4 TPH Fundamentals

Petroleum release sites are often evaluated for potential environmental impact based on screening levels, or risk assessments, of a few individual compounds with well-characterized toxic effects typically found in petroleum products. However, petroleum releases originating from crude oil or crude oil-based products (e.g., gasoline, diesel fuel) contain complex mixtures that must be understood thoroughly to adequately assess risk, especially in scenarios wherein the "typical" toxic compounds are no longer present.

Understanding the properties of petroleum hydrocarbons in the environment (mobile or residual) is essential for developing accurate conceptual site models (CSM) to appropriately evaluate and manage the human health and ecological risks of petroleum hydrocarbons in environmental media (see Human Health Risk and Ecological Risk Assessment).

Petroleum hydrocarbons are unique in environmental site assessment and management because they are complex mixtures of compounds with wide-ranging physical and chemical properties. Following their release into the environment, these complex petroleum mixtures are subject to change due to a multitude of processes commonly referred to as weathering (e.g., volatilization, dissolution, biodegradation, oxidation, etc.).

Assessment of these mixtures is through the estimation of *total petroleum hydrocarbons (TPH)*, a gross quantification without identification of individual constituents. In general, TPH is defined as the measurable amount of petroleum hydrocarbon in an environmental media. It is, thus, dependent on the analytical method used to measure TPH and the medium in which it is found. TPH values can be obtained from several analytical methods. The analytical methods may not limit the quantification solely to just hydrocarbons (i.e., compounds containing only hydrogen and carbon), but can include nonhydrocarbons from naturally occurring organic matter, chemicals, and petroleum-derived metabolites. The mixture will change as it weathers in the environment. Furthermore, compositions of mixtures quantified as "TPH" might be similar for nonaqueous phase liquid (NAPL), residual, and highly contaminated soils, but radically different for either water or air samples. This affects the assessment of risk to humans or ecological receptors. For a general understanding of risk assessment principles and information, see Risk Assessment Guidance for Superfund Sites USEPA 1989, Standard Guide for Risk-Based Corrective Action ASTM 2015a, and ITRC's Risk 3 guidance documents ITRC 2015.

Because the composition of TPH is not consistent (its composition changes spatially and temporally across the contaminant plume), the assessment of health effects and development screening or target levels is problematic. A common approach to estimate risk is to assign TPH into fractions or groups of compounds based on analytical, fate and transport, and exposure considerations derived from the properties of the different petroleum hydrocarbon compound classes.

Essential topics included in this section are organized under the following headings:

- Petroleum chemistry and refining
- Physical and chemical properties of petroleum constituents, TPH carbon ranges (fractions), and metabolites
- Properties of aliphatic and aromatic hydrocarbon fractions
- Alterations of petroleum mixtures in the environment through weathering processes
- Definition of "TPH" in environmental media in risk assessment

4.1 Petroleum Chemistry and Refining

The physical and chemical behavior of a petroleum release is determined by the chemical makeup of the petroleum mixture, as well as site-specific factors, including but not limited to geology, geochemistry, climate, and microbiology.

4.1.1 Petroleum Chemistry/Composition

Crude oil contains hydrocarbons (i.e., molecules consisting only of carbon and hydrogen atoms) primarily with other organic compounds typically containing sulfur, nitrogen, or oxygen (i.e., heteroatoms) and inorganic constituents, such as metals. The chemical composition of unrefined crude varies depending on its source. During the refining process, crude oil is separated into fractions of different boiling point (BP) ranges such as naphtha, gasoline, jet fuel, diesel fuel, and heavier fuel

oils. Crude oil and individual refinery products are typically characterized as TPH in environmental media.

▼*Read more*

4.1.1.1 Crude Oil Refining

Petroleum refining is the process of separating the many compounds present in crude oil by boiling it and taking distillation cuts at different temperatures (Figure 4-1). The hot gases are then passed onto the bottom of a distillation column and, as the gases cool below their BP, they condense to liquids. The liquids are drawn off of the distillation column at specific heights, ranging from heavy residues at the bottom, raw diesel fuels in the midsections and raw gasoline at the top. These raw fractions are then processed further, sometimes with other chemicals added in, into different finished products for industrial and commercial purposes. Heavy compounds and inorganic constituents remain in the residue. Common petroleum products and BP ranges are illustrated in Figure 4-2. This figure also demonstrates that products span a range of BPs and carbon numbers; thus, interpreting analytical data based on carbon number does not tell you exactly which product or products are detected.

The composition of any one of these products can vary based on the refinery involved, time of year, variation in additives or modifiers, and other factors. The chemical composition of petroleum and petroleum-based products can be further affected by weathering and/or biological modification upon release to the environment.

4.1.1.2 Petroleum Hydrocarbons

Petroleum products are complex mixtures of thousands of hydrocarbon compounds, ranging from light, volatile, short-chained organic compounds to heavy, long-chained, branched and cyclic compounds. The exact composition of petroleum products varies greatly because it is based upon the source of the crude oil and the refining practices used to produce them.

Figure 4-1. Typical refinery complex operations TPHCWG 1998a
(Source: Modified after OSHA, 1996.)

Figure 4-2. Common petroleum products and boiling point ranges TPHCWG 1998a.
(Source: TPHCWG, 1998a.)

4.1.1.3 Aliphatics and Aromatics

Petroleum hydrocarbons are organic compounds consisting of carbon and hydrogen atoms arranged in varying structural configurations. Because of differences in their environmental behavior, the most important hydrocarbon compound classes are aliphatics and aromatics. In general, aromatics are more water soluble than aliphatics with similar number of carbon atoms. Structural differences are of great significance in attenuation of the different types of hydrocarbons in the environment and what is present in TPH.

Aliphatic compounds are composed of straight-chained (also called paraffins), branched (isoparaffins), or cyclic compounds (naphthenes) and can be saturated (alkanes) or unsaturated (alkenes [olefins], alkynes, and others). Aromatic compounds have one or more conjugated benzene or heterocyclic rings within their structures and have moderate polarity that accounts for more water solubility. "Saturation" refers to whether all the valence electrons for any given carbon atom are involved in single bonds to other atoms. "Conjugated" refers to the presence of delocalized (shared) electrons within the chemical structure, such as in benzene. Common aliphatic and aromatic compounds are illustrated in Figure 4-3.

Within each hydrocarbon structural family and subfamily, there are *homologous series.* Each member of the series is termed a homolog and differs from adjacent members in the series by a repeating unit such as a methylene (CH_2) group. Within a homologous series, physical properties of compounds change with the number of carbon atoms. For example, there is an increase in the BP of approximately $68^{o}F$ ($20^{o}C$) for each carbon atom added to an *n*-alkane chain. The persistence of petroleum hydrocarbon compounds in the environment increases with an increase in the compound's BP for weathering processes caused by evaporation.

Figure 4-3. Representative aliphatic and aromatic hydrocarbons.

Another key feature of petroleum hydrocarbons is that they typically have a large number of isomers. Isomers are compounds that have the same chemical formula, but have different structural configurations. As the carbon number increases, the number of possible isomers increases rapidly (Table 4-1). The large number of isomers is one of the main reasons why it is not feasible to identify and quantify all individual compounds in TPH.

Table 4-1. Carbon number and isomeric paraffins
(Source: Wikipedia, 2018.)

Carbon Number	Number of Possible Paraffin Isomers
1	1
2	1
3	1
4	2
5	3
10	75
15	4347
20	366,319
25	36,797,588
30	4,111,846,763
40	62,491,178,805,831

▼*Read more*

4.1.2 Aliphatic Compounds

4.1.2.1 Alkanes

The simplest alkane structure is methane (CH_4), composed of a single carbon atom and four hydrogen atoms. Alkanes have the generic molecular formula of C_nH_{2n+2}. In general, straight-chain alkanes are amenable to biodegradation. Highly branched alkanes (isoalkanes) are more resistant to biodegradation.

4.1.2.2 Cycloalkanes

Cycloalkanes (naphthenes) are alkanes in which carbon atoms form cyclic structures. Cycloalkanes can exhibit *configurational isomerism* in that attached groups can differ in their positions relative to the ring. Cycloalkanes have the generic molecular formula of C_nH_{2n}. These types of compounds are relatively less amenable to biodegradation than non-cycloalkanes.

4.1.2.3 Alkenes

Alkenes are hydrocarbons that contain less hydrogen, carbon for carbon, than the corresponding alkane. Alkenes have the generic molecular formula of C_nH_{2n} with one or more double bonds. In the oil industry, alkenes are most often called olefins.

