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Comments Due By:	August 21, 2026
Comment to:	John Fitzgerald
Email Address:	john.j.fitzgerald@mass.gov
Mailing Address:	MassDEP 150 Presidential Way Woburn MA 01801

Characterization of Petroleum Contaminated Sites

Policy #WSC-

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This document provides guidance on how to fulfill the regulatory requirements of the Massachusetts Contingency Plan (MCP, 310 CMR 40.0000) to adequately investigate and assess sites that have become contaminated by a release of a petroleum product, including gasoline, fuel oils, jet fuel, and waste oil. It updates and replaces the MassDEP publication "*Characterizing Risks Posed by Petroleum Contaminated Sites: Implementation of the MADEP VPH/EPH Approach*", which is dated October 31, 2002.

This document is intended solely as guidance. It does not create any substantive or procedural rights, and is not enforceable by any party in any administrative proceeding with the Commonwealth. This document provides guidance on approaches MassDEP considers acceptable for meeting the general requirements set forth in the MCP. Parties using this guidance should be aware that other acceptable alternatives may be available for achieving compliance with general regulatory requirements.

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Millie Garcia-Serrano
Assistant Commissioner
Bureau of Waste Site Cleanup

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List of Acronyms	
AEPMM	Active Exposure Pathway Mitigation Measure
APH	Air-Phase Petroleum Hydrocarbons
AUL	Activity and Use Limitation
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
CAM	Compendium of Analytical Methods (MassDEP)
CEP	Critical Exposure Pathway
CSM	Conceptual Site Model
ELCR	Excess Lifetime Cancer Risk
EPC	Exposure Point Concentration
EPH	Extractable Petroleum Hydrocarbons
eV	Electron Volt
FAME	Fatty Acid Methyl Esters
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
HI	Hazard Index
HQ	Hazard Quotient
HVAC	Heating, Ventilation, Air-Conditioning
IDA	Inclusion Distance Approach
ITRC	Interstate Technology Regulatory Council
LC50	Lethal Concentration 50% (median lethal conc for aquatic organism)
LEL	Lower Explosive Limit
LNAPL	Light Non-Aqueous Phase Liquid
LSP	Licensed Site Professional
MCP	Massachusetts Contingency Plan, 310 CMR 40.0000
MtBE	Methyl tertiary-butyl ether
NAPL	Non-Aqueous Phase Liquid
NSR	No Significant Risk
OHM	Oil and/or Hazardous Material
OTP	Ortho-terphenyl
PFAS	Per- and Polyfluoroalkyl Substances
PAH	Polycyclic Aromatic Hydrocarbon
PCE	Perchloroethylene (AKA Tetrachloroethylene)
PCB	Polychlorinated Biphenyl
PID	Photoionization Detector
ppbV	Parts-per-billion by volume
ppmV	Parts-per-million by volume
QA/QC	Quality Assurance/Quality Control

List of Acronyms	
RAF	Relative Absorption Factor
RC	Reportable Concentration
RfC	Reference Concentration
RfD	Reference Dose
RL	Reporting Limit
RQ	Reportable Quantity
SRM	Substantial Release Migration
SSDS	Sub-Slab Depressurization System
SSGSV	Sub-slab Soil Gas Screening Value (MassDEP)
TCE	Trichloroethylene
TIAC	Typical Indoor Air Concentration
TIC	Tentatively Identified Compound or Total Ion Chromatogram
TMB	Trimethyl benzene
TOV	Total Organic Vapor
TPH	Total Petroleum Hydrocarbons
TPHCWG	Total Petroleum Hydrocarbon Criteria Working Group
TV	Threshold Value (MassDEP indoor air metrics)
UCM	Unresolved Complex Mixture
UST	Underground Storage Tank
VOC	Volatile Organic Compound
VPH	Volatile Petroleum Hydrocarbons

1.0 INTRODUCTION

1.1 Background

Spills and releases of petroleum fuels and lubricating oils are a significant source of environmental contamination in Massachusetts. Because petroleum products are a complex mixture of hundreds of individual hydrocarbon compounds, characterizing the risks to human health and the environment posed by petroleum contaminants in soil, water and air is challenging.

The Massachusetts Department of Environmental Protection (MassDEP) published a document in August 1994 entitled *Interim Final Petroleum Report: Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter*. This publication, which was updated and finalized in November 2003, presented a new toxicological approach to characterize and evaluate risks posed by petroleum-contaminated sites, by breaking down TPH into collective aliphatic hydrocarbon and aromatic hydrocarbon fractions. A supplemental publication, *Sediment Toxicity of Petroleum Hydrocarbon Fractions*, was issued by MassDEP in September 2007.

To support and implement the agency's toxicological approach, MassDEP developed two analytical methods, *Volatile Petroleum Hydrocarbons* (VPH) and *Extractable Petroleum Hydrocarbons* (EPH), to quantify collective concentrations of aliphatic and aromatic hydrocarbon fractions in soil and water. A third method, for *Air-phased Petroleum Hydrocarbons* (APH), was developed to characterize risks posed by hydrocarbon contaminants within air, particularly indoor air. Each of these methods has been modified and fine-tuned over the last 25 years; the latest versions of all methods are available on the agency's web site in its *Compendium of Analytical Methods* (CAM).

MassDEP has integrated the hydrocarbon fraction approach into its Waste Site Cleanup regulations, the *Massachusetts Contingency Plan* (*MCP* – codified as 310 CMR 40.0000), by developing and promulgating soil and groundwater cleanup standards for the aliphatic and aromatic fractions of interest. These standards became effective on October 31, 1997, and have been modified over the years as new toxicological and/or environmental fate and transport information became available. The collective use and application of the toxicological and testing methods developed by MassDEP is generally referred to as the "VPH/EPH/APH" approach.

The first draft of this guidance, *Characterizing Risks Posed by Petroleum Contaminated Sites: Implementation of the MADEP VPH/EPH Approach*, was issued on October 31, 1997, and the final version was issued on October 31, 2002. This update reflects over 20 years of technical and regulatory changes, and an expanded scope that addresses a broader array of site characterization topics. It includes information and reference materials from two other MassDEP guidance documents, which should be consulted as appropriate:

- *Light Nonaqueous Phase Liquids (LNAPL) and the MCP: Guidance for Site Assessment and Closure*, Policy #WSC-16-450, 2016, and
- *Vapor Intrusion Guidance: Site Assessment, Mitigation, and Closure,* Policy #WSC-16-435. 2016

These documents, as well as the MCP, may be downloaded from the MassDEP web site.

Significant changes and updates from the 2002 guidance are summarized in Appendix 1.

1.2 Purpose and Scope

The purpose of this document is to (1) provide a succinct summary of key provisions of the VPH/EPH/APH approach, (2) provide greater detail and specificity on important elements of this approach, and (3) provide technical and regulatory insight, guidance, and ***Rules of Thumb*** to assist

Licensed Site Professionals (LSPs) and others in understanding and applying this approach and characterizing petroleum contaminated sites in an adequate, practical and cost-effective manner.

Rules of Thumb are suggestions and recommendations on how to approach, evaluate, and resolve investigatory, assessment, and remedial issues. Quantitative metrics are in most cases based upon reasonably conservative 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 and suggestions are based upon current information, and are designed to be protective at most, but not necessarily all sites.

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.**

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, including waste oils.

2.0 SUMMARY OF THE MASSDEP VOLATILE PETROLEUM HYDROCARBON (VPH), EXTRACTABLE PETROLEUM HYDROCARBON (EPH) AND AIR-PHASE PETROLEUM HYDROCARBON (APH) 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 primarily a function of (1) the origin and chemistry of the parent crude oil, (2) refining and blending processes, and (3) the use of oxygenates and/or 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 difficult and expensive to identify and quantify every single hydrocarbon compound present in petroleum-contaminated media. Even if this action were accomplished, there are 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 assessment.

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 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/APH approach (MassDEP, 1994). 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 or Reference Concentration) 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: MassDEP Toxicological Approach for Non-Cancer Health Effects

Hydrocarbon Fraction	Reference Dose (mg/kg/day)	Reference Concentration ($\mu g/m^3$)
C5-C8 Aliphatic Hydrocarbons	0.04	200
C9-C18 Aliphatic Hydrocarbons	0.1	200
C19-C36 Aliphatic Hydrocarbons	2.0	N/A (not volatile)
C9-C22 Aromatic Hydrocarbons	0.03	50

The "carbon number" nomenclature in Table 2-1 refers to the number of carbon atoms in a hydrocarbon compound, regardless of its structure. In this manner, a "C6 aliphatic hydrocarbon" includes straight-chained (i.e., n-hexane,) branched chained (e.g., 2-methylpentane), and cyclic (i.e., cyclohexane) compounds that contain 6 carbon atoms. Similarly, a "C9 aromatic hydrocarbon" compound would include 1,2,4 trimethylbenzene and 1-methyl-2-ethylbenzene.

Beyond the threshold health effects described in Table 2-1, **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 MassDEP publication *Updated Petroleum Hydrocarbon Fraction Toxicity Values for the VPH/EPH/APH Methodology*, November 2003, available on the MassDEP web site.

2.2 Hydrocarbon Fractions of Interest in Soil and Water

Although the non-cancer toxicity of petroleum-contaminated media can be adequately described by division into the four hydrocarbon fractions listed in Table 2-1, MassDEP has chosen to designate six hydrocarbon fractions of interest, because of the following analytical and program considerations:

- EPA analytical methods for soil and water 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 MassDEP maintain this distinction. Moreover, because of the large carbon range covered by this 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 (> C_{12}), 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 (< C_9).

- Given the need for two analytical methods for soil and water samples, 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 VPH/EPH Hydrocarbon Fractions

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
C9-C18 Aliphatics	C9-C12 Aliphatics	VPH	0.1
	C9-C18 Aliphatics	EPH	0.1
C19-C36 Aliphatics	C19-C36 Aliphatics	EPH	2.0
C9-C22 Aromatics	C9-C10 Aromatics	VPH	0.03
	C11-C22 Aromatics	EPH	0.03

2.3 Hydrocarbon Fractions of Interest in Air

The MassDEP Air-phase Petroleum Hydrocarbon (APH) test method was developed to quantify hydrocarbon ranges and target analytes of interest in air samples. It is based upon EPA Method TO-15 for volatile organic compounds and quantifies the same spectrum of hydrocarbons as the VPH method: C_5-C_8 Aliphatic Hydrocarbons, C_9-C_{12} Aliphatic Hydrocarbons, and C_9-C_{10} Aromatic Hydrocarbons, along with a specified list of Target Analytes, including benzene, toluene, ethylbenzene, xylenes (BTEX) and naphthalene.

2.4 Target Analytes of Interest

In addition to the quantification of hydrocarbon fractions, the VPH/EPH/APH approach also involves the quantification of a small number of "Target Analytes", such as BTEX, methyl tertiary-butyl ether (MtBE), and naphthalene. This is done for 4 reasons:

- These specific compounds are often detected/associated with petroleum releases.
- These contaminants have well-characterized toxicities and have long been analyzed at petroleum contaminated sites.
- In a number of cases, these contaminants are the most important "risk drivers", particularly in groundwater, where they may constitute the bulk of the water-soluble fraction of spilled petroleum product(s).

- The list of Target Analytes includes carcinogens, such as benzene, that are needed to define non-threshold/cancer health effects.

Most of the Target Analytes chromatographically elute within the hydrocarbon fractions of interest. In order to avoid "double counting", the VPH, EPH, and APH methods specifically require their subtraction from the range value (similar to analytical surrogate and/or internal standard compounds).

2.5 Relationship of VPH/EPH to Total Petroleum Hydrocarbon (TPH) and Gasoline Range Organics (GRO)

A variety of TPH and GRO test methods have been developed over the years by different parties. Unfortunately, it is often difficult to evaluate and compare these procedures, given a lack of universal and/or transparent details on key analytical parameters, such as extraction/purging procedures, detectors, chromatographic ranges, and peak and "hump" integration procedures. Moreover, most of these procedures do not segregate the more toxic aromatic hydrocarbons from the aliphatic hydrocarbons.

For perspective, an overall relationship between TPH, GRO, VPH, EPH, and Target Analytes is graphically displayed in **Figure 2-1.**

As can be seen in Figure 2-1, if the concentrations of the three EPH fractions and target PAH analytes were added together, the total concentration would be about the same as a traditional "TPH" value. Similarly, if the three VPH fractions and BTEX/MtBE/naphthalene concentrations were added together, the total concentration would be about the same as a GRO value (though this collective value would not include Ethanol, which chromatographically elutes prior to C5-C8 Aliphatic Hydrocarbons). 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, due to analytical and programmatic factors, is further discussed in Section 4.2.2, and graphically illustrated in **Figure 2-2.**

Note that there is no overlap in the aromatic fractions: the C_9-C_{10} Aromatic fraction from the VPH method ends just before the chromatographic elution of naphthalene, and the C_{11}-C_{22} Aromatic fraction from the EPH method starts just after the chromatographic elution of naphthalene.

3.0 ANALYTICAL METHODS

In order to use the VPH/EPH/APH toxicological approach, it is necessary to be able to measure the collective concentrations of aliphatic and aromatic hydrocarbon fractions in impacted media. Because conventional TPH and EPA test methods cannot produce this type of data, MassDEP developed and published detailed analytical methods for the analysis of the volatile and extractable ranges of hydrocarbons in soil and water, and vapor-phase hydrocarbons in air. All of these methods are modifications of existing EPA procedures and use a variety of analytical techniques to separate and quantify the aliphatic and aromatic fractions of interest.

None of these methods are perfect, given the need to strike a balance between accuracy, complexity, and testing costs. Analytical and interpretative assumptions and biases have been incorporated into each method in an effort to help ensure that resultant data and decisions for most sites are reasonably (but not overly) conservative, and thus health protective.

3.1 Gas Chromatography

The VPH/EPH/APH analytical methods utilize the principles of gas chromatography, in combination with a variety of detectors. While most data users focus on the quantitative data produced by these

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

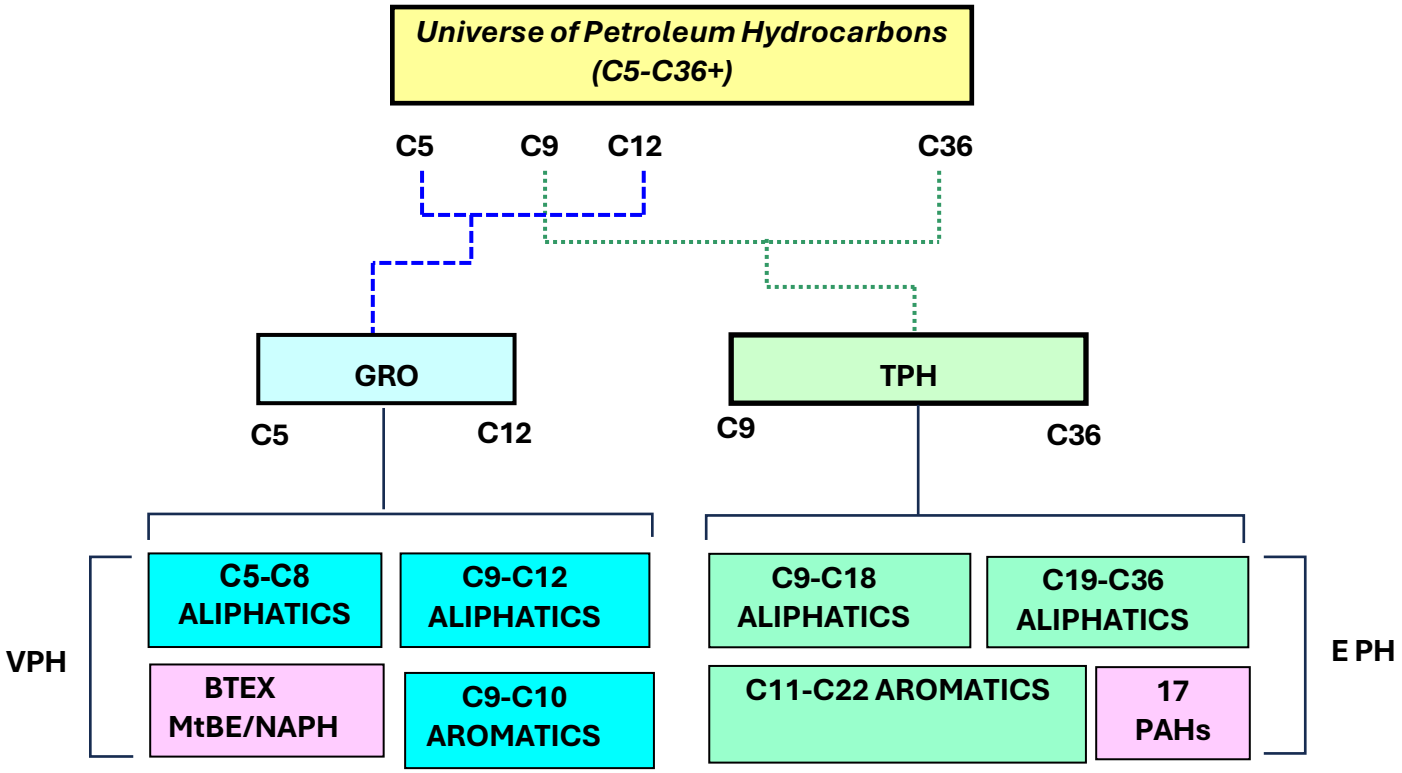
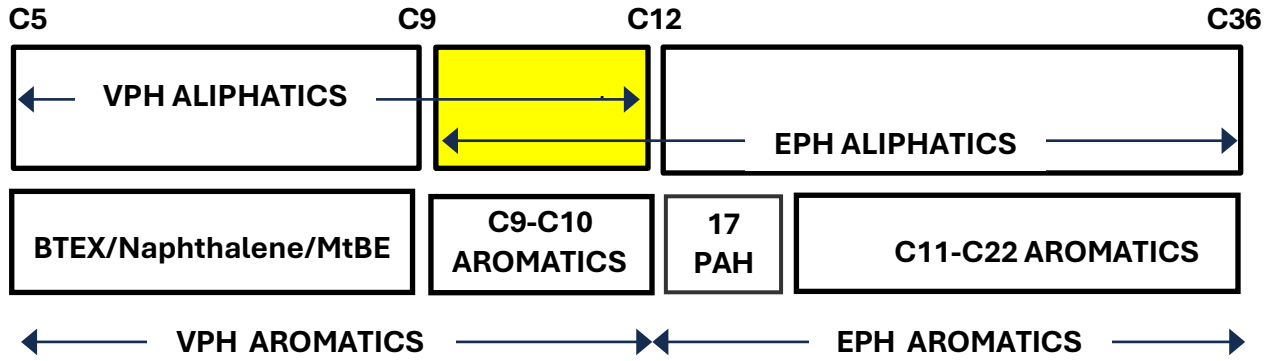


Figure 2-2: Overlap of VPH and EPH Test Methods



procedures, the qualitative information provided by the chromatographic "fingerprints" generated for each sample in each method are often overlooked. This is unfortunate, given the often-valuable insights these chromatograms provide on hydrocarbon chemistry, product type(s), degree of weathering, presence of non-petroleum contaminants, and, in water samples, high-bias results due to the presence of undissolved NAPL.

Chromatography is the separation of compounds or groups of compounds in a complex mixture. In gas chromatography, hydrocarbons in water and soil samples are transferred to the vapor phase by purging (VPH method) or heating (EPH method). The gaseous sample then flows through a (30 – 100 meter long +/-) *capillary column* to a detector, "pushed" along by an inert *carrier gas*, such as nitrogen or helium. 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 retained 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/or boiling point of the compound.

Once they elute from the column, analytes pass through a detector, which ionizes the eluting compounds, producing a small electrical current. 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 or tentatively 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. For methods that use a mass spectrometer detector, compounds tentatively identified on the basis of retention time can be positively confirmed via an evaluation of mass spectra.

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 appropriate sorbents. This trap is then rapidly heated to desorb the analytes, and load them onto a chromatographic column. Volatiles within soil samples 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/APH 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 MassDEP analytical methods use detector selectivity, chemical exchange processes, and extracted ions to fractionate samples, but other techniques may also be acceptable and cost-effective, including comprehensive two-dimensional gas chromatography (GC x GC) approaches.

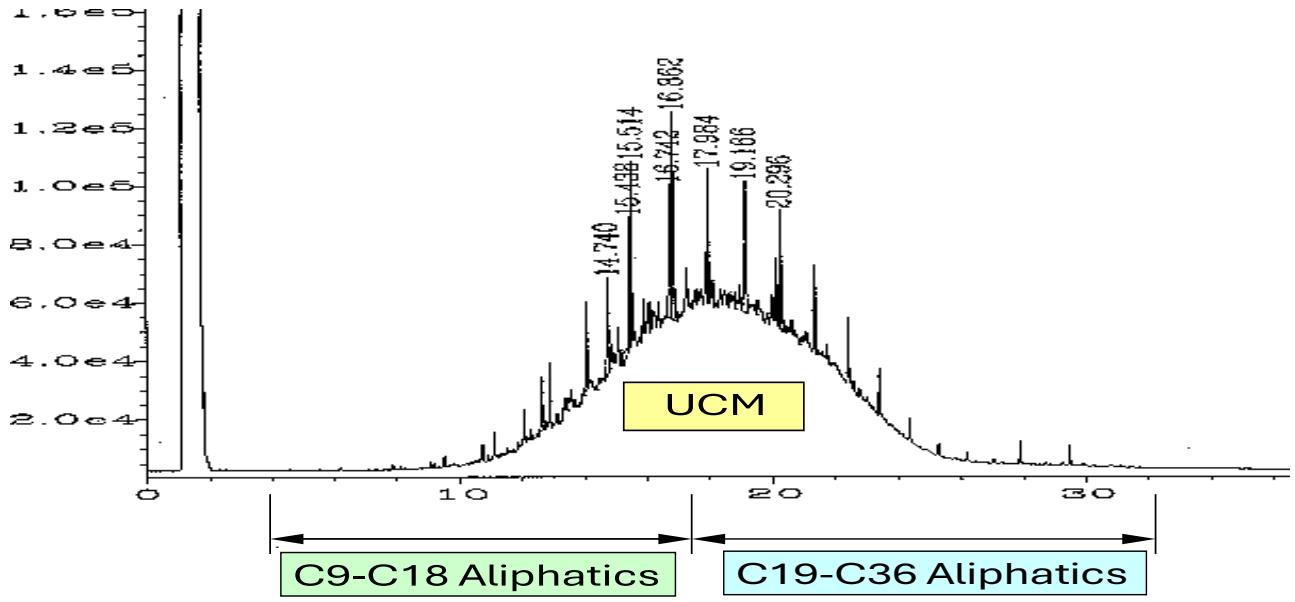
An example of an EPH (GC/FID) chromatogram of the aliphatic portion of a weathered #2 Fuel Oil contaminated soil sample is provided in **Figure 3-1**.

Note that the “x” axis in Figure 3-1 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 MassDEP Analytical Methodologies

The VPH/EPH/APH methods separate complex mixtures of hydrocarbons into collective fractions of aliphatic and aromatic hydrocarbons, and produce data that can be incorporated into the MCP risk assessment process and compared to MCP Method 1 cleanup standards. The analytical methods, along with required steps and documentation required to obtain “Presumptive Certainty” status for data quality, are available in the MassDEP *Compendium of Analytical Methods* (CAM) on the MassDEP web site, and are summarized below.

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



3.2.1 *Volatile Petroleum Hydrocarbons (VPH)*

MassDEP has published two different methodologies to quantify Volatile Petroleum Hydrocarbons (VPH) in water and soil samples: one using a gas chromatograph with in-series photoionization and flame ionization detectors (GC/PID/FID), and one using a gas chromatograph/mass spectrometer (GC/MS). In addition to determining the collective fractions of aliphatic and aromatic hydrocarbons, the VPH methods may also be used to concurrently identify and quantitate individual concentrations of the *Target VPH Analytes* BTEX, methyl-tertiary-butyl ether (MtBE); and naphthalene.

VPH by GC/PID/FID

The VPH by GC/PID/FID method was initially released by MassDEP in January 1998. A modification of EPA Method 8020, it was designed to be a GC procedure that most laboratories could run, including facilities without a mass spectrometer (MassDEP, 2018a).

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 concentration of hydrocarbons in the C9 through C10 range (which are assumed to be aromatic hydrocarbons, and thus classified as C9 through C10 Aromatic Hydrocarbons).

The FID chromatogram is used to determine the collective concentrations of all hydrocarbons within the C5 through C8 and C9 through C12 ranges, with "marker" compounds used to establish the beginning and end of the hydrocarbon ranges of interest. The collective concentration of the PID Target Analytes and the C9 through C10 Aromatic Hydrocarbon range are then subtracted from the collective FID concentrations of all hydrocarbons in the C5 through C8 and C9 through C12 ranges, respectively, to determine the concentrations of C5 through C8 Aliphatic Hydrocarbons and C9 through C12 Aliphatic Hydrocarbons.

This methodology 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 typically 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, in theory, 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 (especially in water samples), this analytical over-quantification is not deemed to be 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 over quantification of the aromatic fraction.

Steps can be taken to minimize over-quantitation 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.

<u>VPH by GC/MS</u>

The VPH by GC/MS method was issued by MassDEP in January 2017, given the greater availability of laboratories with mass spectroscopy capabilities. It is a modification of EPA Method 8260.

As in the VPH by PID/FID method, volatile petroleum compounds are introduced into a gas chromatograph using a purge-and-trap technique. Hydrocarbons exiting from a capillary column in a temperature-programmed oven are directed to a 70-eV mass spectrometer operating in an electron impact mode, with a minimum scan rate of 35 to 250 atomic mass units every three seconds or less (MassDEP, 2017).

Identification of Target VPH Analytes is accomplished in a manner consistent with EPA Method 8260, by comparing analyte retention time and mass spectra with the retention time and mass spectra of standards obtained under identical analytical conditions. Concentration values are determined using Quantitation Ions specific to the Target Analytes, consistent with EPA Method 8260.

The collective concentrations of hydrocarbons are calculated in the C5 through C8 and C9 through C12 ranges using the total ion chromatogram and average response factors (or calibration curves) determined using an aliphatic hydrocarbon standard mixture. The collective concentrations of C9-C10 Aromatic Hydrocarbons are quantitated using extracted ions m/z 120 and m/z 134, where m/z is the ratio of mass to charge, using an average response factor (or calibration curve) determined using an aromatic standard mixture.

The collective concentration of the Target Analytes and the C9 through C10 Aromatic Hydrocarbon range are then subtracted from the total ion chromatographic concentrations of all hydrocarbons in the C5 through C8 and C9 through C12 ranges, respectively, to determine the concentrations of C5 through C8 Aliphatic Hydrocarbons and C9 through C12 Aliphatic Hydrocarbons.

Methodological Biases in MassDEP VPH Methods

Systemic bias in the two VPH methodologies can result from two factors:

- Detector response and selectivity, which can influence the quantitation of Target Analytes and hydrocarbon ranges; and
- The data manipulation steps in each method, which requires the subtraction of Target Analytes from both Aliphatic Hydrocarbon ranges, and subtraction of C9-C10 Aromatic Hydrocarbons from the C9-C12 Aliphatic Hydrocarbon range.

On the basis of a Round Robin study conducted by MassDEP on samples analyzed by both methods (MassDEP, 2016), the following observations were noted:

- When properly run, both the GC/PID/FID and GC/MS VPH methods appear capable of providing reasonably similar, accurate and health-protective data for gasoline contaminated samples.
- The MS method appears to have a moderate positive bias in quantifying C9-C12 Aliphatic Hydrocarbons (at least in soil samples), while the GC/PID/FID method has a moderate positive bias in quantifying C9-C10 Aromatic Hydrocarbons. Both methods appear to provide similar results for C5-C8 Aliphatic Hydrocarbons and the Target Analytes (e.g., BTEX).
- The positive bias in the MS method for C9-C12 Aliphatic Hydrocarbons appears to be attributable to an increased total ion response for aromatic hydrocarbons that elute in the C9 to C12 hydrocarbon range, compared to the total ion response of aliphatic hydrocarbons. It is not clear if this bias will exist for all mass spectrometers in all states of tune. However, this is unlikely to be an issue at most sites, given that C9-C12 Aliphatic Hydrocarbons are not expected to be a risk or cleanup driver.
- The positive bias in the PID/FID method for C9-C10 Aromatic Hydrocarbons is attributable to minor though collectively significant PID response to aliphatic hydrocarbons that elute within this range. Due to the low solubility of aliphatic hydrocarbon compounds, this is unlikely to be a significant issue in water samples, though it may be more of a concern in soil samples classified as “S-1” under the MCP.

Additional information on the comparison of both methods is available in the June 2016 MassDEP publication *Evaluation of MassDEP Volatile Petroleum Hydrocarbon (VPH) Methods*.

3.2.2 Extractable Petroleum Hydrocarbons (EPH)

The MassDEP EPH Method 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 and 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*, or, for Diesel/#2 Fuel Oil, the four *Diesel PAH analytes*: naphthalene, 2-methylnaphthalene, phenanthrene, and acenaphthylene (MassDEP, 2018b).

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 MassDEP 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 under quantitation of aromatic and aliphatic ranges. For this reason, the method specifies the 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 GC 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 these 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 to TPH reporting and cleanup standards.

3.2.3 Air-Phase Petroleum Hydrocarbons (APH)

The MassDEP APH method *is a GC/MS procedure*, and is a modification of EPA air testing method TO-15. 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, BTEX, Methyl-tertiary-butyl ether (MtBE), naphthalene, and 2-methylnaphthalene (MassDEP, 2009).

Samples are collected in 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

non-silanized glass beads. Following preconcentration, the sample is refocused at the head of a capillary column on a gas chromatograph using a cryo-focusing accessory.

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 quantified using retention times/characteristic ions and quantitation ions. Similar to the VPH by GC/MS method, collective concentrations of C9-C10 Aromatic Hydrocarbons are quantified using extracted ions m/z 120 and m/z 134. Collective concentrations of aliphatic hydrocarbon fractions are quantified using a total ion chromatogram, subtracting out Target APH Analytes and C9-C10 Aromatic Hydrocarbons

As with the VPH and EPH test methods, certain methodological limitations and biases are known to exist in the APH test procedure. Most notably, and similar to the VPH by GC/MS method, there is likely to be a moderate positive bias in quantifying C9-C12 Aliphatic Hydrocarbons. However, of greater interest and potential impact is the decision bias that can result from not understanding and/or considering the wide variety of non-petroleum compounds that may be present within indoor air, which can over quantify risk posed to building occupants.

As noted in Section 4.4 and Table 6 of the APH method, certain organic compounds not associated with an environmental release of petroleum products may be detected and may contribute to the collective response quantified within an aliphatic or aromatic hydrocarbon range. This is most common and problematic in the C5-C8 and C9-C12 Aliphatic Hydrocarbon ranges, where common indoor air "background" chemicals may be present, including ethanol, acetone, isopropyl alcohol, ethyl acetate, freons, limonene, pinene, and terpenes. In most cases, these chemicals are off gassing from building materials and/or common consumer/commercial products, which are not regulated under MGL c. 21E and the MCP. Importantly, the APH method, in Sections 9.6.2 and 11.2, provides a mechanism to identify and eliminate these compounds from being quantified as aliphatic range hydrocarbons – which in some cases will mean the difference between being above or below "typical" range concentrations, which has implications to site closure.

Conversely, not all non-petroleum compounds within indoor air are attributable to "background" sources, including chlorinated hydrocarbons such as PCE and TCE, which could be related to a subsurface vapor intrusion pathway – and could be posing unacceptable risks to building occupants.

> On an APH total ion chromatogram, the presence of a non-petroleum peak soon after the elution of benzene and prior to the elution of toluene could be TCE; a non-petroleum peak just after toluene and before ethylbenzene could be PCE.

Lastly, and unique to the APH method, are the complexities involved in differentiating petroleum hydrocarbons within indoor air originating from (non-regulated) in-home sources, including lawn mowers/snow blowers, as well as fuel oil tanks and heating systems, from (regulated) vapor intrusion pathways emanating from contaminated soil, groundwater, and/or LNAPL.

The recommended approach to address these issues is as follows:

- Except within buildings where the presence of chlorinated hydrocarbons within indoor air has previously been ruled out by EPA Method TO-15 or other air testing methods, the total ion chromatogram for initial APH samples should be visually reviewed by the lab analyst or LSP/site investigator to rule out the presence of significant chromatographic peaks that are not related to sample surrogates/internal standards or consistent with a petroleum "fingerprint". In such cases, the lab should be instructed to identify or tentatively identify the peak(s) based

upon mass spectra, as outlined in Section 11.2.1 of the APH method.

