



## 9.2 PETROLEUM CONTAMINATED SITES

A discussion of target chemicals of potential concern and the evaluation of petroleum releases is included in Volume 1 and Appendix 1 of the EHE guidance document (HDOH, 2008). This guidance is summarized and expanded below.

Petroleum is a complex mixture of hundreds of different compounds composed of hydrogen and carbon or "hydrocarbon" compounds (API, 1994). The bulk of these compounds are evaluated collectively under the all-inclusive category of total petroleum hydrocarbons (TPH), typically measured in three ranges: gasoline, middle distillates, and residual fuels. Gasoline-range TPH is a petroleum mixture characterized by a predominance of branched alkanes and aromatic hydrocarbons with carbon ranges of C6 to C12 and lesser amounts of straight-chain alkanes, alkenes, and cycloalkanes of the same carbon range (see also HDOH, 2008, Volume 2, Appendix 7; NEIWPC, 2003). TPH associated with middle distillates (e.g., kerosene, diesel fuel, home heating fuel, jet fuel, etc.) is characterized by a wider variety of straight, branched, and cyclic alkanes, polynuclear aromatic hydrocarbons (PAHs) (especially naphthalenes and methyl naphthalenes), and heterocyclic compounds with carbon ranges of approximately C9 to C25. Residual fuels (e.g., Fuel Oil Nos. 4, 5, and 6, lubricating oils, mineral oil, used oils, and asphalts) are characterized by complex polar PAHs, naphthenoaromatics, asphaltenes, and other high-molecular-weight saturated hydrocarbon compounds with carbon ranges that in general fall between C24 and C40.

Due to the complex nature of petroleum mixtures, petroleum contamination should be evaluated in terms of both TPH and target "indicator chemicals" for the specific type of petroleum product released (e.g., benzene, toluene, ethylbenzene and xylenes [BTEX], methyl tertiary butyl ether [MTBE], PAHs, etc.). Target indicator chemicals typically make up only a small fraction of the total petroleum present but are important players in the assessment of environmental hazards posed to human health and the environment.

### 9.2.1 Recommended Target Analytes for Petroleum Contaminated Soil and Groundwater

Recommended target analytes for petroleum contaminated soil and groundwater are provided in Table 9-5.



**Section 9**  
**Supplemental Guidance for**  
**Select Contaminants of Concern**  
*Petroleum Contaminated Sites*

**Table 9-5 Target Analytes for Releases of Petroleum Products**

Petroleum Product	Media	Recommended Target Analytes
<b>Gasolines</b>	Soil	TPH, BTEX, naphthalene, MTBE and appropriate additives and breakdown products (e.g., DBA, TBA, lead, ethanol, etc.)
	Soil Vapor	Same as soil plus methane
	Groundwater	Same as soil
<b>Middle Distillates</b> (diesel, kerosene, Stoddard solvent, heating fuels, jet fuel, etc.)	Soil	TPH, BTEX, naphthalene, and methylnaphthalenes (1- and 2-)
	Soil Vapor	TPH, BTEX, naphthalene, and methane
	Groundwater	Same as soil
<b>Residual Fuels</b> (lube oils, hydraulic oils, mineral oils, transformer oils, Fuel Oil #6/Bunker C, waste oil, etc.)	Soil	TPH, *VOCs, naphthalene, methylnaphthalenes (1- and 2-), the remaining 16 priority pollutant PAHs, PCBs, and heavy metals unless otherwise justified
	Soil Vapor	TPH, BTEX, naphthalene, and methane
	Groundwater	same as soil

\* = VOCs includes BTEX and chlorinated solvent compounds

The eighteen priority pollutant PAHs are listed in the USEPA Regional Screening Level (RSL) guidance (USEPA, 2008b):

