



COMMONWEALTH OF MASSACHUSETTS  
 EXECUTIVE OFFICE OF ENVIRONMENTAL AFFAIRS  
**DEPARTMENT OF ENVIRONMENTAL PROTECTION**  
 ONE WINTER STREET, BOSTON, MA 02108 617-292-5500

JANE M. SWIFT  
 Governor

BOB DURAND  
 Secretary

LAUREN A. LISS  
 Commissioner

**Characterizing Risks Posed by Petroleum Contaminated Sites:**  
*Implementation of the MADEP VPH/EPH Approach*

**FINAL POLICY**

**October 31, 2002**

**Policy #WSC-02-411**

This Policy provides guidance for parties conducting response actions under the Massachusetts Contingency Plan (MCP) on the use and application of the Volatile Petroleum Hydrocarbons (VPH) and Extractable Petroleum Hydrocarbons (EPH) methods to characterize risks posed by releases of petroleum products to the environment. This Policy updates and replaces draft documents that were issued on October 31, 1997 and June 2001. Parties who are currently using criteria and guidance contained in the June 2001 draft document may do so until May 1, 2003. A summary of significant changes between these earlier drafts and this Final Policy is provided in Appendix 6.

*The information contained in this document is intended solely as guidance. This Policy does not create any substantive or procedural rights, and is not enforceable by any party in any administrative proceeding with the Commonwealth. This Policy provides recommendations and guidance on approaches the Department considers acceptable for meeting the performance standards set forth in the MCP and discussed in this document. These performance standards include, but are not limited to, the Response Action Performance Standards of section 310 CMR 40.0191 of the MCP. Parties using this guidance should be aware that there may be other acceptable alternatives for achieving and documenting compliance with the general regulatory requirements and performance standards of the MCP, including those of 310 CMR 40.0191. The regulatory citations in this document should not be relied upon as a complete list of the applicable regulatory requirements.*

This Policy and further information on the development and application of the aliphatic/aromatic hydrocarbon evaluative technique employed by the Department, referred to as the "VPH/EPH" approach, may be obtained at [http://www.state.ma.us/dep/bwsc/vph\\_eph.htm](http://www.state.ma.us/dep/bwsc/vph_eph.htm)

10/31/02

*Signature on Original*

Date

Deirdre C. Menoyo  
 Assistant Commissioner  
 Bureau of Waste Site Cleanup

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## LIST OF ACRONYMS

AAS	Atomic Absorption Spectroscopy
APH	Air-Phase Petroleum Hydrocarbons
AQWC	Ambient Water Quality Criteria
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
CEP	Critical Exposure Pathway
EDB	Ethylene Dibromide
EPA	Environmental Protection Agency
EPC	Exposure Point Concentration
EPH	Extractable Petroleum Hydrocarbons
eV	Electron Volt
FID	Flame Ionization Detector
GC	Gas Chromatography or Gas Chromatograph
GC/FID	Gas Chromatograph/Flame Ionization Detector
GC/MS	Gas Chromatograph/Mass Spectrometer
GRO	Gasoline Range Organics
GW	Groundwater
HVAC	Heating, Ventilation, Air-conditioning
ICP-AES	Inductively coupled plasma atomic emissions spectroscopy
IR	Infra-red
LNAPL	Light Non-Aqueous Phase Liquids
LSP	Licensed Site Professional
MADEP	Massachusetts Department of Environmental Protection
MCP	Massachusetts Contingency Plan
MtBE	Methyl tertiary butylether
NAPL	Non-Aqueous Phase Liquids
NRS	Numerical Ranking System
OTP	Ortho-terphenyl
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PID	Photoionization Detector
ppbV	Parts-per-billion by volume
ppmV	Parts-per-million by volume
QA/QC	Quality Assurance/Quality Control
RAF	Relative Absorption Factor
RAO	Response Action Outcome
RfC	Reference Concentration
RfD	Reference Dose
RL	Reporting Limit
SIM	Selective Ion Monitoring
SW	Surface Water
TIC	Tentatively Identified Compound
TOV	Total Organic Vapor
TPH	Total Petroleum Hydrocarbons
TPHCWG	Total Petroleum Hydrocarbon Criteria Working Group
UCL	Upper Concentration Limit
UCM	Unresolved Complex Mixture
UST	Underground Storage Tank
UV	Ultra-violet
VOC	Volatile Organic Compound
VPH	Volatile Petroleum Hydrocarbons
WSC	Waste Site Cleanup

# 1.0 INTRODUCTION

## 1.1 Background

Spills and releases of petroleum fuels are the leading source of environmental contamination in Massachusetts. Because petroleum products are a complex and highly variable mixture of hundreds of individual hydrocarbon compounds, however, characterizing the risks posed by petroleum-contaminated soil and water has proven to be difficult and inexact.

Traditional approaches have focused on the identification and evaluation of specific indicator compounds, like benzene, and/or the quantitation of a “Total Petroleum Hydrocarbon” (TPH) value. The limitations of an “indicator only” approach have long been recognized, especially at gasoline-contaminated sites, and it is clear that focusing on a select few compounds cannot adequately characterize the risks posed by all hydrocarbons present. While the quantitation of a TPH value is a step in the right direction, in that an attempt is being made to account for all compounds present, traditional TPH methods and approaches provide little or no information on the composition or toxicity of generated data.

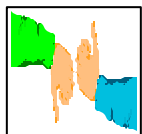
In response to these shortcomings, the Massachusetts Department of Environmental Protection (MADEP) published a document in August 1994 entitled *Interim Final Petroleum Report: Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter*. This document presented a new toxicological approach to characterize and evaluate risks posed by petroleum-contaminated sites, by breaking down TPH into collective aliphatic and aromatic fractions.

To support and implement this new toxicological approach, MADEP developed two analytical methods that differentiate and quantitate collective concentrations of aliphatic and aromatic hydrocarbons in soil and water. These methods, for *Volatile Petroleum Hydrocarbons* (VPH) and *Extractable Petroleum Hydrocarbons* (EPH), were issued in draft form in August 1995, and as final procedures in January 1998. At present, MADEP is in the process of finalizing a method for *Air-Phase Petroleum Hydrocarbons* (APH), which will allow for the collective quantitation of aliphatic and aromatic hydrocarbons in air. A draft APH method was issued by the agency in February 2000.

MADEP has integrated this new approach into the Massachusetts Contingency Plan (MCP), by developing and promulgating soil and groundwater cleanup standards for the aliphatic and aromatic ranges of interest. These standards became effective on October 31, 1997. Parties undertaking cleanup actions at petroleum-contaminated sites in Massachusetts now have the means to quickly and easily address risks posed by these complex mixtures, by the optional use of the generic *Method 1* cleanup standards. Conversely, such parties may elect to develop site-specific cleanup standards via use of a *Method 2* or *Method 3* risk assessment process.

## 1.2 Purpose and Scope

The purpose of this document is to (1) provide a succinct summary of key provisions of the “VPH/EPH” approach, (2) provide greater detail and specificity on important elements of this new approach, and (3) provide technical and regulatory insight, guidance, and **Rules of Thumb** to assist Licensed Site Professionals and others in understanding and applying this approach in a practical and cost-effective manner.



**Rules of Thumb** are suggestions and recommendations on how to approach, evaluate, and resolve investigatory, assessment, and remedial issues. In most cases, they are based upon reasonably conservative or “worst case” assumptions and considerations, and are intended to assist competent professionals in “ruling out” items of concern, or affirming a need to proceed to a more comprehensive level of evaluation. These rules are based upon current information, and are designed to be protective at most, but not all sites.

Derivation details are provided in “Background/Support Documentation for the Development of Publication Guidelines and Rules of Thumb”, available at: [http://www.state.ma.us/dep/bwsc/vph\\_eph.htm](http://www.state.ma.us/dep/bwsc/vph_eph.htm).

**Rules of Thumb may only be applied to the specific situations described in this document, as such guidelines are predicated upon a designated scenario and are reflective of the totality of conservative assumptions incorporated into that scenario. Changing any developmental element of these guidelines and/or applying them to situations not detailed in this document may not be sufficiently protective. Moreover, the use of these rules may not be appropriate at sites with complex or highly heterogeneous contaminant conditions or migration pathways, or at sites or portions of sites with highly sensitive receptors (e.g., drinking water wells).**

*While striving to be as useful and complete as possible, nothing in this document should be viewed as limiting or obviating the need for the exercise of good professional judgment.*

## 1.3 Applicability

The provisions of this document are applicable at sites contaminated by releases of one or more petroleum fuels and/or lubricating oils. The guidance contained in this policy is designed to help Licensed Site Professionals (LSPs) and others comply with the risk-based/performance-based requirements of the MCP to adequately investigate and assess releases of oil and waste oil to the environment.

The MCP – since 1988 – has required that parties conducting response actions at disposal sites document or achieve a level of no significant risk of harm to human health, safety, public welfare, and the environment. Because the MCP is performance-based, it does not dictate the specific means by which one demonstrates compliance with these standards. From a practical point of view, however, most parties did not have ready access to the tools and procedures needed to adequately characterize the total risks posed by petroleum contamination – until promulgation of the VPH/EPH approach, analytical methodologies, and Method 1 cleanup standards in 1997. For this reason, MADEP has adopted a prospective and retrospective position on the application of the VPH/EPH approach:

### *1.3.1 Site Closure on or after October 31, 1997*

Since October 31, 1997, MADEP has provided parties conducting response actions a means to easily and adequately assess risks posed by petroleum contaminants. Therefore, all sites closed on or after this date (e.g., by filing of a Response Action Outcome Statement) must demonstrate compliance with this standard, by use of the VPH/EPH approach, or by use of another scientifically valid and health-protective approach. In these cases, the use of an “indicator only” approach is NOT acceptable.

There are no “grand fathering” provisions for sites that were not closed out prior to October 31, 1997. However, this document provides guidance on how one might utilize and/or “convert” old data obtained prior to this date, to more fully assess risks pursuant to the VPH/EPH approach, and support a post-1997 closure submittal.

Notwithstanding the implementation of this new approach, it should be noted that the MCP retains a cleanup standard for Total Petroleum Hydrocarbons (TPH), which is set conservatively at the lowest EPH fractional cleanup standard (typically C<sub>1</sub>-C<sub>22</sub> Aromatic Hydrocarbons). Parties may continue to use a TPH approach to characterize heavier petroleum products (i.e., >C<sub>9</sub>), using the EPH method (in the TPH screening mode) or other scientifically valid and defensible method (See Section 3.7.1).

### *1.3.2 Site Closure Prior to October 31, 1997*

In general, MADEP will not require reevaluation of petroleum-contaminated sites properly closed prior to October 31, 1997. Nonetheless, the agency reserves the right to do so, in cases where direct and compelling exposure concerns are believed to be present, and where human health is being directly threatened. Such concerns may exist at sites where (1) a release of gasoline has impacted a drinking water well, or (2) a release of gasoline has resulted in persistent, long-term odors or vapors within an occupied structure.

In cases where parties voluntarily conduct VPH/EPH testing at sites closed prior to October 31, 1997 (e.g., pursuant to a property transfer evaluation), the applicable “re-opener” language is contained at 310 CMR 40.0317(17). Under the provisions of this section of the MCP, a notification obligation would exist for this newly obtained VPH/EPH data if such information would change or negate the findings of the closure document (e.g., RAO, LSP Evaluation Opinion).

## 2.0 SUMMARY OF VPH/EPH APPROACH

### 2.1 The Concept

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 composition of petroleum products released to the environment are complex and variable, and are a function of (1) the origin and chemistry of the parent crude oil, (2) refining and blending processes, and (3) the use of performance-enhancing additives. Once released to the environment, the chemistry of a petroleum product is further altered by contaminant fate and transport processes, such as leaching, volatilization, and biodegradation.

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

Based upon an evaluation of information and data available on the chemistry and toxicity of petroleum products, however, it is possible to make some broad observations and conclusions:

- ◇ petroleum products are comprised mainly of aliphatic/alicyclic and aromatic hydrocarbon compounds;
- ◇ aromatic hydrocarbons appear to be more toxic than aliphatic compounds; and
- ◇ 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** toxicity of petroleum-contaminated media is established by (1) determining the collective concentrations of specified ranges of aliphatic and aromatic hydrocarbons, and (2) assigning a toxicity value (e.g., Reference Dose) to each range. Toxicity values are determined on the basis of a review and/or extrapolation of available toxicological data on hydrocarbon mixtures and specific hydrocarbon compounds. The complete breakdown for all ranges of interest is summarized in Table 2-1.

**Table 2-1: Toxicological Approach for Non-Cancer Health Effects**

Hydrocarbon Fraction	Reference Dose (mg/kg/day)
C5-C8 Aliphatic Hydrocarbons	0.04 <sup>a</sup>
C9-C18 Aliphatic Hydrocarbons	0.1 <sup>a</sup>
C19-C36 Aliphatic Hydrocarbons	2.0 <sup>a</sup>
C9-C22 Aromatic Hydrocarbons	0.03

<sup>a</sup> updated values (2002)

**Cancer effects** are evaluated separately, by the identification and quantitation of those specific hydrocarbon compounds, like benzene and certain polycyclic aromatic hydrocarbons (PAHs), which are designated carcinogens. Additional information and details on this approach are provided in the MADEP publication *Interim Final Petroleum Report: Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter*, August, 1994, and as amended, available at [http://www.state.ma.us/dep/bwsc/vph\\_eph.htm](http://www.state.ma.us/dep/bwsc/vph_eph.htm)

## 2.2 Hydrocarbon Fractions of Interest

Although the non-cancer toxicity of petroleum-contaminated media can be adequately described by division into the four hydrocarbon fractions listed above, MADEP has chosen to designate six hydrocarbon fractions of interest, because of the following analytical and program considerations:

- ◇ EPA analytical methods have traditionally used one approach for the analysis of volatile organics (i.e., purge and trap), and another for the analysis of 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), while, 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 use of 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 method. In this manner, it would only be necessary to use the VPH procedure to characterize gasoline releases.



For these reasons, it was necessary and desirable to divide the aliphatic and aromatic hydrocarbon ranges of interest into six separate entities; three detected by the VPH method, and three detected by the EPH Method, as listed in Table 2-2.

**Table 2-2: Hydrocarbon Fractions of Interest**

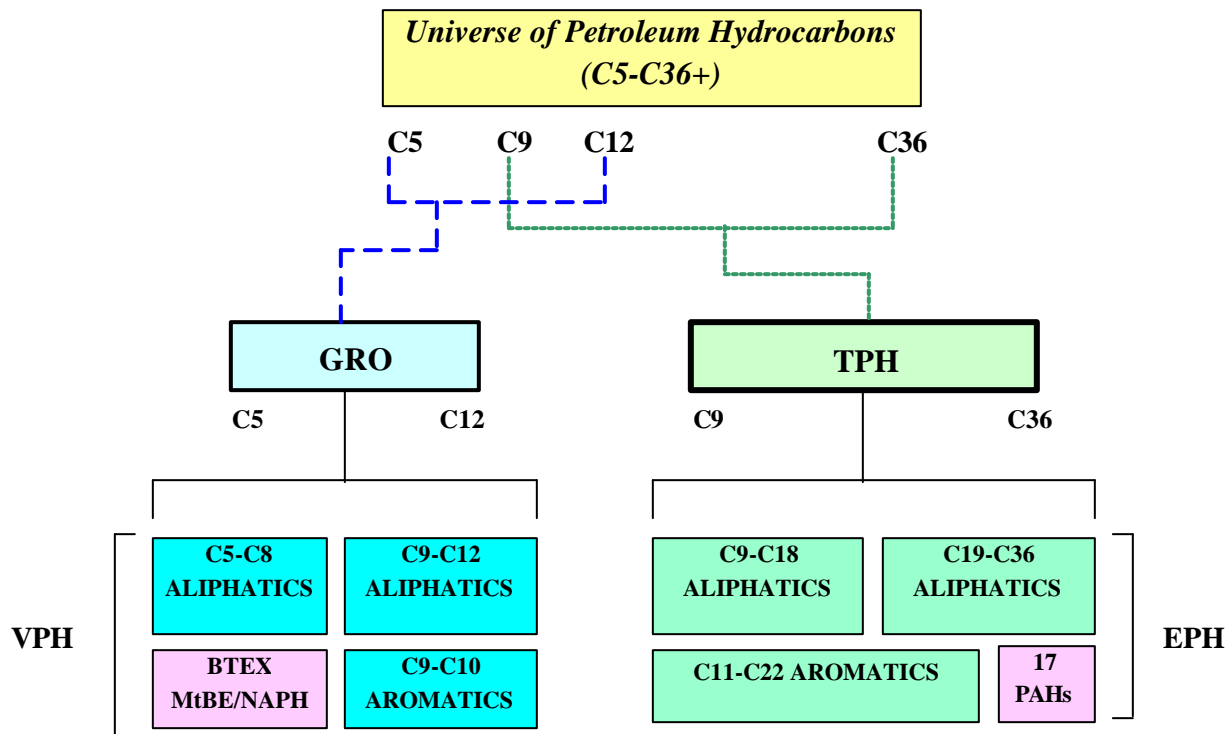
Toxicologically Defined Hydrocarbon Fraction	Analytical/Program Defined Hydrocarbon Fraction	Analytical Method	Reference Dose (mg/kg/day)
C5-C8 Aliphatics	C5-C8 Aliphatics	VPH	0.04 <sup>a</sup>
C9-C18 Aliphatics	C9-C12 Aliphatics	VPH	0.1 <sup>a</sup>
	C9-C18 Aliphatics	EPH	0.1 <sup>a</sup>
C19-C36 Aliphatics	C19-C36 Aliphatics	EPH	2.0 <sup>a</sup>
C9-C22 Aromatics	C9-C10 Aromatics	VPH	0.03
	C11-C22 Aromatics	EPH	0.03

<sup>a</sup>updated value (2002)

### 2.3 Relationship of VPH/EPH to TPH and Gasoline Range Organics (GRO)

The relationship between TPH, GRO, VPH and EPH is graphically displayed in Figure 2-1.

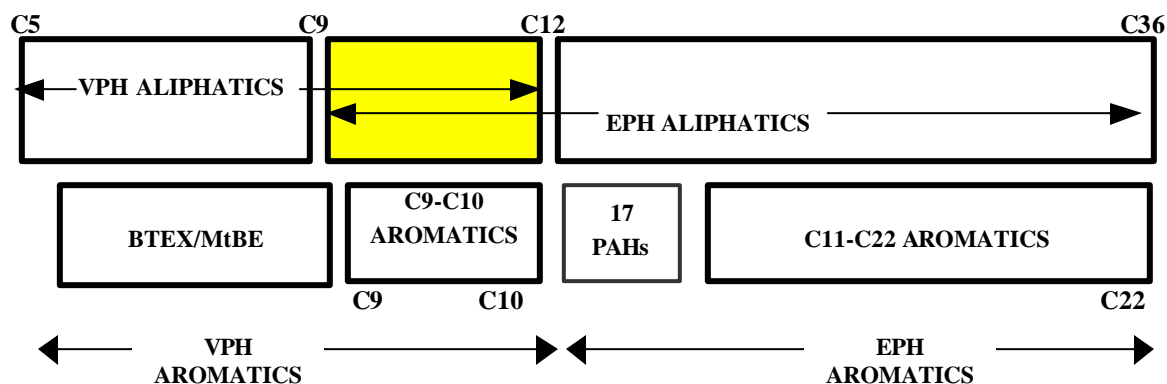
**Figure 2-1: Relationship of GRO, TPH, VPH, and EPH**



As can be seen in Figure 2-1, if the concentrations of the three EPH fractions and target PAH analytes were added together, it would be equal to a traditional "TPH" value. Similarly, if the three VPH fractions and BTEX/MtBE/naphthalene concentrations were added together, it would equal a GRO value.

It may also be noted that an overlap exists between the VPH and EPH methods, in that C9-C12 aliphatic hydrocarbons are quantitated by both methods. This overlap, further discussed in Section 4.2.3, is graphically illustrated in Figure 2-2.

**Figure 2-2: Overlap of VPH and EPH Test 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.

## 2.4 Additional Research and Data Needs

MADEP continues to gather and review information and data on petroleum hydrocarbon chemistry and toxicity. Recent efforts have focused on the review and evaluation of previously unavailable oral and inhalation toxicological data, which has led to some revisions to the recommended RfD and RfC values for hydrocarbon fractions of interest (see Table 4.13). Additional study is also needed to better evaluate ecological risks posed by aliphatic and aromatic hydrocarbons.

On a national level, the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) has published a number of documents relating to this subject. TPHCWG is comprised of representatives from the oil industry, Department of Defense, EPA, state agencies, environmental consulting firms, and academia. This group has recommended an aliphatic/aromatic fractional approach similar to the MADEP approach. Additional information and recommendations have also been provided on petroleum chemistry, hydrocarbon fate and transport, and analytical methodologies.

A number of TPHCWG publications are available on the World Wide Web at <http://www.aehs.com/>

## 3.0 ANALYTICAL METHODS

In order to use the VPH/EPH toxicological approach, it is necessary to be able to measure the collective concentrations of aliphatic and aromatic hydrocarbons in impacted media. Because conventional TPH and EPA test methods cannot produce this type of data, MADEP has developed and published two detailed analytical methods for Volatile Petroleum Hydrocarbons (VPH) and Extractable Petroleum Hydrocarbons (EPH). Both methods are gas chromatography (GC) techniques, and are modifications of traditional EPA procedures contained in SW-846. As such, most laboratories that have conducted volatile and extractable organic analyses in the past should be able to perform these techniques.

### 3.1 Gas Chromatography

Chromatography is the separation of compounds or groups of compounds in a complex mixture. In gas chromatography, hydrocarbons in a sample are transferred to the vapor phase by purging (VPH) or heating (EPH). The gaseous sample then flows through a (100 meter long +/-) *capillary column* to a detector. A chemical coating on the walls of the column first sorbs, and then desorbs each compound in the sample, with the heavier molecular weight compounds being "detained" longer than the lighter compounds. In this manner, analytes exit or *elute* from the column in a predictable and reproducible manner, based upon the structure, molecular weight, and boiling point of the compound.

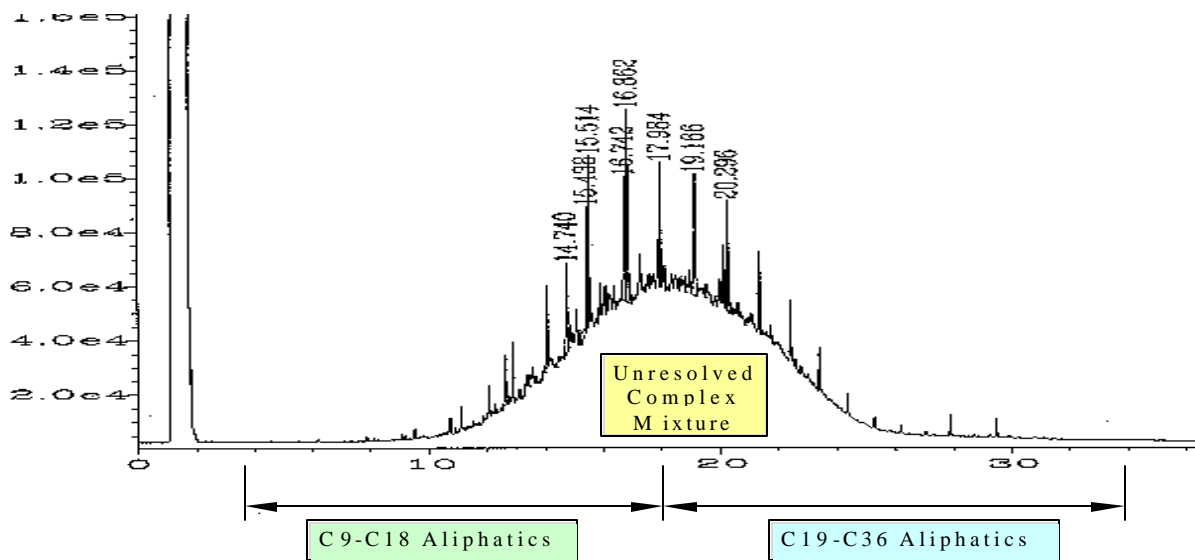
Once they elute from the column, analytes pass through a detector, where the presence of each compound produces a small electrical current, proportional to its mass. This current is then amplified and used to produce a chromatogram, which is simply a plot of electrical (detector) response over time. Each peak on a chromatogram represents one or more individual compounds. Compounds are identified based upon their *retention times*, which is the time (in minutes) it takes the compound to travel through the column. Compounds or ranges of interest are quantitated by an *integration* process that calculates the area beneath the chromatographic peak(s), for comparison to mass/area ratios derived from the injection of *calibration standards* of known mass or concentration.

To transfer the hydrocarbons within a sample medium into a gas chromatograph, and into a gaseous phase, various sample preparation techniques may be used. Volatiles within water samples are generally *purged* with an inert gas, which strips the dissolved volatile compounds from the aqueous phase into the gaseous phase, where they are initially retained on a *trap* containing an appropriate sorbent. This trap is then rapidly heated to desorb the analytes, and load them onto a chromatographic column. Volatiles within soils are first extracted with a solvent (e.g., methanol), then mixed with water and purged. Heavier non-volatile hydrocarbons in both water and soil samples are generally extracted with a solvent (e.g., methylene chloride); the extract is then injected into a gas chromatograph, where it is heated and vaporized into a gaseous state.

A key and novel requirement of the VPH/EPH approach is the need to separate or *fractionate* hydrocarbon mixtures into collective groupings of aliphatic and aromatic hydrocarbons. This fractionation is something that is not done in conventional TPH or Gasoline Range Organic analyses, or the EPA volatile/extractable methodologies detailed in SW-846. There are several different ways to accomplish this task, each with advantages and disadvantages. The recommended MADEP analytical methods use detector selectivity and a chemical exchange process to fractionate samples, but other techniques may also be acceptable and cost-effective.

An example of an EPH (GC/FID) chromatogram of the aliphatic portion of a weathered #2 Fuel Oil soil sample is provided in Figure 3-1.

**Figure 3-1: Sample Chromatogram - #2 Fuel Oil**



Note that the “x” axis is the retention time, in minutes, and the “y” axis is the detector signal strength. The retention time of some of the individual peaks are printed above those peaks. Note also the presence of a large chromatographic “hump” between 10 and 26 minutes, indicating the presence of an *Unresolved Complex Mixture (UCM)*; this feature is an important issue discussed in more detail below.

### 3.2 MADEP Analytical Methodologies

MADEP has developed and published two analytical methodologies for the detection of Volatile Petroleum Hydrocarbons (VPH) and Extractable Petroleum Hydrocarbons (EPH) in soil and water. Both methods separate complex hydrocarbon

mixtures into collective fractions of aliphatic and aromatic hydrocarbons, and produce data that can be directly compared to MCP *Method 1* cleanup standards. MADEP has also issued a draft methodology for the detection of Air-Phase Petroleum Hydrocarbons (APH), to identify and quantitate collective ranges of aliphatic and aromatic hydrocarbons in air and soil gas.

