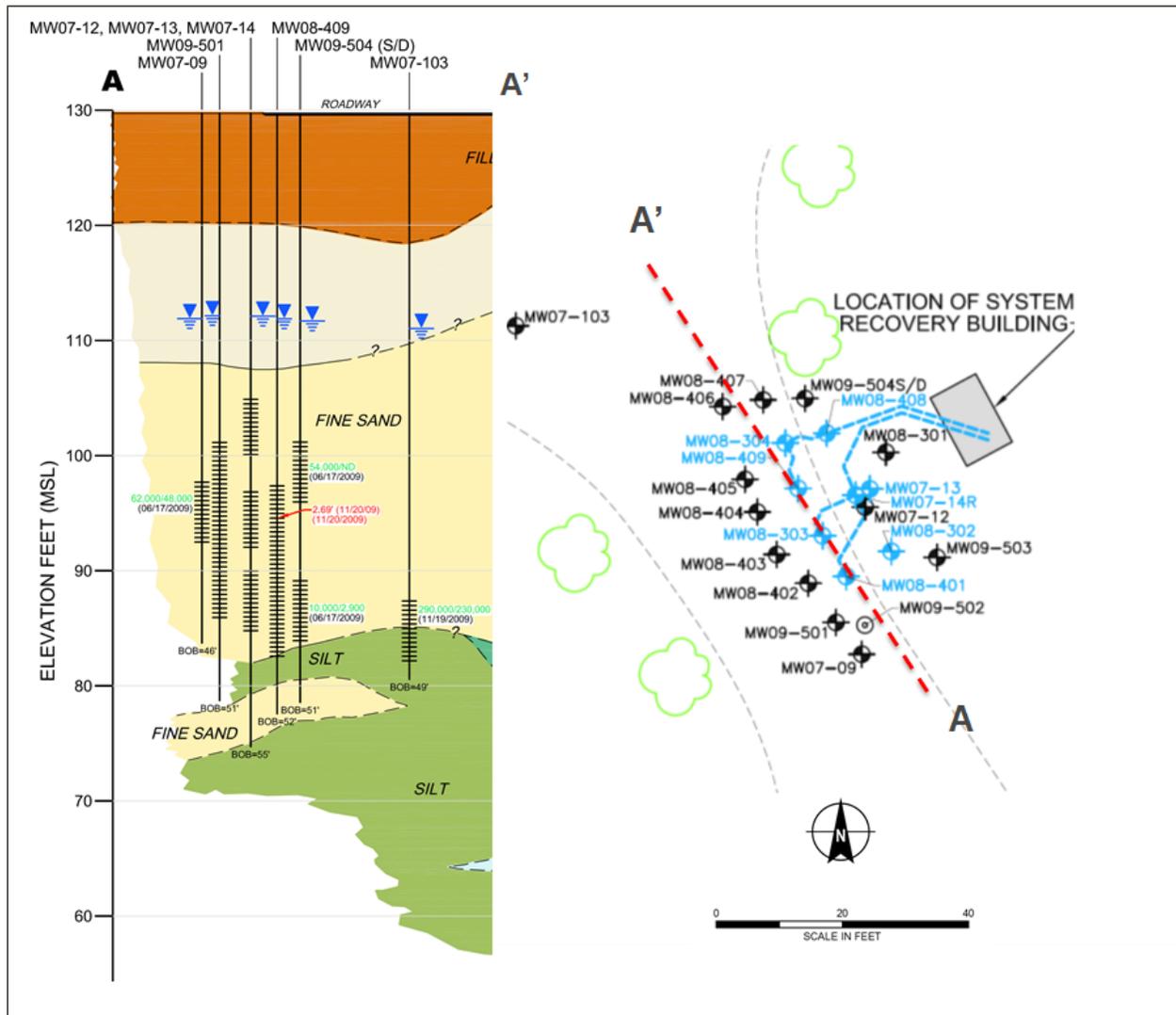


Figure 10. Cross-section through demonstration area (from GZA, 2011). Wells with current and/or historical DNAPL occurrence are shown as blue.

4.3 DNAPL OCCURRENCE

DNAPL recovery wells were installed in the planned demonstration area from 2007 to 2009. The well locations are shown in **Figure 11**. The recovery wells are generally screened from 30 to 45 feet bgs. The selection of the screen depth intervals was based on visual evidence of DNAPL in soil cores at depths ranging from 35 to 45 feet bgs (GZA, 2011).

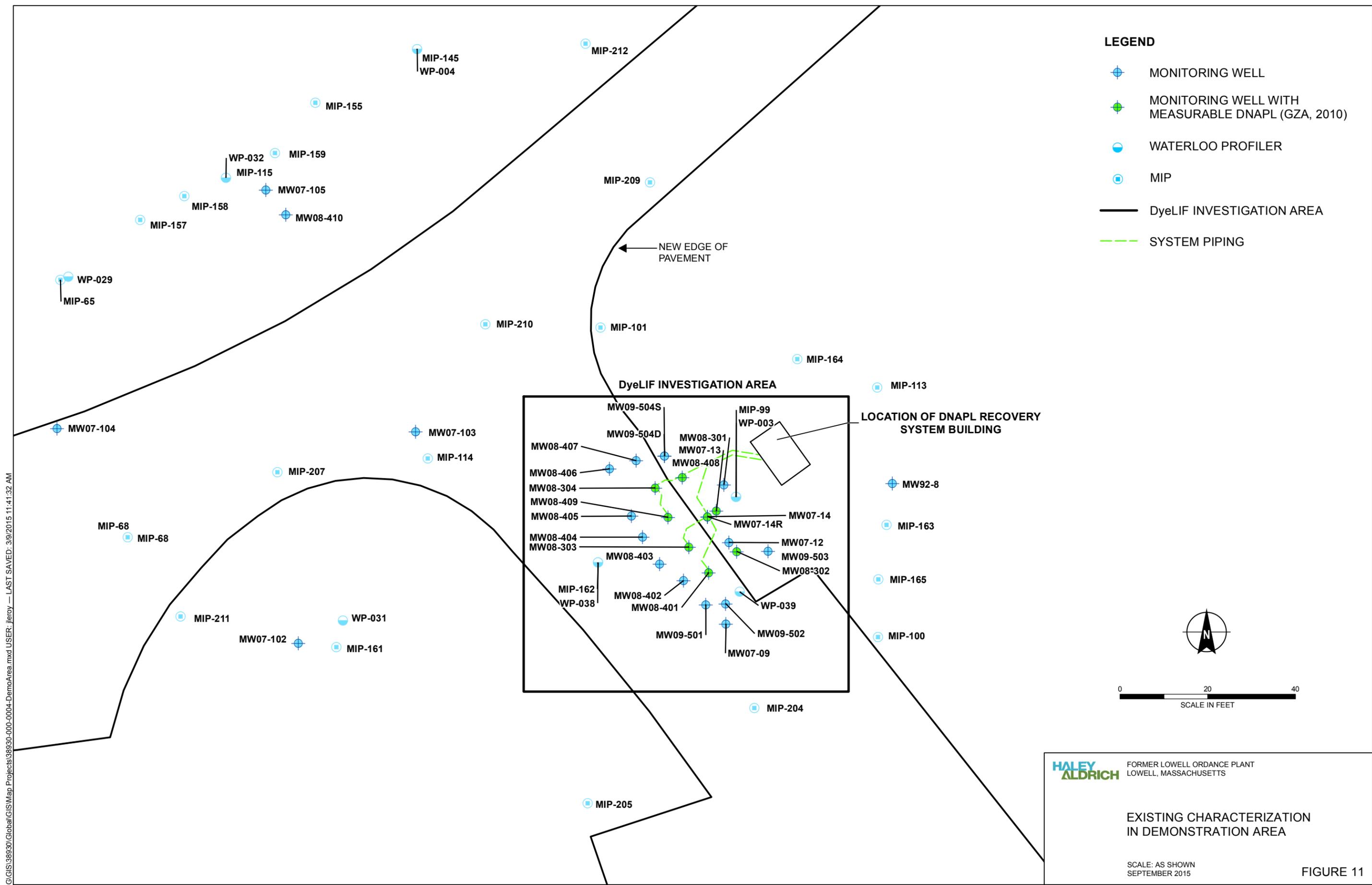
The recovery system had recovered 338 gallons as of December 2010 (GZA, 2011). Historically, the majority of DNAPL has been recovered from wells MW08-303, MW08-304, MW08-401, and MW07-14R. Other wells (MW07-13, MW08-32, MW08-408, and MW08-409) have had sporadic occurrences of DNAPL; however, DNAPL has not been observed recently in those wells (GZA, 2011).

4.4 OTHER HIGH RESOLUTION SITE CHARACTERIZATION DATA SETS

In addition to DNAPL recovery data, other HRSC data is available for the Demonstration Area, including MIP and Waterloo Profiler borings. The MIP tool was described previously in Section 1.1. The Waterloo Profiler is a tool used for collecting multiple groundwater samples at different depths from the same DP boring. The version of the Waterloo Profiler used at the Site was Stone Environmental's Waterloo Advanced Profiling System (Waterloo^{APS}) [<http://www.stone-env.com/profiling/index.php#waterloo>]. The tool works by injecting a steady stream of water into the subsurface as the tool is advanced (Pitkin et al., 1999). This helps prevent clogging of the sampling screen with sediments and also provides high-resolution information on the hydraulic properties of the formation by continuous monitoring of pressures and injection rates providing a parameter referred to as index of hydraulic conductivity (I_k). When a target depth interval for groundwater sampling is reached, the water flow is reversed and a groundwater sample is collected after sufficient purging to ensure the water pumped is representative of formation groundwater, which is also verified via monitoring / stabilization of various parameters with a multi-parameter probe while purging. The location of Waterloo^{APS} and MIP borings are shown in **Figure 12**. Additional discussion of those data sets is provided in the following sections.

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- LEGEND**
-  MONITORING WELL
 -  MONITORING WELL WITH MEASURABLE DNAPL (GZA, 2010)
 -  WATERLOO PROFILER
 -  MIP
 -  DyeLIF INVESTIGATION AREA
 -  SYSTEM PIPING



HALEY ALDRICH FORMER LOWELL ORDNANCE PLANT
LOWELL, MASSACHUSETTS

**EXISTING CHARACTERIZATION
IN DEMONSTRATION AREA**

SCALE: AS SHOWN
SEPTEMBER 2015

FIGURE 11

5.0 TEST DESIGN

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

The field demonstration included two components. The first component was completed during the first week of the demonstration and included a grid of closely spaced DyeLIF probes advanced in the suspected DNAPL source area. The second component, completed during the second week of the demonstration, included high-resolution vertical sampling of soil cores collected from soil borings advanced adjacent to selected DyeLIF probes.

5.2 BASELINE CHARACTERIZATION ACTIVITIES

No intrusive baseline characterization activities were completed for the field demonstration. As described above, a number of closely-spaced DNAPL recovery wells are located in the demonstration area. In addition, a number of soil borings, MIP probes, and groundwater profiling data were available for the demonstration area (**Figure 11**) from prior investigations. This data provided adequate baseline characterization for the subsequent DyeLIF probing.

5.3 FIELD TESTING

As described above, the field demonstration included two components, one week of DyeLIF probing and a second week of follow-on soil coring. The DyeLIF program is described below in Section 5.3.1; the follow-on soil coring is described in Section 5.3.2. Direct-push drilling services for both weeks were provided by Stone Environmental using a Geoprobe 7822DT rig [<http://geoprobe.com/7822DT>]. A second Geoprobe rig from Dakota was onsite and completed a portion of the DyeLIF probing the first week while the other Geoprobe rig from Stone performed the re-entry grouting.

5.3.1 DyeLIF Probes

DyeLIF probes were advanced throughout the suspected DNAPL source area the week of October 7, 2013. Probes were advanced to a depth of approximately 70 feet bgs. This depth was selected based on available characterization data for the suspected DNAPL source area which indicated DNAPL potentially extended down to this depth interval.⁸ DyeLIF probe locations are shown in **Figure 12**. A “DL-XX” naming convention was used for the DyeLIF probes. For example the first DyeLIF probe advance was denoted as “DL-01”. In certain locations duplicate DyeLIF probes were advanced next to the original DyeLIF probe.⁹ Because the duplicate probes were only approximately one foot away from the original probes, they are not shown in **Figure 12** in order to improve the readability of the figure.

A second, shorter DyeLIF investigation was completed March 15-17, 2014. That investigation included the advancement of 11 CPT probes to depths of approximately 70 feet bgs. The

⁸ Data indicating the likely maximum depth of DNAPL in the source area consisted of depth-discrete groundwater samples from a downgradient sampling transect. Results from the DyeLIF study confirmed the initial prediction of maximum DNAPL depth obtained from the downgradient HRSC transect, validating the “transect approach”

⁹ Duplicate in the sense that the “duplicate” boring was advanced adjacent to the original DyeLIF boring.

objective of that mobilization was to test the new CPT version of the DyeLIF and that event did not include the detailed soil sampling that was a component of the larger two week field study completed 2013.

5.3.2 Co-located Soil Borings

During the second week of the field demonstration, a Geoprobe® rig was used to advance closed-piston soil samplers adjacent to select DyeLIF probes that had indicated DNAPL was present at a particular location. Continuous soil cores were collected across the suspected DNAPL depth interval – i.e. cores were collected beginning at a depth several feet above the suspected DNAPL interval and were then collected continuously to a depth several feet below the suspected DNAPL zone. There were two objectives for the soil boring program. The first was to qualitatively compare the inferred “in-situ” DNAPL distribution from Dye-LIF probing with high resolution soil sampling in a co-located soil boring. The second objective was to collect soils that had a wide range of DNAPL pore saturations for aboveground analysis. Those samples ranged from soils with no DNAPL to soils most heavily impacted by DNAPL with the highest documented saturations at the Site (based on DyeLIF responses).

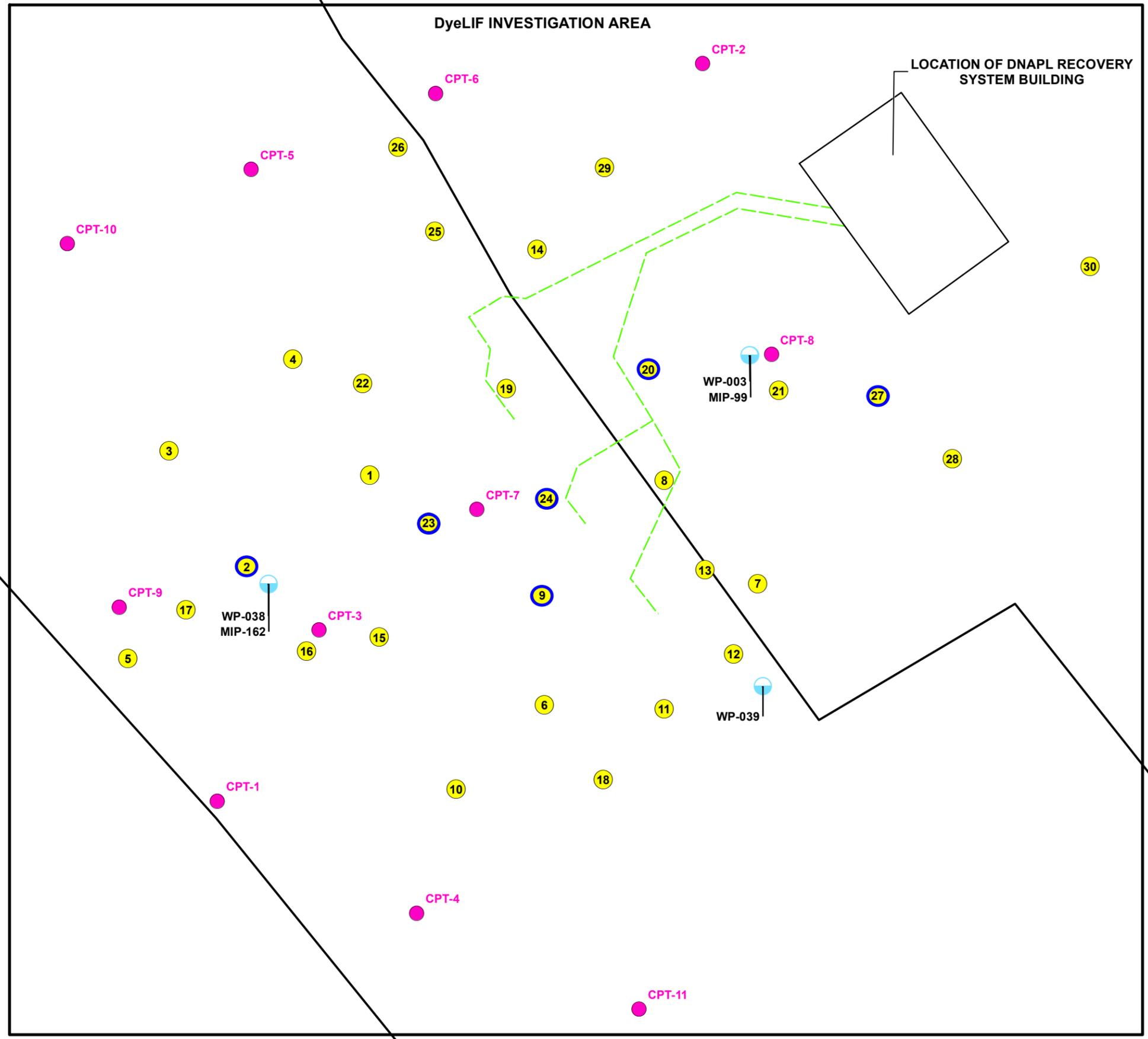
The strong spatial variability in the occurrence and saturation of residual DNAPL in the subsurface makes it difficult to quantitatively compare results from a DyeLIF probe to data (chemical data or visual tests using hydrophobic dyes) collected from nearby borings. Because of the expected variability in the distribution of residual NAPL, it is not reasonable to expect that NAPL will occur at the same depths and concentration /saturation in borings located even one foot away. Early field demonstrations of LIF technologies in the 1990s relied on this type of “verification” but, not surprisingly, often found poor correlation between LIF responses and data from soil samples collected from borings drilled just a few feet away.

To reduce (but not eliminate) biases resulting from the heterogeneous distribution of DNAPL in the subsurface, replicate samples for various types of testing were collected from the same depth interval from within the same soil core. At each sampling interval, four sub-cores were collected: one sub-core was analyzed with tabletop DyeLIF; one sample was field-preserved in methanol for subsequent laboratory analysis; one was collected for moisture content analysis, and a fourth sub-core underwent a dye “shake test” using a visual hydrophobic dye (Oil-Red-O). PID readings were also collected at each depth interval. The sub-core data was used for quantitatively evaluating the performance metrics described in Section 3.0. More details on the coring and sub-sampling methods are included in Section 5.3.3 below.

A total of eight (8) borings were advanced adjacent to selected DyeLIF probes. The corehole/sample IDs for the borings in the data summary table are denoted by the DyeLIF boring the soil boring was co-located with. For example, a soil boring advanced adjacent to DL-27 would be denoted with the same designation of “DL-27.” In some locations, more than one co-located soil boring was advanced next to the original DyeLIF location. This was done primarily to try different coring methods in an attempt to improve soil core recovery. For example, three co-located soil borings were advanced next to DL-23. The letter A, B, and C were used to denote successive co-located borings. For example, at DL-23, the three co-located are denoted as “DL-23A,” “DL-23B,” and “DL-23C.” Because the soil borings were only approximately one

foot away from the original DyeLIF borings, they are not shown in **Figure 12** in order to improve the readability of the figure.

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- LEGEND**
- WATERLOO PROFILER
 - MIP
 - 2013 DyeLIF
 - 2014 CPT AND DyeLIF
 - DyeLIF INVESTIGATION AREA
 - - - SYSTEM PIPING
 - SOIL BORING ADVANCED ADJACENT TO DyeLIF PROBE



0 7 14
SCALE IN FEET



FORMER LOWELL ORDNANCE PLANT
LOWELL, MASSACHUSETTS

DyeLIF PROBE AND SOIL BORING LOCATIONS

SCALE: AS SHOWN
SEPTEMBER 2015

FIGURE 12

5.3 SOIL SAMPLING METHODS

Achieving a high percentage of core recovery during the soil sampling portion of the field demonstration proved difficult due to the fine sands and soft silts at the Site. Different coring methods, run lengths, and operating variables were attempted in an effort to improve recovery. The best recovery was achieved using a modified version of the Geoprobe Macro-Core MC7™ sampler [<http://geoprobe.com/mc7>], which provides 3-inch diameter cores.¹⁰ The MC7 tool was adapted to include a sealed piston above the soil core which was tied off in a fixed position while the core barrel was advanced through the target core interval (method adapted from Zapico et al., 1987) with the goal of providing higher recovery and retention of pore fluids. Run lengths of 3 feet were used based on initial trials to maximize recovery. However, recovery still only ranged from about 50% to 85%, with an average of 65%. Part of the reason for lower recovery was the smaller diameter cutting shoe (~68 millimeters [mm]) versus the sample tube diameter (~75 mm), such that the soft sediments expanded out in the larger tube length and compressed accordingly (under these conditions the maximum recovery expected is about 83%). Based on this, a correction factor was applied to convert sub-sample positions in the core tubes to inferred “in-situ” depths.

The following procedure was used to complete the high-resolution soil sampling described above:

- The cores were split longitudinally on their vertical axes.
- Large drywall scrapers were used to scrape off the top layer of soil, which were decontaminated between intervals to avoid cross-contamination within the cores.
- The cores were quickly photographed and covered with aluminum foil to minimize volatile losses.
- When it was time to sample a given depth interval, a thin layer of the foil was peeled back to expose the soil core. Note that the vertical spacing between sampling intervals ranged from approximately 0.1 to 0.5 feet, with tighter spacing in and around DNAPL zones.
- At each sample depth interval, four sub-cores were collected using 10 mL disposable plastic syringes with the end cut off allowing the subsampler to be pushed into the core (taking care to avoid the outer edges):
 - One sub-core was collected for field screening with Oil-Red-O. The Oil-O-Red screening was completed by ejecting the soil into a pre-prepared 20-milliliter (mL) Volatile Organic Analysis (VOA) vial that contained a few mL of water and Oil-Red-O powder. The vial was then sealed and shaken and visually analyzed for a colorimetric response.
 - One sub-core was collected for subsequent laboratory analysis of VOCs. The soil from the sub-core was ejected into a pre-weighed 40-mL VOA vial containing 15

¹⁰ The larger core diameters were required in order to collect multiple sub-cores at the same depth interval.

mL of methanol preservative, reweighed to determine the wet soil mass and then placed in coolers pending shipment to the contract laboratory (Stone Environmental).

- One sub-core was collected for subsequent laboratory analysis of moisture content which was weighed in the field shortly after collection to determine the wet soil mass, and weighed again in the lab after drying to determine the dry soil mass (used to report VOCs results in terms of dry weight and wet weight).
- One sub-core was collected for aboveground tabletop screening with DyeLIF. This was completed by ejecting the soil into a 20-mL VOA and then adding the DyeLIF dye solution. The VOA vial was then placed on top of the DyeLIF sapphire window for measurements with DyeLIF. The VOA vial was slowly rotated while a series of DyeLIF measurements were collected.¹¹
- Immediately after subsampling at each depth interval, field screening with a PID was completed. This was done by inserting the PID probe tip (air inlet) into one of the “holes” created by the sub-coring and then covering the hole with a nitrile gloved hand to minimize air exposure. When DNAPL was present, the detector reading usually went above the maximum value of the instrument.
- After sampling was completed at one depth interval, the process was completed at the next depth interval.

Appendix B includes a series of photos that depict the sub-coring and sampling process, as well as additional information on the calibration of analytical equipment, quality assurance sampling, decontamination procedures, and grouting methods used for the DyeLIF and soil borings.

5.4 SAMPLING RESULTS

5.4.1 DyeLIF Results

As described above, three types of data products were generated in the field from the DyeLIF data. The first data product is the raw DyeLIF log. That log depicts the total response verses depth. As described in Section 2.1.2, the fluorescence vs. depth plots depict a composite color based on the individual peaks in the waveform plots. For example, a blue-shifted composite waveform where the blue peak dominates results in a bluish color fill. The raw DyeLIF logs also depict the flow rate of the dye solution and the measured backpressure aboveground.¹² The raw DyeLIF logs are included as **Appendix C**.

The second data product is the multi-panel plot that shows the raw waveform to the far left and the various waveforms in the Basis Set to the right (internal instrument background, non-solvated dye, sand, and DNAPL). This graphic facilitates field analysis of which types of fluorescence are

¹¹ The bottom of the VOA vial remained on the probe window while the vial was turned counter-clockwise. The VOA vials were not rotated end-over-end.

¹² The raw DyeLIF logs also depict a column for “P Dwn”. This is the backpressure measured with a downhole pressure transducer. The downhole pressure logging feature was added by Dakota Technologies prior to the CPT-delivery field demonstration in 2014 to improve the hydraulic profiling capabilities of the tool.

contributing most the overall raw fluorescence and helps to identify smaller DNAPL generated fluorescence peaks that might otherwise be lost in a plot showing just the raw fluorescence. The multi-panel plots depicting the results of the ADA are included as **Appendix D**.

The third data product produced from the DyeLIF data is the multi-panel DNAPL plot. This graphic plots five foot increments of the DNAPL waveform plot on the same printout, which facilitates identification of thinner DNAPL layers and can be extremely useful when probing to deeper depths such that regular plots do not provide adequate resolution. The multi-panel DNAPL plots are included as **Appendix E**.

5.4.2 Soil Sampling Results

Table 3 summarizes the soil coring program. It includes fields for boring location, the sampling method,¹³ the sampling depths in feet bgs, the total sampling interval length in feet, the percent recovery achieved, and the number of sub-core intervals within each soil core. As summarized in **Table 3**, a total of 260 depth intervals were sampled.

Table 4 summarizes the sub-coring sampling results. It includes a unique sample identification number for each sub-core sampling interval and additional fields for boring location, sample depth, VOC sampling results,¹⁴ estimated DNAPL saturation¹⁵, Oil-Red-O dye shake test results, tabletop DyeLIF testing, and PID screening results.

¹³ As described in previous sections, three different coring methods were attempted in an effort to determine which method yielded the best recovery.

¹⁴ 133 of 260 sub-core sampling intervals were submitted for laboratory analysis of VOCs.

¹⁵ DNAPL saturation was estimated from VOC concentrations using the procedures described above.

Table 3. Summary of Soil Coring Program

Date	Corehole ID	Run#	Depth from (ft bgs)	Depth to (ft bgs)	Interval (ft)	Recovery (ft)	Recovery (%)	Method	# Soil VOC Samples	Notes
10/14/2013	DL-20	1	15	20	5	2.2	44.0	MC-5	0	
10/14/2013	DL-20	2	20	25	5	2.1	42.0	MC-5	0	
10/14/2013	DL-20	3	25	28	3	2.1	70.0	MC-5	4	
10/14/2013	DL-20	4	28	30	2	1.5	75.0	MC-5	3	
10/14/2013	DL-20	5	30	34	4	3.1	77.5	MC-7	16	
10/14/2013	DL-20	6	34	37	3	2.3	76.7	MC-7	11	
10/14/2013	DL-20	7	37	40	3	0.7	23.3	MC-7	0	piston vibrated down through core sediments
10/14/2013	DL-20D	1	30	33	3	1.7	56.7	MC-5*	6	
10/14/2013	DL-20D	2	33	36	3	2	66.7	MC-5*	9	
10/14/2013	DL-20D	3	36	39	3	2	66.7	MC-5*	0	tube sandlocked in core barrel (more disturbed)
10/15/2013	DL-23A	1	30	33	3	2	66.7	MC-7	11	
10/15/2013	DL-23A	2	33	36	3	2	66.7	MC-7	13	
10/15/2013	DL-23A	3	50	53	3	0.4	13.3	MC-7	0	piston vibrated down through core sediments
10/15/2013	DL-23B	1	30	33	3	2	66.7	MC-7*	12	
10/15/2013	DL-23B	2	33	36	3	2	66.7	MC-7*	14	
10/15/2013	DL-23B	3	50	53.5	3.5	2.1	60.0	MC-7*	7	
10/15/2013	DL-23B	4	53.5	56.5	3	1.4	46.7	MC-7*	4	
10/16/2013	DL-23C	1	50	53	3	1.9	63.3	MC-7*	7	tube sandlocked in core barrel (more disturbed)
10/16/2013	DL-23C	2	53	56	3	1.7	56.7	MC-7*	9	
10/16/2013	DL-24A	1	30	33	3	1.7	56.7	MC-7*	9	
10/16/2013	DL-24A	2	33	36	3	2.1	70.0	MC-7*	9	
10/16/2013	DL-24A	3	36	39	3	1.5	50.0	MC-7*	7	
10/16/2013	DL-24A	4	39	42	3	1.9	63.3	MC-7*	6	
10/16/2013	DL-24A	5	50	53	3	2	66.7	MC-7*	13	
10/16/2013	DL-24A	6	53	56	3	1.8	60.0	MC-7*	10	
10/17/2013	DL-24A	7	56	59	3	1.4	46.7	MC-7*	5	
10/17/2013	DL-24A	8	59	62	3	2.6	86.7	MC-7*	16	
10/17/2013	DL-9A	1	30	33	3	2.1	70.0	MC-7*	8	
10/17/2013	DL-9A	2	33	36	3	2.1	70.0	MC-7*	11	
10/17/2013	DL-9A	3	36	39	3	1.8	60.0	MC-7*	9	
10/17/2013	DL-9A	4	55	58	3	1.8	60.0	MC-7*	9	
10/17/2013	DL-2A	1	30	33	3	2.3	76.7	MC-7*	12	
10/17/2013	DL-2A	2	33	36	3	1.9	63.3	MC-7*	7	
10/17/2013	DL-2A	3	36	39	3	1	33.3	MC-7*	3	core sediments pushed up around piston
10/18/2013	DL-27	1	20	25	5	3.7	74.0	MC-7	0	
10/18/2013	DL-27	2	25	30	5	2	40.0	Waterloo PCB	0	
10/18/2013	DL-27	3	30	35	5	2	40.0	Waterloo PCB	0	lost 1.3 ft out end (no catcher)
Totals					121.5				260	

* adapted method including piston

Table 4. Summary of Sub-Core Sampling Results

Sample ID	Corehole ID	Run Interval (ft bgs)	Corrected Depth ¹ (ft bgs)	Total VOC (mg/kg)	Estimated DNAPL Saturation ² (%)	Oil-Red-O Detection ^{3,4}	DYE-LIF Detection ^{3,4}	PID (ppm)
210	DL-9A	33-36	33.13	111,320	31	1	1	12
211	DL-9A	33-36	33.39	95,260	28	1	1	20.6
187	DL-24A	59-62	59.23	72,100	20	1	1	0.9
088	DL-23B	33-36	33.40	71,220	21	1	1	1.3
186	DL-24A	59-62	59.11	71,120	19	1	1	131
062	DL-23A	33-36	33.27	60,180	17	1	1	29.4
065	DL-23A	33-36	33.67	52,095	15	1	1	2.1
212	DL-9A	33-36	33.65	48,110	14	1	1	15.5
089	DL-23B	33-36	33.53	45,180	13	1	1	55.4
086	DL-23B	33-36	33.13	44,140	12	1	1	159
091	DL-23B	33-36	33.80	44,110	13	1	1	14.9
022	DL-20	30-34	33.68	39,034	11	1	1	7.1
164	DL-24A	50-53	51.33	37,180	10	1	1	0.8
061	DL-23A	33-36	33.13	37,120	10	1	1	1.5
090	DL-23B	33-36	33.67	37,099	11	1	1	0.5
087	DL-23B	33-36	33.27	34,120	9.6	1	1	3.9
066	DL-23A	33-36	33.80	32,058	9.3	1	1	4.1
136	DL-24A	33-36	33.13	29,052	7.9	1	1	8
207	DL-9A	30-33	32.60	29,051	8.1	1	1	61.4
020	DL-20	30-34	33.19	28,032	8.0	1	1	53.7
137	DL-24A	33-36	33.33	27,046	7.7	1	1	24.8
249	DL-2A	30-33	32.53	23,540	6.7	1	1	219
044	DL-20D	33-36	34.07	21,734	6.2	1	1	63.4
209	DL-9A	30-33	32.47	21,664	6.1	1	1	118
063	DL-23A	33-36	33.40	21,064	6.0	1	1	40.1
085	DL-23B	30-33	32.53	18,556	4.9	1	1	92
171	DL-24A	53-56	53.14	18,200	4.8	1	1	280
019	DL-20	30-34	32.94	13,840	3.8	1	1	149
042	DL-20D	33-36	33.53	12,420	3.5	1	1	207
084	DL-23B	30-33	32.40	12,231	3.3	1	1	254
213	DL-9A	33-36	33.91	12,119	3.3	1	1	201
064	DL-23A	33-36	33.53	11,736	3.2	1	1	124
083	DL-23B	30-33	32.27	8,829	2.4	1	1	480
059	DL-23A	30-33	32.53	7,936	2.1	1	1	343
082	DL-23B	30-33	32.13	7,068	1.9	1	1	194
092	DL-23B	33-36	33.93	5,600	1.4	0	0	148
195	DL-24A	59-62	60.36	5,100	1.3	1	1	2
172	DL-24A	53-56	53.42	5,047	1.2	1	0	0.2
188	DL-24A	59-62	59.34	4,608	1.1	1	1	1.2
250	DL-2A	30-33	32.71	4,190	1.0	1	1	1.6
021	DL-20	30-34	33.43	3,412	0.78	1	1	10
041	DL-20D	33-36	33.27	2,320	0.50	1	1	73.1
058	DL-23A	30-33	32.27	2,216	0.44	1	0	102
223	DL-9A	36-39	36.84	2,024	0.39	0	0	25.3
165	DL-24A	50-53	51.47	1,944	0.34	1	0	156
043	DL-20D	33-36	33.80	1,345	0.18	1	1	87.2
179	DL-24A	53-56	55.38	993	0.090	1	0	21.3
170	DL-24A	50-53	52.40	882	0.045	0	0	104
222	DL-9A	36-39	36.56	731	0.006	1	0	631
190	DL-24A	59-62	59.57	631	0.00	1	0	605
220	DL-9A	33-36	34.04	510	0.0	1	0	410
214	DL-9A	33-36	34.17	450	0.0	1	0	485
229	DL-9A	36-39	36.70	400	0.0	1	0	98.2
221	DL-9A	36-39	36.28	400	0.0	1	0	103
045	DL-20D	33-36	34.33	370	0.0	0	0	1.1
259	DL-2A	36-39	36.83	360	0.0	0	0	82.7

Table 4. Summary of Sub-Core Sampling Results

Sample ID	Corehole ID	Run Interval (ft bgs)	Corrected Depth ¹ (ft bgs)	Total VOC (mg/kg)	Estimated DNAPL Saturation ² (%)	Oil-Red-O Detection ^{3,4}	DYE-LIF Detection ^{3,4}	PID (ppm)
118	DL-23C	53-56	53.14	357	0.0	0	0	94.4
138	DL-24A	33-36	33.52	350	0.0	1	0	38.3
219	DL-9A	33-36	35.60	340	0.0	0	0	180
215	DL-9A	33-36	34.43	340	0.0	0	0	3.4
224	DL-9A	36-39	37.12	340	0.0	0	0	319
217	DL-9A	33-36	34.95	330	0.0	0	0	336
049	DL-20D	33-36	35.40	320	0.0	0	0	292
067	DL-23A	33-36	33.93	320	0.0	0	0	207
140	DL-24A	33-36	33.91	320	0.0	0	0	1.0
216	DL-9A	33-36	34.69	320	0.0	0	0	1.1
189	DL-24A	59-62	59.45	310	0.0	1	0	0.8
228	DL-9A	36-39	38.24	310	0.0	0	0	1.2
139	DL-24A	33-36	33.72	300	0.0	0	0	1.8
218	DL-9A	33-36	35.28	300	0.0	0	0	1.4
256	DL-2A	33-36	35.05	280	0.0	0	0	0.8
093	DL-23B	33-36	34.07	280	0.0	0	0	112
095	DL-23B	33-36	34.47	280	0.0	0	0	48.5
141	DL-24A	33-36	34.17	280	0.0	0	0	57.5
255	DL-2A	33-36	34.64	271	0.0	0	0	23.2
046	DL-20D	33-36	34.60	270	0.0	0	0	1.6
142	DL-24A	33-36	34.56	260	0.0	0	0	1.8
047	DL-20D	33-36	34.87	250	0.0	0	0	1.0
163	DL-24A	50-53	51.20	250	0.0	0	0	2.0
094	DL-23B	33-36	34.20	250	0.0	0	0	2.8
196	DL-24A	59-62	60.59	240	0.0	0	0	198
197	DL-24A	59-62	60.81	230	0.0	0	0	60.1
121	DL-23C	53-56	53.79	221	0.0	0	0	42.6
048	DL-20D	33-36	35.13	220	0.0	0	0	10.1
145	DL-24A	36-39	36.30	218	0.0	0	0	5.2
147	DL-24A	36-39	36.90	216	0.0	0	0	20.8
144	DL-24A	33-36	35.34	213	0.0	0	0	28.2
151	DL-24A	36-39	38.10	207	0.0	0	0	39.2
177	DL-24A	53-56	54.54	204	0.0	0	0	50.5
143	DL-24A	33-36	34.95	203	0.0	0	0	54.5
149	DL-24A	36-39	37.50	184	0.0	0	0	23.2
120	DL-23C	53-56	53.57	164	0.0	0	0	17.3
194	DL-24A	59-62	60.13	164	0.0	0	0	431
119	DL-23C	53-56	53.36	150	0.0	0	0	699
153	DL-24A	39-42	39.68	107	0.0	0	0	155
198	DL-24A	59-62	61.04	94	0.0	0	0	486
254	DL-2A	33-36	34.23	90	0.0	0	0	323
191	DL-24A	59-62	59.68	81	0.0	1	0	167
155	DL-24A	39-42	40.50	69	0.0	0	0	29.6
173	DL-24A	53-56	53.70	48	0.0	1	0	10.5
081	DL-23B	30-33	32.00	47	0.0	0	0	16.1
208	DL-9A	30-33	32.34	45	0.0	1	0	3.8
162	DL-24A	50-53	51.07	39	0.0	0	0	16.4
060	DL-23A	30-33	32.13	30	0.0	0	0	75.8
193	DL-24A	59-62	59.91	29	0.0	0	0	9.9
192	DL-24A	59-62	59.79	23	0.0	0	0	16
176	DL-24A	53-56	54.26	21	0.0	0	0	110
134	DL-24A	30-33	31.86	18	0.0	0	0	210
247	DL-2A	30-33	32.34	16	0.0	1	1	80
117	DL-23C	50-53	52.46	13	0.0	0	0	0.2
167	DL-24A	50-53	51.73	11	0.0	0	0	3.2
135	DL-24A	30-33	32.15	10	0.0	0	0	37

Table 4. Summary of Sub-Core Sampling Results

Sample ID	Corehole ID	Run Interval (ft bgs)	Corrected Depth ¹ (ft bgs)	Total VOC (mg/kg)	Estimated DNAPL Saturation ² (%)	Oil-Red-O Detection ^{3,4}	DYE-LIF Detection ^{3,4}	PID (ppm)
116	DL-23C	50-53	52.19	9	0.0	0	0	16.2
166	DL-24A	50-53	51.60	8	0.0	0	0	180
251	DL-2A	33-36	33.27	6	0.0	0	0	190
232	DL-9A	55-58	55.70	5	0.0	0	0	280
168	DL-24A	50-53	51.87	5	0.0	0	0	3.0
175	DL-24A	53-56	53.98	5	0.0	0	0	45
174	DL-24A	53-56	53.84	5	0.0	0	0	10.5
206	DL-9A	30-33	32.21	4	0.0	0	0	1.2
178	DL-24A	53-56	54.96	3	0.0	0	0	1.8
180	DL-24A	53-56	55.17	3	0.0	0	0	0.8
231	DL-9A	55-58	55.42	2	0.0	0	0	0.3
040	DL-20D	30-33	32.29	2	0.0	0	0	2.6
080	DL-23B	30-33	31.73	1	0.0	0	0	57
161	DL-24A	50-53	50.93	1	0.0	0	0	10.1
183	DL-24A	56-59	57.07	1	0.0	0	0	5.6
245	DL-2A	30-33	31.85	1	0.0	0	0	15.4
181	DL-24A	56-59	56.15	0.2	0.0	0	0	89
050	DL-23A	30-33	30.13	0.1	0.0	0	0	175
233	DL-9A	55-58	55.98	0.1	0.0	0	0	24.1
248	DL-2A	30-33	32.22	0.1	0.0	0	0	45.1
246	DL-2A	30-33	32.10	0.1	0.0	0	0	24.6
001	DL-20	25-28	25.71	NA	NA	0	0	2000
002	DL-20	25-28	26.30	NA	NA	0	0	2000
003	DL-20	25-28	26.95	NA	NA	0	0	3000
004	DL-20	25-28	27.60	NA	NA	0	0	2434
005	DL-20	28-30	28.63	NA	NA	0	0	3000
006	DL-20	28-30	29.25	NA	NA	0	0	2073
007	DL-20	28-30	29.75	NA	NA	0	0	1000
008	DL-20	30-34	30.25	NA	NA	0	0	550
009	DL-20	30-34	30.49	NA	NA	0	0	1470
010	DL-20	30-34	30.74	NA	NA	0	0	2039
011	DL-20	30-34	30.98	NA	NA	0	0	1030
012	DL-20	30-34	31.23	NA	NA	0	0	1848
013	DL-20	30-34	31.47	NA	NA	0	0	1431
014	DL-20	30-34	31.72	NA	NA	0	0	1464
015	DL-20	30-34	31.96	NA	NA	0	0	834
016	DL-20	30-34	32.21	NA	NA	0	0	1615
017	DL-20	30-34	32.45	NA	NA	0	0	1090
018	DL-20	30-34	32.70	NA	NA	0	0	1602
023	DL-20	30-34	32.82	NA	NA	0	0	1846
024	DL-20	34-37	34.25	NA	NA	0	0	1901
025	DL-20	34-37	34.49	NA	NA	0	0	1800
026	DL-20	34-37	34.74	NA	NA	0	0	2000
027	DL-20	34-37	34.99	NA	NA	0	0	1779
028	DL-20	34-37	35.23	NA	NA	0	0	2050
029	DL-20	34-37	35.48	NA	NA	0	0	2603
030	DL-20	34-37	35.73	NA	NA	0	0	607
031	DL-20	34-37	35.97	NA	NA	0	0	2400
032	DL-20	34-37	36.22	NA	NA	0	0	1680
033	DL-20	34-37	36.47	NA	NA	0	0	1581
034	DL-20	34-37	36.71	NA	NA	0	0	990
035	DL-20D	30-33	30.57	NA	NA	0	0	2000
036	DL-20D	30-33	31.15	NA	NA	0	0	1878
037	DL-20D	30-33	31.72	NA	NA	0	0	1740
038	DL-20D	30-33	31.43	NA	NA	0	0	972
039	DL-20D	30-33	32.01	NA	NA	0	0	1771

Table 4. Summary of Sub-Core Sampling Results

Sample ID	Corehole ID	Run Interval (ft bgs)	Corrected Depth ¹ (ft bgs)	Total VOC (mg/kg)	Estimated DNAPL Saturation ² (%)	Oil-Red-O Detection ^{3,4}	DYE-LIF Detection ^{3,4}	PID (ppm)
051	DL-23A	30-33	30.40	NA	NA	0	0	2455
052	DL-23A	30-33	30.67	NA	NA	0	0	2400
053	DL-23A	30-33	30.93	NA	NA	0	0	2618
054	DL-23A	30-33	31.20	NA	NA	0	0	2500
055	DL-23A	30-33	31.47	NA	NA	0	0	2000
056	DL-23A	30-33	31.73	NA	NA	0	0	1908
057	DL-23A	30-33	32.00	NA	NA	0	0	647
068	DL-23A	33-36	34.20	NA	NA	0	0	1430
069	DL-23A	33-36	34.47	NA	NA	0	0	1504
070	DL-23A	33-36	34.73	NA	NA	0	0	2694
071	DL-23A	33-36	35.00	NA	NA	0	0	1765
072	DL-23A	33-36	35.27	NA	NA	0	0	1475
073	DL-23A	33-36	35.53	NA	NA	0	0	254
074	DL-23B	30-33	30.13	NA	NA	0	0	1225
075	DL-23B	30-33	30.40	NA	NA	0	0	2500
076	DL-23B	30-33	30.67	NA	NA	0	0	1000
077	DL-23B	30-33	30.93	NA	NA	0	0	1300
078	DL-23B	30-33	31.20	NA	NA	0	0	1000
079	DL-23B	30-33	31.47	NA	NA	0	0	362
096	DL-23B	33-36	34.73	NA	NA	0	0	1551
097	DL-23B	33-36	35.00	NA	NA	0	0	81.3
098	DL-23B	33-36	35.27	NA	NA	0	0	1293
099	DL-23B	33-36	35.53	NA	NA	0	0	1085
100	DL-23B	50-53.5	50.28	NA	NA	0	0	140
101	DL-23B	50-53.5	50.70	NA	NA	0	0	470
102	DL-23B	50-53.5	51.12	NA	NA	0	0	280
103	DL-23B	50-53.5	51.54	NA	NA	0	0	223
104	DL-23B	50-53.5	51.96	NA	NA	0	0	180
105	DL-23B	50-53.5	52.38	NA	NA	0	0	914
106	DL-23B	50-53.5	52.80	NA	NA	0	0	262
107	DL-23B	53.5-56.5	53.96	NA	NA	0	0	320
108	DL-23B	53.5-56.5	54.42	NA	NA	0	0	2500
109	DL-23B	53.5-56.5	54.88	NA	NA	0	0	105
110	DL-23B	53.5-56.5	55.34	NA	NA	0	0	822
111	DL-23C	50-53	50.14	NA	NA	0	0	240
112	DL-23C	50-53	50.55	NA	NA	0	0	66.3
113	DL-23C	50-53	50.96	NA	NA	0	0	396
114	DL-23C	50-53	51.37	NA	NA	0	0	470
115	DL-23C	50-53	51.78	NA	NA	0	0	439
122	DL-23C	53-56	54.00	NA	NA	0	0	358
123	DL-23C	53-56	54.22	NA	NA	0	0	382
124	DL-23C	53-56	54.43	NA	NA	0	0	984
125	DL-23C	53-56	54.86	NA	NA	0	0	220
126	DL-23C	53-56	55.29	NA	NA	0	0	582
127	DL-24A	30-33	30.14	NA	NA	0	0	233
128	DL-24A	30-33	30.50	NA	NA	0	0	470
129	DL-24A	30-33	30.72	NA	NA	0	0	190
130	DL-24A	30-33	30.93	NA	NA	0	0	236
131	DL-24A	30-33	31.15	NA	NA	0	0	206
132	DL-24A	30-33	31.36	NA	NA	0	0	491
133	DL-24A	30-33	31.58	NA	NA	0	0	587
146	DL-24A	36-39	36.60	NA	NA	0	0	255
148	DL-24A	36-39	37.20	NA	NA	0	0	374
150	DL-24A	36-39	37.80	NA	NA	0	0	609
152	DL-24A	39-42	39.27	NA	NA	0	0	383
154	DL-24A	39-42	40.09	NA	NA	0	0	547

Sample ID	Corehole ID	Run Interval (ft bgs)	Corrected Depth ¹ (ft bgs)	Total VOC (mg/kg)	Estimated DNAPL Saturation ² (%)	Oil-Red-O Detection ^{3,4}	DYE-LIF Detection ^{3,4}	PID (ppm)
156	DL-24A	39-42	40.91	NA	NA	0	0	315
157	DL-24A	39-42	41.32	NA	NA	0	0	280
158	DL-24A	50-53	50.13	NA	NA	0	0	350
159	DL-24A	50-53	50.40	NA	NA	0	0	362
160	DL-24A	50-53	50.67	NA	NA	0	0	220
169	DL-24A	50-53	52.13	NA	NA	0	0	124
182	DL-24A	56-59	56.61	NA	NA	0	0	1900
184	DL-24A	56-59	57.53	NA	NA	0	0	220
185	DL-24A	56-59	57.99	NA	NA	0	0	1577
199	DL-24A	59-62	61.27	NA	NA	0	0	105
200	DL-24A	59-62	61.49	NA	NA	0	0	546
201	DL-24A	59-62	61.72	NA	NA	0	0	1229
202	DL-9A	30-33	30.26	NA	NA	0	0	180
203	DL-9A	30-33	30.78	NA	NA	0	0	155
204	DL-9A	30-33	31.30	NA	NA	0	0	390
205	DL-9A	30-33	31.82	NA	NA	0	0	370
225	DL-9A	36-39	37.40	NA	NA	0	0	26.2
226	DL-9A	36-39	37.68	NA	NA	0	0	598
227	DL-9A	36-39	37.96	NA	NA	0	0	20.8
230	DL-9A	55-58	55.14	NA	NA	0	0	336
234	DL-9A	55-58	55.84	NA	NA	0	0	83.0
235	DL-9A	55-58	56.26	NA	NA	0	0	21
236	DL-9A	55-58	56.68	NA	NA	0	0	1213
237	DL-9A	55-58	57.10	NA	NA	0	0	59
238	DL-9A	55-58	57.52	NA	NA	0	0	300
239	DL-2A	30-33	30.12	NA	NA	0	0	78.3
240	DL-2A	30-33	30.49	NA	NA	0	0	250
241	DL-2A	30-33	30.86	NA	NA	0	0	656
242	DL-2A	30-33	31.11	NA	NA	0	0	70.7
243	DL-2A	30-33	31.36	NA	NA	0	0	895
244	DL-2A	30-33	31.60	NA	NA	0	0	130
252	DL-2A	33-36	33.55	NA	NA	0	0	18.4
253	DL-2A	33-36	33.82	NA	NA	0	0	5.3
257	DL-2A	33-36	35.46	NA	NA	0	0	334
258	DL-2A	36-39	36.33	NA	NA	0	0	272
260	DL-2A	36-39	37.33	NA	NA	0	0	27.2

Notes:

1. Corrected sub-core depth accounts for soil recovery percentage in the associated soil core.
2. Orange highlighting: NAPLANAL software calculated DNAPL present.
3. Red highlighting: test (Oil-O-Red or DyeLIF) indicated DNAPL was present in sub-sample.
4. Blue highlighting: test (Oil-O-Red or DyeLIF) indicated DNAPL was **NOT** present in sub-sample.

6.0 PERFORMANCE ASSESSMENT

6.1 CORRELATION BETWEEN SUB-CORES

As described in Section 5, continuous soil cores were collected across suspected DNAPL depth interval – i.e. cores were collected beginning at a depth several feet above the suspected DNAPL interval and collected continuously to a depth several feet below the suspected DNAPL zone. Closely spaced soil samples were then collected from each soil core at a sampling interval ranging from about 0.1 to 0.5 feet with tighter spacing in and around DNAPL layers. At each sampling interval, four sub-cores were collected: one sub-core was analyzed with tabletop DyeLIF above ground; one sample was field-preserved in methanol for subsequent laboratory analysis; one sample was collected for moisture content analysis and a fourth sub-core underwent a dye “shake test” using a visual hydrophobic dye (Oil-Red-O). The aboveground tabletop DyeLIF testing was then compared with the dye shake tests and laboratory analysis.

The performance objective for chemical analysis was 70% consistency between positive DyeLIF responses and samples when laboratory results indicated DNAPL saturations greater than 5%.¹⁶ The demonstration results showed 100% consistency between chemical analysis and DyeLIF for saturations down to 1.9% (35 of 35 samples), and 95% consistency for estimated saturations greater than 0.5% (40 of 42 samples). Therefore, the performance objective for chemical analysis was exceeded.

The performance objective for the dye shake tests was 70% consistency between a positive DyeLIF response and a positive colorimetric response with the dye shake test when the DNAPL saturation was estimated to be above 5%. For the dye shake tests, the demonstration results showed 100% consistency between DyeLIF and the shake tests at saturations down to 1.3% percent (37 of 37 samples).¹⁷ There was 98% consistency between DyeLIF and dye shake tests when saturations were above 0.5% (41 of 42 samples). Therefore, the performance objective for dye shake tests was exceeded.

One issue that was identified during the field program was that at low saturations the DNAPL would sometimes separate out of the sand and cling to the glass in the upper portions of the vial. This proved problematic for the tabletop DyeLIF testing as the protocol used was to place the bottom of the sample vial on the laser window and rotate it while readings were collected. This resulted in LIF readings being taken in the soil rather than up on the glass sidewalls where the DNAPL had preferentially accumulated. Greater consistency at low saturations (< 0.5%) would have likely been achieved by reading the glass sidewalls with DyeLIF rather than the soil at the bottom of the glass vials (making it equivalent to visual dye methods whose detections are enhanced by preferential adherence of the red-colored DNAPL to the sidewalls). Therefore, while this testing indicated a detection limit of around 0.5% saturation, the detection limit in-situ is likely much lower.

¹⁶ DNAPL saturations were estimated from laboratory analytical results using the software NAPLANAL. The NAPLANAL code uses equilibrium partitioning theory to estimate DNAPL saturations.

¹⁷ For one of the samples, both the DyeLIF test and the dye shake test indicated no DNAPL was present. Therefore the samples were consistent with each other but contradicted the lab data. This data suggests that there may have been some intra-core heterogeneity.

6.2 TOOL DURABILITY AND PRODUCTION RATE

The hammering and stress of percussive drilling over the one week drilling program allowed the project team to evaluate the durability of the DyeLIF tool. A performance objective of 90% uptime was the specified goal in the work plan for the field demonstration. A performance objective was also established for the average linear feet of drilling production achieved per day. A performance goal of 150 feet per day was proposed in the work plan.

In the field demonstration, 100% uptime was achieved by having a second set of downhole tooling (DyeLIF sub and probe rods pre-strung with DyeLIF cables) available that could be utilized in the event that minor maintenance of the first set of downhole tooling was required. This approach is also by most MIP contractors as a way to prevent project downtime while repairs to the MIP system are made. During the weeklong field event, the downhole tooling had to be swapped out one time when the DyeLIF encountered a minor issue requiring repair.¹⁸

The production rate for the week of DyeLIF probing averaged over 400 feet of probing per day, greatly exceeding the 150 feet per day goal. The production rate was helped by a second rig on site that was performing some of the re-entry grouting. This approach limited any downtime of the DyeLIF rig during grouting. We estimate the production rate would have decreased approximately 20% if the DyeLIF rig also performed the re-entry grouting. Dakota Technologies has maintained a running average production rate for its TarGOST LIF tool over many years and dozens of sites probed of 334 feet per day. A 20% reduction in the achieved production rate would have been consistent with the running TarGOST average of 334 feet per day.

The production rate, coupled with the extremely fine vertical resolution of DyeLIF (~ one data point per 0.5 cm probed) is a result of the extremely high data acquisition rate of the DyeLIF tool. Using the running TarGOST production rate average of 334 feet probed per day, the number of data points generated per day would be greater than 20,000. Considering the excellent correlation between DyeLIF and colorimetric dye shake tests, one day of DyeLIF probing is essentially equivalent to conducting 20,000 colorimetric dye shake tests, something that would take several months of soil coring and detailed sub-coring to complete.

6.3 NO DRAG-DOWN OF DNAPL

As described in Section 3.3, no drag-down of DNAPL was observed in the DyeLIF logs. This is consistent with the thousands of LIF probes advanced in NAPL sources by Dakota Technologies. The absence of drag-down in this project or other LIF NAPL investigations is primarily because CPT and other DP tools displace 100% of the volume of the DP probe, creating a seal against the DP rods and tooling as they are being advanced. This can be contrasted with soil borings, where the soil is physically removed from the subsurface, thereby increasing the potential for vertical migration of DNAPL.

The concern of vertical migration is further mitigated by employing appropriate grouting techniques – either retraction or re-entry grouting. For the field demonstration, re-entry grouting

¹⁸ This repair required approximately one hour to make. Therefore, if the second set of tooling had not been onsite, the uptime would have still been close to 100%.

was used. This involves reentering the hole with DP rods equipped with a sacrificial tip.¹⁹ Once the depth of the previous boring was reached, the rods were retracted, causing the sacrificial tip to dislodge. Grout was then pumped into the rods as they were retracted, analogous to a tremie pipe. Retraction grouting and “grouting while advancing” techniques have also demonstrated for DP applications (Lutenegger and DeGroot, 1995).

6.4 THREE-DIMENSIONAL GRAPHICAL DEPICTION OF DNAPL SOURCE ZONE

The data acquisition rates and vertical resolution of the DyeLIF generates high-resolution datasets that can be used for three-dimensional rendering of chlorinated solvent DNAPL source zones at a resolution and accuracy previously not possible before with conventional technologies and approaches. 3-D renderings of the actual DNAPL source zone at the demonstration site are shown below in **Figure 13**.

As shown in **Figure 13**, the majority of the DNAPL at the field demonstration site is located at approximately 35 feet bgs, with smaller intervals of DNAPL located at deeper depths. The three-dimensional rendering of the DNAPL source zone is consistent with laboratory experiments (Christ et al., 2010; Fure et al., 2006; Kaye et al., 2008; Ostrom et al., 1999) and numerical modeling (Basu et al., 2008; Christ et al., 2005; Lemke et al., 2004; Park and Parker, 2005) of DNAPL migration which has demonstrated that DNAPL tends to pool and migrate laterally when encountering permeability changes.

The authors of this study suggest that the 3-D depictions of the DNAPL in **Figure 13** constitute the most detailed and accurate definition of subsurface DNAPL ever obtained at a non-research field site. That level of DNAPL delineation is clearly invaluable for optimizing source zone remediation efforts.

¹⁹ The DyeLIF rods are pre-strung with the dye injection tubing and the LIF cables. A separate set of rods that are not pre-strung with the DyeLIF cables were used for grouting purposes.

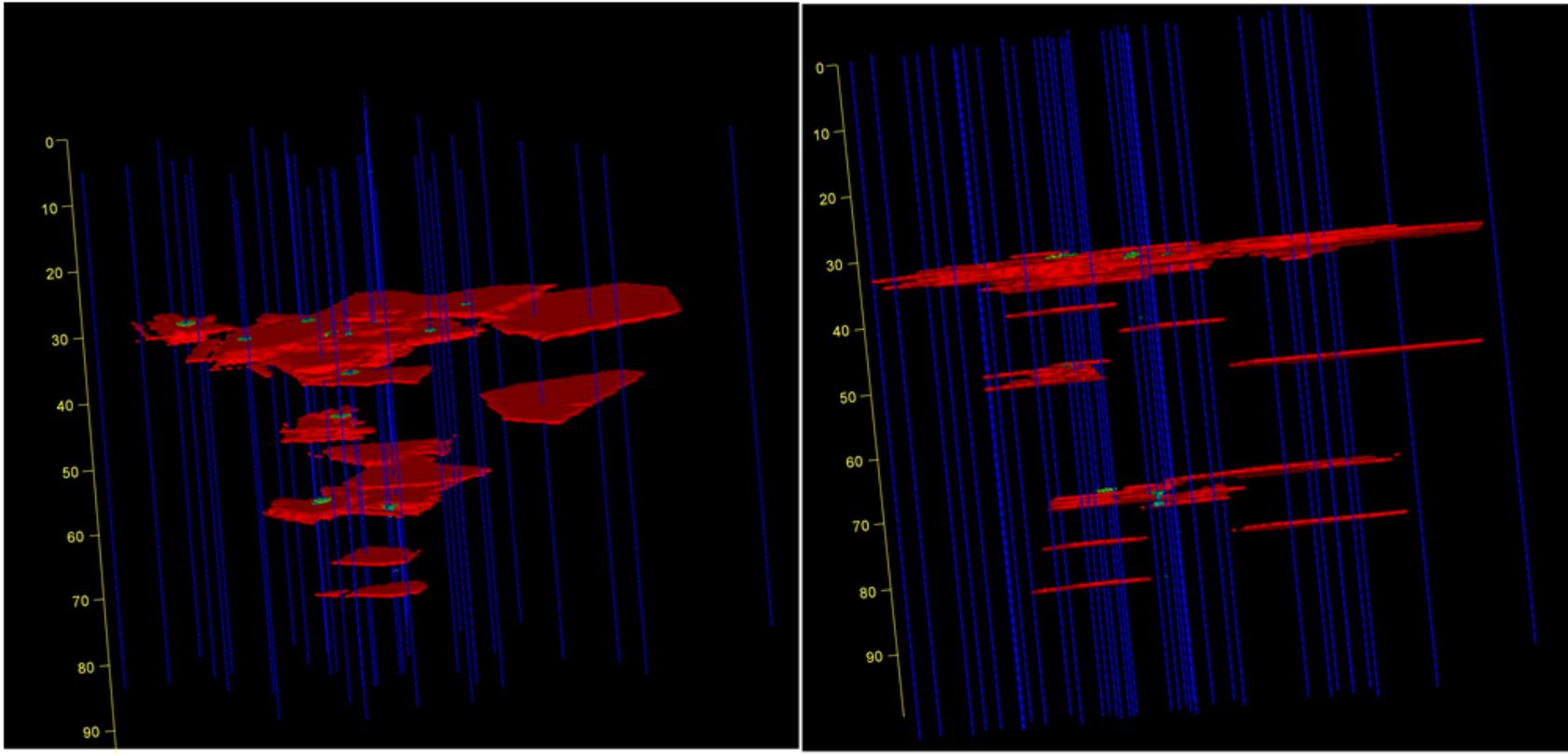


Figure 13. Three-dimensional graphical depiction of DNAPL source zone at demonstration site.

7.0 COST ASSESSMENT

7.1 COST MODEL

The cost model for the DyeLIF tool is straightforward and includes two components. The first component is the daily rate for DyeLIF. Based on the success of this demonstration project, Dakota began to offer the DyeLIF tool commercially in summer 2014. DyeLIF is offered from Dakota for a rate of \$3,500 per day. This includes the DyeLIF equipment and an operator from Dakota to operate the DyeLIF system. Dakota's equipment and services are typically used in conjunction with a Geoprobe or CPT rig that is retained locally. While Dakota can provide Geoprobe® services for projects located within driving distance from Fargo, North Dakota, it is more common for Dakota to ship the DyeLIF (or TarGOST) equipment to a given project site and rely on a local DP contractor to provide Geoprobe® or CPT services. For the cost model it is assumed that a local DP rig is provided at a cost of \$1,500/day such that the total cost for the DyeLIF equipment and the DP rig is \$5,000/day. Mobilization costs for DyeLIF range from \$3,500 to \$4,000 depending on logistical challenges. This includes the travel for the DyeLIF operator.

The second component is an assumed daily production rate. As described in previous sections, Dakota maintains a long-term running average production rate for the TarGOST tool. The current running average production rate is approximately 334 feet per day of probing. In the demonstration study, the average production rate exceeded 400 lineal feet of probing per day. This number was inflated somewhat however given that a second rig was used for some of the grouting work. For cost estimating purposes a number of 325 feet per day was selected as a more appropriate production rate assuming one rig does both probing and grouting.

To estimate the cost for a DyeLIF investigation, one can simply divide the total lineal feet of estimated probing by the assumed production rate to determine the estimated number of days required to complete the DyeLIF investigation. For example, if 30 probes advanced to 50 feet bgs were planned for a DyeLIF investigation, the total lineal feet of probing would be 1,500 feet. Dividing this number by the assumed production rate of 325 feet/day yields a total of 4.6 days of probing. Rounding this up to 5 days and multiplying by the daily rate of \$5,000 days yields a total cost of \$25,000 for the DyeLIF investigation. Note that this cost does not include oversight from the site consultant, mobilization fees, utility clearance for probing locations, and any reclamation work required to repair probed locations.²⁰ Because Dakota has the ability to email the DyeLIF logs out to the project team after each push, a single onsite field person from the site consultant's firm is appropriate.

7.2 COST DRIVERS

The primary cost driver for a DyeLIF investigation is the area and depth of the investigation. In Section 8.0 we discuss the use of a near-source transects of MIP probes or groundwater profiling to map high-concentration plume cores. Mapping high-concentration plume cores helps define

²⁰ A more detailed estimate that includes mobilization, per diem, and consultant oversight is included in Section 7.3.

the lateral (perpendicular to groundwater flow) and vertical dimensions of the suspected DNAPL zone that can then be targeted for the DyeLIF investigation. This preliminary step will typically greatly reduce the area and depth of the investigation.

The other cost driver is the spacing of the DyeLIF probes. Because of the complexity of most chlorinated solvent DNAPL source zones we recommend probing offsets on the order of 10 to 20-feet for most sites (i.e. we do not recommend increasing probing offsets in order to decrease the total amount of probing).

7.3 COST ANALYSIS

In Section 1.1, alternative DNAPL characterization technologies are discussed. The technology most comparable to the DyeLIF technology is high-resolution soil sampling and subsequent field screening using dye shake tests. Sub-cores could also be analyzed via an onsite lab with high-throughput chemical analysis (e.g. Direct Sampling Ion Trap Mass Spectrometer [DSITMS]). As described in previous sections, field screening with dye shake tests was performed during the second week of the field demonstration and correlated extremely well with DNAPL impacted intervals.

While the effectiveness of simple dye shake tests and the use of onsite laboratories with high-throughput sample analyses makes high-resolution vertical sampling of continuous cores feasible, there is still a large amount of labor required to collect soil samples at such a high vertical resolution. This limits the overall production rate (i.e., linear feet drilled and sampled per day) that can be achieved. During the field demonstration for example, 121.5 feet of coring was completed over 4.5 days of drilling (average of 27 feet/day). Total core recovery was 70.9 feet (average of 16 feet/day). The production rate was limited somewhat due to experimentation with different coring methods in an attempt to improve core recovery. Therefore, the average production rate during the field demonstration is likely an underestimate of what could typically be achieved per day. However even doubling the production to approximately 50 feet per day is still significantly less than the production rate achieved with the DyeLIF tool.

A cost comparison of high-resolution soil sampling and DyeLIF is included below in **Table 5**. It is assumed that a closed-piston, large-diameter soil sampler (e.g. Geoprobe MC7) would be utilized to provide greater core recovery and enough sample volume to collect multiple samples at each depth interval. It is assumed that PID screening would be completed every 0.167 feet (~5 cm) and that 25% of the PID locations (75 total samples) would undergo dye shake tests and be analyzed with the onsite laboratory. As shown in **Table 5**, due to the higher production rate and higher vertical resolution of the DyeLIF, the costs per data point are significantly lower. The costs per data point for DyeLIF, dye shake test, and onsite laboratory are \$0.40, \$58.67, and \$98.67 per data point, respectively.

Table 5. Cost Comparison of DyeLIF and High-Resolution Soil Sampling

DyeLIF	High Resolution Soil Sampling (50 feet per day assumption)¹
<p>Costs:</p> <ul style="list-style-type: none"> • DyeLIF: \$3,500 • Mobilization: \$700² • DyeLIF operator per diem: \$150 • Geoprobe rig: \$1,500 • Mobilization: \$100³ • Geoprobe operator per diem (2 persons @ \$150/day): \$300 • Consultant field staff (1 person, 10 hours @ \$100/hour): \$1,000 <p>Total Cost: \$7,250</p>	<p>Costs:</p> <ul style="list-style-type: none"> • Geoprobe rig: \$1,500 • Mobilization: \$100³ • Geoprobe operator per diems (2 persons @ \$150/day): \$300 • Consultant field staff (2 persons, 10 hours @ \$100/hour): \$2,000 • Consultant field supplies (VOA vials/equipment): \$500 • Onsite laboratory¹: \$3,000 <p>Total Costs Without lab: \$4,400 Total Cost With Lab: \$7,400</p>
<p>Production Rate:</p> <ul style="list-style-type: none"> • 300 feet of probing per day • Vertical sampling resolution: 0.5 cm • Total data points generated per day (300 feet/0.5 cm): 18,288 data points per day 	<p>Production Rate:</p> <ul style="list-style-type: none"> • 50 feet of probing per day • Vertical PID screening resolution: 0.167 ft (~5 cm) • Total PID screening locations: 300 • Total dye shake and lab samples @ 25%: 75
<p>Cost per Data Point:</p> <ul style="list-style-type: none"> • $\\$7,250/18,288 = \\$0.40/\text{data point}$ 	<p>Cost per Data Point:</p> <ul style="list-style-type: none"> • Dye shake test: $\\$4,400/75 = \\$58.67/\text{data point}$ • Onsite lab sample: $\\$7,400/75 = \\$98.67/\text{sample}$

Notes:

1. Assumes high-throughput onsite lab that can process around 80 samples per day.
2. Assumes mobilization costs of \$3,500 spread out over 5 day event.
3. Assumes \$500 mobilization fee spread out over 5 days.

