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STRATEGIES FOR CHARACTERIZING SUBSURFACE RELEASES OF GASOLINE CONTAINING MTBE

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Strategies for Characterizing Subsurface Releases of Gasoline Containing MTBE

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EXECUTIVE SUMMARY

The greatest concerns associated with gasoline releases have traditionally been non-aqueous phase liquids (NAPL) and dissolved-phase benzene, toluene, ethylbenzene, and xylenes (BTEX). The site characterization techniques commonly used by industry were originally developed to meet regulatory requirements for NAPL and BTEX. Over the past decade, however, there has been increased use of oxygenated compounds in gasoline, particularly methyl tertiary-butyl ether (MTBE). The chemical properties and subsurface behavior of oxygenated fuel additives are different from those of BTEX or other petroleum hydrocarbons, and so a reevaluation of traditional site characterization procedures is warranted.

This technical bulletin uses the principles of risk-informed decision making to guide the evaluation of sites affected by MTBE or other oxygenates. It includes an introduction to the properties and uses of MTBE, provides guidance for conducting assessments at MTBE release sites, and reviews modern assessment tools and techniques for characterizing and monitoring MTBE in the subsurface. While the primary focus of this study is on MTBE, other fuel oxygenates are also addressed.

Risk-informed decision making is a management strategy that adds exposure and risk considerations to the traditional technical, social, and economic components of the corrective action process. The risk-informed approach presented in this bulletin uses site-specific risk factors to help determine the appropriate level of assessment at oxygenate release sites. It includes a review of the various risk factors associated with oxygenate sources, pathways, and receptors. Based on these factors, three levels of assessment are recognized. The standard level is appropriate for the greatest number of sites: it includes moderate sample spacing with some vertical characterization, as well as horizontal characterization. The limited level is appropriate at sites with fewer risk factors: it includes relatively large sample spacing with emphasis on horizontal characterization. The detailed level is warranted for sites with the most risk factors: it requires the highest level of effort for each characterization task, with relatively close sample spacing, and extensive vertical characterization of chemical concentrations and hydraulic properties.

The appropriate level of assessment is initially determined based on receptor information, since receptor data are typically easier to obtain than source or pathway data. Detailed information about

receptors can normally be obtained from a survey of nearby wells and land uses. Receptor characterization should consider current uses and probable future uses of affected groundwater. Once receptors are characterized and an initial level of effort is established, a subsurface investigation may then be conducted to obtain detailed information about sources and pathways. The source and pathway data should be carefully reviewed as it is collected, and the level of assessment should be “upgraded” or “downgraded” accordingly.

This bulletin includes a detailed overview of the tools and techniques used in the field for source and pathway characterization and subsequent monitoring at oxygenate release sites. Since traditional assessment approaches have been addressed in previous API publications, this bulletin focuses on newer technologies that allow rapid collection and field analysis of soil, soil-gas, and groundwater samples. The bulletin includes a review of the expedited site assessment process, which is particularly well suited for oxygenate assessment. It also provides a comprehensive guide to modern direct-push assessment and monitoring tools, with emphasis on their proper use at MTBE-affected sites.

Section 1

INTRODUCTION

The 1990 Federal Clean Air Act Amendments (CAAA) mandated the use of cleaner burning gasoline in metropolitan areas throughout the United States. One effect of this legislation was an increase in the use of oxygenated compounds in gasoline, particularly methyl *tertiary*-butyl ether (MTBE). During the 1990s, MTBE was used more commonly in gasoline, and at higher concentrations, than in previous decades.

As oxygenate usage has grown, however, so have concerns regarding the potential impacts of these compounds on groundwater quality. Traditionally, the greatest concerns associated with gasoline releases have been non-aqueous phase liquids (NAPL) and dissolved-phase benzene, toluene, ethylbenzene, and xylenes (BTEX). The assessment techniques commonly used by industry (API, 1996a) were originally developed to meet regulatory requirements for NAPL and BTEX characterization. However, many fuel oxygenates are more mobile and persistent in groundwater than BTEX or other petroleum hydrocarbons. These differences have important implications for subsurface assessment; for example, a small surface release of conventional fuel may have no apparent impact on shallow groundwater, while an equivalent release of oxygenated fuel may result in unacceptable concentrations of dissolved-phase MTBE. Furthermore, dissolved-phase MTBE plumes may be more difficult to detect and delineate than dissolved-phase BTEX plumes. In light of these differences, a reevaluation of traditional assessment procedures is warranted.

This study uses the principles of risk-informed decision making to guide the evaluation of sites affected by MTBE or other ether oxygenates. The risk-informed decision making framework uses information about sources, pathways, and receptors to guide site management decisions to reduce or eliminate risks from exposures to chemicals released in the environment.

Section 2 of this publication provides a brief review of MTBE and other fuel oxygenates, including summaries of current environmental, analytical, and regulatory issues. General background information about the chemical structure and properties of fuel oxygenates is included in Appendix A. Section 3 provides a risk-based guidance for conducting assessments at MTBE release sites, while Section 4 reviews modern assessment tools and techniques for characterizing and monitoring MTBE in the subsurface. The primary focus of this study is on MTBE, but the guidance outlined in Sections 3 and 4 should be broadly applicable to other ether oxygenates, which share generally similar properties. This guidance is not necessarily appropriate for ethanol or other alcohol oxygenates, since alcohols are generally more biodegradable than ethers.

The guidance provided in this document is not intended to supercede any local, state or federal policies regarding the assessment of oxygenate releases. Rather, it provides a framework for making assessment decisions to supplement existing policies and procedures, and to provide a framework where agency-specific guidance does not exist.

It should be noted that any and all comments regarding technologies and comments herein are for informational purposes only. Neither the contractor nor API endorses such products or technologies.

Section 2

MTBE AND OTHER FUEL OXYGENATES

2.1 GENERAL PROPERTIES

Two types of oxygenates are commonly added to gasoline: ethers and alcohols. The historical usage of oxygenates in gasoline is discussed in more detail in Section 2.2.

MTBE is currently the most commonly used ether oxygenate due to its high octane properties and availability. Other ethers that are used (or that could potentially be used) as fuel oxygenates include *tertiary*-amyl methyl ether (TAME), *tertiary*-amyl ethyl ether (TAEE), ethyl *tertiary*-butyl ether (ETBE), and diisopropyl ether (DIPE).

Ethanol is by far the most commonly used alcohol oxygenate. Other alcohols that are used (or which could potentially be used) as fuel oxygenates include methanol and *tertiary*-butyl alcohol (TBA). TBA is also of interest as an impurity in MTBE and MTBE-containing fuel, and as a product of MTBE degradation (see Appendix A.2.7).

The most significant environmental issues associated with fuel oxygenates are discussed in Section 2.3. The subsurface behavior of oxygenates is primarily affected by the following characteristics:

- **Oxygenates occur at relatively high concentrations in oxygenated fuels.** For example, oxygenated fuels commonly contain up to 15 % MTBE by volume, or up to 7.3 % ethanol by volume.

- **Fuel oxygenates have a relatively strong affinity for groundwater.** The solubility of MTBE is about 25 to 300 times higher than the solubility of BTEX compounds. The solubilities of ethanol and other alcohols are even higher.

- **Dissolved-phase oxygenates are relatively mobile and persistent.** In general, dissolved-phase oxygenates have a low tendency to adsorb to soil or to volatize into soil vapor. For ether oxygenates (such as MTBE), this problem is magnified by an apparent resistance to biodegradation under field conditions.

A more detailed review and comparison of the chemical structures and properties of BTEX, ether oxygenates, and alcohol oxygenates is included in Appendix A.

2.2 USE OF OXYGENATES IN GASOLINE

The commercial use of fuel oxygenates in the United States began in 1979 following the phase-out of leaded gasoline. Oxygenates were originally valued for their high octane ratings (MTBE has an octane rating of 110, while ethanol has an octane rating of 112.5), and they were used primarily as octane boosters in premium gasolines. In 1981, the U.S. EPA approved the use of MTBE in gasoline at levels up to 10 percent by volume (California EPA, 1997). MTBE was widely used as an octane booster during the 1980s, commonly at concentrations of about 2 to 9 percent by volume in premium gasoline, and at concentrations of less than 1 percent in regular gasoline (Ellis and Gavas, 1996).

Oxygenates were subsequently used at higher concentrations to reduce vehicle emissions and improve air quality. The first oxygenated fuel program was conducted in the Denver area during January and February 1988. The 1990 CAAA established two new fuel programs administered by the U.S. Environmental Protection Agency, that required the use of “federal oxygenated gasoline” or “federal reformulated gasoline.” These two programs greatly expanded the use of oxygenates nationwide. At present, approximately 30 percent of the gasoline sold in the United States contains oxygenates for air quality improvement purposes (U.S. EPA, 1998).

Federal oxygenated gasoline has been used in some 40 metropolitan areas throughout the United States, beginning in October 1992. It is primarily intended to reduce carbon monoxide emissions, and its use is mandated only during winter months. Federal oxygenated gasoline normally must contain at least 2.7 percent oxygen by weight, but no particular oxygenate is specified. This oxygen requirement can be met by using 15 percent MTBE by volume, or 7.3 percent ethanol by volume. The oxygen requirement is subject to local modification. In California, for example, federal oxygenated gasoline need only contain 1.8 to 2.2 percent oxygen by weight. In other areas, federal oxygenated gasoline may contain up to 3.5 percent oxygen by weight (U.S. EPA, 1999c).

Federal reformulated gasoline (RFG) has been used in some 28 metropolitan areas throughout the United States, beginning in January 1995. It is primarily intended to reduce ozone production, and its use is required year round. Federal RFG must contain at least 2.0 percent oxygen by weight during the summer ozone season, but no particular oxygenate is specified. This oxygen requirement can be met by using 11 percent MTBE by volume, or 5.4 percent ethanol by volume.

In April 1996, the State of California mandated the use of "California Phase 2 Reformulated Gasoline" on a statewide, year-round basis. The prescriptive formula for California RFG calls for 1.8 to 2.2 percent oxygen by weight, but this requirement can be waived if equivalent emissions reductions can be achieved using alternative formulations. Thus, California RFG (unlike federal RFG) may or may not contain oxygenates. However, the use of federal RFG (which must contain oxygenates) is still mandated in those parts of California that are required by the CAA to participate in the federal RFG program.

Efforts have been made in several states to discontinue the use of MTBE in gasoline. In such cases, ethanol has typically been adopted or proposed as a replacement oxygenate. The State of California has requested a waiver from all requirements for federal oxygenated gasoline and federal RFG, on the grounds that California RFG can meet federal gasoline performance standards without oxygenated additives of any kind.

2.3 ENVIRONMENTAL ISSUES

2.3.1 Sources

High concentrations of MTBE or other oxygenates in groundwater are typically associated with point sources of fuels, such as storage tanks or pipelines. Specific source release scenarios include subsurface NAPL releases from underground tanks, piping, and sumps; surface NAPL releases from aboveground spills; and subsurface vapor releases from underground tanks or vapor recovery systems. MTBE releases are most commonly associated with older fuel storage tank systems, but they may occur even with systems that meet 1998 federal standards (SWRCB, 1999). There is evidence that even relatively small releases of oxygenated fuels (such as leaking automobile gas tanks, "backyard" fuel storage, or storage tank overfills) can lead to measurable concentrations of

MTBE in shallow groundwater (Maine Bureau of Health, 1998). The similarities and differences between BTEX and oxygenate sources are discussed in more detail in Section 4.2.1.

Nonpoint sources of oxygenates may also affect shallow groundwater, particularly in urban areas. Recent studies have found detectable concentrations of dissolved-phase MTBE in precipitation, storm-water runoff, and surface water bodies (such as rivers, reservoirs, and lakes). The available evidence suggests that infiltration of affected water from such nonpoint sources could lead to low concentrations of oxygenates in shallow groundwater (Pankow *et al.*, 1997; Zogorski *et al.*, 1997). For example, Squillace *et al*. (1997) estimated that precipitation in some urban areas could have MTBE concentrations as high as 3 µg/l, with even higher concentrations possible in the immediate vicinity of MTBE vapor sources (such as parking garages, gas stations, or roads). Moran *et al*. (1999) estimate that precipitation could contribute MTBE to shallow groundwater in concentrations as high as 20 µg/l. MTBE concentrations in the 10 to 50 µg/l range have been found in water samples from lakes and reservoirs used by recreational watercraft (Reuter *et al*., 1998).

2.3.2 Oxygenates in Soil Vapor

MTBE and other oxygenates generally have high vapor pressures, and they tend to volatilize readily from NAPL. On the other hand, oxygenates have relatively low Henry's Law Constant (K_H) values, and so they partition strongly into soil moisture. Vapor-phase migration will be much faster in dry soil and much slower in moist soil (see Appendix A.2.6).

Oxygenates have little tendency to volatilize from groundwater, and so the soil vapor in the vicinity of a dissolved-phase plume may only contain low, or even non-detectable, oxygenate concentrations. Volatilization will be particularly low if there is significant groundwater recharge: in that case, fresh water will accumulate on top of the dissolved-phase plume as it migrates downgradient (Rivett, 1995). The dissolved oxygenate molecules will then have to diffuse upward through the fresh water wedge before they can volatilize, and this process can take decades.

Oxygenates, like other fuel components, can migrate in the vapor phase to receptors in overlying buildings. At present, the potential risks posed by this pathway are not clear. Many oxygenates (particularly MTBE) have little tendency to sorb to soil (see Section A.2.2), and they are resistant to biodegradation (see Section A.2.7). These factors would increase the potential for vapor-phase migration. On the other hand, vapor-phase oxygenates partition strongly into soil moisture, as noted above. Any precipitation (or other forms of recharge) migrating downward through the vadose zone would readily “capture” vapor-phase oxygenates, thereby reducing (or even eliminating) the potential for vapor-phase migration. Other differences between vapor-phase BTEX and vapor-phase oxygenates are discussed in Section 4.2.4.

2.3.3 Oxygenates in Soil

MTBE and other oxygenates generally have low organic carbon partition coefficient (K_{oc}) values relative to BTEX hydrocarbons (See Section A.2.2). Thus, in dry soils, oxygenates are less likely to occur in soil samples because they are less likely to be adsorbed to naturally occurring organic carbon. On the other hand, oxygenates also tend to have relatively high solubilities (see Section A.2.1), and so they are more likely to be dissolved in soil moisture. In moist or water-saturated soils, such as those collected within the saturated zone, oxygenates may be readily detectable, although such samples are subject to biases as discussed in Section 4.2.4.

2.3.4 Oxygenates in Groundwater

Even a relatively small release of oxygenated fuel can impact local groundwater; this is the principal environmental concern associated with MTBE and other oxygenates. The effective solubilities of fuel oxygenates are commonly higher than those of BTEX hydrocarbons, since oxygenates are more soluble and may occur at higher concentrations in oxygenated fuels (see Section A.2.1). Other properties of oxygenates compound this problem. Oxygenates generally have low K_{oc} values (Section A.2.2) and low K_H values (Section A.2.4); ether oxygenates also have low biodegradation rates (Section A.2.7). Dissolved-phase ether oxygenates therefore tend to remain in groundwater, instead of sorbing to soil, volatilizing to soil vapor, or biodegrading (Figure A-2).

Since oxygenates have relatively low K_{oc} values, they also have low retardation factors and high plume migration velocities (see Section A.2.5). MTBE plumes can advance downgradient at relatively high rates in many hydrogeologic settings, even when the associated BTEX plumes are significantly retarded. Furthermore, MTBE plumes appear to naturally attenuate at slower rates, and so they may continue to advance even after the associated BTEX plume has stabilized. The similarities and differences between dissolved-phase oxygenate and BTEX plumes are discussed in more detail in Section 4.2.2.

2.4 ANALYTICAL AND REGULATORY ISSUES

2.4.1 Analytical Methods

The most common analytical techniques for fuel oxygenates in soil or groundwater are EPA Methods 8020, 8021, and 8260, and a modified version of ASTM Method D4815 (Happel *et al.*, 1998). In all of these techniques, analytes are stripped from the sample by purge and trap (P&T) and separated by gas chromatography (GC). However, there are significant differences in other aspects of these techniques, and they are not all equally reliable.

EPA Methods 8020 and 8021 are relatively inexpensive techniques, and they have been widely used to evaluate soil and groundwater samples for MTBE (however, Method 8020 is no longer recognized by U.S. EPA). These methods use photoionization detectors (PIDs) to identify and quantify hydrocarbons and oxygenates. The major drawback to this approach is that certain gasoline hydrocarbons, if present at sufficiently high concentrations, can interfere with the PID and affect the measurement of MTBE. This interference may result in overestimation of MTBE concentrations, or even false identification of MTBE when none is present. For example, Happel *et al*. (1998) used Methods 8020 and 8021 to evaluate MTBE, ETBE, DIPE, and TAME in solutions containing varying concentrations of total petroleum hydrocarbons (TPH). These methods provided good results at a TPH concentration of 500 micrograms per liter (µg/L); however, greatly elevated oxygenate detection limits were needed at TPH concentrations of 5,000 and 50,000 µg/L to prevent false-positive ether oxygenate identifications.

EPA Method 8260 is another widely available technique, although it is more expensive than Methods 8020 or 8021. This approach uses mass spectrometry (MS) to detect analytes. Happel *et al*. (1998) found that Method 8260 provided good results at all TPH concentrations for MTBE, ETBE, DIPE, TAME, and TBA. Limitations include high oxygenate detection limits for NAPL samples and the inability to measure ethanol or methanol.

ASTM Method D4815 was originally developed to test gasoline, but a modified version using P&T has been developed for soil and groundwater samples. This method uses a GC equipped with two different columns and a flame ionization detector (FID). Happel *et al*. (1998) found that the modified Method D4815 provided good results at all TPH concentrations for all tested oxygenates, including MTBE, ETBE, DIPE, TAME, ethanol, methanol, and TBA. However, the commercial availability and regulatory acceptance of this technique is currently limited.

In summary, the lower-cost Methods 8020 and 8021 should only be used for MTBE analysis where there is no significant matrix interference with other hydrocarbons. In general, they may be more reliable near the downgradient end of an MTBE plume than near the source area. Comparative analyses, using Methods 8260 or D4815, may be needed to determine if Methods 8020 or 8021 are appropriate. If a sample analyzed by Methods 8020 or 8021 contains both MTBE and significant concentrations of TPH (over 500 µg/L), then confirmatory analysis by Methods 8260 or D4815 is definitely warranted. Method 8260 appears to be appropriate for all ether oxygenates, although it may not be able to detect them at low concentrations in NAPL. Method D4815 is the most versatile method, but it is not as well known or as widely available as Methods 8020, 8021, and 8260. API (1999) provides additional information on the selection of methods for oxygenate analysis.

2.4.2 Environmental Standards

In 1992, the U.S. EPA proposed a Draft Health Advisory of 20-200 micrograms per liter (µg/l) for MTBE in drinking water. In 1997, this was modified to 20-40 µg/l in a “Consumer Acceptability Advice and Health Effects Analysis” (U.S. EPA, 1997a). Neither of these standards is enforceable. Due to the lengthy regulatory procedures involved, it is unlikely that any enforceable standards for MTBE will be enacted at the federal level in the near future (Happel *et al*., 1998).

The 1992 or 1997 U.S. EPA advisories have been used to establish groundwater cleanup standards in certain states. Other states have adopted lower standards. In 1999, for example, California proposed a Primary Maximum Contaminant Level for MTBE, based on human health criteria, of 13 µg/l. California has also adopted an enforceable Secondary Maximum Contaminant Level for MTBE, based on aesthetic (taste and odor) criteria, of 5 µg/l. Current state standards are listed by U.S. EPA (1999c).

Section 3

RISK-INFORMED DECISION-MAKING AND MTBE ASSESSMENT

3.1 RISK-BASED DECISION-MAKING

3.1.1 Introduction

Traditionally, site management decisions have been based primarily on technical, social, and economic factors. Risk-based decision making is a management strategy that adds exposure and risk considerations to the traditional components of the corrective action process. This strategy may be more accurately termed risk-*informed* decision making, because risk typically supplements, rather than replaces, the other factors (Rice *et al.*, 1998). Risk-informed decision making provides a consistent, technically defensible process for making corrective action decisions that are protective of human health and the environment, while also using resources efficiently. The tiered risk-informed decision making process is further summarized in Appendix B, and in API Publication 1628B (API, 1996c).

The risk-informed decision-making process is used to determine the objectives and scope of environmental site assessments and corrective actions. This process can be readily applied to subsurface releases of MTBE and other oxygenates because the properties of these compounds are understood sufficiently to allow reasonably conservative assumptions to be used. This publication uses the principles of risk-informed decision-making to determine the appropriate level of effort for the characterization of oxygenate release sites.

Some oxygenates do not have well established toxicity values (Appendix A). However, such chemicals can still be addressed using a tiered risk-based framework because other relevant, measurable criteria can be used in place of health-risk-based concentration targets. Such criteria may include aesthetic considerations (e.g., odor, taste, discoloration) that may affect the future use of a site or resource, even after chemical concentrations have been reduced to levels posing no further health or environmental concern. For example, California has established a Secondary Maximum Contaminant Level for MTBE of 5 µg/l, based on aesthetic (taste and odor) criteria. This value is, in fact, lower than typical health-risk-based drinking water standards for MTBE

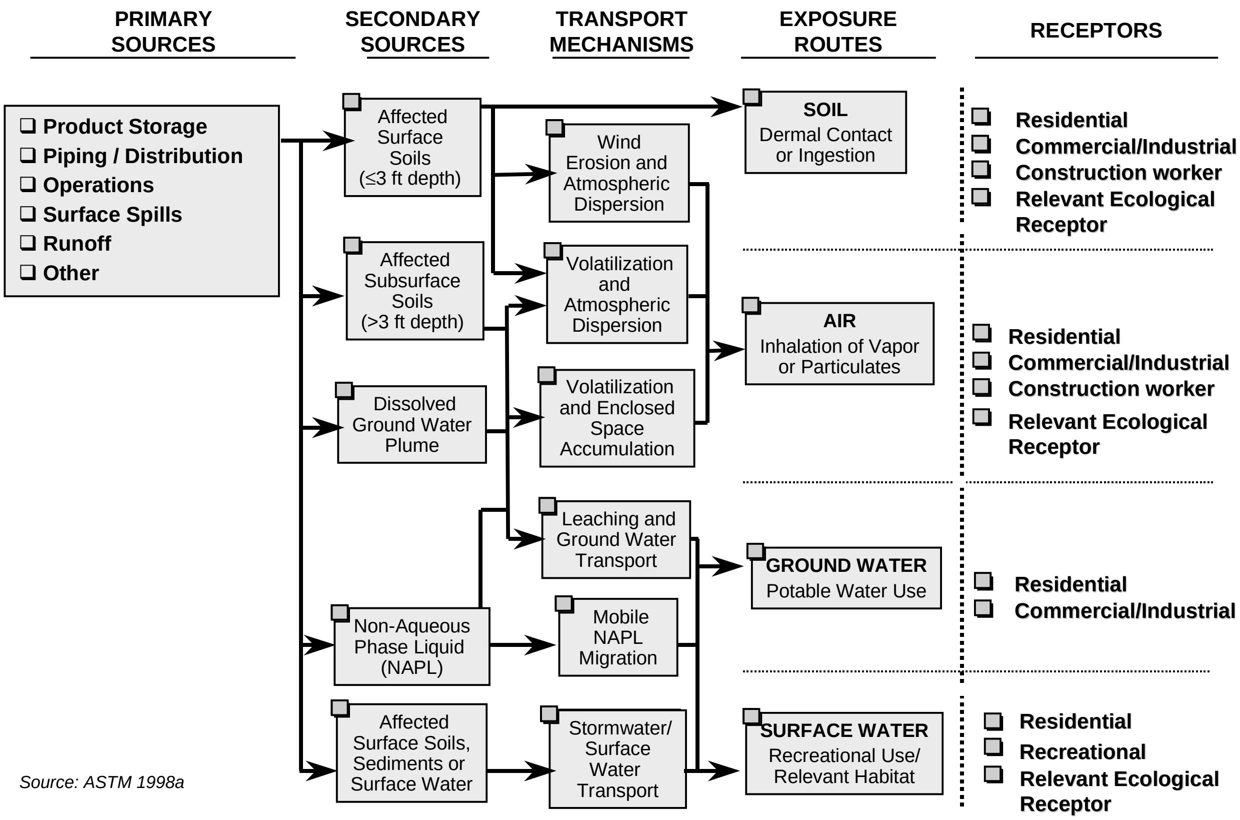
(Section 2.4.2), including California's Proposed Primary Maximum Contaminant Level of 13 µg/l. Resource protection may be a policy objective, and may have associated criteria, even if the resource has no current beneficial use. In addition, other factors, such as legal and economic value considerations, may affect the selection of the remedy(s). These factors can be included in the decision process, usually after health-risk-based cleanup levels have been identified. The tiered process provides a structured way of making assessment and corrective action decisions, regardless of whether health risk is the primary criterion.

Risk-informed decision making should not be confused with quantitative risk assessment. The site characterization process described in this document considers risk factors in a *qualitative* sense; it would not usually involve *quantitative* calculations of health risk. If more exact estimates of health risk were needed for remedial decisions, a quantitative risk assessment could be conducted after the site characterization was completed.

3.1.2 Conceptual Site Model

An essential component of risk-informed decision making is the conceptual site model (CSM) of the chemical release and the site setting. A CSM is an inventory of the actual and potential sources, pathways, and receptors related to the chemical release. **Sources** include the *primary* release of the chemical into the environment (e.g., surface spill or UST system leak). Sources also include the regions of affected soil or groundwater adjacent to the original release, which act as *secondary* sources of chemical to the surrounding environment. **Pathways** include the *mechanisms* by which a chemical may migrate from the source to a point of potential exposure (e.g., groundwater migration, vapor migration). Pathways also include the *route* by which a receptor is exposed to the chemical (e.g., ingestion, inhalation, and dermal contact). **Receptors** may include any organism (human or other ecological species) or habitat that may be adversely affected by exposure to the chemical.

A conceptual site model can be summarized in a variety of ways, such as a written summary, a table or matrix, a flowchart, or a schematic figure. An example of a conceptual site model, expressed as an exposure pathway flowchart, is shown on Figure 3-1. A conceptual model may distinguish between current (actual) exposures, and future (potential) exposures.



Source: ASTM 1998a

Figure 3-1. Example of an Exposure Pathway Flowchart

At the initial stages of an investigation, the conceptual model may be no more than a set of simplified, conservative assumptions about site conditions (sources, pathways, and receptors). As additional knowledge of the site is obtained, the conceptual model is verified or refined. The conceptual site model is the basis for all investigation tasks, whereby data needs regarding sources, pathways, or receptors are identified, and then fulfilled, as the field investigation proceeds. After some subsurface data is collected, the conceptual model would also include a written or graphical summary of the subsurface conditions at the site. This would include a summary of the extent of affected soil and groundwater, and any significant geologic and hydraulic influences on the potential migration of chemicals in the subsurface. The use of the CSM as applied to Accelerated Site Characterization is further discussed in Section 4.3.

The conceptual model is used in several ways:

- To communicate site conditions to decision makers and stakeholders;
- To define potential exposure pathways for further investigation and evaluation;

- To derive pathway-specific, risk-based remedial goals; and
- To select pathway-specific remedies to meet remedial goals.