- If non-petroleum compounds are so identified, steps should be taken by the LSP to ascertain whether the compound is likely related to a "background" source within the building or whether it is likely related to a vapor intrusion pathway. Of most concern are the chlorinated ethenes, which include tetrachloroethylene (PCE) (potentially emanating from dry-cleaned clothing or automotive solvents) and trichloroethylene (TCE) (present in some oven cleaners, self-defense sprays, automotive solvents). While **the presence of the degradation product cis 1,2-Dichloroethylene is almost always indicative of a vapor intrusion pathway**, adequate steps must be taken to reasonably rule out a vapor intrusion pathway at all sites where significant levels of chlorinated solvents are identified. While all non-petroleum peaks may be subtracted from the hydrocarbon range in which they elute, evidence of a non-petroleum vapor-intrusion pathway may require notification to MassDEP and follow-up assessment/mitigation. If the presence of a chemical within indoor air is unrelated to a vapor intrusion pathway or release of OHM to the environment (e.g., from a consumer product) , though not mandated by the MCP, it is highly recommended that the building occupants be informed of any elevated levels of potential concern, so they can decide whether to take steps to avoid using the offending products or materials.
- For samples where large anomalous peaks are not present, no further review is necessary, unless one or more hydrocarbon ranges exceed a risk or remedial metric (e.g., typical indoor air concentrations). In such cases, it is recommended that the total ion chromatogram be more closely scrutinized, to determine if the "fingerprint" of hydrocarbon contamination is likely associated with a "fresh" in-home source of fuel (e.g., gasoline or fuel oil), as opposed to a more "weathered" signature of environmental vapor intrusion pathway.

3.2.4 VPH/EPH/APH Target Analytes

Although both the VPH by GC/PID/FID 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. This concern does not exist for the VPH by GC/MS or APH methods, as they identify analytes using both retention time and mass spectra, and determine concentration based upon quantitation ions specific to the analyte of interest.

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. Positive identification and quantification of the VPH Target Analytes can be accomplished using the VPH by GC/MS method, or by use of EPA Method 8260.

To save money, it may be worthwhile to quantitate Target Analytes using the EPH and VPH by GC/PID/FID 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.

3.3 Sampling Procedures and Requirements for the VPH/EPH/APH Methods

Sample collection and preservation are important elements of the VPH, EPH, and APH Methods. A summary of requirements in this regard is provided in **Table 3-1**; detailed step-by-step sampling recommendations are provided in **Appendix 2**.

Table 3-1: Sample Collection, Preservation, and Holding Times				
Method	**Matrix**	**Container**	**Preservation[b]**	**Holding Time[b]**
VPH	Aqueous[a]	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 ≤ 6ºC but not frozen.	14 days
	Soil	VOC vial or container; add 15g to 40mL vial; 25g to 60 mL vial	1 mL methanol per 1g soil (+/- 25%) to cover soil; cool to ≤ 6ºC but not frozen	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 ≤ 6ºC but not frozen	Extract sample < 14 days; analyze extract within 40 days
	Soil	4-oz (120 mL) +/- Wide-mouth amber glass jar with Teflon-lined screw cap	cool to ≤ 6ºC but not frozen	Extract within 14 days; analyze extract within 40 days
APH	Air & Soil Vapor	Certified clean, leak-free, stainless steel polished or silica lined passivated air sampling canisters	None	30 days

[a] see method if using heated purge procedure [b] see method for option to freeze

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 the addition of acids (e.g., HCl to pH <2) or by the addition of bases (e.g., Trisodium Phosphate Dodecahydrate to pH > 11).

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. 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.

3.4 Data Report Forms

The VPH/EPH/APH procedures have specific reporting formats that are detailed in the methods. These formats are designed to succinctly convey and document key sample preservation, analyses, QA/QC, and data adjustment steps. While laboratories are free to make some modifications to the actual reporting form, all required information must be provided in a clear manner.

Hydrocarbon Range Adjustments

A unique element in the VPH report forms is the need for the laboratory to notate "unadjusted" hydrocarbon range concentration data, along with the elution range of the Target Analytes. In this

context, unadjusted range data is defined to be the collective detector response to compounds eluting within the range, including all Target Analytes (e.g., BTEX), and, in the case of C9-C12 Aliphatic Hydrocarbons, including any aromatic compounds that may elute in that range.

In the VPH by PID/FID method, the FID response is used to quantify all compounds eluting between n-pentane and naphthalene and calculate the concentration of "unadjusted" C5-C8 and C9-C12 Aliphatic Hydrocarbons (this value is "unadjusted" because it may include Target Analytes and aromatic hydrocarbons). The PID detector is used to quantify the concentration of the Target Analytes (e.g., BTEX) as well as all compounds eluting between o-xylene and naphthalene, to quantify a concentration of "unadjusted" C9-C10 Aromatic Hydrocarbons.

In the VPH by GC/MS method, the total ion response of the mass spectrometer is used to quantify collective peak elutions between n-pentane and naphthalene and calculate the concentration of "unadjusted" C5-C8 and C9-C12 Aliphatic Hydrocarbons. Extracted ions m/z 120 and m/z 134 are used to quantify the collective concentration of aromatic hydrocarbons eluting between o-xylene and naphthalene and calculate the concentration of "unadjusted" C9-C10 Aromatic Hydrocarbons.

There is a need to calculate and notate "unadjusted" range concentration data on the Data Report Form. As previously detailed, in addition to calculating the collective concentrations of the numerous aliphatic and aromatic compounds that are present in petroleum products, the VPH method also quantifies the discrete concentrations of a small number of Target Analytes (e.g., BTEX compounds). Importantly, these discrete Target Analyte compounds represent peak elutions within the various aliphatic and aromatic ranges, even though they are individually identified, quantified, and notated in the report forms. As such, it is necessary to subtract their contributions from the collective hydrocarbon ranges in which they elute (i.e., are present within). If this step is not done, the concentration of these hydrocarbon ranges would be inflated, by "double counting" the Target Analytes. And in the case of unadjusted C9-C12 Aliphatic Hydrocarbons, it is further necessary to subtract the concentration of C9-C10 Aromatic Hydrocarbons, which elute in the C9-C12 Aliphatic Hydrocarbon range.

The final concentration value after these adjustments is simply the unmodified hydrocarbon range name, e.g., C5-C8 Aliphatic Hydrocarbons (absent the "unadjusted" modifier). It is this "final" value that is compared to MCP Method 1 standards and/or used in a Method 3 risk characterization process (including the MassDEP Shortforms). MassDEP requires laboratories to report unadjusted range data in order to allow the data user to ensure that hydrocarbon range adjustments were made correctly.

In the EPH method, the only adjustment required is to subtract the concentrations of the Target Analytes (which are all aromatics) from the concentration of unadjusted C11-C22 Aromatic Hydrocarbons. Because fractionation in the EPH method is accomplished chemically (with silica gel), there is no overlap of aliphatic and aromatic fractions. Although data adjustments are also made in the APH method, unadjusted hydrocarbon range values need not be disclosed on the report form.

Surrogate Standards

Sample Surrogates

Like most water and soil testing methods, surrogate standards are used in the VPH and EPH test methods to evaluate and document analytical accuracy. 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%.

EPH Fractionation Surrogates

In the EPH method, in addition to sample surrogates there are two compounds that are used to evaluate and document the accuracy of the fractionation process that is used to separate hydrocarbons into aliphatic and aromatic portions. Specifically, 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 recommended fractionation surrogates in the EPH method are 2-Fluorobiphenyl and 2-Bromonaphthalene - two compounds that are not normally present in petroleum, and that have polarities similar to naphthalene.

Laboratories are required to indicate the percent recovery of each sample surrogate, and in the EPH data report form, the percent recoveries of the fractionation surrogates, along with the acceptable ranges. 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.

Other Elements of the Data Report Forms

Although a comprehensive review of all QA/QC information and data is beyond the ability and/or resources of most data users, in addition to an evaluation of surrogate standard data 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 reviewing the information and data required in the data report form:

- ***All sample information should be provided, describing the sample matrix, condition of containers, and sample preservation***. VPH soil 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., µ/g, mg/kg, or µg/kg for soil; µg/L or mg/L for water; $\mu g/m^3$ and/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 quantify 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 150 µg/L; expected RLs for the aliphatic and aromatic ranges in soil are between 5 and 20 µg/g; expected RLs for the aliphatic and aromatic fractions in air are between 10 and 12 $\mu g/m^3$.

3.5 Data Quality and Presumptive Certainty

There is at present no requirement in the MCP to use a MassDEP certified laboratory to conduct VPH/EPH/APH analyses. Moreover, there is at present no program at MassDEP to certify laboratories to conduct these analyses (though other states and jurisdictions may have such programs).

Broad, performance-based requirements for data quality are specified at 310 CMR 40.0017 of the MCP. While not mandatory, MassDEP has published guidance in its "*Compendium of Analytical Methods*" (CAM) on ways parties can meet these broad performance standards, and obtain "Presumptive Certainty". The concept and process of Presumptive Certainty is discussed in detail in the MassDEP document WSC-CAM_VII A *Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP),* September 30, 2025, and as updated.

In order to achieve Presumptive Certainty for analytical data, including VPH/EPH/APH data, parties must (a) use the analytical method specified for the selected CAM protocol, (b) incorporate all required QA/QC elements specified for the selected CAM protocol, (c) implement, as necessary, required corrective actions for all non-conforming analytical performance standards, (d) evaluate and narrate, as necessary, all identified CAM protocol non-compliances, and (e) comply with all the reporting requirements specified in WSC-CAM-VII A, including retention of reported and unreported analytical data and information for a period of ten (10) years.

In achieving "Presumptive Certainty" status, parties will be assured that analytical data sets:

- satisfy the broad QA/QC requirements of 310 CMR 40.0017 and 40.0191 regarding the scientific defensibility, precision and accuracy, and reporting of analytical data; and
- may be used in a data usability and representativeness assessment, as required in 310 CMR 40.1056(2)(k) and 40.1057(2)(k) for Permanent and Temporary Solution submittals, respectively, consistent with the guidance described in MassDEP Policy #WSC-25-350, *MCP Representativeness Evaluations and Data Usability Assessments*.

Most Massachusetts environmental laboratories are familiar with the MassDEP CAM protocols and the concept of Presumptive Certainty, and if directed will conform to the CAM protocol documents for the VPH/EPH/APH test methods. These protocols, identified below, are available on the MassDEP web site:

- WSC-CAM_IV A–- *Quality Control Requirements and Performance Standards for the Analysis of Volatile Petroleum Hydrocarbons (VPH) by Gas Chromatography/Photoionization Detector/Flame Ionization Detector in Support of Response Actions under the Massachusetts Contingency Plan (MCP)*
- WSC-CAM_IV C–- *Quality Control Requirements and Performance Standards for the Analysis of Volatile Petroleum Hydrocarbons (VPH) by Gas Chromatography/Mass Spectrometry (GC/MS) in Support of Response Actions under the Massachusetts Contingency Plan (MCP)*
- WSC-CAM-IV B–- *Quality Control Requirements and Performance Standards for the Analysis of Extractable Petroleum Hydrocarbons (EPH) in Support of Response Actions under the Massachusetts Contingency Plan (MCP)*
- WSC-CAM-IX A–- *Quality Control Requirements and Performance Standards for the Analysis of Air-Phase Petroleum Hydrocarbons (APH) by Gas Chromatography/Mass Spectrometry (GC/MS) in Support of Response Actions under the Massachusetts Contingency Plan (MCP)*

A key element of the CAM protocols for Presumptive Certainty is the requirement that the laboratory complete and sign a one-page MassDEP Analytical Protocol Certification Form that contains a series of yes or no questions pertaining to sample integrity, QA/QC procedures and results, and method modifications.

It is possible to achieve "Presumptive Certainty" even if (a) some QC standards were not achieved, (b) certain Reporting Limits were above method designation, and/or (c) some Method Analytes were omitted. However, all such issues must be fully narrated by the laboratory, and the use of such data by the data user must be justified per the requirements of the MCP at 310 CMR 40.1056(2)(k) and 310 CMR 40.1057(2)(k), and as further discussed in MassDEP guidance #WSC-25-305, *MCP Representativeness Evaluations and Data Usability Assessments*.

3.6 Other Hydrocarbon Testing Methods

The VPH/EPH/APH methods were developed to provide data on the chemistry and toxicity of complex hydrocarbon mixtures, to facilitate risk evaluations and comparisons to MCP 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 mandated and/or be more appropriate and cost-effective.

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

3.6.1 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.

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	Applicable for low levels of C9 and heavier hydrocarbons in soil (i.e., when TPH concentrations will likely be less than 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; isotope analyses	Not always definitive; requires interpretative expertise

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 [C9] 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 on soil and water samples involved the use of an extraction/concentration step, which leads to the loss of lighter hydrocarbons (<C9) 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 for soil or groundwater:

- The TPH method and resultant data may only be used to characterize releases of petroleum products that consist of hydrocarbons primarily in the C9 to C36 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 Section 4.2.2.
- In addition to the TPH analysis, all appropriate Target Analytes must also be addressed. Guidance in this regard is contained in Section 4.2.3 and Section 4.2.4.
- 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 (e.g., PAH compounds, non-petroleum compounds) from soil and water samples.

Although 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 310 CMR 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 concentrations 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, MassDEP expects all such methods to achieve a level of QA/QC consistent with the VPH and EPH methods.

> If EPH data are needed for risk assessment purposes at disposal sites, and TPH data is required by contaminated soil receiving facilities, EPH test data can be converted to TPH data by adding the concentrations of C9-C18 Aliphatics, C19-C36 Aliphatics, C11-C22 Aromatics, and all PAH Target Analytes.

3.6.2 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(s) present and/or the source of their release to the environment. Analytical testing techniques are available to facilitate evaluations of this nature, though not all laboratories have this capability.

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

- Initially, soil, water, or NAPL 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), and degree of weathering. In some cases, the data obtained in this manner are 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 MassDEP EPH method and

EPA Method 8270, there are in fact many more PAH compounds present in petroleum products. Using a GC/MS technique and appropriate 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) aromatic hydrocarbons from combustion-derived (pyrogenic) aromatic hydrocarbons (given that the latter are predominated by the parent PAH compound, while the former are predominated by the alkylated side chain PAH compounds) (Stout et al., 2015).

- Data on the distribution of alkylated PAHs can often provide sufficient 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 selective 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 (Stout et al., 2015).

Advanced chemical fingerprinting remains a 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 recommended that data users seek out facilities and personnel with the appropriate expertise and experience.

3.7 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 significant. 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/APH 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/APH 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 fully documented, 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 3-3**.

3.7.1 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:

- understand the application and limitations of the screening method(s) of interest;
- consider site-specific contaminant/mixture chemistry and fate/transport processes; and
- 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 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 aliphatic hydrocarbons, than to* accurately quantitate collective aliphatic hydrocarbons, and estimate aromatic *hydrocarbons*. 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 effective for clay or organic-rich soils, due to partitioning efficiencies.
- Screening techniques for volatile petroleum vapor or air samples, such as a PID meter, are appropriate for soil gas/sub-slab soil gas monitoring and detection of significant vapor intrusion point discharges (e.g., cracks, annular spaces, or preferred pathways), but are not sensitive or accurate enough for indoor air characterization.

Table 3-3: VPH/EPH/APH Analytical Screening Techniques					
Technique	**Description**	**Range**	**Applications**	**Limitations**	**Recommendations**
PID Headspace	Soil or water samples are placed in sealed containers & headspace is allowed to develop. PID meter is then used to test the headspace for total volatile organic compounds (VOCs). Reference: Recommended DEP jar headspace procedure (see Appendix 3)	VPH & EPH	Excellent screening tool for gasoline; good tool for kerosene, jet fuel and fresh fuel oil. Best used to increase data density and support representativeness evaluations, direct remedial operations, and optimize VPH/EPH testing. PID preferentially responds to the more toxic aromatic compounds.	Not appropriate for heavy mineral/ lube/fuel oils or weathered diesel/#2 fuel oil. PID response can be non-linear and/or erratic for gasoline headspace vapors > 150 ppmv (Fitzgerald, 1989) PID response lessened by high humidity/moisture (instrument dependent). Additional confirmatory analyses are usually required for key decisions	For gasoline, excluding clays & organic soils, soil headspace readings less than 10 ppmv usually means that BTEX compounds are below 2 µg/g (MassDEP, 2026). Confirmatory analyses are needed. See Section 4.1.1
PID Soil Gas	Soil gas is extracted from a probe and analyzed with a PID meter.	VPH & EPH & APH	Use to investigate soil gas/indoor air pathways, and evaluate GW-2 sites with GW concentrations > GW-2 Method 1 standards. PID preferentially responds to more toxic aromatic compounds.	Instrument response is flow-dependent; must ensure adequate flow rates. PID response can be affected by high moisture & high petroleum vapor concentrations (>150 ppmv).	See Section 4.1.1
UV Fluorescence & Absorbance	The absorbance or fluorescence of a UV light source is used to directly quantitate the aromatic content of a soil sample. Extraction solvent, such as methanol or	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	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	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. Confirmatory analysis recommended for

Table 3-3: VPH/EPH/APH Analytical Screening Techniques					
Technique	**Description**	**Range**	**Applications**	**Limitations**	**Recommendations**
	isopropyl alcohol, must be used.		the more toxic aromatic fractions.		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 recommended for gasoline.	For diesel/#2 fuel oil, conservatively assume 50% C11-C22 Aromatics and 50% 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.	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 have 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 is also possible.	Response decreases with increasing solubility; response to benzene is 10 times less than p-xylene. Significant calibration/ cleaning requirements between uses.	Insufficient information available to offer general recommendations.

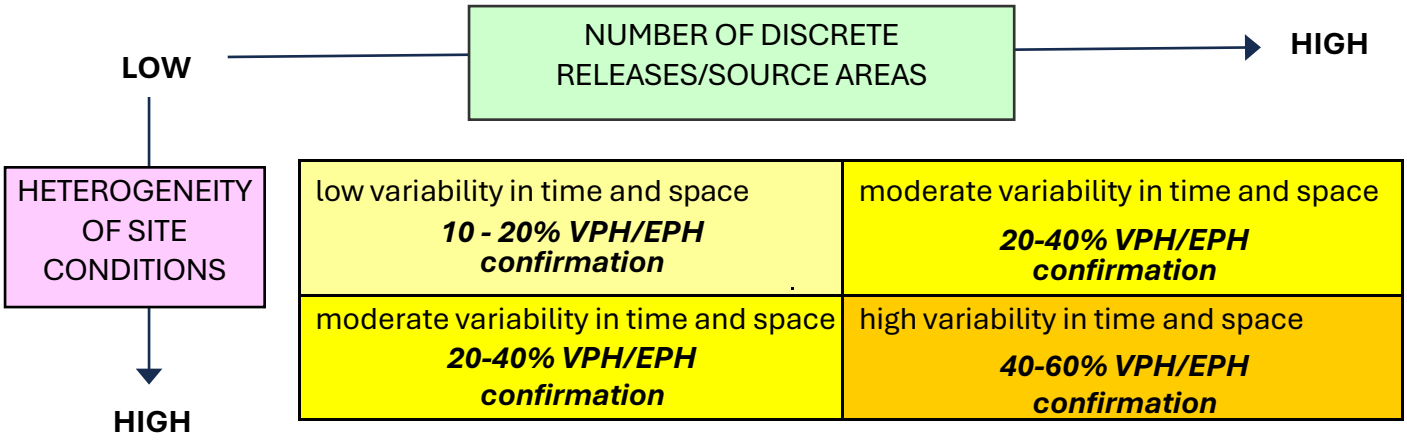
3.7.2 Recommended Approach

Site characterization is inherently probabilistic; more data means higher certainty. Most of the uncertainty in site characterization efforts is usually attributable to the lack of data, as opposed to the quality of available data. And the lack of data is usually attributable to the cost of "laboratory" analytical data.

The proper use of low-cost screening techniques can allow for the production of robust amounts of data in a cost-effective manner, which can substantially increase data density and significantly improve representativeness evaluations. For releases of gasoline and diesel/#2 fuel oil, PID headspace data (soil and groundwater) is an excellent option, as the PID preferentially responds to the more toxic components of these fuels (aromatics), and the more volatile compounds tend to be of greater concern, with respect to mobility (groundwater and vapor-phase transport). As with any analytical tool, however, reliable results can only come with proper procedures (see Section 4.1.1).

For small sites, such as a residential fuel oil release sites, screening techniques are perhaps best used to direct soil removal operations, identify areas for assessment and/or confirmatory VPH/EPH/APH 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/APH laboratory data may provide a better and less expensive approach to site characterization. Generalized *Rules of Thumb* in this regard are provided in **Figure 3-2** for soil samples. Note that additional confirmatory sampling would be indicated if sufficient correlation could not be established between the VPH/EPH values and screening/TPH values.

Figure 3-2: Soil Samples: Recommended Confirmation Data Needed to Support Analytical Screening



3.8 Drinking Water Testing Methods

When testing a potable drinking water supply, the use of the VPH by GC/PID/FID or 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 for public water supplies and EPA Method 8260D (as updated) for private drinking water wells. See Section 4.2.6 for additional information on sampling of private drinking water wells.

4.0 SITE CHARACTERIZATION

The MCP requires that disposal sites be adequately characterized, with respect to the nature and extent of contamination, and current and foreseeable risks posed to pollutant receptors. These regulations are implemented in Massachusetts by Licensed Site Professionals (LSPs) in a semi-privatized program, with specific requirements established for reporting releases of oil/hazardous materials to the environment, conducting assessment and remedial actions, and closing out sites when they have achieved a condition of No Significant Risk to human health, safety, public welfare, and the environment. Summary flowcharts noting key elements in this regulatory structure are provided in **Appendix 4.**

The nature and extent of investigative actions are necessarily site-specific, based upon (a) the toxicity and fate/transport properties of the oil and/or hazardous material (OHM), (b) the complexity of site/geologic conditions, and (c) sensitivity of potential pollutant receptors. There are numerous site assessment guidance documents that detail how to investigate contaminated sites, with respect to the development of a Conceptual Site Model (CSM), installation of borings/monitoring wells, and sampling techniques for soil, groundwater, soil gas, and indoor air. These publications, by the US EPA, MassDEP, Interstate Technology Regulatory Council (ITRC), and others should be consulted as appropriate. The purpose of this section is to succinctly summarize and focus on key assessment concepts and recommendations relevant to petroleum contaminated sites in Massachusetts.

4.1 Sampling Approach and Procedures

More data translates into a higher level of certainty in site assessment conclusions. However, conventional approaches are expensive, which may limit the number of samples collected, which often leads to less-than-optimal levels of certainty. As such, steps should be taken to achieve the maximum amount of relevant information and data for a given budget. This can be done through an understanding of a site's Conceptual Site Model and use of adaptive field investigations and analytical screening procedures, as described in the EPA Triad approach (US EPA, 2001)

4.1.1 Photoionization Detector (PID) Analytical Data

The use of a PID meter to screen and/or quantitatively analyze soil, groundwater, and soil gas samples can produce a large data set in a cost-effective manner, in order to characterize the extent and degree of contamination of volatile petroleum contaminants, including gasoline and diesel/#2 fuel oil. The use of the MassDEP jar headspace procedure (**Appendix 3**) can significantly improve the accuracy and precision of PID screening data for soil and water samples, compared to use of plastic bags or "waving" a PID wand over contaminated media. These data can then be used to reduce the needed number and optimize the selection of samples for VPH, EPH, and APH analysis, as well as to support decisions on the extent and degree of contamination at a site.

PID data should generally be reported in units of ppmV as isobutylene, except for work at underground storage tank (UST) closure sites per 310 CMR 40.0313(2), which will need to be converted to ppmV as benzene, using the appropriate response or correction factor specified by the PID manufacturer.

The utility, capabilities, and limitations of PID data are further described below:

- The PID responds well to the double bonds present in aromatic hydrocarbons, which are generally the most water-soluble and toxic constituents of petroleum fuels.
- While a PID meter may be able to provide semi-quantitative indoor air data with some utility in the evaluation of gross contaminant levels (e.g., fuel oil spill in a building), such instruments

are incapable of discerning and adequately characterizing the low ppbV breathing zone levels within indoor air that may be associated with a vapor intrusion pathway. However, because the vapor intrusion pathway is generally characterized by discrete entry points into the structure, a PID meter can be an excellent tool to look for evidence of these entry points (and thus the possible existence of a pathway), by slowly screening suspect locations, including annular spaces around utility penetrations, floor drains, foundation cracks, and the floor/wall interface of a basement slab. Sudden "bump ups" of PID readings are often observed into the ppmV levels, and are generally reproducible in repeat or subsequent screening operations.

- When screening soil or water samples, research has demonstrated that the MassDEP (dynamic) jar headspace procedure (**Appendix 3**) will generally achieve about 75% of equilibrium headspace conditions in 15 minutes, with the PID headspace concentration reduced by about 50% when piercing the aluminum foil seal and sampling the headspace with a PID meter (Fitzgerald, 1989).
- For soil samples, the partitioning relationships are such that a MassDEP PID jar headspace concentration of less than 10 ppmV as isobutylene will generally be associated with soil concentrations of BTEX of 2 µg/g or less. BTEX concentrations are often the risk and remedial drivers in soil, except for fresh gasoline releases (MassDEP, 2026). Confirmatory VPH analyses are necessary (see Section 3.7.2).
- For groundwater samples, the partitioning relationships are such a PID jar headspace of 25 ppmV or less will generally indicate aqueous concentrations of BTEX below their GW-2 standards. BTEX concentrations are generally the risk/remedial driver in groundwater (MassDEP, 2026). Confirmatory VPH analyses are necessary (see Section 3.7.2).
- For diesel/#2 fuel oil spills, soil samples with less than 10 ppmV jar headspace concentrations will generally meet Method 1 S-1 soil cleanup standards, with the possible exception of naphthalene and 2-methylnaphthalene in S-1/GW-1 areas (MassDEP, 2026). Confirmatory EPH analyses are necessary (see Section 3.7.2).

The following is required in order to obtain and use PID data for comparison with quantitative criteria contained in this guidance:

- The PID meter must be in good working order, equipped with at least a 10.0 eV lamp source, and have known sensitivities to humidity.
- The state of calibration of the PID meter must be confirmed at least every 20 analyses or daily, whichever is more frequent, by testing with an isobutylene gas standard, with percent recoveries in the range of 80% to 120%.
- All calibration-check data and site data must be recorded and included in site submittals.
- All calibration/maintenance and data acquisition procedures must be memorialized in a written SOP that is approved and implemented by a Licensed Site Professional.

4.1.2 Soil vs Groundwater vs Soil Gas Data

The primary utility of VPH and EPH soil data is for human health risk assessment, including comparison of soil EPCs to MCP Method 1 standards. As such, it is necessary to obtain sufficient data for this purpose, generally using a judgmental sampling approach (e.g., sampling in source areas and location of highest PID meter readings). While a judgmental approach may lead to a

conservative bias in site EPCs, considerably more VPH/EPH data would be required via a systematic (e.g., grid) sampling program to obtain representative EPC values.

Generally, soil samples collected for EPH analysis should be composite samples, comprised of 3 to 5 subsamples from the same general area. It is never permissible, however, to composite sub-samples from apparent "hot spot" areas (PID/visual/olfactory) with samples from less contaminated areas. Compositing of VPH samples (collected in methanol) can be accomplished by the immediate immersion of sub-samples into the methanol.

Whether in discrete or composite samples, the amount of soil analyzed in the VPH and EPH analyses is small – generally 10 grams, the volume of about 5 stacked quarter dollars. Given the heterogeneity of LNAPL/hydrocarbon distribution in vadose/smear zone soils, the use of VPH/EPH data to define extent of contamination is inefficient and expensive. A more cost-effective and data-dense option is to use visual, olfactory, and PID data for this purpose, and to guide where confirmatory VPH/EPH samples will be taken. For gasoline and diesel/#2 fuel oil, downgradient VPH/EPH groundwater samples, beyond providing information on drinking water concerns (GW-1 areas) or vapor-intrusion concerns (GW-2 areas), are also a good "barometer" of soil contamination/source-area concerns, and line of evidence in the evaluation of the representativeness of (10-gram) soil data. Similarly, soil gas data can be a useful line of evidence in determining the extent of gasoline in vadose zone source areas, and #2 fuel oil beneath building slabs – in addition to providing information on potential vapor intrusion pathways.

4.1.3 Soil

Of particular interest when sampling soil is the need to ensure that "hot spot" areas are discretely sampled and analyzed. For releases of gasoline and diesel/#2 fuel oil, this can be accomplished via PID headspace analysis; for heavier oils, visual/olfactory factors would be appropriate.

A common scenario for petroleum releases is a contamination assessment in an UST grave or release area for the purpose of determining an Exposure Point Concentration (EPC). For gasoline and fresh diesel/#2 fuel oil releases, this action may be easily accomplished by headspace analysis of samples from the sidewall/bottom of the excavations using a PID meter. Soil samples from areas within the groundwater interface/smear zone with PID jar headspace results more than 10-times surrounding areas should be discretely collected for appropriate VPH/EPH analysis as a potential "hot spot", except at sites where all PID jar headspace readings are relatively low (i.e., less than 50 ppmV).

4.1.4 Nonaqueous Phase Liquid (NAPL)

Virtually all petroleum products used and spilled in Massachusetts are less dense than water, and thus are considered Light Non-Aqueous Phase Liquids (LNAPL) when released into the environment. In many cases, remedial soil excavation activities extend to/into the groundwater table, allowing for a visual inspection for the presence or absence of LNAPL. Where groundwater is not encountered, the installation and gauging/sampling of a monitoring well would be expected if (a) a drinking water well is located within 500 feet, or (b) if $\geq$ 10 gallons of oil was likely released to the environment and (i) the depth to an overburden groundwater table was likely less than 15 feet from the ground surface or (ii) soil remaining at the site contains volatile hydrocarbons equal to or greater than 100 ppmV on a PID jar headspace test procedure. The need to install monitoring wells at sites where the groundwater table is within bedrock is a site-specific decision.

Detailed guidance on the required and recommended steps to investigate, assess, and remediate sites with LNAPL is provided in *Light-Nonaqueous Phase Liquid (LNAPL) and the MCP; Guidance*

for Site Assessment and Closure, MassDEP Policy #WSC-16-450. Key initial investigative steps recommended in Policy #WSC-16-450 are summarized below:

Site history–- Information should be obtained for the area under investigation, including information and data on past storage or uses of petroleum products and petroleum spills.

Monitoring wells–- When installed, groundwater monitoring wells must be screened across the groundwater fluctuation zone in overburden unconfined formations. After installation, all groundwater monitoring wells must be adequately developed. Parties who elect to use monitoring wells that are less than 2 inches in diameter shall include with relevant submittals a discussion of the steps that were taken during the installation, development, and gauging process to ensure the validity of LNAPL thickness measurements.

Monitoring well network–- Where significant amounts of mobile LNAPL are present, barring unavoidable site constraints, the spacing of a monitoring well network should generally be in the range of 15 to 30 feet within the core and at the perimeter of the LNAPL plume. The placement of wells must reflect the location of any sensitive LNAPL receptors, which include surface waters, buildings, sumps, and utilities/subsurface structures within the groundwater fluctuation/LNAPL smear zone.

Gauging–- LNAPL thickness measurements should be made using an oil/water interface probe to eliminate accuracy concerns associated with measuring the thickness of LNAPL observed in a bailer. Each time a well is gauged for LNAPL thickness, the elevation of the groundwater/LNAPL interface must be observed and recorded, to ensure that the top of the well screen is not below the groundwater table. After gauging, it is recommended that free-phase petroleum product be evacuated from the well, to help ensure that the well remains in good hydraulic communication with the surrounding formation and accurately reflects dynamic site conditions.

All gauging data (NAPL/groundwater) must be included in reports submitted to MassDEP

Gauging frequency–- At sites where Non-stable LNAPL is present or potentially present, wells within and just downgradient of an identified LNAPL plume must be gauged on at least a monthly basis until stability is demonstrated. At sites where stable LNAPL is present or likely present, wells within and just downgradient of an identified LNAPL plume should be gauged on at least a quarterly basis for a minimum of one year, with gauging events occurring at both high and low water table conditions.

The presence of LNAPL in a monitoring well, excavation, or subsurface structure requires notification to MassDEP within 72 hours if present at a measured/visible thickness equal to or greater than ½-inch (0.04 feet), or within 120 days if present at a measured/visible thickness of equal to or greater than 1/8-inch (0.01 feet). In the case of Volatile LNAPL (e.g., gasoline) within 30 feet of a School, Daycare, Child Care Center or occupied Residential Dwelling, notification is required within 72 hours as a Condition of Substantial Release Migration if the Volatile LNAPL is present at a measured/visible thickness of equal to or greater than 1/8-inch (0.01 feet). See 310 CMR 40.0300.

4.1.5 Groundwater

Monitoring wells installed at petroleum contaminated sites are generally limited to water table installations in which a 10-foot well screen straddles the groundwater fluctuation zone. This is appropriate, in order to be able to detect the presence of visible LNAPL, and is generally sufficient,

given the tendency of dissolved hydrocarbon plumes to bio-attenuate before significant hydrodynamic "dipping" occurs. However, data obtained from these wells must consider issues and limitations related to the Conceptual Site Model, with respect to when and how such data should be obtained.

