

Technical Justification for Groundwater Media-Specific Criteria

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1 INTRODUCTION

The purpose of this document is to supplement and provide technical justification for groundwater media-specific criteria described in the General Criteria and Media Specific Criteria sections of the Low-Threat Underground Storage Tank (UST) Case Closure Policy (Policy). Media-specific criteria for vapor and soil are discussed in the documents *Technical Justification for Vapor Intrusion Media-Specific Criteria*, and *Technical Justification for Soil Screening Levels for Direct Contact and Outdoor Air Exposure Pathways*, respectively.

2 BACKGROUND

The background section presents information on petroleum chemistry, free product, plume studies, and the use of Conceptual Site Models (CSMs).

2.1 *Petroleum Chemistry*

Petroleum is defined as crude oil, or any fraction thereof, which is liquid at standard conditions of temperature and pressure, which means 60 degrees Fahrenheit and 14.7 pounds per square inch absolute. Petroleum enters the subsurface as an immiscible fluid which is a mixture of constituents. These petroleum constituents are unique in the subsurface and their fate is predictable.

The composition of the dissolved phase from unweathered petroleum products (including gasoline, kerosene, jet fuel, diesel, Bunker C fuel, and motor oil) and unweathered crude oils have been studied and investigated under laboratory conditions by several researchers using various analytical methods (Coleman, et al. 1984; Shi, et. Al. 1990; Thomas and Delfino 1991; Bruya and Friedman 1992; Chen, et al. 1994; and Potter 1996). The results from these studies are consistent, and provide clear evidence that the petroleum hydrocarbons, which comprise the measurable dissolved phase of unweathered crude oil and refined products, are limited primarily to these discrete constituents:

- Six to eleven carbon atoms (C⁶ to C¹¹) monoaromatics (benzene, toluene, ethylbenzene, and xylenes [BTEX] and the alkylated benzenes);
- C¹⁰ to C¹⁴ polyaromatic hydrocarbons (PAHs) (naphthalene, alkylated naphthalenes, acenaphthene, fluorene, phenanthrene, and anthracene); and
- C⁶ and smaller aliphatics.

These studies focused on the hydrocarbon constituents of unweathered crude oil and refined products in the dissolved phase; however, the same principles apply to weathered products. Blending agents or additives which are polar in their molecular structure, such as oxygenates, have both relatively high

pure-compound solubilities and large mole-fractions within the product mixture; therefore, they can represent a large proportion of the dissolved phase of a given product. This is why methyl tertiary butyl ether (MTBE) is present in plumes in much higher concentrations than the hydrocarbons. Note that polar molecules have slightly charged negative and positive ends, and therefore are more soluble in water, which is also polar.

The scientific community has known for more than 15 years that the vast majority of risk posed to human health and water quality is driven by the aromatics within the BTEX suite (benzene in particular) and the oxygenate MTBE. The BTEX compounds have relatively high toxicity and are the hydrocarbon constituents with the highest effective solubility in gasoline. MTBE has very high effective solubility, has relatively low biodegradation potential, and therefore creates longer plumes. MTBE has lower toxicity than benzene, but it has a low taste and odor threshold, therefore its California Maximum Contaminant Level (MCL) is low as well. While the rest of the hydrocarbons make up the majority of the mass in the product that may be present, they account for very little risk posed to human health or groundwater quality due to their lower toxicity and/or lower mobility in the environment.

2.2 Free Product

Free product or light non-aqueous phase liquid (LNAPL) exists in three conditions in the subsurface: 1) residual or immobile LNAPL (LNAPL that is trapped in the soil pore spaces by capillary forces and is not mobile), 2) mobile LNAPL (enough LNAPL is present in the soil pore spaces to overcome capillary forces so that the LNAPL can move), and 3) migrating LNAPL (mobile LNAPL that is migrating because of a driving head). Residual, mobile, and migrating LNAPL are described in detail in several peer-reviewed technical documents, including the 2009 Interstate Technology Regulatory Council (ITRC) Technical/Regulatory Guidance *Evaluating LNAPL Remedial Technologies for Achieving Project Goals*. (ITRC, 2009)

The term free product is primarily equivalent to migrating LNAPL (a subset of mobile LNAPL), and secondarily equivalent to mobile LNAPL. Whether LNAPL is mobile (and therefore could potentially migrate) or not is usually tested by observing recharge of LNAPL after removing LNAPL from a monitoring well. Whether LNAPL is migrating or not is tested by monitoring the extent of the LNAPL body (usually using the apparent product thickness in monitoring wells) at a certain water level elevation over time. If the extent at that water level elevation does not expand, then the LNAPL is not migrating. Therefore, LNAPL must be removed to the point that its migration is stopped, and the LNAPL extent is stable. Further removal of LNAPL is required to the extent practicable at the discretion of the local agency.

Removal of LNAPL from the subsurface is technically complicated, and removal of LNAPL to the maximum extent practicable is based on site-specific factors (such as soil properties, varying groundwater elevations, and varying lateral groundwater flow velocities) and includes a combination of objectives for the LNAPL removal (such as whether the LNAPL is a significant source of dissolved constituents to groundwater or volatile constituents to soil vapor, or whether there is a high likelihood that hydrogeologic conditions would change significantly in the future which may allow the mobile LNAPL to migrate) and technical limitations. The typical objectives for LNAPL removal, technologies for

LNAPL removal and technical limitations of LNAPL removal are discussed in several peer-reviewed technical documents within ITRC (2009).

Studies in California show that once the contaminant source is removed and the plume stabilizes, natural degradation proceeds at substantial rates, sometimes at 50-60% per year (Rice et. al., 1995). Therefore, if free product is removed to the maximum extent practicable and natural degradation is occurring, then it is reasonable to expect that attenuation would continue.

2.3 Plume Studies

Plume length studies recognize that petroleum plumes stabilize in length due to natural attenuation. Various researchers have conducted multi-site studies of groundwater plume lengths at petroleum release sites across the United States. These studies considered sites where active remediation was performed and sites where no active remediation was performed. Many studies focused on benzene plumes (Rice, et al. 1995; Rice et al. 1997; Busheck et al. 1996; Mace, et al. 1997; Groundwater Services, Inc. 1997; American Petroleum Institute (API) 1998); other researchers (Dahlen et al. 2004; Shih et al. 2004) studied both benzene and oxygenate plumes, including MTBE. Many of the researchers recognized benzene, MTBE, and total petroleum hydrocarbons as gasoline (TPHg) as key indicator constituents for groundwater plume lengths. Researchers' technical justification for using these three constituents as key indicators relied on the facts that: 1) benzene has the greatest toxicity of the soluble petroleum constituents, 2) MTBE typically has the greatest plume lengths, and 3) TPHg represents the additional dissolved hydrocarbons that may be present resulting from a typical petroleum release. The peer-reviewed study of plume lengths at 500 petroleum UST sites in the Los Angeles area is widely accepted as representative of plume lengths at California UST sites (Shih et. al., 2004). Shih et. al. (2004) reports benzene, MTBE and TPHg plume characteristics as follows:

Table 1: Plume characteristics reported by Shih et. al. (2004).

Constituent (and plume limit concentration)	Average Plume Length (feet)	90 th Percentile Plume Length (feet)	Maximum Plume Length (feet)
Benzene (5 µg/l)	198	350	554
MTBE (5 µg/l)	317	545	1,046
TPHg (100 µg/l)	248	413	855

Notes:

1. Plume lengths were measured from the source area.
2. Total petroleum hydrocarbons as gasoline (TPHg) is shown for comparison purposes only. The Policy does not set criteria for TPH.
3. Constituent concentrations measured in micrograms per liter (µg/l).

Although the California maximum contaminant level for benzene is 1 micrograms per liter (µg/l), the Shih et al. (2004) study used a benzene concentration of 5 µg/l to determine plume length because of the statistical uncertainty associated with concentrations near the 0.5 µg/l laboratory reporting limit. Benzene plume lengths measured at a 1.0 µg/l concentration limit could be expected to be slightly longer than those tabulated above.

Ruiz-Aguilar et al. (2003) studied releases of ethanol-amended gasoline (10% ethanol by volume) at UST release sites in the Midwest. Ruiz-Aguilar et al. (2003) found that benzene plume lengths may increase by 40% to 70% when gasoline is formulated with 10% ethanol substituted for MTBE. Ethanol preferentially biodegrades prior to benzene, which results in a longer benzene plume.

Natural attenuation of petroleum hydrocarbon and oxygenate plumes has been documented by many researchers since the 1990s. This body of work demonstrates that natural attenuation of petroleum hydrocarbons and MTBE occurs under both aerobic and anaerobic conditions (Howard, 1990). Advances in compound-specific stable isotope analyses make it possible to accurately measure the shift in the ratio of the isotopes in MTBE in water at low concentrations. The fractionation of the MTBE that has not degraded becomes the equivalent to a metabolic product that is used to document biodegradation. This makes it possible for the first time to unequivocally identify and measure anaerobic biodegradation of MTBE at field scale (U.S. EPA, 2005). The rate of degradation/attenuation depends on the constituent and the plume bio/geochemical conditions.

2.4 Conceptual Site Model

A CSM is used to identify contaminant source(s), transport mechanisms or exposure pathways, and potential receptors based on site-specific and regional conditions. It provides a conceptual understanding of contaminant transport and risk assessment at a site. The CSM is a fundamental element of a comprehensive site investigation and contains sufficient detail to make decisions at the site, and comprehensive enough to show compliance with all of the policy media-specific criteria and State and federal laws and/or regulations. The CSM is an iterative thought process that is always implemented at a leaking underground fuel tank (LUFT) site, whether or not it is recorded as a tangible document, graphic, or depiction. To discuss and make decisions about LUFT sites, one must visualize the source and the movement of contaminants in the subsurface and create a model or analogy. Although the term conceptual site model is not found in California law or regulations, the thought process is fundamental to scientific inquiry and is directly applicable to decision-making at LUFT sites.

The objectives of the CSM are:

- To convey an understanding of the origin, nature, and lateral and vertical extent of contamination;
- To identify potential contaminant fate-and-transport processes and pathways. This includes but is not limited to identifying the site topography, regional and site-specific geologic and hydrologic conditions, designated beneficial uses of groundwater beneath the site, and plume stability;
- To identify potential human and environmental receptors that may be impacted by contamination associated with the site;
- To guide site investigation activities and identify additional data needed (if any) to draw reasonable conclusions regarding the source(s), pathways, and receptors; and
- To evaluate risk to human health, safety, and the environment posed by releases at a LUFT site.

3 GENERAL CRITERIA

The Policy indicates the following general criteria must be satisfied by all candidate sites:

- a. The unauthorized release is located within the service area of a public water system;
- b. The unauthorized release consists only of petroleum;
- c. The unauthorized (primary) release from the UST system has been stopped;
- d. Free product has been removed to the maximum extent practicable;
- e. A conceptual site model that assesses the nature, extent, and mobility of the release has been developed;
- f. Secondary source has been removed to the extent practicable;
- g. Soil or groundwater has been tested for MTBE and results reported in accordance with Health and Safety (Health & Saf.) Code § 25296.15; and
- h. Nuisance as defined by Wat. Code § 13050 does not exist at the site.

This section focuses on providing technical justification for the general criteria that pertain to groundwater.

3.1 Public Water Systems

The Policy requires that a low-risk site be located within the service area of a public water system for low-threat site closure. The Policy limits low-threat sites to areas with available public water systems to reduce the likelihood that new wells in developing areas will be inadvertently impacted by residual petroleum in groundwater. The Policy defines a public water system as a system for the provision of water for human consumption through pipes or other constructed conveyances that has 15 or more service connections or regularly serves at least 25 individuals daily at least 60 days out of the year.

Existing programs through the California Department of Water Resources (DWR) and California Department of Public Health (CDPH) provide protective measures to limit new water supply locations in areas with potential poor water quality. DWR's Bulletin 74-81, *Water Well Standards: State of California* (1981), provides guidance on installing new wells to limit poor water quality intrusion. Additionally, CDPH implements their Drinking Water Source Assessment Program (DHS, 2000), which requires an inventory of possible contaminating activities within source areas and protection zones prior to use of a new supply well.

Water suppliers understand the groundwater basins used for water supply. Municipal wells tend to preclude shallow impacts by using deep screens and good surface sanitary seals. Municipal wells have significant dilution due to large pumping volumes. Public water systems have a greater opportunity for blending supplies in the unlikely event a new well captures an old plume. Additionally, residences in a public water system are unlikely to have a private domestic well that could be impacted by a low-threat

site. It is unlikely that shallow domestic wells will be installed where a reliable source of water already exists.

Sites within a public water system that have potential to impact the water supply within a public water system would be considered high-risk and would not qualify as a low-threat site. If a water supplier determines that a site that is being considered for closure under the low-threat scenario is likely to impact future water supplies, the site may have unique conditions that could require additional remediation.

3.2 Release Consists only of Petroleum

The Policy requires that the unauthorized release consists only of petroleum for consideration as a low-threat site. While recalcitrant contaminants may require specific conditions to degrade, petroleum hydrocarbons and MTBE have shown to undergo biodegradation/natural attenuation under both aerobic and anaerobic conditions (Howard, 1990). Other non-petroleum contaminants may have different chemical properties and risks to consider and are therefore beyond the scope of the Policy.

3.3 Primary Release has been Stopped

The Policy requires that the tank, pipe, or other appurtenant structure that released petroleum into the environment has been removed, repaired or replaced for consideration as a low-threat site. This is to prevent the ongoing release of petroleum contamination from continuing in the future. If the mechanism for the primary release is not removed, repaired, or replaced, the petroleum-impacted groundwater plume is unlikely to remain stable or decrease with time and would not qualify as being a low-risk site.

3.4 Free Product Removal

The Policy requires that free product be removed to the maximum extent practicable in order to be considered a low-risk site. Free product is the primary source of contamination from LUFT sites which contributes to secondary sources and groundwater contamination. The Policy is consistent with California Code of Regulations (CCR), Title 23, Division 3, Chapter 16, §2655 et seq. that free product is required to be removed to the maximum extent practicable, and the abatement of migration shall be the predominant objective in the design of the free product removal system. Free product shall be removed in a manner that minimizes the spread of contamination into previously uncontaminated zones. For most sites, stable or declining concentrations of dissolved constituents in groundwater indicate that petroleum is no longer acting as a significant source. Therefore, removing the primary source of contamination limits the development of a secondary source (e.g., soil and groundwater). Rice et. al. (1995) has shown that if the source is removed and groundwater is stable, this can promote natural degradation and expedites compliance with the Water Quality Objectives (WQOs).

3.5 Conceptual Site Model

The Policy requires that a CSM assess the nature, extent, and mobility of the release has been developed in order to be considered a low-risk site. The CSM is a tool that uses current and historical information to evaluate whether a site is currently low-risk site and likely to remain a low-risk site in the future. It describes the dynamics of a system and is used to assess risk based on data from the site and from nearby properties. It captures current and historical surrounding property-use that impact or may impact contaminant transport at a site. It also provides a method for predicting conditions which can affect the nature, extent, and mobility of the contamination (such as soil properties, varying groundwater elevations, and varying lateral groundwater flow velocities).

3.6 Secondary Source Removal

A secondary source is defined as petroleum-impacted soil or groundwater located at or immediately beneath the point of release from the primary source. The Policy requires that the secondary source be removed to the maximum extent practicable. To the maximum extent practicable means implementing a cost-effective corrective action which removes or destroys-in-place the most readily recoverable fraction of source-area mass as determined by the implementing agency. In some cases, site attributes prevent the removal of groundwater contamination (e.g. physical or infrastructural constraints exist where removal or relocation would be technically or economically infeasible). This may result in residual concentrations to remain in groundwater above the WQOs.

Rice et al. (1995) shows that soil microorganisms severely limit the movement of plumes by digesting the balance of the petroleum-based contaminant. Data from a number of counties in California show that contaminant plumes rarely exceed 250 feet and stabilize quickly. Once contaminant sources are removed and plumes stabilize, natural degradation proceeds at substantial rates, sometimes at 50-60% per year (Rice et al., 1995). Allowing the residual contamination to remain after the secondary source removal is performed generally results in a ten-fold reduction in plume contaminant mass within one to three years.

3.7 Testing for MTBE

The Policy requires that soil and groundwater have been tested for MTBE and results reported in accordance with Health & Saf. Code §25296.15. MTBE is recognized as one of the indicator constituents for most petroleum-impacted groundwater plumes and typically has the greatest plume lengths. For these reasons, MTBE is a good indicator of plume characteristics and is useful for evaluating historical trends and refining the CSM.

3.8 Nuisance

As part of the general criteria for the Policy, a site must remediate all nuisances per Wat. Code §13050 to be considered for closure under the low-threat scenario. There can be a scenario where remaining contamination in groundwater is not a risk to human health or the environment but is a nuisance (e.g.,

dewatering in basement at adjoining property). This requirement would eliminate sites from being considered low-risk where there is a current or future potential that a nuisance condition exists.

Wat. Code §13050 defines nuisance as anything which meets all of the following requirements:

- Is injurious to health, or is indecent or offensive to the senses, or an obstruction to the free use of property, so as to interfere with the comfortable enjoyment of life or property;
- Affects at the same time an entire community or neighborhood, or any considerable number of persons, although the extent of the annoyance or damage inflicted upon individuals may be unequal; and
- Occurs during, or as a result of, the treatment or disposal of wastes.

The petroleum vapor intrusion and direct contact and outdoor air exposure pathways criteria listed in the Policy (and related Technical Justification documents) outline the conditions that the site must satisfy for protection of public health and for immediate unrestricted use of the property. If all general criteria are satisfied for the site, it is unlikely that the shallow groundwater will be used before water quality objectives are restored by natural attenuation.

In the unlikely event that shallow groundwater becomes a nuisance through construction dewatering, basement sump dewatering, or other activities where the shallow groundwater is contacted but not consumed, the Policy provides for abatement of nuisance conditions.

4 MEDIA-SPECIFIC CRITERIA FOR GROUNDWATER

This criteria is used to determine that threats to existing and anticipated beneficial uses of groundwater have been mitigated or are de minimus. State Water Board Resolution 92-49, *Policies and Procedures for Investigation and Cleanup and Abatement of Discharges under Water Code § 13304*, directs that water affected by an unauthorized release attain either background water quality or the best water quality that is reasonable if background water quality cannot be restored. Any alternative level of water quality less stringent than background must be consistent with the maximum benefit to the people of the State, not unreasonably affect current and anticipated beneficial use of affected water, and not result in water quality less than that prescribed in the regional water quality control plan (Basin Plan) for the basin within which the site is located. The following illustrates the method and rationale for a low-threat facility to comply with State Water Board Resolution 92-49.

4.1 Low-Threat Groundwater Justification

In general, the Low-Threat Groundwater Classes are classified on stable or decreasing plumes, status of free product removal, distance to the nearest groundwater or surface water receptor from the plume boundary, and other factors that may be required to demonstrate low-threat. Of importance, a factor of safety is applied to each class for separation distances to potential groundwater and surface water receptors. It should be noted that these groundwater plume class criteria (concentrations, plume lengths and separation distances) are only one component of the overall evaluation of site conditions that must be satisfied to be considered for closure as a low-threat site under the Policy.

For the purpose of this Policy, the length of a plume is the maximum extent from the point of release of any petroleum related constituent in groundwater that exceeds the WQOs. The plume boundary is where the constituent(s) furthest from the point of release concentration level equals the WQOs.

A plume is considered stable or decreasing if a contaminant mass has expanded to its maximum extent: the distance from the release where attenuation exceeds migration. There are two common ways to demonstrate plume stability. The first common way is to routinely observe non-detect values for groundwater parameters in down-gradient wells. The second common way is to show stable or decreasing concentration levels in down-gradient wells at the distal end of the plume. It should be noted that concentration levels may exhibit fluctuations due to seasonal variations. These variations may be also attributed to man-made factors, including but not limited to: varying sampling techniques, false positive results, or laboratory inconsistencies.

Based on the plume studies presented in the above sections, a total separation distance from the source area to the receptor of about 500 feet should be protective for 90% of plumes from UST sites, and a total separation distance from the source area to the receptor of about 1,000 feet should be protective for virtually all plumes from UST sites. Additionally, low-threat classes require a known maximum stabilized plume length, and meet all of the additional characteristics of one of the five classes of sites. Requiring that a plume must be stable or decreasing reduces uncertainty as to how long the plume might become in the future. The Policy addresses the potential for longer plumes of ethanol-enhanced gasoline by applying separation distance safety factors of 100% to 400%.

The use of separation distances is consistent with other State and local practices regarding impacts to groundwater caused by other anthropogenic releases. For example, State and local agencies establish required separation distances or setbacks between water supply wells and septic system leach fields (typically 100 feet), and sanitary sewers (typically 50 feet; [DWR 1981]).

In order to accommodate varying plume sizes, remaining free product, higher constituent concentrations, and distances to surface water and groundwater receptors, factors of safety are incorporated into low-threat groundwater classes explained in the following sections. As the associated risk increases, so does the margin of error, thus the factor of safety also increases progressively between 100 and 400 percent (%).

4.2 *Low-Threat Groundwater Classes Defined*

The following paragraphs present and discuss the key rationales for low-threat plume lengths, maximum concentrations, and separation distances for each low-threat class as discussed in the Policy. Note that the specified concentrations are maximums, and typically occur in source area monitoring wells; the average concentrations in the plume would be lower. These groundwater plume class criteria (concentrations, plume lengths and separation distances) are only one component of the overall evaluation of site conditions that must be satisfied to be considered for closure as a low-threat site under the Policy.

Class 1: The short, stabilized plume length less than 100 feet (plume boundary is less than [$<$] 100 feet from point of release) is indicative of a small or depleted source and/or very high natural attenuation

rate. The plume boundary must be greater than 250 feet distance to a receptor. This represents an additional 250% plume length safety factor in the event that some additional unanticipated plume migration is to occur.

Class 2: The moderate, stabilized plume length (plume boundary is <250 feet from point of release) approximates the average benzene plume length from the cited studies. The maximum concentrations of benzene (3,000 µg/l) and MTBE (1,000 µg/l) in groundwater are conservative indicators that free product is not present. These concentrations are approximately 10% and 0.02%, respectively, of the typical effective solubility of benzene and MTBE in unweathered gasoline. The plume boundary must be greater than 1,000 feet distance to a receptor. This represents an additional 400% plume length safety factor in the event that some additional unanticipated plume migration is to occur. Also note that Health & Saf. Code §25292.5 requires that UST owners and operators implement enhanced leak detection for all USTs within 1,000 feet of a drinking water well. In establishing the 1,000 feet separation requirement the legislature acknowledged that 1,000 feet was a sufficient distance to establish a protective setback between operating petroleum USTs and drinking water wells in the event of an unauthorized release.

Class 3: The moderate, stabilized plume length (plume boundary is <250 feet from point of release) approximates the average benzene plume length from the cited studies. The on-site free product and/or high dissolved concentrations in the plume remaining after secondary source removal to the maximum extent practicable as per the General Criteria in the Policy require that the plume has been stable or decreasing for a minimum of five years of monitoring to validate plume stability/natural attenuation (i.e., to confirm that the rate of natural attenuation exceeds the rate of LNAPL dissolution and dissolved-phase migration). The plume boundary must be greater than 1,000 feet distance to a receptor. This represents an additional 400% plume length safety factor in the event that some additional unanticipated plume migration is to occur, and is consistent with Health & Saf. Code §25292.5 as discussed above.