The VPH, EPH, and APH methods were developed to allow a meaningful evaluation of the risks posed by hydrocarbon mixtures. Other procedures may also be available to fulfill this objective, or, perhaps more importantly, other data quality objectives. For example, it may be more cost-effective to use (or initially use) EPA Method TO-14 to evaluate indoor air quality, and establish whether a subsurface hydrocarbon transport pathway is present at a disposal site; if there is no pathway, there is no need to evaluate risks via the APH procedure.

### 3.2.1 Volatile Petroleum Hydrocarbons (VPH)

The MADEP VPH Method (1998) is a *Purge and Trap, GC/PID/FID* procedure. Using this method, the collective concentrations of C5-C8 Aliphatic, C9-C12 Aliphatic, and C9-C10 Aromatic Hydrocarbons can 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 VPH Analytes* benzene, toluene, ethylbenzene, and xylenes (BTEX); Methyl-tertiary-butylether (MtBE); and naphthalene.

Samples are analyzed using a *purge-and-trap* sample preparation/concentration procedure. The gas chromatograph is temperature-programmed to facilitate separation of hydrocarbon compounds. Detection is achieved by a photoionization detector (PID) and flame ionization detector (FID) in series. 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 is used to determine 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.

The MADEP VPH method relies upon the selectivity of the PID detector 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) *sigma* bonds. Because aromatic compounds have at least one benzene ring with three double bonds, they 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. In theory, the FID will detect the total concentrations of all petroleum hydrocarbons in the sample, and the PID will detect only (or mostly) aromatic compounds. By subtracting the PID from the FID response, it would be possible to quantitate just the aliphatic compounds. However, reality deviates from this theoretical ideal in the following ways:

- ◆ *Pi* bonds are present in hydrocarbon compounds other than aromatics - most notably alkenes, which are present in gasoline. Therefore, alkenes will be quantitated as aromatics. However, this bias is not deemed to be a major methodological limitation, due to the fact that (a) alkenes are typically not found in high concentrations in most petroleum products, and (b) alkenes may be more toxicologically similar to aromatics than to aliphatics.
- ◆ A more problematic issue is the fact that aliphatic compounds will produce some measurable response on a PID, especially heavier-molecular-weight branched and cyclic alkanes. Collectively, this response can become significant if there are a lot of these types of aliphatic compounds present, and will result in a falsely inflated quantitation of aromatics. Since a good portion of the hydrocarbons in the C9-C12 range of gasoline are in fact substituted aromatic compounds, this analytical overquantitation is not a major problem. However, other products, like kerosene and Jet A fuel, contain predominately aliphatic compounds within this range, and therefore use of the PID/FID approach can lead to significant overquantitation of the aromatic fraction.

Steps can be taken to minimize overquantitation of the aromatic fraction. Using a low energy PID lamp (e.g., 9.5 eV) will further diminish aliphatic response. Where essential, other techniques, such as chemical fractionation and/or use of a GC/MS approach, may be used to ensure more accurate data in this regard.

### 3.2.2 Extractable Petroleum Hydrocarbons (EPH)

The MADEP EPH Method (1998) is a *solvent extraction/fractionation GC/FID* procedure. Using this method, the collective concentrations of C9-C18 Aliphatic, C19-C36 Aliphatic, and C11-C22 Aromatic Hydrocarbons can be quantitated in soil or water matrices. In addition to these fractional ranges, the EPH method may also be used to concurrently identify and quantitate individual concentrations of the 17 Polycyclic Aromatic Hydrocarbon (PAH) *Target EPH Analytes*.

Soil and water samples are extracted with methylene chloride, solvent 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.

There are two important methodological elements that should be considered when reviewing EPH data:

- ◆ The MADEP EPH method relies upon a solvent-exchange/silica-gel-fractionation process to differentiate aromatic hydrocarbons from aliphatic hydrocarbons. This fractionation process is a sensitive yet critical element of the analytical approach; small errors at this stage can result in significant over or underquantitation of aromatic and aliphatic ranges. For this reason, the method specifies use of *Fractionation Surrogates* to verify proper separation of the aliphatic and aromatic fractions.
- ◆ 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 weathered products. (See Figure 3-1). 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 are included in the sample quantitation calculation, and 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.**

The EPH method also contains an option to forego the solvent-exchange/silica-gel-fractionation process, to obtain a Total Petroleum Hydrocarbon (TPH) concentration. While this data will provide little information on the chemistry or toxicity of the petroleum mixture, it can provide a cost-effective analytical screening value, for comparison with TPH reporting and cleanup standards.

### 3.2.3 Air-Phase Petroleum Hydrocarbons (APH)

The draft MADEP APH method (2000) is a *GC/MS* procedure. Using this method, the collective concentrations of C5-C8 Aliphatic, C9-C12 Aliphatic, and C9-C10 Aromatic Hydrocarbons can be quantitated in air or soil gas matrices. In addition to these fractional ranges, the APH method may also be used to concurrently identify and quantitate individual vapor-phase concentrations of the *Target APH Analytes* 1,3-butadiene, benzene, toluene, ethylbenzene, and xylenes (BTEX); Methyl-tertiary-butylether (MtBE), naphthalene, and 2-methylnaphthalene.

Samples are collected in SUMMA ® passivated stainless steel canisters (other collection techniques are permissible and may be more appropriate for certain data quality objectives). A specified volume of sample is withdrawn from the canister through a mass flow controller using a vacuum pump. The sample is cryogenically concentrated to a volume of less than one mL in a nickel trap filled with nonsilanized glass beads. Following preconcentration, the sample is refocused at the head of a capillary column on a gas chromatograph using a cryofocusing accessory. This step further reduces the sample volume to less than one microliter for injection.

The sample is then injected into a gas chromatograph, which is used to separate the compounds and hydrocarbon fractions of interest. All compounds are detected using a mass spectrometer. Target APH Analytes are identified and quantitated using characteristic ions. Collective concentrations of C<sub>9</sub>-C<sub>10</sub> Aromatic Hydrocarbons are quantitated using extracted ions. Collective concentrations of aliphatic hydrocarbon fractions are quantitated using a total ion chromatogram, subtracting out Target APH Analytes and C<sub>9</sub>-C<sub>10</sub> Aromatic Hydrocarbons. It is important to note that the final APH method may contain modifications of the above procedures.

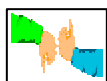
Air testing, whether by the APH procedure or other methodologies, is a specialty service that is not as widely available as soil and water analytical services. However, unlike the VPH and EPH methods, MADEP does not expect use of the APH method will be required at most petroleum contaminated sites, for the reasons listed below:

- ◆ Most releases of petroleum products do not result in an indoor air impact;
- ◆ For those sites where an indoor air impact is a potential concern, it is usually possible to evaluate and/or rule-out indoor air contamination problems using low-cost soil gas analytical screening techniques, as further detailed in Section 4.3.1; and
- ◆ Where indoor air sampling is required to evaluate a potential subsurface vapor transport pathway, traditional EPA procedures (e.g., EPA Method TO-14) may be used to determine if an impact is likely (based upon concentration of target analytes and qualitative presence of hydrocarbon peaks). The use of the APH (or similar) procedure would only be necessary if contamination is confirmed, and a quantitative risk assessment is required.

### 3.3 VPH/EPH Target Analytes

Although both the VPH and the EPH methods are capable of providing quantitation of Target Analytes (concurrent with the quantitation of aliphatic and aromatic ranges), because they are GC methods which identify analytes solely on the basis of retention times, they can produce “false positive” or over-inflated concentration data for these individual compounds. For example, the large peak eluting at 14.740 minutes in Figure 3-1 may be identified by the EPH method as hexadecane, because a hexadecane standard run as part of the calibration procedures eluted at this retention time. However, it is possible that hexadecane is not present in this sample at all, and some other (unknown) hydrocarbon compound is present which elutes at precisely this same time; or it is possible that hexadecane is indeed present, but that 2 or 3 other hydrocarbon compounds are *co-eluting* with hexadecane at precisely this time, which will lead to an overquantitation of the hexadecane concentration.

Although the sample-extract cleanup and fractionation procedures specified in the EPH method will tend to minimize interferences of this nature (by removing aliphatic compounds that may co-elute with the PAH Target Analytes), the only way to get positive identification and quantitation of these Target Analytes is to use a GC/MS analytical technique, like 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. This approach is acceptable, although it may increase analytical costs.



*To save money, it may be a worthwhile gamble to quantitate Target Analytes using the VPH/EPH Methods for samples that are believed to be relatively free from contamination - for example, when trying to confirm a “clean closure” at a tank removal site. If significant concentrations of Target Analytes are in fact found to be present, a re-analysis can be done using GC/MS, to provide a definitive determination in this regard (if the laboratory was instructed to retain the sample extract from the VPH/EPH samples, the cost for this re-analysis would be reduced).*

### 3.4 Sampling Procedures and Requirements for the VPH/EPH Methods

Sample collection and preservation are critical elements in the VPH and EPH methodologies. A summary of requirements in this regard is provided in Table 3-1; detailed step-by-step sampling recommendations are provided in Appendix 1.

Sample preservation is essential. **VPH and EPH aqueous samples must be preserved in a manner that prevents biodegradation of hydrocarbons. Simply cooling these samples is not sufficient.** Biodegradation can be prevented by addition of acids (e.g., HCl to pH <2) or by the addition of bases (e.g., Trisodium Phosphate Dodecahydrate to pH > 11). *Note that acid preservation can significantly degrade levels of MtBE in aqueous samples (see Appendix 1).*

**VPH soil samples must be preserved in a manner that (1) prevents sample losses due to volatilization, and (2) prevents sample losses due to biodegradation.** There is now considerable evidence and data demonstrating substantial losses of volatile petroleum hydrocarbons from unpreserved sampling containers. The recommended preservation technique is to immerse VPH soil samples in methanol *at the time of collection*. Alternative techniques will be considered only if sufficient data are available to demonstrate the efficacy of sample preservation. Currently, only one alternative has been shown to provide acceptable preservation: the use of specially designed sealed-tube devices that obtain an air-tight soil sample.

**Table 3-1: Sample Collection, Preservation, and Holding Times**

Method	Matrix	Container	Preservation	Holding Time
VPH	Aqueous	40 mL VOC vial w/Teflon-lined septa screw caps; fill completely to zero headspace	pH <2 (add 3-4 drops of 1:1 HCl); cool to 4°C. Where MtBE is of concern, use 0.40– 0.44 grams TSP to raise pH > 11 (see Appendix 1)	14 days
	Soil	VOC vial or container; add 15g to 40mL vial; 25g to 60 mL vial	1 mL methanol per 1g soil (+/- 25%); cool to 4°C	28 days
EPH	Aqueous	1-Liter amber glass bottle with Teflon-lined screw cap	pH<2 (add 5 mL of 1:1 HCl); cool to 4°C	Extract within 14 days; analyze extract within 40 days
	Soil	4-oz (120 mL) +/- widemouth amber glass jar with Teflon-lined screw cap	cool to 4°C	Extract within 7 days; analyze extract within 40 days

Such devices have been shown to maintain sample integrity for 48 hours, by which time the sample must be extruded and preserved in methanol. Additional detail on the preservation of VPH aqueous and soil samples is provided in Appendix 1. Information and guidance on shipping methanol-preserved samples is contained in Appendix 2.

### 3.5 Modifications of the VPH/EPH/APH Methods

The MADEP VPH, EPH, and APH analytical techniques are “performance-based” methods, which means that modifications to specified procedures are allowable, as long as acceptable performance is demonstrated and documented.

The most common modification of the VPH and EPH methods involves the use of a GC/MS technique to identify and quantitate collective ranges of aliphatic and/or aromatic hydrocarbons. Under this approach, a mass spectrometer is used to break up the hydrocarbon molecules in a sample into fragments with certain masses and charges. A computer program is then used to search for specified fragments that are indicative of an aliphatic and/or aromatic hydrocarbon structure. Quantitation of a collective hydrocarbon range is accomplished by comparing the total mass of these selected fragments with the mass of fragments produced by calibration standards.

While MADEP believes that a GC/MS approach has promise, it has not yet issued guidelines or recommendations in this regard. Until such time as this occurs, all laboratories conducting such modifications must be able to provide complete documentation on their procedures, and must be able to demonstrate that their methodology is capable of generating data of a known level of accuracy and precision. Specific questions that a data user might want to address to laboratories include:

- ◆ *What “ions” (fragments) were used to quantitate specific aliphatic and/or aromatic hydrocarbon ranges? How were these ions chosen? Because hydrocarbon molecules fragment in different manners and proportions, how do the fragmentation patterns of the calibration standards correlate to the fragmentation patterns of the hydrocarbons likely contained in the sample?*
- ◆ *What studies did the laboratory do to validate the method? Were “neat” petroleum products analyzed? Fresh and/or “weathered”?*
- ◆ *Based upon the choice of quantitating ions and the results of the validation studies, under what (sample chemistry) conditions would a positive or negative identification and/or quantitating bias be expected?*

While MADEP encourages laboratories to develop “better mouse traps”, ultimately, it is the responsibility of the data user to determine the validity and application of data obtained from modified methods. Parties unfamiliar with analytical chemistry and/or laboratory operations are advised to seek expert advice in such matters, and understand the nature, extent, and implication of all method modifications.

### 3.6 Data Quality and Report Content

Because the VPH and EPH methods are performance-based, and because MADEP does not (at this time) have a laboratory certification program for non-drinking/non-wastewater matrices, it is incumbent upon the laboratory and data users to take steps to ensure and document the quality of analytical data, consistent with the provisions and requirements of 310 CMR 40.0017.

The VPH and EPH methods have detailed and specific Quality Assurance and Quality Control (QA/QC) requirements, and a required data reporting content, which is provided in Appendix 3. The reporting content is designed to ensure that data users can easily ascertain (1) what is being reported, (2) basic sample and QA/QC information, (3) whether significant modifications were made to the recommended methods, (4) whether all recommended QA/QC steps were taken, and (5) whether all specified QA/QC and performance standards were met. *While it is not necessary to obtain and provide data in exactly the same form and order detailed on the reporting sheets provided in Appendix 3, data users should insist that all indicated information and statements be provided.*

Although a comprehensive review of all QA/QC information and data is beyond the ability and/or resources of most data users, there are several quick and easy steps that can and should be taken to help ensure the accuracy and reliability of VPH/EPH/APH data, by simply reviewing the information and data required in the data report:

- ◇ **All sample information specified in Appendix 3 should be provided, describing the sample matrix, condition of containers, and sample preservation.** VPH samples that were not preserved in the field with methanol (or sampled/preserved in an acceptable alternative manner) are highly suspect.
- ◇ **The dates of sample collection, receipt by laboratory, extraction (EPH) and analyses should be provided.** Samples held beyond the recommended holding times are suspect, especially EPH soil samples that are preserved only by refrigeration.
- ◇ **A percent moisture value should be reported for all soil samples,** to ensure that such data have been adjusted to a “dry weight” reporting basis.
- ◇ **The analytical units must be clearly indicated,** and should be appropriate for the matrix under evaluation (i.e., µg/g, mg/kg, or µg/kg for soil; µg/L or mg/L for water; µg/m<sup>3</sup> or ppbv for air).
- ◇ **Reporting Limits (RLs) should be specified for each aliphatic and aromatic range and each Target Analyte.** The VPH, EPH, and APH methods contain specific procedures and requirements on how to establish Reporting Limits, which are the minimum concentration values that a laboratory can discern and report with sufficient confidence. These values must be experimentally determined by each laboratory. Note that expected RLs for the aliphatic and aromatic ranges in water are between 50 and 100 µg/L; expected RLs for the aliphatic and aromatic ranges in soil are between 2 and 10 mg/kg; expected RLs for the aliphatic and aromatic fractions in air are between 25 and 100 µg/m<sup>3</sup>.
- ◇ **The percent recovery of sample surrogates should be provided, along with the acceptable range.** A surrogate is a (non-petroleum) chemical compound added (“spiked”) into each VPH and EPH water and soil sample prior to extraction and analyses. The purpose of surrogate spiking is to determine the efficiency and accuracy of sample extraction (EPH), sample purging (VPH), and instrument analyses. Surrogate recovery is expressed in terms of percent recovery; for example, if 1000 µg of the surrogate compound ortho-terphenyl (OTP) is spiked onto a 10 gram soil sample that is to be analyzed by the EPH method (yielding a theoretical concentration of 100 µg/g), and the resultant analysis quantified OTP at 70 µg/g, the percent recovery would be 70%. Although sample data with surrogate recoveries outside of the stated acceptance range should be carefully evaluated, they need not be summarily dismissed or considered categorically unusable. For example, data associated with a surrogate recovery greater than specified limits may be appropriate to use as an “upper limit” value; data associated with a surrogate recovery lower than specified limits may be appropriate to use as a “lower limit”, and would constitute knowledge of a release if exceeding Reportable Concentrations. Note that low recoveries are not uncommon (or unexpected) in clay/organic soil matrices. Also, low recoveries of sample surrogates may be observed in VPH soil samples with high moisture content.
- ◇ **For the EPH Method, the percent recovery of Fractionation Surrogates should be provided, along with the acceptable range.** In the EPH method, a sample extract is loaded onto silica gel, followed by a hexane rinse, to



remove and collect aliphatics, and a methylene chloride rinse, to remove and collect aromatics. However, because of the weakly polar nature of naphthalene and substituted naphthalenes, they are easily “stripped” into the aliphatic fraction - an especially problematic occurrence in water samples, as the naphthalenes constitute a large percentage of the water-soluble fraction of fuel oils. To monitor whether this action is occurring, Fractionation Surrogates are added directly to the sample extract just prior to the silica gel fractionation step (as opposed to the sample surrogates, which are added to the soil and water samples prior to extraction, to evaluate extraction efficiency). The currently recommended Fractionation Surrogates are 2-Fluorobiphenyl and 2-Bromonaphthalene - two compounds that are not normally present in petroleum, and that have polarities similar to naphthalene. Both compounds should be detected in the aromatic fraction within the specified acceptable percent recovery ranges.

Note: Changes and refinements to the EPH Method may affect the use and selection of Fractionation Surrogates.

- ◇ ***The laboratory should clearly indicate whether the reported VPH/EPH/APH fractional range concentrations include or do not include the concentration of Target Analytes, and the range(s) in which the Target Analytes elute.*** By definition, these ranges exclude Target Analytes, which are evaluated separately. (Absent this exclusion, Target Analytes like BTEX and PAHs would be “double counted” - once in the collective range concentrations, and once in a separate Target Analyte evaluation). If the laboratory did not subtract out the concentrations of these Target Analytes (perhaps they only provided range data), the data user may make this adjustment. It is also permissible for a data user to adjust a range concentration value by excluding the concentration(s) of non-petroleum analytes eluting within that hydrocarbon range (e.g., TCE eluting within a C5-C8 Aliphatic Hydrocarbon range). Note that unadjusted data are also acceptable to MADEP - they are just overly conservative.
- ◇ ***The laboratory must clearly indicate whether significant modifications were made to MADEP VPH/EPH/APH methods, and if so, should detail the nature and extent of these modifications.*** Examples of “significant modifications” are specifically listed in Section 11 of each method. Note that MADEP encourages innovation, where appropriate.
- ◇ ***The laboratory should clearly indicate whether it has followed and met the QA/QC program and performance standards specified by the MADEP VPH/EPH/APH Methods.*** Such an affirmation is contained in the required laboratory report content. Note that on some samples, it will not be possible to meet all QA/QC specifications, and that such data need not be summarily dismissed as unacceptable, as long as an appropriate explanation is provided, and as long as limitations inherent in the data are acceptable for the given application and use of the data.
- ◇ ***A report narrative should be provided, if necessary, to document and explain any deviations from the method, analytical problems, and/or QA/QC issues.*** Laboratories using modifications of the method should have on file a written Standard Operating Procedure, which should be referenced or provided as appropriate. While a failure to perform or meet the data reporting and performance standards specified above does not necessarily mean that the provided data are not of sufficient quality, it does place the burden on the data user to make this determination.
- ◇ ***The laboratory should certify under the pains and penalties of perjury that the information contained in the data report form is accurate and complete.*** This attestation should be done via the signature of a responsible laboratory representative.

While minimum standards are specified in the methods, to ensure a minimum level of quality for all data, there is an expectation that laboratories should be able to achieve better results on most samples. In selecting a laboratory, a data user should make sufficient inquiry into the experience of the laboratory performing these (and any other) analytical methods, and on the QA/QC program in operation to monitor, document, and improve analytical quality. In addition, the scope of laboratory services should be negotiated and clearly articulated “up front”, to ensure that the data user is procuring (and the laboratory is receiving compensation for) all desired information and data (e.g., QA/QC data, narrative reports, data usability discussions, etc.).

Additional guidance and recommendations on data quality issues for the VPH/EPH methods (as well as most other common EPA methods) can be downloaded from MADEP at: <http://www.state.ma.us/dep/bwsc/files/data/QAQCDocs.htm>

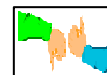
**Analytical data and testing should not be viewed as a commodity, but as a highly technical and sophisticated professional service, requiring the same level of scrutiny and oversight as any other professional service that will be relied upon by a Licensed Site Professional in rendering a waste site cleanup opinion.**

### 3.7 Other Hydrocarbon Testing Methods

The VPH and EPH methods were developed to provide data on the chemistry and toxicity of complex hydrocarbon mixtures, to facilitate risk evaluations and to complement MADEP Method 1 cleanup standards. However, in cases where the total concentrations of hydrocarbons are relatively low, use of these fractionation procedures may be “overkill”, and a “total petroleum hydrocarbon” (and Target Analyte) evaluation may suffice. Moreover, risk characterization is not the only site assessment objective or concern at disposal sites; other characterization needs may include: petroleum product identification, petroleum source identification, and/or Remediation Waste characterization. In these cases, other analytical procedures may be more appropriate and cost-effective.

A summary of other possible analytical approaches and methodologies in this regard is provided in Table 3-2.

**Table 3-2: Other Analytical Approaches**



Objective	Analytical Approach	Conditions/Caveats/Comments
Characterization of Remediation Wastes	TPH, VOCs, and/or jar headspace screening. Metals, PCBs and/or TCLP often required	Need to check with disposal or recycling facility for requirements
Risk Assessment & Compliance with Cleanup Standards	TPH via an appropriate methodology. Characterize Target Analytes as needed with EPA SW-846 methodologies	Applicable for low levels of C9 and heavier hydrocarbons (i.e., when TPH concentrations will likely < TPH cleanup standards)
Determining Type of Petroleum Product	High resolution GC/FID; advanced GC/MS chemical fingerprinting	Also recommended to differentiate petrogenic vs. pyrogenic PAHs
Determining Source of Petroleum Product	High resolution GC/FID; advanced GC/MS chemical fingerprinting; quantitation of biomarkers	Not always definitive; requires interpretative expertise

#### 3.7.1 Total Petroleum Hydrocarbons (TPH)

Though a widely used and conceptually-simple testing parameter, there is no universal definition of TPH, and the term is essentially defined by the analytical method chosen by the laboratory. To further complicate this matter, many laboratories use undefined and inconsistent “modifications” of published methodologies to detect and quantitate TPH concentration values (e.g., Modified EPA Method 8100). This situation has led to a significant degree of confusion over the application, comparability, and quality of TPH data.

The MCP provides a definition of TPH at 310 CMR 40.0006:

*Total Petroleum Hydrocarbons and TPH each mean the total or cumulative concentration of hydrocarbons with boiling points equal to or greater than 150°C [C<sub>9</sub>] and associated with a petroleum product, as measured by standard analytical techniques and/or by procedures approved by the Department, excluding the individual compounds listed at 310 CMR 40.0974(2).*

This definition reflects the fact that the vast majority of “TPH” analyses traditionally conducted in Massachusetts involved the use of an extraction solvent (e.g., Method 418.1), which leads to the loss of lighter hydrocarbons (<C<sub>9</sub>) present in the sample. Based upon this definition, the following rules and recommendations would apply to parties electing to use a TPH analytical method to support a risk assessment or document compliance with an MCP Method 1 TPH cleanup standard:

- The TPH method and resultant data may only be used to characterize releases of petroleum products that consist of hydrocarbons primarily in the C<sub>9</sub> to C<sub>36</sub> range. In other words, it may only be used in lieu of an EPH procedure, not a VPH procedure. Guidance on when an EPH procedure is appropriate is contained in Table 4-6.
- In addition to the TPH analysis, all appropriate Target Analytes must also be addressed. Guidance in this regard is contained in Tables 4-3 and 4-5.

- For analytical procedures that utilize a GC/FID technique, the TPH quantitation value must be based upon the integration to baseline of all peak areas from n-Nonane (C9) to n-Hexatriacontane (C36).
- As the MCP specifically excludes “individual compounds listed at 310 CMR 40.0974(2)” from its definition of TPH, it is acceptable to adjust gross TPH values by subtracting out the collective concentrations of these individual compounds. Note that, for all intents and purposes, the “individual compounds listed at 310 CMR 40.0974(2)” are synonymous with the EPH Target Analytes listed in Tables 4-3 and 4-5.

While the MCP defines TPH to be C9 and heavier hydrocarbons, there are some TPH and/or “Gasoline Range Organics” methodologies that may collectively quantitate lighter hydrocarbons in the range of C5-C12. Typically, these methods involve the use of a purge-and-trap or headspace development technique, followed by a GC/FID analytical procedure. While these procedures may NOT be used to obtain TPH data for comparison to the MCP Method 1 cleanup standards (because of the definition of TPH at 40.0006), they can be used as a screening tool for VPH range contaminants. Specifically, if the TOTAL concentration of hydrocarbons within the C5-C12 range (excluding VPH Target Analytes) is less than the lowest VPH Method 1 standard (usually C9-C10 Aromatic Hydrocarbons), it would be safe to assume that hydrocarbon levels are within all fractional standards.

While use of TPH methods may offer certain advantages, it is the responsibility of the party using and submitting such data to ensure that the specific technique and procedure(s) used is appropriate for the disposal site in question, and that appropriate Quality Assurance and Quality Control (QA/QC) measures are taken to monitor and document the quality and usability of the generated data. In general, MADEP expects all such methods to achieve a level of QA/QC consistent with the VPH and EPH methods.

A tabulation of commonly and/or historically available TPH analytical techniques is provided in Table 3-3.

**Table 3-3: Common/Available TPH Testing Methods**

Method	Technique	Comments
MADEP EPH	Extraction with methylene chloride & GC/FID analysis	Use in the “TPH” screening mode by eliminating the fractionation step per Section 1.5 of EPH Method
EPA Method 1664	Extraction with n-hexane & gravimetric analyses	New method (1999) to replace Method 418.1 (Freon extraction with IR analyses)
Modified EPA Method 8100	Extraction with appropriate solvent & GC/FID analysis	Must ensure quantitation in C9-C36 range with forced baseline integration if data is used to support MCP TPH cleanup standard
Modified EPA Method 8015	Purge-and-trap or headspace sample preparation & GC/FID analysis	Must ensure quantitation in the C5-C12 range with forced baseline integration if data is to be used to screen samples for compliance with MCP VPH cleanup standards

### 3.7.2 Environmental Forensic Techniques

In conducting a characterization of a petroleum-contaminated site, it may be necessary and/or desirable to identify the types of petroleum product present and/or the source of their release to the environment. In recent years, new analytical testing techniques have evolved to facilitate evaluations of this nature, and support an evolving specialization known as “environmental forensics”.