In the early stages of many site assessments, very little may be known about the releases, migration and exposure pathways, or potential receptors. Consequently, the CSM may be generalized at the beginning of the assessment, but it will become more representative of actual site conditions as more site information is obtained. The initial site assessment may include only limited information about potential sources, pathways, and receptors, and so conservative assumptions are commonly used in the initial conceptual site model. For example, if a receptor is found to exist near the site and no other information is known about sources or pathways, then the conceptual model would typically make the conservative assumption that the pathway is complete. Further site characterization data would be used to evaluate this assumption and refine it accordingly. The development of the conceptual site model is further discussed in ASTM, 1995b and ASTM, 1998a.

In order to determine the appropriate level of investigation, the risk factors associated with sources, pathways, and receptors must be evaluated. Risk factors are those aspects of sources, pathways, and receptors that significantly influence the potential for adverse effects. Examples of risk factors are given in the next section.

3.2 RISK FACTORS

3.2.1 Risk Factors Related to Receptors

The most common receptors affected by subsurface releases of oxygenates are the current and future users of potable or non-potable water from municipal or private water wells. The risk factors depend on the beneficial uses of groundwater, and on the proximity and intensity of these uses:

- *The current and future beneficial uses of the affected (or potentially affected) groundwater*. Groundwater that has current, actual potable usage poses a higher risk factor than groundwater that may be used in the future, or has no anticipated beneficial use. An example of an *actual* affected beneficial use would be ongoing potable use of groundwater from private or municipal wells that extract from a region of groundwater affected by released oxygenates. An example of a *future* affected beneficial use would be where a shallow water-bearing zone contains affected groundwater that is not currently withdrawn for potable uses, but where potable uses can be reasonably expected to occur before the concentrations of released oxygenates have attenuated. Future beneficial groundwater usage is more likely in locations where there is rising water demand (for example, due to population growth), and where the natural groundwater quality and yield are adequate for the intended beneficial use. For regulatory jurisdictions that have developed groundwater classification schemes, actual beneficial use can be different than groundwater classification. Actual use (or reasonably anticipated future use) should be considered when assessing risk factors, rather than relying solely on groundwater classification.

- *The density and proximity of water wells, and the depth interval(s) screened by water wells near the release*. Sites that are located near potable-use wells pose higher potential risks than sites that are not near potable-use wells. Similarly, sites that have a small degree of vertical separation from the screened zones of potable-use wells pose higher potential risks than sites that have a large degree of vertical separation from the screened zones of potable-use wells. Sites located in areas with a high density of potable-use wells are more likely to create adverse impacts than sites in areas of low water-well density. Although distance to receptors is an important consideration, subsurface conditions such as stratigraphy can strongly influence the potential for migration, and are important modifiers to any distance criterion.

3.2.2 Risk Factors Related to Pathways

Several MTBE migration pathways are possible, including migration in air and soil gas, surface water, groundwater, and along utility conduits. As discussed in Section 2.3.2, risks related to inhalation exposures resulting from subsurface migration of oxygenate vapors are not clear at present, but are expected to be low. This publication assumes that MTBE migration in groundwater is the principal pathway of concern. The following general risk factors associated with the groundwater pathway should be evaluated:

- *The potential for the release to reach groundwater*. If a release has occurred, but has not reached groundwater, the potential for future migration to groundwater may need to be evaluated. The potential for impact is higher under particular hydrogeologic conditions, such as sites with highly permeable soils or fractures, high rates of groundwater recharge, and a shallow groundwater table. Releases that have resulted in elevated soil gas concentrations may allow migration in the gas phase to the water table, particularly through relatively dry soils.

- *The potential for a dissolved plume to impact a drinking water aquifer*. If a release has affected groundwater quality in the shallowest water-bearing materials, the potential for future horizontal or vertical migration may need to be evaluated. For example, consider a site where the shallow affected water-bearing zone is not used for beneficial purposes, but potentially recharges deeper water-bearing zones that have current beneficial uses. In such a case, the magnitude and direction of groundwater flow would need to be evaluated, including the effects of groundwater pumping on plume migration. The degree of hydraulic connection between shallow and deep zones –- due to natural geologic conditions and to man-made conduits, such as long-screened and/or abandoned wells –- can affect the potential for oxygenates in the shallowest water-bearing zone to affect groundwater quality in deeper zones.

- *The immediacy of the impact*. The rate of migration from source to receptor determines whether an impact is likely to be either imminent, several years in the future, or highly unlikely. The timing of a potential impact depends on the distance to the receptor (a receptor risk factor) divided by the migration velocity (a pathway risk factor). The groundwater velocity and proximity of the release to current receptors are important risk factors.

- *The potential for affected groundwater to discharge to surface water*. If affected groundwater has the potential to migrate to nearby surface water (such as a gaining reach of a stream, or groundwater discharge into a reservoir), the potential for future migration of affected groundwater should be evaluated. The potential for impact is higher under particular hydrogeologic conditions, such as sites with nearby rivers, streams or lakes; highly permeable soils or fractures; high rates of groundwater migration; or a shallow groundwater table. The proximity of the release to groundwater discharge zones is a risk factor.

A thorough understanding of local and regional hydrogeology is usually required to address risk factors related to the groundwater pathway. For example, evaluating the degree of interconnectedness between shallow and deep zones may require several lines of hydrogeologic information, such as comparing groundwater levels in shallow and deep zones, monitoring water level fluctuations within each zone (especially when deep pumping wells are turned on or off), assessing inorganic geochemistry, and/or conducting hydraulic tests to assess the hydraulic properties of the intervening materials.

If subsurface vapor-phase migration and inhalation is a pathway of concern, the following general risk factor associated with this pathway may need to be evaluated:

- *The potential for the release to affect indoor or outdoor air quality*. If a subsurface release has occurred, the potential for vapor migration to air may need to be evaluated. The potential for impact is higher under particular hydrogeologic conditions, such as sites with highly permeable soils or fractures, or coarse, dry soils. Shallow subsurface releases and poorly ventilated buildings (especially those with basements) may also pose greater risks.

3.2.3 Risk Factors Related to Sources

The most common sources of oxygenates in the subsurface are leaks from underground storage tank systems, and spills associated with fuel transfer and dispensing, including releases from pipelines. The risk factors for these potential sources include:

- *Age, integrity, and design of fuel storage and delivery systems*. Storage and delivery systems that are old and/or poorly maintained and improperly operated are more likely to experience releases. The type of vapor recovery system may also affect the potential for subsurface releases of oxygenates (SCVWD, 1999).

- *Volume of fuel stored and/or dispensed*. Over time, facilities that handle larger volumes of fuel and/or oxygenates are more likely to experience releases. For a given level of operational integrity, a site with a higher throughput has a higher risk factor than a site with a lower throughput.

- *The length of time that oxygenates have been used at a particular facility*. Some areas of the country began using gasoline containing MTBE or other oxygenates earlier than in other areas. Facilities that have been using MTBE for longer periods of time have a higher probability of release.

- *Magnitude of release*. If a release is verified, the volume of the release is an important risk factor. Greater volumes of released chemicals pose greater potential risks. In most cases, the volume of released material is highly uncertain, and estimates based on subsurface samples are of limited utility.

- *Concentration and extent of secondary source*. A common situation arises where a release is verified, but the volume and mechanism of release are not known. In this situation, the composition (oxygenate content) of the NAPL, the extent of NAPL, highly affected soil, and/or highly affected groundwater can give an indication of the potential for adverse effects.

It may be possible to evaluate the relative magnitude and significance of the release based on the integrity of the product storage and handling systems and procedures. However, in certain site settings (shallow groundwater, high infiltration rates), small, incidental releases of gasoline containing ether oxygenates may result in unacceptable groundwater concentrations (Lahvis and Rehmann, 1999).

3.3 RISK-INFORMED ASSESSMENT DECISION FRAMEWORK

The tiered risk-informed decision-making process provides a framework for determining the objectives and scope of environmental site assessments. Sites with greater risk factors require the most intensive assessment of contaminant receptors, pathways, and sources. Sites with fewer risk factors warrant a more limited amount of assessment to confirm whether receptors, pathways, and sources require further investigation or corrective action.

Information about receptors can usually be obtained earlier in the site characterization process than information about pathways and sources. Consequently, receptor information is used to estimate the level of effort required for subsequent characterization tasks. The suggested order of the characterization tasks is:

1. Gather information about receptors.
2. Use receptor information to determine an initial level of effort for pathway and source characterization tasks.
3. As characterization proceeds, verify or update the site conceptual model.
4. If warranted, revise the level of effort for subsequent characterization tasks. The level of effort may be revised upward if site conditions show a higher potential for risk than previously assumed. Conversely, the level of effort may be revised downward if site conditions show a lower potential for risk than previously assumed.
5. Continue characterization and monitoring until sufficient information has been collected to make an acceptable interim or final remedy decision.

In the following sections, the level of detail for site assessment tasks is divided into three categories:

- **Limited level:** This is a screening-level assessment requiring a relatively low level of effort. For example, sample spacing would be relatively large, with a greater relative emphasis on horizontal rather than vertical characterization. The limited level of assessment may also constitute the first stage of data collection for more detailed assessments.
- **Standard level**: This level of assessment would require a moderate level of effort. For example, for characterization tasks that require sampling, it would typically involve moderate sample spacing, some degree of vertical characterization, and moderate use of depth-discrete sampling methods.
- **Detailed level**: This is the most comprehensive level of assessment, requiring the highest level of effort. This would usually involve a closer sample spacing, extensive vertical characterization of chemical concentrations and hydraulic properties, and more frequent use of depth-discrete soil sampling and multi-level groundwater sampling methods.

The remainder of Section 3.3 discusses these characterization tasks and levels of assessment in more detail.

3.3.1 Receptor Characterization Tasks

The objective of receptor characterization is to identify any receptors that could be affected by an oxygenate release. Human receptors are typically of greatest concern, but relevant ecological receptors and habitats should be addressed as well. The initial CSM includes working hypotheses regarding potential receptors, particularly those using local wells or surface-water bodies for potable water supply. These hypotheses should be verified by a review of local groundwater usage, including a survey of potable water-supply wells, before undertaking a subsurface investigation. A well survey should search for domestic wells within a minimum 0.25-mile radius of the release, and for municipal wells within a minimum 0.5-miles radius.

Relevant information on water usage is commonly available from local or regional water management authorities, state water agencies, water utilities, or municipalities. In California, for example, an Internet-accessible database is being developed to provide information on the location, yield, and screened intervals of public water wells (Dooher and Happel, 1999). In some cases, agency records may need to be supplemented by a field well survey downgradient of the source, in order to identify older, unregistered, potable-use wells.

In addition to the well survey, state and local laws, regulations, and policies should be reviewed to determine if any groundwater classifications or designations are applicable to the site. For example, jurisdictions with anti-degradation policies may require specific action, even if there are no current or future potable groundwater uses. Regulatory agencies may also provide guidance regarding the appropriate points of compliance for water quality objectives, and the allowable time frames for compliance to be achieved.

The receptor characterization tasks are summarized in Table 3-1.

Table 3-1. Receptor Identification Tasks

Task 1. Receptor Identification
Perform well survey for domestic wells within a minimum 0.25-mile radius of the release, and for municipal wells within a minimum 0.5-miles radius. Collect relevant information on current and future water usage from local or regional water management authorities, state water agencies, water utilities, or municipalities. Review state and local laws, regulations, and policies to determine groundwater classifications, specific actions, or compliance goals applicable to the site. Consider relevant ecological receptors and habitats.

An *initial* level of effort and detail for subsequent investigation tasks may be selected after a review of local water usage data, as shown in Table 3-2. This table addresses both the general groundwater usage throughout the basin in which the site is located, and the site's immediate proximity to specific water wells (or other potential receptors). The groundwater usage categories in Table 3-2 are defined as follows:

Current Municipal Use. Relatively large volumes of groundwater are obtained for potable use by municipal water systems. In such cases, groundwater withdrawals commonly represent a significant fraction of the overall groundwater basin water balance. The region of hydraulic capture of production wells extends across a large portion of the groundwater basin.

Current Domestic Use via Private Wells. Relatively small volumes of groundwater are obtained for potable use by private water wells. In such cases, groundwater withdrawals usually represent a lower proportion of the overall groundwater basin water balance. The region of hydraulic capture of each private water well would typically be small, and would extend over a small portion of the groundwater basin. However, large numbers of these wells may be scattered throughout the basin.

Little or No Current Use, but Future Use is Planned or Likely. Most of the groundwater within the basin is not currently used for potable purposes. However, due to favorable water quality, well yields, and future land use plans, potable uses can be expected to increase within a reasonable time frame.

No Current Use, and Future Use is Unlikely. Little or no groundwater within the basin is currently used for potable purposes. Furthermore, potable uses are unlikely to occur within a reasonable time frame, due to unfavorable water quality, poor well yields, or future land use plans,

Nearby Wells. As noted above, the well survey will normally search for domestic wells within a minimum 0.25-mile radius of the release, and for municipal wells within a minimum 0.5-mile radius. Greater search radii may be used if deemed appropriate.

Table 3-2. Initial Level of Assessment Based on Basin Groundwater Usage and Proximity to Potable-Use Wells

Predominant Usage within Groundwater Basin	**Initial Level of Assessment if nearby wells are present**	**Initial Level of Assessment if no nearby wells are present**
Current Municipal Use	Detailed	Standard
Current Domestic Use via Private Wells	Detailed	Standard
Little or No Current Use, but Future Use is Planned or Likely	Standard	Limited
No Current Use, and Future Use is Unlikely	Not Applicable	Limited

Table 3-2 indicates that the initial level of assessment effort is based solely on receptor conditions. This approach reflects the fact that data about receptors can typically be obtained more easily than data regarding pathways or sources. At most subsurface release sites, detailed information about potential receptors is readily available (from the sources described above), whereas detailed information about sources or pathways is initially lacking. Since the receptor information is likely to be the most complete at the start of an investigation, this data should be used to determine the initial level of assessment effort.

Subsurface sampling and analysis will typically be necessary to obtain further information regarding sources and pathways. As additional source and pathway data become available, the CSM and the tentative category of assessment may change. In such cases, the initial level of assessment effort can be “upgraded” or “downgraded” as appropriate (see Section 3.4.).

Source and pathway investigation tasks are listed in Table 3-3 and described below. The following discussion of investigation tasks is not a comprehensive treatise on environmental site characterization. It builds on existing documents (API, 1996; EPA, 1997, Arulanantham and

Buscheck, 1999), while focusing on topics of particular relevance to the characterization of oxygenated fuel releases.

Tasks 2a through 2d in Table 3-3 are initial *pathway* characterization tasks, and Task 3 (and, to a lesser extent, Task 2c) are initial *source* characterization tasks. The activities in Task 4 are performed to collect and interpret periodic monitoring data in order to provide further information about sources and pathways over time. Although these tasks are listed separately, data for several of these tasks (flow system characterization, geologic characterization, initial chemical delineation, and source zone characterization) are likely to be collected and interpreted together, depending on the methods employed.

Table 3-3. Characterization Tasks and Level of Assessment

Investigation Tasks		**Level of Assessment**		
		Detailed	**Standard**	**Limited**
Task 2. Pathway Characterization	**a. Flow System Characterization**	Review regional information; develop conceptual model of flow system between site and groundwater receptor(s) Define horizontal and vertical flow system (potentiometric contours) Evaluate vertical flow potential (use site-specific water level measurements to estimate vertical hydraulic gradients) Assess hydraulic communication between source and receptor wells Estimate horizontal and vertical migration rates If refined estimates of migration rates are needed, perform hydraulic tests If refined estimates of potential for migration to receptor are needed, conduct simulations of groundwater flow, including the effects of expected groundwater pumping	Review regional information; develop conceptual model of flow system between site and groundwater receptor(s) Define horizontal flow system (potentiometric contours) Evaluate vertical flow potential (use regional or site-specific water level measurements to evaluate vertical gradients) May include hydraulic tests and assessment of vertical hydraulic communication	Review regional information; develop conceptual model of flow system between site and groundwater receptor(s) Define horizontal flow system (potentiometric contours) Similar in detail to historical BTEX investigation

Table 3-3. Characterization Tasks and Level of Assessment (continued)

Investigation Tasks		Level of Assessment		
		Detailed	**Standard**	**Limited**
Task 2. Pathway Characterization	**b. Geologic Characterization**	Define geological controls on groundwater movement and the location and integrity of confining units between a release and existing receptor wells Generate detailed geologic cross-sections using high-resolution characterization methods, such as CPT or geophysical logging.	Define geological controls on groundwater movement and the location and integrity of confining units between a release and potential receptor wells Generate geologic cross-sections with limited use of high-resolution characterization methods	Define geological controls on groundwater movement between a release and potential receptor wells Collect and interpret geologic data using conventional well logs or other lower-resolution methods
	c. Plume Delineation	Define the horizontal and vertical extent of oxygenate plume Extensive use depth-discrete soil and groundwater sampling methods for vertical and horizontal delineation Summarize extent using isoconcentration contour maps, plume cross sections	Define the horizontal extent of oxygenate plume Limited delineation of the vertical extent of oxygenate plume May use depth-discrete soil and groundwater sampling methods for horizontal and vertical delineation Summarize extent using isoconcentration contour maps	Define the horizontal extent of oxygenate plume May include some vertical delineation May use depth-discrete soil and groundwater sampling methods for horizontal and vertical delineation Level of detail similar to historical BTEX investigation
	d. Potential Conduit Survey	Extensive: identify the location and details of abandoned water wells, cathodic protection wells, dry wells, sewers, utility lines, etc. that could facilitate migration to receptors	Less extensive	Minimal

Table 3-3. Characterization Tasks and Level of Assessment (continued)

Investigation Tasks		**Level of Assessment**		
		Detailed	**Standard**	**Limited**
Task 3. Source Characterization	**Source Zone Delineation**	Review existing information concerning the suspected release If downward gradient exists and/or supply wells are within ½- mile, perform an intrusive investigation to further delineate the source zone Sample any NAPL encountered to assess the fraction of oxygenate remaining in the NAPL If source treatment (including removal) is warranted, define the horizontal and vertical extent of free-phase and/or residual NAPL containing oxygenate	Review existing information concerning the suspected release If strong downward gradient and/or other conduits exist, perform a limited intrusive investigation to further delineate the source zone	Review existing information concerning the suspected release No additional intrusive investigation of source zone required if other tasks confirm low risk status

Table 3-3. Investigation Tasks and Level of Assessment (continued)

Investigation Tasks		**Level of Assessment**		
		Detailed	**Standard**	**Limited**
Task 4. Verification Monitoring	**a. Groundwater and Chemical Monitoring**	Minimum of two seasonal variations in water levels and concentrations Multiple monitoring wells with short screened intervals, installed in affected and unaffected zones Potentiometric contour maps (horizontal and vertical) Isoconcentration contour maps	Minimum of two seasonal variations in water levels and concentrations May use one or more monitoring wells with short screened intervals, installed in affected zones Potentiometric contour maps (horizontal and possibly vertical) Isoconcentration contour maps	Minimum of two seasonal variations in water levels and concentrations Traditional monitoring well network, installed in affected zones
	b. Assess Source Depletion and Hydraulic Influences	Plot concentration versus time for individual wells to assess source depletion and hydraulic influences	Plot concentration versus time for individual wells to assess source depletion and hydraulic influences	Plot concentration versus time for individual wells to assess source depletion and hydraulic influences
	c. Assess Plume Stability	Plots of concentration versus distance for centerline wells over multiple time periods	Plots of concentration versus distance for centerline wells over multiple time periods	Plots of concentration versus distance for centerline wells over multiple time periods

Modified after Arulanantham and Buscheck, 1999.

3.3.2 Pathway Characterization Tasks

API (1996) reviewed the general elements of pathway characterization at petroleum release sites. The pathway characterization tasks listed in Table 3-3 are summarized below. Some topics with particular relevance to ether oxygenate releases are discussed in more detail.

3.3.2.1 Flow System Characterization (Task 2a)

The purpose of flow system (hydraulic) characterization tasks is to understand the local and regional groundwater flow system and its impact on the migration of a dissolved plume. Regional groundwater studies and/or agencies with groundwater management authority should be reviewed to determine the overall pattern and intensity of groundwater usage in the groundwater basin. Information from these sources may indicate the location and magnitude of the primary sources and sinks of groundwater within the basin. This information can be used to anticipate the rates and directions of groundwater flow at a site, and the trajectory of a dissolved-phase plume, if one is present.

Groundwater flow systems are typically comprised of recharge areas and discharge areas. The geometry of an oxygenate plume can be affected by its location within the groundwater flow system, so this factor should be incorporated into the conceptual site model as hydraulic and hydrogeologic information is obtained.

Oxygenate plumes in recharge areas tend to slowly migrate downward as the plume migrates downgradient (Weaver *et al.*, 1999). Clean water from precipitation accretes on top of the plume (Figure 3-2). A sharp change in concentration may exist between the clean water "wedge" and the underlying plume because the only mechanism for mixing is transverse vertical dispersion, a typically weak process (Rivett, 1995). If a clean water wedge is present, then a sample collected at the water table (above the plume) may provide a false negative result. For a plume to "dive" below downgradient monitoring wells due to accretion of clean recharge, the rate of accretion must satisfy the following relationship:

$$I \geq \frac{Vd}{x} \qquad \text{(Equation 3-2)}$$

Where:

I = Accretion rate (ft/yr) (= recharge rate divided by porosity, where the recharge rate is the net annual recharge to groundwater in ft/yr)
V = Horizontal groundwater seepage velocity (ft/yr) (= specific discharge / porosity)
x = Distance from release to downgradient monitoring well (ft)
d = Depth of monitoring well screen below the water table (ft)

For example, consider a site where the distance from a release to a downgradient monitoring well is 200 feet, and the downgradient monitoring well screen extends 10 feet below the water table. At this site, the accretion rate would have to exceed 5 percent of the horizontal groundwater velocity in order to result in a false negative at the downgradient monitoring well. If the horizontal velocity were 100 feet per year, then the accretion rate would need to exceed 5 feet per year. Assuming a total porosity of 30 percent, this condition would require a recharge rate that exceeds 1.5 feet per year. Other hydraulic influences, such as pumping in deeper zones, may increase the rate of vertical migration. A more detailed method for estimating the extent of plume diving is presented by Weaver (2000).

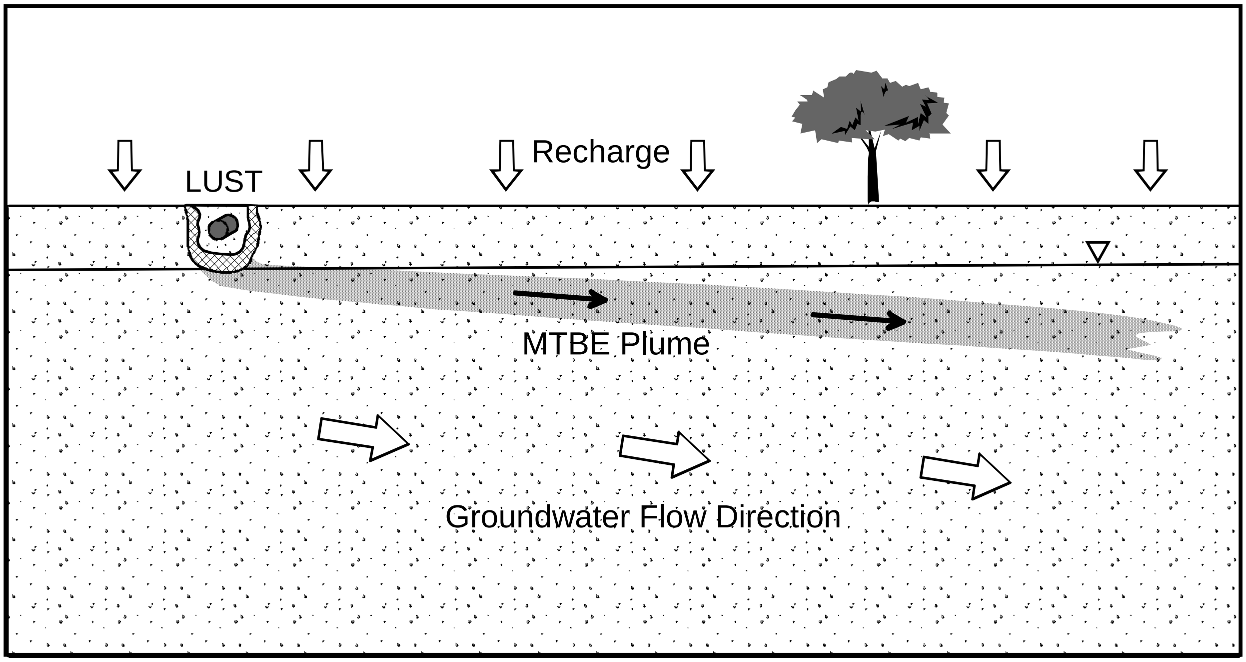


Figure 3-2. Plunging MTBE Plume in a Regional Groundwater Recharge Area

MTBE plumes in groundwater discharge areas tend to migrate upward with groundwater as the plume migrates downgradient (Figure 3-3). Oxygenate plumes of this type may discharge to surface water bodies, or be released to the atmosphere by evaporation or transpiration.

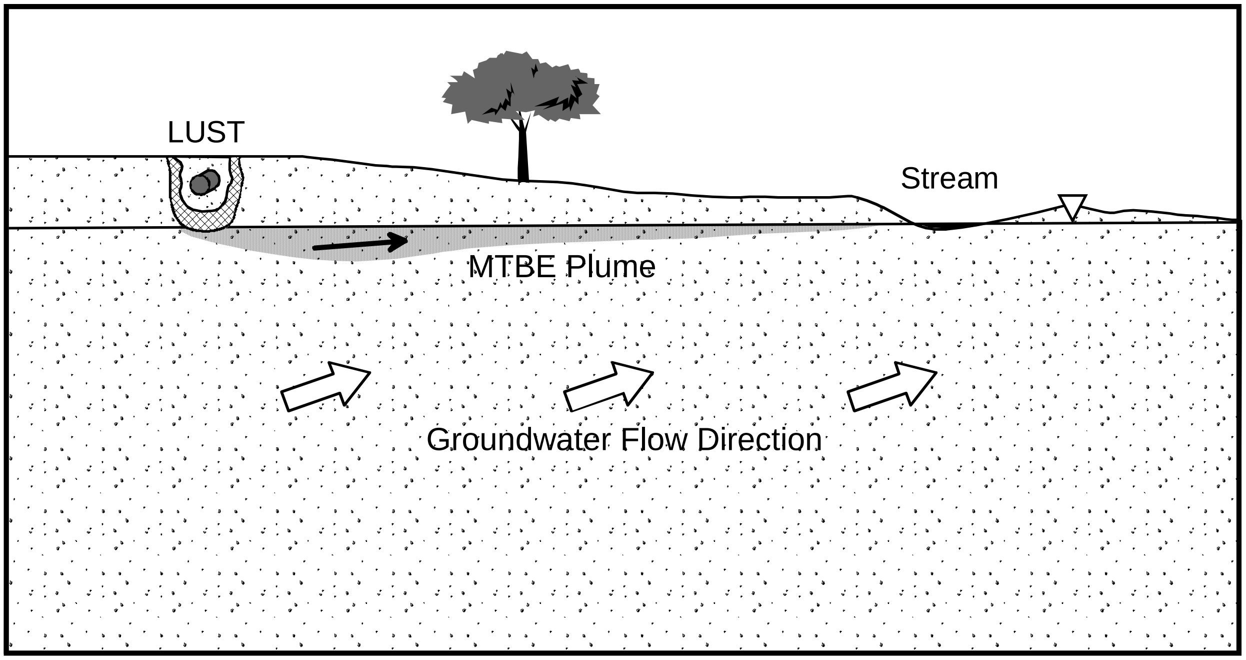


Figure 3-3. Rising MTBE Plume in a Regional Groundwater Discharge Area

Groundwater pumping can have a major effect on the location and ultimate fate of many contaminant plumes. Pumping wells create converging groundwater flow lines, thereby drawing the contaminant plumes into their well screens. Concentrations in the pumping well will be diluted if part of the captured water is affected groundwater, and part of the captured water originates from unaffected areas or water-bearing layers.

