

Using Laser-Induced Fluorescence Based Passive Samplers

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ABSTRACT

ARCADIS and Dakota Technologies deployed two types of in-situ NAPL screening tools in order to characterize coal tar NAPL in river sediments adjacent to a former MGP site. A Tar-specific Green Optical Screening Tool (TarGOST®) was used to log NAPL vs. depth successfully in most areas. Unfortunately, TarGOST characterization of sediments within a gas line buffer zone area was deemed too dangerous due to the direct push machinery used to advance TarGOST. As a solution, Dakota developed customized Dart™ samplers which consist of stiff rods coated with solid phase extraction (SPE) media, which attracts and sorbs PAHs. The Darts were manually installed into the upper 6 to 12 ft of sediments, left in place for 24 hours, and retrieved. Subsequent laser-induced fluorescence (LIF) analysis of the Dart's SPE media indicated the presence and relative availability of PAHs from the sediments in the buffer zone. Site-specific NAPL mixed with clean site sediments were later applied to Darts in the lab in order to improve our understanding of the in-situ Dart sampler's quantitative/qualitative behavior at this particular site.

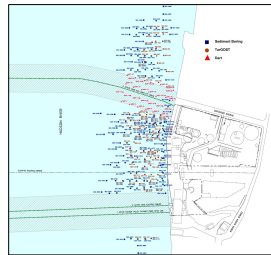


FIGURE 1. Site map showing utility corridor of concern along with TarGOST and Dart locations (Dart locations in red).

Dart Samplers: How they function and how they're analyzed

The Dart samplers are basically fiberglass rods covered with a non-fluorescent SPE media, similar to that used in solid-phase micro-extraction (SPME) analytical methods. With a Kow ranging from 3 to 6, the hydrophobic PAHs prefer to be in NAPL (or similar organic material). The Dart's organic SPE cladding has a high affinity for PAHs, which they sorb into readily. The PAHs contained in MGP NAPL (coal tar) fluoresce poorly under ultra-violet excitation. But those same PAHs, having transferred into "solid solution" in the Dart's SPE cladding, fluoresce much more intensely. This fluorescence can be sensitively analyzed along the entire length of the Dart with LIF, resulting in a log of the PAH concentration along the Dart's length. The LIF log represents the PAH exposure that occurred while the Dart was exposed to the sediment column.

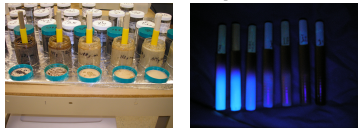


FIGURE 2. A visual demonstration of how Darts glow in response to various concentrations of MGP NAPL on Fisher Scientific sea sand.

Visual observations with a handheld lamp, while "handy" and intuitive, do not generate the sensitive and quantitative digitized readings that laser-induced fluorescence systems such as UVOST can provide. In order to "read" the sorbed PAHs' fluorescence along the Darts entire length and circumference, a lathe-like device is used to rotate the Dart while the UVOST system logs a detailed reading of the PAH fluorescence vs. "depth".

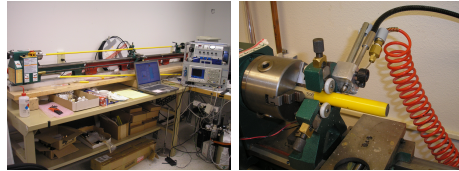


FIGURE 3. Dart logging system including lathe-based reader and UVOST system - full system (left) and close-up of optics system (right).

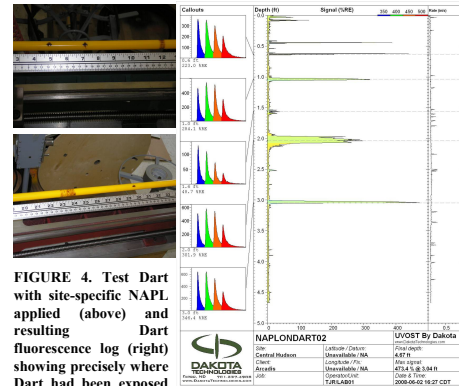


FIGURE 4. Test Dart with site-specific NAPL applied (above) and resulting Dart fluorescence log (right) showing precisely where Dart had been exposed to NAPL.

Field Deployment

The Dart samplers are inserted into the sediments and left in place for 24 hours to allow PAHs to transfer into the SPE cladding. Buoys were used to pre-mark the Dart locations and divers placed the Darts into the sediment by hand, on occasion using a small customized drive hammer to achieve full penetration. Short lengths of floating cord attached to each Dart allowed the divers to find the Darts 24 hours later and retrieve them. After retrieval, the Darts were wrapped in aluminum foil and taken to shore for UVOST analysis. Analysis of each Dart takes about 30 minutes.