Another cost that is important to consider is the impact that a DyeLIF investigation would have on remediation costs. More accurate mapping of the DNAPL source zone allows for much more targeted and focused source zone remediation, particularly if in-situ remedial options such as chemical oxidation or thermal treatment are selected (Kueper et al., 2014; Stroo et al., 2012). As described in Section 1.1 a major limitation of the MIP tool and groundwater profiling is the inability to distinguish NAPL from high-concentration dissolved /sorbed phase contamination. This limitation is particularly important when considering our improved understanding of dissolved-phase plume morphology downgradient of DNAPL source zones. Early conceptualizations of dissolved phase plumes predicted that there would be large amounts of homogenization and mixing as contaminants migrated downgradient away from the DNAPL source. However, studies that have employed high-resolution characterization of the dissolved phase plume along one or more transects oriented perpendicular to the groundwater flow direction have shown that hydrodynamic dispersion (mixing) is much less than was originally assumed, and high concentration plume cores can maintain their strength and structure over relatively long travel distances (Einarson et al., 2010; Guilbeault et al., 2005). The implication of this in relation to characterization of DNAPL source zones with MIP or groundwater profiling is that the DNAPL source zone and inferred mass of DNAPL could appear much larger than they actually are because 1) high-concentrations typically extend well downgradient of the residual DNAPL due to limited mixing and 2) MIP/groundwater profiling is unable to differentiate between DNAPL and high concentration dissolved-phase VOCs.

This limitation of MIP and groundwater profiling in terms of DNAPL delineation was apparent at the field demonstration site. Two transects of MIP probes were advanced downgradient of the DNAPL source several years prior to the DyeLIF investigation. The Electron Capture Detector (ECD; the detector specific to chlorinated compounds in the MIP) maxed out along both transects at horizontal and vertical depth intervals corresponding to upgradient DNAPL. MIP probes MIP-114 and MIP-210 along the first transect and MIP-115, MIP-155, MIP-158 and MIP-159 along the second transect all maxed out (**Figure 14**). In addition, a depth-discrete groundwater sample exceeded 10 milligrams per liter of TCE (>1% of solubility, suggesting DNAPL presence) along this second transect. The DNAPL source delineated using DyeLIF was only approximately 15 feet parallel to flow by 45 feet perpendicular to flow in plan-view (**Figure 14**). The second MIP/groundwater sampling transect was approximately 100-feet downgradient of the edge of the DNAPL source. This illustrates how, when using the MIP tool, the DNAPL source zone could be misconstrued as being much larger than it actually is. Therefore, in addition to investigation cost savings, there is the potential for large remediation cost savings by focusing DNAPL source remediation on only the portions of the subsurface that actually contain DNAPL.

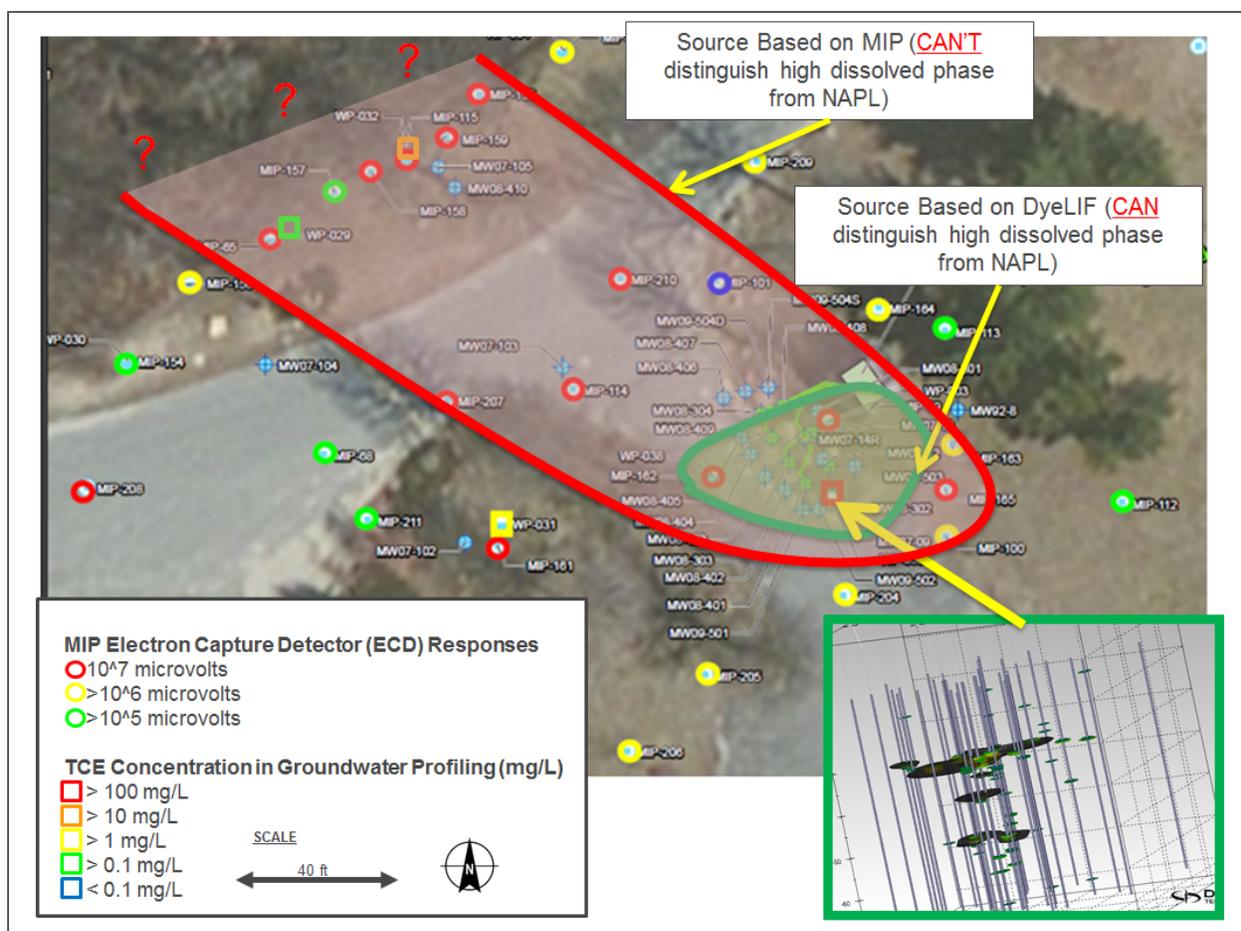


Figure 14. Comparisons of DNAPL source zone delineation using DyeLIF and MIP with depth-discrete groundwater sampling.

While this section has described some of the limitations of MIP and high-resolution soil sampling related to DNAPL source zone investigation, it is noted that these tools are complementary to the DyeLIF technology if utilized correctly. For example, mapping the high-concentration dissolved-phase plume cores downgradient of DNAPL source zones can result in a more focused DNAPL investigation using DyeLIF. Because of the limited mixing of the dissolved-phase plume that occurs downgradient of the DNAPL, a near-source transect of MIP probes and/or high resolution groundwater sampling using profiler tools (e.g. Waterloo APS™) helps to define the approximate width (i.e., perpendicular to flow) and vertical extent of the DNAPL source zone.

Once the DNAPL source zone has been mapped with DyeLIF, targeted soil sampling can be used to evaluate DNAPL composition and other properties. High-resolution soil sampling can also be used to evaluate the extent that dissolved-phase VOCs have penetrated into adjacent low permeability zones and could serve as a source of back-diffusion following source zone treatment (Adamson et al., 2015; Chapman and Parker, 2005; Parker et al., 2004). The integration of these different high-resolution tools is described in the following section.

The authors of this report believe that the new DyeLIF technology will be a “game-changer” for characterizing DNAPL sites in the U.S. and around the world. There are many examples where source zone remediation has been performed, only to learn later that only a portion of the residual DNAPL was removed or treated. In response, many remediation system designers now err on the side of conservatism and overdesign source zone remediation systems. The additional and ongoing costs of ineffective and overly conservative source zone remediation are staggering. EPA estimates that \$209B is needed to fully remediate hazardous waste sites in the U.S. (USEPA 2004). An expert panel with the National Research Council (NRC) considers that figure an underestimate of the actual costs that will be incurred, partially because the distribution of the sources of the contamination remains undefined (National Research Council 2013). The NRC authors stress that improved long-term management of hazardous waste sites requires a much better understanding of the spatial distribution of the contaminants in the subsurface, which can be obtained by the application of emerging diagnostic tools (e.g., DyeLIF). Thus, development and application of the new DyeLIF technology to quickly and fully delineate subsurface DNAPL in three dimensions will likely be a game-changing new site assessment technology that will lead to much more focused and effective source zone remediation programs. The cost savings achieved via better delineation of the remediation targets will likely be measured in billions of dollars.

8.0 TECHNOLOGY IMPLEMENTATION

8.1 POTENTIAL IMPLEMENTATION ISSUES

No major implementation issues were identified during the field demonstration. However a key limitation for any direct-push technology is suitability of the geological conditions for direct-push probing, i.e. absence of cobbles or other conditions that would cause tool damage and preclude advancing the probes. A frequently asked question about the dye is the potential for regulatory resistance to the technology because of the injection of dye as the probe is advanced into the subsurface. The project team does not anticipate regulatory resistance to the technology based on the following:

- The dye is relatively non-toxic (Rat LD50 (intraperitoneal) 4170 mg/kg) and is not a known or suspected carcinogen. From a toxicity standpoint, the dye is therefore similar to fluorescent groundwater tracing dyes that are released in much greater quantities during tracer studies.
- A de minimis quantity of dye is injected (only 0.11 grams per meter of probe penetration).
- Analytical testing on water left in contact with the dye for several days yielded no detectable levels of any listed VOCs or semi-VOCs.
- The dye is extremely hydrophobic and therefore it is expected that there is very little transport of the dye in groundwater away from the probed location.
- Because the DyeLIF tool is used to assess DNAPL in the subsurface, the dye is being injected at a de minimis quantity into a portion of the subsurface that is already heavily impacted by chemicals that are toxic and carcinogenic.

Another potential issue evaluated was that in plastic soils (stiff clays for example) there is potential for the thickness of the dye interaction zone to increase to approximately 1-2mm. Intuition suggests that this thicker layer of dye solution might interfere with sensing of DNAPL globules located in the soil on the far side of the dye layer that is in contact with the soil. Laboratory studies performed at Dakota's facility to investigate this potential issue show that the indicator dye fluid is fairly transparent to the DyeLIF's excitation laser beam. In laboratory tests with a 2mm thick layer of dye solution, there was only a modest (~15%) loss in fluorescence measured at the back of the dye layer vs. the dye in direct contact with the sapphire window (no fluid layer).

8.2 RECOMMENDATIONS FOR TECHNOLOGY IMPLEMENTATION

Based on the technology demonstration and additional work with the DyeLIF technology over the past several years, the project team offers the following recommendations for technology usage:

- As described in Section 1.1, because of the heterogeneity of NAPL source zones, the majority of dissolved phase contamination migrating away from the source zone is typically concentrated in a number of heterogeneous plume cores. Recent high-resolution

characterization studies have shown that the degree of mixing downgradient of source zones is typically minor such that high-concentration plume-cores can maintain their strength and structure over relatively long travel distances (Einarson et al., 2010). A near-source transect of MIP or groundwater profiling probes oriented perpendicular to groundwater flow and located just downgradient of the DNAPL source zone is therefore an excellent first step for defining the DNAPL source zone architecture. Because of the limited mixing that occurs, the plume-cores can be traced back upgradient to the suspected DNAPL source zones. This exercise therefore helps to define the approximate depth and width (perpendicular to flow) of the DNAPL in the subsurface. A grid of DyeLIF borings can then be used to quickly determine the full three-dimensional extent of the DNAPL and differentiate between high-concentration dissolved-phase plume-cores and DNAPL. Guilbeault et al. (2005) detail an excellent case study demonstrating the benefits of a near-source transect for initial DNAPL delineation.

- Because of the complexity of DNAPL source zones, the project team recommend against a “step-out” approach where a single “clean” probe is used to delineate the boundary of the DNAPL source zone. During the field demonstration for this project, a few “clean” (i.e. DNAPL absent) DyeLIF probes were advanced within the overall areal extent of the DNAPL source zone. The field team should therefore remain committed to completing a grid of DyeLIF locations that corresponds to the width and depth of the high-concentration, dissolved-phase plume cores. As an added layer of conservatism, two clean DyeLIF probes (as opposed to one) could be used to define the perimeter of the DNAPL source zone.
- This demonstration project has documented that DyeLIF is significantly more efficient than high-resolution soil sampling in delineating the three-dimensional distribution of DNAPL in the subsurface. Unlike DyeLIF, however, chemical analysis of soil samples yields quantitative information about the concentration and composition of the DNAPL as well as information on the phases (dissolved / sorbed / DNAPL) of contamination instead of focusing only on DNAPL presence / absence. It also provides important information on contaminant distribution including presence of contaminant mass in low-permeability zones, which is a key factor in remediation effectiveness. Consequently, the project team recommends that high-resolution soil sampling be performed at select depths and locations indicated by the DyeLIF results to determine the exact chemical composition of the DNAPL and the overall contaminant distribution. Targeting invasive soil sampling on intervals/locations where DyeLIF indicates that DNAPL is present would result in significant cost savings.²¹
- Finally, high-resolution soil sampling and groundwater profiling should be performed adjacent to a select number of DyeLIF probes where DyeLIF indicates DNAPL pools are located adjacent to low-permeability zones. This will help determine the extent to which VOCs have diffused into the low permeability and estimate the amount of back diffusion that may occur after DNAPL has been removed from the accessible, higher permeability

²¹ This is analogous to targeting the depths and locations of groundwater samples based on the results of MIP probing.

zones. See Adamson et al. (2015) and Chapman and Parker (2005) for examples of this approach.

9.0 REFERENCES

- Adamson, D.T. et al., 2015. Characterization and Source History Modeling Using Low-k Zone Profiles at Two Source Areas. *Groundwater Monitoring & Remediation*, 35(2): 52-69.
- Basu, N.B., Fure, A.D. and Jawitz, J.W., 2008. Simplified contaminant source depletion models as analogs of multiphase simulators. *Journal of contaminant hydrology*, 97(3): 87-99.
- Bumberger, J. et al., 2012. Carry-Over Effects of the Membrane Interface Probe. *Groundwater*, 50(4): 578-584.
- Chapman, S.W. and Parker, B.L., 2005. Plume persistence due to aquitard back diffusion following dense nonaqueous phase liquid source removal or isolation. *Water Resources Research*, 41(12): n/a-n/a.
- Christ, J.A., Lemke, L.D. and Abriola, L.M., 2005. Comparison of two-dimensional and three-dimensional simulations of dense nonaqueous phase liquids (DNAPLs): Migration and entrapment in a nonuniform permeability field. *Water resources research*, 41(1).
- Christ, J.A., Ramsburg, C.A., Pennell, K.D. and Abriola, L.M., 2010. Predicting DNAPL mass discharge from pool-dominated source zones. *Journal of contaminant hydrology*, 114(1): 18-34.
- Christy, T.M., 1996. A Driveable Permeable Membrane Sensor for the Detection of Volatile Compounds in Soil, Tenth National Outdoor Action Conference and Exposition. NGWA, May 13-15, 1996, pp. 169-177.
- Cohen, R.M., Bryda, A.P., Shaw, S.T. and Spalding, C.P., 1992. Evaluation of visual methods to detect NAPL in soil and water. *Groundwater Monitoring & Remediation*, 12(4): 132-141.
- Einarson, M.D., Mackay, D.M. and Bennett, P.J., 2009. Sampling transects for affordable, high-resolution plume characterization and monitoring. *Ground water*, 48(6): 805-808.
- Fure, A.D., Jawitz, J.W. and Annable, M.D., 2006. DNAPL source depletion: Linking architecture and flux response. *Journal of contaminant hydrology*, 85(3): 118-140.
- Griffin, T.W. and Watson, K.W., 2002. A comparison of field techniques for confirming dense nonaqueous phase liquids. *Groundwater Monitoring & Remediation*, 22(2): 48-59.
- Guilbeault, M.A., Parker, B.L. and Cherry, J.A., 2005. Mass and flux distributions from DNAPL zones in sandy aquifers. *Groundwater*, 43(1): 70-86.
- GZA, 2010. Phase IV Status and Remedial Monitoring Report No. 15. October, 2010.
- GZA, 2011. Phase IV Remedy Implementation Plan. February, 2011.
- Kaye, A.J. et al., 2008. Laboratory investigation of flux reduction from dense non-aqueous phase liquid (DNAPL) partial source zone remediation by enhanced dissolution. *Journal of contaminant hydrology*, 102(1): 17-28.
- Kram, M.L., Keller, A.A., Rossabi, J. and Everett, L.G., 2001. DNAPL characterization methods and approaches, Part 1: Performance comparisons. *Groundwater Monitoring & Remediation*, 21(4): 109-123.
- Kueper, B. and Davies, K., 2009. Assessment and delineation of DNAPL source zones at hazardous waste sites, United States Environmental Protection Agency, Publication EPA/600/R-09/119. Washington, DC: Author.
- Kueper, B.H. and Davies, K.L., 2014. DNAPL Source Zone Characterization and Delineation, Chlorinated Solvent Source Zone Remediation. Springer, pp. 63-82.

- Kueper, B.H., Redman, D., Starr, R.C., Reitsma, S. and Mah, M., 1993. A field experiment to study the behavior of tetrachloroethylene below the water table: Spatial distribution of residual and pooled DNAPL. *Groundwater*, 31(5): 756-766.
- Kueper, B.H., Stroo, H.F., Vogel, C.M. and Ward, C.H., 2014. Chlorinated solvent source zone remediation. Springer.
- Lemke, L.D., Abriola, L.M. and Goovaerts, P., 2004. Dense nonaqueous phase liquid (DNAPL) source zone characterization: influence of hydraulic property correlation on predictions of DNAPL infiltration and entrapment. *Water Resources Research*, 40(1).
- Lutenegger, A.J. and DeGroot, D.J., 1995a. Techniques for sealing cone penetrometer holes. *Canadian Geotechnical Journal*, 32: 880-891.
- Mariner, P.E., Jin, M. and Jackson, R.E., 1997. An algorithm for the estimation of NAPL saturation and composition from typical soil chemical analyses. *Groundwater Monitoring & Remediation*, 17(2): 122-129.
- McAndrews, B., Heinze, K. and DiGuseppi, W., 2003. Defining TCE plume source areas using the membrane interface probe (MIP). *Soil and sediment contamination*, 12(6): 799-813.
- National Research Council (NRC), 2013. *Managing the Nation's Complex Contaminated Groundwater Sites*. National Academies Press.
- Oostrom, M., Hofstee, C., Walker, R. and Dane, J., 1999. Movement and remediation of trichloroethylene in a saturated heterogeneous porous medium: 1. Spill behavior and initial dissolution. *Journal of Contaminant Hydrology*, 37(1): 159-178.
- Park, E. and Parker, J., 2005. Evaluation of an upscaled model for DNAPL dissolution kinetics in heterogeneous aquifers. *Advances in Water Resources*, 28(12): 1280-1291.
- Parker, B., Cherry, J., Chapman, S. and Guilbeault, M., 2003. Review and analysis of chlorinated solvent dense nonaqueous phase liquid distributions in five sandy aquifers. *Vadose Zone Journal*, 2(2): 116-137.
- Parker, B.L., Cherry, J.A. and Chapman, S.W., 2004. Field study of TCE diffusion profiles below DNAPL to assess aquitard integrity. *Journal of Contaminant Hydrology*, 74(1): 197-230.
- Pitkin, S.E., Cherry, J.A., Ingleton, R.A. and Broholm, M., 1999. Field Demonstrations Using the Waterloo Ground Water Profiler. *Ground Water Monitoring and Remediation*, 19(2): 122-131.
- Ravella, M., Fiacco Jr, R.J., Frazier, J., Wanty, D. and Burkhardt, L., 2007. Application of the membrane interface probe (MIP) to delineate subsurface DNAPL contamination. *Environmental Engineer: Applied Research and Practice*, 1.
- Stroo, H.F. et al., 2012. Chlorinated ethene source remediation: Lessons learned. *Environmental science & technology*, 46(12): 6438-6447.
- USEPA, 1997. *Expedited Site Assessment Tools for Underground Storage Tank Sites—A Guide for Regulators*. 510-B-97-001.
- USEPA, 2004. *Cleaning Up the Nation's Waste Sites: Markets and Technology Trends*. 542-R-04-015.
- Zapico, M.M., Vales, S. and Cherry, J.A., 1987. A wireline piston core barrel for sampling cohesionless sand and gravel below the water table. *Groundwater Monitoring & Remediation*, 7(3): 74-82.

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- Steve Posten of AMEC for technical support.

Appendix A: Points of Contact

POINT OF CONTACT	ORGANIZATION	PHONE EMAIL	PROJECT ROLE
Murray Einarson	Haley & Aldrich 1956 Webster Street Suite 450 Oakland, CA 94612	650-400-0248 meinaron@haleyaldrich.com	Principal Investigator (PI)
Dr. Adrian Fure		510-693-0139 afure@haleyaldrich.com	Co-PI
Randy St. Germain	Dakota Technologies 2201-A 12 th St. N Fargo, ND 58102	701-237-4908 stgermain@dakotatechnologies.com	Co-PI; service provider of DyeLIF
Dr. Beth Parker	G360 Centre for Applied Groundwater Research School of Engineering University of Guelph 50 Stone Road East Guelph, Ontario, N1G 2W1, Canada	519-824-4120 x53642 bparker@g360group.org	Co-PI
Steven Chapman		506-847-2379 schapman@g360group.org	Co-PI; Field lead for detailed soil coring

Appendix B: Additional Details on Soil Sampling Methods

B.1 FIELD QA/QC PROCEDURES

B.1.1 CALIBRATION OF ANALYTICAL EQUIPMENT

The only field analytical equipment used during the field trials was a photoionization detector (PID). A MiniRAE 3000 PID was utilized for the field trial. The instrument was calibrated each day per the manufactures instructions using a fresh air reading and calibration gas (isobutylene at 100 parts per million) provided by instrument rental company.

B.1.2 QUALITY ASSURANCE SAMPLING

The following quality assurance (QA) samples were collected:

- **Trip Blanks:** one trip blank sample was included with each cooler shipped to the laboratory. There were no VOCs detected in the trip blanks.
- **Duplicates:** seven duplicate samples were collected (approximately 5% of all samples collected).
- **Equipment Blanks:** No equipment blanks were collected because disposable syringes were used in the field.

B.1.3 DECONTAMINATION PROCEDURES

Disposable sampling syringes were utilized so no decontamination of sampling equipment was required. The drilling rods were decontaminated using a stiff bristle brush and a solution of Alconox and water.

B.1.4 SAMPLE DOCUMENTATION

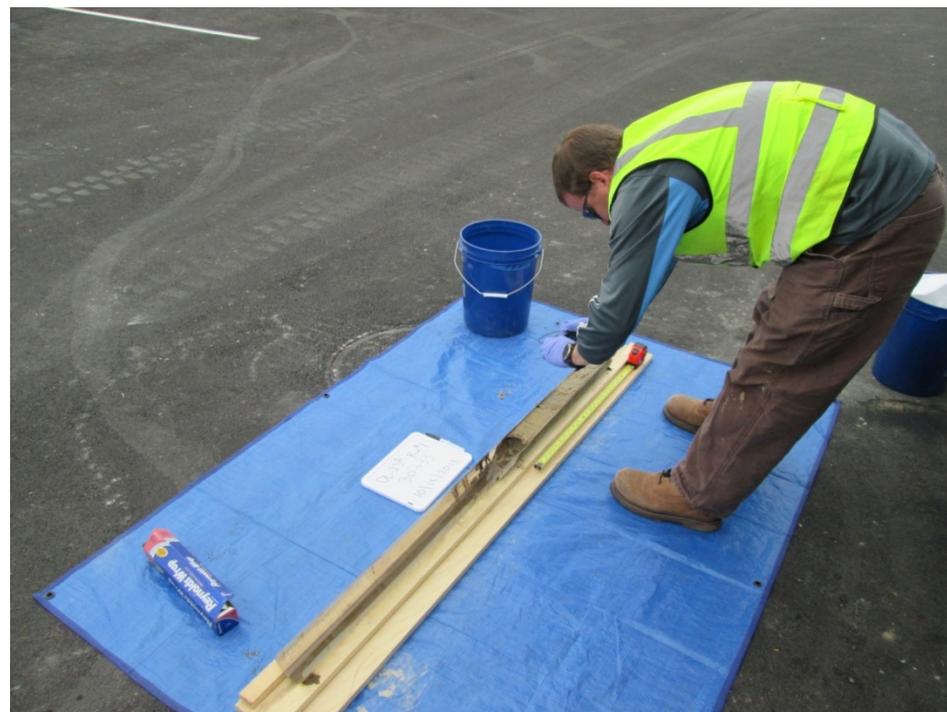
Sample documentation field forms are essentially reproduced in Tables 3 and Table 4. Laboratory samples were submitted with standard chain of custody forms. Each cooler was sealed with a chain of custody seal.

B.2 ADDITIONAL SOIL SAMPLING DETAILS

A series of photographs are included below which summarize the soil sampling procedure. Beneath each photograph is a description of the sampling step displayed in that particular photograph.



Step 1. After the ore is split open, a large drywall tapping knife was used to scrape off the top layer of soil.



Step 2. A photograph of the core was taken. The dry-erase board shown indicates the location ID and core run



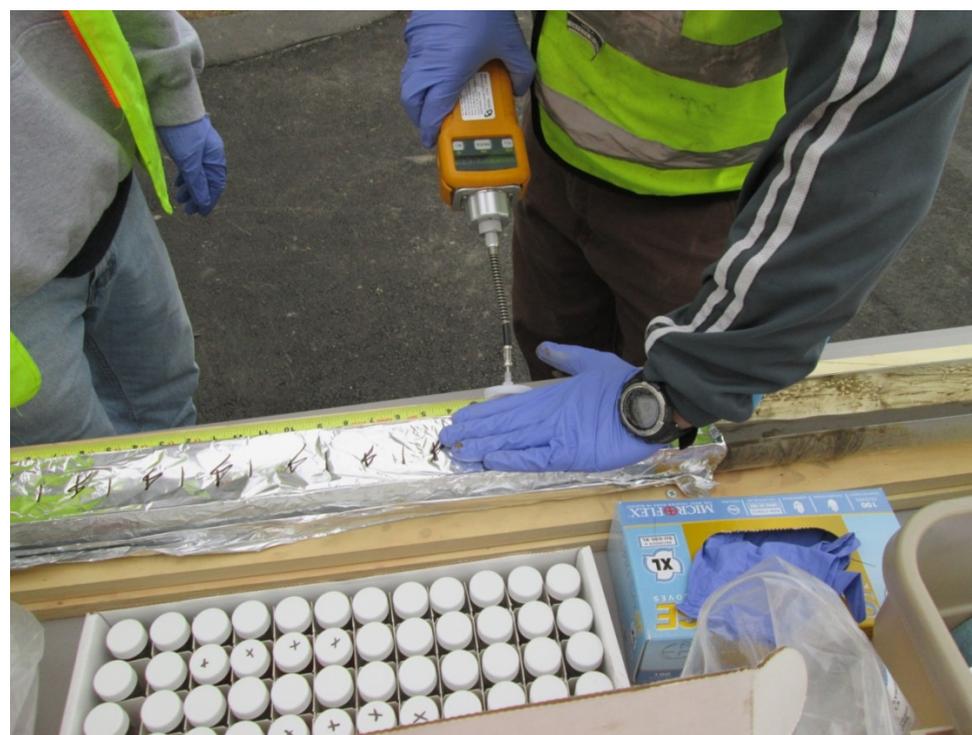
Step 3. After the core was photographed it was quickly covered with foil in order to minimize volatile losses.



Step 4. A marker was used to demarcate the sampling intervals on the aluminum foil. When it was time to sample a particular interval, the foil was pulled back. Four subsamples were collected at each depth interval for laboratory analysis of VOCs, Oil-Red-O dye shake tests, DyeLIF screening, and moisture content.



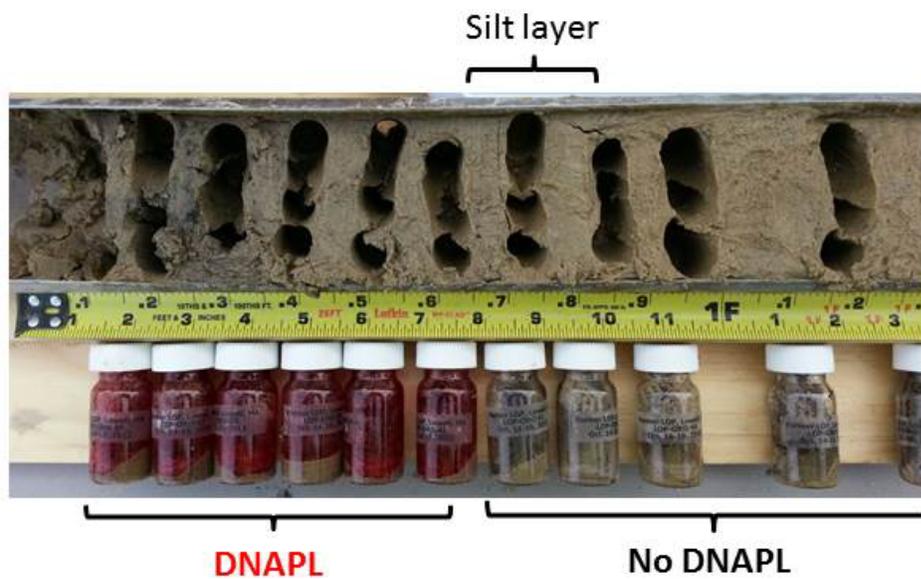
A second person is used to expedite the sampling procedure.



Step 5. After the subsamples are collected, a PID measurement is collected by placing the PID tip in one of the holes made by the subsampling and covering the whole with a plastic glove.



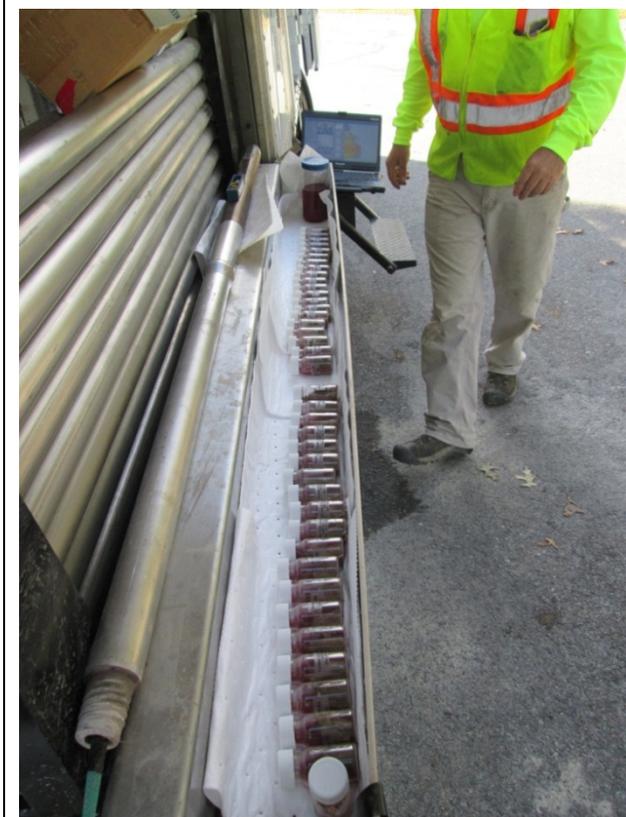
Step 6. After sampling is completed at one depth interval, foil from the next interval is peeled back and the process is repeated.



This photograph is a close-up of a core after the sampling process has been completed. Note the four subcore holes at each interval. The photograph also depicts positive shake test results for the DNAPL.

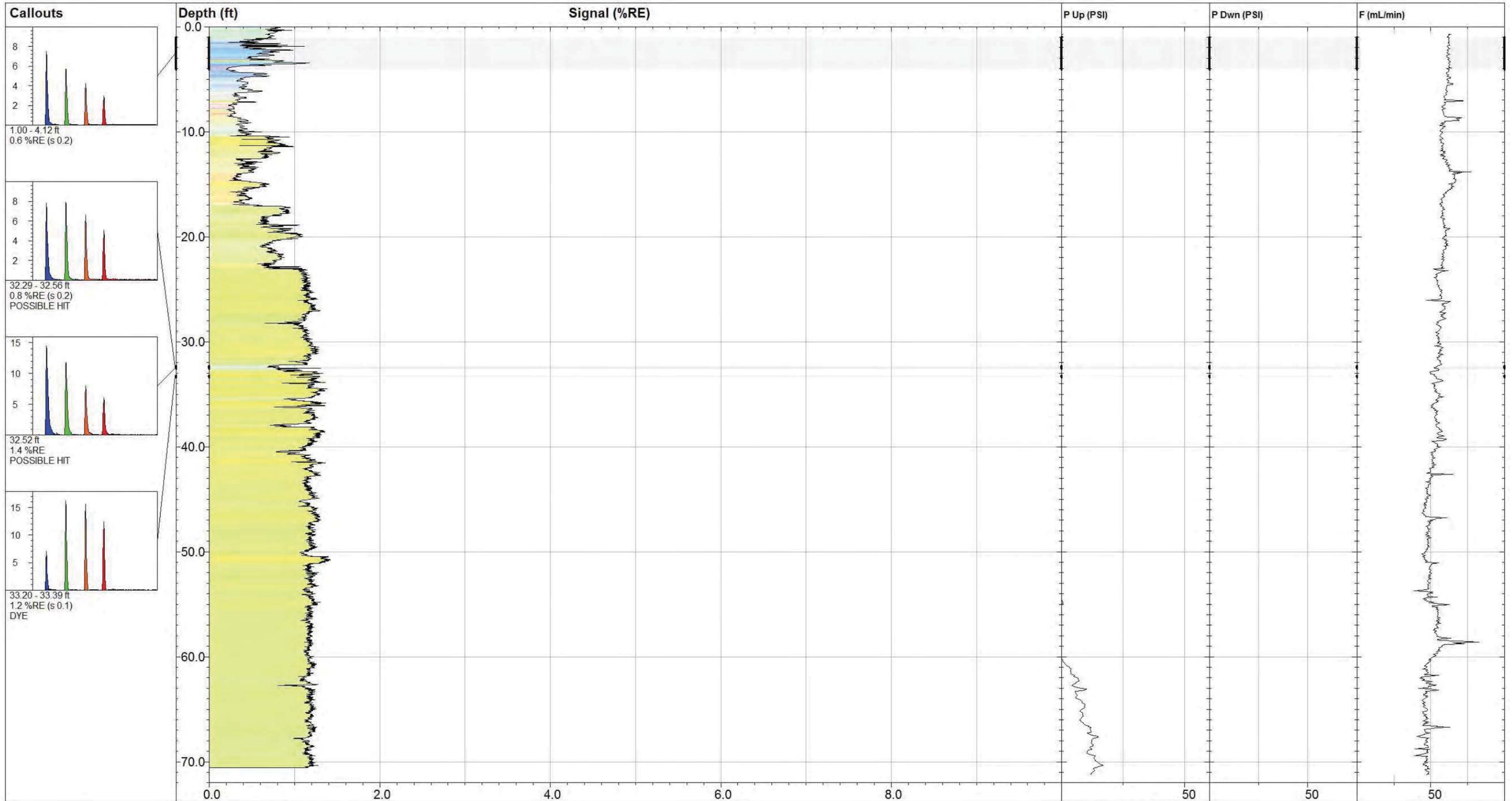


This photograph depicts the procedure used for the aboveground DyeLIF testing. A small amount of dye solution is added to the sample vial and the vial is placed on the probe laser/window and slowly rotated while reading are collected.

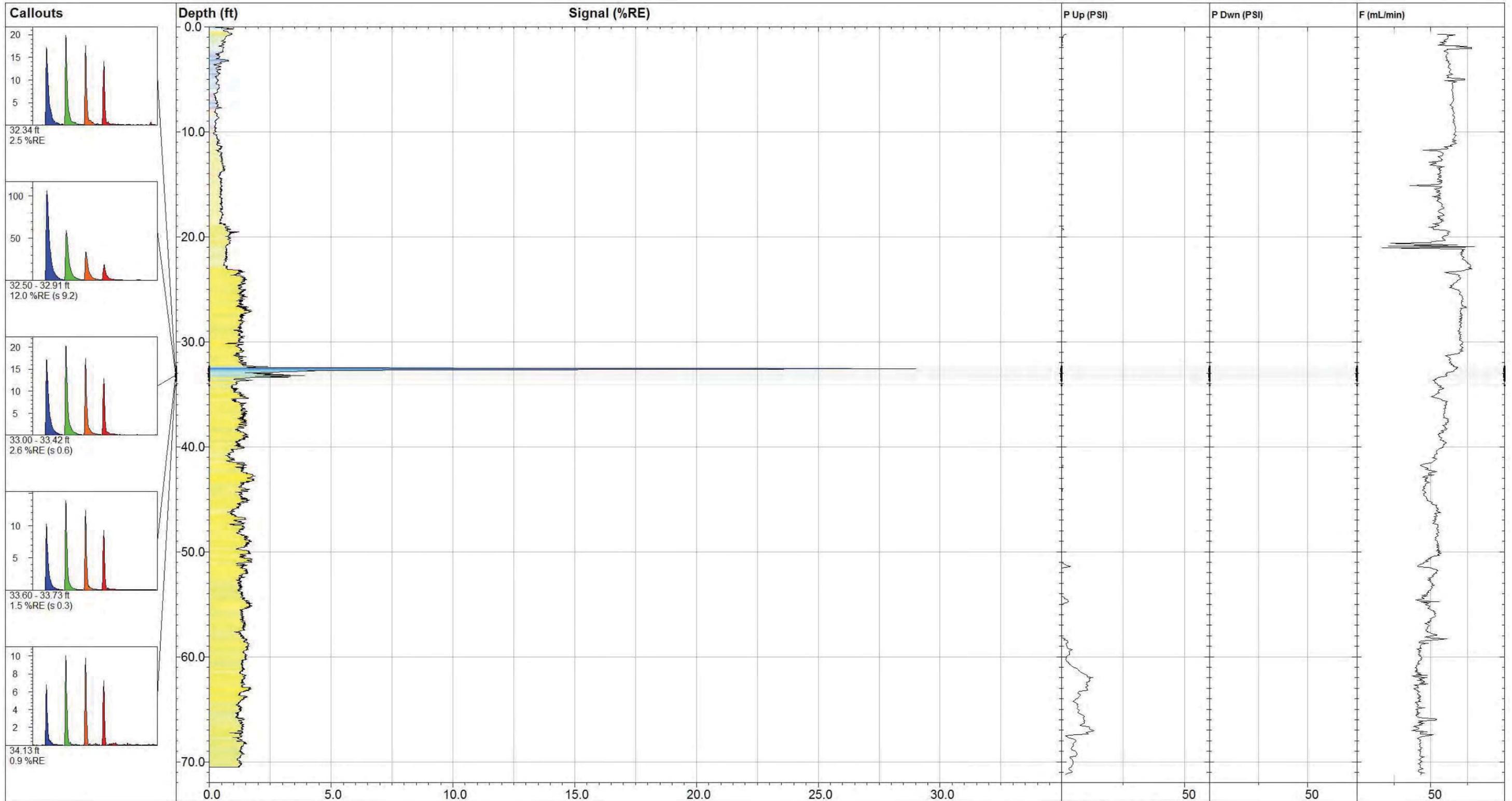


This photograph shows a row of aboveground DyeLIF samples ready for analysis.

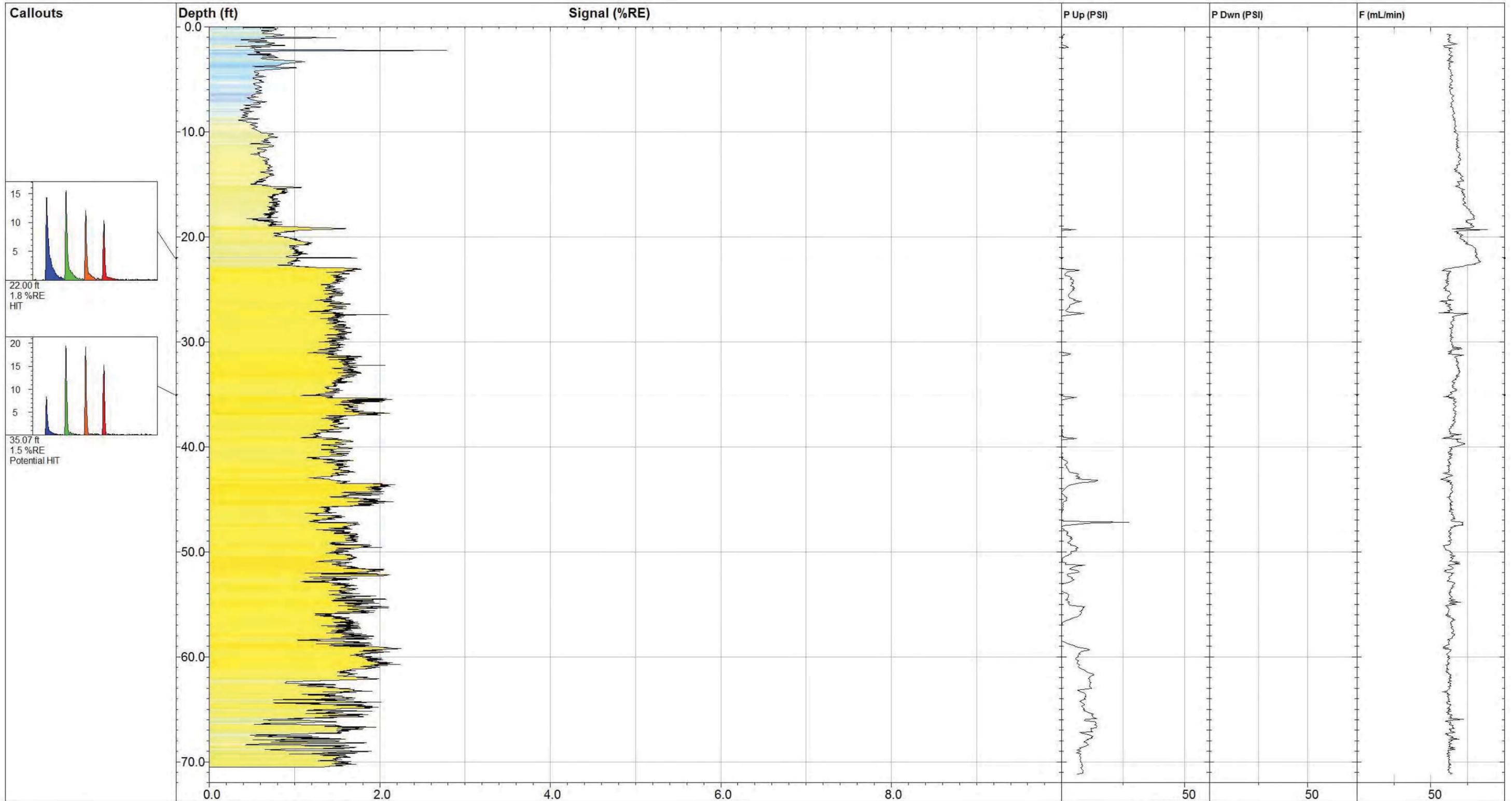
Appendix C: Raw DyeLIF Logs



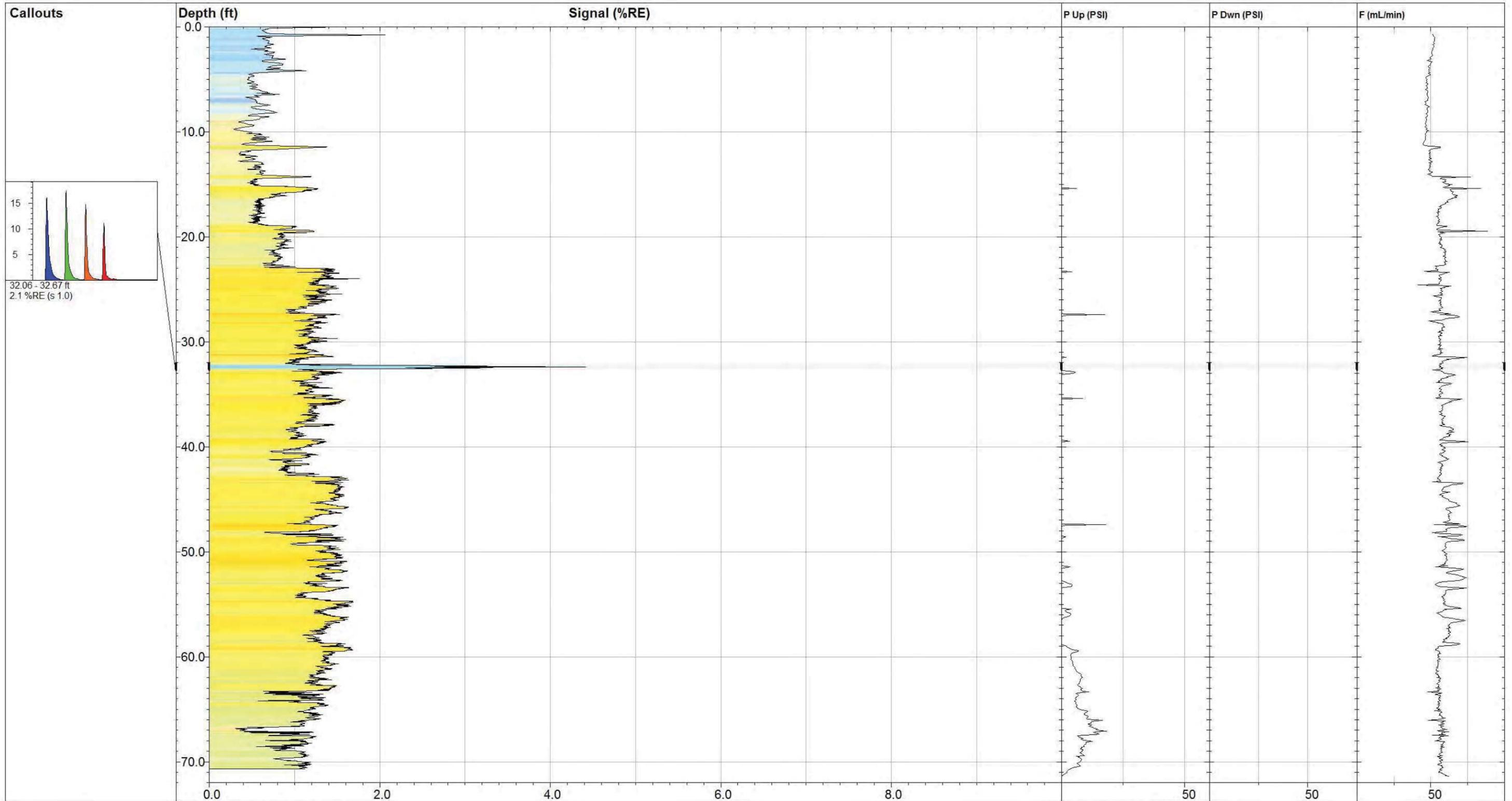
DyeLIF 001		DyeLIF By Dakota www.DakotaTechnologies.com	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047911.6 / SPS	Final depth: 70.55 ft	
Client / Job: ESTCP /	X Coord.(Lng-E) / Fix: 712475.6 /	Max signal: 1.4 %RE @ 50.71 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-07 09:12 CDT	



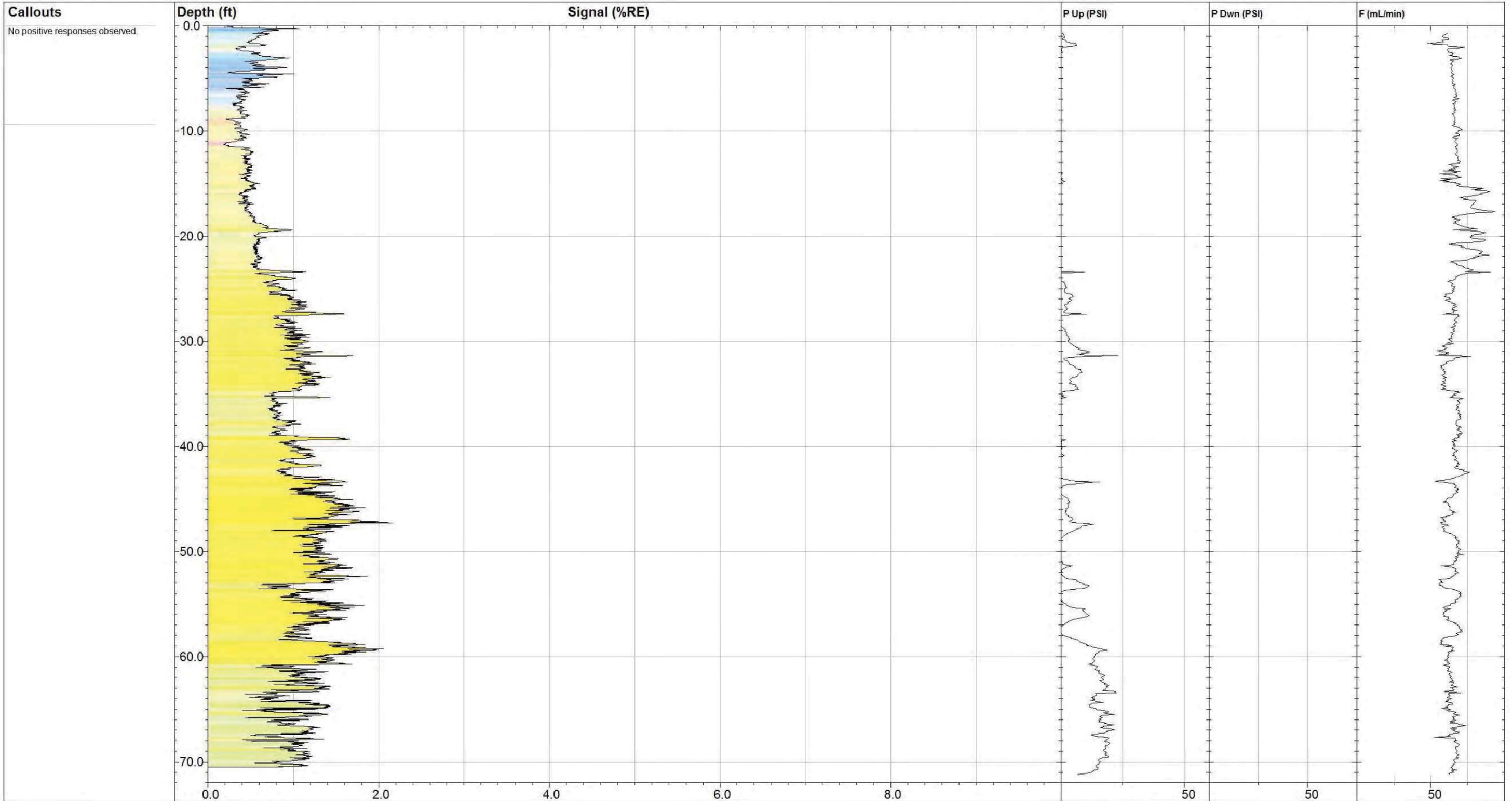
DyeLIF 002		DyeLIF By Dakota www.DakotaTechnologies.com	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047905.6 / SPS	Final depth: 70.51 ft	
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712467.6 I	Max signal: 29.2 %RE @ 32.56 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-07 10:42 CDT	



DyeLIF 002 DUP		DyeLIF By Dakota www.DakotaTechnologies.com	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047911.6 / SPS	Final depth: 70.49 ft	
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712475.6 I	Max signal: 2.8 %RE @ 2.26 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-10 09:35 CDT	



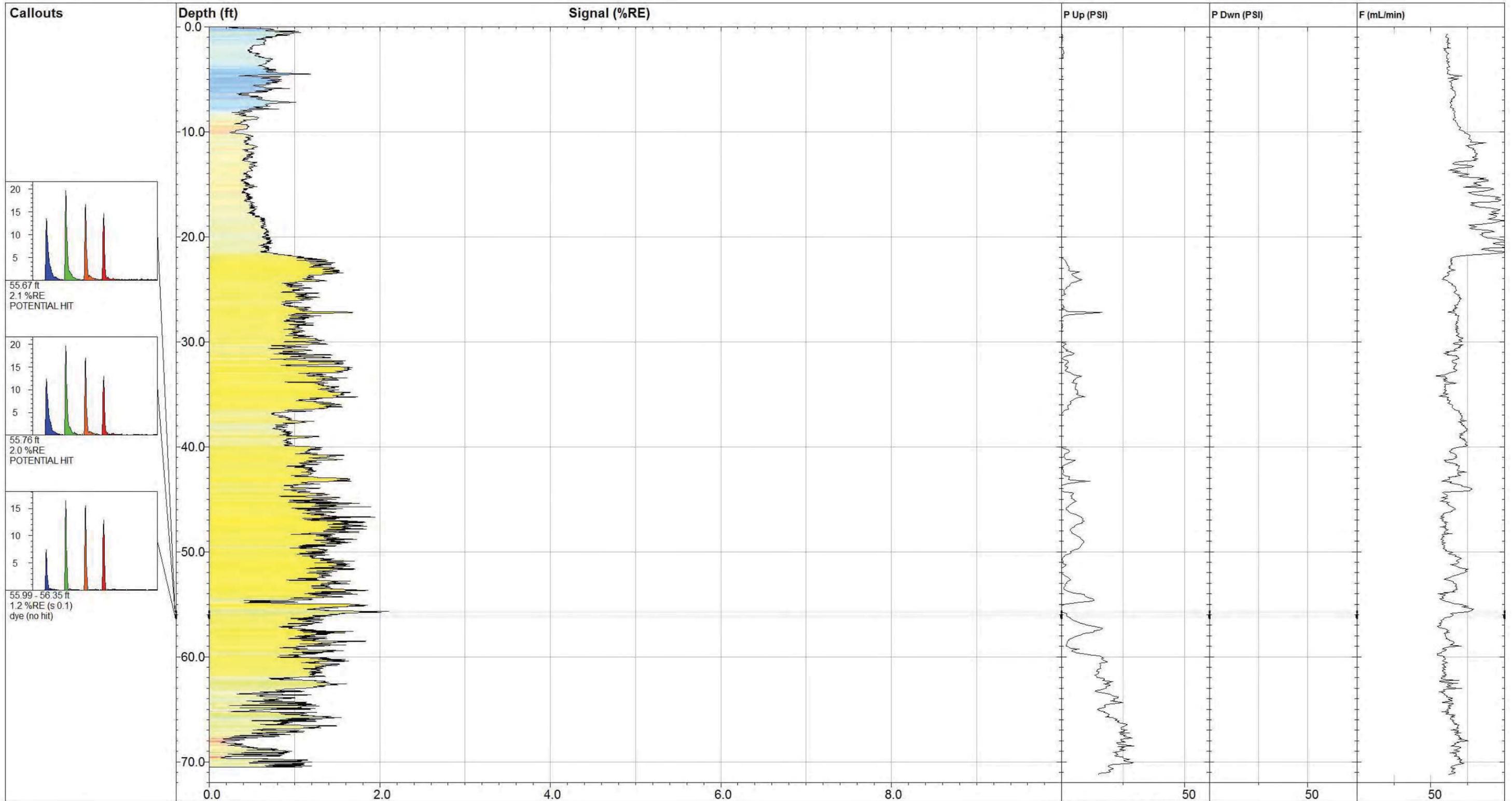
DyeLIF 002 TRIP		DyeLIF By Dakota www.DakotaTechnologies.com	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047911.6 / SPS	Final depth: 70.69 ft	
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712475.6 I	Max signal: 4.9 %RE @ 32.39 ft	
Operator / Unit: RWS/JTL / TG1005	Elevation: Unavailable	Date & Time: 2013-10-16 11:05 EDT	



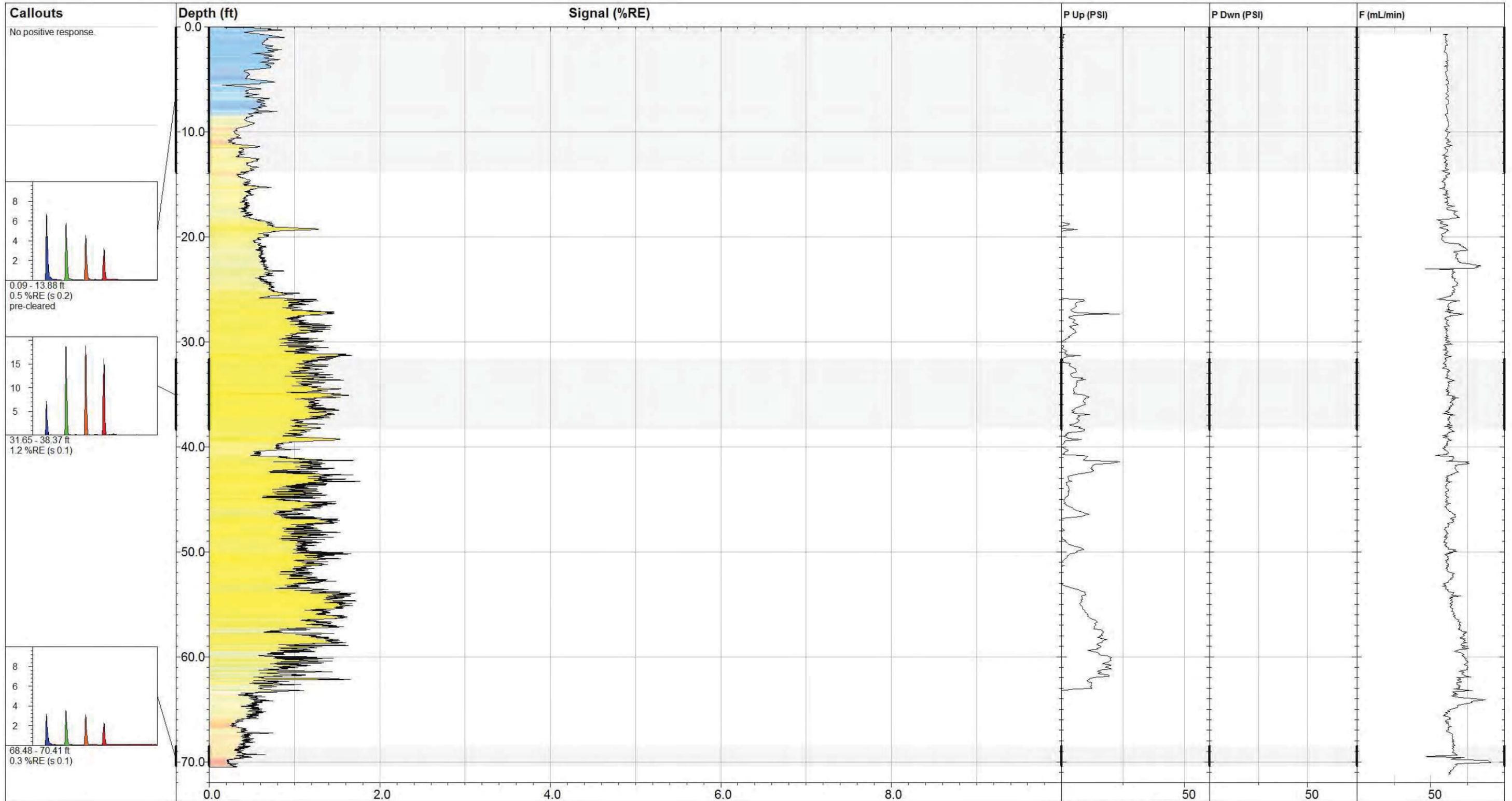
Callouts
No positive responses observed.