In aquifers that are not separated by effective aquitards, downgradient pumping can create strong downward hydraulic gradients that draw contaminants downward (Figure 3-4). At one site in Southern California, trace concentrations of a dissolved-phase MTBE plume have migrated at least 76 ft below the water table, probably caused by pumping in deeper layers (Rong, 1999).

The portion of the aquifer that contributes groundwater flow to a pumping well is known as the capture zone of the well. In addition to plumes directly upgradient of the well, the capture zone may draw in plumes that are located cross-gradient of the well (Figure 3-5). If a water-supply well is affected by ether oxygenates, definition of the capture zone may help to identify the sources that are responsible (Figure 3-6).

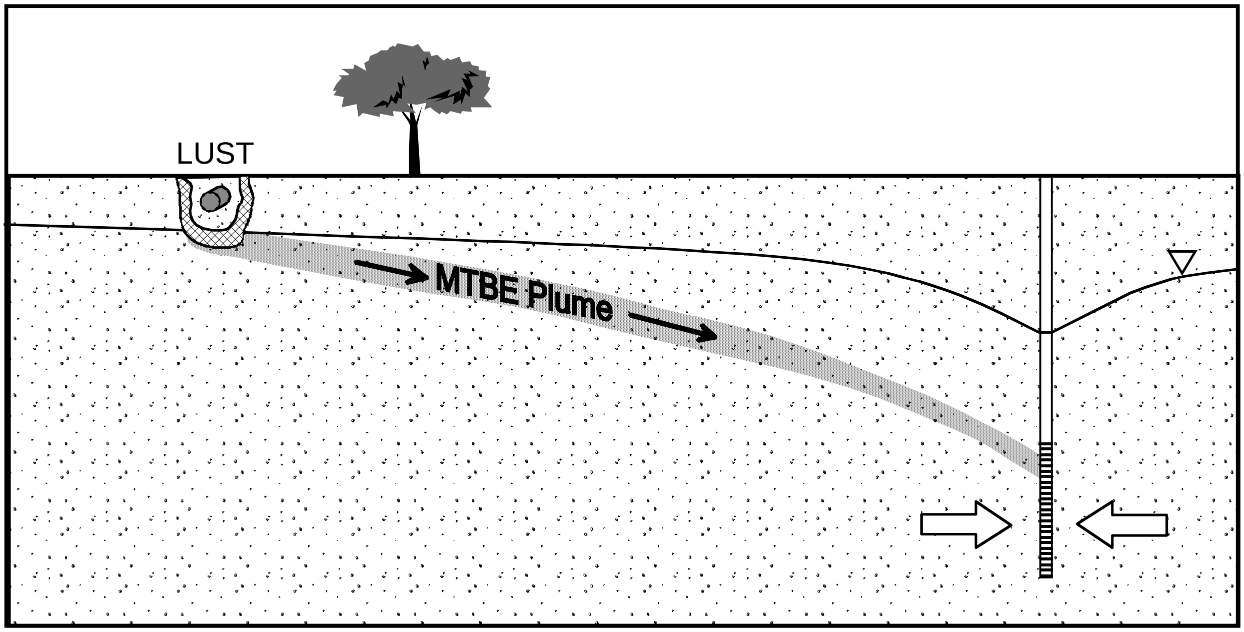


Figure 3-4. Plunging MTBE Plume Caused by Groundwater Pumping

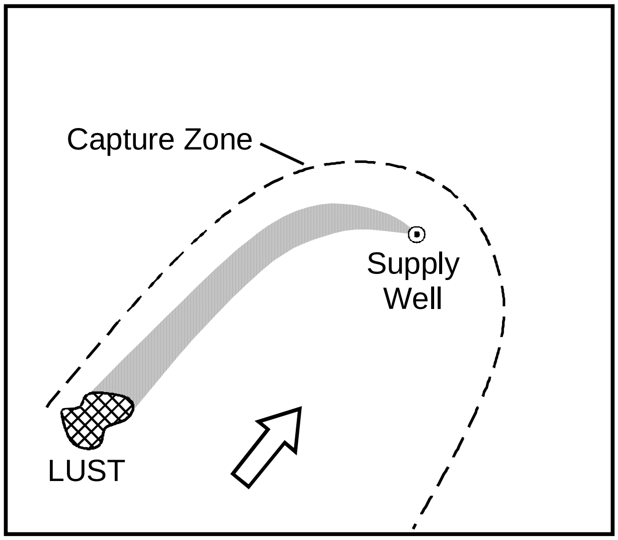


Figure 3-5. MTBE Plume Captured by Supply Well

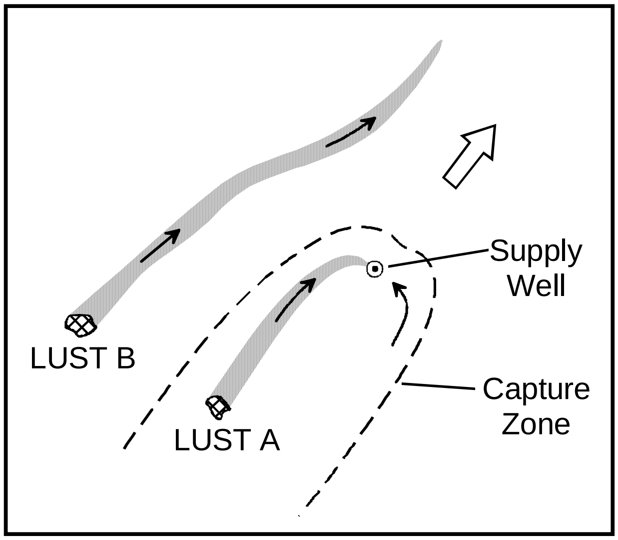


Figure 3-6. Defining the Capture Zone of the Supply Well May Identify Sources

Maps depicting the capture zones of supply wells may be available from water companies, water agencies, or environmental regulatory agencies. If necessary, capture zone maps can be generated using simple analytical equations (Todd, 1980), or numerical groundwater flow models. It is important to note that capture zones are three-dimensional, and that they can vary significantly with changing groundwater flow directions and intermittent or seasonal pumping of the supply wells. A discussion of hydraulic capture zones is presented in Andersen and Woessner (1992).

Groundwater elevations from on-site or nearby monitoring wells should be interpreted using potentiometric contour maps. For sites where vertical migration is a concern, clustered wells can be used to evaluate vertical gradients. Clustered wells are wells where the horizontal distance between wells is small relative to the vertical distance between screened intervals (Figure 3-7). Horizontal and vertical gradients should be interpreted carefully; a hydraulic gradient represents the *driving force* for flow, but does not indicate the *magnitude* of the flow. Steep vertical or horizontal gradients can indicate regions where there are barriers to flow (or major changes in hydraulic conductivity), where the rate of recharge is high, or where a large flux of groundwater is occurring (e.g., near a pumping well), or a combination of these conditions. Geologic controls on groundwater flow should be considered when interpreting groundwater levels, gradients, and potential flow directions.

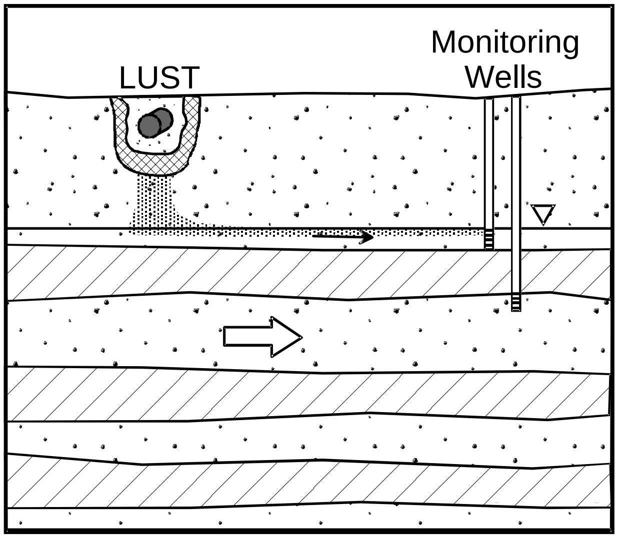


Figure 3-7: Using a Well Cluster to Evaluate Contaminant Migration Controlled by Geologic Stratification

Water levels should be monitored and interpreted for at least 8 quarters to determine whether flow conditions have seasonal variations that could affect the migration of a dissolved plume. Sites that require a more detailed level of characterization may require a longer period (or higher frequency) of water level monitoring.

For sites that require a more detailed level of assessment, hydraulic tests may be used to indicate the flow properties of the subsurface materials. This information can be used to refine estimates of horizontal and/or vertical groundwater flow velocities.

For sites where the magnitude of horizontal or vertical flow between water-bearing zones is uncertain, and where this information is important in estimating the future migration of a dissolved-phase plume towards a receptor, hydraulic interactions can be assessed through a variety of means. Water level changes in response to pumping or natural influences can be evaluated to estimate the degree of hydraulic interconnection between two locations. Groundwater budgets can be estimated to help evaluate the relative magnitude of horizontal and vertical flows. Numerical groundwater flow models can be used to represent and evaluate water inputs, outputs, and other flow features with a wide range of potential detail. In addition to the hydraulic and geologic data discussed in Tasks 2a and 2b, water quality data, such as inorganic chemistry and stable isotope data, can often aid in interpreting the subsurface flow system.

A high degree of hydraulic connection potentially exists where shallow and deep zones are poorly separated by thin layers of moderate or variable vertical hydraulic conductivity, and where water level monitoring data indicate that the upper and lower zones exhibit similar hydraulic responses over time. A high degree of hydraulic connection may also occur as a result of man-made or geologic structures, such as conduit wells, excavations, or erosional contacts between layers. A moderate degree of hydraulic connection potentially occurs where shallow and deep zones are separated by thicker layers of moderate or variable vertical hydraulic conductivity, or where conduit wells are less abundant. A low degree of hydraulic connection would typically occur where zones are separated by thick aquitards, or where water levels in shallow and deep zones are significantly different through time. A low potential for downward migration could also exist where persistent upward hydraulic gradients prevent the migration of groundwater from shallow affected zones to supply wells screened in deeper zones.

3.3.2.2 Geologic Characterization (Task 2b)

The purpose of geologic characterization is to identify the subsurface geologic features that affect the flow of groundwater and the migration of contaminants. Water-bearing zones are rarely homogeneous. Subsurface fine-grained geologic units (aquitards) often exert a strong control on contaminant migration. In many cases, aquitards can help protect potential receptors from a release. API (1996a) and ASTM (1999a) summarize and compare various drilling and logging methods for obtaining geologic information. Additional information on selected new geologic characterization technologies is presented in Section 4. Some of the geologic influences on the migration of contaminant plumes are described below.

In stratified aquifers, the migration of contaminant plumes is typically horizontal (Figure 3-7). On a regional scale, a thick, laterally continuous aquitard may prevent a shallow oxygenate plume from being drawn into the well screens of a deeper pumping well, even when there are strong downward hydraulic gradients (Figure 3-8). A discontinuous aquitard, on the other hand, can allow a shallow oxygenate plume to be drawn into a deeper aquifer (Figure 3-9).

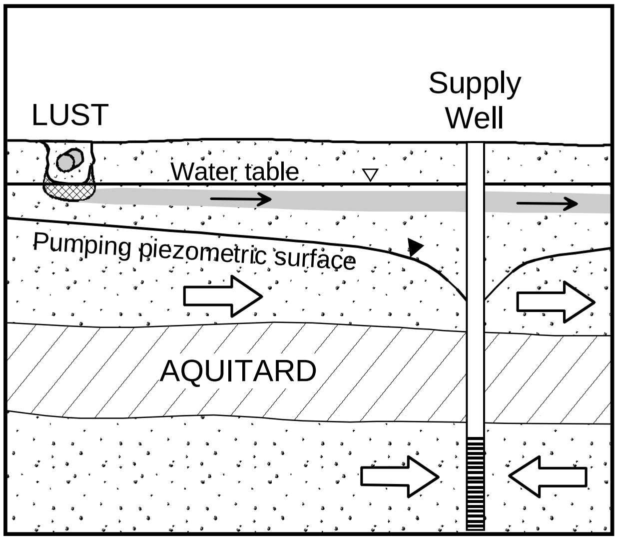


Figure 3-8. Thick Aquitards Can Protect Deeper Groundwater Supplies, Even When Downward Hydraulic Gradients Exist

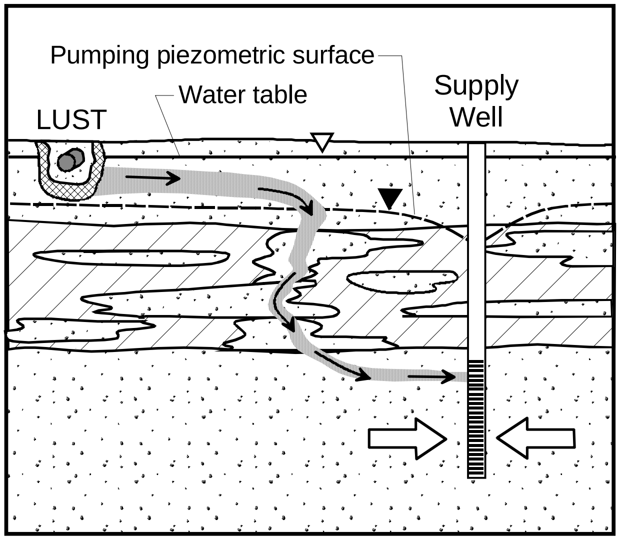


Figure 3-9. MTBE Plume Migrating Through a Leaky Aquitard

Laterally continuous aquitards tend to be associated with marine, estuarine, and lacustrine deposits, while discontinuous aquitards are characteristic of fluvial deposits. Descriptions of geologic units are frequently available from federal or state geological surveys. The type and extent of local geologic units should be identified as part of the conceptual site model.

3.3.2.3 Plume Delineation (Task 2c)

The purpose of plume delineation is to estimate the extent (and to a lesser degree, the magnitude) of a subsurface release of oxygenated fuel. The degree of plume definition necessary at a given site depends on the degree of risk posed by the release to potential receptors. For example, limited plume definition would be warranted at a small oxygenate release site where there are no current or future beneficial uses of the groundwater. Conversely, more detailed plume definition may be necessary at an oxygenate release site that affects a sole-source drinking water aquifer, in order to ensure that corrective actions are effective. A detailed level of assessment would typically include depth-discrete soil samples, and multi-level, short screened wells for vertical and horizontal dissolved chemical delineation. To minimize the possibility for vertical cross-contamination, wells need to be properly constructed. Where feasible, direct-push technologies (described further in Section 4) can be used to collect depth-discrete soil and groundwater samples. The extent of affected groundwater should be interpreted and summarized using isoconcentration contour maps. Sites that warrant a standard level of site assessment would use depth-discrete soil and groundwater sampling methods with less frequency and intensity. Sites that warrant a limited level of site assessment would be less likely to require depth-discrete soil and groundwater sampling methods.

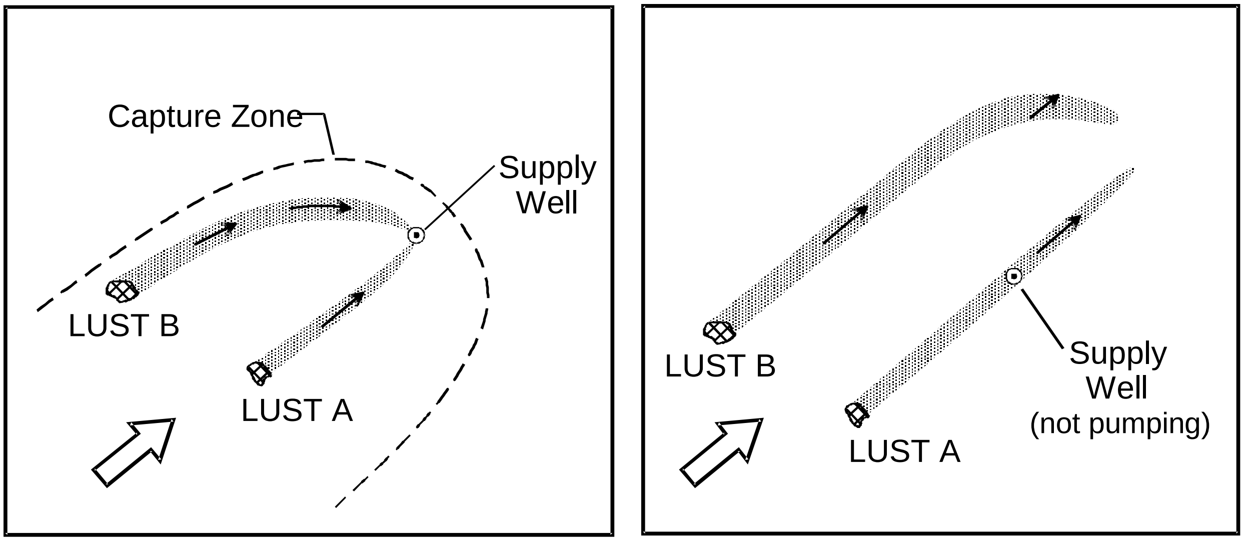
API (1996a) and ASTM (1999a) summarize and compare various chemical sampling methods for delineating subsurface releases. Additional information on selected new sampling technologies is presented in Section 4. Some considerations for chemical delineation of dissolved oxygenate plumes are discussed below.

It can be time-consuming and expensive to locate a relatively narrow and thin oxygenate plume in a regional flow system. The locations and depths of groundwater samples should therefore be selected after careful consideration of the three-dimensional conceptual site model of potential sources, pathways, and receptors. Sampling should begin near the suspected release where the dissolved plume will be located at relatively shallow depths (see Section 3.3.3). For sites that warrant a detailed level of assessment, multiple depth-discrete samples should be collected initially to identify the depth and thickness of the dissolved plume; multiple samples may not be needed at every location after these factors have been determined. The locations of downgradient sampling points should be selected based on the results of previous sampling results. Under the “expedited” approach (see Section 4.3), chemical analysis is performed onsite or offsite with rapid turn-around. In this way, groundwater sampling proceeds until the plume is adequately defined. Several innovative tools have been developed to rapidly collect depth-discrete groundwater samples in a variety of geologic environments (see Section 4.4).

Plume length and apparent plume velocity can be used to estimate the timing of potential impacts to downgradient receptors. The measured plume length can be divided by the approximate time since the release, if known, to provide an estimate of the plume migration rate. Since most releases of oxygenated fuels occurred relatively recently (see Section 2.2), the approximate time of release can often be estimated with greater accuracy than releases of non-oxygenated fuel.

Under certain conditions, dissolved BTEX plumes and oxygenate plumes from the same release may tend to disassociate over time (Happel *et al.*, 1998). Detached MTBE plumes may occur as a result of high groundwater velocity and high recharge rates, which cause higher dissolution rates from NAPL sources (Small and Weaver, 1999). Effective source removal may also result in plume detachment (Weaver *et al.*, 1999). For sites with these conditions, the need for offsite groundwater sampling should be evaluated.

Plume delineation may be complicated if an oxygenate release affects a downgradient water supply well. In such cases, the water supply well is typically shut down. The most obvious assessment approach is to sample along a line between the suspected source areas and the affected well. This approach is appropriate for suspected sources located directly upgradient of the affected well; however, it is not appropriate for suspected sources located in other parts of the capture zone of the well (Figure 3-10). After the pumping well is shut off, the oxygenate plume will continue to migrate downgradient, following the regional groundwater gradient. The distance that the plume migrates after well shutdown can be conservatively estimated by multiplying groundwater seepage velocity by the time since the well was shut off. Analytical or numerical flow models may help to estimate the extent or occurrence of a dissolved plume prior to selecting sampling locations. In some cases, it may be advantageous to continue pumping the affected supply well to maintain plume capture. This could prevent the plume from migrating to other downgradient wells.



Plume locations during pumping.

Plume locations after supply well shut off. Plumes migrating downgradient with regional groundwater flow.

Figure 3-10. Plume Delineation Affected by Pumping Patterns

In steady groundwater flow systems, measurements of geochemical indicators of redox conditions may help to define the “trajectory” that an oxygenate plume will eventually follow. At some sites, historical releases of conventional fuel preceded more recent releases of oxygenated fuel. In such cases, natural attenuation usually limits the length of the older dissolved BTEX plumes, but the degradation of this BTEX by indigenous microorganisms can also deplete many of the dissolved electron acceptors (such as oxygen, nitrate, or sulfate) in the aquifer. This anaerobic “shadow” can travel in the groundwater flow system (at the same velocity as groundwater) until it disappears due to dispersion or reaches a discharge area (Figure 3-11). This approach can help to identify (or rule out) potential receptors of the younger oxygenate release, although it is appropriate only if the current groundwater flow system is similar to the flow system that created the anaerobic “shadow” in years past.

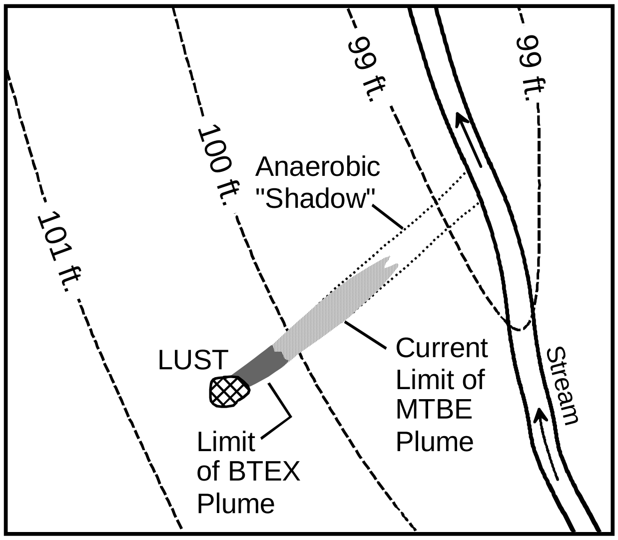


Figure 3-11. Defining an Anaerobic “Shadow” Can Help Define the Trajectory of an MTBE Plume

3.3.2.4 Potential Conduit Survey (Task 2d)

The purpose of a potential conduit survey is to identify any artificial subsurface features that could influence the migration of a released chemical. Near-surface man-made pathways, such as sewer lines, storm drains, and utility corridors, may act as “short circuits” for NAPL or dissolved contaminants. In the vadose zone, these shallow pathways can control the exposure of receptors to subsurface vapors. In the saturated zone in some areas, especially in agricultural areas that have been urbanized, improperly constructed or abandoned water supply wells or monitoring wells can allow rapid transport of dissolved contaminant plumes to deeper aquifers. These old wells penetrate important regional aquitards and can cause “short circuiting” of a contaminant plume, potentially drawing some portion of a plume into a deeper pumped aquifer.

Identification of these potential conduits requires collaboration with water companies, permitting agencies, environmental agencies, and local well drillers. Historical aerial photos can help to identify the general locations of old water wells, and geophysical tools can be used to locate old well casings. Careful mapping of hydraulic heads in a shallow aquifer may show an area of groundwater flow convergence that corresponds to the location of an abandoned well acting as a flow conduit between aquifers.

3.3.3 Source Characterization Tasks

3.3.3.1 Source Zone Delineation (Task 3)

The purpose of the source zone delineation is to estimate the magnitude (and to a lesser degree, the extent) of highly affected soil and groundwater near a subsurface release of oxygenated fuel. As indicated in Table 3-3, source zone characterization may be needed to estimate the magnitude of the release if a site warrants a detailed level of assessment (e.g., if a downward hydraulic gradient exists and/or supply wells exist within ½-mile of the release). Source zone characterization may be warranted for a standard level of assessment if strong downward gradients exist or if potential conduits are identified. Source zone characterization is not required for a limited level of assessment if other investigation tasks confirm the low-risk status of the site.

For higher levels of assessment, the areal extent and vertical saturation distribution of any NAPL may be evaluated in order to estimate the longevity of the associated dissolved-phase oxygenate plume. Since oxygenates generally have a low affinity for soil, residual or mobile NAPL may be regarded as the only persistent subsurface source that can continue to create a high-concentration dissolved-phase oxygenate plume. Mass estimates based on subsurface data are highly uncertain, consequently the amount of mass in a source zone should be considered in a qualitative manner, rather than in a quantitative manner. A site with high dissolved concentrations (or NAPL) extending over a large region represents a larger amount of mass than a site with lower or less extensive concentrations. The amount of mass should be considered during site characterization and corrective action decisions: for sites that pose a potential to impact receptors, sites with larger amounts of mass warrant a higher level of assessment than sites where small amounts of mass have been released.

Developing a Conceptual Model of the Source Zone

Source zone characterization starts with a careful review of available data, such as fuel inventory records, tank and piping integrity reports, anecdotal information from employees, plans of existing and former fuel tanks, piping systems, and vent lines, and plans of potential conduits, such as sewer or drain lines. Surface geophysical instruments, ranging from simple metal detectors to sophisticated ground penetrating radar, are often useful for defining the layout of underground tanks, piping systems, vent lines, and utility lines, especially when construction records are poor or unavailable.

The available data should be used to estimate the location and history (e.g., chronic, catastrophic, or discontinuous), of the release, and then to estimate the extent of the subsurface source (or sources). These estimates may be extremely rough, but they represent the starting points for the investigation. The potential effects of hydrogeologic factors should be considered: for example, soil type affects the residual saturation of NAPL (API 1996a, Table 6), while a rising water table may submerge residual NAPL. For complex, high-risk sites, computer models that estimate the location and dissolution rates of NAPL spills can be useful (Weaver *et al*., 1994). Other models are available; see ASTM (1999b) for a list of computational models appropriate for use in a RBCA framework. Because of the complexity and sensitivity of many flow and transport models, models should only be applied when the modeling objectives, assumptions, and sensitivities are clearly understood, and when adequate field data are available.

Previous characterization work at a given site may not have included oxygenate analyses. However, it still may be possible to determine if MTBE or other oxygenates were present in previously collected samples through a review of old laboratory chromatograms.

Investigating Oxygenate Vapor Releases

Oxygenates tend to volatilize readily from unsaturated zone NAPL, and in dry soil they will migrate horizontally and vertically in soil gas (see Section 2.3.2). Soil gas surveys may be useful at suspected release areas, since the presence of oxygenates in soil vapor samples could demonstrate that a release has occurred. In moist soil, however, oxygenate vapors may not migrate far from the residual NAPL (see Section A.2.6). The absence of oxygenates in soil vapor samples, especially in moist soil, does not necessarily demonstrate the absence of an oxygenate release. Other fuel components may be more useful for evaluating suspected releases in moist soil; for example, low molecular-weight alkanes (in the C_4 to C_8 range) also have relatively high partial pressures in fresh NAPL, but compared to oxygenates, they have a lower affinity for soil moisture.