In order to identify the types and/or source of petroleum products that were detected at a site, (up to) a three-step analytical regiment is recommended:

- Initially, samples should be analyzed by a high-resolution gas chromatography/flame ionization detection (GC/FID) methodology. Such techniques have been utilized for many years, and are a useful “first cut” to help identify the boiling-point range of the hydrocarbon mixtures present in the sample, which can then be used to make judgments on the type(s) of petroleum product(s) released at the site (e.g., #2 fuel oil vs. #6 fuel oil). In some cases, the data obtained in this manner is sufficiently conclusive to satisfy site characterization objectives.

In other cases, however, the contamination is highly weathered, and/or intermingled with hydrocarbons of pyrogenic origin (e.g., coal ash, soot, engine emissions).

- In situations where a GC/FID evaluation is inconclusive, additional analytical characterization by a gas chromatography/mass spectrometry (GC/MS) “advanced chemical fingerprinting” technique may be advisable. These methodologies focus on the identification and quantitation of polycyclic aromatic hydrocarbons (PAHs). Although most people are familiar with the 17 priority pollutant PAH compounds quantitated by the MADEP EPH method and EPA Method 8270, there are in fact many more PAH compounds present in petroleum products. Using a GC/MS technique and sophisticated quantitation algorithm, it is possible to identify and quantitate collective groupings of these PAH compounds based upon their structure, e.g., naphthalene with a side chain containing 1 carbon atom; naphthalene with a side chain containing 2 carbon atoms, etc. The presence and distribution of these side chains can then be used to help establish the type of petroleum product(s) present at the site. Moreover, this same information – often plotted as histograms – may also be used to differentiate petroleum-derived (petrogenic) hydrocarbons from combustion-derived (pyrogenic) hydrocarbons (given that the latter are predominated by the parent PAH compound, while the former are predominated by the alkylated side chain PAH compounds).
- Data on the distribution of alkylated PAHs can often provide definitive information on the type(s) of petroleum products present at a site, and even some evidence on the specific source(s) of release. However, in order to obtain more definitive proof of the source of a petroleum release, one additional analytical tool should be considered: the identification and quantitation of biomarkers. Biomarkers are chemical compounds present in petroleum products that are the remnants of the biological life (e.g., algae, plants, bacteria) that help create the parent crude oil. While certain biomarkers are identifiable using a GC/FID methodology (e.g., pristane and phytane), the most useful compounds in this regard (e.g., terpanes and steranes) are identified using a GC/MS technique in a selected ion monitoring (SIM) mode. Because each crude oil source has a distinct “fingerprint” of biomarkers, it is often possible to identify the specific source of a release of petroleum at a site using this approach (e.g., using a statistical/multivariate component analyses), though weathering processes may sometimes decrease confidence in such conclusions.

At the present time, advanced chemical fingerprinting is an innovative technology used by only a small number of laboratories. Given this status, and given the sophistication, complexity, and professional judgment inherent in these approaches, it is essential that data users seek out facilities and personnel with the appropriate expertise and experience.

### 3.8 Analytical Screening Techniques

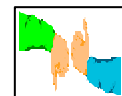
The use of analytical screening techniques is encouraged, to provide timely and cost-effective data. As the sophistication and reliability of so-called “field” methods continue to increase, the distinction between conventional laboratory and analytical screening techniques becomes less defined, and less important. However, with this increased capability and performance comes an increased need to demonstrate and document a commensurate level of quality assurance/quality control (QA/QC), consistent with the provisions and requirements of 310 CMR 40.0017.

Various levels/approaches are possible:

- ◇ Screening techniques may be used solely to direct remedial actions and/or sampling programs for conventional VPH/EPH testing. Because such screening data will not be used in a “stand alone” capacity, QA/QC requirements are not as critical.
- ◇ Screening techniques may also be employed to obtain data that will be used, in whole or in part, to assess risks and/or determine compliance with cleanup standards, and/or to support the representativeness of (“lab”) data used in the risk assessment process. While it is understood that such screening methodologies may lack the qualitative or quantitative accuracy of conventional VPH/EPH testing, *the same level of QA/QC will be expected, within the limits and bounds of the stated application of the data.*

The use of screening techniques depends upon, or may be enhanced by, the use of assumptions and conditions. This approach is acceptable, as long as conservative assumptions are made, and the use of such methods and assumptions are appropriate, given contaminant chemistry, site conditions, and area receptors. A tabulation of commonly used screening techniques, and recommended applications and *Rules of Thumb*, are provided in Table 3-4.

**Table 3-4  
VPH/EPH Analytical Screening Techniques**



Technique	Description	Range	Applications	Limitations	Recommendations
PID/FID Headspace	Soil or water sample is placed in sealed container & headspace is allowed to develop. PID and/or FID meter is then used to test the headspace for total volatile organic compounds (VOCs). Reference: Recommended DEP jar headspace procedure	VPH	Excellent screening tool for gasoline; good tool for kerosene, jet fuel and fresh fuel oil. Best used to direct remedial operations, and provide first-cut site characterization data. PID preferentially responds to the more toxic aromatic compounds.	Not appropriate for heavy mineral/lube/fuel oils or weathered diesel/#2 fuel oil. PID can be non-linear and/or erratic for gasoline headspace vapors > 150 ppmv. PID response lessened by high humidity/ moisture (instrument dependent). Additional confirmatory analyses usually required.	For gasoline, excluding clays & organic soils, headspace readings less than 100 ppmv usually means that all VPH fractions are below 100 µg/g. Confirmatory analyses needed.
PID/FID Soil Gas	Soil gas is extracted from a probe and analyzed with a PID and/or FID meter. Reference: see Section 4.3.1.1	VPH & EPH	Use to investigate soil gas/indoor air pathways, and evaluate sites with g.w. concentrations > GW-2 Method 1 standards. PID preferentially responds to the more toxic aromatic compounds.	Instrument response is flow-dependent; must ensure adequate flow rates. PID response affected by high moisture & high petroleum vapor concentrations (>150 ppmv). FID will respond to pipeline/naturally-occurring methane.	See recommendations in Section 4.3.1.1 and Table 4-9.
UV Fluorescence & Absorbance	The absorbance or fluorescence of a UV light source is used to directly quantitate the aromatic content of soil sample. Extraction solvent, such as methanol or Isopropyl alcohol, must be used. Reference: ASTM 5831-95	VPH & EPH	Good screening tool for petroleum products with significant aromatic content (e.g., diesel/#2 fuel oil and gasoline). UV Fluorescence has lower detection limits than absorbance, but is not as linear. UV methods target the more toxic aromatic fractions.	Does not respond to aliphatics; not appropriate for petroleum products that are primarily aliphatics (mineral oils or dielectric fluids). May pick up naturally occurring humic acids - calcium oxide can be used to decrease interference.	Calibrate with aromatic standard, like C11-C22 EPH standard, for direct measurement of aromatic hydrocarbons. For diesel/#2 fuel oil, assume aliphatic content is twice aromatic. This approach may significantly over-predict aliphatic content of highly weathered diesel/#2 fuel oil. Confirmatory analysis recommended for representative/worst-case samples.
Emulsion-Based TPH Methods	Hydrocarbons are extracted from a soil sample with a solvent (e.g. methanol), and a surfactant is added to create an emulsion. Optical sensor is used to measure extract turbidity	EPH	Gives "TPH" screening values, quantitating both aromatic and aliphatic hydrocarbons. Best correlation shown with diesel/#2 fuel oil.	Does not discriminate between aliphatics and aromatics. Interference possible in organic-rich and clay soils. Not recommend for gasoline.	For diesel/#2 fuel oil, assume 60% C11-C22 Aromatics and 40% C9-C18 Aliphatics.
Immunoassay Test Kits	Soil or water samples analyzed by antibody-antigen reaction. Enzyme conjugates used to allow colorimetric analysis of antigen (contaminant) conc. Soil extraction with methanol. Reference: EPA 4030/4035	VPH & EPH	Can be used to detect specific compounds or groups of compounds (e.g., BTEX and PAHs). "TPH" methods usually target naphthalene, and assume correlation to TPH.	Because antibodies bind with specific antigens (contaminants), cannot directly quantitate collective aliphatic/aromatic fractions or total hydrocarbons. Not effective for lube/hydraulic oils.	No general assumptions can be made. Each kit and application has to be individually evaluated.
Fiber-Optic Chemical Sensors	Probe with hydrophobic/organo-phyllic optical fiber is lowered into a well. Change in refraction index used to est. hydrocarbon conc. in groundwater	VPH & EPH	Allows in-situ measurements of volatile and semi-volatile dissolved hydrocarbons. Results calibrated to a p-xylene response. In-situ vapor measurement also possible.	Response decreases with increasing solubility; response to benzene 10 times less than p-xylene. Significant calibration/cleaning requirements between uses.	Insufficient information available to offer general recommendations.

### 3.8.1 Principles of Operation, Biases, and Calibration

All screening techniques and instruments are predicated upon certain principles of operation, detection, and calibration. Many have limitations and biases that need to be understood and accommodated. For example, an immunoassay “TPH” test method may be designed to detect the presence of naphthalene, and then extrapolate a TPH concentration based upon an assumption on the percentage of naphthalene in fresh fuel oil. Thus, two important assumptions and biases are present: (a) the concentration of a single compound (naphthalene) can be used to determine the concentration of a product which is made up of numerous (perhaps hundreds of) hydrocarbon compounds, and (b) the chemistry of a fresh fuel oil standard can be used to estimate the chemistry of a field sample. As such, a highly weathered fuel oil sample, or a fuel product low in naphthalene (e.g., mineral oils) may not yield reliable results.

To effectively use analytical/screening techniques, especially for risk and cleanup decisions, it is incumbent upon the data user to:

1. understand the application and limitations of the screening method(s) of interest;
2. consider site-specific contaminant/mixture chemistry and fate/transport processes; and
3. determine the precision and accuracy boundaries of the generated data, to see if they meet the desired data quality objectives and site characterization needs (e.g., if data can be considered accurate at 100 µg/g +/- 300%, and the cleanup standard is 500 µg/g, it may be acceptable).

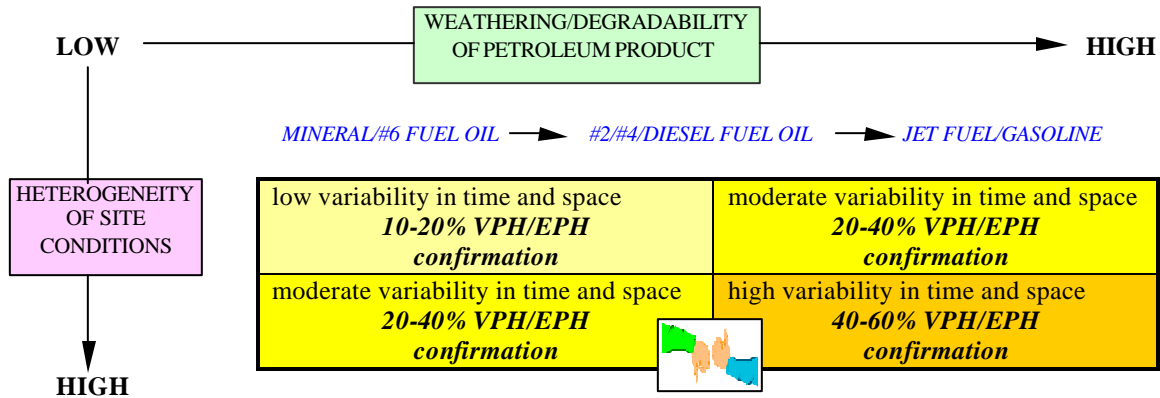
In general, the following recommendations are offered:

- ◇ Techniques that detect a structural class and/or range of compounds are preferred, as opposed to methods that rely upon one specific indicator compound. Techniques that detect a range of compounds include PID/FID headspace techniques, UV absorbance/fluorescence, and emulsion-based TPH techniques. Procedures that target a single indicator compound require sufficient site-specific correlative and confirmatory data.
- ◇ Techniques that target aromatic hydrocarbons are preferred, as opposed to methods that target aliphatic compounds, due to the fact that aromatic hydrocarbons are, as a class, more toxic and mobile than aliphatic hydrocarbons. *On the whole, it is better to be able to accurately quantitate collective aromatic hydrocarbons, and estimate aliphatics, than to accurately quantitate collective aliphatic hydrocarbons, and estimate aromatics.* Techniques that target aromatics include PID headspace and UV absorbance/fluorescence.
- ◇ Techniques that involve a quick “shake out” extraction technique for soil analyses may not be sufficient for clay or organic-rich soils, due to partitioning efficiencies.

### 3.8.2 Recommended Approach

For small sites, such as residential underground storage tank (UST) excavations, screening techniques are perhaps best used to direct soil removal operations, identify areas for assessment and/or confirmatory VPH/EPH laboratory analysis, and/or provide a database to support the representativeness of decision-quality data. For larger sites, the use of screening data as a substitute and complement for VPH/EPH laboratory data may provide a better and less expensive approach to site characterization. For example, for the price of a single EPH test (approximately \$200), it may be possible to perform 4 to 10 field screening analyses. So, for a sampling and analytical budget of \$2000, it may make sense to take 8 EPH samples, and 8 to 20 field-screening samples, rather than (just) 10 EPH samples. The minimum number of VPH/EPH laboratory samples needed to understand contaminant chemistry, and provide confidence in screening data, is necessarily site-specific. The key variables are the heterogeneity of site conditions (stratigraphic/microbiological), source vs. migration areas, and the degradability of the petroleum product(s). Generalized *Rules of Thumb* in this regard are provided in Table 3-5. Note that additional confirmatory sampling would be indicated if sufficient correlation could not be established between the VPH/EPH values and screening/TPH values.

**Table 3-5: Recommended Minimum VPH/EPH Laboratory Confirmation Data Needed to Support Analytical Screening**



### 3.9 Drinking Water Testing Methods

When testing a potable drinking water supply, the use of the VPH/EPH analytical methods should be limited to quantitation of hydrocarbon ranges of interest; specific analytes of interest should be quantitated using the appropriate EPA “500” series drinking water methods.

## 4.0 CLEANUP STANDARDS

The Massachusetts Contingency Plan (MCP) provides three methods to assess risks and determine *how clean is clean enough*:

- ◇ Method 1 - generic cleanup standards in soil and groundwater
- ◇ Method 2 - site-specific modification of generic cleanup standards
- ◇ Method 3 - completely site-specific risk assessment

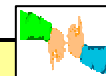
The easiest approach is Method 1, in that cleanup standards have already been established by MADEP. In support of the VPH/EPH approach, 6 generic standards have been developed and promulgated for the aliphatic and aromatic fractions of interest. A conservative TPH standard has also been retained, to allow continued use of such methods. *Note that it is not necessary to meet a TPH cleanup standard (or Reportable Concentration) if all 3 EPH fractional standards are achieved [see 310 CMR 40.0973(7) and 40.0360(2)].*

Because the Method 1 standards are generic, and were calculated assuming conservative site conditions, they can overestimate risk at some sites. In such cases, use of a Method 2 or 3 alternative approach may be advisable and cost effective. Guidance and recommendations in this regard are provided in Table 4-1.

For complete information and guidance on the use of the MCP risk assessment methods, consult the Massachusetts Contingency Plan at 310 CMR 40.0900, and MADEP’s *Guidance for Disposal Site Risk Characterization in Support of the Massachusetts Contingency Plan*, available at <http://www.state.ma.us/dep/ors/orspubs.htm>.



**Table 4-1: Choosing an MCP Risk Assessment/Cleanup Method**



Method	Consider Using If.....	Significant Limitations
1	<ul style="list-style-type: none"> <li>◆ simple/small site</li> <li>◆ contamination in soil and gw only</li> <li>◆ cleanup to Method 1 standards is feasible</li> </ul>	<ul style="list-style-type: none"> <li>◇ cannot be (solely) used if sign. sediment contam</li> <li>◇ cannot be (solely) used if sign. indoor air impacts [see 40.0942]</li> </ul>
2	<ul style="list-style-type: none"> <li>◆ groundwater concentrations &gt; GW-2 standards</li> <li>◆ groundwater concentrations &gt; GW-3 standards</li> <li>◆ sites in GW -1 areas and C9-C10 or C11-C22 Aromatic fraction(s) in soil &gt; Method 1 stds</li> </ul>	<ul style="list-style-type: none"> <li>◇ can't use if sign. sediment contamination</li> <li>◇ can't use if sign. indoor air impacts [see 40.0942]</li> </ul>
3	<ul style="list-style-type: none"> <li>◆ complex/large sites</li> <li>◆ sites with indoor air impacts</li> <li>◆ sites with sediment contamination</li> <li>◆ sites with soil/gw &gt; Method 1 standards</li> </ul>	<ul style="list-style-type: none"> <li>◇ can't achieve permanent solution if: (1) more than 0.5 inches NAPL, or (2) above drinking water std in GW-1 area; or (3) soil conc above Upper Conc Limits (UCLs) unless deeper than 15' or below engineered barrier; or (4) gw conc &gt; UCL</li> </ul>

## 4.1 Exposure Point Concentrations

Regardless of the risk assessment method selected, it is necessary to calculate Exposure Point Concentrations in media and pathways of interest.

### 4.1.1 Groundwater EPCs

In accordance with the provisions of 310 CMR 40.0924(2)(a)(1.), when using a Method 1 or 2 Risk Characterization approach, EACH well and/or groundwater monitoring point is a separate Exposure Point, and data from each well is considered a separate Exposure Point Concentration. Accordingly, the (temporal) average concentration of dissolved analytes in EACH monitoring well cannot exceed appropriate GW -1, GW-2, and/or GW-3 standards (i.e., spatial averaging of data among wells is not permitted). More flexibility is allowed in a Method 3 risk assessment, with the exception of GW-1 areas [40.0924(2)(b)(2.)].

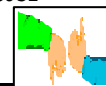
Because groundwater is a dynamic medium, a single “snapshot in time” is generally not sufficient to characterize contaminant levels, and calculate Exposure Point Calculations. ***Except for petroleum products with a low water soluble fraction, it is generally not possible to adequately characterize groundwater quality on the basis of a single round of sampling.*** Seasonal and antecedent precipitation events can significantly influence groundwater quality in any given well on any given day. Over the course of a year, temporal fluctuations in the concentration of dissolved analytes in monitoring wells can be substantial; variation by factors of 2-3 are common at most sites, and factors of up to 5-10 are possible, especially for water table wells, and when monitoring low levels of analytes (i.e., < 50 µg/L).

The amount of spatial and temporal monitoring data needed to make reasonable and meaningful conclusions on groundwater quality is necessarily a site-specific decision, based upon (1) the type/water-solubility of the petroleum product(s) released, (2) the homogeneity of the formation, (3) the sensitivity of potential pollutant receptors, (4) the magnitude of contaminant concentrations (with respect to the standard(s) of interest), and (5) the degree of confidence and understanding of the Conceptual Site Model.

Table 4-2 provides the minimum recommended number of rounds of groundwater sampling at petroleum-contaminated sites where NAPL is not present. A preferred approach is to obtain at least 4 measurements over a 1-year period, coinciding with seasonal variations. **In cases where less than 1 year of quarterly monitoring has been performed, it is necessary to consider and address expected variations in analyte concentrations over time (especially in cases where limited sample data is just below the applicable standard).**



**Table 4-2 Minimum Recommended Quarterly Rounds of Groundwater Monitoring at Sites Where NAPL is Not Present**



Location/GW Category	Gasoline/ JP-4	Diesel/#2-4 Fuel/Kerosene	Mineral/Lube/#6 Fuel Oil
< 800 feet from water supply	4+	3-4	2-3
GW -2	2-3	2	1
GW -3	1-2	1-2	1

It is important to stress that the recommendations provided above are for *quarterly* sampling efforts, with each quarter comprising a 3-month time period coinciding with spring, summer, fall, and/or winter conditions. Multiple sampling rounds in any given season, while providing potentially useful site data, cannot be considered equivalent to multiple samples over multiple seasonal conditions.

Beyond the general concerns and recommendations provided above for all sites, additional monitoring efforts are necessary at sites where groundwater remediation has been undertaken, to determine if contaminant “rebound” has occurred (i.e., a significant increase in dissolved groundwater contaminant concentrations that occurs as contaminants partition and diffuse from and near soil solids). In such cases, groundwater monitoring should be systematically conducted for at least 6 - 9 months after the termination of all remedial activities.

#### **4.1.2 Soil EPCs**

A general discussion of issues and recommendations for the development and calculation of soil Exposure Point Concentrations (EPCs) is contained in *Guidance for Disposal Site Risk Characterization in Support of the Massachusetts Contingency Plan*. Of particular interest at petroleum-contaminated sites is the evaluation of subsurface soil contamination associated with releases from Underground Storage Tanks (USTs). In this regard, when obtaining soil samples at an UST grave for the purposes of determining an EPC, it is necessary to specifically investigate whether a “hot spot” exists within the groundwater table fluctuation zone (i.e., the “smear zone”). For gasoline and fresh diesel/fuel oil releases, this action may be easily accomplished by headspace analysis of samples from sidewall excavations using a PID meter. In cases where headspace concentrations within this smear zone are equal to or greater than 10 times other locations on the sidewall, soil samples from this zone should be discretely collected/composited (either as the sidewall sample or with other sidewall samples) for appropriate analyses.

#### **4.1.3 Indoor Air EPCs**

Extensive guidance on this subject is provided in the *MADEP Indoor Air Sampling and Evaluation Guide*, available at <http://www.state.ma.us/dep/ors/files/indair.pdf>. When evaluating indoor air impacts at disposal sites, however, it is important to understand and differentiate sampling and evaluation objectives and requirements.

Specifically, when the objective is to calculate indoor air EPCs for the purpose of conducting a quantitative risk assessment, temporal and/or spatial averaging of data may be appropriate. Conversely, when the objective is to determine whether a Critical Exposure Pathway (CEP) is present at a home or school, averaging of this nature is NOT appropriate; rather, data from “worse case” site conditions are of interest. Additional discussions in this regard are provided in Section 4.3.

## **4.2 Method 1 Cleanup Standards**

Generic soil and groundwater cleanup standards have been developed by MADEP for the 3 hydrocarbon fractions detected using the VPH analytical procedure (i.e., C5-C8 Aliphatics, C9-C12 Aliphatics, and C9-C10 Aromatics) and the 3 hydrocarbon fractions detected using the EPH analytical procedure (i.e., C9-C18 Aliphatics, C19-C36 Aliphatics, and C11-C22 Aromatics). These standards are designed to be protective at most sites, and were developed using a series of conservative site scenarios to evaluate risks to human health, public welfare, and the environment via a number of exposure pathways and concerns, including direct contact, ingestion, leaching (soil), and volatilization (groundwater).

Method 1 cleanup standards have been developed for 3 categories of groundwater (see 310 CMR 40.0932):

- ◇ **GW-1 Standards** - applicable in (GW -1) areas where groundwater is or may be used for drinking water purposes. The GW -1 standards are based upon ingestion/use of groundwater as a potable water supply.
- ◇ **GW-2 Standards** - applicable in areas within 30 feet of an occupied structure if the depth to groundwater is less than 15 feet from the ground surface. GW -2 standards are based upon inhalation exposures that could occur to occupants of a building impacted by volatile compounds which partition from shallow groundwater.
- ◇ **GW-3 Standards** - applicable at all sites. GW -3 standards consider impacts to aquatic receptors in surface water bodies that receive recharge from a contaminated groundwater plume.

Based upon the above, it can be seen that any given disposal site may fall in one, two, or all three categories. At sites where more than one category applies, groundwater contaminants must be at or below all applicable GW standards in all applicable categories in order to demonstrate a condition of “No Significant Risk” per Method 1.

Method 1 cleanup standards have also been developed for 3 categories of soil (see 310 CMR 40.0933):

- ◇ **S-1 Standards** - applicable to soils that are accessible or potentially accessible, and where the frequency and/or intensity of exposure is high.
- ◇ **S-2 Standards** - applicable to less accessible soils, with lower exposure potential.
- ◇ **S-3 Standards** - applicable to isolated soils, and/or soils where the frequency and/or intensity of exposure is low.

Because all soil standards consider leaching impacts to underlying groundwater, and because there are 3 groundwater categories, there is a matrix of nine possible Method 1 soil standards for each contaminant (e.g., S-1/GW -1, S-1/GW -2, etc.). As with the GW standards, any given disposal site may fall in one or more of these nine soil standards. At sites where more than one category applies, soil contaminants must be at or below all applicable “S-x/GW-y” standards in all applicable categories in order to demonstrate a condition of “No Significant Risk” per Method 1.

In addition to the human health and environmental exposures described above, all Method 1 standards are bounded by certain *basement* and *ceiling* conditions established by MADEP. As a lower limit, no Method 1 standard is set below a background or analytical reporting limit, even if the risk-based concentration was less than this value. On the other extreme, no Method 1 standard is set above a series of “ceiling” concentrations established for classes of soil and groundwater contaminants. Ceiling levels were established to account for exposure pathways and factors that were not considered in developing these generic standards, including “public welfare” concerns related to odors. The ceiling level in groundwater is set at 50,000 µg/L; the ceiling levels in soil are 100, 500, 1000, 2500, and 5000 µg/g, depending upon the soil category (i.e., S-1, S-2, or S-3) and the vapor pressure and/or Odor Index of the compound or hydrocarbon range of interest. Additional information on ceiling levels and Method 1 standards are provided in the MADEP publication *Background Documentation for the Development of the MCP Numerical Standards*, April 1994, and as amended, which is available and may be downloaded from <http://www.state.ma.us/dep/ors/orspubs.htm>

#### **4.2.1 Using Method 1 VPH/EPH Fractional Standards**

Using Method 1 to characterize a petroleum release is a two step process:

- Step 1 - identify and evaluate individual Target Analytes of interest, to address specific hydrocarbon constituents of concern, including carcinogenic compounds; and
- Step 2 - identify and evaluate aliphatic/aromatic fractions of interest, to address the rest of the hydrocarbon mixture.

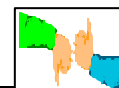
*Note: When using Method 1 fractional standards, it is necessary to have some actual (VPH/EPH) fractional range data. Although it is possible to make assumptions on the aliphatic/aromatic breakdown of TPH and GRO data, and demonstrate compliance with cleanup standards without any VPH/EPH data, such actions must be undertaken as part of a Method 3 Risk Characterization process. Alternatively, TPH data may continue to be compared directly to Method 1 TPH standards, at sites contaminated by heavier petroleum products.*

## 4.2.2 Target Analytes

Target Analytes are those constituents of petroleum which have traditionally been used to characterize environmental pollution, and for which MADEP has specific Method 1 cleanup standards: benzene, toluene, ethylbenzene, xylenes, MtBE, lead, Ethylene Dibromide, and the 17 “priority pollutant” PAHs. *By definition, Target Analytes are not counted within the VPH and EPH Aliphatic and Aromatic hydrocarbon fractions.*

It is not necessary to test all media and all petroleum releases for all Target Analytes; this decision is site-specific, based upon (1) the type (chemistry) of the petroleum product(s) released, (2) fate and transport considerations, and (3) the sensitivity of area receptors. Guidance and *Rules of Thumb* on the most commonly released petroleum products, based upon Total Organic Vapor (TOV) headspace screening and/or TPH data, are provided in Table 4-3.