Class 4: The long, stabilized plume length (plume boundary is <1,000 feet from point of release) approximates the maximum MTBE plume length (Shih et al., 2004). The plume boundary must be at least 1,000 feet distance to a receptor. This is an additional 100% plume length safety factor in the event that some additional unanticipated plume migration is to occur, and is consistent with Health & Saf. Code §25292.5 as discussed above.

Class 5: Other low-threat site-specific scenarios not captured in Class 1 through 4. Should a site not fall in one of the four classes discussed above, an analysis of site specific conditions will be used to determine if the contaminant plume poses a low-threat to human health and safety and to the environment and if the water quality objectives will be achieved within a reasonable time frame.

5 DISCUSSION

This Technical Justification for Groundwater Media-Specific Criteria document should be used in conjunction with the Policy, the Direct Contact and Outdoor Air Exposure Pathways Criteria, and Vapor

Intrusion Criteria documents to determine if a site is low-threat to human health, safety and the environment.

6 REFERENCES

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Technical Justification for Groundwater Plume Lengths, Indicator Constituents, Concentrations, and Buffer Distances (Separation Distances) to Receptors

The purpose of this document is to provide technical justification for the four classes of low-threat groundwater plumes that are described in the Groundwater section of the Low-Threat UST Closure Policy (the Policy). The fifth plume class is a site-specific evaluation.

The Policy Stakeholder Group chose benzene, MTBE, and TPHg as adequate indicator constituents for the groundwater *plume lengths* discussed in the Policy. The technical justification for using these three constituents, discussed in more detail below, relies heavily on the facts that (1) benzene has the highest toxicity of the soluble petroleum constituents, (2) MTBE typically has the longest plume lengths, and (3) TPHg represents the additional dissolved hydrocarbons that may be present resulting from a typical petroleum release. Although TPHd is not used to describe plume lengths (largely because the hydrocarbons in the TPHd carbon range are of low solubility), other technical considerations associated with the use of TPHd data are discussed below.

Benzene and MTBE are used in research studies as key indicator constituents for the threat (human health risk and nuisance) posed by groundwater plumes from petroleum releases because (1) benzene has the highest toxicity of the soluble petroleum constituents, and (2) MTBE typically has the longest plume lengths and has a low secondary MCL (taste and odor threshold of 5 micrograms/liter [ug/l]).

Several significant multi-site studies of groundwater plume lengths from petroleum release sites have been conducted across the U.S. since the mid-1990s. These studies included sites where remediation had been performed and sites where no active remediation had been performed. Most of these studies focused on benzene plumes (e.g., Rice, et al. 1995; Rice et al. 1997; Buscheck et al. 1996; Mace, et al. 1997; Groundwater Services, Inc. 1997; API 1998); three studied benzene and oxygenate plumes (including MTBE) (Dahlen et al. 2004; Shih et al. 2004; Kamath et al. in press). Most of these plume studies are further discussed in detail in the Fate and Transport chapter of the California LUFT Manual.

In summary for all of these multi-site studies, the average benzene plume length was less than 200 feet and 90% of the benzene plumes were less than 400 feet long. The peer-reviewed study by Shih et al. (2004) of plume lengths at 500 UST sites in the Los Angeles area is widely relied upon as representative of current knowledge of plume lengths at UST sites in California. Results for benzene, MTBE and TPHg from Shih et al. (2004) are as follows:

Constituent (and plume limit concentration)	Average Plume Length (feet)	90 th Percentile Plume Length (feet)	Maximum Plume Length (feet)
Benzene (5 ug/l)	198	350	554
MTBE (5 ug/l)	317	545	1,046
TPHg (100 ug/l)	248	413	855

Data are from Shih et al. (2004). Plume lengths were measured from the source area.

Although the California MCL for benzene is 1 ug/l, Shih et al. (2004) used a plume limit concentration of 5 ug/l because of statistical uncertainty with concentrations too close to the laboratory reporting limit. The benzene plume lengths at a 1 ug/l concentration limit would be expected to be slightly longer than those shown here.

Ruiz-Aguilar et al. (2003) studied UST sites in the Midwest with releases of ethanol-amended gasoline (10% ethanol by volume) and found that benzene plume lengths may increase by 40% to 70% due to the addition of ethanol in gasoline (replacing MTBE). Ethanol is preferentially biodegraded over the benzene, which results in a longer benzene plume. However, the Policy addresses this potential for expansion of the plume lengths by adding safety factors of 100% to 400%.

It is well documented that, due to effective solubility, the hydrocarbons that will dissolve at measurable amounts into groundwater from a petroleum fuel release (including gasoline, kerosene, jet fuel, diesel or heavier fuels) are limited to primarily the very small aliphatics (less than C7) and the C14 or smaller aromatics (e.g., Shiu et al. 1990; Coleman et al. 1984). The C15 and larger hydrocarbons have very low effective solubilities and are not found in the dissolved phase of a petroleum fuel release. The carbon range of the potential dissolved hydrocarbons (less than or equal to C14) is largely covered by the TPHg carbon range (approximately C5 to C12). Therefore, TPHg should be sufficient to represent the dissolved hydrocarbons that may be present in addition to benzene and MTBE from virtually any type of product release. TPHd was not included as an indicator constituent for groundwater plume length because the vast majority of the TPHd carbon range (approximately C12 to C22) is higher than the carbon range for the possible dissolved hydrocarbons (less than or equal to C14). Oxygenates other than MTBE were not included as indicator constituents because Shih et al. (2004) documented that MTBE had the longest plume length of any of the oxygenates (MTBE, TBA, DIPE, TAME, ETBE) at any percentile, and Kamath et al. (in press) found that TBA plumes were comparable in length to MTBE plumes. Therefore, MTBE can be used as a conservative indicator for the other oxygenates including TBA.

For groundwater samples analyzed for TPHd for comparison to Water Quality Objectives (WQOs), a silica gel cleanup (SGC) should be included for the following reasons. It is well known that the TPHd analysis (Method 8015B) is not specific to hydrocarbons unless a SGC is used; otherwise the reported TPHd concentration can include polar non-hydrocarbon compounds in addition to the hydrocarbons that may be present in a water sample (e.g., Zemo and Foote

2003). These polar compounds can be from various sources, including metabolites from biodegradation of petroleum (primarily alcohols and organic acids, with possible phenols, aldehydes and ketones). At sites with biodegrading petroleum, the majority of the organics being measured as “TPHd” (without SGC) can be polar compounds and not dissolved hydrocarbons. WQOs for diesel-range petroleum hydrocarbons for health risk or taste and odor concerns are based on the properties of the dissolved hydrocarbons assumed to be present and not on the properties of the polar compounds. For example, the health-based ESL for TPHd is based on the assumption that 100% of the TPH has a toxicity equivalent to the C11 to C22 aromatics, and the taste and odor value for TPHd is based on the dissolved phase of fresh diesel/kerosene (which would be primarily the C14 and smaller aromatics) (SFRWQCB 2008). The San Francisco Bay RWQCB recognized that reported TPHd concentrations may include polar compounds and issued a guidance memorandum recommending that SGC be routinely used so that “..... decisions could be made based on analytical data that represents dissolved petroleum.” (SFRWQCB 1999). Only the hydrocarbon component of the TPHd concentration should be compared to the TPHd WQOs, and thus SGC is necessary to separate the hydrocarbons from the polar compounds in a groundwater sample prior to analysis. It is well established that a SGC does not remove the dissolved hydrocarbons in a sample (e.g., Lundegard and Sweeney 2004). Further, the potential for removal of hydrocarbons by a SGC is always monitored as part of the routine laboratory quality assurance reporting where lab control samples are spiked with a hydrocarbon (surrogate), are subjected to a SGC, and recovery of the surrogate is measured and must be within acceptable ranges.

The four classes of stabilized plume lengths and buffer distances from the plume edge to the closest water supply well or surface water (receptors) that are defined as “low threat” in the Policy are initially based upon the plume lengths from the studies cited above, but also are based on additional safety factors that the Stakeholder Group considered applicable to be protective in a state-wide policy document. For example, based on the plume studies, *a total separation distance from the source area to the receptor of about 500 feet should be protective for 90% of plumes from UST sites, and a total separation distance from the source area to the receptor of about 1,000 feet should be protective for virtually all plumes from UST sites.* Conversely, the “low-threat classes” require a known maximum stabilized plume length (which reduces uncertainty as to how long the plume might become in the future), and include additional safety factors and concentration limits developed by the Stakeholder Group.

Stakeholder Group participants also recognize and acknowledge that this Policy is consistent with other State and local practices regarding impacts to groundwater caused by other anthropogenic releases. For example, State and local agencies establish required separation distances or “setbacks” between water supply wells and septic system leach fields (typically 100 feet), and sanitary sewers (typically 50 feet; [DWR 1981]).

The Stakeholder Group acknowledges that the biodegradation/natural attenuation of petroleum hydrocarbon and oxygenate plumes has been documented by many researchers since the 1990s.

All of this work shows that biodegradation/natural attenuation of petroleum hydrocarbons and MTBE occurs under both aerobic and anaerobic conditions, but the rate of degradation/attenuation depends on the individual constituent and the plume geochemical conditions. The maximum concentrations for benzene and MTBE specified in the low-threat classes below are expected to biodegrade/naturally attenuate to WQOs within approximately 10 to 30 years, based on commonly-accepted rate constants for typical plume conditions and calculations (e.g., Wilson 2003; USEPA 2002). A time period of multiple decades or longer to reach WQOs has been determined to be “reasonable” for plumes of limited extent in existing State Water Board closure orders for UST sites (e.g., Order WQ 98-04 [Matthew Walker]).

TBA is a byproduct of biodegradation of MTBE, and TBA concentrations can build up temporarily in the anaerobic portion of a plume. With respect to the natural attenuation of TBA, Kamath et al. (in press) recently studied benzene, MTBE and TBA plumes at 48 UST sites (30 sites in California) and found that (1) most (68%) of the TBA plumes were stable or decreasing in size, and (2) in the stabilized plumes, the median attenuation rate for TBA was similar to the rates for MTBE and benzene. These findings indicate that TBA should not pose a significant threat to groundwater resources, and are consistent with the finding from Williams (in press) that TBA and MTBE have been detected in only a very limited number of public drinking water supply wells in California between 1996 and 2010. The average annual detection frequencies at any concentration and at concentrations greater than the WQO (12 ug/l for TBA and 5 ug/l for MTBE), through 2010 are: 1.4% and 0.2% for TBA, respectively, and 1.6% and 0.8% for MTBE, respectively (Williams, in press).

The following paragraphs present and discuss the key rationales for low-threat plume lengths, maximum concentrations, and separation distances for each low-threat class. Note that the specified concentrations are maximums, and would likely occur in only a few wells; the average concentrations in the plume would be lower. Note also that these groundwater plume class criteria (concentrations, plume lengths and separation distances) are only one component of the overall evaluation of site conditions that must be satisfied to be considered for closure as a low-threat site under the Policy.

Class 1: The “short” stabilized plume length (<100 feet) is indicative of a small or depleted source and/or very high natural attenuation rate. The 250 feet distance to a receptor from the edge of the plume represents an additional 250% “plume length” safety factor in the event that some additional unanticipated plume migration was to occur.

Class 2: The “moderate” stabilized plume length (<250 feet) approximates the average benzene plume length from the cited studies. The maximum concentrations of benzene (3,000 ug/l) and MTBE (1,000 ug/l) are conservative indicators that a free product source is not present. These concentrations are approximately 10% and 0.02%, respectively, of the typical effective solubility of benzene and MTBE in unweathered gasoline. These concentrations are expected to biodegrade/naturally attenuate to WQOs within a reasonable time frame. The potential for vapor

intrusion from impacted groundwater must be evaluated separately as per the vapor intrusion section of the Policy. The 1,000 feet distance to the receptor from the edge of the plume is an additional 400% “plume length” safety factor in the event that some additional unanticipated plume migration was to occur. Also note that California Health and Safety Code §25292.5 requires that UST owners and operators implement enhanced leak detection for all USTs within 1,000 feet of a drinking water well. In establishing the 1,000 feet separation requirement the legislature acknowledged that 1,000 feet was a sufficient distance to establish a protective setback between operating petroleum USTs and drinking water wells in the event of an unauthorized release.

Class 3: The “moderate” stabilized plume length (<250 feet) approximates the average benzene plume length from the cited studies. The on-site free product and/or high dissolved concentrations in the plume remaining after source removal to the extent practicable (as per the General Criteria in the Policy) require five years of monitoring to validate plume stability/natural attenuation (i.e., to confirm that the rate of natural attenuation exceeds the rate of NAPL dissolution and dissolved-phase migration). The potential for vapor intrusion from free product or impacted groundwater must be evaluated separately as per the vapor intrusion section of the Policy. The 1,000 feet distance to the receptor from the edge of the plume is an additional 400% “plume length” safety factor in the event that some additional unanticipated plume migration was to occur, and is consistent with H&S Code §25292.5 as discussed above.

Class 4: The “long” stabilized plume length (<1,000 feet) approximates the maximum MTBE plume length from Shih et al. (2004). The maximum benzene and MTBE source area concentrations (1,000 ug/l each) in the stable plume are expected to biodegrade/naturally attenuate to WQOs within a reasonable time frame. The maximum benzene concentration would not pose a vapor intrusion risk over the extent of the plume (assuming that five feet of bioreactive vadose zone is available over the extent of the plume; see justification for vapor intrusion screening criteria for details). The 1,000 feet distance to the receptor from the edge of the plume is an additional 100% “plume length” safety factor in the event that some additional unanticipated plume migration was to occur, and is consistent with H&S Code §25292.5 as discussed above.

Notes on Free Product Removal

State regulation (CCR Title 23, Division 3, Chapter 16, Section 2655) requires that “responsible parties“... remove free product to the maximum extent practicable, as determined by the local agency...” (Section 2655a) “... in a manner that minimizes the spread of contamination into previously uncontaminated zones”... (Section 2655b), and that “[a]batement of free product migration shall be the predominant objective in the design of the free product removal system” (Section 2655c). Over the years there has been debate on the meaning of the terms “free product” and “maximum extent practicable”. Product (light non-aqueous phase liquid [LNAPL]) can exist in three conditions in the subsurface: residual or immobile LNAPL (LNAPL that is

trapped in the soil pore spaces by capillary forces and is not mobile), mobile LNAPL (enough LNAPL is present in the soil pore spaces to overcome capillary forces so that the LNAPL can move) and migrating LNAPL (mobile LNAPL that is migrating because of a driving head). “Residual LNAPL”, “mobile LNAPL” and “migrating LNAPL” are described in detail in several peer-reviewed technical documents, including the 2009 Interstate Technology Regulatory Council (ITRC) Technical/Regulatory Guidance “Evaluating LNAPL Remedial Technologies for Achieving Project Goals”. Given the predominant objective of abatement of migration, the term “free product” in the State regulation is primarily equivalent to “migrating LNAPL” (which is a subset of “mobile LNAPL”), and secondarily equivalent to “mobile LNAPL”. Whether LNAPL is mobile (and therefore could potentially migrate) or not is usually tested by observing recharge of LNAPL after removing LNAPL from a monitoring well. Whether LNAPL is migrating or not is tested by monitoring the extent of the LNAPL body (usually using the apparent product thickness in monitoring wells) at a certain water level elevation over time. If the extent at that water level elevation does not expand, then the LNAPL is not migrating. Therefore, LNAPL must be removed to the point that its migration is stopped, and the LNAPL extent is stable. Further removal of non-migrating but mobile LNAPL is required to the extent practicable at the discretion of the local agency. Removal of mobile LNAPL from the subsurface is technically complicated, and the definition of “extent practicable” is based on site-specific factors and includes a combination of objectives for the LNAPL removal (such as whether the mobile LNAPL is a significant “source” of dissolved constituents to groundwater or volatile constituents to soil vapor, or whether there is a high likelihood that hydrogeologic conditions would change significantly in the future which may allow the mobile LNAPL to migrate) and technical limitations. The typical objectives for LNAPL removal, technologies for LNAPL removal and technical limitations of LNAPL removal are discussed in several peer-reviewed technical documents including the 2009 ITRC Guidance (see especially Section 4 “Considerations/Factors Affecting LNAPL Remedial Objectives and Remedial Technology Selection”, Table 4.1 [Example Performance Metrics], Table 5-1 [Overview of LNAPL Remedial Technologies], and Table 6-1 [Preliminary Screening Matrix]).

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Technical Justification for Vapor Intrusion Media-Specific Criteria

(Final 03-21-2012)

1 EXECUTIVE SUMMARY

For petroleum-related volatile organic compounds (VOCs), current risk-based screening levels (such as the California Human Health Screening Levels [CHHSLs]) for evaluating risk from vapor intrusion at underground storage tank (UST) sites are conservative. This conservatism is caused by not considering biodegradation in site screening which generally drives further unnecessary site evaluation. Recent models and field studies show that bioattenuation of petroleum hydrocarbons at UST sites is significant (Abreu et al., 2009; API, 2009; Davis, 2009; Lahvis, 2011). Petroleum hydrocarbon VOCs (such as, benzene, toluene, ethylbenzene and xylenes -BTEX) concentrations have been shown to attenuate by several orders of magnitude within short vertical distances (e.g., < 2-3 m) in the unsaturated zone due to biodegradation. The hydrocarbon VOC attenuation generally increases by an additional order of magnitude (or more) when transport across a building foundation to indoor air is also considered (U.S. EPA, 2008). The characteristic occurrence of rapid hydrocarbon attenuation in the unsaturated zone is amenable to a site-screening methodology for vapor intrusion based on exclusion distances. Exclusion distances are defined as VOC source-receptor (building) separation distances beyond which the risk of vapor intrusion is assumed negligible. Note the source may be located in soil and/or groundwater. Exclusion distances can be broadly defined for two types of sources: low-concentration (e.g., dissolved-phase) and high-concentration (e.g., light non-aqueous-phase liquid – LNAPL) sources which differ substantially in chemical vapor composition and are unique with respect to their vapor intrusion risk potential.

Recent modeling studies and evaluations of field (soil-gas) data from numerous UST sites and sampling locations demonstrate that biodegradation is sufficient to limit the potential for vapor intrusion at sites with “low-concentration” (dissolved-phase) hydrocarbon sources (Abreu et al., 2009; Davis, 2009; Davis, 2010; Lahvis, 2012). For example, there is less than a 5% probability that benzene concentrations in soil gas would exceed a low screening-level for vapor intrusion ($30 \mu\text{g}/\text{m}^3$) at distances of 5 ft (~2 m) or more above a dissolved-phase benzene concentration in groundwater < 1,000 $\mu\text{g}/\text{L}$. (Note, for comparison, the CHHSL for benzene in soil gas is $83 \mu\text{g}/\text{m}^3$ for buildings on engineered fill.) Additional attenuation (i.e., a shorter exclusion distance) is predicted to occur by transport modeling for dissolved-phase sources displaced laterally from the building foundation (Abreu and Johnson, 2005). Vapor intrusion risks are thus expected to be rare to non-existent at sites with low-concentration sources.

At sites with “high concentration” hydrocarbon sources (un-weathered residual light non-aqueous phase liquid (LNAPL) in soil and/or un-weathered free-phase LNAPL on groundwater), transport modeling shows that hydrocarbon VOCs will attenuate below levels of concern in the unsaturated zone within a distance of approximately 20 ft (~7 m) of the source. The transport modeling is based on assuming reasonable approximations of source concentration and transport within the unsaturated zone

(including biodegradation rate). Soil-gas data collected at numerous UST, terminal, and manufacturing sites with LNAPL sources would suggest that the model predicted attenuation above LNAPL sources is conservative. Analysis of the field data at these types of sites shows that hydrocarbon VOCs are attenuated below screening-level concentrations within 8 – 13 ft (~3 - 4 m). Biodegradation accounts for more than 1,000x additional attenuation within 5 ft vertical distances of benzene sources in soil-gas up to 10,000,000 $\mu\text{g}/\text{m}^3$. Again, the attenuation is predicted to increase further for high (e.g., LNAPL) sources displaced laterally from building foundations (i.e. the soil gas concentrations would attenuate in even shorter distances).

The purpose of this document is to provide a technical justification for the proposed low-threat vapor intrusion scenarios. The justification is based on current, state-of-the-art science on separation distances between source and receptor that are human-health protective. A few of the most recent studies cited below are awaiting publication (but are available for review). All cited studies should be considered in the development of a rational, technically defensible approach to vapor intrusion screening.

The four scenarios presented in the *Low-Threat UST Closure Policy* are:

Scenario 1: Un-weathered LNAPL on groundwater

30 ft vertical source/building separation (exclusion) distance for un-weathered (residual or free-phase) LNAPL on groundwater

Scenario 2: Un-weathered LNAPL in soil

30 ft lateral and vertical separation (exclusion) distance between a building foundation and an un-weathered LNAPL (residual or free-phase) source in soil.

Scenario 3: Dissolved phase benzene concentrations in groundwater

- 5 ft. vertical separation distance between a dissolved-phase source < 100 $\mu\text{g}/\text{L}$ benzene and a building foundation (no oxygen (O_2) measurement)
- 10 ft. vertical exclusion distance for a dissolved-phase source < 1,000 $\mu\text{g}/\text{L}$ benzene (no O_2 measurement)
- 5 ft. vertical separation distance between a dissolved-phase source < 1,000 $\mu\text{g}/\text{L}$ and a building foundation (measured O_2 in soil gas $\geq 4\%$)

Scenario 4: Direct measurement of soil gas concentrations

Application of an additional attenuation factor of 1000x to risk-based soil-gas criteria (i.e. vapor sources) located 5 ft. from a building foundation

For each of these scenarios, screening criteria have been proposed that if met will identify the site as posing a low human health threat resulting from the vapor intrusion pathway. The screening criteria and low-risk scenarios are based on the science presented in this document; additional safety factors were incorporated as a policy decision. For the two un-weathered LNAPL scenarios (Scenarios 1 and 2), the current science indicates that soil vapors above an LNAPL source will attenuate within a distance of 20 feet or less. However the two LNAPL scenarios include an additional safety factor of 10 feet so that the exclusion criteria for these cases are set to 30 feet. This buffer distance should take into account any uncertainties with respect to water-table fluctuation. Likewise, in Scenario 3, the scientific studies

and field data indicate that the risk of vapor intrusion is negligible for building foundations located more than 5 feet above plumes with much higher benzene concentrations (up to 15,000 µg/L in groundwater). Again, the proposed screening criteria incorporate additional safety factors which account for uncertainties in the water-table elevation. Management strategies to monitor and prevent groundwater from coming in contact with building foundations should, however, be considered in cases where the vertical separation distance between the building foundation and the dissolved-phase hydrocarbon source is < 5 ft. In Scenario 4, research indicates that soil gas concentrations will attenuate by more than 3 orders of magnitude within a vertical distance of 5 feet. However, the “bioattenuation factor” applied in Scenario 4 is conservatively defined at 3 orders of magnitude (1000-fold attenuation). The proposed bioattenuation factor (in Scenarios 3 and 4) also requires that measured O₂ concentrations in soil gas are greater than or equal to 4%. The practitioner should refer to local regulatory guidance for information on how to collect these measurements. Biodegradation has been shown to be significant at concentrations between 1 and 4 % (DeVaul, 2007). In conclusion, each of the scenarios, by design, had safety factors included and therefore the exclusion criteria will appear to be more conservative than would be otherwise indicated if only basing the results on the modeling results and field data presented in this document.

