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To: Interested Parties

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Subject: *Comparison of HIDOH Total Petroleum Hydrocarbon (TPH) Action Levels to Data for Water Samples*

This memorandum provides additional information regarding use of Hawai'i Department of Health (HIDOH) Environmental Action Levels (EALs) for Total Petroleum Hydrocarbon (TPH) for screening of water data, including groundwater, tapwater and surface water. The basis for this described approach is provided in the attachment to the memorandum.

Three categories of petroleum fuel and associated TPH EALs are presented in the EAL lookup tables: 1) Gasolines (TPH_{gasolines}), 2) Middle Distillates (TPH_{middle distillates}) and 3) Residual Fuels (TPH_{residual fuels}). "Middle Distillate" fuels include diesel, kerosene and jet fuel. "Residual Fuels" include motor oil and other heavy fuels and petroleum products. The action levels apply to the single, total concentration of non-specific (e.g., non BTEXMN) hydrocarbon and hydrocarbon-related degradation compounds (aka "Hydrocarbon Oxidation Products" or "HOPs") present in a water sample and known or assumed to be associated with one of the three-noted categories of fuel. The most conservative action levels should be used for comparison to sample data if the specific type of fuel released cannot be determined or contamination is associated with a mixture of fuel two or more of the noted fuel categories.

Scrutiny of groundwater sample data following the 2021 jet fuel release at the Navy's Red Hill facility in Honolulu identified concerns that the total concentration of TPH-related compounds in a sample was not being adequately quantified. This led to confusion regarding comparison of fuel-specific, TPH EALs to sample data for individual ranges of organic compounds in a sample often reported separately by laboratories.

In short, there is only one concentration of TPH-related contaminants in a sample. The concentration of "TPH" in a water sample derived for comparison to a corresponding TPH action level should be calculated as the sum of the concentration of Total Purgeable Organics for

volatile compounds plus the concentration of Total Extractable Organics for semi-volatile and non-volatile compounds. Volatile compounds are commonly reported as “Gasoline Range Organics (GRO)”, for example using a combined gas chromatography and mass spectrometry (GC-MS) analysis such as Method 8260. Semi-volatile and non-volatile compounds are commonly and reported as “Diesel Range Organics (DRO)” and “Residual Range Organics (RRO)”, for example using gas chromatography Method 8015. The concentration of TPH in a sample is therefore calculated as:

$$\text{TPH} = \text{Total Purgeable Organics} + \text{Total Extractable Organics};$$

or in terms of individual fuel ranges:

$$\text{TPH} = \text{GRO} + \text{DRO} + \text{RRO}.$$

Test methods for Purgeable Organic Compounds and Extractable Organic Compounds can overlap the same carbon range. Volatile compounds reported under purgeable test methods are largely lost in processing of samples to be tested using extraction methods, however. Potential double counting is therefore minimal and does not need to be considered.

The identification of middle distillate-related, organic compounds in a water sample based only on gas chromatography becomes unreliable below a laboratory Method Reporting Limit (“MRL”, aka “Laboratory Quantification Limit”) of approximately 200 µg/L. Samples of drinking water and groundwater that are a current or potential source of drinking water with reported concentrations of Total Extractable Organics (e.g., “DRO” or “RRO”) below this concentration should be retested for individual compounds using a combined GC-MS method such as Method 8270. The resulting data should be reviewed by a chemist experienced in petroleum forensics to determine if the compounds are associated with petroleum-related contamination or other, nonpetroleum-related organic matter in the water. Concentrations of organic matter below the MRL should not be reported as “TPH” until such verification has been made.

Questions and comments should be directed to Roger Brewer with HIDOH (roger.brewer@doh.hawaii.gov).

References

HIDOH, 2024, *Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater – Hawaii Edition (Draft Spring 2024)*: Hawai’i Department of Health, Office of Hazard Evaluation and Emergency Response.