Need to Sample Groundwater - 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 small releases of product (less than 5 gallons), or sites with a deep vadose zone (>15 feet to the groundwater table), if there are no sensitive receptors (e.g., no groundwater withdrawal wells or potentially impacted structures). Regardless of the type of petroleum product released, groundwater characterization should be undertaken at any site where the distance to a drinking water well is less than 500 feet. 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.

Number of Groundwater Monitoring Wells – When such monitoring is necessary, a minimum of three monitoring wells should be installed. The wells should not be installed in a line but in a triangular manner so that groundwater flow direction can be evaluated.

Rounds of Groundwater Monitoring – Because groundwater is a dynamic medium, a single "snapshot in time" is generally not sufficient to characterize contaminant levels, and calculate Exposure Point Concentrations. Except for petroleum products without a significant 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 (McHugh et al., 2011). Experience in Massachusetts by agency staff suggest variations 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 should be 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 4-1 provides the minimum recommended number of rounds of groundwater sampling at petroleum-contaminated sites, from wells that do not contain LNAPL. A preferred approach is to obtain at least 4 measurements over a 1-year period, coinciding with seasonal variations. Multiple sampling rounds in any given season, while providing potentially useful site data, cannot be considered equivalent to multiple samples over multiple seasonal conditions. 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).

Antecedent Precipitation - At all sites, the sampling of water table wells must occur at a time and in a manner that will satisfy data quality objectives. This is complicated by potential dilutional effects in these wells following significant rainfall events, by "short circuiting"

Table 4-1: Minimum Recommended Quarterly Rounds of Groundwater Monitoring*			
Location/GW Category	**Gasoline/ JP-4**	**Diesel/#2-4 Fuel/Kerosene**	**Mineral/Lube/#6 Fuel Oil**
< 500 feet from water supply	4+	3-4	2-3
GW-2	2-3	2	1
GW-3	1-2	1-2	1

*in wells where LNAPL is not present

mechanisms, or normal unsaturated zone infiltration fluxes.

A data usability analysis must be conducted on any data obtained from a water-table well 5 or less days after a significant rainfall event (i.e., ≥ 2 total inches of rain in this preceding period of time). Key elements of this evaluation may include surface cover (e.g., paved vs unpaved), groundwater elevation trends, and concentration data trends.

Vapor Intrusion Evaluation - In GW-2 areas, sampling of groundwater is generally required in order to assess vapor intrusion concerns. In addition to the consideration of antecedent precipitation events, the location of where the groundwater sample is obtained in the well is also of interest, as vapor intrusion is a water table phenomenon. In general, samples obtained for the purpose of characterizing vapor intrusion concerns should be obtained via low-flow sampling techniques, in which sample withdrawal occurs 6 to 12 inches below the water table elevation at the time of sampling. Passive sampling bags may also be appropriate, at this depth interval, if sufficient evidence is provided of their efficacy.

Sumps - 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.

Filtering 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 over-quantitation 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) sorbing dissolved hydrocarbon contaminants, and/or (2) removing colloids that are in fact contaminants that are moving through a formation.

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 (US EPA, 2017).

General guidelines on filtering groundwater samples are provided below:

- 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 should be undertaken, 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.

Entrainment of LNAPL – When trying to characterize dissolved hydrocarbon contamination, water samples should generally not be obtained from wells with visible LNAPL, as any entrained LNAPL will greatly and inappropriately inflate resulting VPH and/or EPH concentration data. Moreover, even wells that are currently free of visible LNAPL can still produce inflated data, if visible LNAPL was present in or near that well in the past. In such cases, aggressive well purging or sampling techniques (particularly use of a bailer) can create shear forces that will dislodge very small globules of LNAPL in the well screen, packing, or surrounding formation, entraining them in the sample, where they will be purged or extracted along with the dissolved hydrocarbons, greatly inflating analytical results.

With respect to EPH data, as discussed in Section 7.3, a likely sign of LNAPL entrainment in a groundwater sample is the reporting of hydrocarbon fraction concentrations in excess of their likely solubility limits, i.e.,

C9-C18 Aliphatic Hydrocarbons > 0.5 mg/L;

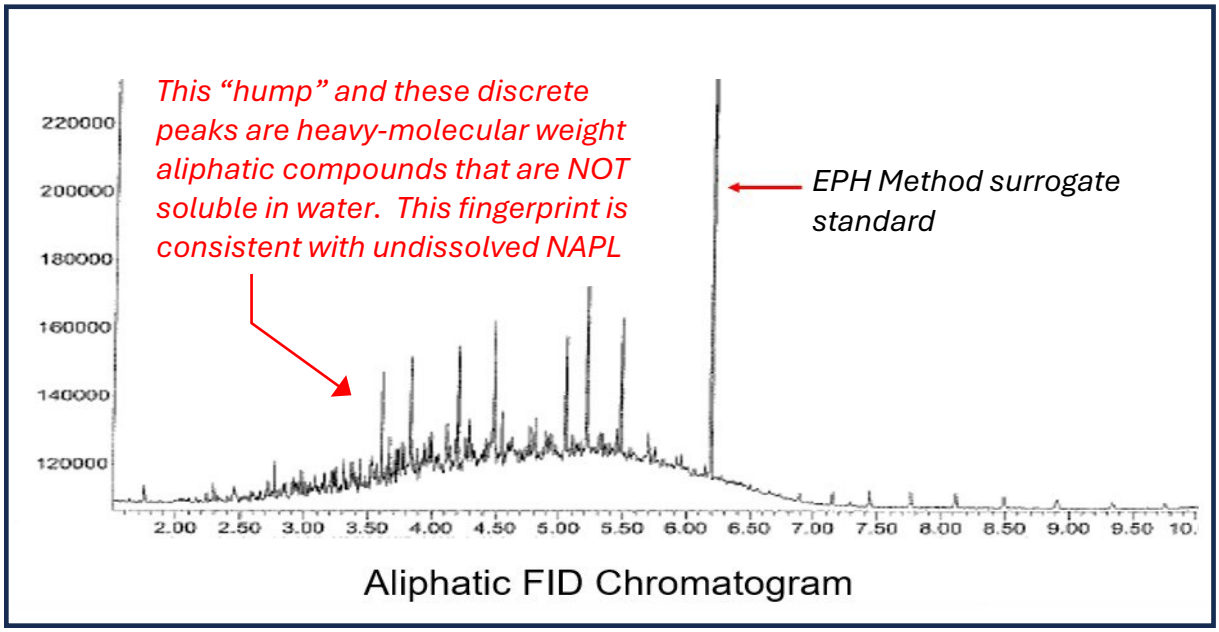
C19-C36 Aliphatic Hydrocarbons > 0.01 mg/L; or

C11-C22 Aromatic Hydrocarbons > 5 mg/L.

Where entrainment of LNAPL is suspected, the chromatogram(s) for the sample(s) should be obtained and examined. The "fingerprint" of dissolved hydrocarbons is much different from that of LNAPL, with the dissolved fraction dominated by BTEX, low molecular weight alkyl-aromatic hydrocarbons (e.g., trimethylbenzenes), and in diesel/#2 fuel oil, naphthalenes and substituted naphthalenes. The chromatogram for a sample with entrained LNAPL will be comprised of a "hump", with discrete spikes throughout the hump if the LNAPL globule was not highly weathered.

An example in this regard is provided in **Figure 4-1**, which is a chromatogram associated with EPH data from the site of a home heating fuel release, where the sample was obtained using a bailer. The associated concentrations of the EPH hydrocarbon fraction exceeded MCP Method 1 standards, which prevented closure of the site. Resampling was conducted by MassDEP using a low-flow technique, with all EPH fractions and target analytes well below Method 1 standards, and a flat chromatogram with no significant peaks.

Figure 4-1: #2 Fuel Oil LNAPL Entrainment in a Groundwater Sample



4.1.6 Indoor Air and Soil Gas Sampling

Samples of indoor air and soil gas (generally sub-slab soil gas) are typically obtained and analyzed via the MassDEP APH test method. Indoor air samples are generally 8-hour or 24-hour time weighted whole-air samples obtained in 2 to 6-Liter canisters from a basement and first floor level. Sub-slab soil gas samples are generally 5 to 15 minute "grab" samples, obtained at a low flowrate (< 300 cc/min) or some other manner to minimize "short circuiting". Other techniques, including grab or continuous samples analyzed by on-site or portable gas chromatographs also have utility, and can appreciably increase data density in a cost-effective manner. Extensive testing by MassDEP has shown that indoor air "grab sample" data compares favorably to 24-hour time weighted samples in single-family homes, especially basement samples (MassDEP, 2016).

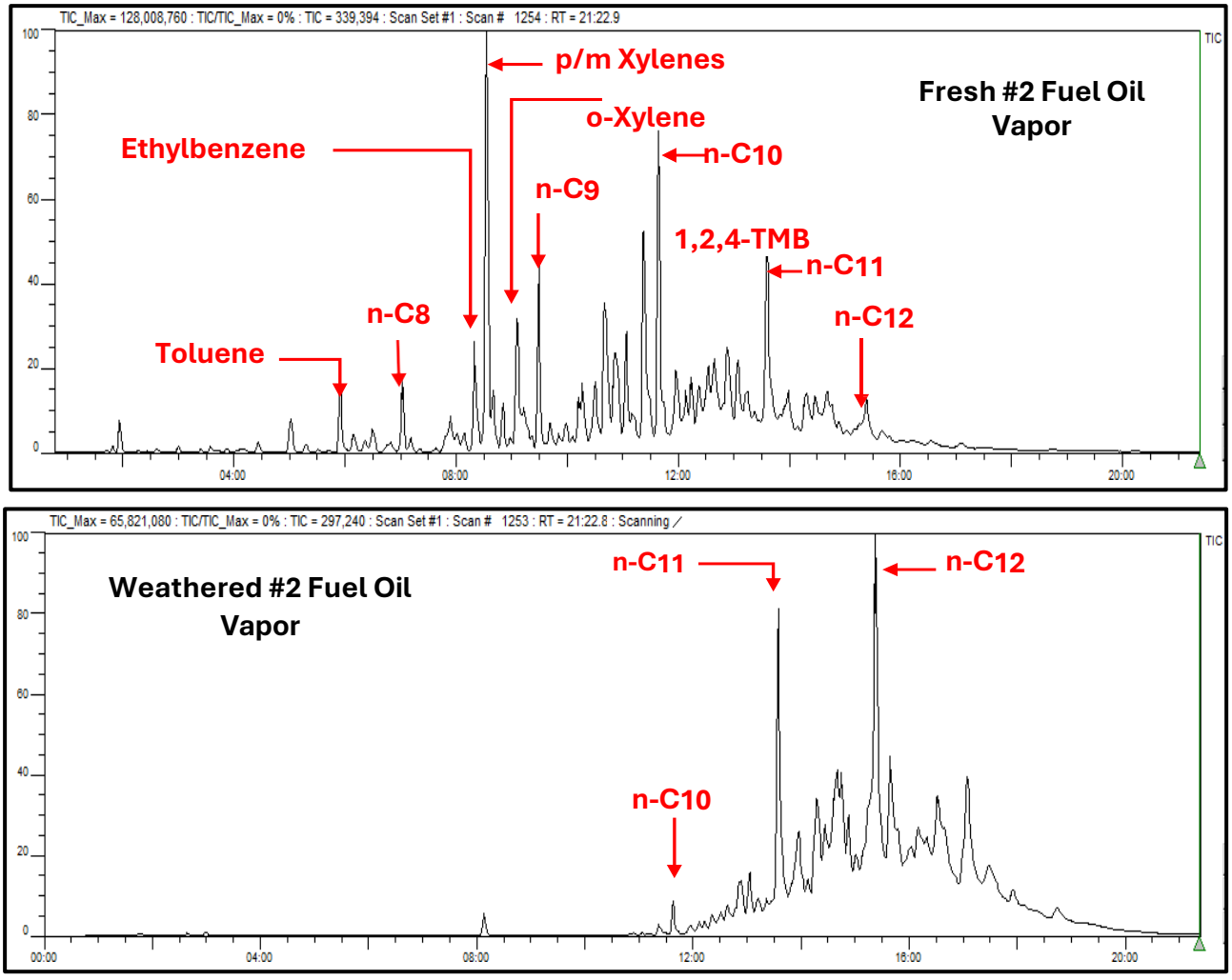
As notated in Section 3.2.3, the MassDEP APH method can significantly overquantify the concentration of collective ranges of hydrocarbons within indoor air, most notably C5-C8 Aliphatic Hydrocarbons, followed by C9-C12 Aliphatic Hydrocarbons, due to the presence of common indoor air contaminants associated with various consumer products (e.g., ethanol, acetone, isopropyl alcohol, ethyl acetate, freons, limonene, pinene, and terpenes).

It is recommended that laboratory personnel be instructed to adjust APH range concentration values by eliminating the contribution of non-petroleum compounds, as allowed by the APH method in Sections 9.6.2 and 11.2. To save money, the laboratory can be instructed to undertake this adjustment only if the initial (unadjusted) values exceed a specified concentration value (e.g., the indoor air "Threshold Values (TV) established by MassDEP).

While the elimination of chlorinated ethenes (e.g. PCE, TCE) from the C5-C8 Aliphatic Hydrocarbon range is appropriate, their presence within indoor air is of concern, and steps must be taken to rule out a vapor intrusion pathway. This can be done by comparing the concentrations of these compounds in soil gas and indoor air; if the concentrations in soil gas are significantly higher than in the indoor air, or if cis-1,2 Dichloroethylene is present within the indoor air, a chlorinated ethene vapor intrusion pathway may be present and must be further assessed.

Additionally, at some sites, it may be necessary to differentiate between in-building sources of hydrocarbon contaminants and hydrocarbon vapors infiltrating into the building from a vapor intrusion pathway. In these cases, an evaluation or comparison of the chromatograms for the indoor air and/or sub-slab vapor samples can be helpful. As presented **in Figure 4-2**, a "fresh" hydrocarbon mixture (perhaps from a home heating fuel tank or other in-building petroleum product) will have elevated concentrations of BTEX compounds, and significant amounts of C5-C10 Aliphatic Hydrocarbon compounds. A more weathered fingerprint, perhaps associated with a sub-slab/environmental (vapor intrusion) source, will lack these lighter compounds, and be dominated by a C10 to C12+ unresolved complex mixture ("hump"). A synoptic comparison between sub-slab vapor samples and indoor air samples can provide a useful line of evidence on whether a vapor intrusion pathway is significantly impacting indoor air quality.

Figure 4-2: Total Ion Chromatograms of Fresh and Weathered #2 Fuel Oil



4.2 Contaminants of Concern

In the MassDEP VPH/EPH/APH approach, the hundreds of individual compounds that comprise petroleum products are categorized as hydrocarbon fractions of interest, Target Analytes, and additives. The presence of non-petroleum compounds in samples is also of interest, as failure to identify/address such compounds can lead to a significant over quantification of risk – or a significant under quantification of risk – to exposed populations.

4.2.1 Non-Petroleum Contaminants

Initial site investigative activities should include steps to conclusively rule out the presence of chlorinated solvents and other non-petroleum environmental contaminants. Exceptions may be appropriate at single family homes where such concerns can be reasonably ruled out and where drinking water wells are not present within 500 feet of contaminated areas.

The most efficient and cost-effective manner to rule-out non-petroleum contaminants at a site of interest is to obtain at least one groundwater sample in the area of highest petroleum contamination and/or area of suspected non-petroleum sources, for analysis of VOCs by EPA Method 8260, at a minimum. This sample should also be analyzed for PFAS contaminants by EPA Method 1633 in GW-1 areas where Aqueous Film Forming Foams (AFFF) were used or likely used, including tanker or vehicle accidents.

The presence of elevated concentrations of chlorinated hydrocarbon compounds in groundwater, most notably PCE, TCE, and/or cis-1,2-dichloroethylene, may be indicative of a vapor intrusion pathway – which may be of much greater concern than the petroleum contaminants being investigated

4.2.2 Hydrocarbon Fractions of Interest for Soil and Groundwater Samples

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 on ranges of interest, as determined by either the VPH or EPH test method, is provided in **Table 4-2** for the most commonly released petroleum products.

When using a Method 1 or 2 Risk Characterization approach, each VPH/EPH fraction is treated as if it were a single entity or unique chemical. The general rules that apply to the calculation of Exposure Point Concentrations, such as averaging data and hot spot determinations, also apply to these aliphatic and aromatic fractions.

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, the VPH value for C9-C12 Aliphatic Hydrocarbons need not be considered in a risk characterization, 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. 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/concentration process. *Accordingly, in such cases, the highest reported value should be used.*

Table 4-2: When to Test for VPH and/or EPH				
Petro Product	**Media**	**VPH**	**EPH**	**Comments/Caveats**
Gasoline	soil	✓		
	GW	✓		
Fresh Diesel/#2 Fuel	soil	✓	✓	"Fresh" assumed unless MassDEP PID Jar headspace < 100 ppmv
	GW	✓	✓	EPH testing is only required in GW-1 areas (see Section 7.3)
Weathered[2] Diesel/#2 Fuel	soil		✓	"Weathered" defined as soil with MassDEP PID Jar headspace < 100 ppmv
	GW		✓	EPH testing only required in GW-1 areas (Section 7.3); VPH testing also required if ≤ 500 ft drinking water well
#3-#6 Fuel Oil Hydraulic Oil	soil		✓	
	GW		✓	
Mineral/Di-electric Fluids	soil		✓	
	GW		✓	
Jet Fuel JP-4 JP-8	soil	✓	✓	May eliminate/reduce VPH testing if MassDEP Jar headspace < 100 ppmv
	GW	✓	✓	
Jet Fuel Jet A Kerosene	soil		✓	
	GW		✓	EPH testing required only if in GW-1 area
Waste Crankcase Oil	soil	✓	✓	
	GW	✓	✓	
Unknown Oils	soil	✓	✓	
	GW	✓	✓	

All groundwater samples obtained within 500 feet of a public or private drinking water supply well should be initially tested by both the VPH and EPH methods, including BTEX and the four diesel/#2 fuel oil PAHs.

Soil and groundwater samples consistent with a weathered Diesel/#2 Fuel Oil need not be tested for VPH or VOCs for the purposes of identifying a potential Critical Exposure Pathway per 310 CMR 40.0313(4)(f).

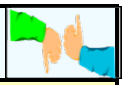
4.2.3 Target Analytes

Target Analytes are those constituents of petroleum which have traditionally been used to

characterize environmental contamination, and for which MassDEP has specific MCP Method 1 cleanup standards: the BTEX compounds, MtBE, lead, ethylene dibromide (EDB), 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. 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	MassDEP Jar Headspace	TPH	Recommended Target Analytes[1]
Gasoline	soil			BTEX compounds, naphthalene, and appropriate additives (e.g., MtBE, lead, and/or EDB).
	GW			BTEX, naphthalene, and appropriate additives (e.g., MtBE, lead, and/or EDB).
#2 Fuel/Diesel	soil	≥100 ppmV		BTEX (required unless MassDEP jar headspace PID data < 100 ppmV)
			>500 µg/g	acenaphthene, naphthalene, 2-methylnaphthalene, phenanthrene
	GW[1]			for GW-1 only: acenaphthene, naphthalene, 2- methylnaphthalene, phenanthrene[3] If soil samples > 100 ppmV jar headspace, or site within 500 feet of a drinking water well, also test for BTEX
#3-#6 Fuel Jet Fuels Kerosene Lube Oils Hydraulic Oils	soil			17 priority pollutant PAHs, unless justification not to
	GW[2]			BTEX and 17 priority pollutant PAHs, unless justification not to do so
Waste Oils	soil			VOCs, PAHs, PCBs, heavy metals
	GW[2]			VOCs, PAHs, PCBs, heavy metals

[1]See Sect 4.2.6 for analysis of drinking water wells

[2]VPH and EPH testing (with target analytes) should be conducted if within 500 feet of a drinking water well

[3]PAH compounds not soluble enough to exceed GW-2/GW-3 Method 1 Standards (Section 7.3)

In addition to the analytes listed in Table 4-3, testing for Per- and Polyfluoroalkyl Substances (PFAS) compounds must be considered at sites located in a GW-1 area where fire-fighting foam was applied (e.g., accidents involving significant gasoline and jet fuel releases or threats of release). In such cases, sample analyses should be performed via EPA Method 1633.

4.2.4 Gasoline Additives

Since 1923, organic, inorganic, and/or organo-metallic compounds have been added to gasolines 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** (Gibbs, 1990).

Table 4-4: Past and Present Gasoline Additives in 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 lead via EPA 6010C, EPA 6020A, or EPA 7010; followed by alkyl lead methods if necessary
		2-4 grams/gal	1920s-present (aviation gasoline)	
ethylene dibromide (EDB)	"scavenger" in leaded gasoline	variable	1923-1981 (still used in aviation gasoline)	EPA Method 8260D
MtBE	octane enhancer	1-8% by volume	1979-1991	MassDEP VPH; EPA Method 8260D[a]
	oxygenate	10-15 % by volume	1991-2006	MassDEP VPH; EPA Method 826OD[a]
ethanol	oxygenate	10- 15% by volume	2005 – present	EPA 8260D with heated purge & trap

[a] acidification of aqueous samples can lead to significant breakdown of MtBE

Rules of Thumb on the selection and analysis of specific petroleum product additives in contaminated media are provided below:

- *Lead* and *Ethylene Dibromide (EDB)* were removed from automotive gasolines in 1988, and routine testing for these additives is no longer necessary. However, leaded gasolines are still being produced and used in small quantities, most notably in aviation (Avgas), racing cars, and some off-road-only vehicles. Accordingly, spills of such fuels, or any fuel known or suspected to contain lead, should include analyses of lead and EDB, at a minimum, in GW-1 groundwater samples, and, for releases occurring less than 20 years prior to assessment, all impacted soil categories in GW-1 areas (due to leaching/source concerns). The lead added to gasoline is in the form of alkyl leads, most notably tetraethyllead and tetramethyl lead. These organo-metallic complexes will generally degrade (biologically and/or chemically) in soil over time but can persist for years within gasoline NAPL. As such, while the initial testing of soil and groundwater samples may be via conventional "total lead" techniques (e.g., EPA 6010C, 6020A, or 7010), if elevated results are obtained, follow-up testing for alkyl leads should be

conducted, at a minimum, on surficial soils and groundwater samples near or within drinking water wells.

Based upon maximum lead content past and present (4-5 grams/gallon gasoline), a single release of leaded gasoline (e.g., tanker spill) is unlikely to result in lead concentrations in soil above the RCS-1 value of 200 µg/g, though repeated releases (e.g., leaking underground storage tank) can result in significantly higher concentrations.

- *MtBE* has been largely phased and out but may still be present at older sites, and remains a Target Analyte in the MassDEP VPH methods.
- *Ethanol* comprises up to 10% by volume of most gasoline currently sold in Massachusetts. There is no MCP Method 1 cleanup standard for ethanol, though it is a listed hazardous material in 310 CMR 40.1600 with Reportable Concentrations (RCs) in soil and groundwater. Like most listed hazardous materials without Method 1 cleanup standards, the RCs for ethanol are not (directly) risk-based but are rather generically assigned values based upon the Reportable Quantity for Ethanol (which is 10 gallons).

  Ethanol is not a Target Analyte in the MassDEP VPH method, but it can be detected and quantified using a modified EPA Method 8260D with a heated purge and trap unit. In the vast majority of cases, however, it is not necessary to test soil or groundwater for ethanol, given its rapid biological degradation at dilute concentrations in groundwater, which generally prevents its migration beyond source areas. However, this rapid degradation can quickly deplete oxygen (and nutrient) levels in the source areas and extend the anoxic core of the plume, thereby potentially reducing biodegradation rates of petroleum compounds, which may then lead to longer plumes of BTEX and other dissolved gasoline hydrocarbons.

4.2.5 Biofuels

Biofuels, most notably E85 ethanol/gasoline blends and biodiesel and biodiesel heating fuel blends, are a growing segment of Massachusetts petroleum product inventories. These product blends can have different physical (e.g., specific gravity, viscosity), chemical (e.g., solubility, vapor pressure), and biological (e.g., biodegradation rate) properties, compared to conventional gasoline and diesel fuels (ITRC, 2011).

The two most significant issues to be concerned with when assessing spills of biofuels are as follows:

- The preferential degradation of biofuels over petroleum hydrocarbons (including BTEX compounds) can diminish available electron acceptors, potentially increasing the length of hydrocarbon plumes and/or creating localized reducing conditions that can mobilize redox-sensitive metals such as iron, manganese, and arsenic.
- The anaerobic degradation of biofuels can lead to the copious production of methane gas, which can concentrate to explosive levels in subsurface structures in source areas, and migrate as a dissolved gas to downgradient properties, where it can off-gas and impact the overlying vadose zone and/or overlying structures. The appearance of methane can be delayed for months or years after the initial release of the biofuel.

Accordingly, when assessing spills of gasoline, diesel fuel, or diesel heating fuel containing more than 10% biofuel components (e.g., ethanol, Fatty Acid Methyl Esters (FAME), etc.), the buildup of methane in subsurface utilities and structures within 25 to 50 feet should be evaluated and documented, at 6 months and 12 months following the release, and thereafter as warranted, using

an infrared meter or other suitable instrument. This testing may not be done solely by a catalytic explosive gas (LEL) meter, which does not provide accurate data in oxygen-deficient atmospheres, nor by a PID meter, which does not detect methane. In situations where the excessive buildup of methane gas is occurring, and likely attributable to ethanol degradation, additional groundwater testing may be advisable for ethanol, methane and/or intermediate breakdown products such as acetate.

4.2.6 Drinking Water Wells

In general, beyond the recommendations contained above, it is not necessary to routinely test for additional analytes at petroleum (only) contaminated sites. At disposal sites where releases of gasoline or diesel fuel have impacted drinking water supplies, however, samples of the impacted private drinking water should be analyzed at least once by (a) EPA Method 8260D (as updated) for all method analytes, and (b) for the metals listed in Method EPA 6010C, excluding the common "background" elements calcium, iron, manganese, and sodium. As noted in WSC-CAM Section IIA, subsection 3.1, an evaluation of tentatively identified compounds (TICs) is not necessary, if site contamination is limited to petroleum releases. For public drinking water supply wells, testing should be conducted using the EPA "500" series (and other) methods to the extent required by the drinking water regulations. Such an action is appropriate given (i) the wide variety of chemical additives in petroleum products, including biofuels, (ii) the relative mobility of volatile organic compounds and certain metal salts and complexes, and (iii) the sensitivity of the exposure pathway.

4.3 Vapor Intrusion Pathway

The possible existence of a vapor intrusion pathway must always be considered/investigated for significant releases of petroleum with some level of volatility, including volatile LNAPL. In Policy #WSC-16-450, MassDEP has defined "Volatile LNAPL" to include "*gasoline, petroleum naphtha, mineral spirits, kerosene, jet fuels and any petroleum mixture where more than 25 percent of component hydrocarbons (by mass) have a boiling point below 218°C (424°F), and any single component (or predominantly single-component) LNAPL with a boiling point below 218°C*." Of most concern is gasoline, due to its toxicity, volatility, and explosivity.

The MCP at 310 CMR 40.0313(4)(f)(3) requires notification within 72 hours of $\geq$ 1/8-inch of Volatile LNAPL located within 30 feet of a home, school, or daycare facility, as this combination of volatility and sensitive receptors mandates expeditious investigation. However, even petroleum products that are not considered "Volatile LNAPL" may still pose chronic long-term concerns that may require evaluation before a Permanent Solution may be achieved. This includes LNAPLs of diesel/#2 fuel oils and any other petroleum products with a potential to impact the indoor air of a structure through a vapor intrusion pathway to a degree that could pose a significant risk to human health or public welfare.

In some cases, impacts are obvious (e.g., odors, LEL/PID readings), and steps must be taken immediately to characterize and/or mitigate acute exposure conditions. In other cases, impacts may be more subtle and insidious, only discoverable by site investigation activities. MassDEP has published detailed general guidance on this topic in *Vapor Intrusion Guidance: Site Assessment, Mitigation, and Closure*, Policy #WSC-16-435.

Guidance specific to petroleum contaminated sites is provided below, ranging from the use of conservative metrics applied to preliminary and/or limited site data, to less conservative criteria applied to more comprehensive data sets, presented as a series of options:

OPTION 1: To attempt to reasonably rule out vapor intrusion concerns in buildings downgradient of a petroleum release, consider use of the MassDEP Modified Inclusion Distance Approach.

OPTION 2: To attempt to reasonably rule out vapor intrusion concerns in a building on a site at which a fuel oil spill occurred, elect to use screening data compared to conservative evaluation metrics.

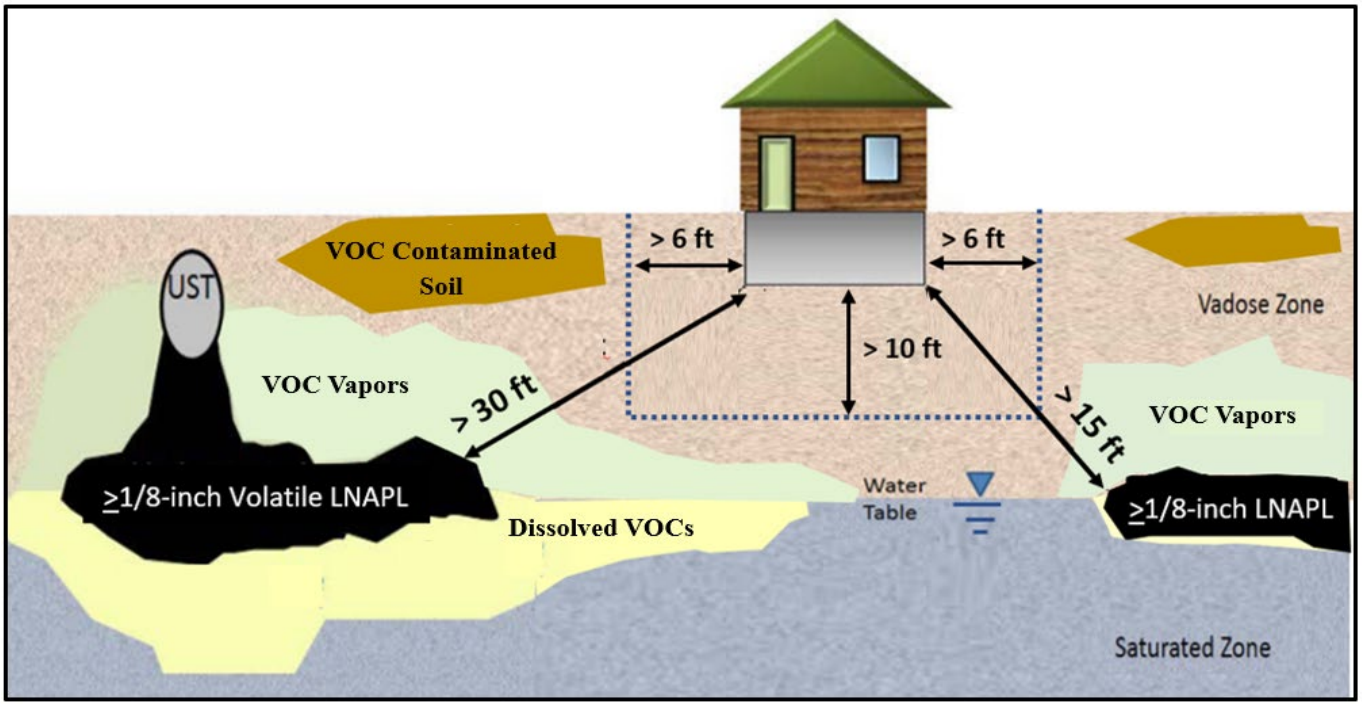
OPTION 3: At any site, or if Options 1 and 2 are unsuccessful, undertake a Multiple Lines of Evidence Approach to determine if a vapor intrusion pathway of concern is likely present at the site.

For spills of gasoline or fuel oils with more than 10% biofuel components (e.g., ethanol, FAME, etc.), an additional vapor intrusion concern would be the generation and migration of methane gas.

4.3.1 Modified Inclusion Distance Approach (IDA) for Downgradient Buildings

Developed by the US EPA, the Inclusion Distance Approach (IDA) for downgradient buildings is based upon years of empirical data demonstrating that petroleum hydrocarbons are generally readily biodegraded in the vadose zone under aerobic conditions (US EPA, 2015). As such, the existence of an aerated "clean zone" of sufficient thickness between a hydrocarbon source and nearby building should generally be capable of attenuating soil gas concentrations to levels unlikely to significantly impact indoor air. MassDEP has modified the EPA criteria to be consistent with the notification criteria at 310 CMR 40.0313(4)(f), including the differentiation of LNAPL by volatility This modified criteria is presented in **Figure 4-3**.

