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Special Issue on

TPH (Total Petroleum Hydrocarbon)

Article summaries

Strategy for risk-based management of TPH .................... 2

This article, from the total petroleum hydrocarbon criteria working group, gives an overview on TPH: how it is defined, indicator compounds, identification, analytical methods, toxicity criteria and risk-based methodology.

Massachusetts’ VPH/EPH approach ............................ 6

This article describes Massachusetts’ VPH/EPH approach, consisting of volatile petroleum hydrocarbon and extractable petroleum hydrocarbon methods.

Washington state’s interim policy on TPH fractions ..... 9

Washington state’s interim policy on TPH fractions was developed to interpret existing regulations. It gives guidance on using surrogates to calculate cleanup levels for TPH.

Fate and transport considerations of TPH fractions ... 11

This article, focusing on the third volume of the TPH criteria working group, summarizes methods for delineating TPH into equivalent carbon number fractions based on fate and transport considerations.

Information sources ................................................... 14

This article lists phone numbers, addresses, and e-mails of recent publications and other sources of information.

Other articles on TPH appeared in UTTU Volume 6, No. 2, April 1992

• Petroleum product chemistry
• Analytical tests for petroleum hydrocarbons
• Wisconsin’s approach to petroleum analysis
• Selecting, understanding and interpreting petroleum hydrocarbon test results
• 1991-92 TPH survey results
• TPH references

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Strategic Plan for Risk-Based Management of TPH

The following article is abstracted from a paper written by Wade Weisman of the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG). His paper appeared recently in the Journal of Soil Contamination.

No consistent strategy exists across the United States for assessing human health risk at petroleum-contaminated sites. The TPHCWG, or Working Group, convened in 1993 to address the large disparity among cleanup requirements used by states at sites contaminated with petroleum hydrocarbons. These requirements usually focus on total petroleum hydrocarbon (TPH), with numerical standards ranging from 10 to thousands of milligrams of TPH per kilogram of soil.

Recognizing these standards are not based on a scientific assessment of human health risk, the Working Group developed a flexible approach for establishing soil cleanup levels that protect human health from all exposure routes. The Working Group’s approach, culminating in the development of fate and transport fraction toxicity criteria, represents a scientifically sound technical basis for risk-based corrective action. While the approach does not address ecological risk or aesthetic criteria, the strategy for developing the Working Group approach can be modified to address ecological concerns.

The Working Group has more than 400 active participants from industry, government and academia. Their data has or will be published in the following volumes:
1: Petroleum Hydrocarbon Analysis of Soil and Water in the Environment
2: Composition of Petroleum Mixtures
3: Selection of Representative TPH Fractions Based on Fate and Transport Considerations
4: Development of Fraction-Specific Reference Doses (RfDs) and Reference Concentrations (RfCs) for TPH
5: Application of the TPHCWG Methodology Within the ASTM Risk-Based Corrective Action Framework

This article focuses on the following aspects of TPH:
• what TPH is
• selection of TPH fraction and indicator compounds
• identification of fractions with similar fate and transport characteristics
• analytical methods for characterizing petroleum-contaminated soils and water
• development of toxicity criteria for fate and transport fractions
• risk-based methodology for deriving soil cleanup levels at petroleum-contaminated sites
• integration of TPHCWG approach into the ASTM RBCA framework

What TPH is
TPH may consist of hundreds or even thousands of individual constituents, of which 250 have been identified. The Working Group collected and evaluated available data regarding the composition of petroleum products, including gasoline, crude oil, jet fuels, kerosene, diesel, home-heating oil and lubricating oils. With this data, the Working Group first quantified how many of the 250 constituents are found in each product. They then summarized this information. Compilation of this data aided the Working Group in identifying which TPH constituents/fractions should be the focus of human health risk-based cleanup levels.

Selection of TPH fraction and indicator compounds
To analyze all soil samples for all TPH constituents would be excessive and cost-prohibitive. Even if concentration data existed for all TPH constituents, the toxicity and fate and transport data needed for assessing human health risk do not exist for each constituent. Thus, the Working Group considered if human health toxicity associated with petroleum contamination should be evaluated on the basis of
• whole products with similar compounds grouped into fractions
• indicator compound toxicity

Figure 1 illustrates this point. The whole product approach applies toxicity criteria for unweathered whole products to the petroleum mixture. The indicator approach describes the mixture’s toxicity of one or more potent constituents. This approach is often used to assess the carcinogenic potential of complex mixtures. The fraction (whole product) approach involves resolving petroleum constituents into fractions based on chemical and physical properties and then assigning representative toxicity criteria to each fraction.

Although the whole product approach may be more appropriate with fresh spills, the Working Group selected a hybrid approach that employs fractions along with indicator compounds. They chose this approach because, in general, petroleum products at contaminated sites are weathered. The Working Group advocates the use of benzene and carcinogenic polycyclic aromatic hydrocarbons (PAHs) as indicator compounds to evaluate cancer risk. To assess non-cancer risk, the Working Group identified 13 TPH fractions to be evaluated (see Table 1, page 4).

Identification of TPH fractions with similar fate and transport characteristics
Exposure considerations are usually the primary factor in determining risk to human health. The fate and transport of TPH constituents vary according to the constituents’ individual chemical and physical properties, which the Working Group evaluated to establish fate and transport parameters for the fractions. Researchers formed these fractions by modeling the potential for individual TPH constituents to leach from soil to groundwater and to volatilize from soil to air. Modelers obtained equations from...
Researchers grouped individual TPH constituents into fractions. Each fraction had no greater than an order of magnitude difference in the modeled environmental behavior of the constituents. Researchers chose this order of magnitude criterion for defining fractions after considering the level of uncertainty in performing toxicity assessments and exposure assessments. Once the researchers defined these fractions, they assigned appropriate fate and transport parameter values to each fraction based on average values of the individual constituents within each fractions (see Table 1). These values can be used to determine exposure to each fraction. Aliphatic and aromatic components are considered separately because their environmental behavior differs so greatly.

Researchers subdivided each chemical group according to equivalent carbon number index. This index, related to the boiling point of individual constituents, is equivalent to the retention time of the compounds in a boiling point gas chromatography (GC) column, normalized to the n-alkanes. Researchers empirically determined the relationship between equivalent carbon number and boiling point. (Knowing the boiling point of a chemical, one can calculate its equivalent carbon number.)

The TPHCWC’s Volume 3 contains a detailed account of fate and transport fractions derivation and their equivalent carbon numbers. Separating TPH constituents into fate and transport fractions simplifies environmental modeling. The physical parameters listed in Table 1 can help modelers estimate partitioning in the soil-water-air system. Thus the fraction is treated like a single chemical, and modelers can more accurately estimate potential human exposure.

