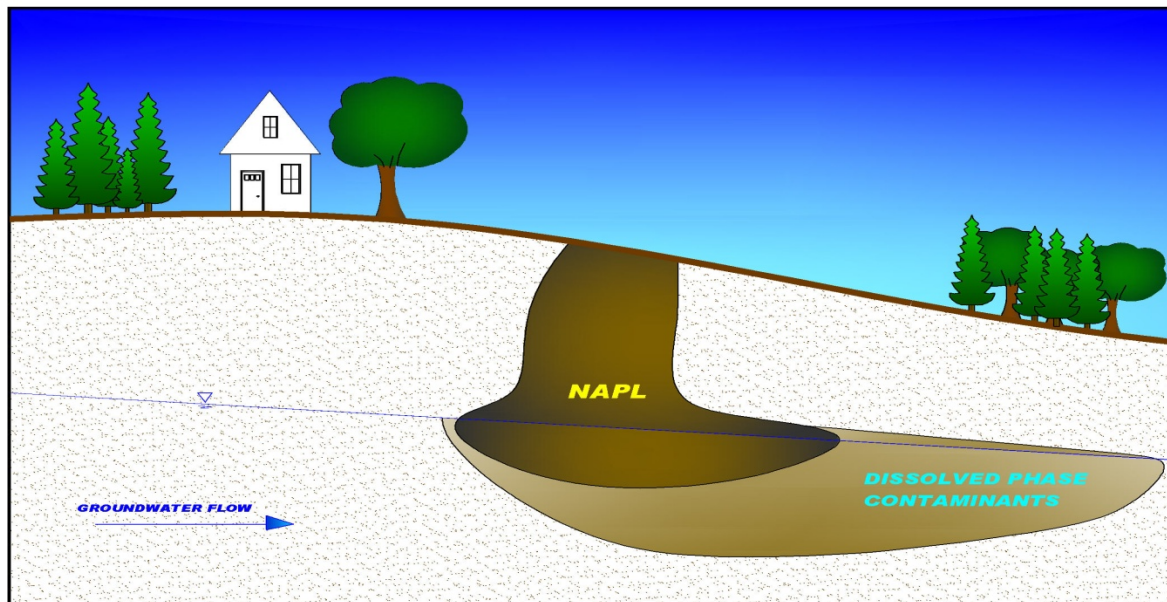


# ***NON-AQUEOUS PHASE LIQUID (NAPL) CHARACTERIZATION, REMEDIATION, AND MANAGEMENT FOR PETROLEUM RELEASES***

REMEDICATION AND REDEVELOPMENT DIVISION  
RESOURCE MATERIALS



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*In order to promote a consistent and informed approach for Michigan Department of Environmental Quality (MDEQ) staff, this document was developed to provide information to MDEQ staff and contractors for characterizing, remediating and managing non-aqueous phase liquids (NAPL) related to petroleum releases.*

*This document is available as a technical reference to assist any party conducting investigations and evaluating NAPL associated with petroleum releases to support recovery and risk management decisions.*

*This document is explanatory and does not contain any regulatory requirements. It does not establish or affect the legal rights or obligations for petroleum NAPL management. It does not have the force or effect of law and is not legally binding on the public or the regulated community. Any regulatory decisions made by the MDEQ regarding NAPL management related to petroleum releases will be made by applying the governing statutes and Administrative Rules to relevant facts.*

A handwritten signature in blue ink, appearing to read 'Robert Wagner', written over a horizontal line.

Approved:

Robert Wagner, Chief  
Remediation and Redevelopment Division  
June 24, 2014



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## SUMMARY

This document is provided as a resource for MDEQ staff and other environmental professionals working on characterizing, remediating, evaluating risk, and managing non-aqueous phase liquids (NAPL) resulting from releases of petroleum products to the environment.

The state of Michigan has thousands of sites that are contaminated with petroleum NAPL. These petroleum-based liquids have limited solubility in water and can degrade over time, but typically will remain in the subsurface for many years. The presence of NAPL in the subsurface can lead to unacceptable risks to human health and the environment if improperly characterized, remediated, and/or managed. However, unacceptable risks can be avoided using appropriate management practices that will reduce NAPL toxicity, remove constituents of concern, recover the NAPL, and/or prevent exposures. Characterization of the NAPL, both chemically and geographically, and the identification of all associated risks is critical for developing a conceptual site model (CSM) and implementing an effective and efficient remedial and management strategy. Conceptual site models (CSM) are communication tools that can provide a clear understanding of the characterization, site conditions, and risks.

In some cases, recovery or remediation of the NAPL is necessary to abate risks. The NAPL management decisions will be risk-based, but if mobile NAPL is present at a site and can be easily recovered in an efficient and cost effective manner, then the MDEQ encourages recovery of the NAPL wherever feasible. Recoverability analyses can aid in the decision making and have been demonstrated to be beneficial for determining how much NAPL may be removed and what remedial strategy may be most effective.

The factors outlined above are also important in achieving the goal of closure or no further action for a petroleum release. When the geographic location, chemical composition, and risk posed by the petroleum NAPL are well characterized and documented with a CSM, the resulting risk-based decision making is more protective, efficient, and cost effective.

## 1.0 INTRODUCTION

The non-aqueous phase liquid (NAPL) and management approaches referred to throughout this document are limited to only petroleum. Petroleum and petroleum compounds are commonly used in many industries and applications across the state. Given their widely-used nature, petroleum releases have occurred from a multitude of sources. Sources of petroleum releases include, but are not limited to, releases from oil and gas exploration and production, bulk storage, refining operations, retail sales (underground storage tanks), pipelines, home heating tanks, and industrial/manufacturing operations. Thousands of sites across the state of Michigan have documented releases of petroleum NAPL to the environment that will need to be addressed under statutory requirements, which includes the proper characterization, remediation, and/or management of the NAPL so that it does not pose an unacceptable risk to human health and the environment.

The scope of this document is to describe concepts for NAPL management. The document, in general terms, is broken into the following categories for NAPL management:

- *NAPL and Management Concepts*
- *NAPL Characterization*
- *Conceptual Site Model (CSM)*
- *Risk Assessment*
- *Recovery and Recoverability*
- *Site Closure*

It is not the intent of this document to provide a detailed discussion of every NAPL concept or strategy. A list of selected references, some of which provide a more thorough discussion of the concepts presented in this document, is presented in Appendix A.