Olefins have been found in oils and condensates across the globe Curiale and B. Frolov 1998. Processes that produce alkenes include catalytic cracking, coking, and visbreaking. They are present in gasoline at low concentrations and can be biodegraded.

4.1.3 Aromatic Compounds

4.1.3.1 Monoaromatic Compounds

Aromatic hydrocarbons have ring structures with alternating single and double bonds. Benzene, the simplest aromatic

compound, is a six-membered carbon ring with the chemical formula C_6H_6. Three carbon-to-carbon single bonds alternate with three carbon-to-carbon double bonds. The bonds of benzene have electron pairs that are delocalized across the entire six-membered ring. This gives benzene more "polar" characteristics than alkanes or alkenes, because its electron clouds are easily deformed by opposite charges on other molecules. Other monoaromatic compounds such as toluene, ethylbenzene, and xylenes have side alkyl groups attached to the benzene ring. These compounds are critical for environmental risk assessment, individually and as part of TPH. These compounds have some water solubility and are relatively amenable to biodegradation.

4.1.3.2 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs have two or more fused benzene rings with and without alkyl groups attached to the multi-ringed structure. Figure 4-4 illustrates the 16 target PAHs that are most often required in environmental investigations. Not all PAHs found in the environment are from petroleum sources. They are included in TPH measurements, but they may not be from petroleum-related releases.

The two major mechanisms of formation of PAHs are petrogenic and pyrogenic. Petrogenic PAHs are formed naturally within petroleum reservoirs and coal beds, and common sources include crude oil and refined petroleum products. Pyrogenic PAHs are formed by combustion, and common sources include fires, combustion of fossil fuels and petroleum products, and coal gasification. Because individual PAHs may be found in both petrogenic and pyrogenic sources, it is the distribution of PAHs characteristic to a source that may distinguish it from others. Petrogenic and pyrogenic PAH sources have distinctive chemical fingerprints that can be used to differentiate among the various source contributions of PAHs in sediments. Numerous studies have shown that urban runoff, primarily a source of pyrogenic PAHs, is a major and widespread contributor to PAHs in sediments API 2011; Van Metre, Mahler, and Furlong 2000.

Figure 4-4. EPA target PAHs.

4.1.4 Other Components of Petroleum

Organic compounds containing sulfur, nitrogen, and oxygen may be encountered at significant concentrations in crude oil and in some heavier fuels such as No. 6 fuel oil. Sulfur-containing heterocyclic aromatic compounds are the major constituents in crude oil; sulfur can range between 0.5% and 14% by weight; however, it rarely exceeds 4% by weight and is distributed across various BPs. They are mainly in the form of thiophenes and thiophenic species. Oxygen-containing compounds in crude oil are primarily organic acids. Nitrogen heterocyclics are present as compounds of thiazole and quinoline, although they are present at much lower concentrations than the sulfur compounds. In general, nitrogen compounds in crude oil are between a few ppm to 0.8% by weight, with most crudes containing less than 4%. Nitrogen-containing compounds typically appear in distillation cuts greater than 650°F. These compounds are included in TPH measurements depending on the analytical approach used.

4.2 Physical and Chemical Properties of Petroleum Constituents, TPH Carbon Ranges (Fractions), and Metabolites

Understanding the key physical and chemical properties of petroleum constituents and mixtures is critical to interpreting the partitioning processes by which chemicals are distributed in a multiphase system. Molecular structure, size, and polarity of hydrocarbons are key factors that determine how they will partition and be transported in environmental media (air, soil, water) and also correlate to toxicological effects. Because of the fundamentally different chemical structures of aliphatics, aromatics, and metabolites, and their resulting degrees of solubility, volatility, and adsorption, the compounds partition uniquely within the different media (Table 4-2). This can also result in different chromatographic patterns (see Conceptual Site Models and the Chromatograms Fact Sheet of the mixtures in water and soil vapor compared to those from LNAPL and soil.

The chemical structure, size, and polarity of a compound (or fractions) determine their volatility in soil, volatility in water, solubility in water, and adsorption to soil particles, as well as how it will be processed for measurement in an analytical laboratory (see Conceptual Site Models).

4.2.1 Impact of Chemical Structure and Polarity on Partitioning of Hydrocarbons and Metabolites

Molecular structure, polarity, and chain length are some of the properties that lead to competing tendencies of petroleum hydrocarbons and their degradation products to partition in different media and determine their distribution into soil, water, vapor, and mobile/residual LNAPL phase. This is exemplified in Figure 4-5, where the competing partitioning effects are shown to affect solubility and vapor pressure and ultimately partitioning into different media.

The absolute concentration in each medium depends on the initial concentration in the LNAPL, partitioning laws, chemical transformation (discussed in Section 4.4, Alterations of Petroleum Mixtures in the Environment Through Weathering Processes), and mixture effects. The longer and more complex (e.g., branched) organic compounds are, the less they tend to volatilize. In general, branching lowers BP and cyclization increases BP for compounds with the same carbon number. For example, branched molecules of hexane have lower BPs than n-hexane and cyclohexane and benzene have higher BPs than n-hexane. Stability and BP generally increase with number of carbons for polar and nonpolar molecules.

Addition of oxygen to hydrocarbons molecules increases the polarity of the molecules and leads to increased solubility in water for carboxylic acids, alcohols, aldehydes and ketones compared to the parent hydrocarbon (e.g., hexanonic acid, hexanol, hexanal, and hexanone compared to n-hexane; Figure 4-5 Zemo 2016. With higher solubility, these polar compounds tend to partition more into the water phase. Therefore, they are less likely to volatilize (Figure 4-5).

Figure 4-5. Vapor pressure and aqueous solubility relationships of significant gasoline constituents () and select metabolite
(Source: Reisinger, et. al.,1989.)

Table 4-2. Summary of TPH fraction properties TPHCWG 1997b
(Source: TPHCWG, 1997b.)

Fraction	BP (°C)	EC	MW (g/mole)	S (mg/L)	VP (atm)	H (cm³/cm³)	Log K$_{oc}$
ALIPHATICS							
EC 5-6	5.1E+01	5.5E+00	8.1E+01	3.6E+01	3.50E-01	4.7E+01	2.9E+00
EC > 6-8	9.6E+01	7.0E+00	1.0E+02	5.4E+00	6.30E-02	5.0E+01	3.6E+00
EC > 8-10	1.5E+02	9.0E+00	1.3E+02	4.3E-01	6.30E-03	5.5E+01	4.5E+00
EC >10-12	2.0E+02	1.1E+01	1.6E+02	3.4E-02	6.30E-04	6.0E+01	5.4E+00
EC >12-16	2.6E+02	1.4E+01	2.0E+02	7.6E-04	4.80E-05	6.9E+01	6.7E+00
EC >16-21	3.2E+02	1.9E+01	2.7E+02	2.5E-06	1.10E-05	8.5E+01	8.8E+00
AROMATICS							
EC 5-7	8.0E+01	6.5E+00	7.8E+01	2.2E+02	1.10E-01	1.5E+00	3.0E+00
EC > 7-8	1.1E+02	7.6E+00	9.2E+01	1.3E+02	3.50E-02	8.60E-01	3.1E+00
EC > 8-10	1.5E+02	9.0E+00	1.2E+02	6.5E+01	6.30E-03	3.90E-01	3.2E+00
EC > 10-12	2.0E+02	1.1E+01	1.3E+02	2.5E+01	6.30E-04	1.30E-01	3.4E+00
EC > 12-16	2.6E+02	1.4E+01	1.5E+02	5.8E+00	4.80E-05	2.80E-02	3.7E+00
EC > 16-21	3.2E+02	1.9E+07	1.9E+02	6.50E-01	1.10E-06	2.50E-03	4.2E+00
EC > 21-35	3.4E+02	2.8E+01	2.4E+02	6.60E-03	4.40E-10	1.70E-05	5.1E+00

4.2.2 The TPHCWG Approach and Equivalent Carbon Number Definition

Hydrocarbons have many types of molecular structures with large numbers of isomers. It is not possible or practical to analyze each and every compound present in the environment at petroleum-impacted sites. However, groups of compounds within certain carbon ranges having similar properties can be defined and a representative toxicity for the mixture can be assigned for risk assessment purposes. The TPHCWG developed the concept of equivalent carbon (EC) number by correlating fate and transport of hydrocarbons based on BP to approximate carbon number or EC number. The EC is related to the BP of a chemical normalized to the boiling point of the n-alkane or its retention time in a boiling point gas chromatographic column (Figure 4-6). This relationship was empirically determined. Thus, for chemicals where only BPs are known, an equivalent carbon number can be easily calculated and physical properties estimated. The EC number is analogous to an n-paraffin retention index (RI). The National Institute of Standards and Technology (NIST) maintains an RI database (NIST 17 Gas Chromatography (GC) Method/Retention Index Library) for almost 100,000 compounds NIST 2017.

