Technical Justification for Groundwater Media-Specific Criteria

(Final 04-24-2012)

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 (C^6 to C^{11}) monoaromatics (benzene, toluene, ethylbenzene, and xylenes [BTEX] and the alkylated benzenes);
- C^{10} to C^{14} polyaromatic hydrocarbons (PAHs) (naphthalene, alkylated naphthalenes, acenaphthene, fluorene, phenanthrene, and anthracene); and
- C^6 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 and 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.

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