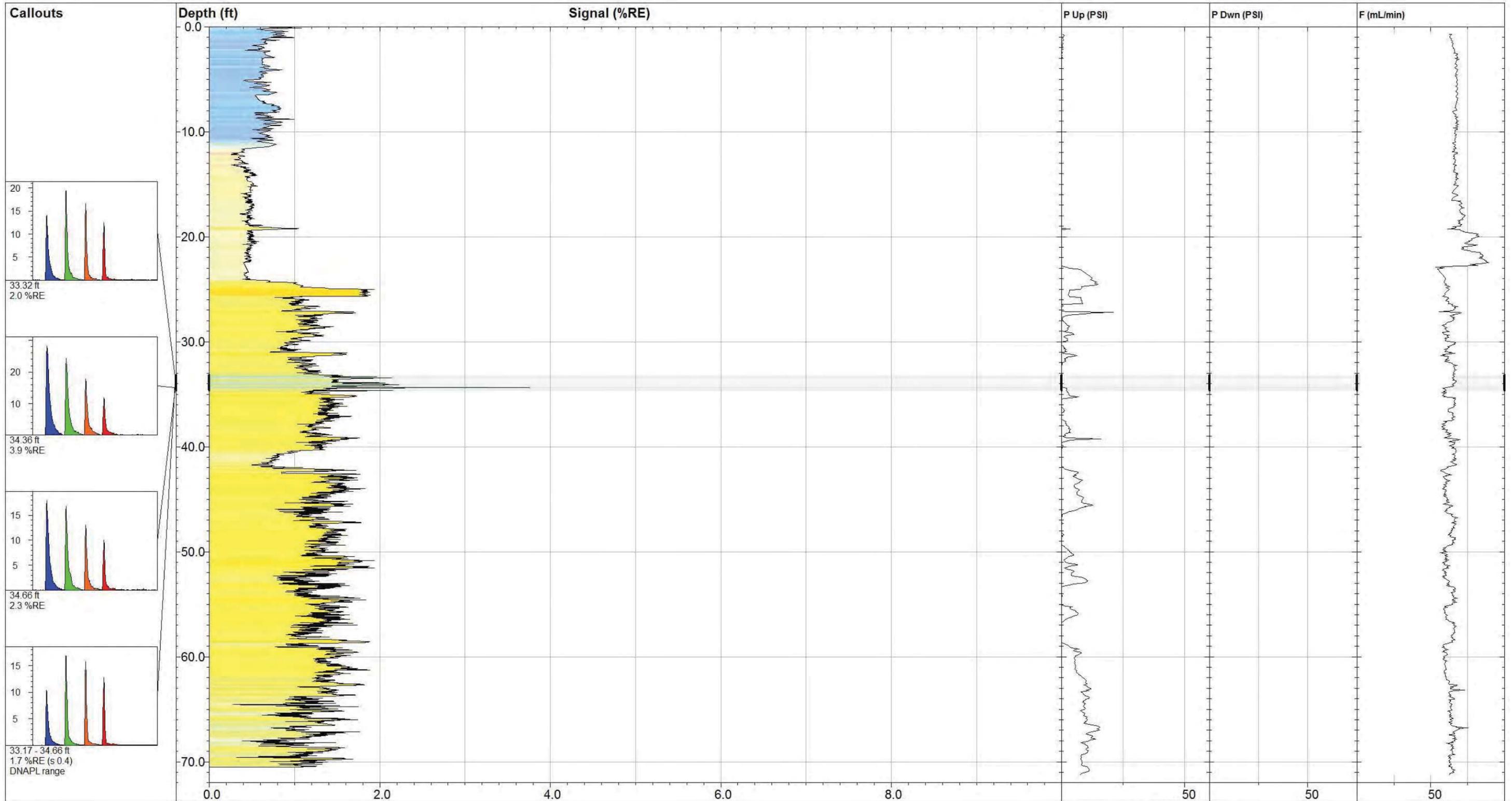
DyeLIF 003		DyeLIF By Dakota <small>www.DakotaTechnologies.com</small>	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047913.2 / SPS	Final depth: 70.50 ft	
Client / Job: ESTCP /	X Coord.(Lng-E) / Fix: 712462.5 /	Max signal: 2.2 %RE @ 47.28 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-07 12:39 CDT	



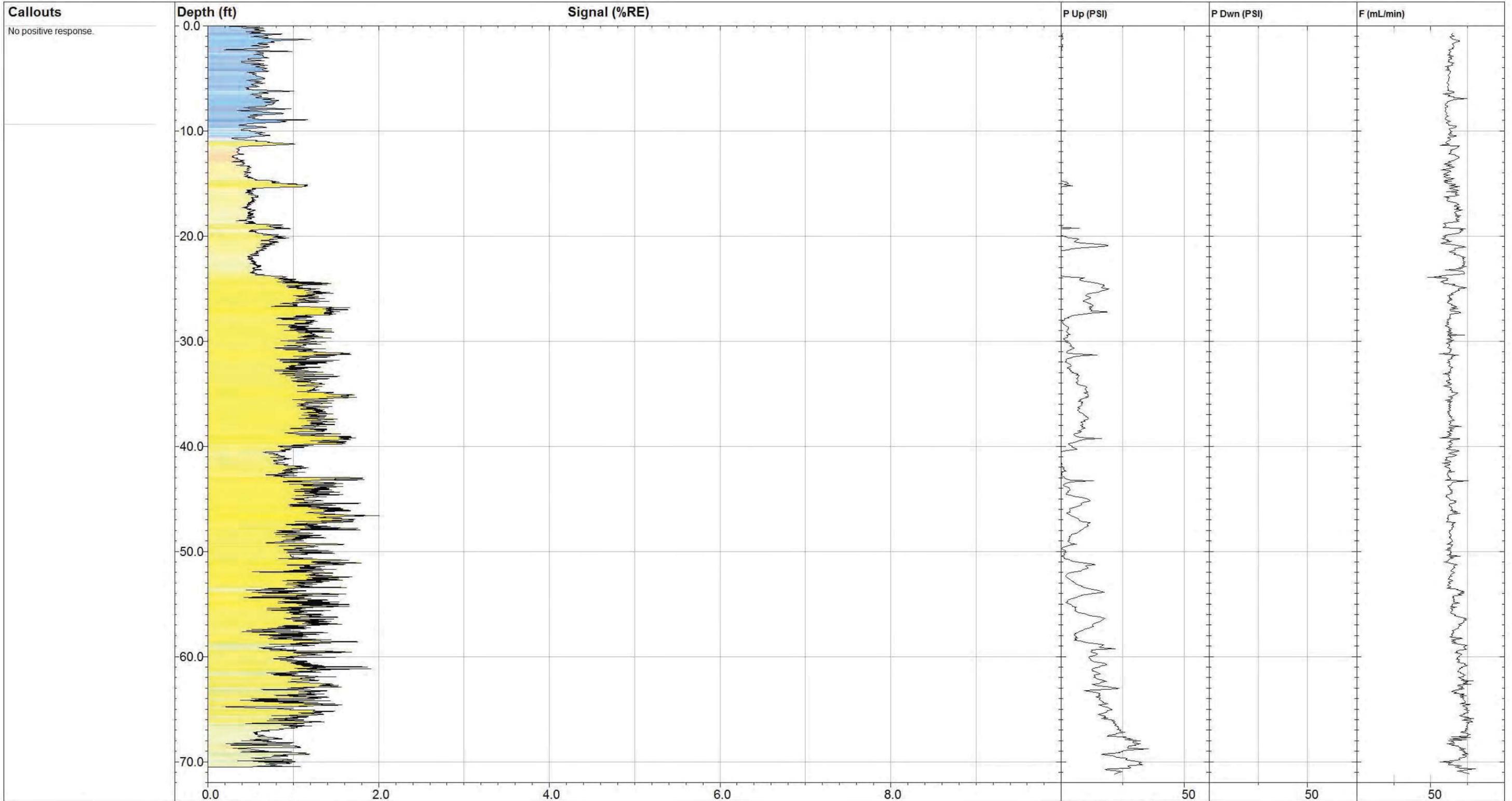
DyeLIF 004		DyeLIF By Dakota www.DakotaTechnologies.com	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047919.1 / SPS	Final depth: 70.52 ft	
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712470.6 I	Max signal: 2.1 %RE @ 55.67 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-07 13:49 CDT	



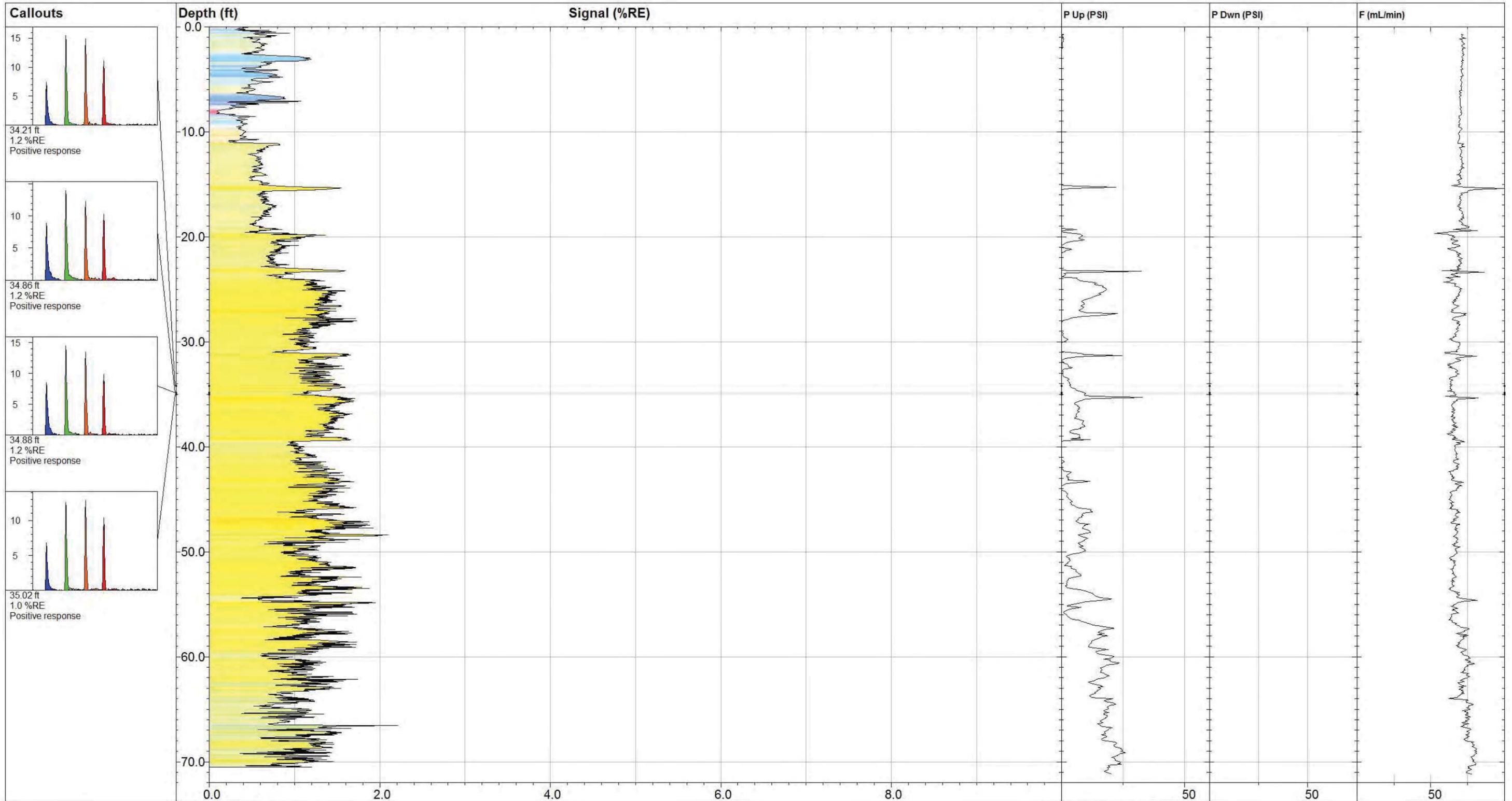
DyeLIF 005		DyeLIF By Dakota www.DakotaTechnologies.com	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047899.6 / SPS	Final depth: 70.52 ft	
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712459.8 I	Max signal: 1.8 %RE @ 43.31 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-08 06:46 CDT	



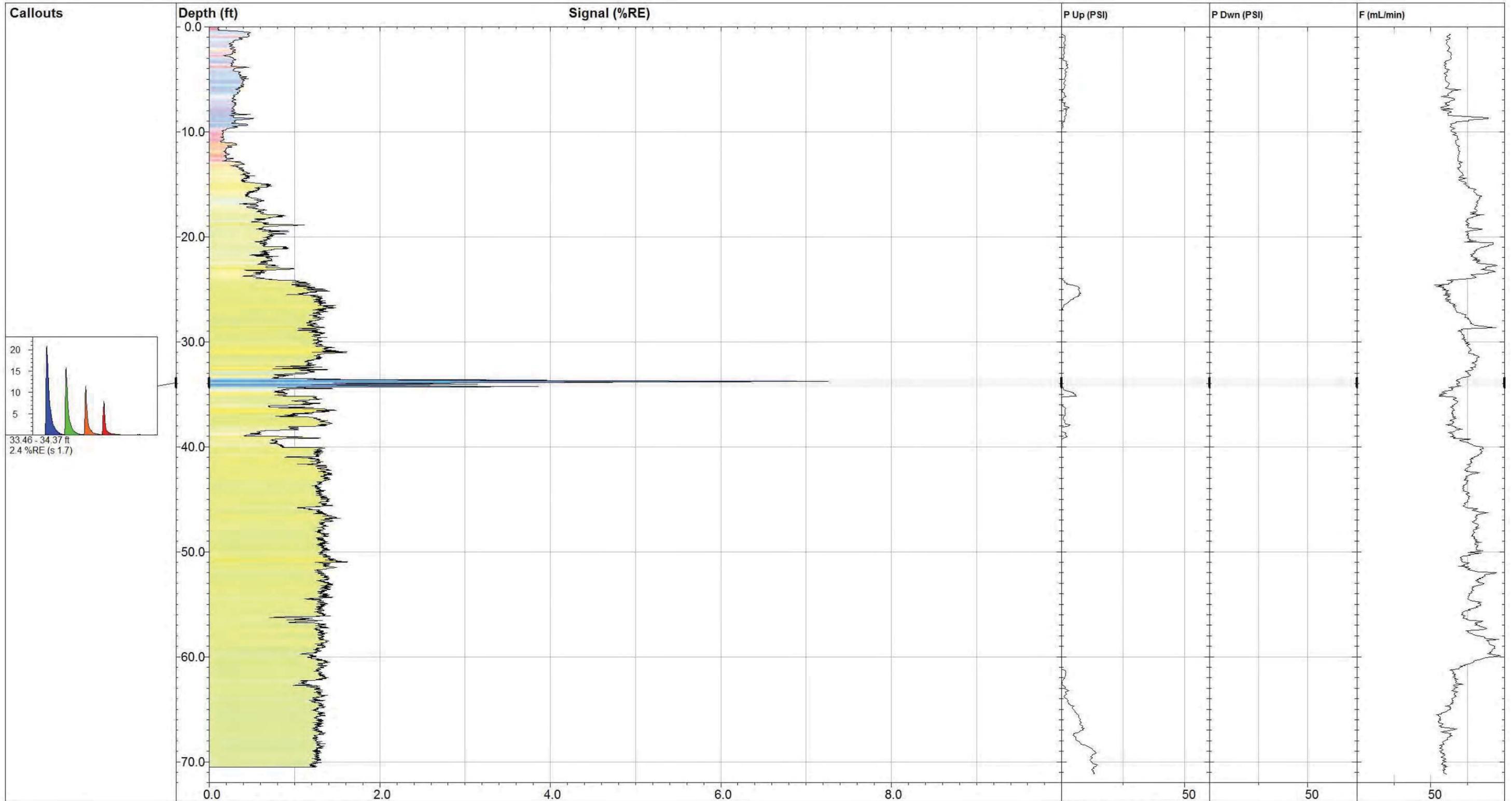
DyeLIF 006		DyeLIF By Dakota www.DakotaTechnologies.com	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047896.6 / SPS	Final depth: 70.52 ft	
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712487.0 I	Max signal: 3.9 %RE @ 34.36 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-08 08:16 CDT	



 DAKOTA TECHNOLOGIES <small>FARGO, ND 701.237.4908 WWW.DAKOTATECHNOLOGIES.COM</small>	DyeLIF 007		DyeLIF By Dakota <small>www.DakotaTechnologies.com</small>
	Site: LOP 2013	Y Coord.(Lat-N) / System: 3047904.5 / SPS	Final depth: 70.49 ft
	Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712501.0 I	Max signal: 2.0 %RE @ 46.60 ft
	Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-08 10:07 CDT



 <p>DAKOTA TECHNOLOGIES FARGO, ND 701.237.4908 WWW.DAKOTATECHNOLOGIES.COM</p>	DyeLIF 008		DyeLIF By Dakota www.DakotaTechnologies.com	
	Site: LOP 2013	Y Coord.(Lat-N) / System: 3047910.1 / SPS	Final depth: 70.51 ft	
	Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712493.4 I	Max signal: 2.2 %RE @ 66.53 ft	
	Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-08 11:47 CDT	

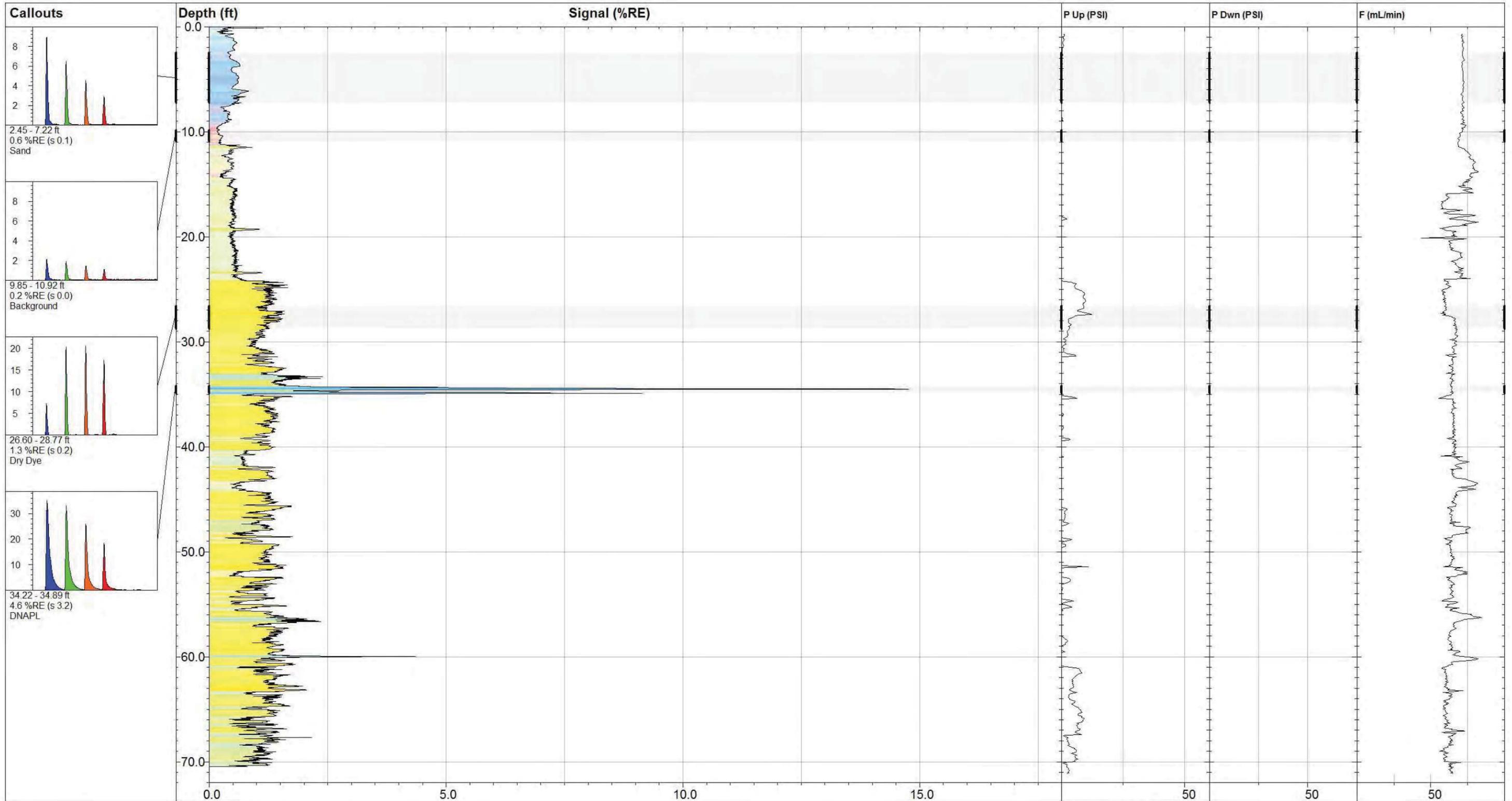


DyeLIF 008 DUP

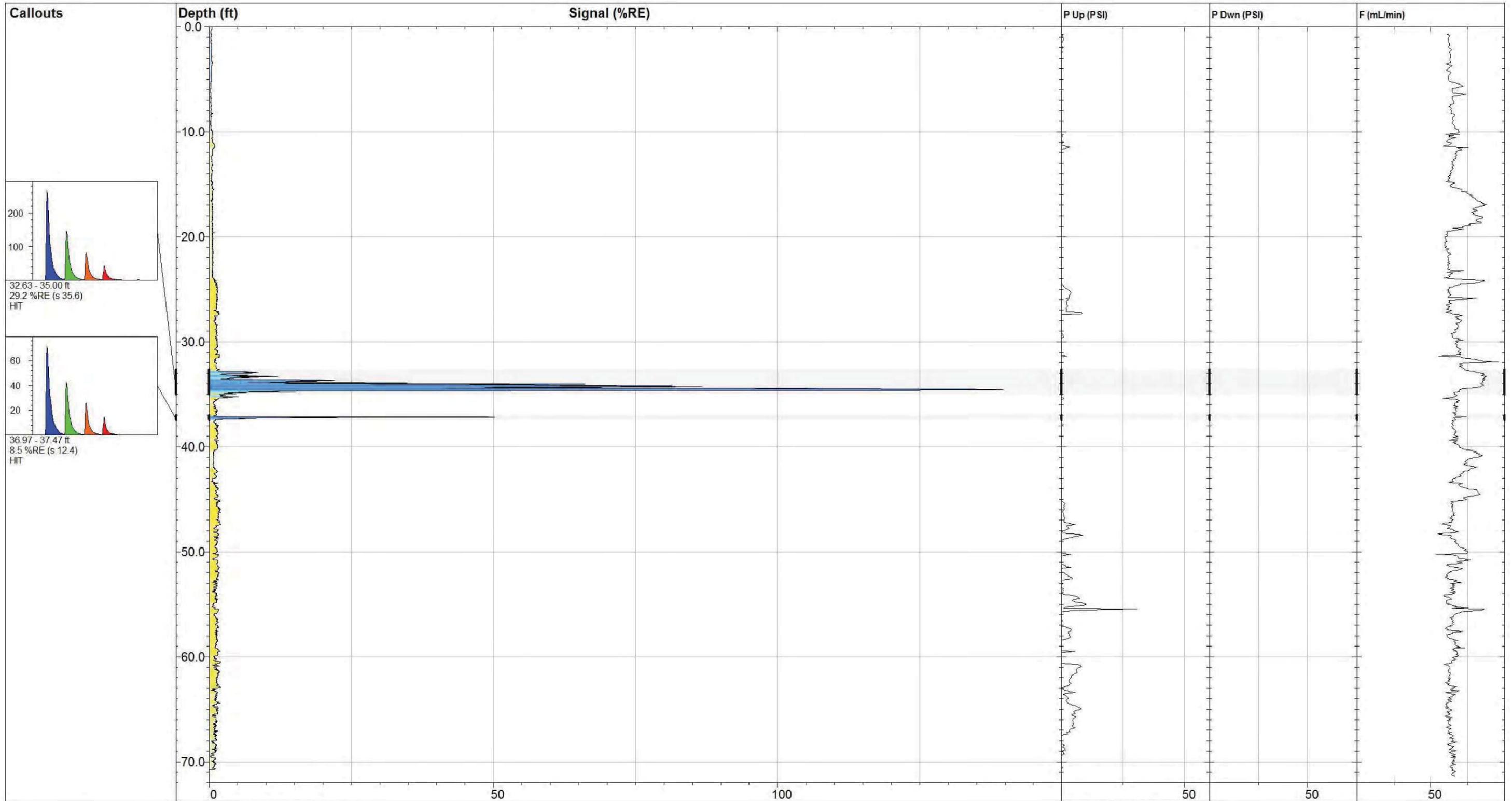
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047911.2 / SPS
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712494.8 I
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable

DyeLIF By Dakota
www.DakotaTechnologies.com

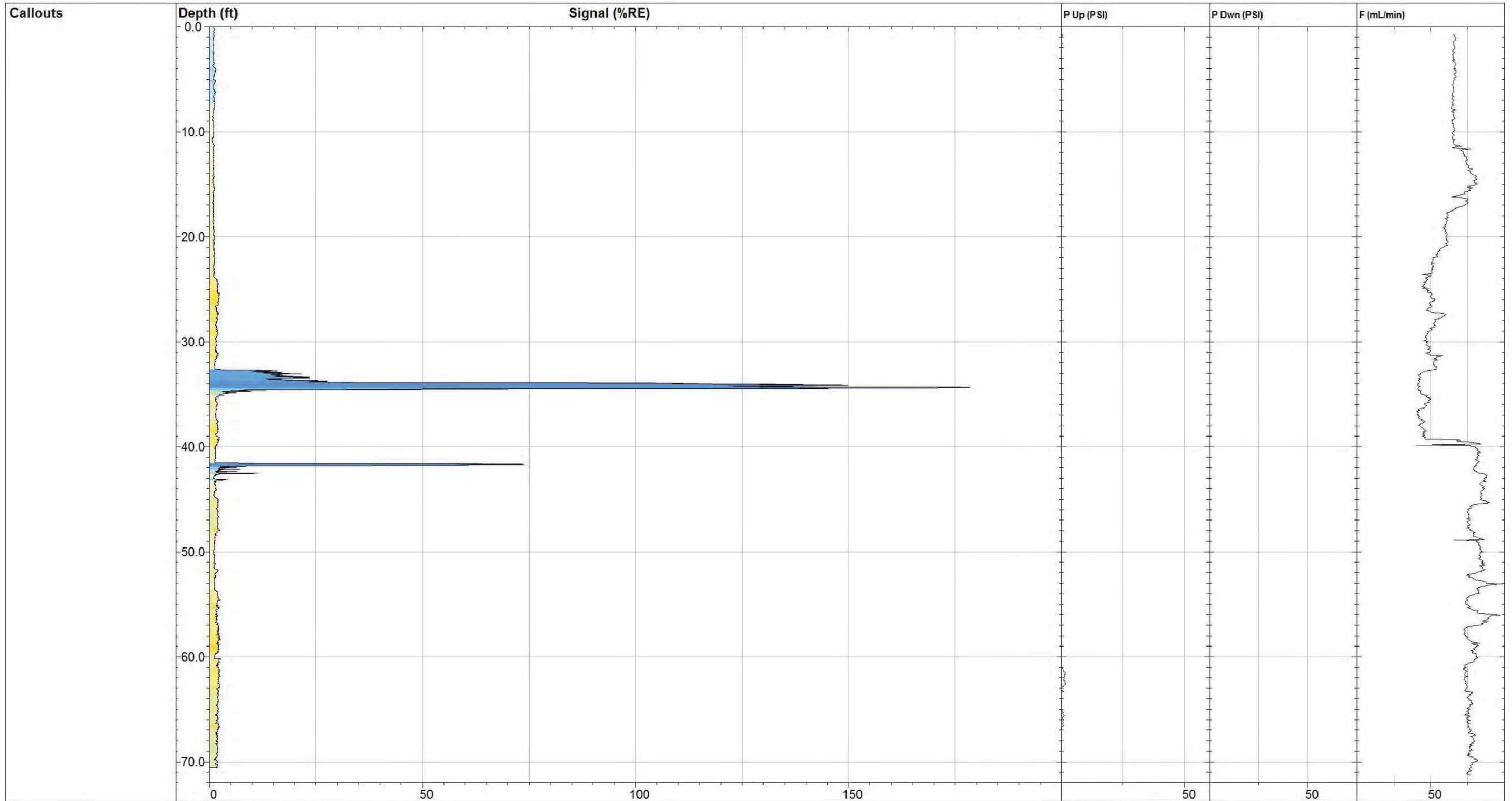
Final depth: 70.51 ft
Max signal: 7.3 %RE @ 33.76 ft
Date & Time: 2013-10-08 13:11 CDT



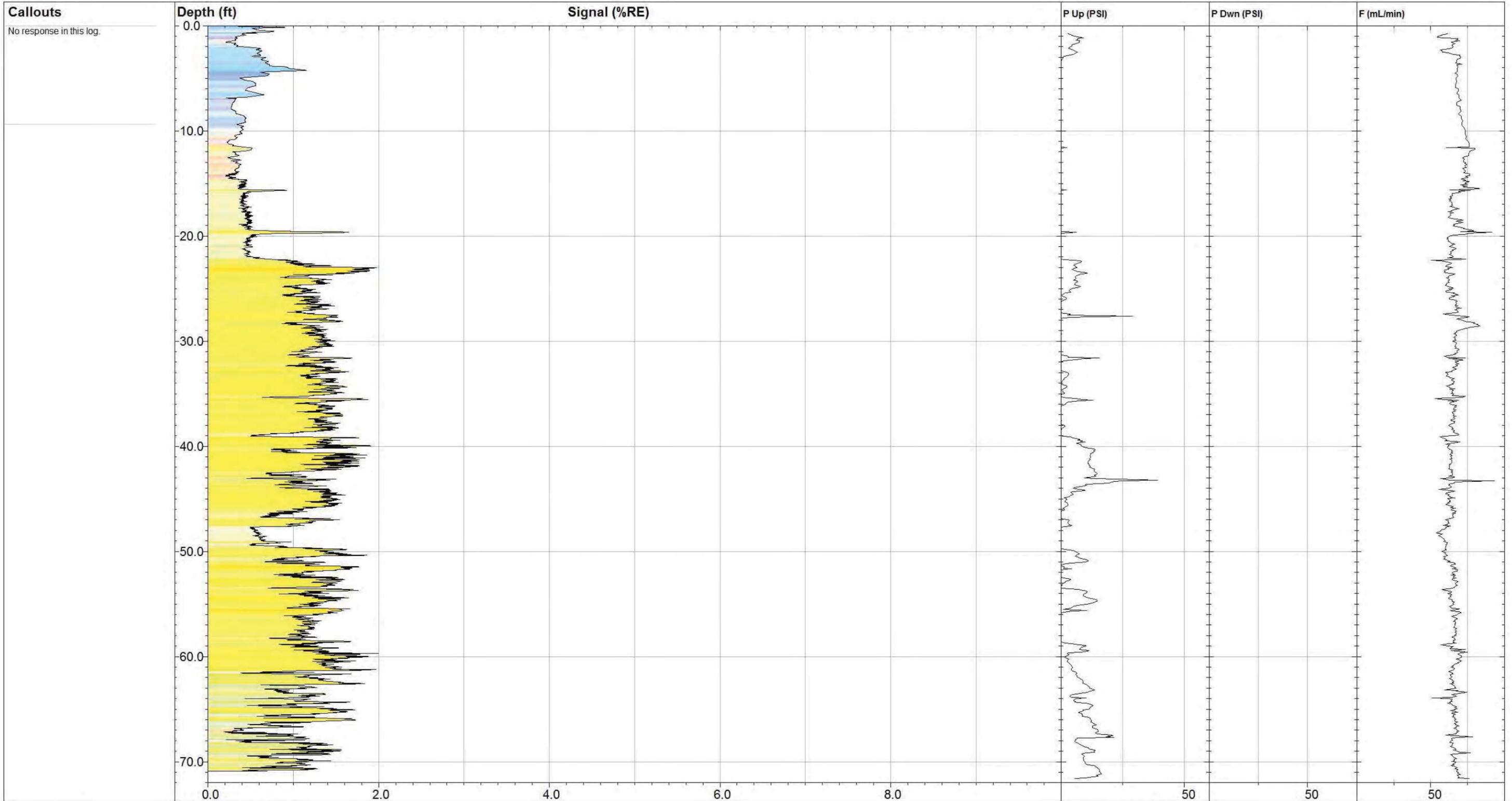
 DAKOTA TECHNOLOGIES <small>FARGO, ND 701.237.4908 WWW.DAKOTATECHNOLOGIES.COM</small>	DyeLIF 009		DyeLIF By Dakota <small>www.DakotaTechnologies.com</small>
	Site: LOP 2013	Y Coord.(Lat-N) / System: 3047903.8 / SPS	Final depth: 70.44 ft
	Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712486.9 I	Max signal: 15.3 %RE @ 34.50 ft
	Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-09 06:35 CDT



DyeLIF 009 DUP		DyeLIF By Dakota www.DakotaTechnologies.com	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047904.8 / SPS	Final depth: 70.71 ft	Max signal: 141.2 %RE @ 34.57 ft
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712486.1 I	Date & Time: 2013-10-09 08:10 CDT	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable		



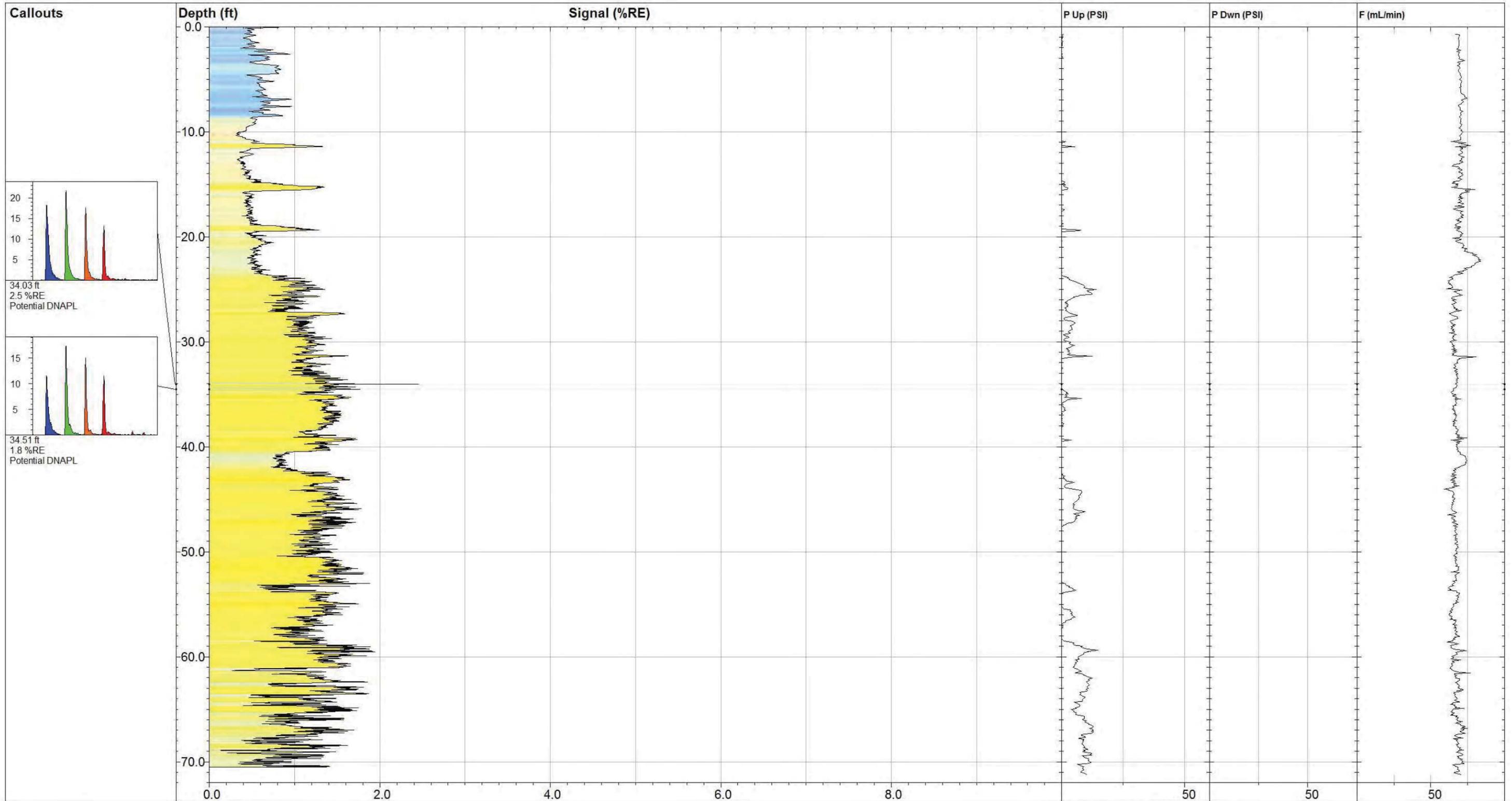
 DAKOTA TECHNOLOGIES <small>FARGO, ND 701.237.4908 WWW.DAKOTATECHNOLOGIES.COM</small>	DyeLIF 009 TRIP		DyeLIF By Dakota <small>www.DakotaTechnologies.com</small>
	Site: LOP 2013	Y Coord. (Lat-N) / System: 3047904.0 / SPS	Final depth: 70.55 ft
	Client / Job: ESTCP I	X Coord. (Lng-E) / Fix: 712485.1 I	Max signal: 179.8 %RE @ 34.34 ft
	Operator / Unit: JTL / TG1005	Elevation: Unavailable	Date & Time: 2013-10-18 09:33 EDT



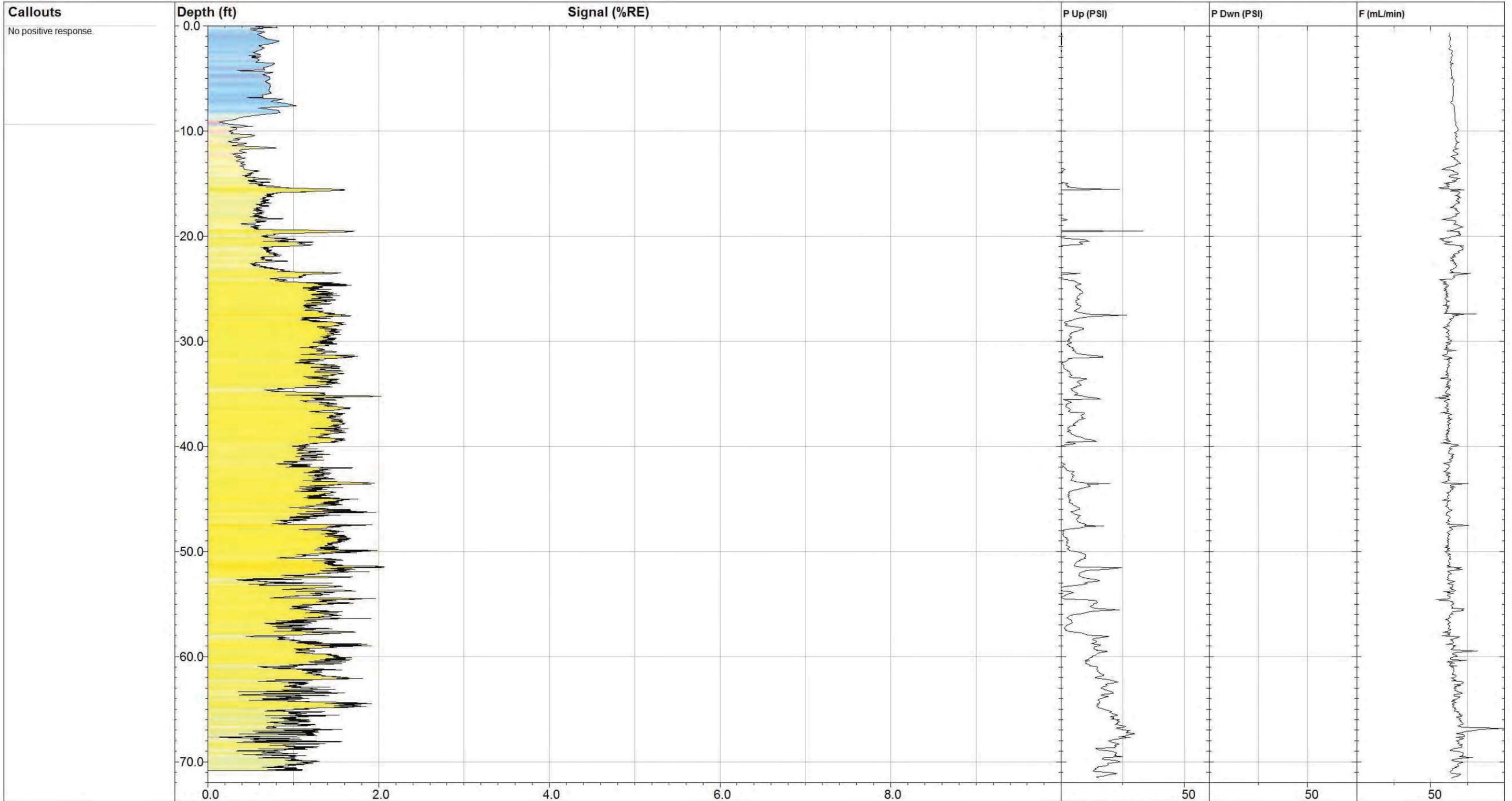
Callouts
No response in this log.



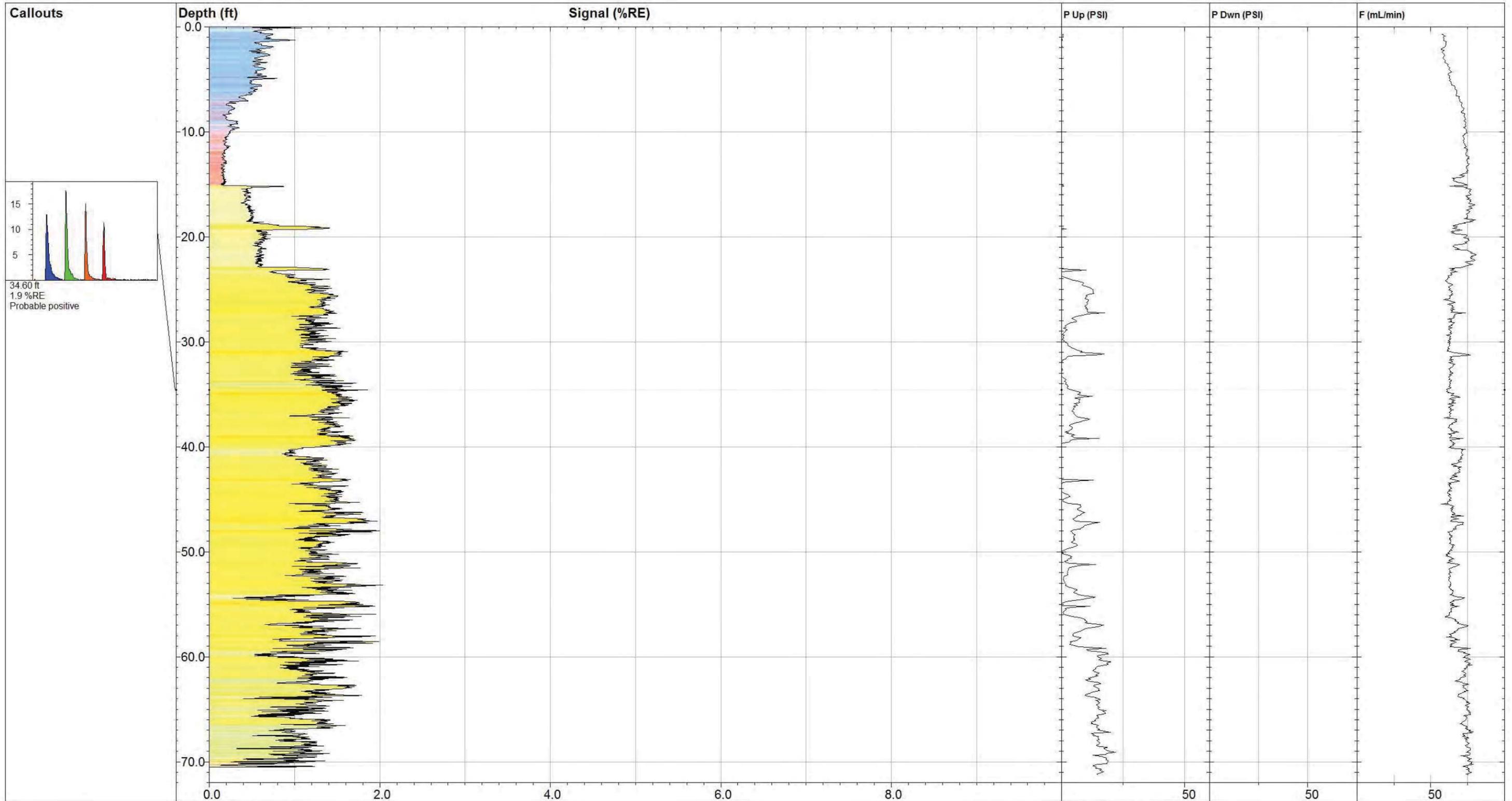
DyeLIF 010		DyeLIF By Dakota <small>www.DakotaTechnologies.com</small>	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047891.1 / SPS	Final depth: 70.88 ft	
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712481.2 I	Max signal: 2.1 %RE @ 59.70 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-09 09:39 CDT	



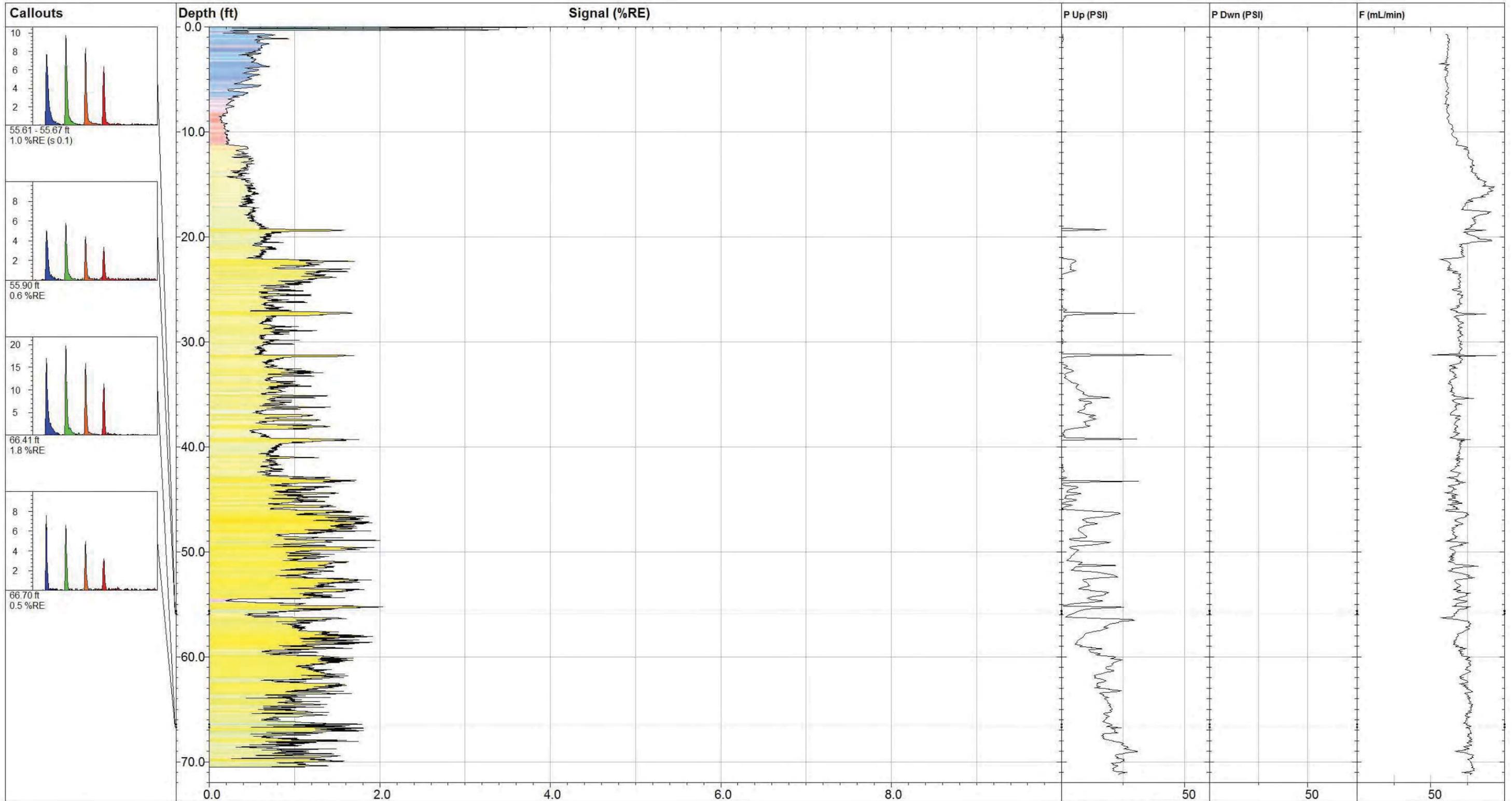
DyeLIF 011		DyeLIF By Dakota <small>www.DakotaTechnologies.com</small>	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047896.3 / SPS	Final depth: 70.51 ft	
Client / Job: ESTCP /	X Coord.(Lng-E) / Fix: 712494.8 /	Max signal: 2.5 %RE @ 34.03 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-09 11:09 CDT	



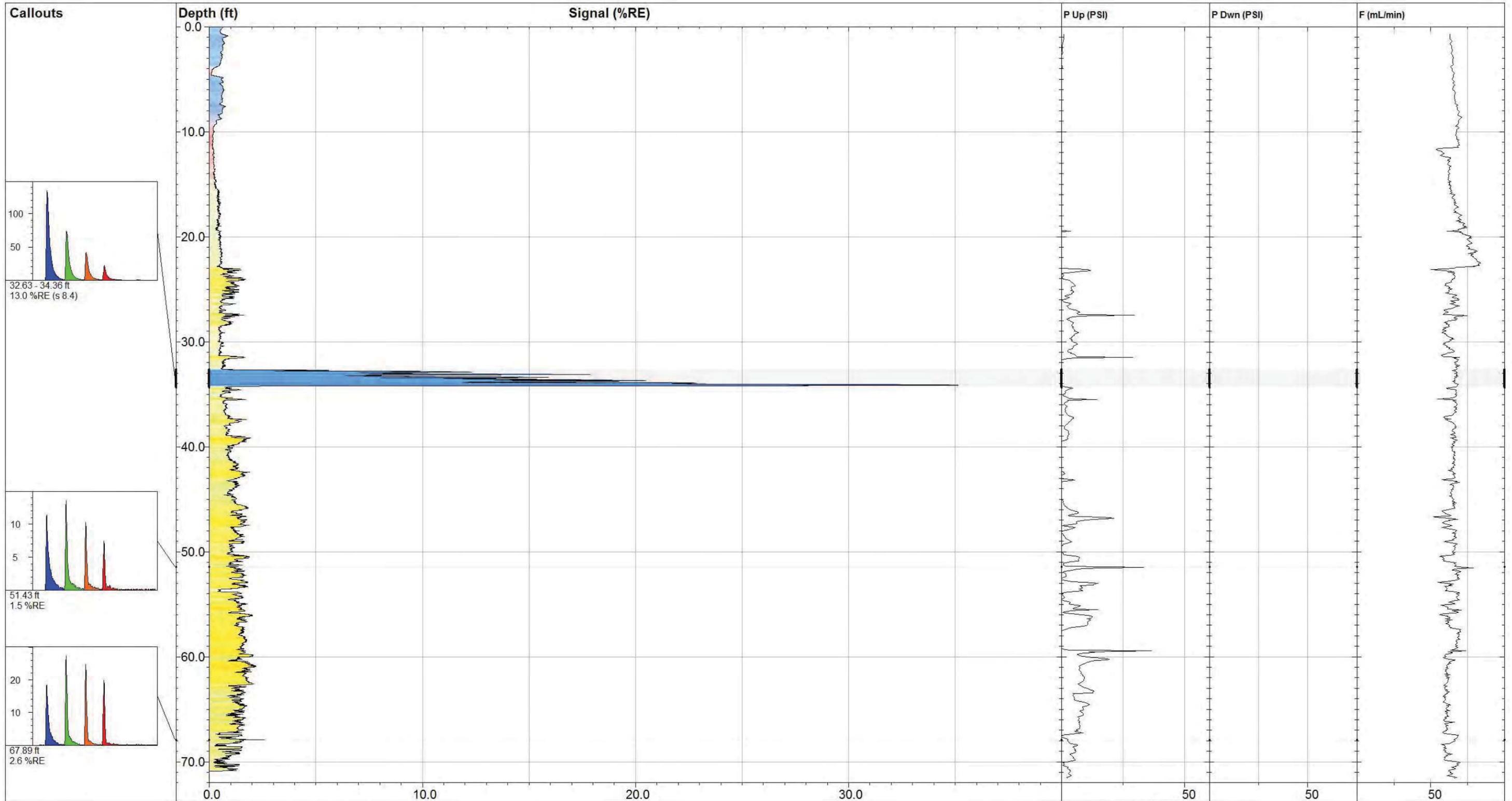
 DAKOTA TECHNOLOGIES <small>FARGO, ND 701.237.4908 WWW.DAKOTATECHNOLOGIES.COM</small>	DyeLIF 012		DyeLIF By Dakota <small>www.DakotaTechnologies.com</small>
	Site: LOP 2013	Y Coord.(Lat-N) / System: 3047899.9 / SPS	Final depth: 70.84 ft
	Client / Job: ESTCP /	X Coord.(Lng-E) / Fix: 712499.4 /	Max signal: 2.1 %RE @ 51.46 ft
	Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-09 12:20 CDT



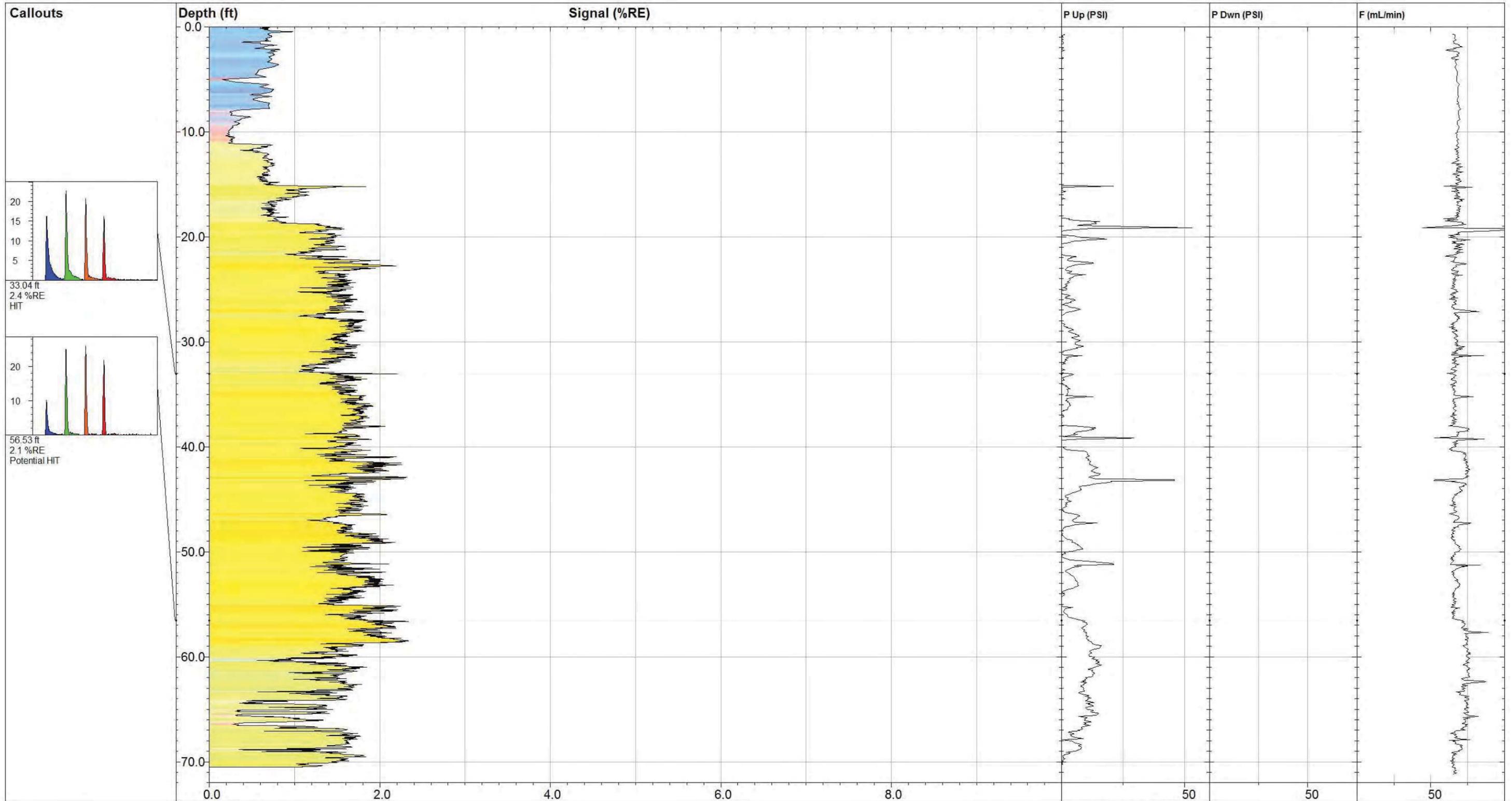
 <p>DAKOTA TECHNOLOGIES FARGO, ND 701.237.4908 WWW.DAKOTATECHNOLOGIES.COM</p>	DyeLIF 013		DyeLIF By Dakota <small>www.DakotaTechnologies.com</small>	
	Site: LOP 2013	Y Coord.(Lat-N) / System: 3047905.4 / SPS	Final depth: 70.50 ft	
	Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712497.5 I	Max signal: 2.1 %RE @ 53.20 ft	
	Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-09 13:32 CDT	



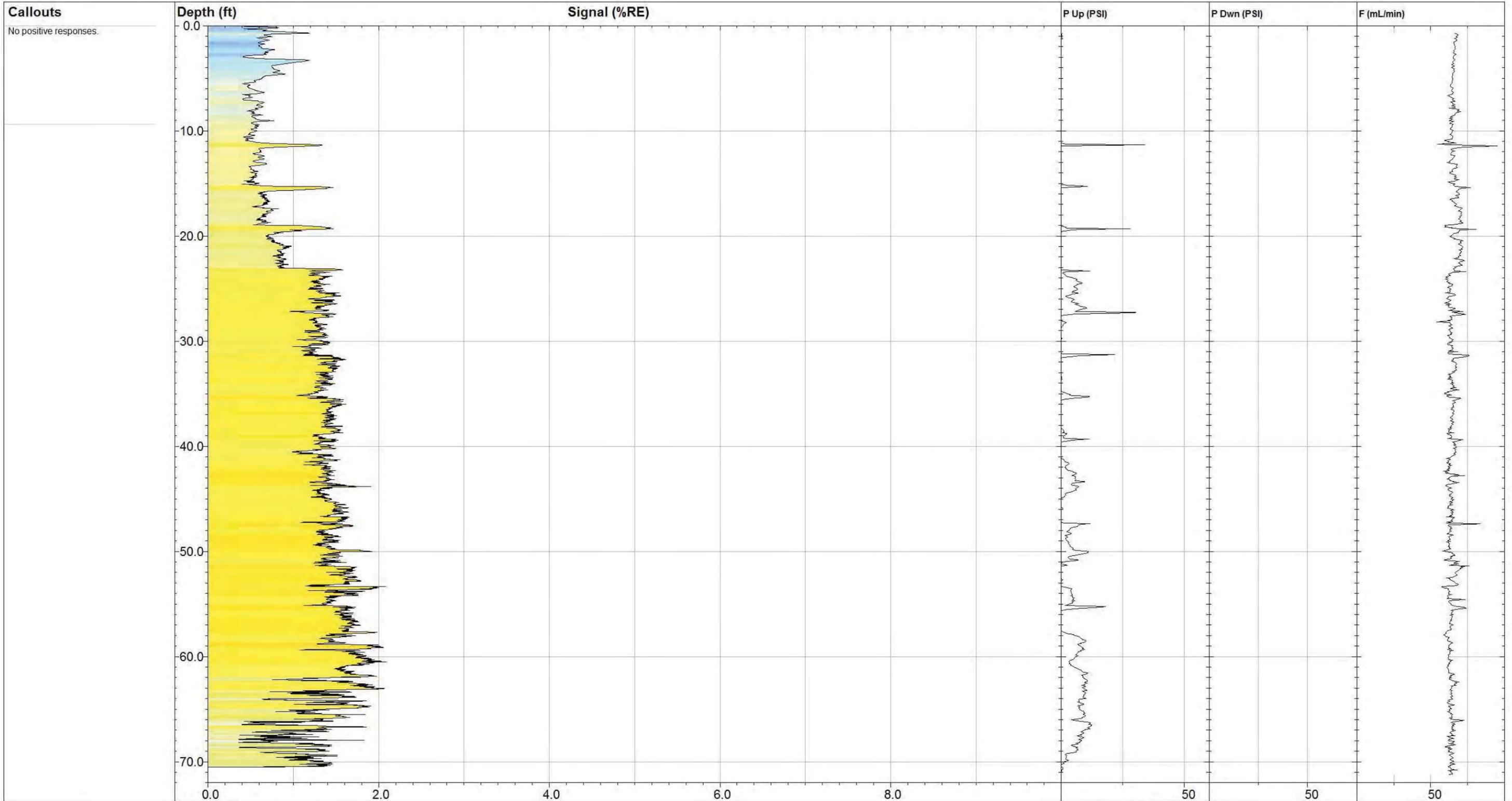
DyeLIF 014		DyeLIF By Dakota www.DakotaTechnologies.com	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047926.3 / SPS	Final depth: 70.52 ft	
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712486.5 I	Max signal: 3.8 %RE @ 0.09 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-09 14:42 CDT	



DyeLIF 015		DyeLIF By Dakota www.DakotaTechnologies.com	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047901.0 / SPS	Final depth: 70.87 ft	
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712476.2 I	Max signal: 36.5 %RE @ 34.14 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-10 06:51 CDT	



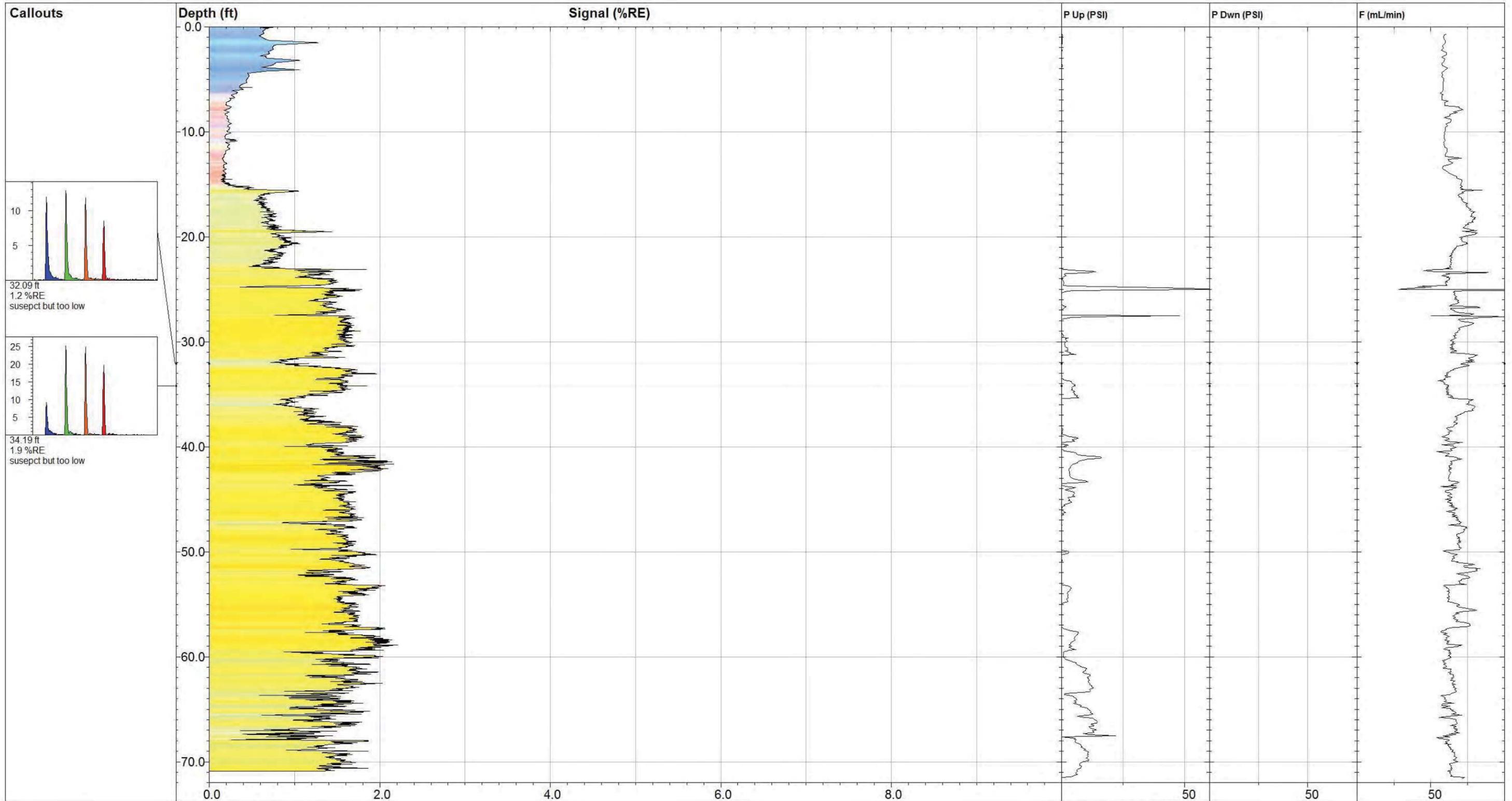
DyeLIF 016		DyeLIF By Dakota <small>www.DakotaTechnologies.com</small>	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047900.1 / SPS	Final depth: 70.49 ft	
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712471.5 I	Max signal: 2.4 %RE @ 33.04 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-10 08:17 CDT	



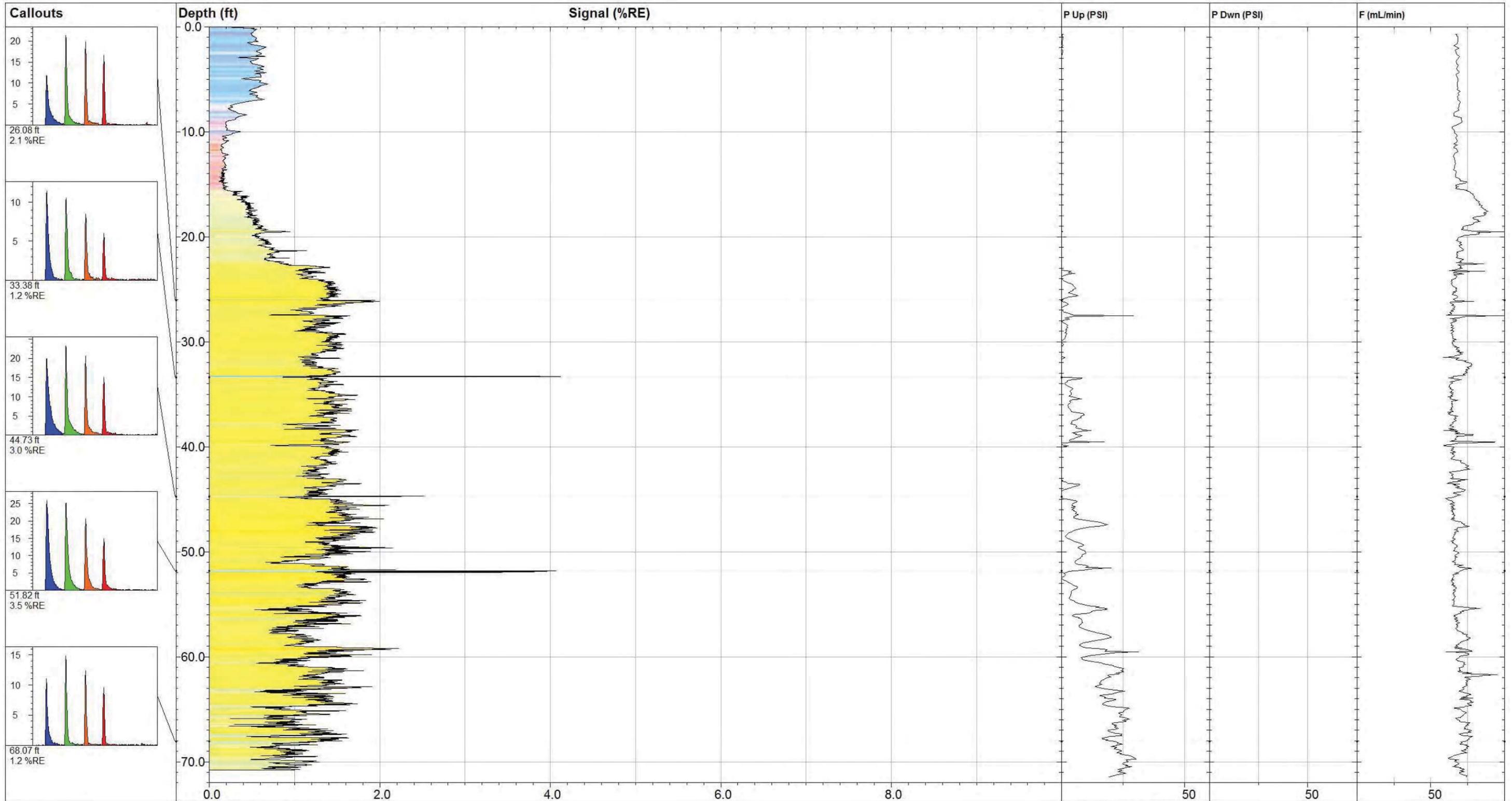
Callouts
No positive responses.



