# **DNAPL** Characterization Using the Ribbon NAPL Sampler: Methods and Results

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#### Abstract

The Ribbon NAPL Sampler (RNS) is a direct sampling device that provides detailed depth discrete mapping of Non Aqueous Phase Liquids (NAPLs) in a borehole. This characterization method provides a yes or no answer to the presence of NAPLs and is used to complement and enhance other characterization techniques. Several cone penetrometer deployment methods are in use and methods for other drilling techniques are under development. The RNS has been deployed in the vadose and saturated zones at four different sites. Three of the sites contain DNAPLs from cleaning and degreasing operations and the fourth site contains creosote from a wood preserving plant. A brief description of the process history and geology is provided for each site. Where available, lithology and contaminant concentration information is provided and discussed in context with the RNS results.

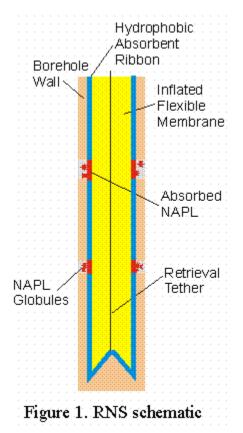
#### Introduction

Dense Non Aqueous Phase Liquids (DNAPLs) such as solvents and dry cleaning fluids migrate downward and are often present in the subsurface as small discrete globules or lenses which are difficult to locate using traditional characterization methods. NAPLs are a common long-term groundwater contamination source. If the long-term source can be found, more aggressive remediation efforts can be used to clean the source and reduce the long-term impact on the aquifer and the associated costs of treating large dissolved contamination plumes.

The Ribbon NAPL Sampler (RNS) provides continuous depth discrete sampling in a borehole and immediate analysis results for the pure phase component. This characterization method provides a yes or no answer to the presence of NAPLs and is used to complement and enhance other characterization techniques. The RNS also works for Light Non Aqueous Phase Liquids (LNAPLs). The Ribbon NAPL Sampler and installation methods are discussed as well as characterization results from four different sites.

# **Materials and Methods**

The Ribbon NAPL Sampler is a direct sampling device that provides detailed depth discrete mapping of NAPLS in a borehole. This characterization technique uses the Flexible Liner Underground Technologies, Ltd. (FLUTe) membrane system (patent pending) to deploy a hydrophobic absorbent ribbon in the subsurface. The system is pressurized against the wall of the borehole and the ribbon absorbs the NAPL that is in contact with it. A schematic of the RNS is shown in Figure 1.



The FLUTe membrane consists of an airtight liner that is pneumatically and/or hydraulically installed in a borehole. The rugged flexible tubular membrane supports and seals the borehole wall and can be installed in the saturated and vadose zones by several techniques. The membrane technology has been used to place sampling ports and sensors in varying sized boreholes to depths of 800 ft. Removal of the membrane is accomplished by turning the membrane inside out by pulling on a tether connected at the bottom of the liner.

The membrane can be reused for multiple deployments.

The absorbent ribbon is a sleeve that covers the FLUTe membrane and is manufactured from a material that will repel water and absorb liquid solvents and petroleum products (NAPLs). This hydrophobic material readily "wicks" NAPL compounds from the adjacent borehole sediments. The primary analysis method uses a hydrophobic ribbon impregnated with a powdered oil dye (Sudan IV). The dye dissolves in NAPLs that are absorbed into the ribbon and stains the ribbon bright red. The ribbon is replaceable for additional deployments with the same FLUTe membrane. A characteristic spot from residual DNAPL detection with the RNS is shown in Figure 2.



Figure 2. Characteristic spot from DNAPL detection with the RNS

In non-collapsing vadose zone boreholes, the Ribbon NAPL Sampler is deployed with air pressure. The hydrophobic ribbon is attached to the membrane and the membrane is everted (turned inside out) from a pressure canister. This eversion method prevents the ribbon from sliding along the borehole and smearing the NAPL on the membrane. The membrane is retrieved and then re-everted at the surface and inspected for the presence of NAPL. The reusable membrane is available in custom lengths and can use any length of the replaceable hydrophobic ribbon. A two-inch diameter membrane is used in CPT boreholes and other diameters are available.

