ARCADIS

Appendix E

Dart Sampling and Laser-Induced Fluorescence Results

1. Introduction

On August 13 and 14, 2013, ARCADIS U.S., Inc. (ARCADIS) conducted Dart sampling at 10 locations in Dawson Cove (three soil locations and seven sediment locations) to qualitatively assess the vertical profile of polycyclic aromatic hydrocarbons (PAHs) and to evaluate the Dart sampling technique for potential future soil and sediment delineation sampling. As discussed in the Downstream Areas Remedial Sampling Plan (ARCADIS 2013), Dart sampling is a technology developed by Dakota Technologies, Inc. (DTI) that uses solid-phase extraction (SPE) and laser-induced fluorescence (LIF) principles to detect PAHs and PAH-containing nonaqueous phase liquids (NAPLs) in soil and sediment. A Dart sampler consists of a rod coated with an SPE medium, which attracts and sorbs PAHs. The sampler is inserted into the soil or sediment, allowed to equilibrate, removed, and analyzed with an LIF reader for PAH/NAPL concentrations as a function of depth[1].

1.1 Dart Sampler Deployment, Retrieval, and LIF Results

At each of the 10 locations (Figure 2-3), field sampling personnel manually pushed 6-foot-long Darts into the soil and sediment locations to a target depth of 3 to 4 feet below soil/sediment surface (bss). During this process, the sampling personnel noted observations of any sheens on the soil or surface water, if present. After 48 hours, the sampling personnel removed the Darts from the soil and sediment locations. Again, the sampling personnel noted any visible sheen, if present. The Darts were subsequently shipped under chain-of-custody procedures to DTI, where the Dart samplers were handled and analyzed by DTI. Prior to analyzing the Dart samplers, the physical condition of each Dart was observed, and the Dart was cleaned to remove any surficial soil, sediment, or visible NAPL. The Dart analyzer consists of a modified lathe and a standard Ultraviolet Optical Screening Tool (UVOST) system paired together to detect PAHs absorbed into the SPE medium. The UVOST and lathe system measures the PAH fluorescence continuously around the circumference of the Dart, along its entire length.

The Dart installation and removal notes, and penetration depth intervals are summarized in Table E-1; Dart logs are provided in Attachment E-1. Additional calibration laboratory studies conducted by DTI to help interpret the field data are summarized in Attachment E-2.

[1] Additional information regarding the Dart technology can be found on DTI's website (http://www.dakotatechnologies.com/index.php/Service/Darts.html), and in Attachment C of the Downstream Areas Remedial Sampling Plan (ARCADIS 2013).

Table E-1: Dart Observations

Dart Location	Dart Penetration Depth (feet)	Observations of Sheen During Installation/Retrieval	Dart Observations/ LIF %RE Intervals > Blank Dart
SO-DA-019	4.25	None	None
SO-DA-021	4.4	None	None
SO-DA-023	4.15	None	None
SED-DA-018	4.4	None	None
SED-DA-019	4.35	None	None
SED-DA-021	3.85	None	None
SED-DA-022	3.3	None	None
SED-DA-023	3.85	None	None
SED-DA-045	4.4	None	0.2 foot to 2.7 feet bss (max %RE[b]=9.7)
SED-DA-052	4.65	None	0.6 to 0.9 foot bss (max %RE=9) 2.3 to 2.5 feet bss (max %RE=13)

Notes:
[a] No sheens were observed to be produced as a result of Dart deployment or retrieval at any of the Dart sampling locations.
[b] Dart fluorescence measurements are normalized to a reference emitter (RE) and reported as percent (%) RE.

As indicated in Table E-1, Dart penetration depths ranged from 3.3 to 4.65 feet. Two of the 10 Dart samples (SED-DA-045 and SED-DA-052) had %RE responses above the "blank" Dart maximum %RE value of approximately 4.6 %RE, which DTI did not attribute to method interferences (blank Darts were those Darts that were taken into the field, not used, and then shipped with the used Darts to DTI). These two locations are near the central drainage pathway within Dawson Cove, and the PAH concentrations in sediment samples obtained at one of these two locations were higher relative to other sample results as reported by the analytical laboratory and discussed below. These results suggest that Dart may be useful as a qualitative tool, by comparing Dart %RE results to those from other Dart samples and "blank" Dart %RE results.

As noted on the Dart logs, DTI interpreted other %RE values above the maximum "blank" response as interferences due to lint on the Dart polymer, or reflection interference from the metallic Dart tip. These occurrences are identified on the Dart logs as single-point, stand-alone responses (Attachment E-1).

1.2 Comparison of Dart Results and PAH Concentrations

1.2.1 DTI "Calibration" Study Using Site-Specific Crude Oil and Sediment

DTI performed a laboratory "calibration" study testing the LIF detection response using prepared standard samples. The standard samples were prepared by spiking a measured mass of clean site sediment (collected from background sediment location SED-DA-BG-012; 0 to 6 inches bss) with a calculated mass of site-specific crude oil, thoroughly homogenizing the crude oil and sediment, leaving Darts in the spiked sediment for 48 hours to simulate field conditions, and analyzing the results with the UVOST system. Results of the calibration study allow %RE values to be compared to known concentrations of crude oil. DTI also measured the %RE response to a Dart exposed to pure site-specific crude oil. The calibration study data and results are presented in Attachment E-2.

The calibration study results suggest a systematic relationship between %RE and crude oil concentrations. The %RE readings increased smoothly and consistently with increasing crude oil concentrations in the standard samples prepared with site-specific crude oil and sediment. However, the calibration study results also suggest that Dart samplers are relatively insensitive within the range of PAH concentrations actually detected in site sediment samples (discussed further below). For example, %RE values as low as 2 to 3 %RE were measured in correlation to approximately 10,000 parts per million (ppm) of site-specific crude oil in prepared standard samples. However, even the "blank" Dart associated with the site-specific data set (which was a new, clean, unused Dart) indicated a %RE response up to 4.6%. These results suggest that Dart sampling does not provide quantitative information regarding site-specific crude oil concentrations at the range of concentrations detected in site sediment.

1.2.2 Dart Readings Compared to PAH Concentrations in Field Samples

Dart readings were also compared to the total PAH (both18 priority+2 list PAHs and long list PAHs) analytical results in co-located core samples to further evaluate the Dart results.

The Dart penetration intervals and co-located core observations (depths and field observations) are provided in Table E-2.

Table E-2: Dart and Co-Located Core Observations

Dart/ Co-Located Core	Dart Penetration Depth (feet)	Core Depth (feet)	Dart Observations/ LIF %RE Intervals > Blank Dart	Photoionization Detector Measurements >1 ppm (ppm)	Sheen Observations
SO-DA-019	4.25	4.0	None	0 to 1 foot bss (7.1 to 12.3)	None
SO-DA-021	4.4	4.0	None	0 to 1 foot bss (2.5 to 3.2)	None
SO-DA-023	4.15	4.0	None	0 to 0.5 foot bss (2.1)	None
SED-DA-018	4.4	3.2	None	0 to 0.5 foot bss (1.1 to 1.4)	None
SED-DA-019	4.35	3.2	None	None	None
SED-DA-021	3.85	3.3	None	None	None
SED-DA-022	3.3	3.0	None	None	None
SED-DA-023	3.85	3.1	None	None	None
SED-DA-045	4.4	1.5	0.2 to 2.7 feet bss (max %RE=9.7)	0.5 to 1 foot bss (1.2 to 3.5)	0 to 0.5 foot bss (sheen)
SED-DA-052	4.65	2.6	0.6 to 0.9 foot bss (max %RE=9); 2.3 to 2.5 feet bss (max %RE=13)	None	None

Qualitatively, Dart readings do not appear to correlate systematically with photoionization detector measurements. SED-DA-045 was the only Dart sampling location where a sheen was observed in the co-located sediment core; the co-located Dart sampler produced the second highest LIF value of the 10 Dart samplers. In addition, this location had the highest reported PAH concentrations among these 10 sediment sampling locations, as discussed below.

The Dart readings were also compared to total PAH concentrations (both18 priority+2 list PAHs and long list PAHs) from soil and sediment samples obtained from the co-located core locations. The average Dart reading over the soil and sediment sample depth interval and the total PAH concentration of the sample interval are plotted on Figures E-1 and E-2.

Figure E-1: Average %RE Compared to Total PAH Concentrations (18 Priority+2 List PAHs)