2 INTRODUCTION

It is well recognized that petroleum hydrocarbons rapidly biodegrade in the presence of O₂ (i.e., when conditions in the unsaturated zone are aerobic). The degree of biodegradation depends mainly on O₂ availability of and the O₂ demand created by the biodegradation reaction. The latter is largely a function of hydrocarbon source type (e.g., LNAPL or dissolved phase). Biodegradation can also be affected at soil moisture content, however, especially if less than the wilting point (i.e., a level sufficient to support plant growth) (Guyman 1997). Unsaturated-zone soils are seldom drier than the wilting point; however, with the exception of near surface soil layers under arid conditions (DeVaul, 1997).

Various researchers (Fischer et al., 1996; Lahvis et al., 1999; DeVaul, 2007; Davis, 2009; and Hartman, (2010) have shown that conditions in the unsaturated zone are aerobic, and that for “low-concentration” sources (weathered residual in soil and/or dissolved concentrations in groundwater), the degree of biodegradation is significant. At these sites, the demand for O₂ resulting from biodegradation generally exceeds O₂ availability. The hydrocarbon concentrations (mainly BTEX) decrease by several orders of magnitude over relatively short (e.g. <2 m) vertical distances. For low concentration hydrocarbon sources, the attenuation will tend to be significant very near the water table (i.e., capillary zone). These assertions are supported both by theory (modeling) (DeVaul, 2007, Abreu et. al. 2009, API, 2009) and by field observation (Lahvis and Baehr, 1996; API, 2009; Davis, 2009). Work by Abreu and Johnson (2005) predicts a greater degree of vapor attenuation at sites where the source is displaced laterally from the building foundation.

Researchers have also documented rapid biodegradation of petroleum vapors at sites underlain by LNAPL sources. At such UST sites, exclusion distances determined by analyzing benzene concentrations in soil gas have been estimated to be in the range of 8 to 15 feet (Davis, 2009; Hartman, 2010; Lahvis, 2011). The greater exclusion distance for LNAPL sources compared to dissolved-phase sources is largely related to the additional demand for O₂ (noted above) created by LNAPL sources and the tendency for

LNAPL sources to be distributed above the capillary zone. Lahvis and Baehr (1996) showed the capillary zone to be an active zone of biodegradation and hydrocarbon attenuation). The presence of residual-phase LNAPL can, however, be difficult to identify because LNAPL may not readily appear in groundwater monitoring wells. In such cases, one may rely on general LNAPL indicator “rules of thumb”, including:

Presence of LNAPL

Direct evidence:

- current or historical evidence of LNAPL in soil (known release area) or at the water table (visible/reported in nearby groundwater monitoring wells)

Indirect evidence:

- hydrocarbon VOC concentrations in groundwater approaching (> 0.2) effective solubilities (Bruce et al., 1991) (e.g., benzene > 3 mg/L; BTEX or TPH gasoline range organics (GRO) > 20 mg/L; TPH diesel range organics (DRO) > 5 mg/L)
- total hydrocarbon VOC concentrations in soil of TPH GRO > 100 - 200 mg/kg⁽¹⁾; TPH DRO > 10 - 50 mg/kg) (see ASTM, 2006, Alaska DEC, 2011)²
- TPH vapor readings from a photo-ionization detector (PID) of > 1,000 ppm (recent gasoline releases), > 100 ppm (recent diesel/historic gasoline releases), and > 10 ppm (historic diesel releases) (Alaska DEC, 2011). Note that weathered LNAPL typically has a significantly reduced VOC content and therefore represents a lesser vapor intrusion risk than un-weathered NAPL.
- proximity (e.g., < 20 ft to a known release area)

It is important to note that although hydrocarbon VOC concentrations approaching effective solubility limits in groundwater can be used as an indirect indicator of residual-phase LNAPL, dissolved-phase hydrocarbon concentrations are not necessarily good metrics for the development of screening criteria (i.e., separation distances) or assessing the vapor intrusion risk potential. Benzene concentrations in soil-gas have shown to be poorly correlated with benzene concentrations in shallow groundwater (Lahvis, 2012). The poor correlation can be attributed to 1) the inability to accurately measure the dissolved-phase source (water-table) concentration (i.e., the actual hydrocarbon vapor source) using conventional ground-water monitoring wells screened across the water table, and 2) hydrocarbon biodegradation between the water table (dissolved-phase source) and the lowermost soil-gas sampling location. Soil-gas and ground-water concentrations are also expected to be poorly correlated in the presence of residual-phase LNAPL sources (Zemo, 2006). Screening (exclusion) distances should therefore be defined on the basis of source type (LNAPL and groundwater) rather than source

¹ TPH (GRO) between 100 to 200 mg/kg may indicate the presence of LNAPL. TPH (GRO) less than 100 mg/kg is a good indication that there is no LNAPL present. The practitioner should refer to local regulatory guidance for TPH sampling and analysis.

² The primary driver for vapor intrusion is benzene. For petroleum-based fuels other than gasoline, benzene is not found at levels that would cause a vapor intrusion problem.

(groundwater) concentration. LNAPL and dissolved-phase hydrocarbon sources are unique with respect to their vapor intrusion risk potential for the following reasons:

- 1) Differences in hydrocarbon vapor diffusion and O₂ demand: hydrocarbon vapor diffusion (mass flux) in the unsaturated zone will be higher for LNAPL sources than dissolved-phase sources because LNAPL contains a higher source mass and is invariably distributed (by water-table fluctuations) above the capillary zone in lower moisture-saturated soil less resistant to vapor transport. The vapor mass flux for LNAPL source zones will also tend to be sustained for longer-periods of time given the larger contaminant mass compared to dissolved sources. The higher rates of vapor diffusion from LNAPL sources will be coupled with greater metabolic demand for O₂ associated with aerobic biodegradation.
- 2) Differences in vapor composition: vapors emanating from dissolved-phase sources are primarily BTEX and other aromatic hydrocarbons and fractionally water-soluble petroleum VOCs. Vapors emanating directly from LNAPL sources contain these constituents and a sizeable fraction of aliphatic and relatively insoluble VOCs, especially if the source is large or un-weathered.

The exclusion distances proposed in policy focus primarily on benzene, which is the primary risk driver for petroleum UST sites. Ethylbenzene and total petroleum hydrocarbon (TPH) data are included in this technical justification only for comparative purposes. Naphthalene is not considered. Rather, the exclusion criteria derived for benzene are assumed to be conservative for naphthalene, which is relatively less volatile than benzene (i.e., has a much lower solubility value and Henry's Law coefficient than benzene) and similarly susceptible to biodegradation (Anderson et al., 2008). Methyl tert-butyl ether (MTBE), which may be considered another potential VOC of concern for vapor intrusion in some regulatory jurisdictions, is also not considered. The exclusion of MTBE can be justified on the basis that no reports of MTBE as a constituent of concern for vapor intrusion are documented in the literature even though MTBE is routinely measured as part of soil-gas sampling (TO-15 air analyses). In addition, long-term (30-yr exposure duration) chronic inhalation risks from MTBE are not expected to occur a because of rapid attenuation of MTBE in source areas. In particular, McHugh et al. (2012) shows MTBE concentrations have decreased in ground water by an average of 85% from 2001 to 2011 in California post the phase out of MTBE as an oxygenate in gasoline in 2000 and its elimination on January 1, 2004.

3 TECHNICAL BACKGROUND – Discussion of Biodegradation Effects

This section presents the results of model studies and field data that support the proposed vapor intrusion exclusion criteria. The results are discussed first for “low-concentration” source cases followed by “high-concentration” sources cases.

3.1 *Low-Concentration Sources (weathered residual in soil and/or dissolved concentrations in groundwater)*

For purposes of this technical justification, low concentration sources at petroleum UST sites are defined as dissolved-phase hydrocarbon concentrations. Low concentration sources are therefore composed primarily of the more soluble (aromatic) VOC LNAPL constituents, benzene, toluene, ethylbenzene, xylenes, and naphthalene. Of these constituents, benzene is the primary risk driver for vapor intrusion

because of its relatively higher toxicity and vapor migration potential. Note: weathered LNAPL is analogous to low-concentration sources in cases where the LNAPL is depleted of VOCs.

3.1.1 Model Studies

Results from numerical (3-dimensional) models (see Figures 3, 4 and 10 below [Abreu et al., 2009]) indicate essentially complete attenuation of benzene soil gas concentrations (between 7 and 14 orders of magnitude – expressed as attenuation factors $\alpha < 1E-07$) within 2 m to 3 m away from a relatively low (< 10 mg/L or $10,000,000$ $\mu\text{g}/\text{m}^3$) benzene source concentration in an unsaturated sand.³ The simulations also assumed biodegradation occurred only in the aerobic portion of the unsaturated zone (i.e., where O_2 concentrations exceed 1%). An aerobic biodegradation rate of 0.79 hr^{-1} was assumed for benzene, which is consistent with the geometric mean of published rates defined by DeVaul (2007). Note that while this degradation rate may seem high, the model only simulates biodegradation in the portion of the unsaturated zone where there is sufficient O_2 ($> 1\%$) to support biodegradation. The modeled hydrocarbon vapor source concentration, < 10 mg/L, is assumed to be consistent with a dissolved-phase source (see Abreu et al. [2009] – Figure 10). Lastly, the attenuation is expected to increase for a similar range of source concentrations and degradation rates in lower permeability soils (e.g., silty clay) (see Figure 19 from API, 2009) and for sources displaced laterally from building foundations (see Figure 9 from Abreu and Johnson, 2005). The attenuation increases for the latter scenario because hydrocarbon transport tends to be vertically upwards (toward the soil surface) rather than laterally towards the receptor. Hence, there is little potential for vapor intrusion to occur at sites where the dissolved-phase source is separated laterally from a building foundation.

The following figures show the results of the modeling studies:

- The figures from Abreu et al. (2009) (Figures 3 and 4) show benzene and O_2 profiles predicted by transport modeling for low-concentration vapor sources and two different foundation configurations (basement and slab, respectively) in a sand unsaturated zone for a reasonable approximation of the hydrocarbon biodegradation rate ($\alpha = 0.79$ hr^{-1}).

³ A 10 mg/L hydrocarbon soil gas source would equate to a ~ 40 mg/L source of BTEX in groundwater assuming a vapor/aqueous phase partition coefficient of around 0.25 (Morrison, 1999).

Figure 3 from Abreu et al (2009).

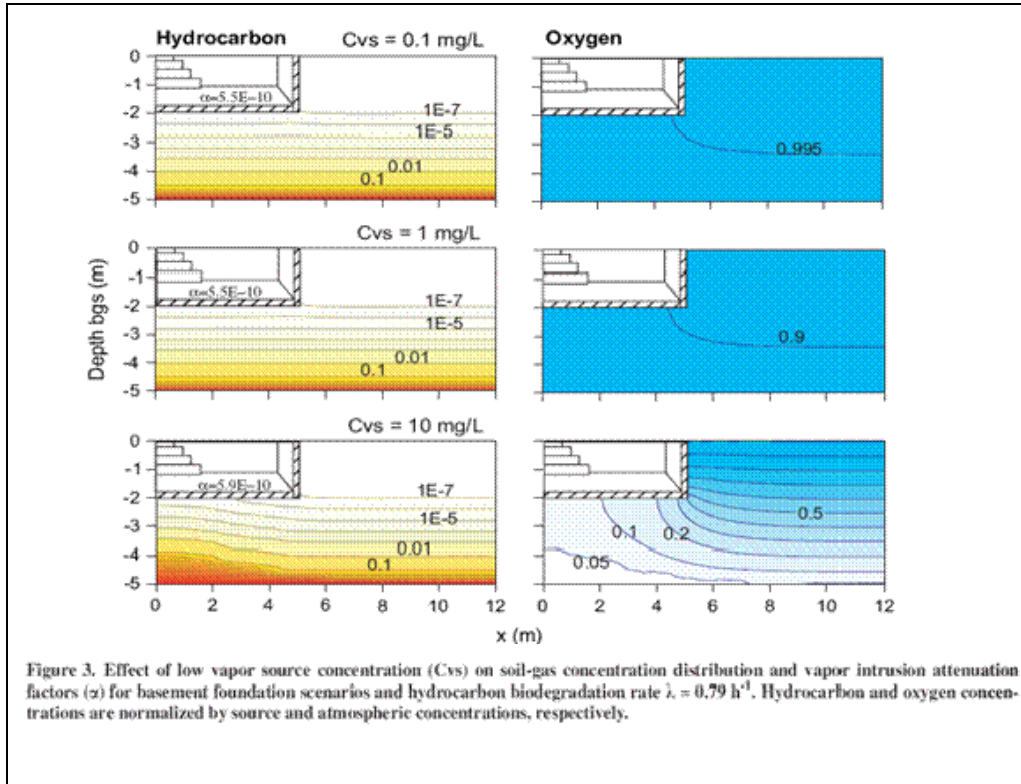
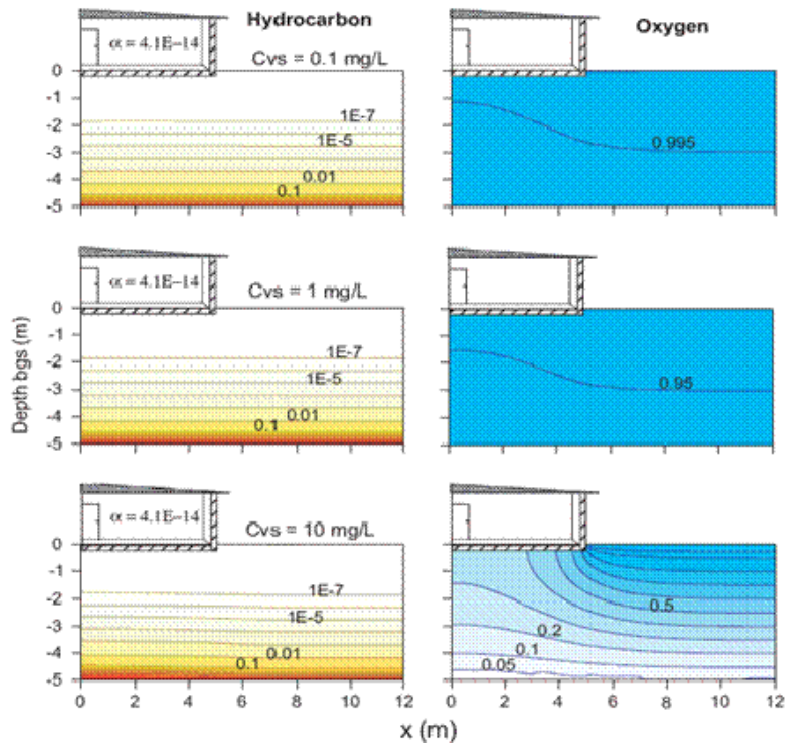


Figure 4 (Abreu et al., 2009)



- Figure 10 from Abreu et al. (2009) is a plot of the hydrocarbon (benzene) attenuation factor in the unsaturated zone versus source vapor concentration for a range of source/building foundation separation distances assuming a representative biodegradation rate ($\lambda = 0.79 \text{ hr}^{-1}$) and a sand unsaturated zone:

Figure 10 from Abreu et al. (2009)

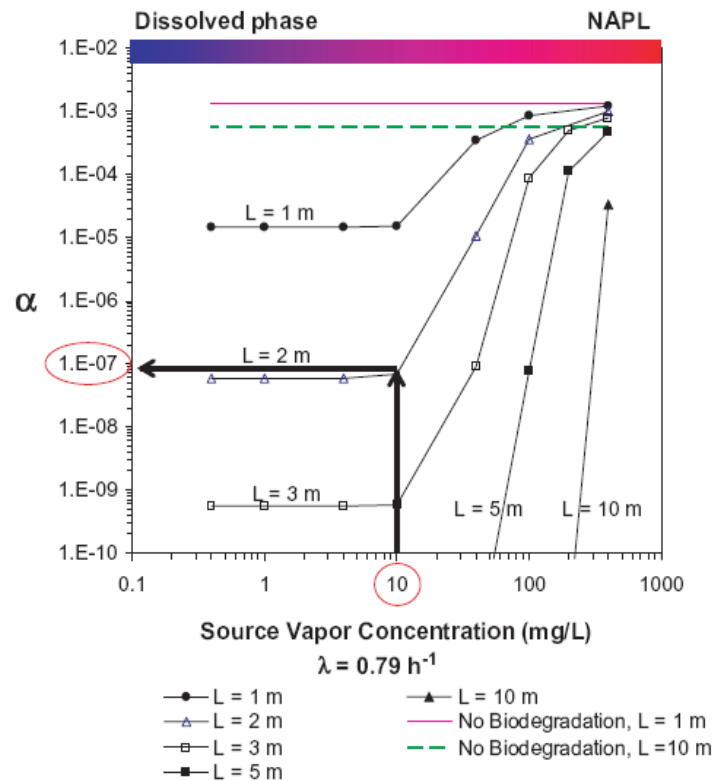


Figure 10. Use of the chart to select a semi-site-specific attenuation factor. For a source concentration of 10,000 $\mu\text{g/L}$ and a source-building separation of 2 m, the attenuation factor would be about $1\text{E-}7$.

- Figure 19 from API (2009) is a plot of the hydrocarbon (TPH-gasoline) attenuation factor in the unsaturated zone versus source vapor concentration for a range of source/building foundation separation distances assuming a representative biodegradation rate and two soil types, sand and silty clay:

Figure 19 from API (2009)

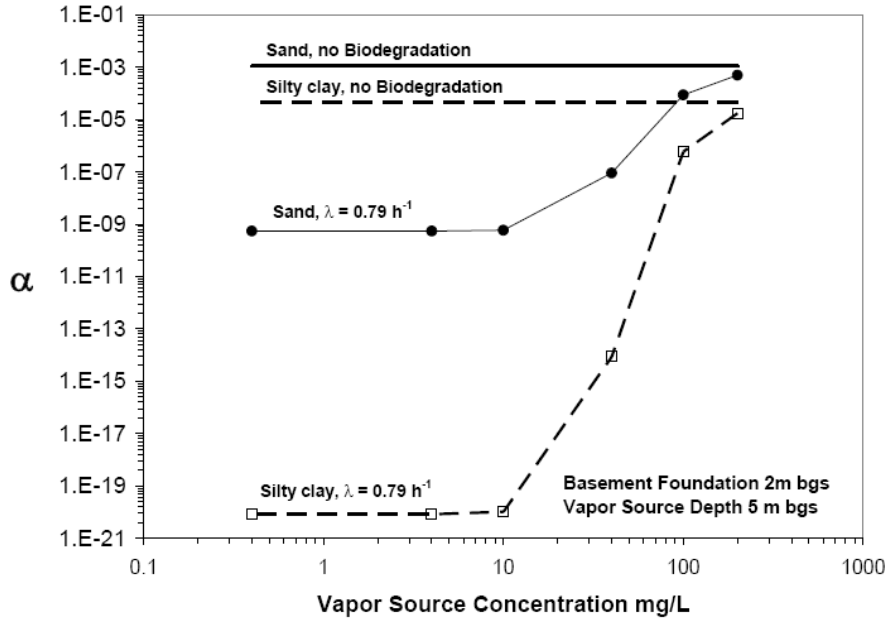


Figure 19—Attenuation factors as a function of soil type and vapor source concentration for a source located at 5 m bgs (3 m below a basement foundation). The graph present results for no biodegradation scenarios and biodegradation scenarios with a first-order biodegradation rate $\lambda = 0.79 \text{ h}^{-1}$. Q_s (sand) = 3.7 L/min and Q_s (silty clay) = 0.05 L/min.

- Figure 9 from Abreu and Johnson (2005) is a plot of the attenuation factor in the unsaturated zone versus source edge-building separation distance predicted in a sand unsaturated zone for a slab-on-grade building foundation. Biodegradation was not considered in the model analysis.

Figure 9 from Abreu and Johnson (2005)

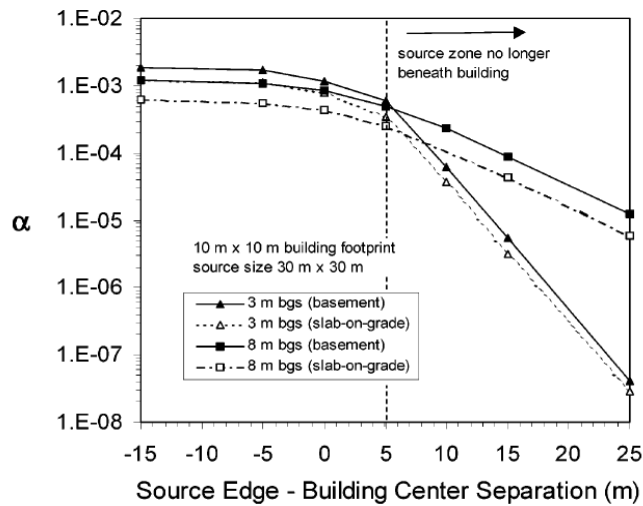
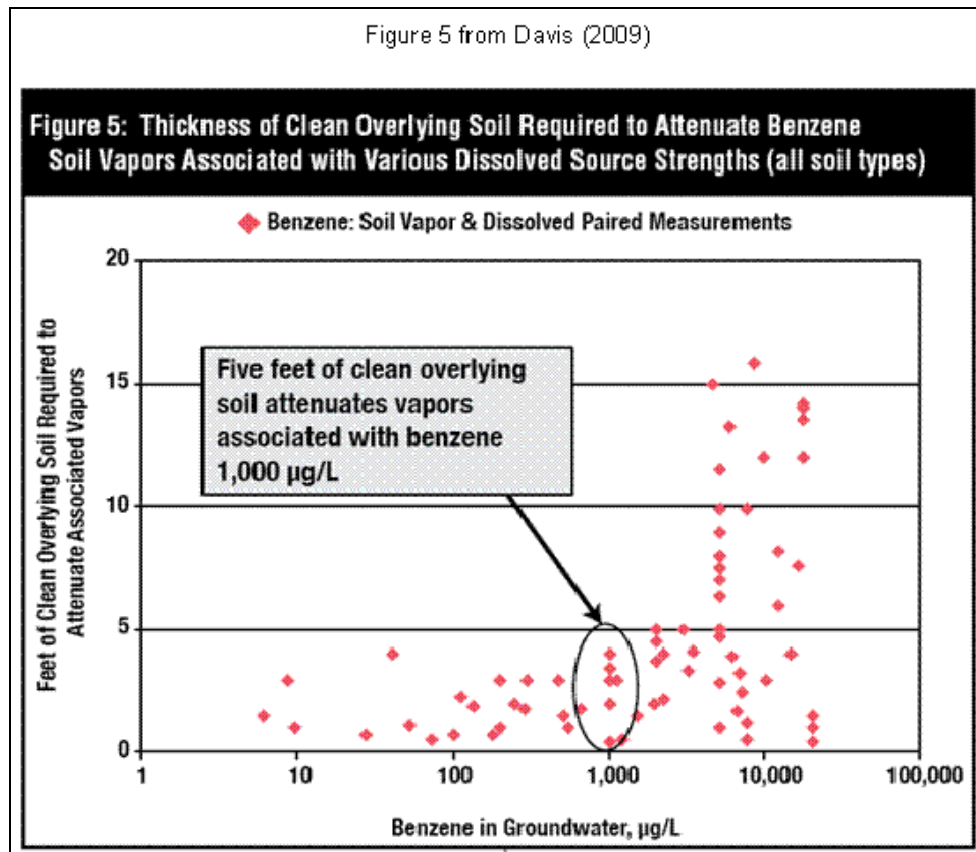


FIGURE 9. Changes in vapor attenuation coefficient (α) with vapor source—building separation and vapor source depth for basement and slab-on-grade foundation scenarios.

