Appendix M
State MTBE Draft Guidelines

FINAL DRAFT – 3/27/2000
Guidelines for Investigation and Cleanup of MTBE and Other Ether-Based Oxygenates

Overview

This document has been developed in response to Executive Order D-5-99 and Senate Bill 989 (Sher -- Chapter 812, Statutes of 1999). It is intended to assist managers and staff at state and local regulatory agencies with the task of overseeing the investigation and cleanup of sites where there have been or may have been releases of MTBE-laden petroleum. This document will serve as a basis for reporting to Cal/EPA and the legislature regarding progress made on cleaning up MTBE.

The essence of this document is the understanding that the standard approach for dealing with petroleum releases employed over the past decade will not suffice for MTBE, because unlike traditional petroleum constituents such as benzene, MTBE moves quickly to pollute water and is slow to degrade in the subsurface environment. Response time is critical for MTBE. A quick response to a release greatly increases the ability to check the spread of the MTBE and to clean up the mass of the release. Because time is critical, regulators will need to prioritize their cases and give first attention to those that pose the greatest risk to groundwater. It is also expected that there will be more need for vertical definition of MTBE plumes and more reliance on active cleanup technologies, such as soil vapor extraction, in situ groundwater remediation, and groundwater pump and treat systems, than there has been for non-MTBE petroleum.

Lead agencies are expected to understand the extent of MTBE releases in their jurisdiction, the proximity of those plumes to nearby receptors (ie. drinking water wells and surface water supplies), and the approximate travel time for the plume to reach the receptor. With this information, lead agencies will be able to direct resources to those sites where the plumes are most likely to impact a nearby receptor. A two-phase priority classification system to allocate resources during investigation and cleanup is presented to help accomplish that task. Technical references are included.

This document does not address the question of when to cease corrective action at an MTBE site. Existing SWRCB policies and resolutions provide guidance for determining the appropriate conditions for site closure.

Introduction

Executive and Legislative Mandates

Governor Davis issued Executive Order D-5-99 on March 25, 1999, and signed Senate Bill 989 on October 8, 1999. These documents recognize that if not managed properly, MTBE can cause significant adverse impacts to current and future beneficial uses of ground and surface water.

The Executive Order contains eleven items that include tasks for various state departments and boards. Among these, item 8 directs the State Board to proceed to identify areas that are most vulnerable to MTBE, prioritize resources, and to provide guidelines for the cleanup of MTBE in groundwater.

> *8. The State Water Resources Control Board (SWRCB), in consultation with the Department of Water Resources and the Department of Health Services (DHS), shall expeditiously prioritize groundwater recharge areas and aquifers that are most vulnerable to contamination by MTBE*

> *and prioritize resources towards protection and cleanup. The SWRCB, in consultation with DHS, shall develop a clear set of guidelines for the investigation and cleanup of MTBE in groundwater at these sites."*

Senate Bill 989, introduced by Senator Sher, also directs the State Board to identify areas most vulnerable to groundwater contamination, prioritize resources, and to develop investigation and cleanup guidelines.

> … "the State Water Resources Control Board, in consultation with the Department of Water Resources and the State Department of Health Services, shall identify areas of the State that are most vulnerable to groundwater contamination by MTBE or other ether based oxygenates. The State Water Resources Control Board shall direct resources to those areas for protection and cleanup on a prioritized basis." …

> … "The Board, in consultation with the State Department of Health Services, shall develop guidelines for the investigation and cleanup of MTBE and other ether-based oxygenates in groundwater. The guidelines shall include procedures for determining, to the extent practicable, whether the contamination associated with an unauthorized release of MTBE is from the tank system prior to the system's most recent upgrade or replacement or if the contamination is from an unauthorized release from the current tank system." …

Applicability

These guidelines are intended for use by Regional Water Quality Control Boards and local agencies to assist in the investigation and cleanup of MTBE impacted sites. The document identifies areas most vulnerable to groundwater contamination, provides a priority ranking of MTBE sites, outlines a decision making framework for determining appropriate actions at sites, and proposes a timeframe for completing site management milestones.

Regulatory Authority

The authority for requiring investigation and cleanup exists in the Porter-Cologne Water Quality Control Act, Health and Safety Code, Underground Storage Tank Regulations, Regional Board Basin Plans, and State Board Policies. These guidelines are not intended to create any new authority, but rather, to help regulators direct resources and manage cases to maximize water quality restoration and protection when faced with widespread MTBE impacts. If the lead agency believes that action other than that described in these guidelines is appropriate, the agency may provide an alternative course of action. These guidelines may not be used by a responsible party to argue that any investigation or cleanup activity should proceed At a slower rate than ordered by the lead agency.

The guidelines are also not intended to set cleanup levels or other closure criteria. Existing SWRCB and RWQCB plans and policies provide guidance for determining the appropriate conditions for site closure. These include SWRCB Resolution 92-49, SWRCB decisions on UST appeal cases, and RWQCB Basin Plans.

Background

Methyl Tertiary Butyl Ether (MTBE) has been added to gasoline to enhance octane and to comply with clean air act mandates. It was approved by the USEPA for use in 1979 and was added to gasoline during the 1980s at approximately 2-5% by volume as an octane booster. In 1992, it was blended at 10-15% by volume for use in some areas in the wintertime oxygenated fuel program. In 1996, it began to be used year round at 11% by volume in the statewide reformulated gasoline program.

