

STATE OF HAWAII
DEPARTMENT OF HEALTH
KA 'OIHANA OLAKINO
P. O. BOX 3378
HONOLULU, HI 96801-3378

In reply, please refer to:
File: RB-21-24

Date: June 12, 2024

To: Interested Parties

Through: Grace Simmons, Program Manager *Gracelda Simmons*
Hazard Evaluation and Emergency Response Office

From: Roger Brewer, PhD *Roger Brewer*
Hazard Evaluation and Emergency Response Office

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 (HIDOH 2018). 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 (TPO) for volatile compounds plus the concentration of Total Extractable Organics (TEO) for semi-volatile

and non-volatile compounds. Volatile compounds are commonly reported as “Gasoline Range Organics (GRO).” Semi-volatile and non-volatile compounds are commonly and reported as “Diesel Range Organics (DRO)” and “Residual Range Organics (RRO).” 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 the volatility of the compounds present:

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

The identification of middle distillate-related, organic compounds in a water sample and quantification of TPH based only gas chromatography becomes unreliable below a laboratory Method Reporting Limit (“MRL”, aka “Laboratory Quantification Limit”) of approximately 200 µg/L. This is because the pattern expressed on the chromatogram becomes lost in background “noise” and is no longer reliably discernable as being related to petroleum. As described in the Forensics Fact Sheet attached to this memorandum, samples of drinking water and groundwater with reported concentrations of Total Extractable Organics below this concentration should be retested for individual compounds using a combined gas chromatograph-mass spectrometry (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 indeed associated with petroleum-related contamination or if they are more likely related to other, nonpetroleum-related organic matter such as algae. Concentrations of organic matter below the MRL should not be reported as “TPH” until such verification has been made.

Questions and comments regarding this Technical Memorandum should be directed to Roger Brewer with HIDOH (roger.brewer@doh.hawaii.gov). Refer also to examples in the use of TPH action levels to assess the risk posed by petroleum-contaminated soil, sediment, water and air are included in a series of petroleum-release case studies published by HIDOH in coordination with experienced consultants (HIDOH 2018).

References

HIDOH, 2018, *Collection and Use of Total Petroleum Hydrocarbon Data for the Risk- Based Evaluation of Petroleum Releases - Example Case Studies*: Hawaii Department of Health, Hazard Evaluation and Emergency Response Office. October 2018.

HIDOH, 2024, *Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater – Hawaii Edition (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). Gas chromatography and Method 8015 is most commonly used to estimate the total sum of petroleum-related compounds in in soil, water or air. Purge-and-trap techniques are used to sum volatile, C5 to C12 compounds present in a sample, referred to as “Total Purgeable Organics (TPO).” Extraction techniques are used to sum semi-volatile, C8 to C36 or higher compounds present in a sample, referred to as “Total Extractable Organics (TEO).” “TPH” is calculated as the sum of TPO and TEO data. Note that overlap of the two methods between C8 and C12 in does not result in significant double counting, since volatile compounds are largely lost in TEO test extraction methods.

Areas under TPO and TEO “humps” on a gas chromatograph (GC) are compared laboratory standards for fuels that primarily fall within these boiling point ranges (Figure 2). For example, the total concentration of volatile, TPO-related compounds present in a sample is estimated based on comparison to a laboratory standard for gasolines. Data for this range are thus often reported by the laboratory as “Gasoline Range Organics (GRO).” The total concentration of semi-volatile, TEO-related compounds is normally estimated by comparison of the mid-boiling point range of the chromatogram (e.g., C8 to C24) to a diesel or other middle distillate fuel standard and the higher boiling point range (e.g., C24-C36+) to a standard for motor oil. The former is often reported by the laboratory as “Diesel Range Organics (DRO)” while the latter is often reported as “Residual Range Organics (RRO).”

Note that the presence of “GRO” range compounds in a sample does not necessarily mean that gasoline is present, only that some compounds within the fuel itself 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 HODOH 2022). This is considered in development of carbon range-weighted, TPH toxicity for neat fuels as well as TPH toxicity factors for vapors from fuels and fuel-specific mixtures of dissolved-phase hydrocarbons in water.