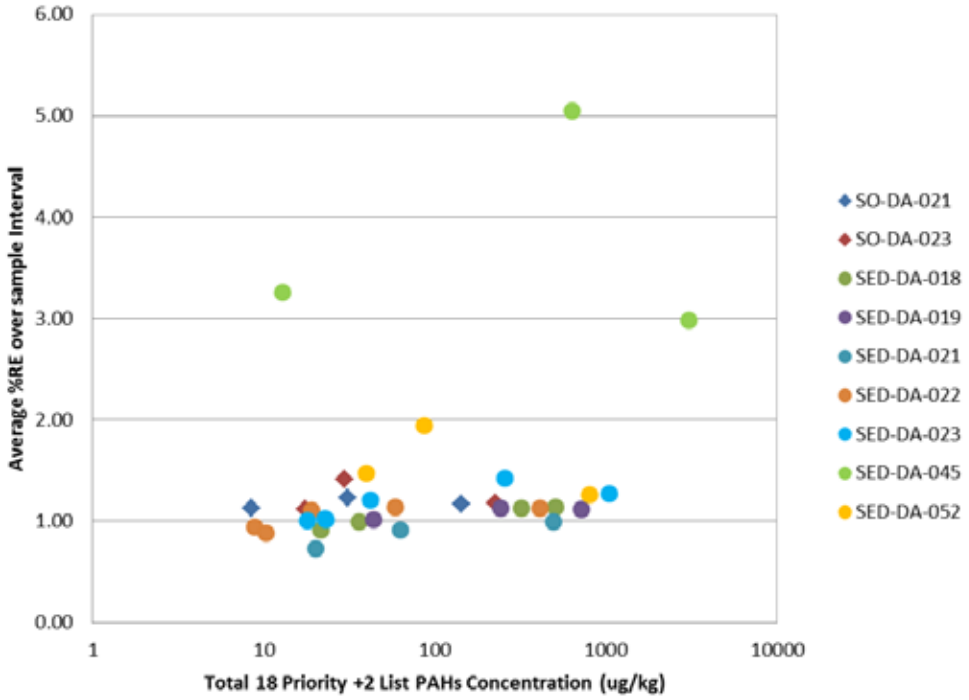
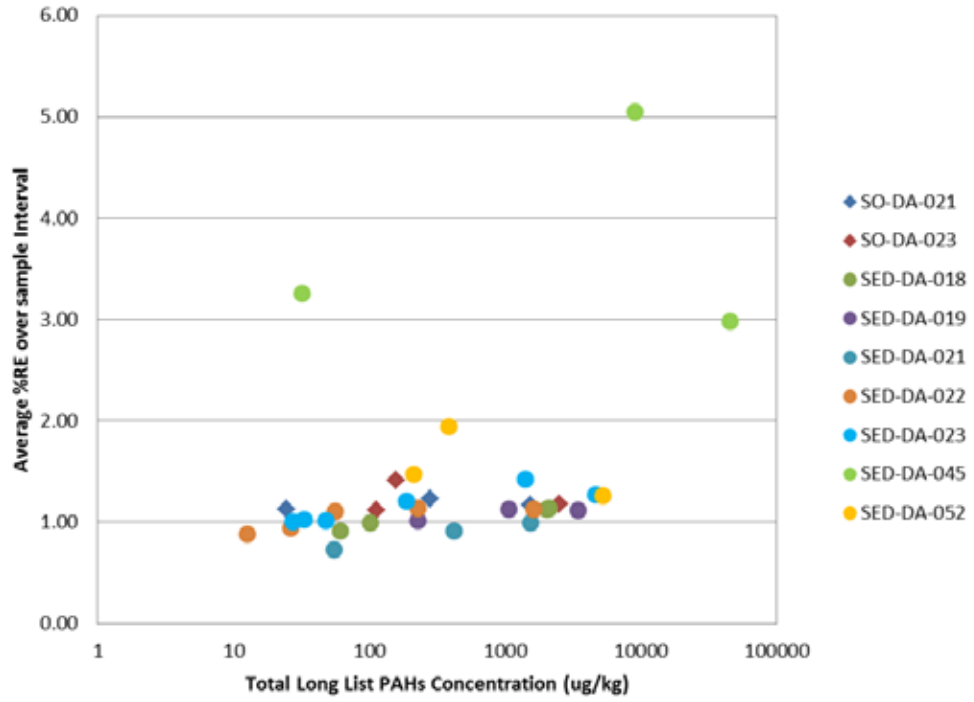


Figure E-2: Average %RE Compared to Total PAH Concentrations (Long List PAHs)



As shown on Figure E-1, the total PAH concentrations (18 priority+2 list PAHs) for the sample intervals that correspond to the Dart data were less than or approximately equal to 1 ppm (1,000 micrograms per kilogram [µg/kg]); the only exception was one sample from location SED-DA-045, which had 3 ppm (3,050 µg/kg) total PAHs. The majority of the average %RE data were between 0.5 and 1.5, whereas PAH concentrations spanned a 2-order-of-magnitude range, indicating that the Dart sampler is insensitive to these lower range total concentrations of the 18 priority+2 list PAHs. Similarly, most of the average Dart %RE responses were consistent across a 3-order-of-magnitude range of these lower range total PAHs using the long list PAH detections in sediment samples (Figure E-2).

Based on the limited and lower range of total PAH concentrations and Dart readings, and the overall spread of the data as shown on Figures E-1 and E-2, Dart sampling does not provide a quantitative indication of PAH concentrations in sediments at this site. Thus, future use of Dart sampling at the site, if any, should be for qualitative, comparative purposes only, and the results should be used with caution.

2. Conclusions

The Dart sampling method appears to have limited use in quantifying crude-oil-related PAHs in sediment and soil at the site. However, Dart samplers may have some utility as a qualitative tool, by comparing the %RE data sets between deployed Darts and unused, "blank" Darts. The Dart samples with the highest %RE values in the data set reported in this appendix also had among the highest PAH concentrations detected in co-located sediment samples; one of the two co-located sediment samples also had a visible sheen after removing the sediment from the coring equipment. Thus, Dart sampling may have some use in evaluating relative PAH concentrations in sediments at the site.

3. Reference

ARCADIS. 2013. Downstream Areas Remedial Sampling Plan. Mayflower Pipeline Incident, Mayflower, Arkansas. July.

Table E-3 – Summary of Dart Results and Corresponding Total PAH Concentrations from Co-located Cores

ExxonMobil Environmental Services Company
Mayflower Pipeline Incident Response, Mayflower, Arkansas
Downstream Areas Data Assessment Report

Dart Location	Sample Interval (feet bss)	Average %RE	Total 18 Priority + 2 List PAHs (µg/kg)	Total HMW & LMW PAHs (Long List) (µg/kg)
SO-DA-019	0-0.5	1.54	NA	NA
SO-DA-019	0.5-1	1.50	NA	NA
SO-DA-019	1-1.5	1.27	NA	NA
SO-DA-021	0-0.5	1.17	142	1527
SO-DA-021	0.5-1	1.23	30.8	280
SO-DA-021	1-1.5	1.12	8.45	24.5
SO-DA-023	0-0.5	1.18	227	2500
SO-DA-023	0.5-1	1.41	29.7	158
SO-DA-023	1-1.5	1.12	17.4	112
SED-DA-018	0-0.5	1.14	507	2091
SED-DA-018	0.5-1	1.13	318	2052
SED-DA-018	1-1.5	0.99	36.1	101
SED-DA-018	1.5-2	0.91	21.5	60.8
SED-DA-019	0-0.5	1.12	719	3450
SED-DA-019	0.5-1	1.13	243	1070
SED-DA-019	1-1.5	1.02	43.6	229
SED-DA-021	0-0.5	1.00	493	1531
SED-DA-021	0.5-1	0.91	62.8	422
SED-DA-021	1-1.5	0.73	20.0	54.9
SED-DA-022	0-0.5	1.13	410	1606
SED-DA-022	0.5-1	1.14	58.8	229
SED-DA-022	1-1.5	1.11	19.0	56.1
SED-DA-022	1.5-2	0.94	8.82	26.5
SED-DA-022	2-3	0.88	10.3	12.6
SED-DA-023	0-0.5	1.27	1046	4640
SED-DA-023	0.5-1	1.42	257	1410
SED-DA-023	1-1.5	1.20	41.8	187.4
SED-DA-023	1.5-2	1.02	22.9	47.7
SED-DA-023	2-3	1.01	17.9	27.3
SED-DA-023	3-3.09	1.03	22.8	32.9
SED-DA-045	0-0.5	2.98	3050	45000
SED-DA-045	0.5-1	5.05	630	9090
SED-DA-045	1-1.5	3.25	12.8	32.2
SED-DA-052	0-0.5	1.26	803	5210
SED-DA-052	0.5-1	1.94	86.3	384
SED-DA-052	1-1.5	1.48	39.5	211
BLANK	0-0.5	0.99	NA	NA
BLANK	0.5-1	0.99	NA	NA
BLANK	1-1.5	1.15	NA	NA
BLANK	1.5-2	0.99	NA	NA
BLANK	2-3	0.97	NA	NA

Notes:

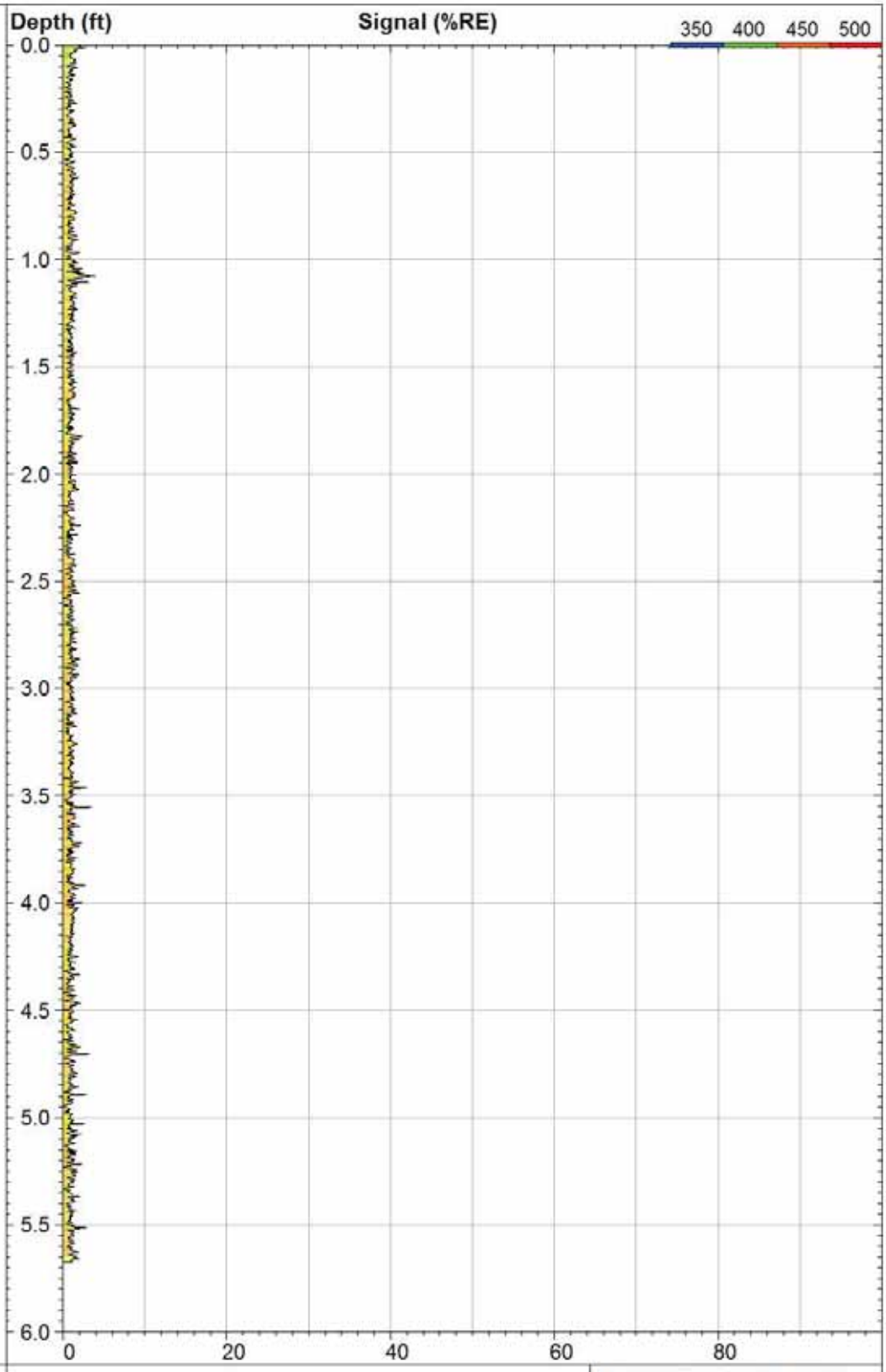
%RE - Dart fluorescence measurements are normalized to a reference emitter (RE) and reported as percent (%)RE
bss - Below soil or sediment surface
NA - Data not available
HMW - High Molecular Weight
LMW - Low Molecular Weight