Relative to other fuel hydrocarbons, MTBE has a high solubility in water. The compound has low retardation in groundwater aquifers, and is slow to biodegrade. These properties, combined with a high percentage in gasoline, cause the potential for high source area concentrations, long plumes in groundwater, and long residence times in the subsurface. It also has taste and odor characteristics that can impair water supplies at very low concentrations.

There have been impacts on drinking water wells at dozens of sites in California, most notably in Santa Monica and South Lake Tahoe. In addition, there are thousands of underground storage tank (UST) sites with MTBE detected in the groundwater. Other sources of MTBE release to the environment include above ground storage tanks, spills, pipelines, etc.

Other Oxygenates and Breakdown Products

Tertiary butyl alcohol (TBA) is often present as a by-product of MTBE production and is also suspected to be a primary breakdown product of MTBE in the environment. In addition, several other ethers have been used as oxygenates in gasoline such as tertiary amyl methyl ether (TAME) and ethyl tertiary butyl ether (ETBE). Because their use has not been as widespread, it is unlikely that they will prove to be as great a threat as MTBE at most sites. However, it is prudent to analyze for these additional compounds during the initial investigation to determine if they are present. If other oxygenates are determined to be present in sufficient quantities to adversely affect beneficial uses, these compounds should be included in the remediation plan for the site. For screening purposes, it may be useful to add the concentration of other ether oxygenates to the concentration of MTBE and treat the sum as “MTBE equivalents”.

The currently accepted analytical protocol for groundwater samples suspected of containing ether oxygenates and TBA is EPA Method 8260B. EPA Method 8020/8021 may be used for MTBE analysis if EPA Method 8260B is used to confirm positive detections. Significant interference and false detections can occur when MTBE is analyzed in the presence of petroleum hydrocarbons using EPA Method 8020/8021. When other hydrocarbons are present in the sample, EPA Method 8260B is the preferred method. The ether oxygenates and TBA are not included in the standard list of analytes for EPA Method 8260B or 8020/8021 and therefore must be specifically requested when submitting samples to a laboratory for analysis. Selected physical properties of MTBE and other oxygenates are presented in Appendix A.

Early Detection of MTBE Releases

Early detection and quick response are key to successful remediation of MTBE releases. Agencies providing investigation and cleanup oversight should work closely with local UST permitting agencies. Appendix D provides a list of actions that may be taken at a site to determine if a UST system is leaking. An effective leak prevention and response plan includes at a minimum:

- UST leak detection systems
- Periodic inspections of UST systems
- Reporting known spills

Role of the Cleanup Fund

The UST Cleanup Fund (Fund) administered by the Division of Clean Water Programs will play a crucial role in implementation of these guidelines. In order for tank owners and operators to meet the time frames specified for higher priority MTBE cases, the Fund will need to process claim applications, letters of commitment, cost approvals and payments in a timely manner. This will likely require the Fund to identify MTBE claims and modify procedures to quickly turn-around approvals and payments for these claims. Fund management should consult with claimants, contractors, and regulators to identify needs, and make any necessary procedural changes consistent with Fund statutes.

Definition of Areas Most Vulnerable to Groundwater Contamination

For the purposes of these guidelines, a site is in a most vulnerable area if it has one or more of the following characteristics:

1) Located within a 1000 ft radius of a drinking water well or surface water body used as a source of drinking water.

2) Located on near-surface fractured bedrock geology that is a source of water supply for a community.

3) Located above an aquifer that is a source of water supply for a community.

4) Located in an area designated as having a high degree of hydrogeologic susceptibility to contamination as shown on the statewide map compiled from Department of Water Resources (DWR) and United States Geological Survey references by the SWRCB in consultation with DWR, the Department of Health Services, and Regional Water Quality Control Boards.

Tracking and Reporting Progress

Tracking the progress of investigations and cleanups is an important aspect of case management. The SWRCB will be creating and distributing a variety of reports based upon data submitted by Regional Boards and local agencies to track the progress of MTBE investigation and remediation in response to the Governor's executive order and SB 989. To accomplish this, accurate and timely data will need to be submitted to the SWRCB by RWQCBs and local agencies who are conducting LUST regulatory oversight through the Geographic Environmental Information Management System maintained by the SWRCB. Some of the questions that will be addressed by these reports are as follows:

- How many sites are in each threat classification?
- Which sites are actively remediating MTBE in soil or groundwater?
- How many pounds of MTBE have been removed?
- Which sites have not received regulatory direction?
- Which sites are delinquent in responding to a regulatory directive?
- Which sites are in enforcement?
- How many sites have been closed?

Site Investigation and Remediation Decision-Making Framework

These guidelines provide a framework for prioritizing resources to work on sites with MTBE or other oxygenates. Lead agencies are in the best position to understand the extent of MTBE releases in their jurisdiction, the proximity of those plumes to nearby receptors, and the approximate travel time for the plume to reach the receptor. With this information, lead agencies can direct resources to those sites where the plumes are most likely to impact a nearby receptor. The site investigation and remediation decision-making framework presented in this section provides a method to accomplish that task.