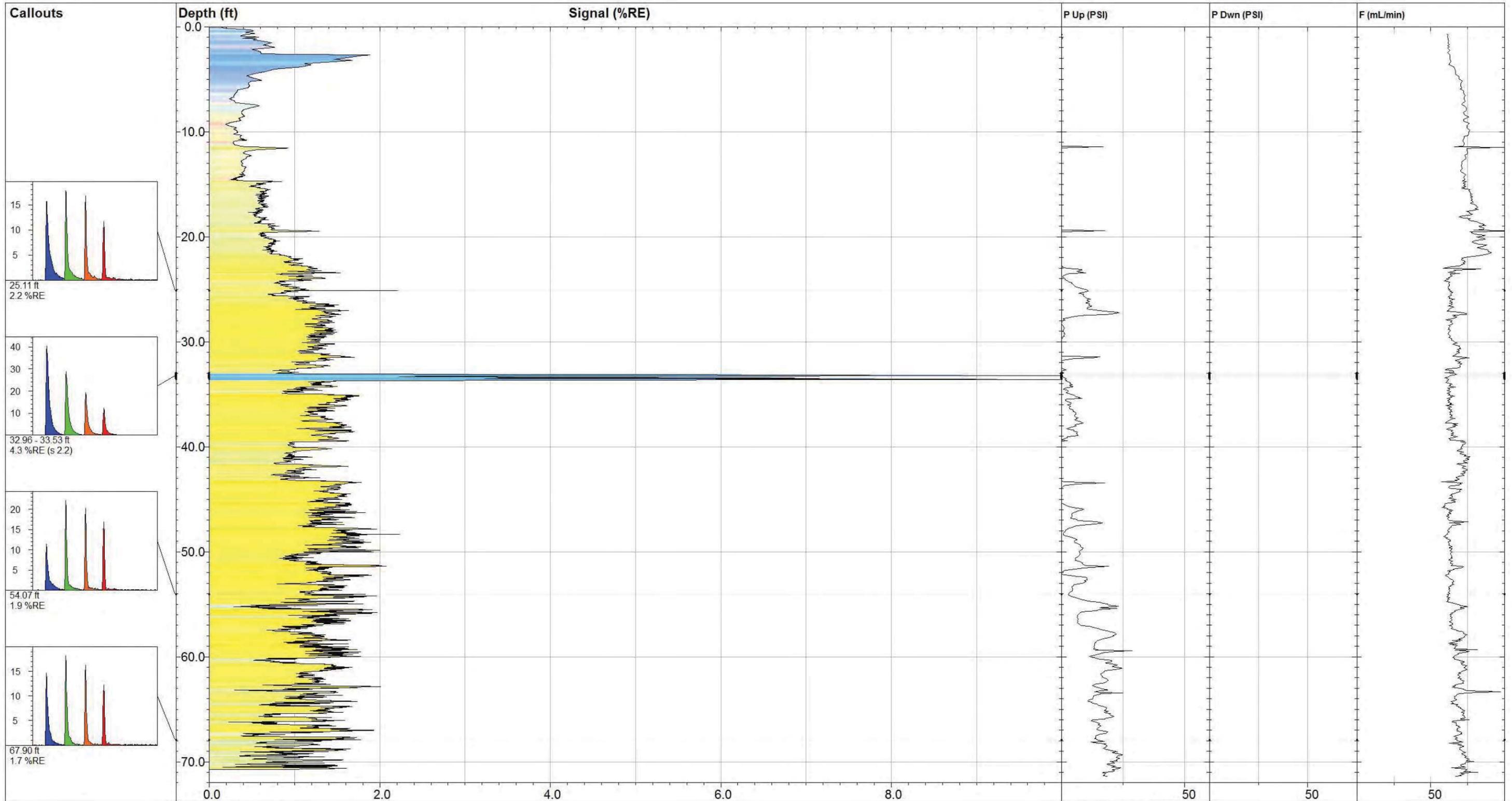
DyeLIF 017		DyeLIF By Dakota <small>www.DakotaTechnologies.com</small>	
Site: LOP 2013	Y Coord. (Lat-N) / System: 3047902.8 / SPS	Final depth: 70.52 ft	
Client / Job: ESTCP I	X Coord. (Lng-E) / Fix: 712463.6 I	Max signal: 2.1 %RE @ 60.49 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-10 10:48 CDT	



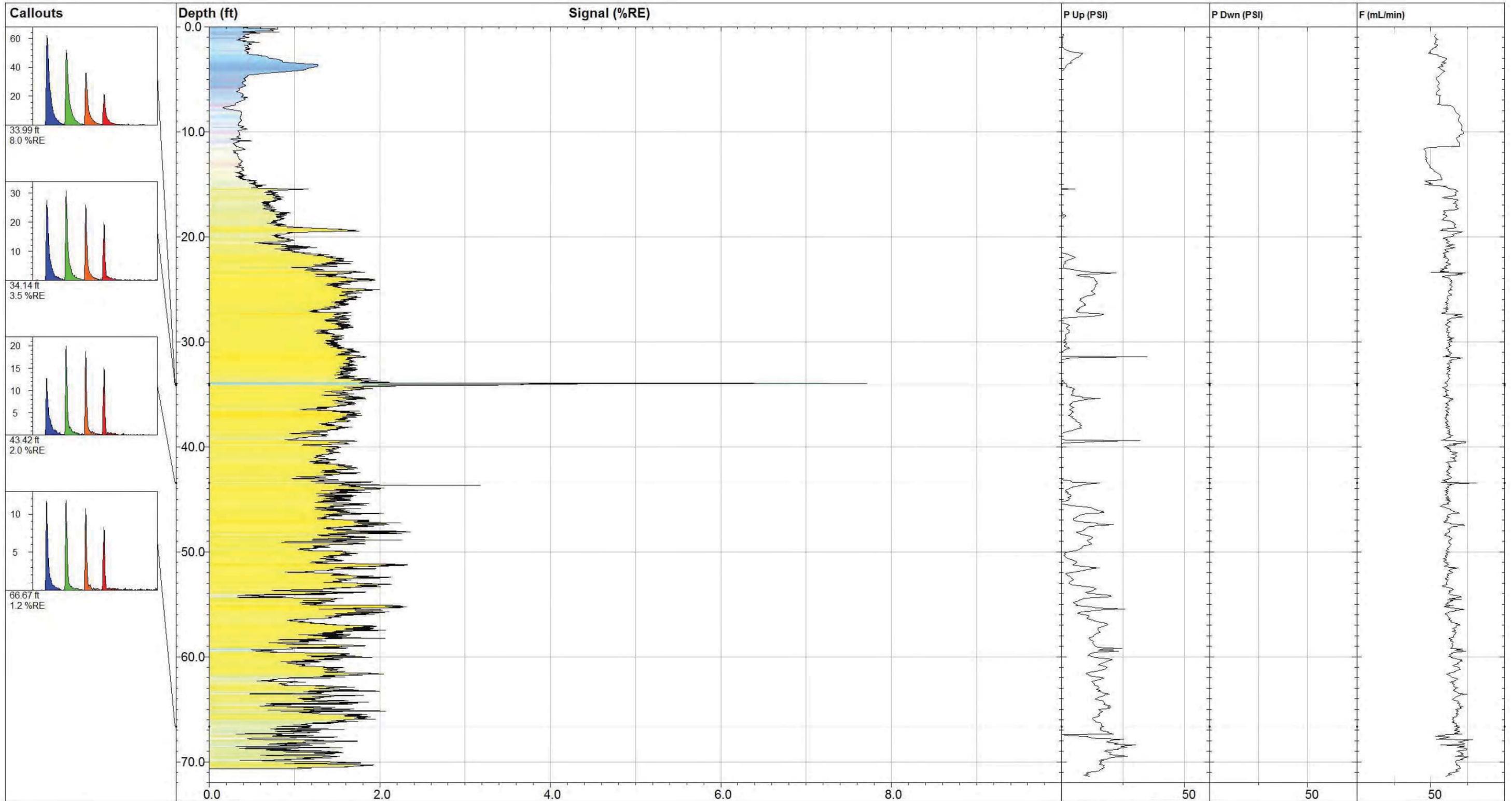
 <p>DAKOTA TECHNOLOGIES FARGO, ND 701.237.4908 WWW.DAKOTATECHNOLOGIES.COM</p>	DyeLIF 018		DyeLIF By Dakota www.DakotaTechnologies.com
	Site: LOP 2013	Y Coord. (Lat-N) / System: 3047891.7 / SPS	Final depth: 70.87 ft
	Client / Job: ESTCP I	X Coord. (Lng-E) / Fix: 712490.9 I	Max signal: 2.2 %RE @ 58.90 ft
	Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-10 12:43 CDT



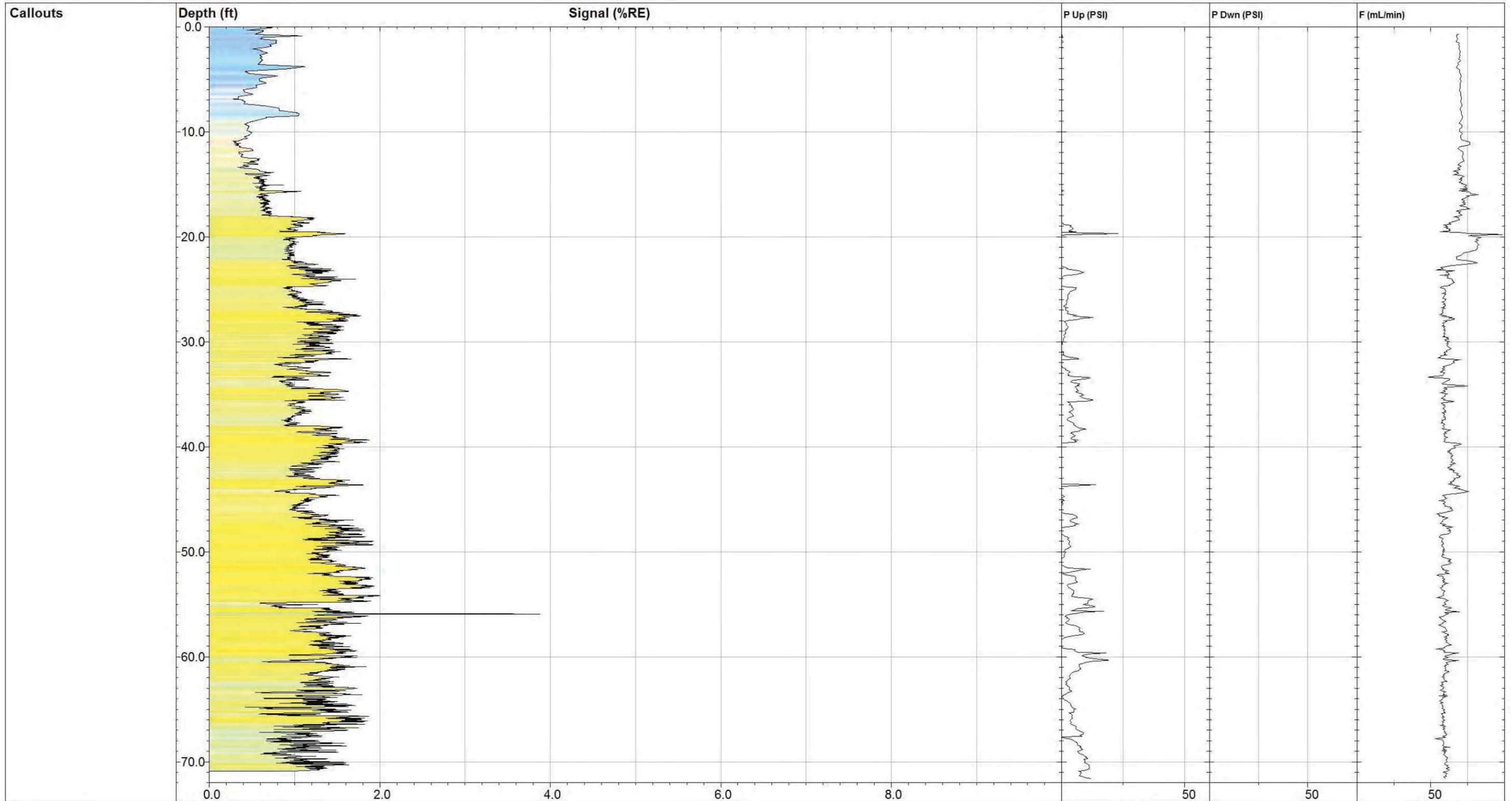
DyeLIF 019		DyeLIF By Dakota www.DakotaTechnologies.com	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047917.2 / SPS	Final depth: 70.76 ft	
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712484.5 I	Max signal: 4.4 %RE @ 33.31 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-10 14:18 CDT	



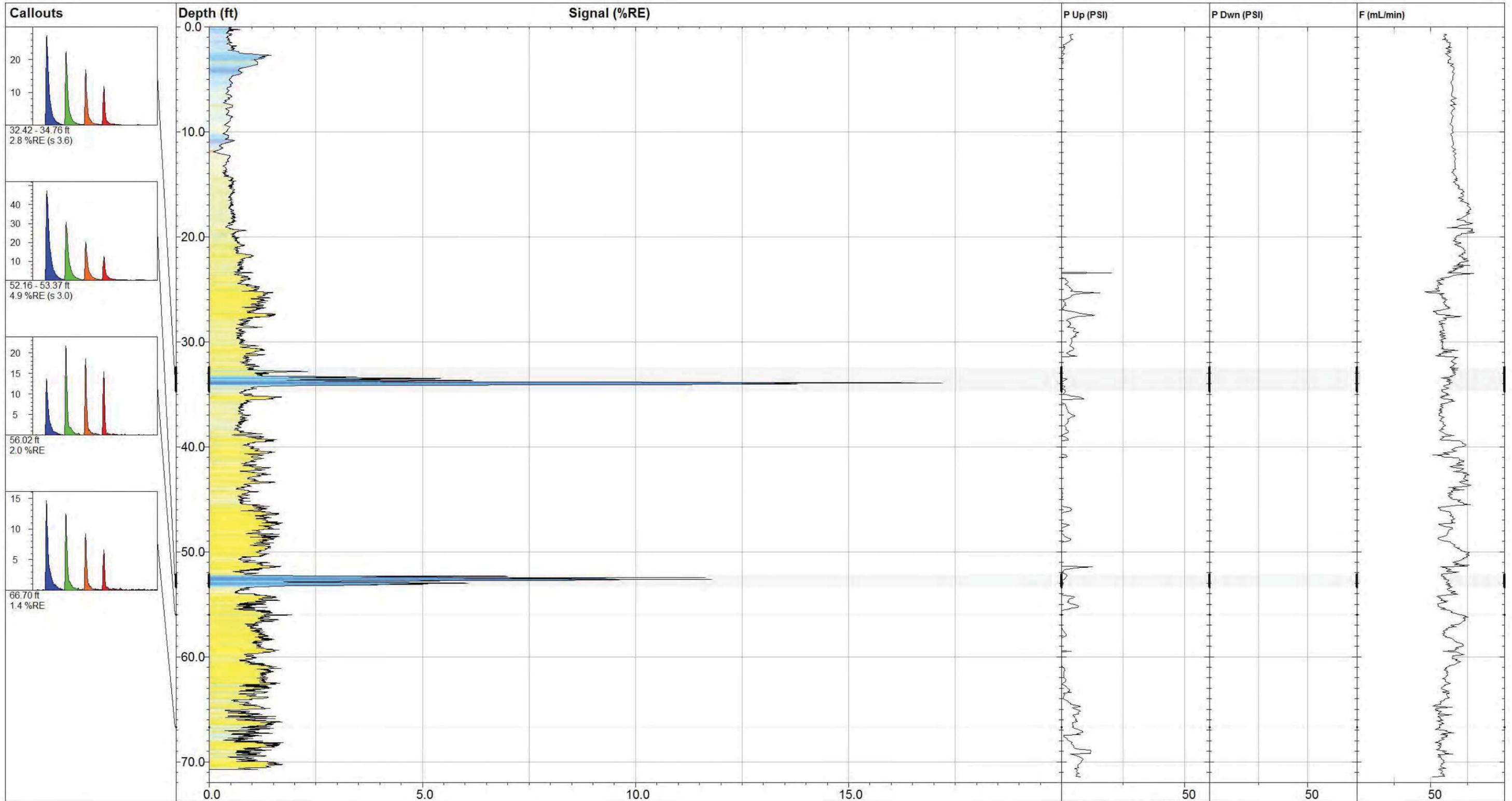
DyeLIF 020		DyeLIF By Dakota www.DakotaTechnologies.com	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047918.5 / SPS	Final depth: 70.71 ft	
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712493.8 I	Max signal: 10.3 %RE @ 33.23 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-10 15:35 CDT	



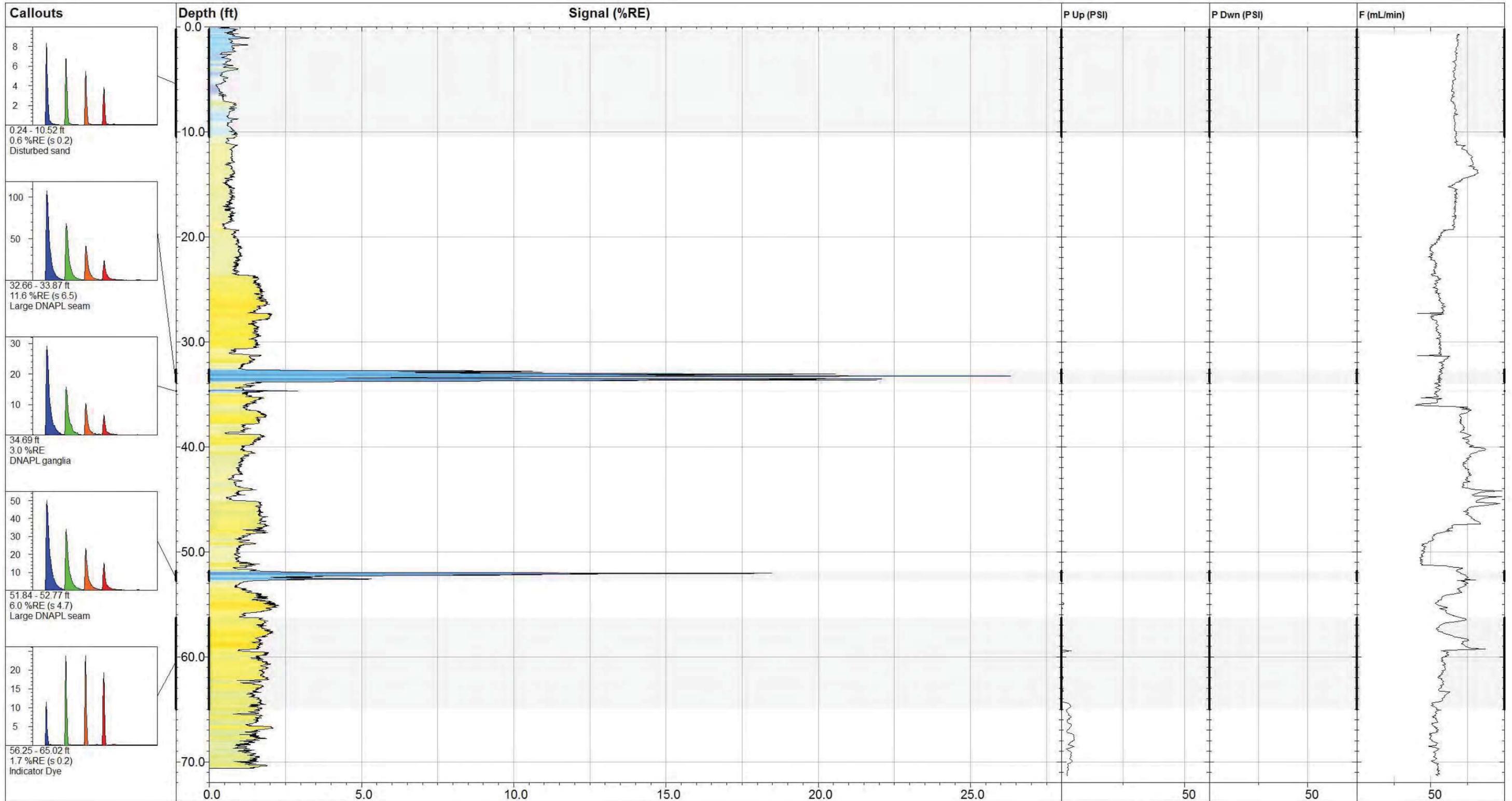
DyeLIF 021		DyeLIF By Dakota www.DakotaTechnologies.com	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047917.1 / SPS	Final depth: 70.67 ft	
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712502.3 I	Max signal: 8.0 %RE @ 33.99 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-11 06:41 CDT	



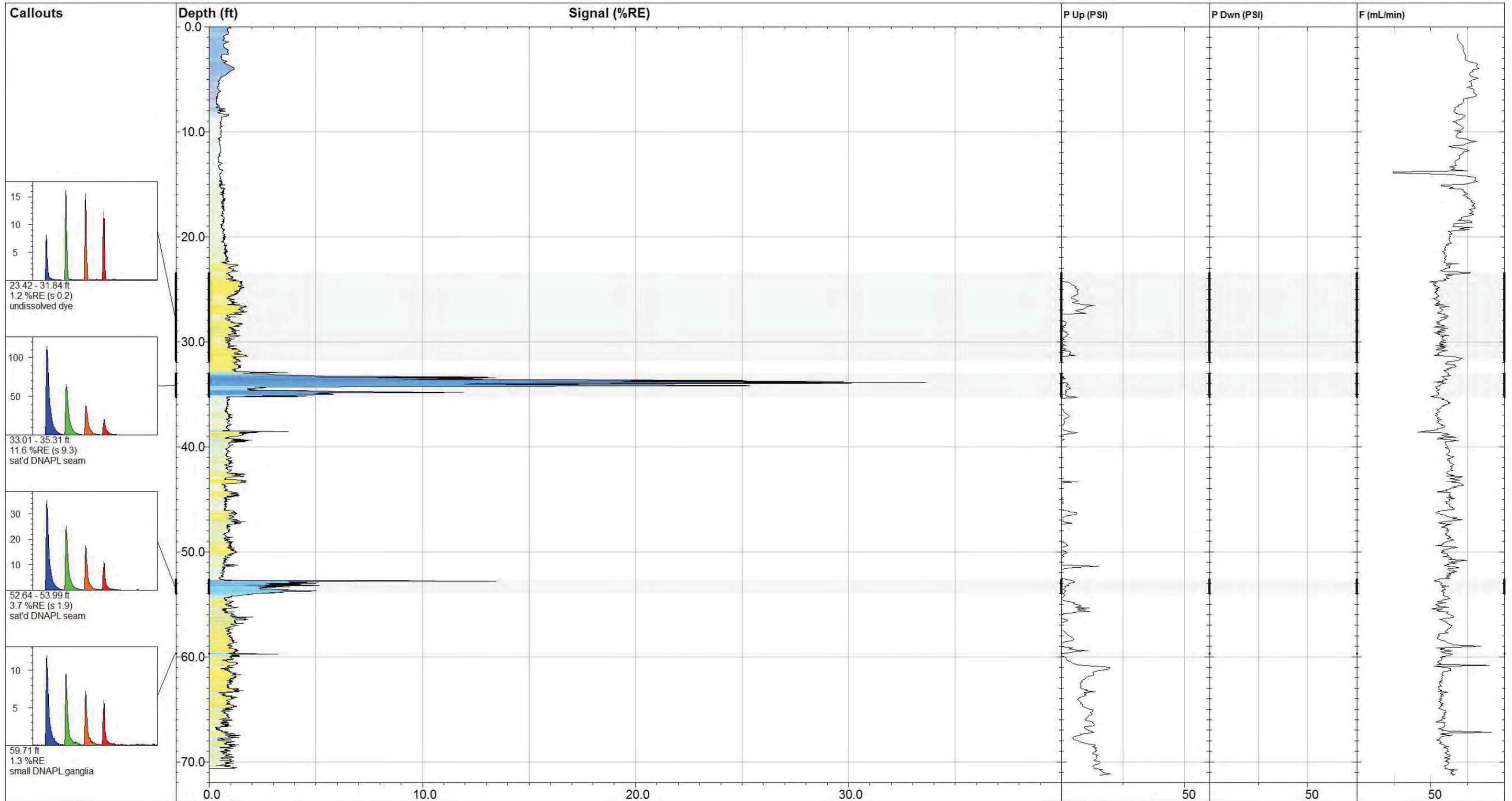
DyeLIF 022		DyeLIF By Dakota <small>www.DakotaTechnologies.com</small>	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047917.6 / SPS	Final depth: 70.90 ft	
Client / Job: ESTCP /	X Coord.(Lng-E) / Fix: 712475.1 /	Max signal: 4.0 %RE @ 55.93 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-11 08:19 CDT	



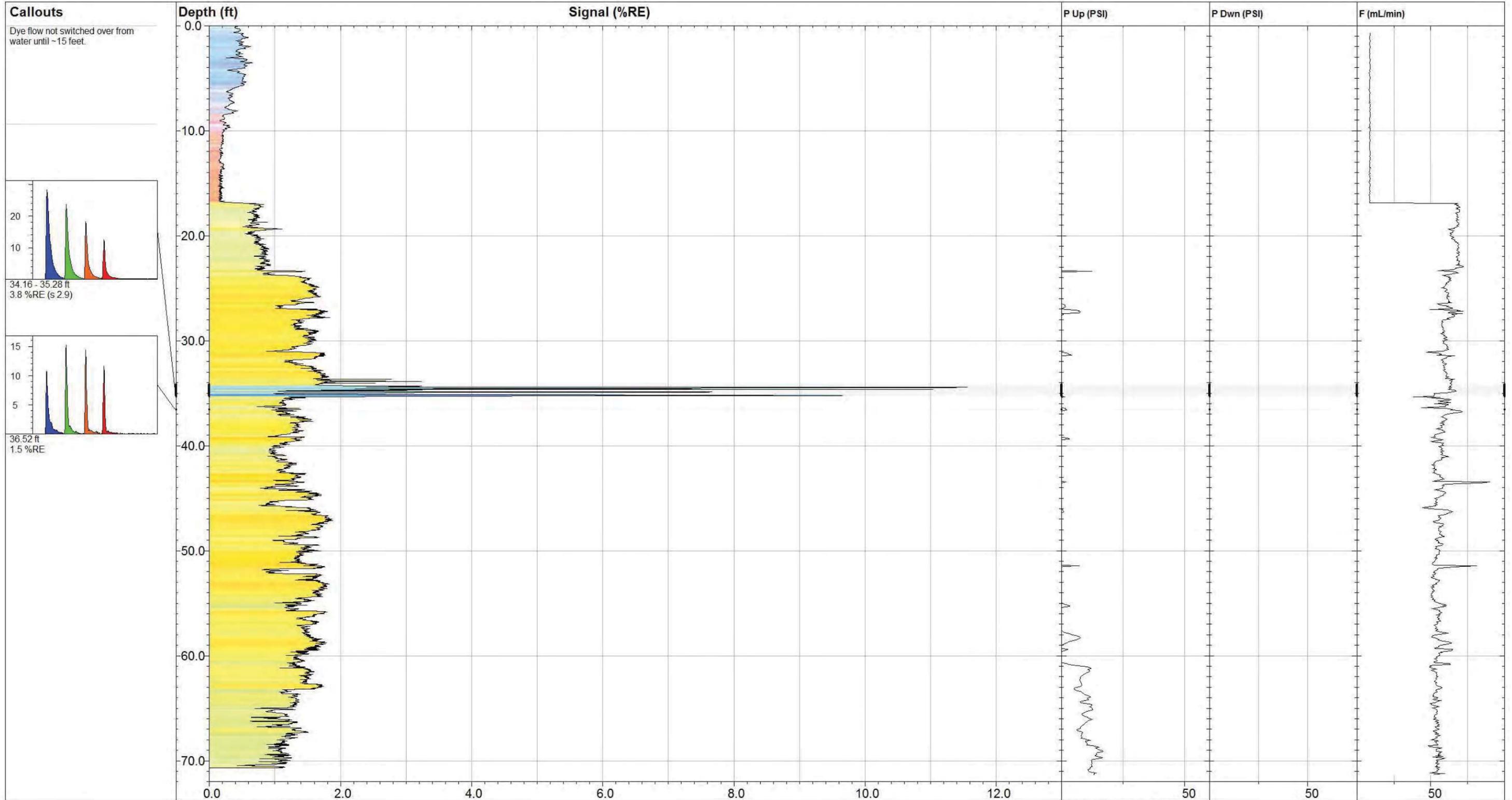
DyeLIF 023		DyeLIF By Dakota www.DakotaTechnologies.com	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047908.5 / SPS	Final depth: 70.73 ft	
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712479.4 I	Max signal: 17.2 %RE @ 33.95 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-11 10:01 CDT	



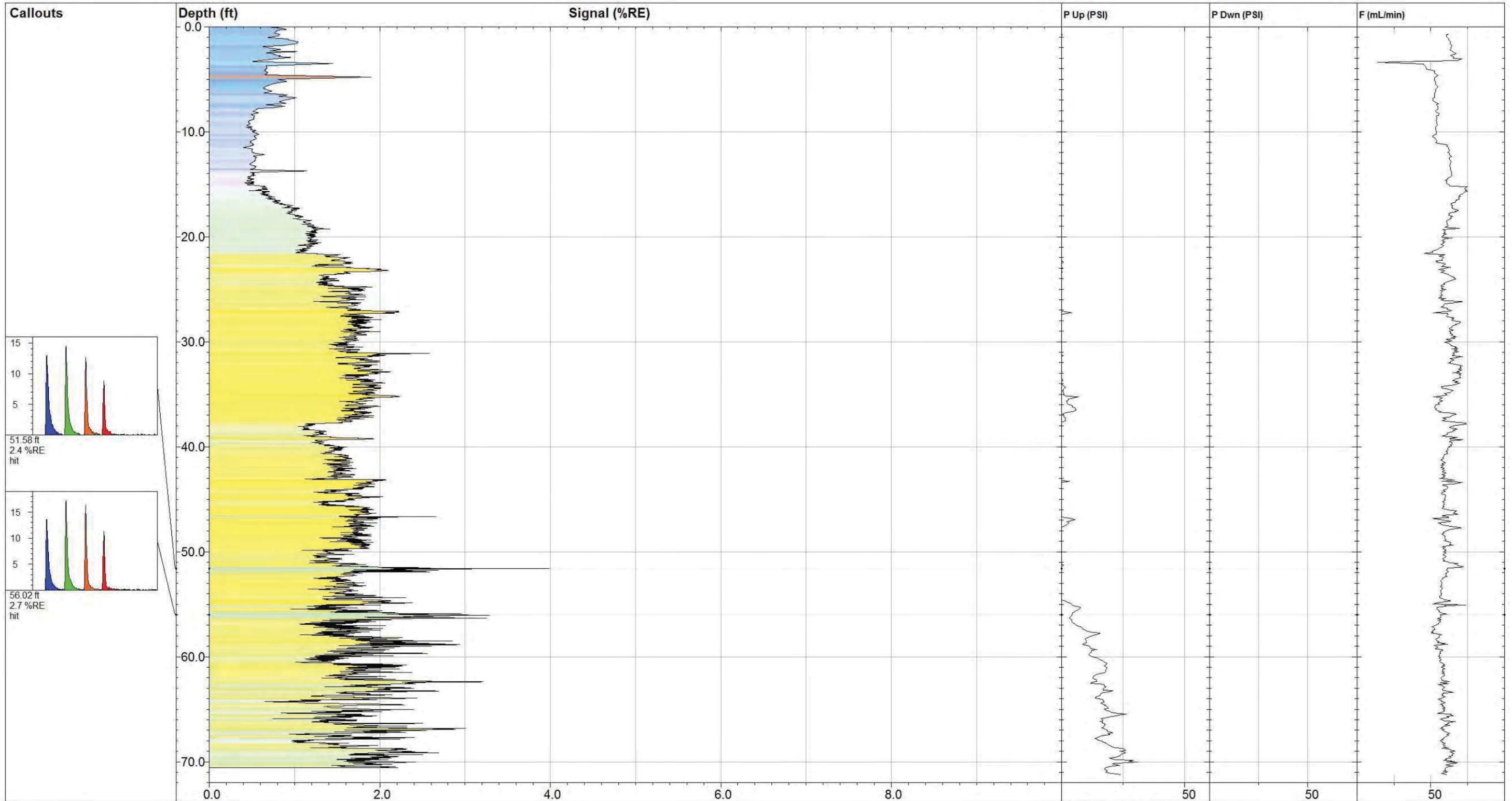
DyeLIF 023 DUP		DyeLIF By Dakota www.DakotaTechnologies.com	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047908.9 / SPS	Final depth: 70.62 ft	
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712479.9 I	Max signal: 26.3 %RE @ 33.27 ft	
Operator / Unit: JTL / TG1005	Elevation: Unavailable	Date & Time: 2013-10-17 10:32 EDT	



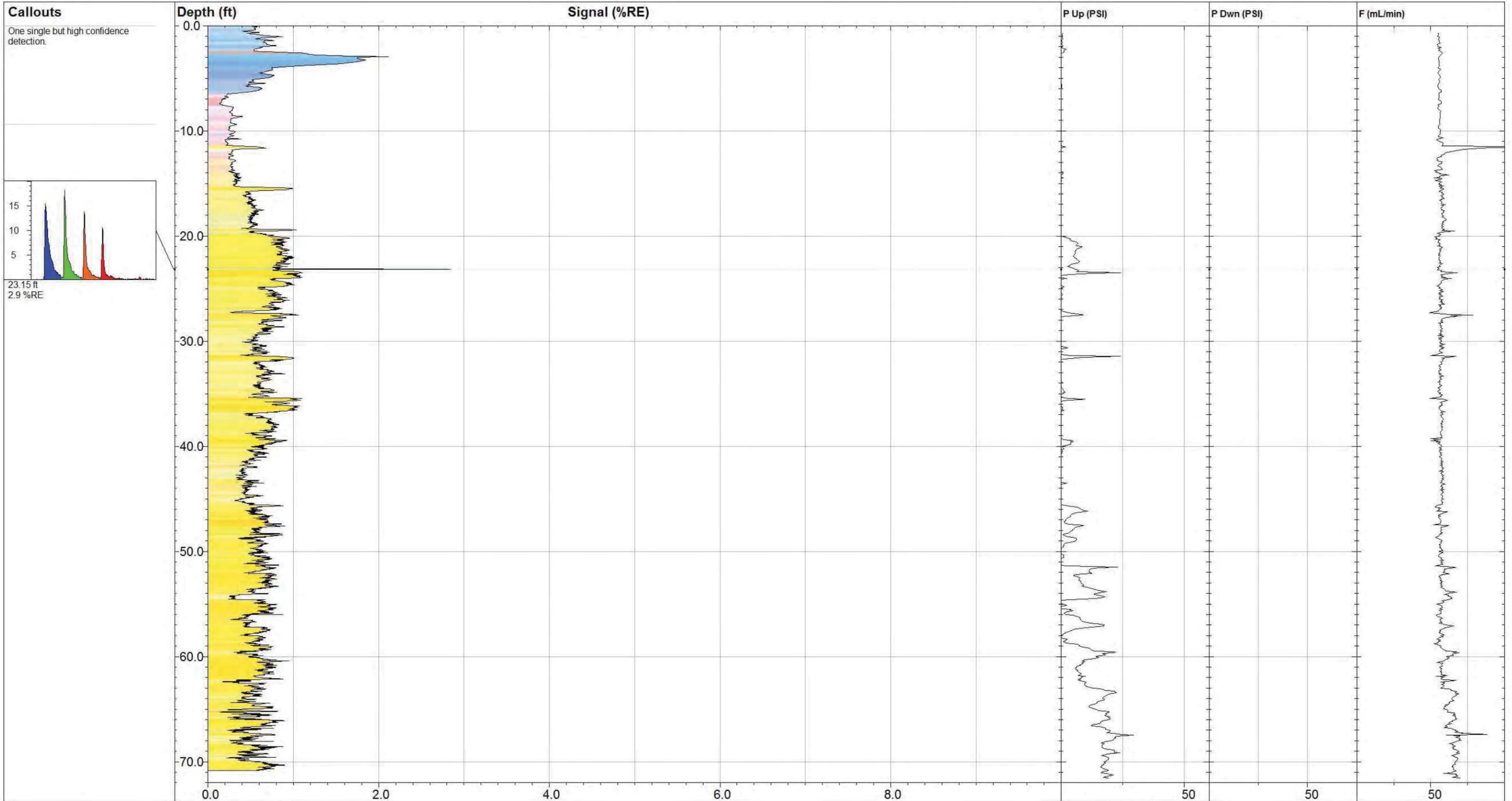
DyeLIF 024		DyeLIF By Dakota www.DakotaTechnologies.com	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047910.1 / SPS	Final depth: 70.61 ft	
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712487.1 I	Max signal: 34.8 %RE @ 33.88 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-11 12:41 CDT	



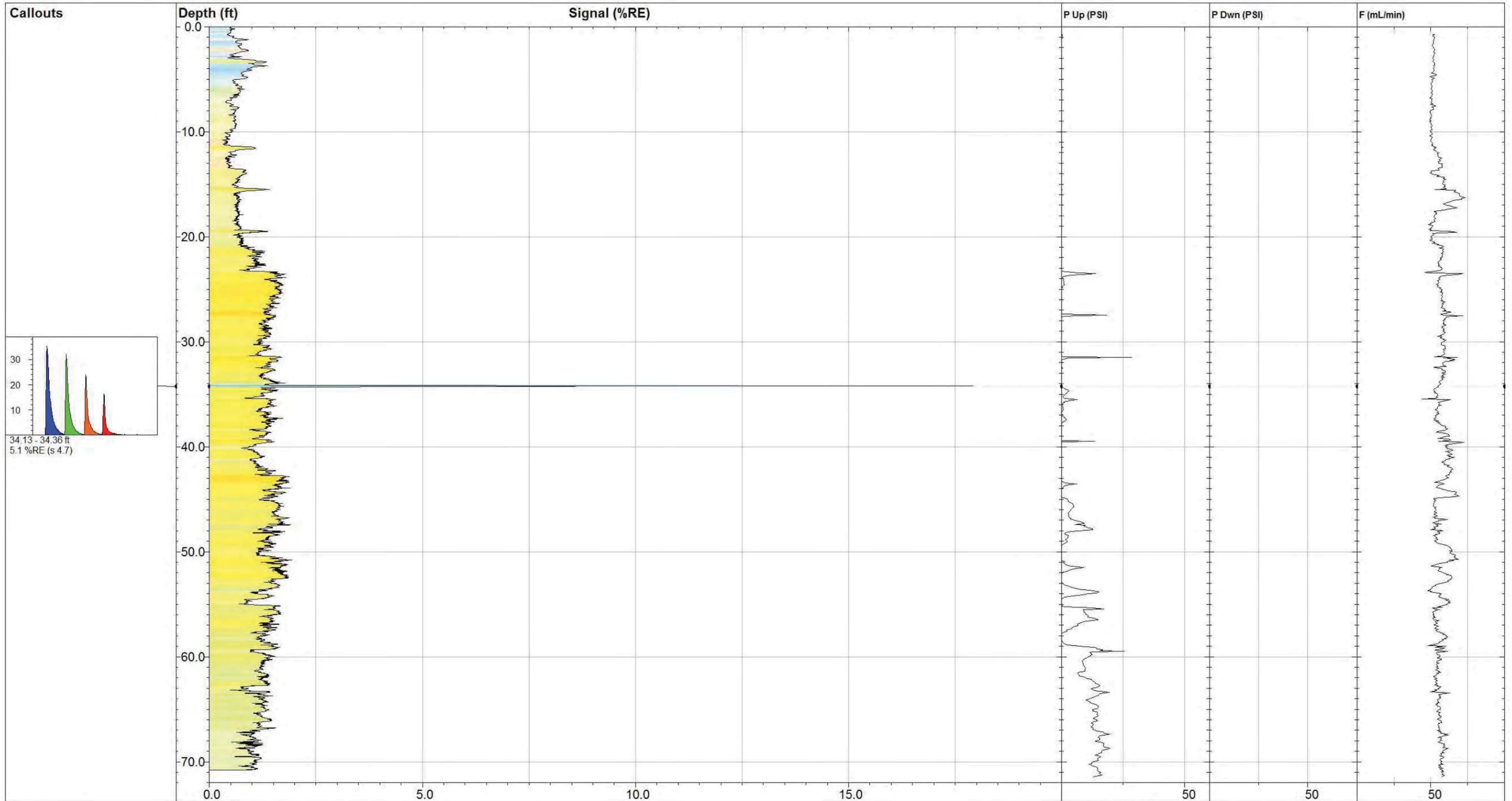
 DAKOTA TECHNOLOGIES <small>FARGO, ND 701.237.4908 WWW.DAKOTATECHNOLOGIES.COM</small>	DyeLIF 024 DUP		DyeLIF By Dakota <small>www.DakotaTechnologies.com</small>
	Site: LOP 2013	Y Coord. (Lat-N) / System: 3047909.1 / SPS	Final depth: 70.67 ft
	Client / Job: ESTCP I	X Coord. (Lng-E) / Fix: 712487.1 I	Max signal: 11.9 %RE @ 34.44 ft
	Operator / Unit: RWS/JTL / TG1005	Elevation: Unavailable	Date & Time: 2013-10-16 07:33 EDT



DyeLIF 025		DyeLIF By Dakota www.DakotaTechnologies.com	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047927.5 / SPS	Final depth: 70.56 ft	Max signal: 4.0 %RE @ 51.59 ft
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712479.9 I	Date & Time: 2013-10-11 13:58 CDT	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable		



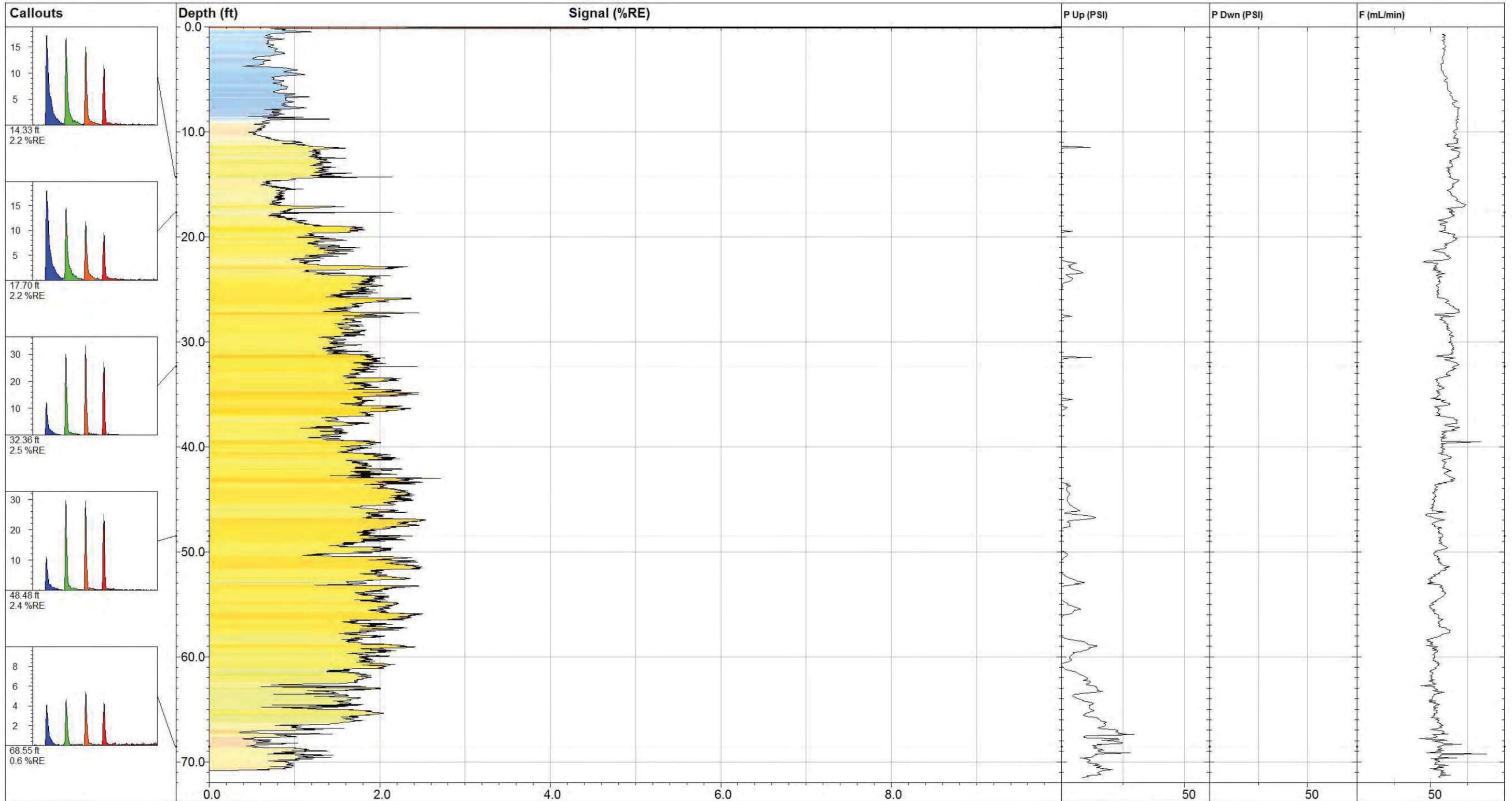
DyeLIF 026		DyeLIF By Dakota www.DakotaTechnologies.com	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047933.0 / SPS	Final depth: 70.82 ft	
Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712477.5 I	Max signal: 2.9 %RE @ 23.15 ft	
Operator / Unit: RWS/SDA / TG1005	Elevation: Unavailable	Date & Time: 2013-10-14 08:55 EDT	



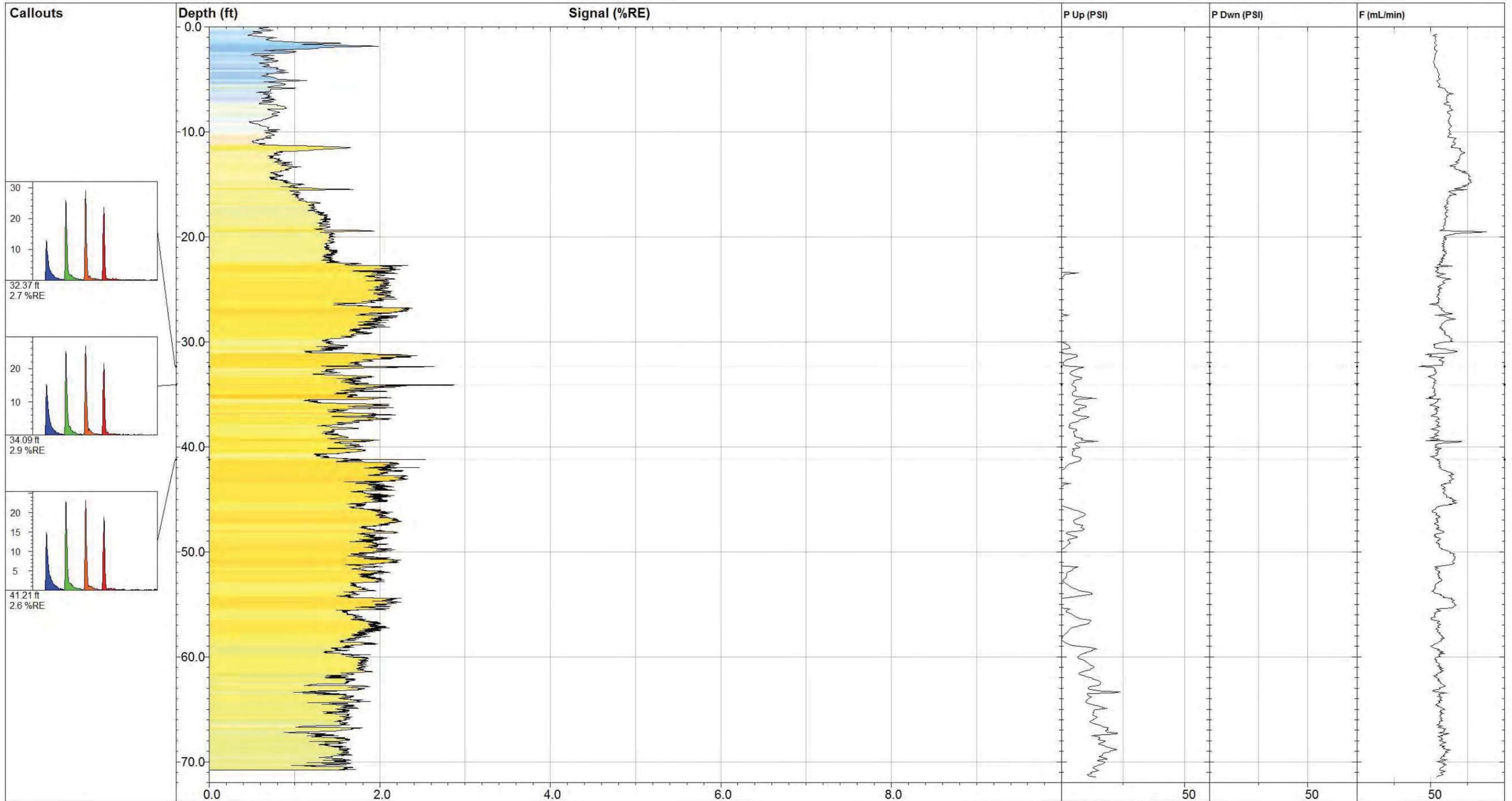
DyeLIF 027
 Site:
LOP 2013
 Client / Job:
ESTCP I
 Operator / Unit:
RWS/JTL / TG1005

Y Coord.(Lat-N) / System:
3047916.8 / SPS
 X Coord.(Lng-E) / Fix:
712508.8 I
 Elevation:
Unavailable

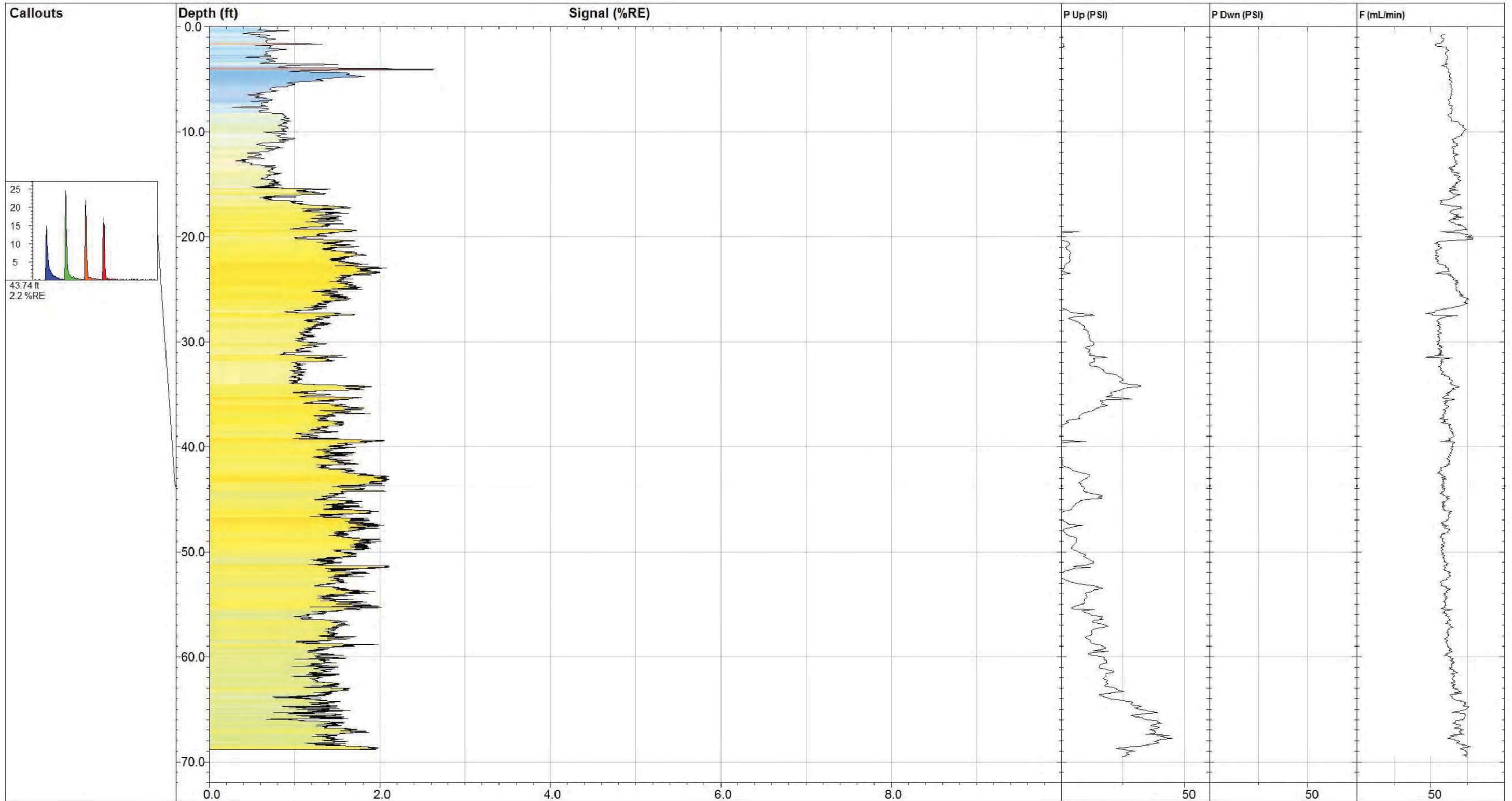
DyeLIF By Dakota
www.DakotaTechnologies.com
 Final depth:
70.76 ft
 Max signal:
18.7 %RE @ 34.20 ft
 Date & Time:
2013-10-15 08:12 EDT



DyeLIF 028		DyeLIF By Dakota <small>www.DakotaTechnologies.com</small>	
Site: LOP 2013	Y Coord.(Lat-N) / System: 3047912.6 / SPS	Final depth: 70.81 ft	
Client / Job: ESTCP /	X Coord.(Lng-E) / Fix: 712513.7 /	Max signal: 30.0 %RE @ 0.01 ft	
Operator / Unit: RWS/JTL / TG1005	Elevation: Unavailable	Date & Time: 2013-10-15 14:20 EDT	



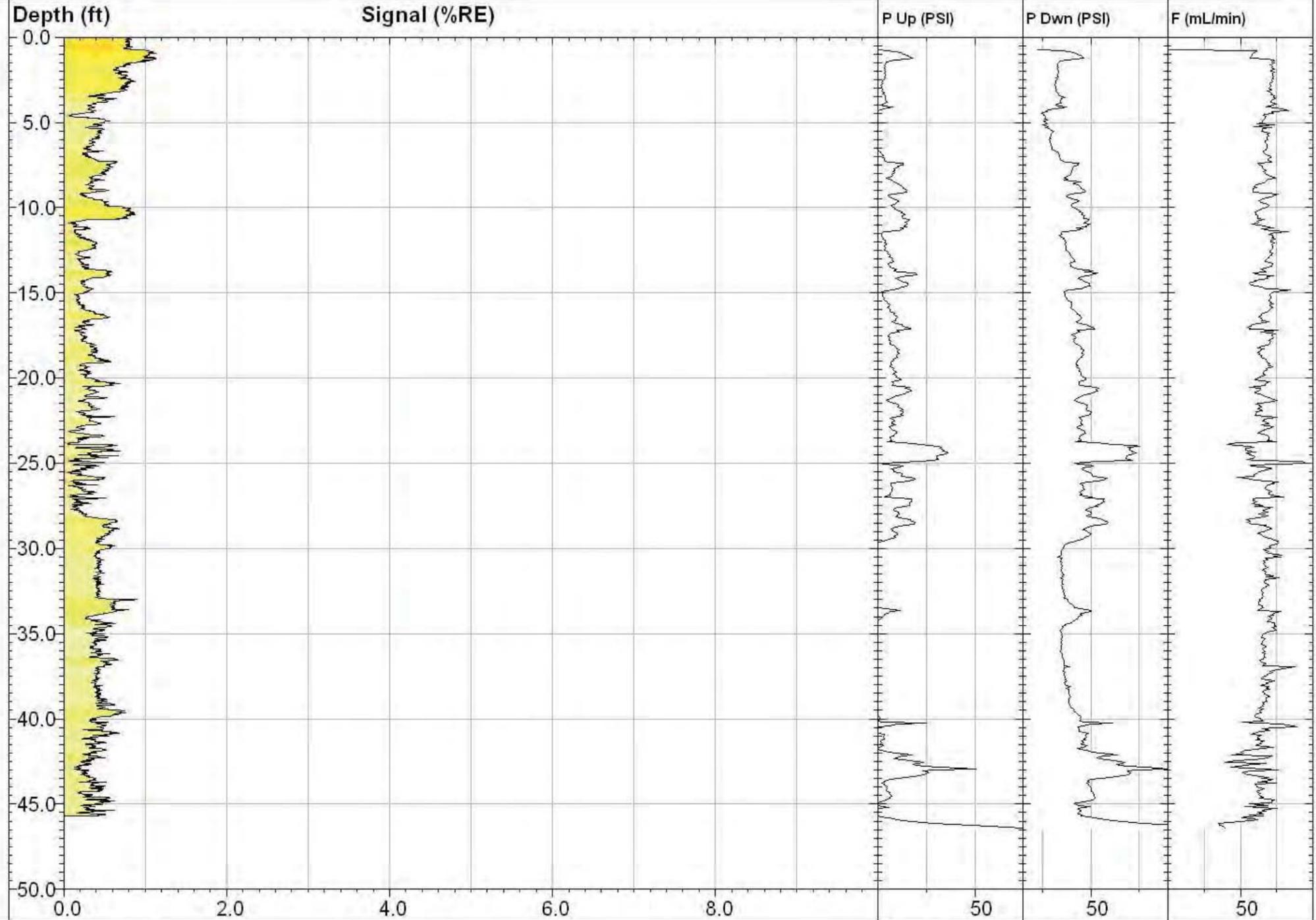
 <p>DAKOTA TECHNOLOGIES FARGO, ND 701.237.4908 WWW.DAKOTATECHNOLOGIES.COM</p>	DyeLIF 029		DyeLIF By Dakota www.DakotaTechnologies.com		
	Site: LOP 2013	Y Coord.(Lat-N) / System: 3047931.6 / SPS	Final depth: 70.76 ft		
	Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712491.0 I	Max signal: 2.9 %RE @ 34.09 ft		
	Operator / Unit: RWS/JTL / TG1005	Elevation: Unavailable	Date & Time: 2013-10-15 16:08 EDT		



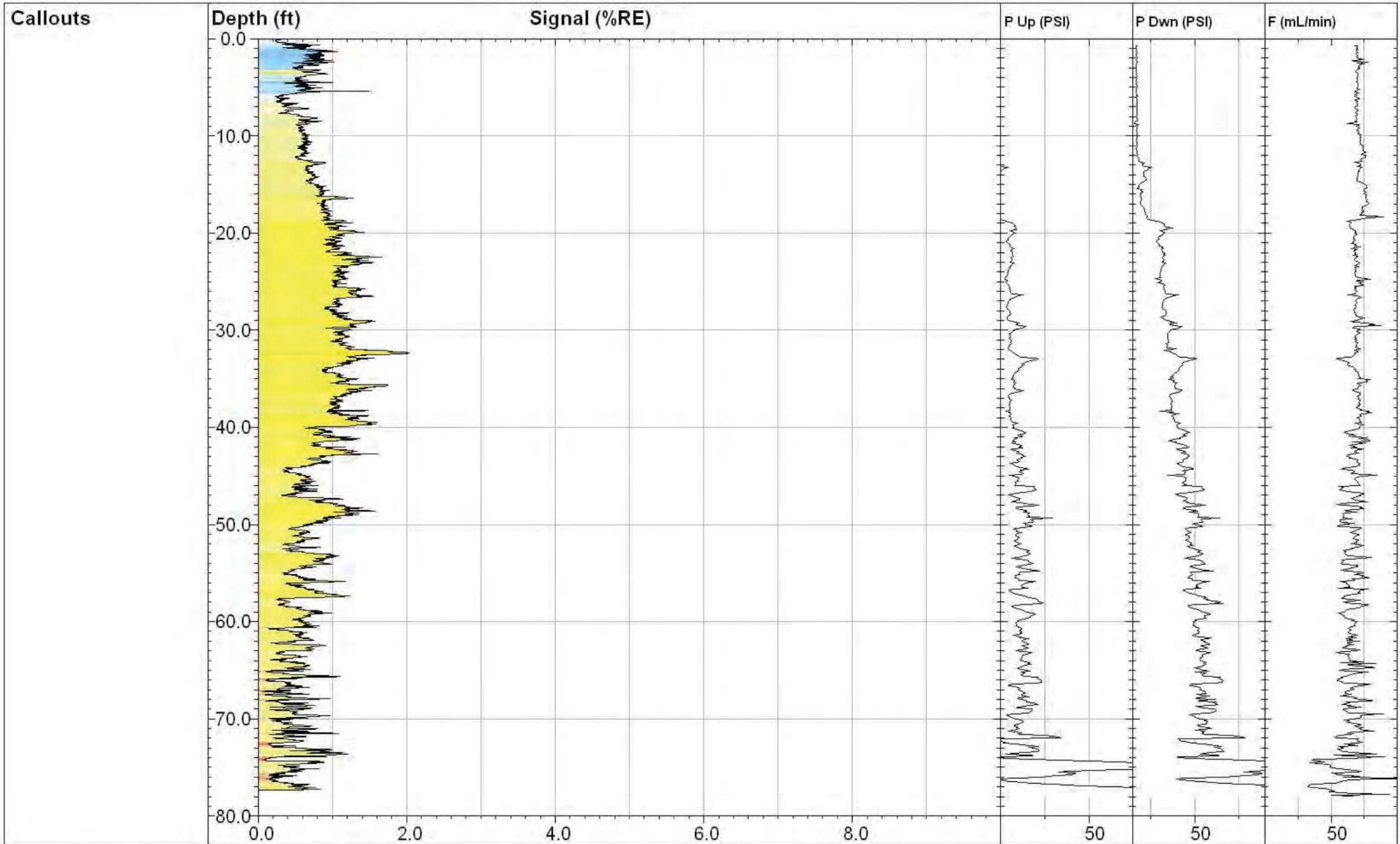
 <p>DAKOTA TECHNOLOGIES FARGO, ND 701.237.4908 WWW.DAKOTATECHNOLOGIES.COM</p>	DyeLIF 030		DyeLIF By Dakota <small>www.DakotaTechnologies.com</small>	
	Site: LOP 2013	Y Coord.(Lat-N) / System: 3047925.2 / SPS	Final depth: 68.82 ft	
	Client / Job: ESTCP I	X Coord.(Lng-E) / Fix: 712522.7 I	Max signal: 2.7 %RE @ 4.07 ft	
	Operator / Unit: RWS/JTL / TG1005	Elevation: Unavailable	Date & Time: 2013-10-16 12:50 EDT	

Callouts

0 represents 28.72' bgs



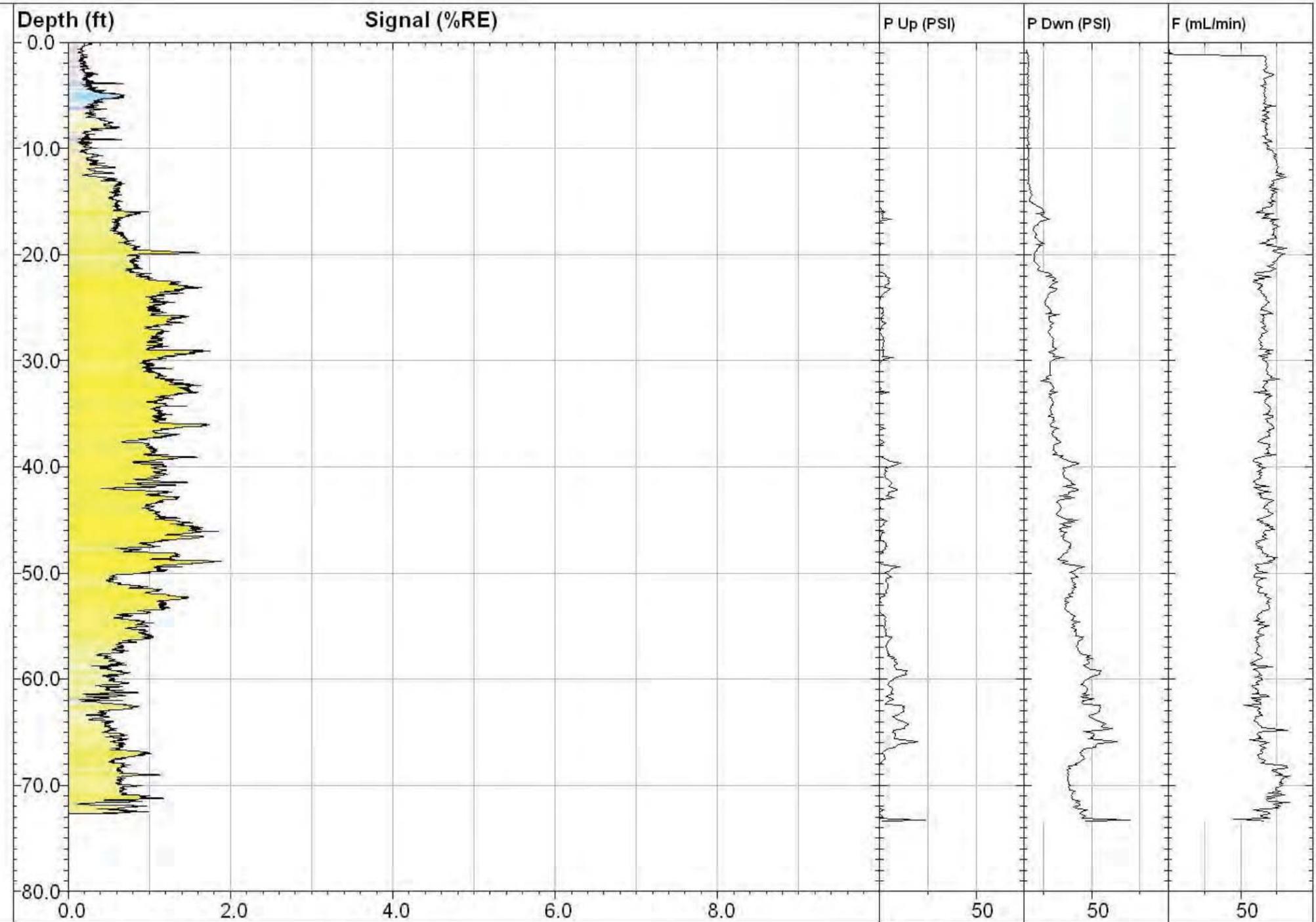
CPTDyeLIF01b		Dye-LIF By Dakota www.DakotaTechnologies.com
Site:	Y Coord.(Lat-N) / System: Unavailable / NA	Final depth: 45.70 ft
Client / Job: /	X Coord.(Lng-E) / Fix: Unavailable / NA	Max signal: 1.1 %RE @ 1.21 ft
Operator / Unit: / TG1001	Elevation: Unavailable	Date & Time: 2014-04-15 13:48 EDT



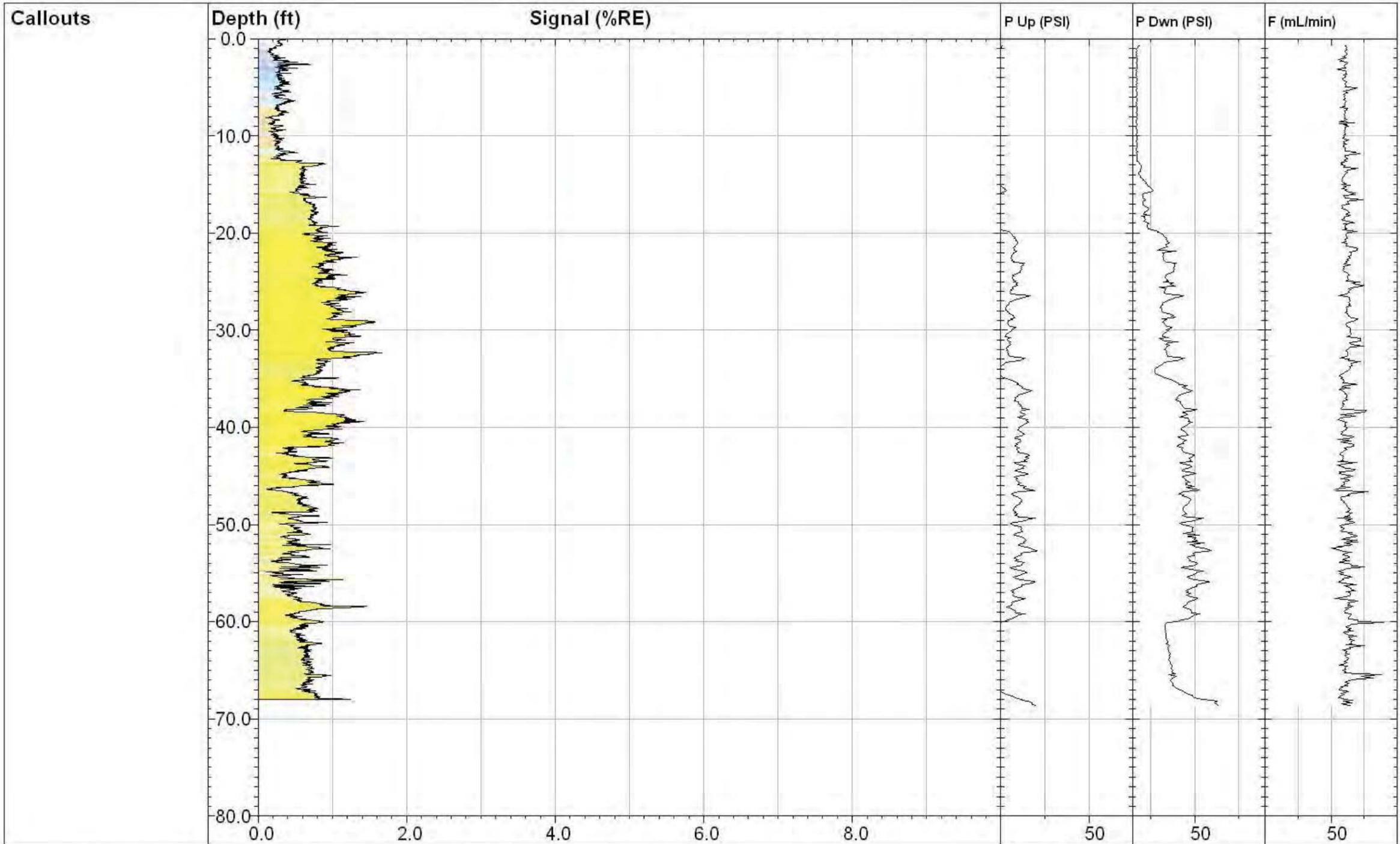
CPTDyeLIF02		Dye-LIF By Dakota www.DakotaTechnologies.com	
Site:	Y Coord.(Lat-N) / System:	Final depth: 77.32 ft	
Client / Job: ESTCP /	X Coord.(Lng-E) / Fix:	Max signal: 2.1 %RE @ 32.37 ft	
Operator / Unit: SDA / TG1001	Elevation:	Date & Time: 2014-04-15 15:18 EDT	
	Unavailable / NA		Unavailable

Callouts

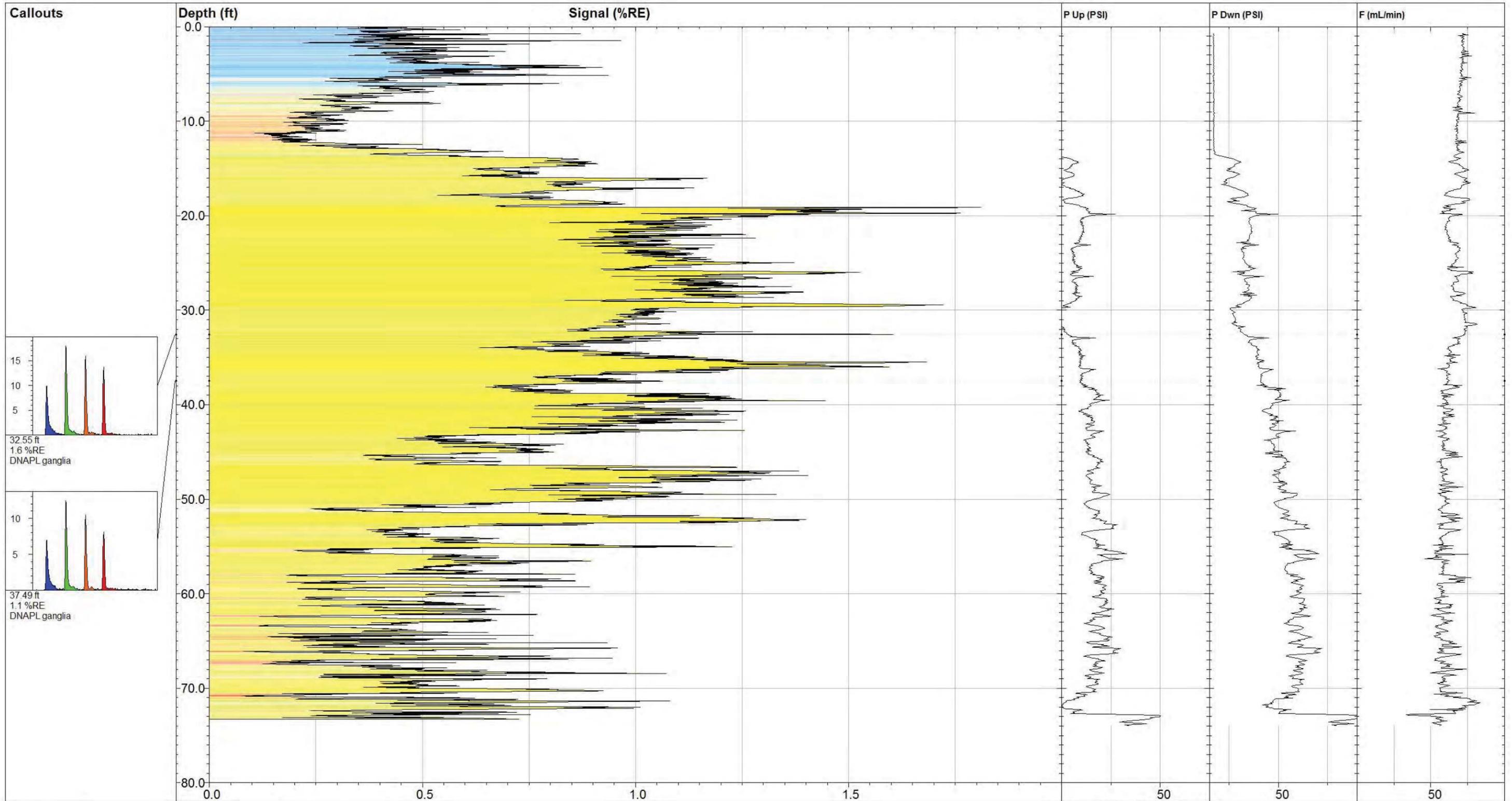
At rod change at 65' while depth was not acquiring a waveform of resembling DNAPL was observed on scope.