Partially oxidized, polar, hydrocarbon-related degradation products will be captured and included in TPO and TEO analysis of a sample. These compounds are also referred to as “Hydrocarbon Oxidation Products” or “HOPs.” The toxicity of the mixture of HOPs compounds is assumed to be identical to that of the original mixture of parent hydrocarbon compounds (HODOH 2024). Polar compounds should in particular not be removed from water samples using silica gel cleanup (SGC) or related methods prior to comparison to TPH action levels. 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

The concentration of TPH in a sample is calculated as the sum of all volatile and semi-volatile, hydrocarbon-related compounds minus the concentration of compounds targeted for individual assessment (e.g., BTEX and PAHs):

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

or in terms of boiling point ranges referenced by the laboratory:

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

Sample data should not be reported as “TPH” by the laboratory unless the data represent the sum of TPO and TEO as noted above. It is otherwise preferable that the laboratory report data in terms of TPO and TEO with the corresponding carbon ranges noted, for example TPO_{C5-C12}, TEO_{C8-C24} and TEO_{C24-C36}. Reference to the sum of the data as “TPH” is an interpretation and second step of the process, assuming that reviews of chromatograms and, as needed, forensic analyses described below, confirm that the main mass of the TPO and TEO is indeed related to petroleum.

Sample data for individual boiling point ranges should not be reported as “TPH” by the laboratory, since the data might not represent to total sum of petroleum-related compounds in the sample. For example, sample data for “GRO” range compounds should not be reported as “TPHg.” Sample data for “DRO” and “RRO” range compounds should not be reported as “TPHd” or “TPHo.”

The resulting summation of TPO and TEO data is compared to the TPH action level applicable to the primary category of fuel released. For example, where there has been a gasoline release, the total concentration of TPO and TEO compounds in a sample (minus BTEX) should be compared to action levels for TPH_{gasolines}. In the case of suspected contamination by diesel or another middle distillate fuel, the sum of TPO plus TEO data is compared to action levels for TPH_{middle distillates}. A similar approach is applied for comparison of laboratory data to action levels for TPH_{residual fuels}. If the nature of the fuel release is uncertain or in cases of releases of multiple fuel types, then the sum of TPO and TEO should be compared to the fuel category with the most conservative action levels unless other supporting information is provided.

Determination of the primary type of fuel released in water based on a review of chromatograms is more complicated for water than for soil or air. Dissolution of hydrocarbons into water will be biased toward more soluble, aromatic compounds. The resulting mix of dissolved-phase compounds in water as reflected in the chromatogram will therefore be different from a chromatogram of the neat 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. Compounds of >C8 aromatics that might elute in the DRO range are likely to be minimal.

As the compounds degrade and become less volatile, however, original GRO-range compounds will begin to elute at a higher boiling point, with some compounds beginning to appear on the chromatogram in the DRO range (Figure 3). The sum of the GRO-range and DRO-range compounds represents the total concentration of TPH for the sample and would be compared to action levels for TPH_{gasolines}. Compounds associated with degraded middle distillate fuels such as diesel or jet fuel could similarly elute in the RRO range of the chromatogram. The estimated concentration of these compounds is added to the estimate concentration of DRO-range compounds to generate a sum TPH concentration for the sample as a whole. This is then compared to action levels for TPH_{middle distillates}.

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 of a chromatogram 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 range of dissolved “TPH” in a sample could therefore span all three ranges on a chromatogram.

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., HDOH 2022).

Preparation of case-specific TPH action levels will normally be undertaken by the responsible party but might need to be generated by HDOH in some instances. In either situation, the case-specific EAL and the rationale for its calculation must be reviewed and approved by HDOH. 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 HDOH 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