The decision-making framework centers around the development and continual modification of the site conceptual model (SCM). The SCM is the progressive assemblage of information regarding the distribution of chemicals at a site and its hydrologic setting. The SCM describes the release scenario, surrounding land use, geology, well locations, and the likely distribution of chemicals at the site, existing and projected water use patterns, and other factors considered when making decisions about a case. It functions as the framework for the investigation, remediation, and ultimately the closure of the site and serves as the basis for communication between responsible parties, regulators, and other interested parties.

Always ready to be changed to better reflect real-world conditions, the SCM is checked and updated when new data become available.

If MTBE is detected in the groundwater at a site, the regulatory caseworker should develop a preliminary SCM, identify the appropriate investigation priority classification, and require the responsible party to conduct the appropriate investigation or interim remediation. The responsible party conducts any required investigation and submits a more detailed SCM to the regulatory agency along with the investigation report. Each subsequent investigation requirement seeks to fill a data gap to clarify the SCM. After the source area and pathways to receptors have been adequately characterized, an appropriate remedial alternative can be selected and implemented. Some sites, however, may require expedited interim remedial action prior to completion of the site investigation. Subsequent reports from responsible parties describe how the information submitted confirm or change the SCM. A suggested format for the SCM is included in Appendix C.

The investigation priority classifications presented below in Step 2 are intended to be *initial* classifications for prioritization of investigation resources. As more detailed information becomes available, the site should be reevaluated and, if appropriate, the investigation priority class changed. When enough information has been collected during the investigation to adequately determine the travel time of the plume to the receptor, a cleanup priority class is assigned and resources directed appropriately. Resources should be directed to those sites that pose the greatest and most immediate threat to nearby receptors.

For further information regarding site investigation, remediation, and the development of site conceptual models, please see the references in Appendix B. A description of the 7-step decision-making framework is included below. It should be noted that the steps listed need not be completed sequentially but may occur whenever the lead agency determines is appropriate.

1) Initial Investigation/Scoping
2) Develop Initial Conceptual Model/Assign Investigation Priority Class
3) Interim Remedial Action
4) Site Characterization/Investigation
5) Update Conceptual Model/Assign Cleanup Priority Class
6) Corrective Action/Remediation
7) Verification Monitoring

Step 1. Initial Investigation/Scoping

The basic data necessary to classify the site is collected during this initial step. These data include the distance to receptors (drinking water wells and surface water supplies) in the vicinity and the concentration of MTBE present in the subsurface at the site.

To determine if MTBE is present at the site, the responsible party should be directed to collect representative groundwater samples for MTBE analysis. If the site is not conducive to groundwater sampling, the lead agency may allow other methods to be substituted during this initial investigation to determine the presence or absence of MTBE. These methods may include collection of soil samples or soil vapor samples beneath areas of suspected release. Expedited site assessment techniques may be useful during this step. Further information on expedited site assessment is contained in the references in Appendix B.

It is assumed that a search of the state GIS mapping database will be the minimum level of effort used to determine the location of wells in the vicinity of the site. A more thorough well search should be completed during the investigation phase and the results reflected in the cleanup priority classification. If wells are suspected to be in the area but their exact locations are unknown, the site should be given a higher investigation priority classification rather than differing classification until more information is available. The investigation priority classification may be changed later if warranted.

Step 2. Develop Preliminary Site Conceptual Model/Assign Investigation Priority Classification

Each agency should examine their portfolio of cases and classify them based on the estimated travel time to the nearest receptor or other factors (such as geology) that the agency feels is pertinent to their jurisdiction. Many sites may have additional information beyond that collected in the initial scoping phase. All relevant site data should be used in this step to obtain the most accurate preliminary SCM and investigation priority classification. Sites which are determined to pose the greatest threat should be given the greatest share of resources and be tracked more closely to assure a timely and effective investigation.

Figure 1. represents an initial estimation of the MTBE travel time to the nearest receptor (drinking water well or surface water source). The curved portion of the two lines separating sections A, B, and C, represent the theoretical contaminant travel time generated by a computer model (the A/B line corresponds to a travel time of 1 year and the B/C line corresponds to a travel time of 20 years). The computer model used is a statistical simulation of a three-dimensional transport equation. The model uses a conservative set of assumptions (groundwater velocities, source area, dispersivity, constant concentration, constant source, and constant velocity). Since the preferred gradient direction (ie. direction of plume travel) is unknown, the model projects that the plume forms an expanding circle around the site. These graphs may be used to screen sites and assign initial investigation priorities, but should not be used as a predictor of actual travel times for plumes.

When a new site is added to the portfolio of active cases, it can be classified according to the criteria listed below. The agency should review the classifications and priorities at least annually to determine if new information has been received that would change the priority of sites. The following is a recommended initial investigation classification system:

