Using Field Screening and Forensic Fingerprinting at Petroleum Hydrocarbon Sites

by Steve Greason, Sitelab Corporation, and
Stephen S. Boynton, P.E., LSP Ambient Engineering, Inc.

When it comes to delineating the extent of petroleum contamination during environmental site assessments and clean up, people would have to collect samples and send them to a laboratory for analysis. Government requires property owners to test the concentration in soil and groundwater in order to determine how much or how little of the contamination is there. Typical applications include underground storage tank (UST) removals resulting from spills and leaks commonly found at gas stations, fuel oils used to heat homes and commercial buildings to much larger sites at military bases, airports, refineries, power plants and old industrial properties.

The problem, however, is that it often takes days or weeks to get test results back from the laboratory, which costs a lot of money, time and headaches. Sound familiar?

Today the process can be significantly improved using new field screening tools to test samples on-site. Portable analyzers that use ultraviolet fluorescence are one such example, and have proven to be a very fast, affordable, easy, and accurate complement to traditional off-site laboratory test methods.

This type of fluorescence technology is capable of detecting concentrations of petroleum hydrocarbons in soil, sediment, groundwater and NAPL oils (Non Aqueous Phase Liquids), with detection limits in the low part-per-billion (ppb) range. Specifically, fluorescence detects aromatic hydrocarbons, which includes carcinogenic compounds such as Benzene, commonly found in gasoline, jet fuels, diesel, heating fuels, crude oil, coal tars and other types of petroleum products.

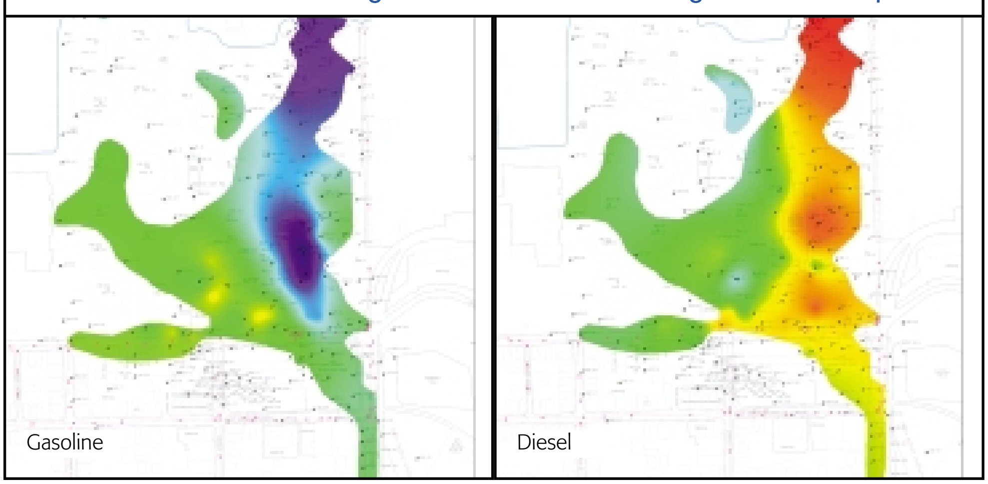
How they work

Depending on the application, the fluorescence analyzers are fitted with optical emission filters which can separately measure the volatile "gasoline" range hydrocarbons (BTEX), from the heavier diesel and oil range hydrocarbons (DRO, TPH), as well as the highly toxic polynuclear aromatic hydrocarbons (PAHs).

Using low cost disposable test kits, samples are collected on a site, extracted in solvent and then placed into the analyzer for analysis. From start to finish, each test only takes five minutes to perform. In addition, certified calibration kits are used to calibrate the analyzers, designed to match and correlate with conventional laboratory test methods using GC/PID, FID and MS instrumentation required by state and federal regulatory agencies.

Unlike the once popular photo-

Normalized Gasoline Range Aromatics and Diesel Range Aromatics Maps



Case Study

In Massachusetts, Ambient Engineering, Inc. has used Sitelab's UVF-3100 analyzer to access a 30-acre petroleum storage terminal in Boston. Assessments include delineating the vertical and horizontal extent of LNAPL contamination, and performing a qualitative forensic evaluation of a large LNAPL plume.