The installation method for the Cone Penetrometer (CPT) allows for installing the Ribbon NAPL Sampler below the water table and in collapsing sediments in the vadose zone. The RNS is fabricated with a bundled ribbon around the membrane and comes assembled to specified lengths from FLUTe Ltd. One of the current designs is for the standard CPT rods with a 1.75 inch OD and 1 inch ID. Once the CPT rods are pushed to depth, the bundled RNS is lowered into the CPT rods and the rods are retrieved a few feet to release the sacrificial tip and anchor the membrane in the sediments. For each CPT rod retrieved, water is measured into the bottom inside of the membrane through the tether tube to expand the membrane and hold the borehole open. Water is also added between the membrane and CPT rods to balance the fluid pressure and reduce friction. Once all the rods are retrieved and the membrane has been in contact with the formation, the RNS is retrieved by pulling the tether up and turning the membrane inside out. The inversion brings the ribbon up on the inside away from the sediments. The water inside the RNS is clean. The RNS is turned right side out and the locations of depth discrete NAPL, indicated by dyed portions of the membrane, are recorded. The RNS can be rebuilt with a new bundled ribbon.

# **Results and Discussion**

The Ribbon NAPL Sampler has been deployed at four different sites in the vadose and saturated zones. Three of the sites contain DNAPLs from cleaning and degreasing operations and the fourth site contains creosote from a wood preserving plant. A brief description of the process history and geology is provided for each site. Where available, lithology and contaminant concentration information is provided and discussed in context with the RNS results.

**SRS A-14 Outfall.** The A-14 Outfall is located in the northern section of the DOE Savannah River Site (SRS). This area housed reactor fuel and target assembly fabrication facilities and laboratory and support facilities whose operations resulted in releases of chlorinated solvents. Beginning in 1952, the process wastes were released through a process sewer system to the A-14 outfall. Between 1952 and 1979, historical records estimate 1,395,000 lbs of solvents were released to the outfall. Of this quantity 72% was tetrachloroethylene (PCE) and 27% was trichloroethylene (TCE). Solvent discharge to the outfall ended in 1979. The outfall is currently used to discharge treated process water and storm water (Jackson et al., 1999). The geologic framework consists of heterogeneous interbedded layers of sand, silt and clay.

Four Ribbon NAPL Samplers were deployed in the vadose zone in open cone penetrometer boreholes at the SRS A-14 Outfall. These deployments were designated HFM-1, HFM-2, HFM-3, and MVE-17. Each of the samplers remained in contact with the borehole for approximately one hour. HFM-1 was installed approximately 20 ft away from the head of the outfall and did not indicate the presence of DNAPL. HFM-2 was deployed to a depth of 60 ft and is above the current outfall discharge. HFM-3 and MVE-17, deployed to a depth of 30 ft, are approximately 15 ft away from HFM-2, within a few feet of each other, and near the headwaters of the current outfall.

CPT information and DNAPL location identified by the RNS for HFM-2, HFM-3, and MVE-17 are presented in Figure 3. The heavier line is the CPT friction ratio where higher values indicate finer grained materials. The lighter line is the sediment resistivity where lower values correspond to more conductive sediments (i.e. wet and/or silty and clayey materials) and the higher values correspond to less conductive sediments (i.e. dry and/or sandy materials). The horizontal lines are the depth discrete location of DNAPL found with the RNS. Note the significant differences in geology between the boreholes and that HFM-2 is dryer than HFM-3 and MVE-17.

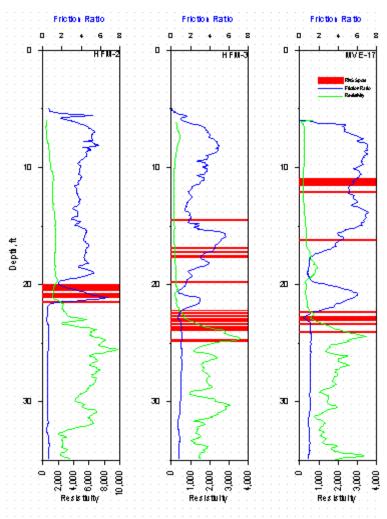


Figure 3. RNS and CPT Results from the SRS A-14 Outfall

DNAPL was found in HFM-2 in the fine-grained materials at approximately 20 ft. DNAPL is present in HFM-3 and MVE-17 in the 22.5-25 ft range which corresponds to the coarser material below the 20 ft fine grained material observed in HFM-2. This inconsistency may be attributed to the constant water infiltration from the outfall moving the DNAPL downward and/or the DNAPL is not coming into contact with the hydrophobic ribbon due to water saturation in the clay. More DNAPL is observed deeper in HFM-3 than in MVE-17 which can be attributed to more coarse grained materials in HFM-3. DNAPL is observed at 12 ft in MVE-17 where downward migration is retarded in the fine-grained material. The nature of the staining on the ribbon indicates the DNAPL is in the form of dispersed globules or very thin lenses and is not present in pools or strong discrete layers.