ARCADIS

Attachment E-1

Dart Result Logs

Callouts



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BLANK-081113

UVOST By Dakota
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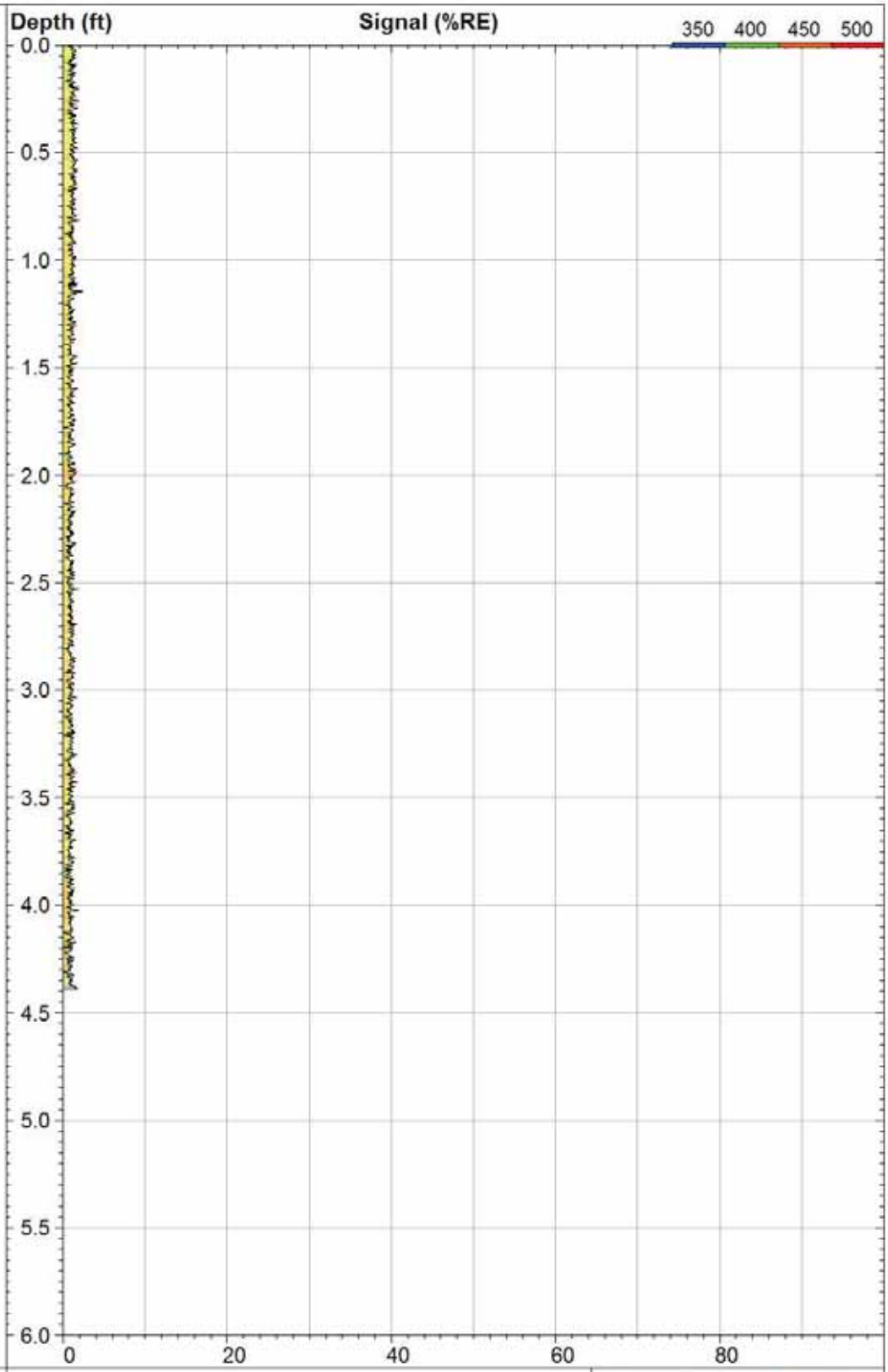
Site: **Mayflower**	*Y Coord.(Lat-N) / System:* **Unavailable / NA**	*Final depth:* **5.67 ft**
Client / Job: **ARCADIS /**	*X Coord.(Lng-E) / Fix:* **Unavailable / NA**	*Max signal:* **4.6 %RE @ 0.00 ft**
Operator / Unit: **RWS / UVOST01**	*Elevation:* **Unavailable**	*Date & Time:* **2013-08-13 15:30 CDT**

Callouts



No %RE response above range detected in Blank-081113.

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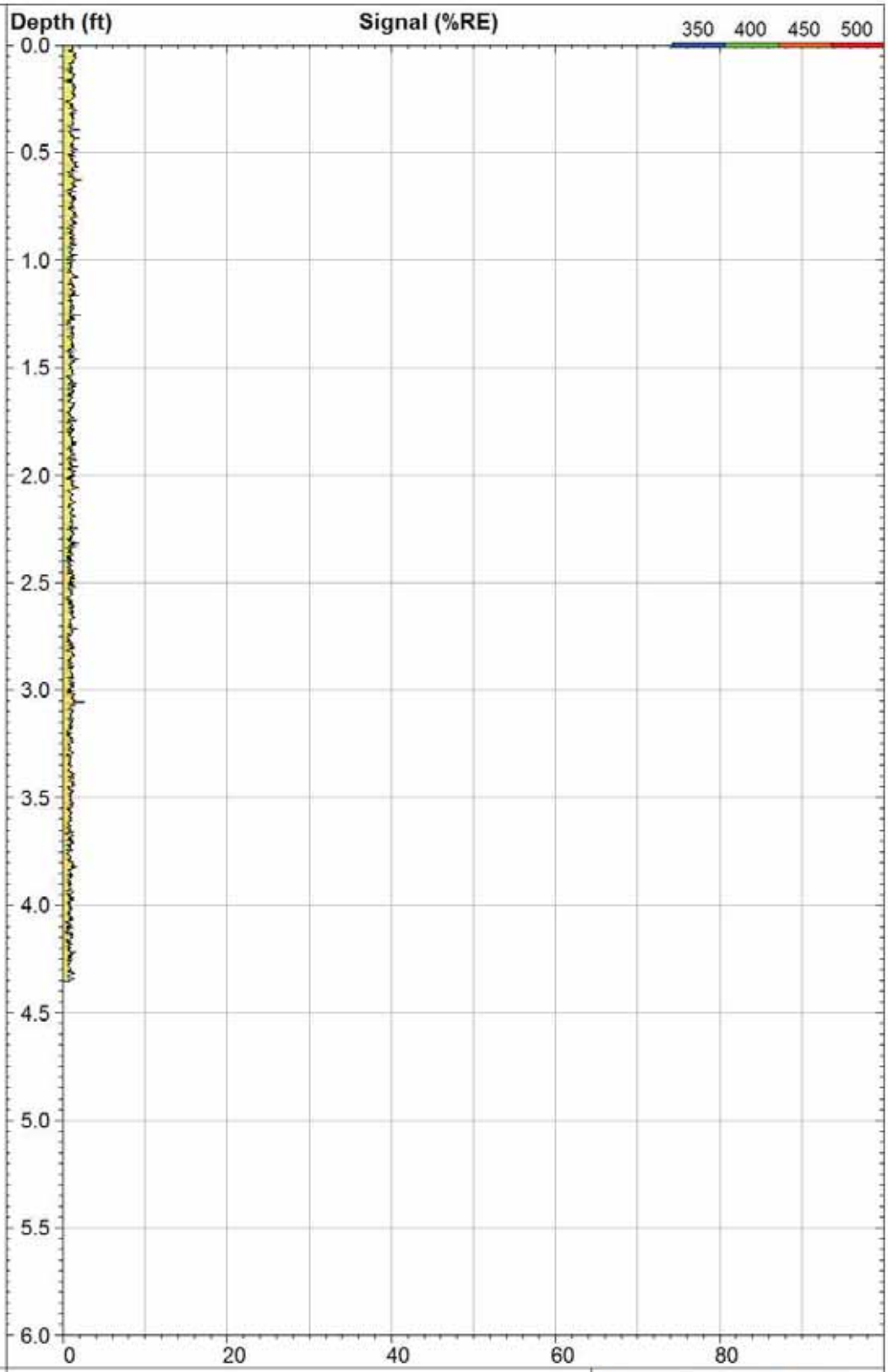
Site: **Mayflower**	*Y Coord.(Lat-N) / System:* **Unavailable / NA**	*Final depth:* **4.39 ft**
Client / Job: **ARCADIS /**	*X Coord.(Lng-E) / Fix:* **Unavailable / NA**	*Max signal:* **2.4 %RE @ 1.15 ft**
Operator / Unit: **RWS / UVOST01**	*Elevation:* **Unavailable**	*Date & Time:* **2013-08-14 11:01 CDT**

Callouts



No %RE response above range detected in Blank-081113.