### Analytical methods

The Working Group also identified and evaluated available analytical methods for hydrocarbons, reported in Volume 1. Methods described use the following techniques:

- gas chromatography
- infrared spectrometry
- gravimetry
- immunoassay
- thin-layer chromatography
- high-performance liquid chromatography

Volume 1 provides guidance on

- the appropriate methods for identifying petroleum hydrocarbons
- limitation of the methods
- how to interpret the methods’ results

For identifying and quantifying fate and transport fractions in soil, the Working Group developed a method that is based on SW-846 EPA Method 3611 (alumina column cleanup and separation of petroleum wastes) and SW-846 Method 3630 (silica gel cleanup). This method fractionates petroleum-derived mixtures into aliphatic, aromatic and polar fractions and resolves and quantifies them. The method may be used to identify contaminants; less expensive methods may then be used to complete the sampling. Application of traditional EPA analytical methods is likely to be necessary to quantify the presence of indicator hydrocarbons.
Developing toxicity criteria for fate and transport fractions

After identifying fate and transport fractions of TPH and developing appropriate analytical methods, the Working Group established toxicity criteria (see Table 2) for these fractions. The Working Group:

• compiled and reviewed available data for individual TPH constituents within each fraction
• reviewed toxicity information for well-defined mixtures that are components of several fractions and for whole products, such as gasoline and fuel oils

In some cases, the same toxicity criterion was assigned to different fate and transport fractions due to the similarity of toxicity findings across fractions or limitations in the available toxicity data. The fractions remained differentiated so that exposure potential could be estimated appropriately. The toxicity criteria can be used like reference doses (RfDs) and reference concentrations (RfCs) because they are derived in a similar manner to USEPA reference doses/concentration. RfDs are estimates of daily exposure to the human population, including sensitive subgroups that are likely to be without appreciable risk of deleterious effects.

### Table 1. TPH fractions derived from fate and transport characteristics and associated properties (based on an equivalent carbon number; from Weisman, 1998).

<table>
<thead>
<tr>
<th>Carbon range</th>
<th>Aliphatic fractions</th>
<th>Aromatic fractions</th>
<th>1 Carbon range equals equivalent carbon number. 2 Benzene is the only compound in this fraction.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solubility (mg/L)</td>
<td>Vapor pressure (atm)</td>
<td>Log K&lt;sub&gt;oc&lt;/sub&gt; (c/c)</td>
</tr>
<tr>
<td>C5 – C6</td>
<td>3.6E + 01</td>
<td>3.5E – 01</td>
<td>2.9E + 00</td>
</tr>
<tr>
<td>&gt;C6 – C8</td>
<td>5.4E + 00</td>
<td>6.3E – 02</td>
<td>3.6E + 00</td>
</tr>
<tr>
<td>&gt;C8 – C10</td>
<td>4.3E – 01</td>
<td>6.3E – 03</td>
<td>4.5E + 00</td>
</tr>
<tr>
<td>&gt;C10 – C12</td>
<td>3.4E – 02</td>
<td>6.3E – 04</td>
<td>5.4E + 00</td>
</tr>
<tr>
<td>&gt;C12 – C16</td>
<td>7.6E – 04</td>
<td>4.8E – 05</td>
<td>6.7E + 00</td>
</tr>
<tr>
<td>&gt;C16 – C21</td>
<td>2.5E – 06</td>
<td>1.1E – 06</td>
<td>8.8E + 00</td>
</tr>
<tr>
<td>C6 – C7</td>
<td>1.8E + 00</td>
<td>1.3E – 01</td>
<td>1.9E + 00</td>
</tr>
<tr>
<td>&gt;C7 – C8</td>
<td>5.2E + 02</td>
<td>3.8E – 02</td>
<td>2.4E + 00</td>
</tr>
<tr>
<td>&gt;C8 – C10</td>
<td>6.5E + 01</td>
<td>6.3E – 03</td>
<td>3.2E + 00</td>
</tr>
<tr>
<td>&gt;C10 – C12</td>
<td>2.5E + 01</td>
<td>6.3E – 04</td>
<td>3.4E + 00</td>
</tr>
<tr>
<td>&gt;C12 – C16</td>
<td>5.8E + 00</td>
<td>4.8E – 05</td>
<td>3.7E + 00</td>
</tr>
<tr>
<td>&gt;C16 – C21</td>
<td>6.5E – 01</td>
<td>1.1E – 06</td>
<td>4.2E + 00</td>
</tr>
<tr>
<td>&gt;C21 – C35</td>
<td>6.6E – 03</td>
<td>4.4E – 10</td>
<td>5.1E + 00</td>
</tr>
</tbody>
</table>

### Table 2. Toxicity criteria for TPH fractions (Weisman, 1998).

<table>
<thead>
<tr>
<th>Carbon range</th>
<th>Aromatic oral RfD (mg/kg/d)</th>
<th>Aromatic inhalation RfC (mg/kg/d)</th>
<th>Critical effect</th>
<th>Aliphatic oral RfD (mg/kg/d)</th>
<th>Aliphatic inhalation RfC (mg/m³)</th>
<th>Critical effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5 – C6</td>
<td>0.2</td>
<td>0.4</td>
<td>5.0</td>
<td>18.4</td>
<td>Nephrotoxicity</td>
<td></td>
</tr>
<tr>
<td>&gt;C6 – C8</td>
<td>0.04</td>
<td>0.2</td>
<td>0.1</td>
<td>1.0</td>
<td>Hepatic and hematological changes</td>
<td></td>
</tr>
<tr>
<td>C5 – C7</td>
<td>0.2</td>
<td>0.4</td>
<td>Decreased body weight</td>
<td>2.0</td>
<td>Hepatic (foreign body reaction) granuloma</td>
<td></td>
</tr>
<tr>
<td>&gt;C7 – C8</td>
<td>Nephrotoxicity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&gt;C8 – C10</td>
<td>0.04</td>
<td>0.2</td>
<td>Decreased body weight</td>
<td>2.0</td>
<td>Hepatic (foreign body reaction) granuloma</td>
<td></td>
</tr>
<tr>
<td>&gt;C10 – C12</td>
<td>0.03</td>
<td>NA</td>
<td>Nephrotoxicity</td>
<td>2.0</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>&gt;C12 – C16</td>
<td>0.03</td>
<td>NA</td>
<td>Nephrotoxicity</td>
<td>2.0</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>&gt;C16 – C21</td>
<td>0.03</td>
<td>NA</td>
<td>Nephrotoxicity</td>
<td>2.0</td>
<td>NA</td>
<td></td>
</tr>
</tbody>
</table>
during a lifetime. RfCs are estimates of continuous inhalation exposure to the human population, including sensitive subgroups that are likely to be without appreciable risk of deleterious effects during a lifetime. The toxicity criteria developed by the Working Group for each fate and transport fraction are based on toxicity data for individual constituents and mixtures. The data provide a representative and conservative estimate of each fraction’s toxicity.

Remediators can use these toxicity criteria within a risk-based decision framework such as ASTM RBCA to calculate non-cancer human health risk-based screening levels (RBSLs). Because carcinogens tend to dictate cleanup requirements, both carcinogenic indicator compounds (evaluated using published slope factor values) and the fate and transport fractions need to be considered when trying to assess health risks.

Risk-based methodology for deriving soil cleanup levels

The Working Group chose ASTM’s RBCA standard as an example framework for establishing soil screening levels at petroleum-contaminated sites. The framework considers

• site assessment
• risk assessment
• risk management
• corrective action

Implementation of the RBCA framework requires an understanding of the petroleum contamination source, the fate and transport pathways that govern contaminant movement, and the existing and potential individuals who are or may be exposed to the contaminants. These elements are incorporated into a three-tiered approach, proceeding from simple to complex, using site-specific analysis as necessary:

• in Tier 1, remediators assess site conditions and contaminant type, and contaminant concentrations are compared with generic risk-based screening levels (RBSLs); if RBSLs are exceeded, the analysis either moves to Tier 2, or corrective action is implemented to reach the RBSLs
• in Tier 2, remediators establish site-specific target levels (SSTLs) based on more detailed site-specific information, including use of relatively simple mathematical models to measure or predict attenuation of contaminants away from the source areas; if SSTLs are exceeded, either corrective action is implemented or analysis proceeds to Tier 3
• in Tier 3, remediators perform a thorough, site-specific risk assessment

As remediators complete each tier, corrective action goals become more site-specific and presumably less conservative and less costly to achieve than those defined by the previous tier. After completion of each tier, the decision maker reviews the results and recommendations and decides if the cost of conducting additional site-specific analyses is warranted by the potential reduction in cost associated with a less costly corrective action plan.