This concept can be applied to mixtures. TPHCWG grouped hydrocarbon fractions of similar partitioning characteristics by using ECs. As seen in Figure 4-6 and summarized in Table 4-2, aliphatic and aromatic hydrocarbons have significantly different water solubilities (within EC fractions) and Henry's law constants and should be addressed separately in evaluation of risk.

Figure 4-6. EC number correlation with boiling point. Water solubility and Henry's law constants correlations to ECs TPHCWG 1997c.
(Source: TPHCWG, 1997c.)

▼*Read more*

The TPHCWG approach is a tiered approach with TPH determined in Tier 1 and aliphatic and aromatic fractions determined in Tier 2, depending on results of Tier 1. A "total TPH" concentration can be calculated from these carbon ranges via the mass percent of each fraction in the whole mixture if data are available for fractions only. Proportion information can be obtained from generic or typical mixture compositions based on historical site information or distinct analysis from site samples TPHCWG 1997a, 1997b.

4.2.3 Texas Commission on Environmental Quality (TCEQ) Fraction Approach

The Texas Risk Reduction Program is similar to TPHCWG in that it is based on a tiered approach and equivalent carbon numbers. In the Texas approach TPH is defined by analytical methods TCEQ 1005 and TCEQ 1006 TCEQ Undated, 2001, 2017a. See Conceptual Site Models for details on EC ranges used.

4.2.4 Massachusetts Department of Environmental Protection (MADEP) Fraction Approach

MADEP divides fractions based on similar toxicity of a certain fraction range and incorporation of EPA-type analytical approaches for volatile petroleum hydrocarbons (VPH) and extractable petroleum hydrocarbons (EPH) to measure TPH. To emphasize the difference from the TPHCWG approach, the MADEP approach focuses on toxicity and has larger TPH fractions that these toxicities are applied to MADEP 2002a. The TPHCWG approach was based on similar transport and fate properties of TPH fractions. Therefore, the fractions are smaller and the approach is more flexible, but the groupings were not based on similar toxicity. Both approaches define aliphatic fractions the same way based on EC as described in 4.2.2.   However, MADEP defines the aromatic ranges by specific compounds and not by EC. Therefore, the aromatic fractions are not equivalent For instance, MADEP C11–C22 range is defined by polycyclic aromatic compounds starting with naphthalene (molecule has 10 carbons but EC of 11.69 or about 12 carbons) and ending with benzo [g, h, i] perylene (22 carbons but EC 34). MADEP's carbon range groupings are shown in Figure 4.7 with clear indication of the different carbon definitions for aliphatic and aromatic fractions MADEP 2002a. TPH results should be interpreted with caution as these approaches are not entirely equivalent.

Figure 4-7. Definition of MADEP hydrocarbon fractions MADEP 2002a.

(Source: MADEP, 2002a.)

It may be noted that an overlap exists between the VPH and EPH methods, in that C9–C12 aliphatic hydrocarbons are quantitated by methods. Note that there is no overlap in the aromatic fractions: the C9–C10 aromatic fraction from the VPH method ends just before naphthalene, and the C11–C22 aromatic fraction from the EPH method starts just after naphthalene.

4.2.5 Limitations of Fractionation Approach

- Most TPH analytical methods are based on gas chromatography (see Conceptual Site Models and Investigative Strategies). The TPHCWG fractions were developed for up to EC35, which is a practical upper range for analysis that can be achieved by most laboratories using standard current chromatographic equipment and encompasses most fuels. Additional work by American Petroleum Institute (API) extended the fractions used by the TPHCWG to EC 44 for aliphatic and aromatic fractions and an additional EC44+ combined aliphatic and aromatic fractions McMillen, Magaw, and Carovillano 2001.
- Crude oils and motor oils can have significant mass above EC 44 but analysis for higher carbons requires the use of high-temperature gas chromatographs, which are not common at commercial environmental laboratories (see Conceptual Site Models and Investigative Strategies). *Excluding* the >EC35 fraction has an impact on calculation of total risk of TPH for the <EC35 fraction, because the relative contribution of the >35 EC fraction is eliminated, meaning the <EC35 now represents 100% of the risk posed by TPH. This has effects on mass balance calculations and risk. For example, the risk of the <EC35 fraction might actually be 70% by mass balance, whereas ignoring the >EC35 fraction would lead to the <EC35 fraction representing 100% of the risk from TPH instead of the real 70% risk. This might lead to over- or underestimation of risk, depending on how much risk the >EC35 fraction contributes and what the composition is. Toxicological and fate and transport data for these heavier hydrocarbons (>EC35) are limited.
- The BP of the compound of interest on a nonpolar GC column is used to derive EC. The relationship between BP and EC is based on n-alkanes as markers. This is not a strict carbon count process. For a homologous series of the same carbon number, branched components have lower BPs than the straight-chain (n-alkane) isomers. Cycloalkanes and aromatic compounds generally have higher BPs than the n-alkane with the same number of carbons. The disparity between actual number of carbons and EC is greater for heavier PAHs. For modeling of transport and fate or risk assessment, it is suggested to select property values (e.g., solubility, etc.) at a midrange or those that represent a "worst-case" scenario. The midrange values appear to be more consistent when varied carbon ranges are applied; the "worst-case" scenario selection can be an order of magnitude more conservative than the average.
- Partitioning of biodegradation products (metabolites) has not been studied. Risk posed from petroleum releases includes risk from TPH and metabolites. The fraction approach only considers partitioning, measurement, and risk from nondegraded TPH. In general, polar metabolites are not accessible by the analyses because of incomplete extraction of metabolites by these methods, SGC removal, and lack of polar standards as standards for analysis.

4.3 Properties of Aliphatic and Aromatic Hydrocarbon Fractions

A summary table for the physical properties of the hydrocarbon carbon ranges fractions, as published by the TPHCWG, is provided in Table 4-2. A summary table of physical properties for example metabolites is provided in Table 4-3. Note that the addition of oxygen to the aliphatics (e.g., alcohols) changes the chemical and physical properties of the molecule. With addition of oxygen, the molecule becomes larger and more polarized. This leads to an increase in BP (and EC number), increased solubility in water, and decreased evaporation tendency compared to nonpolar aliphatics.

Table 4-3. Example metabolite physical properties Kim et al. 2016

(Source: Kim et. al., 2016.)

	Compound	BP (°C)	EC[1]	MW (g/mole)	S (mg/L)	VP (atm)
Carboxylic Acids	Hexanoic Acid	205	11	116.16	$1.03 \times 10+4$	0.000057
Alcohols	Hexanol	157	8.9	102.177	5900	0.0012
Aldehydes	Hexanal	129.6	7.8	100.161	5640	0.0149
Ketone	Hexanone	127.2	7.7	100.161	14.7	0.0153

[1] EC determined from EC boiling point correlation ($EC=4.12 + 0.02(BP) + 6.5e\text{-}5(BP)^2$) of hydrocarbons after TPHCWG 1997b.

4.3.1 Water Solubility of Fractions

When compared within the *same fraction* (e.g., the same EC range, Figure 4-6) TPHCWG 1997c, aromatic hydrocarbons are more soluble compared to aliphatic hydrocarbons as a group. Aliphatics of lower EC (e.g., EC5–EC10) have a similar solubility to aromatics at higher EC (e.g., EC9–EC20). Addition of oxygen atoms to hydrocarbons, for example due to metabolism by bacteria, typically increases solubility. A comparison of the solubility of possible metabolites with the solubility of the corresponding parent hydrocarbon (n-hexane: 9.5 mg/L) shows the following trend: carboxylic acid (e.g., n-hexanoic acid) > alcohol (e.g., n-hexanol) > aldehydes (e.g., n-hexanal) and ketones (e.g., n-hexanone) (Table 4-3) > alkane (e.g., n-hexane; unaltered hydrocarbon). Note also the increase in EC number for the hexanoic acid in response to the increased BP.