Ambient verified the accuracy of the UVF-3100 by testing a number of "split" samples. Samples were tested using the UVF-3100, with the split samples sent to a Massachusetts Certified testing laboratory. Samples were tested for Extractable Petroleum Hydrocarbons.

After verifying the reliability of the UVF-3100 for EPH analysis, Ambient relied extensively on the UVF-3100 to provide cost effective testing. This allowed more samples to be tested within the project budget, resulting in an improved understanding of site conditions. Based on these results, Ambient was able to develop detailed LNAPL cross-sections to aid in understanding the extent and nature of LNAPL contamination.

During the subsurface assessments, it was discovered that the UVF-3100 could be used to perform a qualitative forensic evaluation of LNAPL at the site. By calibrating the analyzer to actual LNAPL samples, Ambient realized that the fluorescence of diluted LNAPL samples could help map the nature of the large co-mingled plume of fuel oil and No. 6 oil at the site. Samples from over forty monitoring wells were collected and analyzed for the presence of diesel range organics and gasoline range organics. The maps (left) clearly show the distribution of product type throughout the terminal.

ionization (PID) meters, which detect only the volatile gases from a sample's headspace, fluorescence technology extracts a sample in solvent and detects volatile, semi-volatile and non-volatile petroleum hydrocarbons. And unlike other extractable test kits available, which require the use of reagents to be added to the extract, the same extract can be analyzed over and over to multiple tests (TPH, PAHs, etc.).

What makes them the better choice

When compared to conventional laboratory GC methods, many tests can be reported in a day right on-site, giving environmental professionals the answers they need more quickly, including the spread and extent of contamination, where to dig next, when to stop digging, as well as determine which samples should be selected for laboratory confirmation.

Economic benefits include savings in laboratory testing, which typically can cost over a hundred dollars per test and take several weeks to complete. In addition, even greater savings can be made by reducing the amount of time spent on labor and equipment on a site, as well as minimizing the volume of soil sent off-site for disposal.

Proven by U.S. EPA to be accurate and reliable

In 2001, the U.S. EPA evaluated fluorescence technology for measuring total petroleum hydrocarbons (TPH) in soil, along with six other competitive products. When compared to the certified laboratory results, this technology was ranked highest in all applicable categories including accuracy, speed, ease of use, detection limits, etc. This was also the only commercially available product capable of separately measuring the gasoline range and diesel range hydrocarbons from one another, just as the laboratory had performed. During the field demonstration, hundreds of samples were provided, including performance evaluation samples spiked with weathered gasoline, diesel fuel and potential interferences.

New qualitative, forensic "fingerprinting" analysis provides additional benefits

Although fluorescence technology cannot detect one compound from another, it does detect specific "fractions" or groups of aromatic hydrocarbons in a given sample. When testing a large number of samples collected from borings, wells or test pits located throughout a site, the proportions of these different fractions can provide qualitative data as to the type or age of petroleum contamination, similar to how forensic fingerprinting techniques are used by conventional laboratories using GC instrumentation.

In Table 1 (below), for example, low or close "EPH to PAH" ratio values indicate samples contain primarily PAHs with heavy or weathered fuel oils and no/little of the volatile GRO hydrocarbons. This is typically encountered in urban fills, coal ash and old fuel oil sites. The opposite is true for sites contaminated with gasoline, jet fuels or fresher, more recent releases of fuel oils where the EPH to PAH ratios are spread very high and the samples contain high proportions of GRO hydrocarbons.