**Table 4-3: Recommended Target Analyte List for Petroleum Products**



Petroleum Product	Media	Headspace TOV	TPH	Recommended Target Analytes
Gasoline	soil	-----	-----	benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene, and appropriate additives (e.g., MtBE, lead, and/or EDB).
	gw	-----	-----	benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene, and appropriate additives (e.g., MtBE, lead, and/or EDB).
#2 Fuel/Diesel	soil	≥100 ppmv	-----	benzene, toluene, ethylbenzene, xylenes, naphthalene
		-----	>500 µg/g	acenaphthene, naphthalene, 2-methylnaphthalene, phenanthrene
	gw	-----	-----	acenaphthene, naphthalene, 2-methylnaphthalene, phenanthrene; in GW -1, test also for BTEX, MtBE <sup>1</sup>
#3-#6 Fuel Jet Fuels	soil	≥100 ppmv	-----	benzene, toluene, ethylbenzene, xylenes, naphthalene
		-----	-----	17 priority pollutant PAHs, unless justification not to
Kerosene	gw	-----	-----	If in GW -1 area, test for BTEX and 17 priority pollutant PAHs
Lube Oils Hydraulic Oils		-----	-----	BTEX/VOCs, PAHs, PCBs, heavy metals
Waste Oils	soil	≥ 10 ppmv	-----	PAHs, PCBs, heavy metals
		-----	-----	BTEX/VOCs, PAHs, PCBs, heavy metals
	gw	-----	-----	BTEX/VOCs, PAHs, PCBs, heavy metals

<sup>1</sup>While MtBE is not an additive in fuel oils, it may become present during the transport and distribution process due to mixing of residue product

### 4.2.2.1 Petroleum Product Additives

The topic of petroleum product additives warrants special consideration with respect to the selection of Target Analytes.

Since 1923, organic, inorganic, and/or organo-metallic compounds have been added to petroleum products to enhance performance characteristics or address operational or air pollution concerns. While additives of this nature have been numerous – and often proprietary – the list of common additives with significant environmental concerns is relatively small. Details in this regard are presented in Table 4-4.

**Table 4-4: Common Gasoline Additives (Massachusetts)**

Additive	Purpose	Amount Added	Peak Years	Analytical Methods (soil/groundwater)
alkyl leads (tetraethyl lead; tetramethyl lead)	anti-knock/octane enhancer	1-2.5 grams/gal	1923-1981 (automotive gasoline)	Total Pb via ICP-AES (EPA 6010B) or AAS (EPA 7000); alkyl Pb by California LUFT/DHS or other proced.
		2-4 grams/gal	1920s-present (aviation gasoline)	
Ethylene Dibromide (EDB)	“scavenger” in leaded gasoline	variable	1923-1981 (cont use in aviation gasoline)	EPA Method 8260B or EPA Method 8021B
MtBE	octane enhancer	1-8% by volume	1979-1991	MADEP VPH; EPA Method 8260B <sup>a</sup>
	oxygenate	10-15 % by volume	1991-present	MADEP VPH; EPA Method 8260B <sup>a</sup>

<sup>a</sup> acidification of aqueous samples can lead to significant breakdown of MtBE

**4.2.2.2 Petroleum Product Additives as Target Analytes**

*Rules of Thumb* on the selection and analysis of specific petroleum product additives as Target Analytes are provided below:

- Given its history of use as an octane enhancer and oxygenate in New England, *MtBE* should always be considered a soil and groundwater Target Analyte of concern (all soil and groundwater categories) at disposal sites where a release of unleaded gasoline occurred or likely occurred after 1979.
- In addition to unleaded gasoline, *MtBE* should also be considered a groundwater Target Analyte of concern within the GW -1 areas of disposal sites where a release of #2 fuel/diesel oil occurred or likely occurred after 1979. Although not (purposely) added to these products, it is believed that trace levels of MtBE are introduced into stocks of #2 fuel/diesel oil during the storage and transportation process. Recent studies have identified the presence of low to moderate concentrations of MtBE within the groundwater at sites contaminated (solely) by a release of #2 fuel/diesel oil.
- Lead* and *Ethylene Dibromide* should be considered groundwater Target Analytes of concern within the GW -1 areas of disposal sites where a release of gasoline occurred or likely occurred prior to 1988. In addition, *Lead* should be considered a soil Target Analyte of concern within the S-1 areas of disposal sites where a release of leaded gasoline occurred or likely occurred prior to 1988. Because alkyl lead complexes are expected to break down into inorganic salts within a 15-year timeframe, use of a “total lead” methodology (e.g., AA/ ICP) is generally appropriate and sufficient in such cases.
- Lead* and *Ethylene Dibromide* should be considered soil and groundwater Target Analytes of concern (all soil/groundwater categories) at disposal sites where a release of leaded gasoline occurred or likely occurred after 1987. Due to their toxicities, it may be necessary to use analytical methods capable of detecting and quantitating the specific alkyl lead compounds of concern (e.g., tetraethyl lead). Although there are few published methods for alkyl lead analysis, one procedure is provided in the California LUFT Manual (<http://www.swrcb.ca.gov/general/publications/docs/luft-manual-1989.pdf>)

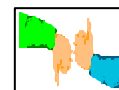


A summary of the above recommendations is provided in Table 4-5.

**4.2.2.3 Ethanol**

Because of its persistence and mobility in the environment, which has lead to wide-scale groundwater contamination, the use of MtBE as a gasoline additive will likely be reduced or eliminated in the coming years. The most likely replacement for MtBE is ethanol, which is already a widely used oxygenate in

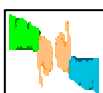
**Table 4-5: Recommended Target Analyte List for Petroleum Additives**



Petroleum Product Released at Site	Date of Release	Recommended Target Analyte(s)	Soil Category			Groundwater Category		
			S-1	S-2	S-3	GW-1	GW-2	GW-3
Unleaded Gasoline	≥1979	MtBE	✓	✓	✓	✓	✓	✓
#2 Fuel/Diesel Oil	≥1979	MtBE <sup>1</sup>				✓		
Leaded Gasoline	≤1987	Total Lead	✓			✓		
		EDB				✓		
Leaded Gasoline	>1987	Lead/alkyl leads	✓	✓	✓	✓		✓
		EDB	✓	✓	✓	✓	✓	✓

<sup>1</sup>While MtBE is not an additive in fuel oils, it may become present during the transport and distribution process due to mixing of residue product

certain parts of the United States, and, in fact, has already been identified at some gasoline release sites in Massachusetts. To date, MADEP has not established a Method 1 standard for ethanol, though it is considered a “hazardous material” under the MCP (see 310 CMR 40.1600). Until such time as the use of ethanol becomes more widespread in Massachusetts, it is not necessary to routinely test for this additive at disposal sites, except as noted below:



- In cases where ethanol is *known* to have been present in gasoline released at a disposal site (e.g., based upon information provided by a service station owner), sampling and analysis for ethanol should be *considered*, based upon the nature of site conditions and sensitivity of surrounding receptors;
- In cases where a release of gasoline has contaminated a drinking water supply, and where ethanol is *known* or *suspected* to be present in the gasoline released at the site (e.g., lack of MtBE contamination), a sample of the drinking water should be analyzed for ethanol.

Note that while ethanol is believed to be less toxic than MtBE, and, unlike MtBE, readily biodegradable under both aerobic and anaerobic conditions, elevated concentrations in the environment may result in certain adverse impacts:

- Due to cosolvency effects, the presence of high concentrations of ethanol may lead to increased levels of gasoline constituents in groundwater, including the Target Analytes benzene, toluene, ethylbenzene, and xylenes (BTEX).
- Because of its highly biodegradable nature, ethanol exerts a high biochemical oxygen demand that can quickly deplete oxygen (and nutrient) levels in the area of contamination, which may lead to longer plumes of BTEX and other dissolved gasoline hydrocarbons. This phenomenon has implications to natural attenuation considerations, and bearing on the design of enhanced and engineered bioremediation systems at such sites.

#### 4.2.2.4 Additional Petroleum Additives

In general, beyond the recommendations contained above, it is not necessary to routinely test for additional petroleum product additives at disposal sites. At disposal sites where releases of gasoline or diesel fuel have impacted drinking water supplies, however, samples of the impacted drinking water should be analyzed (a) by EPA Method 8260B for all method analytes and for Tentatively Identified Compounds (TICs), and (b) for the metals listed in Method EPA 6010B, excluding the common “background” elements calcium, iron, manganese, and sodium. Such an action is appropriate given (i) the wide variety of chemical additives in

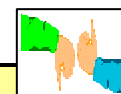
petroleum products, (ii) the relative mobility of volatile organic compounds and certain metal salts and complexes, and (iii) the sensitivity of the exposure pathway.

### 4.2.3 Hydrocarbon Fractions of Interest

It is not necessary to test all media and all petroleum releases for all 6 VPH/EPH hydrocarbon fractions; this decision is also site-specific, based upon (1) the type (chemistry) of the petroleum product(s) released, (2) fate and transport considerations, and (3) the sensitivity of area receptors. Guidance and *Rules of Thumb* on ranges of interest, as determined by either the VPH or EPH test method, are provided in Table 4-6 for the most commonly released petroleum products.

*When using a Method 1 approach, each VPH/EPH fraction is treated as if it were a single entity or unique chemical. The general rules that apply to Method 1 Risk Characterization, such as averaging data and hot spot determinations, also apply to these aliphatic and aromatic fractions.*

**Table 4-6: Hydrocarbon Fractions of Interest**



Petro Product	Media	VPH	EPH	Comments/Caveats
Gasoline	soil	✓		
	gw	✓		
Fresh	soil	✓	✓	“Fresh” is defined as soil/gw with TOV headspace $\geq$ 100 ppmv
Diesel/#2 Fuel	gw	✓	✓	
Weathered	soil		✓	“Weathered” defined as soil/gw with TOV headspace $<$ 100 ppmv
	gw		✓	VPH testing recommended if potentially/impacting a water supply
#3-#6 Fuel Oil	soil		✓	
Hydraulic Oil	gw		✓	VPH testing recommended if potentially/impacting a water supply
Mineral/Di-electric Fluids	soil		✓	
	gw		✓	VPH testing recommended if potentially/impacting a water supply
Jet Fuel JP-4	soil	✓	✓	May eliminate/reduce VPH testing if TOV headspace $<$ 100 ppmv
	JP-8	gw	✓	✓
Jet Fuel Jet A / Kerosene	soil		✓	
	gw		✓	VPH testing recommended if potentially/impacting a water supply
Waste	soil	✓	✓	May eliminate/reduce VPH testing if TOV headspace $<$ 10 ppmv
	Crankcase Oil	gw	✓	✓
Unknown Oils	soil	✓	✓	May eliminate/reduce VPH testing if TOV headspace $<$ 10 ppmv
	gw	✓	✓	

For samples analyzed by both the VPH and EPH test procedure, there are two methodological issues that warrant discussion and clarification:

- ◇ When a (split) sample is analyzed by both the VPH and EPH methods, it is not necessary to quantitate or address a (VPH) value for C9-C12 Aliphatic Hydrocarbons, as these hydrocarbons are included within the C9-C18 Aliphatic Hydrocarbon range detected by the EPH test method. Note that there may be cases where the C9-C12 Aliphatic concentration via the VPH test method exceeds the C9-C18 Aliphatic concentration quantitated by the EPH method – this dichotomy occurs because the VPH method tends to over-quantitate aliphatics in this range (because the FID is also quantitating aromatic compounds). In general, the EPH method should provide more accurate data for this range.

- ◇ In cases where Target Analytes are quantitated by both the VPH and EPH methods, naphthalene will be reported by both procedures. Because it is within the dividing region between purgeable and extractable organics, naphthalene is a problem analyte in both methods: it's the heaviest VPH compound, and difficult to purge, while at the same time being the lightest EPH compound, and therefore subject to volatilization losses during the EPH extraction process. *Accordingly, in such cases, the highest reported value should be used.*

#### **4.2.4 Limitations on the Use of Method 1 Cleanup Standards**

Because of the generic assumptions used in the development of the Method 1 standards, they are not appropriate, and cannot be (solely) used at all sites. The most significant limitations in this regard for VPH/EPH standards are:

- ◆ there must be a Method 1 standard for all Contaminants of Concern (including any non-petroleum contaminants); and
- ◆ the contamination must be limited to just soil and groundwater, and cannot be present in sediments, air, or surface water.

##### **4.2.4.1 Hydrocarbons**

With respect to Contaminants of Concern, if only petroleum products are present at a site, there should be no limitations on the use of the Method 1 standards, as the collective VPH and EPH fractional ranges should address all detected constituents. Note that these collective range standards eliminate problems that arose in the past when laboratories using a GC/MS technique would report petroleum constituents, such as trimethylbenzenes, which did not have a Method 1 Standard - and which therefore called into question the applicability of Method 1. It also follows that this practice of identifying additional petroleum (non-target) analytes is no longer necessary, as long as the compound in question is a petroleum constituent that is collectively quantitated in a hydrocarbon range of interest (e.g., the trimethylbenzenes are picked up in the C9-C10 Aromatic Hydrocarbon range detected by the VPH test method).

##### **4.2.4.2 Additives**

At present, Method 1 standards exist only for lead and MtBE. If other additives are identified at a disposal site, it will be necessary to evaluate risks using a Method 2 or Method 3 risk assessment process.

##### **4.2.4.3 Air-Phase Contamination**

With respect to contamination present in a medium other than soil or groundwater, the most common and problematic limitation occurs when hydrocarbon contaminants are present in the ambient or indoor air at a site. Since this exposure was NOT considered in the development of the Method 1 cleanup standards, a Method 3 assessment must be conducted in such cases.

Volatile non-aqueous phase liquids (NAPL), including separate-phase gasoline, kerosene, jet fuels, and fresh diesel/#2 fuel oils, can result in the generation of significant concentrations of volatile petroleum hydrocarbon vapors in the vadose zone, which can potentially impact the indoor air of nearby structures. Purging a monitoring well containing such NAPL prior to obtaining a groundwater sample may underestimate risks of this nature, as the groundwater sample may contain relatively low concentrations of dissolved hydrocarbons. *For this reason, soil gas investigations should be considered at any site at which volatile NAPL has been identified in monitoring wells or test pits, to characterize the risks posed to indoor air quality, and determine whether use of a Method 1 approach is appropriate.*

#### **4.2.5 Odors**

Odors are an indication that hydrocarbon compounds are present in another medium (air) beyond soil or groundwater (although a lack of odors does not mean that hydrocarbon compounds are not present). Such odors could constitute a significant risk to human health, and/or a nuisance condition that may be considered a significant risk to public welfare.



For this reason, Method 1 cleanup standards should not be used at sites with the following odor conditions:

- ◇ persistent, long term (>3 months) odors in the ambient air at a disposal site; or
- ◇ persistent, long term (>3 months) odors in the indoor air of a building impacted by a disposal site.

***Short term, ephemeral odors, and/or odors noted at depth during subsurface excavation or exploration, would not, by themselves, invalidate the use of a Method 1 approach.***

A tabulation of Method 1 Cleanup Standards for the VPH/EPH hydrocarbon fractions, and TPH, is provided in Appendix 4. Note that these values are current as of the date of this publication, but are subject to change. For a current list of cleanup standards (and Reportable Concentrations), consult the most current version of the Massachusetts Contingency Plan.

### 4.3 Method 2 Risk Characterization

Using Method 2, site-specific fate and transport factors and considerations may be used to modify certain Method 1 standards. The Method 1 standards that are most likely to be exceeded at petroleum contaminated sites, and for which a Method 2 approach may be advisable, are listed in Table 4-7.

**Table 4-7: Method 1 Standards Most Likely to be Exceeded**

Contaminant	Groundwater		Soil (standards based upon leaching)		
	GW-2 (µg/L)	GW-3 (µg/L)	S-1/GW-1 (µg/g)	S-2/GW-1 (µg/g)	S-3/GW-1 (µg/g)
C5-C8 Aliphatics (VPH)	✓	✓			
C9-C12 Aliphatics (VPH)	✓				
C9-C10 Aromatics (VPH)	✓	✓	✓	✓	✓
C9-C18 Aliphatics (EPH)	✓				
C11-C22 Aromatics (EPH)		✓	✓	✓	✓
benzene			✓	✓	✓
2-Methylnaphthalene			✓	✓	✓
naphthalene			✓	✓	✓

A summary of recommended Method 2 assessment approaches and limitations is provided in Table 4-8.

**Table 4-8: Use of Method 2 at Petroleum-Contaminated Sites**

Site Condition	Method 2 Assessment Actions	Limitations
groundwater concentration > GW -2 Std	Evaluate potential for dissolved hydrocarbons in groundwater to impact indoor air of adjacent structures	Assessment limited to demonstration of “no impacts” to structure, based upon actual field data
groundwater concentration > GW -3 Std	Evaluate potential for dissolved hydrocarbons in groundwater to impact receiving surface water body	Cannot modify to exceed an Upper Concentration Limit or have $\geq 0.5$ inches NAPL
soil concentration > Soil Standard	Evaluate potential for hydrocarbons to leach from soil and impact underlying groundwater	Cannot modify to exceed an appropriate “direct contact” soil-exposure concentration [40.0985(6)]

Two important limitations to a Method 2 approach at petroleum-contaminated sites warrant additional emphasis:

- \* Method 2 may **NOT** be used to modify an applicable Method 1 GW -1 standard, including the VPH/EPH fractional standards; and

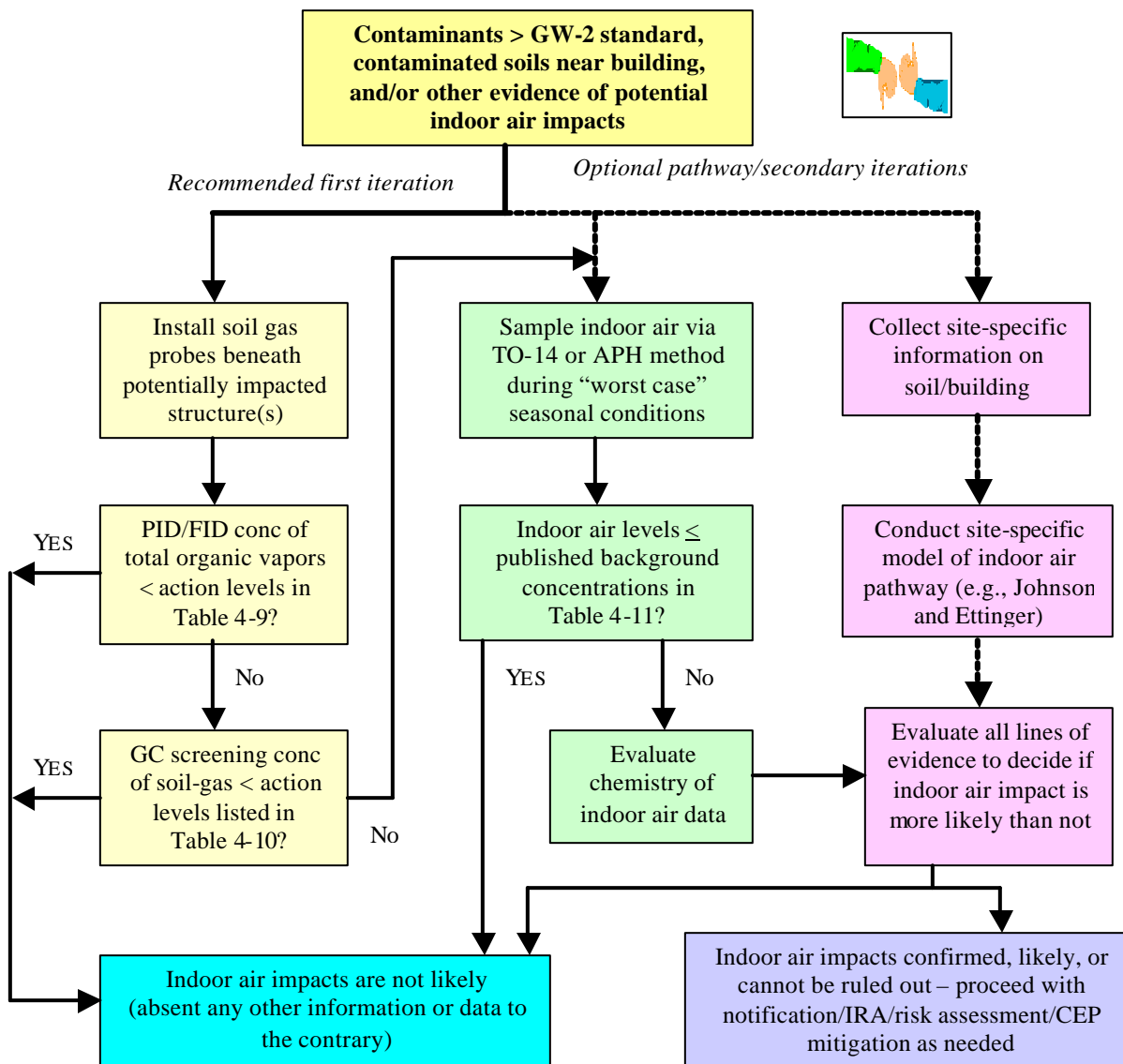


- \* Fate and transport models may **NOT** be (solely) used to evaluate or “rule out” an impact to indoor air from dissolved concentrations of the VPH/EPH fractions in groundwater. This prohibition is due to the fact that the GW - 2 standards for the VPH/EPH fractions were not directly calculated from a modeling exercise, because of a lack of relevant fate/transport and toxicological information. Thus, because there are no generic modeling assumptions for these fractions, there are no direct site-specific modeling modifications possible via a Method 2 approach.

### 4.3.1 Using a Method 2 Approach to Demonstrate “No Impact” to Indoor Air

At sites where a Method 1 GW -2 standard is exceeded for a VPH/EPH fraction and/or Target Analyte, a multi-level, progressively structured investigatory program is recommended, to obtain sufficient information and data to determine whether an impact to indoor air has occurred or is likely to occur. This same approach may be used to investigate concerns over the presence of contaminated soils in close proximity to a building. At some sites, conclusions in this regard are relatively clear; at others, a “tool-box” approach may be needed to establish lines of evidence to make such a determination. In most cases, an optimal and cost-effective tool-box approach is to proceed along a continuum of low-cost/conservative-efforts toward higher-cost/more-accurate-techniques, using the cumulative totality of information to rule out impacts as “unlikely”, or, when such a decision cannot be supported, arrive at a conclusion that such impacts are in fact likely. This process is illustrated in Figure 4-1.

**Figure 4-1: Evaluating Indoor Air Pathway via Method 2**



Initially, a relatively inexpensive soil gas screening effort is recommended, utilizing a series of conservative assumptions, in an attempt to rule out exposure/pathway concerns. Sites not screened out at this stage should consider increasingly more sophisticated and invasive actions, up to and including sampling and analysis of indoor air. Step-by-step recommendations are provided below. Additional guidance may be obtained from the *MADEP Indoor Air Sampling and Evaluation Guide*.

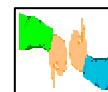
#### 4.3.1.1 Level 1 - Soil Gas Screening

- a) Install at least one or two soil gas sampling probes beneath the structure of concern (e.g., through the concrete slab of a basement floor). For larger structures, additional probes may be needed. If probes cannot be installed within the footprint of the structure, install soil gas sampling probes along the perimeter of the building, as close as possible to the structure. Locations beneath pavement or other impervious surfaces are preferred to obtain representative conditions.

**Soil gas probes located in unpaved areas and/or other areas where rain/snowmelt/surface water infiltration is occurring may not yield representative data. Data from such locations may be biased low, due to displacement and/or solubilization of soil gas vapors during an infiltrative event.**

- b) Install and sample probes placed within the footprint of the structure in a manner that enables the collection of a soil gas sample from just beneath the lowest (floor/slab) elevation. Probes outside of the footprint of the building should be installed and sampled in a manner that enables the collection of a soil gas sample from a point just below the lowest (floor/slab) elevation.
- c) Withdraw a sample of soil gas from each probe, for analysis by a Photoionization Detector (PID) and/or Flame Ionization Detector (FID) meter. The PID should be calibrated to an isobutylene response, the FID to a methane response. Continuous, real-time measurements may be made, or a sample can be pumped to a Tedlar (or equivalent) bag for subsequent PID/FID analyses. Unless a demonstration is made that the sampling technique and equipment is capable of delivering a soil gas sample to the PID/FID meter at an adequate pressure and flow rate, use of the bag technique is recommended. Additional guidance is provided in MADEP's *Policy for the Investigation, Assessment, and Remediation of Petroleum Releases*, April, 1991 (DEP Publication #WSC-401-91), available at <http://www.state.ma.us/dep/bwsc/finalpol.htm>
- D) Compare the readings obtained on the PID and/or FID meters with the screening values in Table 4-9.

**Table 4-9: Soil Gas PID/FID Screening Levels for Evaluating Indoor Air Impacts**



Hydrocarbon Fraction(s) and Target Analytes which exceed applicable Method 1 GW-2 Standards and/or are present in proximate soils	Indoor air impacts unlikely if below listed value for each hydrocarbon fraction & Target Analyte of interest			
	PID ppmV (Isobutylene response)			FID ppmV (methane response)
	< 10.1 eV	10.1 – 11.4 eV	>11.4 eV	
C5-C8 Aliphatic Hydrocarbons	N/A	7	29	25
C9-C12 Aliphatic Hydrocarbons	3	7	33	19
C9-C10 Aromatic Hydrocarbons	28	29	37	21
C9-C18 Aliphatic Hydrocarbons	3	7	33	19
Toluene	11	12	12	10
Ethylbenzene	4	4	4	3
Total Xylenes	25	26	24	22

- On the left side of the table, identify EACH hydrocarbon fraction(s) and/or Target Analyte(s) which exceed an applicable GW-2 groundwater standard and/or are otherwise of concern.
- If a Photoionization Detector (PID) unit was used to analyze the soil gas, identify the energy level of the (UV) lamp in electron-volts (eV). Identify the ppmV reading listed in the appropriate column, and compare this value to the site value for EACH hydrocarbon range and/or analyte of interest. If EACH site value is less than the listed value for the hydrocarbon range(s) and Target Analyte(s) of interest, impacts to indoor air are not likely.
 

