

What Are Chromatograms?

Behind every TPH number calculated using a gas chromatography- (GC) based method, e.g., EPA Method 8015 and TX1005, is a chromatogram. Chromatograms record the magnitude of compounds as they elute off the GC and reveal the carbon range of hydrocarbons present in a sample. Other compounds, such as oxygen-containing compounds, elute at apparent higher carbon numbers than hydrocarbons with the same number of carbons. Compounds will elute according to their boiling point, with the most volatile compounds present on the left side of the chromatogram and the less volatile compounds present at increasing times on the x-axis as shown in Figure A5-1. The exact time a compound will appear in the chromatogram will vary depending on the GC method parameters and the stationary phase in the GC column, so calibration standards are needed to accurately determine the elution time for compounds of interest.

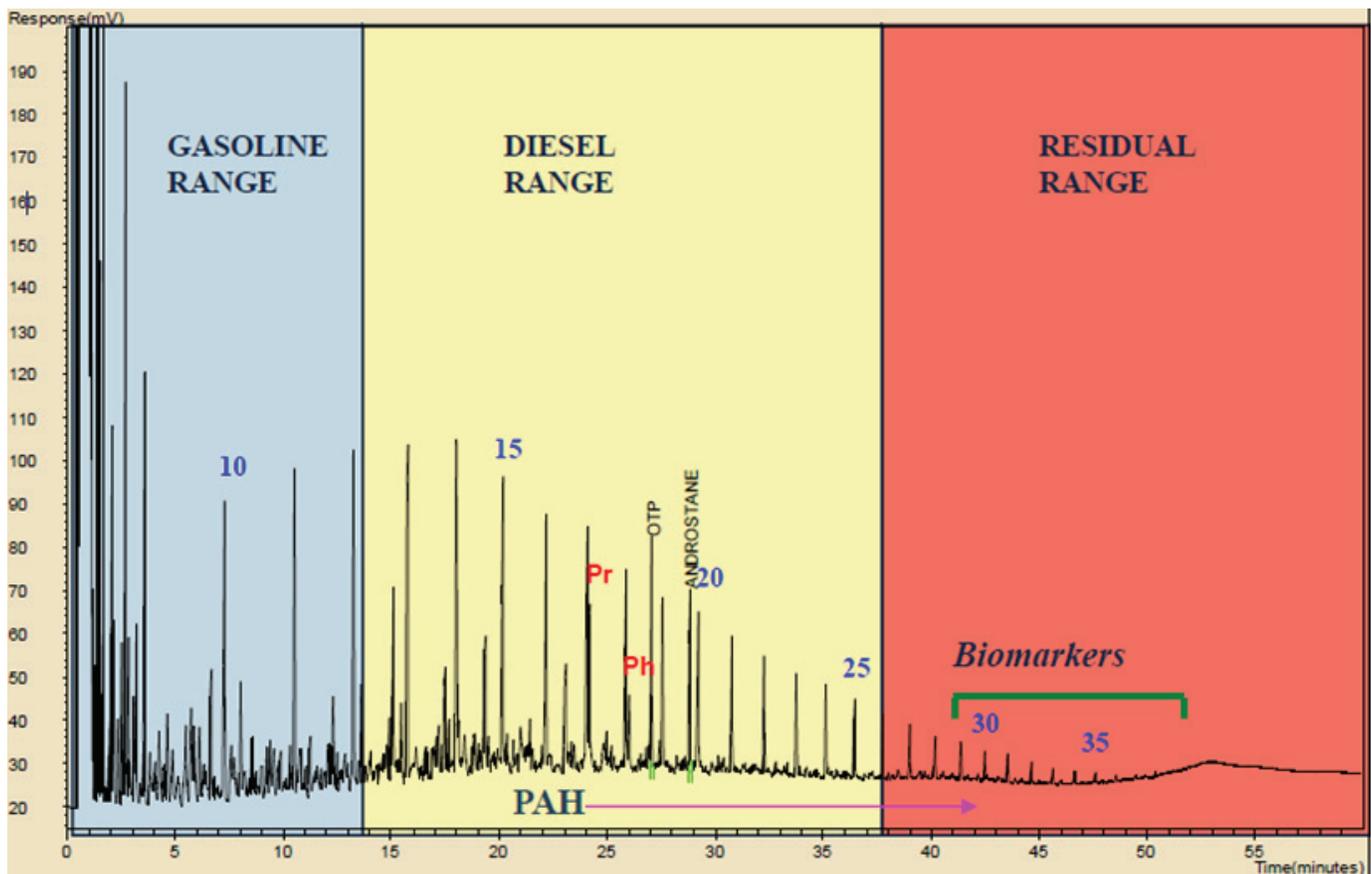


Figure A5-1. Chromatogram of a crude oil. Due to the nonspecific nature of the TPH analysis, TPH chromatograms should be routinely reviewed as part of the QA/QC process before TPH analytical results are used for decision making and if one ever receives questionable TPH results from the laboratory, one of the first actions should be a review of the chromatograms.
(Source: Modified after Chevron, ETC, OT&S, 2018.)

A.5 Chromatograms: A Wealth of Information *continued*

What Can Chromatograms Tell You?

Reviewing chromatograms is useful for reducing uncertainties inherent to TPH analysis. Although individual compounds frequently cannot be identified using the low-resolution GC methods or with nonselective detectors due to the large number of isomers, other valuable information can be obtained, including:

- type of material
- weathering
- presence of nonhydrocarbons
- presence of solvents and other interferents
- poor integration, which can lead to biased TPH concentrations (see Section 4)
- presence of nondissolved compounds.

Figure A5-2 shows typical chromatograms of a crude oil and common products. Because the x-axis is the same for the common products chromatograms, one can directly compare the elution times between the chromatograms. As expected due to the carbon ranges for each of the products, the elution times for the products increases from gasoline to jet to diesel. Crude oil spans the entire carbon range.