Figure 4-3: MassDEP Modified Inclusion Distance Approach for Petroleum Vapor Intrusion



Note: EPH Test Method Hydrocarbon Fractions and Target Analytes are NOT classified as VOCs. VPH Hydrocarbon Fractions and Target Analytes are considered VOCs.

As presented in Figure 4-3, using a modified IDA, a petroleum vapor intrusion pathway of concern is unlikely in a downgradient building if:

- ❖ soil or soil gas impacted with one or more VOCs are NOT present within six feet horizontally from the wall of the structure or within ten feet vertically from the basement floor or foundation. Solely for the purpose of this evaluation, VOC contaminated soil is defined as soil containing one or more VOCs in excess of their RCS-1 notification criteria, and VOC contaminated soil gas is defined as the presence of one or more VOCs in soil gas in excess of their MassDEP sub-slab soil gas screening value (SSGSV) concentration;
- ❖ dissolved VOCs in excess of their Method 1 GW-2 standard(s) are NOT present within 30 feet of the structure, at locations where the average annual depth to groundwater is 15 feet or less;
- ❖ equal to or greater than 1/8-inch LNAPL is NOT present within 15 feet of the structure; and
- ❖ equal to or greater than 1/8-inch Volatile LNAPL is NOT present within 30 feet of the structure.

The use of an IDA approach is limited to those sites where the following applies:

- The extent of LNAPL and groundwater contamination is adequately characterized by the construction of a Conceptual Site Model and acquisition of site data sufficient to ensure that the petroleum plume is stable and that the minimum IDA distances can be reasonably determined, including:
  - ➢ at least two seasonal LNAPL gauging events (high and low groundwater conditions) demonstrating no measurements of LNAPL equal to or greater than 1/8-inch within 15-feet of the building and/or equal to or greater than 1/8-inch Volatile LNAPL within 30 feet of the building, where such well(s) are screened at the water table and situated between the point of LNAPL release or potential release and the downgradient building of interest, in a location(s) that would detect LNAPL; and

- At sites with recent releases of Volatile LNAPL (i.e., within the previous year), or a release of biofuels, soil gas data demonstrating the presence of at least 1% oxygen by volume at a point at least 6-feet horizontally and 10 feet vertically (or just above the groundwater table) from the building (EPA, 2015).

The use of an IDA approach is not appropriate at sites where:

- large-scale petroleum operations have been or are being undertaken (e.g., fuel terminals);
- preferential LNAPL/groundwater/vapor transport pathways are present or likely present;
- aerobic activity may be limited due to exceptionally dry soils (≤ 2% soil moisture) resulting from impervious surfaces and/or highly organic soils (e.g., peat);
- chlorinated solvents or other contaminants are present and/or co-mingled with the petroleum plume; or
- the bedrock surface is less than 3 feet below the building(s) of concern.

4.3.2 Screening Data Approach for Limited On-Site Fuel Oil Spills

Releases from an on-site consumptive use fuel oil storage tank (#2 fuel oil and heavier fuel oils) and/or associated fuel oil transfer piping within or immediately adjacent to a building is not an uncommon oil spill scenario. In some cases, the limited amount of fuel released, the limited extent of impacts and/or the extent of remedial measures are sufficient to conclude with a reasonable degree of certainty that a current or future vapor intrusion pathway of concern is unlikely, even with preliminary and/or limited site data. This "Screening Data" approach, summarized in **Figure 4-4** and detailed below, requires information and/or data on spill volumes, odor conditions, soil and soil gas contamination, groundwater contamination, preferred flow paths, and LNAPL, and applies conservative evaluation metrics to account for the preliminary and limited extent of site characterization. Under this approach, based upon current (e.g., post remedial) conditions, a vapor intrusion pathway of concern is unlikely to exist at a site meeting all of the following conditions and investigatory metrics:

Site Characteristics – Releases occurred from or are related to a single on-site consumptive use fuel oil storage tank.

Volume of Spill – The volume of fuel oil released, based upon a reasonably conservative estimate from tank inventory records and/or other information or observations, was likely less than 10 gallons.

Odors - There are no significant ongoing petroleum odors within the building, even on an intermittent basis. While in many cases such odors are attributable or primarily attributable to the off gassing of hydrocarbons from impacted building materials – which is not regulated by the MCP – a multiple lines of evidence approach is necessary in these cases to adequately establish the origin of odors.

Soil Data – Soil samples obtained from "worst case" impacted areas and/or soils contiguous to impacted soils that had been removed from the site as part of a remedial effort contain levels of contaminants (a) below applicable MCP Method 1 soil standards, or (b) below 10 ppmV total organic vapors via a PID jar headspace procedure.

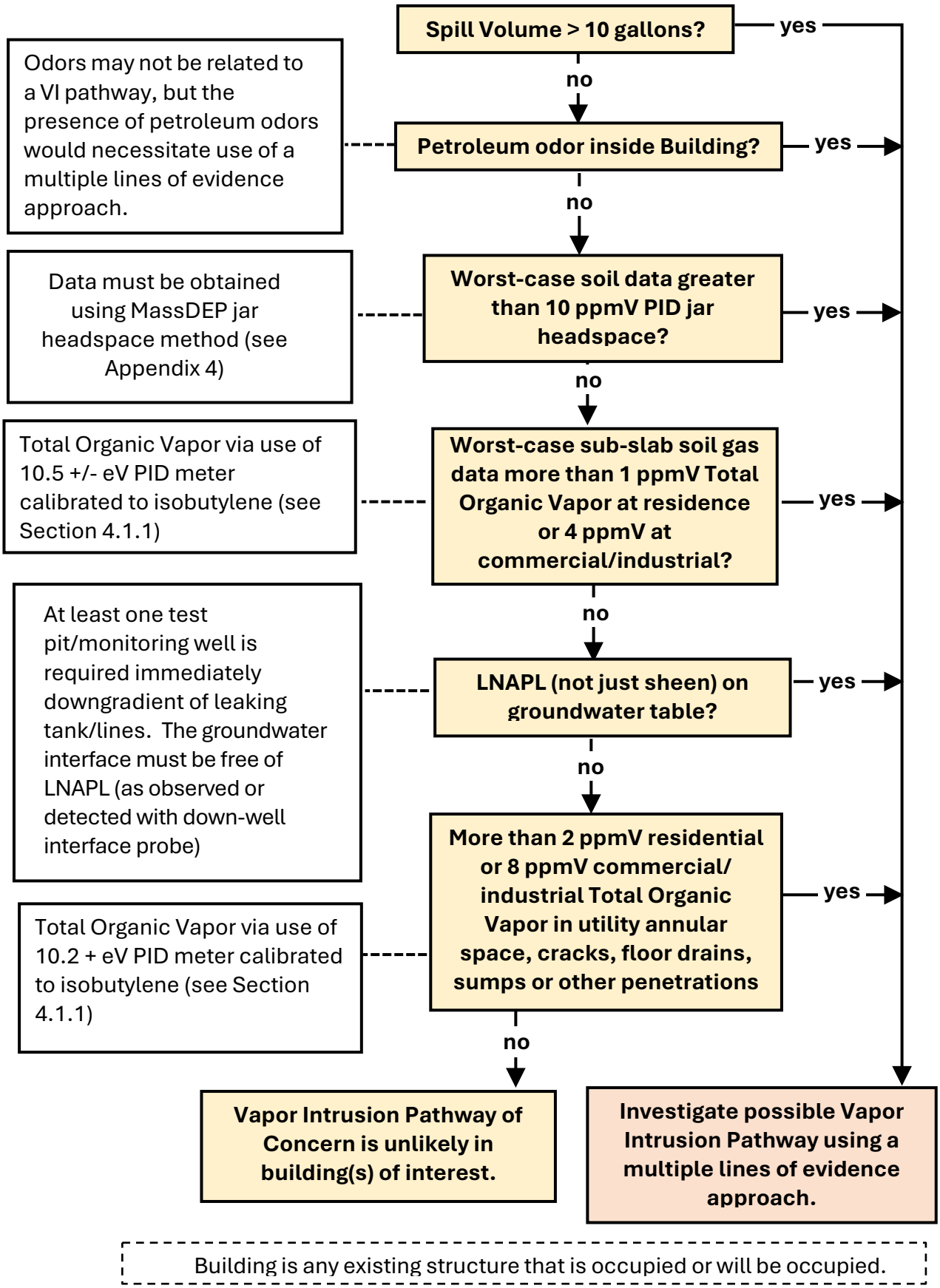
Soil Gas Data – Sub-slab soil gas data obtained from "worst case" areas of impact are equal to or less than 1 ppmV Total Organic Vapors (as isobutylene) on a 10.5 +/- eV PID meter in a residential structure, and less than 4 ppmV in a non-residential structure (MassDEP, 2026).

LNAPL/Groundwater Data – A groundwater monitoring well or test pit excavation advanced in an area or areas immediately downgradient of the storage tank/or leaking transfer line are free of LNAPL in excess of a sheen.

Preferential pathways – PID readings at utility annular spaces, cracks/floor drains/sumps and other subsurface penetrations are equal to or less than 2 ppmV as isobutylene in a residential structure, and less than 8 ppmV in a non-residential structure.

The "Screening Data" approach is solely for the evaluation of vapor intrusion concerns at sites where a small amount of fuel oil has been released to the environment. Additional data (including VPH/EPH/APH) will be needed to address other site characterization concerns and closure requirements.

Figure 4-4: Screening Data Vapor Intrusion Approach for Limited On-Site Fuel Oil



4.3.3 Multiple Lines of Evidence Approach for All Sites

If neither the IDA nor Preliminary Site Data approach was used, or if one or both were used and could not reasonably rule out the likelihood of a vapor intrusion pathway of concern, it will be necessary to proceed to a Multiple Lines of Evidence approach, as described in MassDEP Policy #WSC-16-435. Under this approach, which may be used at any site, groundwater, sub-slab soil gas, and indoor air data are obtained and inputted into a matrix chart, as reproduced in **Figure 4-5**. Key input data for this table for petroleum contaminated sites is reproduced as **Table 4-6**.

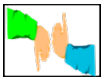
While each line of evidence in isolation has limitations – temporal and sampling variabilities in groundwater data; high spatial variabilities in sub-slab soil gas data, and potentially significant temporal variabilities in indoor air exposures – decisions based on the totality of inputs to the evaluation matrix are believed to provide reasonable and health-protective determinations at most sites.

The first consideration element in this approach is the concentration of volatile petroleum contaminants in groundwater; the next is sub-slab soil gas contaminant levels. If either an MCP GW-2 standard OR a MassDEP Sub-Slab Soil Gas Screening Value is exceeded, indoor air sampling is required; and if an indoor air contaminant level exceeds a MassDEP Threshold Value, a vapor intrusion pathway of concern is likely present at the time of evaluation.

> Of note is the wording of the conclusion generated by use of the Multiple Line of Evidence matrix: is there *likely* a *current pathway of concern*? Beyond the uncertainty conveyed by "likely" is the temporal validity of the conclusion conveyed in "current pathway". Lastly, the matrix is not intended to rule out any level of vapor intrusion, but is rather designed to identify pathways of potential concern, with respect to risk and remedial feasibility issues.

Guidance on the input of data and interpretation of results is provided below:

Groundwater – Of interest is the concentration of volatile petroleum contaminants in the shallow groundwater below the building of concern. Generally, such data do not exist, and as such, conservative values must be designated. In general, these values should be the highest concentrations of VPH and/or VOC contaminants in contiguous and/or upgradient water-table well(s). EPH data are not relevant, as any volatile aliphatics will be reported in the VPH C9-C12 range, and the heavier (C11-C22) aromatic hydrocarbons are highly unlikely to be a vapor intrusion issue, as evidenced by their GW- 2 standard of 50,000 µg/L (likely beyond the solubility limits of this range).



Note that averaging of groundwater data (in space or in time) is not permitted when inputting data into this matrix; in general, the highest concentrations of contaminants in shallow groundwater in the 12 months preceding this evaluation should be the designated groundwater values. As noted in Section 4.1.5, concentration data should be obtained for the upper portions of the saturated zone (6 to 12 inches below the groundwater table) at a point in time when antecedent rainfall events have not significantly diluted contaminant concentrations at the water table interface. In cases where at least 4 recent seasonal rounds of groundwater data have conclusively ruled out the presence of volatile contaminants at and near the groundwater table interface, the inputted groundwater value may be set to zero.

Figure 4-5 - Lines of Evidence Approach for Presence of Likely Vapor Intrusion Pathway (MassDEP #WSC-16-435 and as clarified)
[CHECK SOURCE PUBLICATION FOR POSSIBLE UPDATES]

Residences, Schools and Daycares					
Lines of Evidence					
Groundwater Contaminant Levels	**≤ GW-2 AND**			**> GW-2 OR**	
Sub-Slab Soil Gas Contaminant Levels[a]	**≤ SSGSVr AND**			**> SSGSVr AND**	
Indoor Air Contaminant Levels	**Not Tested**	**≤ TVr**	**>TVr**	**≤ TVr**	**>TVr**
Likely Current Pathway of Concern?	**No**	**No**	**See Footnote[b]**	**No**	**Yes**

Commercial/Industrial Locations					
Lines of Evidence					
Groundwater Contaminant Levels	**≤ GW-2 AND**			**> GW-2 OR**	
Sub-Slab Soil Gas Contaminant Levels[a]	**≤ SSGSVc/i AND**			**> SSGSVc/i AND**	
Indoor Air Contaminant Levels	**Not Tested**	**≤ TVc/i**	**>TVc/i**	**≤ TVc/i**	**>TVc/i**
Likely Current Pathway of Concern?	**No**	**No**	**See Footnote[b]**	**No**	**Yes**

[a] Sub-Slab Soil Gas Screening Values (SSGSVs)

[b] Evaluate potential indoor air sources and/or preferential migration pathways. Indoor air results are not consistent with low subsurface contamination, which raises the possibility of indoor air source(s), preferential pathway(s), or unidentified subsurface sources related to a release. Consult with MassDEP on ambiguous results.

TV_r = MassDEP Residential Indoor Air Threshold Values (applies at schools and daycare facilities)

$TV_{c/i}$ = MassDEP Commercial/Industrial Air Threshold Values

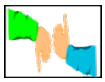
SSGSVr = MassDEP Residential Sub-Slab Soil Gas Screening Value (applies at schools and daycare facilities

SSGSVc/i = MassDEP Commercial/Industrial Sub-Slab Soil Gas Screening Value

Table 4-6: MassDEP Sub-Slab Soil Gas Screening Values (MassDEP #WSC-16-435) [CHECK SOURCE PUBLICATION FOR POSSIBLE UPDATES]				
Compound/Range	**Residential**		**Commercial/Industrial**	
	µg/m³	**ppbV**	**µg/m³**	**ppbV**
Benzene	160	50	800	250
Ethylbenzene	520	120	62,000	14,000
Naphthalene	42	8	190	36
Toluene	3800	1000	310,000	82,000
Xylenes (mixed isomers)	1400	320	6200	1400
C5-C8 Aliphatic Hydrocarbons	4100	NA	23,000	NA
C9-C12 Aliphatic Hydrocarbons	4800	NA	16,000	NA
C9-C10 Aromatic Hydrocarbons	700	NA	3100	NA

When inputting indoor air data to the MassDEP vapor intrusion matrix, make sure to eliminate non-petroleum hydrocarbon compounds for the APH hydrocarbon range data, and, where appropriate, distinguish between "in building" sources and environmental (vapor intrusion) sources. (Section 4.1.6)

Sub-slab soil gas – Given the substantial spatial variability of sub-slab soil gas conditions at some sites, these data are often the least reliable of the three primary lines of evidence. While a high concentration value is a strong indicator of a current or potential future vapor intrusion pathway, low contaminant concentrations in the two probes typically installed in smaller buildings have a more limited utility. Accordingly, the vapor intrusion matrix chart in Figure 4-5 requires indoor air testing at all sites where GW-2 standards are exceeded, even if the soil gas concentrations are below the MassDEP Sub-Slab Soil Gas Screening Values (SSGSV).



It is also noted that elevated concentrations of hydrocarbons in sub-slab soil gas can (infrequently) result from the mass transfer of contaminants from the overlying indoor air into the sub-slab of a building. This can occur through a "barometric" pumping and/or diffusion mechanism, in buildings with elevated levels of non-regulated hydrocarbon vapors within indoor air (e.g., from petroleum storage or spills contained within the building). In these cases, an evaluation of chromatograms for the indoor air and sub-slab soil gas sample may be instructive, in that a soil gas sample impacted by the overlying air space would be expected to contain a substantial amount of lighter molecular weight hydrocarbon compounds associated with gasoline or fresh #2 fuel oil.

Indoor Air – While the most important evaluation metric, indoor air data is not always conclusive in determining whether a vapor intrusion pathway of concern is present. This is especially true with respect to petroleum contamination, given potential "in building" sources, and potential positive biases in the MassDEP APH data. When the reported data is below the MassDEP Threshold Values, this is not a concern. However, if these data are

elevated, steps should be taken to eliminate analytical bias and background sources (see Section 4.1.6).

When an in-building petroleum source has been confirmed (e.g., in-use fuel oil tank, off-gassing from fuel-spill-impacted building materials and/or furnishings), and when a qualitative/quantitative evaluation of the total ion chromatograms of the indoor air and sub-slab soil gas samples confirms the predominance of an in-building petroleum source, the inputted indoor air data for the vapor intrusion matrix may be the highest sub-slab soil gas value divided by 70, based upon the dilution and attenuation factor used in the MassDEP Vapor Intrusion Guidance. Conversely, more detailed modeling or assessments may be undertaken in these situations, to establish the concentrations of hydrocarbons within indoor air attributable to the vapor intrusion pathway, with the understanding that reasonably conservative input parameters must be used (including soil moisture in sub-slab soils in any mathematical models).

No Likely Pathway of Concern - In cases where the conclusion of the vapor intrusion matrix evaluation is no likely current pathway of concern, no further evaluation or consideration of the vapor intrusion pathway is generally necessary, except in cases where there are reasonable questions on the quality or quantity of data, or where there is clear evidence to the contrary (e.g., unexplained odors). If non-petroleum compounds (e.g., chlorinated solvents) were identified and excluded from this evaluation, steps must be taken to ascertain whether those non-petroleum compounds constitute a reportable condition under the MCP [i.e., are from a vapor intrusion pathway where notification is not exempted per 310 CMR 40.0317(16)]. If excluded in-building sources of petroleum hydrocarbons or in-building sources of non-petroleum compounds would constitute a significant risk under the MCP risk management standards, it is recommended that building occupants be apprised of such conditions (though this is not an MCP requirement), so they may choose whether they would like to take steps to reduce their exposures to these (non-MCP) conditions.

Likely Pathway – When the conclusion of the vapor intrusion matrix evaluation is "Yes", and a current pathway of concern is likely, the following steps are necessary.

- In cases where the vapor intrusion pathway constitutes an Imminent Hazard and/or Substantial Release Migration (SRM) condition, provide any needed notification to MassDEP and undertake an Immediate Response Action.
- In cases where the vapor intrusion pathway constitutes a significant risk to human health, safety, or public welfare, take steps to achieve a condition of No Significant Risk.
- In cases where the vapor intrusion pathway does not constitute a significant risk to human health, safety, or public welfare, but nonetheless represents a Critical Exposure Pathway, reduce exposures to the extent feasible.
- If site-specific conditions suggest that a vapor intrusion pathway is not present, conduct additional investigations and/or present additional information and data to refute the presence of a pathway.

Regardless of the outcome of the vapor intrusion evaluation process, if an MCP GW-2 standard is exceeded in any well in a GW-2 area (i.e., temporal average exceeds the GW-2 value), an MCP Method 2 or 3 risk assessment must be conducted for the site.

5.0 RISK CHARACTERIZATION AND 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 for soil and groundwater
- Method 2–- site-specific modification of generic cleanup standards
- Method 3–- site-specific risk assessment

Guidelines and recommendations in this regard are provided in **Table 5-1**. For complete information and guidance on the use of the MCP risk assessment methods, consult the provisions of 310 CMR 40.0900 and available publications on the MassDEP Bureau of Waste Site Cleanup (BWSC) website.

Table 5-1: Choosing an MCP Risk Characterization/Cleanup Method

Method	Consider Using If...	Significant Limitations
1	• simple/small site • contamination in soil and groundwater only • cleanup to Method 1 standards is feasible	• cannot be (solely) used if significant (> 1000 ft^2) sediment contamination • cannot be (solely) used if significant indoor air impacts are present [see 310 CMR 40.0942]
2	• groundwater concentrations > GW-2 standards • groundwater concentrations > GW-3 standards • sites in GW-1 areas and C9-C10 or C11-C22 Aromatic fraction(s) in soil > Method 1 standards	• cannot be (solely) used if significant (> 1000 ft^2) sediment contamination • cannot be (solely) used if significant indoor air impacts are present [see 310 CMR 40.0942]
3	• complex/large sites • sites with indoor air impacts • sites with sediment contamination • sites with soil/gw > Method 1 standards (can be used at any site)	• cannot achieve a Permanent Solution if: (1) Non-Stable NAPL is present at site, or (2) soil conc above Method 3 Ceiling Limits[a] or if coal tar waste deposits are present unless deeper than 15' or below Engineered Barrier; or (3) groundwater conc > Method 3 Ceiling Limits[a]

[a] *Method 3 Ceiling Limits* were formerly known as *Upper Concentration Limits in the MCP* (310 CMR 40.0996)

The easiest and most certain approach is Method 1, in that concentration-based soil and groundwater cleanup standards have already been established by MassDEP. 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 Method 1 TPH cleanup standard (or Reportable Concentration) if all 3 EPH fractional concentrations are below standards [see 310 CMR 40.0973(7) and 40.0360(2)].*

Because the Method 1 standards are generic - 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.

5.1 Exposure Point Concentrations (EPCs)

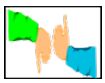
Regardless of the risk assessment method selected, it is necessary to calculate Exposure Point Concentrations (EPCs) in media and pathways of interest (individual data points are generally NOT directly compared to standards). The EPCs are the media and pathway-specific concentration values (µg/g, µg/L, and/or µg/m^3) compared to the Method 1 and Method 2 standards, entered into the MassDEP Shortforms, and/or used in Method 3 site-specific risk characterizations. The performance standard contained in the MCP at 40.0926 is to calculate EPCs that constitute "a conservative estimate of the mean concentration" in the characterized media. Given the spatial and temporal variations in contaminant concentrations in soil, groundwater, and indoor air, this can be a difficult undertaking with significant uncertainties. As such, an understanding of the site Conceptual Site Model and sampling and analytical biases is necessary to fulfill this requirement. Guidance in this regard for media of most interest at petroleum contaminated sites is provided below.

In a Method 1 and 2 Risk Characterization, soil EPCs are based upon the **spatial** average of soil contaminants, and the **temporal** average of groundwater contaminants. In Methods 1 and 2, each individual groundwater measurement point (e.g., monitoring well) is a separate Exposure Point, and averaging of data between these measurement points is not permissible.

5.1.1 Soil EPCs

Soil EPCs in a Method 1 or 2 Risk Assessment are calculated by an evaluation of data points within the same (S-1, S-2, S-3) soil category, as well as 0 to 3 feet below grade. The options available are detailed in the MCP at 40.0926. The most used approach at petroleum sites is the "75/10" method, in which a valid soil EPC exists if, based on a judgmental sampling program: (a) the spatial (arithmetic) mean concentration of soil samples in a data set is less than all applicable standards, (b) 75% of the values in the data set are less than all applicable standards, and (c) no single point in the data set is greater than 10 times any applicable standard (which would constitute a de facto "hot spot"). For complicated sites/systematic sampling approaches, the 90th percentile Chebyshev non-parametric upper confidence limit on the mean should generally be selected as the soil EPC for each contaminant of concern.

Technical judgement must be used to determine the locations and amounts of soil samples needed to assemble a sufficient data set for these calculations. The following are recommendations in this regard:



Analytical Screening – PID screening of gasoline and diesel/#2 fuel oil contaminated soils is highly recommended in judgmental sampling programs to characterize the extent and gradations of soil contamination, optimize selection of samples for VPH and/or EPH analyses to constitute the EPC data set, and provide data points to support a Representativeness evaluation. Use of the MassDEP jar headspace technique (Appendix 3) is recommended to ensure consistent and comparable results.

Underground Storage Tanks (USTs) - 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 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 – unless all PID jar headspace readings are less than 50 ppmV as isobutylene (about 25 ppmV as benzene).

Composite Sampling – When sampling a broad area, the use of composite sampling is recommended: for EPH samples, 3-5 sub-samples; for VPH samples, 2 to 3 sub-samples (deposited directly into methanol in a vial as they are obtained, ensuring the proper ratio of soil/methanol). Composite sampling may NOTt be used in locations where a "hot spot" is likely to exist, based upon visual, olfactory, or analytical screening data, or in systematic (grid) sampling approaches.

5.1.2 Groundwater EPCs

In accordance with the provisions of 310 CMR 40.0924(6)(a), when using a Method 1 or 2 Risk Characterization approach, it is not permissible to conduct spatial averaging of concentration data from different groundwater monitoring points. Rather, EACH individual well and/or groundwater monitoring point is a separate Exposure Point, and data from each well is considered a separate Exposure Point Concentration. In such cases, the EPC is calculated as the arithmetic average of (temporal) concentration data obtained from the various sampling rounds conducted at the monitoring point. In conducting these calculations and establishing valid EPCs:

- concentrations at the monitoring point should NOT be consistently increasing over time, which is suggestive of an unmitigated source area); and
- data more than two years old should not be the sole components of the temporal data set, absent clear and compelling evidence that current concentrations are unlikely to be higher than the data sets used in the EPC calculation.

> The *temporal* averaging of groundwater sample data from an individual well is a simple arithmetic average, and is NOT subject to the "75/10" averaging rules specified for the *spatial* averaging of soil samples.

In a Method 3 risk assessment, there is more flexibility in the calculation of EPCs, and, importantly, in the designation of Exposure Points. However, even in Method 3, per 40.0924(6)(b)(2), in GW-1 areas contaminant EPCs in every groundwater monitoring point must by default not exceed a Massachusetts drinking water standard. (*Note that while the aliphatic and aromatic hydrocarbon ranges (e.g., C9-C10 Aromatic Hydrocarbons) have MCP Method 1 GW-1 standards, they do not have promulgated drinking water standards, and are not subject to this default assumption – see Sections 5.4.1 and 7.6.2).*

In recognition of the typically short length of dissolved hydrocarbon plumes, a conditional exception to the default requirement to meet drinking water standards in every well is available in the MCP at 40.0924(6)(c) and 40.0926(7)(e), for those VPH/EPH Target Analytes (e.g., BTEX) that have drinking water standards:

- the exemption is only available at disposal sites contaminated solely by a release of oil located in a Zone II protective area; and
- must be based upon a Phase II level of effort and 2 years of quarterly monitoring, which demonstrates that the edge of a stable or contracting groundwater hydrocarbon plume is at least 1000 feet from the water supply well(s) of concern.

5.1.3 Indoor Air EPCs

Extensive guidance on indoor air sampling and evaluation is provided in MassDEP's *Vapor Intrusion Guidance (#WSC 16-435)* document. With respect to the calculation of indoor air EPCs at sites contaminated by a release of petroleum, the procurement and evaluation of data are particularly problematic, given the existence of "background" levels of the contaminants of interest, temporal variability, and potential data biases in the APH test method, as detailed in Section 3.2.3.

Once an environmental (vapor intrusion) pathway is confirmed, and any necessary adjustments are made to APH hydrocarbon range data (to remove "background" conditions), available data need to be converted into EPC concentrations for Target Analytes (e.g., BTEX compounds) and hydrocarbon ranges (i.e., C5-C8 and C9-C12 Aliphatic, and C9-C10 Aromatic Hydrocarbons).

Because of the highly variable nature of the vapor intrusion pathway, which can create substantial fluctuations in indoor air concentration values, and the typical lack of temporal indoor air testing data (usually only 2 to 3 samples), **the general expectation is that the highest detected concentration of each analyte of interest is designated as the EPC**. An alternative option is to calculate a conservative EPC that is the 90th percentile Chebyshev non-parametric upper confidence limit on the mean indoor air concentration – which will require substantially more than 3 data points.

As a final note, when evaluating indoor air impacts at disposal sites, it is important to understand and differentiate sampling and evaluation objectives and remedial 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 in some cases be appropriate, as noted above, with sufficient data and compelling rationale. Conversely, when the objective is to determine whether a CEP is present at a home, school, or daycare, averaging of this nature is not appropriate, though a consideration of the likely range of impacts may be a relevant factor in the (cost/benefit) feasibility evaluation that is required to determine if a remedial measure is necessary to mitigate or eliminate the CEP. Additional guidance in this regard is provided in Section 7.7.2.

5.1.4 Odors

The human health risk associated with petroleum odors are addressed generically in the Method 1 and Method 2 standards, and/or on a site-specific basis in a Method 3 risk assessment. Even if not posing a significant risk to human health, however, persistent odors of a certain magnitude can constitute a significant risk to public welfare, which would (a) preclude the use of a Method 1 or 2 risk characterization at a site (given this contribution of risk from the air pathway), and (b) preclude the achievement of a No Significant Risk finding via a Method 3 risk characterization process.

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 consistently or intermittently detectable in ambient or indoor air, and as long as excavation or disturbance of such soils is unlikely, based upon site-specific conditions and/or the institution of an Activity and Use Limitation.

- 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.

5.2 Method 1 Risk Characterization and Use of Generic Cleanup Standards

Generic soil and groundwater cleanup standards have been developed by MassDEP 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). There are no MCP standards for indoor air (APH results are often evaluated using the MassDEP Method 3 Shortform spreadsheets). The soil and groundwater 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 while all sites fall into the GW-3 category, some sites may also be within a GW-2 and/or GW-1 category. At sites where more than one category applies, all 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" using a Method 1 risk characterization method.

Do NOT assume that EPCs below a GW-1 standard will be below a GW-2 and GW-3 standard, or an EPC below a GW-2 standard will be below a GW-3 standard. That is not the case for all OHMs.

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

- **S-1 Standards** - applicable to soils that are accessible or potentially accessible, and where the frequency and/or intensity of exposure at the site is high (includes all exterior soils zero to 15 feet below ground surface at homes/schools/daycares/playgrounds).
- **S-2 Standards** - applicable to less accessible soils, with lower exposure potential.
- **S-3 Standards** - applicable to deep (> 15 feet) and isolated soils, and/or soils where the

frequency and/or intensity of exposure is low (including all soils beneath permanent structures).

Unlike the groundwater categories, the soil categories are mutually exclusive; any given volume of soil can only be S-1, S-2, or S-3. However, it is not uncommon to have different soil categories in different areas of a disposal site (e.g., S-2 in one area/depth range, and S-3 in another).

Changes made to the MCP in 2024 specify that in a Method 1 or 2 Risk Assessment, *the top 3 feet of surface soil shall also represent a separate Exposure Point for current use scenarios* [310 CMR 40.0924(7)(a)(2.)]. While the soil under pavement and concrete hardscape surfaces are consider "surface soil" in this context, soil under a permanent structure is not, unless it is a structure with an earthen floor.

The 2024 MCP changes affect the S-1 and S-3 soil categories on the opposite sides of the Soil Category selection Matrix at Table 310 CMR 40.933(9). Of the two, the S-1 category on the left-hand side of the matrix is of greater interest, as it includes portions of most residential/school/playground properties (i.e., site use high frequency/high intensity, accessible and potentially accessible soils). In this situation, an EPC for current site uses must be calculated for **0-3 feet and 0-15 feet**, for comparison to the appropriate S-1/GW-y standards (where y = 1, 2, and/or 3). A common mistake made in these situations is to calculate EPCs from 0-3 feet and 3-15 feet below grade. This is NOT correct.

Because all soil standards consider leaching impacts to underlying groundwater, and because there are 3 groundwater categories, there is a matrix (310 CMR 40.0993) of nine possible Method 1 soil standards for each contaminant (e.g., S-1/GW-1, S-1/GW-2, etc.). Any given disposal site may fall into 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 minimum and maximum concentration values established by MassDEP. As a lower limit, no Method 1 standard is set below a background or analytical reporting limit, even if the risked-based concentration was less than this value. On the other extreme, no Method 1 standard is set above a series of maximum concentration values established for classes of soil and groundwater contaminants. These maximum 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 staining and odors. The maximum level in groundwater is set at 50,000 µg/L; the maximum 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 (vapor pressure/odor threshold) of the compound or hydrocarbon range of interest. Additional information on minimum and maximum limits in the Method 1 standards is provided in various publications and spreadsheets on the MassDEP website.

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 (note that trimethylbenzenes are included within C9-C10 Aromatic Hydrocarbons); and
- the contamination must be predominantly within soil and groundwater, and cannot be present in any significant amount in sediments, air, or surface water.