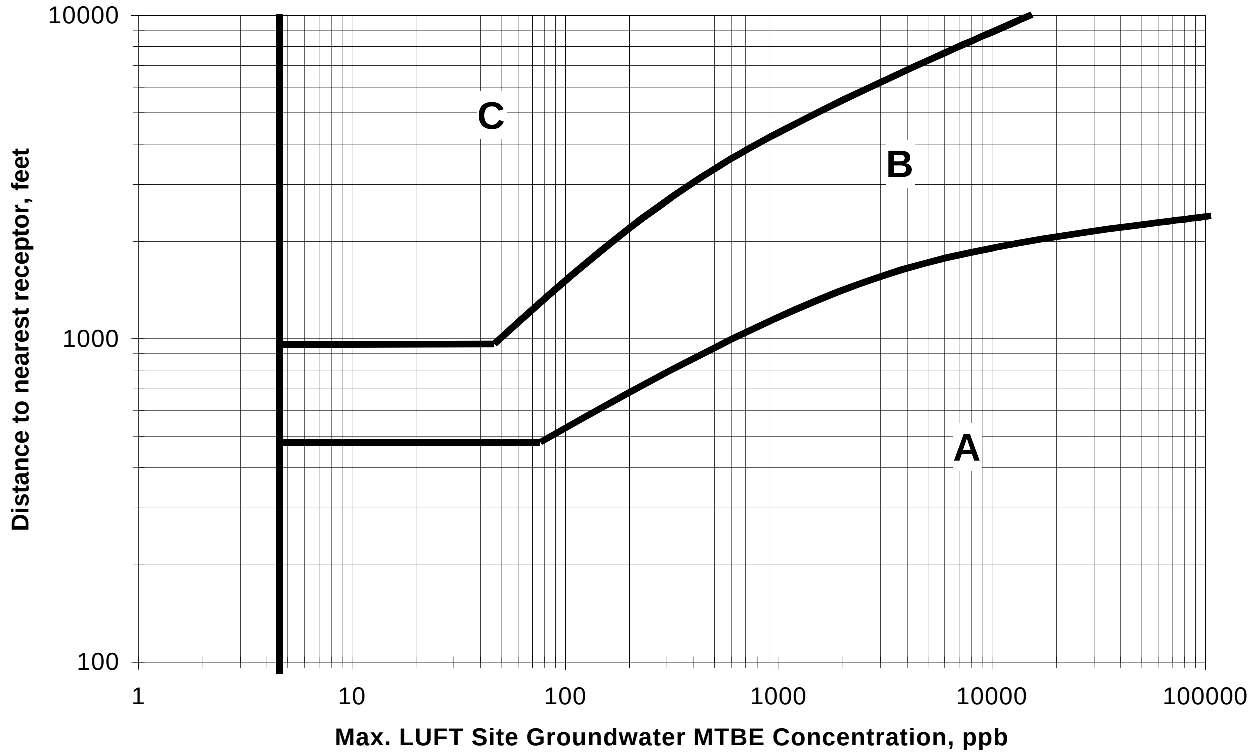
Class A:
Criteria: See Figure 1
Regulatory Response Timing: Conduct case review and send directive letter within 30 days after notification of MTBE release. Determine cleanup priority classification as soon as possible, not later than one year after notification or discovery of MTBE release.

Class B:
Criteria: See Figure 1
Regulatory Response Timing: Determine cleanup priority classification within two years after notification or discovery of MTBE release.

Class C:
Criteria: See Figure 1
Regulatory Response Timing: Determine cleanup priority classification within three years after notification or discovery of MTBE release.

Class D:
Criteria: Not located in an area that is most vulnerable to contamination and has concentrations of MTBE in groundwater over 5 ppb.
Regulatory Response Timing: Determine cleanup priority classification within five years after notification or discovery of MTBE release.

Figure 1. - Investigation Priority Class (A, B, or C)
(Sites Located in Most Vulnerable Areas)
note: log/log scale



Step 3. Interim Remedial Action
Sites with high concentrations and a large release mass should have those concentrations and mass reduced before the plume can spread regardless of their priority classification. For example, sites with free product or persistent concentrations over 10,000 ppb MTBE in the groundwater are candidates for source area remediation as an interim remedial action. Long-term impacts to water quality and financial resources are likely to be reduced if interim remediation is performed in these situations. If the MTBE plume imminently threatens a well, interdiction wells to contain the plume may be necessary. Conversely, if the investigation data indicate a low potential threat, either because the mass of MTBE released is small, migration to drinking water wells is highly unlikely, or other relevant factors exist, then this interim remedial action would not be necessary. The SCM is updated with any new data that is collected while taking interim remedial actions.

It is extremely important for the agency providing cleanup oversight and the tank permitting agency to work together to identify the source of the MTBE in the subsurface (tank, pipe joint, spill bucket, surface spill, etc.) when an ongoing release is suspected at an operating UST. If this step is not completed and an ongoing leak is allowed to continue, the potential success of any attempted remediation will be reduced. A summary of suggested methods for determining the source of leaks in tank systems is included in Appendix D.

Step 4. Site Characterization/Determine Plume Travel Time
In this step, additional data is gathered regarding the distribution of contaminants in the subsurface, the location of any nearby receptors (drinking water wells or surface water sources), and the potential for

migration of contaminants to receptors. Estimating the approximate travel time for a contaminant plume to reach a nearby receptor is a key part of the investigation. This estimation will serve as a basis for the next step in the process, assigning a cleanup priority classification.

Geologic data that has already been collected from nearby sites can provide an overview of what conditions may be encountered beneath the site. For example, an uninterrupted vertical profile of the stratigraphy by continuous core or cone penetrometer can help verify if the regional conceptual model of the geology applies to this site. If the conceptual model using regional data implies that persistent downward vertical groundwater gradients may exist, these gradients and the vertical extent of MTBE impacts should be investigated using cluster wells or other methods. The converse is also true; sites located in areas with known upward gradient may not require site specific assessment of vertical migration.