4.3.2 Volatilization of Fractions from Soil

Aromatics and aliphatics exhibit a similar (i.e., negative) correlation of EC with vapor pressure (VP) for ECs smaller than 25, indicating a higher vapor pressure for low EC compounds TPHCWG 1997c. As a result, the partitioning of aromatics from aliphatics within the same EC range or as groups is not expected, meaning aliphatics and aromatics behave similarly during evaporation from dry soil and are both enriched in soil vapor. Vapor pressure values for equivalent carbon numbers greater than EC25 were excluded due to the low confidence in the measured estimates of vapor pressure values less than 10^{-9} atm. If vapor pressure of metabolites (Table 4-3) is compared to vapor pressure of their respective parent aliphatic hydrocarbons (Table 4-2), vapor pressure of some metabolites may be lower than those of the hydrocarbons. Vapor pressure decreases with chain length of metabolites and increases from acids to alcohols to aldehydes and ketones in the example. Aldehydes and ketones evaporate more readily from soil than alcohols.

4.3.3 Volatilization of Fractions from Water

> TPH in vapors from both gasoline and mid-distillate fuels is generally dominated by low-carbon range aliphatics, while low-carbon range aromatics are minor, though still important.

The Henry's law constant decreases with increasing EC of the aromatics, while it is more or less constant for the aliphatics at all ECs (Figure 4-6) TPHCWG 1997c. Henry's law constants for the aliphatics are generally greater than 1.0, while those for the aromatics are generally less than 1.0 in Figure 4-6. The aromatics generally prefer to be in the aqueous phase compared to the aliphatics, whereas aliphatics prefer the vapor phase. Within EC fractions, aliphatics are also distinctly different from aromatics in their Henry's law constants. This has the effect that TPH in vapors from both gasoline and mid-distillate fuels is generally dominated by low-carbon range aliphatics while low-carbon range aromatics in vapors are a minor, though still important, fraction of TPH in vapors Brewer et al. 2013; ITRC 2014.

4.3.4 Adsorption (Sorption) of Fractions (K_{oc})

The soil organic carbon-water partitioning coefficient (K_{oc}) is the ratio of the mass of a chemical that is adsorbed in the soil per unit mass of organic carbon in the soil per the equilibrium chemical concentration in solution. K_{oc} values are useful in predicting the mobility of organic soil contaminants; higher K_{oc} values correlate to less mobile organic chemicals, whereas lower K_{oc} values correlate to more mobile organic chemicals. The organic carbon content of soil is the primary property controlling sorption of hydrocarbons (non-ionic hydrophobic chemicals), but partitioning can also be influenced by adherence to clay particles. For example, if the soil carbon content is less than 0.001, clay content dominates the partitioning behavior. Furthermore, the kind of clay (kaolinite and montmorillonite, for instance) is also important Jorge 2001.

In general, the higher the ECs, the more aliphatics and aromatics partition into soil compared to fluids. When PAHs and BTEX are compared, K_{oc}s for PAHs are generally higher (at least an order of magnitude), indicating that PAHs are preferentially partitioned into the soil relative to BTEX. Concentrations of the compounds are a function of initial concentration and K_{oc}.

The slope of K_{oc} with EC number of the aliphatics is much steeper than for aromatics with EC range >10–12 TPHCWG 1997c. Compared to the aromatics at the same EC, aliphatics tend to be bound more tightly to soil in the EC10–EC20 range. However, most aliphatics and aromatics have similar K_{oc} (as combined aliphatics and aliphatic groups comprising the complete EC range) and therefore will be found in similar proportions in soil based on the EC-K_{oc} relationship alone.

▼Read more

4.3.5 Applying Physical Properties to Chemical Mixtures

> The critical difference between crude oil or refined product releases (fuels, lubricating products, etc.) versus releases of other types of chemicals is that because the crude oil or product is a mixture, the physical properties of each component in the mixture that relate to partitioning to other phases are less than the "pure component" properties due to what is called the mixture effect.

The preceding sections provided important information about key physical properties for either (1) individual aliphatic or aromatic "equivalent carbon range" fractions, or (2) individual chemicals that are components of a petroleum mixture. The component is a certain proportion of the mixture (always less than 100%). The mixture effect is estimated by Raoult's law for ideal organic mixtures and requires that the component property be multiplied by its proportion (mole fraction) in the mixture. This results in "effective" properties, such as effective solubility (for partitioning from product to water) and effective volatility (for partitioning from product to air).

Water solubility values vary by orders of magnitude for the individual hydrocarbon constituents making up hydrocarbon-derived fuels. For individual compounds, both molecular weight and chemical structure influence the degree of solubility. The concentration or effective solubility of any compound depends on the abundance of the compound in the matrix (in the fuel, for instance). Effective solubilities are even more variable, as these are proportional to the concentration of the individual hydrocarbons in the fuel, the average molecular weight of the fuel, and inherent uncertainties with prediction of mole fraction in multicomponent fuels. Furthermore, component interactions within the organic phase result in deviations from ideality. Mixtures containing compounds that are different in structure (aliphatics and aromatics) deviate from ideal behavior and the oil to water ratio has significant difference in the "effective solubility" Bobra 1992. Other factors affecting effective solubility include the loading rates of water to oil, temperature, ionic strength, and the amount of dissolved organic carbon in groundwater.

Partitioning within the dissolved phase in groundwater in equilibrium with a fresh gasoline or diesel source is primarily limited to BTEX and the small aromatics and very small aliphatics because of their corresponding effective solubilities. The total theoretical aggregate dissolved-phase concentration for the fresh gasoline source is about 100 mg/L versus about 5 mg/L for the fresh diesel source. These results have been proven in many peer-reviewed laboratory partitioning experiments since the 1980s Coleman et al. 1984; Shiu et al. 1990; Thomas and Delfino 1991; Bruya and Friedman 1992; Chen, J. J. Delfino, and Rao 1994; Potter 1996. Effective volatility is why the aliphatics dominate (about 90%) the vapor composition for a fresh gasoline source area, and aliphatics are about 50% of the vapor composition of a fresh diesel source area. Equations for partitioning of individual compounds from the mixture to groundwater or to soil vapor need to incorporate Raoult's law, and must not be based on simple equations that do not account for the fact that the source is a mixture.

Weathering of the petroleum source preferentially reduces the mass fraction of soluble and volatile components of the mixture, and thus reduces their effective solubility and volatility. With continued weathering, the residual petroleum may contain components with very low effective solubility or volatility. Changes in the composition of the mixture due to weathering, and resultant changes in properties of the residual petroleum due to the mixture effect, are a reason why it is critical to obtain TPH fraction data for representative samples at a given site to estimate partitioning to groundwater or to soil vapor.

4.4 Alterations of Petroleum Mixtures in the Environment Through Weathering Processes

The term "weathering" describes physical, chemical, and biological (biochemical) changes that affect hydrocarbons and alter the composition of petroleum hydrocarbon mixtures after they are released to the environment Atlas 1981. When weathering processes reduce the mass of a release, this is often called "natural attenuation." Biochemical processes are catalyzed by microorganisms and collectively known as "biodegradation." Because each petroleum release site is unique and not all weathering processes are of equal importance at all sites, understanding the scientific principles can help with site management decisions.

4.4.1 Overview of Weathering Processes

Different weathering processes can occur simultaneously and/or sequentially. The extent to which a given process occurs depends on the nature of individual hydrocarbons and site characteristics. Not all of these natural changes involve structural transformation or degradation. "Degradation" can mean either a small structural modification (partial degradation) or complete breakdown to single carbon compounds. The fully oxidized carbon can be released as gaseous carbon dioxide (CO_2) or a dissolved inorganic ion bicarbonate (HCO_3^-) in a process called mineralization.

Hydrocarbon degradation always involves oxidation because hydrocarbons are highly reduced chemicals containing only hydrogen atoms at the ends of carbon chains or rings. The hydrogen atoms make the carbon atoms slightly negative and provide excess electrons that can be transferred to oxygen through reactions that produce energy. Biodegradation by microorganisms involves transfer of electrons from the carbon atoms to suitable electron acceptors. This causes one or more of the carbon atoms to become somewhat positive and linked to oxygen atoms. Biodegradation of petroleum hydrocarbon mixtures always involves many steps and produces numerous partial degradation products. These are organic chemicals also known as "metabolites" or "polar compounds" with different characteristics and behaviors in the environment. In polar molecules, electrons are not shared equally among atoms of the same molecule, leading to one end being more positive and another more negative. Thus, the incorporation of oxygen by biodegradation or photooxidation of petroleum hydrocarbons results in formation of oxygen-containing compounds that are more water soluble than the corresponding parent hydrocarbon (see Table 4-3).