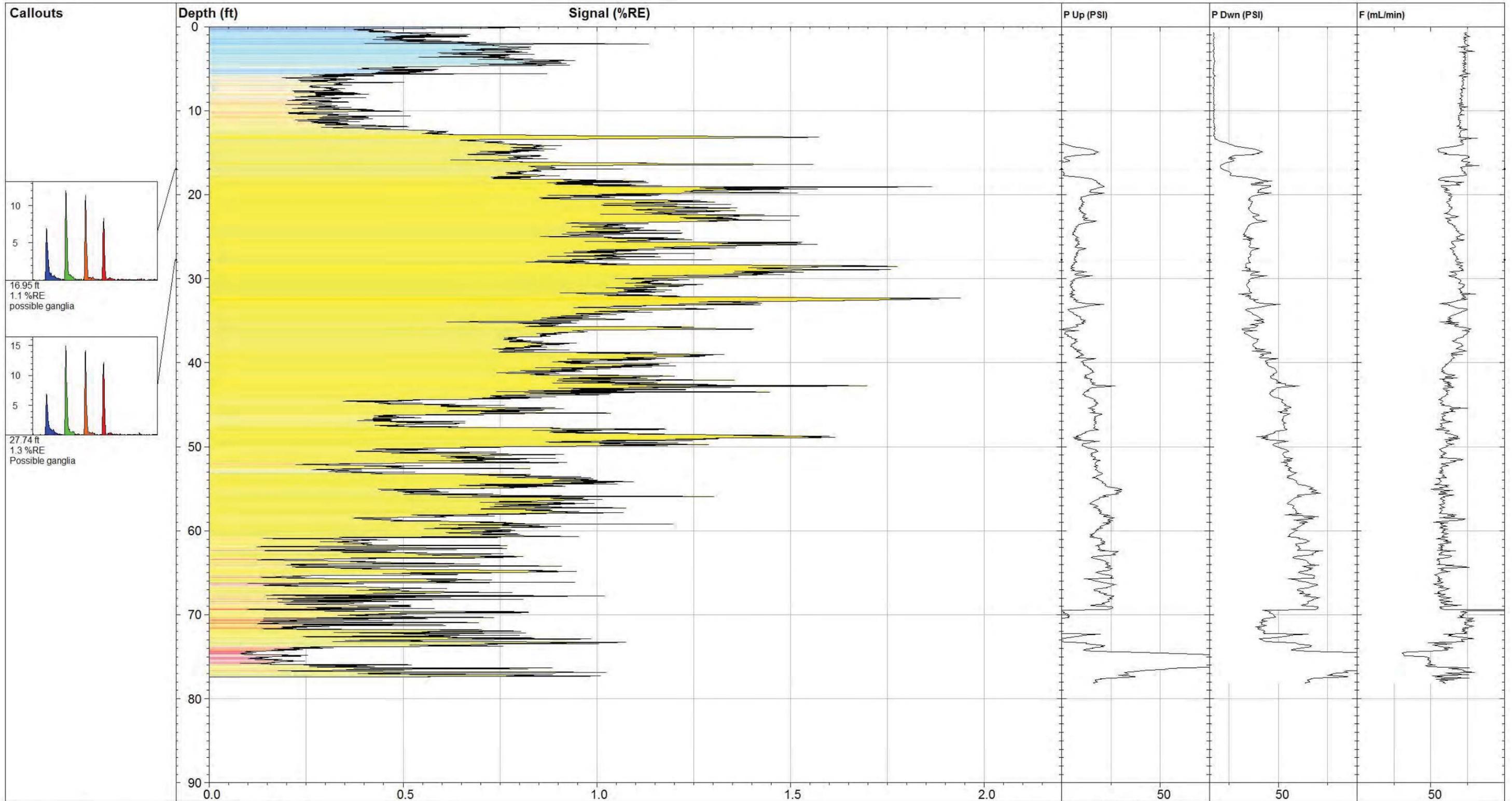
 DAKOTA TECHNOLOGIES <small>FARGO, ND 701.237.4908 WWW.DAKOTATECHNOLOGIES.COM</small>	CPTDyeLIF03		Dye-LIF By Dakota <small>www.DakotaTechnologies.com</small>	
	Site:	Y Coord.(Lat-N) / System:	Final depth:	
	Client / Job:	X Coord.(Lng-E) / Fix:	Max signal:	
Operator / Unit:	Elevation:	Date & Time:		
ESTCP /	Unavailable / NA	2014-04-15 17:04 EDT		
SDA / TG1001	Unavailable			



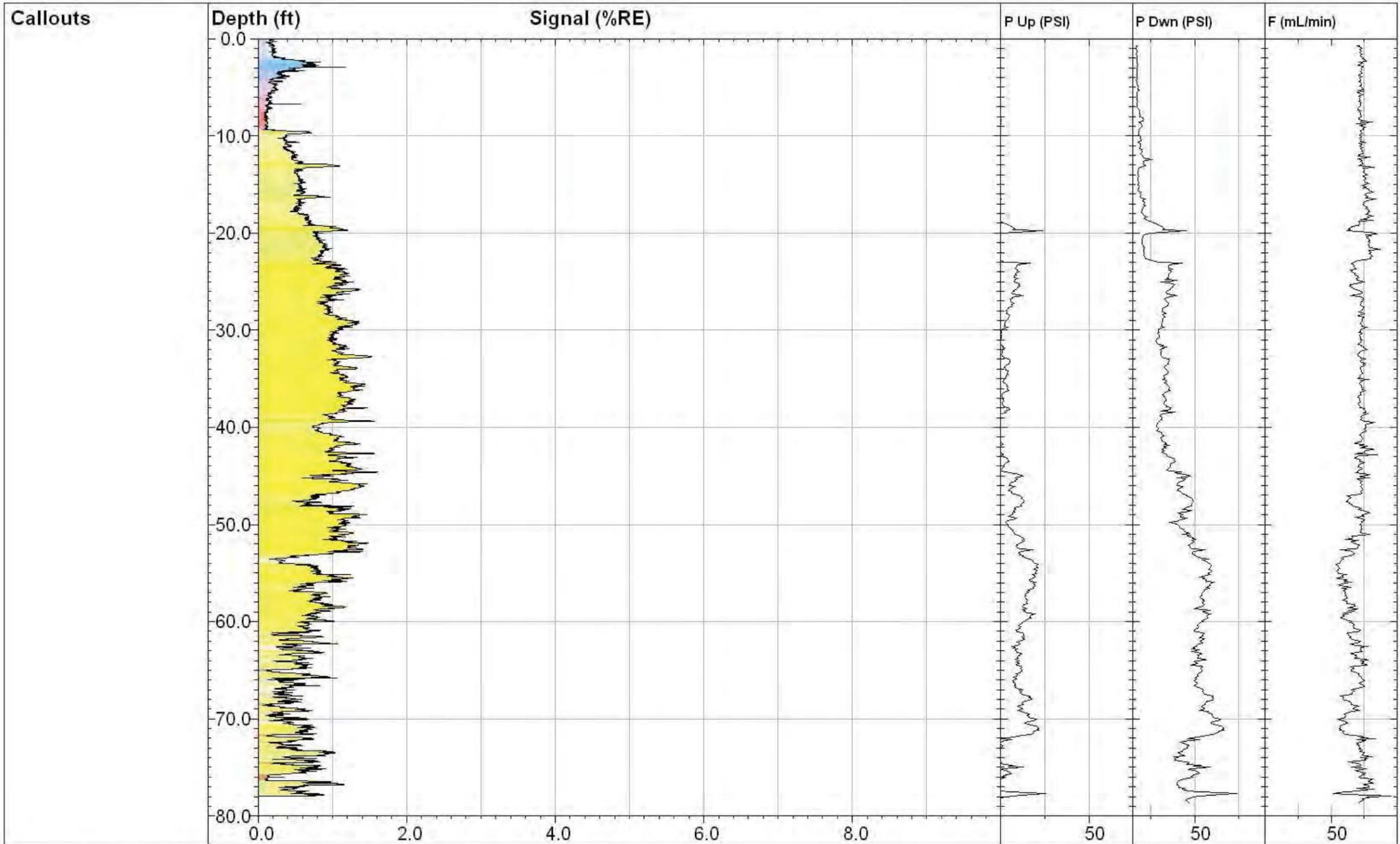
 DAKOTA TECHNOLOGIES <small>FARGO, ND 701.237.4908 WWW.DAKOTATECHNOLOGIES.COM</small>	CPTDyeLIF04		Dye-LIF By Dakota <small>www.DakotaTechnologies.com</small>
	Site:	Y Coord.(Lat-N) / System:	Final depth:
	Client / Job:	X Coord.(Lng-E) / Fix:	Max signal:
	Operator / Unit:	Elevation:	Date & Time:
		Unavailable / NA	68.02 ft
ESTCP /	Unavailable / NA	1.7 %RE @ 32.34 ft	
SDA / TG1001	Unavailable	2014-04-16 09:29 EDT	



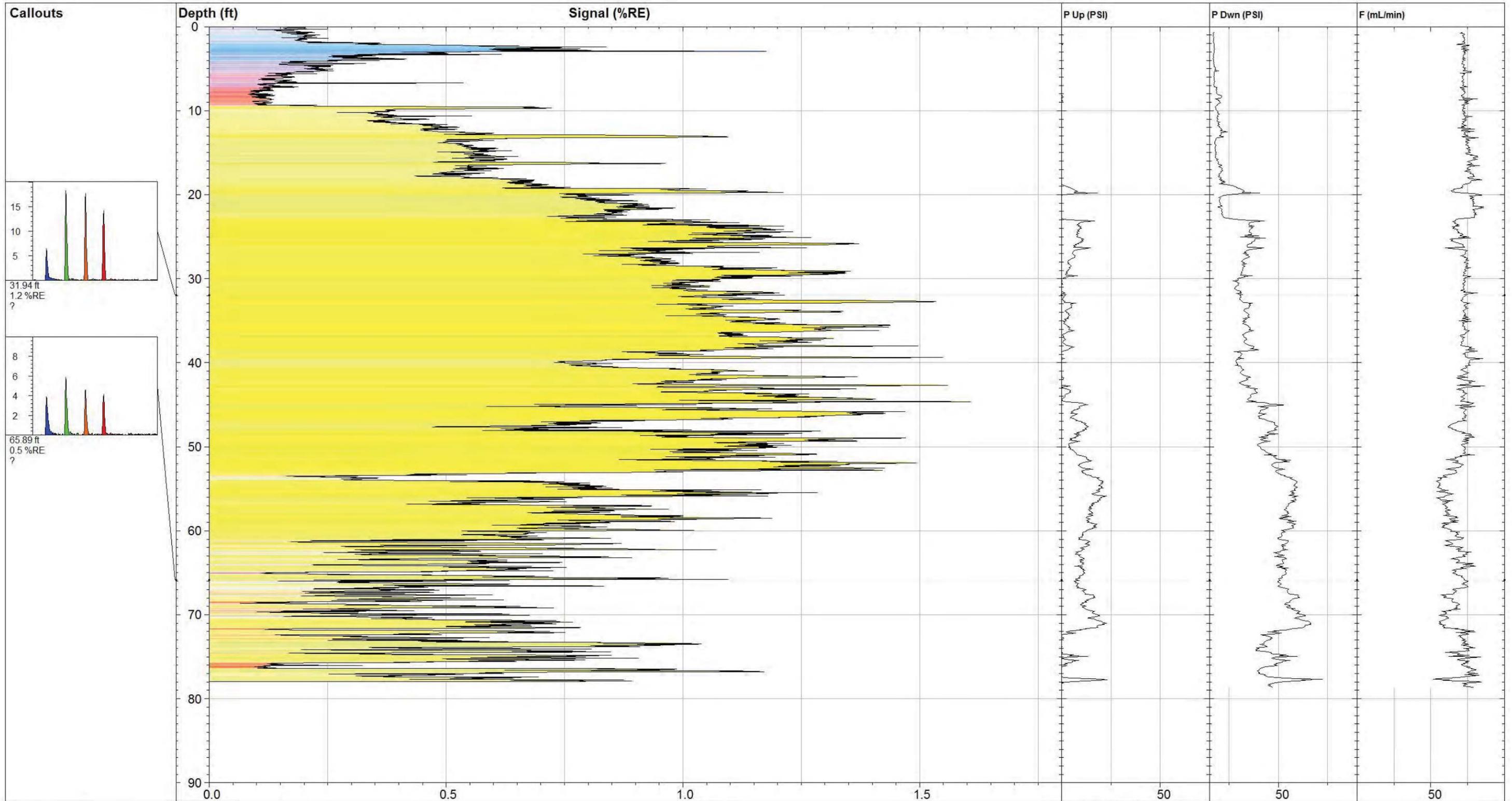
CPTDyeLIF05		Dye-LIF By Dakota <small>www.DakotaTechnologies.com</small>	
Site:	Y Coord.(Lat-N) / System:	Final depth:	
	Unavailable / NA	73.25 ft	
Client / Job:	X Coord.(Lng-E) / Fix:	Max signal:	
ESTCP /	Unavailable / NA	1.9 %RE @ 19.12 ft	
Operator / Unit:	Elevation:	Date & Time:	
SDA / TG1001	Unavailable	2014-04-16 10:47 EDT	



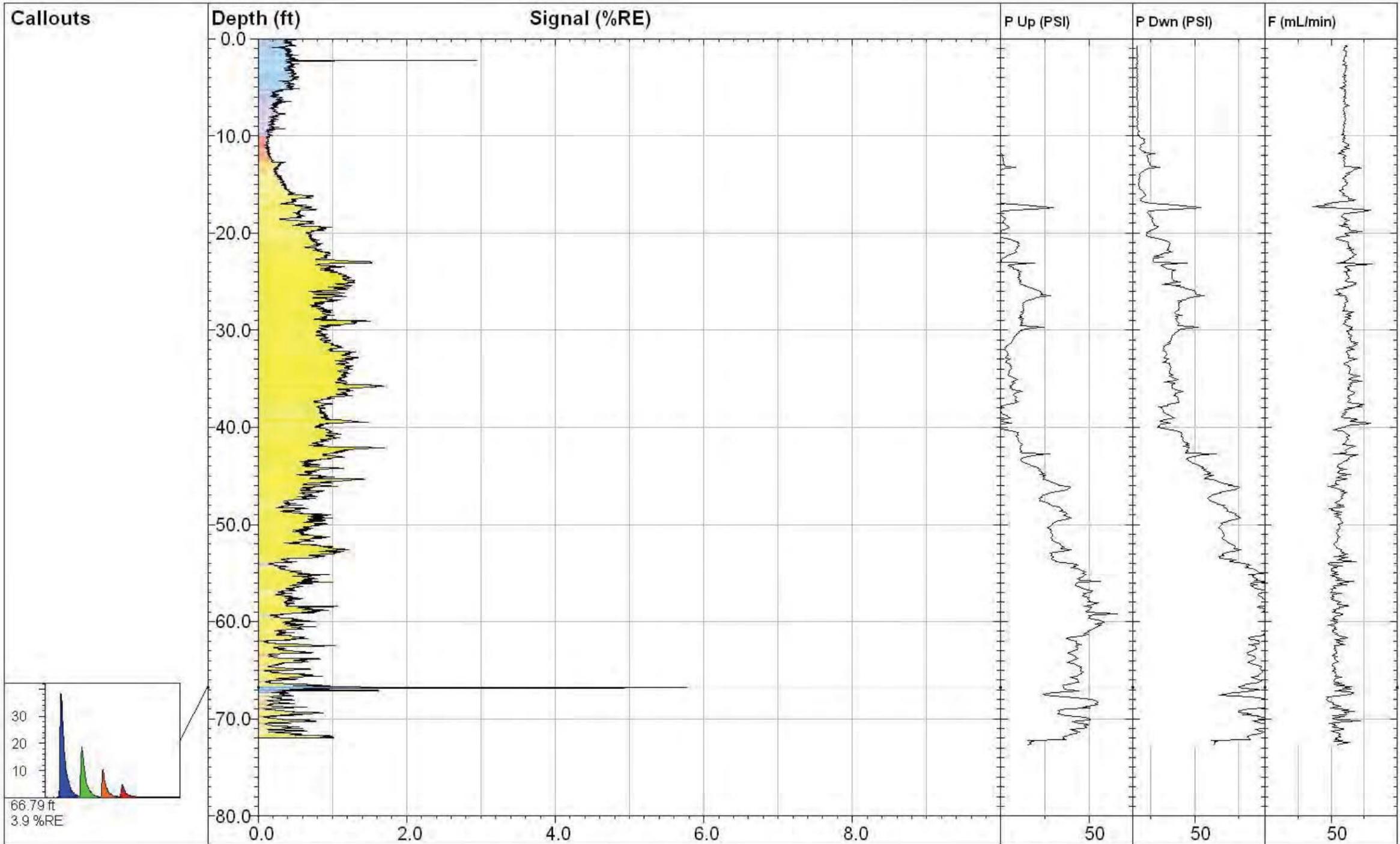
 <p>DAKOTA TECHNOLOGIES FARGO, ND 701.237.4908 WWW.DAKOTATECHNOLOGIES.COM</p>	CPTDyeLIF06		Dye-LIF By Dakota <small>www.DakotaTechnologies.com</small>
	Site:	Y Coord.(Lat-N) / System: Unavailable / NA	Final depth: 77.43 ft
	Client / Job: ESTCP /	X Coord.(Lng-E) / Fix: Unavailable / NA	Max signal: 1.9 %RE @ 32.30 ft
	Operator / Unit: SDA / TG1001	Elevation: Unavailable	Date & Time: 2014-04-16 13:05 EDT



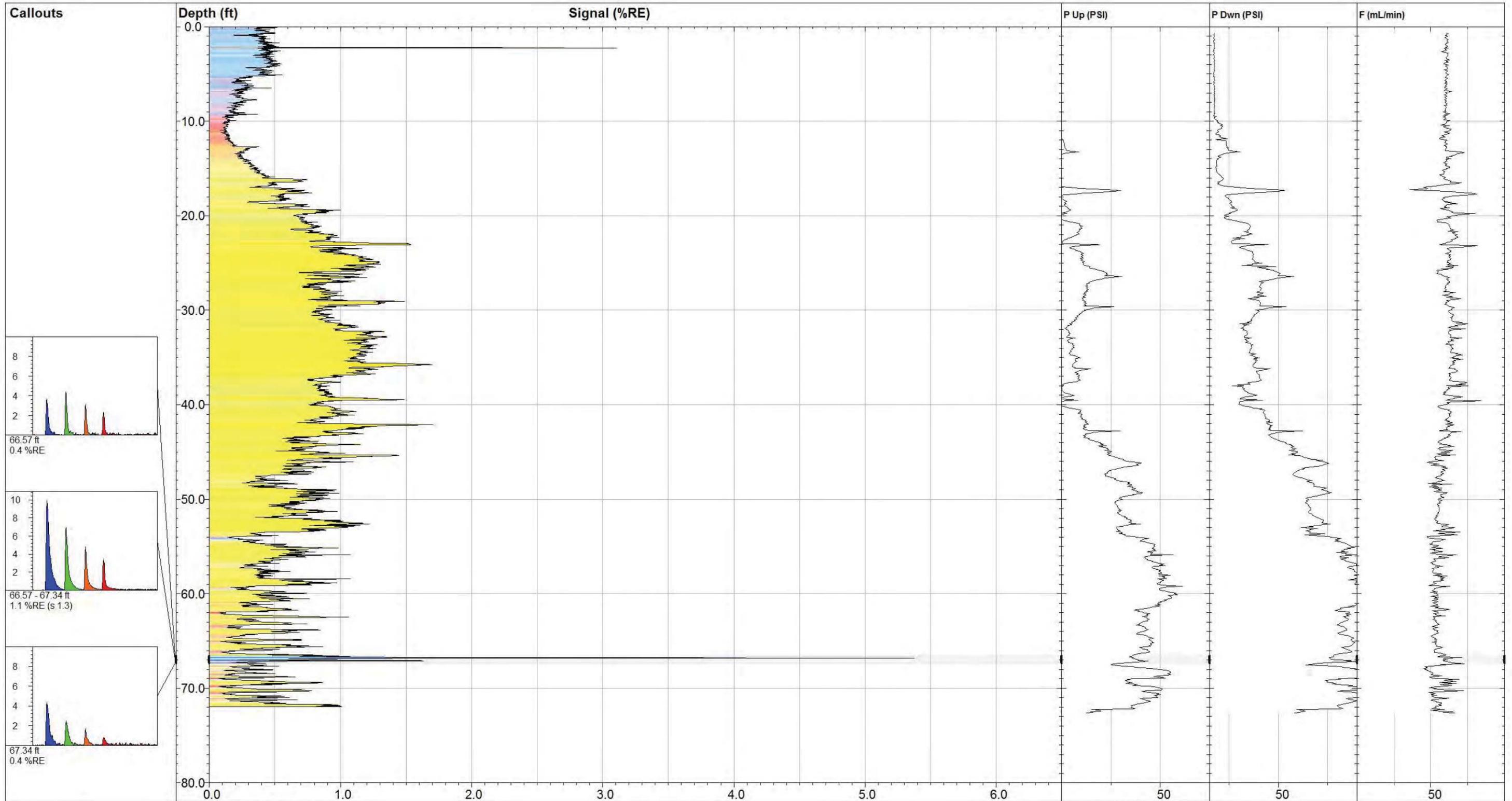
 DAKOTA TECHNOLOGIES <small>FARGO, ND 701.237.4908 WWW.DAKOTATECHNOLOGIES.COM</small>	CPTDyeLIF07		Dye-LIF By Dakota <small>www.DakotaTechnologies.com</small>
	Site:	Y Coord.(Lat-N) / System: Unavailable / NA	Final depth: 77.93 ft
	Client / Job: ESTCP /	X Coord.(Lng-E) / Fix: Unavailable / NA	Max signal: 1.6 %RE @ 44.62 ft
	Operator / Unit: SDA / TG1001	Elevation: Unavailable	Date & Time: 2014-04-16 14:28 EDT



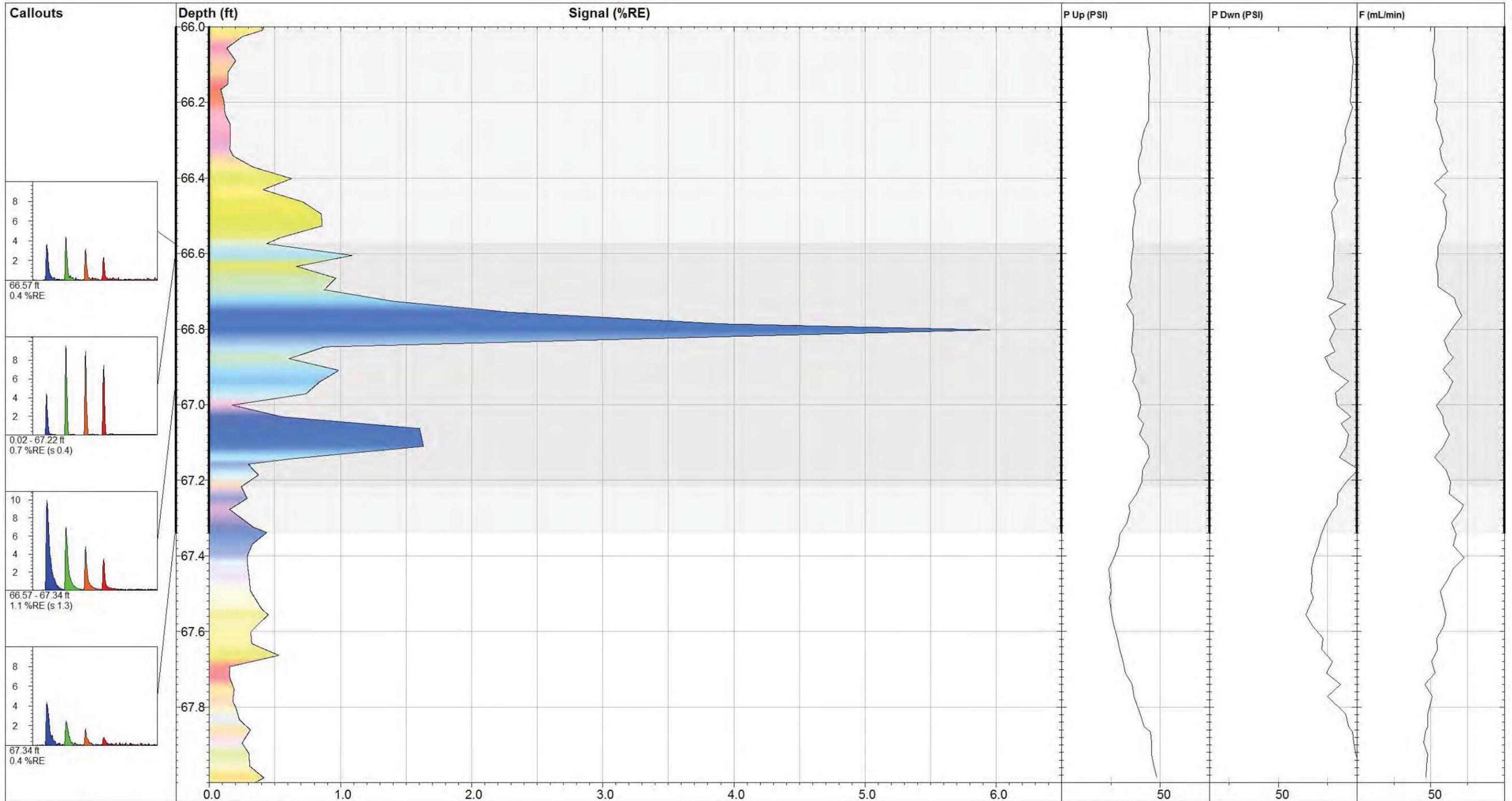
 <p>DAKOTA TECHNOLOGIES FARGO, ND 701.237.4908 WWW.DAKOTATECHNOLOGIES.COM</p>	CPTDyeLIF07		Dye-LIF By Dakota www.DakotaTechnologies.com
	Site:	Y Coord.(Lat-N) / System: Unavailable / NA	Final depth: 77.93 ft
	Client / Job: ESTCP /	X Coord.(Lng-E) / Fix: Unavailable / NA	Max signal: 1.6 %RE @ 44.62 ft
	Operator / Unit: SDA / TG1001	Elevation: Unavailable	Date & Time: 2014-04-16 14:28 EDT

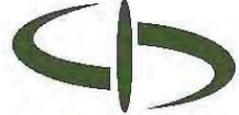


CPTDyeLIF08		Dye-LIF By Dakota www.DakotaTechnologies.com
Site:	Y Coord.(Lat-N) / System: Unavailable / NA	Final depth: 71.95 ft
Client / Job: ESTCP /	X Coord.(Lng-E) / Fix: Unavailable / NA	Max signal: 6.0 %RE @ 66.80 ft
Operator / Unit: SDA / TG1001	Elevation: Unavailable	Date & Time: 2014-04-17 08:50 EDT

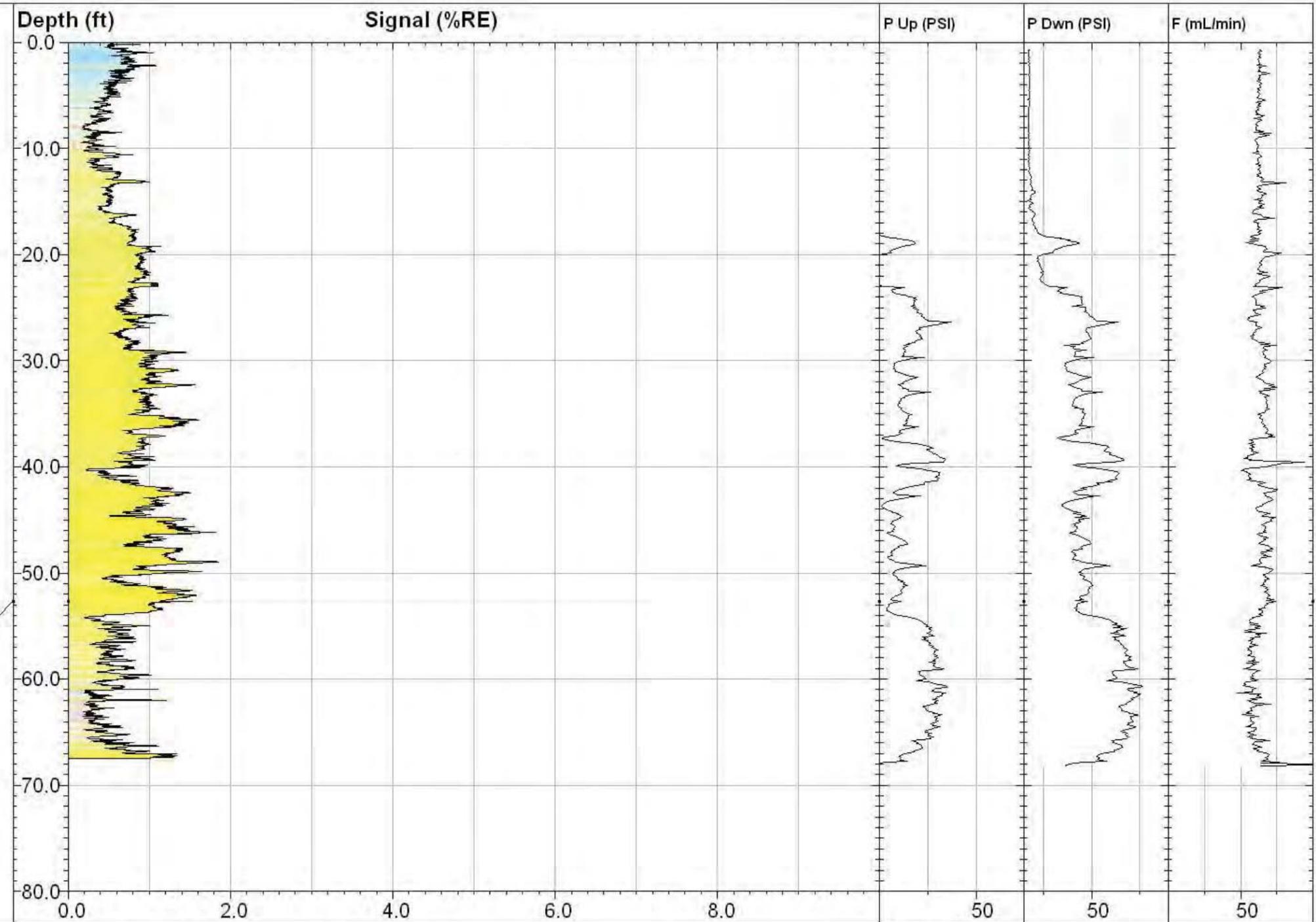
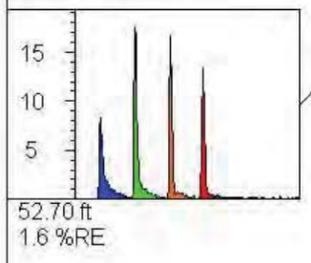


CPTDyeLIF08		Dye-LIF By Dakota www.DakotaTechnologies.com	
Site:	Y Coord.(Lat-N) / System:	Final depth:	
	Unavailable / NA	71.95 ft	
Client / Job:	X Coord.(Lng-E) / Fix:	Max signal:	
ESTCP /	Unavailable / NA	6.0 %RE @ 66.80 ft	
Operator / Unit:	Elevation:	Date & Time:	
SDA / TG1001	Unavailable	2014-04-17 08:50 EDT	



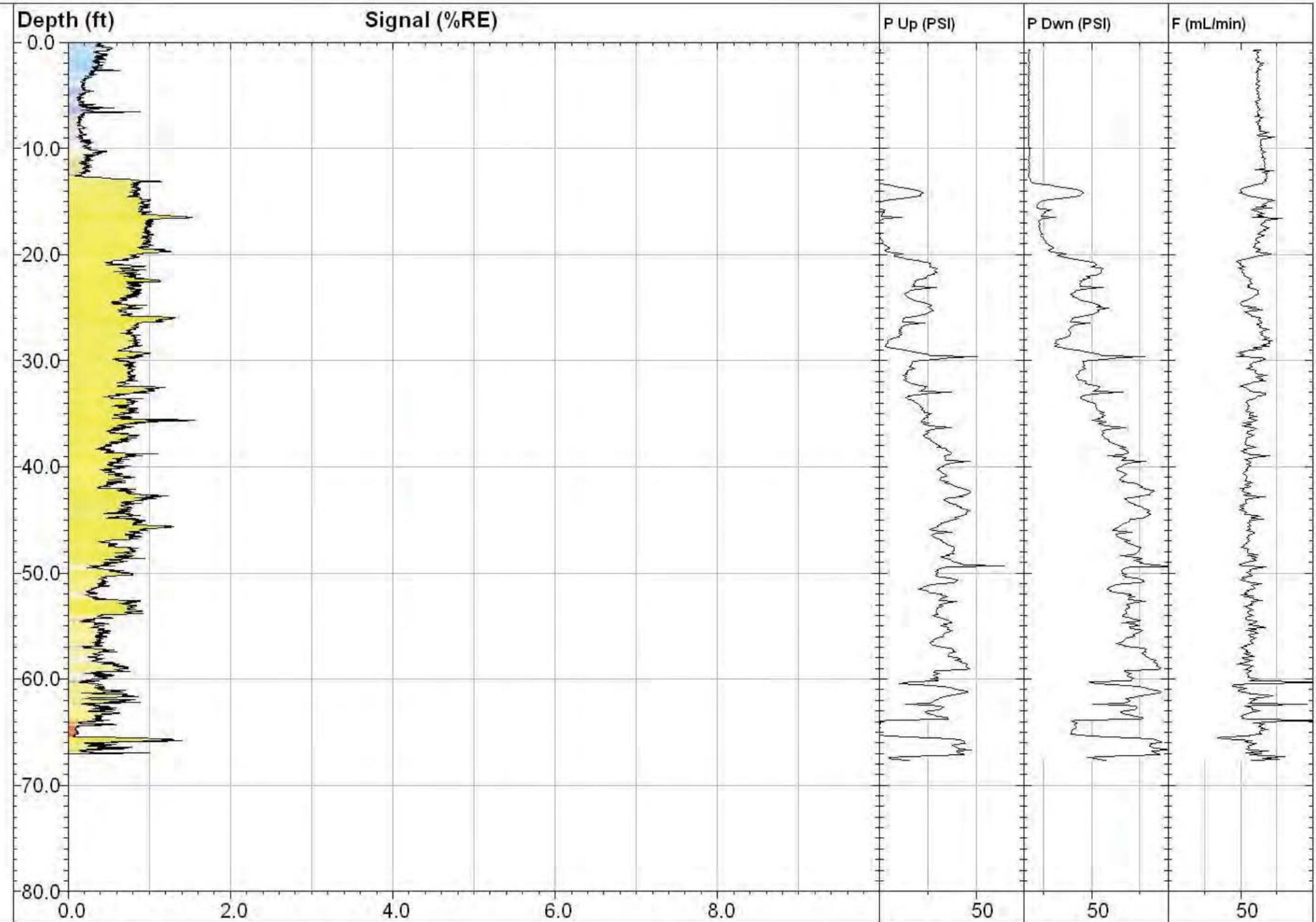
 DAKOTA TECHNOLOGIES <small>FARGO, ND 701.237.4908 WWW.DAKOTATECHNOLOGIES.COM</small>	CPTDyeLIF08		Dye-LIF By Dakota <small>www.DakotaTechnologies.com</small>
	Site:	Y Coord. (Lat-N) / System: Unavailable / NA	Final depth: 71.95 ft
	Client / Job: ESTCP /	X Coord. (Lng-E) / Fix: Unavailable / NA	Max signal: 6.0 %RE @ 66.80 ft
	Operator / Unit: SDA / TG1001	Elevation: Unavailable	Date & Time: 2014-04-17 08:50 EDT

Callouts



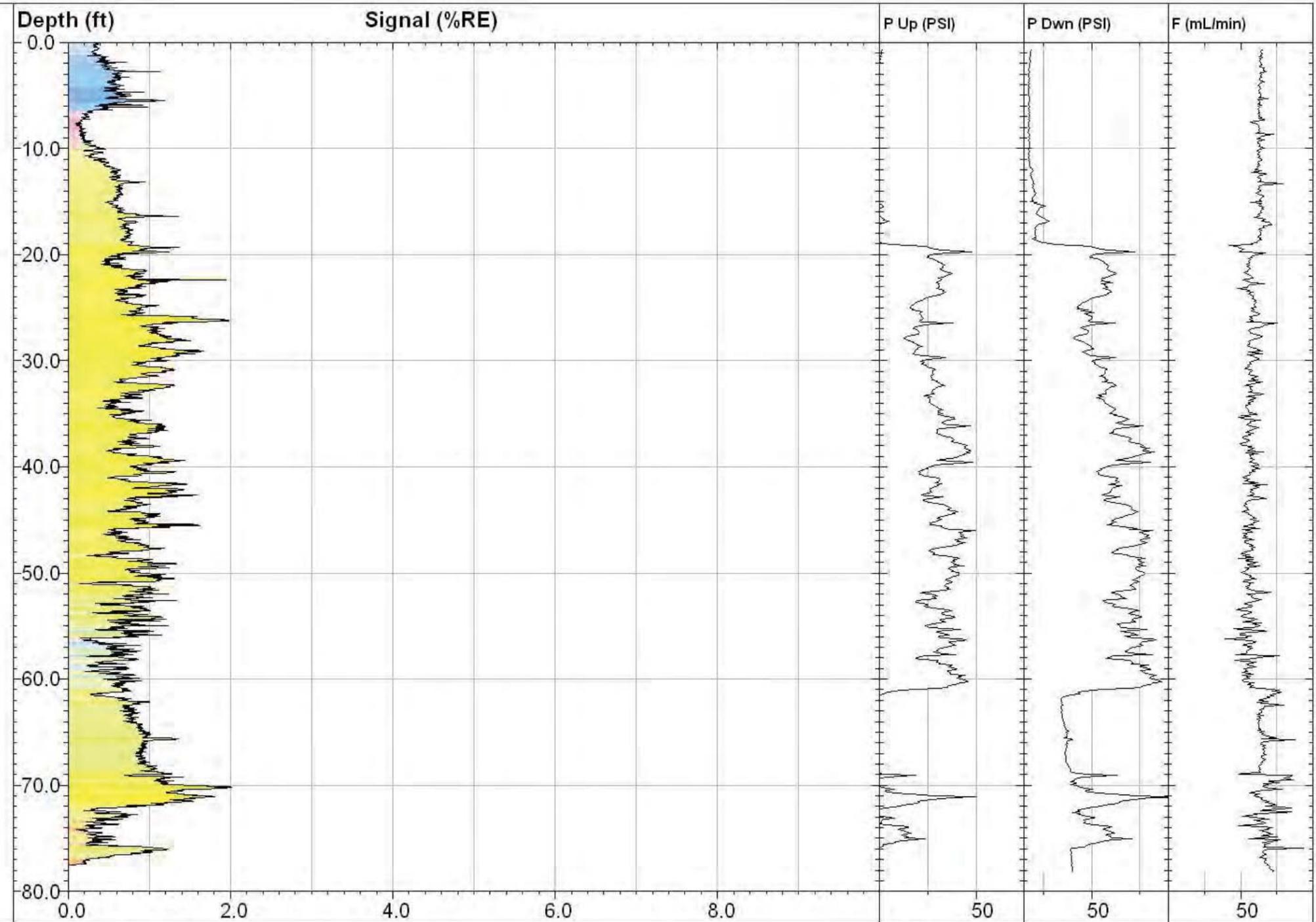
CPTDyeLIF09		Dye-LIF By Dakota <small>www.DakotaTechnologies.com</small>
Site:	Y Coord.(Lat-N) / System: Unavailable / NA	Final depth: 67.47 ft
Client / Job: ESTCP /	X Coord.(Lng-E) / Fix: Unavailable / NA	Max signal: 1.9 %RE @ 48.95 ft
Operator / Unit: SDA / TG1001	Elevation: Unavailable	Date & Time: 2014-04-17 10:12 EDT

Callouts



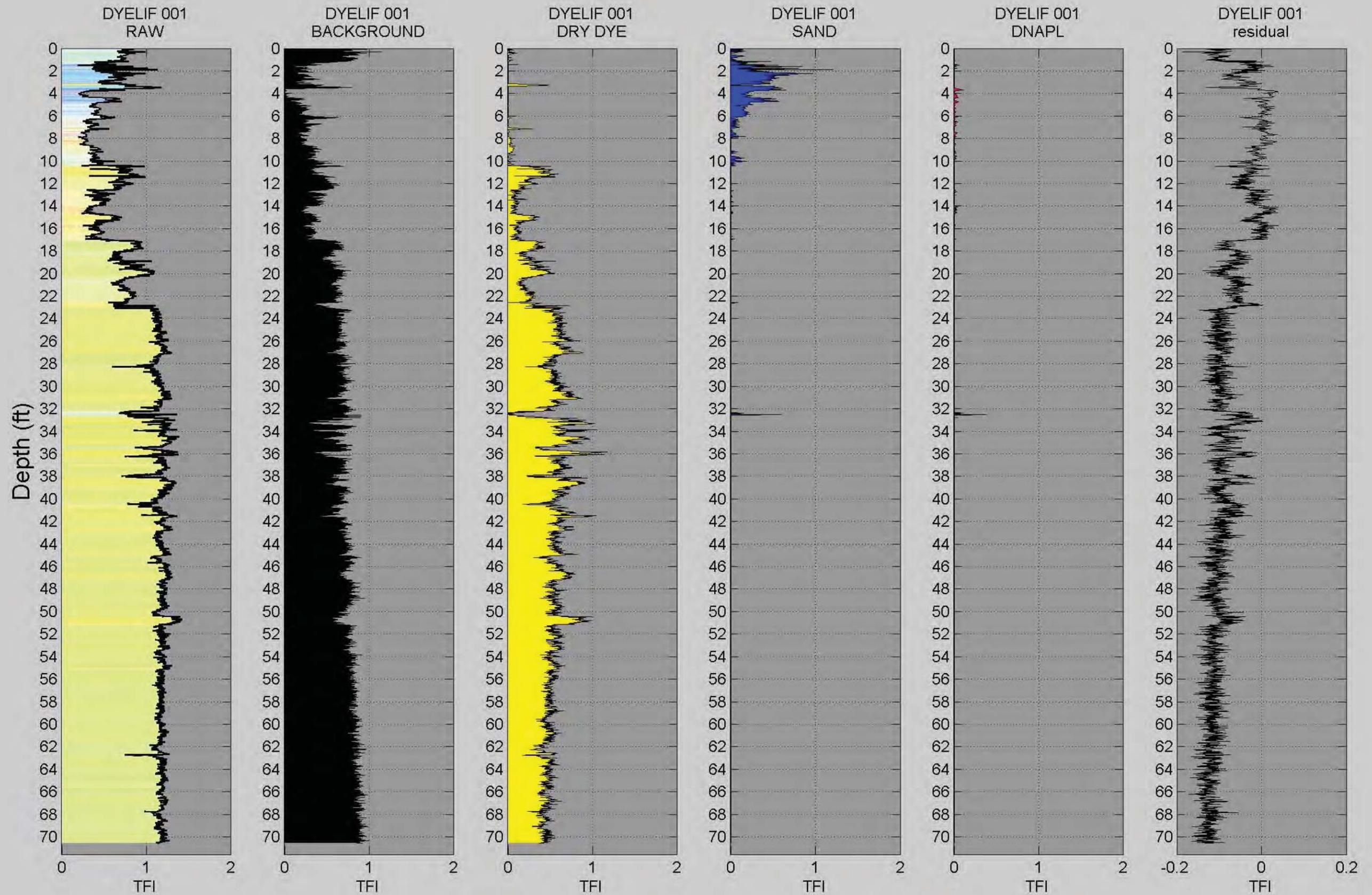
CPTDyeLIF10		Dye-LIF By Dakota <small>www.DakotaTechnologies.com</small>
Site:	Y Coord.(Lat-N) / System: Unavailable / NA	Final depth: 67.04 ft
Client / Job: ESTCP /	X Coord.(Lng-E) / Fix: Unavailable / NA	Max signal: 1.6 %RE @ 35.64 ft
Operator / Unit: SDA / TG1001	Elevation: Unavailable	Date & Time: 2014-04-17 11:22 EDT

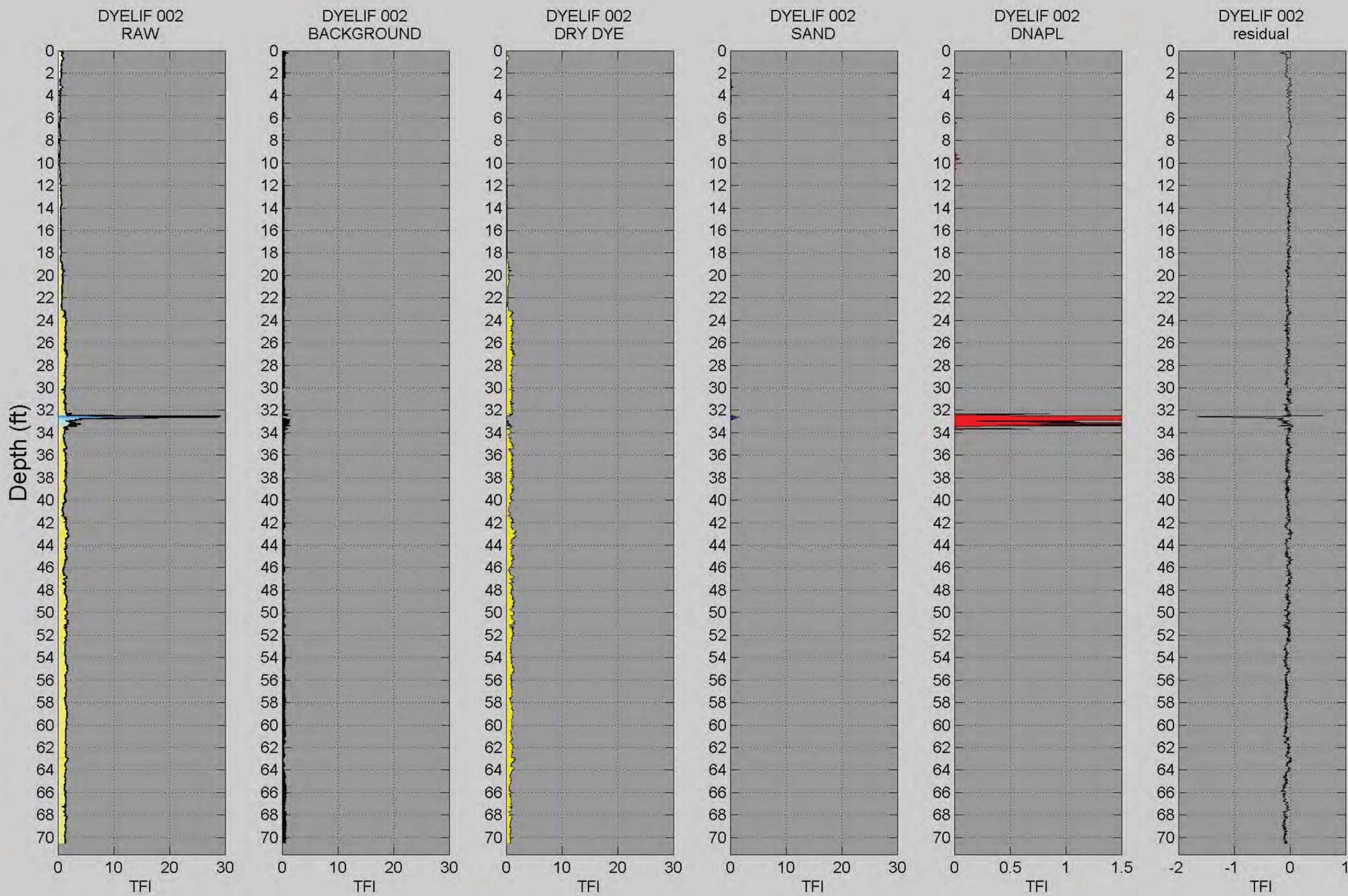
Callouts

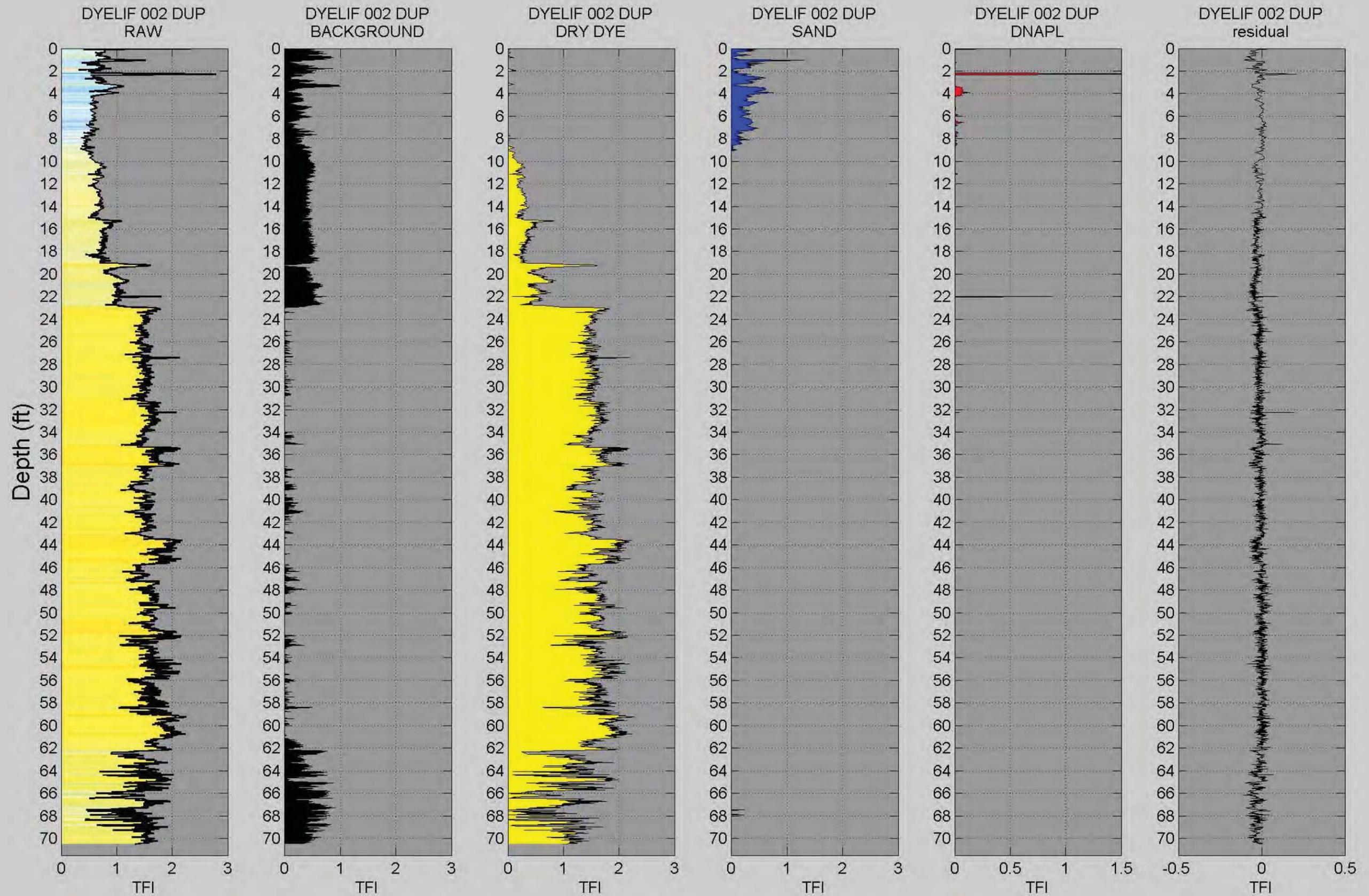


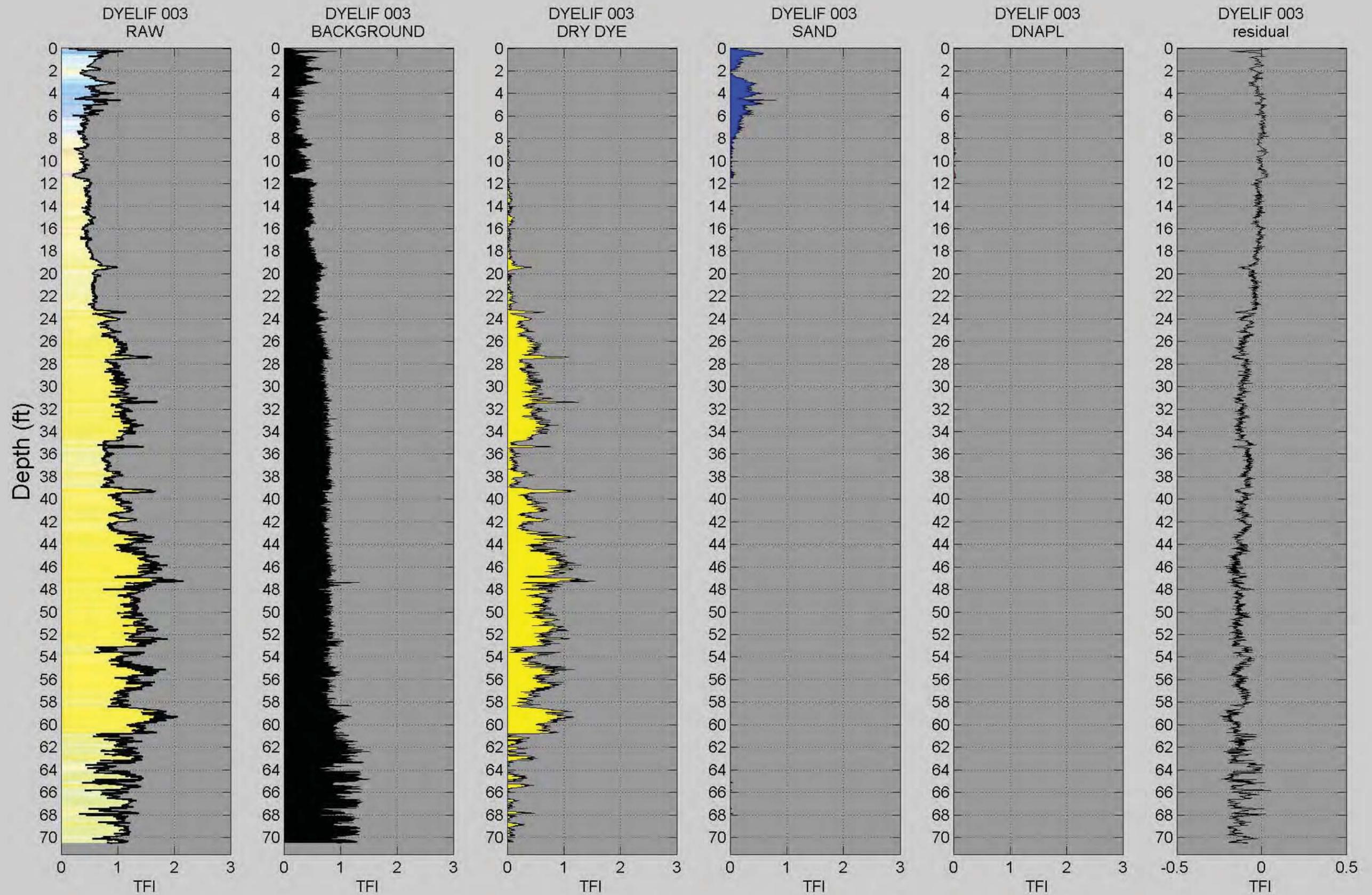
CPTDyeLIF11		Dye-LIF By Dakota www.DakotaTechnologies.com
Site:	Y Coord.(Lat-N) / System: Unavailable / NA	Final depth: 77.47 ft
Client / Job: ESTCP /	X Coord.(Lng-E) / Fix: Unavailable / NA	Max signal: 2.0 %RE @ 70.21 ft
Operator / Unit: SDA / TG1001	Elevation: Unavailable	Date & Time: 2014-04-17 12:59 EDT

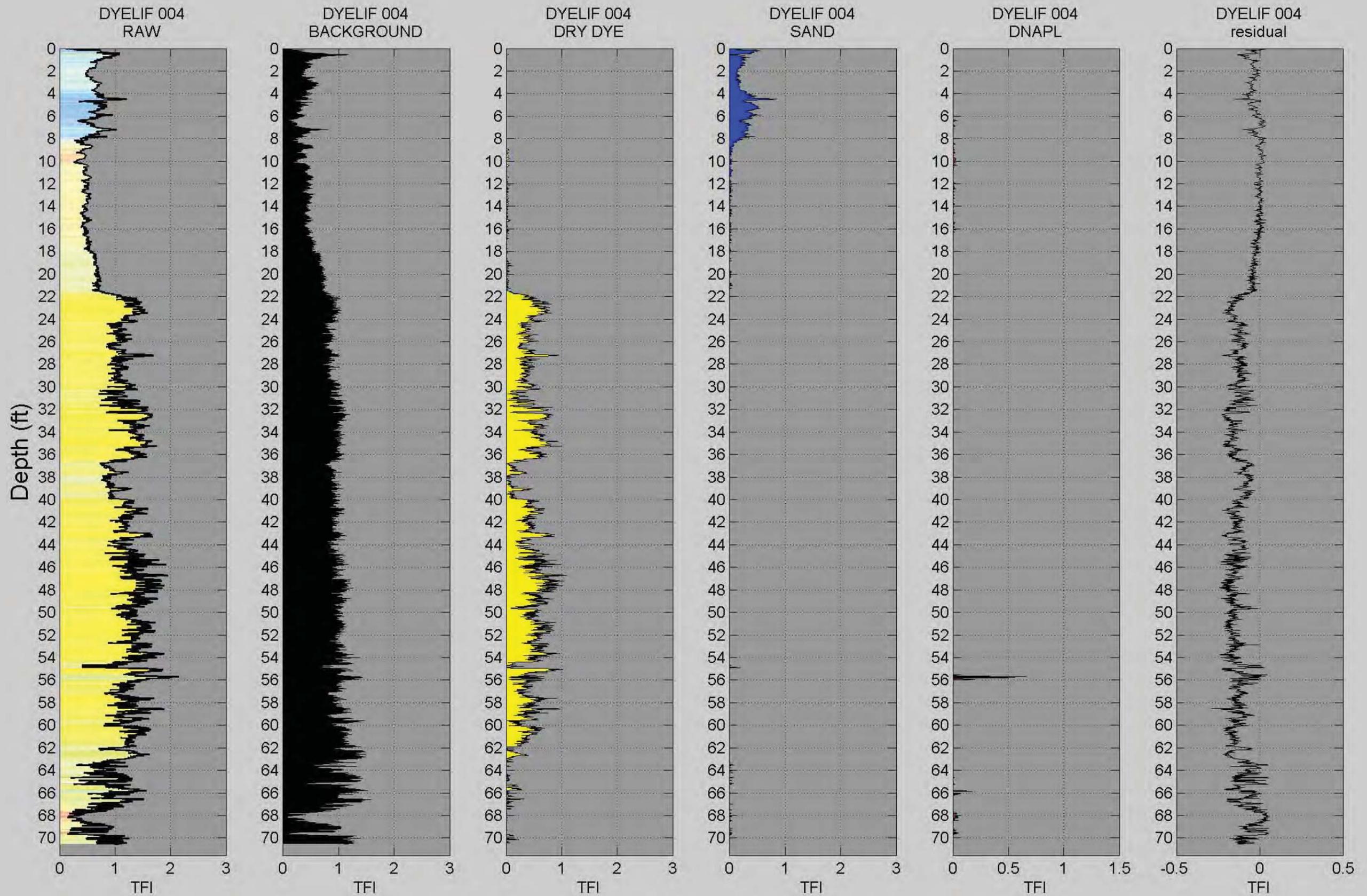
Appendix D: Multi-Panel Plots Showing Results of Advanced Data Analysis