5.2.1 Using Method 1 for Petroleum Contaminants

In a Method 1 risk characterization process, the EPCs of individual Target Analytes (Table 4-3) and aliphatic/aromatic fractions of interest (Table 4-2) are compared to the MCP Method 1 soil and groundwater standards that apply at the site. At most petroleum contaminated sites of limited size and complexity, where a judgmental sampling approach was used and where contamination is present predominantly in soil and groundwater, use of the "75/10" risk assessment process per 40.0926(8)(a)(1.) is recommended for characterizing risks from soil contaminants. A step-by-step summary of this process is provided in **Table 5-2**. For groundwater contaminants, each monitoring well is considered a separate Exposure Point, and spatial averaging of well data to calculate an EPC is not allowed, though temporal averaging of recent and representative sample data from each individual well is permitted.

Table 5-2: The "75/10" Method 1 Risk Assessment Process	
Step 1:	Identify applicable groundwater categories (all sites are GW-3, and some sites or portions thereof may also be GW-1 and/or GW-2). Note that any given area/volume of groundwater can be more than one category.
Step 2:	Identify the appropriate soil categories throughout the site (S-1, S-2, or S-3), per the matrix table at 40.0933(9). Note that any given area/volume of soil can ONLY be one category.
Step 3:	Combine soil "S" categories with underlying "GW" categories (e.g., S-1/GW-2, S-1.GW-3, S-3-GW-2, etc.), based upon the category(ies) of groundwater that underlie each soil category. These are the S-x/GW-y categories.
Step 4:	Compare all EPCs for all contaminants in all groundwater wells with all applicable GW Method 1 standards in 40.0974(2). Each well is its own EPC; spatial averaging is not allowed in Method 1 (though temporal averaging of data in each well is permissible). Temporal averaging for groundwater data is a simple average.
Step 5:	For soil, calculate "presumptive" EPCs for each S-x/GW-y area by taking an arithmetic average of data points contained within that S-x/GW-y area. When necessary, calculate a separate "presumptive" EPC for surface soils (0-3 feet). An EPC will be valid, and will demonstrate a condition of No Significant Risk, if, for EVERY S-x/GW-y (and 0-3 foot) increment and EVERY contaminant, • The arithmetic mean is below the applicable S-x/GW-y Method 1 soil standard in 40.0975(6) • 75% of data points used to obtain the arithmetic average are below the S-x/GW-y Method 1 soil standard; and • No single data point used to obtain the arithmetic average is > 10 times the S-x/GW-y Method 1 soil standard

"Failures" of a Method 1 risk characterization process should be noted; although this approach could not be used to demonstrate a condition of No Significant Risk at the site in question, it's possible that such a demonstration could still be made using a Method 2 or Method 3 evaluation. If not, remediation may be required.

5.2.2 Combined Method 1 and 3 for Indoor Air Contamination

Importantly, in accordance with 40.0971(2), the sole use of a Method 1 risk characterization method is not permissible at a site in which a significant amount of contamination is present in a media other than soil and groundwater. At petroleum contaminated sites, the most common and problematic limitation in this regard is when hydrocarbon contaminants are present within indoor air. These indoor air hydrocarbons could originate from (a) a fuel oil tank/heating system in use at the property, (b) spilled fuel oil off-gassing from a concrete floor, rug, or furnishings within a building, (c) the use of a consumer product, (d) a vapor intrusion pathway from dissolved concentration of hydrocarbon ranges or target analytes in groundwater, and/or (e) a vapor intrusion pathway from contaminated soils and/or volatile light nonaqueous phase liquids, possibly via a preferred pathway. In most cases, sources (a), (b) and (c) can be excluded from the risk assessment as a "background" condition. Guidance in this regard is provided in Section 4.1.6.

In cases where there is evidence of a subsurface vapor intrusion pathway, in accordance with 310 CMR 40.0942(1)(b)1., it is permissible to use a combined Method 1 and Method 3 risk characterization process if it is demonstrated that "the current or foreseeable future human exposure to the oil and/or hazardous materials would occur predominantly through contact with the groundwater or soil." In these cases, EPCs for contaminants in soil and groundwater are compared to the Method 1 standards in the MCP, while Method 3 is used to characterize the risk of harm to public welfare and the environment; no significant risks to public welfare would exist if odors related to a vapor intrusion pathway are not present.

For the purposes of interpreting the language at 310 CMR 40.0942(1)(b)1., and conducting a combined Method 1 and Method 3 risk characterization at petroleum contaminated sites, a conclusion that current and future human exposure to oil contaminants "would occur predominantly through contact with groundwater or soil" may be assumed if:

- the Hazard Index (HI) of all indoor air contaminants present above their MassDEP Threshold Value (e.g., TV_r or $TV_{c/i}$) and associated with a vapor intrusion pathway is equal to or less than 0.1; and
- the Excess Lifetime Cancer Risk (ELCR) of all indoor air contaminants present above their MassDEP Threshold Value (e.g., TV_r or $TV_{c/i}$) and associated with a vapor intrusion pathway is equal to or less than 1×10^{-6}.

Note that a conclusion of the existence of a condition of No Significant Risk in this regard does NOT negate the need to assess and mitigate Critical Exposure Pathways to the extent feasible, as discussed in Section 7.7.2.

5.3 Method 2 Risk Characterization

Using Method 2, site-specific fate and transport factors and considerations may be used to modify certain Method 1 standards, as described in 310 CMR 40.0982(3). Generally, this "modification" is more specifically a demonstration that current site EPCs constitute a condition of No Significant Risk, even though one or more EPCs may exceed a Method 1 standard. In this way, existing site conditions (e.g., groundwater concentrations, absence of a vapor intrusion pathway of concern) can be used in a lines-of-evidence approach to make such a demonstration. In theory, a modified standard greater than a current site EPC is possible, though such an effort would be significantly more difficult, and of little or no benefit.

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 5-3**. A summary of recommended Method 2 assessment approaches and limitations is provided in **Table 5-4**.

Table 5-3: MCP Method 1 Standards Most Likely to be Exceeded						
Contaminant	**Groundwater**			**Soil**		
	GW-1 (µg/L)	**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	✓			✓	✓	✓

Table 5-4: Use of MCP Method 2 Risk Characterization at Petroleum Contaminated Sites		
Site Condition	**Method 2 Assessment Actions**	**Limitations**
Groundwater EPCs > GW-2 Method 1 Standard	Evaluate potential for hydrocarbons in groundwater to impact indoor air of adjacent structures	There must be no significant impacts to indoor air, i.e., H.I. < 0.1 and ELCR < 1×10^{-6}
Groundwater EPCs > GW-3 Method 1 Standard	Evaluate potential for dissolved hydrocarbons in groundwater to impact receiving surface water body	Modified concentration cannot be in excess of a Method 3 Ceiling Limit [40.0996(7)]
Soil EPCs > Method 1 Soil Standard	Evaluate potential for hydrocarbons to leach from soil and impact underlying groundwater	Modified concentration cannot be in excess of a "direct contact" soil-exposure concentration [40.0985(6)]

Four important limitations to a Method 2 approach warrant emphasis:

- in accordance with 40.0926(3), for virtually all sites, fate and transport models may NOT be (solely) used to evaluate or "rule out" an impact to indoor air – actual site data must constitute the primary line(s) of evidence;
- Method 2 may NOT be used to modify an applicable Method 1 GW-1 standard, including the VPH/EPH Aliphatic and Aromatic Hydrocarbon fractional standards
- S-x/GW-y soil standards may not be modified to a level that exceeds the applicable (e.g., S-1, S-2, or S-3) "Table 5 Direct Contact" values at 40.0985(6); and

- groundwater standards (e.g., GW-1, GW-2, and GW-3) may not be modified to a level that exceeds the Method 3 Ceiling Limits established in Table 6 at 40.0996(7).

> In a Method 2 characterization, specific contaminants that exceed Method 1 standards can be "modified" to the site EPC value, if a showing can be made that such a value constitutes a condition of No Significant Risk. The combined use of listed Method 1 standards and such "modified" standards is considered a Method 2 Risk Characterization.

5.3.1 Using Method 2 to Evaluate Exceedances of Method 1 GW-2 Standards

Exceedances of an MCP Method 1 GW-2 standard(s) may be addressed in a Method 2 risk characterization by undertaking a vapor intrusion pathway investigation via the multiple lines of evidence approach specified in Section 4.3.3. If investigations show no significant impacts to indoor air, the Method 1 GW-2 standard of interest may be "modified" to the groundwater EPC value. In this context, no significant indoor air impacts would exist if, for all OHMs related to a vapor intrusion pathway:

- Indoor air concentrations are less than MassDEP Threshold Values (TVs), or
- The indoor air exposures of all OHM so modified represents an HI value of less than 0.1 and ELCR value less than 1×10^{-6}.

Note that use of the existing EPC values in this manner may not be appropriate at locations where significant concentrations of volatile and soluble hydrocarbons are present in the vadose zone beneath pavement or a building, and future removal of such a barrier could lead to significantly higher concentrations of these hydrocarbons in groundwater. Note also the need to address odors (public welfare concern) and/or CEPs (see Section 7.7.2 for residential CEPs).

> Example: The GW-2 EPC at a site for benzene is 1200 µg/L, in excess of the Method 1 GW-2 standard of 1000 µg/L. If it can be demonstrated via a Method 2 characterization that there are no significant impacts to indoor air, the Method 2 modified standard for benzene would be 1200 µg/L.

5.3.2 Using Method 2 to Evaluate Exceedances of Method 1 GW-3 Standards

Method 1 GW-3 standards were derived based upon an assumption that (a) impacts may occur to ecological receptors in a downgradient surface water body at concentrations equal to or greater than the surface water guideline, (b) groundwater from the site is discharging to such a surface water body, (c) dilution via groundwater transport to the downgradient surface water body reduces groundwater contaminant levels by a factor of between 2.5 to 100, based upon contaminant properties, and (d) groundwater contaminants levels are further diluted by a factor of 10 when discharging to the surface water body. A summary and description of currently recommended chemical-specific and fractional water quality guidelines, consisting of a Lethal Concentration 50% (LC50) value divided by 10, is provided in **Table 5-5**.

Using a Method 2 approach, in addition to site data, site-specific fate and transport factors and/or predictive models may be used to support the modification of Method 1 GW-3 standards. Recommended fractional fate and transport parameters are provided in Section 5.4.5**.** Note that per 310 CMR 40.0982(4), a Method 1 GW-3 standard cannot be modified to a concentration in excess of the Method 3 Ceiling Limit for the fraction of interest [40.0996(6)].

Table 5-5: Recommended Surface Water Quality Guidelines (MassDEP, 2024a)		
Analyte/Fraction	**Surface Water Guideline (µg/L)**	**Basis of Guideline**
Benzene	460	Acute LC50/10
Toluene	1400	Acute EC50/10
Ethylbenzene	180	Acute EC50/10
Xylenes	200	Acute EC50/10
Naphthalene	72	Chronic LOEC
C5-C8 Aliphatics	250	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	Acute LC50/10 for trimethyllbenzene (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	5	Mean PAH toxicity

In lieu of site-specific modeling, the conservative dilution factors graphically illustrated in **Figure 5-1** may be used as part of a Method 2 evaluation of groundwater-to-surface-water impacts of dissolved hydrocarbon contaminants. These graphs are generalized, source-area dependent conservative dilution and dispersion curves for dissolved groundwater contaminants, including hydrocarbon range fractions and Target Analytes. They were developed using an analytical transport model (Domenico and Robbins, 1985) assuming an infinite source condition. The only attenuation mechanism considered is hydrodynamic dispersion.

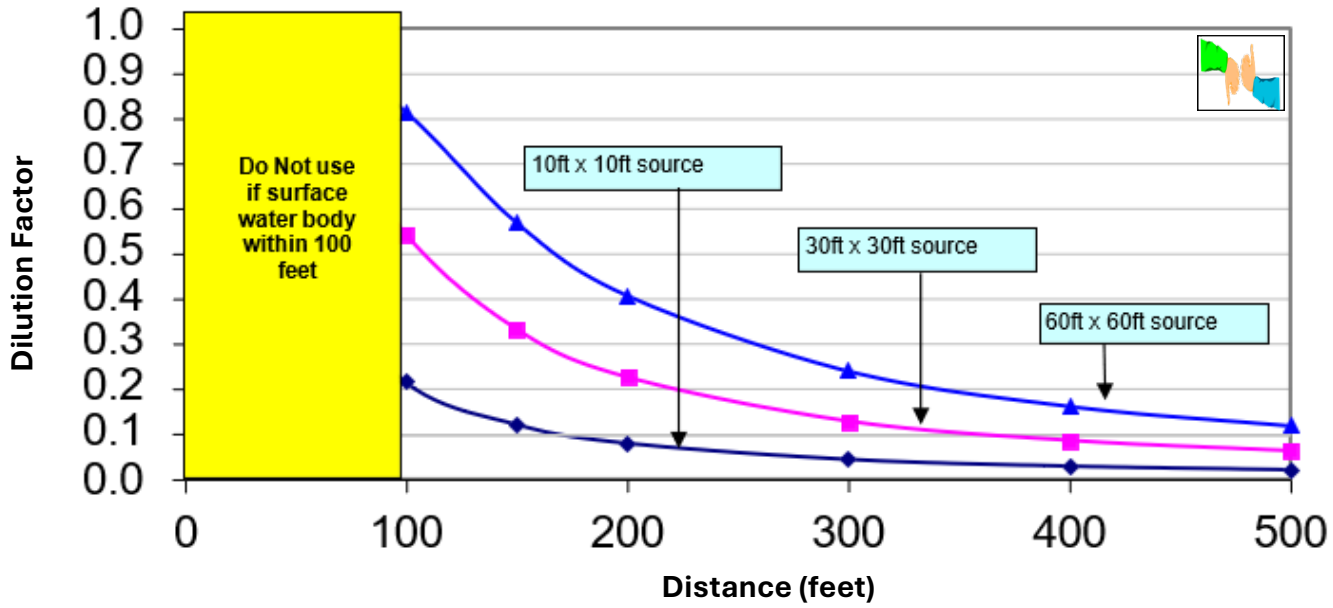
The use of the graphs and equations in Figure 5-1 is limited to sites where ALL of the following conditions are met:

- groundwater/contaminant flow occurs only in an overburden formation;
- there is no “short circuiting” of groundwater/contaminants along preferred flow paths;
- no dissolved contaminant is present at a concentration greater than its Method 3 Ceiling Limit; and
- the nearest downgradient surface water body is at least 100 feet from the impacted well/groundwater area on the site.

Note that these graphs and equations may not (solely) be used to satisfy the requirements in the MCP at 310 CMR 40.0926(7)(e) to establish the point of plume attenuation.

Figure 5-1 should be used to support, not replace, actual site data (groundwater, and, where necessary, surface water data).

Figure 5-1: Groundwater Dilution Factors (DFs) for Dissolved Hydrocarbons



Equations: 10ft x 10ft source area, $DF = 177 \times [\text{distance in feet}]^{-1.455}$
30ft x 30ft source area, $DF = 303 \times [\text{distance in feet}]^{-1.365}$
60ft x 60ft source area: $DF = 237 \times [\text{distance in feet}]^{-1.214}$

In most cases, actual plume attenuation should be significantly more robust, given the biodegradation potential of dissolved petroleum hydrocarbons, which are not considered in the presented graphs. As such, the primary utility of these graphs is to function as a "check" on site data, and/or as a line of evidence where site data is inconclusive.

If the totality of site data and available information demonstrates a condition of No Significant Risk to the environment, the EPC in the monitoring well that exceeded the Method 1 standard would become the Method 2 ("modified" Method 1) GW-3 standard.

Example: at a site in which the source area of contamination is approximately 30ft x 30ft, if the concentration of ethylbenzene in a well located 400 feet from a receiving water body is 7000 µg/L, a (dimensionless) Dilution Factor of 0.09 is obtained from Figure 5-1. Multiplying this Dilution Factor by 7000 µg/L yields 630 µg/L, which would be a conservative estimate of the concentration of ethylbenzene in groundwater before it discharges to the surface water body. An additional site-specific groundwater-to-surface water dilution factor could then be applied to predict the water-column concentration of the hydrocarbon range, for comparison to the values listed in Table 5-5

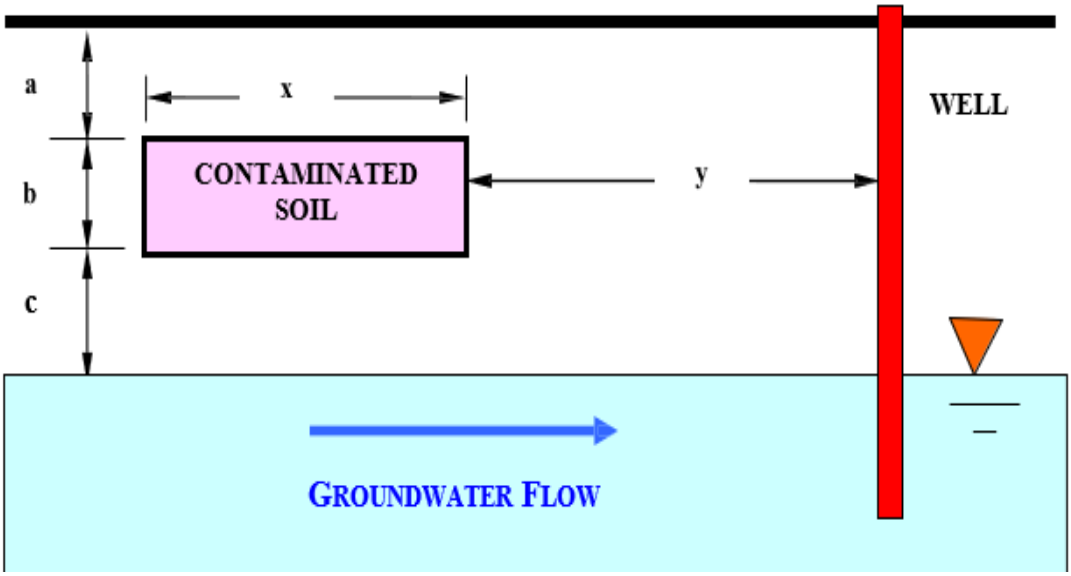
5.3.3 Using a Method 2 to Evaluate Exceedance of S-x/GW-y Soil Standards (Leaching)

Method 1 soil standards were derived via (1) the calculation of a concentration value (µg/g) protective of human health risks (threshold and carcinogenic) from direct contact with contaminated soil, and (2) the calculation of a concentration value (µg/g) that is unlikely to leach and impact underlying groundwater to the point where an applicable GW-1, GW-2, or GW-3 standard would be exceeded. The lower of these values are the S-x/GW-y Method 1 standards in Tables 2, 3 and 4 in 310 CMR 40.0900.

A number of S-x/GW-1 standards are controlled by the leaching pathway, not by direct contact health concerns. For these contaminants, it would be possible to modify a Method 1 soil standard up to the "direct contact" risk limit, if a showing can be made (via Method 2) that the leaching pathway is not of concern at the soil EPC value at the site in question.

The leaching-based component of the Method 1 standards were derived using the SESOIL and AT 123D computer models to evaluate unsaturated and saturated zone transport, as depicted in **Figure 5-2**.

Figure 5-2: Leaching Scenario Used to Develop Method 1 Soil Standards



This modeling exercise was used to determine the maximum (µg/g) concentration of a contaminant in vadose zone soils that would not leach to a degree that would lead to the exceedance of the appropriate (µg/L) groundwater standard (e.g., GW-1, GW-2, and/or GW-3) in a water table monitoring well located some distance downgradient of contaminated soil. The modeled scenario involved a block of soil (**x)** by (**x)** meters wide and (**b)** meters deep, located (**a)** meters below the ground surface and (**c)** meters above the water table, and (**y)** meters from a downgradient monitoring well. The modeling exercise was probabilistic, in that a range of values were inputted for each dimension, leading to a distribution of possible outputs (Dilution and Attenuation Factor), and selection of an appropriate percentile value.

Based upon the assumptions and models used by MassDEP, the only hydrocarbon fraction Method 1 soil standard controlled by leaching concerns is C11-C22 Aromatic Hydrocarbons in GW-1 (drinking water) areas. However, a number of the Method 1 soil cleanup standards for Target Analytes are controlled by the leaching pathway in GW-1 areas (i.e., BTEX, naphthalene, 2-methylnaphthalene, acenaphthene, and phenanthrene) and GW-2 areas (xylenes, naphthalene, 2-methylnaphthalene).

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 the leaching pathway. In most cases, site groundwater data are used to determine if leaching is of concern; contaminants in all wells below the applicable GW-1, GW-2, and/or GW-3 standards are a line of evidence that the MassDEP leaching model was overly conservative at the site in question.

In these situations, the Method 1 S-x/GW-y standard could be "modified" to the site soil EPC value – **as long as that EPC value does not exceed the applicable S-1, S-2, and/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 1000 µg/g, which is the level at which the human health/public welfare risks associated with direct contact controls the setting of this standard.

In order to have sufficient confidence in the use of site groundwater data as the primary basis of a Method 2 modification to a site EPC value(s), the following site and release 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 10 feet;
- the surface(s) overlying most of the contaminated soils are pervious (i.e., no or limited pavement or buildings);
- the number and location of water-table monitoring wells are sufficient to characterize groundwater quality below and downgradient of the zone of soil contamination; and
- at least 4 rounds of monitoring data exist to evaluate seasonal trends.

At sites where the use or sole use of available groundwater data is not appropriate or may not be protective, 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 EPCs 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. Model inputs (e.g., infiltration, depth to groundwater, soil organic carbon content, hydraulic conductivity, etc.) should be site-specific but reasonably conservative.

Recommended fractional fate and transport parameters are provided in Section 5.4.5. For additional information on the calculation of leaching-based Method 1 soil standards, consult the MassDEP web site.

5.4 Method 3 Risk Characterization

Under Method 3, a 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 5-6** and **5-7**, 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* (MassDEP, 1995 and as updated).

5.4.1 Requirements and Limitations of a Method 3 Risk Characterization

While a Method 3 risk 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, MassDEP imposed

Table 5-6: Recommended VPH/EPH/APH 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	0.1	0.03	0.1	2.0	0.03
Subchronic Oral RfD (mg/kg/day)	0.4	1.0	0.3	1.0	6	0.3
Chronic Inhalation RfC (µg/m3)	200	200	50	200	N/A	50
Subchronic Inhalation RfC (µg/m3)	200	600	500	600	N/A	500
Typical Indoor Air 50/75/90 percentile (µg/m3)	58/130/330	68/110/220	ND/ND/44	N/A	N/A	N/A
Chronic RAF - Soil Ingestion	1	1	1	1	1	0.3
Chronic RAF - Soil Dermal	0.2	0.2	0.2	0.2	0.2	0.1
Chronic RAF – Water Ingestion	1	1	1	1	1	1
Subchronic RAF - Soil Ingestion	1	1	1	1	1	0.3
Subchronic RAF - Soil Dermal	0.2	0.2	0.2	0.2	0.2	0.1
Subchronic RAF - Water Ingestion	1	1	1	1	1	1
Ambient Water Quality Guide (µg/L)	250	1800	540	1800	2100	N/A
Sediment Benchmark (mg/kg oc)[a]	1591	2722	236	3167	9883	92
Sediment Benchmark (foc = 0.001)(mg/kg)[a]	1.59	2.72	0.24	3.17	9.88	0.09

[a]mg/kg dry weight

Table 5-7: Recommended VPH/EPH/APH Fractional Properties for Modeling Purposes								
	Equiv Carbon Number (EC)	Molecular Weight	Vapor Pressure (atms)	Solubility in Water (µg/L)	Henry's Constant H*	Partition Coeff, Koc (mL/g)	Diffusion Coeff (cm^2/s)	
							air	water
C5-C8 Aliphatics	6.5	93	0.10	11,000	54	2265	0.08	1×10^{-5}
C9-C12 Aliphatics	10.5	149	8.7×10^{-4}	70	65	1.5×10^{5}	0.07	1×10^{-5}
C9-C10 Aromatics	9.5	120	2.9×10^{-3}	51,000	0.33	1778	0.07	1×10^{-5}
C9-C18 Aliphatics	12	170	1.4×10^{-4}	10	69	6.8×10^{5}	0.07	5×10^{-6}
C11-C22 Aromatics	14	150	3.2 x 10-5	5800	0.03	5000	0.06	1×10^{-5}
C19-C36 Aliphatics	considered immobile							

*dimensionless

maximum limits 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 (e.g., staining and odors). *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 and demonstrate that all such concerns are at or 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 (see 310 CMR 40.0995). Stage I is a screening process used to (1) eliminate from further consideration those sites where exposures are 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 a Method 3 Ceiling Limit. The Method 3 Ceiling Limits (formerly *Upper Concentration Limits*) 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 310 CMR 40.0996(3), these ceiling values are to be applied to the arithmetic mean of the concentration of oil or hazardous materials at a site or within a hot spot. If the mean concentrations of site contaminants exceed an applicable Method 3 Ceiling Limit, remediation

must be undertaken to treat and/or detoxify soil and/or groundwater contaminants, if feasible. If treatment of soil contaminants is not feasible, an Engineered Barrier may allow the achievement of a Permanent Solution (see 310 CMR 40.0998) In cases where it is not feasible to treat or cap contaminated soil, or treat contaminated groundwater, it may be still possible to obtain an interim site closure by filing 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 risk 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. *This means that all oil/hazardous materials in all monitoring wells must be at or below drinking water standards*. While drinking water standards have been promulgated for a number of VPH Target Analytes (e.g., benzene at 5 µg/L), at the present time, the VPH/EPH fractional ranges are not included on this list. Also not included are the target analytes naphthalene, 2-methylnaphthalene, acenaphthene, and phenanthrene. While it is necessary to characterize the risk these target analytes and factional ranges pose to the water supply of concern, it is not necessary to consider these values "analogous health standards."

  For petroleum contaminants with a promulgated drinking water standard, a conditional exemption from the need to meet those standards in Zone II areas is provided at 310 CMR 40.0926(7), as further discussed in Section 5.1.2.

In accordance with 310 CMR 40.0955(2), Imminent Hazards to human health are determined using a Method 3 risk characterization process. Note that petroleum contaminants (Target Analytes and Aliphatic/Aromatic Hydrocarbon ranges) are NOT considered contaminants with "serious effects", per 40.0955(2)(c)(1.). Note that at the present time only a few contaminants fall under the "serious effects" category, namely, TCE, lead, cyanide, perchlorate, methyl mercury, and chromium (VI).

5.4.2 MassDEP Risk Assessment Shortforms

To facilitate Method 3 risk characterizations, including for Imminent Hazard determinations, MassDEP has developed and posted on its website "Shortform" risk assessment (Excel) spreadsheets for soil, groundwater, and indoor air. There are files to calculate total site risks for long-term exposures (to compare to No Significant Risk limits), as well as 'ih" files to evaluate short-term exposures to determine if an Imminent Hazard is present.

To use the Shortforms, simply enter in the EPCs for contaminants of concern, and the spreadsheet will tabulate a Hazard Index (to quantify risk from threshold health effects) and an Excess Lifetime Cancer Risk (to quantify risk from non-threshold/cancer health effects). Be sure to add HI and ELCR values from various spreadsheets (e.g., air, soil), if used, to obtain TOTAL site risk values (HI and ELCR).

It is important to note that when evaluating risks using indoor air data, **it is NOT permissible to adjust site EPC concentration values by subtraction of MassDEP Threshold Values**, as these values do not necessarily represent "background" at any specific site. The utility of TV concentration values is to discern if an OHM is likely present above a background condition; if below a TV value, it may be appropriate to eliminate a chemical from the risk assessment process, if above, it is generally necessary to include the chemical with its unadjusted site-derived EPC, absent a showing that the chemical is unrelated to a vapor intrusion pathway.

Note that in conducting a Method 3 Risk Assessment, including the MassDEP Shortforms, final HI and ELCR values (all media/pathways) must be expressed as one significant figure, for comparison to the (one significant figure) MCP risk management metrics. An **Imminent Hazard** would exist at petroleum contaminated sites if the **HI** value is *equal to or greater than* 10, or if the **ELCR** value is *equal to or greater than* 1×10^{-5}. A condition of **No Significant Risk** would exist if the HI value is *equal to or less than* 1, and the ELCR value is *equal to or less than* 1×10^{-5}.

Additional information about the Shortforms can be found in the Shortform User Guide (SFUG0624). **Any modifications to the Shortforms must be clearly identified, documented and supported with technical justification**.

5.4.3 Recommended Toxicological Parameters

The currently recommended toxicological values for assessing risks associated with the VPH/EPH/APH aliphatic and aromatic hydrocarbon fractions are listed in Table 5-6 presented above (MassDEP, 2024a), along with the typical indoor air concentrations for volatile fractions, indicating the 50th, 75th, and 90th percentile values (MassDEP, 2008), and sediment benchmarks (MassDEP, 2007a).

5.4.4 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, 1997).

Relative to the VPH and EPH hydrocarbon ranges – FOR MODELING PURPOSES ONLY - recommended fractional properties are provided in Table 5-7 presented above. These values were obtained and/or extrapolated from TPHCWG.

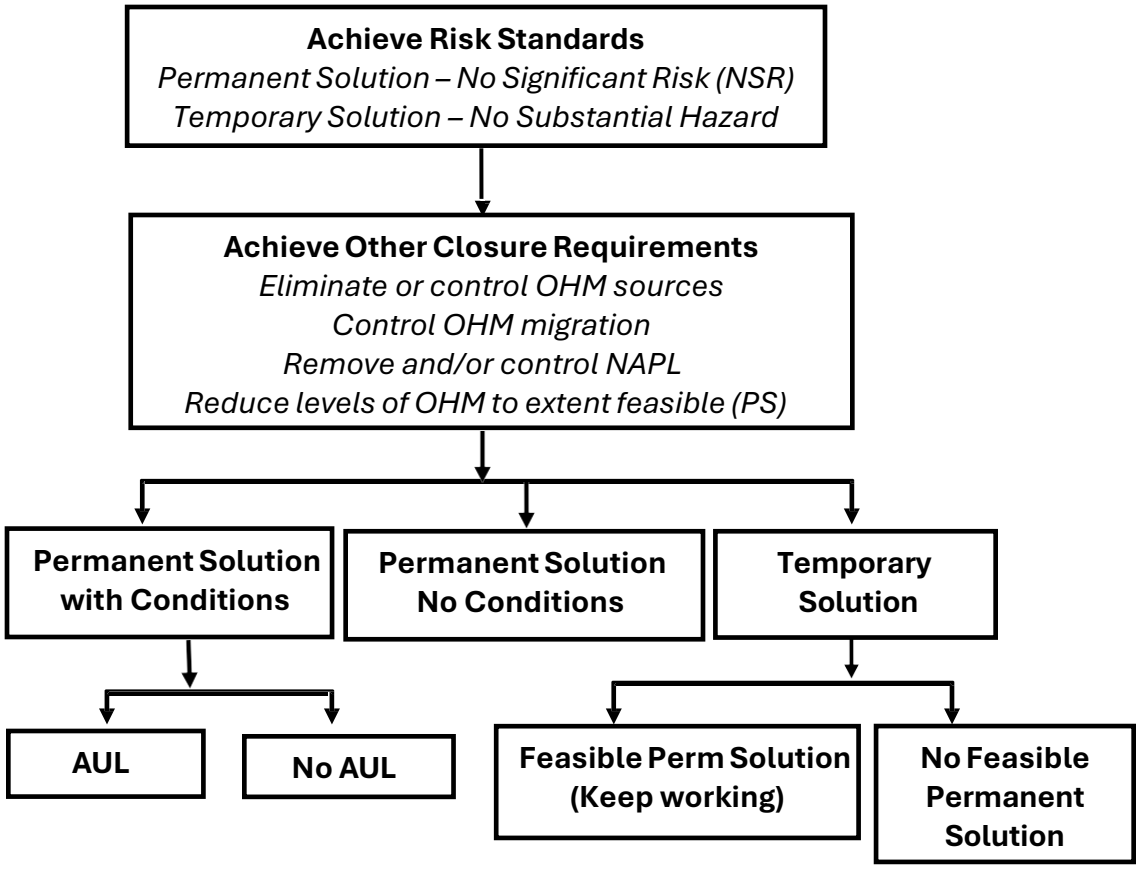
6.0 SITE CLOSURE

The MCP specifies two types of site closures: Permanent Solutions and Temporary Solutions. A Temporary Solution must be filed within 5 years of Tier Classification if (i) there is no feasible Permanent Solution, or (ii) there is a feasible Permanent Solution, but it has not yet been achieved. There are two categories of Permanent Solutions: Permanent Solutions with No Conditions and Permanent Solutions with Conditions. A major bifurcation of the Permanent Solution with Condition category is Permanent Solutions with Conditions including an Activity and Use Limitation (AUL) and Permanent Solutions with Conditions that do not include an AUL. A summary of the site closure process is provided in **Figure 6-1**; a flowchart of the elements of an MCP closure is provided in **Appendix 4**.