In addition, a number of technical terms are used throughout this document when describing various aspects of NAPL assessment and management; this also includes terms used in certain statutes. A glossary of these and other commonly used terms and their definitions/applications are contained in Appendix B. Finally, the information contained in this document reflects basic concepts that are applicable to sites where only petroleum releases have occurred and reflect typical approaches to NAPL management. These approaches and concepts were reviewed by a number of external stakeholders and environmental professionals and where applicable, the comments were incorporated into this document. Appendix C is a list of external stakeholders whose review was sought for the development of this document.

## 2.0 NAPL and MANAGEMENT CONCEPTS

Basic NAPL concepts have been adapted from publications and training prepared by the Interstate Technology & Regulatory Council (ITRC) and ASTM International (ASTM). More detail on basic NAPL concepts is included in Appendix D.

The NAPL Management Strategy is based on three primary concepts:

1) The presence of NAPL should be assumed when there is a known release of petroleum **AND/OR** sustained subsurface petroleum contamination is detected (e.g. sustained vapor or groundwater plumes) **AND/OR** NAPL has been visually observed (e.g. accumulating in a well or excavation). In general, if NAPL was released at a site ("site" in this document is a general term), it is likely present as residual, mobile, and/or migrating NAPL.

2) There are two general stages in the development of the NAPL body after a release: i) the initial or expansion stage, which is generally relatively short in duration after the release has stopped, when the NAPL is actively migrating under a sufficient NAPL gradient; and ii) a stable stage, which is much longer in duration, when migration is minimal to nonexistent after the hydraulic forces driving lateral NAPL migration have declined relative to counteractive mechanisms (e.g. entry pressures, decreasing gradient, etc.) (MPCA, 2010).

3) The NAPL body may act as a long-term origin of chemicals of concern (COC) for the aqueous (dissolved) and vapor phases, referred to as compositional plumes. The NAPL body generally contains much more COC mass than is present in the dissolved and vapor phase, and contains a finite mass of COC. The dissolution or volatilization of the COC from the NAPL body into other phases is the primary mechanism by which most NAPL bodies create unacceptable risks over time. Dissolution, volatilization, and biodegradation, collectively known as natural source zone depletion (NSZD), of COCs from the NAPL body will also deplete the finite over time. The NAPL body may also occasionally release secondary contaminants under certain conditions (e.g. methane), which may result in unacceptable risks.

### 3.0 NAPL CHARACTERIZATION

The NAPL body and any associated compositional plumes (e.g. soil gas, groundwater) will need to be adequately delineated so that migration can be detected to determine plume stability and all risks, both saturational and compositional conditions can be evaluated (ASTM, 2007, Section 3; ITRC, 2009a, Section 3; ITRC, 2009b, Sections 3 and 4). The composition of the NAPL will need to be determined so appropriate investigative techniques, analytical methods, and risk assessments can be implemented (ASTM 2007, Section 6). NAPL characterization can be accomplished either by conventional means or more modern approaches. Conventional means of investigation include drilling accompanied by soil and groundwater sampling; a contemporary approach may include an ultraviolet optical screening tool/laser-induced fluorescence (LIF).

The risk assessment at a site generally requires conventional investigative means to compare concentrations of COCs to risk-based screening levels, and/or generic criteria. Other conventional means of characterization such as analysis of soil for total petroleum hydrocarbons (TPH), gasoline range organics (GRO), diesel range organics (DRO), and/or oil range organics (ORO), can be useful because they allow estimation of the degree of NAPL saturation at a specific, three-dimensional location. Refer to Table 1 below for GRO and DRO concentrations that may be used for screening purposes with soil samples or as a line of evidence. Screening concentrations have not been developed for ORO; however, site specific screening values can be developed using the individual soil and NAPL properties and possibly other lines of evidence. GRO and DRO concentrations greater than those in Table 1 are not automatic indicators of the presence of NAPL or the presence of an unacceptable risk. Additional lines of evidence may be used to determine the presence or absence and/or potential risks posed by the NAPL. These additional lines of evidence can be collected in conjunction with or in lieu of the TPH sampling. There is no prescriptive approach to site characterization because each site and release is unique. Previous site information, geologic and hydraulic information, and release information should guide the characterization phase.



**Table 1 – GRO and DRO Screening Levels**

Material Released / NAPL	Use / Screening Purpose	GRO Concentration (mg/kg)	DRO Concentration (mg/kg)
Gasoline	NAPL not present	≤ 250	N/A
Gasoline	Soil Volatilization to Indoor Air Criteria Applicable	≤ 350	N/A
Gasoline	<0.5% Saturation for Direct Contact	≤ 900	N/A
Diesel	NAPL not present	N/A	≤ 20
Diesel	Soil Volatilization to Indoor Air Criteria Applicable	N/A	≤ 500
Diesel	<0.5% Saturation for Direct Contact	N/A	≤ 1,050

Regardless of the characterization methods used at a particular site, once characterization is complete, it should be evident where the NAPL is located (including below the water table) and its state (residual, mobile, and/or migrating). The presence or absence of NAPL is best determined by multiple lines of evidence. However, one line of evidence is not necessarily superior to another. The weight given to a particular line of evidence would be based on the type of NAPL released and the unique site conditions. Upon completion of the investigation, the location, nature, and extent of the compositional plumes would be well understood.

#### 4.0 NAPL CONCEPTUAL SITE MODEL

It is imperative in risk-based decision making that an adequate CSM is developed and utilized. The *ASTM Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Non-aqueous Phase Liquids Released to the Subsurface* (ASTM 2531) was created to guide the development of a CSM for NAPL. As outlined in ASTM 2531, the CSM is developed using site data for the purpose of assessing risks at a site. Some examples of items to include in a CSM are depth to groundwater, location of the NAPL body, locations of any and all receptors, dissolved phase (groundwater) plume location, and vapor plume locations. For a detailed outline, list of elements commonly incorporated in a CSM, and discussion of the CSM development, refer to ASTM E2531-06 (Sections 6 and 7). The CSM is a dynamic document. As additional data is collected, the data is evaluated in the context of the CSM and appropriate modifications are made to the CSM as needed (ASTM, 2007, Sections 3.1.19.1 and 4.1). The CSM for each release and each site will be unique. The CSM could be developed using existing site data, or it may require new data collection to adequately characterize and understand the risks posed by the release. The land use and the potential risks posed by a site will determine the precision and amount of data necessary to complete the CSM. The CSM, at a minimum, can be made up of **tables** summarizing soil and groundwater contamination and groundwater elevations; **text** describing and summarizing the data and data collection; **boring logs** with lithology, field screening information (e.g. photoionization detector), and any relevant field observations; **hydrographs** showing the NAPL thickness in wells vs. corrected groundwater elevations (if mobile NAPL is observed at a site) and dissolved phase concentrations vs. groundwater elevations; **plan view maps** showing the NAPL body, contaminant distribution, groundwater elevation,



current/future buildings, property boundaries, and other potential receptors; and **cross-sectional maps** showing the NAPL body, groundwater elevations, lithology, contaminant distribution, and potential receptors. The CSM is also useful for identifying any data gaps and evaluating the potential effect they may have on site decision making.