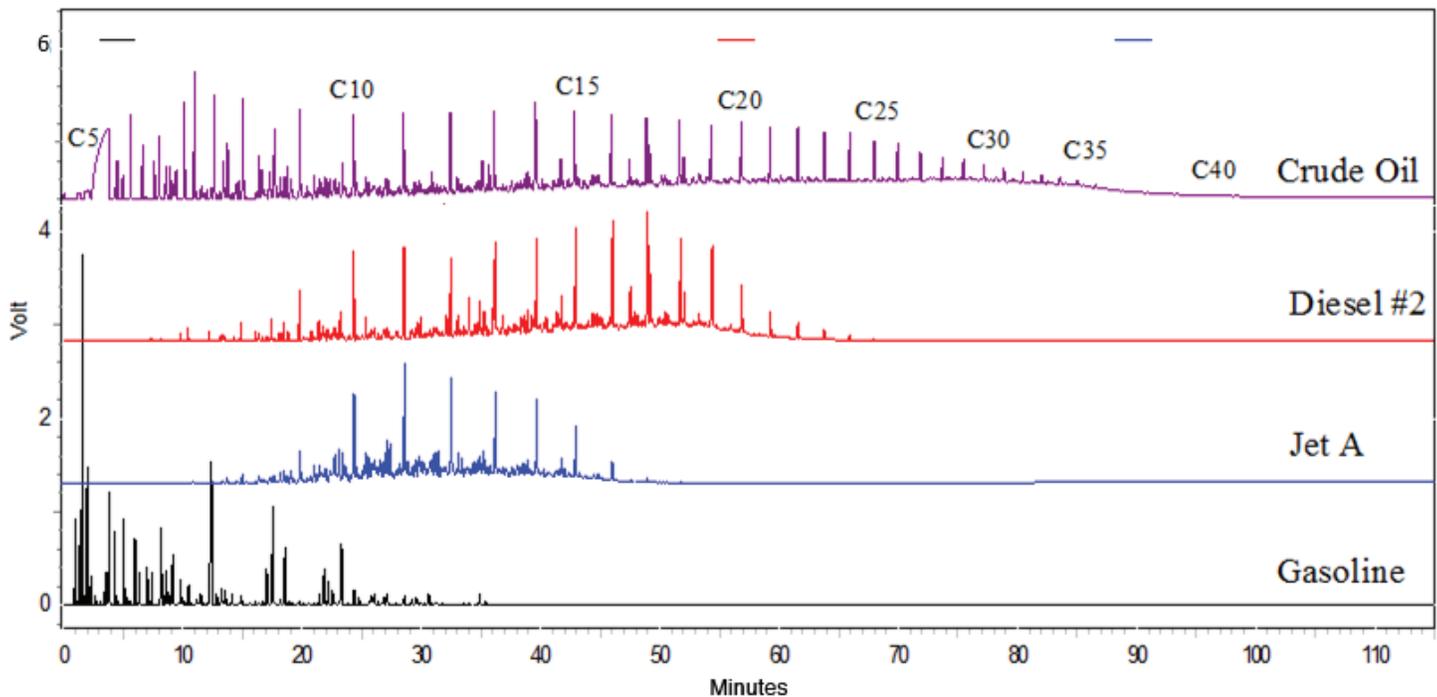


Figure A5-2. Typical chromatograms of a crude oil and common products. Note: The x-axis is the same for all chromatograms.

(Source: Chevron, ETC, OT&S, 2018.)

The chromatographic profile changes with environmental weathering of petroleum mixtures, but in predictable ways. Biodegradation can alter the relative distribution of hydrocarbons. In general, under aerobic conditions, n-alkanes are relatively easy to biodegrade. In most crude oils and middle distillates like diesel, n-alkanes are the most predominant features, as shown by the asterisks on the upper chromatogram of Figure A5-3 (Rhodes 2017). Biodegradation is evident in the bottom chromatogram in Figure A5-3 by the depletion of n-alkanes and the visible residual isoprenoids or highly branched alkanes. The “hump” or unresolved complex mixture (UCM) is largely composed of branched alkanes, cycloalkanes, and naphthene-aromatics. These types of chromatograms are useful in assessing the degree of weathering and in monitoring remediation progress. A good indicator of anaerobic degradation is the loss of toluene and relative increase of ethylbenzene in relation to xylenes with no significant loss of volatiles (Beller et al. 1995).