Figure 4-8 depicts processes contributing to weathering. Physical processes redistribute hydrocarbons in the environment without changing structures. Chemical and biochemical processes change the structures and properties of hydrocarbons mostly through oxidation. For instance, photooxidation can lead to partial oxidation and affects only certain hydrocarbons. Biodegradation is a comparatively slow, stepwise chemical oxidation process that requires the successive action of many different types of microorganisms and a great variety of biological catalysts (enzymes) to process the many different hydrocarbon structures present in a typical petroleum release. Because biodegradation of petroleum hydrocarbons is a complex multistep process, many intermediate breakdown products or metabolites are generated. These undergo increasing oxidation with time and distance from the source zone.

Figure 4-8. Weathering processes that can affect hydrocarbon mixtures.
(Source: U. Johnson, Georgia EPD, 2018.)

Weathering changes the composition of the original mixture because different types of hydrocarbons vary in their susceptibility to physical, chemical, and biological transformation. For example, small aliphatic hydrocarbons evaporate easily and large aromatic hydrocarbons adsorb onto clayey soil. One of the major changes when microorganisms start oxidizing hydrocarbons is that those products (metabolites) move with the water due to their polar nature. Below is a simplified conceptual site model with parent hydrocarbons in yellow and metabolites in red. Understanding the factors involved in the breakdown of hydrocarbons and the limitations of different weathering processes is important for making informed site management decisions.

The conceptual site model (CSM) in Figure 4-9 illustrates key weathering processes and the production of petroleum metabolites in the environment. The parent hydrocarbons are in yellow (in the NAPL phase) and the metabolites are the red "molecules" shown in the different phases of the plume. Parent compounds released at the surface can undergo photooxidation (1) or evaporation following volatilization (2). Metabolites are also produced as a result of photooxidation. As the hydrocarbons travel downward from the surface through the vadose zone, (partial) biodegradation of hydrocarbons (3)

occurs, yielding metabolites, with biodegradation becoming more anaerobic as oxygen levels drop. The NAPL can also penetrate the water table and result in both submerged and vadose zone source areas. Slow anaerobic biodegradation can occur in NAPL but more biodegradation occurs in the fringe. Parent hydrocarbons can also be absorbed onto soil particles (4). Hydrocarbons are transferred from the petroleum mass (NAPL) to water through dissolution (5). The polar metabolites partition preferentially into the water phase. As dissolved hydrocarbons and metabolites move away from the source area, they are subject to dilution (6). Formation of metabolites and further oxidation, as well as fermentation of metabolites, may continue under anaerobic conditions.

Figure 4-9. Conceptual site model for petroleum weathering and metabolites

▼*Read more*

Table 4-4 presents a summary of common weathering processes, the physical parameter that determines a hydrocarbon's susceptibility to that process, and the types of hydrocarbons most susceptible.

Table 4-4. Petroleum hydrocarbon susceptibility to common weathering processes

Weathering Process	Structural Transformation	Change in Fate & Transport	Production of Metabolites	Physical Parameter	Hydrocarbon Susceptibility	Considerations
Volatilization (physical)	No	Yes	No	Boiling point	Low molecular weight Aliphatic > aromatic	Occurs primarily at or near the surface
Dissolution (physical)	No	Yes	No	Solubility in water	Low molecular weight. Aromatic > aliphatic	Generally low
Adsorption (physical)	No	Yes	No	Chemical and structural features	Larger. More aromatic	To inorganic and organic matter
Photooxidation (chemical)	Yes	Yes	Yes	Energy of activation	Aromatic, double bonds	Occurs at the surface only, select hydrocarbons only
Biodegradation (biochemical)	Yes	Yes	Yes	Energy of activation	Structure similar to biological molecules most susceptible	Efficiency varies depending on molecular structure and site factors

4.4.2 Physical and Chemical Weathering Processes

Physical and chemical weathering processes include volatilization (evaporation), dissolution (solubilization), combustion (burning), and photooxidation. As a degradation process that occurs less frequently and proceeds rapidly, combustion is not often considered part of weathering. The susceptibility to a physical weathering process follows simple trends for some classes of hydrocarbons. The chemical properties underlying volatility and solubility are discussed in more detail in Section 4.2, Physical and Chemical Properties of Petroleum Constituents, TPH Carbon Ranges (Fractions), and Metabolites. Although hydrocarbon oxidation is thermodynamically favorable, their chemical and biochemical transformations are driven by the energy of activation, which is a kinetic concept. Because energy barriers make hydrocarbons relatively inert Widdel and Rabus 2001; Labinger and Bercaw 2002; Hostettler et al. 2007; Rabus et al. 2016, they require significant amounts of energy (light, heat) and/or catalysts for degradation under ambient conditions. More background information on the chemistry underlying chemical and biochemical weathering processes is provided in Appendix A.4 (Chemistry of Weathering Processes

Fact Sheet).

Volatilization of hydrocarbons refers to the conversion of some liquid hydrocarbons to vapor. It is a function of a compound's vapor pressure and temperature, or approximately mass and BP. Volatilization results in the selective loss of the lower molecular weight compounds. Aliphatic compounds are generally more volatile than aromatic compounds for a given carbon number. The more branching on the aliphatic compound, the lower the BP. However, cycloalkanes have higher BPs than alkanes with the same carbon number. Volatilization occurs primarily on the surface but can also occur in the subsurface Chaplin et al. 2002; Lahvis et al. 2013.

Dissolution (or solubilization) refers to the transfer of a hydrocarbon from the hydrocarbon mixture to water. It is a function of the molar concentration of a compound in a mixture and the relative solubility in water versus the hydrocarbon mixture. Hydrocarbons with greater water solubility can be partially removed from the hydrocarbon mixtures where there is contact with water. Solubility varies with size (molecular weight) and structure of a molecule. Aromaticity increases solubility. Increasing alkylation generally reduces solubility of similar hydrocarbons. Oxygenated metabolites are generally more soluble than the parent hydrocarbons.

Adsorption refers to the attachment of hydrocarbons onto soil or sediment particles and organic matter. This is often a reversible process and will not be discussed further in this section.

Combustion (burning) of hydrocarbons requires an excess of oxygen and produces carbon dioxide and water. Incomplete combustion results in carbon monoxide, carbon (soot), and polycyclic aromatic hydrocarbons.

Photooxidation refers to a chemical reaction that leads to the oxidation of a hydrocarbon exposed to radiation from the sun. Larger hydrocarbons and hydrocarbons with increasing alkylation are more susceptible to photooxidation. Fully saturated aliphatic compounds (alkanes) are resistant, whereas aromatics are often more susceptible to photooxidation. Alkenes (aliphatic hydrocarbons with one or more double bonds produced during refining) are more susceptible than alkanes.

Biodegradation—the right mix matters:

- Moisture
- Mass
- Microbes

4.4.3 Biodegradation Overview

Biodegradation is a term used to collectively describe a variety of (bio)chemical processes by which microorganisms transform or alter (through metabolic or enzymatic action) the structure of chemicals introduced into the environment. Biodegradation is the most important and universal weathering mechanism. Most hydrocarbon mixtures can be at least partially degraded in the environment due to the presence of ubiquitous microorganisms. Microbes that use oxygen are very effective at breaking down petroleum hydrocarbons. Biodegradation of a hydrocarbon mixture requires many types of microorganisms or a "consortium" of microorganisms, which often consists of different strains of bacteria but can also include fungi, algae, and archaea. The microorganisms are often divided into aerobic and anaerobic species. Aerobic organisms thrive in the presence of oxygen and use oxygen as terminal electron acceptor (TEA). Anaerobic organisms use a variety of alternative TEAs, for example, sulfate or nitrate from the environment. Biodegradation is most rapid where adequate oxygen is available and mixes readily with the hydrocarbons. When conditions turn anaerobic, certain hydrocarbons, including benzene and PAHs, may degrade very slowly. Large quantities of TEAs are required for hydrocarbon breakdown (see Chemistry of Weathering Processes Fact Sheet). Microbial processes that use as TEAs organic molecules generated during their own metabolic activities are sometimes called fermentation. Different types of anaerobic processes can occur at the same site in close proximity Meckenstock et al. 2015. The rate, type, and extent of biodegradation depend on the nature of the hydrocarbons and site-specific factors.