The development and submission of a site-specific CSM improves the understanding of site conditions, potential receptors, and risks and serves as an excellent tool for communicating this information to all parties and stakeholders involved in site decisions. Graphical representations of the CSM are a very efficient way to depict the site and any associated risks. The use of three-dimensional data visualization software (e.g. fence diagrams) and/or volume/mass calculators (e.g. API's LNAPL Distribution and Recovery Model) may also be useful tools for the CSM.

## 5.0 NAPL RISK ASSESSMENT

Once the site is adequately characterized and a site-specific CSM is developed, the important steps of identifying and evaluating the saturational (e.g. presence of migrating NAPL) and compositional risks (e.g. soil gas or groundwater contaminant plumes) follows. This step is useful for identifying any unacceptable risks that would require some type of recovery, remediation, mitigation, exposure control, and/or other means necessary to abate risk(s).

Generic risk-based screening levels (RBSLs) and cleanup criteria have been developed to evaluate potential compositional risks for individual hazardous associated with various exposure pathways. Development of the generic RBSLs and cleanup criteria are based on assumptions regarding exposures, soil and site conditions, and the environmental fate-and-transport of contaminants. Generally, these assumptions do not account for the presence of NAPL in the soils at a site. However, the RBSLs and cleanup criteria may be used to assess risks at sites with NAPL present, but with certain pathways (direct contact and soil volatilization to indoor air) appropriate lines of evidence are necessary to determine applicability.

For exposure pathways that evaluate risk associated with the volatilization of hazardous substances from soil, the absence of NAPL was assumed in the calculations of the RBSLs and cleanup criteria. However, soil analytical data can be compared to the soil volatilization to indoor air inhalation criteria (SVIIC) if either NAPL is not present at that three dimensional location or there is a relatively minor amount of NAPL in the soil so that it can be assumed that aerobic degradation of the petroleum vapors in the soil can occur. Generic SVIIC RBSLs or cleanup criteria may be appropriate for use when GRO concentrations are less than 350 mg/kg for a gasoline release and when DRO concentrations are less than 500 mg/kg for a diesel release and mobile NAPL is not present at that location.

If the concentrations are less than SVIIC and they are applicable (consistent with all assumptions used to calculate the RBSLs or criteria), then no further investigative actions are needed even if residual NAPL is known to exist in the area proximal to the location of evaluation. If mobile NAPL is known to exist in the area proximal to the location of evaluation, then a site-specific risk evaluation would be necessary to evaluate the risk. For a risk assessment of indoor air when NAPL is known to exist, the use of direct measurements (e.g. soil gas) is better and more reliable to assure the protection of public health, especially when the generic assumptions used to calculate criteria are not representative of the site conditions. For the ambient air pathway, if the soil concentrations are lower than the criteria, the assessment is complete. The CSM can be utilized to evaluate the pathways, determine where generic criteria are applicable, and/or determine the need for additional data collection. Additional information regarding vapor intrusion assessment at NAPL sites is provided in Appendix E.





Soil direct contact RBSLs and cleanup criteria may not be appropriate for risk evaluation when mobile NAPL is present and when greater than 0.5% of the soil pore space contains residual NAPL (a degree of saturation that at or below can be reliably assumed to always be residual). Also, at or below this degree of NAPL saturation, this amount of NAPL in the soil is not expected to be significant enough to physically change the soil properties assumed in the direct contact algorithm (e.g. adhesion to skin and intestinal absorption). If the saturation of NAPL in the soil exceeds 0.5% in the pore space or mobile NAPL is present, then the assumption is that a direct contact risk is present at that location unless a site-specific evaluation demonstrates otherwise. The CSM can be utilized to evaluate the pathway, determine the need for additional data collection, and/or conduct a site-specific risk evaluation. Additional information regarding direct contact pathway evaluation at NAPL sites is provided in Appendix F.

## 6.0 NAPL RECOVERY AND RECOVERABILITY

The most cost-effective and efficient way to address new releases is to immediately recover as much NAPL as technically feasible when it is discovered. Generally, practical experience has demonstrated that this will provide the greatest amount of recovery, reduce risk, and save time and money for all parties involved. Once recovery of NAPL associated with a new release is complete, processes outlined in this document may be used to evaluate whether additional recovery is needed, what the threshold for recoverability may be for that release, and aid in the determination of the management practices for the remaining NAPL.

At sites where NAPL is present (which is the majority of sites where NAPL was released), conducting a recoverability analysis allows for better site decisions to be made. A recoverability analysis, which can be conducted for all NAPL, including residual, is a useful tool for determining the quantity of NAPL that may be recovered (hydraulic, excavation, etc.) as well as reviewing recoverability as a part of the overall site and risk assessment. For the recoverability analysis to be the most useful, it should take into account the feasibility of NAPL recovery, current and potential future risks posed by the NAPL, current and future land uses, and other pertinent site factors. Environmental factors, such as the potential seasonal changes in recoverability may make data from multiple events or during different seasons necessary to identify any seasonal affects and complete the analysis (e.g. NAPL could be recoverable during periods of low groundwater elevation and not recoverable during wet seasons with high groundwater elevations). Scientific studies, experience, and risk assessment have shown that in many cases all NAPL cannot be recovered and, in some instances, no recovery is necessary. Consistent with all risk-based corrective actions, if the NAPL (any states) and/or associated COC pose an unacceptable risk (e.g. expanding soil gas and groundwater plumes, threatened receptors, etc.), then the portion of the NAPL body or COCs creating the risk will have to be addressed via removal, destruction, toxicity reduction, and/or exposure elimination (e.g. institutional controls). For exposure elimination to be a feasible option, the NAPL body and all compositional plumes should be stable.