A.5 Chromatograms: A Wealth of Information *continued*

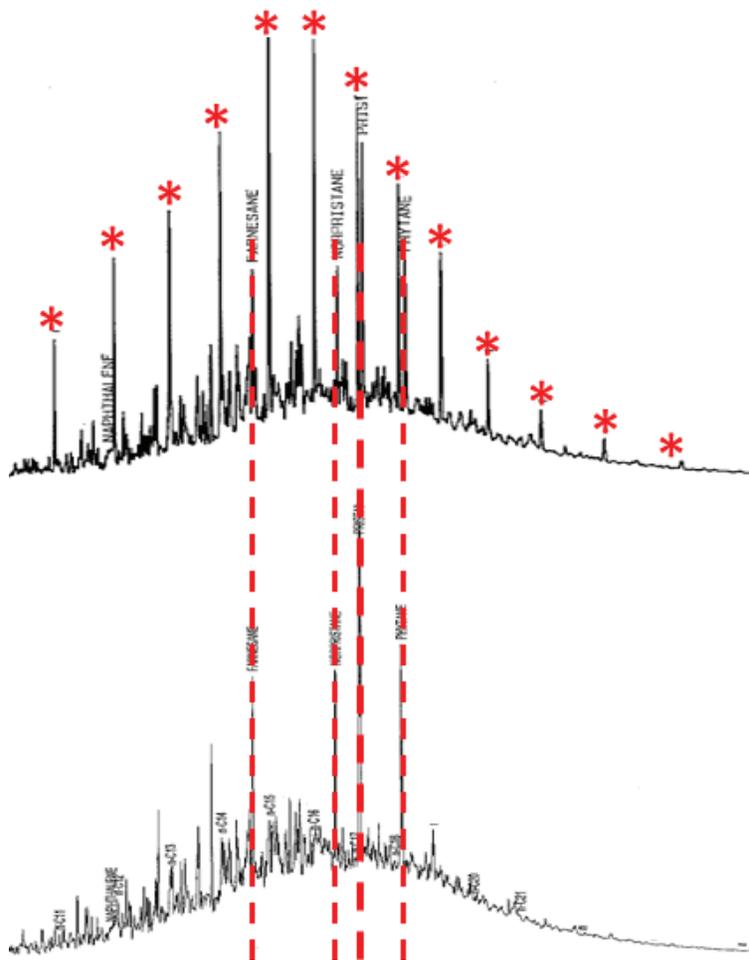


Figure A5-3. Highly branched alkanes remain after biodegradation

Figure A5-4 shows chromatograms of fresh gasolines and gasolines from monitoring wells. It illustrates the use of chromatographic profiles to assess degree and potentially types of weathering. Loss of volatiles is evident by relative reduction in the peaks from compounds lighter than toluene and the relative increase in later-eluting heavier compounds.