Integration of Working Group approach into ASTM’s RBCA

The fate and transport fractions and toxicity criteria developed by the Working Group can be used in the ASTM RBCA framework to derive screening goals for petroleum-contaminated soils. The soil RBSLs calculated for the indicator compounds and fate and transport fractions can be used individually to set cleanup limits, i.e., site remediation is governed by the most restrictive or lowest soil RBSL. Alternatively, researchers can use the composition of the total petroleum mixture present at a site to derive a soil RBSL for TPH. The RBSL for TPH is calculated by summing the RBSLs for the individual compounds and fate and transport fractions, each weighted by their composition in the total petroleum mixture. The Working Group’s Volume 5 provides a thorough discussion of how the approach may be used within the RBCA framework, including risk calculations and results from demonstration sites.

Summary

The Working Group considers impacts of risk to human health by addressing

• carcinogenic risks, by using indicator compounds such as benzene and the carcinogenic PAHs
• non-carcinogenic risks, by using the fraction-specific toxicity criteria shown in Table 2

For each, the Working Group developed analytical methods to determine their relative mass. However, remediators must identify contaminant pathways before the toxicity criteria can be incorporated into the ASTM RBCA framework.

To ensure that TPH soil cleanup levels calculated by the Working Group are protective of human health, this approach must be updated as more data become available regarding the fate and transport properties and toxicity of TPH constituents and mixtures. In addition, the Working Group continues to investigate the use of more rapid, inexpensive methods for analyzing the indicator compounds and fate and transport fractions of TPH as well as for assessing toxicity of these fractions. The streamlined, scientifically sound approach developed by the Working Group represents a significant advance in the management of petroleum-contaminated sites, ensuring the efficient use of resources to maintain and protect human health.

Reference

Massachusetts' VPH/EPH approach

The following article is extracted, sometimes verbatim, from a Massachusetts Department of Environmental Protection (MADEP, 1997) document on characterizing risks at petroleum-contaminated sites using a volatile petroleum hydrocarbons/extractable petroleum hydrocarbons approach (VPH/EPH).

Characterizing the risks posed by petroleum-contaminated soil and water has proved to be difficult and inexact because petroleum products are a complex and highly variable mixture of hundreds of individual hydrocarbon compounds. Traditional approaches have focused on identifying and evaluating specific indicator components, such as benzene, or quantifying a total petroleum hydrocarbon (TPH) value. The limitations of an "indicator only" approach have long been recognized, especially at gasoline-contaminated sites, and focusing on a select few compounds cannot adequately characterize the risks posed by all hydrocarbons present. The quantitation of a TPH value is a step in the right direction because an attempt is being made to account for all compounds present; however, traditional TPH methods and approaches provide little or no information on the composition or toxicity of generated data.

MADEP developed and published a toxicological approach in 1994 that advocated breaking down TPH into aliphatic and aromatic fractions. To support and implement the approach, MADEP also developed two analytical methods that could differentiate and quantitate collective concentrations of aliphatic and aromatic hydrocarbons. Aliphatic compounds are alkanes, alkenes or alkynes or their derivatives; the term denotes compounds that do not have the resonance structure of aromatic compounds. Aromatic compounds are organic compounds that contain a benzene ring in their molecules. The two methods, volatile petroleum hydrocarbons (VPH) and extractable petroleum hydrocarbons (EPH), account for the range of hydrocarbons present in petroleum products of interest. They conform with EPA laboratory approaches for the determination of volatile and extractable organics.

Composition of petroleum

Petroleum is a mixture of hundreds of hydrocarbon compounds. Industry specifications for refined products, such as gasoline and diesel fuel, are based upon physical and performance-based criteria, not upon a specific chemical formulation. As such, the compositions of petroleum products released to the environment are complex and variable, a function of the following:

- the origin and chemistry of the parent crude oil
- refining and blending processes
- addition of performance-enhancing additives

Once a petroleum product is released to the environment, its chemistry is further altered by contaminant fate and transport processes, such as leaching, volatilization and biodegradation.

To identify and quantitate every single hydrocarbon compound present in petroleum-contaminated media would be extremely difficult and expensive. Even if this was accomplished, little toxicological data are available for the vast majority of petroleum constituents. While limited data on the toxicity of some petroleum fuels exist, the chemistry of "weathered" products typically encountered at contaminated sites may be quite different from the chemistry of the fresh product, which was the subject of toxicological evaluation.

An evaluation of data on the chemistry and toxicity of petroleum products, however, suggests the following:

- petroleum products are comprised mainly of aliphatic/alicyclic and aromatic hydrocarbon compounds
- aromatic hydrocarbons appear to be more toxic than aliphatic hydrocarbons
- the toxicity of aliphatic compounds appears to be related to their carbon number/molecular weights

These three precepts are the foundation of the VPH/EPH approach. Specifically, under this approach the non-cancer-causing toxicity of petroleum-contaminated soil or water is established by

- determining the collective concentrations of specified ranges of aliphatic and aromatic hydrocarbons
- assigning a toxicity value (e.g., reference dose) to each range; well-defined compounds within specified ranges are selected as "surrogate" indicators to define the toxicity of the entire range; for example, every aliphatic compound with between 5 and 8 carbon atoms (C5-C8 aliphatic hydrocarbons) is assumed to be as toxic as n-hexane; Table 3 shows the complete breakdown.

<table>
<thead>
<tr>
<th>Hydrocarbon fraction</th>
<th>Surrogate compound</th>
<th>Reference dose (mg/kg/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5–C8 aliphatics</td>
<td>n-hexane</td>
<td>0.06</td>
</tr>
<tr>
<td>C9–C18 aliphatics</td>
<td>n-nonane</td>
<td>0.6</td>
</tr>
<tr>
<td>C19–C36 aliphatics</td>
<td>Eicosane</td>
<td>6.0</td>
</tr>
<tr>
<td>C9–C22 aromatics</td>
<td>Pyrene</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 3. Assigned toxicity values for the four hydrocarbon fractions (MADEP, 1997).

Cancer effects are evaluated separately by identifying and quantifying specific hydrocarbon compounds like benzene and certain polycyclic aromatic hydrocarbons (PAHs) that are designated carcinogens.
Hydrocarbon fractions of interest

EPA analytical methods have traditionally used one approach for volatile organic analysis (i.e. purge and trap) and another for semi-volatile/extractable organics (i.e., solvent extraction). To facilitate use by commercial laboratories accustomed to such division, the VPH and EPH methods developed by MADEP maintain this distinction. Moreover, because of the large carbon range covered by the new approach (i.e., C5 to C36), it would be difficult to detect all fractions using just one method; the volatile/purgeable methods can adequately cover the lighter hydrocarbons but not the heavier fractions (>C12). Due to losses of low-molecular-weight hydrocarbons that occur during the sample preparation process, extractable methods are generally unable to reliably detect lighter fractions (<C9).

Given the need for two analytical methods, and a desire to minimize requirements to use both methods on all samples, a decision was made to break up the C9-C18 aliphatic range to enable detection of all gasoline-range hydrocarbons in the VPH methods. Thus, it would only be necessary to use the VPH procedure to characterize gasoline releases.

