

## Attachment 5

### Technical Justification for Groundwater Media-Specific Criteria 11-7-11

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 (Policy). The fifth plume class is a site-specific evaluation.

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; API 1998); other researchers (Dahlen et al. 2004; Shih et al. 2004) studied both benzene and oxygenate plumes, including MTBE. Many of these plume characteristic studies are discussed in greater detail in the Fate and Transport chapter of the California LUFT Manual (SWRCB, 2010). Many of the researchers recognized benzene, MTBE, and 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* reports benzene, MTBE and TPHg plume characteristics as follows:

Constituent (and plume limit concentration)	Average Plume Length (feet)	90 <sup>th</sup> 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

Note: plume lengths were measured from the source area.

Although the California MCL for benzene is 1 µg/l, the *Shih et al.* 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. found that benzene plume lengths may increase by 40% to 70% when gasoline is formulated with 10% ethanol substituting for MTBE. Ethanol preferentially biodegrades prior to benzene, which results in a longer benzene plume.

Biodegradation/natural attenuation of petroleum hydrocarbon and oxygenate plumes has been documented by many researchers since the 1990s. This body of work demonstrates that biodegradation/natural attenuation of petroleum hydrocarbons and MTBE occurs under both aerobic and anaerobic conditions (Howard, 1990). The rate of degradation/attenuation depends on the constituent and the plume bio/geochemical conditions.

TBA is an intermediate byproduct of the biodegradation of MTBE. TBA concentrations may therefore initially increase in the anaerobic portion of a degrading 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) 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.

### **Diesel**

Researchers do not consider TPHd to be a key indicator of plume lengths largely because the hydrocarbons in the TPHd carbon range are of low solubility and therefore create plumes which are usually shorter than those associated with gasoline releases. Most of the TPHd carbon range (approximately C12 to C22) is greater than the carbon range of the most common solubility-limited hydrocarbons (i.e. those less than or equal to C14).

It is well documented that effective solubility limits the concentrations of hydrocarbons that will dissolve into groundwater from petroleum fuel releases (including gasoline, kerosene, jet fuel, diesel or heavier fuels). Dissolved petroleum constituents are commonly limited to light aliphatic hydrocarbons less than C7 and aromatics less than C14 (e.g., Shiu et al. 1990; Coleman et al. 1984). The C15 and larger hydrocarbons have very low effective solubilities and are not often found in the dissolved phase of a petroleum fuel release. The concentrations of dissolved hydrocarbons in groundwater

whose carbon range is less than or equal to C14 is effectively measured by the TPHg method, which quantifies the concentration of hydrocarbons in the range of approximately C5 to C12. Therefore, a TPHg analysis should be sufficient to quantify dissolved hydrocarbons that may be present in addition to benzene and MTBE from the most common types of petroleum UST releases. 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. Therefore, MTBE can be used as a conservative plume length benchmark for all fuel oxygenates, including TBA. However, if a plume resulting from a petroleum release contains petroleum constituents other than TPHg, benzene, or MTBE (e.g. TBA, toluene, ethylbenzene, etc.) in concentrations greater than water quality objectives, and the plume length exceeds the limiting plume length of the scenario for which it would otherwise qualify, the site should be considered to display “unique site attributes” that disqualify it for consideration of low-threat closure.

Researchers recommend applying silica gel cleanup to groundwater samples prior to analyzing them for dissolved hydrocarbons quantified as TPHd. If SGC is not used, the reported TPHd concentration may include polar non-hydrocarbon compounds (e.g., Zemo and Foote 2003) derived from various sources. These sources often include petroleum biodegradation metabolites (primarily alcohols and organic acids, with possible phenols, aldehydes and ketones), but may also include decay products of naturally occurring organic matter. In some cases researchers have demonstrated that without performing SGC the majority of organics quantified as TPHd are polar compounds and not dissolved hydrocarbons. The San Francisco Bay RWQCB recognized that non-SCG laboratory-quantified TPHd concentrations may include polar compounds. The SFRWQCB 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).

Some regulatory agencies have expressed concern that SGC also removes some fraction of the dissolved hydrocarbons from groundwater samples. Lundegard and Sweeney (2004) concluded that SGC does not remove the dissolved hydrocarbons in a sample. Further, the potential for removal of hydrocarbons by SGC is always evaluated during routine laboratory quality assurance/quality control (QA/QC) procedures. These procedures include analyzing laboratory control samples spiked with a hydrocarbon surrogate, performing SGC, measuring surrogate recovery, and reporting whether the result is within acceptable ranges.

## **Low-Threat Groundwater Classes**

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. Additionally, “low-threat classes” require a known maximum stabilized plume length, which reduces uncertainty as to how long the plume might become in the future. The draft low-threat 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]).

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 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 (<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 µg/l) and MTBE (1,000 µg/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. 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 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 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.

### **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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