3.1.2 Field Data

Two hydrocarbon soil-gas databases were used to support the development of exclusion distance criteria. One was compiled by Davis (2009) and the other by Wright (2011). The cited databases are publically available upon request. Davis (2009) compiled the database from measurements at 58 UST, terminal, and manufacturing sites across several states, including California. The Wright (2011) database includes soil-gas data collected from 124 additional UST, terminal, and manufacturing sites in Australia. Both databases include soil-gas data collected from on and off-site locations. Approximately 16% of the soil-gas data are measurements taken directly below building foundations (i.e., sub-slab). The field data support the model results discussed in the previous section. An analysis by Davis (2009) indicates that benzene concentrations in soil gas are completely attenuated within 5 feet or less of groundwater containing up to 6 mg/L (or $\sim 1,500,000 \mu\text{g}/\text{m}^3$ vapor phase equivalent⁴) benzene (see Figure 5 below from Davis, 2009). The analysis includes data from “non-UST” locations.



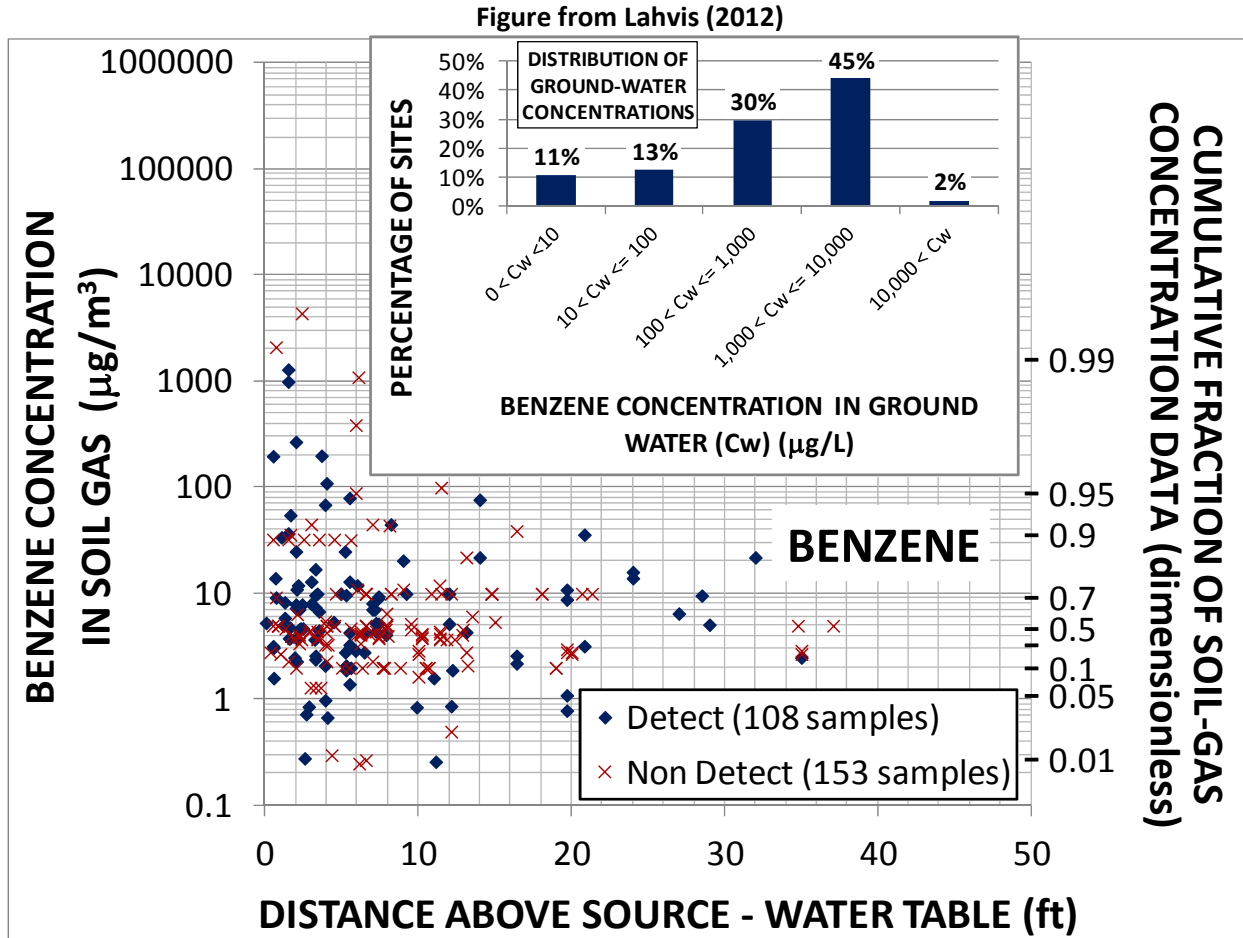
It is important to note in Figure 5, that the exclusion distance (and vapor intrusion risk potential) is relatively independent of the benzene source concentration over the approximate range of dissolved phase concentrations up to 6,000 $\mu\text{g}/\text{L}$. The development of more conservative groundwater

⁴ Assuming equilibrium partitioning between soil-gas and groundwater and a Henry's Law coefficient of $0.25 \text{ m}^3/\text{m}^3$ for benzene. The Henry's Law constant for benzene is only expected to only vary by a factor of 2 (0.09 - 0.18) for anticipated soil temperatures ranging from at 5°C to 20°C (Baehr et al., 1999).

concentration-based exclusion distances (e.g., specific exclusion distance criteria for 100 µg/L and 1,000 µg/L sources) was a policy decision.

Davis (2009) did not screen out sites with potential residual LNAPL sources above the water table (i.e. LNAPL in soil). Note that residual LNAPL in soil and free-phase LNAPL on groundwater will pose similar vapor-intrusion risks. The latter are sites where LNAPL is observed in groundwater monitoring wells located in the source area. However, Davis (2009) found that the thickness of “clean” soil required to fully attenuate vapors to health-protective concentrations (i.e., the exclusion distance) decreased from ~15 feet (Figure 5) to 8 feet when accounting for residual-phase LNAPL sources above the water table (Davis 2010 – see Figure from Davis in Section 3.2.2).

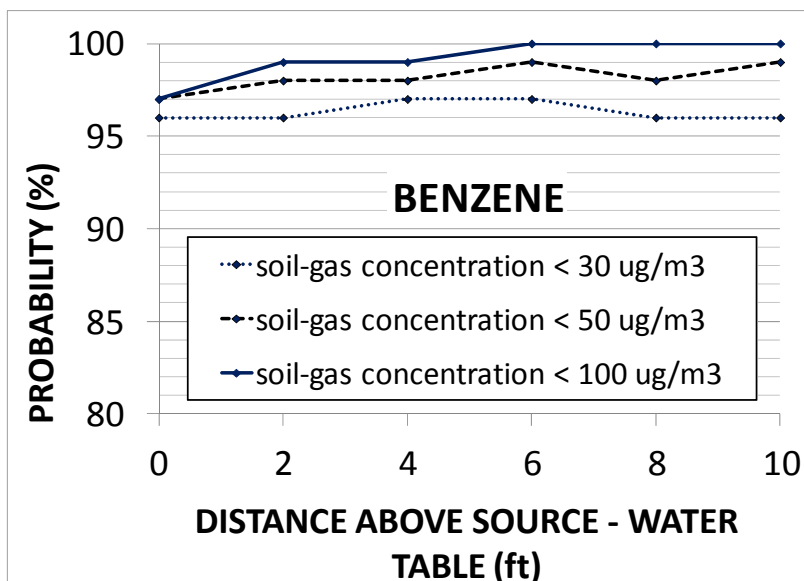
Lahvis (2012) analyzed soil-gas data collected above dissolved-phase sources where efforts were taken to identify and screen out sites with LNAPL above the water table (i.e LNAPL in soil). The analysis filtered out sites with either direct evidence of LNAPL (current, historical) or indirect evidence of LNAPL (soil-gas measurements collected near potential sources (i.e., locations within 20 ft of USTs and dispensers). The analysis did, however, include soil-gas data from sites with dissolved-phase (source) concentrations up to 15 mg/L benzene. Lahvis (2012) included these additional data to assess an “upper bound” on exclusion distances for dissolved-phase sources, realizing that dissolved-phase concentrations greater than 3 mg/L benzene and 20 mg/L BTEX may potentially indicate the presence of a residual-phase LNAPL source (Bruce et al. , 1991). In other words, Lahvis (2012) included soil-gas data from sites with potential LNAPL sources to be conservative in estimating the exclusion distances for dissolved-phase sources. The Lahvis (2012) study included soil-gas data from both Davis (2009) and Wright (2011). Lahvis (2012) shows that benzene in soil vapor is attenuated below a relatively conservative soil-gas screening level of 30 µg/m³ for dissolved benzene sources located 5 vertical feet or greater from the receptor. Note that more than half of the soil-gas measurements were taken from sites with source concentrations of benzene dissolved in groundwater ranging from 1 to 15 mg/L.



The results shown in the figure from Lahvis (2012) were then used to define exclusion distance criteria based on the probability⁵ of the measured soil gas concentration being less than specified (vapor intrusion) screening level concentrations for benzene in soil gas of 30, 50 and 100 $\mu\text{g}/\text{m}^3$. These values are consistent with current U.S. state regulatory soil-gas screening limits for benzene which range from approximately 3 to 300 $\mu\text{g}/\text{m}^3$ (see EnviroGroup Limited - <http://www.envirogroup.com/links.php>). The data were then sorted in a cumulative distribution of specified vertical separation distances from the source (e.g., ≥ 0 , ≥ 2 , ... ≥ 10 ft). The results are shown in the following figure:

⁵ Probability estimated from the concentration distribution calculated by non-parametric Kaplan-Meier method (Kaplan and Meier, 1958)

Figure from Lahvis (2012)



The results indicate that the probability of observing benzene vapor concentrations in excess of a conservative screening level (e.g., $30 \mu\text{g}/\text{m}^3$) at distances greater than 5 ft above the dissolved phase source at UST sites is less than 5%. The water table would have to be essentially in contact with a building foundation for there to be a potential concern for vapor intrusion for this class of low concentration sites. Note there is limited sensitivity to the benzene soil-gas screening limit over the specified range ($30 - 100 \mu\text{g}/\text{m}^3$).

The data from which the vertical exclusion distances were derived encompass a broad range of environmental site conditions, geographic retail markets, and a 14-year time span of sample collection (from 1997 to 2011). The exclusion distances (0 ft for dissolved-phase sources and 13 ft for LNAPL) are thus deemed applicable for the vast majority of petroleum UST sites, including those with differing soil types, land-surface covers (including sub-slab and pavement), subsurface temperatures, and fuel types/compositions. Approximately 67% of the soil-gas samples in the Lahvis (2012) database were collected at UST sites in Utah and Australia where relatively low soil-moisture conditions are likely to have been present. The empirical study comprised data collected throughout the year at UST sites in Utah, Maine, Minnesota, Canada, Australia and California suspected of having highly variable subsurface soil temperatures. The soil conditions at these sites are thus assumed to represent soil conditions encountered at the vast majority of relatively arid UST sites in California.

Additional validation may, however, be warranted at certain unusual sites not statistically captured in the database or by the Lahvis (2012) analysis. These sites include those with high organic matter soils (e.g., peat), a really extensive building foundations at land surface (e.g., large commercial facilities or apartment complexes), and high (85%) ethanol content fuel (e.g., E85) releases.

3.1.3 Summary of Low Concentration Sources

In summary, model and field data from UST petroleum release sites shows minimal vapor-intrusion-to-indoor air risk above dissolved-phase only hydrocarbon sources. At low-concentration sites, benzene, the primary risk driver for vapor intrusion, will be attenuated below conservative soil-gas screening limits within 5 feet above the water table.

3.2 High-Concentration Sources (un-weathered residual in soil and/or free-phase LNAPL on groundwater)

3.2.1 Model Studies

As shown in the attached figures (Figures 5 and 7 from Abreu et al. [2009]), benzene is predicted to completely attenuate in the unsaturated zone above an LNAPL source within $\sim 7\text{ m}$ (20 ft) of the source⁶. Abreu et al (2009) used benzene to represent the greatest potential risk posed by soil vapor from an un-weathered LNAPL vapor source. This LNAPL source will primarily consist of aliphatic hydrocarbons. The model is assumed to be conservative when considering benzene biodegradation assumptions (see note 7 below).

Figure 5 (modified) from Abreu et al. (2009)

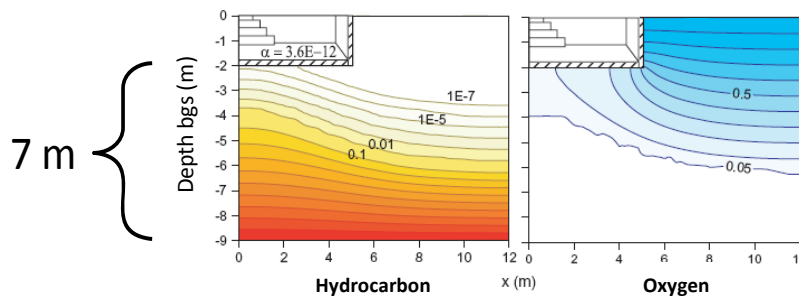


Figure 5. Effect of source depth on the soil-gas concentration distribution and vapor intrusion attenuation factors (α) for basement scenarios with a high vapor source concentration of $100,000\ \mu\text{g/L}$ and biodegradation rate $\lambda = 0.79\ \text{h}^{-1}$. Hydrocarbon and oxygen concentrations are normalized by source and atmospheric concentrations, respectively.

Figure 7 (modified) from Abreu et al. (2009)

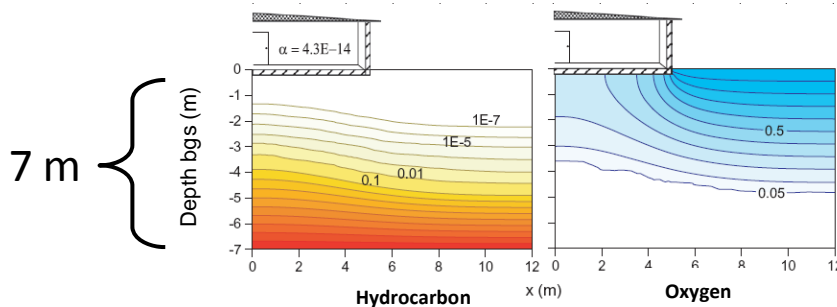


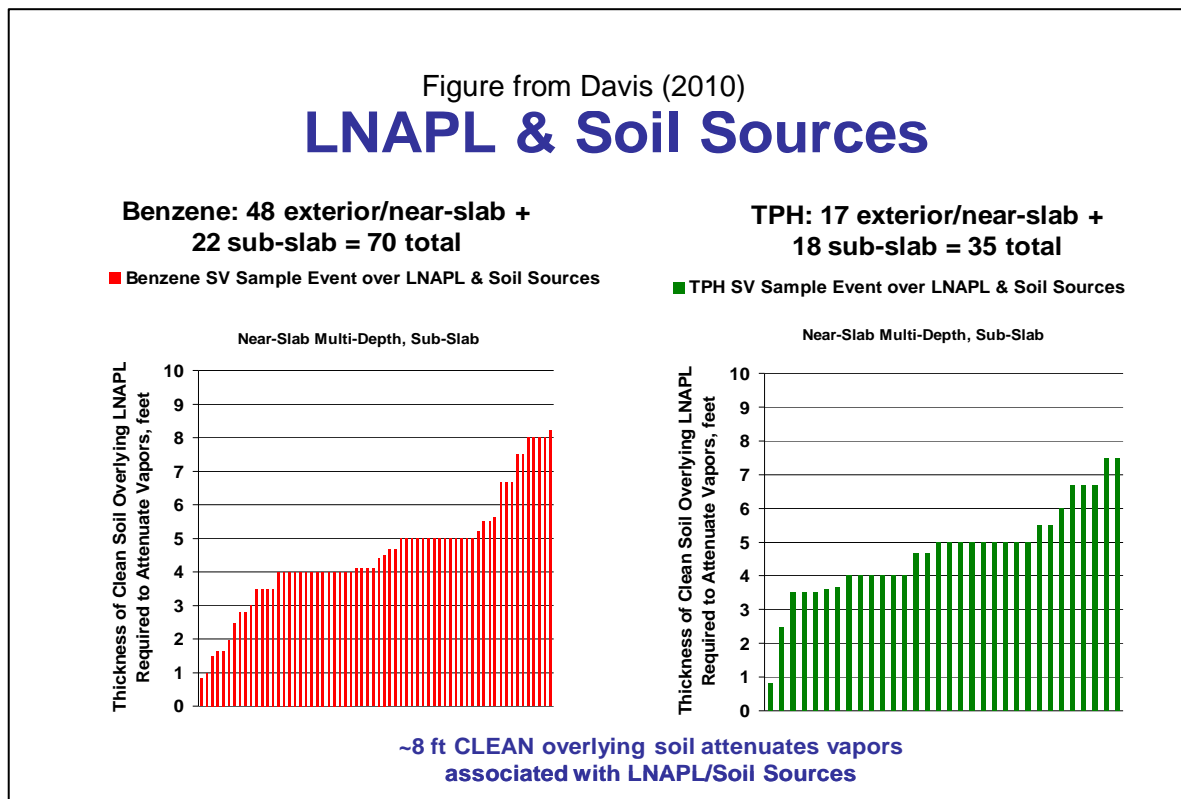
Figure 7. Effect of building type on soil-gas concentration distribution for high vapor source concentration ($100,000\ \mu\text{g/L}$) and biodegradation rate $\lambda = 0.79\ \text{h}^{-1}$. Hydrocarbon and oxygen concentrations are normalized by source and atmospheric concentrations, respectively.

⁶ Note Figures 5 and 7 from Abreu et al. (2009) were slightly modified to highlight the technical justification.

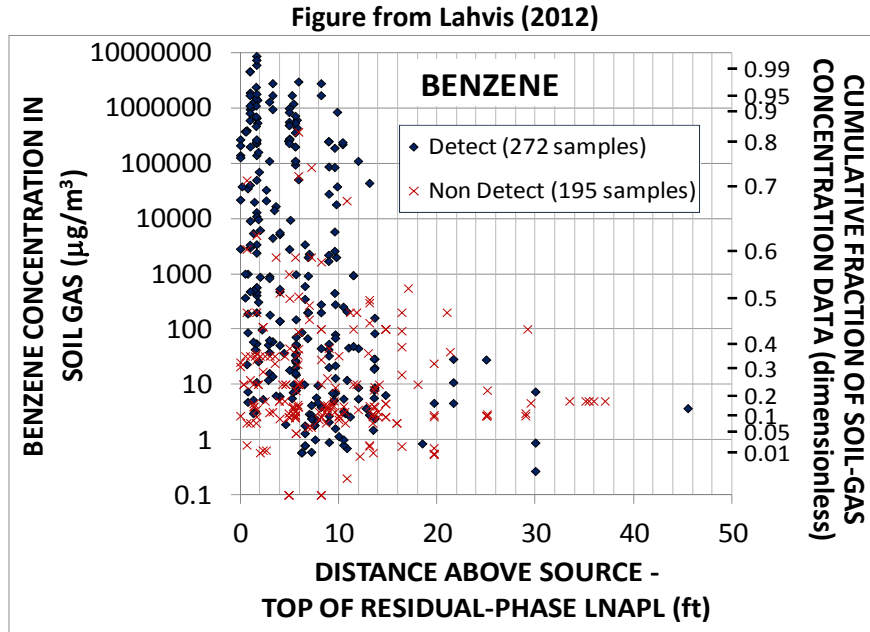
Vapor attenuation is predicted to increase for LNAPL sources displaced laterally from the basement foundation (Abreu and Johnson, 2005).

3.2.2 Field Data

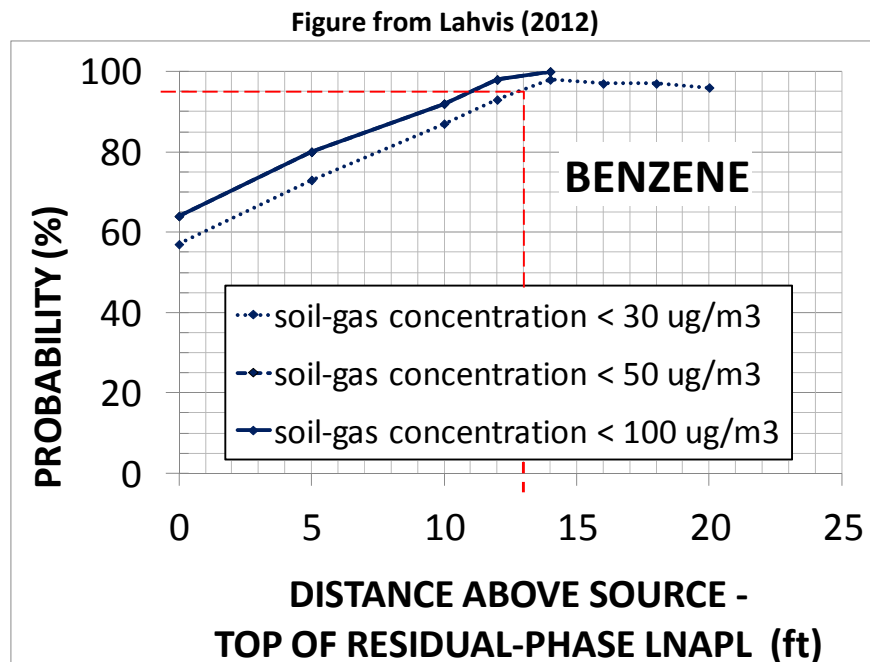
A recent analysis of a soil-gas database by Davis (2010) indicates that the model-predicted attenuation cited above is conservative. Davis (2010) found source-receptor separation distances of only 8 ft. attenuated soil-gas vapors associated with benzene and TPH from LNAPL sources to below health-risk screening criteria (see the following figure from Davis [2010]). The Davis (2010) analysis accounts for residual LNAPL sources in the unsaturated zone.



In addition, Lahvis (2012) demonstrates in the following figure that benzene concentrations in soil gas generally decrease by more than 4 orders of magnitude at source-receptor separation distances of > 13 feet at LNAPL sites:



From a conditional probability standpoint, benzene concentrations in soil gas will attenuate below $30 \mu\text{g}/\text{m}^3$ at distances of $> \sim 13$ ft above the source in greater than 95% of cases.



Again, lateral separation exclusion distances would be expected to be less than the vertical exclusion distances for the reasons previously presented. As noted in Lahvis (2012), the exclusion distance estimate is also relatively insensitive to the presence/absence of a building foundation at land surface.