A.5 Chromatograms: A Wealth of Information *continued*

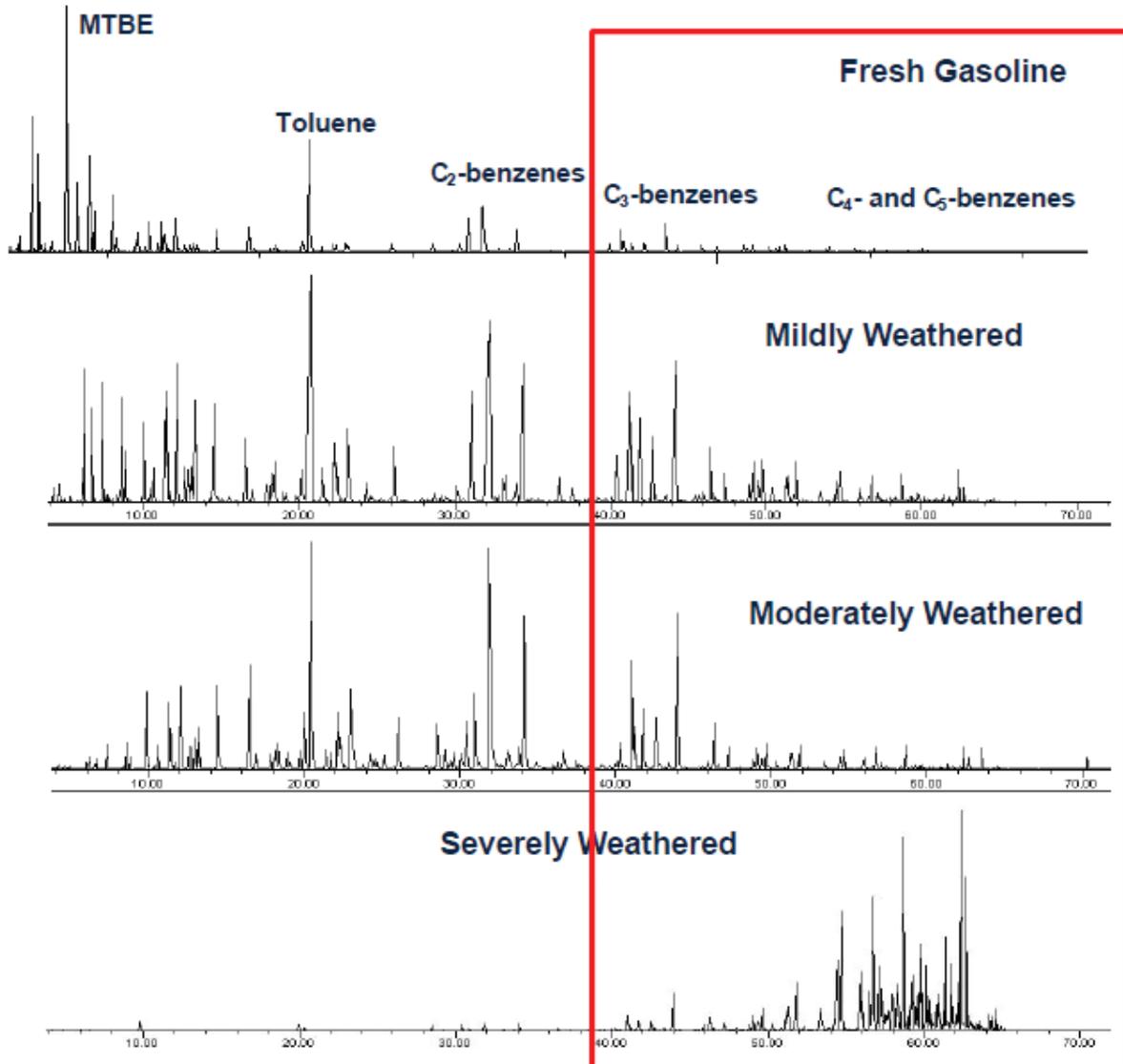
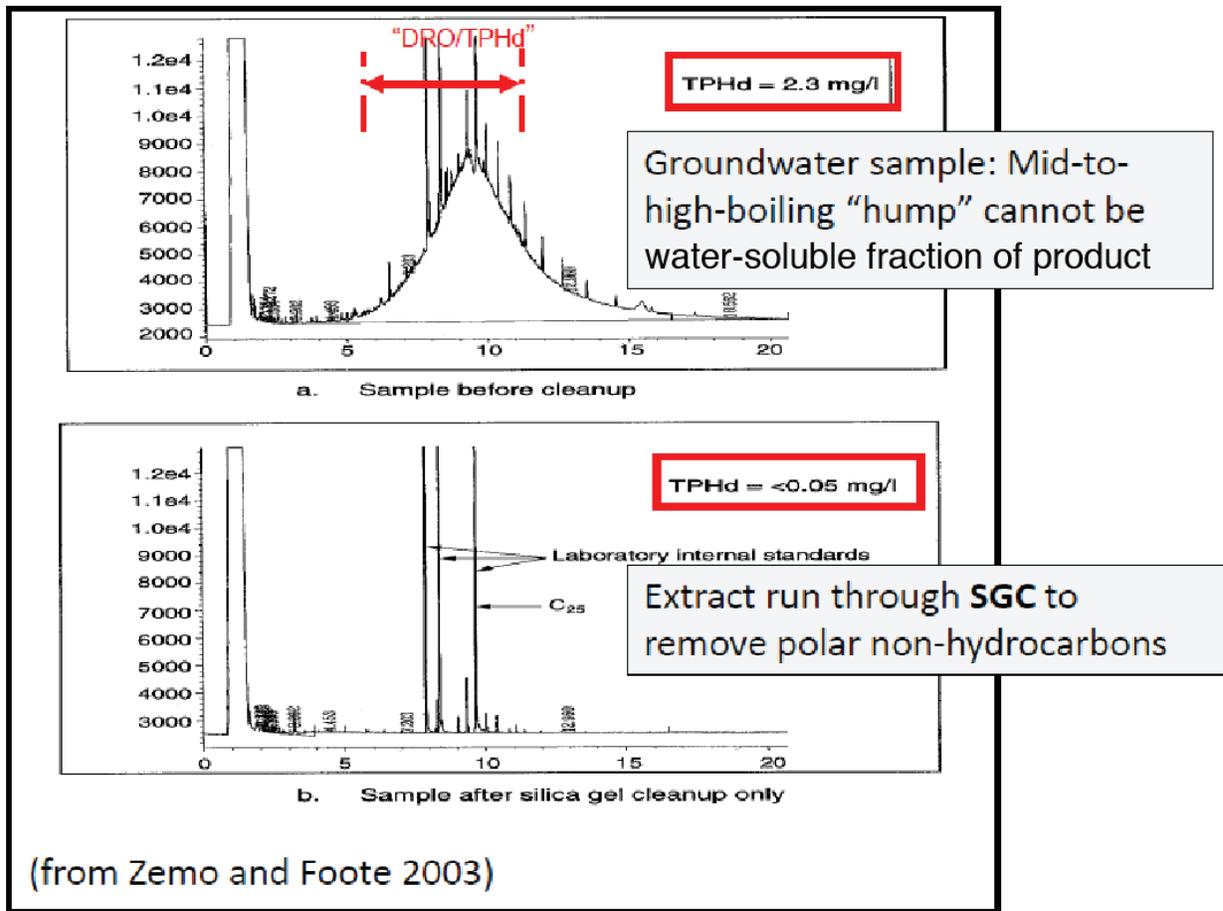


Figure A5-4. Distribution of compounds changes with weathering

(Source: Stout, S.A., Douglas, G.S., and Uhler, A.D., 2006.)