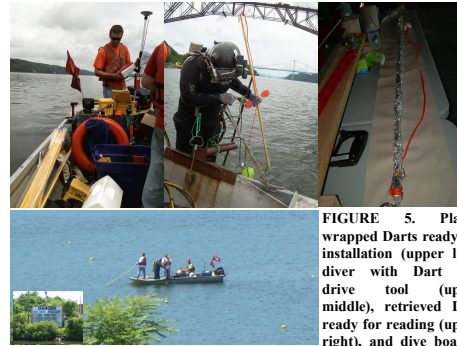


FIGURE 5. Plastic wrapped Darts ready for installation (upper left), diver with Dart and drive tool (upper middle), retrieved Dart ready for reading (upper right), and dive boat in buffer zone (bottom).

Analysis Results

Each Dart was scanned on-site with UVOST LIF. Since the PAHs are now "locked into" the SPE cladding and don't require icing, the Darts could have been shipped to Dakota for reading. A variety of responses were observed. Examples logs from the 28 Dart locations are shown below in Figure 6. Notice that most of the logs show a foot or so of clean sediment near the surface. The "spiky" appearance is due to smearing, streaking, or "hot spots" on one side of the Dart, but not the other.

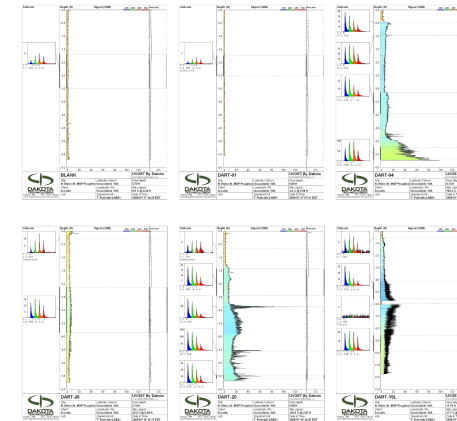


FIGURE 6. Variety of logs generated from the 28 Darts deployed in the buffer zone (utility corridor).

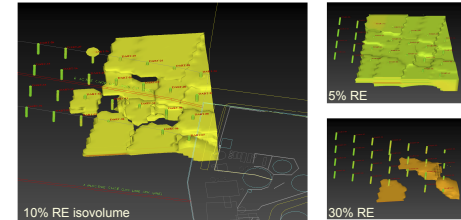


FIGURE 7. 3D visualization of the fluorescence response of the Darts. The fluorescence scaled with PAHs transferred to the SPE of the Darts.

Lab Results

Laboratory experiments were conducted using site sediment (a fine dark organic sediment) and Fisher Scientific brand sea sand to mimic two extremes of soil types. Site NAPL from a nearby well was spiked onto the two soil types. Test Darts were exposed to these sediments for 24 hours and analyzed with UVOST. The samples were also tested with TarGOST for comparison. See Figure 2 for basic approach.

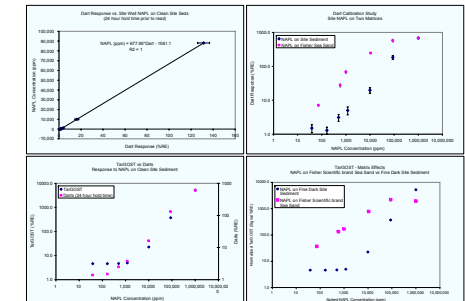


FIGURE 8. Dart and TarGOST response to site-specific NAPL on fine dark organic sediment and Fisher Scientific sea sand.

Conclusions

The use of Dart samplers to delineate the extent of PAH impacted sediments within the gas line buffer zone area was successful. Like TarGOST, the Darts responded monotonically to NAPL concentration as desired. Just as TarGOST responds to PAHs (NAPL) "available" to the sapphire window, Darts respond to PAHs "available" for direct contact with the SPE cladding. Soil matrix effects influence both TarGOST and Darts, similar to how soil type influences a visual core examination by a geologist. The Dart samplers, like TarGOST, are affected by sediment type and have improving limits of detection with increasing porosity (grain size) and decreasing organic content. Determination of an exact %RE threshold that is equivalent to a "NAPL present" visual assessment was difficult because the presence of NAPL at low concentrations is difficult to define or quantify. Site-specific calibration was useful for rigorously quantifying the Dart's in-situ performance and to provide confidence regarding interpretation of the LIF logs generated during the Dart survey.