▼Read more

4.4.3.1 The Diversity of Biological Weathering Processes

Biological weathering (biodegradation) refers to chemical reactions catalyzed by collections (consortia) of microorganisms that alter and break down hydrocarbons in the environment under ambient conditions through actions of enzymes (biological catalysts). As biological molecules, enzymes are very sensitive to the structure of the molecules they bind to and

process. Therefore, hydrocarbons with different structural elements (e.g., aliphatic, aromatic, cyclic/alicyclic, aromatic and/or aliphatic polycyclic, open-chain or branched) require different enzymes and microorganisms. Based on the ease of biodegradation, hydrocarbons can be divided in three groups:

1. simple aliphatic hydrocarbons
2. (alkylated) mono- and diaromatic hydrocarbons
3. branched, cyclic and polycyclic aromatic hydrocarbons (PAHs)

Simple aliphatics are typically easiest to degrade, especially even-numbered hydrocarbons with approximately 10–20 carbon atoms, because these resemble naturally occurring fatty acids after one end is oxidized to a carboxylic acid. Many microorganisms prefer longer Zobell 1946 or medium-length hydrocarbon chains over short ones Rojo 2009; Alvarez, Heathcote, and Powers 1998; Borden et al. 1997. Note that smaller aliphatic hydrocarbons are preferentially removed from the mixture by volatilization. Mono- and diaromatic hydrocarbons (benzenes and naphthalene) can be degraded fairly easily if they are alkylated or if microorganisms with the right alkylating enzymes are part of the microbial consortium of the site. Benzene itself is difficult to degrade. Some hydrocarbons show very little degradation under anaerobic conditions and may even be slow to degrade under aerobic conditions. This group includes larger molecules with various branched and cyclic structures, including PAHs.

Hydrocarbons are generally easily to degrade under aerobic conditions. Under these conditions oxygen is abundant and aerobic microorganisms thrive. For many years (since about 1900) aerobic processes were considered the principal way petroleum mixtures could be degraded in the environment Atlas 1981; Leahy and Colwell 1990 until anaerobic degradation was demonstrated in the late 1980s Heider et al. 1999; Widdel and Rabus 2001 and became more widely discussed only in the following decades Hostettler et al. 2007.

Microorganisms can use hydrocarbons both as a carbon source (making building blocks for cellular molecules) and as an energy source, although hydrocarbons are not a preferred food source Rojo 2009. Aerobic organisms are most efficient at extracting energy from hydrocarbons, which, together with the fuel that hydrocarbons provide, promotes growth of microbial communities and enhanced biodegradation capacities. Aerobic degradation is often observed with small petroleum releases and on the fringes of large releases. Anaerobic processes are predominant at depth in soil and groundwater where biodegradation has used up the available oxygen Aitken 2004; Lueders 2017; Rojo 2009. Although some studies found that TEAs appear to be depleted in a preferred order Wiedemeier 1999; OHEPA 2014, at other sites multiple anaerobic processes have been observed to occur concurrently Bekins, Goodsy, and Warren 1999; Heider et al. 1999.

> ### *Anaerobic Degradation*
>
> Anaerobic organisms break down hydrocarbons differently from aerobic organisms. For example, the activation step often involves addition of fumarate and the formation of an alkyl- or aryl succinate (see Chemistry of Weathering Processes Fact Sheet). The electrons produced during the various oxidation steps are not used to reduce oxygen but are transferred to the preferred electron acceptor, such as SO_4^{2-}, NO_3^-, or Fe^{2+}. Electron transport is independent of O_2 transport.

Compared to aerobic degradation, anaerobic processes are more diverse and more complex; therefore, they are slower and more prone to accumulation of metabolites. They may not readily produce CO_2. Metabolites may be passed from one microorganism to another through syntrophy Schink 1997. Anaerobic microorganisms can use more of these TEAs in lieu of oxygen. Common inorganic TEAs in the environment are sulfate, nitrate, iron, and manganese. Numerous microorganisms have been identified that can use one or more of these ions during the oxidative breakdown of specific types of hydrocarbons. It has recently been shown that several anaerobic processes can occur in close proximity Meckenstock et al. 2015. A special case of anaerobic degradation involves fermentation–degradation in the absence of external electron acceptors. Because in this case one organic molecule or carbon atom must accept the electrons from another, fermentation

leads to reduction of some molecules while others are oxidized. Any significant energy production virtually always involves some CO_2 production even under anaerobic conditions where it may be coupled to methane production (Figure 4-10).

Figure 4-10. Possible distribution of carbon atoms during petroleum biodegradation.
(Source: U. Hellman-Blumberg, California DTSC,2018.)

Figure 4-10 illustrates why hydrocarbon biodegradation in the environment requires many steps. Each arrow represents many chemical reactions. The chemical reactions differ depending on the structure of the hydrocarbon, the conditions at a given site, and the type of microorganisms that thrive there. The top and left side of the schematic show highly reduced molecules, the bottom right corner shows fully oxidized carbon. Hydrocarbon degradation occurs in three stages: initial activation of the carbon atom on one end of the molecule (several steps), breakdown and transformation into smaller molecules or metabolites with increasing oxygen content (many steps, including repetitive and cyclic processes), and

complete breakdown into fully oxidized one-carbon molecules (CO_2 gas or dissolved HCO_3^-). Under certain highly anaerobic, fermentative conditions the final stage may be the breakdown of small metabolites to methane and carbon dioxide, which may involve transfer of hydrogen from one organism to another. Biodegradation of large petroleum releases that become anaerobic often involves syntrophy between aerobic and different types of anaerobic organisms. Persistent metabolites are occasionally generated through co-metabolism or photooxidation (see anthraquinone example in Chemistry of Weathering Processes Fact Sheet).

4.4.4 Factors Affecting Susceptibility to Weathering

4.4.4.1 Molecular Features of Hydrocarbons

The likelihood and extent of physical and chemical weathering affecting a given type of hydrocarbon can often be predicted reasonably well by simple structural features. However, biodegradation rates do not always correlate well with simple structural features, although many attempts have been made to discern and define patterns (see also Table 4-4).

The ability of microorganisms to assimilate, attack, and transform a hydrocarbon typically depends on the extent to which it resembles biological molecules that are normally processed by living organisms. Moreover, different strains or types of microorganisms (bacteria, archaea, and fungi) differ in their ability to activate and/or process certain molecular features. That can explain, for example, why alkylbenzenes are more readily degraded than a plain benzene molecule or why a larger hydrocarbon (longer aliphatic chain) may be more readily degraded than a small one Zobell 1946. In addition, the position of functional groups or side chains is important and large differences in biodegradation have been observed between isomers. For example, most of the microorganisms studied thus far will degrade only two of the three xylene isomers, but the degradation preference and extent of degradation can vary with site conditions Foght 2008.

4.4.4.2 Site-Related Factors

The rate and extent of biodegradation is affected by several factors Das and Chandran 2011. These include the availability of oxygen and/or alternate electron acceptors, soil type, geochemistry, moisture, temperature, and presence of other natural or synthetic chemicals (see box). For example, water is essential for microbial activity. Because most petroleum hydrocarbons in soil occur as a four-phase mixture, biodegradation occurs within that four-phase mixture, typically in locations where petroleum hydrocarbon components partition into (or are adjacent to) soil moisture. Although it has been shown that production of metabolites (partial biodegradation) can occur in small water droplets in oil Meckenstock et al. 2014, anaerobic degradation on the interior of a large NAPL mass can occur only at a very slow rate. Temperature has a major effect on the reaction kinetics (the higher the

Site-Related Factors

That affect biodegradation include:

- total mass of the release
- oxygen levels
- availability of other electron acceptors (geochemistry)
- water chemistry (pH, salinity, availability of nutrients)
- availability of hydrocarbons to microorganisms (soil type)
- soil moisture
- soil organic matter (competition for electron acceptors)
- temperature

temperature, the faster the reaction) and the type of organisms (some like it hot, some not so much) present at a given site. Inorganic TEAs such as sulfate or iron are linked to the geochemistry of the site and affect microbial activity. Together these factors help explain why the rate of attenuation through weathering is site-specific.