For these reasons, MADEP divided the aliphatic and aromatic hydrocarbon ranges of interest into six separate entities: three detected by the VPH method and three by the EPH method as listed in Table 4.

<table>
<thead>
<tr>
<th>Toxicologically defined hydrocarbon fractions</th>
<th>Analytical/program-defined hydrocarbon fraction</th>
<th>Analytical method</th>
<th>Toxicity surrogate</th>
<th>Reference dose (mg/kg/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatics C5-C8</td>
<td>C5-C8</td>
<td>VPH</td>
<td>n-hexane</td>
<td>0.06</td>
</tr>
<tr>
<td>C9-C18</td>
<td>C9-C12</td>
<td>VPH</td>
<td>n-nonane</td>
<td>0.6</td>
</tr>
<tr>
<td>C19-C36</td>
<td>C19-C36</td>
<td>EPH</td>
<td>n-nonane</td>
<td>0.6</td>
</tr>
<tr>
<td>Aromatics C9-C22</td>
<td>C9-C10</td>
<td>VPH</td>
<td>Pyrene</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>C11-C22</td>
<td>EPH</td>
<td>Pyrene</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 4. Aliphatic and aromatic hydrocarbon ranges (MADEP, 1997).

Relationship of VPH/EPH to TPH and gasoline range organics

Traditionally, petroleum fuels have been characterized by identifying and evaluating indicator compounds, like benzene, and/or collective measurements of total petroleum hydrocarbons (TPH). Because TPH is essentially defined by the test method chosen, a universal definition does not exist, and resultant data are notoriously incomparable. Most common methods (e.g., TPH via EPA Method 418.1) involve an extraction technique, and since loss of lighter hydrocarbons can be expected as a result of sample extraction and concentration, TPH can be operationally defined as hydrocarbons with 9 or more carbon atoms (>C9).

Like TPH, the EPH test quantitates hydrocarbons >C9. The EPH method, however, goes one step further, separating the TPH fraction into three sub-fractions (C9-C18 aliphatic hydrocarbons, C19-C36 aliphatic hydrocarbons, and C11-C22 aromatic hydrocarbons) and 17 targeted PAH compounds.

Similarly, gasoline releases have sometimes been characterized by use of a gasoline range organics (GRO) analysis. Like a GRO analysis, the VPH test method is also a purge-and-trap gas chromatography (GC) procedure that detects hydrocarbons in the C5-C12 range. Once again, however, the VPH method goes one step further, separating the GRO fraction into three sub-fractions (C5-C8, aliphatic hydrocarbons, C9-C12 aliphatic hydrocarbons, and C9-C10 aromatic hydrocarbons) and eight target compounds (including BTEX, MTBE and napththalene).

Figure 2 indicates that if the concentrations of the three EPH fractions and target PAH analytes were added together, it would equal a “TPH” value. Similarly, if the three VPH fractions and BTEX/MTBE/napththalene concentrations were added together, it would equal a GRO value. It should be noted that the C9-C12 aliphatic hydrocarbons are quantitated by both methods.

Analytical methods

MADEP developed and published its own analytical methods for VPH and EPH because conventional TPH and EPA test methods are not capable of measuring the collective concentrations of aliphatic and aromatic hydrocarbons. The VPH and EPH methods use gas chromatography (GC) and modifications of traditional EPA procedures such as SW-846. These two analytical methods separate complex hydrocarbon mixtures into collective fractions of aliphatic and aromatic hydrocarbons and produce data that can be directly compared to Massachusetts’ cleanup standards (method 1).

Figure 2. GRO, TPH, VPH and EPH relationships (from MADEP, 1997).
**Volatile petroleum hydrocarbons (VPH) method**

The MADEP VPH method is a purge and trap, GC/PID/FID procedure. This method allows collective concentrations of C4-C8 aliphatic, C9-C12 aliphatic and C9-C10 aromatic hydrocarbons to be quantitated in soil or water matrices. In addition to these fractional ranges, the VPH method may also be used to concurrently identify and quantitate individual concentrations of the target analytes benzene, toluene, ethylbenzene and xylene (BTEX), and methyl-tertiary-butylether (MTBE) and naphthalene.

Laboratory workers analyze samples using purge-and-trap sample preparation/concentration. The gas chromatograph is temperature-programmed to facilitate separation of hydrocarbon compounds. A photoionization detector (PID) and flame ionization detector (FID) in series detect the hydrocarbons. The PID chromatogram is used to determine the individual concentrations of target analytes and the collective fractional concentration of aromatic hydrocarbons in the C9 through C10 range. The FID chromatogram identifies the collective fractional concentrations of aliphatic hydrocarbons within the C5 through C8 and C9 through C12 ranges. Individual “marker” compounds are used to establish the beginning and end of the hydrocarbon ranges of interest.

This approach relies on the selectivity of the PID and FID detectors to differentiate aromatic hydrocarbons from aliphatic hydrocarbons. Specifically, the PID will preferentially respond to hydrocarbon compounds with pi or double carbon (C=C) bonds, but will not respond well to hydrocarbon compounds with single carbon (C-C) bonds. Because aromatic compounds have at least one benzene ring with three double bonds, the aromatic compounds respond well to a PID; straight, branched and cyclic aliphatic compounds with single carbon bonds respond poorly. Conversely, the FID is more of a universal detector and will respond equally well to both aliphatic and aromatic hydrocarbons.

Because the PID can detect sample analytes without destroying them, compounds eluting from the chromatographic column are first passed through the PID and then through the FID, where they are combusted in a hydrogen flame. The FID will theoretically detect the total concentrations of all petroleum hydrocarbons, while the PID will detect mostly aromatic compounds. Subtracting the PID from the FID response can quantitate aliphatic compounds. Reality, however, deviates from the theoretical in two important ways:

First, pi bonds are present in hydrocarbon compounds other than aromatics—most notably alkenes—which are present in gasoline; alkenes, therefore, will be falsely quantitated as aromatics; however, this is not a major limitation because:

- alkenes are not typically found in high concentrations in most petroleum products
- alkenes may be more toxicologically similar to aromatics than to aliphatics

Second, and more problematic, aliphatic compounds will produce some measurable response on a PID, especially heavier-molecular-weight branched and cyclic alkanes. This response can become significant if several aliphatic compounds are present, and it will appear as an inflated quantitation of aromatics. Because a significant portion of the hydrocarbons in the C9-C12 range of gasoline are substituted aromatic compounds, this analysis over-quantitation is not a major problem. Products like kerosene and Jet A fuel, however, contain predominantly aliphatic compounds within this range. Therefore, use of the PID/FID approach can lead to significant over-quantitation of the aromatic fraction.

To minimize over-quantitation of the aromatic fraction and ensure accurate data, lab workers can:

- use a low-energy PID lamp (e.g., 9.5 eV) to further diminish aliphatic response
- use other techniques such as chemical fractionation
- use a GC/MS approach

**Extractable petroleum hydrocarbons (EPH) method**

MADEP’s EPH solvent extraction/fractionation GC/FID procedure quantitates the collective concentrations of C9–C18 aliphatic, C19–C36 aliphatic and C11–C 22 aromatic hydrocarbons in soil or water matrices. In addition to these fractional ranges, the EPH methods may also be used to concurrently identify and quantitate individual concentrations of the 17 polynuclear aromatic hydrocarbon (PAH) target analytes.