*Example: BTEX and aliphatic/aromatic fractions present at site, but GW-2 standards exceeded for only Toluene and C9-C10 Aromatic Hydrocarbons. Soil gas below structure is found to have 25 ppmV (isobutylene calibration) total VOCs via a 10.6 eV PID unit. While this PID reading indicates impacts from C9-C10 Aromatic Hydrocarbons are unlikely (since < 29 ppmV), this data cannot rule out impacts by Toluene (since 25 ppmV > 12 ppmV).*
- If a Flame Ionization Detector (FID) unit was used to sample the soil gas, compare the site value to the value listed in the table. If the site value is less than the listed value for each hydrocarbon range and/or Target Analyte of interest, impacts to indoor air are not likely.
- In situations where soil gas data are available from both a PID and FID, the FID data should be the basis of this evaluation.
- In situations where soil gas data are available from PID units with different lamp (eV) intensities, the data from the highest intensity lamp should be the basis of this evaluation.

The values provided in Table 4-9 are based upon conservative assumptions on (a) likely partitioning and dilution and attenuation factors for the identified hydrocarbon compounds and ranges, (b) response characteristics of commonly available PID and FID units; and (c) empirical observations, experience, and professional judgment. Because of its toxicity and low rate of anaerobic biodegradation, screening values have not been provided for benzene. This table should not be used to rule out impacts for non-listed contaminants, or to rule out impacts at structures with earthen floors, standing water, or open floor sumps.

#### 4.3.1.2 Level 2 - Soil Gas Analysis

If indoor air impacts cannot be ruled out by PID/FID screening, more sophisticated testing is recommended for a soil gas sample obtained in accordance with the recommendations provided in Section 4.3.1.1. Recommendations in this regard follow:

##### GC SCREENING

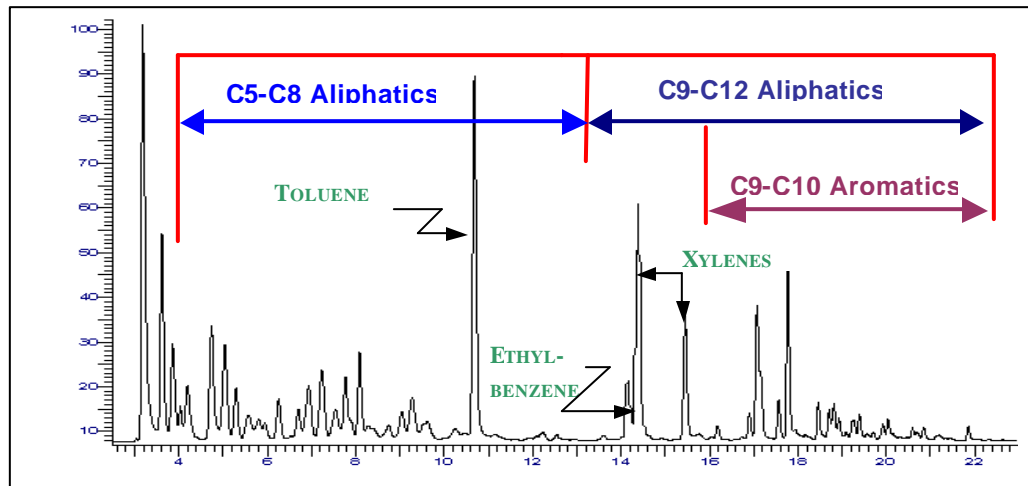
Soil gas samples obtained in a bag, canister, or directly into a gas-tight syringe are analyzed using a GC equipped with a flame ionization detector (FID). In cases where only aromatic contaminants are of interest (i.e., G<sub>9</sub>-C<sub>10</sub> Aromatic Hydrocarbons, toluene, ethylbenzene, and/or xylenes), a GC/PID may be used in lieu of a GC/FID. Even where only aliphatic hydrocarbons are of interest, the use of a PID in series with an FID will lead to more accurate and less conservative data.

A GC/FID sample chromatogram of a fresh gasoline sample is presented in Figure 4-2.

Under this approach, a series of assumptions are used to estimate the concentration of the hydrocarbon range(s) of interest; the more sophistication employed in this effort (i.e., use of GC/PID/FID), the less conservative the assumptions:

*C5-C8 Aliphatic Hydrocarbons:* On a GC/FID, quantitate all peak elutions between n-pentane and just before n-nonane using a response factor from one or several of the normal alkanes which elute in this range (e.g., n-heptane, n-octane).

**Figure 4-2: GC/FID Soil Gas Chromatogram**

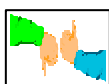


Conservatively assume that this entire concentration value is C5-C8 Aliphatic Hydrocarbons (even though MtBE and some or all of the BTEX compounds also elute in this range). Compare this value (in  $\mu\text{g}/\text{m}^3$ ) with the value listed in Table 4-10. If less than the listed value, measurable indoor air impacts are not likely. If more than this value, consider use of a GC/PID to quantitate MtBE, benzene, toluene, ethylbenzene, xylenes (BTEX), and naphthalene, and “adjust” the C5-C8 Aliphatic Hydrocarbon value previously obtained by subtracting out the GC/PID  $\mu\text{g}/\text{m}^3$  concentrations of compounds eluting within this range. If this adjusted C5-C8 Aliphatic Hydrocarbon value is less than the value listed in Table 4-10, measurable indoor air impacts are not likely. If more than this value, a Level 3 evaluation may be necessary.

**C9-C12 Aliphatic Hydrocarbons:** On a GC/FID, quantitate all peak elutions between n-nonane and just before naphthalene using response factors from one or several of the normal alkanes which elute in this range (e.g., n-nonane, n-decane). Conservatively assume that this entire concentration value is C9-C12 Aliphatic Hydrocarbons (even though some aromatic compounds are also likely eluting in this range). Compare this value (in  $\mu\text{g}/\text{m}^3$ ) with the value listed in Table 4-10. If less than the listed value, measurable indoor air impacts are not likely. If more than this value, consider use of a GC/PID to quantitate BTEX, naphthalene, and C9-C10 Aromatic Hydrocarbon, and “adjust” the C9-C12 Aliphatic Hydrocarbon value previously obtained by appropriate subtraction from the Aliphatic range. If this adjusted C9-C12 Aliphatic Hydrocarbon value is less than the value listed in Table 4-10, measurable indoor air impacts are not likely. If more than this value, a Level 3 evaluation may be necessary.

**C9-C10 Aromatic Hydrocarbons:** On a GC/FID, quantitate all peak elutions just after the last xylene peak and just before naphthalene using the response factor for 1,2,4-Trimethylbenzene. Conservatively assume that this entire concentration value is C9-C10 Aromatic Hydrocarbons (even though some aliphatic compounds are also likely eluting in this range). Compare this value (in  $\mu\text{g}/\text{m}^3$ ) with the value listed in Table 4-10. If less than the listed value, measurable indoor air impacts are not likely. If more than this value, consider use of a GC/PID to quantitate this range in the same manner. If this GC/PID range concentration is less than the value listed in Table 4-10, measurable indoor air impacts are not likely. If more than this value, a Level 3 evaluation may be necessary.

**Toluene, Ethylbenzene, Total Xylenes:** On a GC/PID or GC/FID, identify and quantitate Target Analyte peak via retention times and response factors/curves established for each analyte. Compare these values ( $\mu\text{g}/\text{m}^3$ ) with the values listed in Table 4-10. If all data are less than the listed values, measurable indoor air impacts are not likely. If one or more of the analytes are above their respective values, a Level 3 evaluation may be necessary.



*NOTE: When using a “field” GC screening technique, all appropriate and necessary quality assurance/quality control procedures must be employed. At a minimum, the following steps would generally be expected:*

- Calibration of the GC system at a minimum of 3 concentration levels, using gaseous-phase calibration standards; and
- Daily analysis of a blank sample and mid-range calibration or QC check standard, to ensure and document system performance.

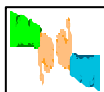
## LABORATORY PROCEDURES

Soil gas samples obtained in a bag, canister, or directly into a gas-tight syringe are analyzed using a VPH procedure (modified by changing sample introduction from purge and trap to direct injection/desorption) or by the APH methodology.

Using either the “screening” or laboratory procedure, the concentration of each fraction (in  $\mu\text{g}/\text{m}^3$ ) should be compared to the soil gas action level indicated in Table 4-10. **NOTE: THESE VALUES MAY NOT BE PROTECTIVE AT BUILDINGS WITH EARTHEN FLOORS OR STANDING GROUNDWATER WITHIN A BASEMENT OR CRAWL SPACE AREA.**

**Table 4-10: Soil Gas GC Screening Levels for Evaluating Indoor Air Impacts**

<b>Fraction/Analyte</b>	<b>Measurable Indoor Air Impacts Not Likely if Below (<math>\text{mg}/\text{m}^3</math>)</b>
C5-C8 Aliphatic Hydrocarbons	111,000
C9-C12 Aliphatic Hydrocarbons	117,000
C9-C10 Aromatic Hydrocarbons	104,000
C9-C18 Aliphatic Hydrocarbons	130,000
Toluene	36,000
Ethylbenzene	13,000
Total Xylenes	94,000



As an alternative to the active soil-gas sampling procedures detailed above, the use of passive/diffusion samplers may also be an appropriate technique to characterize and quantitate hydrocarbon vapors beneath and proximate to structures of concern.

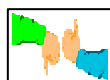
### 4.3.1.3 Level 3 - Indoor Air Analysis

If soil gas analysis cannot rule out an indoor air impact, direct measurement of indoor air is usually necessary. At least one (2-4 hour) time-weighted sample should be obtained from the lowest occupied level of the structure and analyzed using EPA Method TO-14A/15 or the MADEP Air-Phase Petroleum Hydrocarbon (APH) methodology. (While TO-14A/15 may be used to determine if a pathway is present, the APH method is recommended to evaluate risks from such a pathway). Additional (2-4 hour) time-weighted samples on other levels of the structure could be helpful in evaluating the likelihood of a subsurface vapor infiltration pathway in the event that elevated concentrations of contaminants are identified in the lowest level (e.g., higher concentrations in upper levels could be a potential line of evidence contrary to a subsurface infiltration pathway).

Sampling during Winter or early Spring is usually considered a “worst case” evaluation, due to (a) depressurization of the structure that occurs due to the operation of combustion furnaces and chimney stack effects, (b) lack of building ventilation, (c) presence of frost layer impeding diffusion to the atmosphere, and/or (d) presence of a high groundwater table (Spring). At structures with a central air-conditioning system that obtains make-up air from a basement, worst-case conditions may be during summer months. **Sampling during times of the year that are not considered worst case may not conclusively rule out indoor air impacts.**

Concentrations of hydrocarbon fractions and Target Analytes obtained by this analysis should be evaluated to determine if they are in excess of a “background” condition for that structure. In lieu of determining a site-specific background concentration, the generic values presented in Table 4-11 may be used.

**Table 4-11: Estimated Background Indoor Air Concentrations**



Fraction/Analyte	Estimated Generic Background	
	mg/m <sup>3</sup>	ppbV
C5-C8 Aliphatic Hydrocarbons	85	N/A
C9-C12 Aliphatic Hydrocarbons	90	N/A
C9-C10 Aromatic Hydrocarbons	80	N/A
C9-C18 Aliphatic Hydrocarbons	100	N/A
Benzene	21	6.5
Toluene	29	7.5
Ethylbenzene	10	2.2
Total Xylenes	72	17
Naphthalene	5	1
MtBE	3-18*	1-5*

*\* concentration of MtBE in ambient air; may be higher in immediate vicinity of gasoline filling stations or if gasoline storage in building (e.g., lawnmower)*

#### 4.3.1.4 Use of Vapor Transport Models

On occasion, it may be necessary or desirable to use predictive/computer models to help evaluate vapor transport issues at disposal sites. This option is most necessary when it is not possible or feasible to obtain soil gas and/or indoor air measurements, or when such data are ambiguous. While use of these techniques can aid in the understanding of the Conceptual Site Model, and facilitate characterization of current and future exposure pathways, **it is MADEP’s longstanding position that current exposure pathways should be evaluated/validated with actual site data, to the extent feasible.**

Accordingly, unless precluded by unavoidable logistical constraints and/or “background” interference (e.g., toluene migration into a commercial/industrial site where toluene is used as a raw product), *there is an expectation that (some) actual soil gas and/or indoor air data will be generated during the evaluation of sites with an exceedance of GW-2 standards.* Sufficient explanation and justification must be provided in the appropriate report submittals for sites where such data are not obtained.

Most mathematical evaluations of this vapor transport pathway involve use of the Johnson & Ettinger model. Spreadsheet applications of the model are available for downloading free of charge from MADEP at <http://www.state.ma.us/dep/bwsc/files/standard/GW2/GW2.htm> and from the US Environmental Protection Agency at [http://www.epa.gov/superfund/programs/risk/airmodel/johnson\\_ettinger.htm](http://www.epa.gov/superfund/programs/risk/airmodel/johnson_ettinger.htm).

When using models of this nature, all input parameters and values have to be individually justified as appropriate and/or conservative for the specific site in question; it is not permissible to “pick and chose” generic modeling default values absent such justification. A particularly sensitive modeling parameter in this regard is the vadose zone moisture content **below the structure of concern**, which should be empirically determined on a site-specific basis.

#### **4.3.1.5 Vertical Profiling of Groundwater Contaminants to Evaluate Vapor Transport**

In cases where soil gas and/or indoor air data are ambiguous, vertical profiling of groundwater contaminants may provide useful lines of evidence in the evaluation of vapor transport pathways.

Typically, groundwater plumes “dip” as they flow from a source area, due to the infiltration of rainfall and snowmelt. This recharge can result in the formation of a “fresh water lens” above a plume of dissolved contaminants. In such situations, contaminants must diffuse through the (uncontaminated) lens in order to reach the groundwater table/capillary fringe, and partition from the aqueous phase into the gaseous phase. Because of the slow rate of liquid-phase diffusion, the formation of such a fresh water lens can effectively eliminate the vapor transport pathway, by preventing dissolved contaminants from partitioning into the overlying vadose zone.

Predicting the exact point in the path of a plume where vapor generation is “cut off” in this manner is difficult, if not impossible, due to the transient and dynamic nature of the governing parameters. Moreover, plumes that dip will eventually reverse direction and rise toward a groundwater discharge point, where contaminants may again be flowing in close proximity to the groundwater table and aqueous/vapor interface.

Despite these difficulties and unknowns, it may be useful at some sites to profile groundwater contaminant concentrations in the first 5-10 foot interval of the saturated zone, to determine whether a freshwater lens is present at the site in question. Typically, this action is accomplished by advancement of small diameter driven well points, obtaining groundwater samples at 1 to 2 foot depth intervals, for analysis by GC screening or laboratory techniques. Such data, in conjunction with soil gas data and/or other site factors, may provide the necessary weight of evidence to adequately evaluate and/or eliminate this pathway.

#### **4.3.1.6 Response Actions at Sites with Indoor Air Impacts**

Evidence of the migration of petroleum vapors from the subsurface into a school building or occupied residential dwelling (above a background condition) represents a Critical Exposure Pathway and Condition of Substantial Release Migration under the Massachusetts Contingency Plan. In such cases, pursuant to the provisions of 310 CMR 40.0414, an Immediate Response Action must be undertaken to evaluate the risks associated with this infiltration, and determine if there is a feasible remedial measure to prevent or mitigate this continued infiltration. *If feasible mitigative options exist, remedial actions must be taken.*

When considering and implementing mitigative options, a hierarchy of remedial efforts is recommended, from least-invasive/least-costly to most-invasive/most-costly. Details are provided in Figure 4.3.

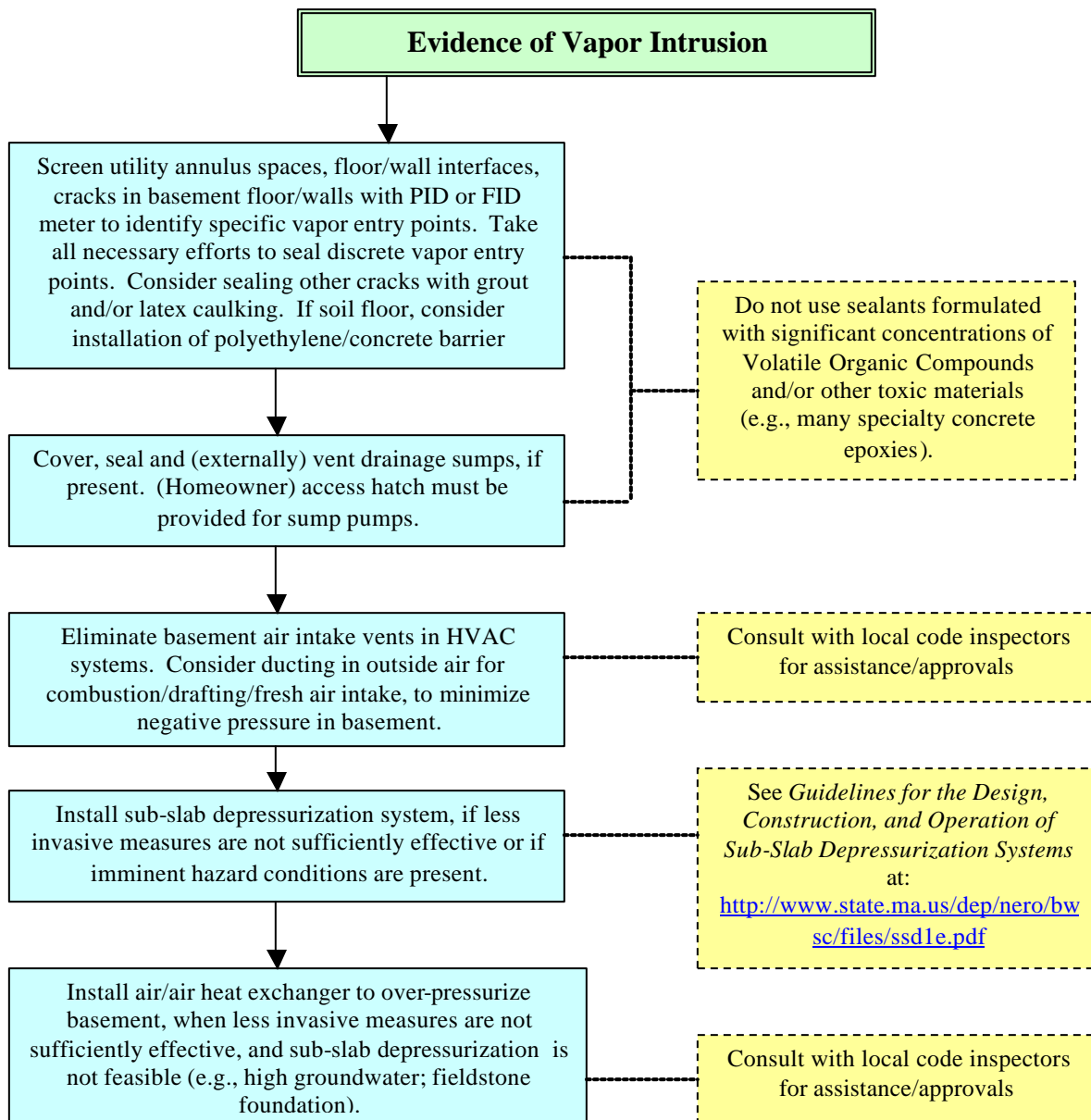
#### **4.3.2 Using a Method 2 Approach to Evaluate Exceedances of Method 1 GW-3 Standards**

The Method 1 GW -3 standard most likely to be exceeded at a petroleum-contaminated site is for C9-C10 Aromatic Hydrocarbons. This standard and all Method 1 GW -3 standards were derived based upon an assumption that (a) impacts may occur to ecological receptors in a surface water body at concentrations equal to or greater than the ambient water quality guideline, (b) groundwater from the site is discharging to such a surface water body, and (c) dilution between the groundwater and surface water body is minimal. A summary and description of currently recommended fractional ambient water quality guidelines is provided in Table 4-12.

Using a Method 2 approach, site-specific data, fate and transport factors, and/or predictive models may be used to modify Method 1 GW -3 standards. Recommended fractional fate and transport parameters are provided in Section 4.6. *Note that per 310 CMR 40.0982(4), a Method 1 GW-3 standard cannot be modified to a concentration in excess of the Upper Concentration Limit for the fraction of interest.*



**Figure 4-3: Recommended Hierarchy of Vapor Mitigation Efforts**



**Table 4-12: Recommended Surface Water Quality Guidelines**

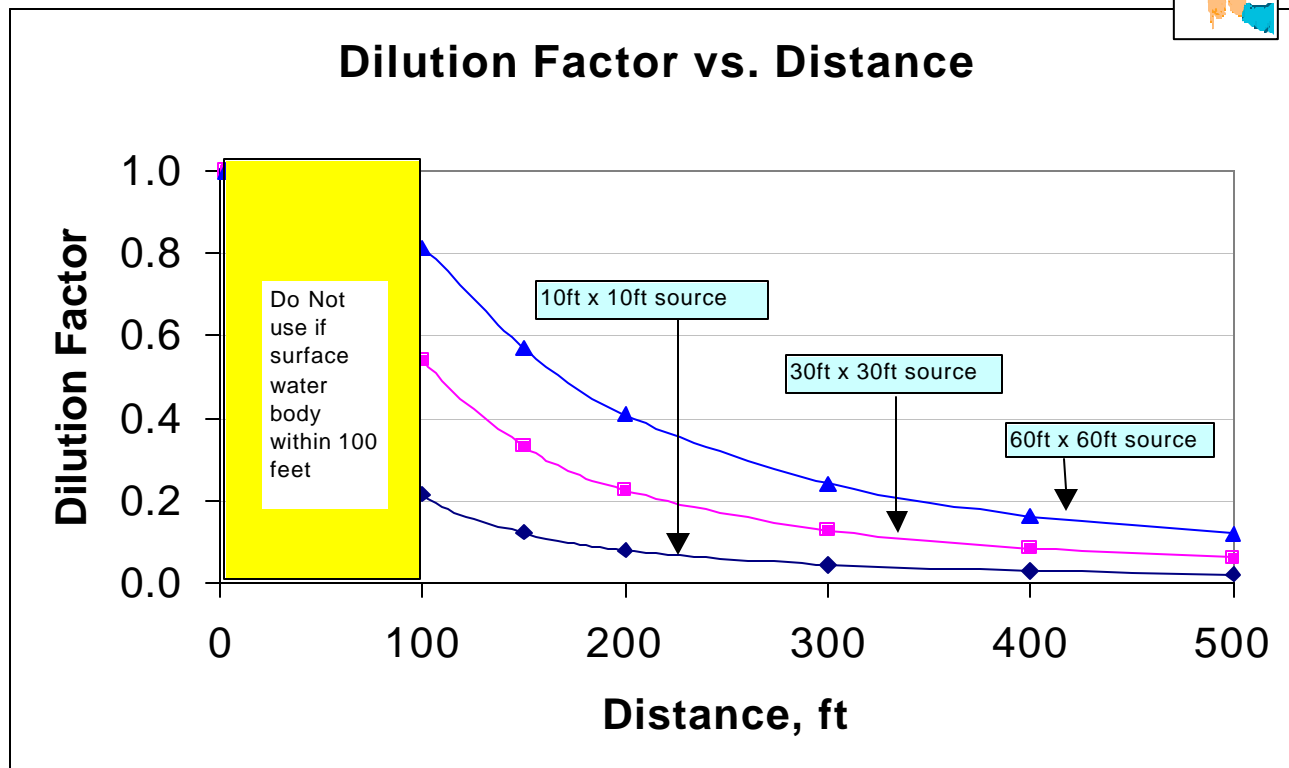
Fraction	Surface Water Guideline (mg/L)	Basis of Guideline
C5-C8 Aliphatics	250 <sup>a</sup>	Acute LC50/10 for Hexane (as surrogate for this range)
C9-C12 Aliphatics	1800	Acute LC50/10 for Decane (as surrogate for this range)
C9-C10 Aromatics	540 <sup>a</sup>	Acute LC50/10 for Trimethylbenzene (as surrogate for this range)
C9-C18 Aliphatics	1800	Acute LC50/10 for Decane (as surrogate for this range)
C19-C36 Aliphatics	2100	Acute EC50/10 for Cyclododecane (as surrogate for this range)
C11-C22 Aromatics	N.A. <sup>a</sup>	Effects may be seen at less than the EPH Reporting Limit; other testing methods (e.g., GC/MS) may be needed on site-specific basis

<sup>a</sup>updated value (2002)



In lieu of site-specific modeling, the conservative dilution factors graphically illustrated in Figure 4-4 may be used as part of a Method 2 evaluation of groundwater-to-surface-water impacts dissolved hydrocarbon contaminants.

**Figure 4-4: Groundwater Dilution Factors for Dissolved Hydrocarbons**



**Equations:**

10ft x 10ft source area,  $DF = 177 (\text{distance in feet})^{-1.455}, r^2 = 0.99$   
 30ft x 30ft source area,  $DF = 303 (\text{distance in feet})^{-1.365}, r^2 = 0.99$   
 60ft x 60ft source area:  $DF = 237 (\text{distance in feet})^{-1.214}, r^2 = 0.99$

The graphs presented in Figure 4-4 are generalized, source-area dependent conservative dilution and dispersion curves for any dissolved groundwater contaminant, including hydrocarbon range fractions and Target Analytes. They were developed using the Domenico and Robbins analytical transport model (1985) assuming an infinite source condition. The only attenuation mechanism considered is hydrodynamic dispersion, and as such may be used for any dissolved organic compound.

The use of these graphs, however, is limited to sites where **ALL** of the following conditions are met:

- ◇ groundwater/contaminant flow is occurring only in an overburden aquifer;
- ◇ there is no “short circuiting” of groundwater/contaminants along preferred flow paths;
- ◇ no fractional range is present at a concentration greater than 100,000 µg/L (i.e., exceeding UCLs); and
- ◇ the nearest downgradient surface water body is at least 100 feet from the impacted well/groundwater area on the site.