4.4.5 Evidence for Weathering

The effects of weathering, including biodegradation, are often readily apparent at typical or simple sites. Even at complex or recalcitrant sites (e.g., significant mass; unique geochemical, microbial, etc., conditions), some biodegradation of hydrocarbons virtually always occurs, but progress in the reduction of environmental contamination may not always be readily apparent. Careful monitoring of weathering and, in particular, biodegradation processes, is the key to regulatory acceptance of monitored natural attenuation (MNA) USEPA 1999. Some, but not all, of the methods below are also commonly used for investigation of natural source zone depletion (NSZD) of LNAPL sources ITRC 2018. NSZD tends to focus on large masses and mass flux regardless of the weathering (attenuation) mechanisms, whereas MNA tends to focus on residual concentrations in environmental media that favor biodegradation. Considering mass flux only in the evaluation of natural attenuation is not sufficient because different types of hydrocarbons or TPH fractions have different toxicities and different susceptibilities to biodegradation or other weathering processes. Multiple lines of evidence are often recommended at complex or recalcitrant sites. A list of methods that can be used for evaluating weathering processes is provided below:

- *Water quality parameters*: Biodegradation of petroleum hydrocarbons causes changes in the chemistry of groundwater. After dissolved oxygen has been depleted, microorganisms use the electrons acceptors (ions) that are available. Tabulating or graphing contour maps that show decreasing TEAs (including O_2) and an increase in byproducts can provide a line of evidence. By quantifying these changes, it may be possible to document that biodegradation is occurring.
- *Chromatograms produced as part of TPH analysis*: Chromatograms typically provide initial qualitative evidence of weathering and can be easily obtained from the testing laboratory.
- *Comparison of duplicate TPH samples processed with and without silica gel cleanup (SGC)*: Lower bulk TPH concentrations with SGC can indicate partial degradation of petroleum hydrocarbon, but site information is also required for proper interpretation CASWB-SFBR 2016b.
- *Molecular methods*: Methods such as quantitative polymerase chain reaction (qPCR) have become readily available in recent years for evaluating sites contaminated with various chemicals and mixtures including petroleum. A qPCR analysis is based on the amplification of genetic signatures that allows identification and quantification of microorganisms or active genes. Quantitation helps predict whether natural attenuation will likely be adequate (see Environmental Molecular Diagnostics, New Site Characterization & Remediation Enhancement Tools ITRC 2013). These methods also may provide information on how biodegradation could be enhanced.
- *Isotope-based methods*: Isotopes have been extensively used for decades in laboratory studies of microbial biodegradation of individual hydrocarbons and mixtures. Several isotopic methods such as compound-specific isotope analysis (CSIA) and stable isotope probing (SIP) are increasingly being used in the field and approved by regulatory agencies for the investigation and management of petroleum sites, for example, see this presentation from Georgia Environmental Protection Division.
- *Production of gases*: Biodegradation produces CO_2 and sometimes methane. Carbon dioxide flux can be an indicator of the natural losses of petroleum mass due to degradation. (See also Evaluating Natural Source Zone Depletion at Sites with LNAPL and the McCoy et al. 2015 article on CO_2) Methane is evidence for methanogenic (anaerobic) degradation, but because methane gas often travels from the location where it is generated methane detections should be interpreted carefully.
- *Temperature*: Monitoring the increase of temperature may be an option at certain sites, particularly when there is significant mass of hydrocarbons. At sites with very active aerobic degradation an increase of temperature has been observed Sweeney and Ririe 2014. (See also Evaluating Natural Source Zone Depletion at Sites with LNAPL).

4.5 Definition of "TPH" in Environmental Media in Risk Assessment

4.5.1 Definition of TPH for Purposes of This Guidance Risk Assessment for Petroleum Releases

One of the important lessons learned from decades of petroleum site investigation and risk assessment is that the more the hydrocarbons, hydrocarbon classes and carbon ranges, and nonhydrocarbon organic components are separated from each other in the definition of TPH, the more accurate the site evaluation will be because the different components can be assigned their respective properties. Therefore, for the purpose of this guidance and based on best practices to improve investigation and risk assessment for petroleum releases, TPH is defined as:

the known or assumed aliphatic and aromatic hydrocarbon mixture (e.g., crude oil, fuel type, mixture of fuel types) originally released to the environment, or the remaining aliphatic and aromatic hydrocarbon mixture after weathering thereof, for <u>*LNAPL in soil, and sediment sample matrices*</u>*, and the dissolved hydrocarbons that have partitioned from the hydrocarbon mixture into groundwater or surface water for* <u>*the water matrix*</u>*, and the volatilized hydrocarbons that have partitioned from the hydrocarbon mixture or the dissolved phase to the soil vapor for* <u>*the air matrix*</u>*.*

Thus, TPH is defined by the aliphatic and aromatic hydrocarbon carbon range fractions covering the applicable carbon range based on the known or assumed original hydrocarbon mixture (or the weathered hydrocarbon mixture thereof), or the hydrocarbon fractions partitioned to water or air. In the case of uncertainty regarding what petroleum type was released to the environment, the aliphatic and aromatic carbon ranges should cover the entire potential range (e.g., EC5–EC35 for aliphatics and EC8–EC35 for aromatics). The analysis is limited to EC35 because most labs have a difficult time getting to EC44 without discrimination and significant column bleed.

TPH is defined by the analytical method used to measure it, and the methods used can be variable from state to state and even from lab to lab. The variability can be due to which organics are included in the analysis and which carbon ranges (BP ranges) are quantified and reported, as well as differences in calibration standards, extraction solvents, detection limits of equipment, and methods. TPH numerical results should be carefully evaluated when looking for trends, for instance, to ensure that apparent changes are due to site condition changes and not to analysis of TPH by different methods and/or labs.

The commonly used bulk TPH analyses are known to include all extractable organics within the specified BP range unless a cleanup is used to isolate the hydrocarbons. The bulk TPH analyses do not distinguish between aliphatic and aromatic hydrocarbons.

The calibration used for quantitation can be a whole product standard or a group of individual hydrocarbons. Besides inconsistency, these factors hinder the ability to accurately evaluate either fate and transport properties or risk posed by the residual petroleum.

In the original TPHCWG program, the individual target compounds of potential concern (such as hexane, BTEX, naphthalene, for instance) are included as "TPH" in the corresponding aliphatic and aromatic fractions, and are not subtracted from their respective carbon range fractions.

For this ITRC document, the approach is to use the TPHCWG procedure for fate and transport calculations; however, as is the long-standing practice in most regulatory programs, the individual compounds of potential concern are typically analyzed for and evaluated separately for risk assessment purposes. The biodegradation metabolites are not always included and not accurately estimated as "TPH" because their properties can be significantly different from hydrocarbons and these metabolites are not always extracted and/or are too polar to be analyzed by gas chromatography. However, some metabolites and/or naturally occurring organic matter can be "measured/ reported" as TPH and bias results.

In the best case, all data collected at the site would be aliphatic and aromatic carbon range fractions, but in reality, the analysis required for these data is relatively expensive and more complex, and there is almost always a need (by responsible parties and state tank funds) to use a less-expensive bulk hydrocarbon carbon range TPH analysis (e.g., hexane to dodecane (nC6–nC12), decane to octacosane (nC10–nC28), etc.) for most samples during site investigation (TCEQ Tier 1 ranges).

The bulk TPH analysis can be useful in an investigative approach for a variety of reasons, including (1) at the beginning to

compare to a bulk hydrocarbon TPH screening level to see if the site or areas of the site "screen out" and do not need further detailed evaluation, (2) to select representative samples for aliphatic/aromatic carbon range (fractionated) analyses, or (3) for "lateral and vertical extent" investigation purposes. The bulk carbon range TPH should be *hydrocarbons only* to be comparable to the aliphatic and aromatic fraction data.

4.5.2 Fraction Approach for TPH for Risk Assessment

Based on the information provided in the previous sections, it is clear that use of the aliphatic and aromatic carbon range fraction approach for TPH is the current best practice for site characterization and risk assessment. This is the best way to account for the large differences in physical properties and toxicities of the different components of the mixture, and to account for changes in the relative proportions of the components in the mixture over time due to weathering.