In order to achieve a Permanent Solution, an MCP Method 1, 2, or 3 risk characterization must demonstrate that the disposal site (or portion thereof) is at a condition of No Significant Risk to human health, safety, public welfare, and the environment, for current and foreseeable exposures. In order to achieve a Temporary Solution, the disposal site must be at a condition of No Substantial Hazard.

In addition to a showing of a condition of No Significant Risk or No Substantial Hazard, there are a number of other site closure performance standards delineated in 310 CMR 40.1003 that must be achieved, including source elimination or control, migration control, NAPL removal, and (for Permanent Solutions) a reduction of contaminant levels to the extent feasible.

Figure 6-1: Site Closure under the Massachusetts Contingency Plan



Under M.G.L. c 21E and the MCP, parties report *releases* and take response actions at *disposal sites*. Releases are assigned Release Tracking Numbers (RTNs) by MassDEP, and disposal sites are created by/associated with one or more releases of OHM. There are several places in the MCP process where RTNs can be consolidated (e.g., IRA Completion Statement, Tier Classification, Permanent and Temporary Solution Statement), to establish a primary RTN for the disposal site. **It is important to note that site closure (Permanent or Temporary Solution) is obtained for disposal sites (or portions thereof), and NOT for releases**. At disposal sites where multiple releases are co-mingled, closure of a defined area/depth of a disposal site can only occur if ALL MCP-regulated contaminants achieve required risk endpoints and performance standards, regardless of who may have liability to take needed response actions. **Simply stated, it isn't clean until it's clean**.

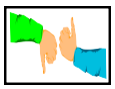
Risk characterization options were discussed in the previous section. Below is guidance on achieving the other performance standards for site closure.

6.1 Source Elimination or Control

Under the provisions of 310 CMR 40.1003(5), a Permanent or Temporary Solution cannot be achieved at a site if a continuing source(s) of environmental contamination is present. Per 40.0006 "Source of OHM Contamination" is defined to include both point discharges as well as intermedia mass transfer of OHM from NAPL and impacted soils.

At petroleum-contaminated sites, the following conditions could constitute a continuing source:

- *Abandoned Storage Tanks* - Any abandoned storage tank containing any amount of NAPL 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 applicable 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 properly closed out or operating in compliance with all applicable regulations.



- *NAPL* - Given requirements that all NAPL must be removed from a site to the extent feasible, petroleum NAPL remaining at a site will generally not be considered a source requiring mitigation unless (a) it is the source of a petroleum vapor intrusion pathway that constitutes a significant risk to human health, safety, or public welfare, (b) it is discharging or periodically discharging to surface water bodies or subsurface utilities or structures, or (c) it contains more than 10% biofuel components and is generating significant quantities of methane gas.

At sites where the above sources cannot be eliminated, the Permanent Solution standard of "eliminated to the extent feasible and controlled" is met if (a) for NAPL-related petroleum vapor intrusion pathways constituting a significant risk, an Active Exposure Pathway Mitigation Measure (AEPMM) is implemented in accordance with 310 CMR 40.1025, and (b) for biofuel NAPL, methane accumulations in structures and utilities are insignificant, e.g., less than 5% of the Lower Explosive Limit (LEL), with or without and AEPMM.

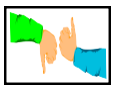
At sites where the above sources cannot be eliminated, the Temporary Solution standard of "eliminate and controlled to the extent feasible" is met if (a) for NAPL-related vapor intrusion pathways constituting a Substantial Hazard, an AEPMM is implemented in accordance with 310 CMR 40.1026, (b) for biofuel NAPL, methane accumulations in structures and utilities do not constitute a significant explosion hazard (i.e., are less than 10% of the Lower Explosive Limit (LEL)), with our without and AEPMM, and (c) for NAPL that is discharging or periodically discharging to surface water bodies or subsurface utilities or structures, sorbent pads, booms, or other containment measure are instituted in accordance with 40.0897 to minimize migration of NAPL in surface water bodies and/or subsurface structures or utilities.

6.2 Migration Control

Under the provisions of 310 CMR 40.1003(6), a Permanent or Temporary Solution cannot be achieved at a site unless the subsurface migration of OHM at and from a disposal site is controlled. The performance standard to achieve in this regard is a showing that the dissolved hydrocarbon plume in groundwater and/or vapor-phase plume in the vadose zone is stable or contracting. This is generally not a problem at petroleum contaminated sites, given that most dissolved hydrocarbon plumes bio-attenuate within about 200 feet from the source area (API, 1998), and significant migration of hydrocarbon vapors in the vadose zone is not generally observed (US EPA, 2015).

A potential concern may exist at sites with NAPL containing more than 10% biofuels, which can extend the length of dissolved hydrocarbon plumes and generate substantial amounts of methane gas. In such cases:

- sufficient investigative data is needed to determine the length and stability of dissolved hydrocarbon plumes in groundwater, and



- the potential migration of methane (vapors and dissolved in groundwater) should be investigated if structures or underground utilities are present within 100 feet of the disposal site.

Due to its limited solubility and volatility, investigative actions are not generally needed to demonstrate migration control at spills of diesel/#2 fuel oil, unless (a) there is a drinking water supply well located within 500 feet of the source area, (b) there is a diesel/#2 fuel oil vapor intrusion pathway within 100 feet of the source area, or (c) the fuel oil contains more than 10% biofuel components,

6.3 NAPL

The presence of a visible non-aqueous phase liquid (NAPL) adds significant complexity to the assessment and remediation of petroleum-contaminated sites. Of primary concern is (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, via intermedia mass transfer processes.

The MCP sets specific cleanup requirements for all NAPLs, including petroleum NAPL. Under 310 CMR 40.1003(7) of the MCP, in order to achieve a Permanent Solution, non-stable NAPL may not be present at a site, and all (stable) NAPL must be removed to the extent feasible. For Temporary Solutions, *Non-stable NAPL* can be present, as long as it is removed or controlled to the extent feasible.

Non-Stable NAPL is NAPL with a footprint that is expanding laterally or vertically by (a) migrating along or within a preferred flow path, (b) discharging or periodically discharging into a building, utility, drinking water well, or surface water body, or (c) spreading as a bulk fluid through or from subsurface media. It is also referred to as NAPL with macro-scale mobility, in contrast to *NAPL with Micro-Scale Mobility* – which is NAPL with a footprint that is not expanding, but which is visibly present in the subsurface in sufficient quantities to migrate or potentially migrate as a separate phase over a short distance and visibly impact an excavation, boring, or monitoring well.

MassDEP has issued detailed guidance on the identification, assessment, and remediation of petroleum LNAPL in *Light Nonaqueous Phase Liquids (LNAPL) and the MCP: Guidance for Site Assessment and Closure*, Policy #WSC-16-450. Included in the LNAPL guidance are specific recommendations and metrics on how to look for, measure, and characterize the stability of LNAPL, and determine the feasibility of LNAPL recovery, when implementing the "Simplified Approach" prescribed in the guidance. The overall flowchart of this recommended process and LNAPL Stability Action Levels are provided in **Figure 6-2**, and **Table 6-1**. A recommended graph on determining the infeasibility of LNAPL recovery is reproduced as **Figure 6-3**.

6.4 Feasibility of Achieving Background Concentrations (Permanent Solutions)

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* [310 CMR 40.1003(5)].

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 toxicants affect human and ecological receptors; these limitations are especially true and problematic when considering

Figure 6-2: Simplified Approach for LNAPL Assessment and Remediation (MassDEP #WSC-16-350)

[CHECK SOURCE PUBLICATION FOR POSSIBLE UPDATES]

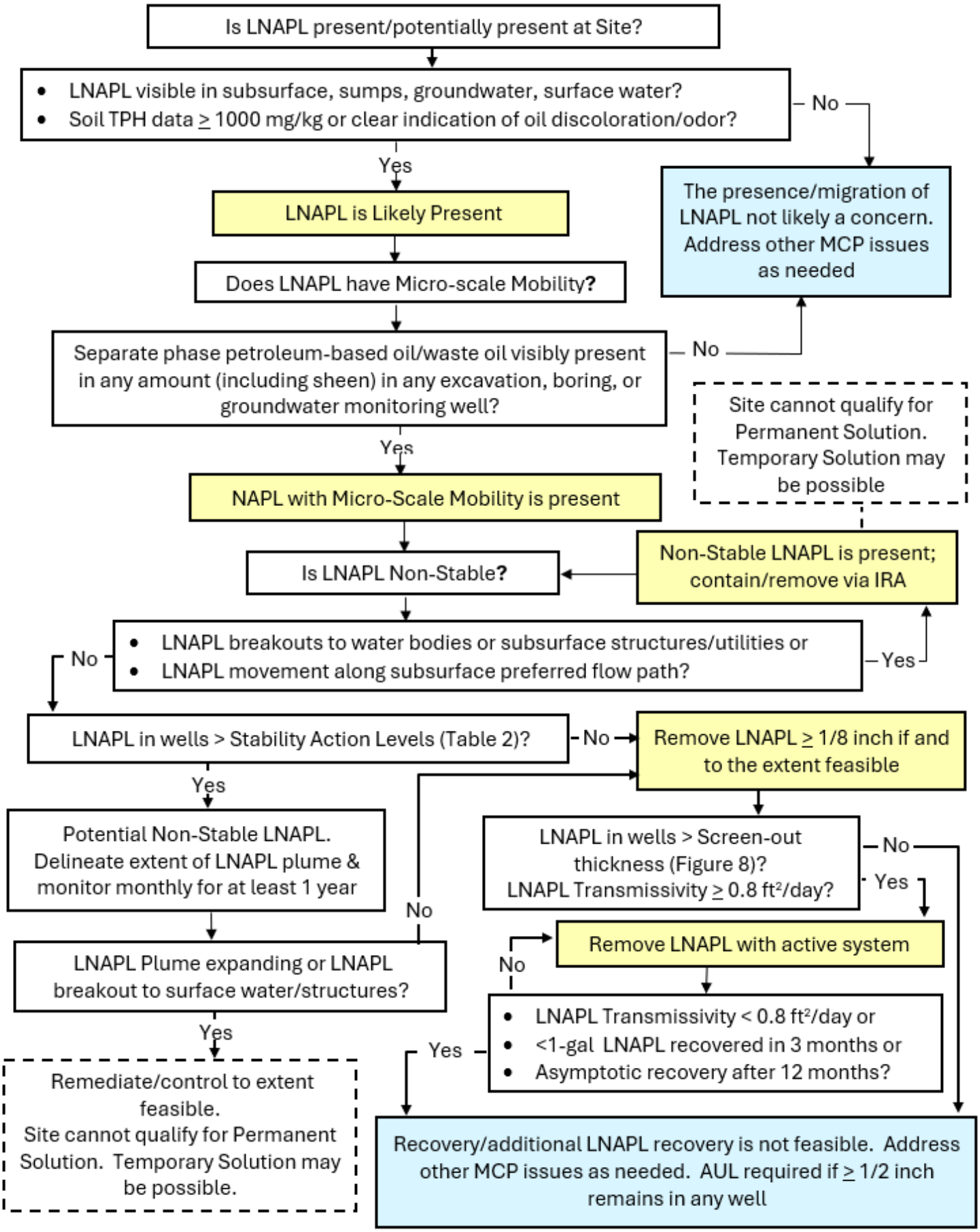
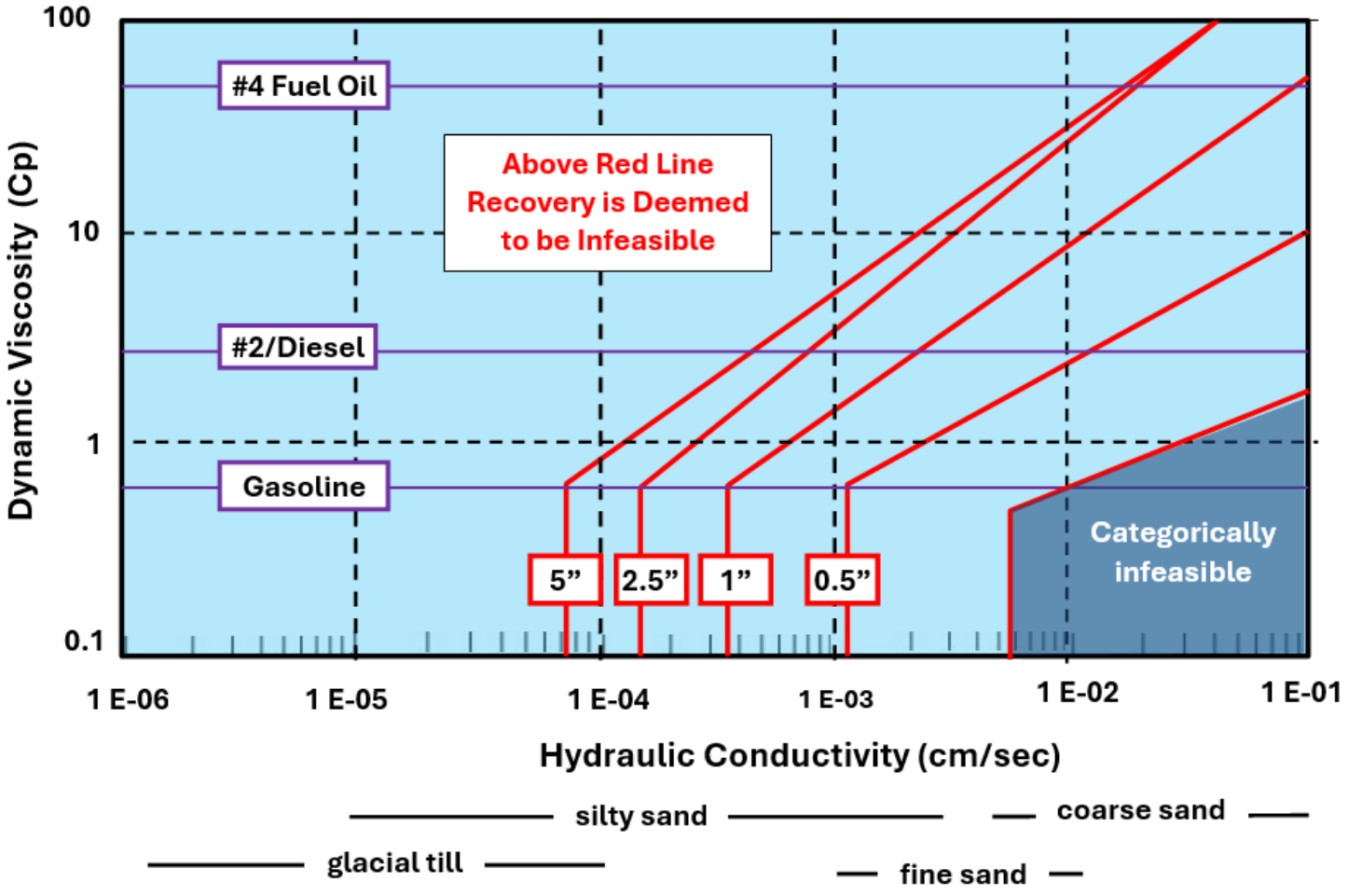


Table 6-1: **LNAPL Stability Action Levels** (Golder Associates, 2008)			
Soil Type*	**Characteristic Fraction**	**Percent Fines (silt and clay)**	**LNAPL Thickness (inches)**
Coarse sand or gravel	> 20% Coarse sand	< 3	**1.2 inch**
Coarse sand or gravel	> 20% Coarse sand	3-10	**2 inches**
Medium sand	Medium sand	< 10	**4 inches**
Fine sand	Fine sand	< 10	**8 inches**
Silty sand	Sand	> 10	**12 inches**

* If soil at a site does not match any of the listed types, professional judgment shall be used to select an available category and metric that is a reasonably conservative approximation.

Figure 6-3: Feasibility of LNAPL Recovery by Conventional Technologies (MassDEP #WSC-16-450)
[CHECK SOURCE PUBLICATION FOR POSSIBLE UPDATES]



Feasibility of LNAPL Recovery Examples

The maximum thickness of Fuel Oil #2 measured in a well at a site is 1 inch, in a fine to silty sand with a conservative hydraulic conductivity value of 1 x 10^{-3} cm/sec. In Figure 6-3, make a point at the intersection of the 1E-03 mark on the "x" axis and the #2/Diesel fuel mark on the '"y" axis. Since that point is above the 1" thickness red line in the graph, recovery by conventional hydraulic/vacuum technologies maybe considered infeasible.

The maximum thickness of gasoline in a monitoring well is 2 inches in a formation with a hydraulic conductivity value of 5 x 10-4 cm/sec. The extrapolated intersection between 5E-04 cm/sec and the gasoline horizontal line is below the extrapolated 2-inch thickness red line, meaning the feasibility of LNAPL recovery by conventional methods cannot be ruled out using this approach.

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.

While it is necessary to consider the feasibility of achieving or approaching background at all MCP 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 where source areas have been addressed, 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 these considerations, certain generic guidelines are offered to streamline background restoration considerations at sites contaminated ONLY with petroleum hydrocarbons:

- Groundwater - Achieving or approaching background concentrations of petroleum hydrocarbons in *groundwater* may generally be considered infeasible.
- Soil - Achieving or approaching background concentrations of petroleum hydrocarbons may generally be considered infeasible in soils, except in cases where only small quantities of contaminated soil are present (less than 20 cubic yards) in readily accessible locations.

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 the feasibility of achieving background may be downloaded from the MassDEP web site (MassDEP 2004).

6.5 Categories of Permanent Solutions

Complete details on the categories and required elements of Permanent Solutions are contained in 310 CMR 40.1000. Guidelines and recommendations specific to petroleum contaminated sites are outlined below:

- *Small spills* - For relatively minor releases of petroleum fuels or products, it is usually feasible to achieve a Permanent Solution with No Conditions, using a Method 1 or Method 2 risk characterization process.

- *Larger spills* - For larger spills and/or more complex sites, it is often necessary to file a Permanent Solution with Conditions that may include an Activity and Use Limitation (AUL).

6.6 AULs

An AUL is part of a Permanent Solution at sites where a condition of No Significant Risk exists for current uses, but not all future foreseeable uses. The most common AUL is a Notice of Activity and Use Limitation, as detailed at 310 CMR 40.1074, which involves the attachment of a notice to the deed of a property in cases where the amount of remaining contamination warrants documentation and/or controls.

The three conditions at petroleum contaminated sites most likely to trigger the need for an AUL are (a) the presence of LNAPL with micro-scale mobility, (b) the presence of contaminants in soil that could pose a significant risk to sensitive receptors, and/or (c) the presence of sub-slab soil gas vapors at a level that could create indoor air exposure concerns if the basement/slab were removed or damaged.

LNAPL - The MCP at 310 CMR 40.1012(2)(d) requires the filing of an AUL for all sites where NAPL is visibly present in an excavation, boring, or monitoring well at a measured or anticipated thickness greater than ½-inch and is it not feasible to remove the remaining NAPL.

> At all disposal sites where more than ½-inch of LNAPL was visibility present in any excavation, boring, or monitoring well at any time, an AUL is required when filing a Permanent Solution, unless at least one year of at least four subsequent seasonal gauging efforts has demonstrated less than or equal to 1/2-inch of visible NAPL in every monitoring point during every gauging event.

Soil Contamination - An AUL is also required at sites where contaminated soil down to 15 feet below grade is safe for the current site use (e.g., commercial lot or beneath a residential building footing) but is not safe for any future use or exposure pathway (e.g., if the soil is excavated and deposited at the ground surface at a residential home or playground). When using a Method 1 or 2 risk assessment process, this means that one or more contaminant Exposure Point Concentrations in the soil exceeds the Method 2 S-1 "direct contact" standards at 40.0985(6).

> A Method 3 risk characterization can be conducted in cases where an AUL would be required due to exceeding one or more Method 2 S-1 "Direct Contact" standards at 310 CMR 40.0985(6). An AUL would not be required if the Method 3 assessment demonstrated a condition of No Significant Risk for any site use or soil exposure scenario (e.g., if the soil was excavated and brought to a residence or playground). However, this assessment must also evaluate risks to public safety, the environment, and public welfare – including soil odors.

Sub-slab Vapors – Just as soil contamination at depth is a concern for future/foreseeable exposures, hydrocarbon vapors below a building slab have the potential to create indoor air exposures if some portion of the basement/slab structure is removed or damaged. An AUL is required to notate this condition, and the need to maintain the integrity of the building slab/foundation, if the concentrations of sub-slab vapors are high enough to warrant concern.

Such a determination involves an estimation of the future dilution and attenuation factor (DAF) between sub-slab soil gas and overlying indoor air. Absent a defensible site-specific DAF determination, MassDEP considers a value of 70 to be reasonable estimation. Using this DAF value, a simplified approach for determining whether an AUL is required to address future vapor

intrusion concerns is provided in **Table 6-2**, based upon risk metrics or Typical Indoor Air Concentrations (TIAC)

Table 6-2: Simplified Approach for Determining Need for AUL to Address Sub-Slab Soil Gas

Contaminant	Acceptable Indoor Air Value ($\mu g/m^3$)	Odor Threshold ($\mu g/m^3$)	Basis of Acceptable Indoor Air Value	Max Allowable Sub-Slab Conc with 70X DAF ($\mu g/m^3$)	Sub-Slab Conc Requiring AUL ($\mu g/m^3$)
Benzene	2.3	4900	TIAC	160	>160
Toluene	1000	30,000	HQ = 0.2	70,000	>70,000
Ethylbenzene	200	2000	HQ = 0.2	14,000	>14,000
Xylenes	20	440	HQ = 0.2	1400	>1400
Naphthalene	0.6	440	HQ = 0.2	42	>42
C5-C8 Aliphatics	58	--	TIAC	4100	>4100
C9-C12 Aliphatics	68	--	TIAC	4800	>4800
C9-C10 Aromatics	10	--	HQ = 0.2	700	>700

Note that the acceptable indoor air concentrations in Table 6-2 for the listed compounds and hydrocarbon fractions are based upon human health risks (Hazard Quotient = 0.2) or TIAC value, whichever is higher, consistent with risk characterization under the MCP. Cancer risks are not an issue as the only volatile carcinogen, benzene, has an assumed background concentration higher than the concentration equivalent to an ELCR of 1×10^{-6}. Accordingly, this means the acceptable indoor air values for Toluene and Ethylbenzene are significantly higher than their MassDEP Threshold Values, which for those chemicals, are not risk based.

Given the need to address public welfare (e.g., odors) as well as human health risks, odor threshold values for the listed compounds (MassDEP 2024b) were compared to the acceptable indoor air and sub-slab concentration values (odor threshold values are not available for the hydrocarbon fractions). While it is not possible to rule out localized and episodic emissions of odorous concentrations of Toluene, Ethylbenzene, and Xylene from the subsurface, expected dilution within the breathing zone suggests odor concerns are unlikely to be an issue, and not rise to the level of constituting a significant risk to public welfare.

An alternative approach to evaluate the need for an AUL to address sub-slab vapors is to calculate the total Hazard Index for measured concentrations of sub-slab contaminants (e.g., using the MassDEP Shortform). If the Total Hazard Index is equal to or less than 70, an AUL would not be needed to address non-cancer risks. For benzene, it would also be necessary to show that the ELCR value is less than 7×10^{-4}, or less than the DAF x the acceptable indoor air concentration.

Given the heterogeneous nature of sub-slab vapor concentrations and emission pathways, the highest concentration value recorded in any sub-slab soil gas probe for any contaminant should be used as the input value for the DAF calculations. The use of any other value must be justified, based upon the number of sub-slab probes installed (which should generally be more than the 2-3 installed in most single-family homes) and/or the use of a high-volume soil gas sampling program.

7.0 HOMEOWNER FUEL OIL SPILLS

There are a large number of single-family owner-occupied homes in Massachusetts in which #2 fuel oil is used for heating purposes. The scale and commonality of issues associated with oil spills in these homes warrants a focused review in this guidance document.

Spills from a free-standing heating oil storage tank and/or filter assembly within a home/basement/ garage are the most common residential fuel oil release mechanisms, followed by leakage from the fill line between the oil tank and furnace/boiler. Spills from underground storage tanks and filling/delivery operations are the next most frequent cause of fuel oil releases. Environmental impacts from residential fuel oil spills can range from relatively minor amounts of soil contamination to migration/discharge of significant quantities of NAPL to drains and surface water bodies. While it is impossible to address the full range of potential impacts, guidance is provided on the most common situations and concerns. Of foremost importance is the amount of remediation required (and not required) by the MCP.

It is usually not necessary to under-pin a home and/or remove large quantity of contaminated soils from beneath the structure to comply with the regulatory requirements of the MCP. While some parties may elect to take such extreme measures to restore property value or avoid filing an Activity and Use Limitation for their property, homeowners should be informed that such actions are not generally deemed necessary or advisable by MassDEP.

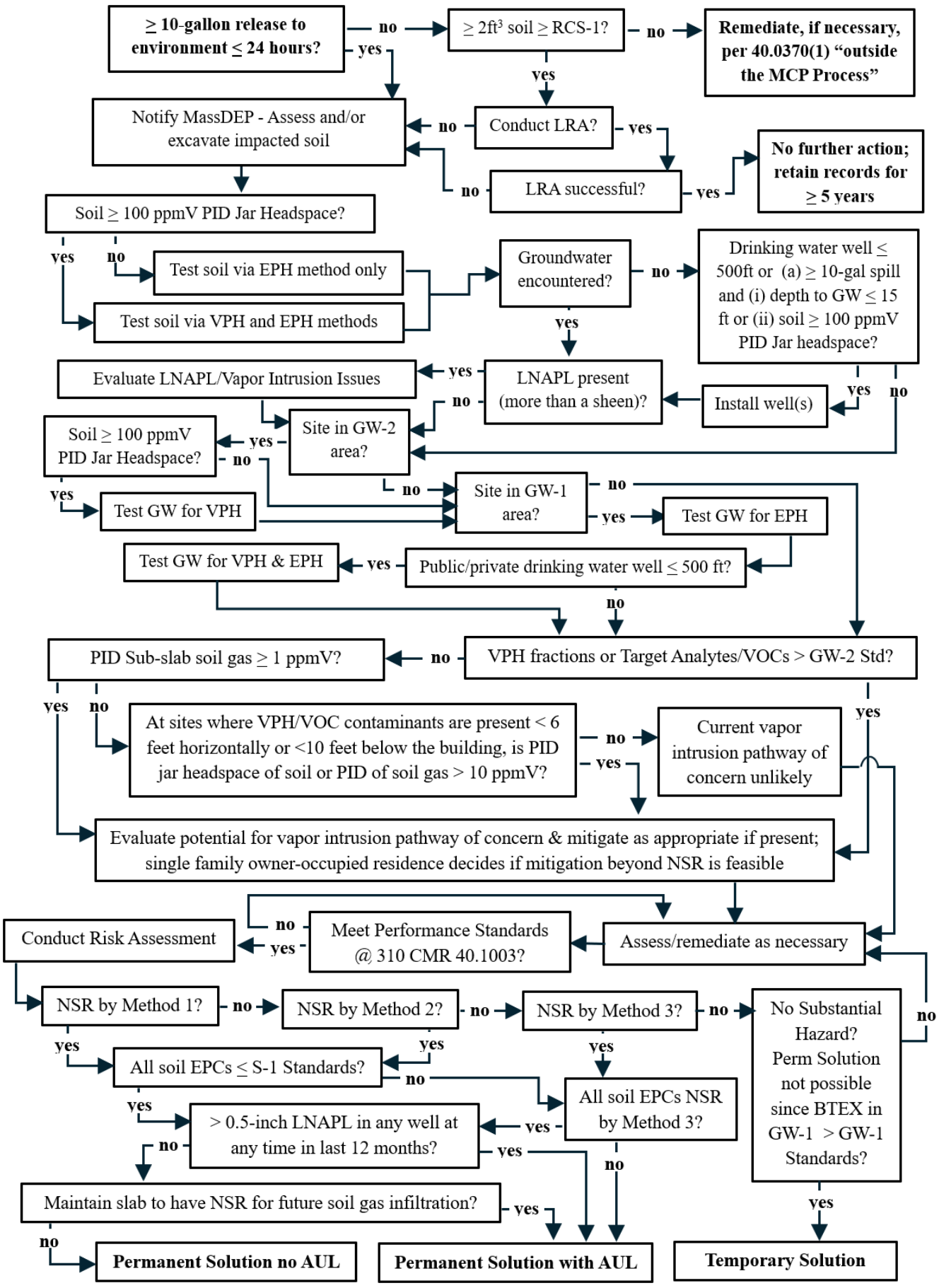
A flow chart summarizing investigative and site closure requirements and recommendations for homeowner sites is provided in **Figure 7-1** and discussed in additional detail below.

7.1 Reporting Sudden Spills

The Reportable Quantity (RQ) for a "sudden spill" of #2 fuel oil is 10-gallons within any 24-hour time period. Importantly, this metric is applied ONLY to releases (or threats of release) of oil to the environment. For spills of oil into a basement or building slab, an estimate must be made of not only the amount of oil discharged into the basement/slab, but also the amount of oil that likely exited the structure and migrated into the environment (e.g., soil beneath/around structure). A 2-hour reporting obligation for a sudden spill of oil would only exist if it were likely that 10 or more gallons of oil has reached the environment.

Spills of oil onto earthen floors comprising all or part of a basement will generally be considered a release to the environment. The volume of spilled oil transported through cracks in a concrete floor and at the wall/slab interface is difficult to estimate, though anecdotal experience suggests it can be significant. It appears that the width of cracking is more important than the length of cracking in this regard, and that hairline cracks (e.g., less than 50 microns (0.05 mm) in width) are not likely to be of significance. (Wang et al., 1997)

Figure 7-1: Response Action Flowchart for Fuel Oil Spills at Single-Family Owner-Occupied Building



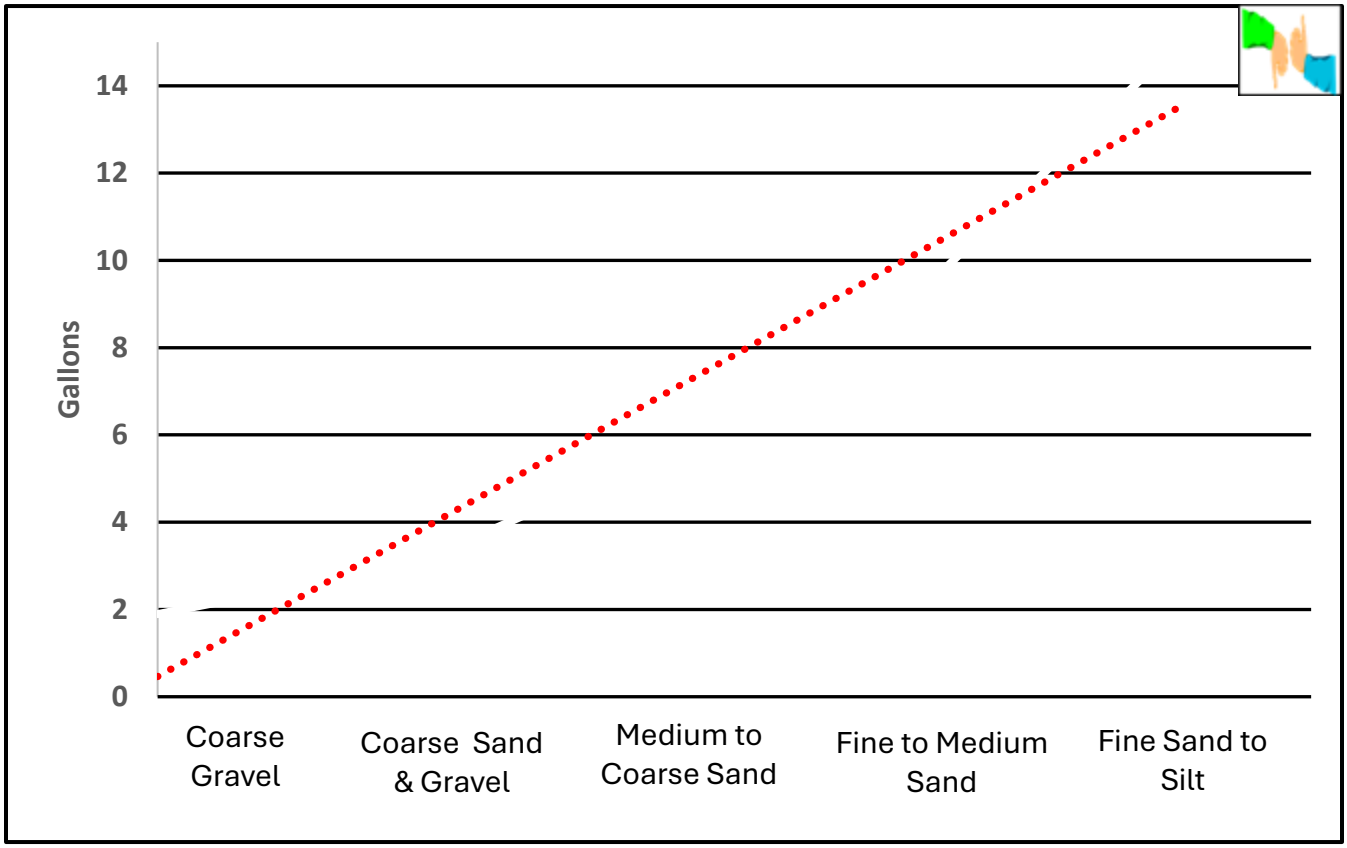
Even where notification to MassDEP is not required, per the requirements of 310 CMR 40.0370, parties are still obligated to conduct cleanups if site conditions are posing a significant risk (though such work is done "outside the MCP process", complying with all applicable requirements, including disposal of contaminated media).