**Because of modeling uncertainties, and limitations that typically exist on the availability of temporal and spatial groundwater monitoring data, the graphs and equations contained in Figure 4-4 may not be used at sites where the distance to surface water is less than 100 feet.**

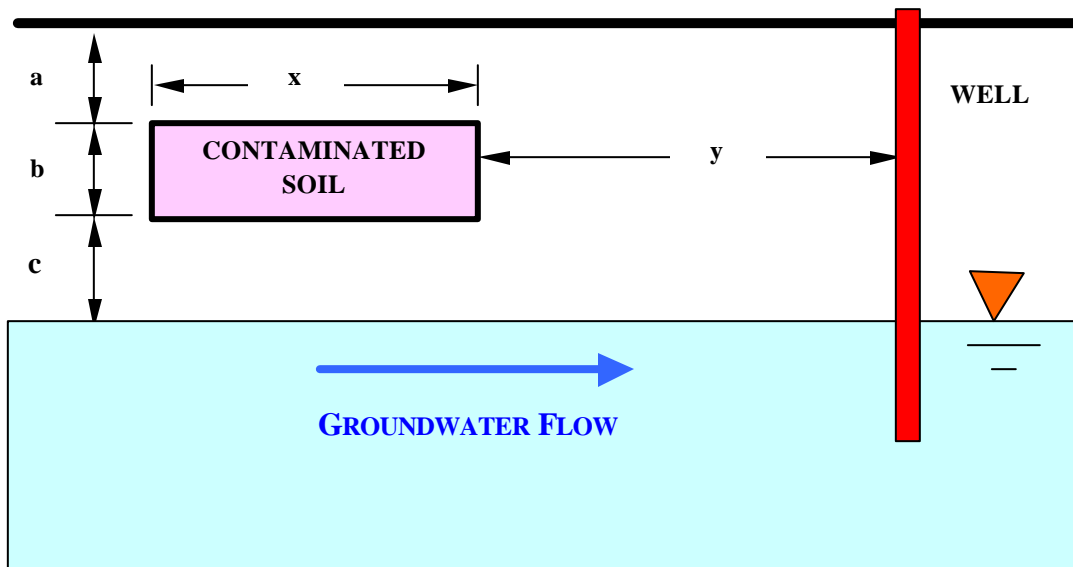
Using Figure 4-4, it is possible to conservatively calculate the concentration of a hydrocarbon range or Target Analyte of interest at some distance from a site (typically, a monitoring well located at a site). For example, at a site in which the source area of contamination is approximately 30ft x 30ft, if the concentration of C<sub>9</sub>-C<sub>10</sub> Aromatic Hydrocarbons in a well located 400 feet from a receiving water is 600 µg/L, a (dimensionless) Dilution Factor of 0.09 is obtained from Figure 4-4. Multiplying this Dilution Factor by 600 µg/L yields 54 µg/L, which would be a conservative estimate of the maximum concentration of C<sub>9</sub>-C<sub>10</sub> Aromatic Hydrocarbons in groundwater that would migrate to this point. An additional dilution factor may then be applied to account for the mixing of groundwater with the surface water, based upon site-specific information and data.

Parties wishing to provide alternative ambient water quality guidelines for the VPH/EPH fractions, and/or provide a site-specific evaluation of environmental impacts, must do so via a MCP Method 3 approach.

#### 4.3.3 Using a Method 2 Approach to Evaluate Leaching

All Method 1 soil standards consider leaching impacts to underlying groundwater. The leaching-based component of the Method 1 standards were derived using the SESOIL and AT123D computer models to evaluate unsaturated and saturated zone transport, as depicted in Figure 4-5.

**Figure 4-5: Leaching Scenario Used to Develop Leaching-Based Method 1 Soil Standards**



The standards developed by MADEP in 1993 were based upon a deterministic modeling effort, using “point” value input parameters (i.e., in Figure 4-5 a, b, and c = 1 meter, x and y = 10 meters). More recent efforts by MADEP have involved use of a probabilistic modeling approach, using ranges or distributions for input parameters. In all cases, “Dilution and Attenuation Factors” were developed to relate concentrations of soil contaminants in the source area to concentrations of those contaminants in a hypothetical “point of compliance” downgradient monitoring well.

Based upon the assumptions and models used by MADEP, the only VPH/EPH Method 1 soil standard controlled by leaching concerns is C11-C22 Aromatics in GW-1 (drinking water) areas. However, the Method 1 soil cleanup standards for two important Target Analytes - naphthalene and 2methylnaphthalene - are also controlled by leaching considerations.

Using a Method 2 approach, site-specific data, fate and transport factors, and/or predictive models may be used to modify a Method 1 soil standard that is based upon leaching concerns. In such an exercise, the site-specific soil concentration(s) of a hydrocarbon fraction or Target Analyte of interest is used to predict maximum groundwater concentrations that may be expected in areas beneath and downgradient of the contaminated soil. These

groundwater concentrations are then compared to the appropriate Method 1 or 2 groundwater standards. A modified soil standard derived in this manner is acceptable if:

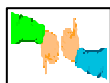
- ◇ the maximum predicted groundwater concentration of the contaminant of interest downgradient of the zone of soil contamination is at or below the appropriate Method 1 or 2 GW standard; and
- ◇ the modified soil standard does not exceed the appropriate S-1, S-2, or S-3 levels which are protective of direct-contact exposure concerns [as listed at 310 CMR 40.0985(6)].

Example: under a Method 2 approach, the S 1/GW-1 Method 1 standard for C11-C22 Aromatic Hydrocarbons can be modified, based upon site-specific leaching considerations, to a maximum concentration of 800 µg/g, which is the level at which the human health risks associated with direct contact controls the setting of this standard.

*Note that while the generic Method 1 standards were predicated on a specified or probabilistic downgradient receptor of concern, (e.g., 10 meters downgradient of the source area), actual site-specific conditions and receptors should be used when undertaking a Method 2 evaluation effort (e.g., buildings, surface water bodies, GW-1 areas).*

Recommended fractional fate and transport parameters are provided in Section 4.6. For additional information on the calculation of leaching-based Method 1 soil standards, consult *Background Documentation for the Development of the MCP Numerical Standards* (MADEP, 1994 and as amended).

In lieu of or in conjunction with predictive models, the use of groundwater monitoring data is often an acceptable and cost-effective means to evaluate site-specific leaching concerns. In order to have sufficient confidence in such an approach, however, the following site conditions are desirable:



- ◇ the release occurred at least 24 months ago;
- ◇ the depth between the zone of soil contamination and groundwater table is less than 6 feet;
- ◇ the surface(s) overlying the contaminated soil is pervious (i.e., no pavement or buildings);
- ◇ the number and location of monitoring wells are sufficient to characterize groundwater quality below and downgradient of the zone of soil contamination; and
- ◇ sufficient temporal monitoring data exist to evaluate seasonal trends.

## 4.4 Method 3 Risk Characterization

Under Method 3, a completely site-specific evaluation is conducted to determine risks to human health, safety, public welfare, and the environment. Recommended toxicological and fate and transport values for the VPH/EPH fractions in this regard are provided in Tables 4-13 and 4-14, respectively. Although it is not necessary to use any of these values in a Method 3 risk characterization effort, the burden is on the party conducting the assessment to document and defend the selection of alternative assumptions, parameters, and values. Complete details on the Method 3 risk assessment process are provided in *Guidance for Disposal Site Risk Characterization* (MADEP, 1995 and as amended).

### 4.4.1 Requirements and Limitations of a Method 3 Characterization

While a Method 3 characterization allows a significant degree of flexibility, there are important obligations and limitations:

- ◇ **Site-specific risks to public welfare must be evaluated.** Under the Massachusetts “superfund” legislation (MGL c. 21E), risks to public welfare are given the same weight as risks to human health, safety, and the environment. In deriving the Method 1 standards, MADEP imposed ceiling levels on acceptable concentrations of contaminants, in an attempt to ensure that each standard would be set at a low enough level to rule out significant impacts to public welfare. “Public welfare” is a difficult standard to articulate, and it is much easier to define a *de minimis* condition, than to define a precise point where a risk to public welfare becomes significant. Nevertheless, parties conducting a Method 3 assessment must make an independent evaluation of all relevant public welfare concerns, and conclude that all such concerns are below a level of *No Significant Risk*.
- ◇ **Site-specific risks to ecological receptors must be evaluated.** Under the MCP, environmental risk assessment is done via a two-stage process. Stage I is a screening process used to (1) eliminate from further consideration those sites where exposures are clearly unlikely to result in environmental harm, or, on the other extreme, (2)

eliminate from further consideration those sites where harm is readily apparent (i.e., it is clear that remediation is needed, and additional study is not necessary). Those sites that are not eliminated must proceed to a Stage II evaluation, which involves a quantitative, site-specific characterization of the risk to ecological receptors.

- ◇ **A Method 3 approach cannot be used to modify or eliminate Upper Concentration Limits.** Upper Concentration Limits (UCLs) are “gross” levels of contamination in soil and groundwater that, by their very presence in the environment, constitute a significant risk to public welfare and the environment. Under the provisions of 40.0996(2), the UCL standards are to be applied to the arithmetic average of the concentration of oil or hazardous materials at a site or within a “hot spot”. If the average concentrations of site contaminants exceed an applicable UCL value, remediation must be undertaken to treat or encapsulate areas of concern, if feasible. In cases where it is not feasible to remediate such conditions, it may be still possible to obtain an interim site closure by filing a Class C Response Action Outcome, representing a Temporary Solution.
- ◇ **A Permanent Solution cannot be achieved if drinking water standards are exceeded in a GW-1 area.** In conducting a Method 3 assessment, all applicable or suitably analogous health standards must be identified and achieved. Under the provisions of 310 CMR 40.0993(3)(a), the Massachusetts Drinking Water Quality Standards promulgated in 310 CMR 22.00 are considered applicable in all GW -1 areas. While drinking water standards have been promulgated for a number of Target Analytes (e.g., benzene at 5 µg/L), at the present time, the VPH/EPH fractional ranges are not included on this list. While it is necessary to characterize the risk these fractional ranges pose to the water supply of concern, it is not necessary to consider these values “analogous health standards”.

#### 4.4.2 Impacts to Indoor Air

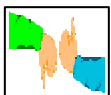
Relevant guidance contained in Section 4.3.1 should be considered by parties undertaking an evaluation of impacts to indoor air as part of a Method 3 risk assessment process. The use of the inhalation RfC values provided in Table 4-13 would be a conservative means to quantitate risks via the inhalation pathway, and use of the estimated background concentration values listed in this table would be a conservative means to evaluate Critical Exposure Pathways.

#### 4.4.3 Odors as a Significant Risk to Public Welfare

Under the provisions of 310 CMR 40.0994, the existence of a nuisance condition shall be considered in a characterization of risks to public welfare. Given the low odor recognition thresholds of many petroleum constituents (and breakdown products), the presence of odors at petroleum-contaminated sites can constitute a nuisance condition, and preclude achievement of a condition of No Significant Risk to Public Welfare, *even if a condition of No Significant Risk to Human Health has been achieved.*

Definitive and quantitative guidelines and standards on when a petroleum odor constitutes a nuisance condition and significant risk to public welfare are difficult to articulate. In the context of petroleum-contaminated sites, however, the following **Rules of Thumb** are suggested for when an odor condition would generally NOT be considered a nuisance condition:

- ◇ Odors observed in the subsurface during excavation or boring advancement would generally not be considered a nuisance condition, as long as such odors are not detectable in ambient or indoor air, and as long as there are no plans to excavate or disturb such areas.
- ◇ Odors observed in the breathing zone of the ambient air, or indoor air of an impacted structure, would generally not be considered a nuisance condition, if such odors do not persist for more than 3 months.
- ◇ Odors observed in the breathing zone of the ambient air would generally not be considered a nuisance condition if they are discernable less than 10 days a year.
- ◇ Odors observed in the ambient air or indoor air of an impacted structure would generally not be considered a nuisance condition if the occupants of such a structure do not believe such odors significantly affect or degrade their quality of life.



#### 4.4.4 MADEP Petroleum-Contaminated Site Risk Assessment Short Forms

To streamline the Method 3 risk assessment process, MADEP has developed a series of Risk Assessment “Short Forms” which incorporate the aliphatic and aromatic fractional ranges, for optional use at sites contaminated by various petroleum products. Like other MADEP Short Forms, these spreadsheet-based tools incorporate standardized exposure assumptions and toxicological profiles, and allow the user to input site-specific concentration data. The output is a series of summary tables that describe chemical-specific, medium-specific, and cumulative (total site) risks, which may be used and/or applied as part of a Method 3 risk assessment at petroleum-contaminated sites.

The Short Forms, and supporting documentation, are available for downloading from the MADEP Web site, at <http://www.state.ma.us/dep/ors/orspubs.htm>

### 4.5 Recommended Toxicological Parameters

The currently recommended toxicological values for assessing risks associated with the VPH/EPH aliphatic and aromatic hydrocarbon fractions are listed in Table 4-13. Note that these values are subject to change as additional information and data become available to MADEP.

**Table 4-13: Recommended VPH/EPH Toxicological & Risk Assessment Parameters**

	C5-C8 Aliphatics	C9-C12 Aliphatics	C9-C10 Aromatics	C9-C18 Aliphatics	C19-C36 Aliphatics	C11-C22 Aromatics
Chronic Oral RfD (mg/kg/day)	0.04 <sup>a</sup>	0.1 <sup>a</sup>	0.03	0.1 <sup>a</sup>	2.0 <sup>a</sup>	0.03
Subchronic Oral RfD (mg/kg/day)	0.4 <sup>a</sup>	1.0 <sup>a</sup>	0.3	1.0 <sup>a</sup>	6 <sup>a</sup>	0.3
Chronic Inhalation RfC (mg/m3)	200	200	50 <sup>a</sup>	200	N/A	50 <sup>a</sup>
Est. Background Indoor Air (mg/m3)	≤85	≤90	≤80	≤100	N/A	≤50
Chronic RAF - Soil Ingestion	1 <sup>a</sup>	1 <sup>a</sup>	1 <sup>a</sup>	1 <sup>a</sup>	1 <sup>a</sup>	0.36 <sup>a</sup>
Chronic RAF - Soil Dermal	1 <sup>a</sup>	0.5 <sup>a</sup>	0.5 <sup>a</sup>	0.5 <sup>a</sup>	0.1	0.1 <sup>a</sup>
Chronic RAF – Water Ingestion	1	1	0.91	1	1	0.91
Subchronic RAF - Soil Ingestion	1 <sup>a</sup>	1 <sup>a</sup>	1 <sup>a</sup>	1 <sup>a</sup>	1 <sup>a</sup>	0.36 <sup>a</sup>
Subchronic RAF - Soil Dermal	1 <sup>a</sup>	0.5 <sup>a</sup>	0.5 <sup>a</sup>	0.5 <sup>a</sup>	0.1	0.18
Subchronic RAF - Water Ingestion	1	1	0.91	1	1	0.91
Ambient Water Quality Guide (mg/L)	250 <sup>a</sup>	1800	540 <sup>a</sup>	1800	2100	N.A.. <sup>a,b</sup>

<sup>a</sup> updated value (2002)

<sup>b</sup> see table 4-12

### 4.6 Recommended Fate and Transport Parameters

For recommended approaches, procedures, and values to conduct fate and transport evaluation/modeling of Target Analytes and hydrocarbon ranges, consult *Volume 3: Selection of Representative TPH Fractions Based on Fate and Transport Considerations*, a (1997) publication prepared by the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG), available at <http://www.aehs.com/whatsnew.htm>.

Relative to the VPH and EPH hydrocarbon ranges – FOR MODELING PURPOSES ONLY - recommended fractional properties are provided in Table 4-14.

**Table 4-14 : Recommended VPH/EPH Fractional Properties for Modeling Purposes**

	Equivalent Carbon Number (EC)	Molecular Weight	Vapor Pressure (atms)	Solubility in Water (mg/L)	Henry's Constant, H (dimensionless)	Partition Coeff, Koc (mL/g)	Diffusion Coeff (cm <sup>2</sup> /s)	
							air	water
C5-C8 Aliphatics	6.5	93	0.10	11,000	54	2265	0.08	1 x 10 <sup>-5</sup>
C9-C12 Aliphatics	10.5	149	8.7 x 10 <sup>-4</sup>	70	65	1.5 x 10 <sup>5</sup>	0.07	1 x 10 <sup>-5</sup>
C9-C10 Aromatics	9.5	120	2.9 x 10 <sup>-3</sup>	51,000	0.33	1778	0.07	1 x 10 <sup>-5</sup>
C9-C18 Aliphatics	12	170	1.4 x 10 <sup>-4</sup>	10	69	6.8 x 10 <sup>5</sup>	0.07	5 x 10 <sup>-6</sup>
C19-C36 Aliphatics	considered immobile							
C11-C22 Aromatics	14	150	3.2 x 10 <sup>-5</sup>	5800	0.03	5000	0.06	1 x 10 <sup>-5</sup>

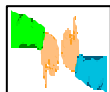
#### 4.7 Non-Aqueous Phase Liquids (NAPL)

The presence of non-aqueous phase liquids (NAPL) adds significant complexity to the assessment and remediation of petroleum-contaminated sites. Of primary concern are (1) the bulk fluid migration of petroleum NAPL, and potential discharge into underground structures, utilities, and/or surface water bodies, and (2) NAPL acting as a continuing source of soil, groundwater, and/or soil gas contamination. Due to these concerns, under the provisions of 310 CMR 40.0996(4), the presence of a non-aqueous phase liquid having a thickness equal to or greater than 0.5 inches in *any environmental medium* is considered an exceedence of an Upper Concentration Limit (UCL).

##### 4.7.1 Upper Concentration Limits

A *single* measurement of  $\geq 0.5$  inches NAPL in a *single* groundwater monitoring well does not necessarily constitute exceedence of a UCL standard:

- ◇ The standard applies to the formation, not a groundwater monitoring well. Typically, the thickness of NAPL measured in a monitoring well does not correspond to the thickness of NAPL in the surrounding formation. Moreover, seasonal and short-term water table fluctuations and tidal influences will affect apparent levels of petroleum product thickness in monitoring wells, with thickness levels often increasing with a declining water table, and decreasing or “disappearing” with a rising water table. Although the relationship between the thickness of NAPL in a monitoring well and the surrounding formation is not easily established, there may be methods and sites for which reasonable assumptions and conclusions can be reached, based upon:



- \* an evaluation of formation properties, especially the thickness of the capillary fringe;
- \* an evaluation of test pit, split-spoon, and/or analytical screening observations within the presumed NAPL “smear zone”; and
- \* an evaluation of sufficient spatial and temporal monitoring well data, relative to the observed thickness of the NAPL and the elevation of the potentiometric surface.

- ◇ As with all UCL standards, averaging of data is permissible. In the case of NAPL, however, temporal averaging of data from monitoring wells is generally not appropriate, due to distortions introduced by a falling and rising water table.

- ◇ It is permissible to spatially average wells within the contiguous area of the NAPL plume, excluding “hot spots”, which are defined by the MCP to be discrete areas where the thickness of NAPL is more than 10 times the thickness of surrounding areas.

##### 4.7.2 Apparent NAPL Thickness vs. Actual NAPL Thickness

The occurrence, detection and migration of non-aqueous phase liquids in the subsurface are a complex phenomenon. Many investigators have attempted to develop theoretical and/or empirical methods to correlate the apparent



thickness of NAPL, as measured in a monitoring well, to the actual thickness of that NAPL in the surrounding formation. Most of these methods involve relationships based upon the density of the liquid hydrocarbon (de Pastrovich *et al.*, 1979), properties of the geologic medium (Hall *et al.*, 1984), height of the capillary fringe (Blake and Hall, 1984; Ballesterro *et al.*, 1994; and Schiegg, 1985), and/or idealized capillary pressures in homogeneous porous media (Farr *et al.*, 1990; and Lenhard and Parker, 1990). Unfortunately, none of the methods or approaches presented to date appears to be sufficiently reliable or reproducible at field sites, especially when significant fluctuations occur in the elevation of the groundwater table.

Despite these limitations, at most sites, it is likely that the *maximum* apparent (measured) thickness of light non-aqueous phase liquid (LNAPL) in a monitoring well is significantly greater than the actual thickness of that LNAPL in the surrounding formation. This phenomenon occurs when a monitoring well is installed into a formation in which mobile LNAPL is pooled on top of the capillary fringe above the water table. In such cases, LNAPL will flow into the monitoring well, depressing the true elevation of the potentiometric surface, until such time as equilibrium is achieved with the level of the LNAPL above the capillary fringe, and the weight/density of the hydrocarbon liquid in the well.

**While LNAPL occurrence and measurement is a complicated matter, it is possible to make one simple conclusion: it is usually not possible to adequately characterize this concern without sufficient temporal gauging data. At a minimum, monitoring activities should include at least 4 rounds of gauging during the 4 seasons of the year.**

Until such time as additional guidance is available on this topic, site investigators must undertake a “weight of evidence” approach to determine compliance with the 0.5 inch NAPL standard. A conservative approach would be to assume that the maximum (temporal) LNAPL thickness *observed* in a monitoring well is equivalent to the *actual* thickness of LNAPL in the formation. If the spatial average of these values within an area of concern (excluding hot spots) is less than 0.5 inches, compliance has been achieved. If the average of these values – or of a hot spot area – is greater than 0.5 inches, additional evaluations/calculations are needed to relate the observed/apparent thickness to actual formation thickness.

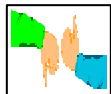
#### 4.7.3 NAPL and Vapor/Indoor Air Impacts

Volatile non-aqueous phase liquids (NAPL), including separate-phase gasoline, kerosene, jet fuels, and fresh diesel/#2 fuel oils, can result in the generation of significant concentrations of volatile petroleum hydrocarbon vapors in the vadose zone, which can potentially impact the indoor air of nearby structures. Purging a monitoring well containing such NAPL prior to obtaining a groundwater sample may underestimate risks of this nature, as the groundwater sample may contain relatively low concentrations of dissolved hydrocarbons. *For this reason, soil gas investigations should be considered at any site at which volatile NAPL has been identified in monitoring wells or test pits, to characterize the risks posed to indoor air quality, and determine whether use of a Method 1 approach is appropriate*

## 4.8 Elimination of Continuing Sources

Under the provisions of 310 CMR 40.1003(5), a permanent solution cannot be achieved at a site if a continuing source(s) of environmental contamination is present. At petroleum-contaminated sites, the following conditions could constitute a continuing source:

- ◇ *Abandoned Storage Tanks* - any abandoned storage tank containing any amount of mobile and/or soluble petroleum product would be considered a continuing source of environmental contamination, regardless of its current condition, unless such a tank has been closed pursuant to all applicable federal, state, and local regulations.
- ◇ *Septic Tanks/Dry Wells* - any wastewater storage, conveyance, or disposal system containing significant quantities of Non-Aqueous Phase Liquids (NAPL) would be considered a continuing source of environmental contamination, unless such systems are operating in compliance with all applicable federal, state, and local regulations.



- ◇ *Gasoline NAPL* - measurable amounts of gasoline NAPL could constitute a continuing source of environmental contamination, unless modeling, groundwater and/or soil gas monitoring data can demonstrate decreasing concentrations of dissolved and/or vapor-phase contaminants over time.
- ◇ *Gasoline/VPH-contaminated soils* - concentrations of VPH fractions in soil above applicable Method 1 standards could constitute a continuing source of environmental contamination, unless modeling, groundwater and/or soil gas monitoring data can demonstrate decreasing concentrations of dissolved and/or vapor-phase contaminants over time.


## 4.9 Feasibility of Achieving Background Concentrations

Under the provisions of MGL c. 21E and the MCP, a permanent solution shall, *at a minimum*, achieve a condition of No Significant Risk. However, the statute and regulations go one step further: a permanent solution shall also include measures to reduce contaminant levels in the environment to concentrations that achieve or approach a “background” condition, *to the extent such measures are feasible*. Thus, remedial decisions under the MCP are predicated on two distinct evaluation processes: risk and feasibility. Generic and site-specific procedures and criteria to evaluate and eliminate significant risk are extensively detailed in the MCP and associated guidance documents. Procedures and criteria to evaluate the feasibility of achieving or approaching background are less defined, and are typically considered on a site-by-site basis.

A feasibility evaluation of this nature identifies and weighs the benefits and costs of eliminating or minimizing the mass or volume of contaminants in the environment, beyond a “risk-based” endpoint. The costs of such actions can be generally calculated. The benefits are less quantifiable, but include property-value/economic and non-pecuniary benefits, as well as potential health benefits. With respect to the latter, it is important to understand that all risk-based standards have inherent uncertainties, due to limitations in our understanding of how toxins affect human and ecological receptors; these limitations are especially true and problematic when considering potential synergistic effects of multiple contaminants, and exposures to sensitive populations (e.g., children). While most standards are thought to be conservative, better studies and future data may lead to a different conclusion. A good example in this regard is the risk-based GW-1 standard for MtBE, which in recent years has been lowered by MADEP from 700 µg/L to 70 µg/L (and which may be lowered even further in the future).

While it is necessary to consider the feasibility of achieving or approaching background at petroleum-contaminated sites, certain attributes of petroleum hydrocarbons are germane to the benefit/cost evaluation, and allow for generalized conclusions and recommendations on feasibility issues. Specifically, most of the petroleum hydrocarbons contained in gasoline and lighter fuel oils are biodegradable, under both aerobic and anaerobic conditions. At most sites, residual levels of such contaminants will naturally degrade to levels that achieve or approach a background condition, in a foreseeable time period. In such cases, the “benefit” side of the feasibility equation becomes more an issue of timing than of concentration endpoints: is the benefit of *accelerating* this mass reduction worth the cost?

Based upon the above, certain generic guidelines are offered to streamline background restoration considerations at sites contaminated ONLY with petroleum hydrocarbons:

- ◇ Given the typical “asymptotic” response for contaminant reduction in aquifer systems, at sites contaminated solely by releases of gasoline or diesel fuel oil, achieving or approaching background concentrations of petroleum hydrocarbons in *groundwater* may generally be considered infeasible, provided that indigenous or enhanced microbial populations present at the site of concern would be expected to naturally degrade petroleum hydrocarbon concentrations.
- 
- ◇ Achieving or approaching background concentrations of petroleum hydrocarbons may generally be considered infeasible in soils that are located beneath a permanent structure.
  - ◇ Achieving or approaching background concentrations of petroleum hydrocarbons may generally be considered infeasible at sites where such remedial activities would interrupt vital public services and/or threaten public safety (e.g., energy interruption; traffic disruption).

**It is important to stress that the above guidelines pertain only to the feasibility of remediation beyond a risk-based endpoint.** Under the MCP, all sites must achieve a condition of No Significant Risk.

Additional policy documents on this subject are currently under development by MADEP; refer to the BWSC publication page at <http://www.state.ma.us/dep/bwsc/pubs.htm> to track progress/provide input in this regard.



## 5.0 IMPLEMENTATION ISSUES

### 5.1 Site Characterization

#### 5.1.1 Analytical Parameters

Recommended Target Analytes and VPH/EPH hydrocarbon ranges of interest for the most commonly released petroleum products are detailed in Tables 4-3, 4-5, and 4-6.

#### 5.1.2 Site and Media Characterization

Site characterization may involve evaluation and/or testing of NAPL, soil, groundwater, surface water, soil gas, ambient air, indoor air, or freshwater or marine sediments. Decisions of this nature are necessarily site-specific, based upon the type and quantity of petroleum product(s) released, depth to groundwater, and sensitivity of potential pollutant receptors.

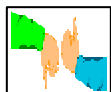
**Rules of Thumb** for the most commonly released petroleum products and problematic situations are provided below:

##### NAPL

- ◇ When gauging a well for the purpose of monitoring the presence and thickness of NAPL, it is essential that all free-phase petroleum product be evacuated from the well after each gauging round, to help ensure that the well remains in good hydraulic communication with the surrounding formation, and accurately reflects dynamic aquifer conditions.
- ◇ Generally, it is not possible (or meaningful) to attempt to measure the concentration of dissolved petroleum product in a monitoring well which contains a measurable thickness of NAPL.