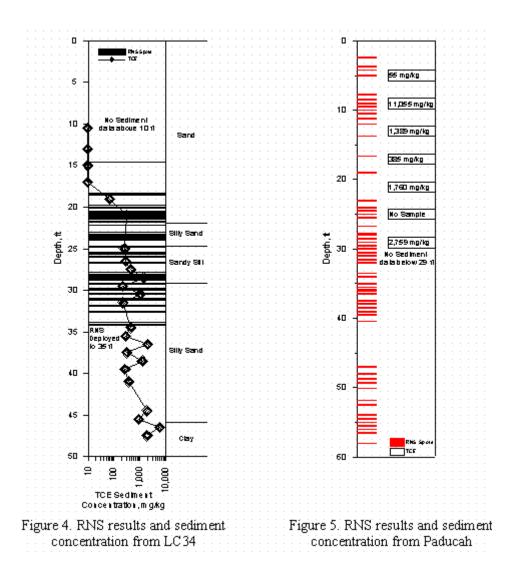
**Cape Canaveral Air Station Launch Complex 34.** Launch Complex 34 (LC34), was constructed during 1959-1960 for the Saturn I and IB rockets, which served as launch vehicles during the early Apollo manned space program. The Saturn rocket engines were cleaned while on the launch pad with solvents, predominantly trichloroethylene (TCE), and the solvent was discharged to a nearby drainage pit. Engine parts were also cleaned with TCE at a nearby support building. These on-site cleaning activities ceased in 1968 with the termination of operations at the complex. The geologic framework consists of an upper unit of relatively uniform fine grained sand 23-27 ft thick from grade, a middle unit of silty and clayey fine sand 1-17 ft thick, a lower sand unit of silty fine sand 15 ft thick, and a confining clay unit at approximately 45 ft below grade. The water table was about 4 ft below surface during the deployment.

The Ribbon NAPL Sampler was deployed in the saturated zone through the cone penetrometer rods to a depth of 35 ft below ground surface. The deployment of the sampler took approximately 1.5 hours and it

remained in contact with the borehole for approximately 45 minutes. The staining on the sampler showed residual DNAPL (TCE) is present from approximately 18 ft to 35 ft with a higher density sitting on top of the middle fine unit and at the bottom the middle fine unit. The spotty nature of the staining on the ribbon indicates the DNAPL is in the form of dispersed globules and is not present in pools or strong discrete layers. The location of DNAPL found with the RNS is shown in Figure 4 along with TCE sediment concentrations from a nearby boring completed during previous characterization work. At this particular site, DNAPL is present when sediment concentrations are between 250 and 450 mg/kg (Eddy-Dilek et al., 1999). The sediment sampling was conducted at 1 ft intervals to a depth of 48 ft.

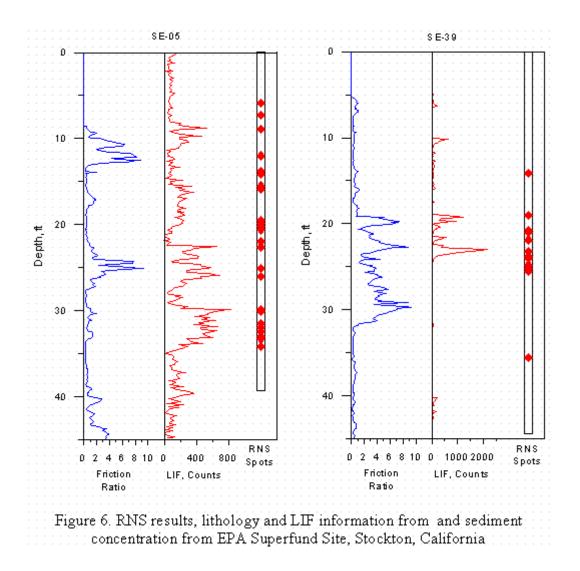
**Paducah Gaseous Diffusion Plant.** The TCE leak site is located near a building used for degreasing, cleaning, and testing of components used in the gaseous diffusion process. One release at this site is from effluent leaking from a subsurface pipe carrying discharge from a sump in the building to a storm sewer. It was not known that the sump discharged to the storm sewer and the release may have begun as early as the 1950s. A pump station used to offload TCE from tank cars into a storage tank had leaked and been repaired several times in the past and released an unknown but significant quantity of TCE to the subsurface. The geologic framework consists of an upper 60 ft section of heterogeneous interbedded layers of clay, silt, sand, and gravel (CH2M Hill, Inc., 1999). The water table was located at about 40 ft below the surface.