Using the fraction approach as the primary site information for risk evaluation is consistent with regulatory programs in several states (see States Survey) (Regulatory Framework). Specific details are not captured by the bulk carbon range TPH methods. The use of bulk data to define TPH can result in poor understanding of the potential environmental mobility and/or toxicity of the petroleum present. If bulk TPH methods are used, it is highly recommended to request and submit chromatograms along with the result to the regulating agency and examine chromatograms for potential interferences from nonhydrocarbon sources, single or multiple chemicals from other sources, or the degradation stage. Additionally, if the bulk carbon range TPH did not include a cleanup to isolate hydrocarbons, the TPH is essentially a total extractable organics measurement and may or may not have relevant relationship to aliphatic and aromatic hydrocarbon content. As discussed previously, *bulk* carbon ranges for TPH could be used for initial site screening purposes or as a practical cost-saving measure for "lateral and vertical extent" characterization purposes after fractionated data are collected.

The typical TPH carbon range fractions (all are "equivalent carbon numbers" in terms of BPs relative to n-alkanes) for analysis and evaluation are shown in Figure 4-11 below.

Aliphatics: EC5–EC6; >EC6–EC8; >EC8–EC10; >EC10–EC12; >EC12–EC16; >EC16–EC21; >EC21–EC35

Aromatics: >EC8–EC10; >EC10–EC12; >EC12-EC16; >EC16–EC21; >EC21–EC35

If using bulk hydrocarbon TPH data, the above carbon range fractions could be approximated by using EC6–EC12, >EC12–EC21, >EC21–EC28, >EC28–EC35

Figure 4-11. TPH carbon range fractions.

These carbon ranges are generally consistent with the TPHCWG and those used by most states that have a fractionated approach and use BTEX to represent the EC6–EC9 aromatics fraction.

4.5.3 Biodegradation Metabolites

Some metabolites from biodegradation (as well as other oxygen-containing molecules present in the background and not a result of the release, e.g., phthalates, humic acids, etc.) can be included in a bulk carbon range TPH analysis if SGC is not used because the bulk TPH analysis provides an aggregate measure of all extractable organics and is not specific to petroleum hydrocarbons. The frequency and magnitude of the inadvertent inclusion of the metabolites in a bulk TPH analysis was brought to the attention of regulators, consultants, and responsible parties in the late 1990s Zemo and Foote 2003. Prior to that it was assumed by most regulatory programs and environmental practitioners that the entire bulk TPH quantitation was hydrocarbons.

The nature, fate, and toxicity of metabolites in groundwater at petroleum release sites has been the subject of recent active research Zemo et al. 2017; Mohler et al. 2013; Bekins et al. 2016, and whether or not to include the metabolites as TPH has been an active debate involving some regulatory agencies for the past couple of years HIDOH 2017; CASWB-SFBR 2016b. However, due to two important factors, it is best practice to differentiate the metabolites from parent TPH. These factors are:

- metabolites have significantly different chemical and physical properties than the hydrocarbons due to their polar molecular structure (e.g., much higher solubility),
- the toxicity of metabolite mixtures may be different from the toxicity of the hydrocarbons presumed to be

present as TPH.

Improper identification of nonhydrocarbons such as metabolites and naturally occurring organic matter as TPH may mislead site characterizations and could confound investigations in the following ways:

- the location and concentration of the hydrocarbons could only be estimated
- concentration trends for the hydrocarbons would not be observed or understood
- site assessment and remediation strategies can also be compromised without a clear understanding of what's there: hydrocarbons vs. metabolites. You can select (or design) the wrong type of remediation if you do not know what you have. Hence, the need for a comprehensive, three-dimensional site characterization and development of a detailed CSM that is continually updated as new data/information become available.

▼Read more

All of these are critical reasons to separate the hydrocarbons and the metabolites in the definition of TPH for the purpose of this ITRC guidance document, in the pursuit of more accurate site investigation and risk assessment. Just like the hydrocarbons before biodegradation, metabolites are present in soil and groundwater as complex mixtures, and it is impossible to analyze for all potential metabolites individually. If the metabolites are of potential concern, there are two potential options to separately evaluate them using currently available analytical methods.

The first potential option would be to analyze samples using bulk extractable carbon range TPH without and with SGC to separate the bulk hydrocarbon and bulk polar (assumed to be metabolites) portions (see Section 5.9, TPH Analytical Methods). The BPs of the metabolites are typically higher than those for hydrocarbons with the same number of carbons, but many "small" metabolites can be quantified within the nC10+ range (e.g., extractable or "diesel" range). In this way, the extractable metabolites would not be included as TPH but would be otherwise evaluated separately.

Note that at present there is not a mechanism to separate hydrocarbons and metabolites for the bulk organics purgeable or "gasoline" range TPH. It is also critical that one or more representative background sample(s) are collected to assist in differentiating the naturally occurring oxygenated compounds and those originating from the petroleum release.

The second potential option would be to select potential individual metabolites that have known regulatory toxicity factors (e.g., 2-hexanone; several alkylphenols) and for which standards are available, and analyze for those specific metabolites separately using quantitative discrete-constituent analyses (GC/mass spectrometry).

Potential human toxicity and potential aquatic toxicity of the metabolites mixtures at biodegrading petroleum release sites, and recommended mechanisms to evaluate the potential risk posed by the metabolites, are discussed in detail in Human Health Risk and Ecological Risk Assessment.

4.5.4 Individual Constituents

Individual compounds, shown in Table 4-5, are individual chemicals such as BTEX, MTBE, tert-butyl alcohol (TBA), naphthalene, and PAHs that have well-established chemical-specific toxicity values. The use of individual compounds as the basis for risk evaluation is well established ASTM 2015b, and the choice of surrogate compounds is dictated by the petroleum fuel release and the regional or state regulatory programs. If the release type(s) is unknown, then all of the individual compounds should be analyzed for, with the possible exception of organic lead and lead scavengers. For petroleum hydrocarbon oil, a set of individual chemicals is used in some regulatory programs but may include only a small fraction of the total oil compositional mass. Therefore, a possibility exists that all individual concentrations may meet or fall below individual chemical screening levels or criteria, but the remaining total oil concentration (or TPH) might still exceed risk-based levels (see Conceptual Site Models).

> *Even at petroleum-contaminated sites where BTEX, naphthalene, PAHs, etc., are not present or at concentrations below their applicable Tier 1/screening levels, TPH should still be assessed for risk.*

It is important to emphasize that TPH is a way to assess what else may be in the environment that cannot be accounted for by determination of individual indicator compounds. Although the indicator compounds are often the risk drivers, there are situations when there are no target compounds above regulatory thresholds but the "unknown" mixture that is considered "TPH" may be triggering a more in-depth investigation.

Table 4-5. Recommended individual compounds for assessment of petroleum releases in addition to TPH

Compound(s)	Gasoline	Aviation Gasoline	Jet Fuel	Diesel	Heavier Fuels and Crude Oil
n-hexane	Y	Y	N	N	N
BTEXN	Y	Y	Y	Y	Y
2-MN	Y	Y	Y	Y	Y
MTBE, TBA	Y	N	N	N	N
Organic (Alkyl) Lead (total and speciated)*	Y, for pre-1977 releases only, product only	Y	N	N	N
Lead Scavengers (EDB, EDC)	Y, for pre-1997 releases only	Y	N	N	N
16 Priority Pollutant PAHs	N	N	N	N	Y

Notes: Y = yes; N = no.

BTEXN = benzene, toluene, ethylbenzene, xylenes, naphthalene; 2-MN= 2-methylnaphthalene.

MTBE, TBA= methyl tert-butyl ether, tert-butyl alcohol (MTBE and other oxygenates were used approx. early 1990s to 2005; TBA is primarily a biodegradation metabolite from MTBE).

n-Hexane and 2-MN are analyzed so that conservative toxicity values for their respective carbon range fractions based on these two chemicals do not have to be used for risk assessment.

16 priority pollutant PAHs are from 40CFR401.15 CWA list. Other compounds may be required for waste oil releases. Recommended analytical methods for each matrix are provided in TPH Analytical Methods.

*Alkyl lead should be used only from GC/mass spectrometry (MS) or GC/electron capture detector (ECD) methods where the individual species are determined.

In addition to higher-quality concentration data provided by targeted analyses (e.g., GC-MS), analysis of individual compounds affords the opportunity to not have to default to the most conservative toxicity value for a TPH fraction that is based on a specific compound (e.g., n-hexane or 2-methylnaphthalene). For example, in some TPH risk-based regulatory programs, it may be possible to demonstrate that a specific surrogate (e.g., 2-methylnaphthalene) may not actually be present in the mixture and, if so, it may be possible to use an alternate surrogate to assess the potential toxicity of an individual fraction. It is also good practice to check any guidance pertinent to the jurisdiction of the site in question to identify whether this approach is acceptable (see Regulatory Framework).