##### Soil

- ◇ When obtaining samples at an UST grave for the purposes of determining an Exposure Point Concentration (EPC), it is necessary to specifically investigate whether a “hot spot” exists within the groundwater table fluctuation zone (i.e., the “smear zone”). For gasoline and fresh diesel/fuel oil releases, this action may be easily accomplished by headspace analysis of samples from sidewall excavations using a PID meter. In cases where headspace concentrations within this smear zone are equal to or greater than 10 times other locations on the sidewall, soil samples from this zone should be discretely collected/composited (either as the sidewall sample or with other sidewall samples) for appropriate analysis.

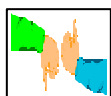


##### Groundwater

- ◇ Regardless of the type of petroleum product released, groundwater characterization should be undertaken at any site where the distance to a groundwater withdrawal well is less than 500 feet.
- ◇ In most cases, it is necessary to obtain groundwater samples to adequately characterize releases of gasoline, aviation gasoline, and military jet fuels. Exceptions may include: very small releases of product (less than a few gallons), or sites with a deep vadose zone (>30 feet to the groundwater table), **IF** there are no sensitive receptors (e.g., no groundwater withdrawal wells or potentially impacted structures). At sites where the groundwater table is located in bedrock, the use of passive and/or active soil gas sampling is recommended to help determine if NAPL or significant concentrations of dissolved constituents are present in the groundwater.
- ◇ At sites where there has been a release of diesel/#2 fuel oil, and where excavation is being accomplished to remove a tank or contaminated soil, an attempt should be made to reach the groundwater table using on-site equipment. If reached, visible observations of the presence or absence of NAPL should be documented, and a groundwater and/or soil sample (from within the groundwater fluctuation zone) should be obtained

for analysis by a TPH or EPH methodology. If not reached, the installation of a groundwater monitoring well would generally not be necessary if (a) site data, before or after remediation, document concentrations of EPH fractional ranges below appropriate Method 1 standards, and (b) there are no groundwater withdrawal wells within 500 feet. Further guidance on tank removal is available in *Commonwealth of Massachusetts Underground Storage Tank Closure Assessment Manual*, DEP Policy # WSC-402-96, April, 1996.

- ◇ At gasoline-contaminated sites, particular attention and emphasis should be placed on the characterization of MtBE in groundwater. This compound, an additive in unleaded gasoline, is extremely soluble and mobile, and can migrate significant distances in groundwater. While most petroleum hydrocarbon plumes tend to biodegrade before significantly “dipping” below the groundwater table, MtBE plumes can “sink” below the typical 10-foot water table well screens in monitoring wells with increasing distance from a source area, necessitating consideration of deeper wells in downgradient plume areas (i.e., beyond about 100 meters from the source area). Moreover, unlike BTEX and other petroleum hydrocarbons, MtBE may not be a good candidate for natural attenuation, as it does not tend to volatilize, sorb to soils, or readily biodegrade. *Recent information and data developed by the USEPA (2002) have disclosed that conventional sampling and analysis techniques can significantly underestimate MtBE concentration in groundwater; additional details and recommendations are provided in Appendix 1.*
- ◇ When investigating vapor partitioning/transport concerns due to the presence of an open groundwater collection sump in a basement structure, it is recommended that 3-5 sump volumes of water be evacuated (as permitted by site/recharge conditions) immediately prior to sampling, to ensure collection of a representative sub-slab groundwater sample.



#### **Soil Gas/Indoor Air**

- ◇ Testing of soil gas and/or indoor air should be considered at any site where (a) a groundwater sump is present within a potentially impacted structure, (b) an earthen floor is present within a potentially impacted structure, (c) volatile LNAPL is present beneath or near a potentially impacted structure, or (d) contaminated soils are located within 5 feet of a potentially impacted structure (including beneath a basement slab). Note that the current MCP Method 1 soil standards do NOT consider the direct partitioning of volatile contaminants from impacted soils to an overlying or nearby structure, or impacts from groundwater that infiltrates a structure.
- ◇ When the objective for indoor air sampling is to determine whether a Critical Exposure Pathway (CEP) is present at a home or school, testing must be conducted under “worst case” site conditions; spatial and temporal averaging of indoor air data, while potentially appropriate for determining Exposure Point Concentrations for risk assessment purposes, is NOT appropriate when evaluating CEP conditions. Additional discussions in this regard are provided in Section 4.3.

#### **5.1.3 Filtering of Groundwater Samples**

The objective of a groundwater characterization program is to determine the concentrations of contaminants within, and moving through, an aquifer or formation. Groundwater monitoring wells are installed to help meet this objective. However, monitoring wells are not perfect instruments for this purpose, as they can introduce a (false-positive) bias in the form of (a) suspended sediments containing significant concentrations of sorbed (non-dissolved) hydrocarbons, and/or (b) colloidal suspensions of non-aqueous phase liquids (NAPL). In either case, the analyses of water samples from such wells can provide an overquantitation of contaminant levels of concern. For this reason, groundwater samples are sometimes filtered prior to analyses, generally through a 0.45 micron filter. However, filtering in such a manner can produce a (false-negative) bias, by (1) removing particles smaller than 0.45 microns, and/or (2) removing colloids that are in fact contaminants that are moving through a formation.

Recommendations on this issue are outlined below:

- ◇ The use and sampling of properly installed, constructed, and developed groundwater monitoring wells, using low-flow sampling techniques, is a preferred alternative to filtering. Recommended guidance and a standard operating procedure for low-flow/low-stress groundwater sampling is available from the EPA Region I website at: <http://www.epa.gov/region01/measure/well/wellmon.html>

- ◇ Samples obtained from potable water supply wells should NOT be filtered prior to analysis.
- ◇ Filtering should generally NOT be conducted in monitoring wells outside the “source area” of a petroleum release. Such wells are designed to determine the dissolved plume migration of petroleum contaminants, and should not contain suspended sediments with significant concentrations of sorbed hydrocarbons, or any NAPL.
- ◇ When filtering samples, the use of an “in line” device is recommended, to minimize handling and disturbance of the sample.
- ◇ When filtering samples, the collection and analysis of a separate (split) non-filtered sample may be appropriate, to help discern biases present in the characterization process, and determine compliance with characterization objectives.

**Because of the potential to produce a false-negative/bias, all site investigations that rely upon data obtained from filtered groundwater samples must include an adequate discussion and justification for using such techniques.**

## 5.2 Use of Old and New TPH Data

While the use of the VPH/EPH approach is a preferred means to characterize risks from petroleum products released to the environment, there are significant amounts of historical Total Petroleum Hydrocarbon (TPH) data that have been obtained in the past for contaminated sites. Moreover, the future use of new TPH data may also be appropriate, to screen out problems in a cost-effective manner. For this reason, in addition to the VPH/EPH aliphatic and aromatic range standards, TPH reporting and cleanup standards have been retained in the Massachusetts Contingency Plan. Note, however, that many of the (post 1997 MCP) standards have been changed, in that the TPH standards are now set at the lowest EPH fractional standard (usually C11-C22 Aromatics), as a “worst case” assumption on hydrocarbon chemistry.

There are two ways to use TPH data:

- ◇ TPH data may be used *directly*, by comparison to TPH Reportable Concentrations and Cleanup Standards; or
- ◇ TPH data may be used *indirectly*, by using (conservative) assumptions on hydrocarbon chemistry to break down and “convert” the TPH data into aliphatic and aromatic ranges.

### 5.2.1 Comparing TPH Data to Reportable Concentrations, Method 1 Cleanup Standards, and UCLs

Soil and groundwater data obtained from a TPH test method may be directly used to ascertain reporting obligations, compliance with MCP Method 1 cleanup standards, and compliance with Upper Concentration Limits (UCLs). Because the TPH standards assume that the entire hydrocarbon mixture is comprised of the most toxic/problematic hydrocarbon fraction, in theory, use of TPH data would be viewed as a conservative screening effort. However, parties electing to proceed in such a fashion should be aware of the following practical conditions and concerns:

- ◇ Effective October 31, 1997, the MCP defines TPH as “the total or cumulative concentration of hydrocarbons with boiling points equal to or greater than 150°C (C9) and associated with a petroleum product...” All data termed TPH must meet this performance standard. Given the lack of standardized testing, calibration, and reporting techniques for TPH test methods, and methodological biases for techniques such as EPA Method 418.1 (Infra-red detection), demonstrating compliance with this definition is a burden that must be met by data users.
- ◇ In lieu of using an ill-defined TPH methodology, parties seeking to use this screening tool should consider using the EPH test method in the “TPH mode”. Specifically, the EPH method provides an option to forego the aliphatic/aromatic fractionation step, and generate a GC/FID TPH quantitation value. If this value is low, and below the TPH cleanup standard, compliance has been achieved. If this value is above the TPH cleanup standard, the laboratory can be instructed to then

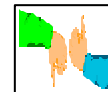
proceed to the fractionation step, to produce more toxicologically relevant and less conservative fractional data.

- ◇ Because common TPH test techniques employ a solvent extraction and concentration step, which can lead to significant losses of hydrocarbons lighter than C9, the use of such methods are not appropriate in the characterization of light petroleum products, such as gasoline, aviation gasoline, and certain military jet fuels.
- ◇ Because the EPH fractional ranges provide a better characterization of hydrocarbon chemistry and risks, such data will take precedence over TPH data. For example, parties that exceed a TPH Method 1 cleanup standard have the option of obtaining EPH fractional range data, to see if the individual fractions comprising the TPH value are within listed standards. Similarly, under the provisions of 310 CMR 40.0360(2), parties that exceed a TPH Reportable Concentration have 120 days to obtain EPH fractional data, and demonstrate that NONE of the fractions exceeds an applicable Reportable Concentration, to avoid reporting.

### 5.2.2 Converting TPH Data into EPH Fractional Ranges

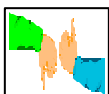
Since TPH is essentially a summation of the 3 EPH fractions (i.e., C9-C18 Aliphatics, C19-C36 Aliphatics, and C11-C22 Aromatics), it is possible to “convert” TPH data into the EPH fractional ranges, by making informed and reasonably conservative judgments on the chemistry of the TPH data. Compositional assumptions for soil data that are believed to be protective at most sites are provided in Table 5-1.

**Table 5-1: Recommended TPH Compositional Assumptions in Soil**



Petroleum Product	C11-C22 Aromatics	C9-C18 Aliphatics	C19-C36 Aliphatics
Diesel/#2/Crankcase Oil	60%	40%	0%
#3-#6 Fuel Oil	70%	30%	0%
Kerosene and Jet Fuel	30%	70%	0%
Mineral Oil Dielectric Fluid	20%	40%	40%
Unknown Oil	100%	0%	0%

For water data, only conservative assumptions can be made:



- ◇ For TPH water data, all of the TPH should be assumed to be the most conservative EPH fractional standard for the groundwater category(ies) of interest, although it is permissible to subtract out the concentrations of Target PAH analytes (e.g., naphthalene), if known;
- ◇ For Gasoline Range Organic (GRO) water data, the entire GRO concentration should be assumed to be the most conservative VPH fractional standard for the groundwater category(ies) of interest, although it is permissible to subtract out the concentration of Target BTEX/MtBE analytes, if known.

For old GRO soil data, a conservative assumption would be to consider all of the non-BTEX/MtBE hydrocarbons greater than C8 to be C9-C10 Aromatics. (All non-BTEX/MtBE compounds lighter than C9 are aliphatic hydrocarbons). **Note, however, that if the GRO soil sample was not preserved in methanol, the integrity and validity of this data would be suspect.**

In using and applying assumptions on the composition of petroleum hydrocarbons, it is essential that all relevant factors be carefully considered, including (1) level of certainty of identification of petroleum product(s) released at the site, (2) reliability, validity, and bias of TPH/screening techniques, and (3) sensitivity of pollutant receptors. Given the wide variability in “TPH” analytical methods, and inherent biases of these methods, the determination of a true TPH concentration is not a trivial exercise.

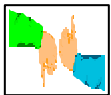
*When evaluating risks for Critical Exposure Pathways, such as drinking water wells, the use of assumptions is generally not appropriate, unless it can be demonstrated that such assumptions represent “worst case” conditions.*

### 5.3 VPH/EPH Compositional Variability/Recommended Approach

Because of fate and transport processes that act upon hydrocarbon compounds and mixtures when they are released to the environment, the chemical composition of petroleum contamination will vary across a site of concern. Accordingly, it is not possible to analyze one soil or groundwater sample by the VPH or EPH methods to establish a compositional template, and apply that template to break down TPH data from other parts of the site into aliphatic/aromatic fractional ranges. For example, soil in the saturated zone in the plume migration area will be contaminated with higher concentrations/proportions of more soluble compounds (e.g., aromatics); soils in older spill sites will have higher concentrations/proportions of less soluble/degradable compounds, such as heavy aliphatics and 3-5 ring PAH hydrocarbons.

For small sites, it may be more cost-effective to simply analyze all impacted media samples by VPH and/or EPH test methods, though use of field screening techniques would be desirable to optimize the selection and support the representativeness of such samples. For larger sites, however, cost savings may be realized by using a combination of VPH/EPH test methods and screening techniques to determine the nature and extent of contamination, and calculate Exposure Point Concentrations (EPCs). In such cases, the following would be recommended:

1. obtain VPH/EPH data from *key areas* and *exposure pathways*;
2. supplement VPH/EPH data with screening/TPH data;
3. consider the chemistry of the petroleum products released to the environment, fate and transport factors, the VPH/EPH data, and the conservative compositional parameters recommended in Table 5-1; and
4. determine conservative fractional composition/EPCs for risk assessment purposes and/or comparison with Method 1 standards.

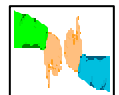


### 5.4 Other Program Issues

#### 5.4.1 Numerical Ranking System (NRS)

Under the provisions of 310 CMR 40.1500, sites are classified as either Tier I or Tier II on the basis of a numerical score, and scoring criteria are contained within a number of tables throughout this section. Recent additions to the MCP (1999) have provided (human) toxicity scoring criteria for the VPH/EPH fractions at 310 CMR 40.1511. Future revisions to the MCP will include additional VPH/EPH scoring criteria for mobility and persistence; until that occurs, scoring may be accomplished using the values listed in Table 5-2.

**Table 5-2: Mobility and Persistence Scoring Criteria for VPH/EPH Fractions**



Fraction	Mobility and Persistence Values and Scores										
	Solubility (mg/L)		Vapor Press (mm Hg)		K <sub>ow</sub>		Degrad Potential		Specific Gravity		Total Score
	Value	Score	Value	Score	Value	Score	Value	Score	Value	Score	
C5-C8 Aliphatics	11	5	80	10	<E+04	5	NP	0	<1	0	20
C9-C12 Aliphatics	0.07	0	0.7	5	>E+04	0	NP	0	<1	0	5
C9-C10 Aromatics	51	5	2	10	<E+04	5	NP	0	<1	0	20
C9-C18 Aliphatics	0.01	0	0.2	5	>E+04	0	NP	0	<1	0	5
C19-C36 Aliphatics	N/A	0	N/A	0	N/A	0	P	10	<1	0	10
C11-C22 Aromatics	5.8	5	0.02	5	>E+04	0	NP	0	<1	0	10

#### **5.4.2 Characterization of Remediation Wastes**

For the purpose of characterizing Remediation Wastes, as well as other purposes, the sum of the 3 EPH fractions (i.e., C9-C18 Aliphatics, C19-C36 Aliphatics, and C11-C22 Aromatics) is equivalent to a TPH concentration, as defined by the MCP.

#### **5.4.3 Characterization of Remedial Air Emissions**

Requirements for the evaluation and/or treatment of remedial air emissions are specified in the MCP at 310 CMR 40.0049. Further guidance in this regard is provided in *Off-Gas Treatment of Point-Source Remedial Air Emissions*, Policy #WSC-94-150, available at <http://www.state.ma.us/dep/bwsc/finalpol.htm>

For the purposes of characterizing remedial air emissions at petroleum-contaminated sites, the following guidelines may be applied:

- The specification in 310 CMR 40.0049(5) to achieve 95% removal of emitted oil and hazardous materials applies to the collective concentrations of all influent/effluent hydrocarbons, not to individual target analytes and/or hydrocarbon ranges. Therefore, if monitored by the APH method, the collective concentration of all influent Target Analytes and hydrocarbon ranges is compared to the collective concentration of all effluent Target Analytes and hydrocarbon ranges.
- Consistent with the recommendations contained in Section 5.0 of *Off-Gas Treatment of Point-Source Remedial Air Emissions*, it is permissible to monitor influent and effluent vapor concentrations using a portable PID or FID unit. In such cases, the PID unit should be calibrated to an isobutylene response standard, and the FID unit should be calibrated to a methane response standard. At sites where gasoline vapors are being emitted, the PID must be equipped with a minimum 10.0 eV lamp. When using a PID or FID unit to monitor vapor emissions, a reading of 1 ppmV or less can generally be considered a "background" concentration.
- It is permissible to evaluate off-gas remedial emissions using the Emission-Distance Graphs contained in Section 7.3 of *Off-Gas Treatment of Point-Source Remedial Air Emissions*. When using these graphs, the C5-C8 Aliphatic, C9-C12 Aliphatic, and C9-C18 Aliphatic Hydrocarbon ranges are considered "Group 4" contaminants, and the C9-C10 Aromatic and C11-C22 Aromatic Hydrocarbon Fractions are considered "Group 3" contaminants.

#### **5.4.4 Characterization of Coal Tar Contaminated Sites**

MADEP is evaluating the applicability of the VPH/EPH approach in the characterization of sites contaminated by coal tars. As an interim recommendation, the use of VPH and EPH would appear to be an appropriate approach to characterize the risks posed by the aliphatic and aromatic hydrocarbons that comprise coal tars; because of the chemistry of this material, aliphatic and aromatic ranges quantitated by both the VPH and EPH methods would appear to be necessary, along with all method Target Analytes except MtBE (i.e., BTEX and the 17 Target PAHs). In addition to the aliphatic and aromatic ranges and Target Analytes, additional contaminants of concern for coal tars would include phenolics, cyanide, and trace metals.

**APPENDIX 1**  
**Collecting and Preserving VPH Samples**  
**Page 1 of 3**

**SOIL SAMPLES**

**OPTION 1: In-Field Methanol Preservation Technique**

**PERFORMANCE STANDARD:** Obtain undisturbed soil sample and immediately preserve with methanol at a ratio of 1 mL methanol per 1 gram soil (+/- 25%).

Step 1: Choose appropriate sampling container:

60 mL wide mouth packer bottle; or  
60 mL straight sided wide mouth bottle; or  
60 mL VOA vial; or  
40 mL VOA vial

All sampling containers should have an open-top screw cap with Teflon-coated silicone rubber septa or equivalent.

Step 2: Pre-label each container with a unique alpha/numerical designation. Obtain and record tare (empty) weight of each container to nearest 0.1 gram. *This information must be available to the laboratory performing the analyses.*

Step 3: Add 25 mLs of purge and trap grade methanol to 60 mL containers, or 15 mL to 40 mL containers. *It is essential that the methanol be purge and trap grade or equivalent quality.* Immediately cap the container. Make a mark on the 60 mL containers approximately 15 mL above the level of methanol, or a mark on the 40 mL container approximately 10 mL above the level of methanol. The objective is to obtain 25 grams of soil in the 60 mL container, or 15 grams of soil in the 40 mL container, which is approximately 15 and 10 mL of soil volume, respectively, depending upon soil type and moisture content. Other masses of soil are permissible, as long as the ratio of [grams soil]/[mL methanol] is 1:1, +/- 25%. Store at 4°C. *The use of a methanol trip blank prepared in this manner is recommended.*

Step 4: In the field, carefully add soil to the sample container, until the level of methanol in the vial reaches the designated volumetric mark. For wet soil, add slightly beyond the mark. **IN NO CASE, HOWEVER, MAY THE LEVEL OF SOIL IN THE CONTAINER RISE ABOVE THE LEVEL OF METHANOL.** The use of a 10-30 mL disposable syringe with the end cut off is recommended to obtain an undisturbed soil sample from freshly exposed soils. In such cases, obtain and extrude the soil into sample container, avoiding splashing methanol out of the container.

*Optional: use a field electronic balance to ensure addition of desired mass of soil (25 grams to 60 mL containers, 15 grams to 40 mL containers).*

Step 5: Use a clean brush or paper towel to remove soil particles from the threads of the sample container and screw cap. Tightly apply and secure screw cap. Gently swirl sample to break up soil aggregate, if necessary, until soil is covered with methanol. **DO NOT SHAKE.** Duplicate samples obtained in this manner are recommended. A split-sample must also be obtained for a determination of soil moisture content. This sample must NOT be preserved in methanol. **HINT:** fill this container 1/2 full, to allow screening of the sample headspace by the field investigator or the laboratory.

Step 6: Immediately place containers in cooler for storage in an upright position. Sample vials may be placed in separate sealable bags to protect containers in case of leakage during transport. Transport to analytical laboratory using appropriate chain-of-custody procedures and forms.



**APPENDIX 1**  
**Collecting and Preserving VPH Samples**  
**Page 2 of 3**

**SOIL SAMPLES (Continued)**

**OPTION 2: Use of a Sealed-Tube Sampling/Storage Device**

**PERFORMANCE STANDARD:**      **Obtain undisturbed soil sample and immediately seal in air-tight container, for shipment to laboratory and immersion in methanol within 48 hours.**

Step 1:                      Obtain pre-cleaned and/or disposable samplers/containers that allow the collection and air-tight storage of 5- 25 grams of soil.

Step 2:                      In the field, obtain an undisturbed sample from freshly exposed soil. Immediately seal container, and place in a cooler. Obtain a duplicate sample to enable the determination of soil moisture content (this may be stored/sealed in a conventional container). Transport to analytical laboratory using appropriate chain-of-custody procedures and forms.

Step 3:                      Samples must be extruded and immersed in purge and trap (or equivalent) grade methanol at the laboratory within 48 hours of sampling, at a ratio of 1 mL methanol to 1 gram soil. In no case, however, shall the level of soil in the laboratory container exceed the level of methanol (i.e., the soil must be completely immersed in methanol).

*NOTE: Documentation MUST be provided/available on the ability of the sampler/container to provide an air-tight seal in a manner that results in no statistically significant loss of volatile hydrocarbons for at least 48 hours.*

**OPTION 3: Use of Alternative Collection/Storage/Preservation Techniques**

**PERFORMANCE STANDARD:**      **Obtain and store an undisturbed soil sample in a manner that ensures the chemical integrity of the sample by (1) preventing the volatilization of petroleum hydrocarbons heavier than C5, and (2) preventing the biological degradation of petroleum hydrocarbons.**

*NOTE: The onus is on the user of such techniques to demonstrate the validity of the procedures used, via reference to published literature and/or other pertinent data.*

**SAFETY**

***Methanol is a toxic and flammable liquid, and must be handled with appropriate care. Use in a well-vented area, and avoid inhaling methanol vapors. The use of protective gloves is recommended when handling or transferring methanol. Vials of methanol should always be stored in a cooler with ice at all times, away from sources of ignition such as extreme heat or open flames.***



**APPENDIX 1**  
**Collecting and Preserving VPH Samples**  
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**AQUEOUS SAMPLES**

**MOST VPH/VOC AQUEOUS SAMPLES**

All aqueous samples that will not be analyzed within 4 hours of collection must be preserved by pH adjustment, in order to minimize analyte losses due to biodegradation. For most samples, this can be accomplished by acidification of the sample to pH <2, by adding 3-4 drops of 1:1 HCl to a 40 mL vial. The sample should then be stored at 4°C until it is analyzed. In lieu of acidification, samples may also be preserved with an appropriate base to pH > 11.0 (see below).

**SAMPLES TO BE ANALYZED FOR MtBE**

**ISSUE**

Traditionally, VPH and VOC aqueous samples have been preserved by addition of an acid (e.g., HCl) to lower the pH of the sample to less than 2.0. While this is still an acceptable approach for petroleum hydrocarbons and most VOC analytes, recent information and data have indicated that such a technique can lead to significant losses (up to 89%) of MtBE and other ethers (White, H., Lesnik, B., Wilson, J., *Analytical Methods for Fuel Oxygenates*, LUSTLINE Bulletin #42, New England Interstate Water Pollution Control Commission, 2002 (<http://www.epa.gov/swrust1/mtbe/LL42Analytical.pdf>)). Specifically, the combination of a low pH and high temperature sample preparation technique (e.g., heated purge and trap) hydrolyze the ether bonds present in the sample, converting the ethers into alcohols (e.g., TBA).

**PRESERVING  
MtBE  
SAMPLES**

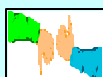
To prevent ether hydrolysis, samples should either (a) not be acidified or (b) not be heated. Because heating the sample may be necessary to achieve proper analyte purging/partitioning, an alternative to acidification is likely to be the most efficient means to prevent hydrolysis. Because ethers are not subject to base-catalyzed hydrolysis, raising the pH of the sample is an acceptable alternative to acidification. Studies by the USEPA have shown that preservation of aqueous samples to a pH greater than 11.0 using trisodium phosphate dodecahydrate will effectively prevent biological degradation of dissolved analytes, and will not result in deleterious effects on other dissolved oxygenates or on BTEX analytes.

**PROTOCOL**

A recommended protocol to achieve a pH level > 11.0 is to add between 0.40 and 0.44 grams of trisodium phosphate dodecahydrate to a 40 mL vial. For convenience, this can be done in the laboratory prior to sample collection in the field. Because it is more convenient to measure the required amount of trisodium phosphate dodecahydrate on a volume basis rather than by weight, the use of a precalibrated spoon is recommended. In the field, each vial is filled with the aqueous sample and sealed without headspace – as is traditionally done for acidified samples. The sample is then stored at 4°C until it is analyzed.

**WHEN IS  
THIS  
NEEDED?**

Given the Method 1 standard for MtBE in GW-2 and GW-3 areas (i.e., 50,000 µg/L), MADEP will generally not expect or require the use of alternative preservation or analytical protocols for disposal sites located ONLY in such areas, with respect to demonstrating attainment of a condition of No Significant Risk. Nevertheless, such efforts should be considered, and may be necessary, on a case-specific basis, to investigate other site assessment objectives, such as extent of contamination, source identification, etc.



For gasoline releases in GW-1 areas, it is generally expected that some level of assessment will be conducted to confirm the concentration of MtBE using alternative preservation and/or analytical procedures to prevent hydrolysis of ethers. In particular, confirmatory samples would be recommended in the “source area” and in the outer plume (or N.D.) monitoring wells. When sampling a private or public drinking water supply well that is proximate to a release of gasoline and/or #2 fuel oil, it is generally expected that all such samples will be evaluated for the presence of MtBE by use of an alternative preservation and/or analytical procedure.

## APPENDIX 2 SHIPPING METHANOL PRESERVED SAMPLES

### Shipping of Hazardous Materials

Methanol is considered a hazardous material by the US Department of Transportation (DOT) and the International Air Transport Association (IATA). Shipments of methanol between the field and the laboratory must conform to the rules established in Title 49 of the Code of Federal Regulations (49 CFR parts 171 to 179), and the most current edition of the IATA Dangerous Goods Regulations. Consult these documents or your shipping company for complete details, as these regulations may change without notice.