The Ribbon NAPL Sampler was deployed through the cone penetrometer rods to a depth of 59 ft below ground surface. The deployment of the sampler took approximately 2 hours and it remained in contact with the borehole for approximately 45 minutes. The staining on the sampler showed residual DNAPL (TCE) is present throughout the sampled interval with the highest densities located at approximately 10 ft, 25-40 ft, and 50-55 ft. The spotty nature of the staining on the ribbon indicates the DNAPL is in the form of dispersed globules and is not present in pools or strong discrete layers. The location of DNAPL found with the RNS is shown in Figure 5 along with TCE sediment concentrations from a nearby boring completed during previous characterization work (CH2M Hill, Inc., 1999). The sediment sampling was conducted at 4 ft intervals to a depth of 29 ft. Unlike conventional sediment sampling and analysis, the Ribbon NAPL Sampler provides continuous sampling in a borehole with immediate field results.



**EPA Superfund Site, Stockton, California.** McCormick & Baxter Creosoting Co. formerly operated a wood-preserving facility on a 32-acre site in a light industrial area near the Port of Stockton. From 1942 to 1990, utility poles and railroad ties were treated with creosote, pentachlorophenol (PCP), and arsenic compounds. Waste oils generated from the wood-treatment processes were disposed of in unlined ponds and concrete tanks on-site. Previous characterization found soils throughout the site were contaminated with constituents of creosote. The geologic framework consists of heterogeneous interbedded gravel, sand, silt, and clay. The water table is located approximately 10-15 ft below surface (U.S. Army Corps of Engineers, Seattle District, 1999).

Two Ribbon NAPL Samplers were deployed through the vadose zone into the saturated zone through the CPT rods. Each of the samplers remained in contact with the borehole for approximately one hour and was deployed near previous CPT and laser induced fluorescence (LIF) characterization pushes. Location SE-05 was deployed to a depth of 39 ft and SE-39 was deployed to 44 ft. CPT and LIF information and DNAPL location identified by the RNS are presented in Figure 6. The CPT friction ratio is a measure of sediment types where higher values indicate finer grained materials. The LIF counts indicate the location of the creosote contaminants. At creosote contaminated sites, the creosote stains the ribbon a dark black or brown and overshadows the red dye staining.



In SE-05 the staining on the sampler showed DNAPL (creosote) is present throughout the sampled interval. The location of DNAPL found with the RNS correlates with some of the LIF peaks especially in the 30-35 ft range. The discrepancy can be attributed to the heterogeneity (retarded downward movement caused by the fine material at 10 and 25 ft) and the resulting dispersed, residual nature of the DNAPL in this area. The RNS was deployed within approximately 5 ft of the CPT push. In SE-39, the DNAPL found with the RNS correlates well with the LIF data. At this location, the DNAPL is primarily located in the upper portion of the 10 ft thick interbedded sand, silt, and clay zone starting at 20 ft.

# Conclusions

The Ribbon NAPL Sampler has proven to be a robust method for determining the depth discrete location of DNAPL in the subsurface. The sampler is easily deployed with CPT in both the vadose and saturated zones. Deployment methods for both larger and smaller diameter drilling techniques are under development. The results from four DNAPL sites show DNAPL is present as dispersed globules and does not exist in pools or layers and is strongly controlled by lithology. Comparative results of sediment sampling and the RNS prove soil sampling is prone to missing the small dispersed globules of DNAPL whereas the RNS provides continuous sampling in a borehole. The RNS provides a complementary characterization technique for NAPL field screening and for verification of the presence and location of NAPL.

# References

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