If mobile NAPL is present at a thickness greater than 0.2 feet in monitoring wells, transmissivity testing is a suitable tool to help determine recoverability. NAPL transmissivity is an indicator of the ability of the NAPL to flow in the subsurface and is a function of both the media and the NAPL properties. For more information on NAPL transmissivity, see ASTM E2856-11, *Standard Guide for Estimation of LNAPL Transmissivity*. In general, if the transmissivity of the NAPL is greater than 0.5 ft<sup>2</sup>/day, recovery is beneficial to reduce the saturation and the ability of the NAPL to flow and the NAPL can be recovered



in a cost effective and efficient manner. However, a demonstration may be made to show that recovery may not be necessary if the NAPL and risks can be appropriately managed.

Factors that comprise a recovery demonstrations may include, but would not be limited to, composition of the NAPL, net benefit of NAPL recovery (e.g. environmental and/or societal), costs, distance to property boundaries, distance to nearest receptors, plume stability, and uncertainties. See ASTM 2531-06 Section 7.12 and ITRC 2009b Section 4 for descriptions of NAPL recovery metrics. The metric of transmissivity for NAPL recovery is a secondary metric and would be utilized after the risks are adequately abated, removed, and/or managed since the primary metric for remediation, exposure elimination, and recovery will be determined by the risks at a site. In some cases, the recovery of NAPL that results in transmissivity below 0.5 ft<sup>2</sup>/day may not reduce the risks at a site; however, this will likely reduce the length of time it takes for a site to attenuate (reduce the legacy of the site). Both ASTM and ITRC guidance advocate for setting sound NAPL remedial objectives consistent with a CSM, using a systematic, science-based approach to select the most suitable NAPL remediation technology(ies), and implementing the technology(ies) to the fullest benefit (ASTM, 2007, Section 7.5; ITRC, 2009b, Section 1.5).

Federal law, 40 CFR 280.64, requires NAPL recovery to the “maximum extent practicable” (determined by the implementing agency) with a minimum standard of minimizing migration. The MDEQ interprets “maximum extent practicable” to mean the recovery of all NAPL that can be recovered in a cost-effective and efficient manner. Again, if the NAPL has a transmissivity greater than 0.5 ft<sup>2</sup>/day, it is likely that the NAPL can be recovered in a cost-effective and efficient manner unless a demonstration is made to show otherwise. If migrating NAPL is present at a site, recovery and/or containment are necessary to stop or prevent migration.

## **7.0 NAPL AND NO FURTHER ACTION OR CLOSURE**

No further action or closure is achievable at sites where residual and/or mobile NAPL are present and risks are abated or managed. Demonstration that risks are appropriately abated or managed include the following: 1) recoverable NAPL has been recovered to the “maximum extent practicable;” 2) all unacceptable risks (e.g. expanding plumes, exposed or threatened receptors) have been abated; and 3) proper institutional controls are recorded on the deed, if necessary, to notify current and future property owners of the presence of NAPL and to ensure that land use changes do not alter site conditions without proper evaluation. Providing data for these demonstrations that clearly indicate all plumes and the NAPL body are stable or decreasing in size and mass will generally allow for a more efficient and expedited review of the documentation. The amount and timing of the data, as well as the length of time required for monitoring, is dependent upon the risks, the proximity to potential receptors, and the proximity to property boundaries.

Since the environment is dynamic, there may be some expected transient or seasonal expansions and contractions in plume sizes. Any transient expansions should be insignificant when compared to the distance to receptors and property boundaries. Risk-based assessments for sites with mobile NAPL may be more complex with additional data collected that is necessary to support the conclusions, account for potential uncertainties, and assure that the risks are properly managed. However, the data necessary to support risk abatement and management are based on site-specific conditions and are most effectively communicated in a clear, concise CSM.

## Appendix A.

### References

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## Appendix B.

### Definitions/Terminology

The following terms are defined and if used for assessment, correspondence, and documentation of petroleum release sites regulated under NREPA will aid in clearer communications. When appropriate, a brief discussion of how these terms relate to light NAPL (LNAPL) or petroleum NAPL follows the definition (Note – The Part 213 statutory definitions are in all **CAPS** and **BOLD** text).

- **NAPL -- MEANS A NONAQUEOUS-PHASE LIQUID OR A NONAQUEOUS-PHASE LIQUID SOLUTION COMPOSED OF 1 OR MORE ORGANIC COMPOUNDS THAT ARE IMMISCIBLE OR SPARINGLY SOLUBLE IN WATER. NAPL INCLUDES BOTH DNAPL AND LNAPL.**
- **LNAPL -- MEANS A LIGHT NONAQUEOUS-PHASE LIQUID HAVING A SPECIFIC GRAVITY LESS THAN 1 AND COMPOSED OF 1 OR MORE ORGANIC COMPOUNDS THAT ARE IMMISCIBLE OR SPARINGLY SOLUBLE IN WATER, AND THE TERM ENCOMPASSES ALL POTENTIAL OCCURRENCES OF LNAPL.**
  - This term addresses all states of LNAPL. It should only be used conceptually and generically in regards to LNAPL issues. Use of this term in lieu of the term free product should be avoided and instead the more descriptive terms residual LNAPL, mobile LNAPL, and migrating LNAPL should be applied.
- **'MIGRATING NAPL' – MEANS NAPL THAT IS OBSERVED TO SPREAD OR EXPAND Laterally or vertically or otherwise result in an increased volume of the NAPL extent, usually indicated by time-series data or observation. Migrating NAPL does not include NAPL that appears in a well within the historical extent of the NAPL due to a fluctuating water table.**
  - Migrating petroleum NAPL occurs when the vertical and/or horizontal extent of this NAPL is expanding. It is only likely to be present shortly after a release occurs or if the release is ongoing. However, site-specific conditions or changes in site conditions may allow petroleum NAPL to migrate for extended periods of time. All migrating petroleum NAPL is also mobile NAPL.
- **MOBILE NAPL -- MEANS NAPL THAT EXCEEDS RESIDUAL SATURATION, AND INCLUDES MIGRATING NAPL, BUT NOT ALL MOBILE NAPL IS MIGRATING NAPL.**
  - The term mobile NAPL can be used when petroleum NAPL is present and is at a high enough saturation to be hydraulically connected in the pore spaces so that it can flow. If a well is placed in a location with mobile petroleum NAPL present, this NAPL will accumulate in the well. Mobile petroleum NAPL has the potential to move or expand its footprint, but it is not spreading vertically or laterally. Mobile petroleum NAPL is potentially hydraulically recoverable, but recovery depends on several factors. Examples of mobile petroleum NAPL include: NAPL first observed to accumulate in a well or boring at a site prior to completion of a conceptual site model (CSM), or petroleum NAPL observed in a well due to a change of water levels.