- acenaphthene
- acenaphthylene
- anthracene
- benzo(a)anthracene
- benzo(b)fluoranthene
- benzo(g,h,i)perylene
- benzo(a)pyrene
- benzo(k)fluoranthene
- chrysene
- dibenzo(a,h)anthracene
- fluoranthene
- fluorene
- indeno(1,2,3)pyrene,
- methylnaphthalenes (1 & 2)
- naphthalene
- phenanthrene
- pyrene



Separate Environmental Action Levels (EALs) for 1- and 2-methylnaphthalenes are presented in the updated, 2008 EHE guidance document (HDOH, 2008). The suite of PAHs that should be tested at a given site depends on the type of the petroleum product released (after MADEP, 2002a). As indicated in the Table 9-5, naphthalene is the only PAH to test at gasoline release sites. Both methylnaphthalenes and naphthalene should be tested at sites with releases of middle distillates (diesel, jet fuel, etc.). The full suite of PAHs should be considered at sites with releases of heavier petroleum fuels and waste oil, unless site-specific information on the product released justifies eliminating specific PAHs.

1- and 2- methylnaphthalenes are unlikely to drive potential vapor intrusion hazards at petroleum release sites due to their relatively low volatility and concentration in most middle distillates and residual fuels. Testing for these compounds in soil vapor is also difficult and requires different sample collection and analytical methods. For these reasons, 1- and 2- methylnaphthalenes do not need to be included in soil vapor studies at petroleum release sites unless otherwise directed by HDOH.

Volatile components of petroleum that are not specifically identified as target indicator compounds in Table 9-5 but reported as separate compounds by the laboratory using EPA Method 8260 or similar methods can in general be ignored (e.g., alkanes, alkenes, alkyl benzenes and other aromatics not specifically identified as target indicator compounds; refer to Section 2.11 in the EHE guidance document [HDOH, 2008]). These compounds are included under the umbrella analysis for TPH in general and do not need to be evaluated (or even reported) separately. This is based on the assumption that the toxicity factors selected for TPH are adequately conservative for the mixture of compounds present in fuels beyond the target compounds noted in Table 9-5.

Soil, groundwater, and soil vapor samples must always be tested for TPH (or equivalent) in addition to targeted, individual chemicals. Laboratory analysis for TPH as gasolines and middle distillates is generally carried out using gas chromatography, modified for "gasoline-range" organics ("Volatile Fuel Hydrocarbons") and "diesel-range" organics ("Extractable Fuel Hydrocarbons"), respectively (e.g., EPA Method 8015). Analysis for TPH as residual fuels up to the C40 carbon range can be carried out by gas chromatography, infrared absorption, or gravimetric methods. The



latter methods are rarely used, however, due to their inability to discriminate the type of the petroleum present and interference with organic material in the soil. Analysis of soil vapor for TPH is commonly reported as Total Volatile Hydrocarbons (TVH). Consult a laboratory with expertise in analysis of total hydrocarbon fractions in soil vapor for additional information.

Note that the breakdown of heavy petroleum can lead to an increase in volatile petroleum compounds (Chaplin, 2002). This necessitates the collection of soil vapor samples at sites contaminated by heavier fuels, as well as gasolines and middle distillates.

Reported concentrations of unidentified hydrocarbons as gasoline, diesel or oil indicate that the chromatogram generated for the sample does not match standards used to quantify TPH. Reported concentrations of TPH should be considered approximate, but adequate for comparison to HDOH action levels. A more detailed evaluation through petroleum carbon range analysis can be carried out on a site-specific basis as warranted.

### **9.2.2 Petroleum Contamination Encountered During Subsurface Soil Excavation**

Unanticipated petroleum (free product) or petroleum-contaminated soil is sometimes encountered during construction work where subsurface soil is being excavated. The HEER Office has a Guidance Fact Sheet, consistent with the Hawai'i Environmental Response Law (HRS 128D), to assist project managers, contract workers, safety and health personnel or anyone involved in construction and excavation of soils when petroleum is encountered on a site. This document, "Guidance Fact Sheet for Use When Petroleum Contamination is Encountered During Subsurface Soil Excavation", is provided in Appendix 9-D.