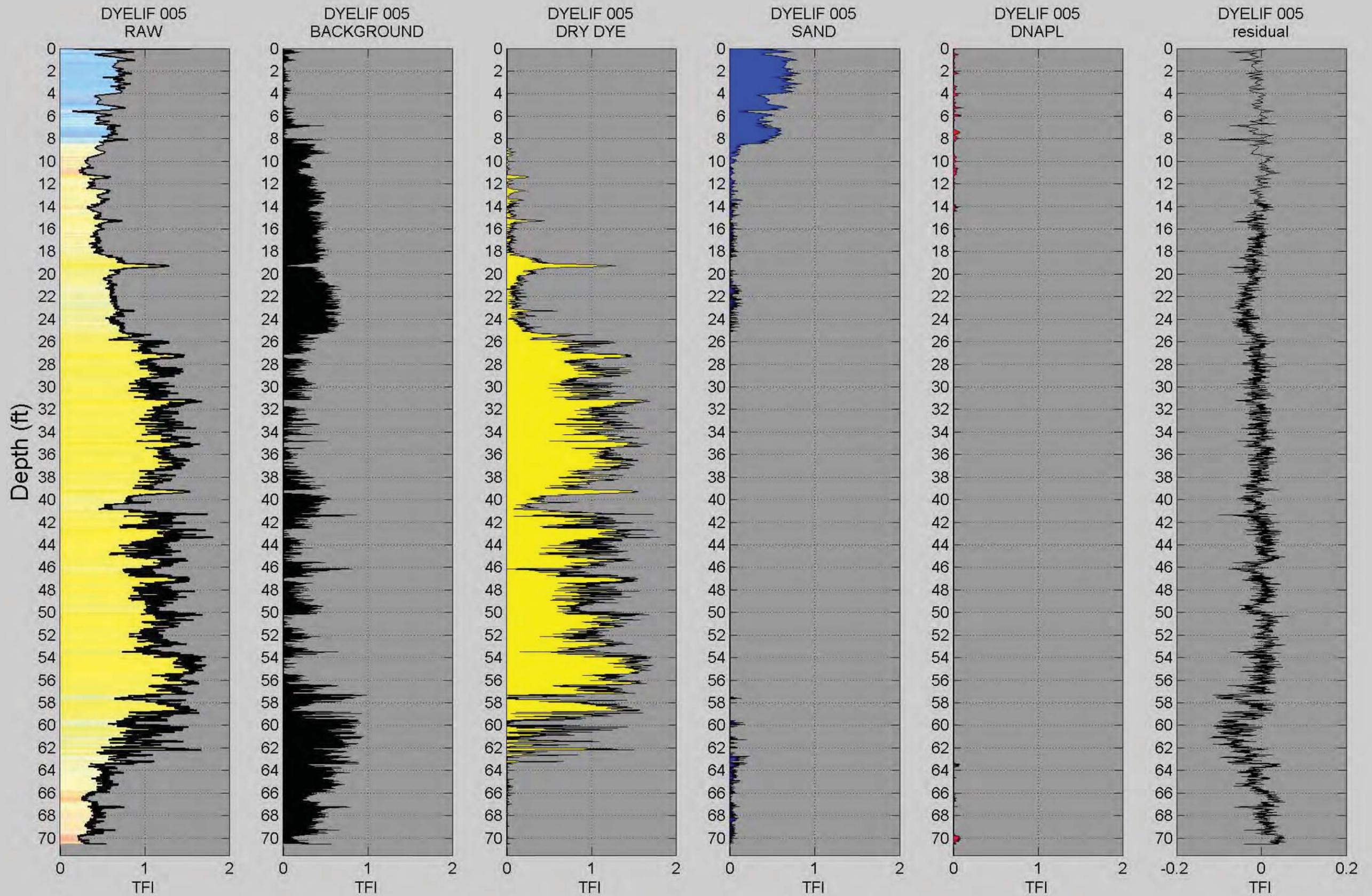


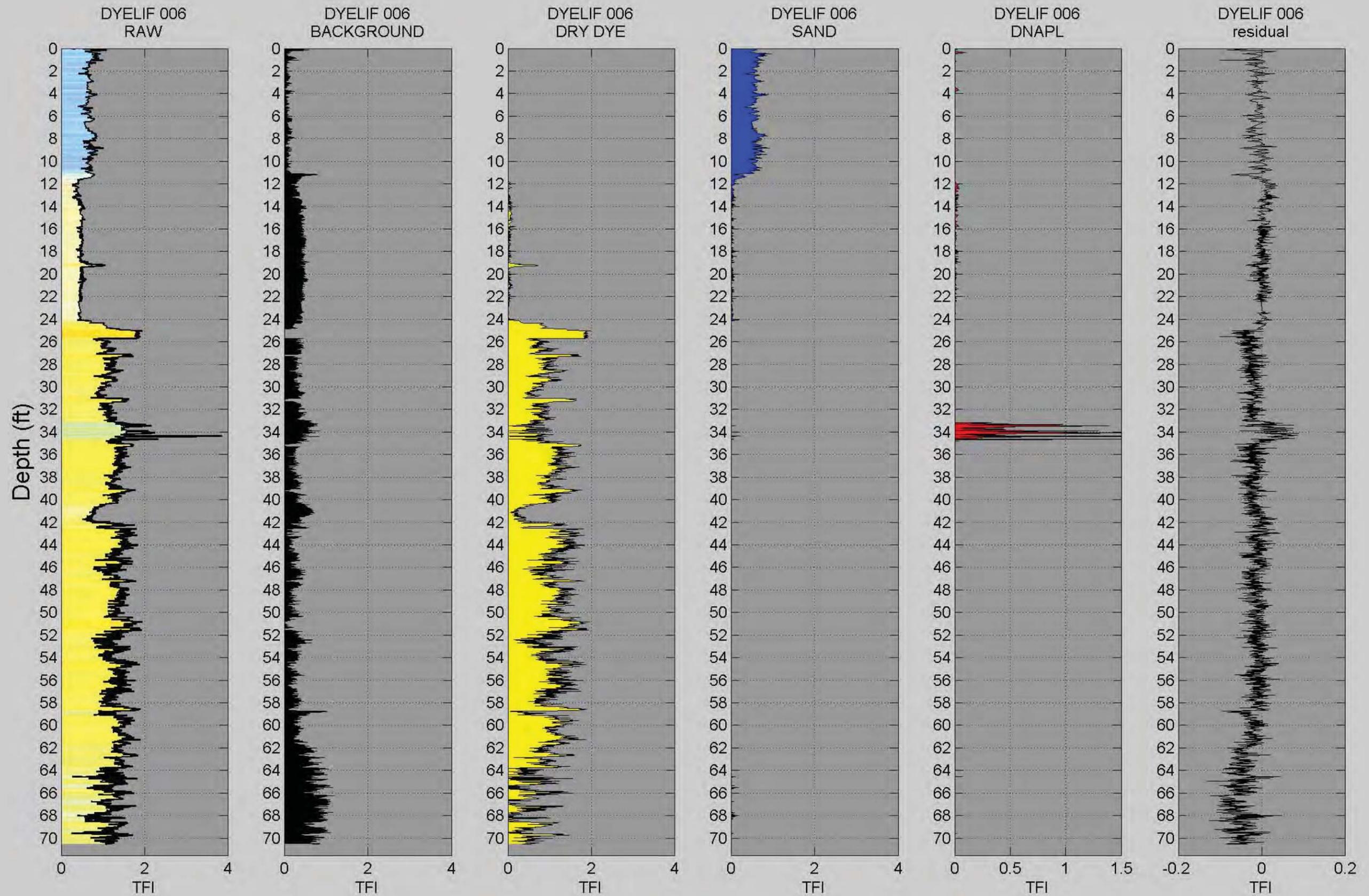


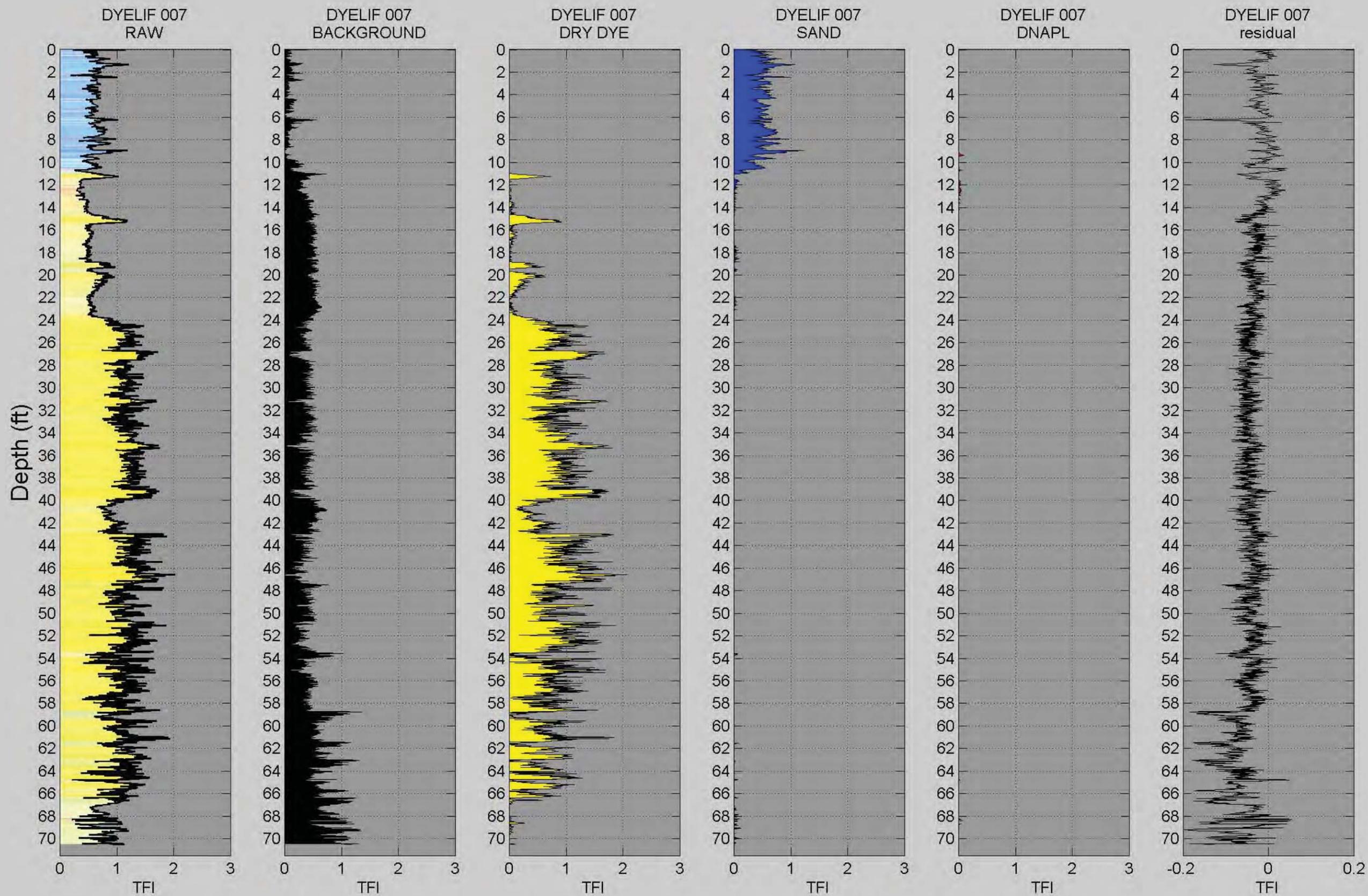


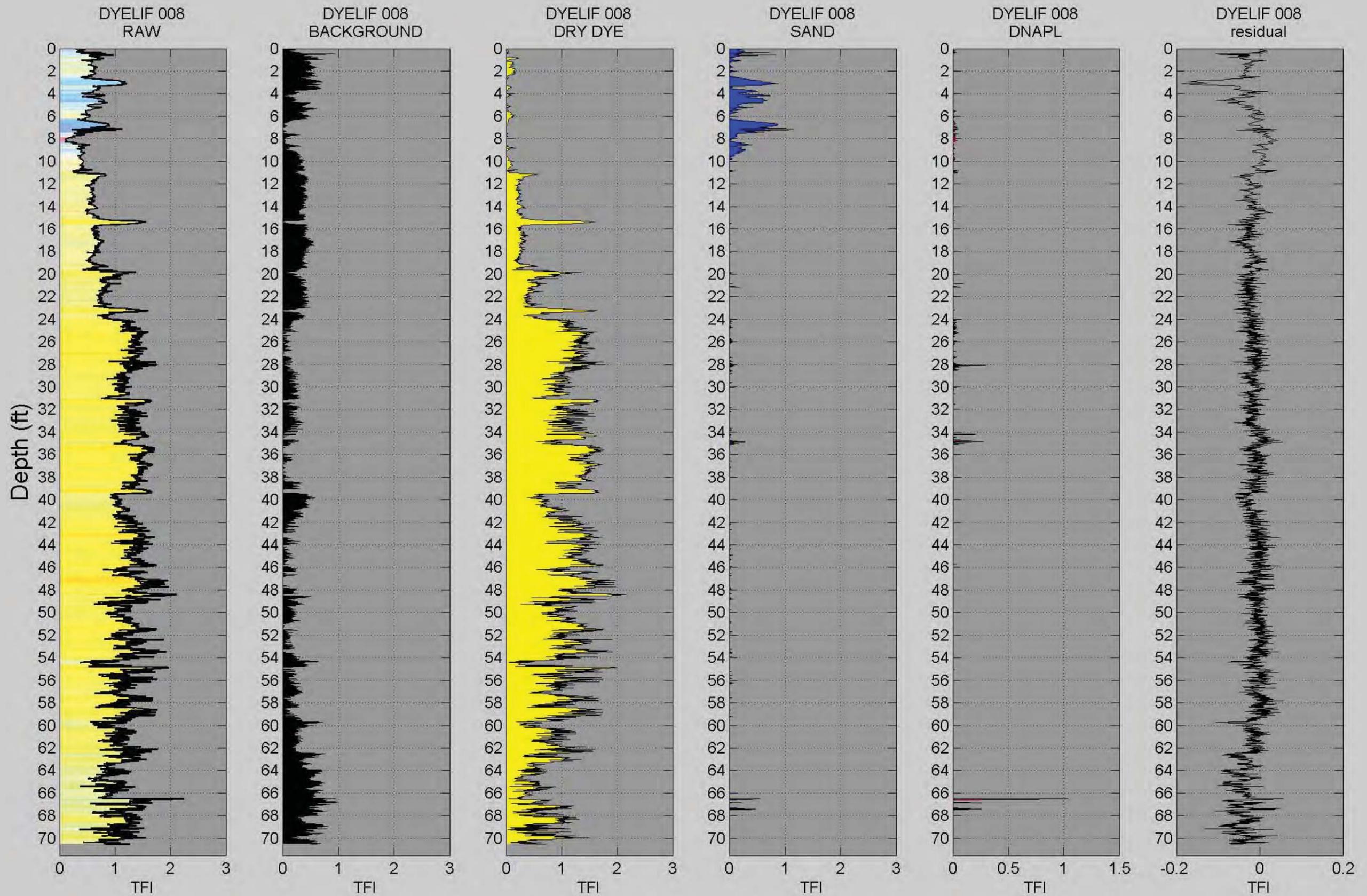


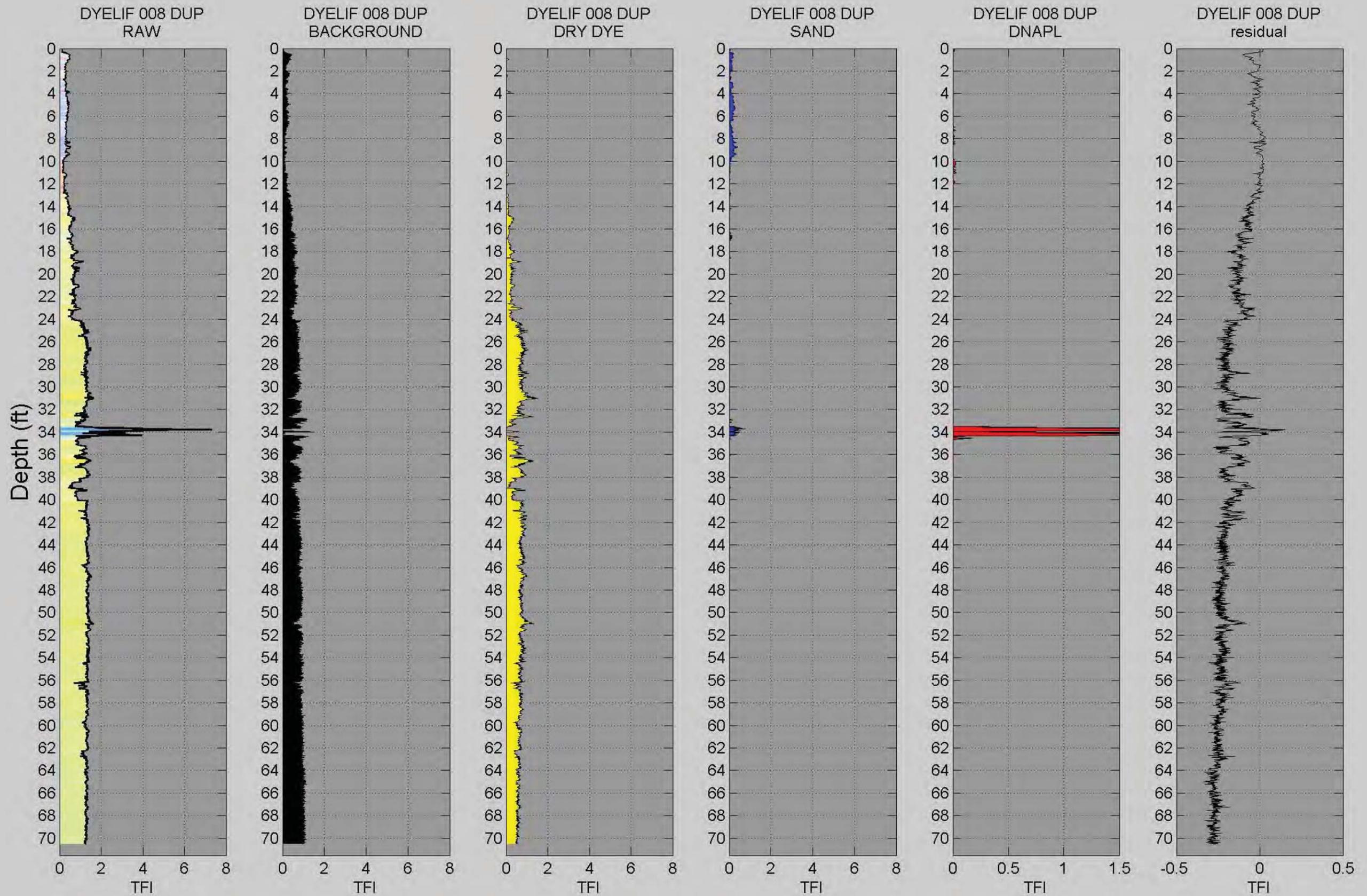


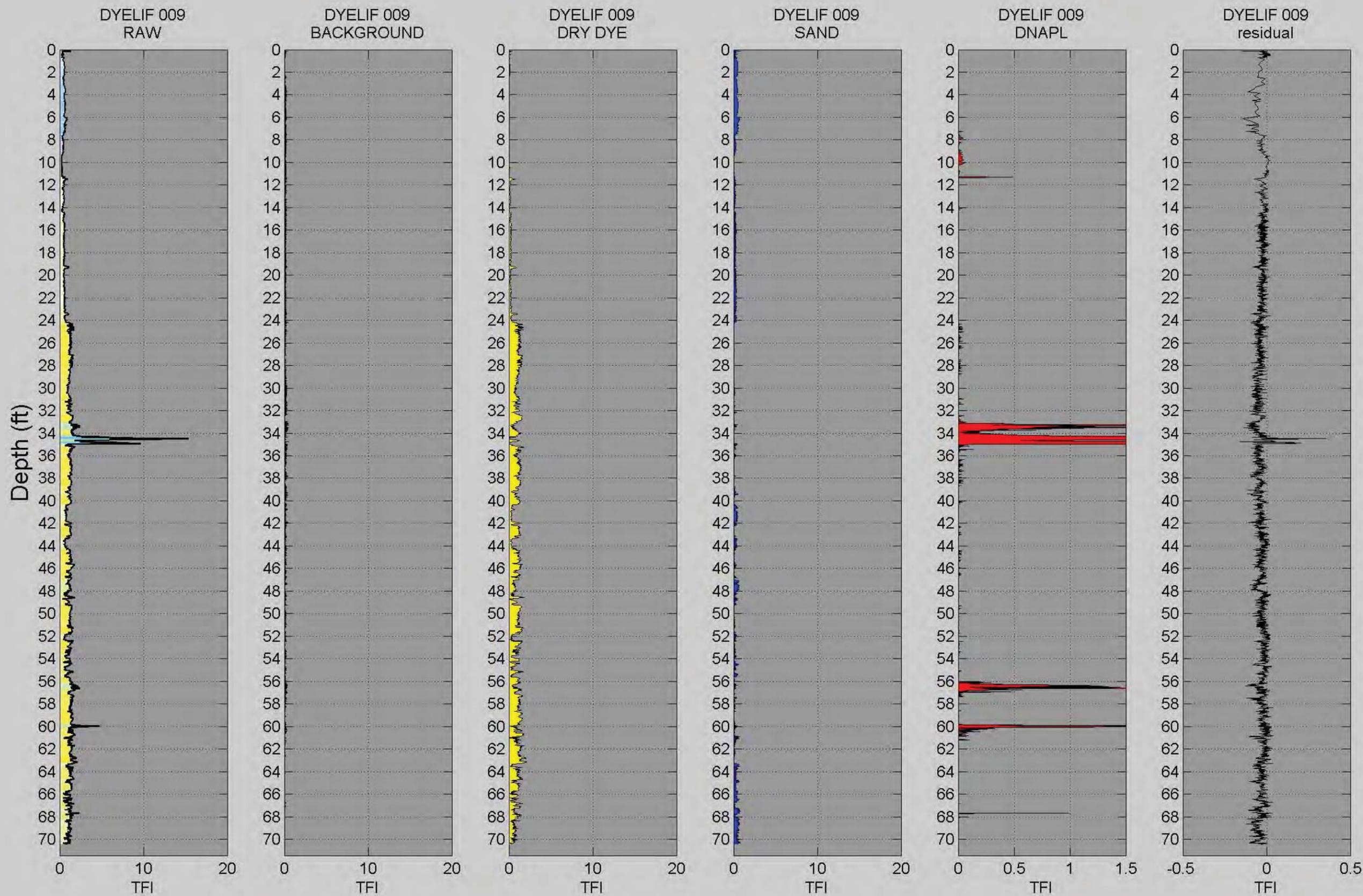


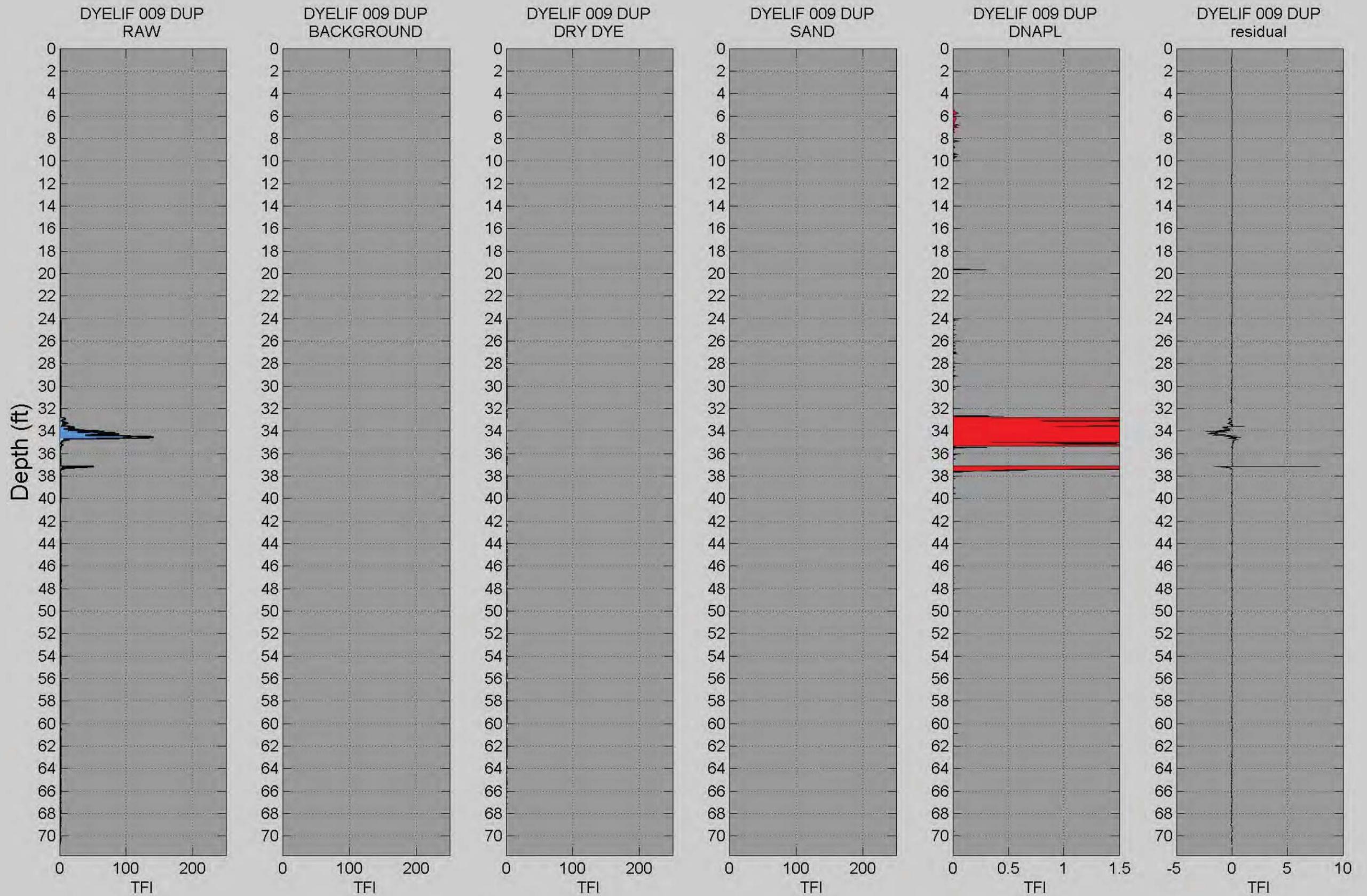


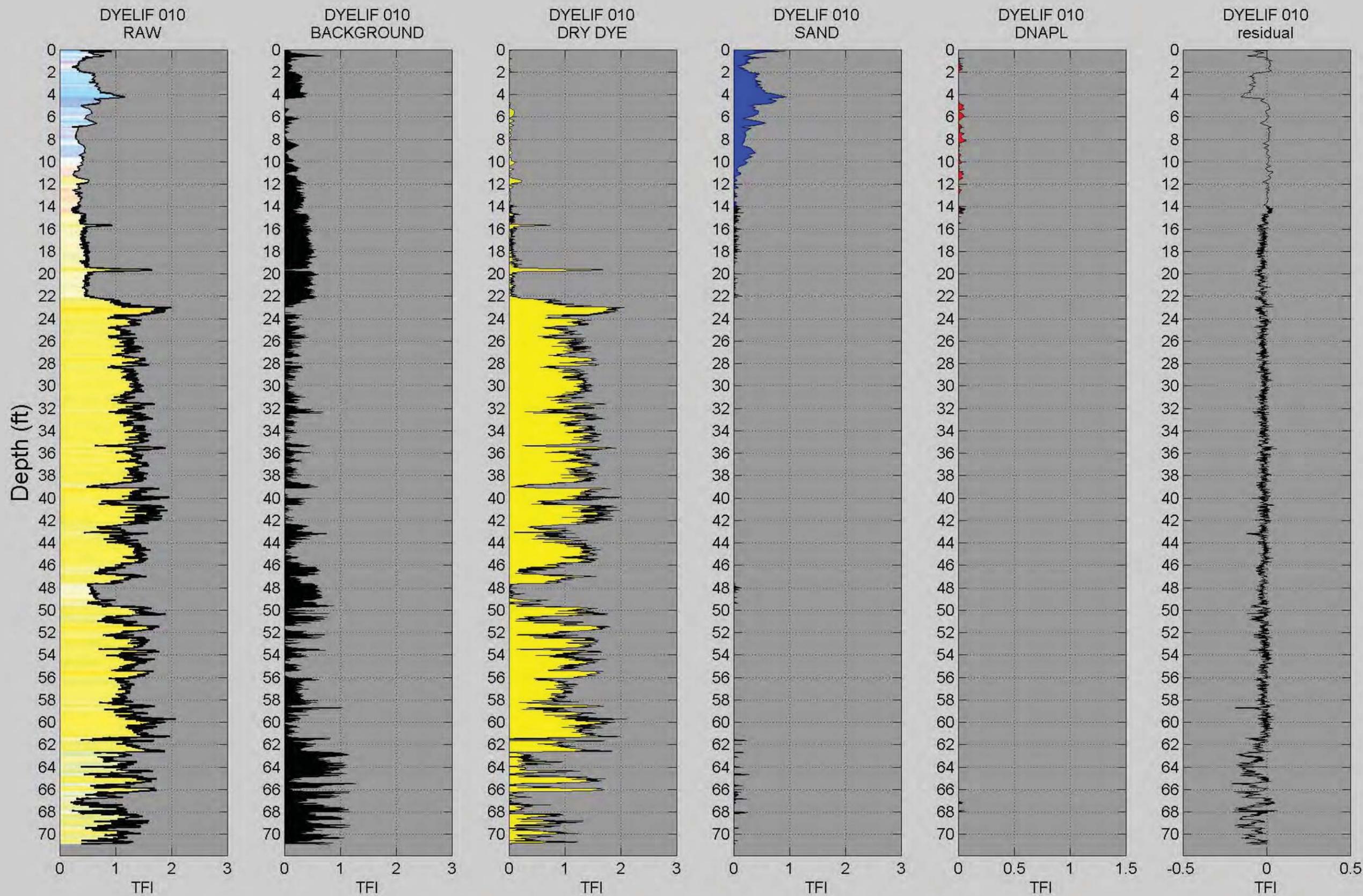


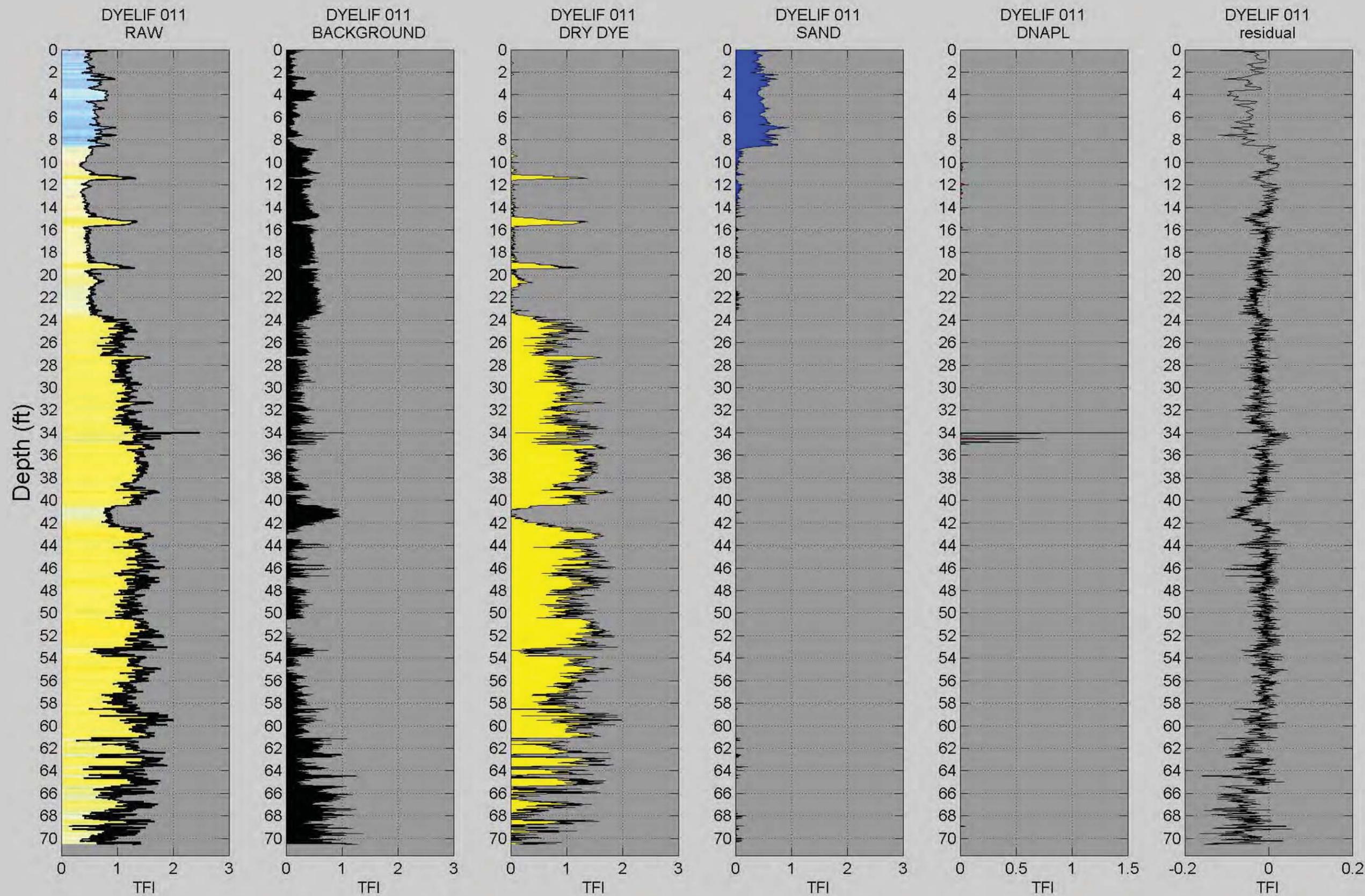


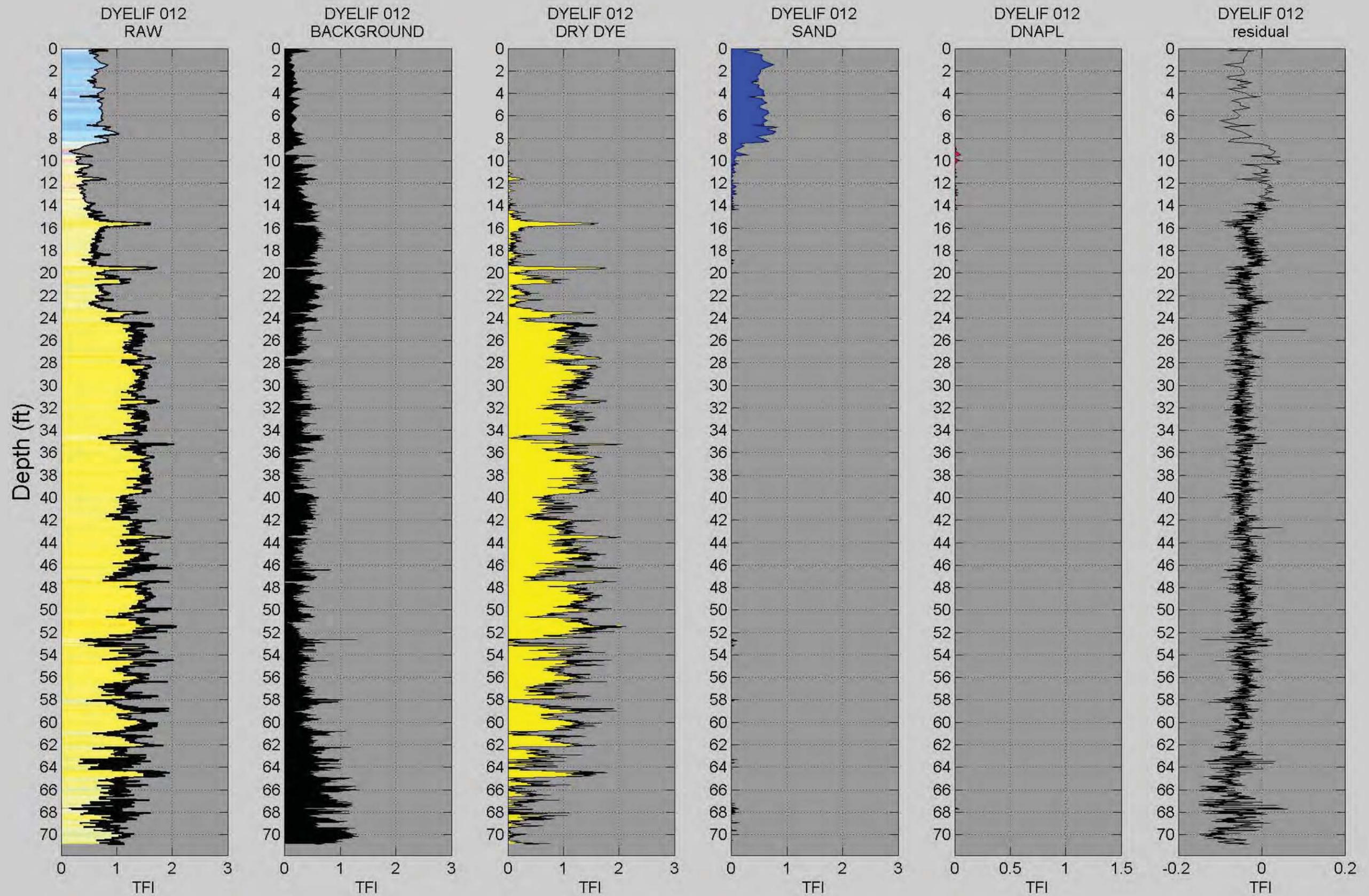


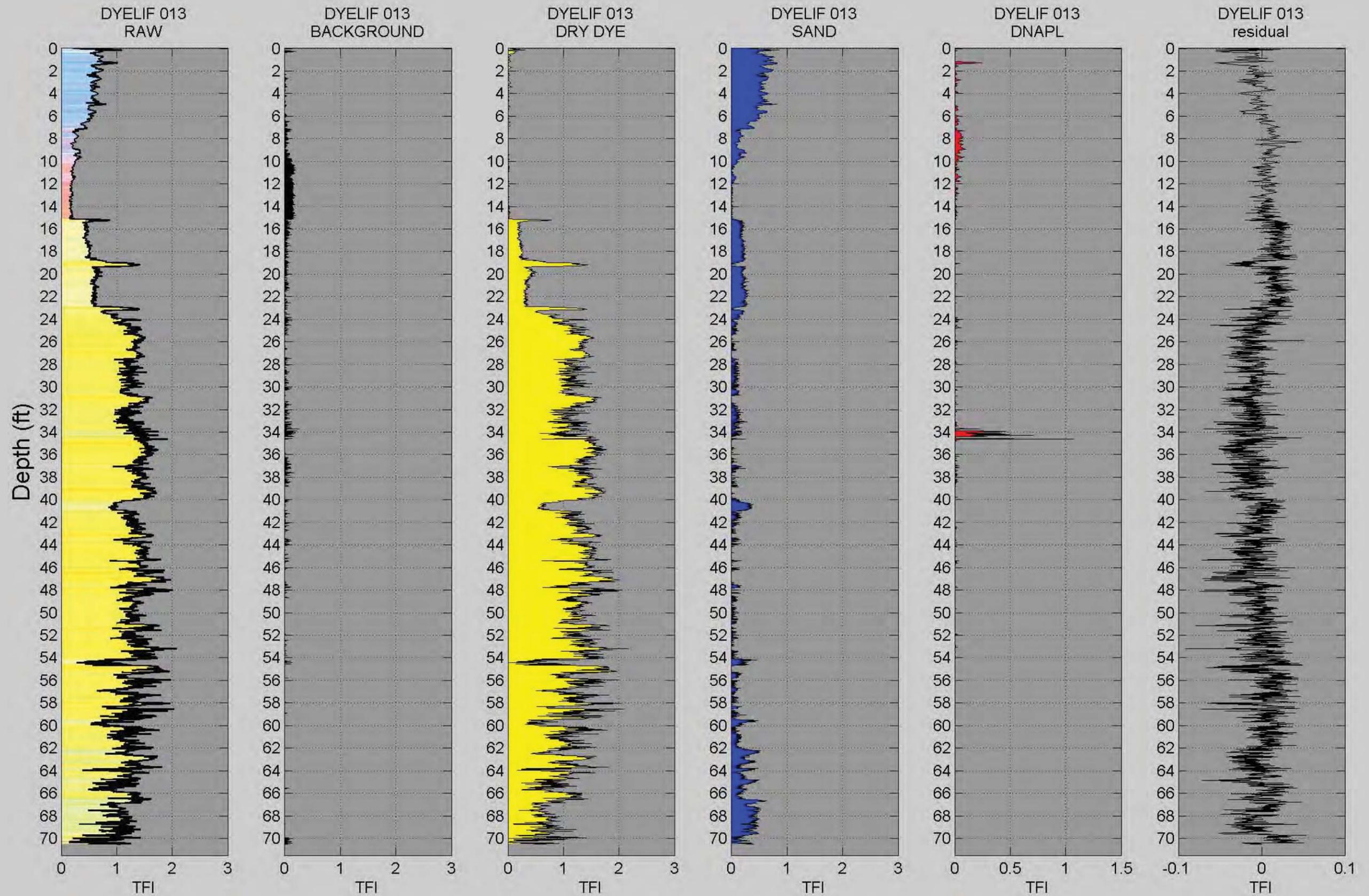


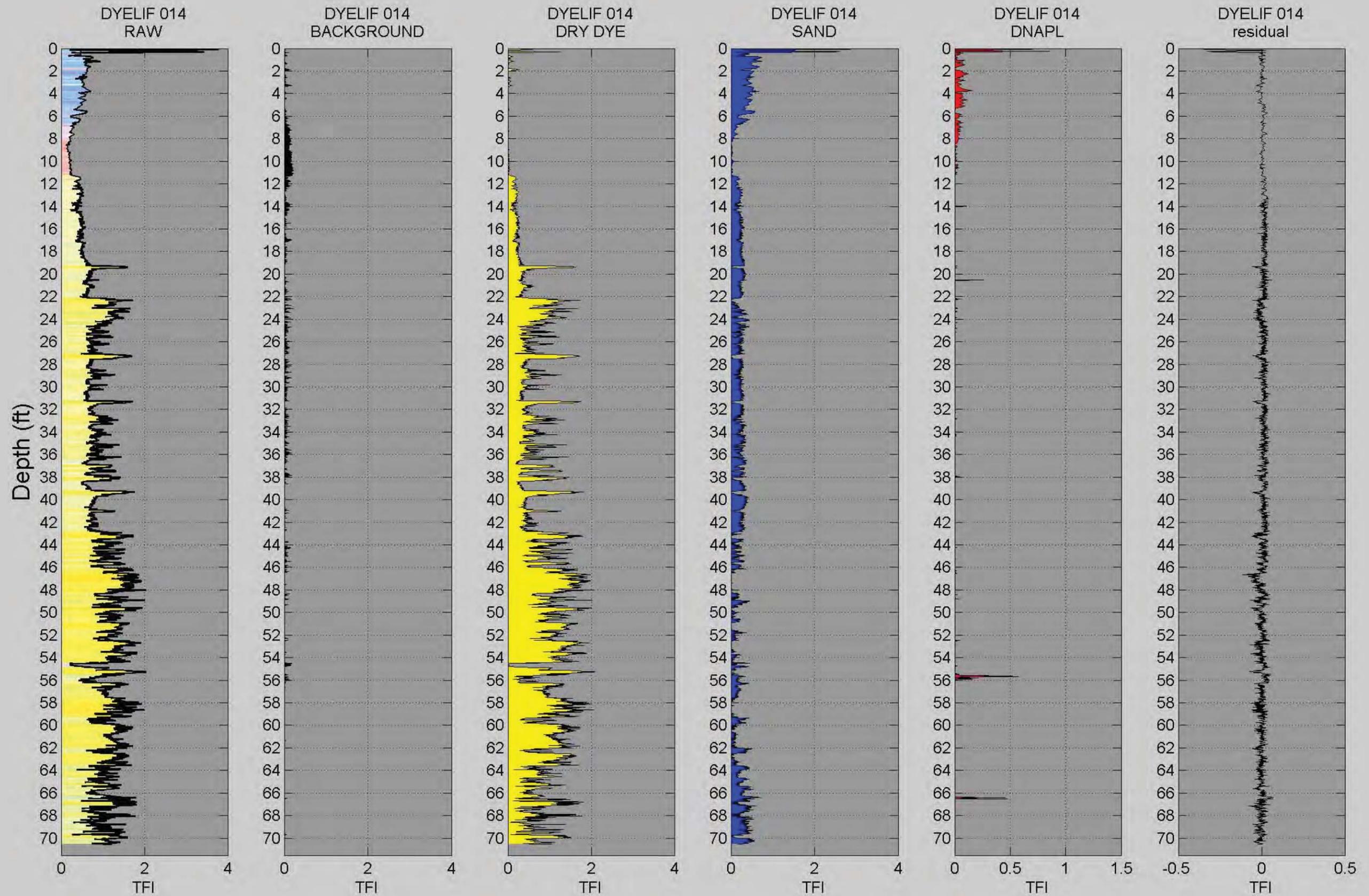


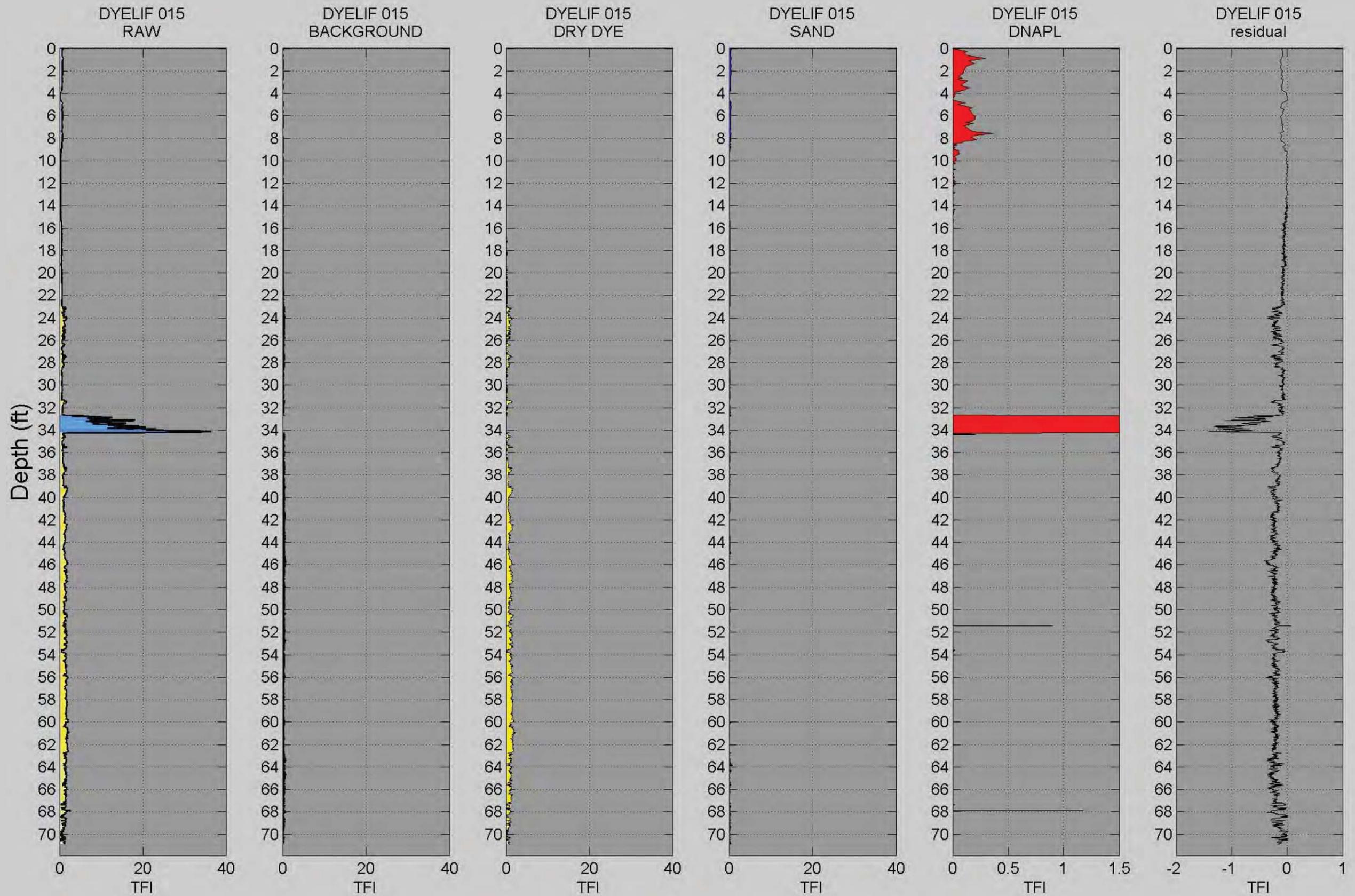


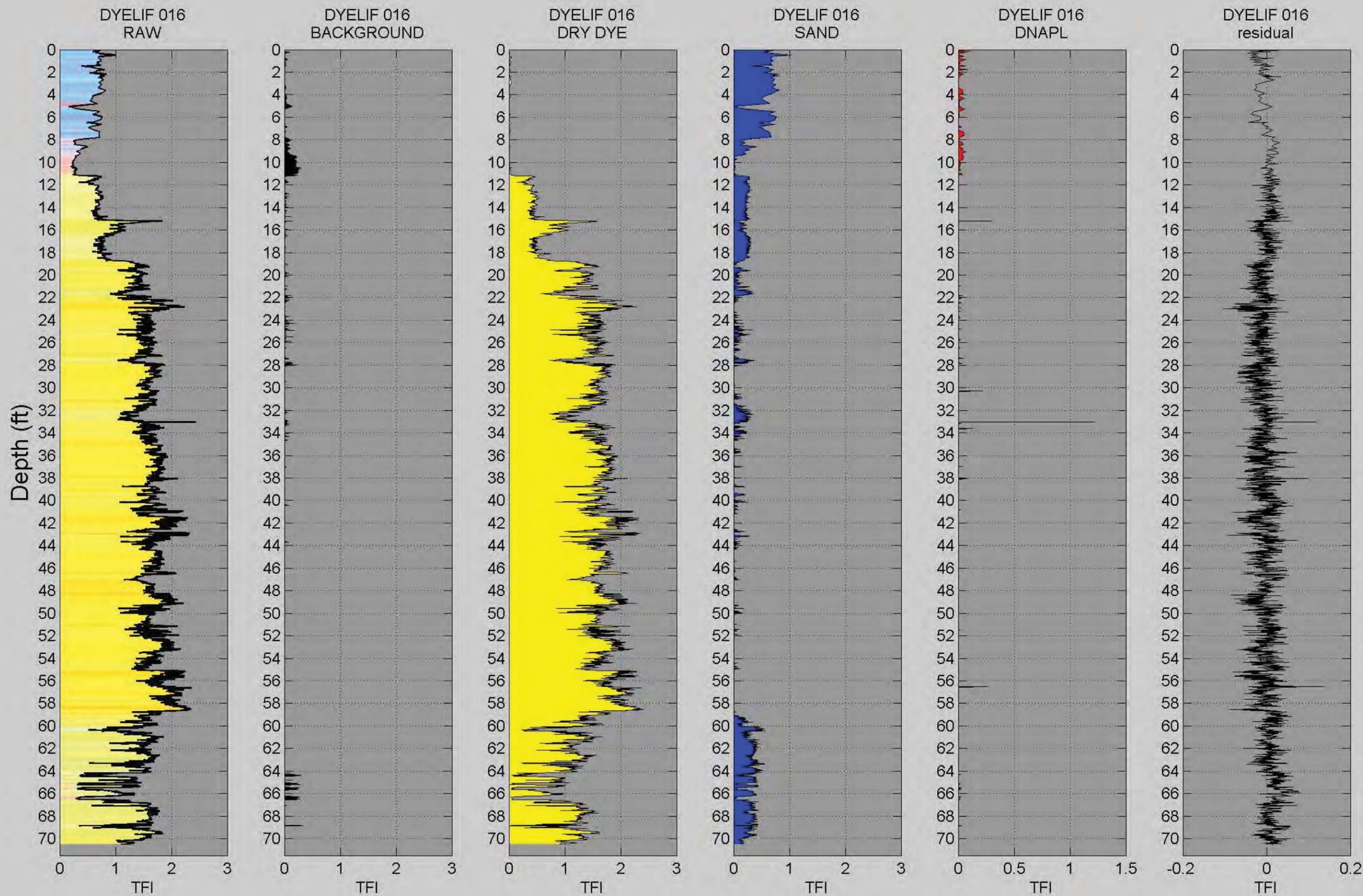


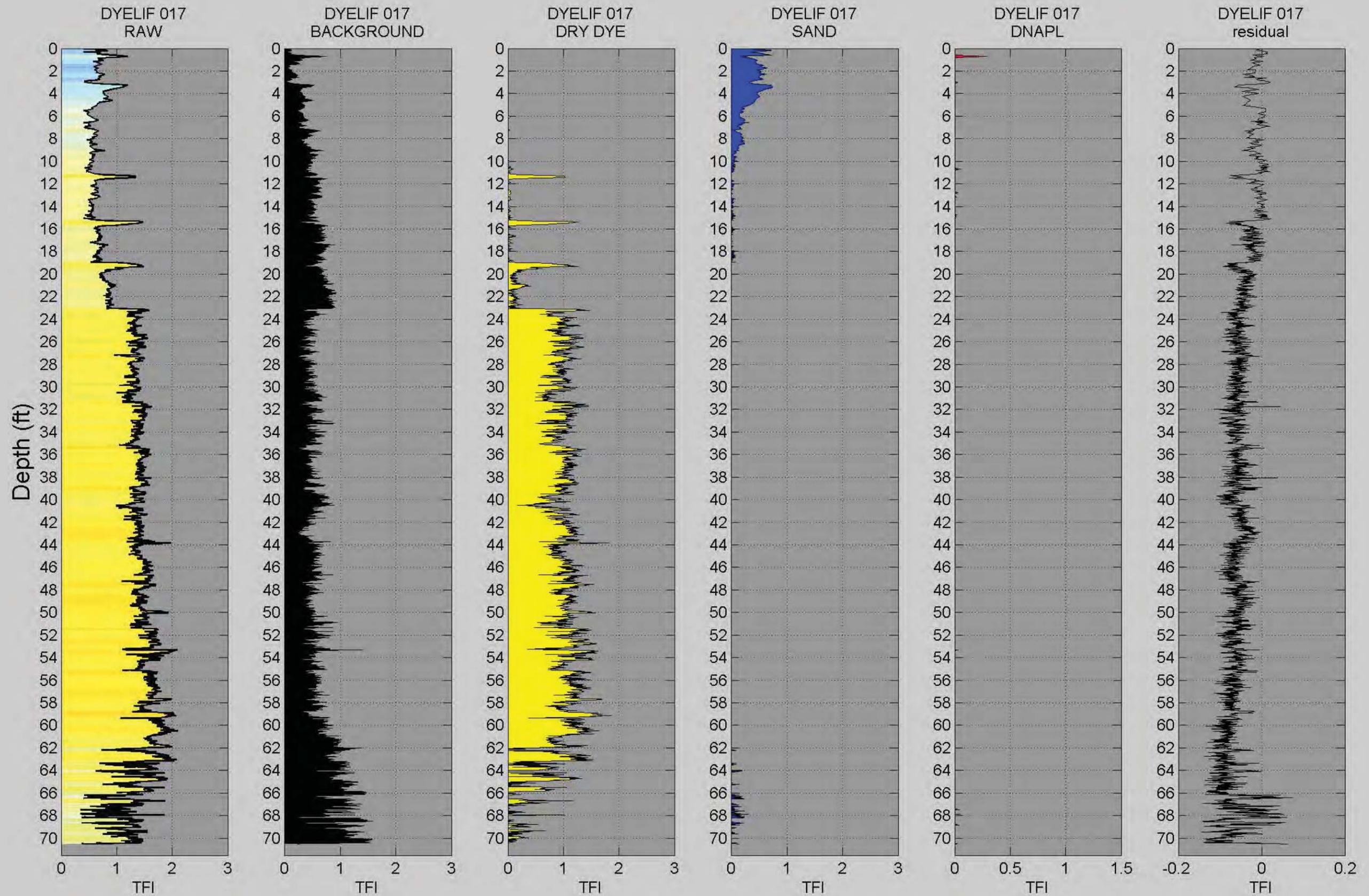


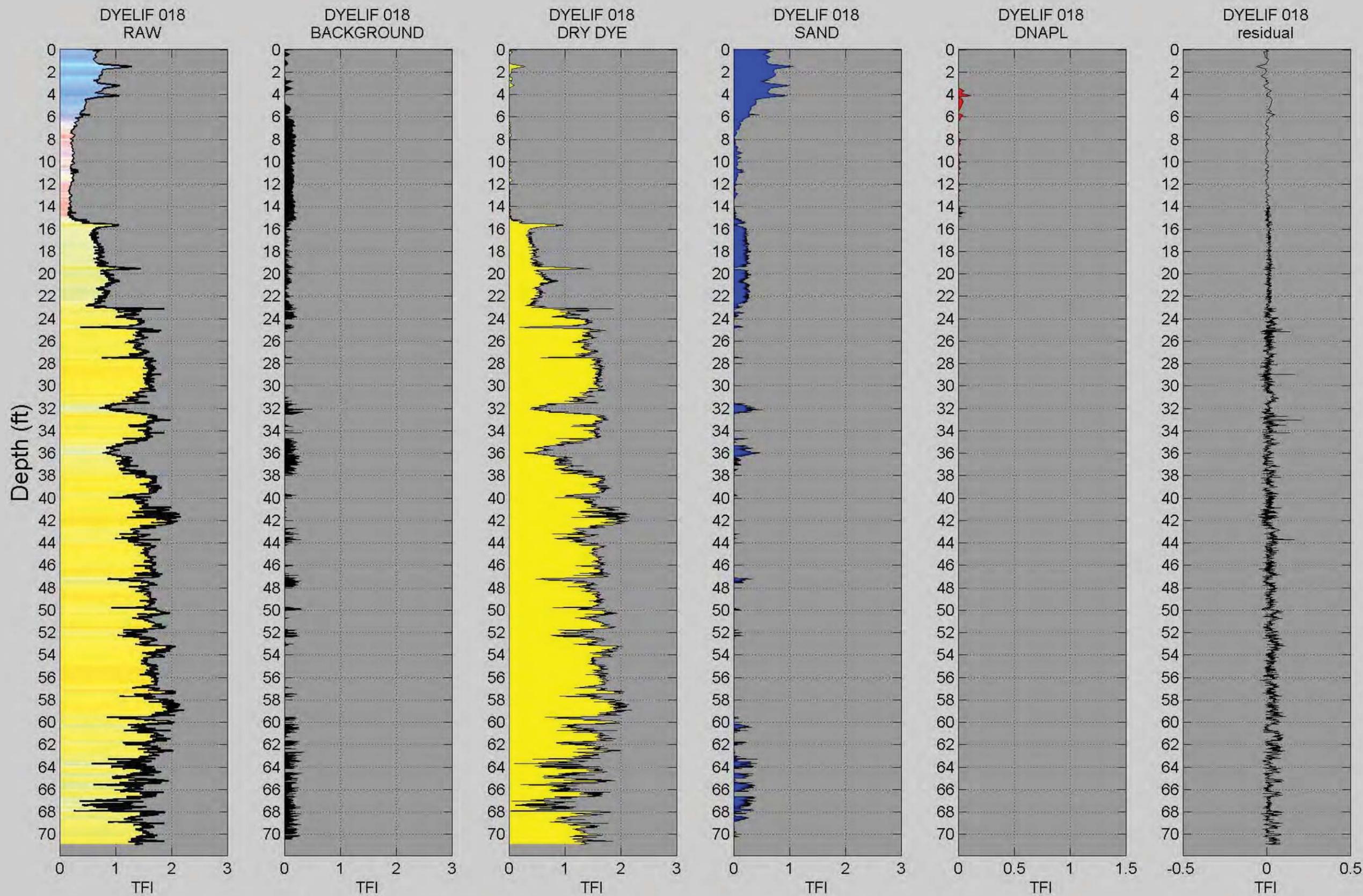


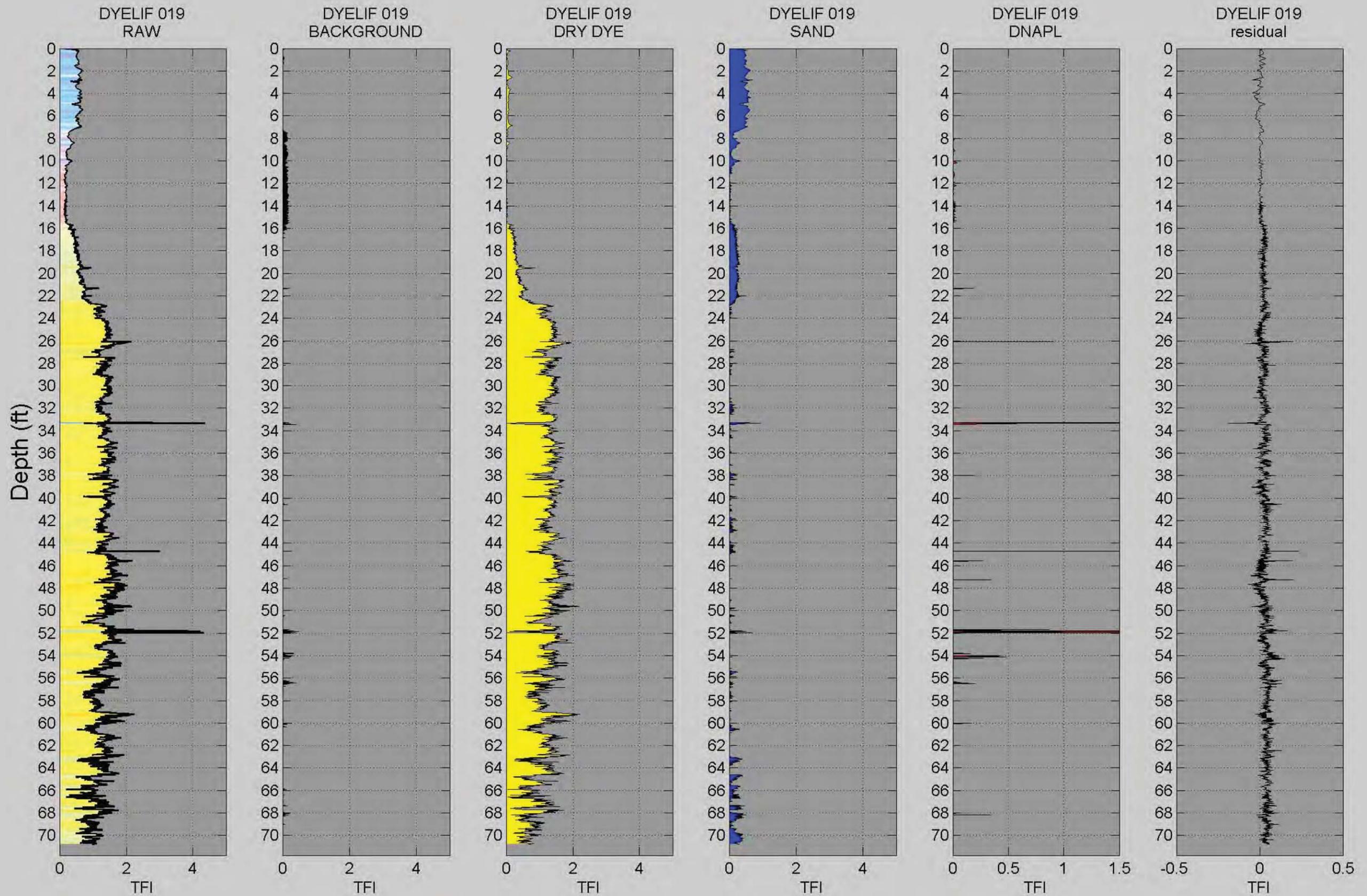


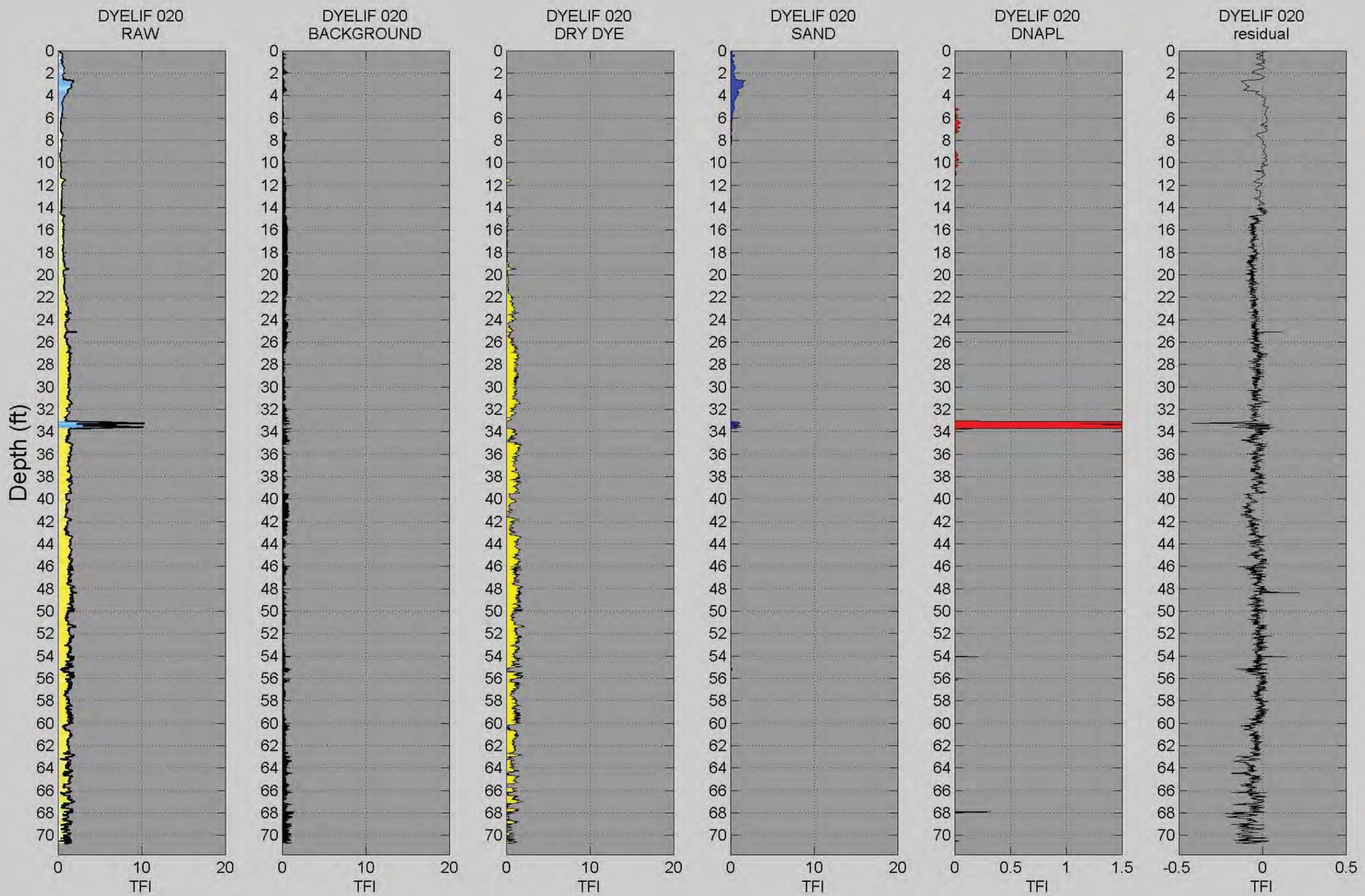


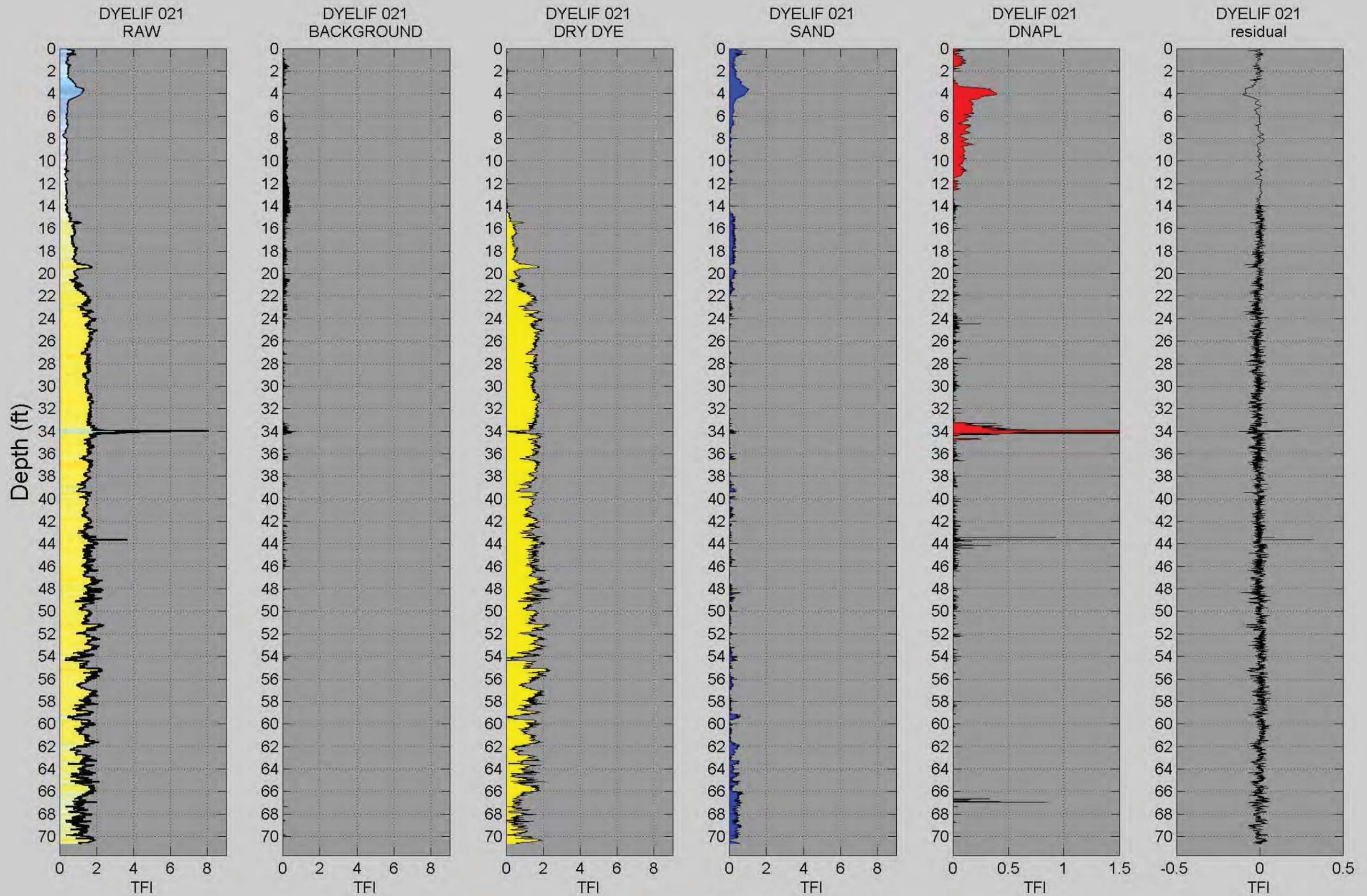


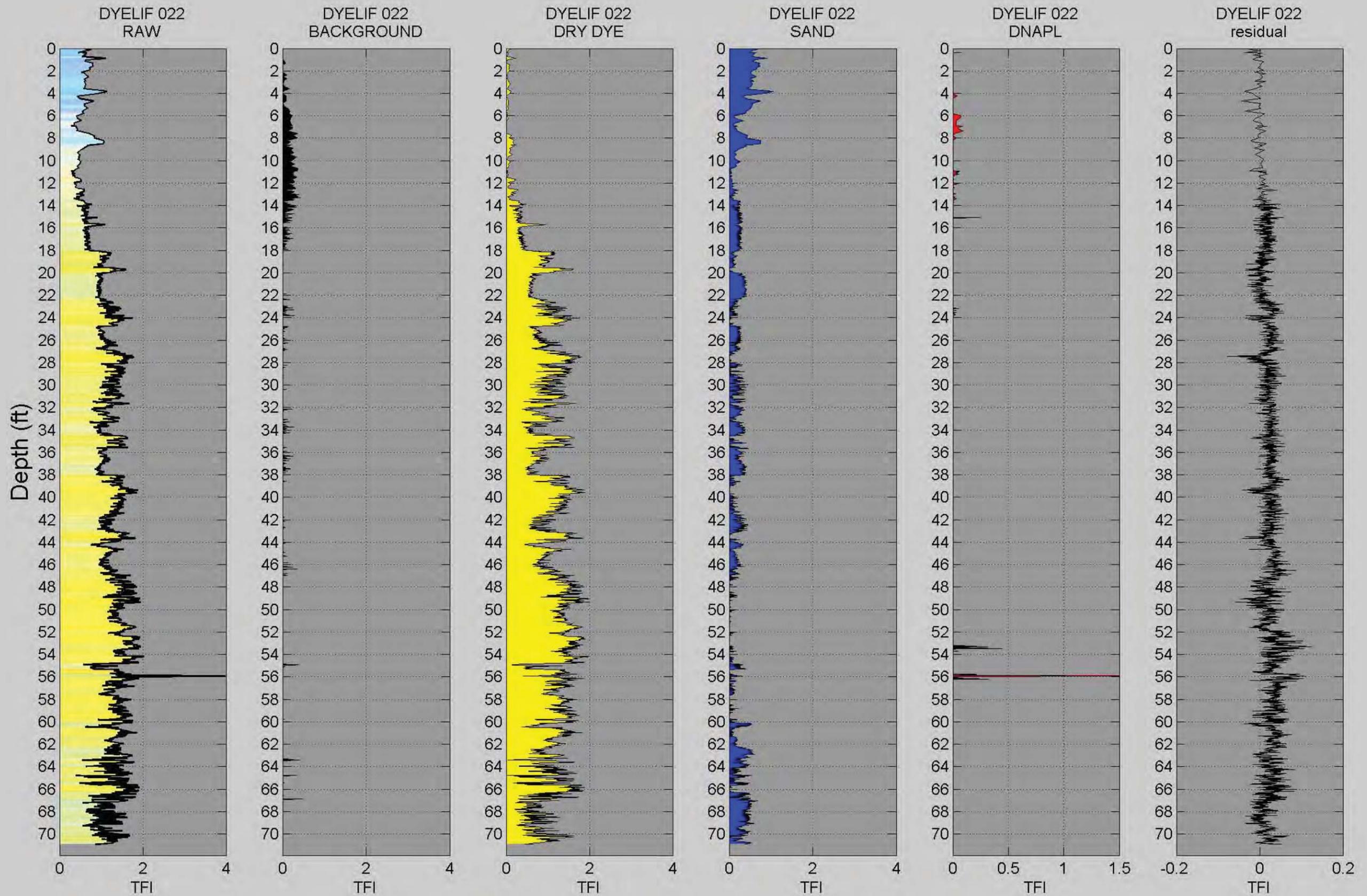


