

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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