NewFields

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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: Example FID Chromatogram

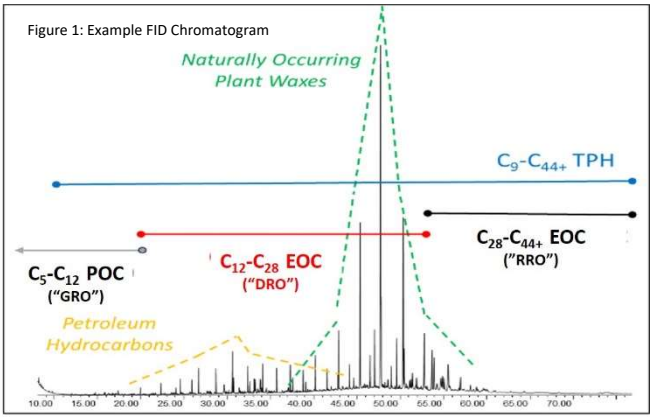


Figure 1 provides an example of a water sample with both petroleum hydrocarbons and naturally occurring plant waxes. In this example the EOC (DRO and RRO) measurements include impacts from both petroleum and naturally occurring chemicals and contain a high bias due to non-petroleum constituents. EPA 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 C_5-C_{12} purgeable organics and Method 8270E C_8-C_{44+} 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 C_5-C_{12} purgeable organics and C_8-C_{44+} 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 HIDOH guidance for appropriate use of data for potential assessment of risk beyond initial forensic analysis (HIDOH 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 HIDOH 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).

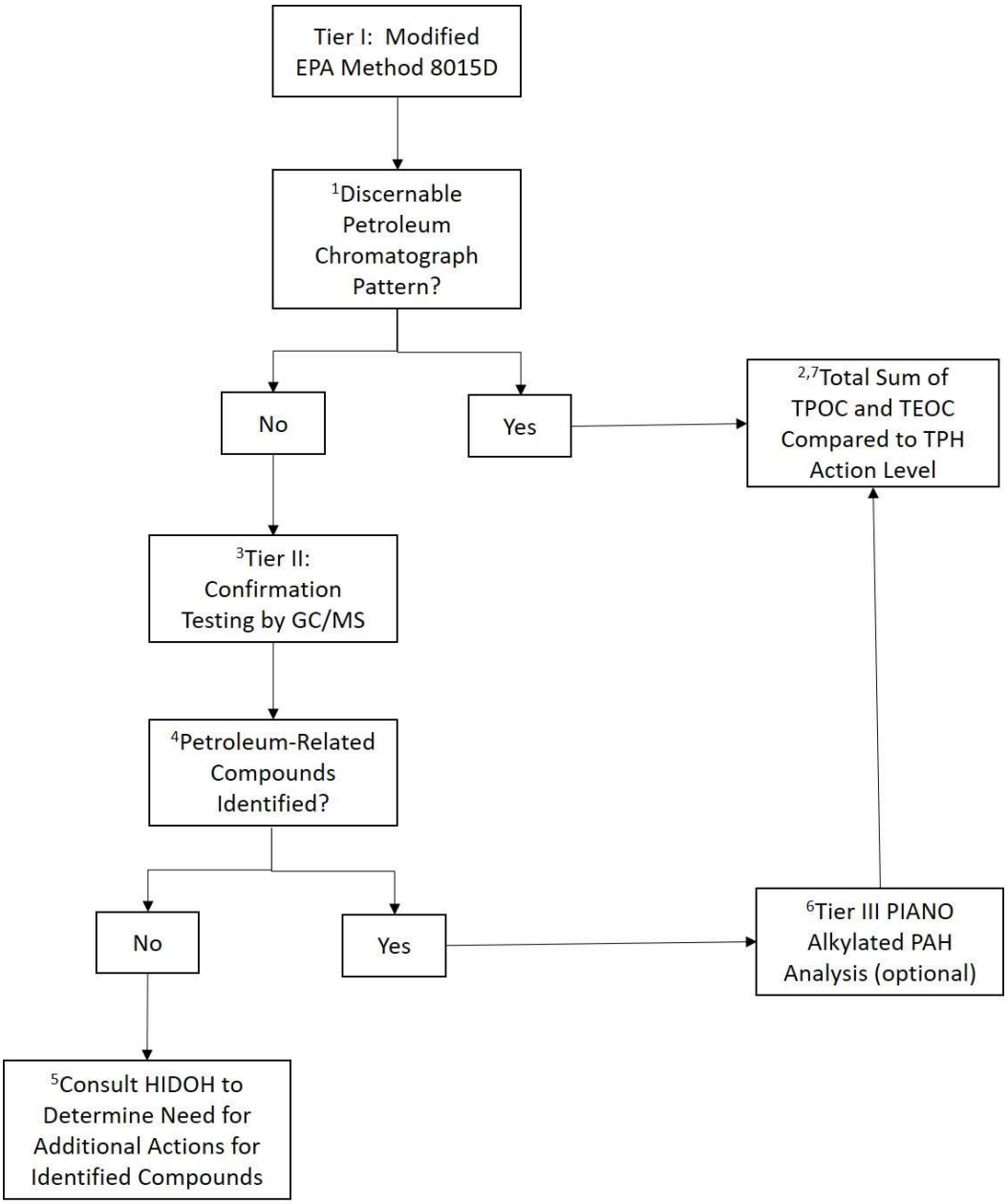
References:

HIDOH, 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.



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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, C_5-C_{12}) is 50 µg/L. The HIDOH target MRL for petroleum-related DRO and RRO (i.e. Total Extractable Organic Compounds, C_8-C_{44}) 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 C_5-C_{12} purgeable organic compounds and Method 8270E C_8-C_{44+} 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 BTEXNN 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.