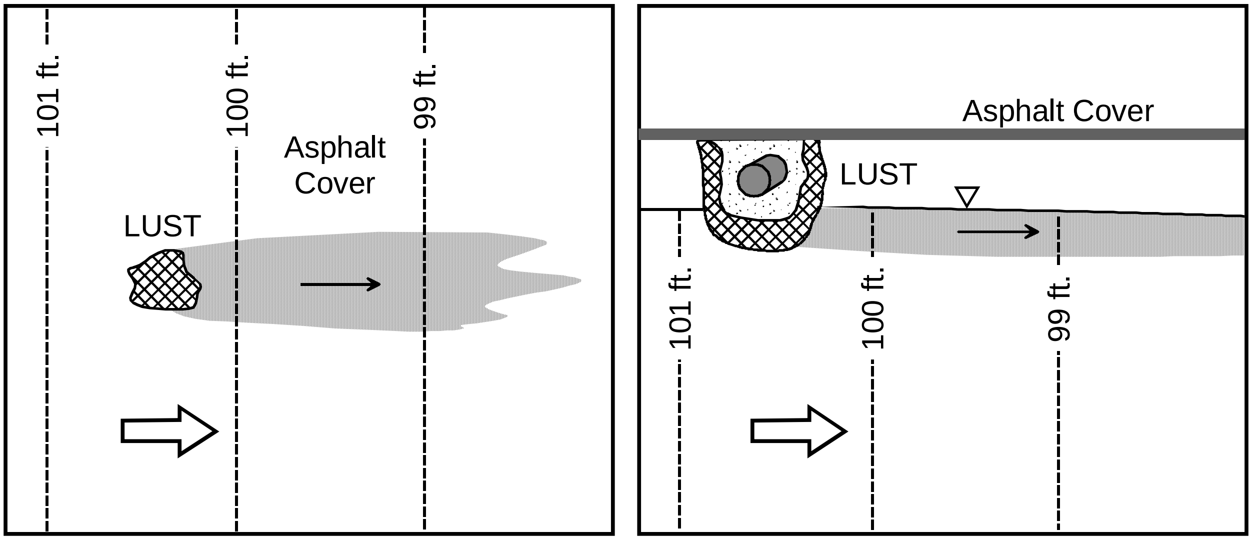
At some sites, releases of petroleum vapors in the vadose zone and subsequent partitioning into groundwater may be a significant release mechanism (see Section 4.2.1). This hypothesis can be tested by collecting depth-discrete soil vapor samples, including a sample just above the capillary fringe, along with depth-discrete groundwater samples below the water table. Vapor releases may be more likely at UST installations with assisted vapor recovery systems than with balanced vapor recovery systems (SCVWD, 1999). If this pathway exists, then the expected result would be a thin plume of dissolved oxygenates near the water table.

Assessing Potential Releases to Groundwater

At many sites, the presence of oxygenates in groundwater may be suspected, but not documented. In such cases, groundwater samples should be collected immediately downgradient of the suspected release area to determine if groundwater has been affected and to estimate the magnitude of the release. These groundwater samples should be collected near the water table as close as possible and downgradient from the suspected source location.

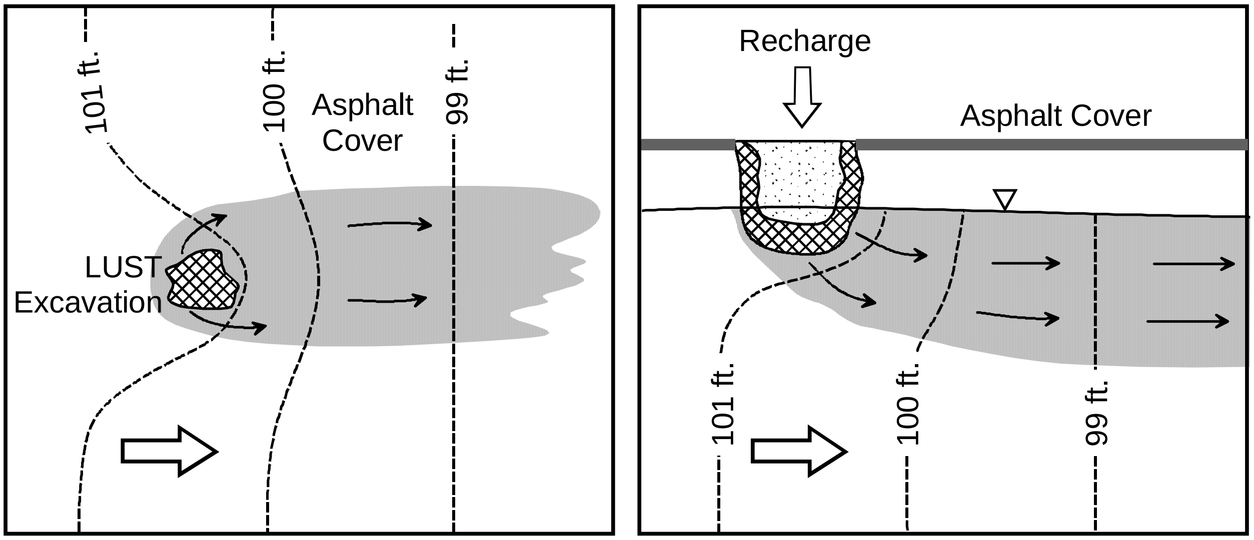
In some cases, the groundwater flow direction may be well defined based on previous work, and the number of sampling locations can be kept to a minimum, provided that groundwater flow conditions have not changed appreciably. In other cases, the groundwater flow direction may fluctuate or may be poorly defined, so a greater number of sampling points may be warranted. Dissolved-phase oxygenate plumes may be relatively narrow and thin (see Section 4.2.2), so closer sample spacing may be needed to detect them.

A special (but not uncommon) case exists when USTs have been removed and the excavation has been filled with sand or gravel backfill. At these sites, preferential recharge through the backfill causes radial flow through the source zone, creating a wider and thicker contaminant plume (Figure 3-12). This localized disruption of the groundwater flow field can create flow lines quite different than the regional flow system, and may therefore warrant a greater number of sampling points. The conceptual site model should consider the likelihood of this condition (e.g., by evaluating annual precipitation rates and the infiltration characteristics of the backfilled area relative to other parts of the site). If necessary, the presence or absence of this condition can be quickly evaluated during a field investigation by installing monitoring wells or temporary piezometers, and measuring hydraulic heads in and near the backfilled area.



MTBE Plume in a Uniform Flow System (plan view)

MTBE Plume in a Uniform Flow System (cross section)



Wider MTBE Plume Resulting From Preferential Recharge through Tank Excavation (plan view)

Thicker MTBE Plume Resulting From Preferential Recharge through Tank Excavation (cross section)

Figure 3-12. Example MTBE Source Conditions

The vertical resolution of groundwater samples collected during a source zone investigation depends on the level and objectives of the assessment. If the purpose of the investigation is simply to determine whether or not a release has occurred, then a single groundwater sample at each location is usually adequate. This is consistent with the “limited level of assessment” as indicated in Table 3-3. Caution is necessary, however; at many sites, the depth of the water table is poorly defined, so this single sample may be collected below the contaminant plume, especially when short-screened DP water sampling tools are used (Figure 3-13). For screening-level investigations, DP water sampling tools or monitoring wells with long screens (5 feet or more) could be considered near the source area to ensure that the plume is not missed, although the samples collected with long-screened tools will typically result in lower oxygenate concentrations due to dilution.

After the presence and extent of oxygenates in groundwater has been documented, it may be necessary to establish the highest concentrations of dissolved-phase oxygenates migrating from the source zone. This may be useful at sites that warrant a detailed level of assessment. In such cases, multiple depth-discrete groundwater samples may be needed at several locations.

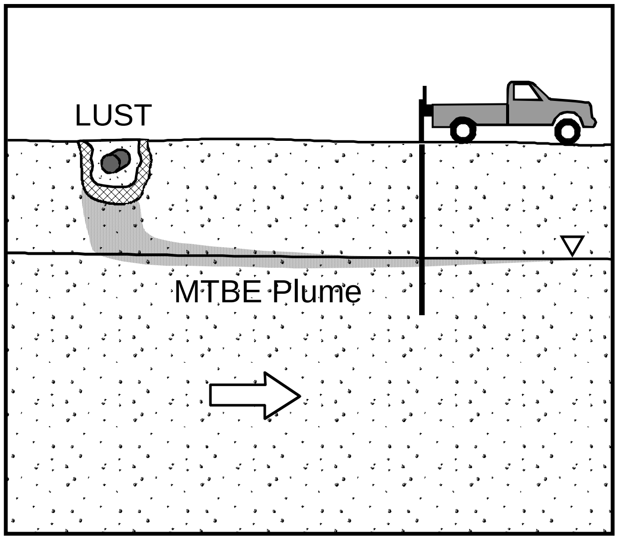


Figure 3-13. Missing the Plume by Collecting a Single-Depth Groundwater Sample Below the Zone of Contamination

Determining Whether NAPL is Present in the Subsurface

The presence or absence of NAPL is an important factor at oxygenated fuel release sites. If little or no residual NAPL is present, then there will be no significant mass of oxygenates to “feed” the dissolved-phase plume. Desorption of oxygenates in soil is generally not a significant factor, since oxygenates (unlike BTEX compounds) do not sorb significantly to organic material in the aquifer matrix (see Section 2.3.3).

If existing site wells contain NAPL, samples of the NAPL should be collected and analyzed for oxygenates (see Section 2.4.1). The analysis should determine whether oxygenates are present in the NAPL, and if they do occur, the analysis should estimate the mole fraction of oxygenate in the NAPL. A low mole fraction may indicate that most of the oxygenates have already been leached or volatilized from the NAPL; alternatively, it may indicate that the NAPL was derived from an older, conventional fuel product that contained only small amounts of oxygenated compounds (see Section 2.2). Historical factors may help to identify the most likely hypothesis.

Many sites have complex release histories; undetected small volume releases may have occurred over time from UST systems. Oxygenates may therefore occur in NAPL in one part of a given site, yet be absent in NAPL in another part of the same site. Oxygenated NAPL may occur only in a small area where the most recent release occurred. The conceptual site model should consider all available historical information to help define potential oxygenate source areas.

Under some circumstances, no NAPL will be detected in wells even when NAPL exists beneath the site. One reason may be that the wells are in the wrong locations. Alternatively, the NAPL may only be present at its residual saturation, and may not flow into a monitoring well. Charbeneau *et al*. (1999) discuss the use of monitoring wells to estimate subsurface NAPL volumes in more detail. Huntley and Beckett (1999) and Rixey and Joshi (1999) discuss the dissolution and longevity of MTBE in residual LNAPL.

Three other NAPL indicators are often used in subsurface investigations: fluorescent light, hydrophobic dyes, and measured concentrations in soil samples. Hydrophobic dyes are colored powdered dyes that dissolve in organic liquids, but not in water. A small amount of dye is placed in a vial with water and soil. The sample is then shaken to mix the soil, water, and dye; if NAPL is present, the dye will visibly partition into it. Many of the hydrophobic dyes (especially Sudan IV) are hazardous materials, and must be used and disposed of properly. Cohen and Mercer (1993), Cohen *et al*. (1992), Feenstra (1990), and Pankow and Cherry (1996) discuss the use of fluorescent light and hydrophobic dyes.

Soil samples are often collected and analyzed to determine whether free-phase NAPL is present in the source zone. The results are not necessarily obvious; for example, if MTBE occurs in soil at a concentration of 20 mg/kg, does that indicate that free-phase NAPL is present? This question can be addressed by estimating a few physical properties of the soil and assuming saturation concentrations in the various phases.

MTBE in vadose-zone soil can occur in four phases: in NAPL, dissolved in pore water, in gas molecules in soil pores, and sorbed onto soil particles. Laboratory analysis will extract MTBE from all four phases and measure the total (assuming that no MTBE is lost during sample collection or preparation). If the concentration of MTBE in the pore water is assumed to be at saturation concentrations, it is then possible to calculate the maximum concentration of MTBE that can be present within that soil sample without a NAPL being present (Feenstra *et al.*, 1991). If the soil sample contains MTBE above that calculated concentration, then MTBE is likely present in residual NAPL.

The maximum soil concentration without free-phase NAPL (C_t) may be calculated using bulk density (ρ_b), Henry's Law coefficient (K_H), the soil-water partition coefficient (K_d), the effective solubility of the oxygenate (S_e), the soil porosity (ϕ), and the volumetric water saturation (S_w), where

$$C_t = \left[\frac{\phi}{\rho_b} \left\{ S_W + K_H \left(1 - S_W\right) \right\} + K_d \right] S_e \qquad \text{(Equation 3-2)}$$

In this example, MTBE was detected at a concentration of 20 mg/kg in vadose-zone soil. Assuming $\rho_b = 1.86$ g/cm^3, $K_H = 0.0216$, $K_d = 0.011$ l/kg, $S_e = 3{,}500$ mg/l (consistent with a NAPL that is somewhat depleted in MTBE), $\phi = 0.35$, and $S_w = 0.30$, then the calculated upper limit soil concentration $C_t = 241$ mg/kg. Since this value is above the measured 20 mg/kg concentration, this result suggests that free-phase NAPL is not present in the soil.

One difficulty with the application of this equation is determining an accurate value of S_e. The mole fraction of MTBE in NAPL can be determined by direct analysis of a representative NAPL sample; the mole fraction of MTBE can then be multiplied by the theoretical solubility of MTBE to obtain S_e (see Section A.2.1). Alternatively, S_e can be measured directly by equilibrating a representative NAPL sample in clean water and then analyzing the water (Feenstra *et al.*, 1991).

3.3.4 Verification Monitoring

3.3.4.1 Groundwater and Chemical Monitoring (Task 4a)

Periodic groundwater monitoring is used to supplement the initial assessment data, and to confirm assumptions about the site conceptual model. The objectives of groundwater monitoring 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.

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 monitor well spacing.

Sites that warrant a detailed level of assessment would usually require a monitoring period of at least two seasonal variations in water levels and concentrations (Table 3-3). Data from periodic monitoring should be interpreted and summarized using potentiometric contour maps and isoconcentration contour maps. Sites that warrant a standard or limited level of assessment would usually require a similar monitoring period and data summary (Table 3-3).

3.3.4.2 Assess Source Depletion, Hydraulic Influences, and Plume Stability (Tasks 4b and 4c)

Variations in concentration over time at individual wells can be used to understand source depletion and potential hydraulic influences on plume migration. The purpose of analyzing concentrations over distance along a plume centerline is to assess plume stability. 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 groundwater flow. The trend in concentrations at these points will determine 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 decline with distance from the source). This analysis must be done carefully because short-duration concentration changes (“spikes”) can occur due to water level fluctuations, changes in groundwater flow direction, or recharge events. Depth-discrete monitoring can reduce the uncertainty in assessing source depletion, hydraulic influence, and plume stability. Methods for display and interpretation of groundwater concentration data are summarized in ASTM, 1998b.

3.4 CONFIRMATION OF CONCEPTUAL SITE MODEL AND EXAMPLE LEVELS OF ASSESSMENT

The assessment process outlined in this document uses readily available receptor data to tentatively determine the initial level of assessment for the site (see Section 3.3.1). As the investigation proceeds, more information about the receptors, pathways, and sources will become available, and the assumptions used to determine the initial level of assessment should be reevaluated. The level of assessment for the site may be upgraded or downgraded as appropriate; for example, the results of an initial limited assessment may indicate that a standard level of effort is warranted.

In most cases, there will be no simple “bright lines” or “litmus tests” to indicate when a higher or lower degree of characterization is necessary. *The decision to upgrade or downgrade the level of assessment should be based on whether the available information is sufficient to make a protective site management decision*.

For example, suppose that a standard-level assessment has found a subsurface MTBE release at a hypothetical site, and that the released MTBE has affected a nearby potable-use well. Although this situation may fulfill the criteria for a detailed level of assessment, the results of the standard-level assessment also show that the hydrogeologic setting is straightforward, and that the MTBE release is completely captured by the potable well. In this case, the existing assessment information may be sufficient to implement a protective remedy to protect current and future beneficial uses of groundwater. Effective corrective actions, such as source removal combined with wellhead treatment and hydraulic containment, could be implemented with the existing assessment information. Thus, an upgrade to a more detailed level of assessment would not be necessary.

Table 3-4 presents a matrix of example receptor, pathway, and source conditions that can be used to help determine the appropriate overall level of effort. Once site characterization is relatively complete, sites with similar conceptual models (and similar risk factors) should have similar overall levels of effort. This section provides some example site conditions and levels of effort to serve as a confirmation on the appropriate overall level of assessment.

The conditions in Table 3-4 are presented as examples only; they should be considered together, using a weight-of-evidence approach, since it is unlikely that all of the conditions at a given site will consistently suggest the same level of assessment. Furthermore, the example conditions listed in Table 3-4 are qualitative in nature. Quantitative definitions for such terms as “low”, “moderate”, or “high” in the context of this table should be determined by the user, in accordance with applicable regulatory guidelines.

The example conditions shown in Table 3-4 are not intended to encompass all site conditions or considerations. For example, other criteria or risk factors may warrant a higher level of assessment, such as ecological risk considerations, or potential human exposures via pathways other than groundwater ingestion.

Table 3-4. Example Conditions Associated with Different Levels of Assessment

	Level of Assessment		
	Detailed	**Standard**	**Limited**
Receptor Conditions			
Local usage of shallow groundwater	Used for potable purposes	Little or no current use for potable purposes	Not currently used for potable purposes due to insufficient yield or quality
Local usage of affected groundwater	Used for potable purposes	Not currently used for potable purposes	Not currently used for potable purposes
Horizontal/vertical separation between affected soil/groundwater and potable-use wells	Little or no separation	Moderate degree of separation	High degree of separation
Pathway Conditions			
Estimated rate of groundwater migration	High	Moderate	Low
Presence of groundwater recharge area	Site is located in a groundwater recharge area	Site is not located in a groundwater recharge area	Site is not located in a groundwater recharge area
Estimated rate of groundwater recharge	High	Moderate	Low
Discharges of groundwater to surface water	Groundwater from the site discharges to surface water close to the site	Groundwater from the site does not discharge to surface water, or discharges at a moderate distance from the site	Groundwater from the site does not discharge to surface water, or discharges at a large distance from the site
Downward vertical gradients due to pumping or diffuse recharge	Known to occur	Existence uncertain	Not known to occur
Source Conditions			
Presence/extent of oxygenate release	Sampling data suggest that a significant oxygenate release has occurred	Sampling data suggest that an oxygenate release has occurred	Sampling data suggest that no release has occurred
Oxygenate concentrations in soil/groundwater	Preliminary data indicate high oxygenate concentrations	Preliminary data indicate moderate oxygenate concentrations	Preliminary data indicate low oxygenate concentrations
Extent of affected soil/groundwater	Preliminary data indicate large extent of affected soil/groundwater	Preliminary data indicate moderate extent of affected soil/groundwater	Preliminary data indicate very limited extent of affected soil/groundwater

Section 4

MTBE ASSESSMENT AND MONITORING

4.1 OBJECTIVES

The objective of a site assessment is to obtain information in an efficient and cost-effective manner that is sufficient to make site management decisions to achieve remedial goals. Assessment data are needed to validate the initial site conceptual model, to evaluate the potential risks to receptors, and to design and implement corrective actions, if the potential risks are unacceptable. These general points apply to site assessments for any chemical, not only oxygenates.

Periodic groundwater monitoring is often needed to supplement the initial assessment data, particularly when groundwater migration is the primary pathway of concern, as it is for oxygenates. The objectives of monitoring 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.

4.2 ETHER OYXGENATE ASSESSMENT VS. HYDROCARBON ASSESSMENT

The general approaches for assessing an oxygenated fuel release are similar to those used for a conventional fuel release. In either case, sound conceptual site models must be developed to guide the investigation, and the same sampling tools and analytical techniques can be employed. However, the subsurface behaviors of ether oxygenates and hydrocarbons differ in several important respects, as outlined below. These differences should be addressed in the assessment of any known or suspected release of oxygenated fuel.

4.2.1 Sources

Fuel oxygenate sources are not necessarily the same as fuel hydrocarbon sources. Subsurface BTEX plumes are typically derived from large NAPL releases, such as those associated with storage tank or pipeline failures. Small NAPL releases are unlikely to act as significant secondary BTEX sources, since BTEX attenuates relatively readily. Ether oxygenates, on the other hand, attenuate less readily; it appears likely that even small releases of oxygenated fuel can affect shallow groundwater quality (see Section 2.3.1). This factor may greatly increase the difficulty of source detection. BTEX in groundwater at a given site is commonly attributable to a tank release or some other large source; MTBE in groundwater may be related to a variety of sources, large or small.

Oxygenate source identification is further complicated by the potential for vapor-phase migration to groundwater (see Section 2.3.1). Vapor migration to groundwater has not been regarded as significant for BTEX compounds, since they have relatively low partial pressures in NAPL and biodegrade relatively rapidly in aerobic soils. However, it does represent a theoretically viable pathway for the migration of MTBE and other ether oxygenates, since these compounds have relatively high partial pressures and biodegrade less readily (Stocking *et al*., 1999; Lahvis and Rehmann, 1999). In other words, MTBE vapors could migrate out of underground tank systems, and then migrate downward to the underlying groundwater, either in the vapor phase or dissolved in soil moisture, or both.

4.2.2 Plume Geometry

Dissolved-phase oxygenate plumes may display different geometries than dissolved-phase BTEX plumes. However, the expected plume geometries depend on hydrogeological and historical factors. MTBE was used as an octane booster in gasoline as early as 1979, but most oxygenated fuel programs in the U.S. were not initiated until 1992 to 1996 (see Section 2.5.1). Thus, MTBE releases are often younger than BTEX releases. Such historical considerations must be addressed during the site assessment process.

If BTEX and ether oxygenates are released simultaneously at a given site, then the plume lengths are unlikely to remain equal. The BTEX plume will be more subject to retardation and biodegradation, so it will be more likely to remain near the source area. The ether oxygenate plume will be more mobile and persistent, and so it is likely to extend further downgradient. If BTEX attenuation rates are relatively high, then a single release of oxygenated fuel may ultimately produce two distinct dissolved-phase plumes: a BTEX plume near the source and an ether oxygenate plume further downgradient. In other words, the oxygenate plume from a given fuel release may extend far offsite, even when the associated BTEX plume from the same release remains onsite. The potential need for offsite groundwater sampling should be considered in any planned assessment of oxygenated fuel releases, because the resulting complications can lead to significant schedule delays.

If a BTEX release at a given site predates an ether oxygenate release, then the BTEX plume may be as long (or even longer) than the oxygenate plume. However, the older BTEX plume is more likely to have been affected by changing flow directions or fluctuating water levels, while the younger oxygenate plume is more likely to have experienced fewer variations in groundwater conditions. Given these factors, the older BTEX plume may be wider and thicker, and the younger oxygenate plume may be narrower and thinner. Thus, an ether oxygenate plume may be more difficult to detect and delineate, even when its overall length is similar to that of the associated BTEX plume.

Dissolved-phase MTBE plumes vary in length, as do BTEX plumes. Mace and Choi (1998) evaluated fuel release sites in Texas; they found that 90 percent of the MTBE plumes were less than 386 feet long. Happel *et al*. (1998) conducted a similar study of sites in California, and found that 90 percent of the MTBE plumes were less than 325 feet long. The two studies obtained different results on the relative lengths of benzene and MTBE plumes. Mace and Choi (1998) found that 90 percent of the benzene plumes were less than 325 feet long, and that they tended to be shorter than MTBE plumes. On the other hand, Happel *et al*. (1998) found that 90 percent of the benzene plumes were less than 400 feet long, and that they tended to be longer than MTBE plumes. Happel *et al*. (1998) noted that this result could reflect the greater age of the BTEX plumes, and that the BTEX plumes were more likely to stabilize or shrink over time, while the MTBE plumes were more likely to grow. Happel *et al.* (1998) also examined a smaller group of plumes for which several years of monitoring data were available; for this group, MTBE appeared to be more mobile than BTEX compounds.

Analyses of MTBE plume stability are limited by the availability of monitoring data. Mace and Choi (1998) tentatively concluded that many MTBE plumes in Texas are stable or receding due to natural attenuation. Hydrogeologic factors may have affected this conclusion: most of the sites reviewed by Mace and Choi (1998) were located in clay-rich sediments. Most of the California sites reviewed by Happel et al. (1998) were located in alluvial sediments, and did not have sufficient monitoring data for temporal analysis.

4.2.3 Biodegradation

Hydrocarbons are subject to relatively high rates of natural biodegradation, and it is often feasible to evaluate geochemical indicators of biodegradation at BTEX release sites (API, 1997b; ASTM, 1998b; Wiedemeier *et al*,. 1995; EPA, 1999b). However, the available evidence suggests that the rates of natural biodegradation of MTBE and other ether oxygenates are lower than the rates for BTEX in most natural groundwater environments (see Section A.2.6). However, monitoring for geochemical indicators of biodegradation may still provide useful information regarding the migration and attenuation of dissolved-phase ether oxygenate plumes. If geochemical evidence of biodegradation is observed at an oxygenate release site, it could be related to the biodegradation of BTEX or other organic carbon sources, rather than to the biodegradation of oxygenates.

For any dissolved plume, the primary evidence for biodegradation (or other attenuation processes) is plume stability, which requires collecting water quality data over time using an appropriate network of monitoring locations (ASTM, 1998b). Potential differences in plume geometry may require different monitoring locations to assess plume stability.

4.2.4 Sample Media Biases

The differing chemical characteristics of oxygenates and hydrocarbons need to be considered when interpreting analytical results. For example, whenever groundwater samples are collected, some fraction of the dissolved-phase chemicals will be lost to volatilization. These losses should be much smaller for MTBE and other oxygenates than for BTEX compounds because oxygenates generally have a much greater affinity for water.

For soil samples collected in areas away from residual LNAPL, moisture content has an important influence on sample analytical results. MTBE and other oxygenates generally have high solubilities and low K_{oc} values relative to BTEX hydrocarbons, so they are more likely to be detected in soils with higher water contents. If present, oxygenates should be readily detectable in moist or wet soils, including soils collected within the saturated zone. However, the reported oxygenate concentrations in such soil may be biased by lithological factors. Coarse-grained soil is more likely to lose moisture (and therefore dissolved oxygenates) during the sample collection and preparation processes. Fine-grained soil is more likely to retain moisture (and oxygenates, if oxygenates occur in the pore fluid).

Soil moisture may also affect vapor samples. Oxygenates in a released NAPL have relatively high partial pressures, and so they volatilize readily from NAPL. However, oxygenates also have relatively low K_H values, and so vapor-phase oxygenates are readily dissolved in soil moisture. If there is sufficient groundwater recharge, lateral migration of vapor-phase MTBE away from the release may be significantly reduced.

4.3 EXPEDITED ASSESSMENT

In recent years, “expedited” site assessments (ESAs) have been used to improve the quality and reduce the time required to conduct site characterization at fuel release sites. ESAs are particularly applicable to sites affected by MTBE or other ether oxygenates. The general principles of ESAs, as contrasted with those of conventional site assessments (CSAs), are discussed below.

4.3.1 Conventional Site Assessments

Both CSAs and ESAs begin with the development of a conceptual site model (CSM) and the identification of data gaps. In a CSA, these gaps are addressed by preparing a rigid sampling and analysis plan, with a predefined number of sampling points in predetermined locations. These sampling points are commonly groundwater monitoring wells. The sampling and analysis plan is then implemented by junior field staff. Laboratory analyses and data syntheses are usually performed off-site, and may take weeks or months to complete. The main objective of most CSAs is to delineate the boundaries of the contaminant plume in two dimensions (i.e., plan view). Multiple phases of investigation are typically required to achieve this goal.

CSAs tend to be time consuming and expensive. Each phase of investigation may require weeks or months, from the beginning of field work to the submittal of a preliminary report. Furthermore, multiple phases of investigation are usually needed, and so corrective action decisions may be delayed for months or even years. Finally, the site conditions reported by CSAs are often incomplete. CSAs generally emphasize plume boundary mapping; however, this approach often fails to address many significant issues, such as source area conditions, the location of the most significant contaminant mass, or the three-dimensional nature of contaminant migration.