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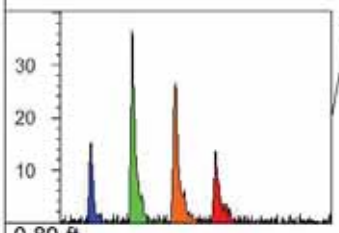
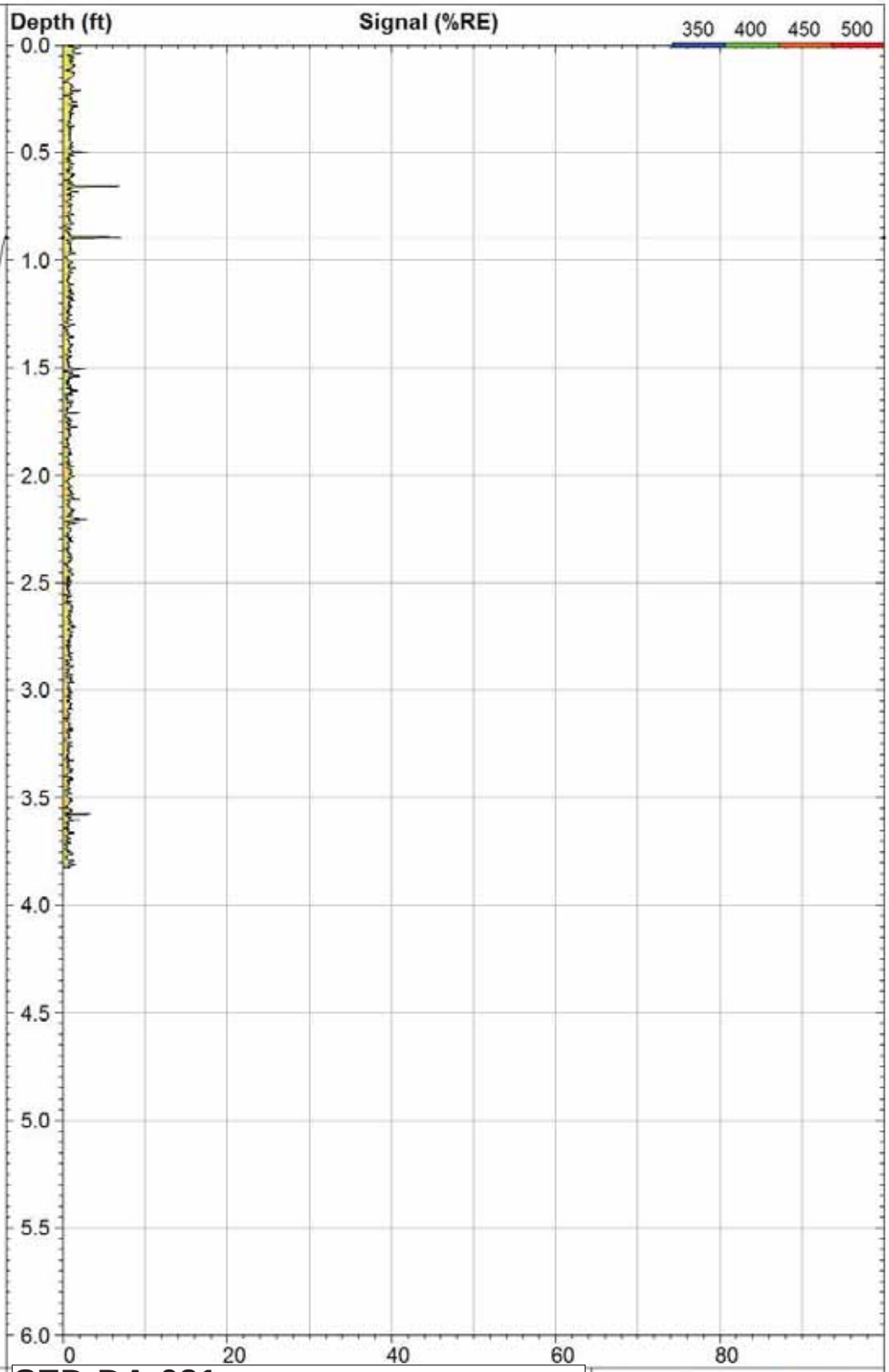
Site: **Mayflower**	*Y Coord.(Lat-N) / System:* **Unavailable / NA**	*Final depth:* **4.35 ft**
Client / Job: **ARCADIS /**	*X Coord.(Lng-E) / Fix:* **Unavailable / NA**	*Max signal:* **2.7 %RE @ 3.06 ft**
Operator / Unit: **RWS / UVOST01**	*Elevation:* **Unavailable**	*Date & Time:* **2013-08-14 09:32 CDT**

Callouts



0.89 ft
7.3 %RE
lint - disregard



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SED-DA-021 Dart originally mislabeled in the field, reported as SED-DA-021 II and later determined to be SED-DA-021.

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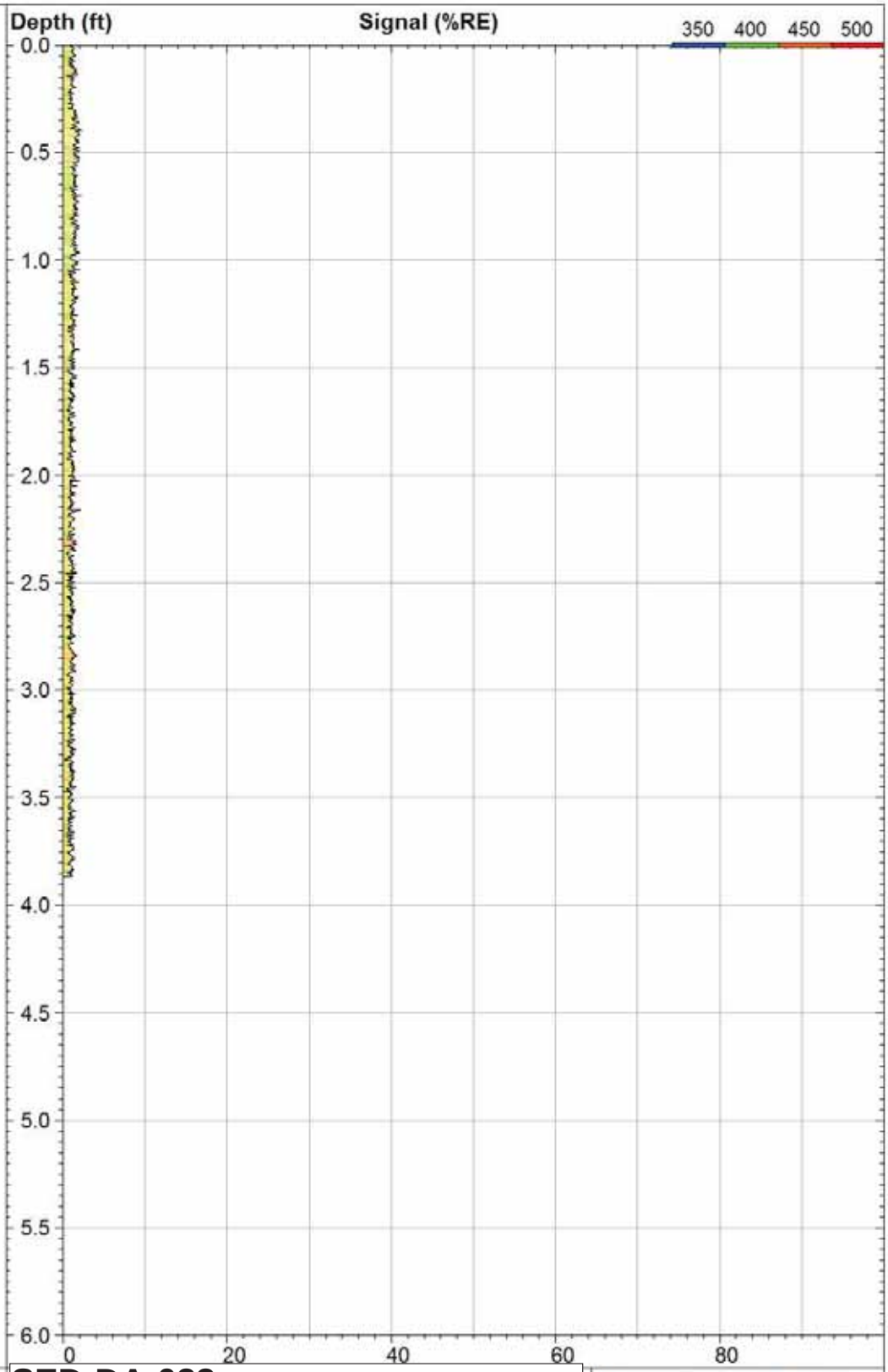
Site: **Mayflower**	*Y Coord.(Lat-N) / System:* **Unavailable / NA**	*Final depth:* **3.82 ft**
Client / Job: **ARCADIS /**	*X Coord.(Lng-E) / Fix:* **Unavailable / NA**	*Max signal:* **7.3 %RE @ 0.89 ft**
Operator / Unit: **RWS / UVOST01**	*Elevation:* **Unavailable**	*Date & Time:* **2013-08-14 12:39 CDT**

Callouts



No %RE response above range detected in Blank-081113.