At some sites, there may be information available that will allow an estimation of the magnitude of petroleum released (ie. amount of free product, amount of impacted soil, inventory records documenting a release, etc.). Although these data can help infer whether the release was relatively large or small, detailed estimates of mass or volume released have historically proven to be highly inaccurate. Therefore, while knowledge of the relative magnitude of the release can help guide remedial decisions, attempting to precisely quantify the number of gallons or pounds released is not recommended.

The SCM is continually updated during this process. Also, the SCM should be compared to the SCM for other sites in the agency's portfolio on a regular basis. If it becomes apparent that the site in question does not pose a threat to any nearby receptors in the near future and other sites may pose a higher threat, resources should be directed to those other sites before the investigation is fully completed.

Note: Determining the plume travel time is not intended to be an end in itself nor a detailed effort requiring extensive computer fate and transport modeling. Conservative estimates based upon literature values for aquifer properties, average site groundwater gradients, and zero retardation can be quickly made. Installation of a guard well in the down gradient direction can provide early detection if the rough estimate of travel time is not sufficiently accurate.

Step 5. Update Conceptual Model/Assign Cleanup Priority Classification

This step, assigning a cleanup priority, occurs after sufficient data has been collected to estimate the travel time for the contaminant plume to reach a receptor. At this point in the process, the site is given a priority for remediation based upon the estimated plume travel time to the nearest down-gradient receptor, timeframe for intended use of the aquifer, or other criteria determined by the lead agency. At a minimum, each agency should review their cases annually to determine if the site's priority classifications should be changed based upon new data that has been received. It should be noted that non-water quality related issues may require work sooner than expected (e.g. legislative requests, redevelopment, property transfers, etc.).The following is a suggested cleanup priority system, summarized in Table 1:

Class 1:
Criteria: Groundwater MTBE plume travel time to nearest downgradient receptor: < 5 years

Regulatory Response Timing: Implement remedial action plan as soon as possible, not later than 1 year after determination of cleanup priority class:

Class 2:
Criteria: Groundwater MTBE plume travel time to nearest downgradient receptor: > 5 years and < 20 years

Regulatory Response Timing: Implement remedial action plan within 5 years after determination of cleanup priority class.

Class 3:
Criteria: Groundwater MTBE plume travel time to nearest downgradient receptor: > 20 years

Regulatory Response Timing: Direct cleanup resources to these sites after sites in classes 1 and 2 have been addressed.

Table 1 - Cleanup Priority Classification Criteria

Cleanup Priority Class	Groundwater plume travel time to nearest downgradient receptor (years)	Regulatory Response Timing (years)
1	< 5	1
2	5 - 20	5
3	> 20	-

Step 6. Corrective Action / Remediation
When the lead agency determines that a site requires remedial action, those actions should be taken expeditiously. In general, the type of response actions taken at MTBE release sites will be similar to the type of actions taken at traditional petroleum releases. The primary difference is that responses to MTBE will need to be swifter and more aggressive to reduce the spread of MTBE to a wider area. Remedial alternatives may include, but are not limited to, the following either individually or in combination:

- Soil excavation and/or dewatering of source areas
- Soil vapor extraction
- Groundwater extraction and above-ground treatment
- Flow-through remediation cells/in-situ bioremediaton
- Free product removal
- In-situ air sparging
- Soil vapor extraction/dual phase extraction

Removing MTBE from the subsurface at high concentrations is much more cost effective than extracting water or vapor with low concentrations. At many sites, aggressive interim remediation in the source area can help diminish the chances of creating a large diluted plume of MTBE. Large dilute plumes are more difficult to remediate and have impacts that are more widespread. In many cases, source area remediation may reduce subsurface impacts sufficiently to protect surrounding water quality. Sites with plumes that could impact drinking water wells may need to have plume containment measures implemented. This may include groundwater extraction and treatment at onsite or offsite remedial extraction wells. For more information regarding the details of implementing these technologies, please refer to the references in Appendix B.

Step 7. Verification Monitoring

Periodic groundwater monitoring is used to supplement the initial assessment data, and to confirm assumptions about the site conceptual model. The objective of groundwater monitoring is to determine if the site conditions will meet regulatory requirements and may include evaluating seasonal changes in site conditions, documenting evidence of source depletion, evaluating plume stability or migration, or assessing the effectiveness of corrective actions. If there is reason to believe downward migration of contaminants may be occurring, clustered monitoring wells or other methods of determining vertical gradients should be used to determine the extent that vertical migration occurs.

While assessment strategies may differ between BTEX and oxygenates, periodic monitoring strategies are similar. The potentially more rapid rate of migration of oxygenates should be considered when determining an appropriate sampling frequency and monitoring well spacing.
Data from periodic monitoring should be interpreted and summarized using potentiometric contour maps and isoconcentration contour maps.

Variations in concentration over time at individual wells can be used to understand source depletion and potential hydraulic influences on plume migration. Concentrations may be analyzed over distance along a plume centerline to assess plume stability and thus potential threat to nearby receptors. Concentrations of oxygenates and other constituents of concern can be determined over time at appropriately located monitoring points downgradient of the source and oriented along the direction of ground water flow. The trend in concentrations at these points will confirm whether the plume is shrinking, stable, or expanding (e.g. if the plume is shrinking, concentrations will decrease over time or space; if the plume is stable, concentrations will remain relatively constant over time and space). For further discussion, refer to the references listed in Appendix B.