- **RESIDUAL NAPL SATURATION -- MEANS THE RANGE OF NAPL SATURATIONS GREATER THAN ZERO NAPL SATURATION UP TO THE NAPL SATURATION AT WHICH NAPL CAPILLARY PRESSURE EQUALS PORE ENTRY PRESSURE AND INCLUDES THE MAXIMUM NAPL SATURATION, BELOW WHICH NAPL IS DISCONTINUOUS AND IMMOBILE UNDER THE APPLIED GRADIENT.**
  - This defines the saturation below which petroleum NAPL become discontinuous and no longer has the ability to flow (residual NAPL). The petroleum NAPL is essentially trapped in the pores and under normal conditions and gradients, the NAPL will not move. The term residual NAPL is used to describe the state of NAPL below this saturation. This petroleum NAPL cannot be recovered by hydraulic means (e.g. pumping); however, with the use of technologies such as excavation, dual-phase extraction, or air sparge/soil vapor extraction, some fraction of the residual NAPL can be remediated or recovered.
  - This term is used when petroleum NAPL has been released at a site, but other lines of evidence suggest mobile or migrating petroleum NAPL is not present. For example, if a boring log or other evidence (e.g. petroleum staining, high photoionization detector (PID) concentrations, laser-induced fluorescence (LIF), dye tests, etc.) indicates the presence of petroleum NAPL in the soil and/or aquifer material, but a properly developed well installed in the same location does not contain mobile NAPL, the NAPL is residual. If there is a sustained groundwater plume or vapor plume present at a site, but no observed mobile or migrating petroleum NAPL, residual NAPL is present. Residual petroleum NAPL could lead to the appearance of mobile NAPL with changes in site conditions, such as a drop in groundwater elevation.
  - Residual petroleum NAPL can exist above and beneath the water table, and will have to be assessed in both the vadose zone and aquifer for the delineation of the petroleum NAPL body, mass calculations, and the development of the CSM. Residual petroleum NAPL can also be the source of compositional plumes (dissolved phase and/or vapor phase) from the NAPL body.

**NOTE:** Although ASTM 2531-06 has been incorporated by reference into the amended Part 213, some terms defined within the ASTM standard differ from the terms defined within the amended Part 213 (e.g. mobile NAPL has different meanings in each document – in Part 213 mobile NAPL has the ability to move but in ASTM 2531-06 mobile NAPL is moving). ASTM terms to become familiar with include:

- Free LNAPL – LNAPL that is hydraulically connected in the pore space and has the potential to be mobile in the environment. This is the same as mobile LNAPL as defined in amended Part 213.
- Residual LNAPL – LNAPL that is hydraulically discontinuous and immobile under prevailing conditions. Residual LNAPL cannot move through hydraulic mechanisms (unless prevailing conditions change), but can be a source for chemicals of concern (COC) dissolved in groundwater or in the vapor phase in soil gas.



### Appendix C.

#### Stakeholder List

Below is the list of individuals outside of the Michigan Department of Environmental Quality (MDEQ) who received the Petroleum Non-Aqueous Phase Liquids (NAPL) Management Policy and Procedure. The list also shows external affiliations and if comments were provided.

Stakeholder Name	Affiliation	Provided Comments (Yes/No)
Grant Trigger	Racer Trust	No
Mark Adamski	BP America	Yes
Pete Bosanic / Stephen Zayko	PM Environmental	Yes
Abed Houssari	DTE Energy	No
Cheryl Kehres-Dietrich	Soil and Materials Engineers, Inc.	Yes
John Robbins	Shell Oil	Yes
Sanjay Garg	Shell Global Solutions	Yes
Robert Steede	Enbridge Energy	No
Keith Aragona	Haley Aldrich	No
Curt Roebuck	DLZ Michigan	Yes
Steve Crider	NTH Consultants	No
Brad Koons	ARCADIS	Yes
John Rabideau	AMEC E&I, Inc.	Yes
Erik Johnson	Blarney Castle Oil	No
Mike Wolfe	AECOM Environment	Yes
Joe Berlin	BLDI Inc.	No
Dana Bradt	ATC Associates	Yes
Greg Kernosek	Envirosolutions, Inc.	Yes
Tiffany Yusko-Kotimko	Barr Engineering	Yes
Gary Dyke	CH2MHill	No
Donal Brady	Inland Seas Engineering	Yes
Andrew Kirkman	BP America	Yes

## Appendix D.

### Basic Petroleum Non-Aqueous Phase Liquids Concepts

The migration of petroleum non-aqueous phase liquids (NAPL) requires that the NAPL displace air and water from the soil pores. It takes less force for NAPL to displace air than water; therefore, NAPL preferentially enters air-filled pores. It takes less pressure for NAPL to enter a larger pore; however, in an air-NAPL system (no water), the NAPL will also be in smaller pore spaces because it is the wetting fluid in that system. Geologic heterogeneity, pore geometry, and the presence and amount of water in the pores all strongly affect NAPL migration. NAPL can migrate below the surface of the groundwater; the depth of submerged NAPL will be determined by the degree of heterogeneity and the NAPL head. NAPL can also be present in perched and hydraulically-confined stratigraphic units in the presence of soil/lithology heterogeneity.

After a release, NAPL infiltrates into the pores and is driven downward by gravitational forces through the unsaturated (vadose) zone. As NAPL migrates through the vadose zone, some will remain immobile and trapped in the pores. This residual NAPL in the vadose zone is part of the NAPL body and can act as a source for compositional plumes. If a sufficient volume of NAPL is released to overcome the holding capacity of the vadose zone, the NAPL will reach the water table and, despite it generally having a lower density than water, can be driven into the saturated zone by the vertical NAPL head. For the NAPL to migrate in the saturated zone, it must first displace the water from the pore spaces. NAPL will continue to migrate downward into pores below the water table until vertical equilibrium is reached; this occurs when the NAPL head (downward force) is less than or equal to the sum of the buoyancy force (with LNAPL only) and the entry pressure of the aquifer pores (upward forces). Vertical equilibrium usually occurs before horizontal equilibrium, and the NAPL will continue to spread laterally until horizontal equilibrium is reached. The vertical and horizontal spread of NAPL is limited by buoyancy, capillary forces, NAPL conductivity, and the declining hydraulic force of the NAPL gradient. The NAPL will persist as a separate phase in the pores within both the vadose zone and saturated zone after the NAPL body is spatially stable. All of the NAPL in all of the states (residual, mobile, and migrating) within the saturated zone and the vadose zone make up the entire NAPL body.