4.3.2 Expedited Site Assessments

The ESA process is a framework for rapidly characterizing site conditions and providing input into corrective action decisions. It has been described with other names, including accelerated site characterization, rapid site characterization, and expedited site investigation. The U.S. EPA (1997b) and ASTM (1999a) provide detailed guidance on performing ESAs. In ESAs, unlike CSAs, the sampling and analysis plan is dynamic; as new site information is generated, it is used to direct the assessment. The field-generated data are used to validate or refine the CSM until it no longer changes appreciably. While new to the environmental industry, the general ESA philosophy has been used by earth scientists for over a century (Chamberlin, 1897).

ESAs, like CSAs, start with the development of a conceptual site model. The CSM should be based on a review of existing information on past and current land uses, potential sources of contamination, and potential migration pathways and receptors. Potential future land and groundwater uses should also be investigated. Much of the required data may already be available as part of a previous Phase I Environmental Site Assessment; otherwise standard Phase I sources and techniques may be used (ASTM, 1997). In addition, the regional hydrogeology, including local water-supply systems, must be considered (see Section 3.3). Relevant hydrogeologic data can often be obtained from federal and state geological surveys, state or local environmental and water agencies, private water companies, and university geology and civil engineering departments. The initial CSM is typically summarized on large-scale maps of the site area, showing geologic and hydrogeologic features, cross sections, groundwater flow directions and velocities, anticipated sources, plume location and extent, receptors, and other relevant factors. Data gaps can then be readily identified.

In an ESA, the data gaps are addressed by a flexible sampling and analysis plan. ESAs emphasize innovative technologies, such as surface geophysical methods, direct-push sampling and monitoring tools, and on-site mobile laboratories. Traditional monitoring well installation is minimized. Analytical data are generated and interpreted on-site whenever possible. The sampling and analysis plan is implemented by senior field managers, who have both the experience to interpret results in the field and the authority to select new sampling locations and approaches as judged necessary. The field manager continually refines or validates the CSM as field data are collected and evaluated. New sampling depths and locations are chosen to test specific aspects of the CSM, and the assessment proceeds until the CSM no longer changes enough to affect remedy decisions. The ESA should be completed in a single intensive phase of investigation that typically lasts several days. Any data gaps should be filled and any anomalies should be resolved prior to demobilization.

ESAs have been made possible in recent years by the development of improved, cost-effective methods for rapid collection and field analysis of soil, soil-gas, and groundwater samples. When appropriate, conventional sampling and analytical methods can also be used in the ESA process. For example, an air rotary drilling rig may be used in consolidated material, or an off-site stationary laboratory analysis may be used to verify field analytical methods. The ESA process emphasizes the appropriate use of technologies in a way that minimizes the time required for complete characterization, and maximizes the data available for making corrective action decisions.

ESAs are particularly applicable to MTBE release sites. In CSAs, multiple phases of field work and reporting are usually required to evaluate a contaminant plume. The time and effort required for the CSA approach may be magnified at an oxygenate release site because such sites are commonly characterized by relatively small source zones, and long, thin, dissolved-phase plumes (see Section 4.2.2). MTBE and other ether oxygenate plumes can be delineated most effectively when groundwater samples are collected and analyzed in the field, thereby allowing the site investigator to select new sampling locations (i.e., to “chase the plume”) based on the most recent sampling results.

4.4 INNOVATIVE TECHNOLOGIES

The environmental industry has witnessed explosive growth in innovative technologies for site assessment in the last decade. Direct push (also referred to as direct drive) methods for collecting soil, soil gas, and groundwater samples are replacing conventional drilling techniques as the primary means of collecting subsurface data at fuel release sites. Surface geophysical surveying tools have been improved and refined, and now provide low-cost information about source zones and contaminant pathways. On-site analytical instruments are now frequently used, providing rapid turnaround of soil, soil gas, and groundwater samples at economical prices. Many mobile labs have passed the same rigorous certifications as fixed-location laboratories. Some mobile labs offer GC/MS analyses as well as conventional GC methods for analyzing petroleum hydrocarbons.

The U.S. EPA (1997b) presents a thorough discussion of these innovative technologies. A summary of the various direct push (DP) characterization and monitoring technologies – in the context of MTBE release assessments – is presented in the following sections. A table listing the applicability of some of the innovative technologies for MTBE assessment and monitoring is presented in Table 4-1.

Note that DP sampling tools and mobile laboratories are not appropriate for all MTBE site assessments. At release sites overlying bedrock, for example, a drill rig may be necessary to install conventional monitoring wells. Conventional site characterization tools and well installation procedures are outlined in API (1996a).

Table 4-1. Innovative Technologies for MTBE Assessment and Monitoring

Technology	Specific Type	Investigation Task				Comments
		Long-Term Groundwater Quality and Water-Level Monitoring	Geologic Pathway Characterization	Dissolved Plume Delineation	Source Zone Delineation	
Surface Geophysical Surveys	Resistivity, electomagnetic, ground-penetrating radar	NA	2	4	1	Can quickly define locations of USTs and associated piping systems, old excavations, shallow trenches, utility lines, shallow geologic pathways, abandoned water supply wells. Identification of geologic anomalies typically requires confirmatory subsurface investigations.
Passive Soil Gas Sampling Kits	Adsorptive material buried in soil	NA	4	4	3	Useful for measuring potential exposure to surface receptors. Not generally useful for defining source zone or plume location. Usefulness limited because of MTBE's affinity for water.
Active Soil Gas Sampling Tools	Small-diameter probes	NA	4	4	2	Can be useful to help define location of initial release and zones of residual hydrocarbons in source area vadose zone. Not very useful for plume delineation because of MTBE's affinity for water.
DP Soil Sampling Tools	Non-sealed samplers	NA	2	NA	1	Example: Standard Penetration (SPT) samplers. Non-sealed tool typically used with a hollow-stem auger (HSA) rig. HSA cases hole as augers are advanced preventing cross contamination of soil samples collected with non-sealed sampler.
	Piston samplers	NA	2	NA	1	Most common soil sampling tool used with DP rigs. Sampler is sealed while it is pushed to sample zone. Piston is released and tool is advanced further, collecting depth-discrete soil sample.

Explanation: 1 = very useful; 2 = useful; 3 = somewhat useful; 4 = not very useful; NA = not applicable

Table 4-1 (continued). Innovative Technologies for MTBE Assessment and Monitoring

Technology	**Specific Type**	**Investigation Task**				**Comments**
		Long-Term Groundwater Quality and Water-Level Monitoring	**Geologic Pathway Character-ization**	**Dissolved Plume Delineation**	**Source Zone Delineation**	
DP Groundwater Sampling Tools	Well points	2	4	3	3	Open screen points driven to depths less than 30 feet in coarse-grained soil. Subject to clogging if driven through silt or clay. Can be contaminated if driven through NAPL or heavily contaminated soil.
	Sealed screen samplers	3	3	1	1	Most common type of one-time, "snapshot" groundwater sampling tool. Examples: HydroPunch® and BAT EnviroProbe®. Samplers pushed to target depth then opened to collect sample. Frequently advanced ahead of HSA or rotary drilled borehole to collect depth-discrete samples at depths greater than 100 feet.
	Vertical profilers	3	3	1	2	Designed to collect depth-discrete groundwater samples in a single push. Examples: Waterloo Groundwater Profiler®, Cone Sipper®, and Geoprobe® Groundwater Profiler. Rapid collection of multiple depth-discrete groundwater samples in coarse-grained soil.

Explanation: 1 = very useful; 2 = useful; 3 = somewhat useful; 4 = not very useful; NA = not applicable

Table 4-1 (continued). Innovative Technologies for MTBE Assessment and Monitoring

Technology	**Specific Type**	**Investigation Task**				**Comments**
		Long-Term Groundwater Quality and Water-Level Monitoring	**Geologic Pathway Characterization**	**Dissolved Plume Delineation**	**Source Zone Delineation**	
Small-diameter monitoring wells	Single interval	1	4	2	2	Provides repeated access to measure hydraulic heads and collect groundwater samples over time. Installed with most DP sampling rigs. Sampling methods are limited. Small-diameter annular seals may not be allowed in some jurisdictions. Can be installed in clusters to allow collection of depth-discrete samples.
	Multi-level	1	4	2	3	As above but provides depth-discrete samples and hydraulic head measurements at several depths in one borehole. Allows more complete vertical definition of contaminant plume. Several systems being developed but not widely available at the time of publication (early-2000). Small-diameter annular seals may not be allowed in certain jurisdictions. Care must be taken when constructing wells to avoid cross-contamination within the borehole. Should not be installed in areas where free-phase NAPL exists.

Explanation: 1 = very useful; 2 = useful; 3 = somewhat useful; 4 = not very useful; NA = not applicable

Table 4-1 (continued). Innovative Technologies for MTBE Assessment and Monitoring

Technology	**Specific Type**	**Investigation Task**				**Comments**
		Long-Term Groundwater Quality and Water-Level Monitoring	**Geologic Pathway Character-ization**	**Dissolved Plume Delineation**	**Source Zone Delineation**	
CPT and Other Specialized Tools	Cone Penetrometer Testing (CPT or Piezocone)	NA	1	NA	3	Excellent tool for rapid characterization of heterogeneous stratigraphy and preferential geologic pathways. CPT rigs are also frequently used to advance DP soil, soil gas, and groundwater sampling tools (see above).
	Geophysical and geochemical logging probes	NA	2	3	1	Includes geophysical tools like electrical conductivity probes to define site stratigraphy. Geochemical probes [e.g., Laser-Induced Fluorescence® (LIF) or Membrane Interface Probe® (MIP)] often useful to define zones of NAPL or heavily contaminated soil in source areas.
	SimulProbe®	NA	3	2	2	A combination DP tool used to collect soil, soil gas, or groundwater samples from a single zone. Usually advanced with larger DP sampling rigs or conventional drilling rigs.

Explanation: 1 = very useful; 2 = useful; 3 = somewhat useful; 4 = not very useful; NA = not applicable

4.4.1 Direct Push Sampling Technologies

Direct push (DP) tools are used for subsurface investigations by driving, pushing, and/or vibrating small-diameter hollow steel rods into the ground. By attaching sampling tools to the end of the steel rods, they can be used to collect soil, soil gas, and groundwater samples. DP rods can also be equipped with probes that provide continuous *in situ* measurements of subsurface properties (e.g., stratigraphy, contaminant distribution). DP equipment can be advanced with various methods ranging from 30-pound manual hammers to trucks weighing 40 tons.

DP technologies are most applicable in unconsolidated sediments, typically to depths less than 100 feet. In addition, they are increasingly being used to install small-diameter (i.e., less than 2 inches) temporary or permanent monitoring wells, and small-diameter piezometers. Penetration is limited in semiconsolidated sediments and is generally not possible in consolidated formations, although highly weathered bedrock (i.e., saprolite) is an exception for some equipment.

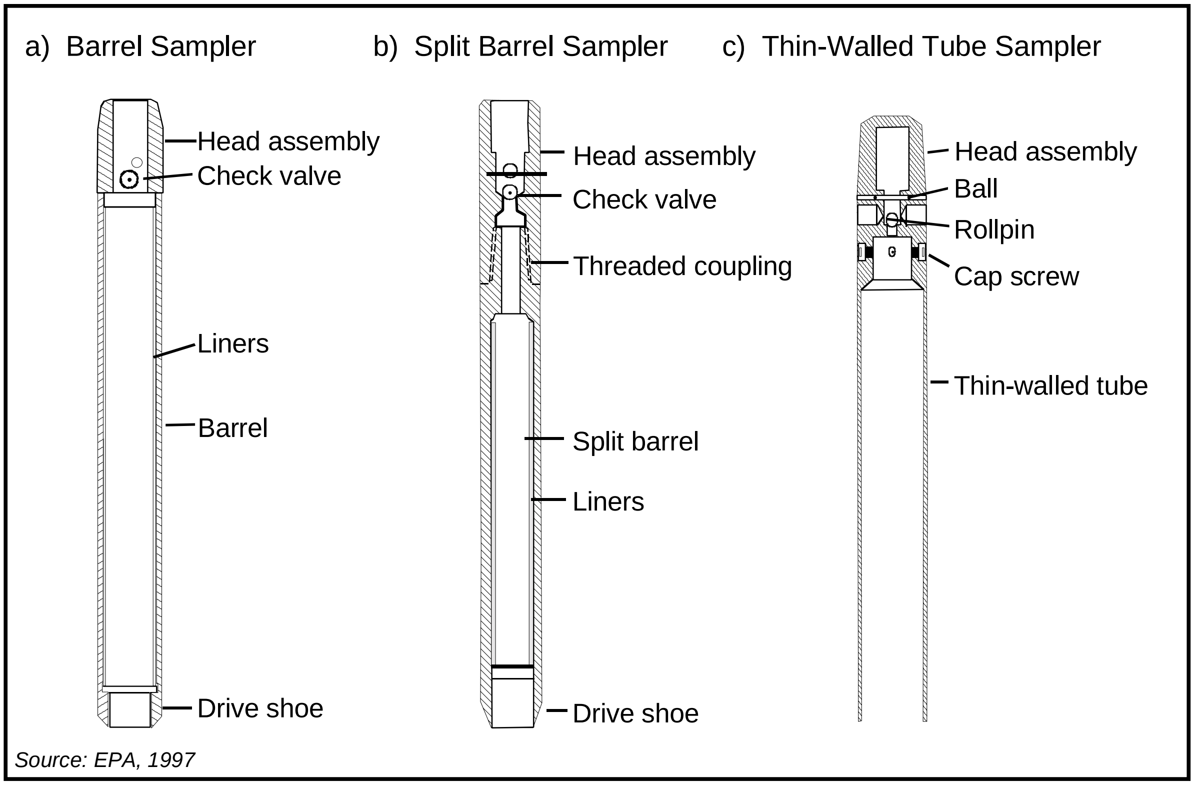
Soil Sampling Tools

Soil samples are collected for two primary reasons during MTBE site assessments: hydrogeologic characterization and source-zone chemical characterization. Soil cores are collected to define the subsurface stratigraphy and hydrogeologic properties of the soil (e.g., grain size, porosity, permeability, bulk density). In fine-grained strata, soil cores are often the only way to identify the presence of features like desiccation cracks or root holes that can dramatically increase the secondary permeability of the soil. At complex, heterogeneous sites, continuous soil cores are needed to define the subsurface geology. At other sites, spot-coring may be all that is necessary to confirm the conceptual geologic model of the site. Soil coring is typically needed to confirm the results of surface geophysical surveys and to calibrate the reading from a cone penetrometer testing (CPT) rig.

Chemical analysis of soil cores is typically done to define the nature and extent of the NAPL release in and around the source zone. Visual inspection of the core, with or without the aid of hydrophobic dyes, can identify zones of NAPL. Chemical analysis of the cores can provide evidence of residual NAPL, even when none is visible (Section 3.3.3).

Collection of saturated or unsaturated soil samples for chemical analysis outside of the source zone or outside of highly affected groundwater rarely provides useful information at MTBE release sites, however. As discussed in Section 2, dissolved MTBE occurs almost exclusively dissolved in the pore water, with only a small amount sorbed onto the aquifer matrix. Therefore, in the area of the dissolved plume, chemical analyses should be focused on samples of groundwater and not on soil.

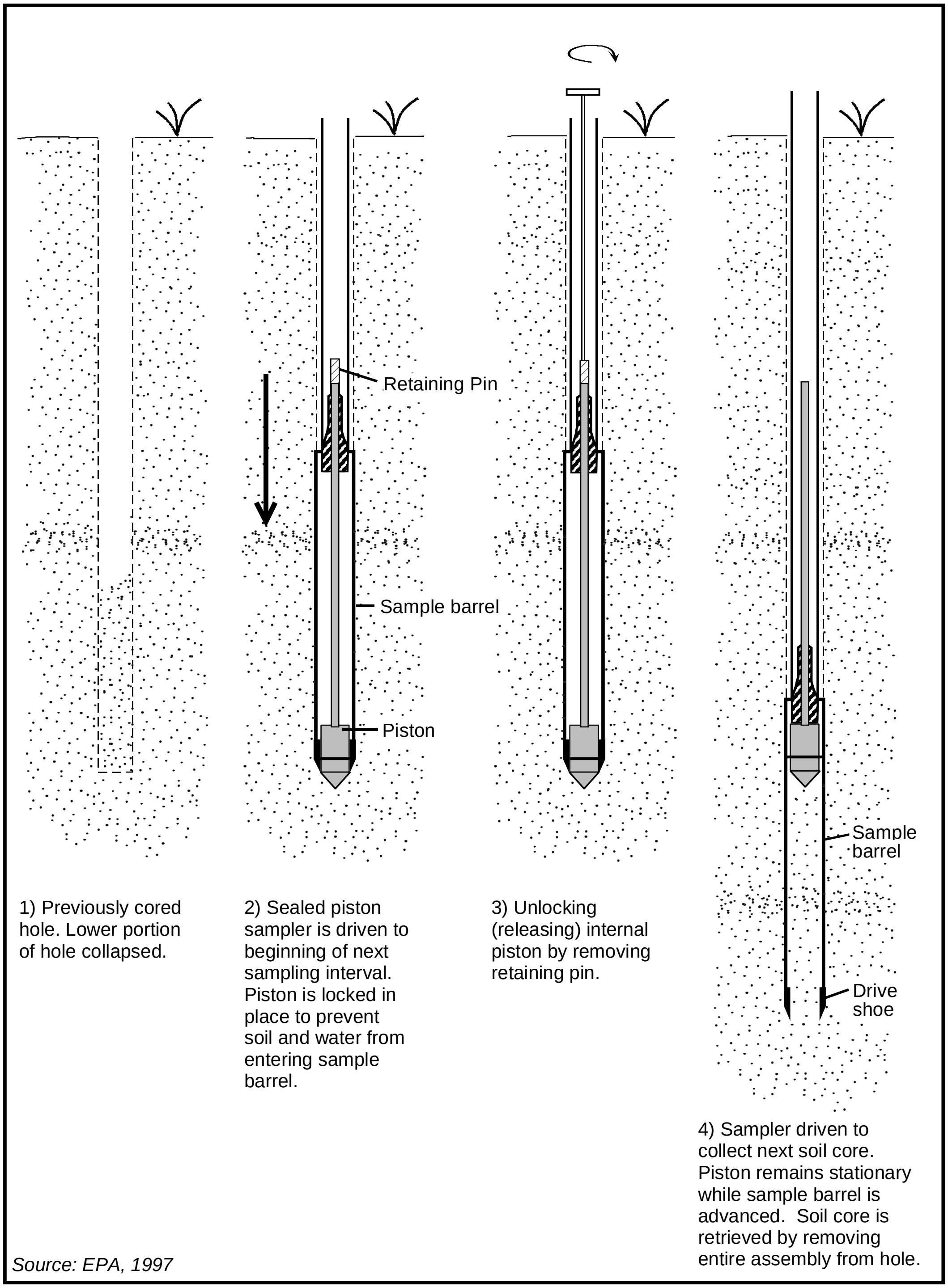
There are two primary types of soil sampling tools. The first is referred to as “non-sealed” samplers or sample barrels. These tools include barrel samplers, split barrel samplers (e.g., Standard Penetration (SPT) samplers) and thin-walled tube samplers (e.g., Shelby tubes; see Figure 4-1). The tools are open at the end, allowing the soil to enter the sample barrel as it is driven into the ground. Open barrel samplers should only be used when they are advanced through hollow-stem augers or a drive casing (in the case of a dual-tube DP system) that prevents slough from cross-contaminating the soil sample.



Source: EPA, 1997

Figure 4-1. Examples of Non-Sealed Soil Samplers and Sample Barrels

The second type of soil sampling tool is a sealed barrel or “piston sampler.” Piston samplers are the most commonly used types of soil sampling tools used during DP environmental assessments. Piston samplers are sealed with a watertight piston as they are pushed to the desired sampling depth. The piston is then released. Continued pushing of the tool allows the soil sample to enter the sample barrel (Figure 4-2). When the sample barrel is full, withdrawing the sampling rods retrieves the sample. Subsequent samples are collected in the same way. The primary advantage of piston samplers is that they are sealed until they reach the desired sampling depth. This allows the tool to be pushed through heavily contaminated soil or water without cross-contaminating the soil sample collected at a deeper depth. Piston soil samplers are commonly used with single rod DP systems.



1) Previously cored hole. Lower portion of hole collapsed.

2) Sealed piston sampler is driven to beginning of next sampling interval. Piston is locked in place to prevent soil and water from entering sample barrel.

3) Unlocking (releasing) internal piston by removing retaining pin.

4) Sampler driven to collect next soil core. Piston remains stationary while sample barrel is advanced. Soil core is retrieved by removing entire assembly from hole.

Source: EPA, 1997

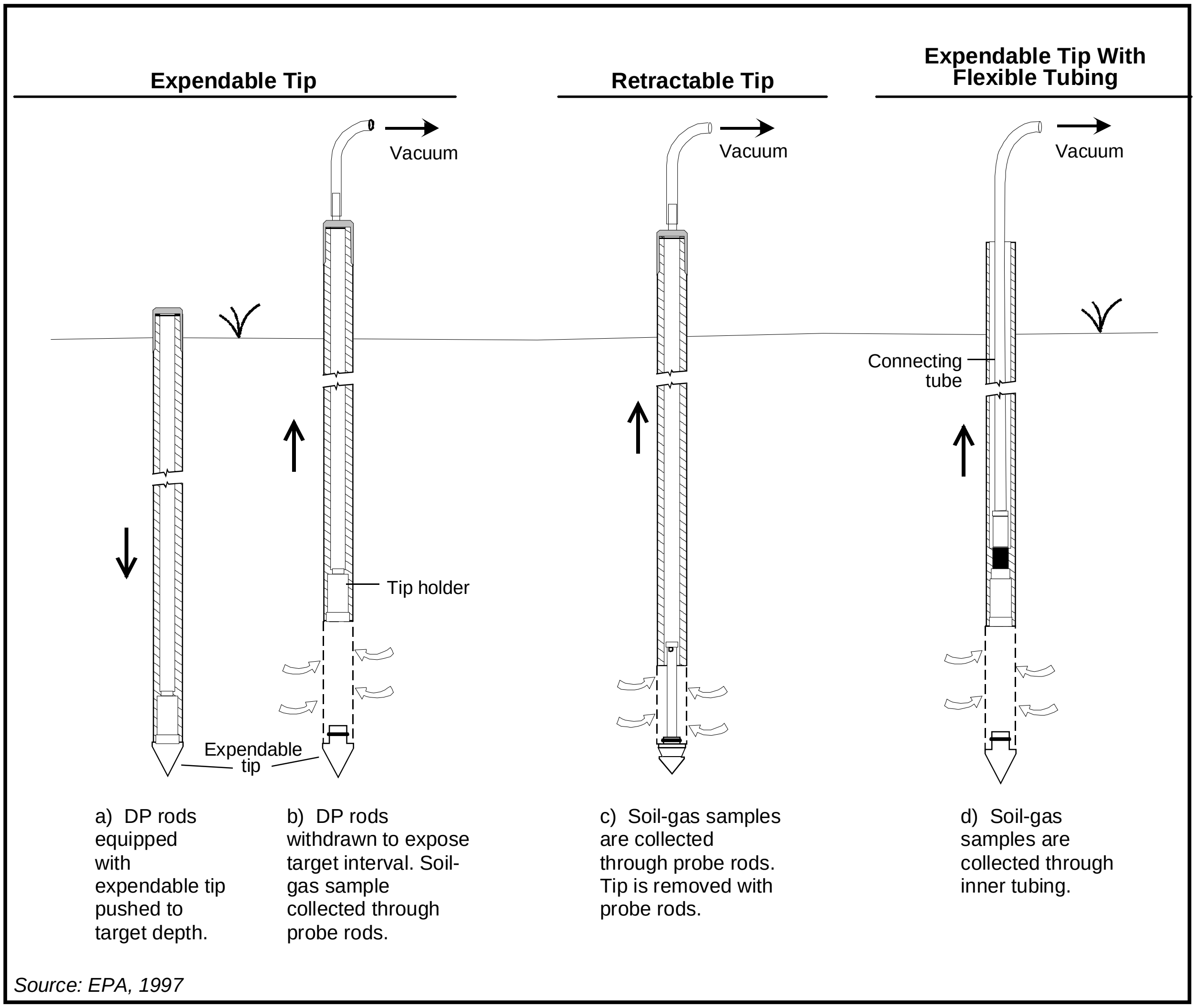
Figure 4-2. Example of a Piston Soil Sampler

Soil Gas Sampling Tools

Collecting vertical profiles of gaseous concentrations of MTBE and other petroleum hydrocarbons can provide valuable information about the release mechanism (e.g., vapor releases), or the location and extent of residual NAPL in the vadose zone. Because of the affinity of MTBE for water, however, soil gas surveys can rarely be used to identify the location of dissolved plumes of MTBE (see Section 2 and Appendix A).

A wide variety of soil gas sampling tools exist, some of which are depicted in Figure 4-3. Some use an expendable tip to seal the rods as they are advanced to the target depth. Others use a retractable tip. Still others use an expendable or retractable tip equipped with flexible tubing through which the sample is extracted.

Soil gas samples are typically extracted using a vacuum pump and are collected in stainless steel Summa® canisters, Tedlar® bags, or syringes. Soil gas samples should be analyzed as soon as possible (ideally on site) to prevent diffusive losses or biodegradation of the samples.



Source: EPA, 1997

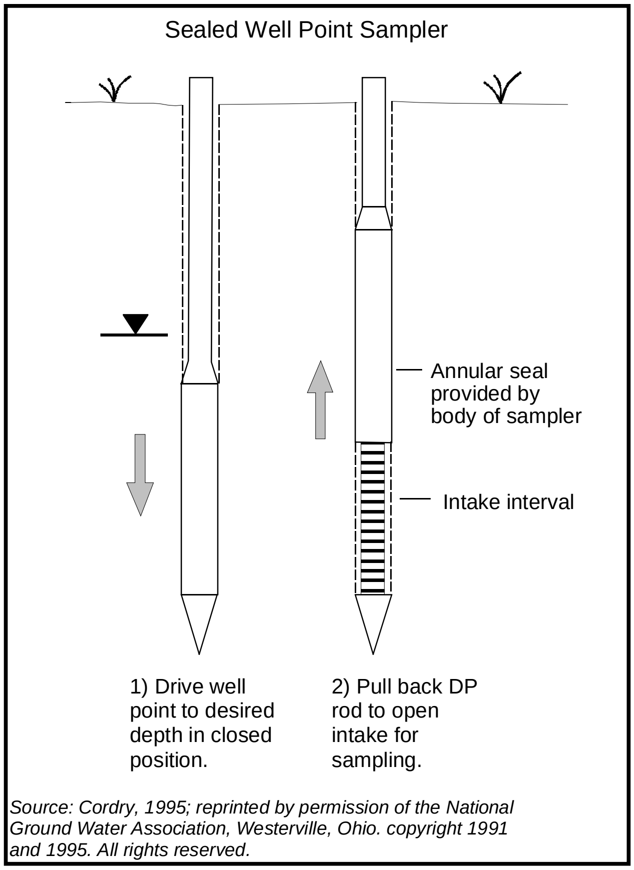
Figure 4-3. Examples of Soil Gas Sampling Tools

Groundwater Sampling Tools

Collection of groundwater samples constitutes one of the primary activities of MTBE field investigations, especially when definition of the dissolved plume is necessary. Because of MTBE's tendency to partition into water (due to the chemical's low Henry's constant), one can expect to sustain fewer negative biases due to volatile losses during the sampling process than would occur with more volatile compounds. In short, it is difficult to lose significant mass of MTBE with most DP groundwater sampling methods. While this does not excuse sloppy sampling procedures, it does eliminate some concerns regarding negative biases that are thought to be caused by some sampling techniques (e.g. bailers, peristaltic pumps) used to sample more volatile compounds.