Appendices:

A Physical/chemical properties of oxygenates
B Technical references
C Site conceptual model reports
D Finding leaks in tank systems

Appendix A
Physical Properties of BTEX and Oxygenates

	Pure Phase Solubility[1]	log K_{oc}[2]	Vapor Pressure[3]	Henry's Law Constant[4]	Retardation Factor[5]	
	mg/L	log l/kg	mm Hg	Dimensionless	Soil Condition A[6]	Soil Condition B[7]
Benzene	1,780	1.5 - 2.2	76 - 95.2	0.22	1.59	3.38
Toluene	535	1.6 - 2.3	28.4	0.24	1.75	3.99
Ethylbenzene	161	2.0 - 3.0	9.5	0.35	3.66	11.6
m-Xylene	146	2.0 - 3.2	8.3	0.31	4.34	14.4
Ethanol	Miscible	0.20 - 1.21	49 - 56.5	0.00021 - 0.00026	1.04	1.17
Methanol	Miscible	0.44 - 0.92	121.6	0.00011	1.04	1.16
TBA	Miscible	1.57	40 - 42	0.00048 - 0.00059	1.31	2.25
MTBE	43,000 - 54,300	1.0 - 1.1	245 - 256	0.023 - 0.12	1.09	1.38
ETBE	26,000	1.0 - 2.2	152	0.11	1.33	2.34
TAME	20,000	1.3 - 2.2	68.3	0.052	1.47	2.89
DIPE	2,039 - 9,000	1.46 - 1.82	149 - 151	0.195 - 0.41	1.37	2.47

Notes:

Data from Zogorski et al. (1997). Values at 20 or 25 °C
TBA: tertiary butyl alcohol
MTBE: methyl tertiary butyl ether
ETBE: ethyl tertiary butyl ether
DIPE: di-isopropyl ether

1 = The propensity of a chemical to dissolve into water, expressed in milligrams of chemical per liter of water.

2 = The propensity of a chemical to adsorb to soil. Defined as the ratio of the concentration of the chemical adsorbed onto organic carbon to the concentration of the chemical dissolved in water

3 = The propensity of a chemical to migrate from NAPL to the gas phase. The vapor pressure of a chemical is the pressure exerted by the gas phase when it is in equilibrium with the liquid phase.

4 = The propensity of a chemical to partition between the dissolved phase and the gas phase. The Henry's Law Constant is defined as the ratio of the equilibrium concentration of the chemical in the gas phase to the equilibrium concentration of the chemical in water.

5 = The average velocity of plume migration for a chemical will typically be lower than the average velocity of the associated groundwater. The retardation factor is the ratio of the velocity of the groundwater to the velocity of the associated chemical plume. This factor is calculated; a function of soil bulk density, soil effective porosity, soil organic carbon content, and the organic carbon partitioning coefficient of the chemical.

6 = Soil Condition A: $f_{oc=}$0.001 mg/mg, bulk density=1.75 kg/L, porosity=0.25

7 = Soil Condition B: $f_{oc=}$0.004 mg/mg, bulk density=1.75 kg/L, porosity=0.25

Appendix B

Technical References

Site Investigation / Conceptual Model

1. Expedited Site Assessment Tools For Underground Storage Tank Sites – A Guide For Regulators (USEPA, Office of Underground Storage Tanks, March 1997)

2. Strategies for Characterizing Subsurface Releases of Gasoline Containing MTBE, American Petroleum Institute, API Publication No. 4699

3. Course manual "Assessment and Management of MtBE Impacted Sites", SWRCB & USEPA, 1999

4. Guidelines for Hydrogeologic Characterization of Hazardous Substance Release Sites, Cal/EPA, 1995

5. Standard Guide for Accelerated Site Characterization for Confirmed or Suspected Petroleum Release Sites, ASTM E1912-98

Remediation

6. How to Evaluate Alternative Cleanup Technologies For Underground Storage Tank Sites, USEPA, EPA 510-B-94-003, 1994

7. Pump-and-Treat Ground-Water Remediation, A Guide for Decision Makers and Practitioners, USEPA – Office of Research and Development, EPA/625/R-95/005

8. The Performance and Cost of MTBE Remediation Technologies, Proceedings of the 1998 Petroleum Hydrocarbons and Organic Chemicals in Water conference, D.N. Creek, J.M. Davidson

9. Treatment Technologies for Removal of Methyl Tertiary Butyl Ether (MTBE) from Drinking Water, MTBE Research Partnership: Western States Petroleum Association, Association of California Water Agencies, Oxygenated Fuels Association, 1998

10. Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water, in *Health and Environmental Assessment of MTBE, UC TSR&TP Report to the Governor of California*, Keller, AA, OC Sandall, RG Rinker, MM Mitani, B Bierwagen, MJ Snodgrass, 1998.