NAPL body behavior can be characterized partly by the NAPL saturation, which is the percentage of total pore volume occupied by the NAPL. The remaining pore volume is occupied by air and water (soil moisture) in the vadose zone, and by water in the saturated zone. At vertical equilibrium in the saturated zone, the relative amount of NAPL in the pores varies with depth, and higher NAPL saturations are usually observed near the top of the saturated zone. Over time and as the groundwater elevation fluctuates, some of the NAPL may be vertically and locally redistributed. Some of the NAPL will eventually become hydraulically disconnected, leaving independent globules of NAPL in some pores. As the NAPL migrates and the degree of saturation of NAPL decreases, the NAPL will approach residual saturation. NAPL saturation at or below residual saturation is neither mobile nor hydraulically recoverable. NAPL saturation above residual saturation is mobile, potentially migrating, and potentially hydraulically recoverable. Even though residual NAPL is not mobile, it can still act as a significant source of contaminant mass for vapor and groundwater plumes. Conversely, in some instances, it is possible that the residual NAPL may not be in contact with groundwater, may not be leaching to groundwater, and may not be a vapor risk and can be left in place using institutional controls, if necessary.

The presence of mobile NAPL in a given well does not necessarily mean that the NAPL body is migrating; the NAPL just has the potential to migrate. In order for migration to occur at the edges of the



NAPL body (expansion), the NAPL head (e.g. potential energy or gradient) must be high enough to overcome the entry pressure of adjacent soil pores. As the NAPL body spreads, the degree of NAPL saturation decreases, which reduces the NAPL conductivity. Once the counteracting mechanisms (decreasing conductivity, decreasing gradient, and entry pressure combined with loss mechanisms of biodegradation, dissolution, and volatilization) are greater than the NAPL head, the NAPL body will eventually become spatially stable under prevailing conditions, even though mobile NAPL may remain in the core of the NAPL body.

The detection of visible or measurable NAPL in a well (analogous to a large soil pore) indicates that some of the NAPL in the immediate vicinity of the well exceeds residual saturation and is mobile. The lack of visible or measurable NAPL in a well does not necessarily mean that there is no NAPL in the vicinity of the well; there may be residual NAPL. Moreover, mobile NAPL may be trapped within the saturated zone due to the stronger force needed to displace water from the pores. That is why NAPL may appear or accumulate in greater volumes in a well after the elevation of the groundwater decreases. Thus, water table fluctuations must be accounted for when evaluating saturations, recovery, and the potential for migration of NAPL. Water table fluctuations also affect NAPL recharge rates and recovery trends.

NAPL will generally contain more mass of the constituents of concern (COC) than what is dissolved in groundwater, volatilized to soil gas, and adsorbed to soil particles; however, the mass contained in the NAPL is finite. Over time, as compounds dissolve, volatilize, biodegrade, and/or adsorb to soil, depletion of COC in the NAPL occurs, which is referred to as natural source zone depletion (NSZD). Determining the rate of NSZD may be useful in making risk-based, recovery, and remedial decisions.

The transmissivity of the NAPL, defined as the volume of NAPL traveling through a unit width of aquifer per time per unit drawdown, can be utilized as a metric for recoverability and aid in remedial decisions. Transmissivity can also be used as part of the conceptual site model (CSM) for delineating and depicting recovery trends; however, transmissivity does not necessarily provide information regarding the risk posed by the NAPL. The NAPL transmissivity is a function of both fluid (e.g. density, viscosity) and media (e.g. permeability, pore saturation) properties. Currently, the collection, assessment, and evaluation of NAPL transmissivity data is relatively new and may be subject to change as more data are collected. There are generally four means of data collection and analysis of NAPL transmissivity: 1) baildown/slug testing; 2) manual skimming; 3) recovery system data; and 4) tracer testing. For a more detailed discussion of the methods and analyses, see ASTM E2856 – 11, *Standard Guide for the Estimation of LNAPL Transmissivity*.





## Appendix E.

### Assessing Vapor Intrusion Risk at Sites with Petroleum Non-Aqueous Phase Liquids

The presence of petroleum non-aqueous phase liquids (NAPL) in soils can lead to difficulties evaluating the risk associated with the soil volatilization to indoor air pathway, commonly known as vapor intrusion (VI). This is partly attributed to the Michigan Department of Environmental Quality's (MDEQ) use of the Johnson and Ettinger VI model (J&E model) for assessing the risk of this exposure pathway, as well as the evaluation of individual contaminants rather than the multiple contaminants that can occur in NAPL. The United States Environmental Protection Agency (EPA) has identified a number of conditions under which the J&E model may not accurately predict VI risk, which includes the presence of NAPL. There are alternate versions of the J&E model as well as other models, such as the American Petroleum Institute's (API) BioVapor, that have been developed to help assess VI risk associated with NAPL. These alternate models can be utilized with multiple contaminants and also assume some biodegradation of petroleum vapors in the vadose zone; however, the source inputs for the models are groundwater or soil gas contaminant concentrations. As stated in the BioVapor model literature, with residual NAPL in the soil, the model(s) should not be used as a primary line of evidence for risk assessment and may require collection of soil gas data.

The MDEQ developed soil volatilization to indoor air inhalation criteria (SVIIC), assumed to be protective of indoor air. The SVIIC numbers will continue to be utilized to assess VI risk; however, with the inherent uncertainties with any model or calculation or soil gas data is a useful metric to make a direct assessment of the vapor risk. Absent soil gas data, soil analytical data can be compared to the SVIIC values for individual hazardous substances if the soil can be considered to contain a relatively minor amount of NAPL. The MDEQ will consider the SVIIC applicable if NAPL is not present or the concentration of TPH GRO is less than 350 mg/kg for gasoline or TPH DRO is less than 500 mg/kg for diesel. If the other assumptions in the algorithm are appropriate for the site, the soil contains no or relatively minor amount of NAPL and the soil analytical data is less than SVIIC, then no further risk assessment is required, even if residual NAPL is in the area proximal to the location of evaluation. If the soil concentrations exceed the SVIIC (when applicable), the soil is above 350 ppm GRO/500 ppm DRO, and/or mobile or migrating NAPL is present, then additional assessment (e.g. soil gas sampling) or presumptive remedies (e.g. soil vapor extraction or institutional controls) will need to be utilized to evaluate and/or address the pathway.