The Method 8015 Method Detection Level should be no greater than the TPH action level for the subject fuel category (e.g., 91 µg/L for TPH(middle distillates). Sample data for Total Purgeable Organics (e.g., GRO) or Total Extractable Organics (e.g., DRO or RRO) below the laboratory Method 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 TPO range compounds in water. An MRL of 200 µg/L or higher is common for reporting of TEO range compounds, including both “DRO” and “RRO.” Sample data below the MRL are normally qualified with “J” flag in the laboratory report. This indicates that the specific nature of the organic compounds identified is certain. “J-flagged” data should be reported as “TPO” and “TEO” by the laboratory, rather than “TPH.” 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 TEO-related organic matter detected below the typical MRL of 200 µg/L. In cases where J-flagged data could reflect hydrocarbon-related contamination and the sum concentration of TPO and TOE data exceeds the TPH action level, the sample should be immediately retested using Mass Spectrometry (MS) methods (e.g., Method 8260 for volatiles and Method 8270 for semi-volatiles). 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 (refer to attached Forensics Fact Sheet; Newfields 2024). This initially includes direct comparison of Method 8015 TPH data to applicable risk-based action levels. Additional consideration of data based on Non-Volatile Dissolved Organic Carbon (NVDOC) analysis or similar test methods might be required for heavily degraded plumes if Method 8015 data are suspected to underestimate the total concentration of polar, hydrocarbon-related metabolites present (USGS 2024).

If the GC-MS review suggests that the compounds are unlikely to be related to hydrocarbons, then the data do not need to be incorporated into calculation of TPH. Consult with HODOH to determine if identification of nonpetroleum-related compounds requires additional action, including other identified contaminants and/or naturally occurring biogenic matter that could indicate elevated levels of bacteria in the water.

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 this approach differs from the recommended use of the MRL as an action level for other type of contaminants when it exceeds the corresponding action level (refer to Volume 1, Section 2.3 of the EAL guidance). The MRL is not used as an action level in the case of TPH.

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 HODOH.

“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 HODOH.

Quantification of TPH in Other Media

Summation 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.

USGS, 2024, *Distribution of Ancient Carbon in Groundwater and Soil Gas from Degradation of Petroleum near the Red Hill Bulk Fuel Storage Facility, O'ahu, Hawai'i*: U.S. Geological Survey, Scientific Investigations Report 2024–5034.