HIDOH, 2023, *Technical Guidance Manual* (and updates): Hawai’i Department of Health, Office of Hazard Evaluation and Emergency Response, <https://health.hawaii.gov/heer/tgm/>

Laboratory Analysis of Petroleum-Related Compounds

Petroleum fuels are made of hundreds of individual compounds of differing volatility and sorptive capacity (Figure 1). The lowest boiling point compounds are typically referred to by the laboratory as “Gasoline Range Organics (GRO), due to the predominance of such compounds in gasolines. Mid-range boiling point compounds are commonly referred to as “Diesel Range Organics (DRO)” for the same reason with respect to diesel-based fuels. High boiling point and low-volatility compounds are referred to as “Residual Range Organics (RRO).” Volatile, GRO-range compounds (e.g., C5-C12) are identified and quantified using “purge-and-trap” analytical methods. Less volatile DRO-range compounds (e.g., C8-C24 or C10-C24) and RRO-range compounds (e.g., >C24) are identified and quantified using extraction methods.

The area under the resulting “hump” generated on a gas chromatograph (GC) is compared to laboratory standards for the known or assumed fuel type and used to identify the primary type of fuel present. The presence of GRO range compounds in a sample does not necessarily mean that gasoline is present, only that some compounds within the fuel fell within this range. Jet fuels, for example, can consist of hydrocarbon compounds that span both GRO and DRO boiling point ranges (e.g., refer to HIDOH 2022).

Hydrocarbon-related degradation products are assumed to have a similar toxicity as the parent compounds (HIDOH 2024). Polar compounds should therefore not be removed from water samples using silica gel cleanup (SGC) or other methods prior to testing. Comparison of SGC to non-SGC data can, however, assist in determining the overall state of degradation of the petroleum.

Laboratory Reporting Ranges vs TPH Action Levels

Confusion in the application of TPH action levels to water sample data is caused in part by use of the terms “Gasoline Range Organics,” “Diesel Range Organics” and “Residual Range Organics” by laboratories to report sample data. There is only one true concentration of “TPH” for a sample, which is the sum of concentrations of all hydrocarbon compounds detected across the three ranges that are not otherwise targeted for individual assessment (e.g., BTEX and PAHs). That concentration should be compared to the TPH action level applicable to the primary type of fuel released. For example, where there has been a gasoline release, the total concentration of gasoline-related contaminants in a water sample should be compared to action levels for $TPH_{\text{gasolines}}$. Where there has been a diesel release, the total concentration of diesel-related contaminants in a water sample should be compared to action levels for $TPH_{\text{middle distillates}}$. If the nature of the fuel release is uncertain or in cases of release of multiple fuel types, the calculated concentration of TPH should be compared to the fuel category with the most conservative action levels.

Refer again to Figure 1. Two separate types of laboratory methods are required for testing of petroleum-contaminated media, including water. Volatile compounds are reported in terms of Total Purgeable Organics (e.g., “GRO”), using purge-and-trap techniques such as Method 8260. Sem-volatile are reported in terms of Total Extractable Organics (e.g., “DRO” and “RRO”), using extraction methods. Test methods for Purgeable Organic Compounds and Extractable Organic Compounds can overlap the same carbon range. Volatile compounds reported under TPO tests method are largely lost in TEO test extraction methods, however, so double counting is minimal.

Refer next to Figure 2. The case for water samples is more complicated. Dissolution of hydrocarbons into water will be biased toward more soluble, aromatic compounds. The mix of dissolved-phase compounds in water will therefore be different from that of the fuel itself. In the case of water contaminated by gasolines, dissolved-phase compounds such as benzene, toluene, ethylbenzene and xylenes (BTEX) will be reported as part of the GRO range compounds, as expected. As the compounds begin to degrade and become less volatile, however, they will elute on the chromatogram at a higher boiling point, with some compounds potentially eluting within the “DRO” range. Heavier RRO-related compounds are not normally found associated with degraded gasolines but should be included in initial sample data for a site to document that such contamination is not present. The total concentration of dissolved “TPH” in the sample is therefore most appropriately calculated as the sum of the reported concentration for GRO range compounds plus the reported concentration of DRO range compounds ($TPH = DRO + GRO + RRO$).

Dissolved-phase middle distillate fuel, such as JP-5 jet fuel, can include BTEX as well as a significant amount of additional, heavier and less volatile aromatics (e.g., >C8 aromatics). This can lead to compounds falling within both the GRO and DRO ranges even in the absence of degradation (see Figure 2). As the GRO-range compounds degrade, they will again begin to be reported as “DRO.” As the DRO-range parent compounds degrade, they will elute on the chromatogram at a higher boiling point and in some case could reported as “RRO.” The total concentration of dissolved “TPH” in the sample is the sum of the concentrations reported for all three ranges ($TPH = DRO + GRO + RRO$).