This is an important observation with respect to managing risks associated with future building construction.

3.2.2 Summary

Most recent field data analyses indicate 8 to 13 feet of clean soil (soil with no LNAPL present) between source and receptor is sufficient to reduce soil-vapor concentrations to below health-protective levels for the vapor-intrusion-to-indoor air pathway at sites with LNAPL sources in either soil or groundwater.

3.3 Technical Background Conclusions

Researchers have demonstrated that soil-vapor benzene concentrations above low-concentration sources attenuate up to 6 orders of magnitude in the unsaturated zone within short vertical distances (e.g., < 5 ft) due to biodegradation. Biodegradation is sufficient to essentially eliminate these sites from further vapor intrusion consideration.

At sites with high concentration sources (e.g., un-weathered LNAPL sources), 8 to 13 feet of clean soil (i.e. TPH <100 mg/kg) are required to fully attenuate hydrocarbon vapors to health-protective concentrations for the vapor-intrusion-to-indoor air pathway. The attenuation due to biodegradation would be equally or more significant for LNAPL sources separated laterally from building foundations (i.e. a shorter distance would be required for attenuation to health-protective concentrations).

The use of soil-gas data to support the development of vapor intrusion guidance for petroleum hydrocarbon site screening is relatively new. Consequently, the technical justification includes several references to non-peer-reviewed literature. The work of Lahvis (2012) has recently been documented and is intended for publication in peer-reviewed literature. The study is being used to support the development of vapor intrusion guidance for US EPA Office of Underground Storage Tanks. Although the analyses are subject to change as a consequence of the peer review, the non peer-reviewed attachments are based on sound scientific knowledge and fundamental to the validation of model theory and development of vapor intrusion guidance. It is important to consider these “state of the science” results in the development of rational, technically defensible, approaches to vapor intrusion risk assessment. Please note that the Stakeholder Group that developed the Low-Threat UST Policy Petroleum considered the cited technical sources when developing the vapor-intrusion scenarios and associated risk criteria presented in the Low-Threat Policy. In addition, *as a statewide policy consideration*, the Stakeholder Group applied source-to-receptor separation distance and source concentration safety factors that make the proposed vapor-intrusion-to-indoor-air screening criteria *more conservative* than they would otherwise be if considering the scientific literature alone. These safety factors include greater separation distances and lower threshold concentrations than those found by researchers to be health protective.

4 THE FOUR LOW-THREAT VAPOR INTRUSION SCREENING SCENARIOS

The Stakeholder Group convened by the SWRCB considered the available current and relevant scientific studies when developing the following low-threat vapor-intrusion-to-indoor air criteria. The four basic vapor-intrusion scenarios are:

Scenario 1: Un-weathered LNAPL on groundwater

30 ft vertical source/building separation (exclusion) distance for un-weathered (residual or free-phase) LNAPL on groundwater

Scenario 2: Un-weathered LNAPL in soil

30 ft lateral and vertical source/building separation (exclusion) distance for an un-weathered LNAPL (residual or free-phase) LNAPL source in soil and a building foundation

Scenario 3: Dissolved phase benzene concentrations in groundwater

- 5 feet vertical separation distance between a dissolved-phase source < 100 µg/L benzene and a building foundation (no oxygen (O₂) measurement)
- 10 feet vertical exclusion distance for a dissolved-phase source < 1,000 µg/L benzene (no O₂ measurement)
- 5 ft. vertical separation distance between a dissolved-phase source < 1,000 µg/L and a building foundation (measured O₂ in soil gas > 4% ⁷)

Scenario 4: Direct measurement of soil gas concentrations

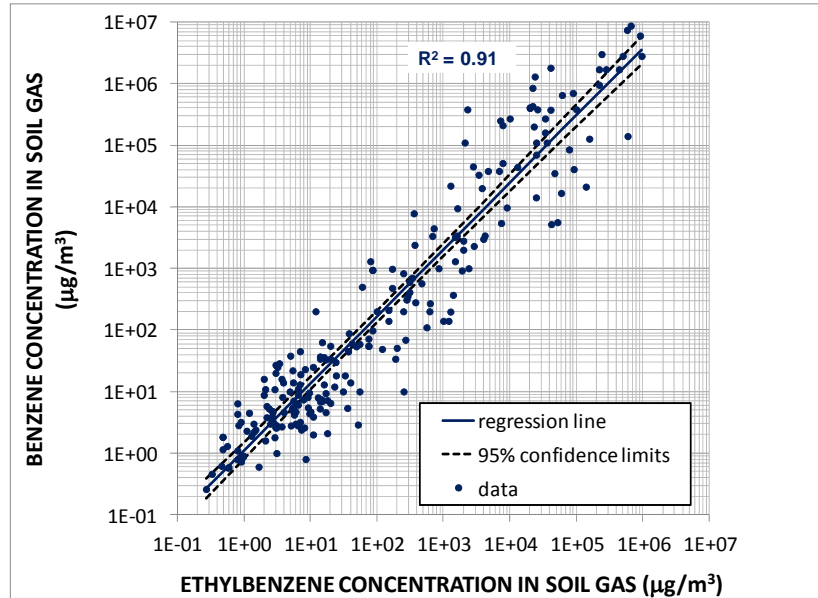
Application of an additional thousand-fold biodegradation attenuation factor to risk-based soil-gas concentration criteria (CHHSLs) when the source is located more than 5 feet from a building foundation

Scenarios 1 and 2 are will usually be associated with “high”-concentration sources. Scenario 3 is associated with a “low” concentration source, and Scenario 4 may be associated with either “low” or “high” concentration sources. The following section details the technical justification(s) for each of the sets of low-threat exclusion criteria expressed in the four scenarios.

The vapor-intrusion exclusion distance criteria determined for benzene are assumed to be health-protective for other potential hydrocarbon VOCs, such as ethylbenzene and naphthalene. For ethylbenzene, this assumption is based on 1) ethylbenzene having similar source concentrations and fate and transport properties as benzene (Abreu et al., 2009), and 2) a strong correlation between benzene and ethylbenzene concentrations in soil-gas measured concurrently from the same soil-gas probe (see following figure from Lahvis [2012]):

⁷ 4% refers to 40,000 ppmv. O₂ concentrations in soil gas sufficient to support aerobic mineralization are reported to be in the range of 1 to 4 % (DeVaull, 2007).

Figure from Lahvis (2012)



The exclusion distance criteria determined for benzene are assumed to be conservative for naphthalene because 1) naphthalene is typically present in gasoline at lower fractions as benzene, 2) naphthalene is likely present at very low concentrations (mass fraction of 0.0026) in diesel (Potter and Simmons, 1998), and 3) naphthalene is less volatile, and has similar (if not, higher) degradation rates as benzene (GSI, 2010).

4.1 Scenario 1: Un-weathered LNAPL on Groundwater

30 ft vertical source/building separation (exclusion) distance for un-weathered (residual or free-phase) LNAPL on groundwater

The proposed 30 feet exclusion distance⁸ is conservative based on:

- Model theory shows full attenuation within 7 m (~ 20 ft) of a high concentration LNAPL source assuming reasonable approximations of the biodegradation rate (see Figures 5 and 7 below from Abreu et al., 2009)⁹. The use of benzene to represent an un-weathered LNAPL vapor source (which will primarily consist of aliphatic hydrocarbons) is assumed to be conservative with respect to benzene biodegradation assumptions (linked to O₂ availability)¹⁰.

⁸ The top of the residual-phase source can generally be assumed to be consistent with the historic high water-table elevation.

⁹ Note Figures 5 and 7 from Abreu et al. (2009) were slightly modified to highlight the technical justification

¹⁰ In this model, biodegradation is linked to O₂ availability. Biodegradation is not simulated when O₂ concentrations in the unsaturated zone fall below 1%. Relative to benzene, aliphatic hydrocarbons are less susceptible to biodegradation because they partition less to the aqueous phase (pore water) where biodegradation takes place. Simulating LNAPL with a single benzene source will thus be conservative with respect to O₂ demand (and benzene biodegradation) compared to simulating LNAPL using a primarily aliphatic hydrocarbons.

Figure 5 (modified) from Abreu et al. (2009)

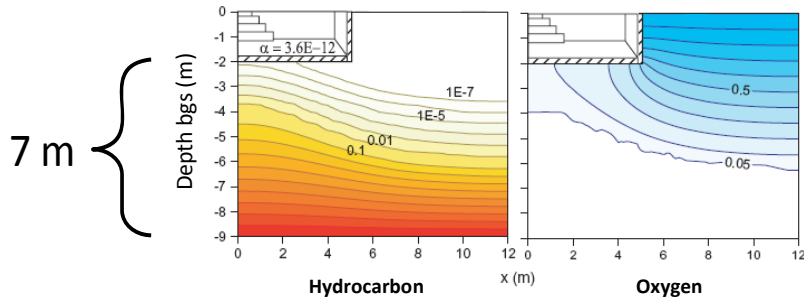


Figure 5. Effect of source depth on the soil-gas concentration distribution and vapor intrusion attenuation factors (α) for basement scenarios with a high vapor source concentration of 100,000 $\mu\text{g/L}$ and biodegradation rate $\lambda = 0.79 \text{ h}^{-1}$. Hydrocarbon and oxygen concentrations are normalized by source and atmospheric concentrations, respectively.

Figure 7 (modified) from Abreu et al. (2009)

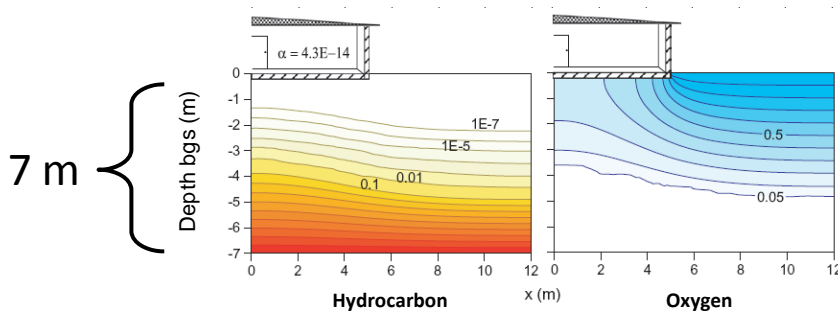
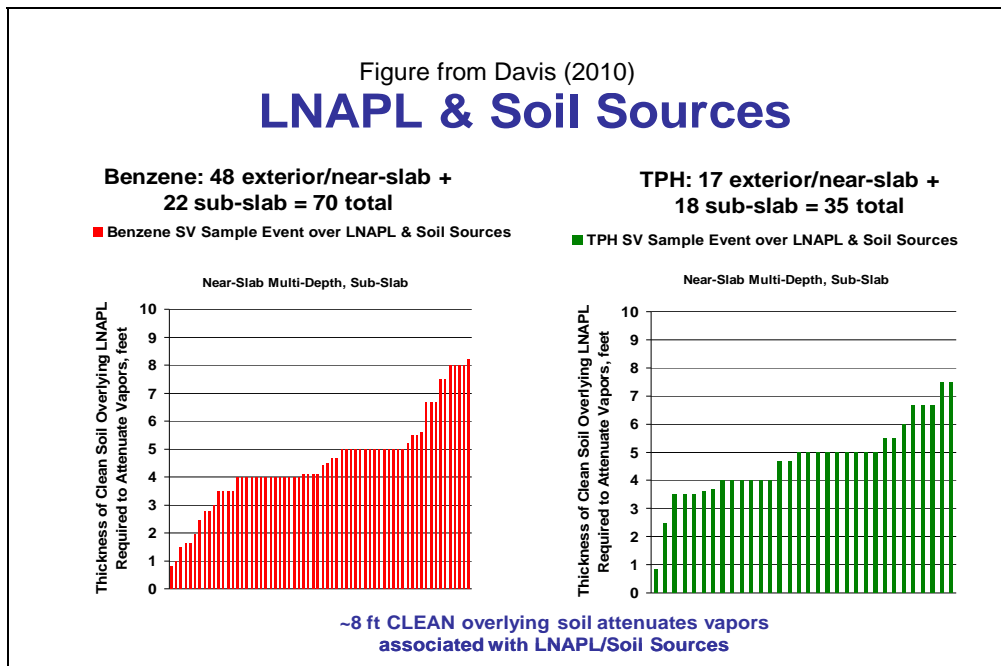
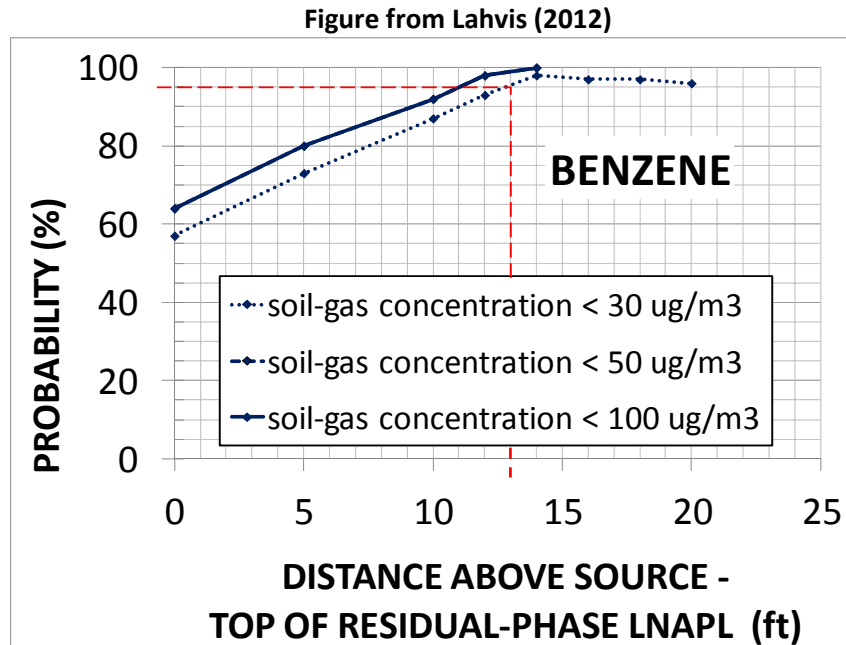


Figure 7. Effect of building type on soil-gas concentration distribution for high vapor source concentration (100,000 $\mu\text{g/L}$) and biodegradation rate $\lambda = 0.79 \text{ h}^{-1}$. Hydrocarbon and oxygen concentrations are normalized by source and atmospheric concentrations, respectively.

- For LNAPL and residual sources, field (soil-gas) data show full attenuation within 8 ft of the source (see figure, below, from R. Davis [2010] – also published in Hartman [2010]).



The following figure from Lahvis (2012) shows a greater than 95% probability that benzene concentrations in soil gas will attenuate below a conservative screening level for benzene in soil gas of $30 \mu\text{g}/\text{m}^3$ (alternatively, a $< 5\%$ probability of observing benzene concentrations $> 30 \mu\text{g}/\text{m}^3$) at distances of $> \sim 13$ ft from a LNAPL (residual or free-phase) source.



4.2 Scenario 2: Un-weathered LNAPL in Soil

30 ft lateral and vertical source/building separation (exclusion) distance for an un-weathered LNAPL (residual or free-phase) LNAPL source in soil and a building foundation

The same technical justification provided for Scenario 1 applies to Scenario 2. The proposed 30 feet lateral off-set distance is even more conservative for sources displaced laterally as indicated in the following figure from Abreu and Johnson (2005). For example, an additional order of magnitude of attenuation is predicted for plume centerlines displaced 10 m (~ 30 ft).

Figure 9 from Abreu and Johnson (2005)

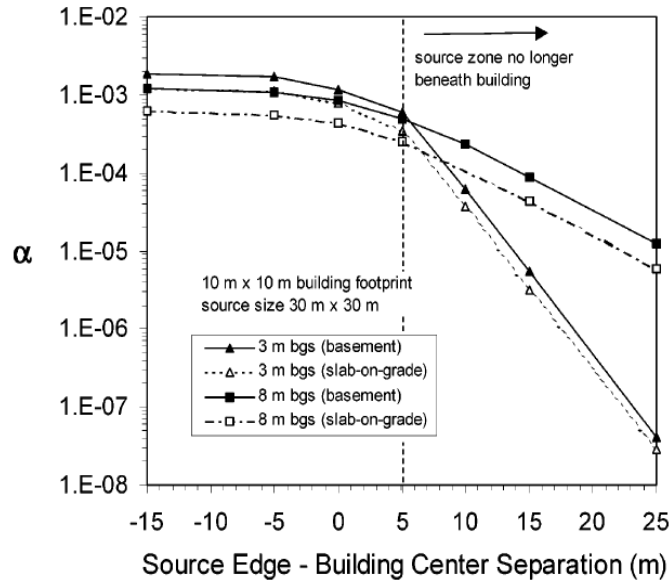


FIGURE 9. Changes in vapor attenuation coefficient (α) with vapor source–building separation and vapor source depth for basement and slab-on-grade foundation scenarios.

As discussed in the technical background section 3.2.2, 13 feet is more than adequate to fully attenuate vapors derived from LNAPL sources in soil and groundwater; therefore providing a 30-ft lateral distance screening criteria provides an additional safety factor.

4.3 Scenario 3: Dissolved Phase Benzene Concentrations in Groundwater

- 5 ft. vertical separation distance between a dissolved-phase source < 100 $\mu\text{g/L}$ benzene and a building foundation (no oxygen (O_2) measurement)
- 10 ft. vertical exclusion distance for a dissolved-phase source < 1,000 $\mu\text{g/L}$ benzene (no O_2 measurement)
- 5 ft. vertical separation distance between a dissolved-phase source < 1,000 $\mu\text{g/L}$ and a building foundation (measured O_2 in soil gas $\geq 4\%$ or 40,000 ppm_v)

These separation distances are conservative with respect to protecting human health based on the following:

- Complete attenuation ($\sim 1\text{E-}07$) is predicted within 2 m (6 ft.) of a soil gas source of benzene < 10 mg/L (or or 10,000,000 $\mu\text{g/m}^3$) (assumes an approximate 40 mg/L dissolved phase benzene concentration, based on an approximation of benzene partitioning between soil gas and groundwater [dimensionless Henry's Law constant = 0.25] - see attached Figure 10 from Abreu

et al. [2009]¹¹). Even greater hydrocarbon attenuation (lesser exclusion distances) is predicted for dissolved-phase sources in other less permeable (e.g., silty clay) unsaturated zone systems (Abreu et al, 2009). The attenuation is complete for the entire vapor (dissolved-phase) concentration range. The dissolved phase concentrations (especially) (i.e., 100 µg/L) and proposed exclusion distance specified in this scenario are therefore assumed to be very conservative. Note: in the figure below, “L” is the distance to the foundation from the source.

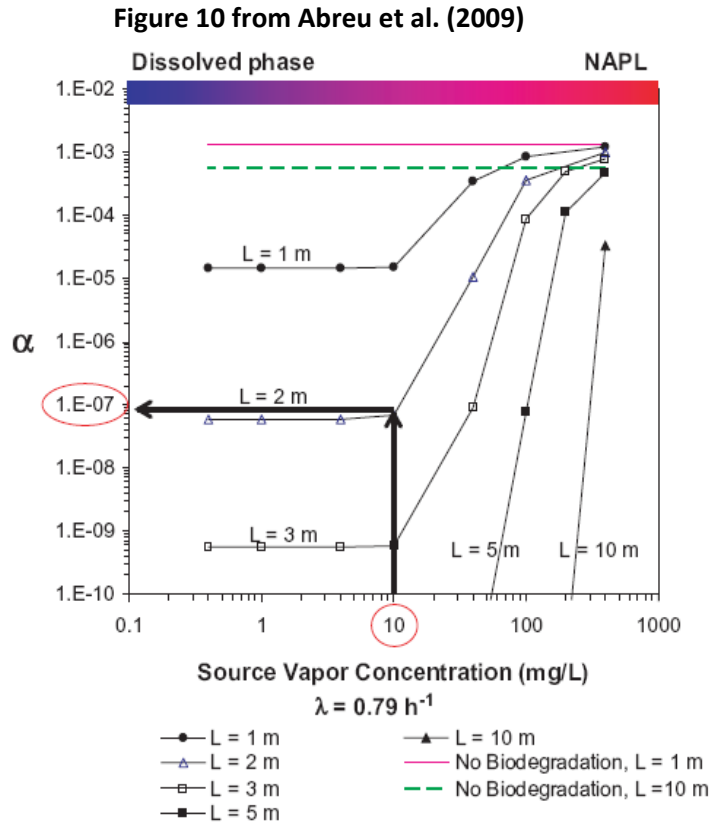


Figure 10. Use of the chart to select a semi-site-specific attenuation factor. For a source concentration of 10,000 µg/L and a source-building separation of 2 m, the attenuation factor would be about 1E-7.

- Model theory shows > 9 orders of magnitude (i.e. complete) attenuation (for reasonable approximations of the biodegradation rate $\lambda = 0.79 \text{ hr}^{-1}$) within a source/building separation distance of $L=3 \text{ m}$ (10 ft) in a sand unsaturated zone (Abreu et al. (2009)). This magnitude of attenuation is applicable for a benzene vapor source $< \sim 10 \text{ mg/L}$ (10,000,000 µg/m³)(or $\sim 40 \text{ mg/L}$ dissolved phase source in groundwater assuming reasonable approximations for benzene partitioning between soil gas and groundwater (i.e., a dimensionless Henry’s Law constant = 0.25). Even greater hydrocarbon attenuation (lesser exclusion distances) is predicted for dissolved-phase sources in other less permeable (e.g., silty clay) unsaturated zone systems

¹¹ Note figure from Abreu et al. (2009) was slightly modified to highlight the technical justification

(Abreu et al, 2009). The attenuation is complete for the entire vapor (dissolved-phase) concentration range. The dissolved phase concentrations (especially) (1,000 $\mu\text{g/L}$) and proposed exclusion distance specified in this scenario are therefore assumed to be very conservative. Note: in the figure below, “D” is the overall source depth and “L” is the distance to the foundation from the source.