Laboratory workers use methylene chloride to extract the samples. Next, the solvent is exchanged into hexane and loaded onto a silica gel cartridge or column. The silica gel cartridge/column is rinsed with hexane to strip aliphatic compounds, and the resultant extract is collected and labeled. The silica gel cartridge/column is then rinsed with methylene chloride to strip aromatic compounds and the resultant extract is collected and labeled. The two extracts are then analyzed separately by direct injection into a temperature-programmed GC/FID. Individual target PAH compounds are identified by GC/FID analysis of the aromatic extract. While using this method, lab workers should keep in mind the following two aspects.

First, this method relies on a solvent/silica gel fractionation process to differentiate aromatic hydrocarbons from aliphatic hydrocarbons. The process is a sensitive, yet critical element of the analytical approach. Small errors at this stage can result in significant over- or under-quantitation of aromatic and aliphatic ranges. For this reason, the method specifies use of a fractionation check solution to verify proper separation of the aliphatic and aromatic fractions.

Second, like any GC/FID procedure, an unresolved complex mixture (UCM) or “hump” will typically be observed on the chromatogram of a heavier molecular weight petroleum product, particularly with weathered products. A UCM is produced when many individual hydrocarbon compounds are eluting from the capillary column at the same time, overwhelming and preventing the detector signal from returning to baseline. Nevertheless, it is important that these compounds be included in the sample quantitation.
calculation. For that reason, the EPH method specifies the use of a forced or projected baseline when integrating chromatographic areas of fractional ranges. If a laboratory does not take steps to ensure this integration technique, resultant fractional range data may significantly under-report true hydrocarbon concentrations.

**Target analytes**

Both VPH and EPH methods can provide quantitation of target analytes. They are GC methods that identify analytes solely on the basis of retention times, thus they can produce “false positive” or over-inflated concentration data for individual compounds.

Although the cleanup and fractionation procedures specified in the EPH methods will tend to minimize interferences of this nature (by removing aliphatic compounds that may co-elute with the PAH target analytes), the only approach to get positive identification and quantitation of these target analytes is to use a GC/MS analytical technique, such as EPA Method 8270 for the PAHs, and EPA Method 8260 for BTEX/MTBE. For this reason, a laboratory may advise a client to use the VPH and EPH methods to quantitate the aliphatic/aromatic fractional ranges, but a GC/MS method to quantitate individual (target) analytes. Although acceptable, the strategy may increase analytical costs.

To save money, workers might risk a gamble by quantitating target analytes using the VPH/EPH methods for samples that are believed to be relatively free from contamination. Trying to confirm a “clean closure” at a tank removal site is a good example. If significant concentrations of target analytes are found, a re-analysis can be done using GC/MS to provide a definitive determination. If the laboratory was instructed to retain the sample extract from the VPH/EPH samples, the cost for this re-analysis would be reduced.

**Alternatives to the VPH/EPH methods**

The MADEP VPH and EPH analytical techniques are “performance-based” methods, which means that modifications to specified procedures are allowable, as long as acceptable performance can be demonstrated. Recommended procedures and criteria by which the performance of modified or alternative methods can be judged and documented will be provided by MADEP with the publication of the final methods. The laboratory must clearly identify the nature of modifications to any method.

**Additional research needs on VPH and EPH methods**

MADEP continues to gather and review information and data on its VPH/EPH approach. Key areas requiring additional development and/or refinement include:

- ecological risks: in addition to the human health considerations addressed by RfD and RfC criteria, information, data and standards are needed to better evaluate ecological risks posed by aliphatic and aromatic hydrocarbons

**Other information contained in MADEP’s report**

The MADEP report contains other information such as:

- sampling procedures and requirements
- reporting requirements
- analytical screening techniques
- cleanup standards
- risk characterization
- site characterization

**Reference**

MADEP, Characterizing Risks Posed by Petroleum-Contaminated Sites: Implementation of MADEP VPH/EPH Approach, October 31, 1997, public comment draft, Commonwealth of Massachusetts, Executive Office of Environmental Affairs, Department of Environmental Protection, One Winter Street, Boston, Massachusetts 02108; 617-292-5500.

**Washington state’s interim policy on TPH fractions**

In 1991, Washington state developed, under the Model Toxics Control Act (MTCA), an interim advisory policy concerning risk-based, site-specific cleanup methods designed to protect air, soil and water (WSDE, 1997). The policy, although not binding on the regulated community, was developed to interpret existing regulations. It does not completely address health effects of vapors or provide cleanup levels that necessarily address residual odors or ecological receptors; the policy does, however, give guidance on how to calculate cleanup levels for TPH using surrogates.

The surrogate approach involves representing complex weathered petroleum mixtures by substituting known data for particular substances, or for ranges of substances. Petroleum spills are often weathered to some degree; therefore, remediaters measure fractions of the petroleum mixtures rather than the whole product mixture at a site. Using surrogates involves

- defining the fractions
- defining the values to be used for those fractions
Petroleum fractions

Fractions of petroleum can be defined by the substance’s molecular size. Because a common analytical technique, chromatography, relies on substance mobility, and mobility is related to molecule size, lab technicians can use chromatography to define and quantify fractions of petroleum mixtures.

Petroleum compounds have molecular structures based on carbon atoms. Molecule shape (straight chain, branched chain, cyclic, etc.) and the size (number of carbon atoms) determine the chemical and physical properties. The relationship between the structure and the chemical and physical properties can also be expressed by how many carbons each substance acts as if it has rather than how many it actually has. This will better allow groups of substances, or “fractions” (fractions of the total), to be combined with similar-acting substances. The fractions referred to in this article for fate and transport use the term “EC” (“equivalent carbons” or “relative carbon index number”), which is not always the same as the actual carbon number.

Petroleum hydrocarbons can be divided into two major fractions based on their structures:
- aliphatic hydrocarbons: straight carbon chains such as normal hexane, branched chains such as 3-ethyl hexane, or cyclic, such as cyclohexane
- aromatic hydrocarbons: typified by benzene, unsaturated 6-carbon-ring-structures

The two fractions tend to have similar compounds within each, both in terms of toxicity and fate and transport properties. Hydrocarbons fall into the following categories:
- single carbon-to-carbon bonds: alkanes
- one or more double carbon-to-carbon bonds: alkenes
- one or more triple carbon-to-carbon bonds: alkynes

Alkynes are rare in petroleum products. From an analytical perspective, it is easier to include most alkenes with aromatics; thus, for the purposes of this article, aromatics include alkenes. Some alkenes, however, especially volatile low-carbon-number alkenes, may be quantified as aliphatics rather than as aromatics.

Human health toxicity using surrogates

WSDE does not yet believe that adequate data exist to support more than one surrogate substance with a corresponding oral reference dose (ORfD) for each of the two groups, aliphatic and aromatic. The chosen surrogate for the aliphatic group is n-hexane, while pyrene is the surrogate for the aromatic group. WSDE previously determined the ORfD for these two chemicals. (Note: surrogates are used to evaluate non-carcinogenic effects; carcinogenic risk is determined by evaluating benzene and, if appropriate, carcinogenic PAHs.)

This interim policy also addresses the additive effect of toxic (non-carcinogenic) substances. Toxic effects can be the sum of everything that produces toxicity. Presently, all toxic effects of all petroleum compounds are not known, and defining them to WSDE’s satisfaction has not yet been accomplished. Thus, WSDE assumes that aliphatics, aromatics or any fraction thereof can cause toxic effects. As described in an earlier regulation, the effects must be summed and the sum cannot exceed a hazard index of 1.