The collection of representative data is always the most appropriate way to evaluate sites. For various reasons, TPH may not always be collected. If soil TPH GRO data has not been collected, then it can be estimated using the soil benzene, toluene, ethylbenzene, and total xylene (BTEX) data. For a gasoline release, multiply the sum of the BTEX concentrations by 40 to estimate the GRO concentration. For a diesel release, estimating the DRO concentration is complex, and site-specific evaluations could be completed.

Soil TPH GRO estimate = Soil BTEX\*40

The following is intended to provide additional information and assistance on assessing VI risk and implementing corrective actions when addressing NAPL releases. One of the key assumptions is that the investigation results in an understanding of where the NAPL is located and where each state (residual, mobile, and migrating) of NAPL occurs. In addition, an adequate conceptual site model (CSM) will depict the location, nature, and extent of the NAPL body and compositional plumes in both plan and cross-sectional views, and properly identify potential receptors. The following options can be



utilized (alone or in combination) for evaluating and addressing the VI risk at NAPL sites using the CSM:

1. If the CSM demonstrates that there is no NAPL or only residual NAPL below the 350 ppm GRO or 500 ppm DRO, and the concentrations of the individual petroleum contaminants of concern (COC) in the soil are less than SVIIC then there will be no further risk assessment of the VI pathway required. Other assumptions in the SVIIC calculation will still need apply to the site. If GRO concentrations are unknown, the values can be estimated as outlined above. However, representative data provides the best information for assessing risks.
2. When NAPL is present, establish the chemical composition of the NAPL and utilize a scientifically defensible VI model that can estimate the rate of VI into buildings and identify the associated health risks. The model utilized will need to account for NAPL. Examples of appropriate NAPL models (in Excel<sup>®</sup> format), their assumptions and use restrictions, and their associated user's guides can be found at:

[http://www.epa.gov/oswer/riskassessment/airmodel/johnson\\_ettlinger.htm](http://www.epa.gov/oswer/riskassessment/airmodel/johnson_ettlinger.htm)

OR

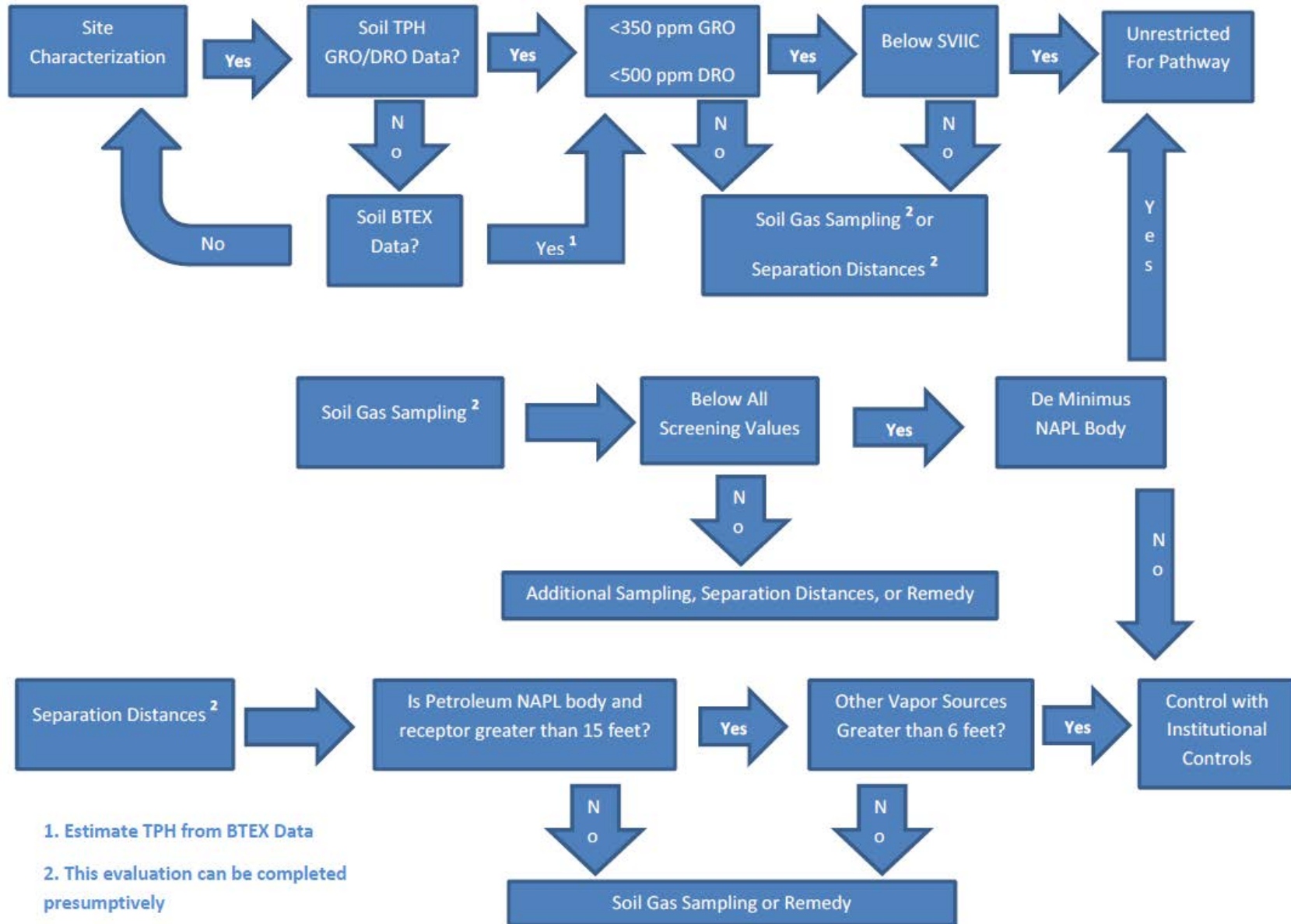
[http://www.epa.gov/oswer/riskassessment/airmodel/johnson\\_ettlinger.htm](http://www.epa.gov/oswer/riskassessment/airmodel/johnson_ettlinger.htm)  
<http://www.api.org/environment-health-and-safety/clean-water/ground-water/vapor-intrusion/biovapor-form>

3. When mobile and/or migrating NAPL is present; **or** the SVIIC (when applicable) is exceeded; **or** the GRO/DRO (350/500 ppm) concentration exceeds the screening value; **or** a structure is less than five meters (15 feet) from a NAPL body (that exceeds screening values); **or** a structure is less than two meters (6 feet) from other vapor sources (that exceeds screening values), then soil gas or sub-slab samples may be collected and analyzed. The soil gas samples should be collected and analyzed in accordance with the sampling strategies identified in the MDEQ's *Guidance Document for the Vapor Intrusion Pathway* or in other scientifically defensible methods. Any detected values can be compared to the screening values published in that document to evaluate if the NAPL poses a risk.
4. If the CSM demonstrates that the NAPL body meets the separation distance of five meters (15 feet) and all other sources of vapor (e.g. impacted soil and dissolved groundwater) are at least two meters (6 feet) from any current, proposed, or planned structure, then the exposure risk is not present and no further risk assessment of the VI pathway is warranted.