Figure 6 from Abreu et al. (2009)

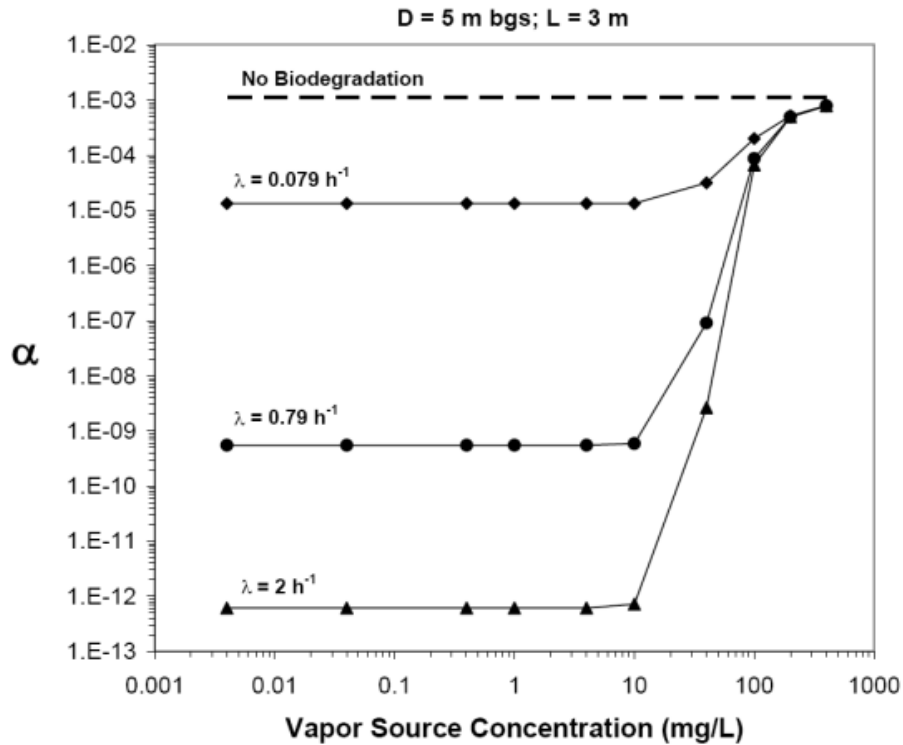
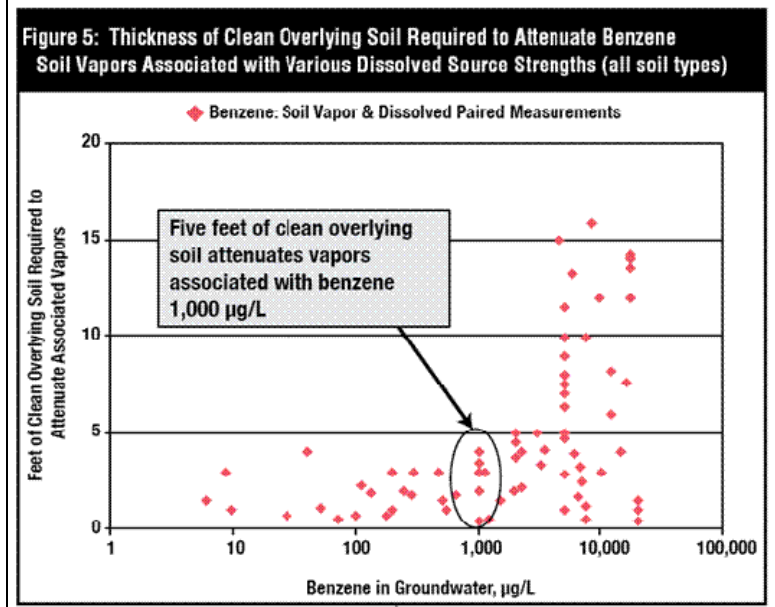


Figure 5—Influence of soil vapor source concentration and first-order biodegradation rates (λ) on vapor intrusion attenuation factors (α) for basement scenarios, homogeneous sand soil and source depth (D) of 5 m bgs (source-foundation separation L = 3 m).

- Field soil-gas data show complete soil-gas attenuation within 5 feet above benzene concentrations in groundwater of up to 6 mg/L (Davis, 2009).

Figure 5 from Davis (2009)



- Field (soil-gas) data from Davis (2009) and Wright (2011) show benzene concentrations in soil gas attenuate below $80 \mu\text{g}/\text{m}^3$ (see Figure 1) and $20 \mu\text{g}/\text{m}^3$ (see Figure 2) within 10 feet above the water table for dissolved-phase benzene concentrations up to $1,000 \mu\text{g/L}$ and $100 \mu\text{g/L}$, respectively at petroleum UST release sites.

Figure 1 - Lahvis (written communication)

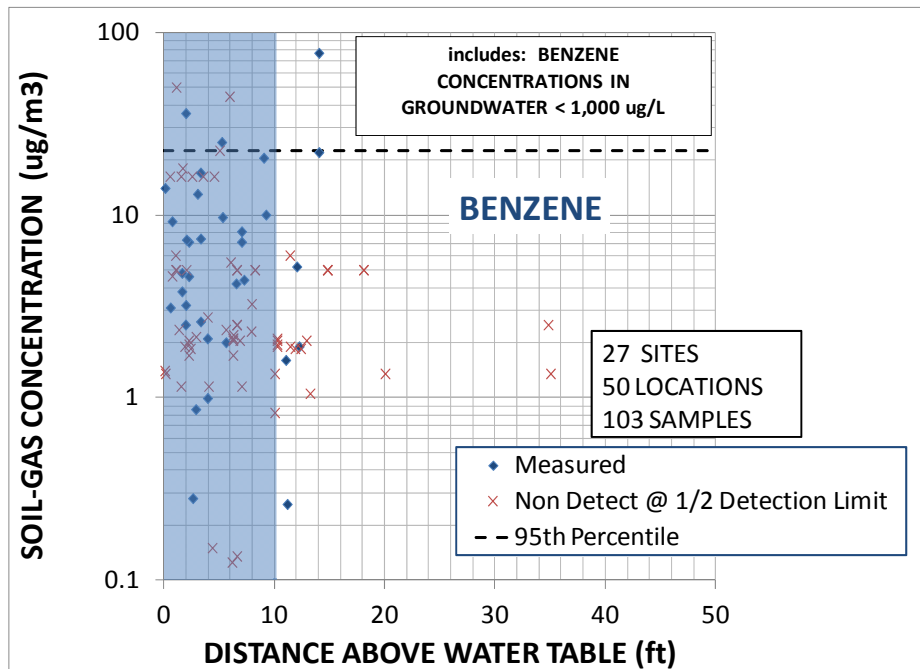


Figure 1. Benzene concentrations in soil gas as a function of distance above the water table for concentrations in groundwater < $1,000 \mu\text{g/L}$. Analysis is based on soil gas data from Davis (2009) and Wright (2011).

Figure 2 - Lahvis (written communication)

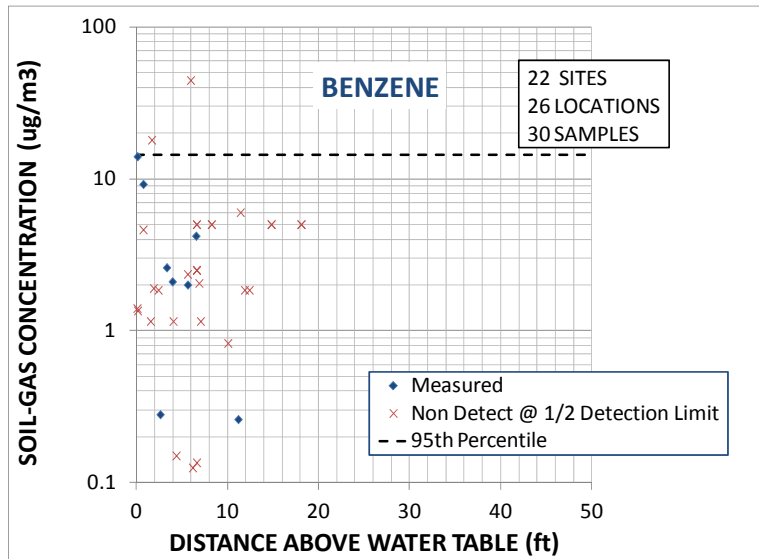


Figure 2. Benzene concentrations in soil gas as a function of distance above the water table for concentrations in groundwater < 100 µg/L. Analysis is based on soil gas data from Davis (2009) and Wright (2011).

- The probability of benzene vapor concentrations near the receptor exceeding a conservative screening level of 50 µg/m³ is less than 5% at petroleum-UST release sites with benzene concentrations in groundwater < 1,000 µg/L. The probability is less than 5% regardless of the source-receptor separation distance (see Figure 3 – Lahvis [written communication]). The water table would have to be essentially in contact with a building foundation to create a potential concern for vapor intrusion at low concentration sites.

Figure 3 from Lahvis (written communication)

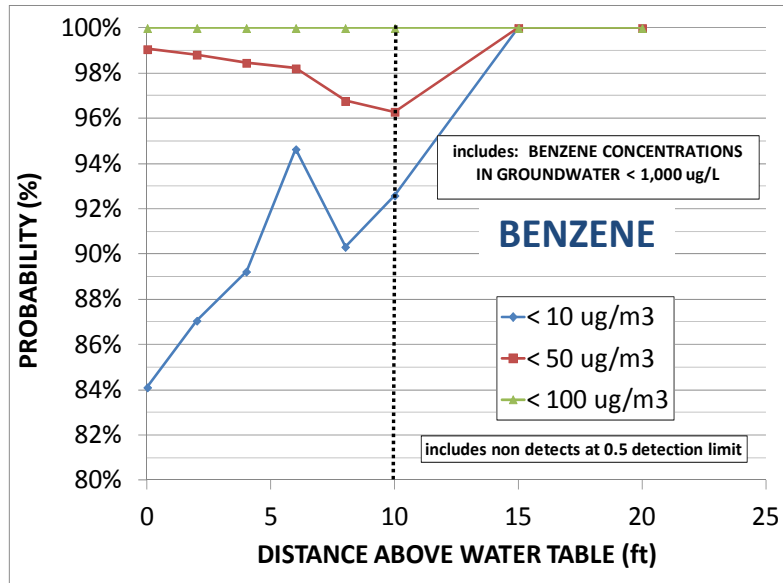


Figure 3. Probability of encountering benzene concentrations in soil gas above conservative screening-level concentrations of 10, 50, and 100 µg/m³ at various distances above the water table at UST-only locations. The data are associated benzene (source) concentrations in groundwater < 1,000 µg/L and are taken from the databases reported in Davis (2009) and Wright (2011).

- The probability of benzene vapor concentrations near the receptor exceeding a (very) conservative screening level (i.e., 10 µg/m³) at petroleum-UST release sites with benzene concentrations in groundwater < 100 µg/L is less than 5% regardless of the source-receptor separation distance (see Figure 4 from Lahvis [written communication]). The water table would have to essentially be in contact with a building foundation to create a potential concern for vapor intrusion at low concentration sites.

Figure 4 from Lahvis (written communication)

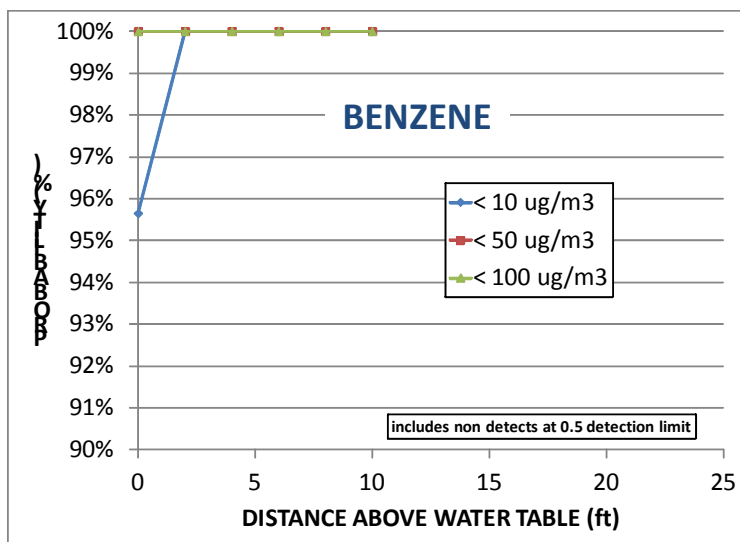


Figure 4. Probability of encountering benzene concentrations in soil gas above conservative screening-level concentrations of 10, 50, and 100 $\mu\text{g}/\text{m}^3$ at various distances above the water table at UST-only locations. The data are associated benzene (source) concentrations in groundwater < 100 $\mu\text{g}/\text{L}$ and are taken from the databases reported in Davis (2009) and Wright (2011).

- The model results from Abreu et al. (2009) (see Figure 3 below) show O_2 concentrations in excess of ~17% ($0.8 * 21\%$) for a hydrocarbon (benzene) vapor source concentration of 1 mg/L (1,000 $\mu\text{g}/\text{L}$) (see plots in middle of the figure). This benzene (or BTEX) vapor source concentration is roughly equivalent to a dissolved phase source concentration of ~4,000 $\mu\text{g}/\text{L}$, which is > the maximum dissolved-phase benzene concentration “1,000 $\mu\text{g}/\text{L}$ ” defined for Scenario 3. This calculation assumes:
 - a) the dissolved-phase source is primarily BTEX (the most soluble hydrocarbon fraction)
 - b) vapor/aqueous partitioning occurs according to Henry’s law, and
 - c) a dimensionless Henry’s Law partition coefficient for benzene (or BTEX) of 0.25.
- Analyses of soil-gas data from Davis (2010) and Wright (2011) show that O_2 concentrations in soil gas are > 4% (40,000 ppm_v) at sites with dissolved-phase sources of benzene in groundwater up to 15 mg/L (see Figure from Lahvis [2012]).

Figure 3 from Abreu et al (2009)

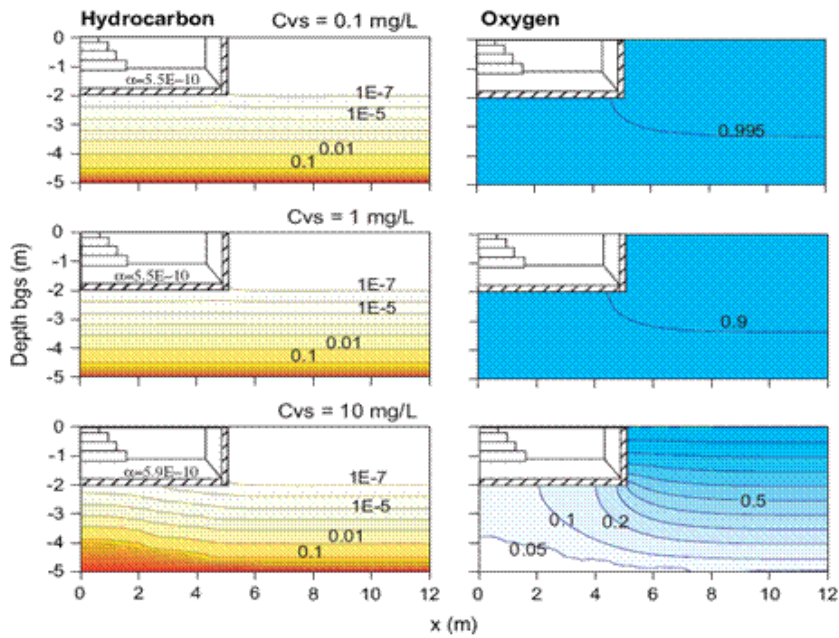


Figure 3. Effect of low vapor source concentration (C_{vs}) on soil-gas concentration distribution and vapor intrusion attenuation factors (α) for basement foundation scenarios and hydrocarbon biodegradation rate $\lambda = 0.79 \text{ h}^{-1}$. Hydrocarbon and oxygen concentrations are normalized by source and atmospheric concentrations, respectively.

Figure from Lahvis (2012)

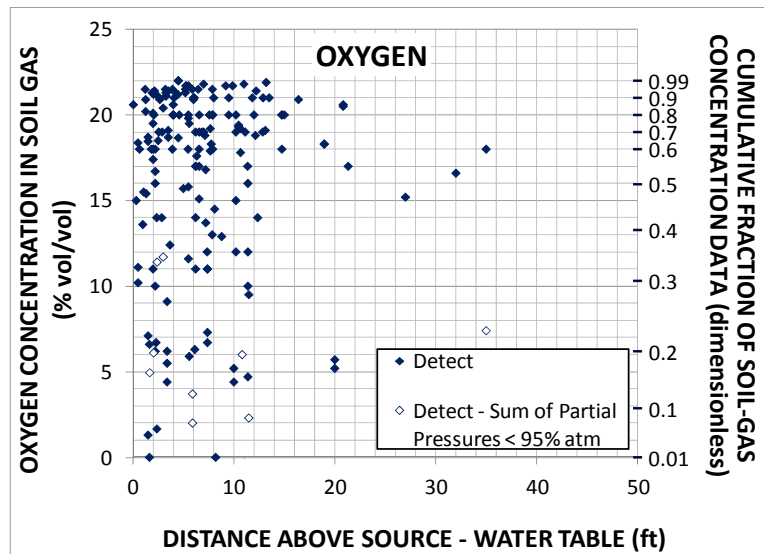


Figure. Plot of measured oxygen concentrations in soil gas as a function of distance above a dissolved-phase hydrocarbon source. Plot includes 192 soil-gas samples collected at 47 UST sites and 128 sampling locations. Non-detect data are omitted. Hollow points indicate selected data where the estimated sum of partial pressures in the sample is less than 95%. The cumulative fraction of all soil gas concentrations is noted on the right vertical axis. The oxygen concentrations are associated with dissolved-phase hydrocarbon (benzene) sources in groundwater with concentrations up to 15 mg/L. Analysis is based on soil gas data from Davis (2009) and Wright (2011).

4.3 Scenario 4: Direct Measurement of Soil Gas Concentrations

Application of a thousand-fold attenuation factor to risk-based soil-gas criteria (i.e. CHSSLs) for sources located more than 5 vertical feet from a building foundation.

- Model results (see Figure 10 from Abreu et al., 2009) show that biodegradation produces an approximate 10,000-fold attenuation of benzene concentrations in soil-gas up to ~10 mg/L or 10,000,000 $\mu\text{g}/\text{m}^3$ within 2 m (5 ft) of a building foundation for reasonable approximations of the degradation rate in a sand unsaturated zone¹². The proposed 1,000-fold additional attenuation for benzene concentrations in soil gas up to 85,000 and 280,000 $\mu\text{g}/\text{m}^3$ located more than vertical 5 feet from a building foundation is thus deemed conservative for residential and commercial settings, respectively.

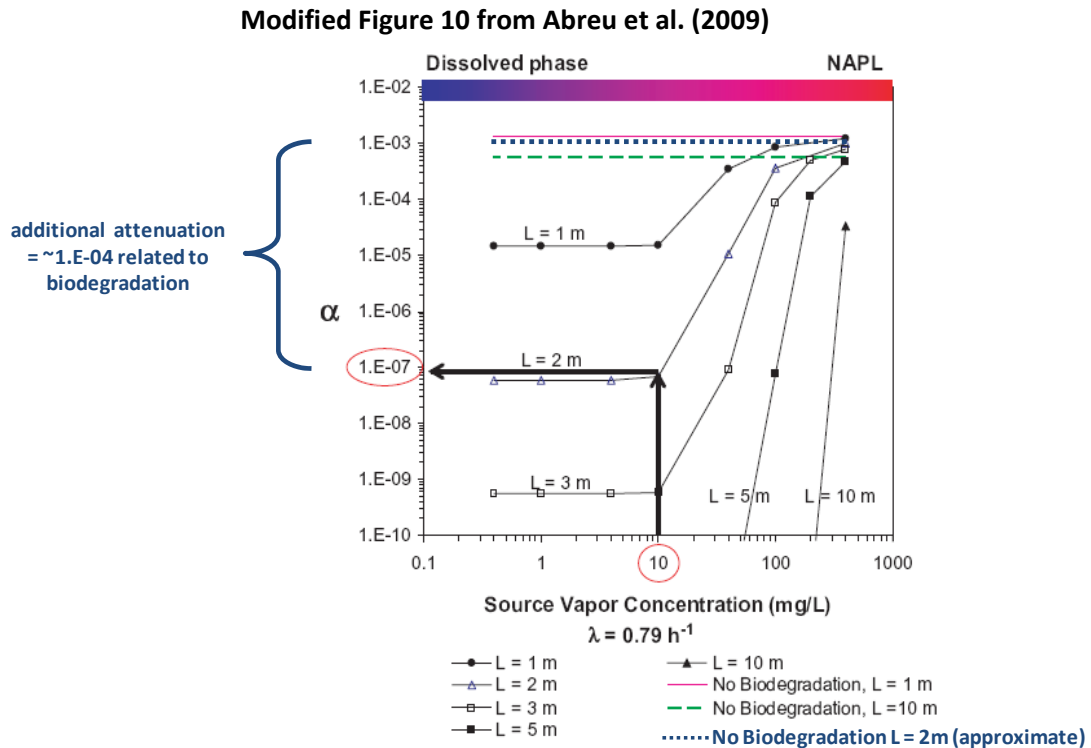


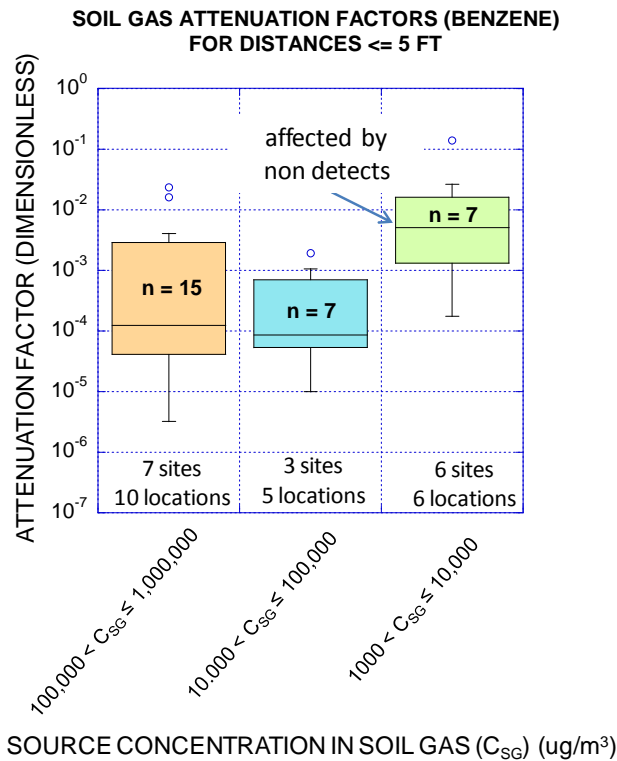
Figure 10. Use of the chart to select a semi-site-specific attenuation factor. For a source concentration of 10,000 $\mu\text{g}/\text{L}$ and a source-building separation of 2 m, the attenuation factor would be about 1E-7.

- Measured field soil-gas (benzene) concentrations from Davis (2009) and Wright (2011) collected from vertically nested vapor probes support the model theory (see Figure below)

¹² Figure modified to show 'No Biodegradation L = 2 m (approximate)' and additional attenuation to highlight technical justification.

from Lahvis [written communication]). More specifically, these data show that benzene attenuation in the unsaturated zone generally exceeds 1000-fold within a 5 feet vertical distance of a benzene (source) soil-gas concentration range between 10,000 and 100,000 $\mu\text{g}/\text{m}^3$ (see Figure 5 – middle box). Similar attenuation is observed for benzene soil gas (source) concentrations ranging between 100,000 and 1,000,000 $\mu\text{g}/\text{m}^3$ (see Figure 5 – left hand box). Less attenuation is observed for benzene soil gas (source) concentrations ranging between 1,000 and 10,000 $\mu\text{g}/\text{m}^3$ (see Figure 5 – right hand box). The statistics for this concentration range are affected, however, by non-detect values reported at $\frac{1}{2}$ the detection limit. The soil-gas data are from the databases described by Davis (2009) and Wright (2011) for petroleum-UST release locations. This finding supports the model theory of Abreu et al. (2009) and the proposed use of a 1000-fold soil-gas bioattenuation factor.

Figure from Lahvis (written communication)



Each box encloses 50% of the data with the median value of the variable displayed as a line. The top and bottom of the box mark the limits of $\pm 25\%$ of the variable population. The lines extending from the top and bottom of each box mark the minimum and maximum values within the data set that fall within an acceptable range defined by the software. Any value outside of this range, called an outlier, is displayed as an individual point.