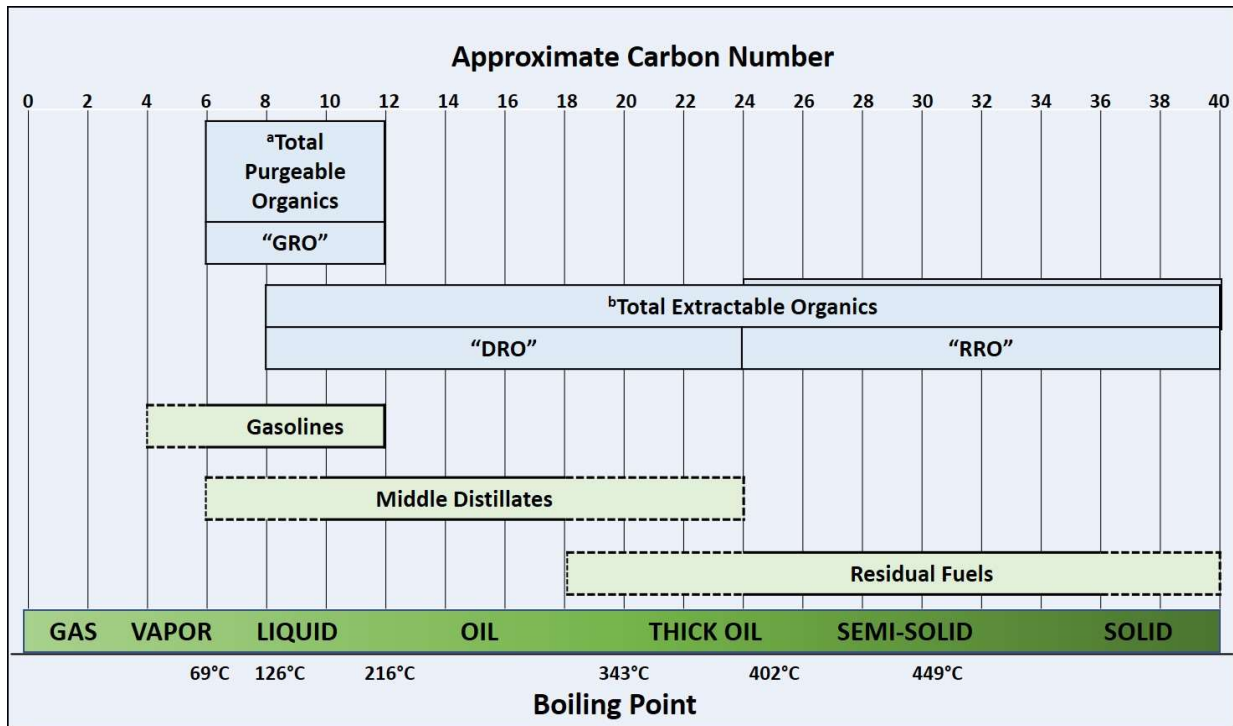


Figure 1. Comparison of fuel categories to laboratory analytical methods and reporting ranges; a) Total Purgeable Organics (TPO) methods are used to quantify volatile compounds (e.g., Method 8260 for “GRO”), b) Total Extractable Organics (TEO) methods are used to quantify semi-volatile compounds (e.g.,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

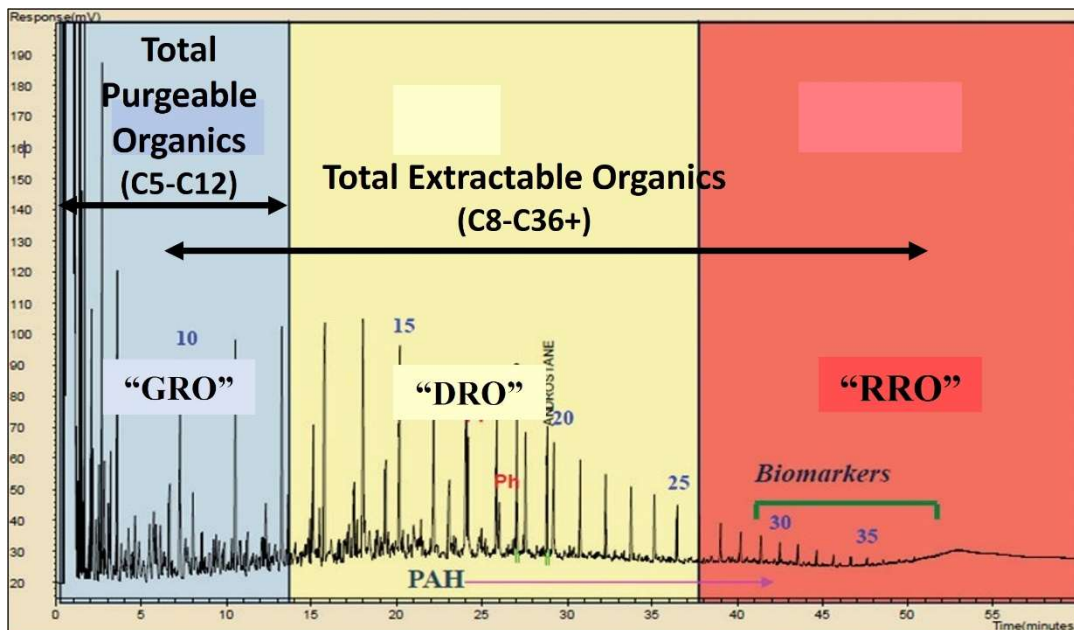


Figure 2. Chromatogram depicting TPO and TEO analytical method ranges and associated “GRO,” “DRO” and “RRO” reporting ranges sometimes used by laboratories. “TPH” is equal to the sum of the full range of petroleum-related compounds in the sample (TPH = TPO+TEO or GRO+DRO+RRO).

