Total Petroleum Hydrocarbons

Diesel was used in Area IV to power vehicles, construction equipment, and back-up generators. This resulted in releases to the environment. Total Petroleum Hydrocarbons (TPH) describes petroleum-derived fuel hydrocarbon mixtures, like kerosene, gasoline, and diesel. A TPH analytical result is reported for a range of carbon atoms in the sample (e.g., C15-C20). TPH with lower carbon range (lighter) fractions usually degrade more quickly than higher (heavier) carbon-range fractions.

California Polytechnic State University evaluated the rate of natural attenuation of TPH in soil in Area IV at SSFL as part of the U.S. Department of Energy's (DOE's) soil treatability studies. Natural attenuation of TPH in soil can potentially result in reduced contaminant concentrations of soil in place and reduce the volume of soil needing to be excavated and hauled off-site.

There were difficulties in achieving accurate analytical TPH results in soils from Area IV at lower concentrations approaching the TPH Method Reporting Limit specified in DTSC's Look-Up Table (5 mg/kg). A follow up study was done to address these issues. The researchers noted that TPH (residual range oil) cleanup levels varied nationwide from 99 mg/kg to 10,000 mg/kg*. The report can be found at: http://www.dtsc-ssfl.com/files/lib_doe_area_iv/soiltreatstudies/evaluation_report/66906_SSFL_AreaIV_STS_TPH_NOM_report.pdf

*The CA-Regional Water Quality Control Board's Case Closure Policy does not contain cleanup criteria for TPH in any medium, and concludes that the potential threat to human health and water quality is adequately captured by the individual "criteria" analytes for each medium. TPH is included in the Case Closure Policy only to ensure that site characterization is adequate.

What's in the soil? Results suggest that the contamination of Area IV soils being characterized as TPH consists of high molecular weight hydrocarbons, suggestive of residual range oil (RRO). These types of hydrocarbons undergo slow natural breakdown. Other compounds identified in the soil include polycyclic aromatic hydrocarbons (PAHs) and organic acids (natural oils), which are suggestive of Natural Organic Material (NOM). These non-petroleum hydrocarbons can be soil or sediment organic matter (i.e., degradation products of plants and animals), or lipids that may be inadvertently included in the TPH measurement. The NOM fraction of TPH in the Area IV soil samples accounted for about 5 to 8% of the total TPH.

Why is this an issue? The NOM can interfere with analytical TPH signals and impact the accuracy of TPH analytical results, especially at lower concentrations. Concentrations may appear higher than that attributable to hydrocarbons from petroleum-based origins. Maintaining a high level of analytical accuracy is critical when determining if low levels of TPH are present as contamination.

How was this issue addressed? Attempts were made to remove compounds associated with NOM prior to TPH analysis through a common method known as silica gel fractionation. Use of the silica gel approach had mixed results, with some samples showing some degree of NOM removal and others showing an increase in TPH. The silica gel approach was found not to fully address the issue of interfering NOM, and may underestimate the contribution of NOM to future TPH measurements.

TPH chromatograms showing results with (top) and without (bottom) use of silica gel preparation for removal of NOM in sample 5D-612

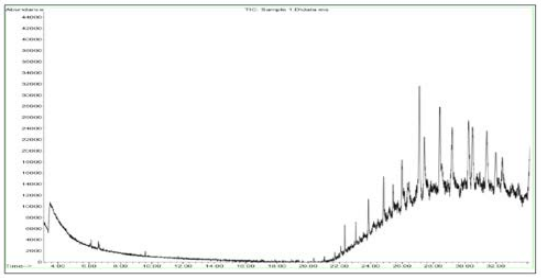

Figure B-1A: Sample 1 (5D-612) with no silica gel prep.

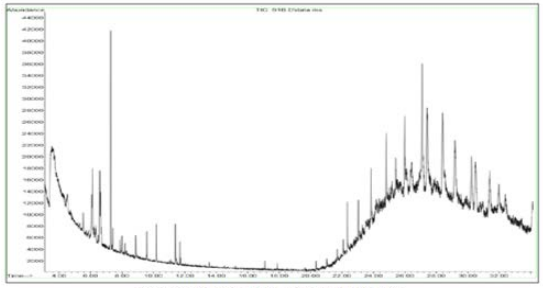

Figure B-1B: Sample 1 (5D-612) with silica gel prep.

Another identified issue: High variability in measured TPH concentrations between laboratories was observed, shown as relative standard deviation in the tables to the right, particularly at low concentrations. Variability may be attributed to localized presence of small rocks, varying fines, "tar balls", etc. as well as inherent difficulties of measuring low TPH concentrations.

Conclusions: Accurately quantifying low levels of TPH during the study (100 to 300 mg/kg), was difficult. The ability to reliably distinguish where contamination exists at the Look-up table value (5 mg/kg) may not be possible due to the elevated variability of sample concentrations at these low levels.

Table 4.1. TPH results from Cal Poly Lab (GC/MS) compared to TPH results of EMAX commercial laboratory

Sample Number	Sample ID	TPH Concentration (mg/kg)						Difference between Cal Poly and EMAX (%)
		EMAX	Cal Poly Lab					
			Rep 1	Rep 2	Average	Std. Dev.	Rel. Std. Dev. (%)	
1	5D-612	ND	208	56	132	108	82	+ ∞
2	5D-885	50	212	41	127	121	95	+154
3	01-BE-B	170	147	176	161	21	13	-5
4	02-LS-C	17	34	87	60	37	62	+256
5	18-B-A	190	219	316	268	69	26	+41

Table 4.2. Effect of silica gel cleanup on measured TPH concentrations by EMAX and Cal Poly

Soil Sample	Soil Sample Location	TPH Concentration (mg/kg)			
		EMAX Results		Cal Poly Results	
		Before Silica	After Silica	Before Silica	After Silica
1	5D-612	-	-	208	209
2	5D-885	50	43	212	99
3	5B- 01-BE-B	170	150	147	168
4	5B-02-LS-C	17	10	34	101
5	5B-18-CB-A	190	180	219	262

Table 4.4. Estimated Contribution of NOM to Measured TPH of the Soil Samples With and Without Silica Gel Cleanup.

	Without Silica Cleanup		With Silica Cleanup	
Soil Sample	Concentration NOM (mg/kg)	Percent of TPH	Concentration NOM (mg/kg)	Percent of TPH
1	9.3	4.03	9.0	4.02
2	16.8	6.89	9.0	7.14
3	9.1	4.95	6.6	3.45
4	4.0	7.94	0.0	0
5	7.4	2.93	0.0	0

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