Figure 5. Box plots based on statistical analysis of benzene soil-gas data collected concurrently from vertically nested probe locations separated by distances \leq 5 ft. The soil-gas data are taken from the databases reported in Davis (2009) and Wright (2011).

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Technical Justification for Soil Screening Levels for Direct Contact and Outdoor Air Exposure Pathways

(Final 03-15-2012)

1 EXECUTIVE SUMMARY

Soil screening levels have been proposed to be used in conjunction with vapor intrusion criteria and groundwater criteria for identifying sites posing a low-threat to human health. That is, these soil screening levels are just one of three sets of criteria that should be evaluated to determine if a site is low-threat.

The soil screening levels discussed in this document have been developed for benzene, ethylbenzene, naphthalene, and polyaromatic hydrocarbons (PAHs). The exposure pathways considered in the conceptual site model are: **incidental ingestion of soil, dermal contact with soil, and inhalation of dust and volatile emissions from soil**. Note these exposure pathways are assumed to occur simultaneously, i.e., the screening levels are protective of exposure from all four exposure pathways for each chemical. Standard U.S. EPA risk assessment equations were used to derive the screening levels. The exposure parameter values, chemical toxicity values, and chemical fate and transport properties are based on default values used in California.

Risks posed by direct exposure to multiple chemicals with similar health effects are considered to be additive or cumulative. For example, the total risk posed by the presence of carcinogenic chemicals is the sum of the theoretical risk posed by each individual chemical. The same is true for chemicals that cause noncarcinogenic health effects. Use of these screening levels for single chemicals is limited to the extent that the screening levels remain protective of human health should other chemicals with similar health effects are present. Assuming all four chemicals are present at the same location and at concentrations at their respective screening levels, the estimated total risk is 4×10^{-6} . For reference, the USEPA National Contingency Plan (NCP) is commonly cited as the basis for acceptable risks in risk management decisions. According to the NCP, an acceptable site-specific lifetime incremental cancer risk falls with the range of 1 in a million (1×10^{-6}) to 100 in a million (1×10^{-4}). Cancer risks below or within the range of 10^{-6} to 10^{-4} are generally considered protective of human health by the USEPA. The estimated total risk for the four chemicals considered in this document (4×10^{-6}) falls within this range.

Two sets of screening levels were developed for two soil horizons: one from 0 to 5 feet below ground surface (bgs) and one from 5 to 10 feet bgs¹ and three exposure scenarios (residential,

¹ There are several definitions of what constitutes surface soil ("near" surface soil is typically the top 6 inches of soil) to quantify potential exposures in health risk assessments. Surface soil can be defined as soil to a depth of 2 feet below ground surface

commercial/industrial, and a utility trench worker) were considered. This document describes the technical background for the development of the soil screening levels.

2 INTRODUCTION

The equations used to develop the soil screening levels are identical to the equations used to derive the USEPA's Regional Screening Levels (RSLs; USEPA 2011). Exposure parameter values were assumed to equal the default values used in California Department of Toxic Substances (DTSC) Office of Human and Ecological Risk (HERO) "Human Health Risk Assessment (HHRA) Note Number 1" (DTSC 2011). The soil screening levels presented in this document are sufficiently protective because the assumptions used to calculate the values are based on conservative assumptions and exposures.

The volatilization factor used in the RSLs was replaced with volatilization factors obtained from the American Society of Testing Material's (ASTM's) Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites (ASTM 1995). The ASTM volatilization factors used to calculate concentrations in outdoor air consider mass balance. The volatilization algorithm used in the RSLs can overestimate the amount of contaminant volatilizing into outdoor air (Cal/EPA, 2005). In the ASTM volatilization algorithm², if the calculated volatilization rate depletes the source before the end of the exposure duration, the volatilization rate is adjusted so that the total source mass is assumed to volatilize by the end of the exposure duration. By using this mass-balance check, it is ensured that the total amount volatilized does not exceed the total amount of contaminant in soil.

For incidental ingestion of soil, dermal contact with soil, and inhalation of dust, the concentration in soil is assumed to be constant at the screening level for the entire exposure duration. This assumption is conservative for volatile chemicals or chemicals that are expected to biodegrade in soil, such as benzene and ethylbenzene.

2.1 Screening Levels vs. Risk

The soil screening levels represent concentrations, below which, indicate the site is a low-threat risk for human health. Multiple conservative assumptions were made when developing these soil screening levels. Actual site risk is expected to be lower than the risk targets used to develop the screening levels. For example, a residential receptor is assumed to come into contact with soil at concentrations

or as indicated in the supporting documentation for the CHHSLs and ESLs, a depth of approximately 10 feet is generally used to delineate between shallow soil, where a potential exists for regular direct contact, and deep soil where only periodic exposure is considered likely.

² The ASTM VF differs from the approach used by USEPA in the development of the RSLs. The VF used to calculate the RSLs assumes infinite sources over a large source area for the dispersion term. The ASTM VF algorithm is considered more appropriate for leaking underground fuel tank (LUFT) sites. Further details on the differences are presented in the Draft California LUFT Guidance Manual, version 2.0, 2010).

equivalent to the screening level every day (350 days/year) for a total of 30 years. While most residential exposures would not occur at the default levels used to derive these screening levels, the defaults are designed to be protective for this hypothetical scenario.

Note that site concentrations that exceed the screening levels do not indicate unacceptable human health risks with regards to these pathways; rather, an exceedance may indicate that a site-specific evaluation of human health risk is warranted.

2.2 Chemicals Considered

Risk-based soil screening levels were developed for benzene, ethylbenzene, naphthalene and PAHs. These constituents are considered the primary risk-driving compounds at petroleum-impacted sites.

Total petroleum hydrocarbons (TPH) were not considered as a chemical of concern. The stakeholders chose not to include TPH in policy for the following reasons:

- TPH consists of a mixture of more than 2000 chemicals.
- Once in soil, the TPH starts weathering immediately changing its composition through time and from one site to the next.
- Bulk TPH measurements, such as those obtained by analytical method 8015M, are not suitable for risk assessment because they do not provide information about the composition with respect to chemical toxicity and fate and transport properties.
- None of the regulatory agencies in California that are responsible for requiring risk assessment have an approved analytical method for evaluating TPH for purposes of risk assessment (such as a fractionation method). In fact, most analytical labs in California are not familiar with TPH fractionation.
- Benzene, ethylbenzene and naphthalene more accurately capture the risk that TPH poses for human health concerns.

Methyl tert-butyl ether (MTBE) was not considered as a chemical of concern for the following reasons:³

For benzene, the USEPA RSL in soil for residential land use is 1.1 mg/kg, which is approximately 1,650-times lower than its soil saturation concentration. For MTBE, the residential soil RSL is 43 mg/kg, which is about 200-times lower than its soil saturation concentration. Even though the MTBE content of gasoline may be 10- to 15-times that of benzene, potential risks from direct contact with soil will still be driven by benzene, which is about 60-times more toxic than MTBE. Currently, USEPA does not evaluate MTBE as a potential human carcinogen. The State of California has developed a cancer slope factor for MTBE based on a combination of data from two animal studies, one study by the inhalation route and the other study by the oral route. Numerous

³ Written communication with the Department of Toxic Substances Control, Human and Ecological Risk Office.

uncertainties have been identified in the animal studies, including severe mortality and lack of histopathological criteria. In addition, the mechanism of MTBE carcinogenicity is not known. Given the uncertainties associated with MTBE carcinogenicity, benzene will be the risk-driving chemical of concern associated with fuel-related hydrocarbons, especially considering that benzene is a known human carcinogen with a known mechanism of action.

The soil screening level for “PAH” is appropriate for comparison with the total concentration of the seven carcinogenic PAHs, as benzo(a)pyrene equivalents (BaPe)⁴. The carcinogenic PAHs typically analyzed during site investigations are: benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene. The toxicity value used for the entire group of carcinogenic PAHs is California’s Office of Environmental Health Hazard Assessment (OEHHA) cancer potency value for benzo(a)pyrene (OEHHA 2010). This is a conservative assumption because the few PAHs that are more carcinogenic than benzo(a)pyrene are typically not found in petroleum mixtures.

2.3 Requirements for Using Screening Levels

There is only one “model” used in calculation of the Screening Levels. This model assumes the following:

- The area of impacted soil where a particular exposure occurs is 25 by 25 meters (approximately 82 by 82 feet) or less. This does not mean that the site or the property has to be less than 25 by 25 meters. If the area of impacted soil where a particular exposure is larger, a site-specific risk analysis may be warranted.
- The receptor is located at the downgradient edge for inhalation exposure. For residential exposures, it is assumed that the receptor is located on site for 24 hours/day for the entire exposure duration. For industrial and utility workers, it is assumed that the worker is located onsite for 8 hours/day.
- The wind speed is assumed to equal 2.25 meters per second (m/s) on average. If the average wind speed is lower, a site-specific risk analysis may be warranted.
- The default input parameters for all exposure scenarios were obtained from DTSC defaults for California hazardous waste sites. If the exposure scenarios are different, a site-specific risk analysis may be warranted.

⁴ The Office of Environmental Health Hazard Assessment (OEHHA) of Cal/EPA has developed potency equivalency factors (PEFs) for carcinogenic PAHs based on their potential toxicity when compared to benzo(a)pyrene [B(a)P]. To estimate B(a)P toxicity equivalents (TEQs; referred to as BaPe), the concentration of each carcinogenic PAH detected in soil is multiplied by the appropriate PEF developed by OEHHA [benz[a]anthracene (0.1), benzo[a]pyrene (1.0), benzo[b]fluoranthene (0.1), benzo[k]fluoranthene (0.1), chrysene (0.01), dibenz(a,h)anthracene (0.34), and indeno(1,2,3-cd)pyrene (0.1)]. The sum of BaPe concentrations for a mixture of PAH results in a total BaPe for each sample; the total BaPe concentrations should be compared to the soil screening level for PAHs.

3 CONCEPTUAL SITE MODEL

This section describes the exposure scenarios and receptors considered in the development of the soil screening levels. Soil screening levels were developed for two different soil horizons. A schematic of the conceptual site model for the two soil horizons is shown in Figure 1.

3.1 Exposure Pathways

The soil screening levels consider four exposure pathways simultaneously:

- incidental ingestion of soil;
- dermal contact with soil;
- inhalation of volatile soil emissions; and
- inhalation of particulate emissions.

Incidental ingestion of and dermal contact with soil are direct exposure pathways, i.e., the receptor is assumed to contact the soil directly and, therefore, the exposure point concentration is the actual concentration in soil. For the inhalation exposure pathways, the exposure medium is outdoor air; the outdoor air concentration must be estimated using volatilization and particulate emission factors.

3.2 Receptors Considered

Soil screening levels were calculated for three exposure scenarios. The exposure scenarios considered were:

- residential;
- commercial/industrial worker; and
- a worker in a utility trench or similar construction project (utility worker).

It is assumed that all four of the exposure pathways (discussed in section 3.1) are potentially complete for each scenario. However, the input parameter values are different for each receptor.

For the residential exposure scenario, it is assumed that the receptor is a child for 6 years and then an adult for 24 years. When calculating carcinogenic risk, the total intake of a chemical over a lifetime is used; therefore, the carcinogenic residential screening levels are protective of the combined child plus adult scenario. For benzo(a)pyrene (PAHs), the mutagenic exposure equations are used for calculating the screening level. In this case, the early life exposures (i.e., 0 to 2 years, 2 to 6 years and 6 to 16 years) are weighted more than they are in the non-mutagenic equations (Table 1). For noncarcinogenic health effects, the intake is not added over the exposure period. In this case, the child is the more sensitive

receptor; therefore the noncarcinogenic screening levels are developed for a child receptor and are protective for the adult resident.

The commercial/industrial exposure scenario assumes that the receptor is an adult and works in an office or outdoors at a site. In this scenario, it is assumed that the receptor works for a total of 25 years at 250 days/year at the same location.

For the utility or construction worker, the exposure duration is assumed to be much shorter than in the other two scenarios (1 year); however, the chemical intake per day is assumed to be higher due to increased incidental ingestion and/or increased inhalation rates.

3.3 *Depths to Which the Screening Levels Apply*

Two sets of screening levels were developed for the residential and commercial/industrial scenarios based on depth of impacted soil: one set applies to 0 to 5 feet bgs and the other set applies to 5 to 10 feet bgs. The full depth of 0 to 10 feet is assumed to contribute to outdoor air concentrations for all scenarios.

For the residential and commercial/industrial exposure scenarios, it is assumed that residents and commercial workers could contact soil at depths between ground surface and 5 feet bgs. For the utility or construction worker, it is assumed that direct contact with soil could occur at depths between ground surface and 10 feet bgs.

4 DERIVATION OF SCREENING LEVELS

This section describes how the soil screening levels were calculated. Except the volatilization term, standard equations from the USEPA RSLs were used. A target risk level of 1×10^{-6} for carcinogens and a target hazard index of 1.0 for noncarcinogens were used.

4.1 *Equations Used*

4.1.1 Exposure Equations

The equations used to develop the soil screening levels are presented in Tables 1 through 3 for each receptor. The variable definitions are presented in Table 4. USEPA considers the carcinogenic PAHs to be “mutagens” and as such, has unique equations to calculate screening levels. The mutagenic equations are for “early life exposures” and therefore only apply to the residential scenario.

4.1.2 Volatilization Factor

The volatilization factor (VF) used to predict an outdoor air concentration due to volatilization from the soil is based on the ASTM guidance (1995). The assumptions in the ASTM volatilization factor algorithm (ASTM 1995) are:

- Dispersion in air is modeled from a ground-level source. It is assumed that the air in the outdoor air “box” is well-mixed;
- The receptor is located onsite, directly over the impacted soil, 24 hours/day for the entire exposure duration; and
- A long-term average exposure point concentration is estimated for the entire exposure duration.

The conceptual model for volatile emissions and inhalation of outdoor air is shown in Figure 2. The assumed receptor location at the edge of the downwind side of the source is the most conservative location that could be used. The dispersion of contaminant in the air, or mixing, is limited to the height of the breathing zone; that is, upward vertical dispersion (i.e., dilution), as the air blows towards the receptor, is not considered in the model.

The ASTM VF is actually composed of two equations as presented in Table 5: one equation assumes an infinite source, and the other one equation includes a mass balance check to limit the volatilization term so that the amount volatilized cannot exceed the total amount of mass in the soil initially. The VF is calculated using both equations and the lower of the two volatilization rates is used for the VF in the exposure equations. The default input values are presented in Table 6. Unless there are site-specific conditions, reasonable estimates for the length and width of the source are 25 meters each (approximately 82 by 82 feet). The thickness of impacted soil is assumed to equal 3.05 meters (10 feet).

4.1.3 Particulate Emission Factor

A particulate emission factor (PEF) is used to estimate the outdoor air concentrations due to chemicals airborne on particulates (dust). The default value used for the PEF for the residential and commercial/industrial scenarios is 1.3×10^9 [(mg/kg)/(mg/m³)] (DTSC 2011). For the utility trench (construction) worker, a PEF value of 1×10^6 [(mg/kg)/(mg/m³)] was used (DTSC 2011).

4.2 Exposure Parameter Values Used

All of the default exposure parameters for the receptors were obtained from DTSC’s “Human Health Risk Assessment (HHRA) Note Number 1” (DTSC 2011). Table 4 presents the default values for each parameter and provides the reference document where each parameter value was obtained.

4.2.1 Ingestion of Soil

Receptors working or playing outdoors may ingest soil through incidental contact of the mouth with hands and clothing. For the residential and commercial exposure scenarios, one of the very conservative assumptions made is that the chemical concentrations remain constant over time in the soil. In reality, this would not be the case, especially for volatile chemicals in the top few feet of soil, where most of the direct contact would occur. Benzene, ethylbenzene and naphthalene are highly fugitive in surface soil, quickly depleting the upper soil depths.

4.2.2 Dermal Contact with Soil

Some soil contaminants may be absorbed across the skin into the bloodstream. Absorption will depend upon the amount of soil in contact with the skin, the concentration of chemicals in soil, the skin surface area exposed, and the potential for the chemical to be absorbed across the skin. Note, USEPA assumes that benzene and ethylbenzene will not be on the skin long enough (due to volatilization) to absorb through the skin.

4.2.3 Inhalation of Volatile and Particulate Emissions in Outdoor Air

The inhalation exposure route includes the inhalation of both volatile and particulate emissions. The inhalation slope factors and noncarcinogenic inhalation reference doses are presented in Table 7.

4.3 Chemical Parameter and Toxicity Values Used

The default chemical parameter values came from the RWQCB 2 Environmental Screening Levels (2007). The toxicity values for noncarcinogenic toxicity came from USEPA’s On-line Risk Information System (IRIS, 2011). The carcinogenic toxicity values for benzene, ethylbenzene, and naphthalene came from OEHHA’s list of cancer potency factors (OEHHA 2009). The carcinogenic oral slope factor for benzo(a)pyrene came from OEHHA’s Public Health Goals for Chemicals in Drinking Water for Benzo(a)pyrene (OEHHA 2010).

5 SOIL SCREENING LEVELS

Table 8 shows the soil screening levels calculated for each exposure scenario.

Table 8: Summary of Soil Screening Levels for different Exposure Scenarios and Receptors

Chemical	Residential		Commercial/ Industrial		Utility Worker
	0 to 5 feet bgs	Volatilization to outdoor air (5 to 10 feet bgs)	0 to 5 feet bgs	Volatilization to outdoor air (5 to 10 feet bgs)	0 to 10 feet bgs
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Benzene	1.9	2.8	8.2	12	14
Ethylbenzene	21	32	89	134	314
Naphthalene	9.7	9.7	45	45	219
PAH*	0.063**	NA	0.68	NA	4.5

Notes:

* Based on the seven carcinogenic PAHs as benzo(a)pyrene toxicity equivalent [BaPe]. The PAH screening level (applicable to total BaPe) is only applicable where soil was affected by either waste oil and/or Bunker C fuel.

** DTSC (2009) reports average ambient PAH concentrations (as BaPe) in California ranging from 0.16 to 0.21 mg/kg, and upper tolerance limits (UTLs) ranging from 0.9 to 1.5 mg/kg. The screening level shown in this table is “risk-based” and is far below the average ambient concentrations for PAHs in California. It is suggested that DTSC citation (2009) be consulted for sites with PAH contamination.

NA = Not Applicable

Note, the screening levels for naphthalene are the same for the top 5 feet and for 5 to 10 feet bgs based on volatilization to outdoor air. This is because naphthalene is only carcinogenic from the inhalation exposure pathway and not from oral or dermal contact. The screening levels based on carcinogenic mode of action and inhalation were the most conservative (i.e., the carcinogenic screening levels were less than the noncarcinogenic screening levels).

6 APPLYING SOIL SCREENING LEVELS

The maximum concentrations of petroleum constituents in soil should be compared to those listed in Table 8 for the specified depth bgs and the receptor scenario. The concentration limits for 0 to 5 feet bgs are protective for ingestion of soil, dermal contact with soil, inhalation of volatile soil emissions, and inhalation of particulate emissions, and the 5 to 10 feet bgs concentration limits are protective for inhalation of volatile soil emissions in outdoor air. Both the 0 to 5 feet bgs concentration limits and the 5 to 10 feet bgs concentration limits for the appropriate site classification (residential or commercial/industrial) shall be satisfied. In addition, if exposure to construction workers or utility trench workers is reasonably anticipated, the concentration limits for the utility worker shall also be satisfied.

7 DISCUSSION

This document has presented soil screening levels to be used to identify sites that are low threat to human health risk for the direct contact pathways from impacted soil. These soil screening levels are designed to be used in conjunction with the Vapor Intrusion Criteria and Groundwater Criteria to determine if the site is a low-threat from all exposure pathways.

OEHHA has indicated that the residential exposure scenario is protective for other sensitive uses of a site. This means that these screening levels are also appropriate for other sensitive uses of the property (e.g., day-care centers and hospitals; OEHHA 2005).