Fate and transport using surrogates

The use of fractions and surrogates is well suited to model petroleum’s fate and transport because petroleum is a complex mixture whose compounds cover a broad range of physical properties. The two fate and transport pathways of major concern are movement from soil to groundwater and from soil to air.

The scientific literature lists numerous models for these pathways, but most apply to single substances or simple mixtures. Modeling of complex petroleum mixtures is still under study, especially with respect to vapor transport.

Analytical approach to surrogates

WSDE’s approach for measuring TPH involves two steps:
- measure volatile petroleum hydrocarbons (VPH) by a “purge and trap” process, followed by gas chromatography (GC), and detection by two detectors that can discriminate between aliphatics and aromatics
- measure extractable petroleum hydrocarbons (EPH) by a solvent extraction and solid-phase extraction/fractionation followed by gas chromatography and a single detector; here, the distinction between aliphatics and aromatics for EPH occurs in the extraction steps

For more on this topic, see also “Massachusetts’ VPH/EPH approach” in this issue of UTTU.

Other individual substances that might be analyzed for are:
- benzene
- ethylbenzene
- toluene
- xylene
- carcinogenic polynuclear aromatic compounds (cPAHs)
- other hazardous substances such as fuel additives

This interim policy also includes:
- a table listing the TPH compound, the fractions and the compounds commonly found in a release of a specific petroleum product
- a table listing fate and transport fractions and surrogate values
- an explanation of Washington’s Method A: lookup tables with media-specific TPH cleanup levels as well as cleanup levels for certain individual constituents (not to be used for surface water or air)
- an explanation of Washington’s Method B and Method C, involving the release’s toxicity evaluation and migration potential and greater detail (with examples) on how to use fractions for a surrogate approach to determine oral reference dose and cleanup levels
- a list of references to other Washington state documents
Fate and transport considerations of TPH fractions

This article, based on Volume Three from the TPH Criteria Working Group (TPHCWG, 1998), summarizes methods used to delineate TPH into equivalent carbon number fractions based on fate and transport considerations.

Many exposure pathways that need to be evaluated for petroleum hydrocarbon-contaminated soils are cross-media (e.g., leaching of chemicals in soils to groundwater) and thus require analysis of chemical fate and transport. Most current approaches use analytical models to estimate chemical movement from the source to a receptor. At present, these methods model individual chemical transport in the environment, which is appropriate for sites that focus on a relatively few chemicals. For sites containing large numbers of individual compounds, however, the analytical approach is inadequate because of excessive analytical and computational requirements, and insufficient fate and transport and toxicological data.

The Working Group proposed to group hydrocarbons into a relatively small number of fractions with similar physical-chemical properties, to simplify modeling their movement in soil-water-air systems. Fate and transport models (simple or complex) can be applied as well.

More than 200 hydrocarbons were considered in the development of fraction-specific properties. A simple screening-level, partitioning model based on the 1995 ASTM Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites (RBCA) was applied to each chemical to quantify, individually, the chemical’s relative ability to leach from soil to groundwater and volatilize from soil to air. Based on the modeling results, the chemicals were grouped into fractions, using an order of magnitude as the cut-off point. Once the fractions were defined, typical fate and transport properties were assigned to each fraction based on an empirical relationship of the boiling point within each fraction. These properties could be used to help determine fraction-specific exposure potential at petroleum-contaminated sites.

Risk assessment paradigm

A chemical’s fate and transport defines its exposure potential. The combination of chemical properties, site properties and information on how individuals or species (receptors) are potentially placed in contact with the chemical all define the exposure scenario. Estimation of chemical concentrations at a receptor location is an exposure assessment. A defined route of exposure describes the way receptor-to-chemical contact could occur (e.g., inhalation, ingestion). A hazard assessment addresses the toxicity of the chemicals to which a receptor could potentially be exposed. This would define an acceptable (“safe”) concentration or loading based on a pre-defined specified risk value (e.g., hazard quotient of +1). A risk characterization would compare the concentrations to which a receptor is potentially exposed and the “safe” concentration. Conversely, acceptable concentrations in specific media, like soil, can be back-calculated from the safe concentration at the point of exposure if certain assumptions about the inter-media partitioning and exposure factors are made. Routinely done in the calculation of soil cleanup goals, this is the approach incorporated into the ASTM RBCA framework and the 1996 U.S. EPA Soil Screening Guidance. The Working Group applied these methods to estimate risk-based screening levels (RBSLs) for TPH.

The fraction approach

Because data are unavailable for many of the individual components of petroleum hydrocarbons, the Working Group used available data from the literature to characterize typical physical-chemical properties for subsets of an entire mixture (called fractions). Fractions are specifically determined based on the range of their physical-chemical properties and simple partitioning models. It is important not to treat an entire mixture as behaving in the environment as a single, pure liquid. Hydrocarbon mixtures separate and partition based on the make-up of individual chemicals. To various degrees, the individual chemicals will

• persist
• degrade
• move
• adhere to soil particles

It is reasonable to assume that chemicals of an aliphatic or aromatic nature and boiling point would behave similarly. The Working Group delineated specific fractions based on an order of magnitude differentiation in these simple partitioning properties, i.e., leaching to groundwater and volatilization to air.

Once the Working Group identified the fate and transport fractions, a fraction-specific toxicity value (reference dose, RfD) for a non-cancer endpoint was determined for each fraction by the Toxicology Technical Advisory Committee. Because toxicity data are even less available for complex mixtures, the same toxicology value could be assigned to different fate and transport fractions. The fractions must,
however, remain differentiated so that the exposure potential estimation remains intact. Fate and transport fractions with their corresponding RfDs are then used to estimate fraction-specific RBSLs for different exposure scenarios. This screening level analysis would simplify the analysis of complex hydrocarbon mixtures at petroleum release sites. Furthermore, the individual RBSLs for each fraction can be combined with a site-specific mixture composition to compute a single mixture-specific TPH RBSL value.

Analytical requirements
The definition of the fate and transport fractions must be consistent with available analytical capabilities. The mass percent of each fraction in the whole mixture or a mixture similar to the type on site is needed when calculating a mixture-specific TPH concentration. The concentration of each fraction in the soil is important for determining which fractions are driving the risk on a site, and concomitantly which fractions pose no threat. Generic or typical mixture compositions based on historical site information could be used, or distinct analysis applied to site samples.

Soil saturation, partitioning and transport
In Volume Three, the Working Group also gives summation equations for determining

- soil saturation concentration of a chemical in soil
- partitioning behavior, dealing with water, vapor and sorbed phases
- transport equations with an emphasis on the routes
  - subsurface soil leaching to groundwater
  - subsurface soil and volatilization to air

Relevant properties of hydrocarbon compounds
Several chemical properties must be known to evaluate how a chemical partitions in tri-phasic (air-water-soil) systems. The TPHCWG document gives a list (not reprinted here; the list is 10 pages long) of chemical properties for about 200 of the most common chemicals found in petroleum products. The chemical properties include

- molecular weight
- aqueous solubility
- vapor pressure
- Henry’s law constant
- boiling point equivalent carbon number
- soil-water sorption coefficient
- octanol-water partition coefficient
- organic-carbon partition coefficient
- air diffusivity
- water diffusivity

Remediators can use these properties to estimate leaching and volatilization factors. The most sensitive properties for estimating a leaching factor are the soil-water sorption coefficient and Henry’s law constant. These properties, in addition to air diffusivity, are important when calculating volatilization from sub-surface soils to air; diffusivity in water is sufficiently low to render negligible the term in the summation equation.