MTBE Properties

11. Fuel Oxygenates and Water Quality: Current Understanding of Sources, Occurrence in Natural Waters, Environmental Behavior, Fate, and Significance. Chapter 2 in *Interagency Assessment of Oxygenated Fuel*, Office of Science & Technology Policy, Executive Office of the President, Washington, D.C., Zogorski, J.S., A. Morduchowitz, A.L. Baehr, B.J. Bauman, D.L. Conrad, R.T. Drew, N.E. Korte, W. W. Lapham, J. F. Pankow, and E.R Washington., 1997

Electronic Information Sources

12. California Environmental Protection Agency (Cal/EPA) www.calepa.ca.gov
13. State Water Resources Control Board (SWRCB) www.swrcb.ca.gov
14. California Department of Health Services (DHS) www.dhs.ca.gov
15. United States Environmental Protection Agency (EPA) www.epa.gov
16. Lawrence Livermore National Laboratory (LLNL) www.llnl.gov
17. Association of California Water Agencies (ACWA) www.acwanet.com
18. American Petroleum Institute (API) www.api.org/mtbe
19. Western States Petroleum Association (WSPA) www.wspa.org
20. American Society of Testing and Materials (ASTM) www.astm.org
21. National Water Research Institute (NWRI) www.ocwd.com/nwri

Appendix C

Site Conceptual Model Reports

The Site Conceptual Model (SCM) is a written or graphical representation of the release scenario, site characteristics (geology, hydrogeology, etc.) and the likely distribution of chemicals at the site. It links potential sources to potential receptors through transport of chemicals in air, soil, and water. It also provides a framework for the entire project and a communication tool for regulators, responsible parties, and other stakeholders. The goals of the conceptual model are listed below:

- Identify how the distribution of chemicals is changing in space and time
- Identify potential current and future receptors
- Identify environmental issues that need to be addressed

Reporting

Reports submitted to regulatory agencies are by necessity specific to the type of information they are presenting. They may contain a summary of activities, backup data to support conclusions, etc. A report that attempts to convey a representation of a SCM needs to meet the goals listed above. To meet these goals, investigation reports usually, at a minimum, contain the following elements:

I. Text
1. Site Description, Land Use, and Water Use
2. Chronology of Events
3. Site Stratigraphy and Hydrogeology
4. Well and Conduit Study
5. Estimation of Release Mass (if available)
6. Source Removal Activities
7. Remediation Activities

II. Figures
1. Site Location Map
2. Site Vicinity Map with Receptor Wells
3. Site Map with Groundwater Gradients, Cross Section Lines, and any known preferential pathways
4. Site Map with Isoconcentration Contours
5. Cross Section - long axis of plume
6. Cross Section - short axis of plume
7. Cross Section of Regional Geology (optional)
8. Concentration vs. Time Plots for Each Well
9. Concentration vs. Distance (optional)

III. Tables
1. Groundwater Elevation Data
2. Groundwater Analytical Data
3. Soil Analytical Data

Appendix D

Finding Leaks in Tank Systems

The purpose of this document is to identify available resources and potential activities that can be performed at suspected release sites to confirm and determine the source of a suspected release from a UST system. The appropriate level of effort for this task is interrelated with the results of groundwater monitoring, extent and type of the release, and other site-specific characteristics.

This investigation may be an iterative process and it is important that all data and findings be maintained and properly documented. A joint effort of a team of clean-up staff and leak prevention staff is needed to oversee activities and analyze the findings. The subsurface contaminant distribution may point to a leak source; e.g., relatively clean tank pit but high contaminant levels around a specific dispenser or near specific piping joint.

I. **Preliminary Site Evaluation –** The local inspector may perform these activities. All activities and findings should be documented item by item.

A. Visual Evaluation and Interviews

1. Check surfaces around UST systems for any visible signs of spills. Evaluate and document the condition of the concrete and asphalt – look for cracks, stains, etc. Pay particular attention to the area around fill pipes and dispenser islands.

2. Interview the operators with respect to unusual operating conditions, known spills and leaks, inventory reconciliation, etc.

3. Check monitoring equipment (all sensors, Line Leak Detectors, ATG, CITLDS) control panel for presence of alarm lights, trouble lights, and power lights. Power light should be on; trouble and alarm lights should be off.

B. Records Review

1. Review records of any water pumped-out from the tanks.

2. Review records of product or water removed from the sumps, spill containment boxes, and dispenser containment boxes.

3. Review records of product spills by customers filling their gas tanks or gasoline delivery trucks and the action taken to clean up the spill.

4. Review inventory records and the results of any Statistical Inventory Reconciliation (SIR) test reports. In the SIR reports, pay attention to the product-gain and inconclusive test results. Compare the test information with the test method specifications listed in the “Leak Detection Equipment and Test Methods List – LG 113”. A quick method of checking inventory records is to count the number of positive and negative daily variances in a month. The number of positives and the number of negatives should be almost equal. (E.g., in 30 days of recording, there should be 15 positives and 15 negatives; 18 of one and 12 of the other is suspicious; 10 of one and 20 of the other indicates a problem of some kind.

5. Review any past tank and piping tests performed at the site. Verify that tests were properly conducted. Compare the test information with the test method specifications listed in the "Leak Detection Equipment and Test Methods List – LG 113". Review the test results closely to determine if the tester did any system fixes (loose valves and connections and loose fill pipes) in order to make the test pass. Determine what follow-up action was taken at the site for reported fail results.

6. Check the spill containment box for presence or indication of product spills from product deliveries.

7. Check all sumps for presence of product, corrosion, or indication of product releases.

8. Check under-dispensing piping for any visible signs of product releases (drips, tarnished piping, etc.). This check should be done both while the dispenser is idle and during dispensing.