A review of chromatograms can also reveal the presence of nondissolved and polar nonhydrocarbons. The upper chromatogram in Figure A5-5 shows organic material extracted from a groundwater sample in the C15 and above carbon numbers. One would not expect to detect this carbon range as part of the water-soluble fraction due to the effective solubility of aromatic compounds with carbon numbers greater than 15 and aliphatic compounds less than C₈. This indicates that either there is a nondissolved hydrocarbon component or there are nonhydrocarbons present. Silica gel cleanup can be used to determine if the “hump” is due to nondissolved hydrocarbons or polar nonhydrocarbons. In the bottom chromatogram of Figure A5-5 the removal of the “hump” and lowered TPH-d concentration indicate that the compounds were polar nonhydrocarbons instead of nondissolved hydrocarbons.

A.5 Chromatograms: A Wealth of Information *continued*



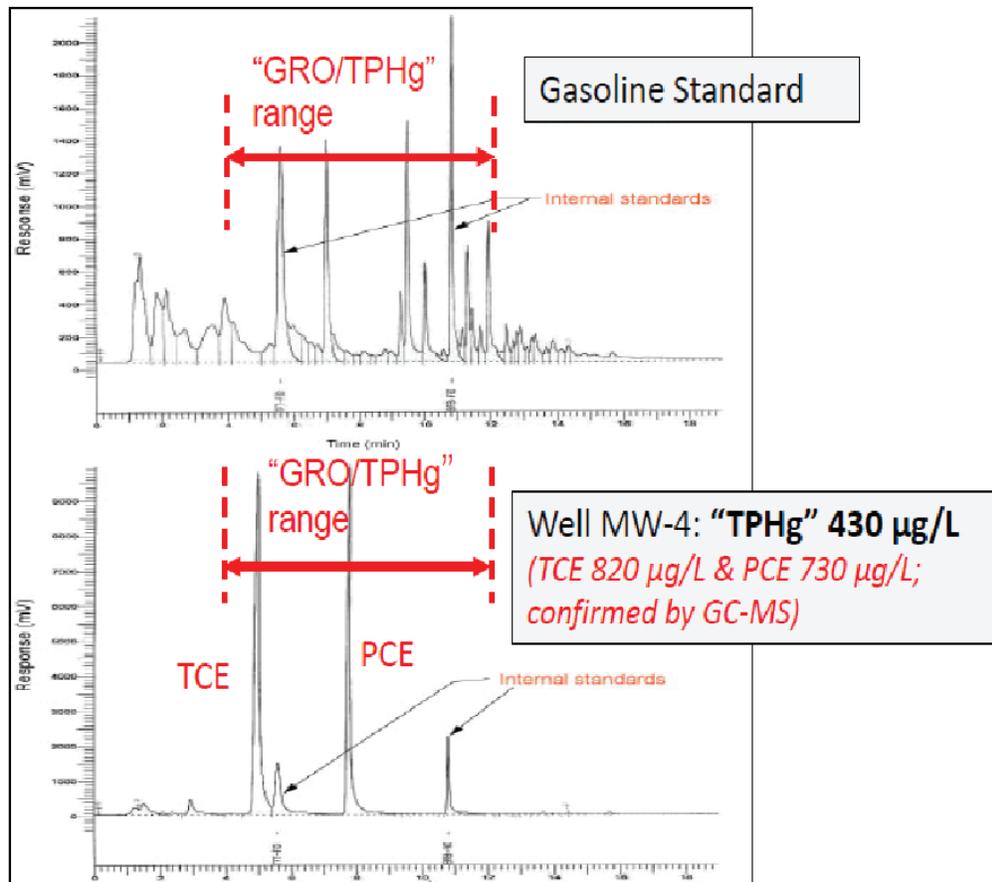
(from Zemo and Foote 2003)

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Figure A5-5. Example of biodegrading metabolites in groundwater within the TPH reporting range (Zemo 2016)
(Source: Zemo and Foote, 2003.)