Three types of DP groundwater sampling tools are commonly used to collect one-time samples of groundwater, yielding “snapshots” of groundwater quality at a particular location. The first type is the conventional well point made of wire-wrapped steel well screens and steel riser pipe. Well points are widely available for shallow water supplies in rural areas. Well points can be left in place as permanent monitoring wells to allow collection of additional groundwater samples over time. Well points are best used in sand and gravel aquifers, since silt and clay formations can plug the exposed well screens as the well points are advanced. Also, well points are susceptible to cross-contamination when the points are pushed through high-concentration portions of a dissolved plume to less contaminated groundwater underlying the plume. This potential bias should be negligible for MTBE assessments, however, because very little MTBE would be sorbed on soil inadvertently pushed to the deeper depths (see Section 4.2.4).

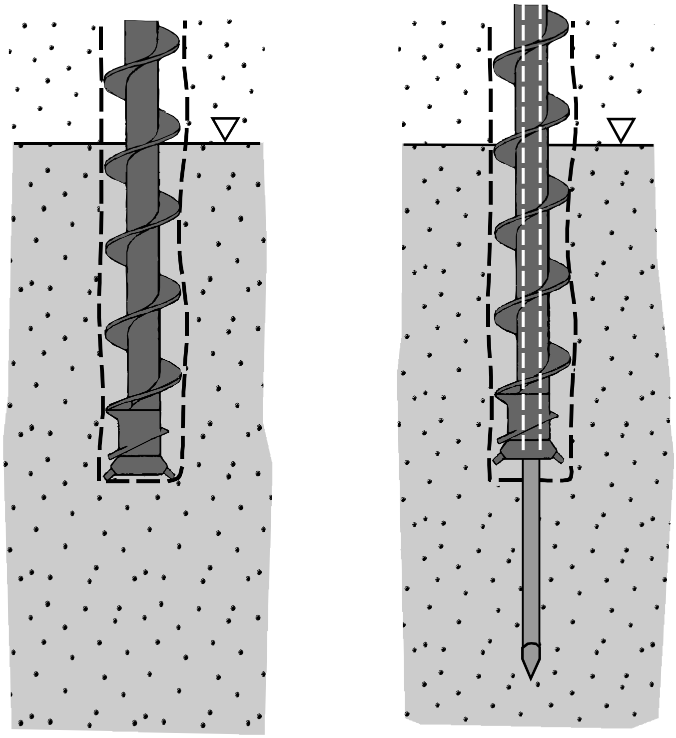
Sealed screen groundwater sampling tools are the most commonly used DP sampling tools (Figure 4-4). The original tools of this sort are the HydroPunch® I and II and the BAT EnviroProbe®, although there are many similar groundwater sampling tools now being used. The main advantage of these types of tools is that they are sealed as they are advanced to the targeted sampling depth, minimizing cross-contamination of the groundwater samples. Sealed screen samplers are commonly used with truck-mounted DP rigs, where the samplers are advanced on the end of steel DP rods. Once advanced to the target depth, the tool is withdrawn a specified distance (ranging from 0.5 to 5 feet), exposing a well screen. Groundwater flows into a reservoir inside of the tool, and can be retrieved by withdrawing the tool, or extracting the water sample with a small sampling pump or bailer. The BAT EnviroProbe® uses an evacuated glass vial to collect water samples under the pressure existing in the aquifer (Berzins, 1993).



Source: Cordry, 1995; reprinted by permission of the National Ground Water Association, Westerville, Ohio. copyright 1991 and 1995. All rights reserved.

Figure 4-4. Example of a Sealed Screen Groundwater Sampling Tool

Sealed screen samplers are often used to collect depth-discrete groundwater samples in conjunction with conventional drilling methods like HSA and mud rotary. These methods are typically used to delineate MTBE plumes that occur at depths greater than can be reached with smaller truck-mounted DP rigs (reasons why MTBE plumes can occur at relatively great depths are explained in Section 3.3.2). To collect a groundwater sample, the sealed screen sampler is lowered down through the inside of the HSA or rotary drill rods, and pushed a few feet into the undisturbed aquifer (Figure 4-5). The sampling tool is pulled back, exposing the wells screens, and water samples are collected as described above.



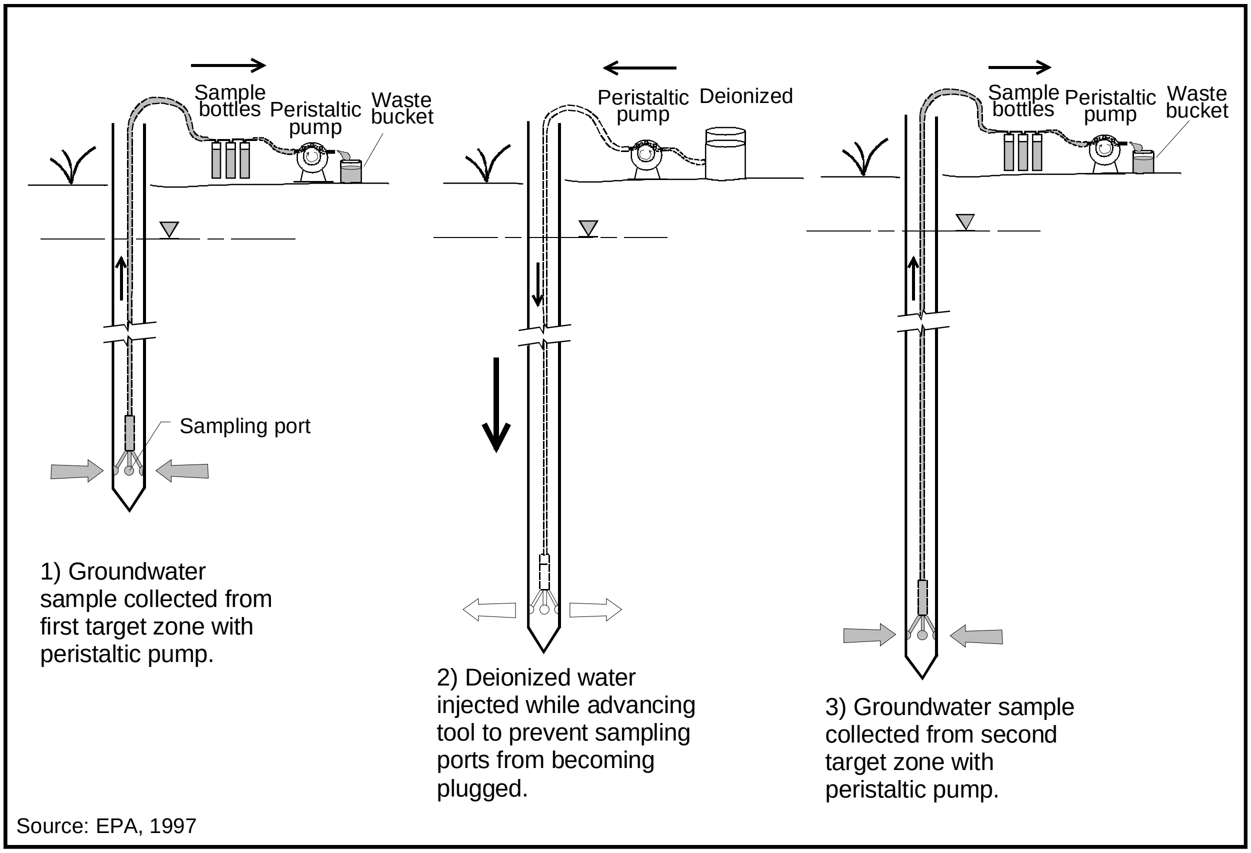
1) Advancing auger to target depth.

2) Pushing the sampling tool ahead of the lead auger.

3) Opening the tool and collecting a groundwater sample.

Figure 4-5. Collecting a Groundwater Sample Ahead of a Hollow Stem Auger Using a Sealed Screen Direct-Push Tool

Another type of groundwater sampling tool, referred to as a groundwater profiler, is used to collect multiple depth-discrete groundwater samples in a single push. Examples include the Cone Sipper® and the Waterloo Groundwater Profiler® (see Pitkin *et al.*, 1998). With a groundwater profiler, groundwater samples are collected through ports located at the bottom of the DP rods (Figure 4-6). Samples are extracted through Teflon® tubing that runs inside of the DP rods from the intake ports to the ground surface. Samples are collected in vials mounted upstream of the peristaltic pump, in order to avoid negative biases caused by sorption of organic molecules to the peristaltic tubing. After a sample has been collected, the flow of water is reversed, and deionized water is pumped slowly down through the Teflon® tubing and out of the sampling ports. This flushes the old sample out of the tubing and keeps the ports from plugging. When the next sampling depth is reached, the flow direction is again reversed, pumping groundwater to the surface. Care should be taken to avoid collection of the first water that is pumped out of the system, since this will consist primarily of deionized water contained within the tubing (the arrival of aquifer water is easily determined by monitoring the electrical conductivity of the effluent). Groundwater profilers are especially useful for delineating stratified contaminant plumes in coarse-grained aquifers.



Source: EPA, 1997

Figure 4-6. Example of a Groundwater Profiler

Another groundwater sampling tool, the SimulProbe®, facilitates the collection of soil and soil gas or groundwater from the same depth interval. The SimulProbe® tool has seen widespread use in MTBE assessments in California in the late 1990s, and is typically used in conjunction with powerful DP or conventional drilling rigs, as described above. SimulProbe® is described in more detail below.

CPT and Other Specialized Probes

CPT is a DP characterization technology, originally developed for geotechnical work, but which has been adapted for environmental assessments. CPT uses sensitive pressure transducers mounted on the tip of the probe rods to measure the tip resistance and sidewall friction of the earth materials as the probe is advanced at a constant rate. Dense sands exert a strong tip resistance with little side wall friction; clays exert less tip resistance and significant sidewall friction due to the cohesion of the clay minerals. Thus, the CPT tool provides a detailed log of the site stratigraphy. Most CPT tools also utilize an additional pressure transducer to measure the dissipation of pore water pressure as the probe is advanced. This measurement, taken with a “piezocone”, provides supplemental information about the hydraulic conductivity of the materials being penetrated. CPT provides a continuous log of the interpreted stratigraphy of the site. CPT tools should be calibrated to site conditions by advancing at least one probe adjacent to a location where a continuous soil core has been collected and logged.

The CPT tools are typically advanced with large 20 to 40 ton trucks, although smaller portable vehicles are also being used. With smaller rigs, reactive mass is usually added by filling water tanks attached to the rig, or placing earth augers or concrete bolts to anchor the sampling rig. CPT rigs are also commonly used to advance a variety of soil, soil gas, and groundwater sampling tools described in the previous sections.

Recently, other tools have been attached to CPT cones to provide supplemental information. These include natural gamma detectors, resistivity and seismic probes, and depth-discrete groundwater sampling tools, such as the Cone Sipper®. Specialized geochemical sensors, such as Laser Induced Fluorescence® and Rapid Optical Screening Tool®, provide relative measurements of residual hydrocarbons in soil. Recent advances in CPT technology include a small video camera that provides a visual log of the soil as the probe is advanced (Lieberman, 1998).

Other manufacturers also make specialized geophysical and geochemical probes. Geoprobe® manufactures an electrical conductivity profiling tool, and the Membrane Interface Probe® (MIP) system that provides a relative measurement of residual petroleum hydrocarbons in soil and/or water. Recent field testing of the MIP system at an API-sponsored MTBE field study in California, however, indicated that the MIP system is currently not effective at delineating MTBE dissolved in water at concentrations as high as 3,000 ug/L (Einarson *et al*., 1999).

SimulProbe®

The patented SimulProbe® is a DP sampling tool that has been successfully used to collect samples of soil, soil gas, and groundwater at MTBE release sites in California and elsewhere. There are four unique features of the SimulProbe® system: 1) it can collect samples of soil and soil gas, or soil and groundwater, from the same depth interval; 2) it uses a patented nitrogen back-pressurization system to prevent cross-contamination of groundwater samples from borehole fluids, and to prevent VOC loss from the groundwater samples; 3) it uses a patented drive cone called the SimulProbe® Latch Activated Tip (SPLAT) which eliminates the use of drive cone control rods and tip release cables; and 4) it uses a patented sliding drive shoe assembly to conceal the screen and fluid entry ports during subsurface deployment of the device.

The system consists of a sealed-barrel piston sampler to collect soil cores coupled with a sealed-screen port assembly to collect either soil gas or groundwater samples (Figure 4-7). Operation of the piston sampler is similar to other systems, except that the piston can be released without the aid of separate release rods. Prior to removing the sampling tool to recover the soil core, soil gas or groundwater samples can be collected from the same depth interval. This is accomplished by withdrawing the tool a few inches, which opens a screened port at the base of the tool. Soil gas or groundwater is conveyed around the outside of the soil core via two small Teflon® tubes mounted in the interior sidewall of the sampling tool. Soil gas samples can be collected by drawing a vacuum on a Teflon® sampling tube that is run inside of the DP rods from the sampling tool to the ground surface. Groundwater samples can be collected by opening the screened ports, allowing groundwater to enter the tool and fill a water canister positioned above the soil sample barrel.

The SimulProbe® tool comes in several sizes, ranging from 2.0 to 3.38 inches in diameter, and can be advanced using standard DP rigs or conventional drilling rigs as described above. As with other heavy-duty sealed-screen sampling tools, SimulProbe® tools have been used to collect depth-discrete groundwater samples to depths greater than 700 feet by pushing the tool below the bottom of a rotary-drilled borehole at regular intervals.

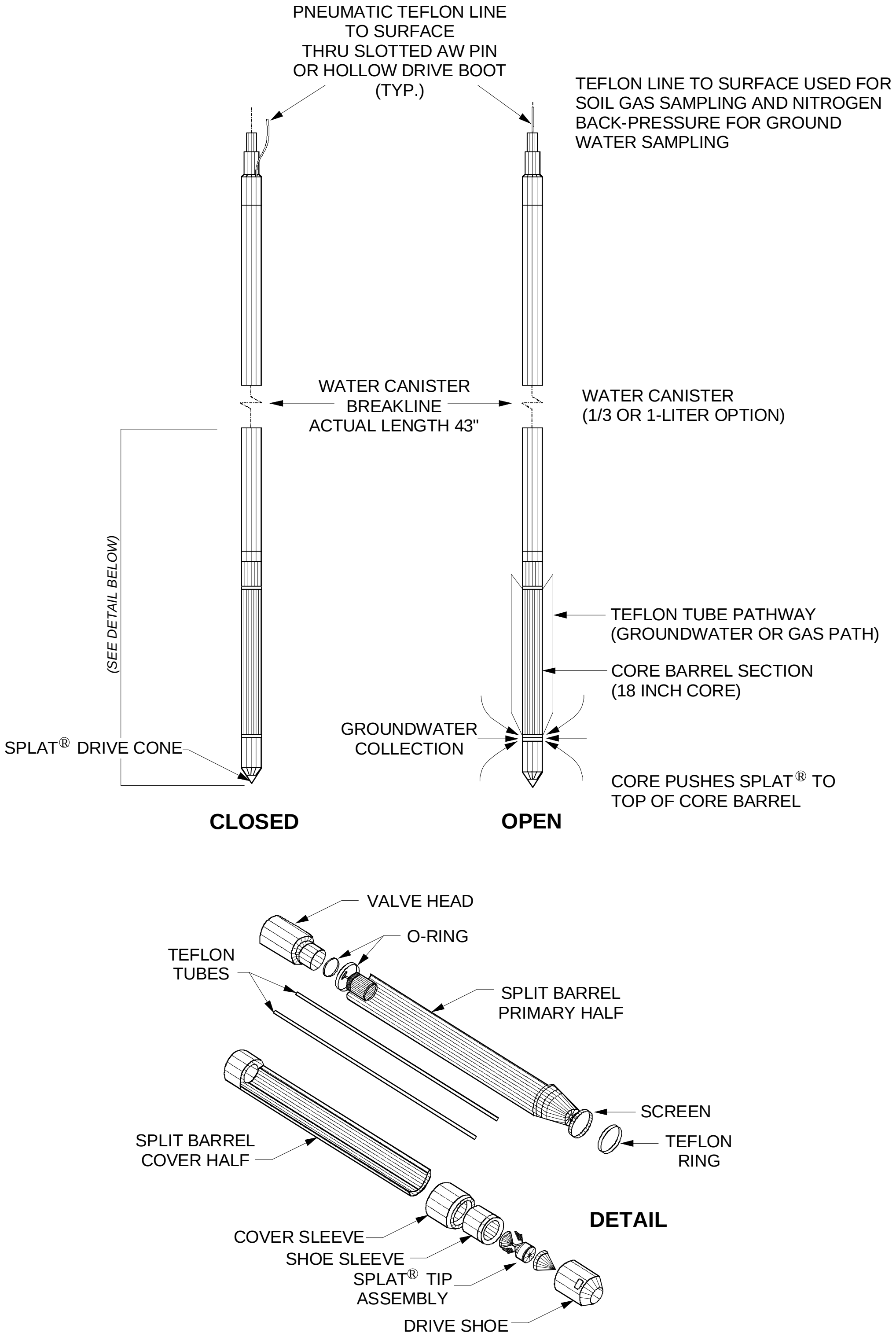


Figure 4-7. The SimulProbe® Sampling System

4.4.2 Small-Diameter Monitoring Wells

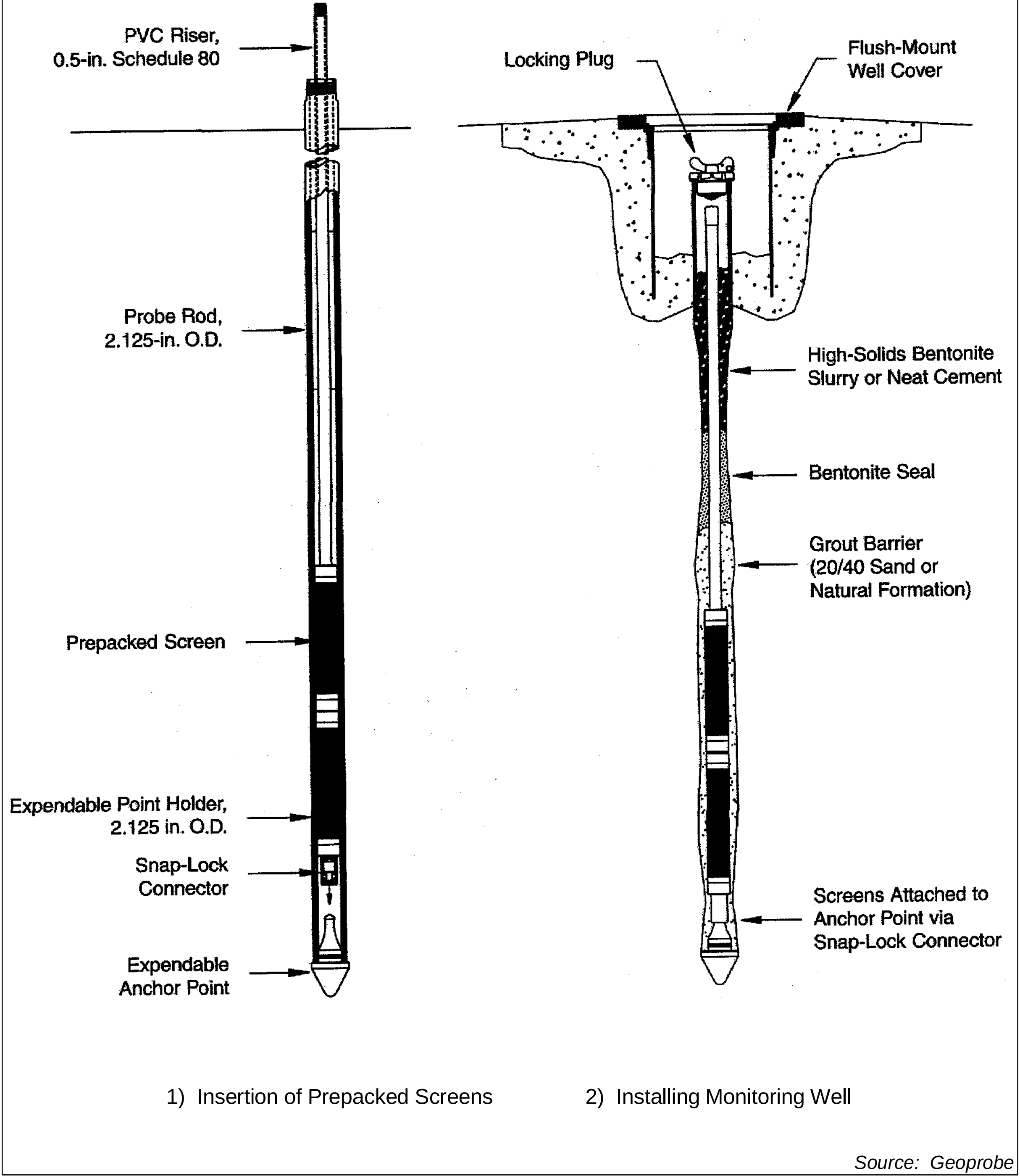
Innovations in DP sampling technology have facilitated the installation of permanent monitoring wells and piezometers. Single interval monitoring wells are most common, and improved designs are continually evolving. Multi-level monitoring wells installed with DP equipment are also currently being developed.

Single Interval Monitoring Wells

Single interval monitoring wells are typically constructed of ½- to 1-inch diameter PVC. Well screens are made of either slotted PVC or stainless drive points containing ports wrapped with stainless steel mesh. Riser pipes are made of PVC or, in the case of stainless steel drive points, ½-inch-diameter polyethylene or Teflon® tubing. The wells are typically installed by advancing a displacement tip on the end of the DP rods. The PVC pipe or tubing can be advanced with the DP rods, or inserted after the DP rods have been pushed to the desired depth.

When the DP rods are pulled out, sand collapses around the well screens and riser pipe. With larger DP rod systems, a pre-packed sand pack can be attached to the well screens (Figure 4-8). Also, cement or bentonite seals can be injected into the annular space as the DP rods are withdrawn. Water samples are collected using peristaltic pumps, small-diameter bailers, check-valve tubing pumps, and airlift pumps. Small-diameter bladder pumps are now available for sampling 1-inch-diameter monitoring wells. Hydraulic heads are measured with standard electric tapes or depth indicators. A number of manufacturers also make electronic pressure transducers that will fit inside of small-diameter monitoring wells.

Methods and technologies for installing permanent small-diameter wells are evolving quickly, and care should be taken to ensure that the wells do not form pathways for the vertical migration of contaminants. Standards for small-diameter monitoring wells installed with DP equipment are currently being developed by ASTM Committee D18.



Source: Geoprobe

Figure 4-8. Single-Interval Monitoring Well Installed With Direct-Push Equipment

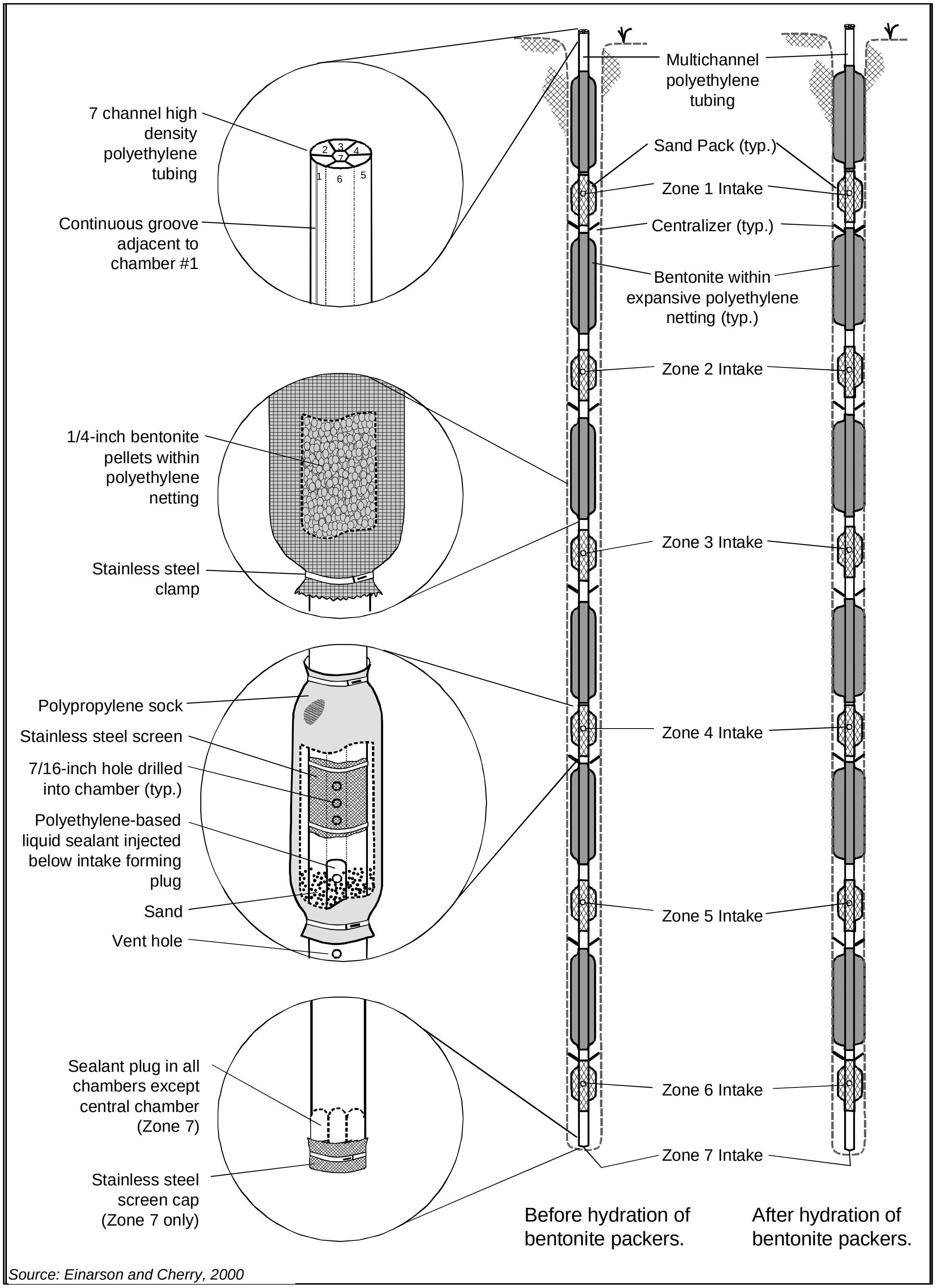
While the effectiveness of small-diameter monitoring wells has been demonstrated at many sites, some state and local regulatory agencies discourage their use because they do not comply with the current well construction ordinances that were developed for supply wells or large-diameter monitoring wells. Always check with the appropriate permitting agency before installing permanent small-diameter monitoring wells.

Multi-Level Monitoring Systems

Collection of depth-discrete samples of groundwater is often necessary during MTBE site assessments. Many times, one-time “snapshot” sampling is all that is necessary to confirm the conceptual site model regarding the nature and extent of the release. At other sites, on-going monitoring is necessary to confirm the effectiveness of a particular remedial action, or to ensure that downgradient receptors are not at risk. Depth-discrete monitoring may be necessary due to the particular characteristics of MTBE plumes (see Section 3.3).