In closing

Since the industrial revolution began over a hundred years ago, man has relied heavily on the use of oil, coal and other fossil fuels. Not surprising, petroleum hydrocarbons are the world's biggest polluter and greatest threat to human health and our environment. By quickly testing soil and water in the field using accurate and reliable tools like fluorescence, which complement traditional laboratory methods, people no longer have to wait. By knowing where and how bad the contamination is, where it came from and where it may be going underground, without having to wait saves everybody time and money. ■

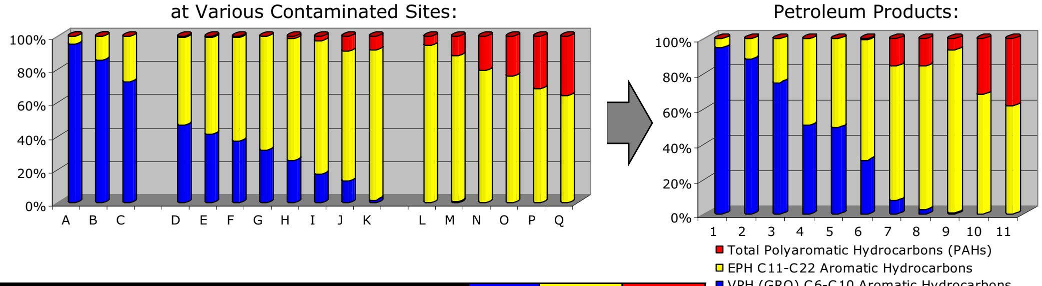
Steve Greason is an Environmental Scientist for Sitelab Corporation. For more information, please contact him at (978) 363-2299 or via e-mail at sgreason@site-lab.com.

Stephen S. Boynton, P.E., LSP, is Vice President of Ambient Engineering, Inc. For more information, please contact him at (978) 369-8188 or via e-mail at sboynton@ambient-engineering.com.

Table 1: Fingerprinting Soils to Petroleum Type

Fluorescence Signatures for Soils at Various Contaminated Sites:

Signatures for Common Petroleum Products:



Example Sites with High VPH (A-C), High EPH (D-K) and High PAHs (L-Q)	VPH	EPH	PAHs
A. Fresh UST Spill at Gas Station, Reading, MA	266	13	0
B. Weathered Jet Fuel Site, Holloman AFB, NM	320	55	0
C. Weathered Gasoline Site, Norwood, MA	1,360	510	0.4
D. Residential Heating Oil Spill (1 week old), Natick MA	1,850	2,085	14
E. Former UST Site, U.S. Army Base, Natick, MA	266	384	2.5
F. UST Diesel Site at Trucking Facility, Southboro, MA	960	1,630	9
G. NAPL Site with No. 2 Diesel Fuel, Boston, MA	2,700	5,910	18
H. NAPL Site with Weathered/Commingled Fuels, Boston, MA	1,200	3,540	60
I. No. 2 Fuel Area: Brownfield Power Plant Site, Savannah, GA	700	3,250	122
J. NAPL Site with Weathered No. 6 Fuel Oil, Boston, MA	80	496	54
K. No. 6 Fuel Area: Brownfield Power Plant Site, Savannah, GA	9.4	507	47
L. River Sediments near Coal Tar Plume at MGP Site, Colorado	10	5,000	278
M. Sediments Downstream at Coal Tar MGP Site, Colorado	5	942	126
N. Catch Basin Debris at Highway Dept, Seattle, WA	0	114	30
O. Coal Pile at US Air Force Base Power Plant, Goldsboro, NC	0	250	80
P. Coal Area 1: Brownfield Power Plant Site, Savannah, GA	0	150	68
Q. Coal Area 2: Brownfield Power Plant Site, Savannah, GA	0	318	177

1. 75% Weathered Gasoline
2. 75% Weathered Kerosene
3. NAPL Weathered Jet Fuel, NM
4. Fresh No. 2 Fuel (home heating oil)
5. Fresh Diesel Fuel
6. 50% Weathered Diesel Fuel
7. Fresh No. 4 Fuel Oil
8. Fresh No. 6 Fuel Oil (Bunker C Oil)
9. NAPL Coal Tar at former MGP Site, CO
10. Coal Ash/Waste at Power Plant, GA
11. 100% Humic Acid (natural organics)