Consideration of Individually Targeted Compounds

The concentration of individually targeted compounds such as BTEX and PAHs should be subtracted from the TPH data to avoid double counting (refer to TGM Section 9.3.1.2). This can be done by the laboratory on request or by the project consultant. In practice, this will make minimal difference in the concentration of TPH used for comparison to EALs, since the proportion of BTEX, PAHs and other individually targeted compounds is normally minimal in comparison to non-specific compounds collectively assessed as “TPH.”

Case-Specific TPH Action Levels

Toxicity, along with physiochemical and other factors considered in the development of TPH action levels for specific fuel types are discussed in Volume 2, Appendix 1, Section 6 of the HDOH Environmental Action Level guidance (HDOH 2024). The assumptions used are intended to address the majority of petroleum-impacted sites in Hawai‘i without the need for a site-specific risk assessment.

Development of “case-specific,” TPH action levels will, however, be required in a small number of cases when assumptions incorporated into the default TPH action levels do not apply to conditions in the field. For example, the TPH action level for middle distillate fuels are based on the assumed, combined toxicity of GRO and DRO components of typical middle distillate fuels. (RRO components are negligible). The action level for drinking water (“tapwater”) also assumes that the fuel is partially oxidized and no longer significantly volatile. This decreases the overall exposure risk and results in a slight increase in action levels over fresh fuel that is still volatile.

If these conditions are not met in the field for a specific case, then a case-specific TPH action level(s) must be generated. For example, if fresh fuel is released and threatens a drinking water

supply, then alternative action levels would need to be developed that take into consideration volatilization of compounds from water and exposure via inhalation (e.g., HIDOH 2022).

Preparation of case-specific TPH action levels will normally be undertaken by the responsible party but might need to be generated by HIDOH in some instances. In either situation, the case-specific EAL and the rationale for its calculation must be reviewed and approved by HIDOH. The responsible party will also have the option to prepare alternative action levels at a later time in the response action, based on changes in site conditions, and provide this to HIDOH for review and approval (e.g., degradation and reduced volatility and toxicity of fuel-contaminated groundwater over time). Supporting field data must be provided to support changes to the initial action level.

Data Below the Method Reporting Limit

Sample data for Total Purgeable Organics (e.g., GRO) or Total Extractable Organics (e.g., DRO or RRO) below the laboratory Reporting Limit for the test method (“MRL”; aka “Limit of Quantification”) cannot directly be assumed to be associated with petroleum-related compounds. This is because the concentration of organic compounds in the sample is too low to generate a recognizable, fuel-related pattern.

An MRL of 50 µg/L is typical for reporting of GRO range compounds. An MRL of 200 µg/L or higher is common for reporting of DRO and RRO compounds. Sample data below the MRL are normally qualified with “J” flag in the laboratory report. This indicates that neither the specific nature of the organic compounds identified, nor the true concentration of the compounds is certain. “J-flagged” data should not be reported as “TPH” by the laboratory. The organic compounds identified might or might not be related to petroleum. Algae and other organic matter are also common in water at these concentrations.

This will primarily be an issue for DRO-range organic matter detected below the typical MRL of 200 µg/L. In cases where there is a concern that J-flagged data could reflect hydrocarbon-related contamination in a sample and cause the sum concentration of Total Purgeable Organics and Total Extractable Organics to exceed the TPH action level, the sample be immediately retested using Mass Spectrometry (MS) methods (e.g., Method 8270). This allows individual compounds to be identified. An experienced chemist can then determine if the compounds are more likely to be associated with dissolved hydrocarbons or hydrocarbon-related degradation products or more likely related to other organic material in the sample, such as algae. A Fact Sheet on the use of mass spectrometry methods as a forensics tool to determine the likely origin of J-flagged compounds is included as an attachment to the memorandum.

If a conclusion is made that the compounds are likely related to hydrocarbons, then the data should be considered for calculation of a final TPH concentration for the sample. If the review suggests that the compounds are unlikely related to hydrocarbons, then the data do not need to be incorporated into calculation of TPH. As a default, J-flagged data should be assumed to reflect hydrocarbon-related compounds in cases where petroleum contamination has otherwise been confirmed unless disproven by more MS or other detailed analysis.