The Working Group does not discuss the chemical’s biodegradation rate, which can affect a model’s outcome by several orders of magnitude and drive decision-making at a site. Biodegradation, however, is not only a function of chemical structure but site parameters such as soil types, dissolved oxygen content, and other electron acceptors. Biodegradation rates can vary significantly from site to site. Remediators typically handle biodegradation losses by assuming that biodegradation equals 0 for the initial screening level analyses (Tier 1) and then obtaining relevant literature data or site-specific data for more detailed iterations (or tiers) in the risk assessment process. It is not in the current scope of the TPHCWG to develop fraction-specific degradation rates, although such research is needed.

Equivalent carbon number, EC
The equivalent carbon number, EC, is related to the boiling point of a chemical normalized to the boiling point of n-alkanes or its retention time in a boiling point gas chromatographic (GC) column. This relationship is empirically determined. Thus, for chemicals where only the boiling points are known, an equivalent carbon number can be easily calculated. For example, hexane contains six carbons and has a boiling point of 69°C. Its equivalent carbon number is six. Benzene, also containing six carbons, has a boiling point of 80°C. Based on benzene’s boiling point and its retention time in a boiling point GC column, benzene’s equivalent carbon number is 6.5. This approach, consistent with methods routinely used in the petroleum industry for separating complex mixtures, is a more appropriate differentiation technique than the chemical’s carbon number. This is typically how analytical laboratories report carbon number for chemicals evaluated on a boiling point GC column. For molecules with higher relative carbon number indices, the disparity (in terms of EC) between aliphatic and aromatic hydrocarbons is great.

Soil water sorption coefficient, Kd
Kd, the soil-water sorption coefficient, expresses the tendency of a compound to be adsorbed onto soil or sediment particles. Kd can be measured as the ratio of the amount of the chemical sorbed per unit weight of soil or sediment to the concentration of the chemical in solution. Sorption of a chemical to soil is typically measured in soil-water bath systems where a known concentration of chemical in water is introduced to known quantities of “clean” soil. Over time, the chemical will migrate from the free water and sorb onto the soil particles. The magnitude of the sorption for most soil/water systems is a function of the hydrophobicity of the chemical as measured by the water solubility and the organic carbon content of the soil. Once the system reaches chemical equilibrium, concentrations
are measured in both the liquid phase and solid phase. $K_d$ is
the slope of the line plotting the liquid phase concentration
vs. the solid phase concentration for various combinations
of soil mass and liquid phase concentrations. There are
several assumptions inherent when using this approach:

- Sorption of one chemical to a solid surface is linear.
  This method assumes that there is no limit to the
  number of binding sites on the soil particles or to
  chemical size in fitting onto binding sites. Studies have
  shown that sorption processes are decidedly non-linear
  for high solute concentrations, ionized chemicals, and
  metals. For non-ionic, hydrophobic chemicals such as
  hydrocarbons with concentrations significantly less than
  the solubility limit, the linear assumption is reasonable.
  Additionally it is assumed that the contact time between
  the chemical and soil is adequate to reach chemical
  equilibrium.

- Implicit in the linear sorption is an assumption that the
  rate of adsorption equals the rate of desorption. Field
  and laboratory studies have shown that for many
  chemicals and soil types, the desorption rate can be
  significantly lower than the adsorption rate.

- Chemical “A” binds to soil “B” equally, regardless of
  soil moisture content. Most chemical-specific sorption
  coefficients found in the literature have been developed
  using bi-phasic systems (soil-water). In these cases, the
  soil is completely saturated, leaving no air spaces, which
  is designed to mimic groundwater systems. However,
  $K_d$ values developed for groundwater systems are
  routinely applied to unsaturated soils during modeling.
  Differences are probably not significant where the soil
  moisture content approaches the soil porosity. In cases
  where the soil moisture content is low, a different
  sorption profile will be obtained, depending on the
  chemical’s Henry’s law constant (the amount of gas
  absorbed by a given volume of a liquid at a given
  temperature is directly proportional to the pressure of
  the gas, applicable only to dilute solutions). This problem
  is not sufficiently addressed in current screening-level
  models, or even in some more “robust” models. Batch
  studies and column studies could be performed to better
  quantify this phenomenon.

- Organic carbon content is the controlling variable. This
  approach assumes that a chemical contaminant in soil
  will bind or sorb to the soil’s organic matter. For soils
  with organic carbon fractions less than 0.001, other
  components of the soil matrix (e.g., inorganic clay
  minerals) will exert greater influence. This is also the
  case for some chemicals with charged functional groups.

In addition to literature values and extrapolations from other
variables, $K_d$ can be measured for site-specific analyses
(usually in Tier 3 analyses). Representative soil samples
may be collected at the site and, using solutes typical of site
conditions, isotherms can be developed and soil-column
break-through curves measured. These results will give a
more realistic picture of chemical binding to site soils. Care
should be taken, however, since soils can vary across a site
and with depth.

**Organic-carbon partition coefficient, $K_{oc}$**

Researchers have found that for non-ionic, hydrophobic
chemicals, the primary soil property controlling sorption is
the soil’s organic carbon content. To compare studies of
the same chemical on different soils, one can calculate the
organic-carbon partition coefficient, $K_{oc}$, which is defined
by $K_{oc} = K_s/F_{oc}$. The $K_{oc}$ values may range from 1 to
10,000,000 cm$^3$/g. These values are usually presented
in the log$_{10}$ form. Fraction of organic carbon, $F_{oc}$, is a function
of soil type and depth. Generally, soil organic carbon is
about 60 percent of the total soil organic matter content.
Typical values of soil organic matter for sandy-loam soils
range from approximately 1 to 4 percent. Sands and clay
soils have less organic carbon (<1%), and loams have up to
10 percent. Peat soils could have up to 50 percent
organic matter. Organic matter content decreases with
depth. A method for estimating $K_{oc}$ is presented in the
referenced document.

**Octanol-water partition coefficient, $K_{ow}$**

$K_{ow}$, the octanol-water partition coefficient, is the ratio of the
chemical’s concentration in the octanol phase to its concen-
tration in the aqueous phase of a two-phase octanol-water
system. $K_{ow}$ equals the concentration in an octanol phase
(mg/L) divided by the concentration in the aqueous phase
(mg/L). Because $K_{ow}$ is an estimated value of a chemical’s
hydrophobicity or partitioning tendency from water to
organic matter, it can be correlated to the compound’s water
solubility and $K_{oc}$. The TPHCWG document gives several
methods for estimating $K_{ow}$.