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SED-DA-023

Dart originally mislabeled in the field, reported as SED-DA-021 and later determined to be SED-DA-023.

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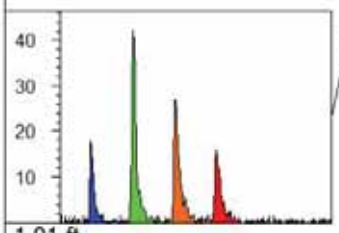
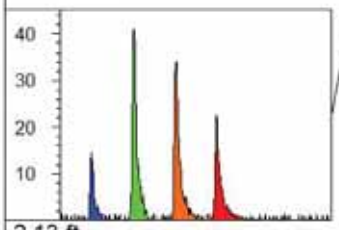
Site: **Mayflower**	*Y Coord.(Lat-N) / System:* **Unavailable / NA**	*Final depth:* **3.86 ft**
Client / Job: **ARCADIS /**	*X Coord.(Lng-E) / Fix:* **Unavailable / NA**	*Max signal:* **2.3 %RE @ 0.70 ft**
Operator / Unit: **RWS / UVOST01**	*Elevation:* **Unavailable**	*Date & Time:* **2013-08-14 09:07 CDT**

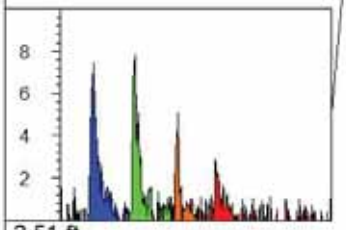
Callouts



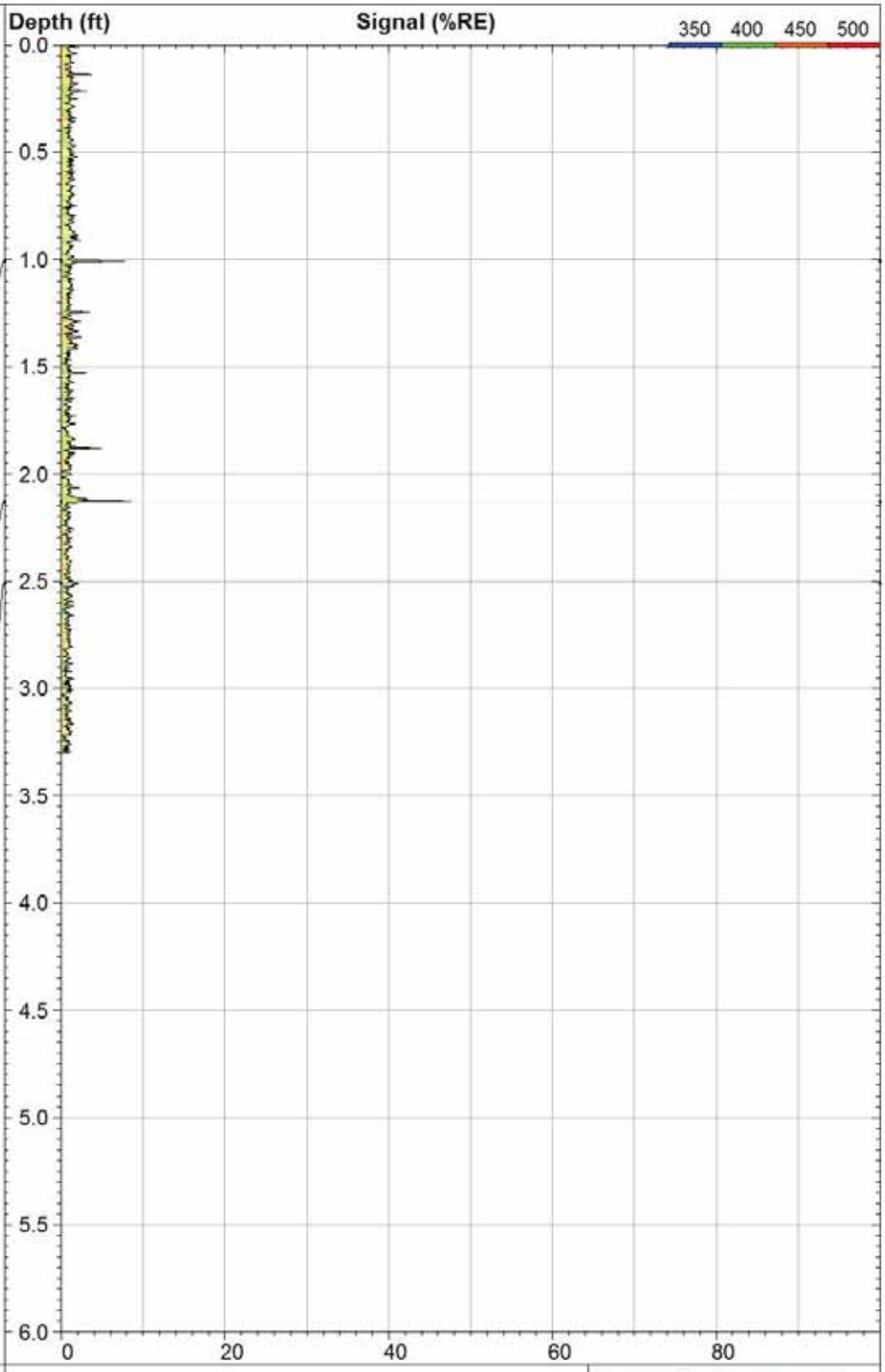
1.01 ft
8.2 %RE
disregard



2.13 ft
8.7 %RE
disregard



2.51 ft
2.1 %RE
?



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SED-DA-022

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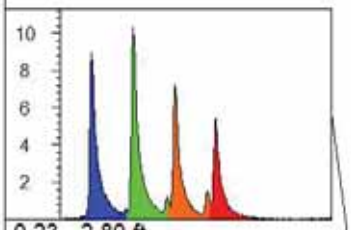
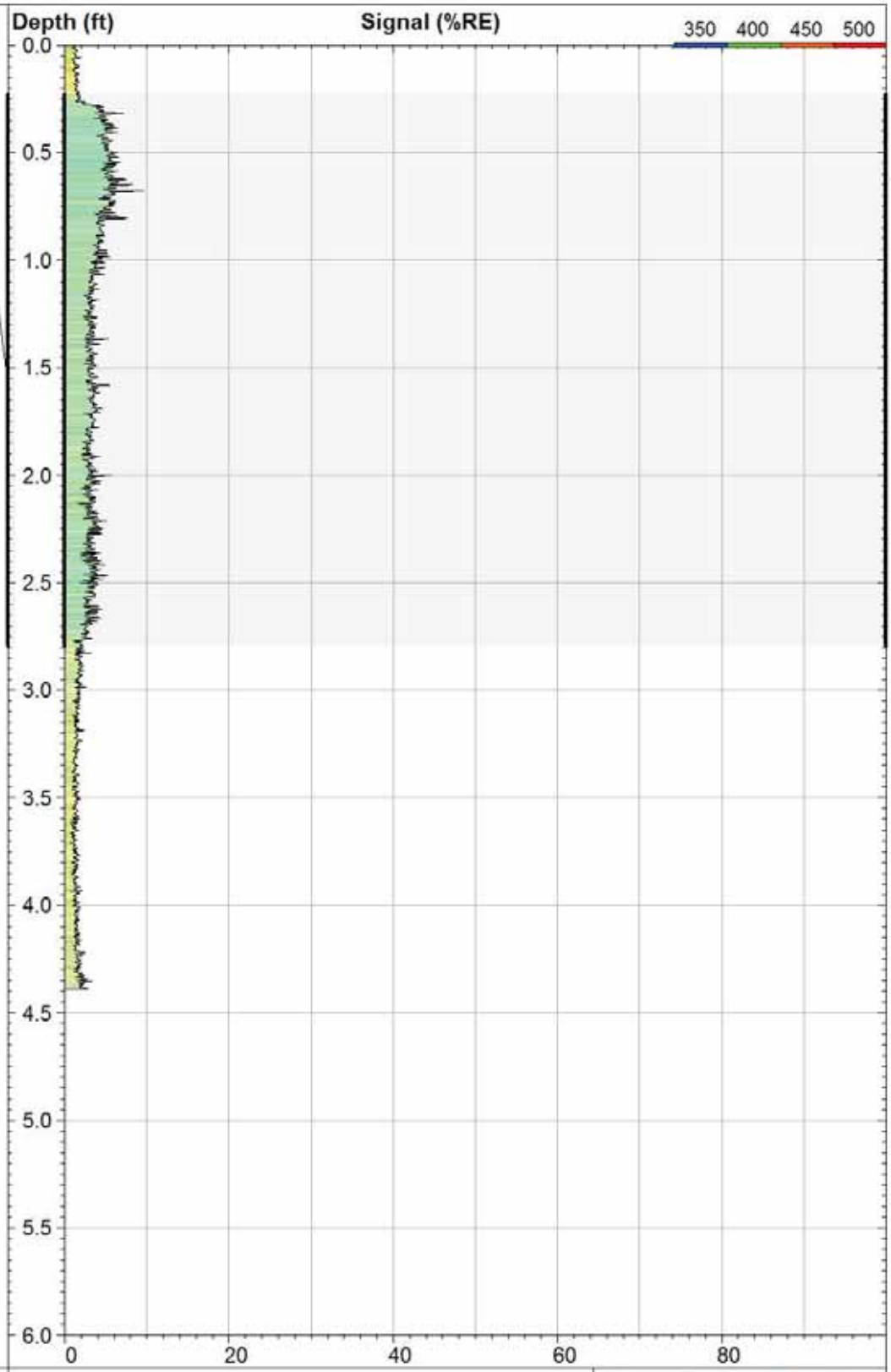
Site: **Mayflower**	*Y Coord.(Lat-N) / System:* **Unavailable / NA**	*Final depth:* **3.30 ft**
Client / Job: **ARCADIS /**	*X Coord.(Lng-E) / Fix:* **Unavailable / NA**	*Max signal:* **8.7 %RE @ 2.13 ft**
Operator / Unit: **RWS / UVOST01**	*Elevation:* **Unavailable**	*Date & Time:* **2013-08-14 11:44 CDT**