Multi-level groundwater monitoring can be accomplished by simply installing clusters of single-interval monitoring wells at different depths. The site-specific hydrogeology and the objectives of the monitoring program determine the number and depths of the individual wells.

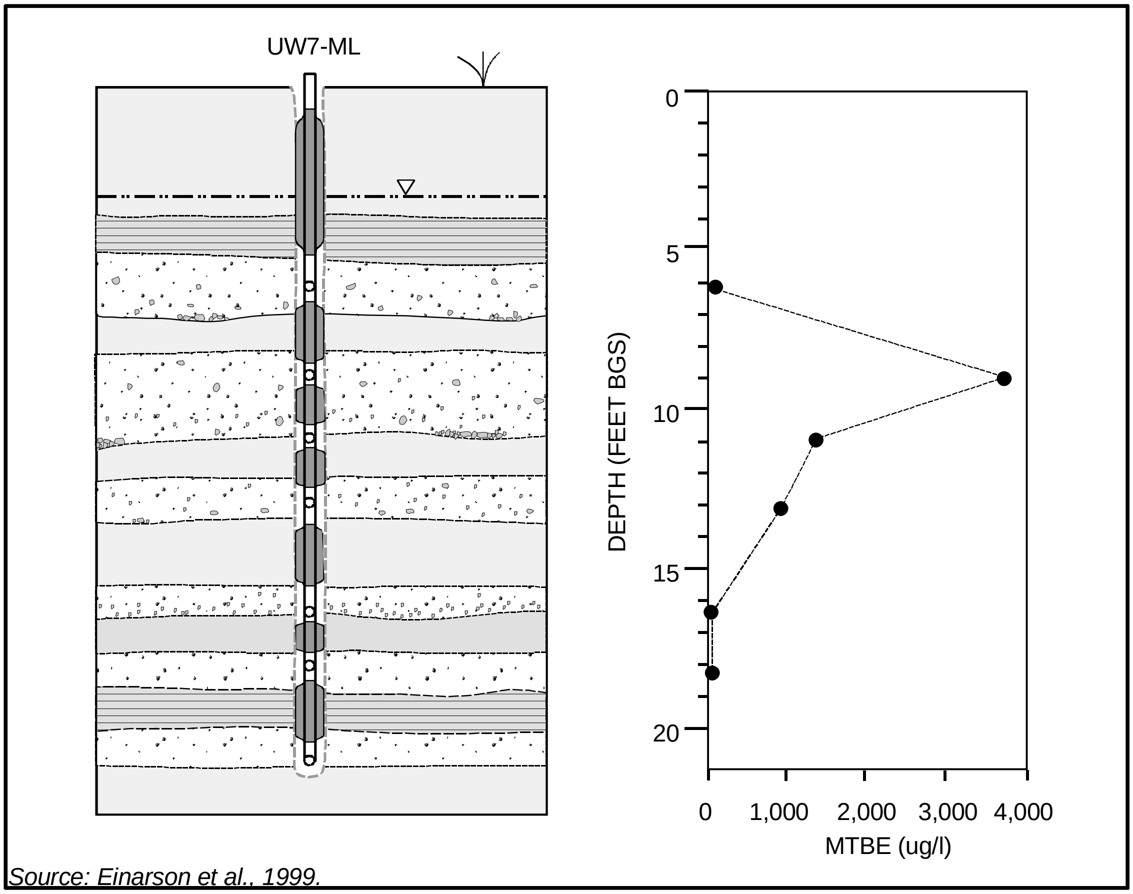
Other multi-level monitoring systems are currently being developed. One system uses custom-made multi-chamber, high-density polyethylene tubing to monitor as many as seven intervals in a single boring (Einarson and Cherry, 2000; see Figure 4-9). Holes are drilled through the outside of the tubing into individual chambers at different depths, creating sampling ports. Pre-packed cylinders of sand and bentonite packer seals can be attached to the tubing. The well, including sand pack and bentonite seals, is built completely above ground and simply inserted into large-diameter DP drive casing to the targeted depth. The drive casing is then withdrawn, allowing water to flow into the borehole, hydrating the bentonite. After about one hour, the bentonite packers have swelled, completely sealing the borehole between the various sampling intervals.



Source: Einarson and Cherry, 2000

Figure 4-9. Direct-Push Multi-Level Monitoring System

The system has been used successfully at an API-funded research site at Vandenberg AFB in California (Einarson *et al.*, 1999). At the Vandenberg site, an uncontrolled release of gasoline from a base service station has resulted in a 1,700-foot-long MTBE plume. The plume is flowing within a complex sequence of thin, coarse-grained alluvial deposits. Sixteen multi-level wells have been installed at the site, providing a detailed picture of the vertical distribution of MTBE, BTEX, and various electron acceptors in the plume. Data from one of the multi-level wells (UW-7ML), located approximately 200 feet downgradient from the source, is presented in Figure 4-10. The MTBE plume at that location is less than approximately 5-feet thick and is strongly controlled by the site geology.



Source: Einarson et al., 1999.

Figure 4-10. Multi-Level Monitoring Well used to Define Distribution of Dissolved MTBE in a Stratified Alluvial Aquifer, Vandenberg AFB, California

Note that with all multi-level monitoring systems, extra care must be taken during construction to avoid creating conditions that would allow dissolved contaminants to migrate between water bearing zones.

REFERENCES

Anderson M.P., and W. Woessner. 1992. *Applied Groundwater Modeling: Simulation of Flow and Advective Transport*. Academic Press, San Diego, CA.

API. 1991. *Chemical Fate and Impact of Oxygenates in Groundwater: Solubility of BTEX from Gasoline-Oxygenate Mixtures*. API Publication No. 4531. American Petroleum Institute. Washington, D.C.

API. 1996a. *A Guide to the Assessment and Remediation of Underground Petroleum Releases*. API Publication No. 1628. American Petroleum Institute. Washington, D.C. Third Edition, July.

API. 1996b. *Natural Attenuation Processes*. API Publication No. 1628A. American Petroleum Institute. Washington, D.C. First Edition, July.

API. 1996c. *Risk-Based Decision-Making*. API Publication No. 1628B. American Petroleum Institute. Washington, D.C. First Edition, July.

API. 1997a. *Field Evaluation of Biological and Non-Biological Treatment Technologies to Remove MTBE/Oxygenates from Petroleum Product Terminal Wastewaters*. API Publication No. 4655. American Petroleum Institute. Washington, D.C.

API. 1997b. *Field Studies of BTEX and MTBE Intrinsic Bioremediation*. API Publication No. 4654. American Petroleum Institute. Washington, D.C.

API. 1998. *Delineation and Characterization of the Borden MTBE Plume: An Assessment of MTBE Transport in Groundwater Over 8 Years*. API Publication No. 4668. American Petroleum Institute. Washington, D.C.

API. 1999. *Selecting Analytical Methods for the Determination of Oxygenates in Environmental Samples and Gasoline*. API Environmental Monitoring Workgroup. http://www.api.org/ehs/oxyMTBE10.doc

Arulanantham R., and T. Buscheck. 1999. Assessment and Management of MTBE Impacted Sites. Course notes. Sponsored by the California Environmental Protection Agency, State Water Resources Control Board. 1999.

ASTM. 1995a. *Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites, E 1739-95*$^{\varepsilon 1}$. American Society for Testing and Materials, West Conshohocken, PA.

ASTM. 1995b. *Standard Guide for Developing Conceptual Site Models for Contaminated Sites, E 1689-95*. American Society for Testing and Materials, West Conshohocken, PA.

ASTM, 1997. *Standard Practice for Environmental Site Assessments: Phase I Environmental Site Assessment Process, E1527-97*. American Society for Testing and Materials, West Conshohocken, PA.

ASTM. 1998a. *Provisional Standard Guide for Risk-Based Corrective Action, PS 104-98*. American Society for Testing and Materials, West Conshohocken, PA.

ASTM. 1998b. *Standard Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Release Sites, E 1943-98*. American Society for Testing and Materials, West Conshohocken, PA.

ASTM. 1999a. *Standard Guide for Accelerated Site Characterization for Confirmed or Suspected Petroleum Releases, E 1912-98*. American Society for Testing and Materials, West Conshohocken, PA.

ASTM. 1999b. *RBCA Fate and Transport Models: Compendium and Selection Guidance*. ASTM Technical and Professional Training, American Society for Testing and Materials, West Conshohocken, PA.

ATSDR. 1996. Toxicological Profile for Methyl *tert*-Butyl Ether. Agency for Toxic Substances and Disease Registry. NTIS PB97-121016. August.

Baehr A.L. 1987. Selective Transport of Hydrocarbons in the Unsaturated Zone Due to Aqueous and Vapor Phase Partitioning. *Water Resources Research. 2*3(10): 1926-1938.

Berzins, N.A., 1993. Use of the Cone Penetration Test and BAT Groundwater Monitoring System to Assess Deficiencies in Monitoring Well Data. In Proceedings of the Sixth National Outdoor Action Conference, May 11-13, 1992. National Ground Water Association, Columbus, OH..

Borden, R.C., Daniel, R.A., LeBrun, L.E., IV, and Davis, C.W. 1997. Intrinsic Biodegradation of MTBE and BTEX in a Gasoline-Contaminated Aquifer. *Water Resources Research*. 33(5): 1105-1115.

Bradley, P.M., J.E. Landmeyer, and F.H. Chapelle. 1999. Aerobic Mineralization of MTBE and *tert*-Butyl Alcohol by Stream-Bed Sediment Microorganisms. *Environmental Science & Technology* 33(11):1877-1979.

Buscheck, T.E., D.J. Gallagher, D.L. Kuehne, and C.R. Zuspan. 1998. *Occurrence and Behavior of MTBE in Ground Water*. National Ground Water Association, Southwest Focused Conference, June 3-4.

California Environmental Protection Agency. 1997. MTBE Briefing Paper. http://www.arb.ca.gov/cbg/cbg.htm.

California EPA. 1998. *Prop 65 Scientific Review Panels Conclude MTBE Is Neither a Reproductive or Developmental Toxicant nor a Carcinogen*. California Environmental Protection Agency, News Release. December 10. http://www.calepa.ca.gov/publications/press/1998/c2898.htm.

California EPA. 1999. *Public Health Goal for Methyl Tertiary Butyl Ether (MTBE) in Drinking Water*. Office of Environmental Health Hazard Assessment. March. http://www.oehha.org/water/phg/pdf/mtbe_f.pdf.

Chamberlin, T.C. 1897. The Method of Multiple Working Hypotheses. *Journal of Geology*. 5(6).

Charbeneau, R.J., R.T. Johns, L.W. Lake and M.J. McAdams. 1999. *Free Product Recovery of Petroleum Hydrocarbon Liquids*. API Publication No. 4682. American Petroleum Institute, Washington, D.C.

Church, C.D., Isabelle, L.M., Pankow, J.F., Rose, D.L., and Tratnyek, P.G. 1997. Method for determination of methyl *tert*-butyl ether (MTBE) and its degradation products in water. *Environmental Science & Technology*, 31(12): 3723-3726.

Cohen, R.B., A. P. Bryda, S.T. Shaw, C.P. Spalding. 1992. Evaluation of Visual Methods to Detect NAPL in Soil and Water. *Ground Water Monitoring Review*, 12(4): 132–141.

Cohen, R.M. and J.W. Mercer. 1993. *DNAPL Site Evaluation*. C.K. Smoley, CRC Press, Inc., Boca Raton, Florida.

Cordry, K.E. 1986. Ground water sampling without wells. In Proceedings of the Sixth National Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring, May 11-13, 1992. National Water Well Association, Columbus, OH.

Cowan, R. M. and K. Park. 1996. Biodegradation of the Gasoline Oxygenates MTBE, ETBE, TAME, and TBA by an Aerobic Mixed Culture. *Proceedings*, 28th Mid-Atlantic Industrial and Hazardous Waste Conference, Buffalo, NY. pp. 523-530.

Delzer, G. C., Zogorski, J.S, Lopes, T.J, Bosshart, R.L. 1996. *Occurrence of the Gasoline Oxygenate MTBE and BTEX Compounds in Urban Stormwater in the U.S., 1991-95*. U.S. Geological Survey Water-Resources Investigation Report 96-4145.

Dooher, B.P., and A.M. Happel, 1999. Evaluating the Feasibility of a Statewide Geographic Information System: Design and Testing of an Internet Accessible Geographic Environmental Information Management System. Lawrence Livermore National Laboratory, Livermore, CA. UCRL-AR-134611, July 1. 15 pp + Appendices.

Ellis P. and F. Gavas. 1996. MTBE… If Ye Seek It, Ye May Well Find It… And Then What? *L.U.S.T. Line*, Bulletin 24. New England Interstate Water Pollution Control Commission. July. p. 7-13.

Einarson, M.D. and J.A. Cherry. 2000. A New Low-Cost Multi-Level Groundwater Monitoring System. Manuscript in preparation.

Einarson, M.D., M. S. Schirmer, D.M. Mackay, R.A. Wilson. 1999. Comparison of Eight Innovative Site Characterization Tools Used to Investigate and MTBE Plume at Site 60, Vandenberg Air Force Base, California. *in* Proceedings of the API/NGWA Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water--Prevention, Detection, and Remediation, Houston, Tex., Nov. 17-19, 1999, p., 147-157.

Feenstra, S. 1990. Evaluation of Multi-Component DNAPL Sources by Monitoring of Dissolved-Phase Concentrations. In Proceedings of the Conference On Subsurface Contamination by

Immiscible Fluids, International Association of Hydrogeologists, Calgary, Alberta, April 18-20, 1990.

Feenstra, S., D.M. Mackay, and J.A. Cherry. 1991. A Method for Assessing Residual NAPL Based on Organic Chemical Concentrations in Soil Samples. *Ground Water Monitoring Review* 11(2):128-136.

Gibbs, L. 1990. Gasoline Additives - When and Why. SAE Tech. Paper 902104, Int'l Fuels and Lubricants Meeting, Soc. Auto. Eng., Warrendale PA.

Happel, A.M., E.H. Beckenbach, R.U. Halden. 1998. *An Evaluation of MTBE Impacts to California Groundwater Resources*. Lawrence Livermore National Laboratory, UCRL-AR-130897; Lawrence Livermore National Laboratory: Livermore, CA, 77 pp.

Hubbard, C.E., J.F. Barker, S.F. O'Hannesin, M. Vandegriendt, and R.W. Gillham. 1994. *Transport and fate of dissolved methanol, methyl-tertiary-butyl-ether, and monoaromatic hydrocarbons in a shallow sand aquifer*. API Publication No. 4601. American Petroleum Institute. Washington, D.C.

Huntley, D. and G.D. Beckett. 1999. Relationship Between Risk Reduction and LNAPL Recovery, *in* Proceedings of the API/NGWA Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water--Prevention, Detection, and Remediation, Houston, Tex., Nov. 17-19, 1999, p., 26-40.

IARC. 1999. Some Chemicals that Cause Tumours of the Kidney or Urinary Bladder in Rodents, and Some Other Substances. *International Agency for Research on Cancer Monographs* 73. http://193.51.164.11/htdocs/monographs/Vol73/73-13.html.

Jensen, H.M. and E. Arvin. 1990. Solubility and degradability of the gasoline additive MTBE, methyl-tert-butyl-ether and gasoline compounds in water. In F. Arendt, M. Hinsenveld and W.J. van den Brink, eds. *Contaminated Soil*. Kluwer, Dordrecht, The Netherlands. p. 445-448.

Keller, A., J. Froines, C. Koshland, J. Reuter, I. Suffet and J. Last. 1998. *Health & Environmental Assessment of MTBE*. Report to the Governor and Legislature of the State of California as Sponsored by SB 521, Volume I, Summary & Recommendations. November.

Landmeyer, J.E., Pankow, J.F., and Church, C.D. 1997. Occurrence of MTBE and tert-butyl alcohol in a gasoline-contaminated aquifer. In American Chemical Society Division of Environmental Chemistry pre-prints of papers, 213th, San Francisco, Calif.: ACS, 37(1): 413-415.

Lahvis, M.A., and L.C. Rehmann. 1999, Simulation of methyl tert-butyl ether (MTBE) transport to ground water from immobile sources of gasoline in the vadose zone, *in* Proceedings of the API/NGWA Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water--Prevention, Detection, and Remediation, Houston, Tex., Nov. 17-19, 1999, p., 247-259.

Lieberman, S. H. 1998. GeoVis Soil Video Imaging System. 50th Annual Meeting of National Ground Water Association, Las Vegas, Nevada, December 1998. National Water Well Association, Columbus, OH.

Mace, R.E. and W-J. Choi. 1998. *The Size and Behavior of MtBE Plumes in Texas*, in Proceedings of the API/NGWA Conference on Petroleum Hydrocarbons and Organics Chemicals in Ground Water, National Ground Water Association, November 11-13.

Mace, R.E., R.S. Fisher, D.M. Welch, and S.P. Parra. 1997. Extent, Mass, and Duration of Hydrocarbon Plumes from Leaking Petroleum Storage Tank Sites in Texas; Bureau of Economic Geology, University of Texas at Austin, Austin, Texas.

Maine Bureau of Health. 1998. *The Presence of MTBE and Other Gasoline Compounds in Maine's Drinking Water -- A Preliminary Report*. Bureau of Health, Department of Human Services; Bureau of Waste Management & Remediation, Department of Environmental Protection; Maine Geological Survey, Department of Conservation. October 13.

Mancini, E.R., A. Steen, G.A. Rausina, D.C.L. Wong, W.R. Arnold, F.E. Gostomski, T. Davies, J.R. Hockett, W.A. Stubblefield, K.R. Drottar, T.A. Springer, and P. Errico. 1999. *Preliminary Calculations of Freshwater and Marine Water Quality Criteria for MTBE*. Poster presented at the 20th Annual Meeting of the Society of Environmental Toxicology and Chemistry (SETAC), 14-18 November,1999, SETAC Annual Meeting Abstract Book #AB99, Philadelphia, PA.

Mo, K., C.O. Lora, A. Wanken, and C.F. Kulpa. 1997. Biodegradation of Methyl Tert-Butyl Ether by Pure Bacterial Cultures. Applied. Microbiol. Biotech. 47: 69-72.

Moran, M.J., Zogorski, J.S., and Squillace, P.J. 1999. MTBE in ground water of the United States--Occurrence, potential sources, and long-range transport, *in* Proceedings of the Water Resources Conference, American Water Works Association, Norfolk, Va., Sept. 26-29, 1999.

Mosteller, D.C, K.F. Reardon, A.W. Bourquin, B. Desilets, D. Dumont, R. Hines, and S. Kilkenny. 1997. Biotreatment of MTBE-Contaminated Ground Water. *Division of Environmental Chemistry Preprints of Extended Abstracts* 37(1):420-421. American Chemical Society, Washington D.C.

NESCAUM. 1999. "The Health Effects of Gasoline Constituents." In: *RFG/MTBE Recommendations and Findings*. Northeast States for Coordinated Air Use Management. Attachment 1. August 1999.

National Toxicology Program. 1999. http://ntp-server.niehs.nih.gov/NewHomeRoc/9thConsideration.html

OFA. 1998. *Taste and Odor Properties of Methyl Tertiary-Butyl Ether and Implications for Setting a Secondary Maximum Contaminant Level*. Oxygenated Fuels Association Technical Memorandum. June 26. http://www.ofa.net/111.pdf.

OSTP 1997. *Interagency Assessment of Oxygenated Fuels*. Office of Science and Technology Policy. National Science and Technology Council. June.

Pankow, J.F., and J.A. Cherry. 1996. *Dense chlorinated solvents and other DNAPLs in ground water*. Waterloo Press. Portland, Oregon.

Pankow, J.F., N.R. Thompson, R.L. Johnson, A.L. Baehr, and J.S. Zogorski. 1997. The Urban Atmosphere as a Non-Point Source for the Transport of MTBE and Other Volatile Organic Compounds (VOCs) to Shallow Groundwater. *Environmental Science & Technology,* 31: 2821-2828.

Pitkin, S. E., J.A. Cherry, R.A. Ingleton, and M. Broholm, 1999. Field Demonstrations Using the Waterloo Groundwater Profiler. Ground Water Monitoring and Remediation, Vol 19., No. 2. Spring 1999.

Reid, J.B, H.J. Reisenger, P.G. Bartholomae, J.C. Gray, and A.S. Hullman, 1999. Comparative M*t*BE Versus Benzene Plume Behavior, BP Oil Company Florida Facilities. Integrated Science & Technology, Inc., Marietta, Georgia. 58 pp.

Reuter, J.E., B.C. Allen, R.C. Richards, J.F. Pankow, C.R. Goldman, R.L. Scholl and J.S. Seyfried. 1998. Concentrations, Sources and Fate of the Gasoline Oxygenate Methyl *ter*t-Butyl Ether (MTBE) in a Multiple-Use Lake. *Environmental Science & Technology,* 32(23): 3666-3672.

Rice, D.W., R.D. Grose, J.C. Michaelson, B.P. Dooher, D.H. MacQueen, S.J. Cullen, W.E. Kastenberg, L.G. Everett, M.A. Marino. 1995. *California Leaking Underground Fuel Tank (LUFT) Historical Case Analyses*. UCRL-AR-122207. Lawrence Livermore National Laboratory. Livermore, CA.

Rice, D.W., W.W. McNab, P.C. Johnson, L.G. Everett, W.E. Kastenberg, M.C. Cavanaugh, S. Pelmulder, M.C Small, and R.C Ragaini. 1998. *Department of Defense Petroleum Hydrocarbon Cleanup Demonstration Program Final Report: Risk-Informed Decision Making as Petroleum Contaminated Sites*. UCRL-AR-131771. Lawrence Livermore National Laboratory. Livermore, CA.

Rivett, M. O., 1995. Soil Gas Signatures from Volatile Chlorinated Solvents: Borden Field Experiments. *Ground Water*, 33(1): 84-98.

Rixey, W.G., and S. Joshi. 1999. Dissolution Characteristics of MTBE, BTEX and 1,2,4-Trimethylbenzene from a Residually Trapped Gasoline Source, *in* Proceedings of the API/NGWA Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water--Prevention, Detection, and Remediation, Houston, Tex., Nov. 17-19, 1999, p., 107-122.

Rong, Y.R. 1999. A Study of Vertical Plume Length for Methyl Tertiary Butyl Ether in the Charnock Wellfield Investigation Area. Environmental Geosciences, 6(3): 123-129.

Salanitro, J.P., L.A. Diaz, M.P. Williams, and H.W. Wisniewski. 1994. Isolation of a bacterial culture that degrades methyl t-butyl ether. *Applied Environmental Microbiology*, 60(7): 2593-2596.

Schirmer, M. and J.F. Barker. 1998. A Study of Long-term MTBE Attenuation in the Borden Aquifer, Ontario, Canada. *Ground Water Monitoring & Remediation*. 18(2): 113-122.

SCVWD, 1999. Summary Report, Investigation of MtBE Occurrence Associated with Operating Underground Storage Tanks, Santa Clara Valley Water District Groundwater Vulnerability Pilot Study, Santa Clara Valley Water District, Santa Clara, California, July 16, 1999. http://www.scvwd.dst.ca.us/wtrqual/factmtbe.htm.

Shen, Y.F., L.J. Yoo, S.R. Fitzsimmons, and M.K. Yamamoto. 1997. Threshold Odor Concentrations of MTBE and Other Fuel Oxygenates. American Chemical Society, Division of Environmental Chemistry, Preprints of Papers Presented at the 213th ACS National Meeting, San Francisco, California, April 13-17, 1997: 37(1)

Small, M.C., and J. Weaver, 1999. An updated conceptual model for subsurface fate and transport of MTBE and benzene, *in* Proceedings of the NGWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water--Prevention, Detection, and Remediation, Houston, Texas, Nov. 17-19, 1999, p. 209-220.

Squillace, P.J., J.F. Pankow, N.E. Korte, and J.S. Zogorski. 1997. Review of the environmental behavior and fate of methyl tert-butyl ether. *Environmental Toxicology and Chemistry*, 16(9): 1836-1844.

Steffan, R.J., K. McClay, S. Vainberg, C.W. Condee, and D. Zhang. 1997. Biodegradation of the Gasoline Oxygenates Methyl tert-Butyl Ether, Ethyl tert-Butyl Ether, and tert-Amyl Methyl Ether by Propane-Oxidizing Bacteria. *Applied and Environmental Microbiology*, 63(11): 4216-4222.

Stocking, A., S. McDonald, B. Woll, and M. Kavanaugh. 1999. Evaluation of Fate and Transport of Methyl Tertiary Butyl Ether (MTBE) in Gasoline Following a Small Spill, *in* Proceedings of the NGWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water--Prevention, Detection, and Remediation, Houston, Texas, Nov. 17-19, 1999, p. 229-244.

Suflita, J.M. and M.R. Mormile. 1993. Anaerobic biodegradation of known and potential gasoline oxygenates in the terrestrial subsurface. *Environmental Science & Technology*, 27(5): 976-978.

Todd, D.K. 1980. *Groundwater Hydrology*, Second Edition, John Wiley & Sons, New York.

U.S. EPA. 1993. Assessment of Potential Health Risks of Gasoline Oxygenated with Methyl Tertiary Butyl Ether. EPA/600/R-93/206, November. Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C., 50 p.

U.S. EPA. 1997a. Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on MTBE. EPA/822/F-97/008. Office of Water, U.S. Environmental Protection Agency, Washington, DC. http://www.epa.gov/OST/Tools/MtBEaa.pdf.

U.S. EPA. 1997b. *Expedited Site Assessment Tools for Underground Storage Tanks Sites*. EPA 510-B-97-001. March. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1998. "Oxygenates in Water: Critical Information and Research Needs", EPA/600/R-98/048. Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1999a. *MTBE Groundwater Clean-up Levels for LUST Sites: Current & Future*. http://www.epa.gov/swerust1/mtbe/mtbemap.htm

U.S. EPA. 1999b. *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites*. Office of Solid Waste and Emergency Response Directive Number: 9200.4-17P, April 21. U.S. Environmental Protection Agency, Washington. D.C.

U.S.EPA. 1999c. “State Winter Oxygenated Fuel Programs”. June 16. U.S. Environmental Protection Agency, Office of Mobile Sources, Washington, D.C. http://www.epa.gov/oms/regs/fuels/oxy-area.pdf

U.S. EPA. 1999d. *Achieving Clean Air and Clean Water: The Report of the Blue Ribbon Panel on Oxygenates in Gasoline*. EPA 420-R-99-021. September 15, 1999. 116p.

Weaver, J.W., R.J. Charbeneau, J.D. Tauxe, B.K. Lien, and J.B. Provost. 1994. The Hydrocarbon Spill Screening Model (HSSM) Volume 1: User's Guide. EPA/600/R-94/039a. Robert S. Kerr Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency. Ada, Oklahoma.

Weaver, J.W., J.E. Haas, and C. Sosik. 1999. Characteristics of gasoline releases in the water table aquifer of Long Island, *in* Proceedings of the NGWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water--Prevention, Detection, and Remediation, Houston, Texas, Nov. 17-19, 1999. p. 260-261.

Weaver, J.W. 2000. Estimated Plume Diving in Simple Hydrogeologic Settings. Submitted to *Ground Water*, in publication.