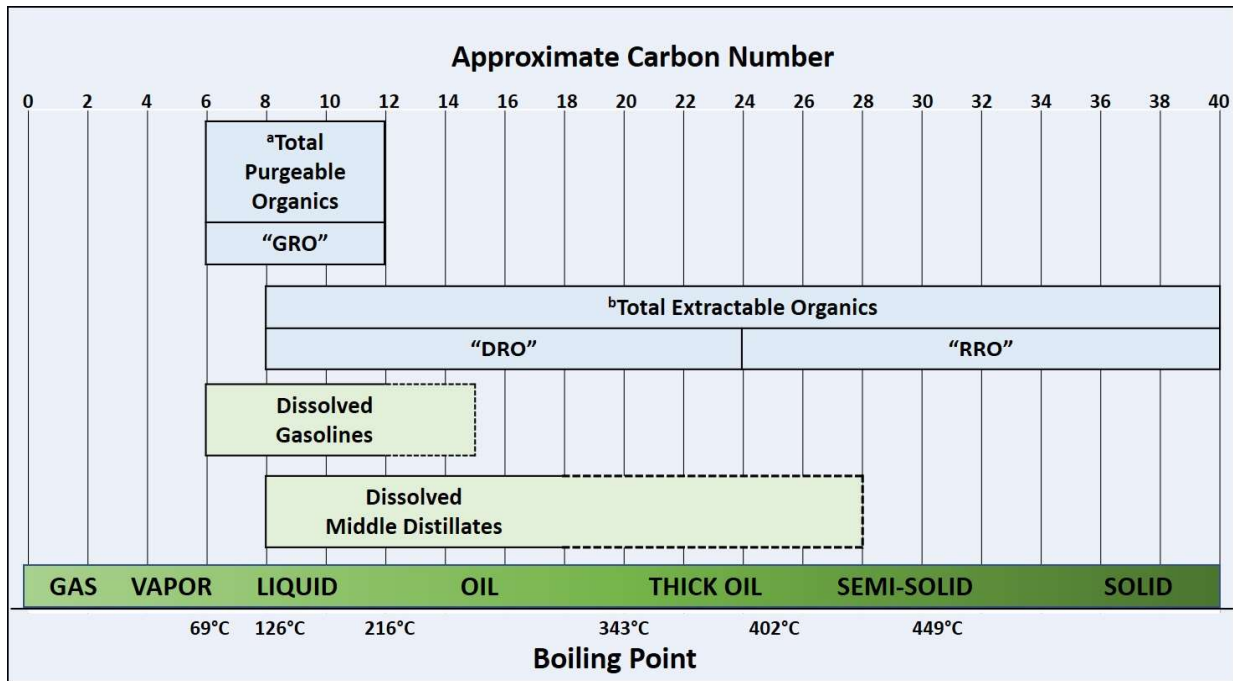


Figure 3. Comparison of partially degraded, dissolved-phased petroleum in water to laboratory analytical methods and reporting ranges. Note potential spread of fuel-related degradation compounds into higher boiling point ranges in comparison to Figure 1.

Forensic Drinking Water Characterization (Newfields, June 2024)

Forensic Water Characterization

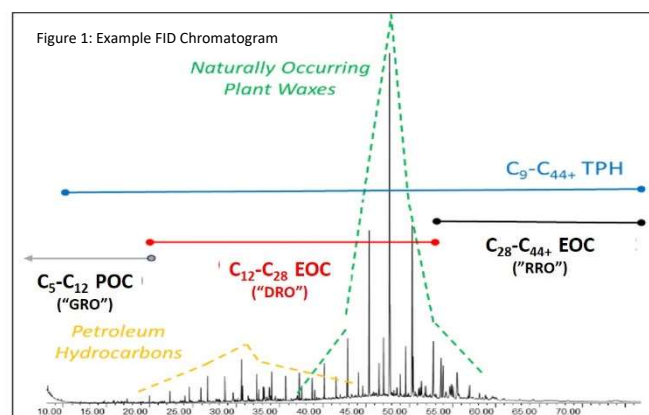
Identifying Purgeable and Extractable Chemicals Included in Total Petroleum Hydrocarbon Measurements
Prepared for the Hawaii Department of Health (HIDOH)

Introduction

Total Petroleum Hydrocarbon (TPH) analysis is a conventional laboratory technique used for monitoring 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 semi-volatile extractable organic compounds (EOC) in the C_8 to C_{44+} carbon range. Total C_8 to C_{44+} EOC is commonly measured in two carbon ranges reported as “Diesel Range Organics (DRO)” and “Residual Range Organics (RRO).” Volatile TPH analysis conducted using methods like USEPA Method 8260D by GC Mass Spectrometry (GC/MS) provide a bulk measurement of the purgeable organic compounds (POC) in the C_5 to C_{12} carbon range and is commonly reported as “Gasoline Range Organics (GRO).” The HIDOH calculates the total concentration of volatile and semi-volatile TPH as the sum of POC + EOC (Figure 1). The HIDOH prefers the terms POC and EOC to indicate that these bulk measurements can include both petroleum and non-petroleum constituents.