Callouts



0.23 - 2.80 ft
3.7 %RE (s 1.1)
positive response



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SED-DA-045

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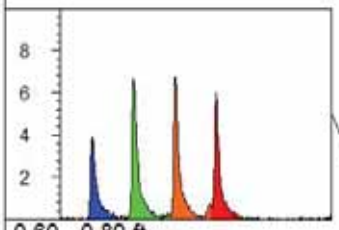
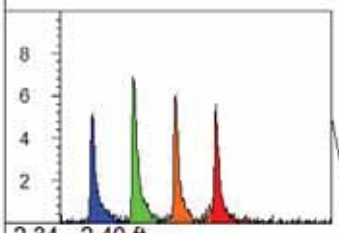
Site: **Mayflower**	*Y Coord.(Lat-N) / System:* **Unavailable / NA**	*Final depth:* **4.39 ft**
Client / Job: **ARCADIS /**	*X Coord.(Lng-E) / Fix:* **Unavailable / NA**	*Max signal:* **9.7 %RE @ 0.68 ft**
Operator / Unit: **RWS / UVOST01**	*Elevation:* **Unavailable**	*Date & Time:* **2013-08-14 08:46 CDT**

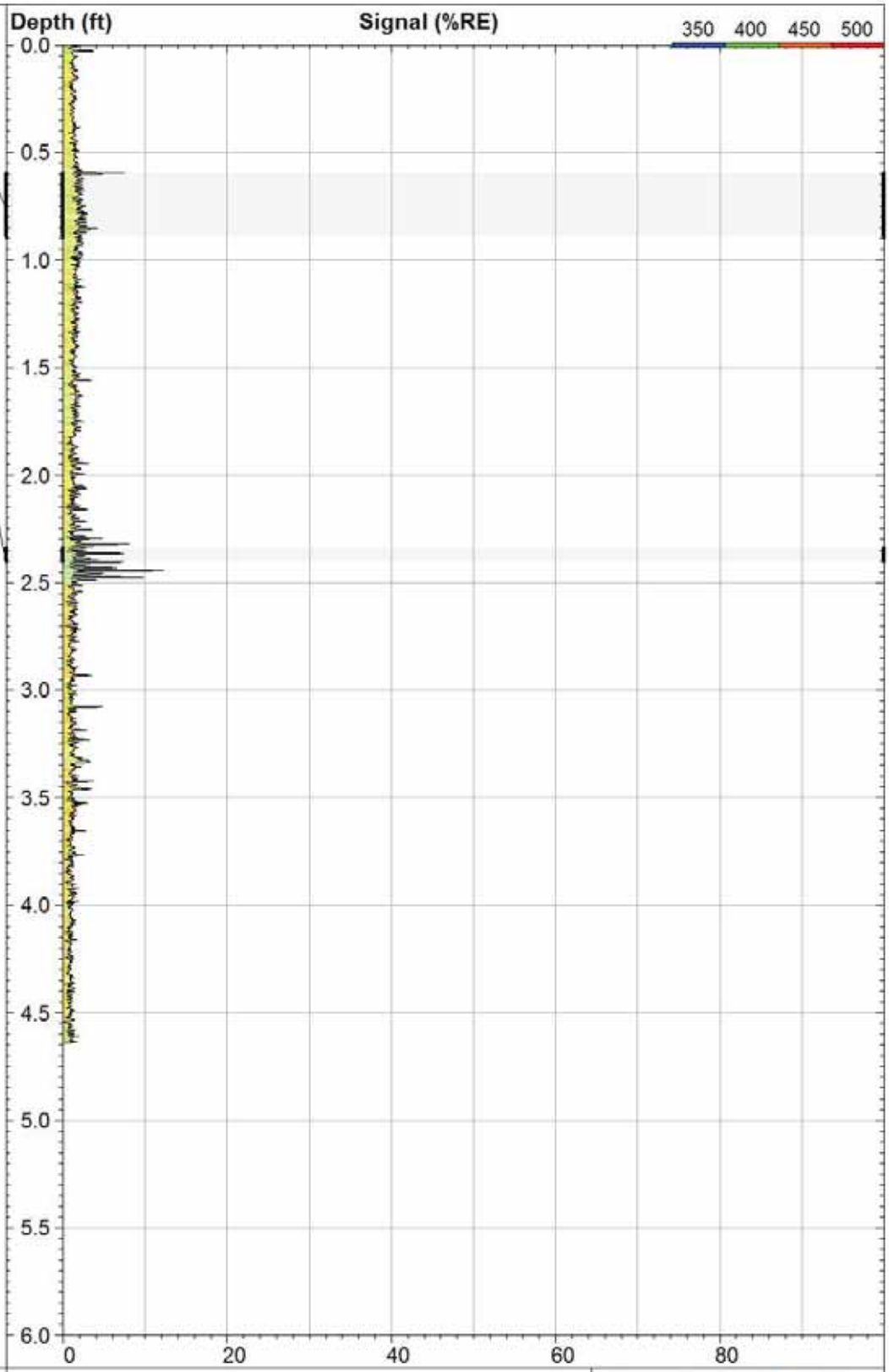
Callouts



0.60 - 0.89 ft
2.1 %RE (s 0.9)
positive response



2.34 - 2.40 ft
2.1 %RE (s 1.8)
positive response



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SED-DA-052

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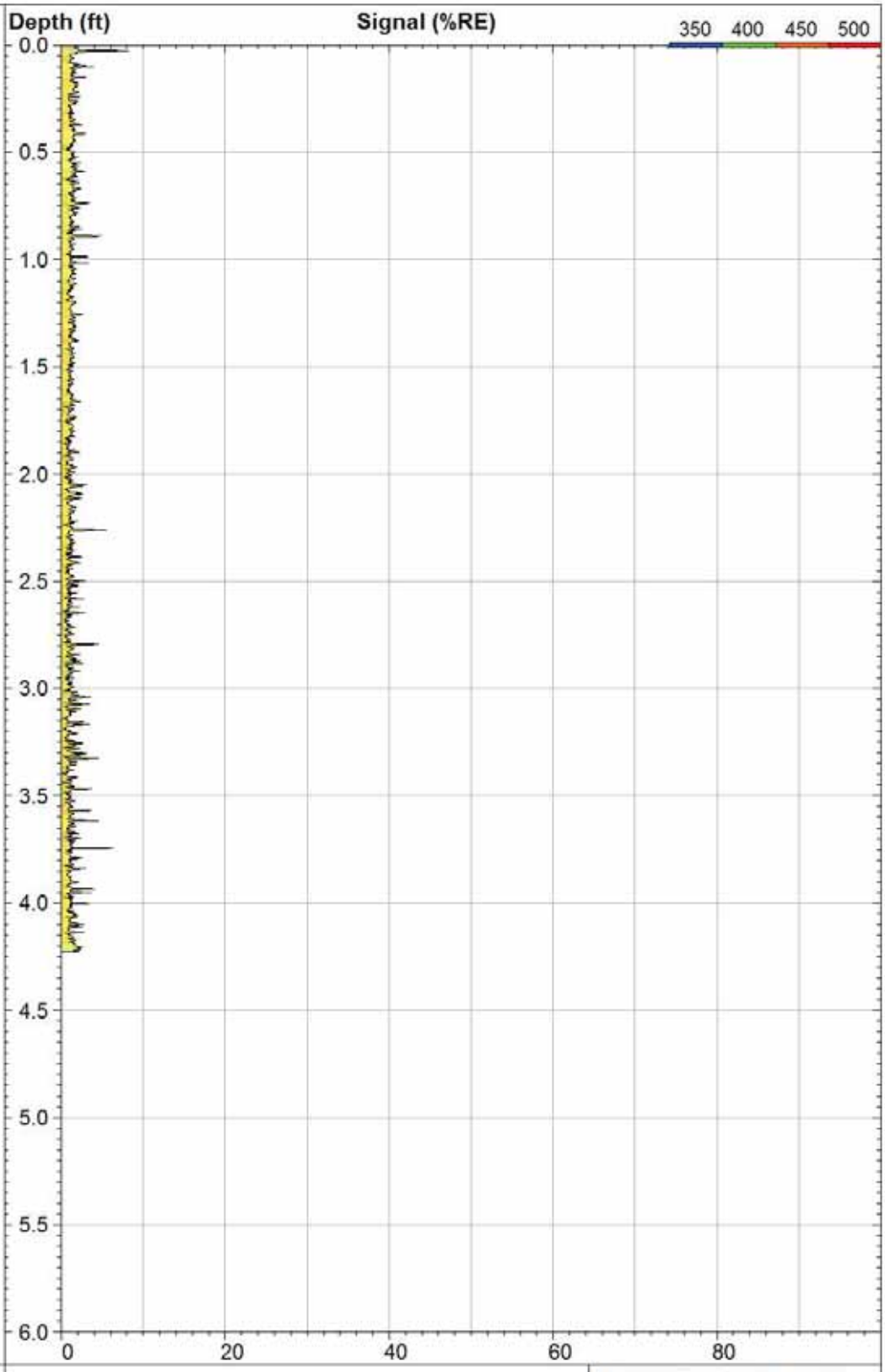
Site: **Mayflower**	*Y Coord.(Lat-N) / System:* **Unavailable / NA**	*Final depth:* **4.64 ft**
Client / Job: **ARCADIS /**	*X Coord.(Lng-E) / Fix:* **Unavailable / NA**	*Max signal:* **13.0 %RE @ 2.44 ft**
Operator / Unit: **RWS / UVOST01**	*Elevation:* **Unavailable**	*Date & Time:* **2013-08-13 16:43 CDT**