7.2 Reportable Concentrations

In cases where evidence does not exist that 10 or more gallons of #2 fuel oil was likely discharged into the environment within any 24-hour period, a 120-day reporting obligation would exist if hydrocarbon concentrations in soil exceed the appropriate Reportable Concentration (RC), which would be RCS-1 for residences. RC values are contained in the MCP at 310 CMR 40.1600 for TPH and PAH compounds and for EPH and VPH Aliphatic/Aromatic Hydrocarbon fractions and Target Analytes. The TPH RC value is based on conservative assumptions on hydrocarbon chemistry, and if it is exceeded, it would be advisable to re-test using the EPH method, to allow for a better and less conservative characterization of potential risks, and obtain data that may be used in lieu of the TPH data [40.0360(2)].

Importantly, per 310 CMR *40.0315(2), a 120-day reporting obligation would only exist for petroleum releases if the total contiguous volume of soil exceeding the RC is equal to or greater than 2 cubic yards*. In cases where a sudden release of oil to the environment is less than 10-gallons in a 24-hour period, what volume of fuel oil release (over any period of time) would be expected to contaminate two or more contiguous cubic yards of soil? This is a difficult and complicated issue that is predicated on soil properties and site conditions. Rough estimates in this regard are provided in **Figure 7-2**, based upon published residual saturation concentrations for middle distillates (Brost, 2000).

Figure 7-2: Theoretical Number of Gallons of #2 Fuel Oil to Contaminate 2 Cubic Yards of Soil



While this theoretical value ranges from about 1.5 gallons for coarse gravels to over 10 gallons for fine sands and silts, absent definitive information on soil conditions beneath a building, a value of 5-gallons would be a reasonable estimate. In cases where there is a reasonable possibility that a soil RC value has been exceeded, there is an expectation that steps will be taken to confirm or refute the existence of a 120-day reporting obligation. This could involve a sub-slab soil sampling effort and/or a sub-slab excavation effort.

In cases where a sub-slab soil exploration and removal program is implemented, and this exploration program confirms the existence of more than 2 contiguous cubic yards of soil with hydrocarbon levels exceeding an RC, notification could still be avoided if a Limited Removal Action (LRA) is conducted in compliance with the provisions of 310 CMR 40.0318 – provided there are no other reporting obligations, including exceeding a groundwater Reportable Concentration, if groundwater is encountered. If groundwater is not encountered, the installation and gauging/sampling of a monitoring well would be expected if (a) a drinking water well is located within 500 feet, or (b) if $\geq$ 10 gallons of oil was likely released to the environment and (i) the depth to an overburden groundwater table was likely less than 15 feet from the ground surface or (ii) soil remaining at the site contains volatile hydrocarbons equal to or greater than 100 ppmV on a PID jar headspace test procedure.

7.3 Solubility of #2 Fuel Oil

The limited solubility of #2 fuel oil in groundwater can be leveraged to reduce sampling and analytical costs at sites that are not located in GW-1 areas. Specifically, the total solubility of #2 Fuel Oil in water has generally been reported to be in the range of 2 to 6 mg/L (API, 1993; API, 1994). Based upon MassDEP's review of EPH data obtained at sites contaminated by #2 Fuel Oil, and theoretical solubility limits of the hydrocarbons comprising the Aliphatic and Aromatic fractions (TPHCWG, 1998), a reasonable upper limit of dissolved concentrations of the EPH fractions, along with the current MCP Method 1 standards (2024b), are presented in **Table 7-1**.

Table 7-1: Solubility of EPH Hydrocarbon Fractions in #2 Fuel Oil

EPH Hydrocarbon Fraction	Concentration [mg/L]			
	Likely Upper Limit of Solubility	GW-1	GW-2	GW -3
C_9-C_{18} Aliphatics	0.5 – 1.0	**0.7**	5	50
C_{19}–C_{36} Aliphatics	< 0.01	14	NA	50
C_{11}-C_{22} Aromatics	1 – 3	**0.2**	50	5

As can be seen in Table 7-1, none of the EPH hydrocarbon fractions are likely to exceed Method 1 groundwater standards for disposal sites in GW-2 or GW-3 areas – and, as discussed in Section 4.1.5, any data report containing concentrations in excess of these limits are likely due to one or more of the following:

- the presence of colloidal suspensions or micro-emulsions of un-dissolved NAPL in the groundwater sample, often present in monitoring wells with a past history of measurable NAPL;
- the presence of sorbed hydrocarbons on suspended sediment in the groundwater sample, generally in turbid samples from source-area wells;
- the presence of non-hydrocarbon compounds and/or biological breakdown products in the groundwater sample (falsely quantitated by the EPH method as a range analyte); and/or

- analytical "noise" (especially problematic for C_{19}–C_{36} Aliphatic Hydrocarbons).

A similar situation exists for the four EPH Diesel/#2 Fuel Target Analytes. While it is true these analytes have published solubility values significantly above MCP Method 1 groundwater standards, it is important to understand that these published data are for single-component systems. The solubility of constituents within organic mixtures such as fuel oil – termed *effective solubility* – is significantly less than these pure-component values, and is function of the compound's (molar) concentration in the mixture (Raoult's Law). For example, naphthalene has a published solubility in water of approximately 32 mg/L. However, using Raoult's Law, the expected maximum effective solubility of this compound in water impacted by a fuel oil release is about 0.5 mg/L (O'Reily et al., 2001). Empirical data have confirmed these theoretical values as upper solubility limits (Lee et al., 1992). A tabulation of relevant data and values is provided in **Table 7-2**.

Table 7-2: Presence and Solubility of PAH Target Analytes in #2 Fuel Oil (Lee et al., 1992)

Chemical	Concentration [mg/L]				
	In Fresh Fuel Oil #2	Water in Contact with Fuel Oil #2	MCP GW-1	MCP GW-2	MCP GW-3
Acenaphthene	100-600	0.004-0.014	0.02	NA	10
Naphthalene	350-1500	0.08-0.5	**0.14**	0.7	20
2-Methylnaphthalene	3500-9000	0.18-0.34	**0.01**	2	20
Phenanthrene	100-1500	0.015-0.025	0.05	NA	10

The data in Table 7-2 indicates that only naphthalene and 2-methylnaphthalene would be expected to be present in a dissolved state in groundwater at concentrations that could exceed a Method 1 GW-1 standard. In non-GW-1 areas, no dissolved PAH Target Analyte would be expected to exceed an MCP Method 1 GW standard.

Accordingly, characterization efforts at #2 fuel oil contaminated sites should focus on whether visible LNAPL is present at the water table interface, and EPH testing of groundwater can be limited to disposal sites in GW-1 areas. In addition to EPH testing of all groundwater within GW-1 areas, VPH testing should also be conducted at any location within 500 feet of a drinking water well.

7.4 Post Spill Testing Regimen

Beyond the general guidelines provided in Section 4.0 of this document, additional recommendations specific to characterization efforts at single family owner-occupied residential homes are provided below:

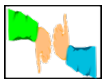
Soil – When soil testing is conducted for risk assessment purposes, initial "worst case" samples from the source area should be tested for EPH hydrocarbon ranges and target analytes. For "fresh" spills (i.e., PID jar headspace ≥ 100 ppmV as isobutylene), samples should also be analyzed for the VPH ranges and target analytes. Further soil VPH testing is not necessary if all VPH target analytes and C5-C8 Aliphatics and C9-C10 Aromatics are below S-1 standards; in such cases, EPH testing alone will suffice (exceedances of C9-C12 Aliphatics in the VPH method are acceptable since hydrocarbons within this range are picked up in the EPH test method). PID jar headspace data should be obtained and recorded and used to direct and limit soil sampling for VPH and EPH

laboratory testing. Soil samples with PID jar headspace concentrations less than 10 ppmV (as isobutylene) are likely indicative of hydrocarbon levels below Method 1 soil standards (MassDEP, 2007b). Confirmatory EPH testing is, however, necessary.

LNAPL – Soil excavations in source areas that encounter groundwater can be used to rule-out (or confirm) LNAPL concerns. If groundwater is not encountered, the installation and gauging/ sampling of a monitoring well would be expected if (a) a drinking water well is located within 500 feet, or (b) if $\geq$ 10 gallons of oil was likely released to the environment and (i) the depth to an overburden groundwater table was likely less than 15 feet from the ground surface or (ii) soil remaining at the site contains volatile hydrocarbons equal to or greater than 100 ppmV on a PID jar headspace test procedure. The need for and feasibility of monitoring well installations at sites where the groundwater table is within bedrock should be considered on a site-specific basis.

Groundwater – If groundwater is encountered in an excavation, or when a monitoring well is installed to determine if LNAPL is present, a sample of the groundwater should be obtained and analyzed using the EPH test method if the site is located in a GW-1 location; testing for EPH is not otherwise required. If a drinking water well is located within 500 feet of the site, or if soil samples were consistent with a "fresh" fuel oil (i.e., > 100 ppmV PID jar headspace), testing of a groundwater sample by the VPH method (and possibly EPA Method 8260) should also be undertaken. Groundwater samples should not be obtained from wells with visible LNAPL or sheens.

Soil Gas – Sub-slab soil gas vapor probes should be installed when (a) sub-slab soils are present or remain beneath the home with PID jar headspace concentrations higher than 10 ppmV as isobutylene, or (b) LNAPL (beyond sheening) is present on the groundwater table beneath or within 15 feet of the building. The probes can be first screened with a PID meter; withdrawing 100 to 300 cc/min for a total of at least 5 minutes. If the maximum concentration recorded during sampling is equal to or less than 1 ppmV as isobutylene, a vapor intrusion concern can be ruled out (MassDEP, 2026). If PID readings are not accomplished or exceed 1 ppmV, the probes should be sampled and analyzed by the MassDEP APH test method.



Indoor Air – The indoor air should be sampled if (a) petroleum odors are continuously or periodically present in the home (following all necessary remedial actions), or (b) soil gas data cannot rule out a vapor intrusion pathway. Samples should generally be obtained from the basement/lowest level and one floor above, and analyzed using the MassDEP APH procedure. The laboratory should be instructed to identify or tentatively identify significant non-petroleum peaks if range concentration values exceed MassDEP residential threshold values, and then adjust those range concentration values accordingly (while noting significant concentrations of peaks identified or tentatively identified as chlorinated ethenes). Of particular concern is TCE, which elutes just after benzene and before toluene, and PCE, which elutes just after toluene and before ethylbenzene. In homes where in-building sources of fuel oil are present (e.g., fuel oil tank; off-gassing impacted building materials or furniture), consider conducting an evaluation of the total ion chromatograms for the sub-slab soil gas samples and indoor air samples, to see if a reasonably conservative allocation of sources (e.g., vapor intrusion vs in building sources) can be made. See Section 4.1.6 for additional discussions of these concerns.

7.5 Condition of Substantial Release Migration

In the MCP, SRM conditions are time-critical contaminant transport/exposure conditions that require notification to MassDEP within 72-hours of obtaining knowledge, per 310 CMR 40.0313(4).

SRMs listed at 310 CMR 40.0313(4) require notification to MassDEP ONLY if associated with a release of OHM that otherwise requires/required notification to MassDEP, at the present time or any time in the past. This means some other reporting obligation (e.g., sudden release > 10 gallons of oil, exceeding a Reportable Concentration) is or was present.

The most common SRMs at residential fuel oil sites are those conditions listed in subparagraph 310 CMR 40.0313(4)(f), relating to vapor intrusion concerns. The criteria in subparagraphs (1.) and (2.) concern VOCs, which are defined in 40.0006 to be those compounds reported by EPA method 8260 and other purgeable organic methods. Thus, this evaluation is limited to VPH and VOC data, and excludes EPH data from consideration.

Guidelines for each item in 310 CMR 40.0313(4)(f) are provided below for sites where VPH and/or VOC testing data is obtained:

Item 1 – VOC contaminants in soil or soil gas under/near home. A vapor intrusion pathway of concern would not be likely, and notification under this provision would not be required, if (a) no soil sample exceeds 10 ppmV as isobutylene using the MassDEP PID jar headspace screening procedure, and (b) no sub-slab soil gas vapor sample exceeds 1 ppmV PID readings as isobutylene. (MassDEP, 2007; MassDEP 2026)

Item 2 – *VOCs in groundwater exceed MassDEP GW-2 standard*. For sites contaminated only with petroleum hydrocarbons, this evaluation is limited to the MassDEP VPH target analytes and hydrocarbon ranges. EPH target analytes and hydrocarbon ranges are not classified as VOCs, and are not relevant to an SRM determination of this nature.

Item 3 – *Volatile LNAPL*. This provision does NOT apply to releases of #2 fuel oil, as it is not considered a Volatile LNAPL. (While not considered an immediate concern, fuel oil vapors still require evaluation as part of a site characterization and closure process).

Item 4 – *Preferential Pathways* – This concern can be ruled out if PID screening of (a) annular spaces around utility pipes entering the home, (b) floor drains, or (c) other potential preferred pathways into the home do not record readings higher than 2 ppmV as isobutylene (above background).

7.6 Method 2 and Method 3 Risk Characterizations

Many residential homes where a reportable oil spill occurred can demonstrate the existence of a condition of No Significant Risk using the MCP Method 1 risk characterization approach, often after some amount of contaminated soil removal. The risk/remedial drivers in these cases vary, depending on whether the site is located within a GW-1 area (drinking water resource area).

Typical risk/remedial driver in non-GW-1 locations are

- C9-C18 Aliphatic Hydrocarbons in soil.

Typical risk/remedial drivers in GW-1 locations are

- C9-C18 Aliphatic Hydrocarbons in soil,
- 2-methylnaphthalene in soil,
- C11-C22 Aromatic Hydrocarbon in groundwater, and/or
- 2-methylnaphthalene in groundwater.

7.6.1 Non-GW-1 Areas

Under the MCP, all soil on a residential property to a depth of 15 feet is classified as soil category S-1, except for soil beneath a building slab/foundation, which is considered soil category S-3.

The MCP Method 1 S-1/GW-2 and Method 1 S-1/GW-3 soil standards for risk driver C9-C18 Aliphatic Hydrocarbons are both 1000 mg/kg. The MCP Method 2 "Direct Contact" standard for S-1 soil is also 1000 mg/kg. This means that the S-1/GW-2 and S-1/GW-3 standards are not based upon leaching concerns, and that a Method 2 Risk Characterization cannot be used to address soil contamination at sites where an EPC exceeds 1000 mg/kg.

The S-3/GW-2 and S-3/GW-3 soil standards for risk driver C9-C18 Aliphatic Hydrocarbons in soil are both 5000 mg/kg, The MCP Method 2 "Direct Contact" standard for S-3 soil is also 5000 mg/kg. This means that the S-3/GW-2 and S-3/GW-3 standards are not based upon leaching concerns, and that a Method 2 Risk Characterization cannot be used to address soil contamination at sites where an EPC exceeds 5000 mg/kg.

While it is usually feasible to clean up to an EPC of less than 5000 mg/kg C9-C18 Aliphatic Hydrocarbons in soils beneath a building slab/foundation, and achieve a condition of No Significant Risk for current site exposures for those S-3 soils under a Method 1 Risk Characterization, an AUL will be required if the soil EPC is greater than the S-1 standard of 1000 mg/kg. In fact, using a Method 1 Risk Characterization process, an AUL will be required anywhere on a residential property (0-15 feet in depth) where the soil EPC for C9-C18 Aliphatic Hydrocarbons exceeds 1000 mg/kg.

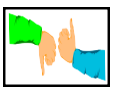
The Method 2 "Direct Contact" standards for C9-C18 Aliphatic Hydrocarbons – which define maximum permissible limits in MCP risk characterization Methods 1 and 2 — are not based upon health risks, but rather on the potential for odors, which can be considered a significant risk to public welfare. For example, the S-1 Direct Contact standard of 1000 mg/kg for C9-C18 Aliphatic Hydrocarbons equates to a human risk Hazard Quotient (HQ) value of 0.07, well below the HQ of 0.2 used for most Method 1 standards to address human health risks.

Additional guidance on use of a MassDEP Shortform Method 3 Risk Characterization in these situations to justify site closures at EPCs of greater than 1000 mg/kg C9-C18 Aliphatic Hydrocarbons without the need for an AUL is provided in Section 7.7.1.

7.6.2 GW-1 Areas

In addition to C9-C18 Aliphatic Hydrocarbons (discussed above), soil concentrations of 2-methylnaphthalene are often the risk/remedial driver at residential fuel oil spills in GW-1 areas. In groundwater, C11-C22 Aromatic Hydrocarbons and 2-methylnaphthalene are most likely to exceed MCP Method 1 standards.

Soil



The S-1/GW-1 Method 1 standard for 2-methylnaphthalene is 0.7 mg/kg, which is controlled by the leaching pathway, given that the Method 2 S-1 Direct Contact standard at 310 CMR 40.0985(6) is 300 mg/kg. In such cases, a Method 2 risk characterization process can be used to justify an EPC above 0.7 mg/kg (but less than 300 mg/kg) as being a condition of No Significant Risk if a showing can be made that 2-Methylnaphthalene is not leaching at the site at a level of concern. This can be accomplished as follows:

- using a Method 2 risk characterization approach, a showing that 2-methylnaphthalene is not present in groundwater above its Method 1 GW-1 standard of 10 µg/L (i.e., the temporal

average in each and every groundwater monitoring well is less than 10 µg/L), or, if that is not the case,

- using a Method 3 risk characterization approach, a showing that the EPC of 2-methylnaphthalene in groundwater will not impact the drinking water well(s) of concern.

Groundwater

In a GW-1 area, it is normally not possible to achieve a Permanent Solution at a site if the EPC in any groundwater monitoring well exceeds the concentration listed for the MCP GW-1 standards. Such an action is prohibited in a Method 2 risk characterization per the provisions of 310 CMR 40.0982(1). Even in a Method 3 risk characterization process – where Method 1 and Method 2 standards do not apply - it is still necessary to meet "all applicable or suitably analogous health standards", per 40.0993(3). In 40.0993(3)(a), the Massachusetts Drinking Water Quality Standards promulgated in 310 CMR 22.00 are specifically defined to be such an applicable standard, and all MCP Method 1 GW-1 standards are set to the same concentration as such drinking water standards. Moreover, per 40.0924(6)(b)(2.), the EPC is in general applied to the "groundwater resource itself", in that all monitoring wells within a GW-1 area must meet the applicable standards,

For petroleum contaminated sites, using a Method 3 Risk characterization process, there are two options available to justify a Permanent Solution for a site in a GW-1 area where a groundwater EPC is greater than an MCP GW-1 standard:

- Per 310 CMR 40.0924(6)(c), in areas classified as GW-1 due to their locations within a Zone II of a public water supply well, the EPC can be applied at the public drinking water well itself, and not throughout the groundwater resource area, as long as a robust monitoring program can demonstrate that the disposal site boundary (e.g., the extent of the hydrocarbon plume) is at least 1,000 feet from the drinking water well(s).
- At disposal sites where no contaminant exceeds a listed drinking water standard, a Method 3 risk characterization can be undertaken to demonstrate that the dissolved (or undissolved) hydrocarbon plume will not reach or impact any drinking water wells. This demonstration is not tied to the characterization requirements or plume stagnation criteria of 310 CMR 40.0924(6)(c).

With respect to petroleum contaminated sites, 2-methylnaphthalene and C11-C22 Aromatic Hydrocarbons are NOT among the promulgated drinking water standards in 310 CMR 22.00 (nor are any of the Aliphatic or Aromatic Hydrocarbon fractions). If no contaminant with a drinking water standard exceeds a GW-1 concentration (including BTEX), a reasonable level of effort may be undertaken to demonstrate that 2-methylnaphthalene and/or C11-C22 Aromatic Hydrocarbons have not and will not impact any drinking water well.

> Using MCP risk characterization Method 3, it could be possible to justify a groundwater EPC value of 2-methylnaphthalene greater than 10 µg/L and C11-C22 Aromatic Hydrocarbons greater than 200 µg/L in a GW-1 area.

For single family owner-occupied homes, this can generally be accomplished by:

- Testing all drinking water wells within 500 feet for VPH and EPH components, and
- documenting the lack of any preferred flow paths or other site conditions that would suggest that 2-methylnaphthalene or C11-C22 Aromatic Hydrocarbons could migrate

more than 500 feet from the source area(s),

Assuming no drinking water wells are impacted by site contaminants, and no conditions exist that would suggest migration beyond 500 feet is likely, the drinking water exposure pathway can be ruled out for 2-methylnaphthalene and C11-C22 Aromatic Hydrocarbons (i.e., EPC = 0).

7.7 Site Closure

7.7.1 Residential AULs

A site can achieve a Permanent Solution if a condition of No Significant Risk (NSR) is demonstrated for current site uses and conditions, via MCP risk characterization Methods 1, 2, or 3. In order to qualify for a Permanent Solution without an Activity and Use Limitation (AUL), however, it must be demonstrated that a condition of NSR also exists for any foreseeable future exposures, which means that (i) all soil EPCs 0-15 feet below ground surface, including soil under a building, are suitable for direct contact by children, (ii) less than 0.5-inches of NAPL remains at the site, and (iii) sub-slab vapor conditions do not present a future risk to building occupants. General guidance in this regard is provided in Section 6.6.

It is not uncommon in residential homes to have high concentrations of EPH hydrocarbon fractions and/or target analytes in pockets of soil below foundation footings or in other areas where excavation is difficult. In risk assessment Methods 1 or 2, these soils would be considered a "hot spot" if any EPC was present at concentrations in excess of ten times an applicable Method 1 soil standard, or, if a Method 2 risk assessment method was used, more than 10 times a modified Method 1 standard. These Hot Spots would constitute separate EPCs that must be compared to the applicable Method 1 or Method 2 soil standards. In a Method 3 risk assessment, a hot spot would be as defined in 310 CMR 40.0006 of the MCP.

In cases where a condition of No Significant Risk for risk-driver C9-C18 Aliphatic Hydrocarbons in soil cannot be demonstrated using a Method 1 or 2 Risk Characterization (including for foreseeable exposures) a Method 3 Risk Characterization should be considered. Using a MassDEP Shortform to address human health risks, it should be possible to justify an EPC value of C9-C18 Aliphatic Hydrocarbons for S-1 soils greater than 1000 mg/kg.

While use of the Residential Soil Shortform can address risk to human health, an evaluation of risk to Public Welfare is more difficult, as odors are subjective. Importantly, site closure under the MCP is for current *and reasonably foreseeable* exposure conditions. As such, the current depth/inaccessibility of contaminated soil and/or odor sensibilities of the current owners of the property are not the final determinants in this matter. Rather, an LSP must consider reasonably foreseeable conditions over a period of the next 30+ years, including building modifications and/or excavation and removal of contaminated soils to off-site locations. If an LSP cannot reasonably rule out concerns of this nature, the site should be closed out using an AUL, to ensure future owners are aware of this concern, and so potential future exposures to contaminants may be avoided.

A reasonable assessment of future public welfare/odor concerns would consider the likelihood of disturbance and volume of contaminated soil, with the latter indicative of (i) the extent and duration of odor conditions should the soil be disturbed or excavated, and (ii) the timeline for on-site contaminated soils to biodegrade.

7

For single family owner-occupied buildings, for most sites, a reasonable case could be made via a Method 3/Shortform assessment to justify a "residential" EPC (without the need for an AUL) of up to 3000 mg/kg of C9-C18 Aliphatic Hydrocarbons if there are currently no significant odors associated with the fuel oil release within the building(s) and the total volume or contaminated soils exceeding 1000 mg/kg is limited (i.e., less than 20 cubic yards).

At sites where it is not possible to demonstrate a condition of No Significant Risk for future exposures (e.g., contaminated soil below the slab/footing), even using a Method 3 Risk Characterization, an AUL will need to be filed as part of the Permanent Solution. To avoid filing an AUL, some homeowners may opt to undertake expensive excavation projects, to reduce contaminant EPCs to levels not requiring an AUL. While this is an allowable option, it is incumbent on LSPs to explain to their clients that such steps are not mandated by state law or regulation, and that AULs were created to provide a sensible and cost-effective means to allow site owners to close out contaminated sites while ensuring that future actions at the site would not create unsafe conditions. If homeowners are concerned about the impact of an AUL on the resale value of their home, they should be advised to consult with a local real estate professional, to ascertain the likely impact, if any, on the value of the property resultant from the recording of an AUL.

7.7.2 Critical Exposure Pathway

A vapor intrusion pathway at an occupied residential structure represents a Critical Exposure Pathway, as defined in 310 CMR 40.0006. If this pathway creates a condition of significant risk, mitigative actions *must be taken* to achieve a condition of No Significant Risk, generally via the installation of a sub-slab depressurization system.

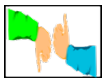
If the vapor intrusion pathway does not pose a significant risk, per the requirements of 310 CMR 40.0414(3) and 310 CMR 40.1020, mitigative actions *must still be taken, to the extent feasible*, with feasibility defined in terms of cost vs. benefit. Guidance in this regard is provided below:

- In a single family owner-occupied residential building, the owner may decide on the degree of benefit associated with exposure reduction actions and may decide that mitigative actions beyond those necessary to achieve a condition of No Significant Risk are not worth the associated costs, and thus not feasible.
- At residential properties where response actions are being undertaken by a party that does not own the property, absent objections by the owner, it is generally feasible to install and activate a sub-slab depressurization system. In such cases, however, if the operation of the system is not necessary to achieve or maintain a condition of No Significant Risk, the long-term operation, maintenance, and monitoring of the system by the non-owner is generally not feasible. In such cases, the property owner can elect to continue to run the system, at their expense, or choose not to run the system.

7.7.3 Sub-Slab Depressurization Systems

Sub-Slab Depressurization Systems (SSDS), considered an Active Exposure Pathway Mitigation Measure (AEPMM) under the MCP, are designed and operated to eliminate or mitigate a vapor intrusion pathway into an overlying building; they are not intended to function as a remedial measure to remove significant mass of contaminants from the environment. However, given the nature of oil spills in residential structures (i.e., most contaminant mass is immediately below the building slab), and the high aerobic biodegradation potential of #2 fuel oil, the installation and operation of an active SSDS can be a component of site closure at residential homes:

- In cases where a vapor intrusion pathway is posing a significant risk, perhaps due to the infeasibility of sub-structure contaminated soil removal, an SSDS can be operated for a period of time to extract hydrocarbon vapors while simultaneously inducing the movement of oxygen into contaminated sub-slab areas. This combination of hydrocarbon vapor removal and enhanced bioremediation will reduce sub-structure contaminant levels. After some period of time, generally 12 to 24 months, the SSDS can be shut down, and, after a period of 2 to 3 weeks, indoor air samples can be obtained from the basement/lowest level and overlying living space. If indoor air concentrations of hydrocarbons (associated with a vapor intrusion pathway) no longer pose a significant risk, the SSDS should remain inactive, until such time as follow-up indoor air testing can be undertaken (3 to 6 months later). If the follow-up test confirms a condition of No Significant Risk, and if at least one round of indoor air testing occurred between November to March, a Permanent Solution can be achieved, assuming all other site closure standards are met. The SSDS can then be re-activated, if desired and feasible, to further mitigate any emissions of hydrocarbons into the structure and continue to enhance sub-slab bioremediation of residual hydrocarbons.



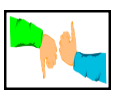
- The operation of an SSDS in the above manner could take place as an IRA, Phase IV/V remedial measure, Remedy Operation Status (ROS), Temporary Solution, or Permanent Solution as an Active Exposure Pathway Mitigation Measures (AEPMM).
- Importantly, the post Permanent Solution operation or continued operation of an SSDS within a residence in which a condition of No Significant Risk exists or has been achieved *without the need to operate the SSDS* (i.e., it is being run to address a CEP condition that does not pose a significant risk) does not need to be operated under any MCP remedial measure and is not subject to the AEPMM requirements of the MCP at 310 CMR 40.1025, as long as remedial emissions do not exceed 100 pounds/year or create risk or odor conditions in downwind areas.

> Active SSD systems at sites that filed a Permanent Solution that are NOT needed to maintain a condition of No Significant Risk are NOT considered AEPMMs subject to the requirements 40.1025. In such cases, SSD Systems can be a cost-effective means to enhance and accelerate the biological breakdown of residual hydrocarbon contaminants while minimizing or eliminating all exposures to subsurface hydrocarbon vapors, hydrocarbon breakdown products (including methane), and radon gas.

7.7.4 Temporary Solution

The filing of a Temporary Solution statement for a 1-4 family owner-occupied residence should be considered in the following cases:

- In GW-1 areas where a Permanent Solution is not feasible due to presence of benzene, toluene, ethylbenzene, or xylenes at concentrations in excess of their MassDEP drinking water standards (per 310 CMR 22.00 – which are the same as their MCP GW-1 standards), assuming (i) no public or private drinking water well is or is likely to be impacted, (ii) soil/NAPL source areas have been adequately removed or addressed, and (iii) all other closure standards of 310 CMR 40.1000 have been achieved. In these cases, it can generally be considered infeasible to implement groundwater remediation, and thus infeasible to obtain a Permanent Solution. The filing of a Temporary Solution would be justified and may be the best option for the homeowner, with the expectation that natural attenuation will address residual contaminants. Designated monitoring wells would then be sampled over time, until drinking water standards are not exceeded in any well, and a Permanent Solution can be achieved.



- At sites where an SSDS is being operated to maintain a condition of No Significant Risk, and where all other closure standards of 310 CMR 40.1000 have been achieved. The filing of a Temporary Solution (or Remedy Operation Status) may be advisable, if it can be shown that SSDS operations will likely lead to a Permanent Solution in time, given mass removal of residual hydrocarbons via volatilization and enhanced bioremediation.

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APPENDIX 1

Significant Changes from 2002 *Characterizing Risks Posed by Petroleum Contaminated Sites: Implementation of the MADEP VPH/EPH Approach*, October 31, 2002, Policy #WSC-02-411

Section	Topic	Discussion
3.2.3	COCs	Need to look for significant chlorinated solvent peaks in APH method in initial samples to rule out this issue
3.7.2	Field vs lab data	Figure 3-2 changed from original document
4.1.1	PID Data	New Section; rules of thumb given
4.1.2	Soil vs gw vs soil gas	New Section – limitations of soil sampling; use of soil gas & composite soil samples
4,1,3	Soil sampling	New Section - use of PID to define hot spots
4.1.4	NAPL	New Section - Rules of Thumb from LNAPL Guidance
4.1.5	Groundwater Sampling	Expanded guidance on groundwater sampling with additional info and Rules of Thumb on when NAPL is inflating dissolved groundwater concentration values
4.1.6	Indoor Air/Soil Gas Sampling	Warning on APH positive bias and steps to take; information and chromatograms on distinguishing vapor intrusion from in-building fuel oil sources
4.2.1	Non-Petroleum Contaminants	Need to rule out chlorinated solvents at disposal site; initial groundwater sample(s) in source area should be tested via EPA 8260
4.2.2	VPH testing	VPH testing not required at Diesel/#2 Fuel Oil release sites if soil or gw samples are characterized as "weathered" (< 100 ppmV PID headspace), including for the purposes of complying with the Critical Exposure Pathway provisions of 310 CMR 40.0313(4)(f)
4.2.2 4.2.3	Tables 4-2 and 4-3	New Provision – EPH groundwater testing for diesel/#2 fuel oil spills only required in GW-1 areas
4.2.5	Biofuels	New Section
4.3	Vapor intrusion	Three options provided for assessing whether a vapor intrusion pathway exists at petroleum sites: Inclusion Distance, Screening, or Multiple Lines of Evidence approach
5.1.1	Soil EPCs	Rules of thumb; description of "75/10" option
5.1.2	Groundwater EPCs	Clarification that the 75/10 rule does not apply to temporal averaging of data from gw monitoring wells
5.1.3	Indoor Air EPCs	General expectation that maximum indoor air data be used as EPC
5.2	Method 1 Risk Assessment	2024 MCP changes on Exposure Points; step by step process for determining soil EPCs and conducting Method 1 assessment
5.2.2	Indoor Air Issue	Definition of insignificant indoor air exposures for combined Method 1 and 3 assessment

Section	Topic	Discussion
5.3	Method 2	Clarification that "modified" Method 1 standard should in general be the site EPC; expanded guidance and examples on conducting Method 2 assessments
5.3.1	Method 2	Definition of no significant indoor air impacts for modified GW-2 standard
5.4.2	Imminent Hazards	Clarification of exactly which OHM have "serious effects" with a Hazard Index of 1
6.0	Site Closure	New Section – includes clarification that one reports releases but remediates disposal sites
6.2	Migration control	Rules of thumb
6.3	NAPL	Includes information/tables from #WSC-16-450 (MassDEP LNAPL Guidance)
6.6	AULs	Expanded guidance on when AULs are required
7.0	Homeowner Spills	New Section - expanded guidance to achieve more cost-effective cleanups.
7.3	Groundwater Issue	Low solubility of #2 fuel oil limits need for groundwater testing and helps identify sampling errors that lead to positive biases
7.4	Testing Regimen	Expanded guidance including acquisition/use of low-cost PID data
7,5	SRM	Guidance/criteria on Substantial Release Migration provisions of 310 CMR 40.0314(4)
7.6	Method 2 & 3 Risk Characterizations	Guidance on when and how to do Method 2 and 3 risk characterization for common petroleum Method 1 exceedances
7.7.2	CEP	Clarification of when long-term operation of SSDS to mitigate a CEP that is not addressing Significant Risk is not feasible
7.7.3	SSDS	Clarification that SSD systems that are not required to eliminate NSR are not subject to the AEPMM performance and submittal requirements.
7.7.4	Temporary Solution	Indicates a Temporary Solution may be best choice for homeowner oil spills in GW-1 area, if source removal completed
App 3	Jar Headspace	Added modified MassDEP Jar Headspace procedure in Appendix 3
App 4	Flowcharts	Added a series of flowcharts for notification and Response Actions in Appendix 4

APPENDIX 2
Collecting and Preserving VPH Samples

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.