9. Dipstick the tank to check for water and product and allow for at least 24-48 hours. Use the tank chart and tank installation information to determine the rate of any losses or gains from the tank (same concept as manual tank gauging). Tank should be locked up and not used during this time. Note: temperature should be stable and no deliveries for a few days before the start of the test. The longer the test the better. A test should run for 48 hours unless the tank size is small. This test may not be appropriate if it significantly interferes with the daily operation of the facility.

10. To the extent possible, document the type, model, and brand of all major UST system components. This information should be reviewed and compared with any data on manufacturer recalls or any other frequently reported manufacturer defects.

II. **Detailed Site Evaluation and Data Collection -** A qualified and authorized contractor should perform these activities with oversight of the local inspector. All hands-on work on equipment must be performed in accordance with the manufacturer's instructions and test procedures, findings should be documented in detail, and all system reports printed.

A. Check for potential overfill events.

1. Check the overfill prevention device and report whether it is functional.

2. If the tank is equipped with an Automatic Tank Gauging System, (ATG) have the contractor check the system for overfill alarms, review product delivery records, and cross check deliveries with ATG system inventory records for consistency to verify proper deliveries.

3. If possible, contact the company delivering product to the facility to find out if they had any overfills (this may be just a nice try!). The ATG may also have a record of overfills. If delivery invoices are available, check to see if they contain before and after stick readings. Look for after delivery readings that are above the tank 95% level. Document results and file.

B. Functional equipment checks – These activities do not lead directly to locating a potential source of release. However, you should verify that leak detection equipment is functional before reviewing past test reports, and using the equipment to test the UST system components. All work must be performed in accordance with the manufacturer's instructions provided in the equipment maintenance manuals.

1. Print and check system set up for any programming errors.

2. Verify that all monitoring equipment and sensors are functional by testing all sensors.

3. Review the system diagnostic information to identify any system problems.

4. Perform a quantitative test on line leak detectors (mechanical and electronic) to determine that they can detect a leak of at least 3 gallons per hour. This is a test where the contractor simulates an artificial leak and the system response to that leak rate is evaluated and compared with the system requirements and the setup information

C. Check alarm history, system failure history, and leak test history reports.

1. Review the history of system alarms including system functional alarms.

2. If the tank is equipped with an ATG review the records of in-tank water and the history of high water alarms.

3. Review the history of leak tests performed by Continuous In-Tank Leak Detection System (CITLDS), ATG systems and electronic line leak detectors. Analyze the test results closely by comparing the test information with the test method specifications listed in the "Leak Detection Equipment and Test Methods List – LG 113"

D. Test all secondary containment.

1. Perform a hydrostatic test of the spill containment box (This is a very crude test method that currently only is performed at the time of installation. Containment box is filled with water; water level is marked or measured, and checked again in 24 hours to verify if the box is liquid-tight. Document the results.

2. Perform a hydrostatic test of all sumps (see item 1 above) and document the results. Also verify that all sensors are functional.

3. Check all piping penetrations and fittings for proper seal, verify secondary containment piping terminates in the sump, and verify that any potential releases from the primary piping into the secondary piping will drain into the sump (i.e. the reducer that was used to isolate the secondary during the installation tightness test has been removed or if a drain port was installed the outlet is not plugged).

4. Conduct a tightness test on the secondary piping and the interstitial space of the tank using an approved test method.

5. If there is dispenser containment present perform a hydrostatic test (see item 1 above) and verify that the leak-sensing mechanism is functional.

E. Activate Leak detection tests using on-site equipment.

1. Put the ATG system in a leak test mode (preferably 0.1 gph mode if available) and review the test result. Note that there should be no product dispensing from the tank until the test is completed. Evaluate the test results, not just for pass/fail. Review the measured leak rates and if needed, extrapolate the number to a full tank leak rate to determine if there may be a release from the tank. Also make sure that in-tank water is recorded before and after the test and look for water ingress during the test.

2. Activate mechanical line leak detector test mode (3gph) and electronic line leak detector test modes (3gph, 0.1 gph and 0.2gph), review the test results, and make note of any alarms or slow-flow or product pump shutdowns. Note that there should be no product dispensed from the piping system until the test is completed.

III. Tank and Line Tests – (These tests must be performed By a Licensed Tester)

A. Have the product lines tightness tested by a licensed tank tester using an approved test method. Be present during the test if possible. Compare the test information with the test method specifications listed in the "Leak Detection Equipment and Test Methods List – LG 113". Make sure the tester performs the test before doing any repairs or system fixes. If the test fails, any fixes should be done before a second test is conducted. All activities, including any repairs need to be documented and reviewed.

B. Have the ullage space of the tank tightness tested by a licensed tank tester using an approved test method.

C. Have the product-filled portion of the tank tested using an approved test method. Do not require the addition of any product to the tank for this test. In the event that the tank is leaking, the contamination may get worse if more product is added to the tank. Evaluate the test results, not just for pass/fail. Review the measured leak rates and if needed, extrapolate the number to a full tank leak rate to determine if there may be a release from the tank. Also make sure that in-tank water is recorded before and after the test and look for water ingress.

IV. External Full-System Evaluation for Vapor and Liquid Releases

Perform an external evaluation.