Callouts

all lint - no positive response



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SO-DA-019

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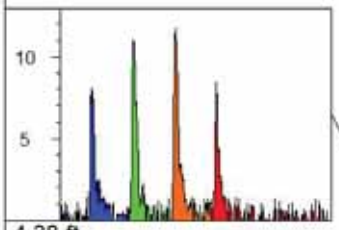
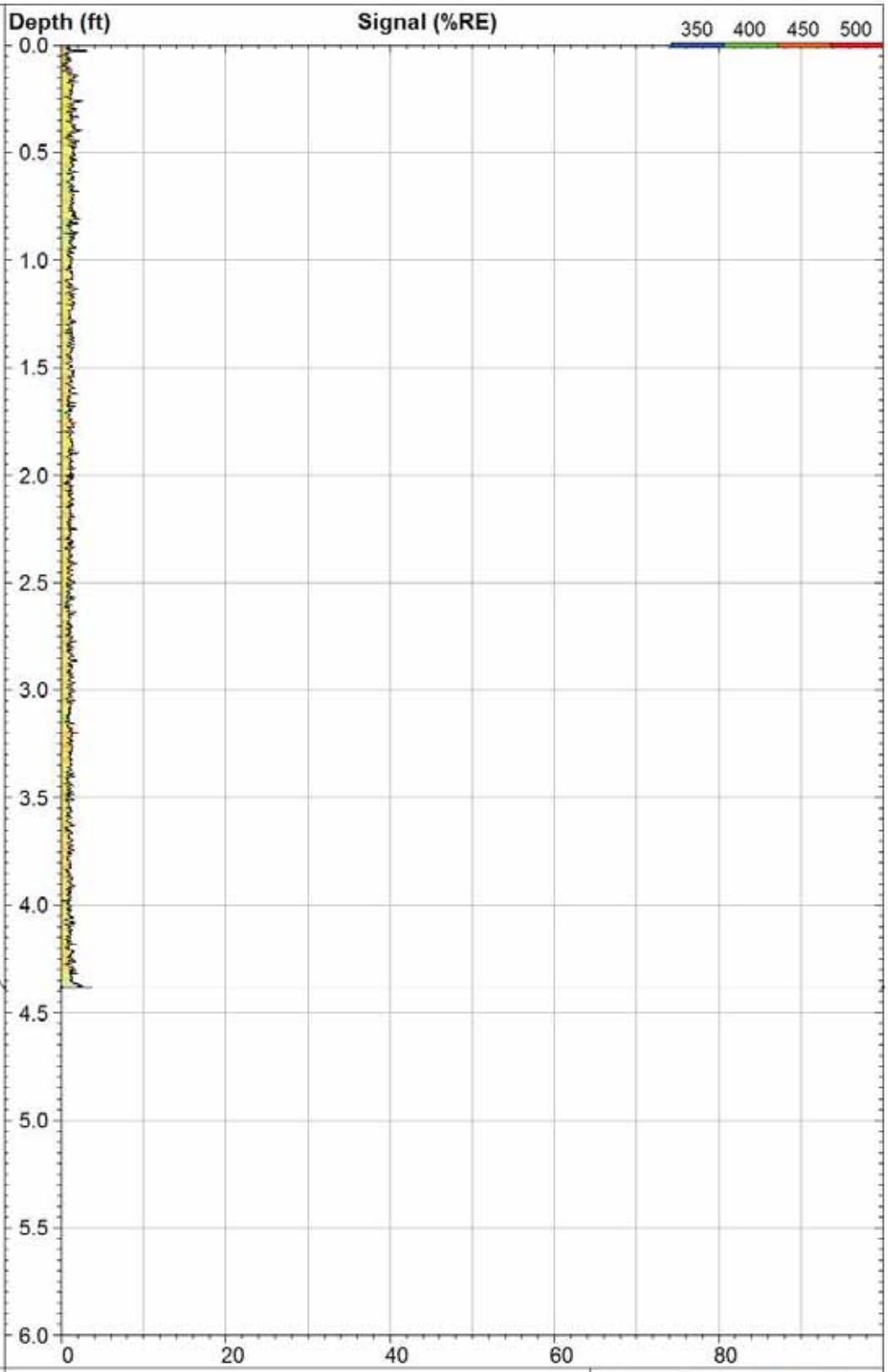
Site: **Mayflower**	*Y Coord.(Lat-N) / System:* **Unavailable / NA**	*Final depth:* **4.23 ft**
Client / Job: **ARCADIS /**	*X Coord.(Lng-E) / Fix:* **Unavailable / NA**	*Max signal:* **8.3 %RE @ 0.03 ft**
Operator / Unit: **RWS / UVOST01**	*Elevation:* **Unavailable**	*Date & Time:* **2013-08-14 08:14 CDT**

Callouts



4.38 ft
3.2 %RE
tip - disregard



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SO-DA-021

UVOST By Dakota
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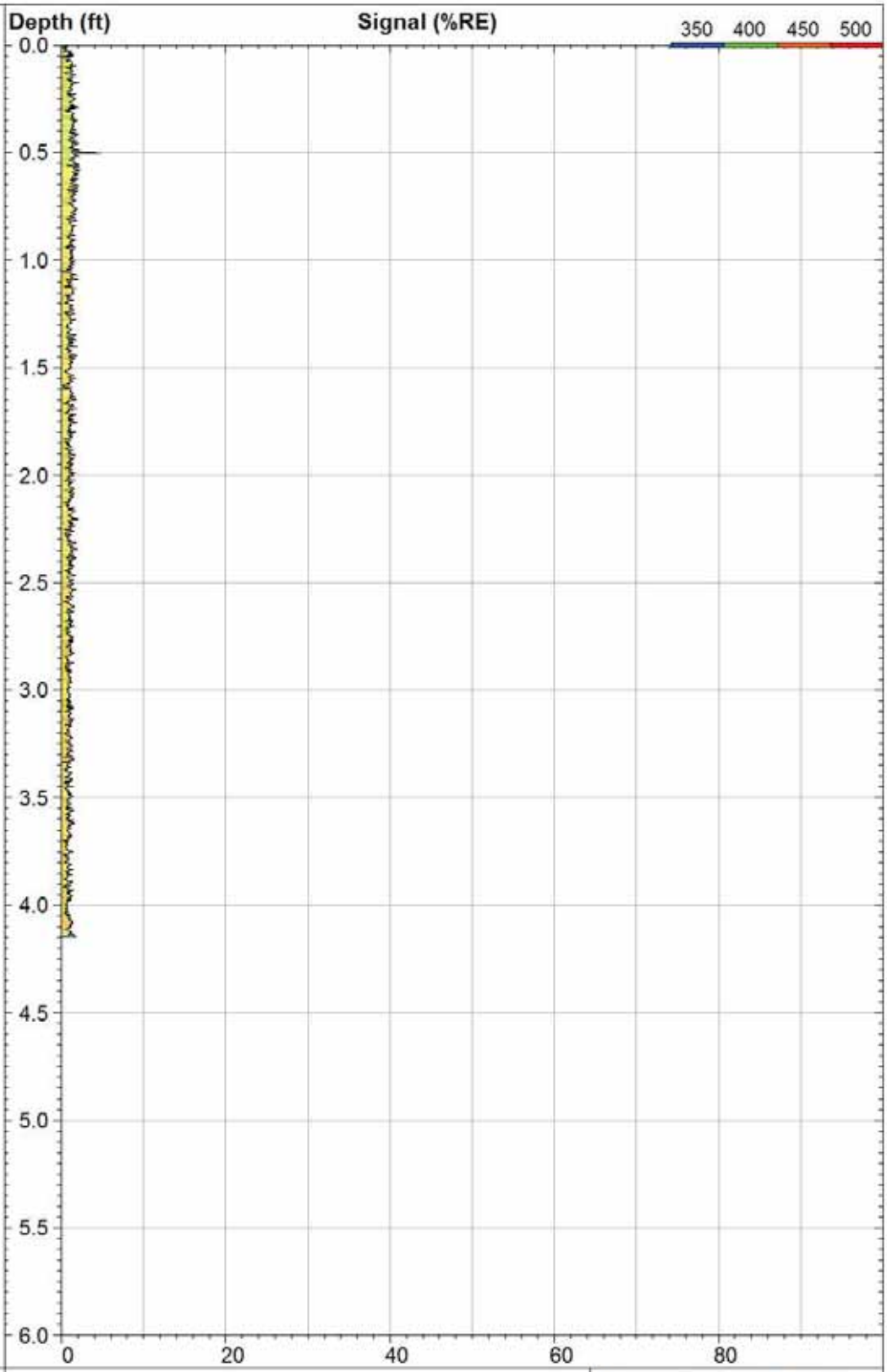
Site: **Mayflower**	*Y Coord.(Lat-N) / System:* **Unavailable / NA**	*Final depth:* **4.38 ft**
Client / Job: **ARCADIS /**	*X Coord.(Lng-E) / Fix:* **Unavailable / NA**	*Max signal:* **3.7 %RE @ 4.38 ft**
Operator / Unit: **RWS / UVOST01**	*Elevation:* **Unavailable**	*Date & Time:* **2013-08-14 11:19 CDT**