GC/FID analysis cannot identify the specific chemicals reported within a bulk measurement. At higher relative concentrations it may be clear that a water sample contains petroleum hydrocarbons, but at low levels confirmation analysis is needed to identify the chemical constituents. When analyzing samples with 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 related to other non-petroleum organic contaminants or naturally occurring biogenic materials (e.g. plant waxes, organic acids).

Figure 1 provides an example of a water sample with both petroleum hydrocarbons and naturally occurring plant waxes. In this example the EOC (DRO and RRO) measurements include impacts from both petroleum and naturally occurring chemicals and contain a high bias due to non-petroleum constituents. EPA Method 8015D analysis cannot differentiate between these classes of chemicals. Volatile POC (GRO) measurements, or semi-volatile EOC (DRO or RRO) measurements performed using a mass specific analysis like GC/MS can more readily differentiate between petroleum- and non-petroleum-related compounds.



Recommended Forensic Analysis for Low-Level TPH Characterization

Forensic methods are designed to characterize source materials and are optimized for low-level sample analysis. To maximize the extraction efficiency of both non-polar and polar hydrocarbons, samples should be prepared following USEPA Method 8270E’s guidance for acid, base and neutral extraction with dichloromethane (DCM)([EPA Method 8270E, 1.4.8](#)). It is important to note that solvents such as hexane have lower relative extraction efficiencies than DCM and may underrepresent polar and oxygenated hydrocarbons measured during sample analysis. Oxygenated hydrocarbon compounds are assumed to have the same toxicity as the parent hydrocarbons under HIDOH guidance (HIDOH 2024). When characterizing low level EOC (DRO or RRO) results it is recommended to follow a tiered analytical approach (Figure 2):

- ❖ 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 petroleum source materials.
- ❖ Tier II: Confirmation Testing by GC/MS
 - Samples reporting low level POC (GRO), or EOC (DRO or RRO) results are further analyzed in Tier II by EPA Method 8260D for C₅-C₁₂ purgeable organics and Method 8270E C₈-C₄₄₊ for extractable organics to screen for the presence of petroleum and other non-petroleum chemicals. This type of GC/MS analysis is used to perform both target and non-target analysis (NTA) and to detect tentatively identified compounds (TICs) that can be used to characterize the purgeable, and extractable constituents present in low level EOC (DRO or RRO) measurements. Tier II analysis will help determine if EOC (DRO or RRO) measurements are truly related to petroleum hydrocarbons or contain other non-petroleum-related constituents. Tier II GC/MS analysis must achieve sufficient instrument sensitivity and should target reporting limits between 1.0 and 5.0 µg/L for C₅-C₁₂ purgeable organics and C₈-C₄₄₊ extractable organics.
 - EICP Petroleum Hydrocarbon Screening: Samples reporting low-level EOC (DRO or RRO) measurements are screened for the presence of petroleum hydrocarbons using GC/MS extracted ion current profiles (EICPs) that include petroleum specific diagnostic ions. EICPs provide a broad screening metric by which samples can be qualitatively evaluated for known chromatographic patterns of target and non-target petroleum hydrocarbon compounds. Samples should be screened for EICPs that monitor saturated hydrocarbons (m/z 43, 57, 85), alkylated benzenes (m/z 78, 92, 106, 120, 134), alkylated naphthalenes (m/z 128, 142, 156, 170, 184) and alkylated phenanthrenes and anthracenes (m/z 178, 192, 206, 220, 234). EICP screening can determine if petroleum hydrocarbons are present above the detection limit.
 - Non-Petroleum NTA and TIC Analysis: If GC/MS chromatograms contain NTA peaks arising from non-petroleum sources, the peaks are further analyzed using mass spectral analysis. The mass spectrum of NTAs is compared to a NIST library of mass spectrum and is assigned a tentatively identified compound name (TIC). TICs should be carefully reviewed for the quality of spectral matches between samples and the NIST library. A project specific threshold should be established for acceptable TIC quality scores (e.g. >50%) and only TICs with acceptable quality scores should be used in low-level TPH characterization.
- ❖ Tier III: Petroleum Characterization
 - If suspected petroleum-related compounds are present, samples can be further analyzed by modified forensic Methods 8260D-PIANO volatile organic compounds (paraffins, isoparaffins, aromatics, naphthenes and olefins) and 8270E-Alkylated PAHs. These methods are designed to chemically characterize petroleum hydrocarbon residues, determine source type, and evaluate the degree of environmental weathering. Consult HODOH guidance for appropriate use of data for potential assessment of risk beyond initial forensic analysis (HODOH 2024).