### Small Quantity Exemption

The volumes of methanol recommended in the VPH method fall under the small quantity exemption of 49 CFR section 173.4. To qualify for this exemption, all of the following must be met:

- ◇ the maximum volume of methanol in each sample container must not exceed 30 mL
- ◇ the sample container must not be full of methanol
- ◇ the sample container must be securely packed and cushioned in an upright position, and be surrounded by a sorbent material capable of absorbing spills from leaks or breakage of sample containers
- ◇ the package weight must not exceed 64 pounds
- ◇ the volume of methanol per shipping container must not exceed 500 mL
- ◇ the packaging and shipping container must be strong enough to hold up to the intended use
- ◇ the package must not be opened or altered while in transit
- ◇ the shipper must mark the shipping container in accordance with shipping dangerous goods in acceptable quantities, and provide the statement:

*“This package conforms to conditions and limitations specified in 49 CFR 173.4”*

### Shipping Papers

All shipments must be accompanied by shipping papers that include the following:

Proper Shipping Name:	Methyl Alcohol
Hazardous Class:	Flammable Liquid
Identification Number:	UN1230
Total Quantity:	<i>(mL methanol/container x the number of containers)</i>
Emergency Response Info:	Methanol MSDS attached
Emergency Response Phone:	<i>provide appropriate number</i>
Shipping Exemption:	DOT-E 173.118, Limited Quantity

### Labeling & Placarding

Labeling and placarding are not required for valid small quantity exemptions (per 173.118)

## APPENDIX 3 - Required VPH Data Report Content

### SAMPLE INFORMATION

<b>Matrix</b>	<input type="checkbox"/> Aqueous <input type="checkbox"/> Soil <input type="checkbox"/> Sediment <input type="checkbox"/> Other:		
<b>Containers</b>	<input type="checkbox"/> Satisfactory <input type="checkbox"/> Broken <input type="checkbox"/> Leaking:		
<b>Sample Preservatives</b>	Aqueous	<input type="checkbox"/> N/A <input type="checkbox"/> pH<2 <input type="checkbox"/> pH>2 Comment:	
	Soil or Sediment	<input type="checkbox"/> N/A <input type="checkbox"/> Samples NOT preserved in Methanol or air-tight container	
		<input type="checkbox"/> Samples rec'd in Methanol: <input type="checkbox"/> covering soil <input type="checkbox"/> not covering soil	
	<input type="checkbox"/> Samples received in air-tight container:		mL Methanol/g soil <input type="checkbox"/> 1:1 +/- 25% <input type="checkbox"/> Other:
<b>Temperature</b>	<input type="checkbox"/> Received on Ice <input type="checkbox"/> Received at 4 °C <input type="checkbox"/> Other:		

### VPH ANALYTICAL RESULTS

<b>Method for Ranges: MADEP VPH 98-1</b>		<b>Client ID</b>						
<b>Method for Target Analytes:</b>		<b>Lab ID</b>						
<b>VPH Surrogate Standards</b>		<b>Date Collected</b>						
PID:		<b>Date Received</b>						
FID:		<b>Date Analyzed</b>						
		<b>Dilution Factor</b>						
		<b>% Moisture (soil)</b>						
<b>Range/Target Analyte</b>	<b>Elution Range</b>	<b>RL</b>	<b>Units</b>					
Unadjusted C5-C8 Aliphatics <sup>1</sup>	N/A							
Unadjusted C9-C12 Aliphatics <sup>1</sup>	N/A							
Benzene								
Ethylbenzene								
Methyl-tert-butylether								
Naphthalene	N/A							
Toluene								
m- & p- Xylenes								
o-Xylene								
C5-C8 Aliphatic Hydrocarbons <sup>1,2</sup>	N/A							
C9-C12 Aliphatic Hydrocarbons <sup>1,3</sup>	N/A							
C9-C10 Aromatic Hydrocarbons <sup>1</sup>	N/A							
PID Surrogate % Recovery								
FID Surrogate % Recovery								
Surrogate Acceptance Range				70-130%	70-130%	70-130%	70-130%	70-130%

<sup>1</sup>Hydrocarbon Range data exclude concentrations of any surrogate(s) and/or internal standards eluting in that range  
<sup>2</sup> C<sub>5</sub>-C<sub>8</sub> Aliphatic Hydrocarbons exclude the concentration of Target Analytes eluting in that range  
<sup>3</sup> C<sub>9</sub>-C<sub>12</sub> Aliphatic Hydrocarbons exclude conc of Target Analytes eluting in that range AND concentration of C<sub>9</sub>-C<sub>10</sub> Aromatic Hydrocarbons

### CERTIFICATION

Were all QA/QC procedures REQUIRED by the VPH Method followed?	<input type="checkbox"/> Yes <input type="checkbox"/> No - Details Attached
Were all performance/acceptance standards for required QA/QC procedures achieved?	<input type="checkbox"/> Yes <input type="checkbox"/> No - Details Attached
Were any significant modifications made to the VPH method, as specified in Sect 11.3?	<input type="checkbox"/> No <input type="checkbox"/> Yes - Details Attached
<i>I attest under the pains and penalties of perjury that, based upon my inquiry of those individuals immediately responsible for obtaining the information, the material contained in this report is, to the best of my knowledge and belief, accurate and complete.</i>	
SIGNATURE: _____	POSITION: _____
PRINTED NAME: _____	DATE: _____

**APPENDIX 3 - Supplemental VPH QA/QC data (Optional)**

**QA/QC DATA**

Range/Target Analyte	Range of Elution	Reporting Limit	Lab Method Blank	Duplicate Sample			Lab Fortified Blank	
				Sample	Duplicate	%RPD	Spiking Conc	% Recov
Unadjusted C5-C8 Aliphatics	N/A						N/A	N/A
Unadjusted C9-C12 Aliphatics	N/A						N/A	N/A
Pentane								
2-Methylpentane								
Methyl-t-butylether								
2,2,4-Trimethylpentane								
Benzene								
Toluene								
n-Nonane								
Ethylbenzene								
m- & p- Xylenes								
Naphthalene								
C5-C8 Aliphatics Hydrocarbons	N/A						N/A	N/A
C9-C12 Aliphatics Hydrocarbons	N/A						N/A	N/A
C9-C10 Aromatics Hydrocarbons	N/A						N/A	N/A
Sample Matrix								
Units								
Sample ID number		N/A						
Date Analyzed		N/A						

**VPH SOIL PRESERVATION DATA**

	Client ID									
	Lab ID									
<b>A</b>	Tare Wt. Jar (g)									
<b>B</b>	Vol Methanol Initially Added (mL)									
<b>C</b>	Wt. Jar & Methanol (g)									
<b>D</b>	Wt Jar, Methanol & Soil (g)									
<b>D-C</b>	Wt. Soil (g)									
<b>E</b>	Est Vol loss Methanol after sampling (mL)									
<b>F</b>	Vol Methanol added after sampling (mL)									
<b>B-E+F</b>	Final Vol Methanol Preservative (mL)									
<b>G</b>	Vol Surrogates/Internal Stds Added (mL)									
<b>H</b>	Volume of Matrix Spikes Added (mL)									

## APPENDIX 3 – Required EPH Data Report Content

### SAMPLE INFORMATION

<b>Matrix</b>	<input type="checkbox"/> Aqueous <input type="checkbox"/> Soil <input type="checkbox"/> Sediment <input type="checkbox"/> Other:
<b>Containers</b>	<input type="checkbox"/> Satisfactory <input type="checkbox"/> Broken <input type="checkbox"/> Leaking:
<b>Aqueous Preservatives</b>	<input type="checkbox"/> N/A <input type="checkbox"/> pH $\leq$ 2 <input type="checkbox"/> pH>2   Comment:
<b>Temperature</b>	<input type="checkbox"/> Received on Ice <input type="checkbox"/> Received at 4 ° C <input type="checkbox"/> Other:
<b>Extraction Method</b>	Water: _____ Soil: _____

### EPH ANALYTICAL RESULTS

Method for Ranges: MADEP EPH 98-1	Client ID					
Method for Target Analytes:	Lab ID					
<b>EPH Surrogate Standards</b> Aliphatic: Aromatic:	Date Collected					
	Date Received					
	Date Extracted					
<b>EPH Fractionation Surrogates</b>	Date Analyzed					
	Dilution Factor					
	% Moisture (soil)					
RANGE/TARGET ANALYTE	RL	Units				
<b>Unadjusted C11-C22 Aromatics<sup>1</sup></b>						
<b>Diesel PAH Analytes</b>	Naphthalene					
	2-Methylnaphthalene					
	Phenanthrene					
	Acenaphthene					
<b>Other Target PAH Analytes</b>						
<b>C9-C18 Aliphatic Hydrocarbons<sup>1</sup></b>						
<b>C19-C36 Aliphatic Hydrocarbons<sup>1</sup></b>						
<b>C11-C22 Aromatic Hydrocarbons<sup>1,2</sup></b>						
<b>Aliphatic Surrogate % Recovery</b>						
<b>Aromatic Surrogate % Recovery</b>						
<b>Sample Surrogate Acceptance Range</b>			40-140%	40-140%	40-140%	40-140%
<b>Fractionation Surrogate % Recovery</b>						
<b>Fractionation Surrogate % Recovery</b>						
<b>Fractionation Surrogate Acceptance Range</b>			40-140%	40-140%	40-140%	40-140%

<sup>1</sup>Hydrocarbon Range data exclude concentrations of any surrogate(s) and/or internal standards eluting in that range  
<sup>2</sup> C11-C22 Aromatic Hydrocarbons exclude the concentration of Target PAH Analytes

### CERTIFICATION

Were all QA/QC procedures <b>REQUIRED</b> by the EPH Method followed?	<input type="checkbox"/> Yes <input type="checkbox"/> No-Details Attached
Were all performance/acceptance standards for the required QA/QC procedures achieved?	<input type="checkbox"/> Yes <input type="checkbox"/> No-Details Attached
Were any significant modifications made to the EPH method, as specified in Section 11.3?	<input type="checkbox"/> No <input type="checkbox"/> Yes-Details Attached
<i>I attest under the pains and penalties of perjury that, based upon my inquiry of those individuals immediately responsible for obtaining the information, the material contained in this report is, to the best of my knowledge and belief, accurate and complete.</i>	
<b>SIGNATURE:</b> _____	<b>POSITION:</b> _____
<b>PRINTED NAME:</b> _____	<b>DATE:</b> _____

## APPENDIX 3 - Recommended TPH Data Report Content

### SAMPLE INFORMATION

Matrix	<input type="checkbox"/> Aqueous <input type="checkbox"/> Soil <input type="checkbox"/> Sediment <input type="checkbox"/> Other:
Containers	<input type="checkbox"/> Satisfactory <input type="checkbox"/> Broken <input type="checkbox"/> Leaking:
Aqueous Preservatives	<input type="checkbox"/> N/A <input type="checkbox"/> pH $\leq$ 2 <input type="checkbox"/> pH $>$ 2   Comment:
Temperature	<input type="checkbox"/> Received on Ice <input type="checkbox"/> Received at 4 ° C <input type="checkbox"/> Other:
Extraction Method	Water: _____ Soil: _____

### TPH ANALYTICAL RESULTS

Method: MADEP EPH 98-1		Client ID						
Method for Target Analytes:		Lab ID						
TPH Surrogate Standards		Date Collected						
		Date Received						
		Date Extracted						
		Date Analyzed						
		Dilution Factor						
		% Moisture (soil)						
Range/Target Analyte		RL	Units					
Unadjusted Total Petroleum Hydrocarbons <sup>1</sup>								
Diesel PAH Analytes	Naphthalene							
	2-Methylnaphthalene							
	Phenanthrene							
	Acenaphthene							
Other PAH Target Analytes								
Total Petroleum Hydrocarbons <sup>2</sup>								
Sample Surrogate % Recovery								
Sample Surrogate Acceptance Range				40-140%	40-140%	40-140%	40-140%	40-140%
<sup>1</sup> Hydrocarbon Range data exclude concentrations of any surrogate(s) and/or internal standards eluting in that range <sup>2</sup> Total Petroleum Hydrocarbons exclude the concentration of PAH Target Analytes								

### CERTIFICATION

Were all QA/QC procedures REQUIRED by the EPH Method (for TPH) followed?	<input type="checkbox"/> Yes <input type="checkbox"/> No-Details Attached
Were all performance/acceptance standards for the required QA/QC procedures achieved?	<input type="checkbox"/> Yes <input type="checkbox"/> No-Details Attached
Were any significant modifications made to the EPH method, as specified in Section 11.3?	<input type="checkbox"/> No <input type="checkbox"/> Yes-Details Attached
<i>I attest under the pains and penalties of perjury that, based upon my inquiry of those individuals immediately responsible for obtaining the information, the material contained in this report is, to the best of my knowledge and belief, accurate and complete.</i>	
SIGNATURE: _____	POSITION: _____
PRINTED NAME: _____	DATE: _____





**APPENDIX 4 - VPH/EPH Cleanup Standards and Reportable Concentrations**  
**October 31, 1997**

**Reportable Concentrations**

Fraction/Parameter	RCS-1 (mg/g)	RCS-2 (mg/g)	RCGW-1 (mg/L)	RCGW-2 (mg/L)
C5-C8 Aliphatic Hydrocarbons	100	500	400	1000
C9-C12 Aliphatic Hydrocarbons	1000	2500	1000	1000
C9-C10 Aromatic Hydrocarbons	100	500	200	4000
C9-C18 Aliphatic Hydrocarbons	1000	2500	1000	1000
C19-C36 Aliphatic Hydrocarbons	2500	5000	5000	20,000
C11-C22 Aromatic Hydrocarbons	200	2000	2000	30,000
Total Petroleum Hydrocarbons (TPH)	200	2000	2000	1000

**Method 1 Cleanup Standards for Groundwater**

Fraction/Parameter	GW-1 (mg/L)	GW-2 (mg/L)	GW-3 (mg/L)
C5-C8 Aliphatic Hydrocarbons	400	1000	4000
C9-C12 Aliphatic Hydrocarbons	4000	1000	20,000
C9-C10 Aromatic Hydrocarbons	200	5000	4000
C9-C18 Aliphatic Hydrocarbons	4000	1000	20,000
C19-C36 Aliphatic Hydrocarbons	5000	N/A	20,000
C11-C22 Aromatic Hydrocarbons	200	50,000	30,000
Total Petroleum Hydrocarbons (TPH)	200	1000	20,000

**Method 1 Cleanup Standards for Soil**

Fraction/Parameter	GW-1 Areas			GW-2 Areas			GW-3 Areas		
	S-1 (mg/g)	S-2 (mg/g)	S-3 (mg/g)	S-1 (mg/g)	S-2 (mg/g)	S-3 (mg/g)	S-1 (mg/g)	S-2 (mg/g)	S-3 (mg/g)
C5-C8 Aliphatic Hydrocarbons	100	500	500	100	500	500	100	500	500
C9-C12 Aliphatic Hydrocarbons	1000	2500	5000	1000	2500	5000	1000	2500	5000
C9-C10 Aromatic Hydrocarbons	100	100	100	100	500	500	100	500	500
C9-C18 Aliphatic Hydrocarbons	1000	2500	5000	1000	2500	5000	1000	2500	5000
C19-C36 Aliphatic Hydrocarbons	2500	5000	5000	2500	5000	5000	2500	5000	5000
C11-C22 Aromatic Hydrocarbons	200	200	200	800	2000	5000	800	2000	5000
Total Petroleum Hydrocarbons (TPH)	200	200	200	800	2000	5000	800	2000	5000

**Upper Concentration Limits (UCLs)**

Fraction/Parameter	Groundwater (mg/L)	Soil (mg/g)
C5-C8 Aliphatic Hydrocarbons	100,000	5000
C9-C12 Aliphatic Hydrocarbons	100,000	20,000
C9-C10 Aromatic Hydrocarbons	100,000	5000
C9-C18 Aliphatic Hydrocarbons	100,000	20,000
C19-C36 Aliphatic Hydrocarbons	100,000	20,000
C11-C22 Aromatic Hydrocarbons	100,000	10,000
Total Petroleum Hydrocarbons (TPH)	100,000	10,000

**Cleanup Standards are subject to change; consult latest version of the MCP for most up to date values!**

## APPENDIX 5 - ADDITIONAL REFERENCE/SUPPORT MATERIALS



### For a Closer Look.....

The following documents and publications provided additional background, information, and insight into the VPH/EPH approach, guidance, and standards

### MADEP Publications

#### VPH/EPH Approach

- ◇ *Interim Final Petroleum Report: Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter, August, 1994* - Original report presenting the toxicological basis of the proposed new VPH/EPH approach.
- ◇ *Issues Paper: Implementation of VPH/EPH Approach, Public Comment Draft, May, 1996* - Detailed discussion and recommendations on how to develop MCP Method 1 cleanup standards, and otherwise incorporate new VPH/EPH approach into the MCP regulatory process.
- ◇ *Beyond TPH: Understanding and Using the New VPH/EPH Approach, June, 1997* - Slides and handouts from a day-long training session presented by MADEP in the Spring of 1997.
- ◇ *#2 Fuel/Diesel Short Form, July, 2002* - An Excel spreadsheet that allows for the site-specific characterization of human health risks for Target Analytes and appropriate aliphatic/aromatic hydrocarbon fractions.
- ◇ *Reports on the Results of the VPH/EPH Round Robin Testing Programs, June 1997 and January 1998* - Detailed reports outlining the methods and results of two interlaboratory "Round Robin" testing programs undertaken by MADEP to help refine and validate the VPH and EPH analytical test methods.
- ◇ *Method for the Determination of Volatile Petroleum Hydrocarbons (VPH), January, 1998* - Detailed analytical procedure for this GC/PID/FID methodology developed by MADEP.
- ◇ *Method for the Determination of Extractable Petroleum Hydrocarbons (EPH), January, 1998* - Detailed analytical procedure for this silica-gel/fractionation GC/FID method developed by MADEP.
- ◇ *Draft Method for the Determination of Air-Phase Petroleum Hydrocarbons (APH), February, 2000* - Proposed analytical procedure for this GC/MS methodology developed by MADEP.
- ◇ *Background Documentation for the Development of VPH/EPH Cleanup Standards and Guidance, October, 2002*, available at [http://www.state.ma.us/dep/bwsc/vph\\_eph.htm](http://www.state.ma.us/dep/bwsc/vph_eph.htm)

#### Related MADEP Regulations and Guidance Documents

- ◇ *Massachusetts Contingency Plan (MCP), 310 CMR 40.0000* - State regulations that govern the cleanup of sites contaminated by oil or hazardous materials; now includes provisions for VPH/EPH approach and standards.
- ◇ *Background Documentation for the Development of the MCP Numerical Standards, April, 1994* - Contains information, data, assumptions, approaches, and spreadsheets for development of the MCP Method 1 cleanup standards, excluding VPH/EPH fractional range standards.
- ◇ *Guidance for Disposal Site Risk Characterization in Support of the Massachusetts Contingency Plan, July, 1995* - Comprehensive guidance on how to characterize risks to human and ecological receptors.

## APPENDIX 5 - ADDITIONAL REFERENCE/SUPPORT MATERIALS (continued)

### Related MADEP Regulations and Guidance Documents (continued)

- ◇ *Commonwealth of Massachusetts Underground Storage Tank Closure Assessment Manual, April, 1996* - Outlines requirements and procedures for conducting a closure assessment of underground storage tanks.
- ◇ *Interim Remediation Waste Management Policy for Petroleum Contaminated Soils, April, 1994* - Procedures, requirements, and recommendations for characterizing, classifying, managing, and recycling/disposing of petroleum contaminated soils.

All MADEP publications available on the World Wide Web at <http://www.state.ma.us/dep/bwsc/pubs.htm>

### Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) Publications

TPHCWG is a national consortium of state regulatory agencies, academia, DOD, DOE, USEPA, ASTDR, petroleum, power and transportation industries, and consulting firms. The goal of this group is to evaluate and propose methods to characterize risks posed by petroleum-contaminated media. TPHCWG has endorsed a toxicological approach similar to the MADEP VPH/EPH approach. Recommendations by this group on evaluating the fate and transport of aliphatic and aromatic hydrocarbon fractions were used by MADEP in developing the cleanup standards and the guidelines and recommendations contained in this policy. TPHCWG plans on publishing a six-volume series of reports on issues of interest; volumes of interest to parties using the VPH/EPH approach are listed below:



- ◇ *Volume I – Analysis of Petroleum Hydrocarbons in Environmental Media (1998)* - Contains an overview of petroleum hydrocarbon characterization and risk assessment, a discussion of available analytical methods, and a proposed GC-Based analytical method, developed by the Working group, that reports hydrocarbon results in equivalent carbon number groups or fractions.
- ◇ *Volume II - Composition of Petroleum Mixtures* – Contains a description of the chemical characteristics and composition of petroleum fuels, with a comprehensive series of tables and references.
- ◇ *Volume III - Selection of TPH Fractions Based upon Fate and Transport Consideration (1997)*- Contains information and data on the physical and chemical properties of hydrocarbons and hydrocarbon mixtures, and recommended algorithms for determining the properties of aliphatic and aromatic fractions.
- ◇ *Volume IV - Development of Fraction-Specific Reference Doses (RfDs) and Reference Concentrations (RfCs) for Total Petroleum Hydrocarbons (TPH) (1997)* - Contains extensive information and data on the toxicological properties of petroleum products and hydrocarbon mixtures, and a proposed approach to characterize risks based upon the collective fractions of aliphatic and aromatic fractions. NOTE: Certain provisions of these recommendations are in conflict with current MADEP positions and requirement, although the agency is currently evaluating recent data presented in this volume.

**TPHCWG Publications are being cited as potentially relevant background/reference materials. MADEP is not necessarily endorsing the conclusions and/or recommendations provided in these various documents.**

TPHCWG Publications available on the World Wide Web at  
<http://www.aehs.com/publications/catalog/contents/tph.htm>

**APPENDIX 6**  
**SUMMARY OF SIGNIFICANT CHANGES MADE TO FINAL IMPLEMENTATION POLICY**

<b>BY SECTION</b>		
<b>Section</b>	<b>Subject</b>	<b>Change/Addition</b>
1.3	Applicability	New explanation of VPH/EPH reporting obligations at closed sites
3.2.3	APH	New explanation of Air-Phase Petroleum Hydrocarbon (APH) method
3.5	Method Modification	New guidance on evaluating modifications to VPH/EPH/APH procedures
3.7	Other Testing Methods	New guidance on use of TPH and other hydrocarbon testing procedures
4.1	Exposure Point Conc.	New Section 4.1 added with additional guidance on determining EPCs
4.2.2	Target Analytes	<b>Modifications of Table 43, additional information and guidance on lead, EDB, MtBE, and other petroleum additives</b>
4.3	Vapor Pathway	Expanded “tool box” approach to investigate (Figure 4-1) and mitigate (Figure 4-3) subsurface vapor infiltration pathways
4.3.1	Soil Gas Screening	Additional guidance on location of soil gas probes; <b>new criteria for PID/FID Level 1 Screening (Table 4-9)</b> ; additional guidance on Level 2 Screening
4.3.1.1	Soil Gas Guidelines	Certain Target Analytes added to Tables 4-9, 4-10, and 4-11; criteria now relevant to soil contamination, as well as GW -2 exceedances
4.3.1.4	Vapor Transport Models	New reference to DEP policy on use/utility of transport models
4.3.1.5	Groundwater Profiling	New guidance on evaluating indoor air pathways by profiling contaminant concentrations at and below the groundwater table
4.3.2	GW -3 Evaluation	<b>New Dilution Graphs (Figure 4-4) and guidance to evaluate plume dispersion</b>
4.5	Toxicological parameters	<b>New RfD and RfC values for certain fractions</b>
4.6	Fate/Transport Parameters	New aqueous diffusivity coefficients for hydrocarbon fractions
4.7	NAPL	Additional guidance on NAPL monitoring and evaluation
5.4.1	NRS	New recommended mobility and persistence scoring criteria (Table 5-2) for hydrocarbon fractions when using Numerical Ranking System
5.4.3	Remedial Air Emissions	<b>New recommendations on monitoring and evaluating off-gas treatment for remedial air emissions</b>
App 1	MtBE analysis	<b>New information/guidelines on preservation of aqueous samples for MtBE analysis (Due to degradation caused by acidification)</b>
App 3	VPH/EPH Report Format	Required Reporting Format for VPH/EPH methods
App 5	References	Additional references/support materials for VPH/EPH approach

**Shading indicates changes that were made AFTER issuance of FINAL DRAFT document (June 2001)**

**APPENDIX 6**  
**SUMMARY OF SIGNIFICANT CHANGES MADE TO FINAL IMPLEMENTATION POLICY**  
**(Continued)**

<b>BY SUBJECT</b>		
<b>Subject</b>	<b>Section</b>	<b>Change/Addition</b>
APH	3.2.3	New explanation of Air-Phase Petroleum Hydrocarbon (APH) method
Applicability	1.3	New explanation of VPH/EPH reporting obligations at closed sites
Exposure Point Conc.	4.1	New Section 4.1 added with additional guidance on determining EPCs
Fate/Transport Parameters	4.6	New aqueous diffusivity coefficients for hydrocarbon fractions
Groundwater Profiling	4.3.1.5	New guidance on evaluating indoor air pathways by profiling contaminant concentrations at and below the groundwater table
GW -3 Evaluations	4.3.2	<b>New Dilution Graphs (Figure 4-4) and guidance to evaluate plume dispersion</b>
Method Modifications	3.5	New guidance on evaluating modifications to VPH/EPH/APH procedures
MtBE analysis	App 1	<b>New information/guidelines on preservation of aqueous samples for MtBE analysis (Due to degradation caused by acidification)</b>
NAPL	4.7	Additional guidance on NAPL monitoring and evaluation
NRS	5.4.1	New recommended mobility and persistence scoring criteria (Table 5-2) for hydrocarbon fractions when using Numerical Ranking System
Other Testing Methods	3.7	New guidance on use of TPH and other hydrocarbon testing procedures
References	App5	Additional references/support materials for VPH/EPH approach
Remedial Air Emissions	5.4.3	<b>New recommendations on monitoring and evaluating off-gas treatment for remedial air emissions</b>
Soil Gas Screening	4.3.1	Additional guidance on location of soil gas probes; <b>new criteria for PID/FID Level 1 Screening (Table 4-9)</b> ; additional guidance on Level 2 Screening
Soil Gas Guidelines	4.3.1.1	Certain Target Analytes added to Table 4-9, 4-10, and 4-11; criteria now relevant to soil contamination, as well as GW -2 exceedances
Target Analytes	4.2.2	<b>Modifications of Table 43, additional information and guidance on lead, EDB, MtBE, and other petroleum additives</b>
Toxicological Parameters	4.5	<b>New RfD and RfC values for certain fractions</b>
Vapor Pathway	4.3	Expanded “tool box” approach to investigate (Figure 4-1) and mitigate (Figure 4-3) subsurface vapor infiltration pathways
Vapor Transport Models	4.3.1.4	New reference to DEP policy on use/utility of transport models
VPH/EPH Report Format	App3	Required Reporting Format for VPH/EPH methods

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