There are many possible organic interferences that will appear in the TPH portion of the chromatogram. Two examples are shown in Figures A5-6 (solvents) and A5-7 (natural organics). The lower chromatogram in Figure A5-6 reveals that only four major compounds are responsible for the "TPH" concentration; however, none of these are petroleum hydrocarbons. Figure A5-7 demonstrates that natural organics can be difficult to differentiate from petroleum hydrocarbons, and in this instance, the spatial relationship to the presumed petroleum source area should be used as supplemental evidence as to the source of the organics.

A.5 Chromatograms: A Wealth of Information *continued*

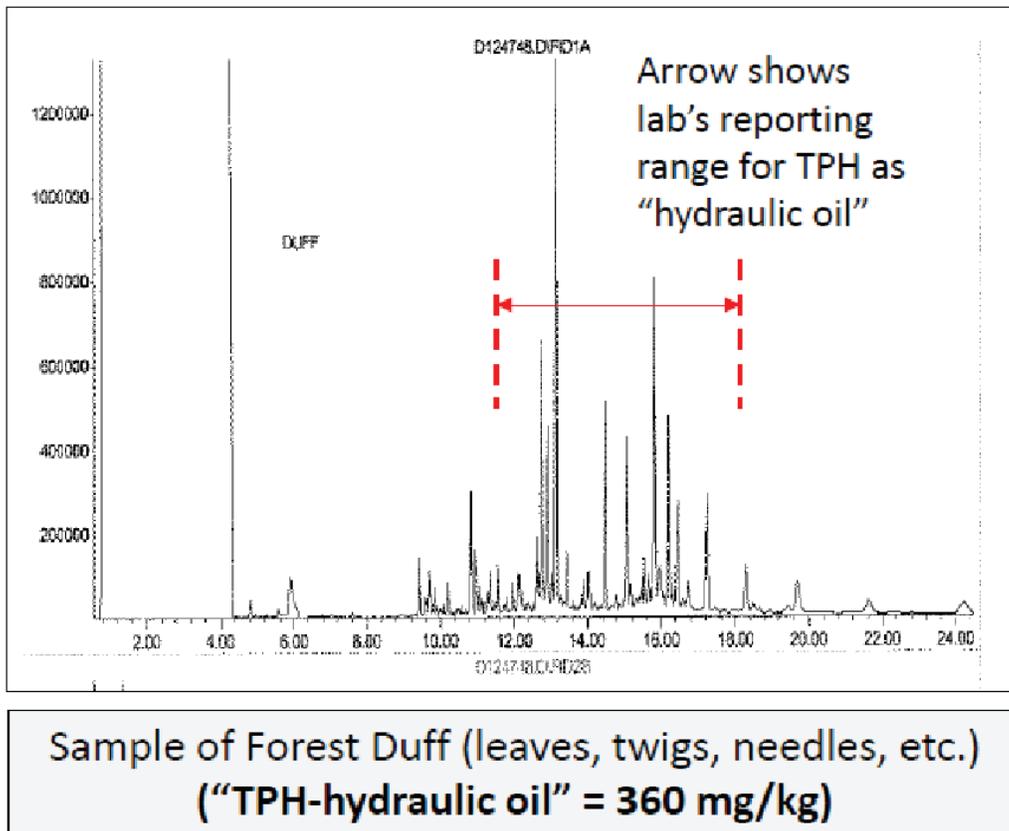


(from Foote and Zemo 2008)

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Figure A5-6. Example of CVOCs in groundwater within the GRO reporting range (Zemo 2016)
(Source: Foote and Zemo, 2008.)

A.5 Chromatograms: A Wealth of Information *continued*



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Figure A5-7. Example of natural organics (vegetative material) within TPH reporting range (Zemo 2016)
 (Source: Zemo and Associates. 2018.)



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