Note that an elevated MRL for a range typically reflects a high concentration of contaminants in one of the other ranges or otherwise in the sample. Discussions regarding next steps can proceed if the sum TPH concentration exceeds the action level for the fuel-type involved. If not, discuss the reasons for the elevated MRL and need for retesting of the sample with the laboratory and the overseeing project manager at HIDOH.

“Non-detects” at the laboratory Method Detection Level (MDL) do not need to be considered in calculation of a final TPH concentration for a sample unless otherwise required by HDOH.

Quantification of TPH in Other Media

Summing of Total Purgeable Organics (e.g., GRO) data and Total Extractable Organics data (e.g., DRO and RRO) for calculation of TPH is generally not necessary for soil samples. Environmental Action Levels for different categories of TPH in soil reflect concentrations that necessitate the presence of free product in the soil. The predominant makeup of “TPH” in the soil sample should more closely match the makeup of the original fuel, even if partially weathered, should in turn be captured by a single reporting range test (see Figure 1).

For example, the concentration of gasoline product in soil should be adequately captured by a purgeable organic compound test method and associated GRO data. The concentration of diesel and other middle distillate fuels in soil should be adequately captured by extractable organic compound test methods and associated DRO data, etc. Reported concentrations of GRO, DRO and RRO in soil can therefore be individually compared to soil action levels for TPH_{gasolines}, TPH_{middle distillates} and TPH_{residual fuels}.

The concentration of TPH in air and soil vapor samples should be reported as the sum of C5 to C12 compounds and the data similarly compared to the indoor air and subslab soil vapor action level appropriate for the fuel in question (Section 7.13.1 of the HDOH *Technical Guidance Manual*, HDOH 2023). Summa canister methods are normally used for reporting of up to C12 hydrocarbons in air and vapor samples. The use of sorbent tube methods is necessary for reporting of >C12 hydrocarbons in air or soil vapor. The *Technical Guidance Manual* currently recommends the use of both Summa and sorbent sampling methods for air and vapor samples associated with middle distillate fuels. Testing of vapors from such fuels has consistently identified insignificant amounts of >C12 compounds, however. This negates the need for sorbent tube vapor sample data at petroleum release sites unless otherwise requested by HDOH or desired by the project consultant. Updates to the TGM to reflect this change are pending.

References

HDOH, 2024, *Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater – Hawaii Edition (Draft Spring 2024)*: Hawai'i Department of Health, Office of Hazard Evaluation and Emergency Response.

HDOH, 2022, *Recommended Risk-Based Drinking Water Action Levels for Total Petroleum Hydrocarbons (TPH) Associated with Releases of JP-5 Jet Fuel*: Hawai'i Department of Health, Hazard Evaluation and Emergency Response, Technical Memorandum from Roger Brewer to Kathleen Ho, April 20, 2022.

ITRC, 2018, *TPH Risk Evaluation at Petroleum Contaminated Sites*: Interstate Technology & Regulatory Council. Washington D.C.