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.

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.

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).

RARE CASES WHERE MTBE IS LIKELY TO BE PRESENT IN GW-1 AREAS

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, 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 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 pre-calibrated 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 □g/L), MassDEP 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, MassDEP will generally not expect or require the use of alternative preservation or analytical protocols for disposal sites, unless there is reason to believe that significant concentrations of MtBE are likely to be present.

APPENDIX 3 - MassDEP Jar Headspace Screening Procedure (Fitzgerald, 1989)

Updated 2026

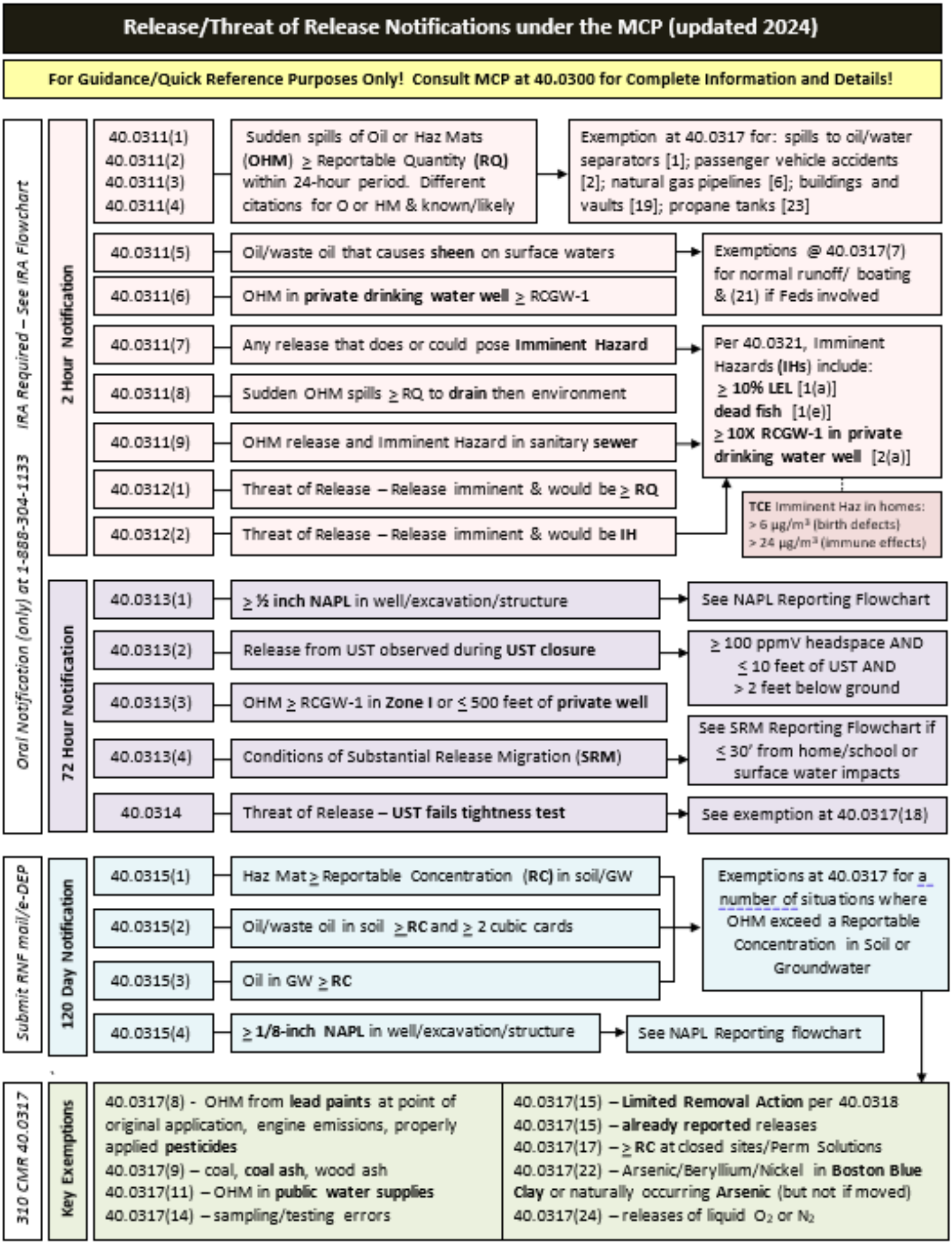
The following is the recommended procedure for conducting analytical screening of contaminated soil or groundwater utilizing a portable Photoionization Detector (PID)

1. Half-fill a clean glass or plastic jar with the sample to be analyzed. Quickly cover the open top with one or two sheets of clean aluminum foil and subsequently apply screw caps to tightly seal the jar. Sixteen-ounce (16 oz.; approximately 500 ml) soil or "mason" type jars are preferred; jars less than 8 oz. total capacity (approximately 250 ml), should not be used.
2. Allow headspace development for at least 10 minutes. Vigorously shake jars for 15 seconds both at the beginning and end of the headspace development period. Where ambient temperatures are below 32º F headspace development should be within a heated vehicle or building.
3. Subsequent to headspace development, remove screw lid/expose foil seal. Quickly puncture foil seal with instrument sampling probe, to a point about one-half of the headspace depth. Exercise care to avoid uptake of water droplets or soil particulate.

   Following probe insertion through foil seal and/or sample injection to the probe, record highest meter response as the jar headspace concentration. Using foil seal/probe insertion method, maximum response should occur between 2 and 5 seconds. Erratic meter response may occur at high organic vapor concentrations or conditions of elevated headspace moisture, in which case headspace data should be discounted.
4. PID field instruments should contain a uV lamp source of at least 10 eV, and be calibrated with an isobutylene standard Data should generally be reported as ppmV (as isobutylene), except for UST closure evaluation conducted per 310 CMR 40.0313, which should be reported “as benzene” (e.g., multiply the response from an isobutylene calibration times the benzene calibration factor of the PID instrument being used). For jar headspace analysis, instrument calibration should be checked/adjusted no less than once every 20 analyses, or daily, whichever is greater.
5. Instrumentation with digital (LED/LCD) displays may not be able to discern maximum headspace response unless equipped with a "maximum hold" feature or strip-chart recorder. Deviations, departures and/or additions to the above procedures should be consistent with 310 CMR 40.0017. In such cases, compelling technical justification must be presented and documented by the methodology proponent.

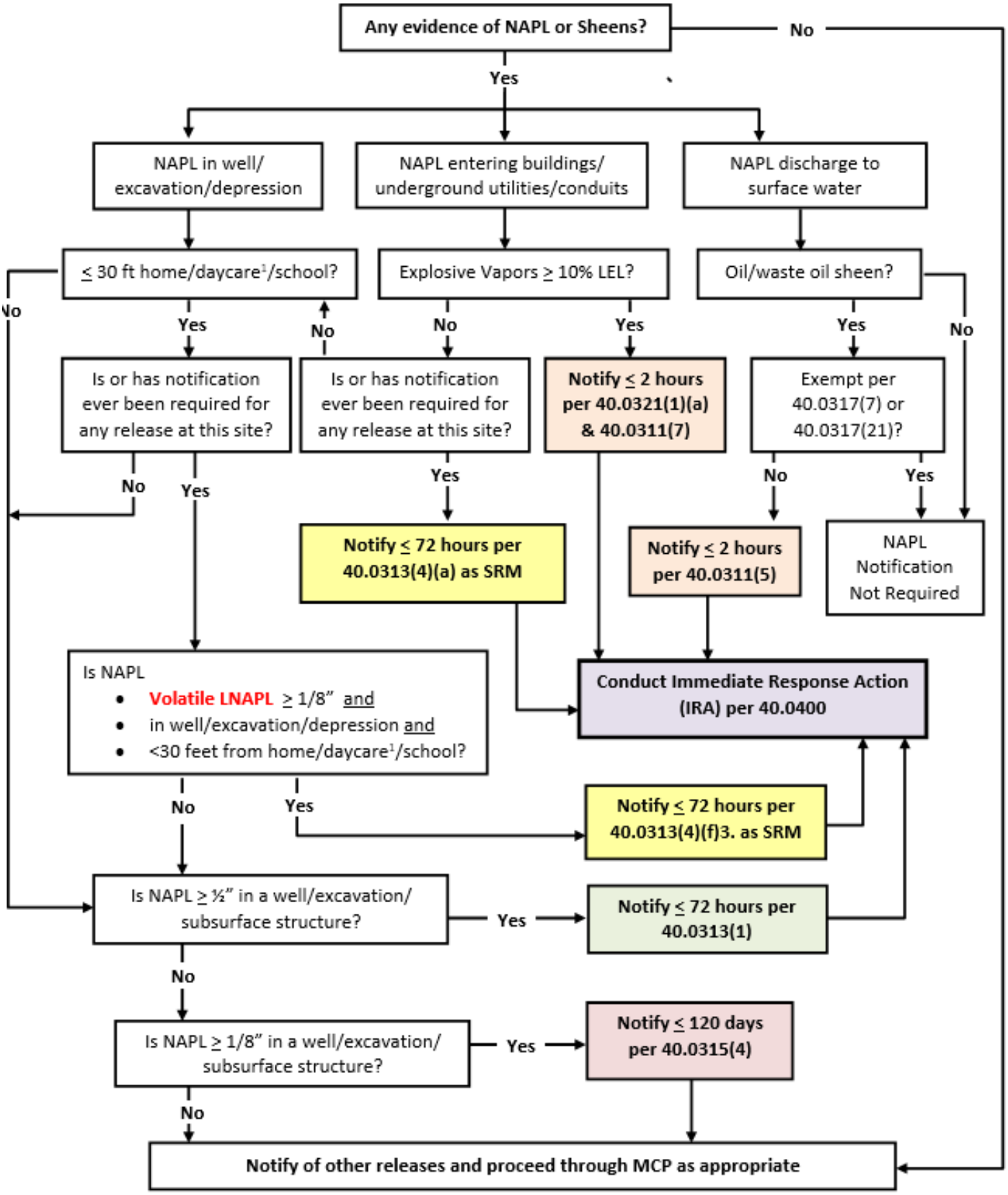
Appendix 4

MCP Notification and Response Action Flowcharts

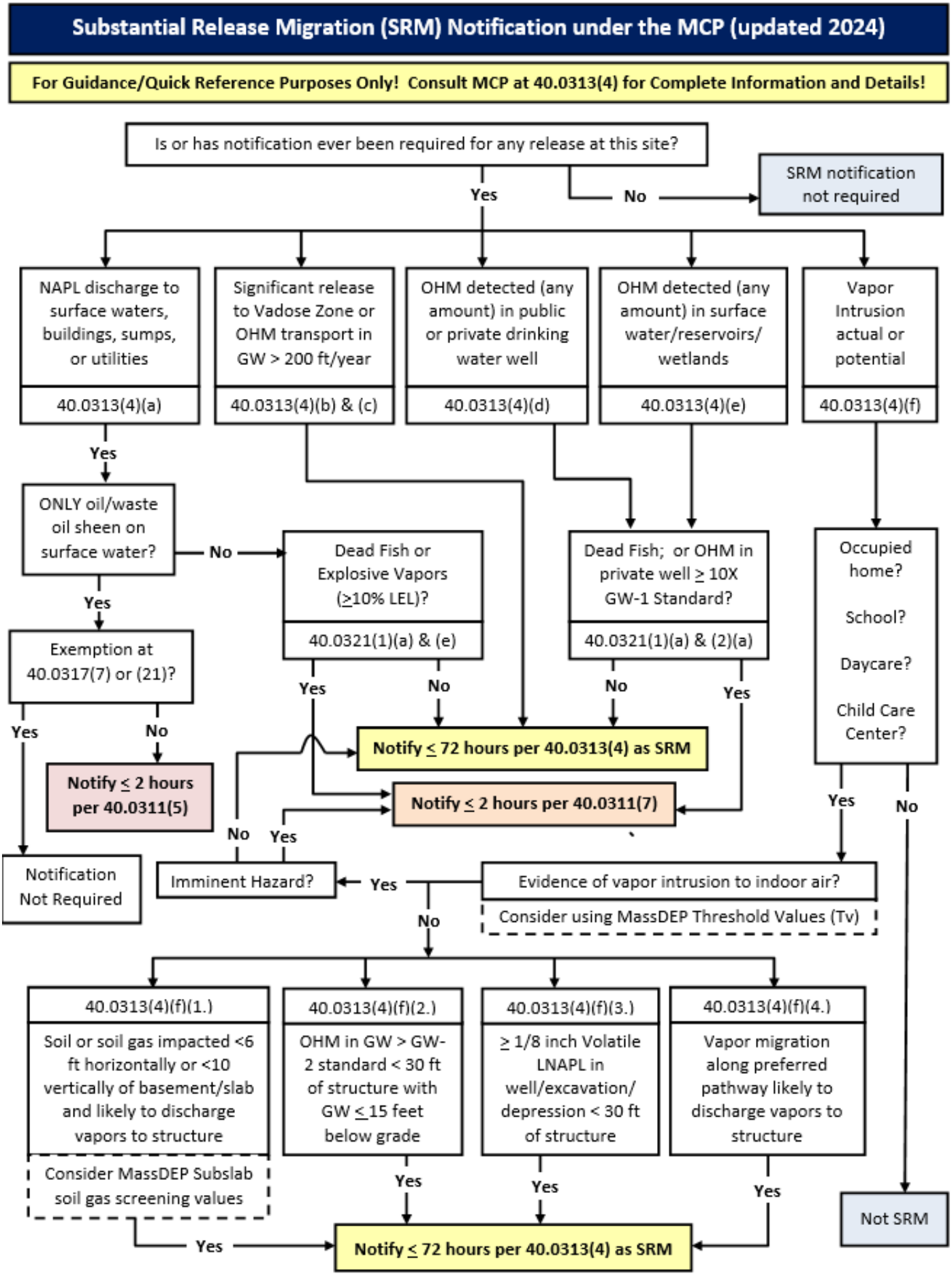

Release/Threat of Release Notifications under the MCP (updated 2024)
For Guidance/Quick Reference Purposes Only! Consult MCP at 40.0300 for Complete Information and Details!
Oral Notification (only) at 1-888-304-1133 IRA Required – See IRA Flowchart
2 Hour Notification
40.0311(1) 40.0311(2) 40.0311(3) 40.0311(4)
Sudden spills of Oil or Haz Mats (OHM) ≥ Reportable Quantity (RQ) within 24-hour period. Different citations for O or HM & known/likely
Exemption at 40.0317 for: spills to oil/water separators [1]; passenger vehicle accidents [2]; natural gas pipelines [6]; buildings and vaults [19]; propane tanks [23]
40.0311(5)
Oil/waste oil that causes sheen on surface waters
40.0311(6)
OHM in private drinking water well ≥ RCGW-1
Exemptions @ 40.0317(7) for normal runoff/ boating & (21) if Feds involved
40.0311(7)
Any release that does or could pose Imminent Hazard
40.0311(8)
Sudden OHM spills ≥ RQ to drain then environment
40.0311(9)
OHM release and Imminent Hazard in sanitary sewer
Per 40.0321, Imminent Hazards (IHs) include:
≥ 10% LEL [1(a)]
dead fish [1(e)]
≥ 10X RCGW-1 in private drinking water well [2(a)]
40.0312(1)
Threat of Release – Release imminent & would be ≥ RQ
40.0312(2)
Threat of Release – Release imminent & would be IH
TCE Imminent Haz in homes:
> 6 µg/m³ (birth defects)
> 24 µg/m³ (immune effects)
72 Hour Notification
40.0313(1)
≥ ½ inch NAPL in well/excavation/structure
See NAPL Reporting Flowchart
40.0313(2)
Release from UST observed during UST closure
≥ 100 ppmV headspace AND ≤ 10 feet of UST AND > 2 feet below ground
40.0313(3)
OHM ≥ RCGW-1 in Zone I or ≤ 500 feet of private well
40.0313(4)
Conditions of Substantial Release Migration (SRM)
See SRM Reporting Flowchart if ≤ 30' from home/school or surface water impacts
40.0314
Threat of Release – UST fails tightness test
See exemption at 40.0317(18)
Submit RNF mail/e-DEP
120 Day Notification
40.0315(1)
Haz Mat ≥ Reportable Concentration (RC) in soil/GW
40.0315(2)
Oil/waste oil in soil ≥ RC and ≥ 2 cubic cards
40.0315(3)
Oil in GW ≥ RC
Exemptions at 40.0317 for a number of situations where OHM exceed a Reportable Concentration in Soil or Groundwater
40.0315(4)
≥ 1/8-inch NAPL in well/excavation/structure
See NAPL Reporting flowchart
310 CMR 40.0317
Key Exemptions
40.0317(8) - OHM from lead paints at point of original application, engine emissions, properly applied pesticides
40.0317(9) – coal, coal ash, wood ash
40.0317(11) – OHM in public water supplies
40.0317(14) – sampling/testing errors
40.0317(15) – Limited Removal Action per 40.0318
40.0317(15) – already reported releases
40.0317(17) – ≥ RC at closed sites/Perm Solutions
40.0317(22) – Arsenic/Beryllium/Nickel in Boston Blue Clay or naturally occurring Arsenic (but not if moved)
40.0317(24) – releases of liquid O_2 or N_2

Notification and Response to NAPL/Sheens under the MCP (updated 2024)

For Guidance/Quick Reference Purposes Only! Consult MCP at 40.0300 for Complete Information and Details!

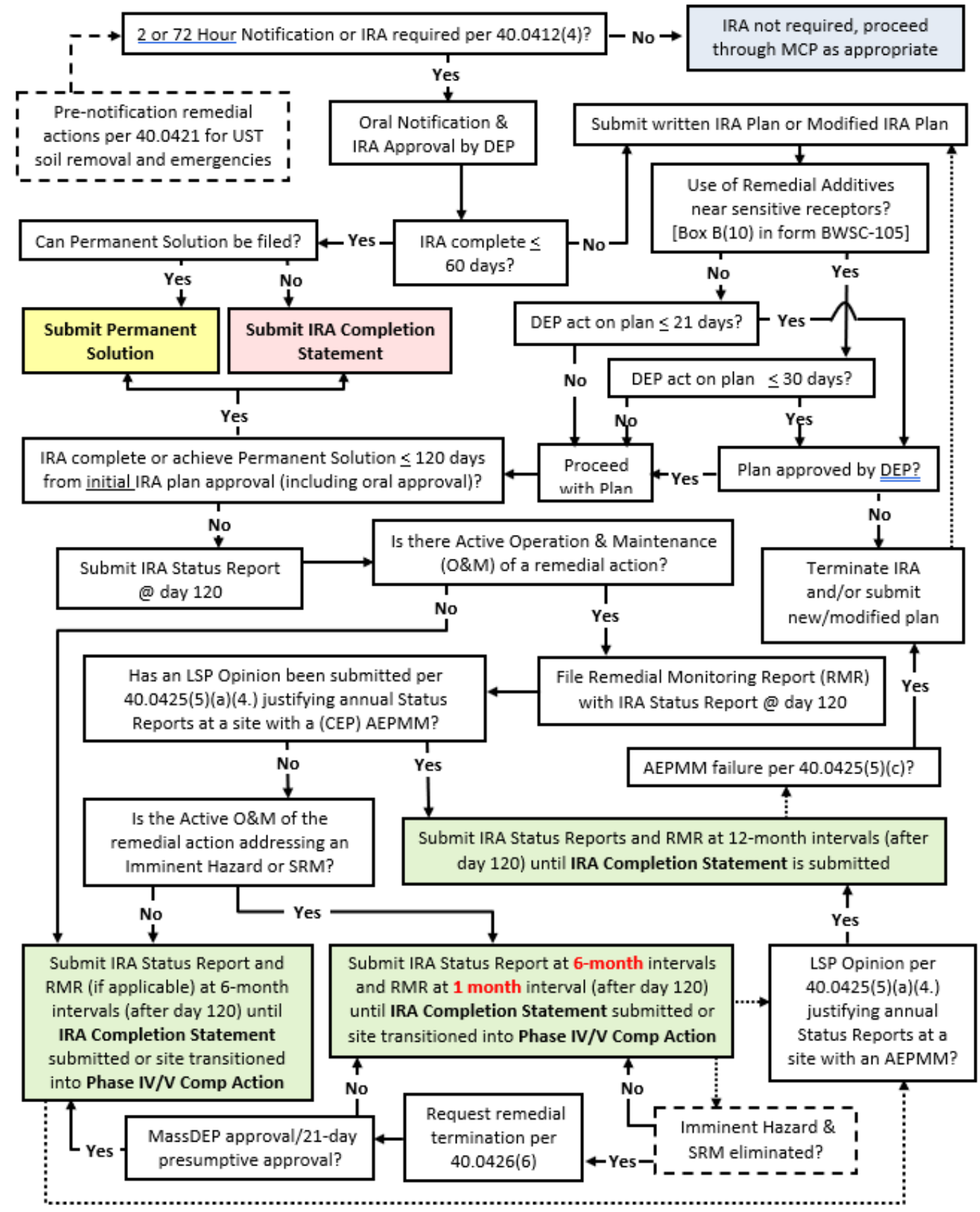


[1] childcare centers as well as daycares


Substantial Release Migration (SRM) Notification under the MCP (updated 2024)
For Guidance/Quick Reference Purposes Only! Consult MCP at 40.0313(4) for Complete Information and Details!
Is or has notification ever been required for any release at this site?
Yes
No
SRM notification not required
NAPL discharge to surface waters, buildings, sumps, or utilities
40.0313(4)(a)
Significant release to Vadose Zone or OHM transport in GW > 200 ft/year
40.0313(4)(b) & (c)
OHM detected (any amount) in public or private drinking water well
40.0313(4)(d)
OHM detected (any amount) in surface water/reservoirs/ wetlands
40.0313(4)(e)
Vapor Intrusion actual or potential
40.0313(4)(f)
Yes
ONLY oil/waste oil sheen on surface water?
No
Yes
Exemption at 40.0317(7) or (21)?
Yes
No
Notify ≤ 2 hours per 40.0311(5)
Notification Not Required
Dead Fish or Explosive Vapors (≥10% LEL)?
40.0321(1)(a) & (e)
Yes
No
Dead Fish; or OHM in private well ≥ 10X GW-1 Standard?
40.0321(1)(a) & (2)(a)
No
Yes
Occupied home?
School?
Daycare?
Child Care Center?
Yes
No
Notify ≤ 72 hours per 40.0313(4) as SRM
Notify ≤ 2 hours per 40.0311(7)
No
Yes
Imminent Hazard?
Yes
Evidence of vapor intrusion to indoor air?
Consider using MassDEP Threshold Values (Tv)
No
40.0313(4)(f)(1.)
Soil or soil gas impacted <6 ft horizontally or <10 vertically of basement/slab and likely to discharge vapors to structure
Consider MassDEP Subslab soil gas screening values
40.0313(4)(f)(2.)
OHM in GW > GW-2 standard < 30 ft of structure with GW ≤ 15 feet below grade
40.0313(4)(f)(3.)
≥ 1/8 inch Volatile LNAPL in well/excavation/ depression < 30 ft of structure
40.0313(4)(f)(4.)
Vapor migration along preferred pathway likely to discharge vapors to structure
Yes
Yes
Yes
Yes
Notify ≤ 72 hours per 40.0313(4) as SRM
Not SRM

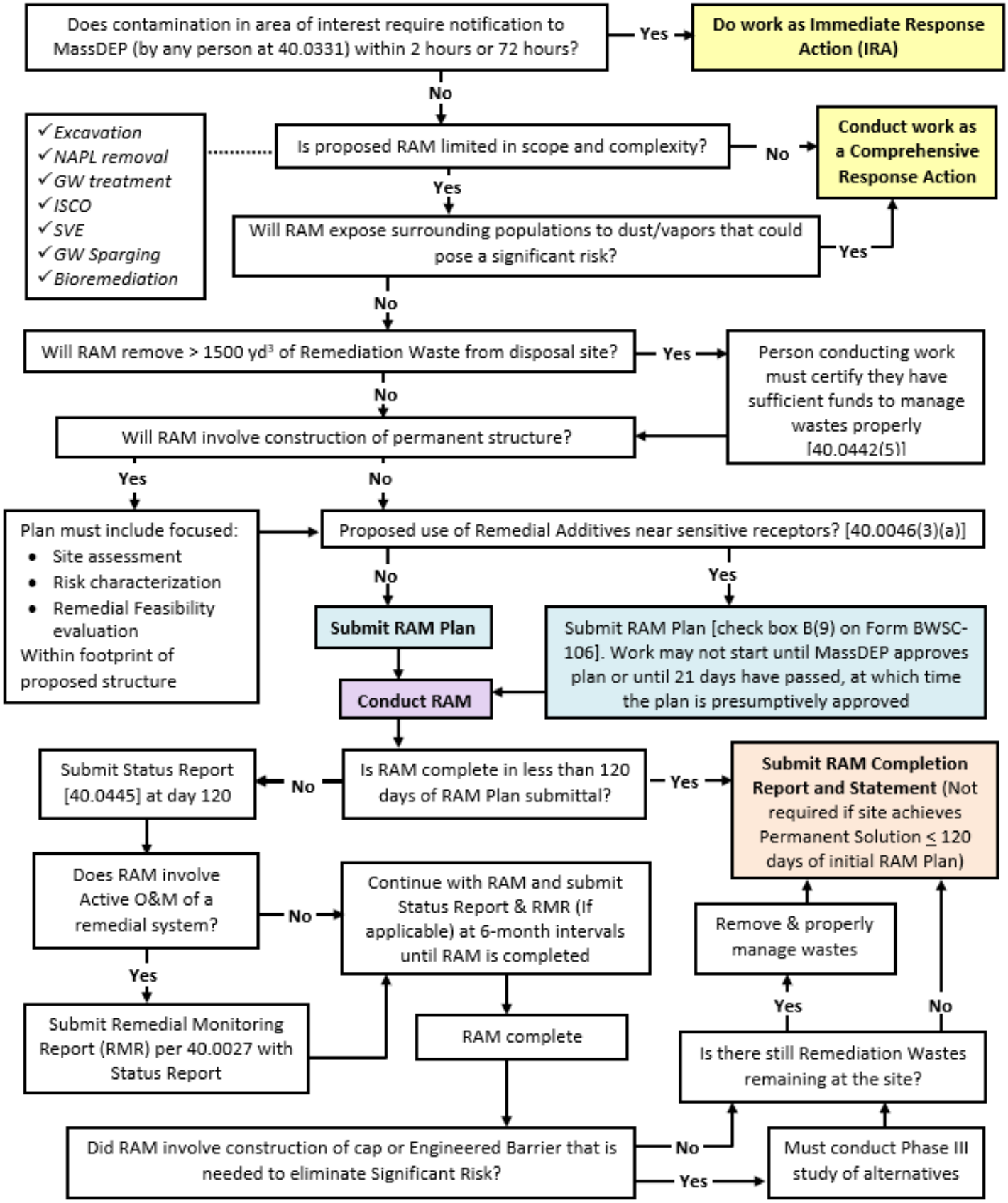
Immediate Response Actions (IRAs) under the MCP (updated 2024)

For Guidance/Quick Reference Purposes Only! Consult MCP at 40.0410 for Complete Information and Details!



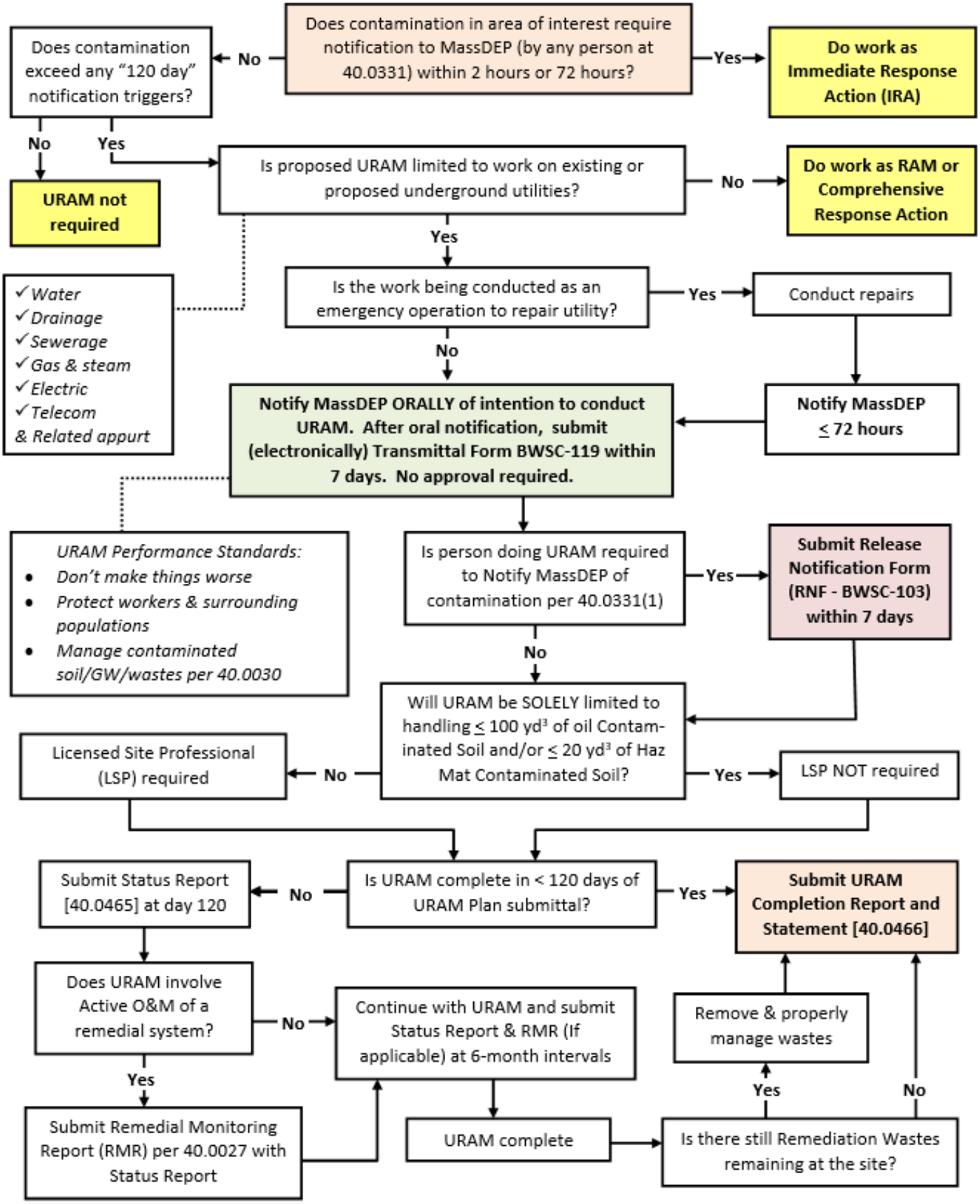
Release Abatement Measures (RAMs) under the MCP (updated 2024)

For Guidance/Quick Reference Purposes Only! Consult MCP at 40.0440 for Complete Information and Details!



Utility-Related Abatement Measures (URAMs) under the MCP (updated 2024)

For Guidance/Quick Reference Purposes Only! Consult MCP at 40.0460 for Complete Information and Details!



Site Closure under the MCP (updated 2024)

For Guidance/Quick Reference Purposes Only! Consult MCP at 40.1000 for Complete Information and Details!