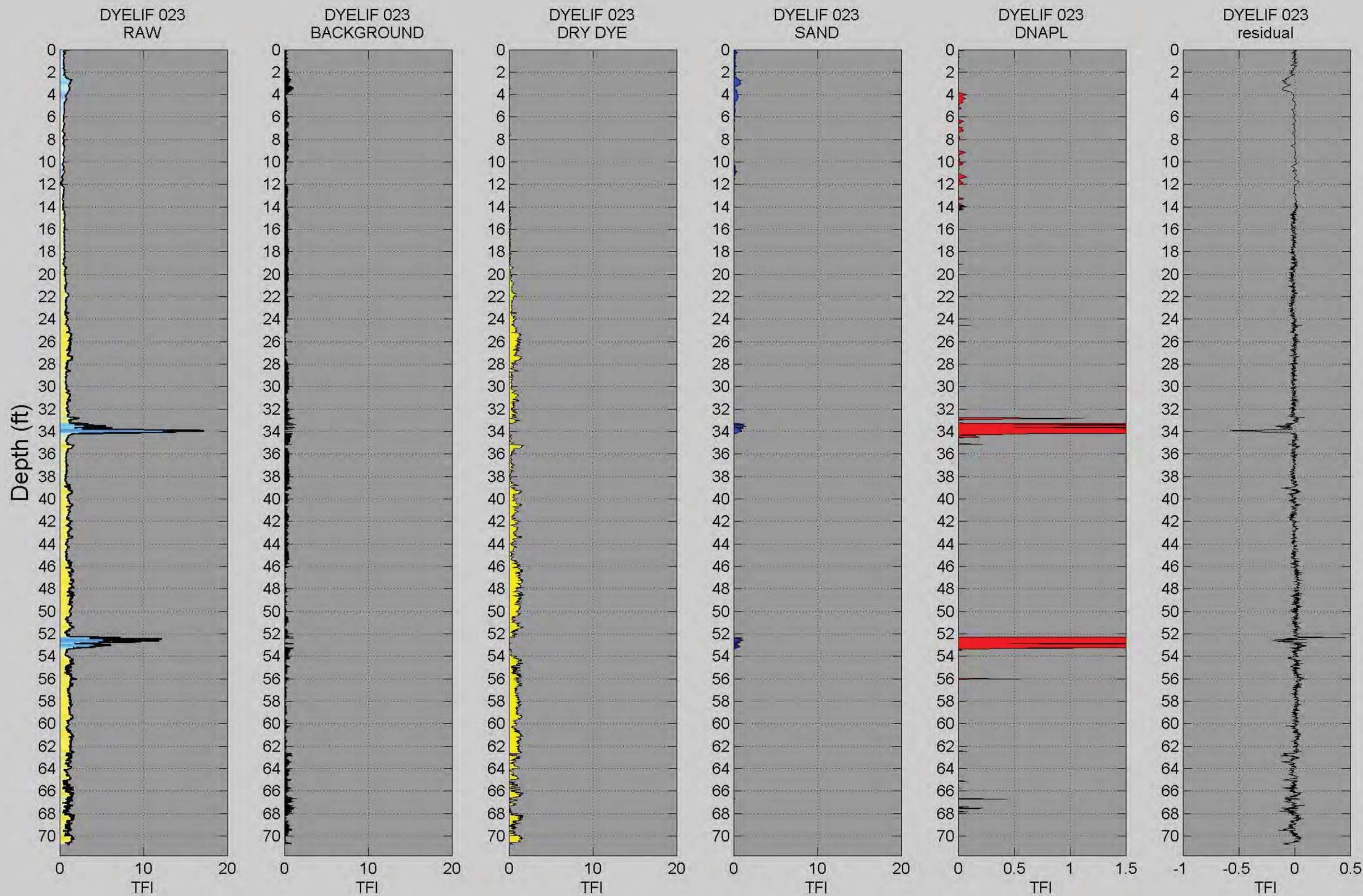


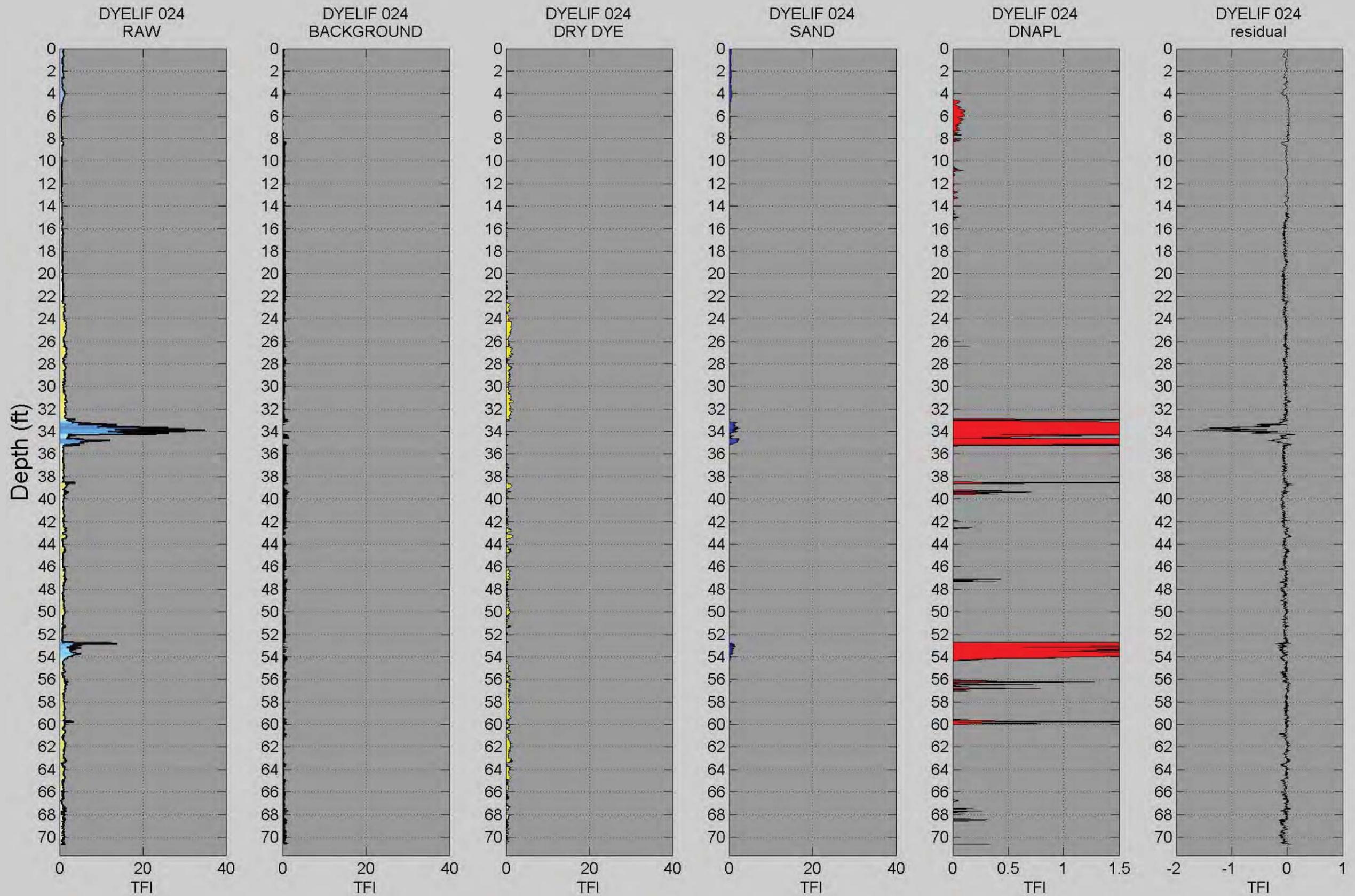


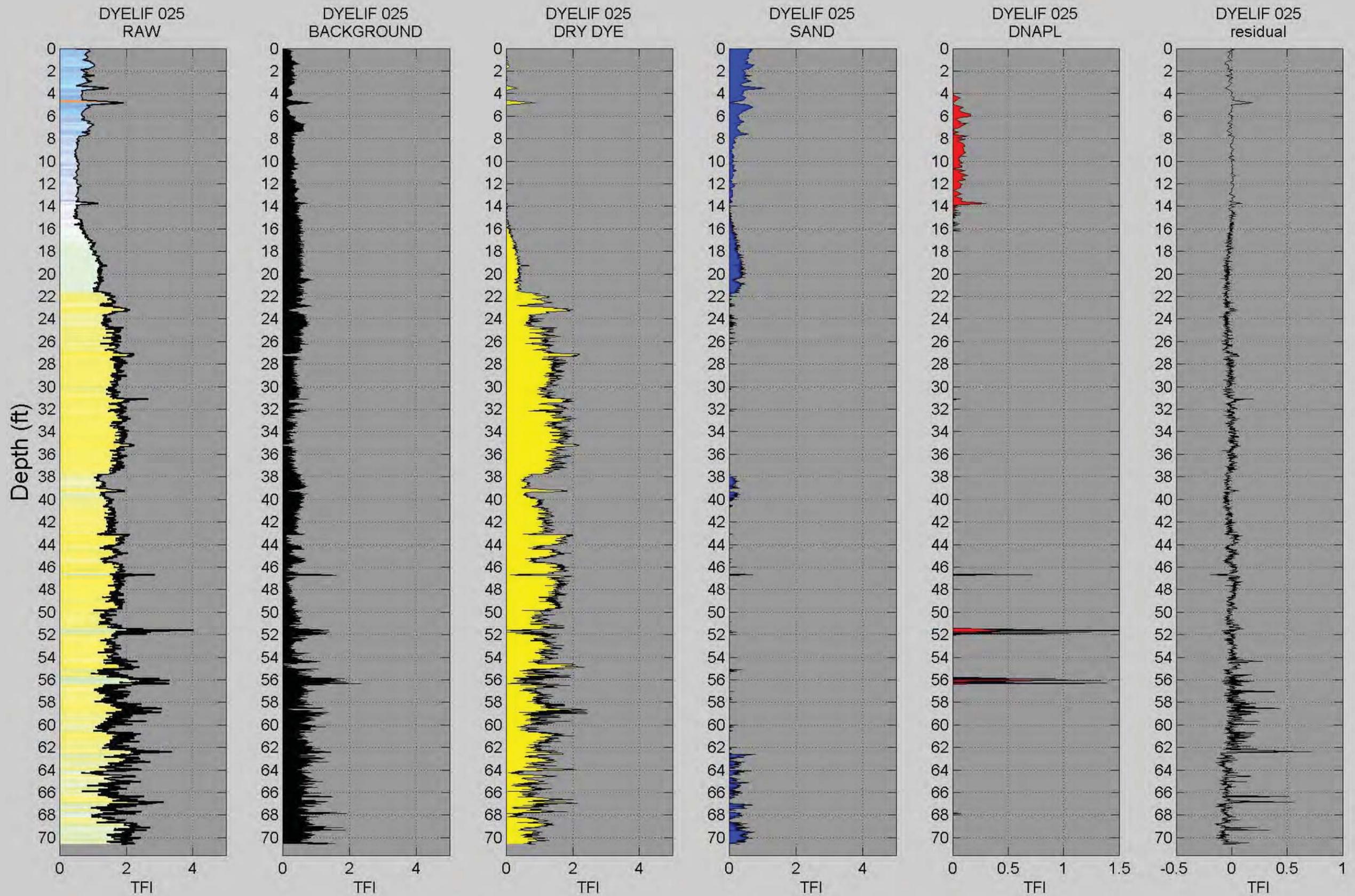


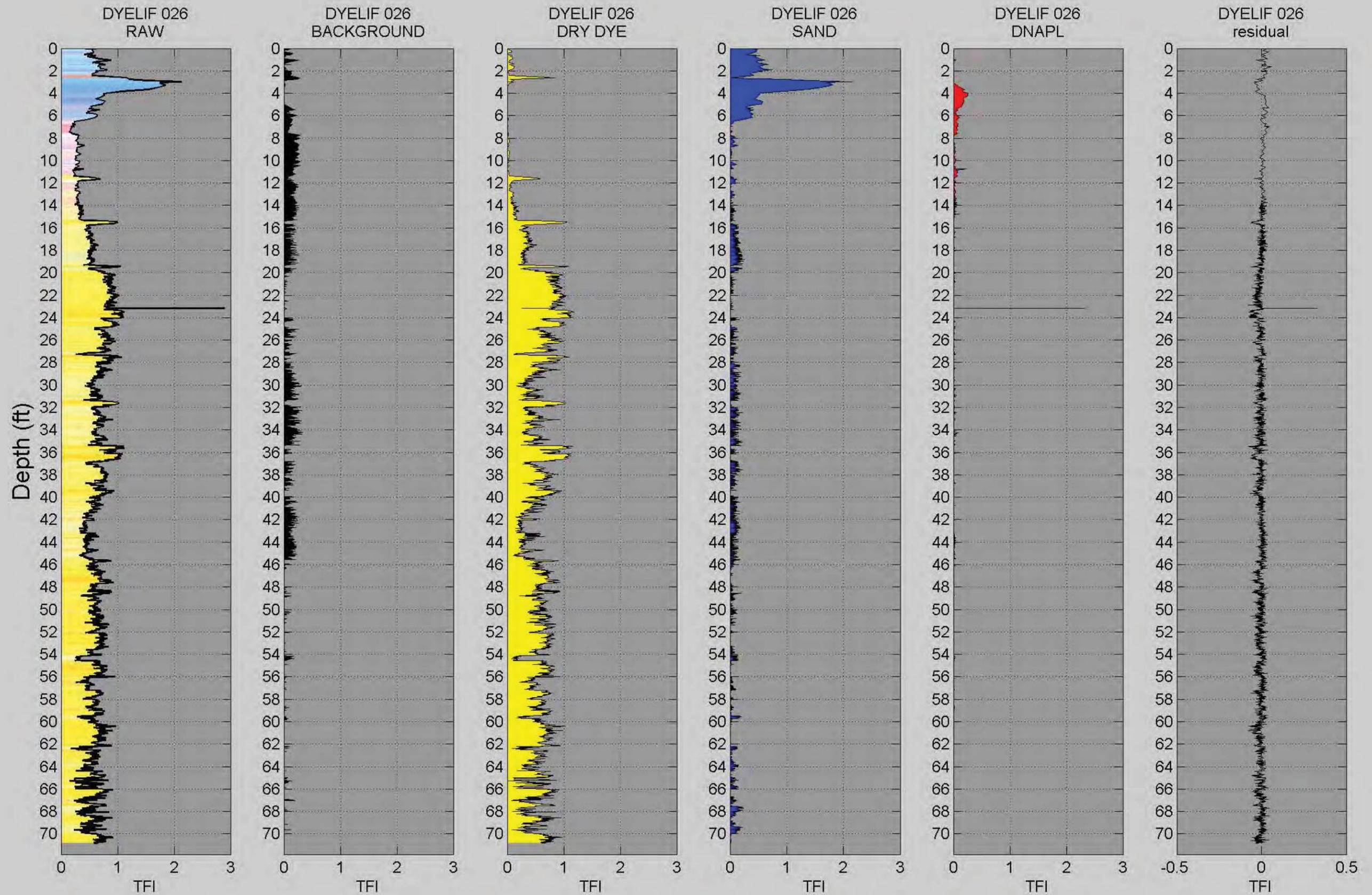


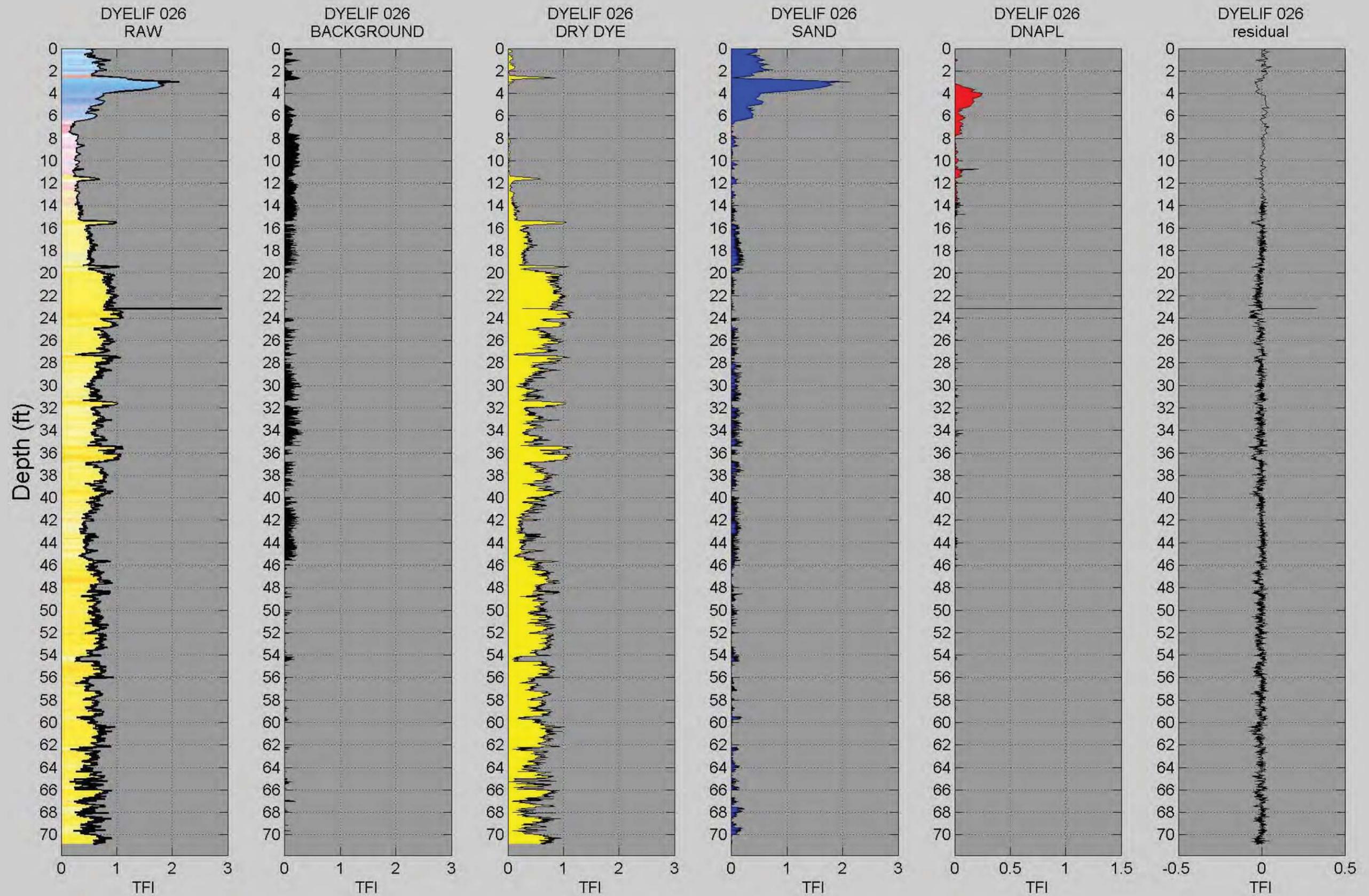


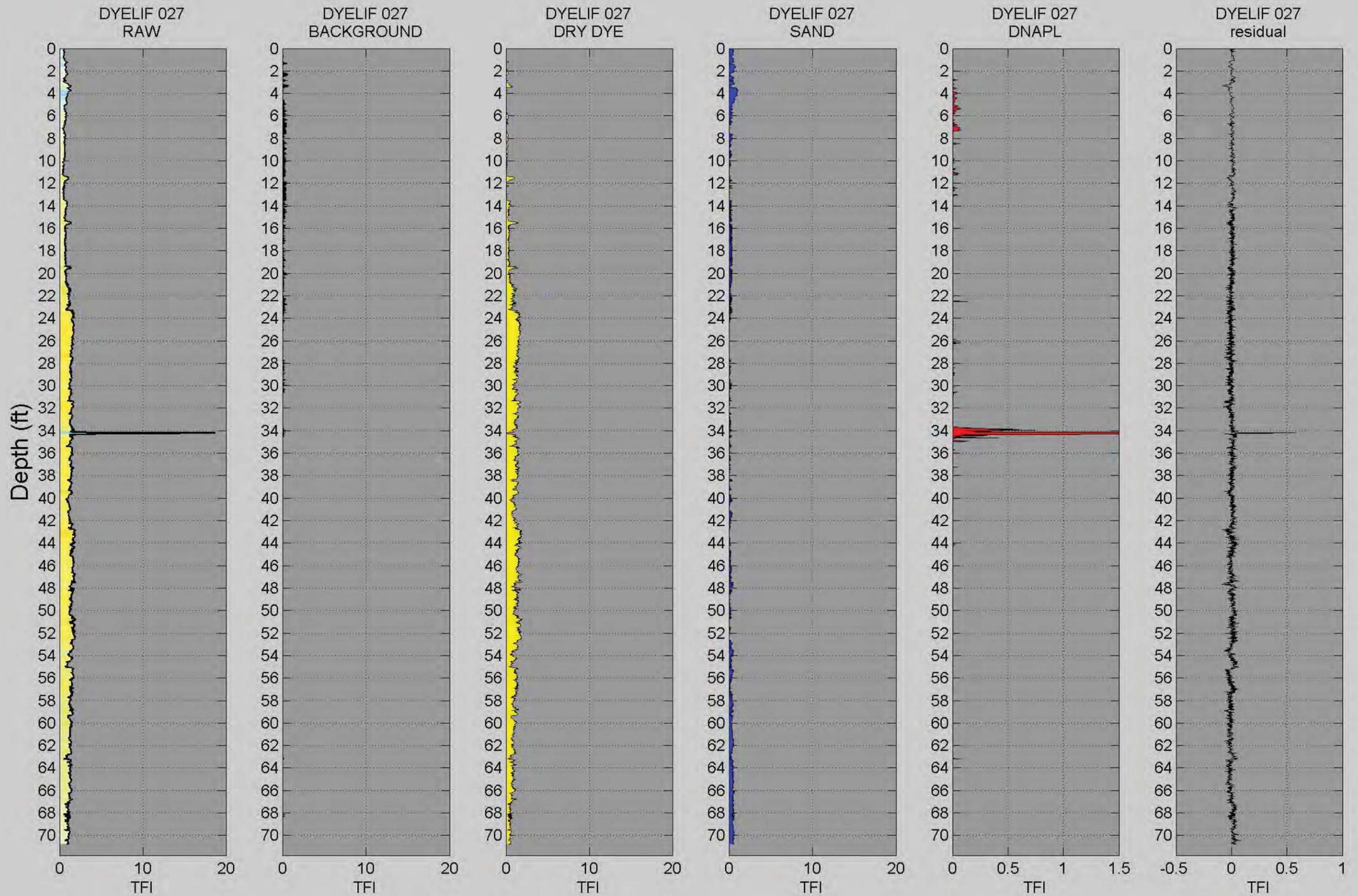


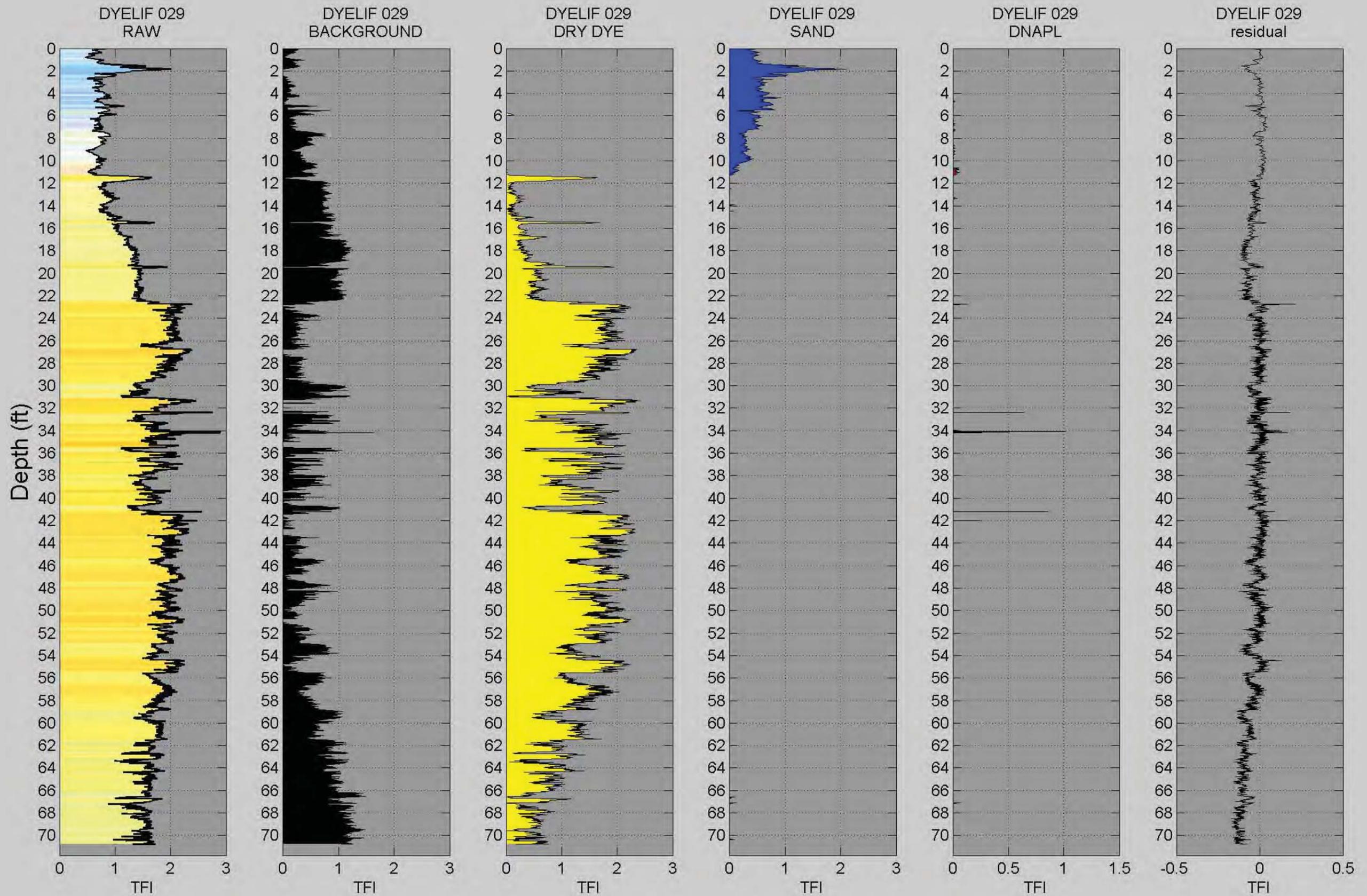


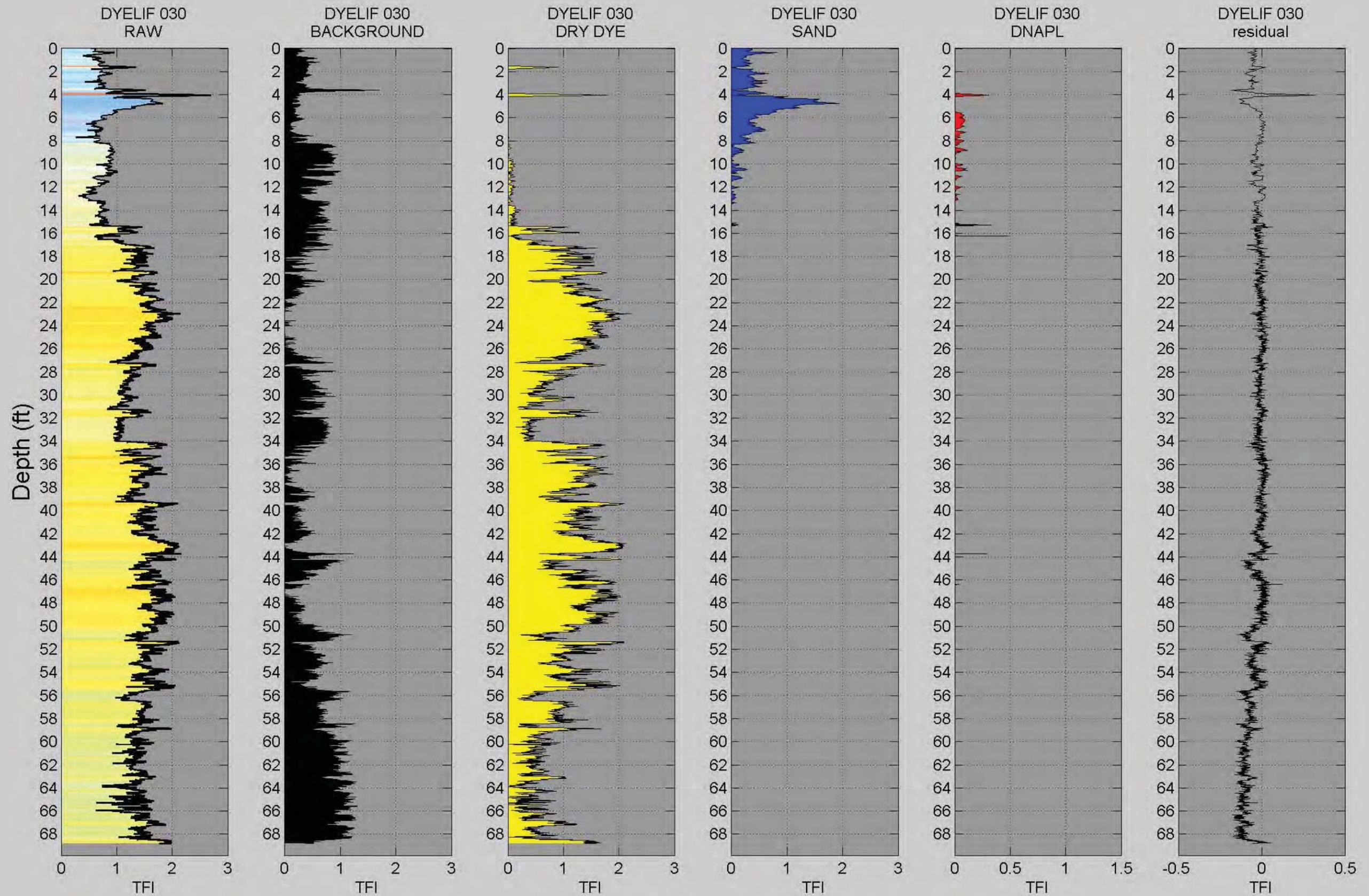


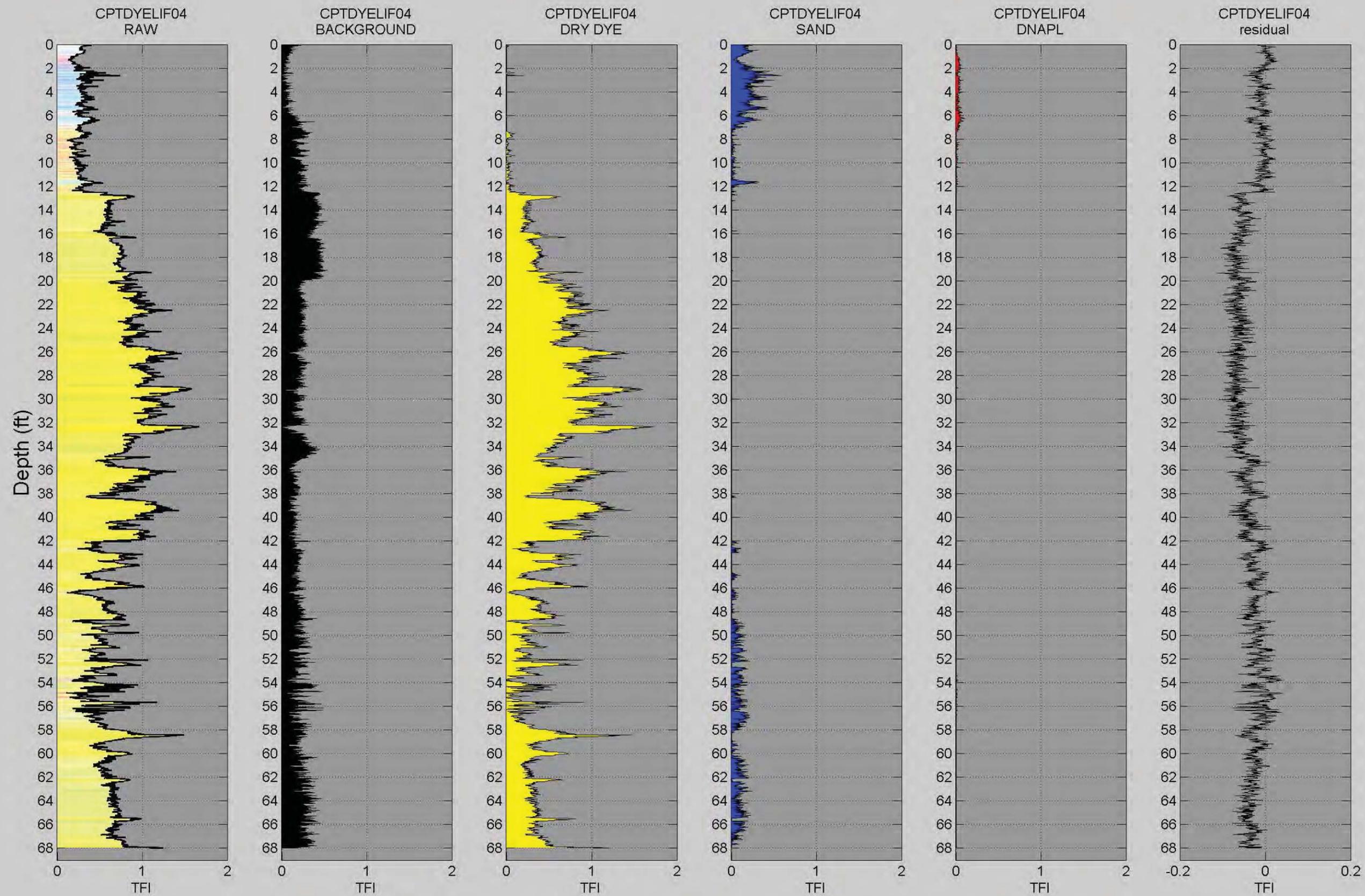


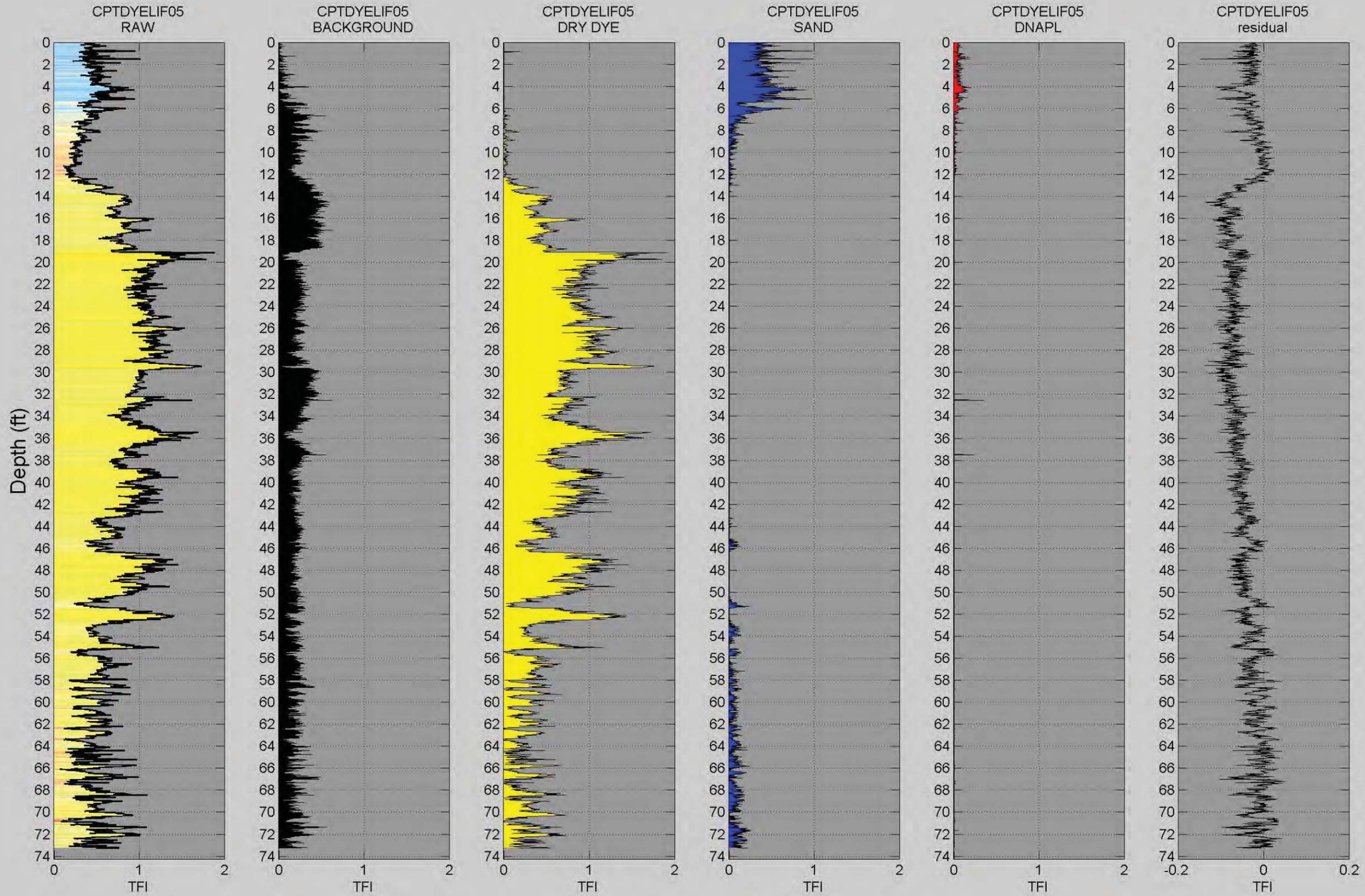


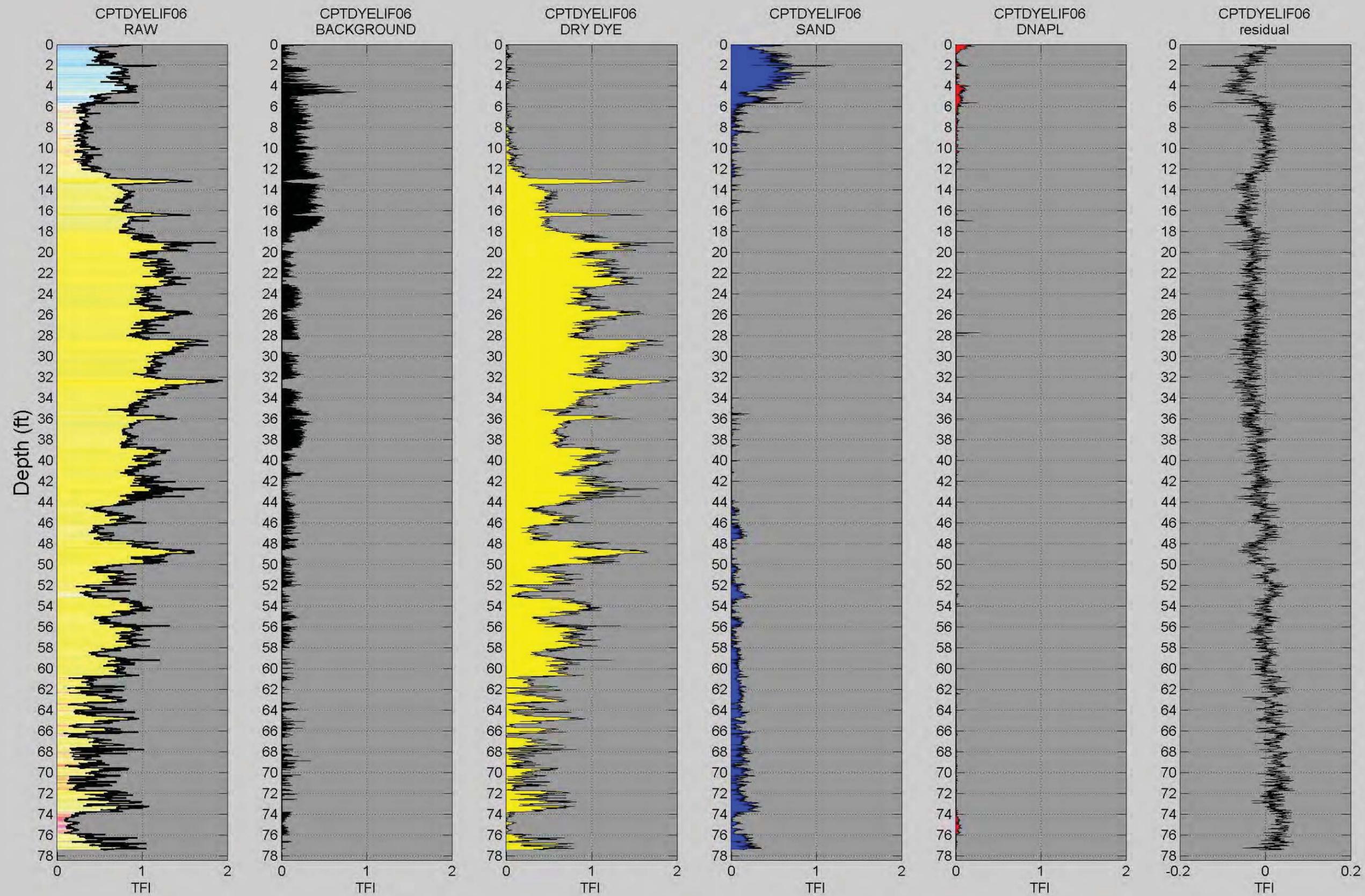


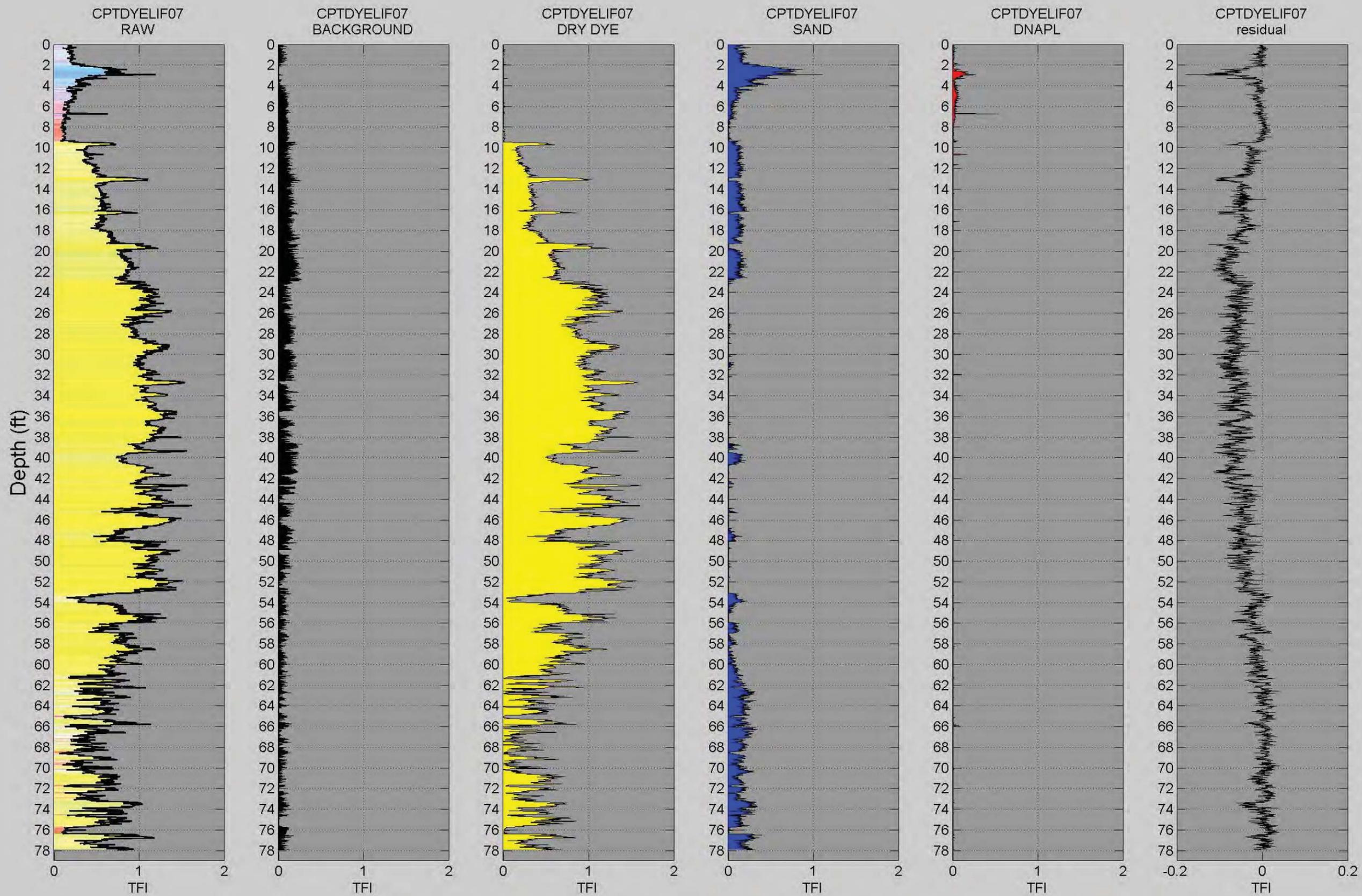


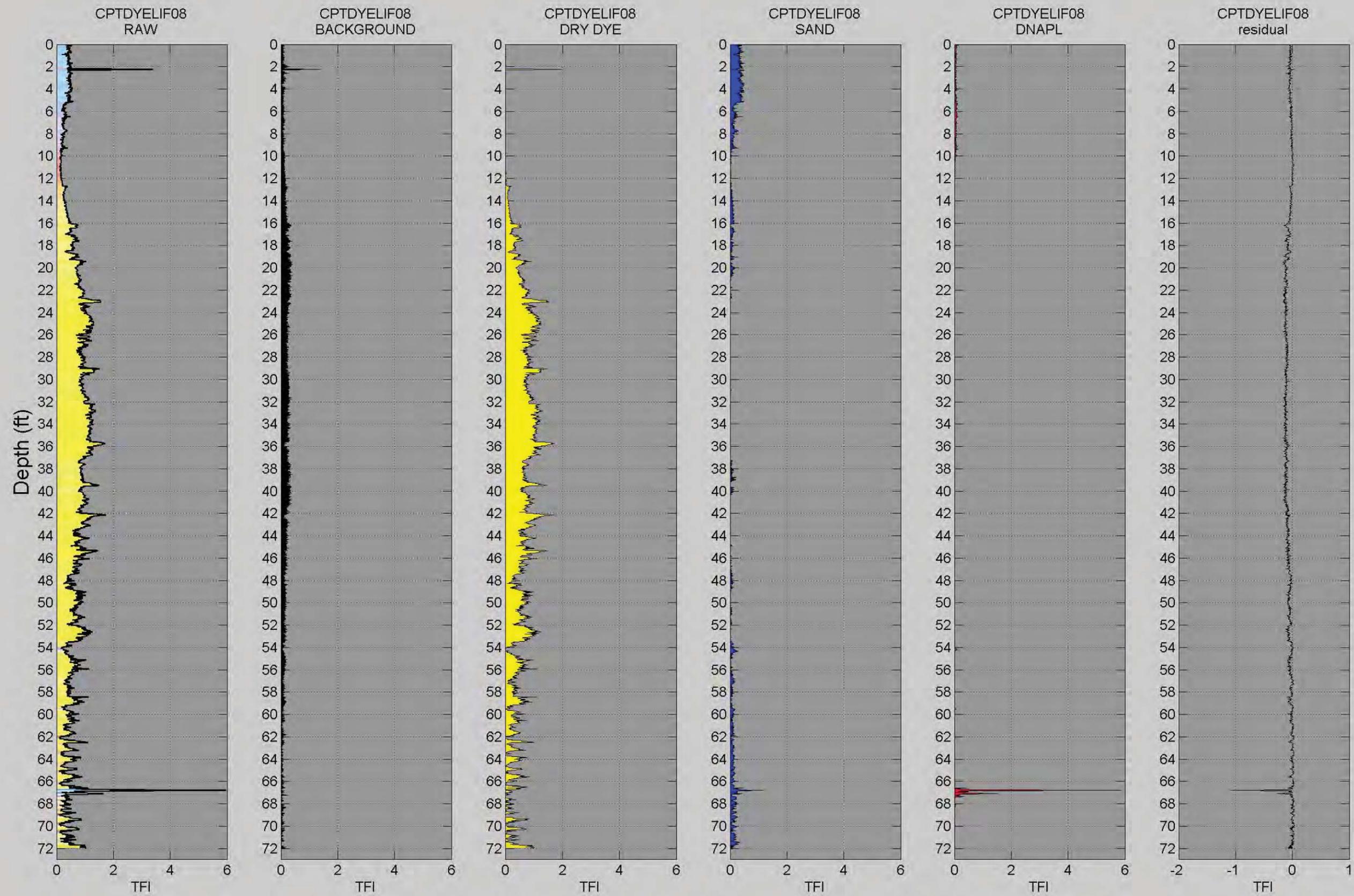


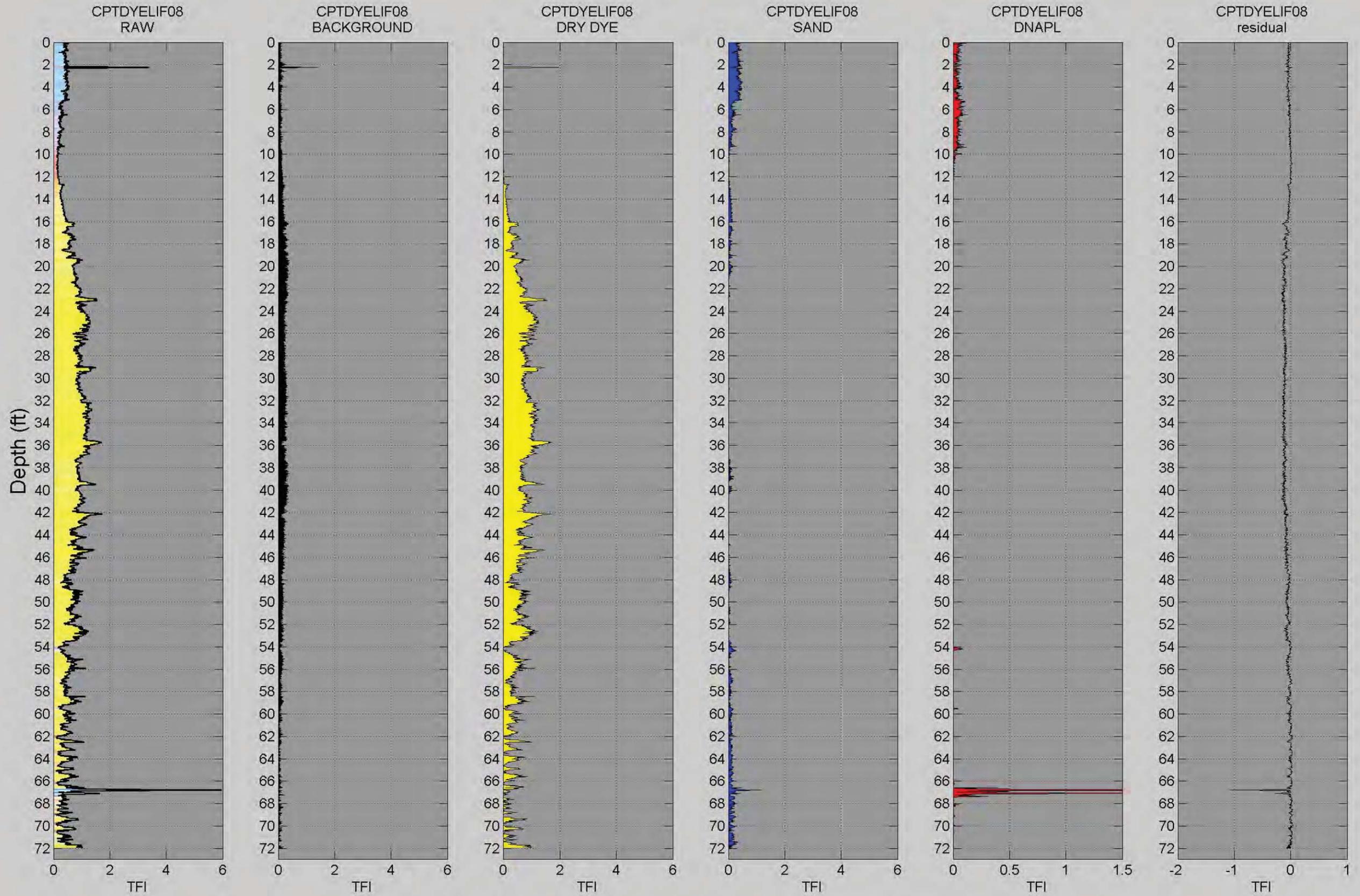


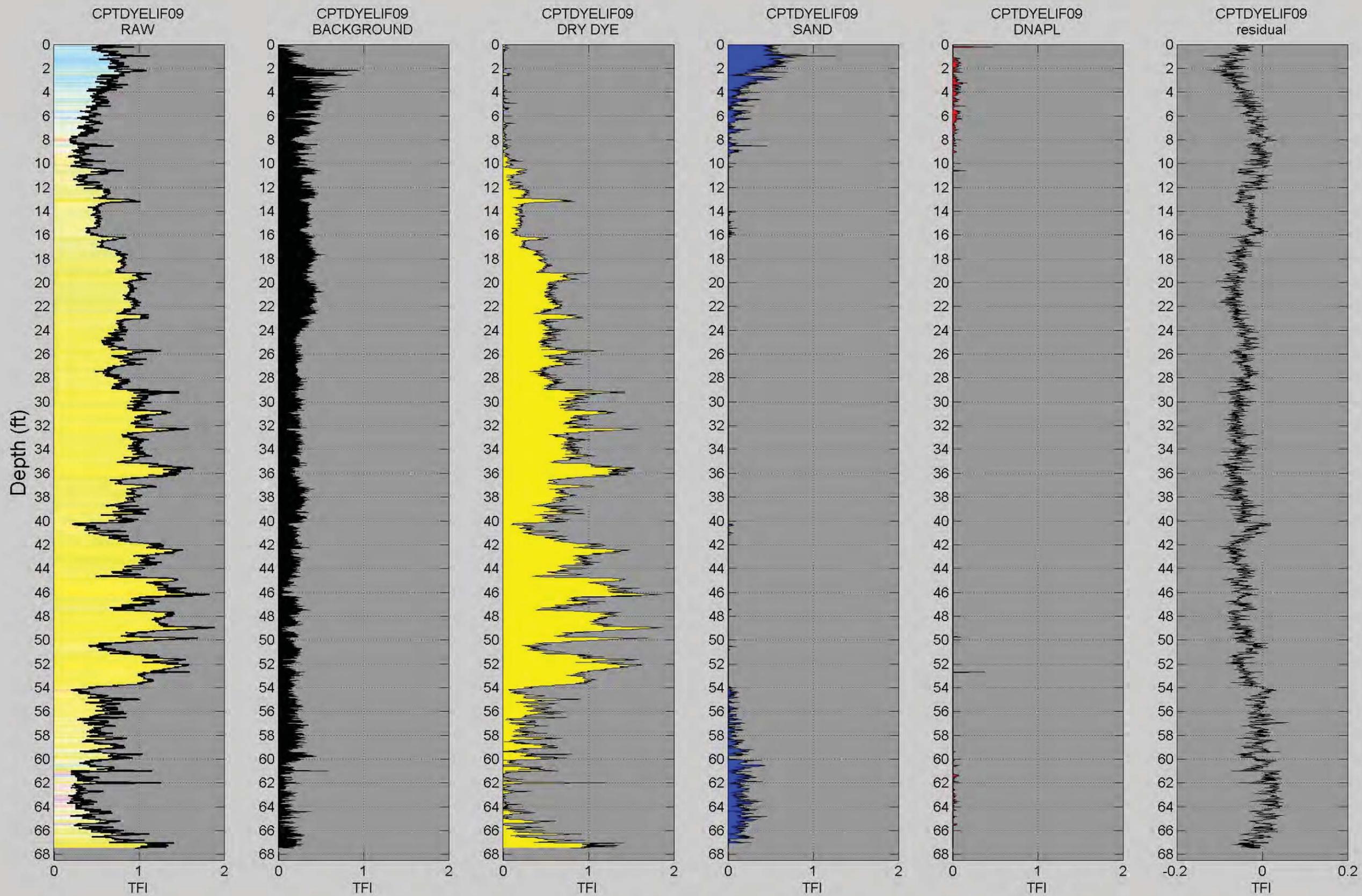


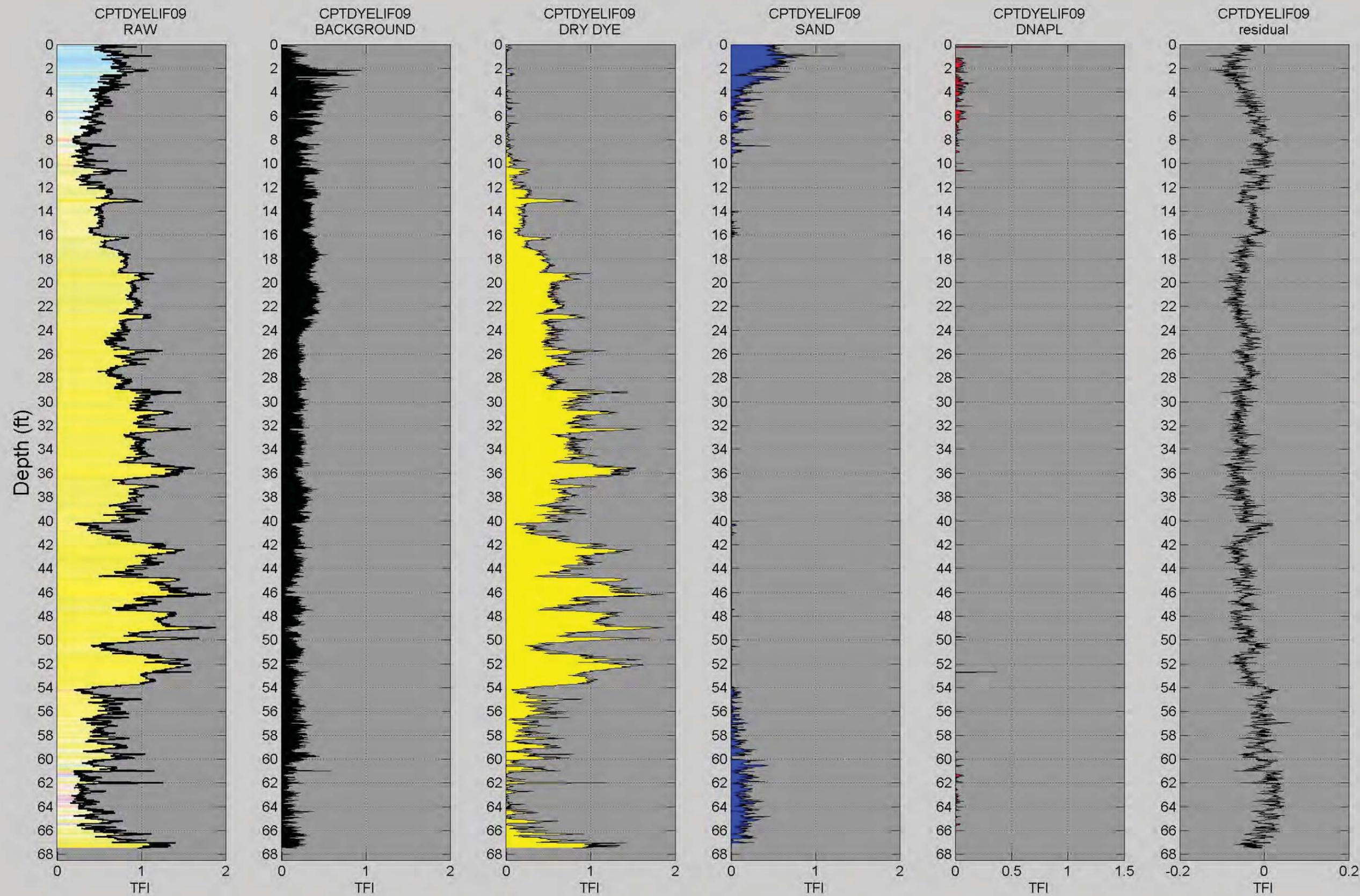


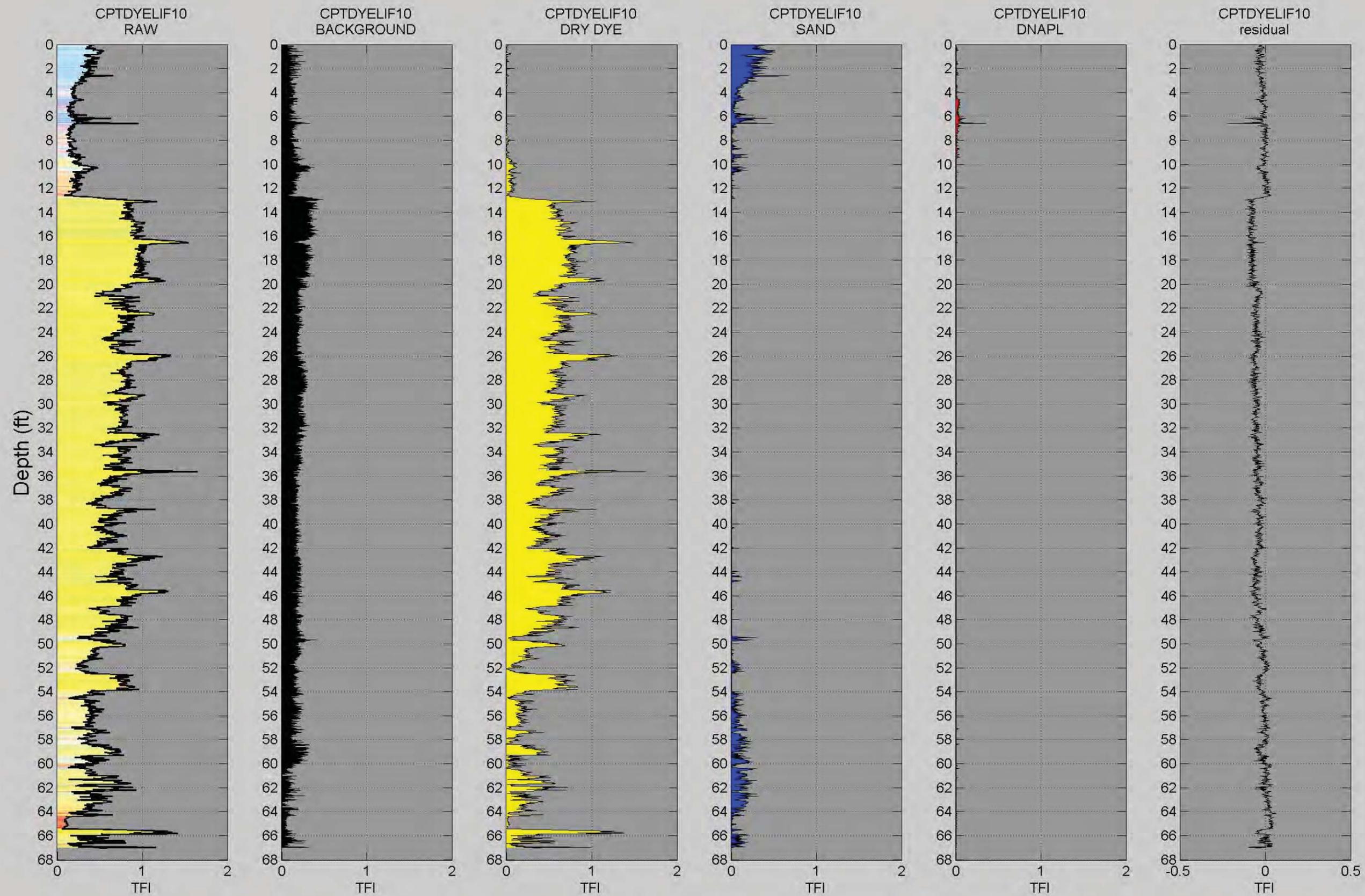


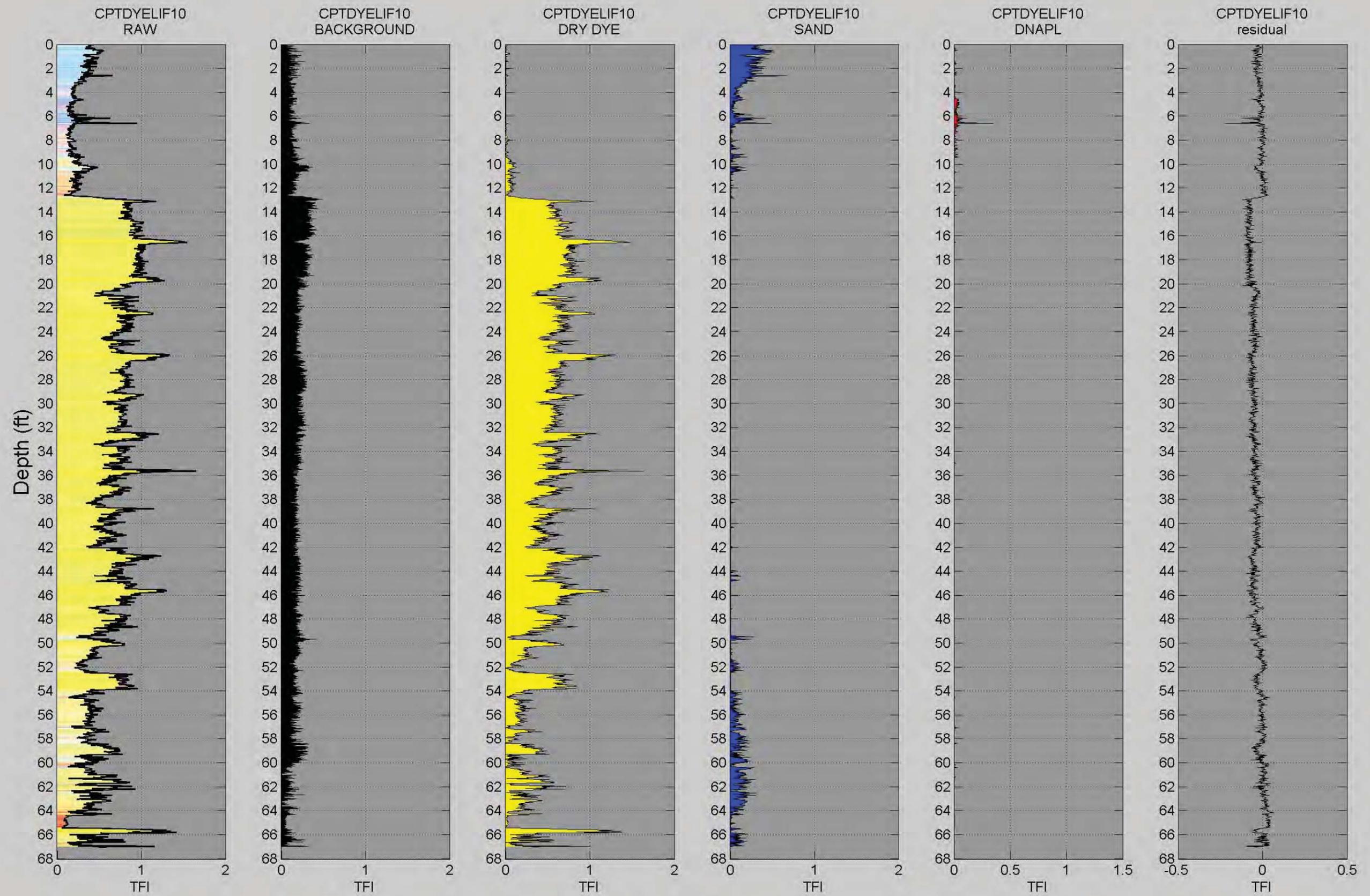


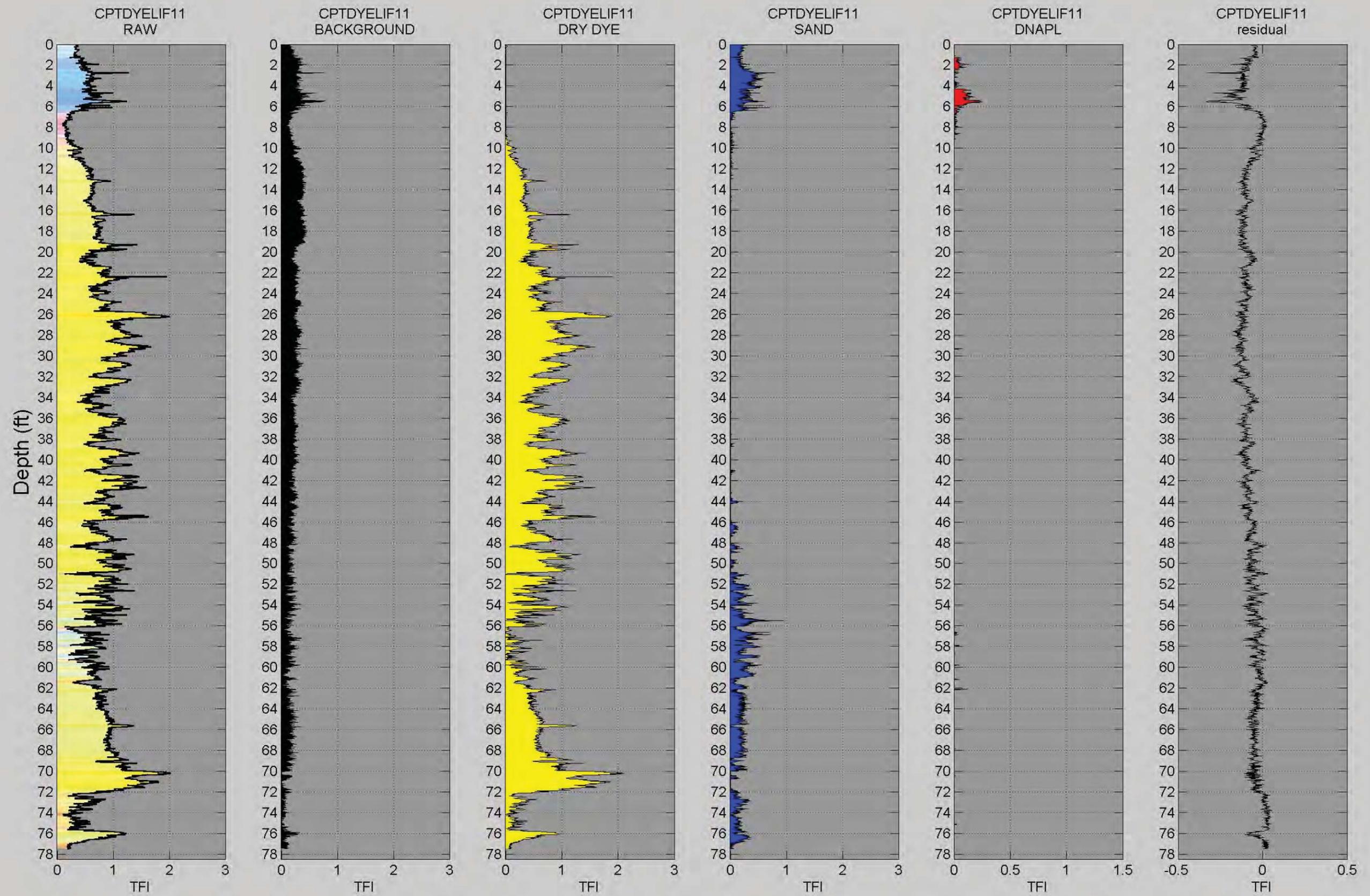




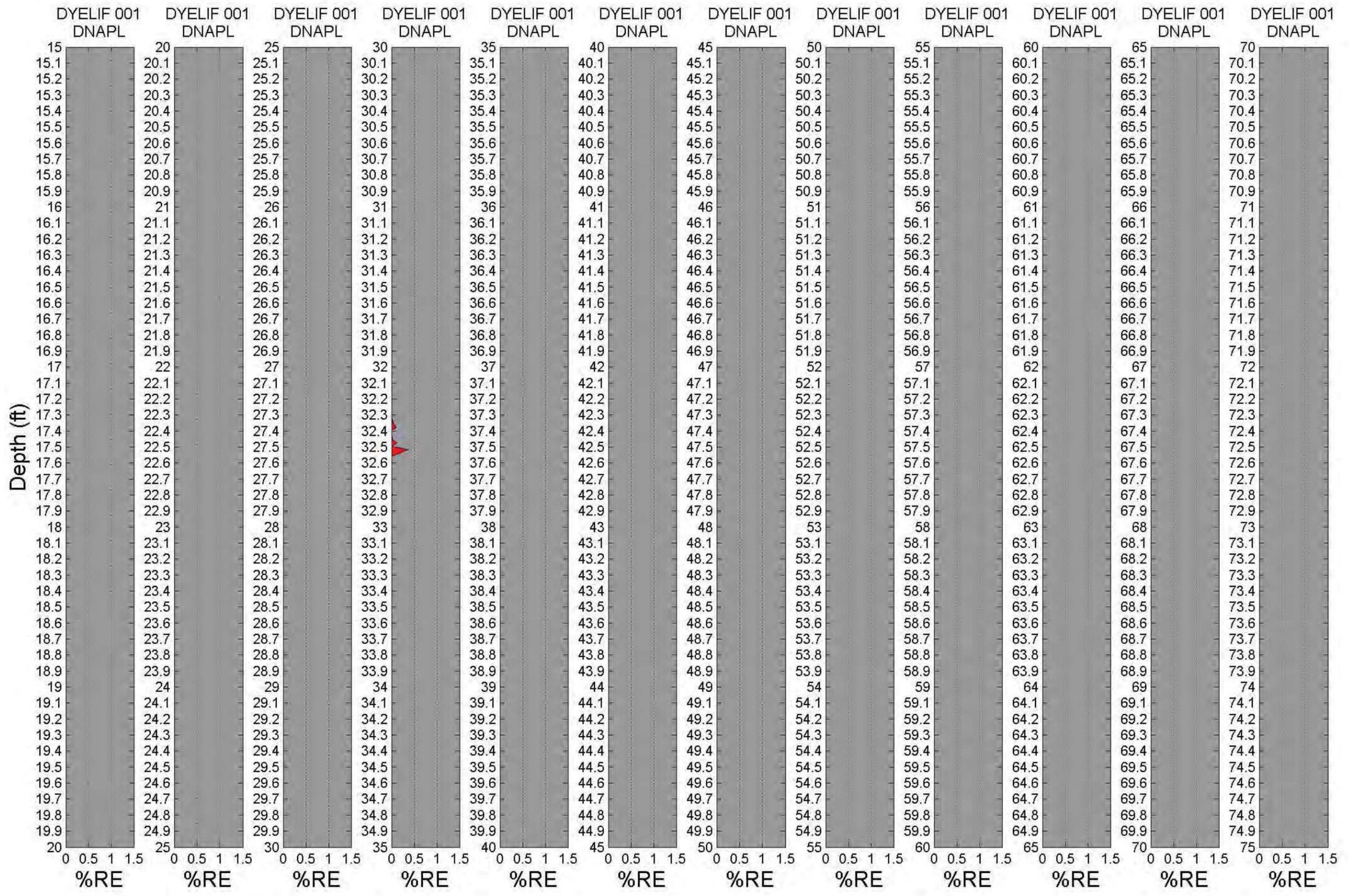