**Henry’s law constant, $H$**

Henry’s law constant, $H$, an air-water partition coefficient,
can be measured as the ratio of a compound’s concentra-
tion in air to its concentration in water at equilibrium:

\[
H = \text{concentration in air [atm]/concentration in water [mole/m}^3]\]

$H$, which is calculated by taking the ratio of a compound’s
vapor pressure to its aqueous solubility, can have units of
atm-m$^3$/mole. $H$ can also be expressed in its concentration-
based form (units of cm$^3$ air/cm$^3$ water) by dividing the
parameterized form of $H$ by the universal gas constant
($R = 8.2 \times 10^{-5}$ atm-m$^3$/mole-K) and temperature, $T$ (in
degrees, K). The Henry’s law relationship is only valid for
dilute solutions where water concentrations are much less
than the compound’s water solubility. When petroleum
concentrations in soils and soil water approach residual
saturation, the relationship may not be valid.
Diffusivity in air, $D_{\text{air}}$

The diffusion coefficient or diffusivity in air, $D_{\text{air}}$, is a measure of the diffusion of a molecule in a gas medium as a result of intermolecular collisions. It is not a measure of turbulence or bulk transport (apparent diffusion). Diffusivity is technically defined as:

$$D_{\text{air}} = \frac{J_B}{\Delta X_B}$$

where $D_{\text{air}}$ = diffusivity of a compound B in compound or mixture A (in this case A is air)

$J_B$ = net molal flux of B [mol/cm²/s]

$\Delta X_B$ = concentration gradient of B [mol/cm³/cm]

Most environmental fluid media are turbulent and therefore controlled by the intensity of turbulent mixing rather than molecular diffusion. Situations where molecular diffusion is significant, or even controlling, include the movement of chemicals at air-water interfaces, the interstitial waters of sediments, and vapor diffusion through soils. Hydrodynamic and mechanical dispersion play a major role in determining chemical concentrations at a receptor (mixing zone effect), but dispersion is usually not considered in simple screening-level models.

Diffusivity in water, $D_{\text{wat}}$

The diffusion coefficient in water, $D_{\text{wat}}$, is a function of solute size, temperature and solution viscosity. $D_{\text{wat}}$ is not a sensitive parameter in this analysis; however, the equation is presented below for completeness:

$$D_{\text{wat}} = \frac{RT}{6 N_w R_B}$$

where

$D_{\text{wat}}$ = diffusivity of compound B in water [cm²/s]

$N_w$ = viscosity of water [cp]

$R_B$ = radius of molecule B [cm]

Additional information contained in this Working Group volume

This particular Working Group volume also includes the following:

- a list of compounds found in petroleum distillate products and crude oils and their relevant physical-chemical properties
- a list of compounds and their relative abundance in specific petroleum products: gasoline, crude oil; JP-4, JP-5, JP-8, kerosene, diesel and home heating oil; also when available, values for their relevant physical-chemical properties
- reference for these values
- explanation of estimation methods used to compute
  - octanol-water partition coefficient
  - organic carbon partition coefficient
  - diffusivity in air

- computation and resulting values (each for aliphatics and aromatics or equivalent carbon numbers) for water solubility, Henry’s law constant, organic carbon partition coefficient, and air and water diffusivity

Reference

TPHCWG, 1998, Selection of Representative TPH Fractions Based on Fate and Transport Considerations, Volume 3; see “recent publications” at the Wright Patterson Air Force Base’s Air Force Research Laboratory, http://voyager.wpafb.af.mil.; also see the Association for the Environmental Health of Soils (AEHS), http://www.aehs.com, or e-mail heather@aehs.com, or write to Amherst Scientific Publishers, 150 Fearing Street, Amherst, Massachusetts 01002.

Information sources

Publications

Ground Water Currents can be ordered by calling 800-490-9198 or 513-489-8190, faxing 513-891-6685, or downloading at http://clu-in.com/techpubs.htm.

Innovative Site Remediation Technology: Phase II is available from the WASTECH Consortium. The seven volumes, which can be ordered from the American Academy of Environmental Engineers (phone 410-266-3390, fax 410-266-7653, or e-mail aaee@ea.net), consist of topics on

- Bioremediation
- Chemical treatment
- Liquid extraction technologies
- Stabilization/solidification
- Thermal desorption
- Thermal destruction
- Vapor extraction and air sparging

Cost and Performance Report: Dual Auger Rotary Steam Stripping, Pinellas Northeast Site and In-Situ Anaerobic Bioremediation, Pinellas Northeast Site can be ordered by contacting Mike Hightower at mmhight@sandia.gov.

The 1998 U.S. Market for Phytoremediation is available by phoning 617-726-5474, or e-mailing DGlassAssc@aol.com.
Websites and electronic documents

Assessing Soil Quality: Four Case Studies: http://members.home.net/terrabyte/papers.htm

Barrier/reaction wall technology information:
Federal Remediation Technologies Roundtable: http://www.frtr.gov/
Groundwater Remediation Technologies Analysis Center (GWRTAC) http://www.gwrtac.org/
Oregon Graduate Institute (zero-valent iron permeable barriers): http://cgr.ee.ogi.edu/iron
Permeable Reactive Barrier Demonstration Profiles: http://www.rdf.org/bardocs.htm#info
Remedial Technologies Development Forum: http://www.rdf.org
SECOR: http://www.secorm/index.htm
U.S. EPA clean-up information: http://clu-in.com/
Biolinks: http://biogroup.gzea.com/biolinks/topics.asp
Bioremediation Field Evaluation: Hill Air Force Base, Utah (EPA 540/R-97/505); http://www.epa.gov/ORD/WebPubs/biorem/
Compendium of State/Territorial Brownfields Program Funding: http://www.astswmo.org/Publications/bookshelf.htm

Environmental Reporting Assist File (ERAFl) and Registry of Lists (ROL) databases and DOS search/retrieve software: http://www.env-sol.com/solutions/MSDS.HTML
Environmental Software: http://www.envsoft.com
Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater: http://clu-in.com/intup.htm#NATO or http://nato.int/ccms, or call 800-490-9198 or 513-489-8190 or fax request to 513-901-6685. One volume contains information on treatment walls and permeable reactive barriers.
Geochemist's Workbench PowerPoint: web@rockware.com
Hydrocarbon Range and Corresponding EPA Analytical Methods appears on GZA GeoEnvironmental, Inc. at http://www.gza.net; go to BioLinks then Environmental Engineering Tools
Laboratory comparison data (fixed vs. mobile): http://members.home.net/terrabyte/papers.htm
Mail lists of interest to geotechnical engineers: http://dialspace.dial.pipex.com/town/terrace/qs21/www

Subscriptions and address corrections

Any person or organization wanting a subscription to Underground Tank Technology Update (UTTU) should send requests and subscription fee (free to state government employees) to Debbie Benell
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Remediation Technologies Development Forum: http://clu-in.com/techpubs.htm, or call 800-490-9198 or 513-489-8190, or fax 513-891-6685.

Remedial technologies in general
www.gwtac.org
www.gnet.org
www.em.doe.gov
www.terratherm.com
www.ecogrount.com
www.haywardbaker.com
www.inquip.com
www.nttc.edu
www.copa.org
www.iridium.nttc.edu
www.nap.edu/readingroom/
www.remedial.com
www.rtdf.org

Search engine for environmental field (environmental, geotechnical, hydrology, mining, geology, petroleum) with nearly 20,000 links: http://www.geoindex.com

Setting cleanup levels spreadsheet that is compatible with RBCA and RNA: http://www.wa.gov/ECOLOGY

Software for environmental applications:
http://www.data-surge.com

The East Garrington Trench and Gate System: It Works:
http://www.geo.ucalgary.ca/hydro/thomas


University of Waterloo: http://www.uwaterloo.ca; also for information on ORC socks: http://darcy.uwaterloo.ca/gwn/july96/nature.html; for software on natural attenuation: www.flowpath.com

UST information, such as UST dimensions: http://www.groundwater.com

Well owner’s checklist: ngwa.org/gwmarket/check.html

**UTTU obtained many of these sites and other information from the Groundwater Mailing List (http://groundwater.com), the Bioremediation Discussion Group (http://biogroup.gzea.com) and TechDirect (http://clu-in.com/techdrct.htm).**

**UTTU thanks the moderators from these groups: Ken Bannister of Groundwater, Richard Schaffner of Biogroup and Jeff Heimerman from U.S. EPA’s TechDirect.**