NOTE: An institutional control would **NOT** be necessary if the evaluation was based on generic residential assumptions and comparison of soil analytical data to SVIIC (if applicable) or comparison of soil gas concentrations to screening levels to assess risk (if the soil gas samples were collected in or immediately adjacent to the NAPL body – “worst case”). Any time an evaluation other than one based on generic residential assumptions or “worst case” soil gas is implemented (e.g. dependence on separation distance), an institutional control or other remedial action will be necessary to prevent future exposures that could result from land use changes.

Further details on the investigation and risk assessment of soil vapors can be found in the MDEQ *Guidance Document for the Vapor Intrusion Pathway*.

Evaluation of the Vapor Intrusion Pathway with Residual Petroleum NAPL



1. Estimate TPH from BTEX Data

2. This evaluation can be completed  
presumptively

Note: De Minimus NAPL body is not defined and will be a site specific decision in considering all site factors



## Appendix F.

### Assessing Direct Contact Risk at Sites with Petroleum Non-Aqueous Phase Liquids

The presence of petroleum non-aqueous phase liquids (NAPL) complicates the evaluation of the soil direct contact (SDC) pathway. Soils containing NAPL can pose a direct contact risk to humans and risks to environmental receptors. The presence of petroleum-saturated soils was not accounted for in the development of the SDC risk-based screening levels (RBSLs)/cleanup criteria (CC) for individual hazardous substances, and may be inconsistent with the underlying assumptions of these criteria. Furthermore, while the Michigan Department of Environmental Quality (MDEQ) has established SDC RBSLs/CC for some of the individual hazardous substances that may be present in common petroleum mixtures, the variability of chemical compositions of petroleum mixtures and the site conditions under which they may exist prevents the development of generic petroleum-mixture RBSLs/CC for state-wide application. To minimize the uncertainties associated with applying the SDC RBSLs/CC when NAPL is present, the MDEQ considers the generic SDC RBSLs/CC appropriate for the evaluation of risk for the SDC exposure pathway when there is less than or equal to 0.5% of the pore space in the soil filled with residual NAPL and there is no evidence of mobile NAPL. At 0.5% saturation of NAPL, it can be reliably assumed that the NAPL is residual and there is not enough mass of NAPL in the soil to physically change the assumed soil properties in the algorithms.

If there is no evidence of mobile NAPL, initial comparisons of the soil concentrations may be made to the lower of the following: generic SDC RBSLs/CC or the individual single compound saturation limit ( $C_{sat}$  or soil in equilibrium with water at the solubility limit of an individual compound). When approximating the average compositions of petroleum, several of the individual  $C_{sat}$  concentrations may represent approximately 0.5% petroleum saturation in the soil pore space. If the lower of the generic SDC RBSLs/CC or  $C_{sat}$  is not exceeded, the MDEQ assumes that less than or equal to 0.5% of the pore spaces in the soil is filled with residual NAPL and no further activities would be required for this pathway.

If the lower of generic SDC RBSLs/CC or  $C_{sat}$  is exceeded, or there is evidence of mobile NAPL, a site-specific evaluation can be conducted to assess the SDC risk. The site-specific evaluation could include the determination of the degree of NAPL saturation and NAPL composition. The degree of NAPL saturation can be determined in the laboratory or estimated using total petroleum hydrocarbon (TPH) analysis and the following equation:

$$S_n = (\rho_b * TPH) / (\rho_n * n * 10^6)$$

Where:

$S_n$  – degree of saturation (unitless)

$\rho_b$  – dry bulk density of soil ( $g/cm^3$ ) – assumed to be 1.6

TPH – TPH analytical value (mg/kg)

$n$  – porosity – assumed to be 0.4 (unitless)

$\rho_n$  – NAPL density ( $g/cm^3$ ) – assumed to be 0.77 for gasoline and 0.85 for diesel fuel

Using the above assumptions, a TPH-gasoline range organics (GRO) concentration of 900 mg/kg and a TPH-diesel range organics (DRO) concentration of 1,050 mg/kg are approximately equal to 0.5% saturation of NAPL in the pore space of the soil. If the TPH concentration is less than or equal to these GRO and/or DRO concentrations or  $S_n$  is less than or equal to 0.5% NAPL saturation using site-



specific values, then the individual hazardous substance concentrations can be compared to the RBSLs/CC for the risk assessment of the SDC pathway.

If the NAPL saturation exceeds 0.5%, then it is assumed that there is a SDC risk associated with the soil, and corrective actions and/or exposure controls will be necessary. Site-specific risk evaluations may also be conducted to determine risks.

Example of an acceptable direct contact pathway risk evaluation:

1. The concentration of xylenes in a soil sample is 400,000 micrograms per kilogram ( $\mu\text{g}/\text{kg}$ ). Comparison to generic SDC RBSLs/CC indicates via footnote that it is necessary to determine if NAPL is present to use this value for comparison. The initial screening comparison then becomes comparison to  $C_{\text{sat}}$ .
2. This concentration exceeds the individual  $C_{\text{sat}}$  screening level of 150,000  $\mu\text{g}/\text{kg}$ . Further evaluation is required to determine if NAPL is present and if additional controls or protections from the NAPL are required.
3. The TPH-GRO concentration in this same soil sample is 750,000  $\mu\text{g}/\text{kg}$ . Using the above assumptions and saturation equation, the GRO value suggests that NAPL saturation is less than 0.5%. This implies that residual NAPL is present at a low enough saturation the SDC RBSL/CC for xylenes of 410,000,000  $\mu\text{g}/\text{kg}$  can be used for comparison.
4. Since the soil concentration of xylenes is less than the SDC RBSL/CC, there is no direct contact risk of total xylenes.