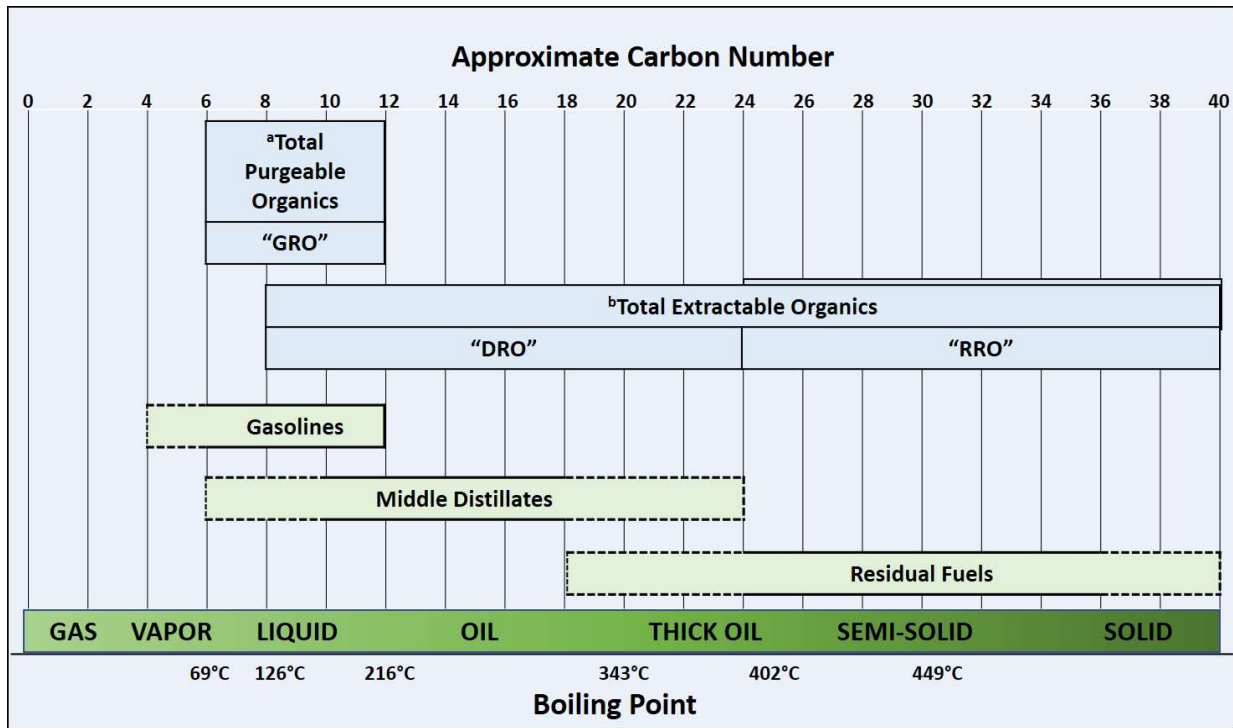


Figure 1. Comparison of fuel categories to laboratory analytical methods and reporting ranges; a) Total Purgeable Organics (TPO) methods are used to quantify volatile compounds (e.g., Method 8260 for "GRO"), b) Total Extractable Organics (TEO) methods are used to quantify semi-volatile compounds (e.g., Method 8015M for "DRO" and "RRO").

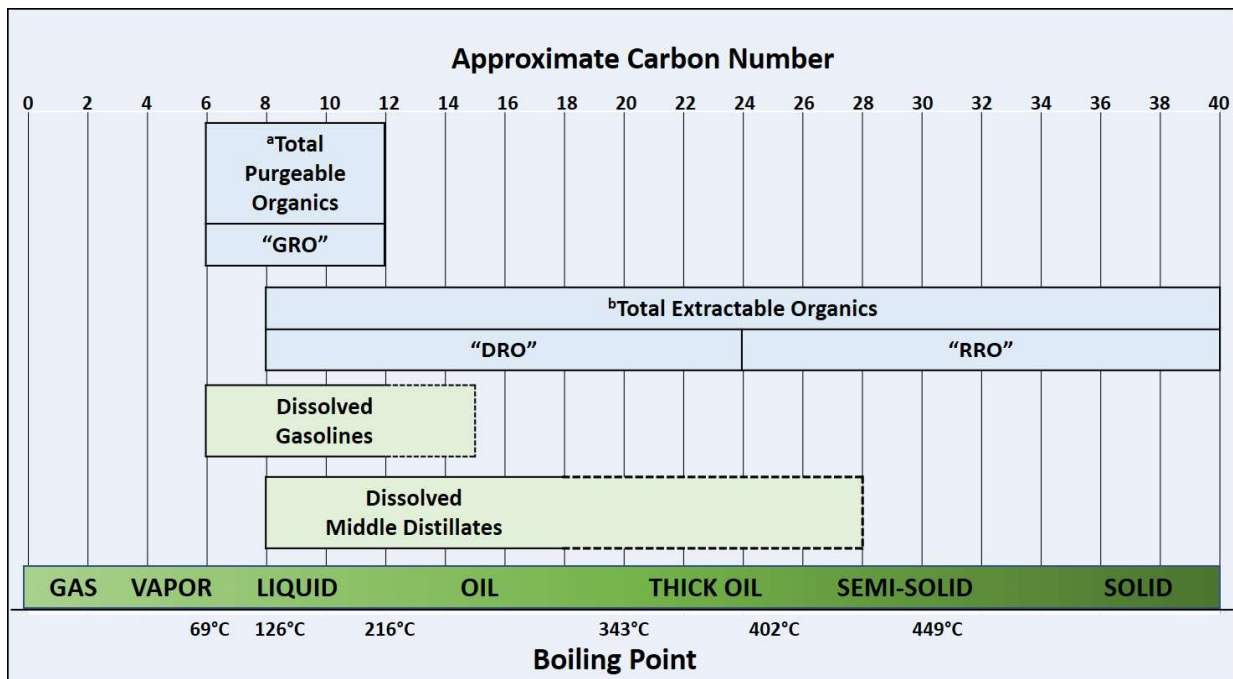


Figure 2. Comparison of dissolved fuels to laboratory analytical methods and reporting ranges. Note potential spread of lower volatility, fuel-related degradation compounds into higher boiling point reporting ranges. This requires addition of reported concentrations "GRO," "DRO" and "RRO" to estimate a total concentration of TPH-related compounds.