Callouts



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SO-DA-023

UVOST By Dakota
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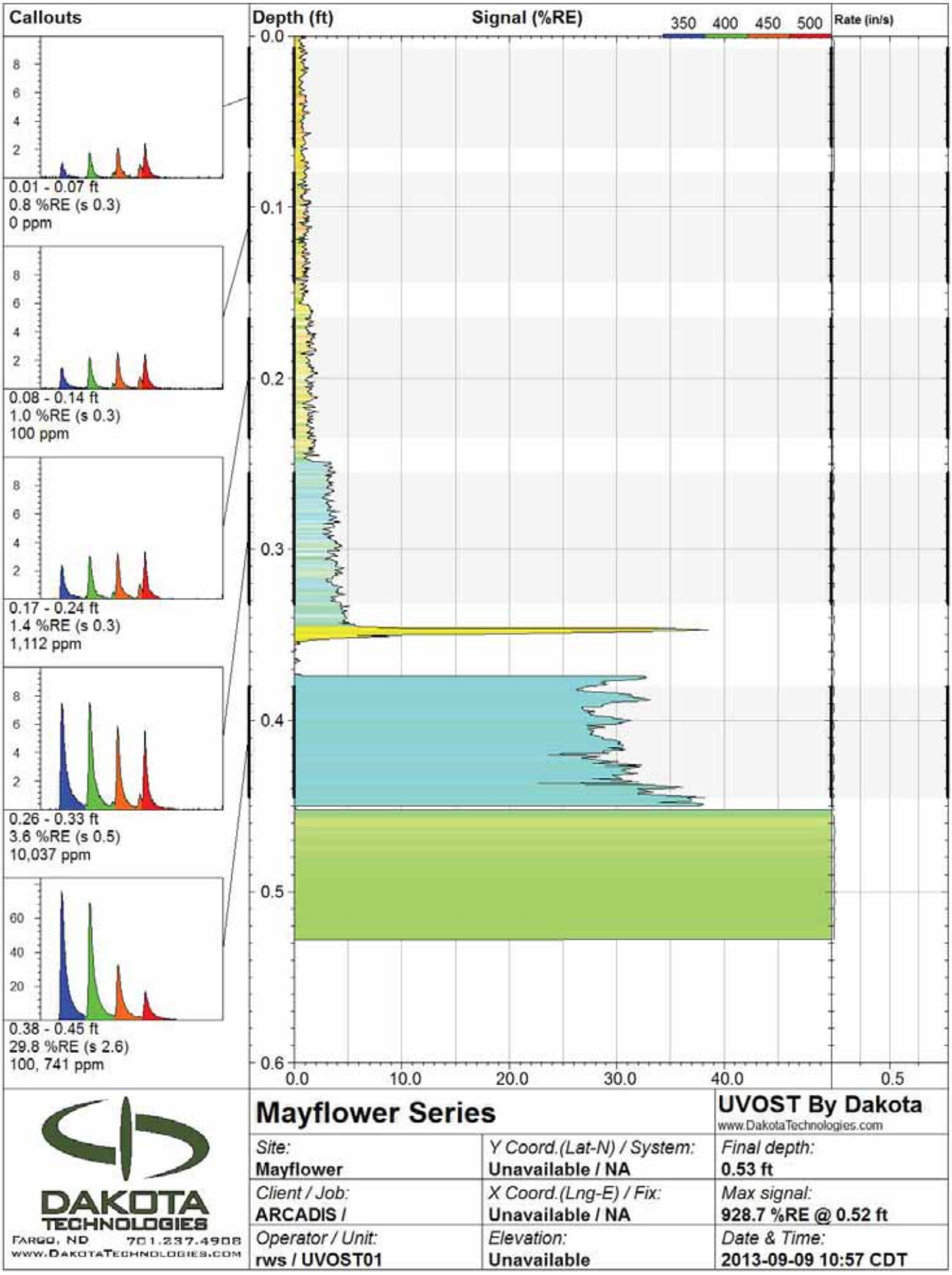
Site: **Mayflower**	*Y Coord.(Lat-N) / System:* **Unavailable / NA**	*Final depth:* **4.15 ft**
Client / Job: **ARCADIS /**	*X Coord.(Lng-E) / Fix:* **Unavailable / NA**	*Max signal:* **5.1 %RE @ 0.50 ft**
Operator / Unit: **RWS / UVOST01**	*Elevation:* **Unavailable**	*Date & Time:* **2013-08-13 15:58 CDT**

ARCADIS

Attachment E-2

Dart Calibration Results



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Mayflower Series

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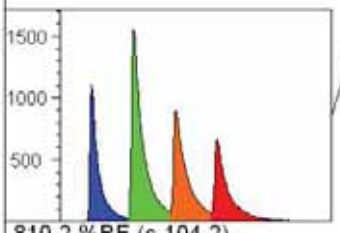
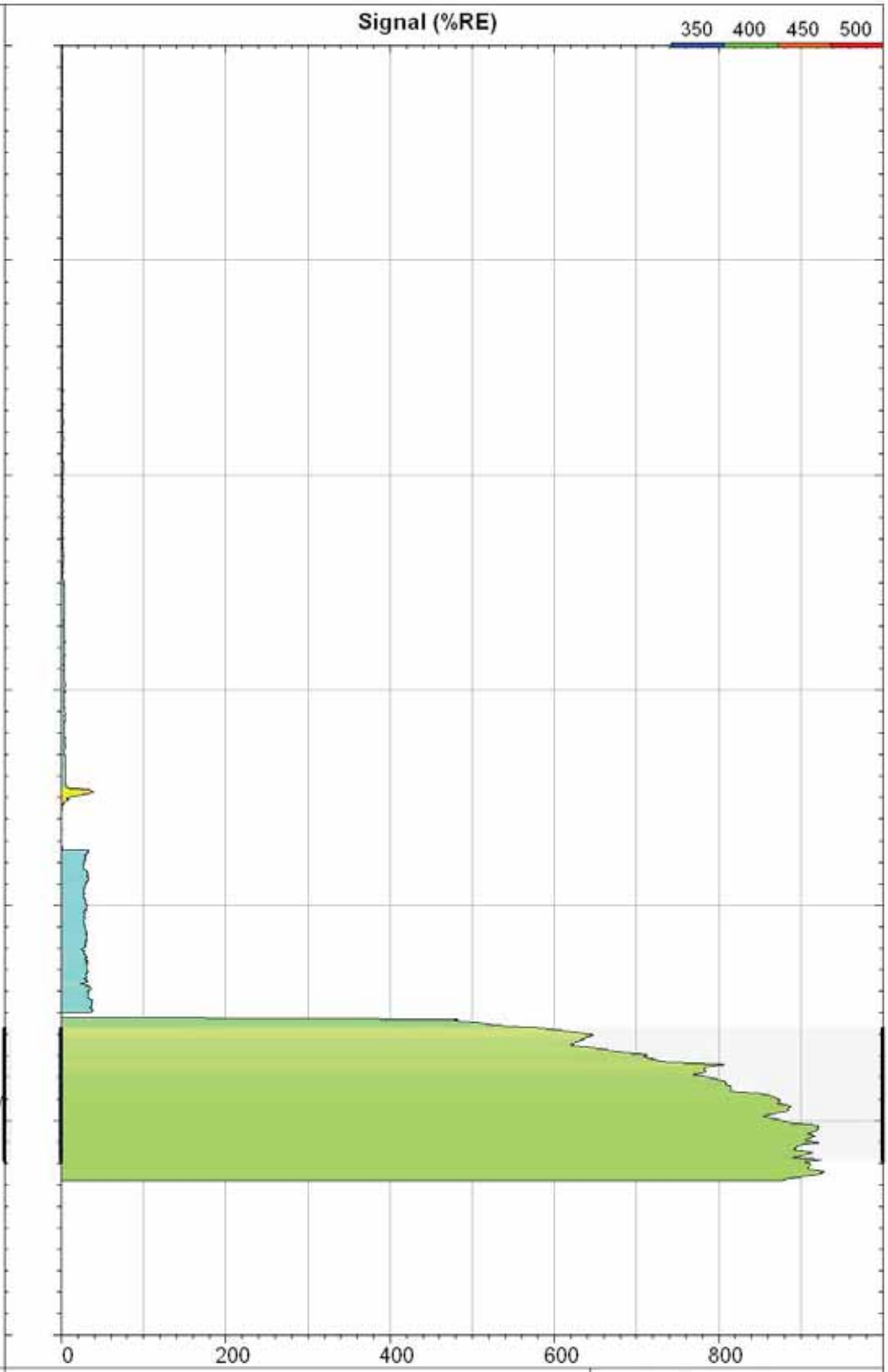
Site: **Mayflower**	*Y Coord.(Lat-N) / System:* **Unavailable / NA**	*Final depth:* **0.53 ft**
Client / Job: **ARCADIS /**	*X Coord.(Lng-E) / Fix:* **Unavailable / NA**	*Max signal:* **928.7 %RE @ 0.52 ft**
Operator / Unit: **rws / UVOST01**	*Elevation:* **Unavailable**	*Date & Time:* **2013-09-09 10:57 CDT**

Callouts



810.2 %RE (s 104.2)
neat oil



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Mayflower Series - Neat Oil

UVOST By Dakota
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Site: **Mayflower**	*Y Coord.(Lat-N) / System:* **Unavailable / NA**	*Final depth:*
Client / Job: **ARCADIS /**	*X Coord.(Lng-E) / Fix:* **Unavailable / NA**	*Max signal:* **928.7 %RE**
Operator / Unit: **rws / UVOST01**	*Elevation:* **Unavailable**	*Date & Time:* **2013-09-09 10:57 CDT**

Dakota Technologies, Inc.
Dart Calibration Study Results for Mayflower Pipeline Incident Response

UVOST Response (%RE)	actual g site sediment	desired concentration (ppm)	g NAPL to add	~ml NAPL to add	actual g NAPL added	Actual Concentration (ppm)	approximate NAPL Density (g/ml)	
810	NA	1,000,000 ppm				1,000,000	0.98	
29.9	49.1	100,000 ppm	5.460	5.571	5.505	100,741	0.98	
3.5	50.5	10,000 ppm	0.510	0.521	0.512	10,037	0.98	
1.4	44.9	1,000 ppm	0.045	0.046	0.050	1,112	0.98	
1	50.2	100 ppm	0.005	0.005	0.005	100	0.98	
0.8	NA	0 ppm		0.000		0	0.98	
Background Corrected								
29.1						100741.1474		
2.7						10036.8541		
0.6						1112.3471		
0.2						99.5917		
0						0.0000