8 REFERENCES

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TABLES

Table 1: Equations Used to Develop Soil Screening Levels for the Direct Contact Pathways for a Residential Exposure Scenario

(page 1 of 3)

Carcinogenic – Residential
<p>Incidental ingestion of soil</p> $SL_{res-sol-ca-ing} = \frac{TR \times AT_{Carc} \times 365d/yr}{SF_o \times EF_r \times IFS_{adj} \times 1E-6 \text{ kg/mg}}$ <p>where</p> $IFS_{adj} = \left[\frac{ED_c \times IRS_c}{BW_c} + \frac{ED_a \times IRS_a}{BW_a} \right]$ <p>Inhalation of particulates and volatiles</p> $SL_{res-sol-ca-inh} = \frac{TR \times AT_{Carc} \times 365d/yr}{IUR \times \left(\frac{1000 \mu g}{mg} \right) \times EF_r \times \left(VF_r + \frac{1}{PEF_r} \right) \times (ED_c + ED_a) \times ET_r \times \left(\frac{1 \text{ day}}{24 \text{ hours}} \right)}$ <p>Dermal Contact with soil</p> $SL_{res-sol-ca-der} = \frac{TR \times AT_{Carc} \times 365d/yr}{\frac{SF_o}{GIABS} \times EF_r \times DFS_{adj} \times ABS_d \times 1E-6 \text{ kg/mg}}$ <p>where</p> $DFS_{adj} = \left[\frac{ED_c \times SAS_c \times AF_c}{BW_c} + \frac{ED_a \times SAS_a \times AF_a}{BW_a} \right]$ <p>Total</p> $C_{res-sol-ca-tot} = \frac{1}{\frac{1}{SL_{res-sol-ca-ing}} + \frac{1}{SL_{res-sol-ca-inh}} + \frac{1}{SL_{res-sol-ca-der}}}$

Table 1: Equations Used to Develop Soil Screening Levels for the Direct Contact Pathways for a Residential Exposure Scenario

(page 2 of 3)

Noncarcinogenic (Hazard) – Residential	
Incidental ingestion of soil	
$C_{res-sol-nc-ing}$	$= \frac{THQ \times BW_c \times AT_{nc} \times ED_c \times 365 d/yr}{EF_r \times ED_c \times \frac{1}{RfD_o} \times IRS_c \times \frac{1E-6 kg}{mg}}$
Inhalation of particulates and volatiles	
$C_{res-sol-nc-inh}$	$= \frac{THQ \times AT_{nc} \times ED_c \times 365 d/yr}{EF_r \times ED_c \times ET_r \times \frac{1 day}{24 hours} \times \frac{1}{RfC} \left(VF_r + \frac{1}{PEF_r} \right)}$
Dermal contact with soil	
$C_{res-sol-nc-der}$	$= \frac{THQ \times BW_c \times AT_{nc} \times ED_c \times 365 d/yr}{EF_r \times ED_c \times \frac{1}{(RfD_o \times GIABS)} \times SAS_c \times AF_c \times ABS_d \times \frac{1E-6 kg}{mg}}$
Total	
$C_{res-sol-nc-tot}$	$= \frac{1}{\frac{1}{SL_{res-sol-nc-ing}} + \frac{1}{SL_{res-sol-nc-inh}} + \frac{1}{SL_{res-sol-nc-der}}}$

Table 1: Equations Used to Develop Soil Screening Levels for the Direct Contact Pathways for a Residential Exposure Scenario

(page 3 of 3)

Carcinogenic – Mutagenic	
Incidental ingestion of soil	
$SL_{res-sol-mu-ing} = \frac{TR \times AT_{Carc} \times 365d/yr}{SF_o \times EF_r \times IFSM_{adj} \times 1E-6 kg/mg}$	
where	
$IFSM_{adj} = \frac{ED_{0-2}(2years) \times IRS_c \times 10}{BW_c} + \frac{ED_{2-6}(4years) \times IRS_c \times 3}{BW_c} + \frac{ED_{6-16}(10years) \times IRS_a \times 3}{BW_a} + \frac{ED_{16-30}(14years) \times IRS_a \times 1}{BW_a}$	
Inhalation of particulates and volatiles	
$SL_{res-sol-mu-inh} = \frac{TR \times AT_{Carc} \times 365d/yr}{IUR \times \left(\frac{1000 \mu g}{mg} \right) \times EF_r \times \left(VF_{s-r} + \frac{1}{PEF_r} \right) \times ET_r \times \left(\frac{1 \text{ day}}{24 \text{ hours}} \right) \times \left(ED_{0-2}(2years) \times 10 + ED_{2-6}(4years) \times 3 + ED_{6-16}(10years) \times 3 + ED_{16-30}(14years) \times 1 \right)}$	
Dermal Contact with soil	
$SL_{res-sol-mu-der} = \frac{TR \times AT_{Carc} \times 365d/yr}{\frac{SF_o}{GIABS} \times EF_r \times DFSM_{adj} \times ABS_d \times 1E-6 kg/mg}$	
where	
$DFSM_{adj} = \left[\frac{ED_{0-2}(2years) \times SAS_c \times AF_c \times 10}{BW_c} + \frac{ED_{2-6}(4years) \times SAS_c \times AF_c \times 3}{BW_c} + \frac{ED_{6-16}(10years) \times SAS_a \times AF_a \times 3}{BW_a} + \frac{ED_{16-30}(14years) \times SAS_a \times AF_a \times 1}{BW_a} \right]$	
Total	
$C_{res-sol-mu-tot} = \frac{1}{\frac{1}{SL_{res-sol-mu-ing}} + \frac{1}{SL_{res-sol-mu-inh}} + \frac{1}{SL_{res-sol-mu-der}}}$	

Table 2: Equations Used to Develop Soil Screening Levels for the Direct Contact Pathways for a Commercial/Industrial Exposure Scenario

Carcinogenic – Commercial/Industrial (c/i)	
Incidental ingestion of soil	
	$SL_{c/i-sol-ca-ing} = \frac{TR \times AT_{Carc} \times 365d/yr \times BW_{c/i}}{SF_o \times EF_{c/i} \times ED_{c/i} \times IRS_{c/i} \times 1E-6kg/mg}$
Inhalation of particulates and volatiles	
	$SL_{c/i-sol-ca-inh} = \frac{TR \times AT_{Carc} \times 365d/yr}{IUR \times \left(\frac{1000 \mu g}{mg} \right) \times EF_{c/i} \times \left(VF_{c/i} + \frac{1}{PEF_{c/i}} \right) \times ED_{c/i} \times ET_{c/i} \times \left(\frac{1 day}{24 hours} \right)}$
Dermal Contact with soil	
	$SL_{c/i-sol-ca-der} = \frac{TR \times AT_{Carc} \times 365d/yr \times BW_{c/i}}{\frac{SF_o}{GIABS} \times EF_{c/i} \times ED_{c/i} \times SAS_{c/i} \times AF_{c/i} \times ABS_d \times 1E-6kg/mg}$
Total	
	$C_{c/i-sol-ca-tot} = \frac{1}{\frac{1}{SL_{c/i-sol-ca-ing}} + \frac{1}{SL_{c/i-sol-ca-inh}} + \frac{1}{SL_{c/i-sol-ca-der}}}$
Noncarcinogenic – Commercial/Industrial	
Incidental ingestion of soil	
	$C_{c/i-sol-nc-ing} = \frac{THQ \times BW_{c/i} \times AT_{nc} \times ED_{c/i} \times 365d/yr}{EF_{c/i} \times ED_{c/i} \times \frac{1}{RfD_o} \times IRS_{c/i} \times \frac{1E-6kg}{mg}}$
Inhalation of particulates and volatiles	
	$C_{c/i-sol-nc-inh} = \frac{THQ \times AT_{nc} \times ED_{c/i} \times 365d/yr}{EF_{c/i} \times ED_{c/i} \times ET_{c/i} \times \frac{1day}{24hours} \times \frac{1}{RfC} \left(VF_{c/i} + \frac{1}{PEF_{c/i}} \right)}$
Dermal contact with soil	
	$C_{c/i-sol-nc-der} = \frac{THQ \times BW_{c/i} \times AT_{nc} \times ED_{c/i} \times 365d/yr}{EF_{c/i} \times ED_{c/i} \times \frac{1}{(RfD_o \times GIABS)} \times SAS_{c/i} \times AF_{c/i} \times ABS_d \times \frac{1E-6kg}{mg}}$
Total	
	$C_{c/i-sol-nc-tot} = \frac{1}{\frac{1}{SL_{c/i-sol-nc-ing}} + \frac{1}{SL_{c/i-sol-nc-inh}} + \frac{1}{SL_{c/i-sol-nc-der}}}$

Table 3: Equations Used to Develop Soil Screening Levels for the Direct Contact Pathways for a Utility Trench Worker or Construction Exposure Scenario

Carcinogenic – Utility Trench Worker (ut)	
Incidental ingestion of soil	
	$SL_{ut-sol-ca-ing} = \frac{TR \times AT_{Carc} \times 365d/yr \times BW_{ut}}{SF_o \times EF_{ut} \times ED_{ut} \times IRS_{ut} \times 1E-6kg/mg}$
Inhalation of particulates and volatiles	
	$SL_{ut-sol-ca-inh} = \frac{TR \times AT_{Carc} \times 365d/yr}{IUR \times \left(\frac{1000 \mu g}{mg} \right) \times EF_{ut} \times \left(VF_{ut} + \frac{1}{PEF_{ut}} \right) \times ED_{ut} \times ET_{ut} \times \left(\frac{1 \text{ day}}{24 \text{ hours}} \right)}$
Dermal Contact with soil	
	$SL_{ut-sol-ca-der} = \frac{TR \times AT_{Carc} \times 365d/yr \times BW_{ut}}{\frac{SF_o}{GIABS} \times EF_{ut} \times ED_{ut} \times SAS_{ut} \times AF_{ut} \times ABS_d \times 1E-6kg/mg}$
Total	
	$C_{ut-sol-ca-tot} = \frac{1}{\frac{1}{SL_{ut-sol-ca-ing}} + \frac{1}{SL_{ut-sol-ca-inh}} + \frac{1}{SL_{ut-sol-ca-der}}}$
Noncarcinogenic – Utility Trench Worker	
Incidental ingestion of soil	
	$C_{ut-sol-nc-ing} = \frac{THQ \times BW_{ut} \times AT_{nc} \times ED_{ut} \times 365d/yr}{EF_{ut} \times ED_{ut} \times \frac{1}{RfD_o} \times IRS_{ut} \times \frac{1E-6kg}{mg}}$
Inhalation of particulates and volatiles	
	$C_{ut-sol-nc-inh} = \frac{THQ \times AT_{nc} \times ED_{ut} \times 365d/yr}{EF_{ut} \times ED_{ut} \times ET_{ut} \times \frac{1day}{24hours} \times \frac{1}{RfC} \left(VF_{ut} + \frac{1}{PEF_{ut}} \right)}$
Dermal contact with soil	
	$C_{ut-sol-nc-der} = \frac{THQ \times BW_{ut} \times AT_{nc} \times ED_{ut} \times 365d/yr}{EF_{ut} \times ED_{ut} \times \frac{1}{(RfD_o \times GIABS)} \times SAS_{ut} \times AF_{ut} \times ABS_d \times \frac{1E-6kg}{mg}}$
Total	
	$C_{ut-sol-nc-tot} = \frac{1}{\frac{1}{SL_{ut-sol-nc-ing}} + \frac{1}{SL_{ut-sol-nc-inh}} + \frac{1}{SL_{ut-sol-nc-der}}}$

Table 4: Default Exposure Parameters (continued)

Parameter	Variable Name	Units	Value	Reference
Averaging time for carcinogens	AT_{carc}	days	365 x 70	70 years by definition (USEPA 1989)
Averaging time for noncarcinogens	AT_{nc}	days	365 x ED	USEPA 1989
Body weight, residential child	BW_c	kg	15	DTSC HERO (2011)
Body weight, residential adult	BW_a	kg	70	DTSC HERO (2011)
Body weight, commercial/industrial	$BW_{c/i}$	kg	70	DTSC HERO (2011)
Body weight, utility worker	BW_{ut}	kg	70	DTSC HERO (2011)
Exposure duration, residential child	ED_c	years	6	DTSC HERO (2011)
Exposure duration, residential adult	ED_a	years	24	DTSC HERO (2011)
Exposure duration, commercial/industrial	$ED_{c/i}$	years	25	DTSC HERO (2011)
Exposure duration, utility worker	ED_{ut}	years	1	DTSC HERO (2011)
Exposure frequency, residential	EF_r	d/year	350	DTSC HERO (2011)
Exposure frequency, commercial/industrial	$EF_{c/i}$	d/year	250	DTSC HERO (2011)
Exposure frequency, utility worker	EF_{ut}	d/year	250	DTSC HERO (2011)
Exposure time for outdoor air, residential	ET_r	hours/day	24	DTSC HERO (2011)
Exposure time for outdoor air, commercial/industrial	$ET_{c/i}$	hours/day	8	DTSC HERO (2011)
Exposure time for outdoor air, utility worker	ET_{ut}	hours/day	8	DTSC HERO (2011)
Soil ingestion rate, residential child	IRS_c	mg/d	200	DTSC HERO (2011)
Soil ingestion rate, residential adult	IRS_a	mg/d	100	DTSC HERO (2011)
Soil ingestion rate, commercial/industrial	$IRS_{c/i}$	mg/d	100	DTSC HERO (2011)
Soil ingestion rate, utility worker	IRS_{ut}	mg/d	330	DTSC HERO (2011)
Soil to skin adherence factor, residential child	AF_c	mg/cm ²	0.2	DTSC HERO (2011)
Soil to skin adherence factor, residential adult	AF_a	mg/cm ²	0.07	DTSC HERO (2011)
Soil to skin adherence factor, commercial/industrial	$AF_{c/i}$	mg/cm ²	0.2	DTSC HERO (2011)
Soil to skin adherence factor, utility worker	AF_{ut}	mg/cm ²	0.8	DTSC HERO (2011)
Skin surface area exposed to soil, residential child	SAS_c	cm ² /d	2900	DTSC HERO (2011)
Skin surface area exposed to soil, residential adult	SAS_a	cm ² /d	5700	DTSC HERO (2011)

Table 4: Default Exposure Parameters (concluded)

Parameter	Variable Name	Units	Value	Reference
Skin surface area exposed to soil, commercial/industrial	SAS_{ci}	cm ² /d	5700	DTSC HERO (2011)
Skin surface area exposed to soil, utility worker	SAS_{ut}	cm ² /d	5700	DTSC HERO (2011)
Particulate emission factor, residential	PEF_r	m ³ /kg	1.3 x 10 ⁹	DTSC HERO (2011)
Particulate emission factor, commercial/industrial	PEF_{ci}	m ³ /kg	1.3 x 10 ⁹	DTSC HERO (2011)
Particulate emission factor, utility worker	PEF_{ut}	m ³ /kg	1.0 x 10 ⁶	DTSC HERO (2011)
Dermal absorption factor from soils	ABS_d	unitless	See Table 7	
Gastrointestinal absorption factor	$GIABS$	unitless	See Table 7	
Oral cancer slope factor	SF_o	1/(mg/kg-d)	See Table 7	
Inhalation Unit Risk	IUR	1/(ug/m ³)	See Table 7	
Oral reference dose	RfD_o	mg/kg-d	See Table 7	
Inhalation reference dose	RfC	mg/m ³	See Table 7	
Target hazard quotient	THQ	unitless	1	OEHHA (2005)
Target individual excess lifetime cancer risk	TR	unitless	1 x 10 ⁻⁶	OEHHA (2005)

References:

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Table 5: Equations Used to Estimate Volatilization and Particulate Emission Factors

Volatilization and Particulate Emission Factors

Effective Diffusion Coefficient (D_{eff})

$$D_{eff} = D_{air} \left(\frac{\theta_a^{10/3}}{\theta_T^2} \right) + D_{water} \frac{1}{H} \left(\frac{\theta_w^{10/3}}{\theta_T^2} \right)$$

Volatilization Factor (VF)

Infinite source:

$$VF \left[\frac{(\text{mg}/\text{m}^3 - \text{air})}{(\text{mg}/\text{kg} - \text{soil})} \right] = \frac{2 \cdot W \cdot \rho_b}{U_{air} \cdot \delta_{air}} \sqrt{\frac{D_{eff} \cdot H}{\pi(\theta_w + \text{FOC} \cdot K_{oc} \cdot \rho_b + H \cdot \theta_a) \tau}} \times 10^3 \frac{\text{cm}^3 \text{kg}}{\text{m}^3 \text{g}}$$

Mass-balance considered:

$$VF \left[\frac{(\text{mg}/\text{m}^3 - \text{air})}{(\text{mg}/\text{kg} - \text{soil})} \right] = \frac{W \cdot \rho_b \cdot d}{U_{air} \cdot \delta_{air} \cdot \tau} \times 10^3 \frac{\text{cm}^3 \text{kg}}{\text{m}^3 \text{g}}$$

Calculate VF using both equations, then use the lower of the two values.

VF_r : Use $\tau = \tau_c + \tau_r$

$VF_{c/i}$: Use $\tau = \tau_{c/i}$

VF_{ut} : Use $\tau = \tau_{ut}$

Table 6: Default Volatilization and Soil-Specific Parameters

Parameter	Variable Name	Units	Value	Reference
Fraction organic carbon in soil	FOC	g OC/g soil	0.01	ASTM (1996)
Thickness of impacted soil	d	cm	305	ASTM (1996) (10 feet)
Wind speed in outdoor air mixing zone	U_{air}	cm/s	225	ASTM (1996)
Width of source area parallel to wind, or groundwater flow direction	W	cm	2500	ASTM (1996)
Outdoor air mixing zone height	δ_{air}	cm	200	ASTM (1996)
Volumetric air content in vadose-zone soils	θ_A	(cm ³ air)/(cm ³ soil)	0.26	ASTM (1996)
Total soil porosity	θ_T	(cm ³ voids)/(cm ³ soil)	0.38	ASTM (1996)
Volumetric water content in vadose- zone soils	θ_W	(cm ³ water)/(cm ³ soil)	0.12	ASTM (1996)
Soil bulk density	ρ_b	g/cm ³	1.7	ASTM (1996)
Averaging time for vapor flux, residential adult	τ_{ur}	s	7.57E8	ASTM (1996) = ED _r in sec
Averaging time for vapor flux, residential child	τ_{uc}	s	1.89E8	ASTM (1996) = ED _c in sec
Averaging time for vapor flux, commercial/industrial	τ_{uci}	s	7.88E8	ASTM (1996) = ED _{c/i} in sec
Averaging time for vapor flux, utility worker	τ_{ut}	s	3.15E7	ASTM (1996) = ED _{ut} in sec
Effective diffusion coefficient in soil	D_{eff}	cm ² /s	Chem. specific	calculated
Diffusion coefficient in air	D_{air}	cm ² /s	Chem. specific	See Table 7.
Diffusion coefficient in water	D_{water}	cm ² /s	Chem. specific	See Table 7.
Organic carbon-water sorption coefficient	K_{oc}	mL/g	Chem. specific	See Table 7.
Henry's Law coefficient	H	(cm ³ water)/(cm ³ air)	Chem. specific	See Table 7.

References:

ASTM. 1996. Standard Guide to Risk-Based Corrective Action Applied at Petroleum Release Sites, ASTM E1739-95, Philadelphia, PA.

Table 7: Chemical Parameter Values

Chemical Parameters	Units	Benzene	Ethyl-benzene	Naphthalene	PAH ¹	Reference
Henry's Law constant	-	0.23	0.32	0.02	2.0E-5	SF RWQCB ESLs
Organic carbon partition coefficient	ml/g	58.9	360	1200	5.5E+6	SF RWQCB ESLs
Diffusion coefficient in air	cm ² /s	0.088	0.075	0.059	ND	SF RWQCB ESLs
Diffusion coefficient in water	cm ² /s	9.8E-6	7.8E-6	7.5E-6	ND	SF RWQCB ESLs
Toxicity Parameters						
Oral slope factor (SF _o)	1/(mg/kg-d)	0.1	0.011	ND	1.7	OEHHA (2009, 2010 – BaP PHG)
Inhalation unit risk (IUR)	1/(µg/m ³)	2.9E-5	2.5E-6	3.4E-5	1.1E-3	OEHHA (2009)
Oral reference dose (RfD _o)	mg/kg-d	0.004	0.1	0.020	ND	USEPA IRIS
Reference concentration (RfC)	mg/m ³	0.060	2	0.009	ND	OEHHA RELs
Dermal absorption factor from soil	-	ND	ND	0.13	0.13	SF RWQCB ESLs
Gastrointestinal absorption factor	-	1	1	1	1	SF RWQCB ESLs

ND = No Data

SF RWQCB ESLs. Regional Water Quality Control Board (RWQCB) Region 2 – San Francisco. 2008. Screening for Environmental Concerns at Sites with Contaminated Soil and Groundwater. Interim Final. May

OEHHA (2009). OEHHA Cancer Potency Values as of July 21, 2009.

OEHHA RELs. OEHHA Chronic Reference Exposure Levels (RELs). <http://www.oehha.ca.gov/risk/chemicaldb/>

USEPA IRIS. USEPA Integrated Risk Information System on-line database.

¹ The chemical properties for benzo(a)pyrene were used as a surrogate for the “PAH” group.

Table 8: Soil Screening Levels for Each Receptor

Chemical	Residential		Commercial/ Industrial		Utility Worker
	0 to 5 feet bgs mg/kg	Volatilization to outdoor air (5 to 10 feet bgs) mg/kg	0 to 5 feet bgs mg/kg	Volatilization to outdoor air (5 to 10 feet bgs) mg/kg	0 to 10 feet bgs mg/kg
Benzene	1.9	2.8	8.2	12	14
Ethylbenzene	21	32	89	134	314
Naphthalene	9.7	9.7	45	45	219
PAH*	0.063**	NA	0.68	NA	4.5

* Based on the seven carcinogenic PAHs as benzo(a)pyrene toxicity equivalent [BaPe]. The PAH screening level is only applicable where soil is affected by either waste oil and/or Bunker C fuel.

** DTSC (2009) reports average ambient PAH concentrations (as BaPe) in California ranging from 0.16 to 0.21 mg/kg, and upper tolerance limits (UTLs) ranging from 0.9 to 1.5 mg/kg. The screening level shown in this table is “risk-based” and therefore in this case is far below the average ambient concentrations for PAHs in California. It is suggested that DTSC (2009) be consulted for sites with PAH contamination.

NA = Not Applicable

FIGURES

Figure 1. Conceptual Site Model for the Soil Screening Levels.

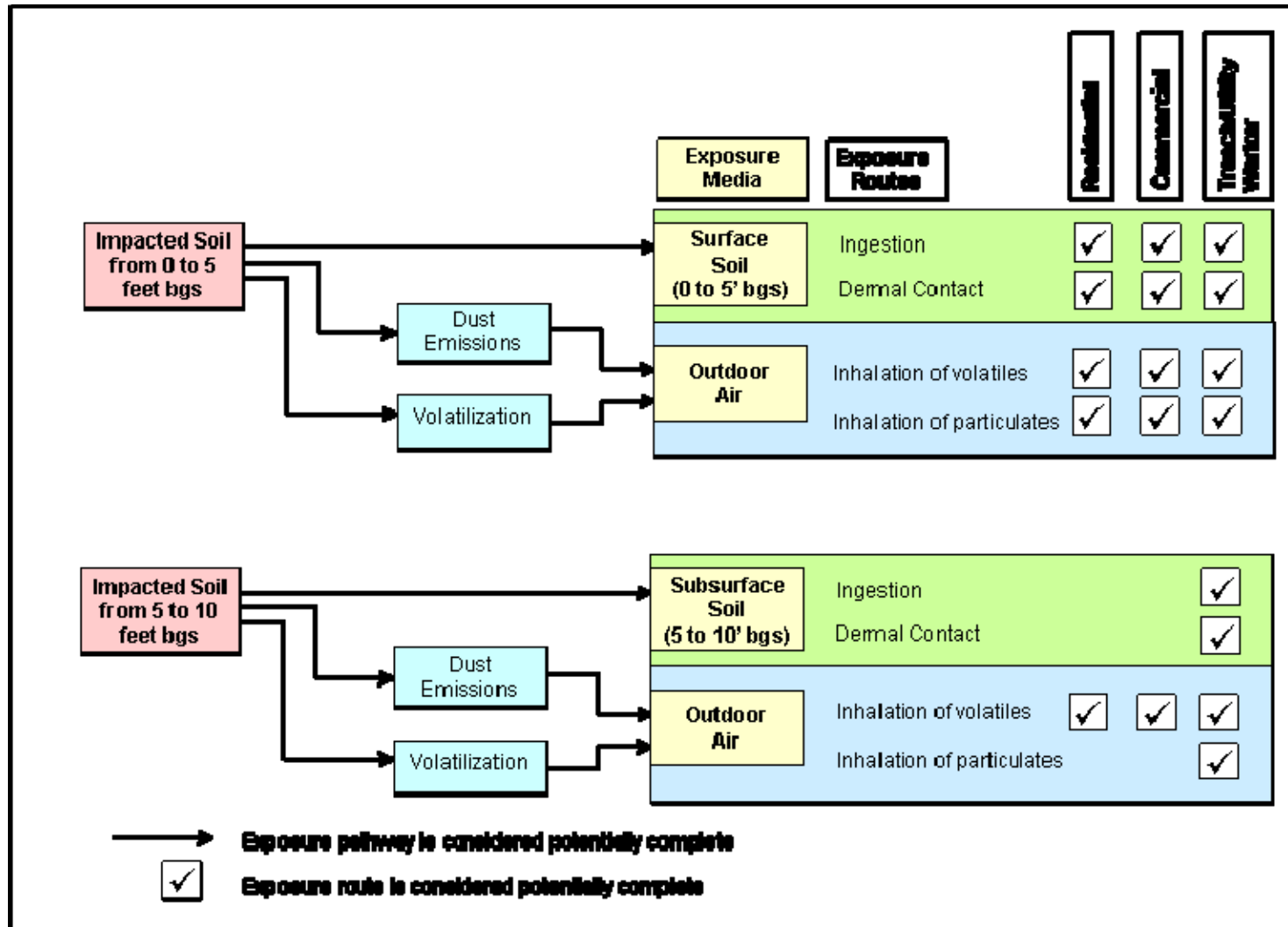


Figure 2. Schematic for the ASTM Volatilization Factor.