If petroleum-related compounds are identified during sample analysis, including the presence of parent and alkylated petroleum hydrocarbons and/or petroleum hydrocarbon-related degradation compounds, then HODOH guidance should be reviewed to determine appropriate additional actions. This can include direct comparison of Method 8015 TPH data to risk-based action levels published by the agency. Additional consideration of data based on Non-Volatile Dissolved Organic Carbon (NVDOC) analysis or similar test methods might be required in some cases to more accurately estimate the total concentration of hydrocarbon-related metabolites present in a sample (USGS 2024).

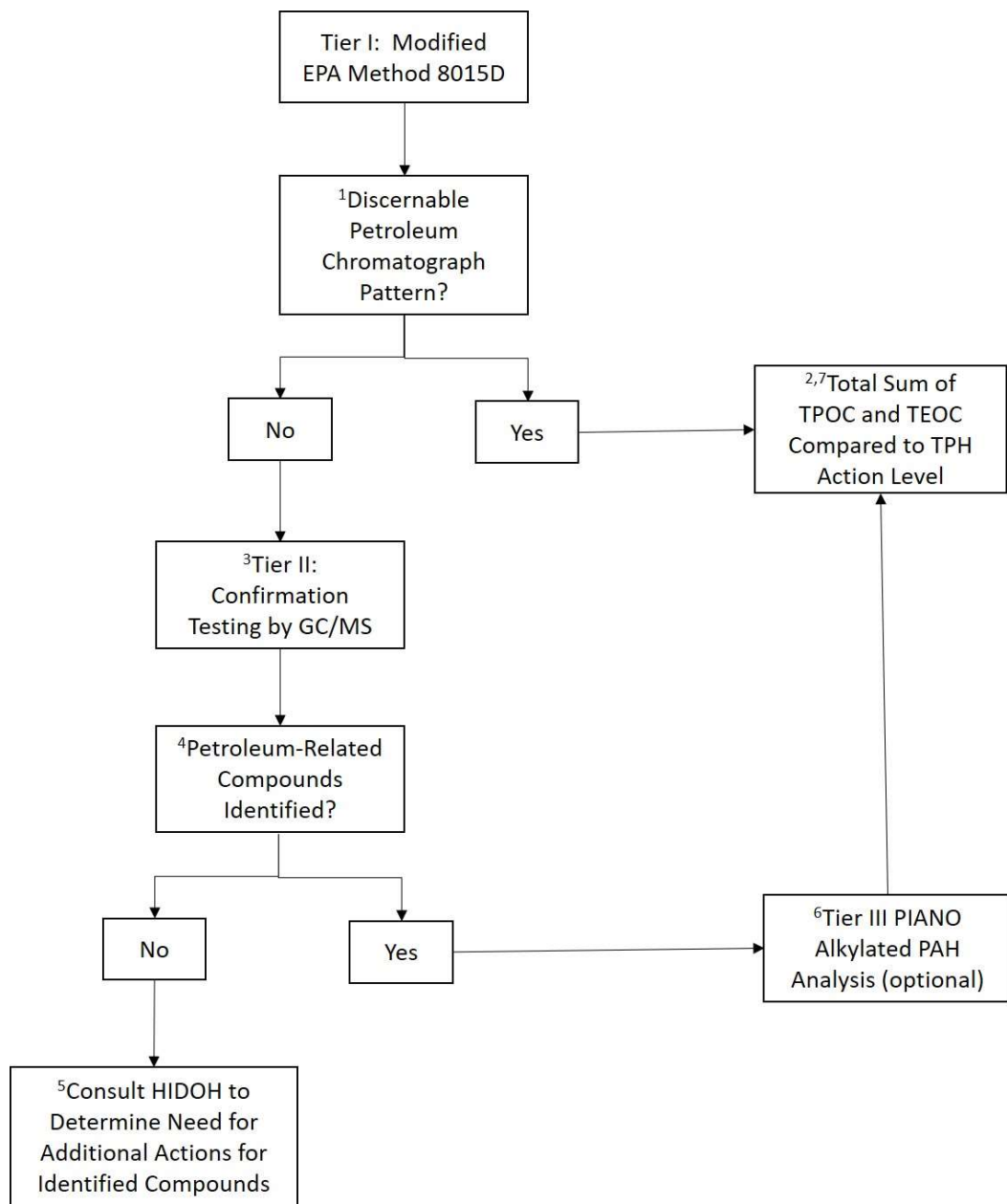
References:

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

USGS, 2024, Distribution of Ancient Carbon in Groundwater and Soil Gas from Degradation of Petroleum near the Red Hill Bulk Fuel Storage Facility, O'ahu, Hawai'i: U.S. Geological Survey, Scientific Investigations Report 2024–5034.

Figure 2. Tiered approach to Forensic Water Characterization (HIDOH 2024).

Follow this tiered approach for samples reporting positive TPH results and consult HIDOH for regulatory guidance.



Hawaii DOH 2024 Technical Notes:

1. **Tier I: (quantitative):** Petroleum hydrocarbon patterns are not generally discernable at concentrations below the laboratory Method Reporting Level (MRL) for GRO, DRO, and RRO methods (i.e. purgeable and extractable organic compounds). The HIDOH target MRL for petroleum-related GRO (Total Purgeable Organic Compounds, C₅-C₁₂) is 50 µg/L. The HIDOH target MRL for petroleum-related DRO and RRO (i.e. Total Extractable Organic Compounds, C₈-C₄₄) is 200 µg/L. High resolution GC/FID fingerprints provide greater separation between carbon ranges and allow for a more accurate assessment of potential source materials
2. **Total Petroleum Hydrocarbons (TPH)** concentrations are estimated by HIDOH as the sum of POC (GRO), and EOC (DRO and RRO) minus the concentration of organic compounds not related to petroleum hydrocarbon sources (HIDOH 2024). TPH results should be compared to the HIDOH petroleum hydrocarbon action level most appropriate for the type of fuel release.
3. **Tier II (qualitative):** Samples are analyzed by EPA Method 8260D for C₅-C₁₂ purgeable organic compounds and Method 8270E C₈-C₄₄₊ for extractable organic compounds to characterize the chemical constituents present in POC (GRO), or EOC (DRO and RRO) measurements. EPA Methods 8260D and 8270E are used to screen samples for the presence of petroleum and other non-petroleum chemicals.
4. **Petroleum-Related Compounds:** Include identifiable petroleum-related hydrocarbon compounds as well as suspected petroleum-related degradation compounds, including partially oxidized aromatics and aliphatics.
5. **Non-Petroleum-Related Compounds:** Consult with HIDOH to determine if identification of non-petroleum-related compounds requires additional action, including other identified contaminants and/or naturally occurring biogenic matter.
6. **Tier III (quantitative):** According to HIDOH guidance, additional testing of a sample using PIANO-VOC and alkylated PAH analyses when petroleum-related compounds have been tentatively identified is optional. Toxicity factors and risk-based action/screening levels may be available for some compounds in addition to benzene, toluene, ethylbenzene, xylenes, naphthalene, and methylnaphthalene (BTEXNM). Note that non-BTEXNM, petroleum-related compounds are by default considered in bulk aromatic and aliphatic carbon range groupings used to develop weighted toxicity factors and risk-based action levels for TPH (refer to Appendix 1, Section 6 of the HIDOH EAL guidance). The individual assessment of petroleum-related compounds other than BTEXNM is not normally necessary since these compounds are included under the umbrella category of TPH. Proposals for separate assessment of individual chemicals and/or use of alternative methods to assess the weighted toxicity of TPH-related compounds should be presented to HIDOH for review and approval.