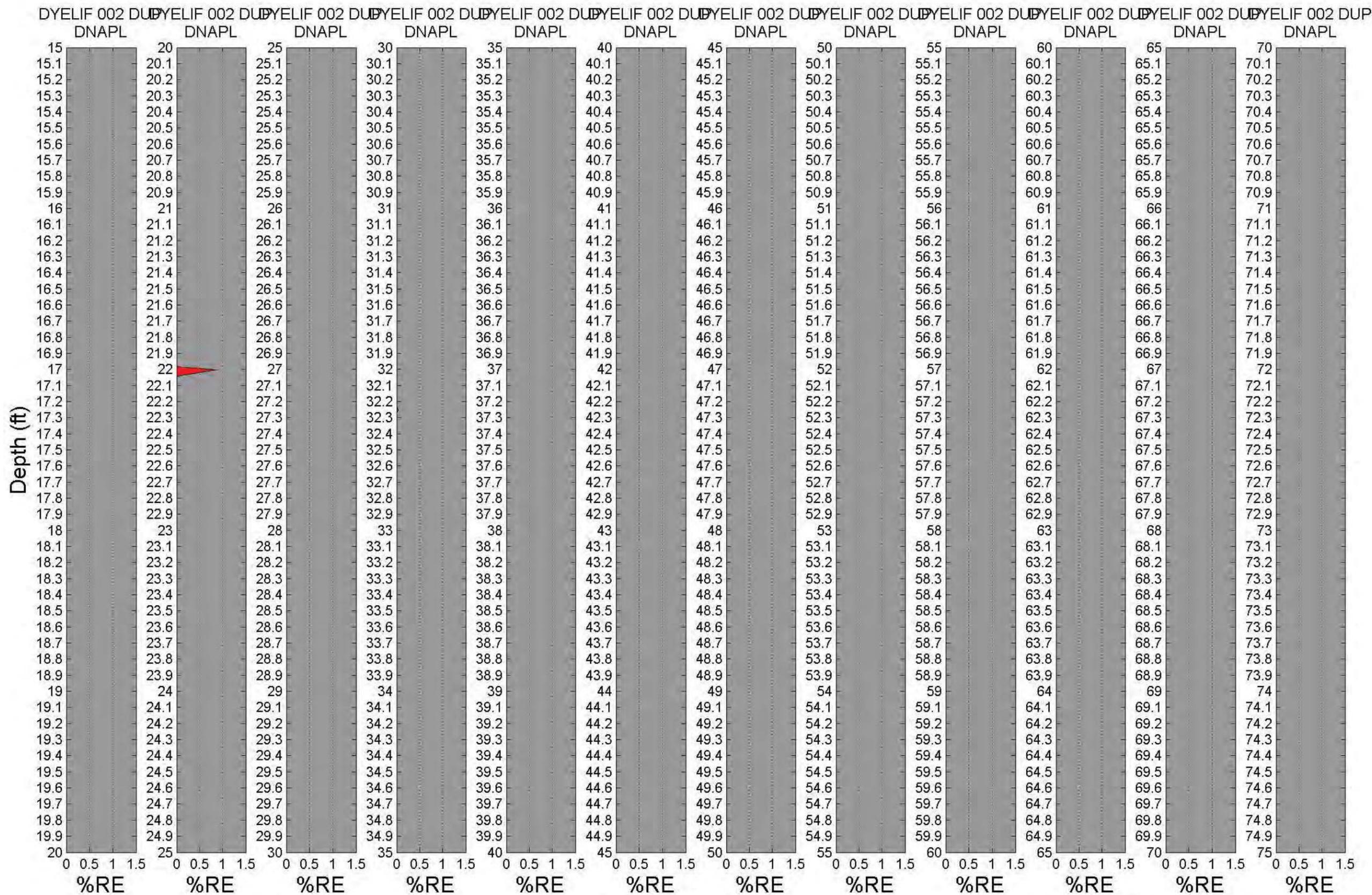


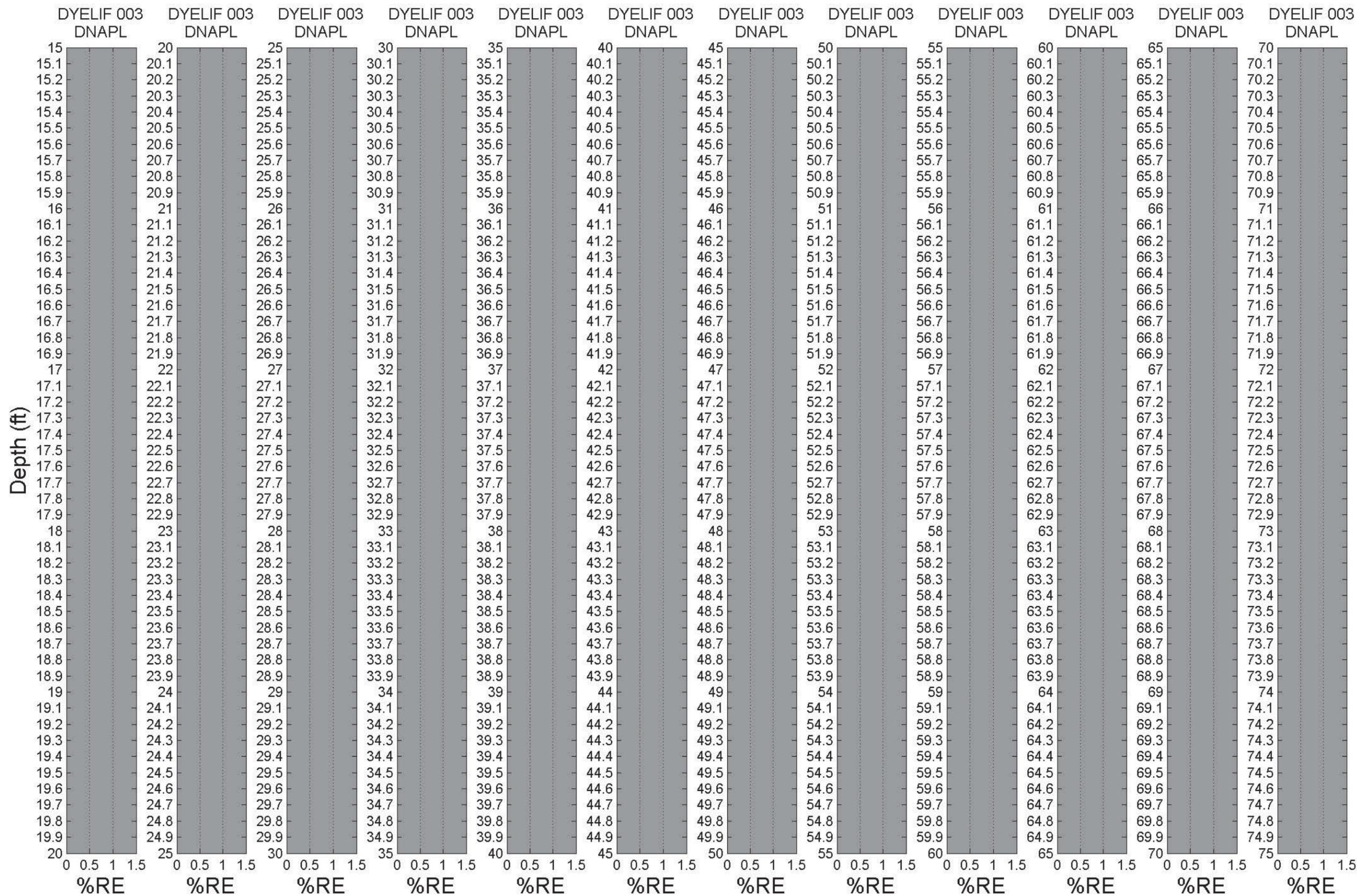


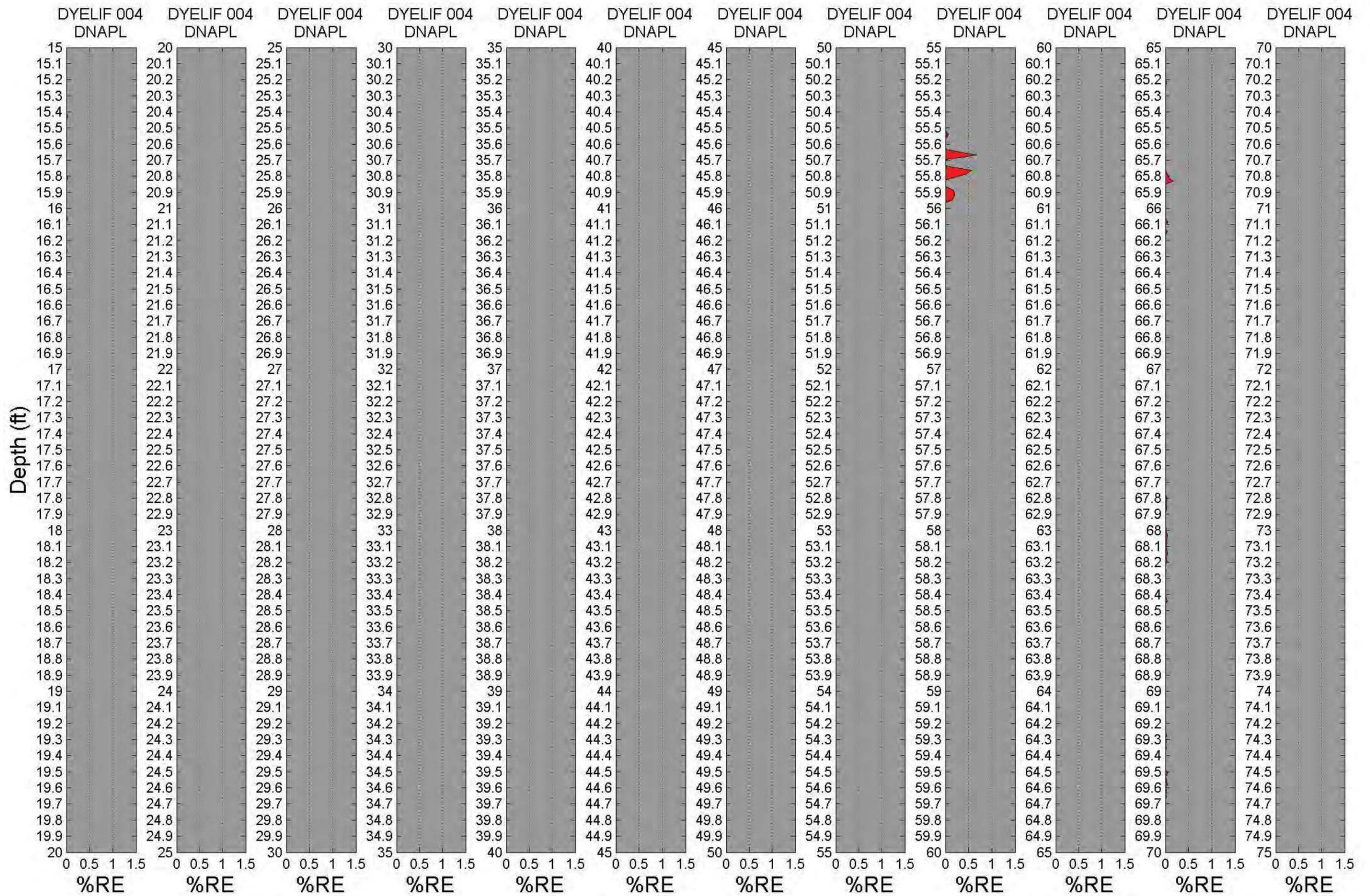


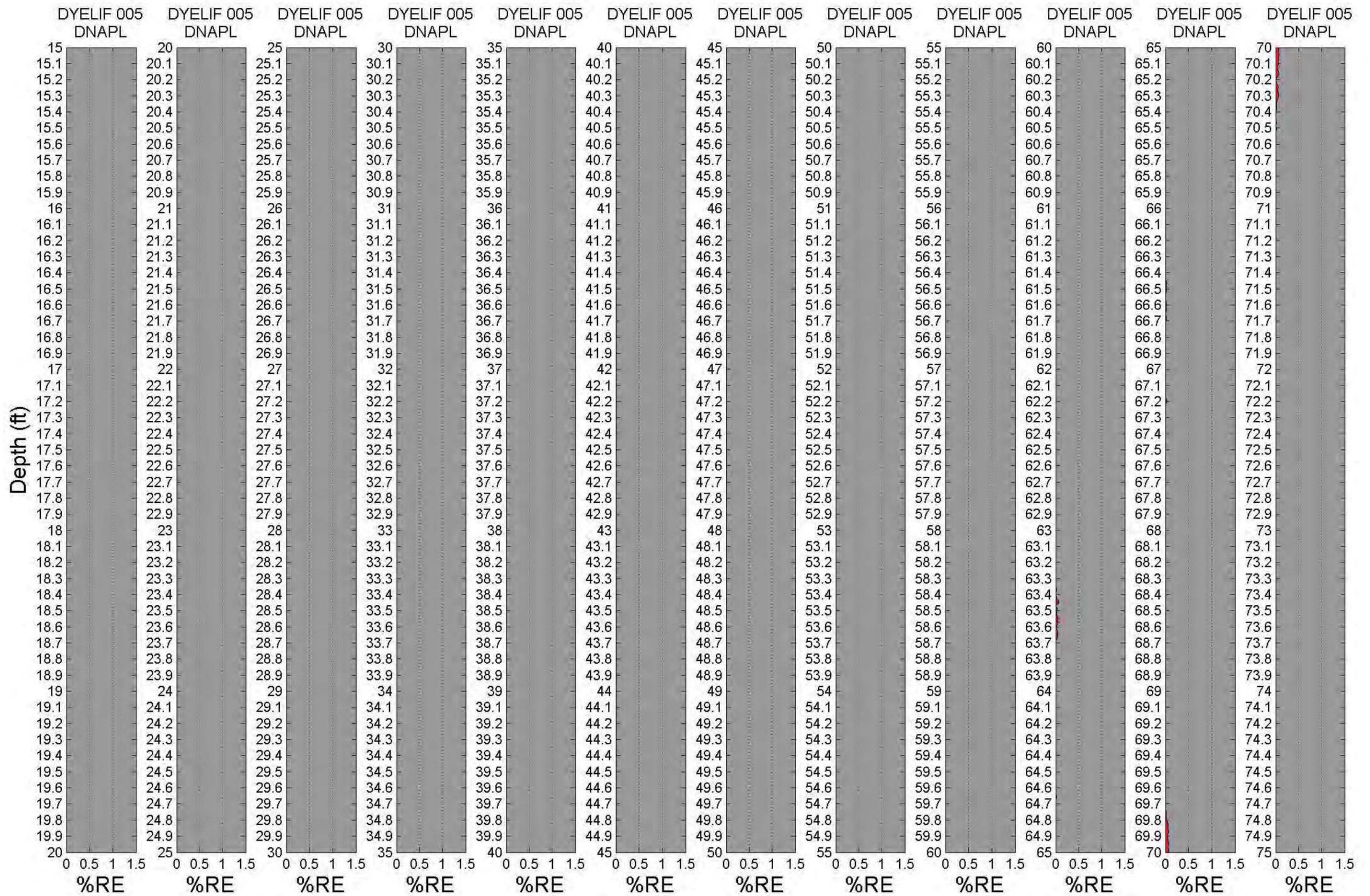
Appendix E: Multi-Panel DNAPL Plots

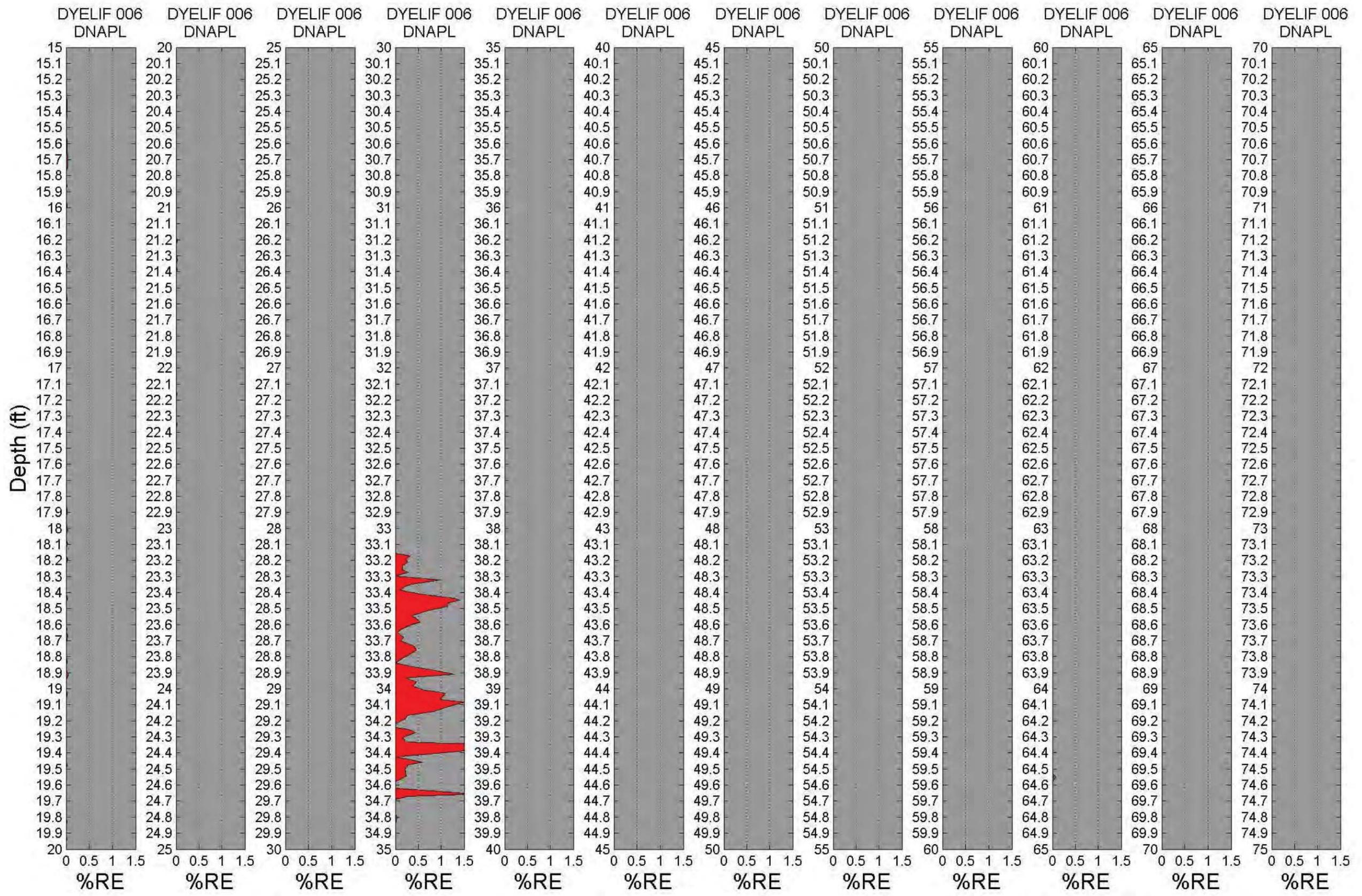


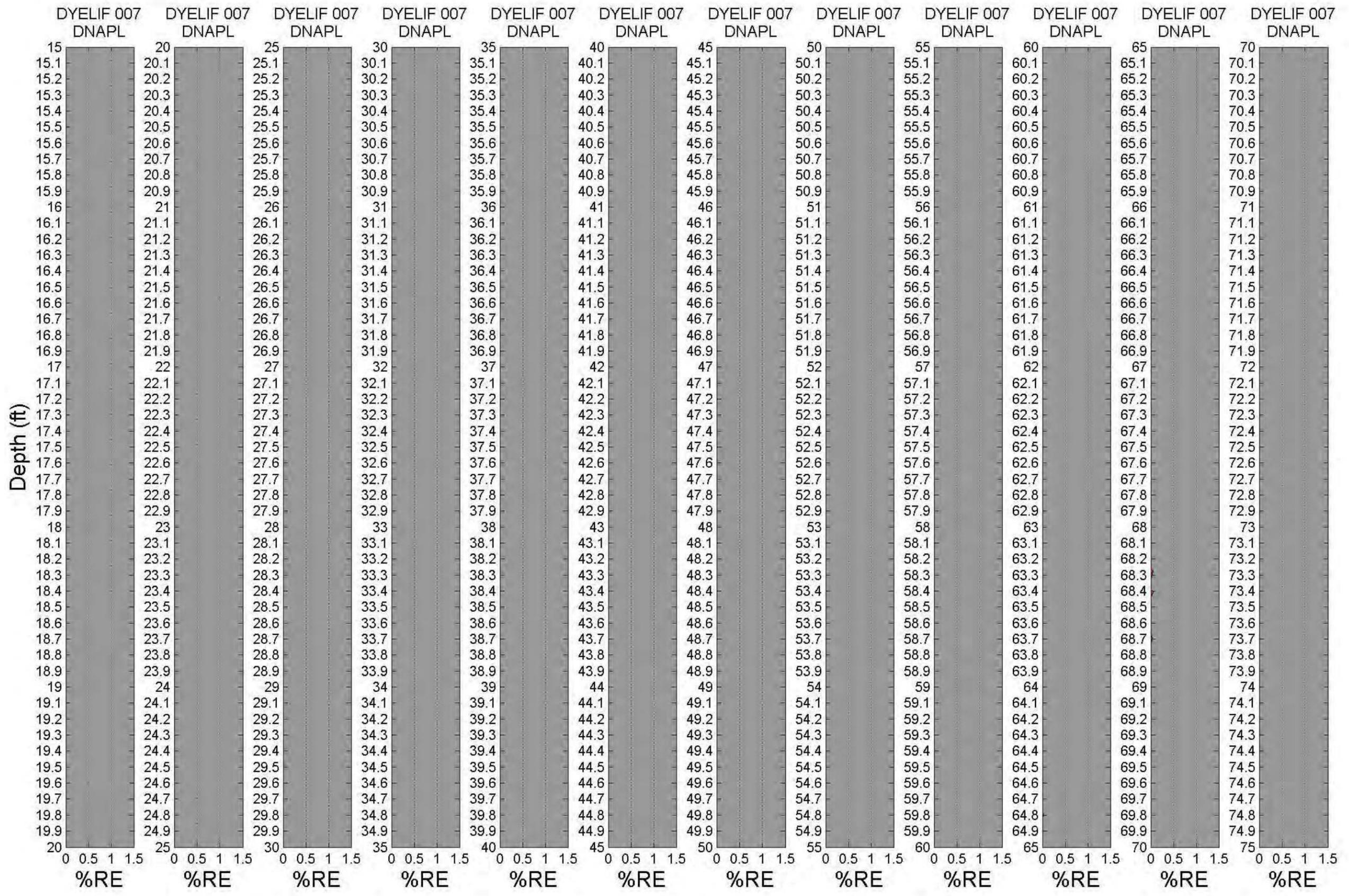


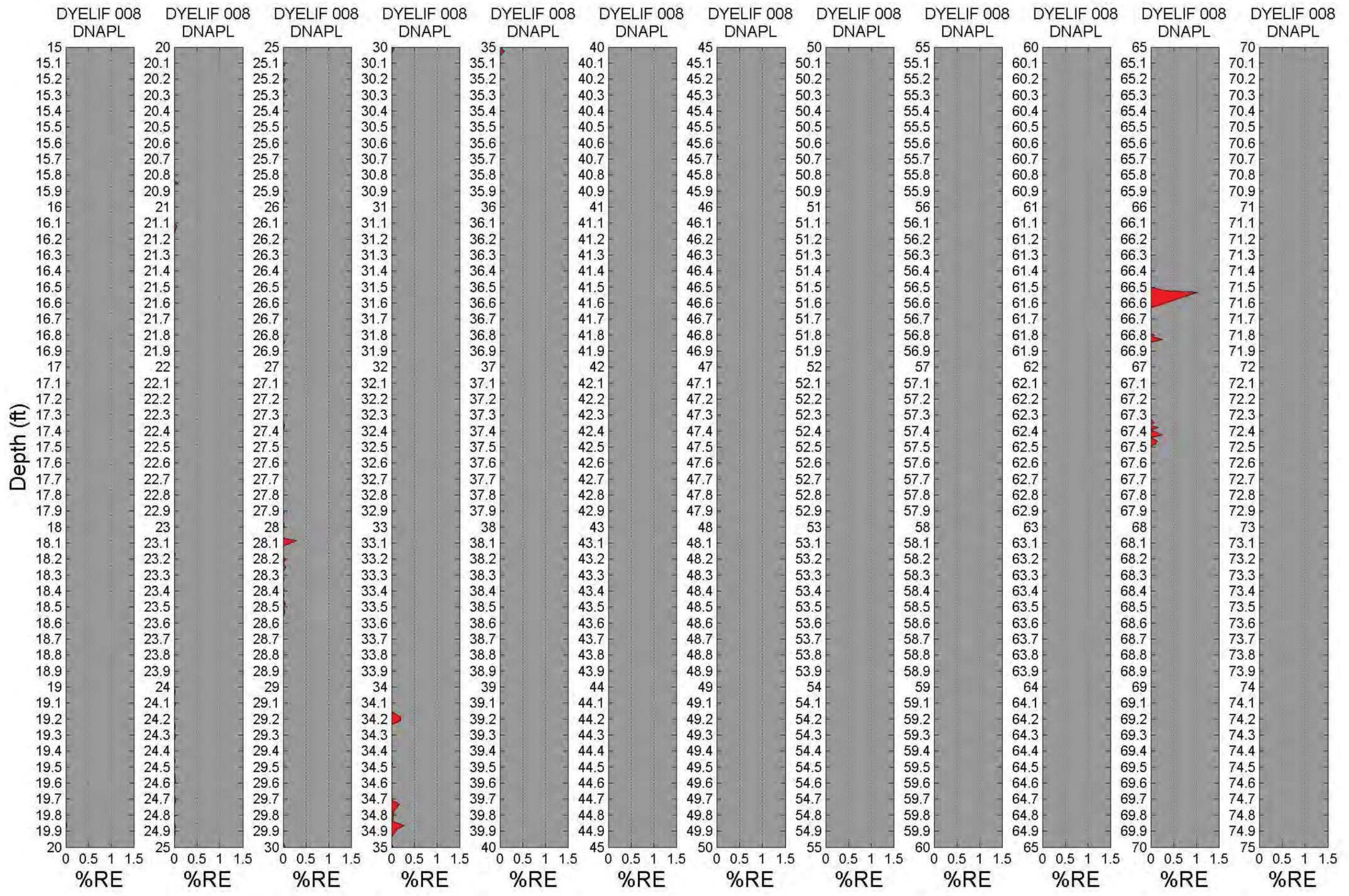


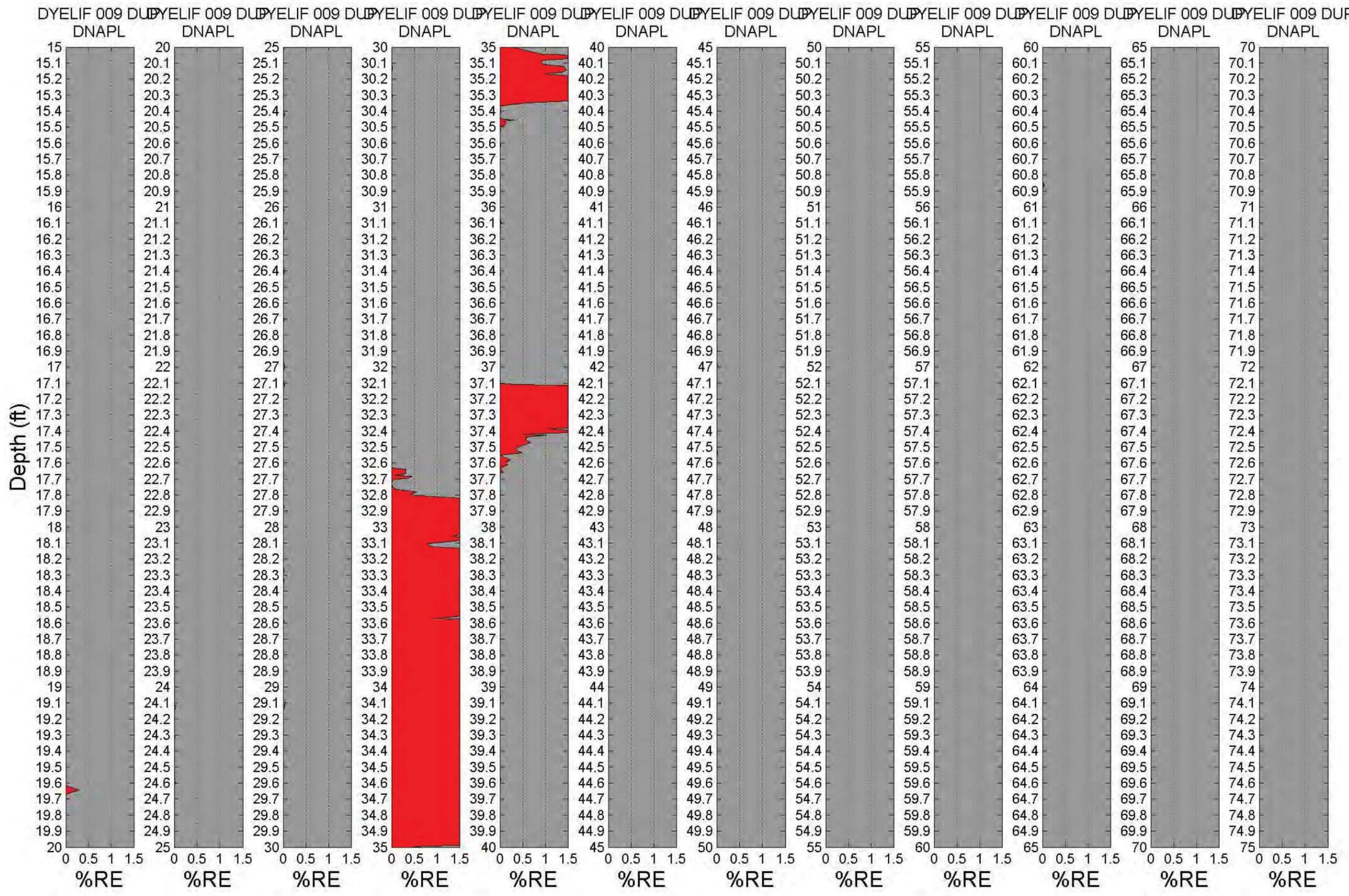


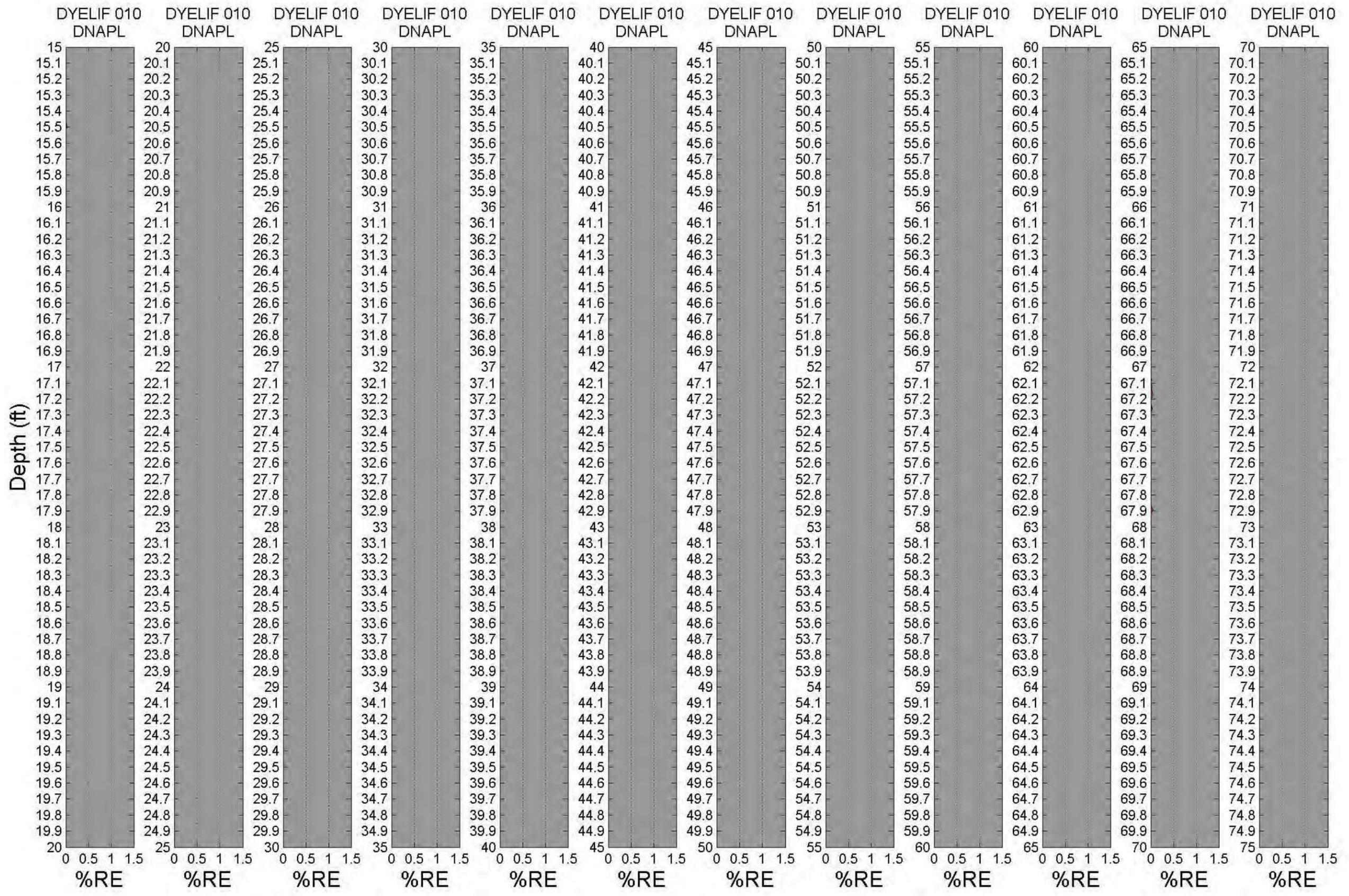


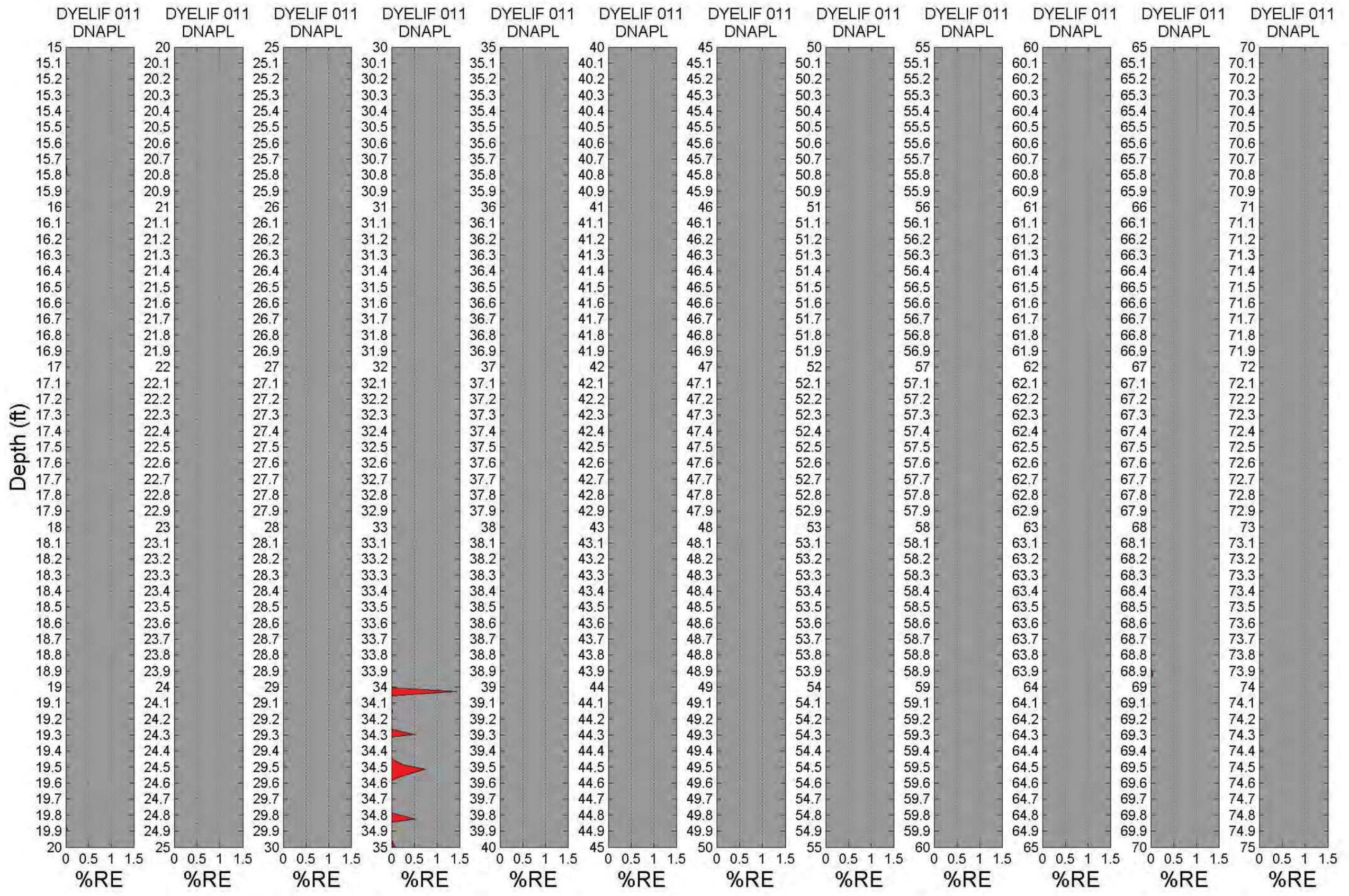


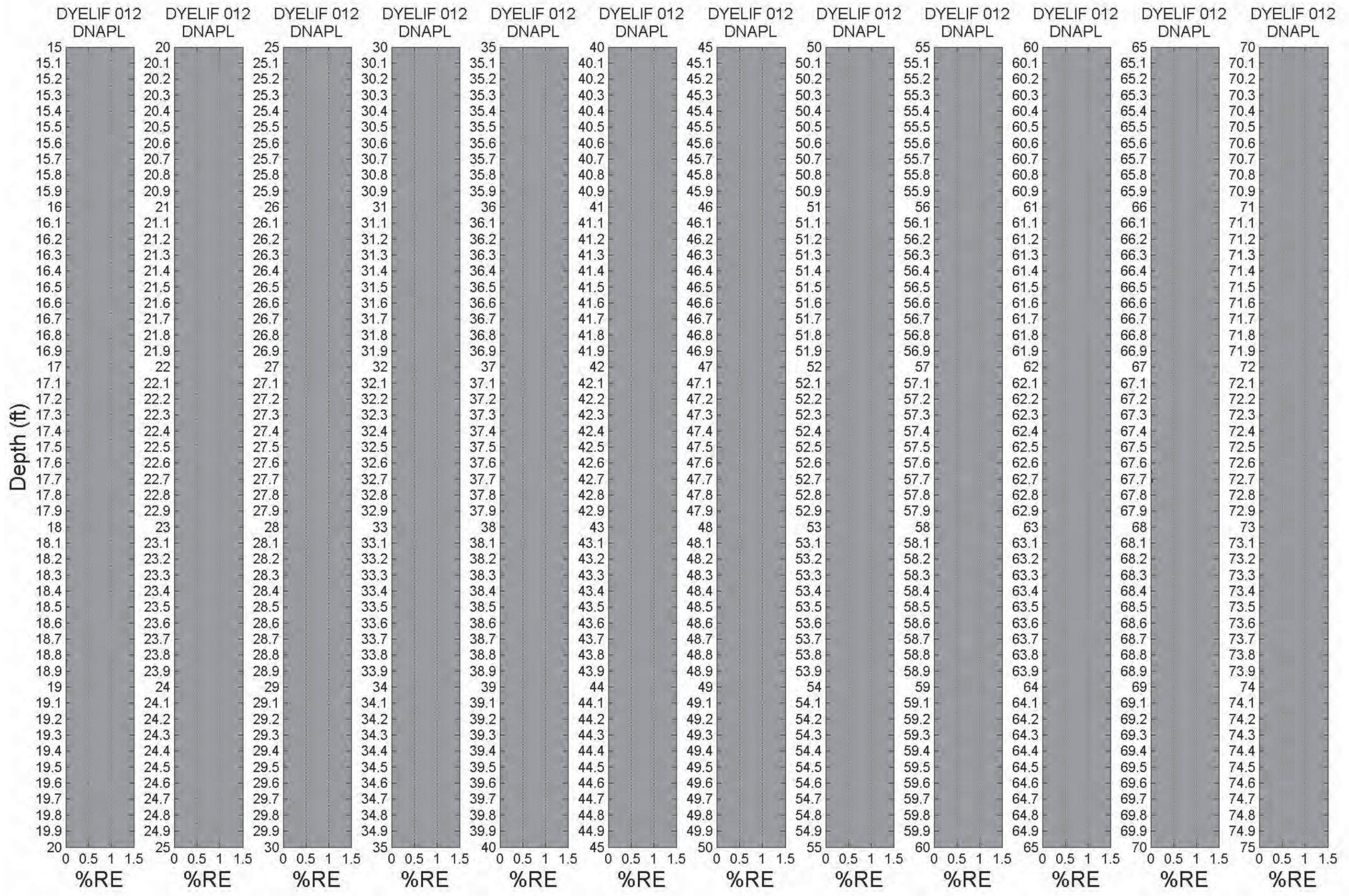


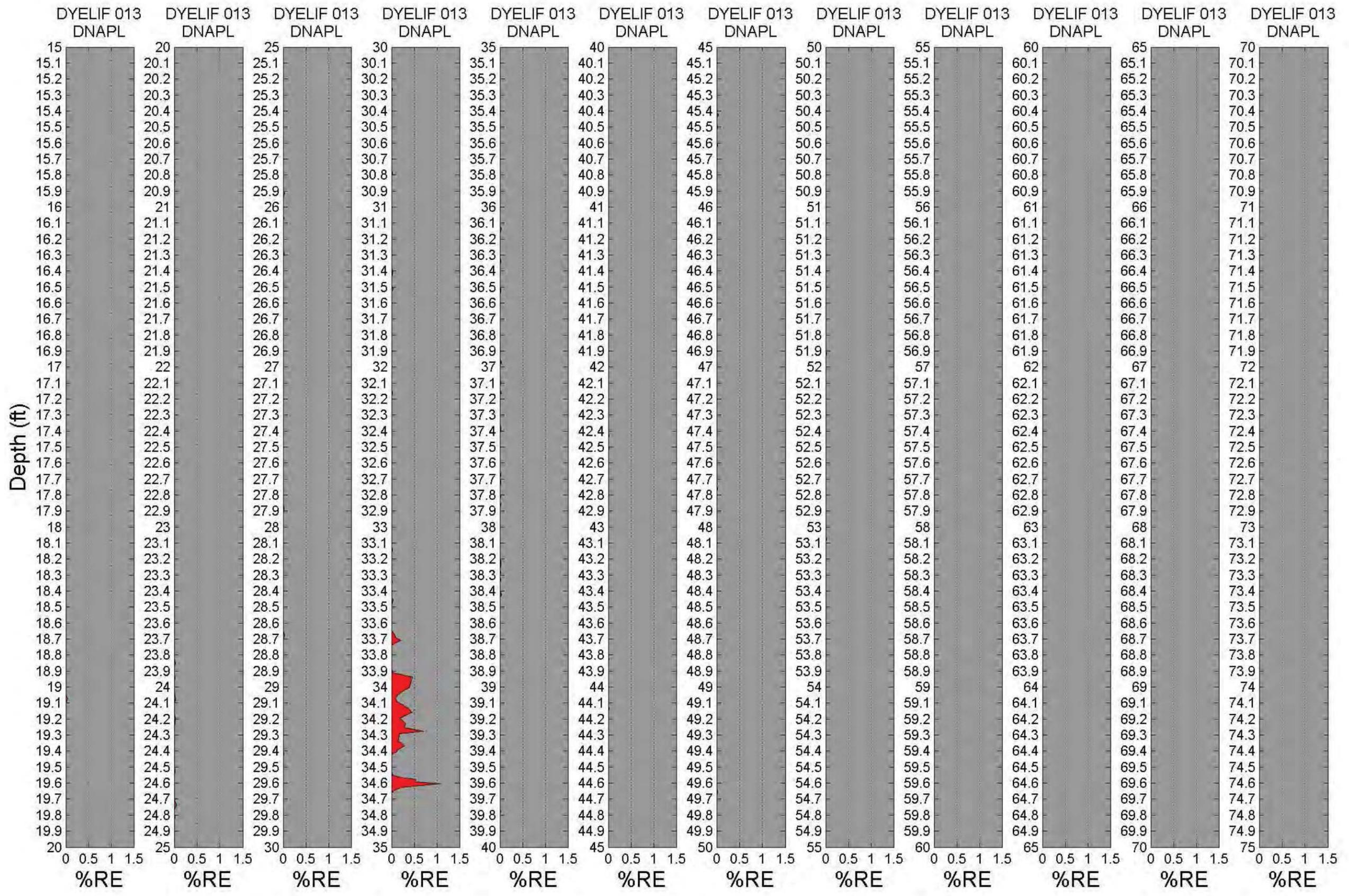


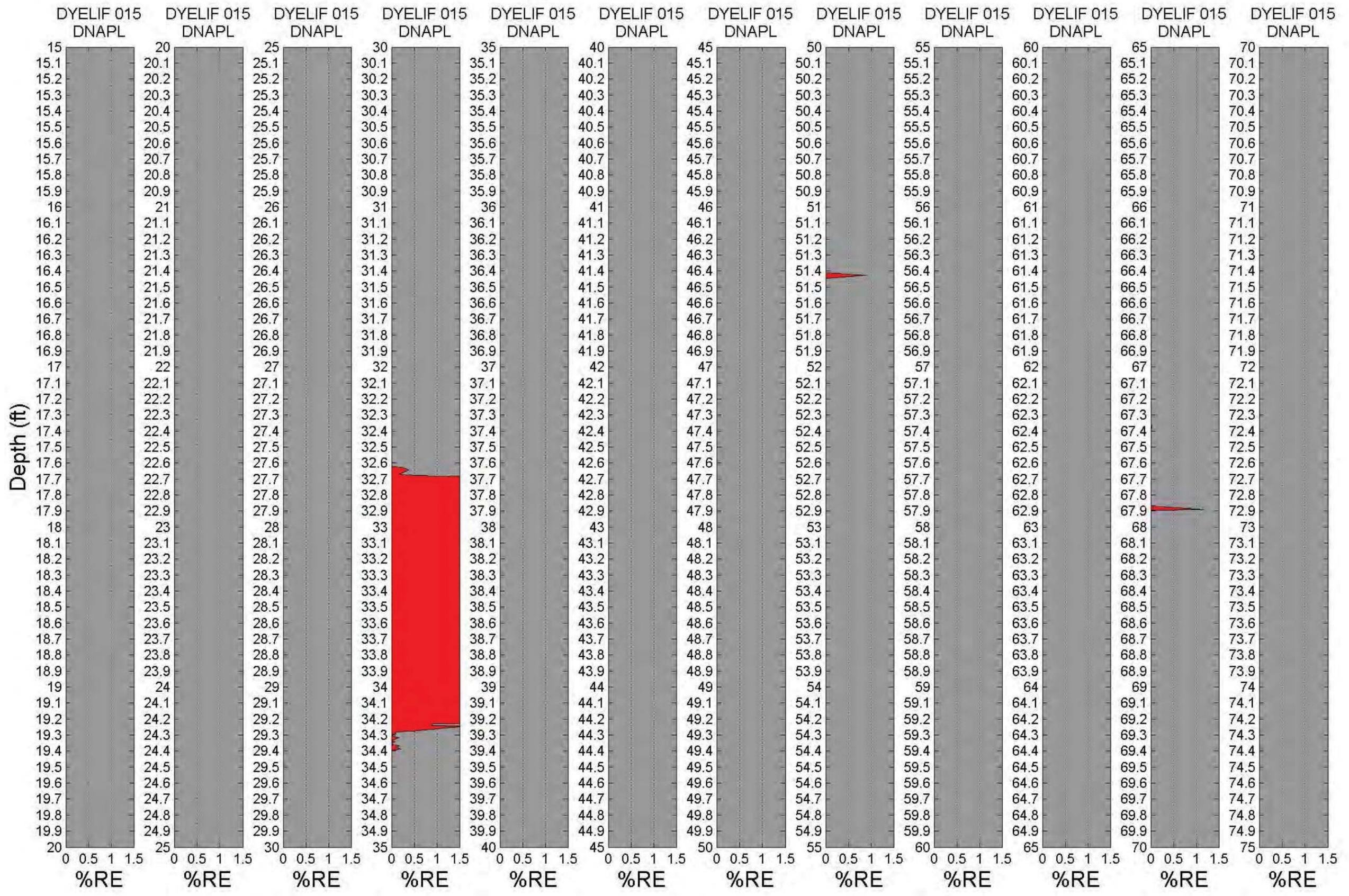


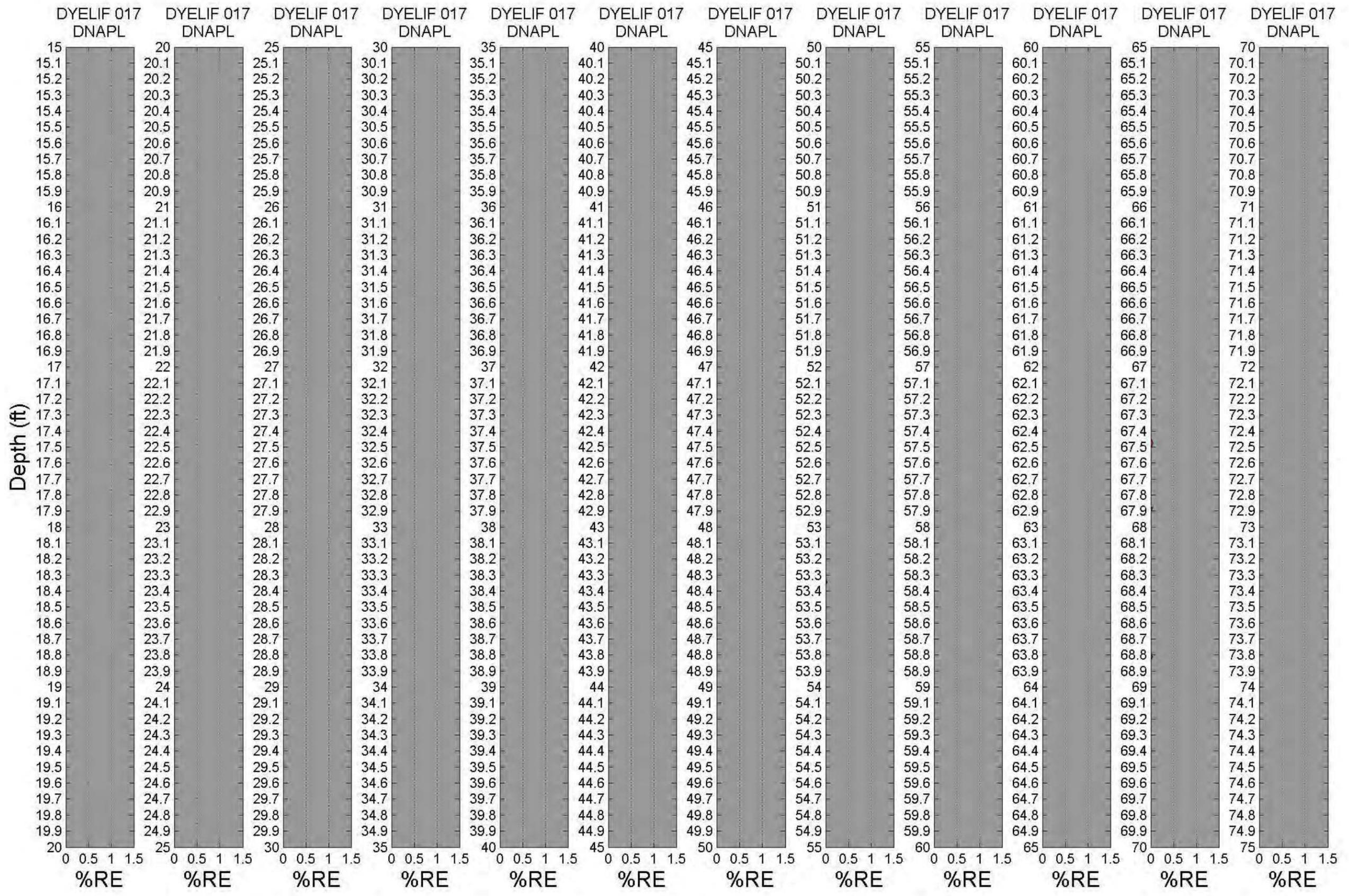


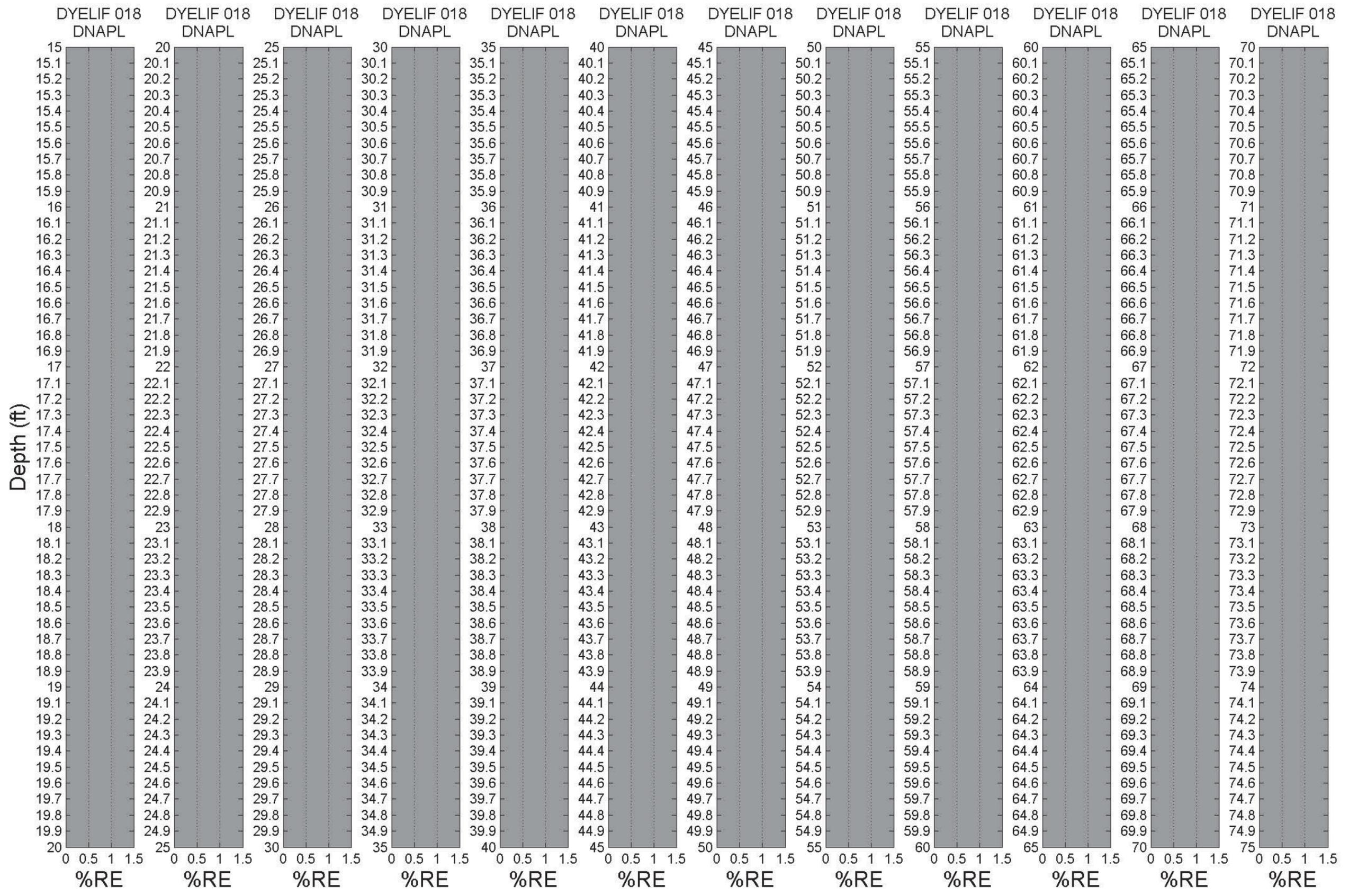


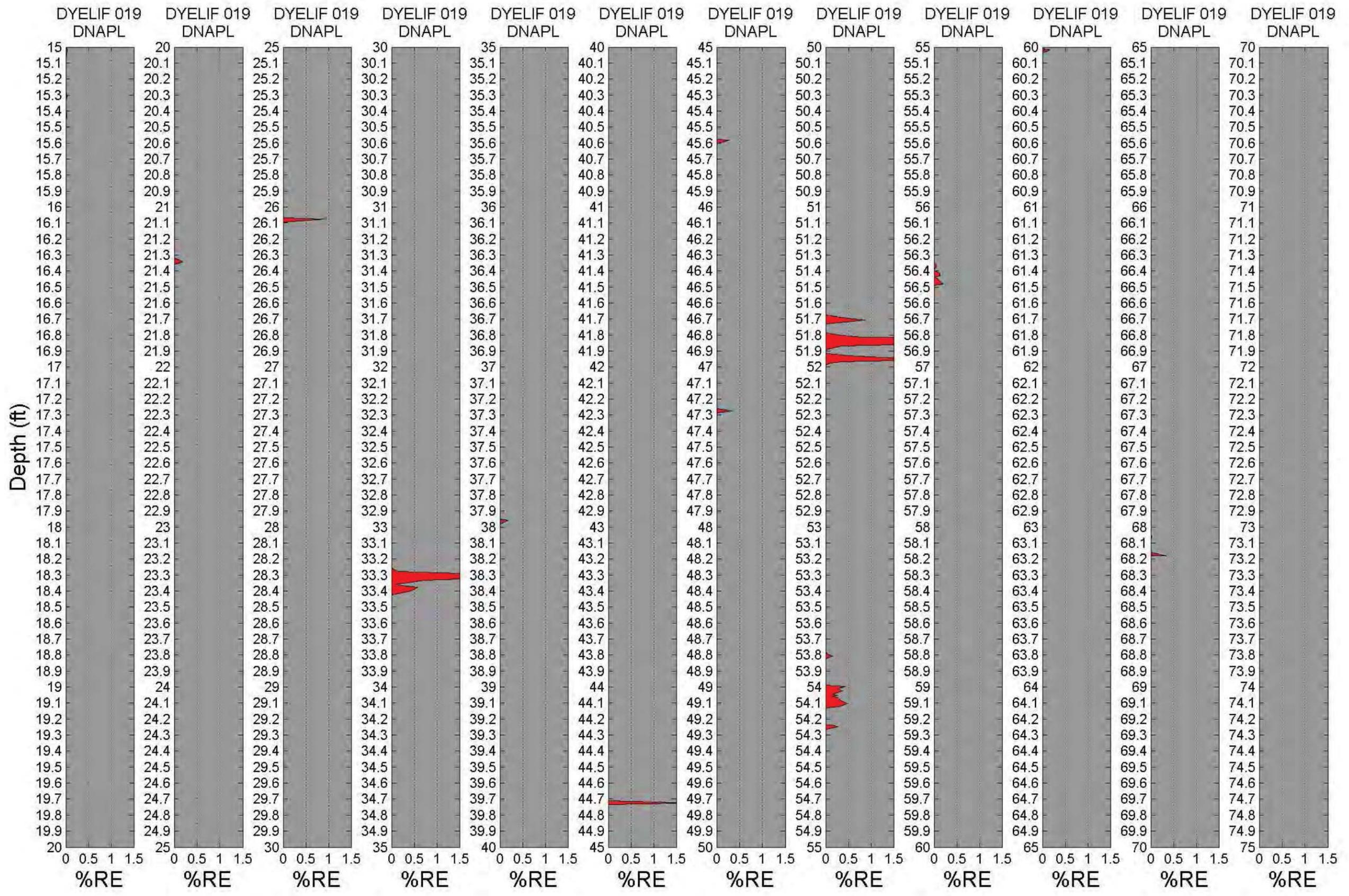


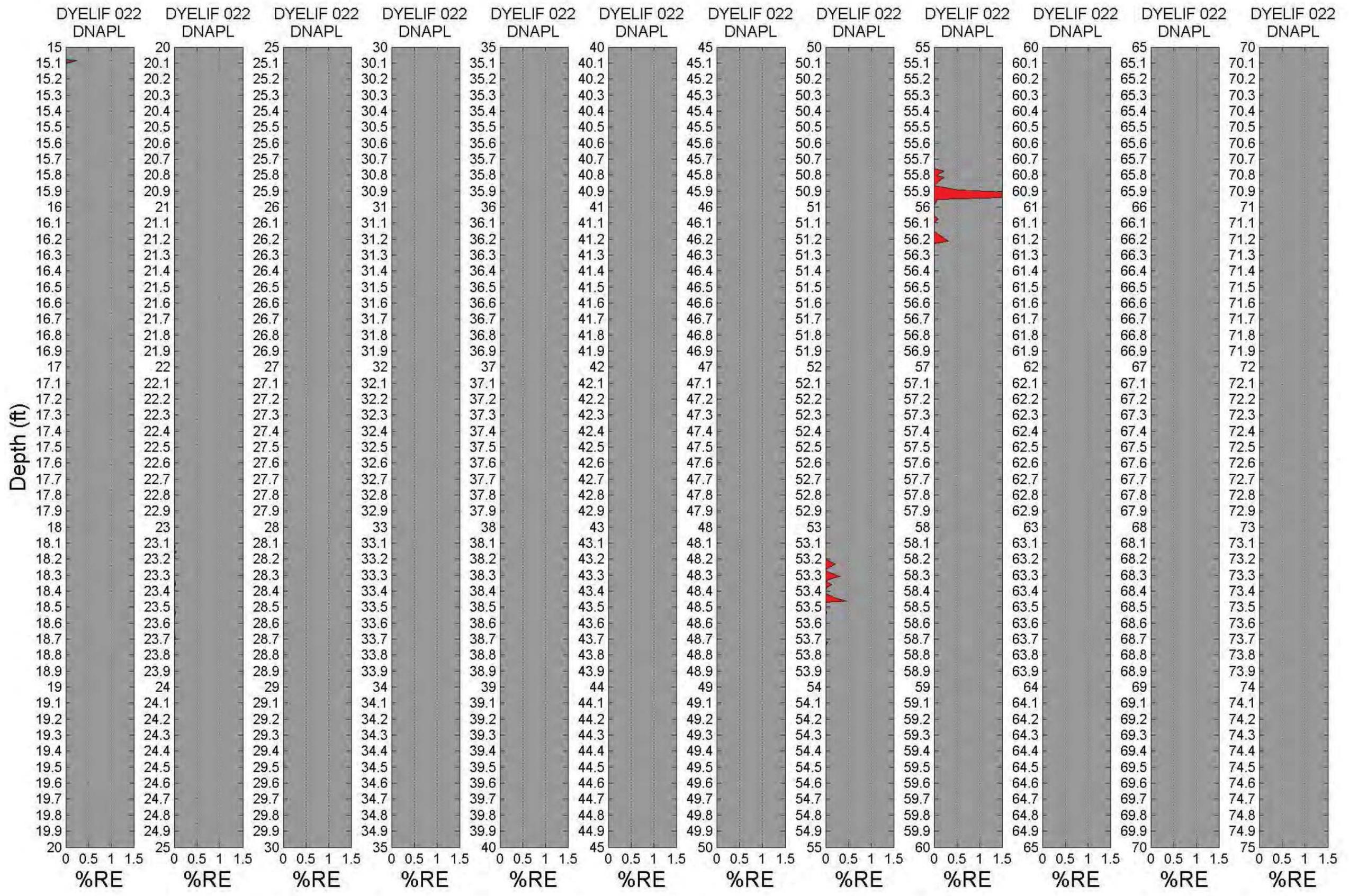


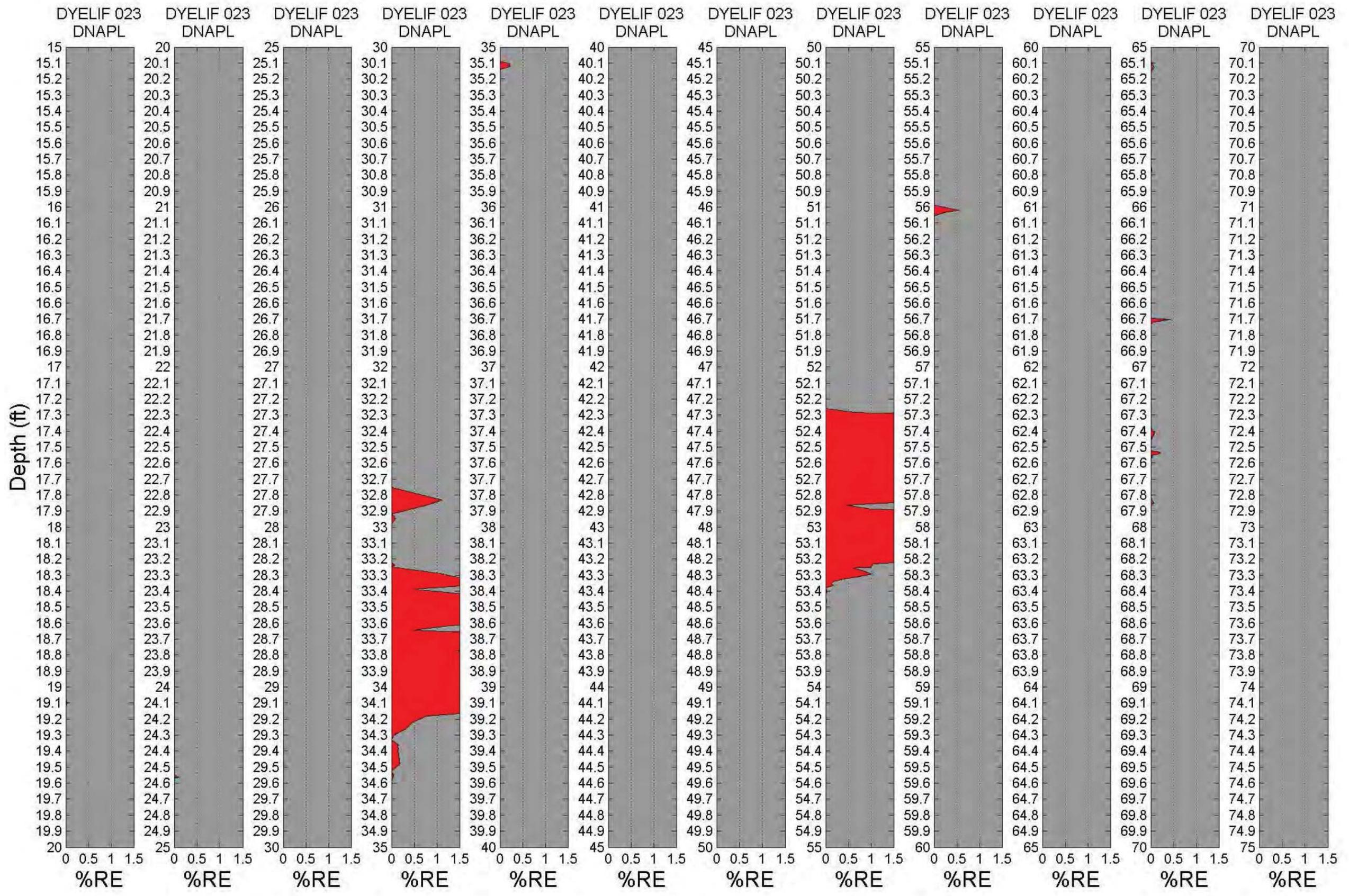












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