Forensic Drinking Water Characterization (Newfields; January 30, 2024)

Forensic Drinking Water Characterization

Identifying Purgeable and Extractable Chemicals Included in Total Petroleum Hydrocarbon Measurements
Prepared for the Hawaii Department of Health

Introduction

Total Petroleum Hydrocarbon (TPH) analysis is a conventional laboratory technique used for monitoring drinking water samples for petroleum hydrocarbons. TPH analyses conducted using methods like USEPA Method 8015D by Gas Chromatography with a Flame Ionization Detector (GC/FID) provides a bulk measurement of extractable organics detected within a defined carbon range (e.g. gasoline range-GRO, diesel range-DRO, oil range-ORO; Figure 1).

However, GC/FID analysis cannot identify the specific chemicals reported within a bulk measurement. At higher relative concentrations it may be clear that a drinking water sample contains petroleum hydrocarbons, but at low levels confirmation analysis is needed to identify the chemical constituents. When analyzing samples with very low levels of organic matter, it is important to identify the specific chemicals present using a method like GC Mass Spectrometry (GC/MS). GC/MS analysis can be used to determine if low-level organic constituents in a sample are truly petroleum hydrocarbons or are actually related to other non-petroleum organic contaminants or naturally occurring biogenic materials like plant waxes or organic acids.

Figure 1 provides an example of a drinking water sample with both petroleum hydrocarbons and naturally occurring plant waxes. In this example the DRO measurements include impacts from both petroleum and naturally occurring chemicals and contain a high bias due to non-petroleum constituents. Conventional TPH analysis cannot differentiate between these classes of chemicals.

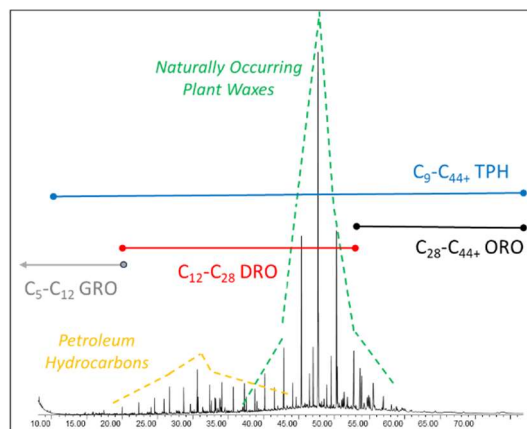


Figure 1. Example Drinking Water GC/FID Chromatogram

Recommended Forensic Analysis for Low Level TPH Characterization

Forensic methods are designed to characterize source materials and are optimized for low level sample analysis. When characterizing low level TPH results it is recommended to follow a tiered analytical approach:

- ❖ Tier I: Modified EPA Method 8015D High Resolution GC/FID Fingerprint
 - High resolution GC/FID fingerprints provide greater separation between carbon ranges and allow for a more accurate assessment of potential source materials.
- ❖ Tier II: Confirmation Testing by GC/MS
 - Samples should then be analyzed by EPA Method 8260D for C₅-C₁₂ purgeable organics and Method 8270E C₈-C₄₄₊ for extractable organics. This type of GC/MS data can be used to perform non-target analysis (NTA) and detect tentatively identified compounds (TICs) that can be used to identify the purgeable, and extractable chemical constituents present in low level TPH measurements. This analysis will help determine if TPH measurements are truly petroleum hydrocarbons or other non-petroleum constituents.
- ❖ Tier III: Petroleum Characterization
 - If petroleum hydrocarbons are present, samples can be analyzed by modified forensic Methods 8260D-PIANO volatile organic compounds and 8270E-Alkylated PAHs. These methods are designed to chemically characterize petroleum hydrocarbon residues, determine source type, and evaluate the degree of environmental weathering.