WHO (World Health Organization). 1999. INTERNATIONAL PROGRAMME ON CHEMICAL SAFETY (IPCS) Environmental Health Criteria 206: Methyl *tertiary*-butyl ether. http://www.who.int/pcs/docs/ehc_206.htm

Wiedemeier, T.H., J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. 1995. *Technical protocol for implementing intrinsic remediation with long-term monitoring for natural* *attenuation of fuel contamination dissolved in groundwater*. U.S. Air Force Center for Environmental Excellence, San Antonio, TX.

Yeh, C.K. and J.T. Novak. 1994. Anaerobic biodegradation of gasoline oxygenates in soils. *Water Environmental Research*, 66: 744-752.

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. 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 Fuels*, Office of Science & Technology Policy, Executive Office of the President, Washington, D.C.

Appendix A

STRUCTURE AND PROPERTIES OF OXYGENATES

A.1 CHEMICAL STRUCTURE

Petroleum fuels consist predominantly of complex mixtures of hydrocarbon molecules. A wide variety of hydrocarbons are typically present, but they all share one common characteristic: they are composed entirely of carbon and hydrogen atoms, linked by carbon-carbon and carbon-hydrogen bonds. Examples include benzene (Figure A-1) and other BTEX compounds.

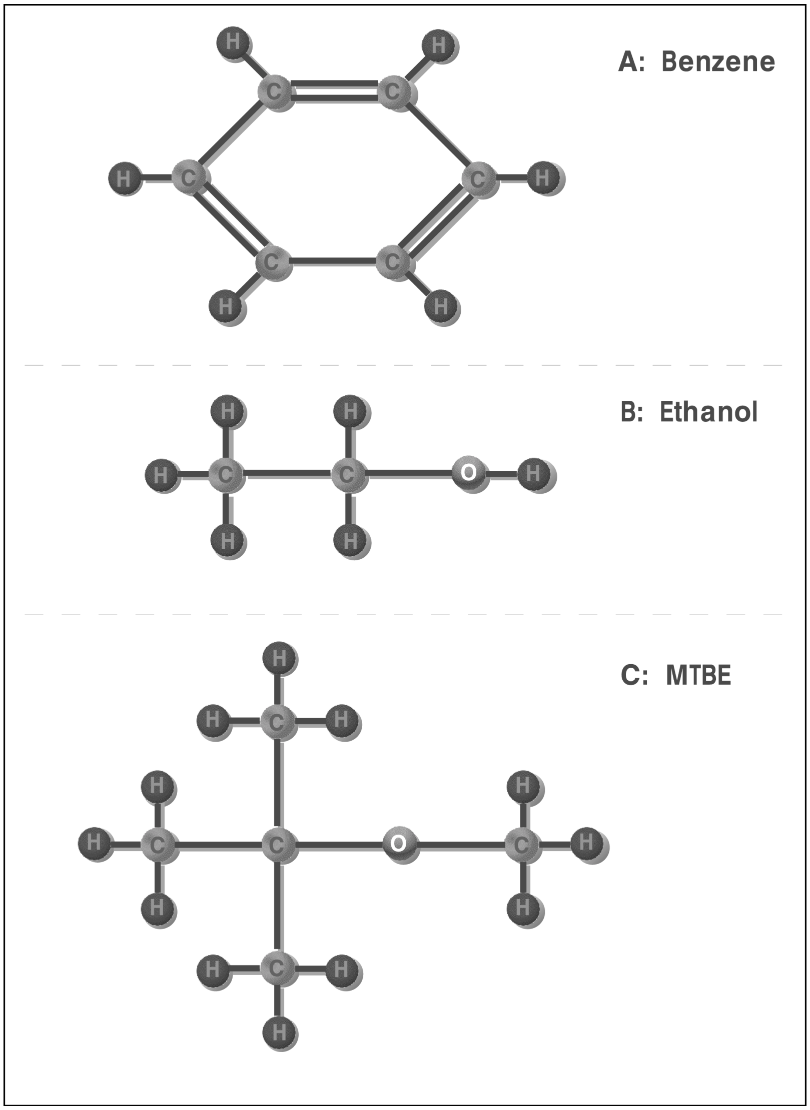


Figure A-1. Chemical Structure of Benzene, Ethanol, and MTBE

Gasoline oxygenates contain oxygen atoms in addition to carbon and hydrogen atoms. The presence of gasoline oxygenates promotes cleaner fuel combustion within the engine, boosts fuel octane values, and reduces vehicle air emissions (Keller *et al.*, 1998). Two types of oxygenates are commonly added to gasoline: alcohols and ethers.

In alcohols, each oxygen atom is linked to a carbon atom and a hydrogen atom, forming a carbon-oxygen-hydrogen sequence. Ethanol (Figure A-1) is by far the most commonly used alcohol oxygenate. Other alcohols that are used (or that could potentially be used) as fuel oxygenates include methanol and *tertiary*-butyl alcohol (TBA). TBA is also of interest as a product of MTBE degradation and a potential impurity from MTBE manufacture (see Appendix A.2.7).

In ethers, each oxygen atom is linked to two carbon atoms, forming a carbon-oxygen-carbon sequence. MTBE (Figure A-1) is by far the most commonly used ether oxygenate due to its high octane properties and availability. Other ethers that are used (or that could potentially be used) as fuel oxygenates include *tertiary*-amyl methyl ether (TAME), *tertiary*-amyl ethyl ether (TAEE), ethyl *tertiary*-butyl ether (ETBE), and diisopropyl ether (DIPE).

A.2 CHEMICAL PROPERTIES

When fuel is released to the subsurface, the components of the fuel may remain in the original NAPL, dissolve into and migrate with any water present in the soil, absorb to solid material in the soil, or volatilize into soil gas. This partitioning between NAPL, water, solids, and gas can be largely described by four chemical properties: solubility in water, solids-water partition coefficient, vapor pressure, and Henry's Law Constant. The movement of fuel components in groundwater is a function of the groundwater flow velocity and the retardation factor, and their persistence in the environment is affected by the biodegradation rate. These properties are briefly reviewed below, with particular reference to BTEX, alcohol oxygenates, and ether oxygenates.

A.2.1 Water Solubility

The propensity of a chemical to dissolve in water is measured by its solubility, commonly expressed as milligrams of dissolved chemical per liter of water (mg/L). If fuel is released to the subsurface, compounds with high solubilities are more likely to dissolve into groundwater, while compounds with low solubilities are more likely to remain in NAPL.

Hydrocarbons, in general, are only slightly soluble in water (Table A-1). For example, the solubilities of BTEX compounds range from approximately 150 to 1,800 milligrams per liter (mg/L). Ether oxygenates tend to have higher solubilities. For example, the solubility of MTBE is about 48,000 mg/l, which is about 25 times higher than the solubility of benzene and about 300 times higher than the solubility of ethylbenzene. Alcohol oxygenates are still more soluble; ethanol, methanol, and TBA are all miscible with water, so their solubilities are essentially infinite.

Table A-1. Comparison of Physical Properties of BTEX and Oxygenates

Chemical	Pure Phase Solubility	log K_{oc}	Vapor Pressure	Henry's Law Constant	Retardation Factor	
	mg/L	log l/kg	mm Hg	Dimensionless	Soil Condition A[1]	Soil Condition B[2]
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:

See text for abbreviations
Data from Zogorski *et al*. (1997). Values at 20 or 25 °C
1 = Soil Condition A: f_{oc}=0.001 mg/mg, bulk density = 1.75 kg/L, porosity = 0.25
2 = Soil Condition B: f_{oc}=0.004 mg/mg, bulk density = 1.75 kg/L, porosity = 0.25

The solubilities listed in Table A-1 are theoretical values; they measure the amount of pure chemical that could dissolve in one liter of water. Theoretical solubilities are useful for comparative purposes. However, petroleum fuels are mixtures of compounds, not pure chemicals, and this affects the solubility of fuel components. The effective solubilities of fuel components dissolving from NAPL are typically much lower than the theoretical solubilities.

The effective water solubility of a fuel component in NAPL may be estimated using the following equation:

$$S_e = S_t X_m \gamma \qquad \text{(Equation A-1)}$$

where S_e is the effective solubility, S_t is the theoretical solubility, X_m is the mole fraction of the compound in the NAPL, and γ is a compound-specific activity coefficient (Squillace *et al.*, 1997). For many common fuel components (including MTBE), X_m is approximated by the volume fraction of the compound in NAPL, while γ is close to 1.

The total S_e of BTEX and all other hydrocarbons in nonoxygenated gasoline NAPL is generally about 120 mg/L (Squillace *et al.*, 1997), while the S_e of MTBE in gasoline may greatly exceed this value. Since modern oxygenated fuels commonly contain 11 to 15 percent MTBE by volume (see Appendix A.5.1), and since the theoretical solubility of MTBE is about 48,000 mg/l (Table A-1), the S_e of MTBE in oxygenated gasoline NAPL could reach levels of approximately 5,000 to 7,500 mg/L. Even an older fuel blend, containing just 2 to 3 percent MTBE by volume as an octane booster, could still have an MTBE S_e of some 1,000 to 1,500 mg/L.

Under field conditions, the dissolved-phase concentrations of fuel components will typically be lower than the S_e values obtained from Equation A-1. For example, dissolved concentrations of MTBE in excess of 1,000 ppm are actually very uncommon. The dissolved-phase concentrations will reach the S_e values only if the water is fully saturated with gasoline, which is likely to occur only in the immediate vicinity of NAPL. Field S_e values may also be affected by NAPL weathering. Certain fuel components are subject to rapid evaporation from NAPL, which may significantly lower their X_m value, and therefore their S_e value. Conversely, other fuel components have little tendency to evaporate from NAPL, and so their X_m and S_e values may increase.

A.2.2 Solids-Water Partition Coefficient

Dissolved compounds in groundwater may adsorb to soil particles. For fuel components, the naturally occurring organic matter in soil is usually the preferred medium for adsorption. The tendency of a fuel component to adsorb to soil is therefore related to the organic carbon partition coefficient (K_{oc}).

K_{oc} is defined as the ratio of the concentration of the chemical adsorbed onto organic carbon to the concentration of the chemical dissolved in water. It is commonly expressed as milligrams of adsorbed chemical per kilogram of organic carbon (mg/kg) divided by milligrams of dissolved chemical per liter of water (mg/L), which simplifies to L/kg. Because K_{oc} values may vary by several orders of magnitude, log K_{oc} values are often used. If fuel components are dissolved in groundwater, compounds with high K_{oc} values are more likely to adsorb to soil, while compounds with low K_{oc} values are more likely to remain dissolved in groundwater.

In general, K_{oc} tends to be inversely proportional to water solubility (Table A-1). The BTEX compounds have log K_{oc} values of approximately 1.5 to 3.2. Alcohol and ether oxygenates have generally lower log K_{oc} values, ranging from about 0.2 to about 2.2. MTBE falls near the middle of this range, with measured log K_{oc} values ranging from about 1.0 to 1.1. It should be noted that these are log values, and so a difference of one actually represents a ten-fold difference in K_{oc}. Thus, the K_{oc} values of BTEX compounds are some 6 to 35 times higher than that of MTBE.

The K_{oc} values listed in Table A-1 are useful for comparative purposes. However, natural soils contain a wide variety of materials, not just organic carbon. The actual propensity of fuel components to adsorb to soil solids is measured by the solids-water partition coefficient (K_d). The K_d value for a given compound in a particular soil is typically much lower than the K_{oc} value.

K_d is the ratio of the concentration of the chemical adsorbed onto soil solids to the concentration of the chemical dissolved in water. It is commonly expressed in L/kg, like K_{oc}. The K_d value of a given compound is determined by the organic carbon fraction (f_{oc}) of the soil and by the K_{oc} value of the compound, in accordance with the following equation:

$$K_d = K_{oc} f_{oc} \qquad \text{(Equation A-2)}$$

Since f_{oc} is a property of soil, K_d values are site-specific. The K_d values for different fuel components in that soil will vary in proportion to K_{oc} values. MTBE and other oxygenates have relatively low K_{oc} values, as noted above. At any given location, the K_d values for oxygenates are always lower than the corresponding K_d values for BTEX compounds.

The effects of this difference are shown graphically in Figure A-2, which contrasts the equilibrium partitioning for benzene and MTBE under a given set of soil conditions ($f_{oc} = 0.005$, porosity = 0.38, bulk density = 1.7 kg/L) and varying degrees of saturation. Compared to MTBE, benzene has a clear affinity for soil: in this case, most of the benzene mass remains sorbed to soil, even as the degree of moisture saturation approaches 100 percent (Figure A-2a). MTBE has a much stronger affinity for water: it partitions readily into soil moisture as the degree of saturation increases (Figure A-2b). Even at only 16 percent saturation, most of the MTBE mass is dissolved in water.

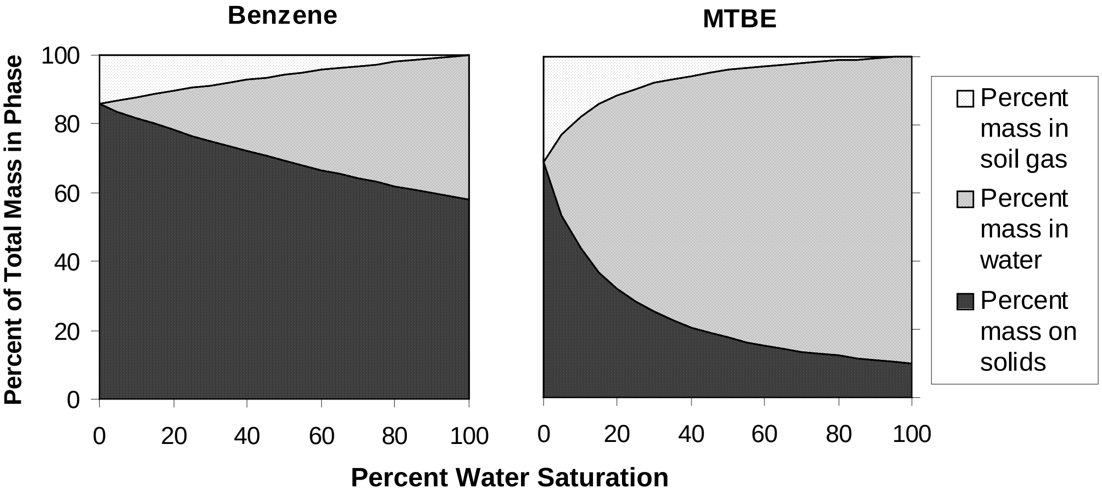


Figure A-2. Comparison of Equilibrium Partitioning for Benzene and MTBE

A.2.3 Vapor Pressure

The propensity of a chemical to migrate from NAPL to the gas phase is measured by the vapor pressure, commonly expressed in millimeters of mercury (mm Hg) at 25°C. The vapor pressure of a given chemical is the pressure exerted by the gas phase when it is in equilibrium with the liquid phase. If fuel is released to the subsurface, compounds with high vapor pressures are more likely to vaporize into soil gas, while compounds with low vapor pressures are more likely to remain in NAPL.

The vapor pressures of BTEX compounds at 25°C range from about 8 to 95 mm Hg (Table A-1). Ether oxygenates generally have higher vapor pressures (Table A-1). For example, the vapor pressure of MTBE at 25°C is about 250 mm Hg. Thus, MTBE and other ether oxygenates have a relatively strong tendency to volatilize from NAPL.

The vapor pressures listed in Table A-1 apply to pure chemicals. The partial pressures exerted by fuel components in NAPL are typically lower than the vapor pressures, just as the effective solubilities of fuel components in NAPL are lower than the theoretical solubilities. The partial pressure of a fuel component in NAPL may be estimated using the following equation:

$$P_p = P_v X_m \qquad \text{(Equation A-3)}$$

where P_p is the partial pressure, P_v is the vapor pressure, and X_m is the mole fraction of the compound in the NAPL.

For MTBE, P_v is higher than the corresponding values for BTEX compounds; X_m may be higher as well, since oxygenated fuels often contain a relatively high proportion of MTBE (see Appendix A.5.1). Thus, the P_p value for MTBE in oxygenated NAPL can be much higher than the value for total BTEX compounds.

Under field conditions, the vapor-phase concentrations of fuel components will typically be lower than the P_p values obtained from Equation A-1. The vapor-phase concentrations may reach the P_p in the immediate vicinity of NAPL. The vapor-phase concentrations may even exceed the calculated P_p values, if the composition of the NAPL changes after its release. Certain fuel components (particularly pentane and other light alkanes) are subject to rapid evaporation; this factor increases the X_m (and therefore the P_p) of the remaining fuel components in the residual NAPL.

A.2.4 Henry's Law Constant

The propensity of a chemical to partition between the dissolved phase and the gas phase is measured by the Henry's Law Constant (K_H). K_H is defined as the ratio of the concentration of the chemical in the gas phase to the concentration of the chemical dissolved in water. If fuel components are dissolved in groundwater, compounds with high Henry's Law Constants are more likely to vaporize into soil gas, while compounds with low Henry's Law Constants are more likely to remain dissolved in groundwater.

The dimensionless K_H values for BTEX compounds range from approximately 0.22 to 0.35 (Table A-1). Ether oxygenates often have lower K_H values; for example, the K_H for MTBE has been estimated at about 0.022 to 0.12. Thus, MTBE and other oxygenates have a relatively low tendency to volatilize from groundwater.

A.2.5 Retardation in Groundwater

Fuel components dissolved in groundwater undergo advective transport; in other words, they migrate with the movement of groundwater. The front of any dissolved-phase plume will therefore tend to migrate in the downgradient direction. However, the average velocity of plume migration for a given chemical (V_c) will typically be lower than the average velocity of the associated groundwater (V_{gw}). This difference is measured by the dissolved-phase retardation factor (R_{dp}), where

$$V_c = \frac{V_{gw}}{R_{dp}} \qquad \text{(Equation A-4)}$$

R_{dp} is a function of soil bulk density (ρ_b), soil effective porosity (θ_e), and K_d (see Appendix A.2.2), as defined by the following equation:

$$R_{dp} = 1 + \frac{K_d \rho_b}{\theta_e} \qquad \text{(Equation A-5)}$$

R_{dp} and V_c depend on soil and groundwater properties, and are therefore site-specific. These parameters are also affected by K_d, which in turn is proportional to K_{oc} (see Appendix A.2.2).

Thus, the differences in the velocities of dissolved-phase plumes in groundwater at a given location are ultimately related to differences in K_{oc}.

Fuel components with moderately high K_{oc} values, such as BTEX hydrocarbons, have moderately high R_{dp} values (Table A-1). Dissolved BTEX compounds, therefore, tend to move somewhat slowly relative to local groundwater. For example, in a sandy aquifer where $\rho_b = 2.1$ kg/l, $\theta_e = 0.25$, and $f_{oc} = 0.001$, the R_{dp} values for BTEX compounds would range from about 1.6 to 4.3. The corresponding chemical velocity values would range from approximately 23 to 63 percent of the groundwater velocity.

Fuel components with relatively low K_{oc} values, such as MTBE and most other oxygenates, have relatively low R_{dp} values (Table A-1). Dissolved oxygenates, therefore, tend to be more mobile in groundwater than dissolved BTEX compounds. For example, under the same aquifer conditions as those described above, the R_{dp} values for alcohol and ether oxygenates would range from about 1.0 to 1.5. The corresponding V_c values would range from approximately 68 to over 95 percent of V_{gw}. MTBE is a relatively mobile oxygenate; its R_{dp} value would be about 1.09, which corresponds to V_c values of about 91 percent of V_{gw}.

Retardation and chemical velocity values are sensitive to changes in f_{oc}, but such changes affect hydrocarbons more than oxygenates (Table A-1). For example, consider the same aquifer conditions outlined above, but with $f_{oc} = 0.004$ instead of $f_{oc} = 0.001$. Given this change in f_{oc}, the R_{dp} value for benzene would more than double (from 1.6 to 3.4), and the corresponding V_c value would drop by more than half (from 63 to 30 percent of V_{gw}). The effects on MTBE would be less pronounced. Given the same change in f_{oc}, the dissolved-phase retardation factor for MTBE would rise slightly (from about 1.09 to 1.38), and the corresponding chemical velocity would drop slightly (from about 91 to 73 percent of groundwater velocity). The practical consequence is that dissolved BTEX will migrate much more slowly in high-organic-carbon soils than dissolved oxygenates.

A.2.6 Retardation in the Vadose Zone

When NAPL is released to the subsurface, some portion will volatilize and migrate in the vapor phase. The transient migration of fuel components in the vapor phase depends on site-specific factors, including ρ_b, the volumetric water content (θ_w), and the volumetric air content (θ_a), as well as chemical-specific factors, including K_d and K_H. Baehr (1987) defined a vapor-phase retardation factor (R_{vp}) as follows:

$$R_{vp} = 1 + \frac{\theta_w + K_d\, \rho_b}{K_H\, \theta_a} \qquad \text{(Equation A-6)}$$

R_{vp} values are particularly sensitive to differences in K_H and θ_w. In dry soils (low θ_w), there is comparatively little difference between the R_{vp} values for oxygenates and BTEX compounds. However, oxygenates generally have lower K_H values than BTEX compounds, and so they partition more strongly into soil moisture. As θ_w increases, the R_{vp} values for oxygenates increase more quickly than the corresponding values for BTEX compounds. The practical consequence is that vapor-phase oxygenates will migrate more slowly than vapor-phase BTEX vapors as soil moisture increases.

A.2.7 Biodegradability

Fuel components released to the subsurface are subject to breakdown by the activity of microorganisms. Such microbiological transformation is known as biodegradation (API, 1996b). Biodegradation rates are extremely variable, depending on the compound and the ambient conditions (particularly the availability of oxygen). It is usually difficult to establish an accurate estimate of the biodegradation rate for a chemical at a particular site. Tier 1 RBCA analyses commonly overcome this uncertainty by making the conservative assumption that biodegradation rates are essentially zero (ASTM, 1995a; API, 1996c).

While absolute biodegradation rates are difficult to quantify, it is possible to rank the relative biodegradability of different compounds. In general, hydrocarbons and alcohols are considered relatively biodegradable, while ethers are considered less biodegradable.

Most available evidence indicates that MTBE in groundwater is relatively difficult to biodegrade (Squillace *et al.*, 1997). Some studies have shown that MTBE biodegradation is possible; Borden *et al*. (1997) and Schirmer and Barker (1998) have published quantitative estimates of biodegradation rates. However, biodegradation often appears to be relatively slow, and it may only occur under specific environmental conditions (Jensen and Arvin, 1990; Suflita and Mormile, 1993; Salanitro *et al.*, 1994; Yeh and Novak; 1994; Hubbard *et al.*, 1994). There is evidence that both MTBE and TBA may be aerobically degraded by microorganisms in streambed sediments (Bradley *et al.*, 1999). Plume studies in Florida and Texas suggest that many MTBE plumes do appear to stabilize, and that biodegradation of MTBE may play a significant role in limiting plume extent (Reid *et al.*, 1999; Mace and Choi, 1998).

An expected degradation product of subsurface MTBE is TBA (Church *et al.*, 1997). However, the presence of TBA in groundwater does not necessarily demonstrate that MTBE is undergoing biodegradation because TBA may also occur in gasoline as an octane booster (Landmeyer *et al.*, 1997), or as an impurity in ether oxygenates.

A.2.8 Human Toxicity

Several organizations have recently conducted comprehensive reviews of the carcinogenicity and toxicity of MTBE including U. S. EPA (1997a), OSTP (1997), NESCAUM (1999), California EPA (1998, 1999), the National Toxicology Program (NTP, 1999), the International Agency for Research on Cancer (IARC, 1999), the Agency for Toxic Substances and Disease Registry (ASTDR, 1996) and the World Health Organization (WHO, 1999). The available data on the human health and animal toxicity of ether oxygenates are limited, particularly for ingestion as the route of exposure. Based on collective evidence, it appears unlikely that MTBE alone induces adverse acute health effects in the general population under common exposure conditions (WHO, 1999). However, the current opinions of these agencies could change as more data become available.

As with other gasoline components, the principal human health concern associated with MTBE are possible cancer effects. Limited laboratory evidence suggests that MTBE may act as a carcinogen in rodents. Animal ingestion studies have shown carcinogenic effects at high levels of exposure

(250,000 micrograms per kilogram animal body weight and higher) (U.S. EPA, 1997). IARC and the National Institute of Environmental Health Sciences (NIEHS) have reviewed all relevant MTBE health studies and indicated that at this time there are not adequate data to consider MTBE a probable or known human carcinogen (USEPA 1999d, 1997).

In studies on animals, MTBE is "moderately" acutely toxic and induces mild skin and eye irritation but not sensitization. Repeated exposure affects primarily the kidney of rats and the liver of mice, with lowest reported adverse effect levels of 440 mg/kg body weight per day in rats following ingestion and 1440 mg/m3 (400 ppm) following inhalation. MTBE has not induced adverse reproductive or developmental effects at concentrations less than those that were toxic to the parents (WHO, 1999).

There are limited data on human populations that may be sensitive to MTBE. Although there is some evidence that fuels containing MTBE could irritate the eyes, as well as cause headaches and rashes, effects attributed to MTBE alone have yet to be proven. (U.S. EPA, 1999d). Limited epidemiological data suggest greater attention should be given to the potential for increased symptom reporting among highly exposed workers (U.S. EPA, 1999d).

There have been no human or animal health effects studies performed for MTBE in drinking water (U.S. EPA, 1999d). However, human and animal studies are currently underway at the U.S. Environmental Protection Agency (U.S. EPA), Health Effects Institute (HEI) and the Chemical Industry Institute of Toxicology (CIIT) to address some of these research needs.

Many of the studies cited above have been used to develop human drinking water advisories, goals or standards. Drinking water containing MTBE at or below the taste and odor levels identified in the U.S. EPA’s Drinking Water Advisory (20 to 40 micrograms per liter) is not expected to cause adverse health concerns for the majority of the population (U.S. EPA, 1999d).

A.2.9 Ecological Toxicity

The available evidence suggests that MTBE in surface waters has limited acute and chronic toxicity for aquatic organisms (California EPA, 1999, p. 65). While research in this area is continuing, ambient water quality criteria for MTBE are likely to be much higher than health-based or aesthetic-based drinking water criteria. For example, Mancini *et al*. (1999) recently calculated preliminary water criteria for MTBE in freshwater and marine environments based on available ecological toxicity data. The freshwater criteria were 151 mg/l (acute) and 51 mg/l (chronic); the marine criteria were 53 mg/l (acute) and 18 mg/l (chronic).

A.2.10 Taste and Odor Thresholds in Drinking Water

At high concentrations, MTBE is considered to have a strong, turpentine-like odor; however, human sensitivity to this odor varies. Individual taste and odor threshold values ranging from 2.5 µg/l to 740 µg/l have been reported (Oxygenated Fuel Association [OFA], 1998, p. 5).

Several recent studies have addressed the odor threshold of MTBE in drinking water. U.S. EPA (1997a, p. 5) concluded that MTBE concentrations in the 20 to 40 µg/l range would “likely avert unpleasant taste and odor effects”, but also noted that “some people may detect the chemical below this range”. Shen *et al*. (1997) found MTBE odor threshold values of 13.5 to 45.4 µg/l in trained panelists. OFA (1998) conducted odor testing with a large consumer panel, and concluded that no more than 5 percent of the tested subjects could detect MTBE at a concentration of 22 µg/l.

OFA (1998) recommended a Secondary Maximum Contaminant Level for MTBE of 15 µg/l, deeming this level protective of more than 95 percent of the consuming population. In 1999, however, California established a Secondary Maximum Contaminant Level of 5 µg/l, based on the lowest observable odor detection threshold level for any individual. This value is lower than standards based on human health criteria (see Section A.2.8). Thus, in some jurisdictions, taste and odor criteria may represent the most stringent standard for MTBE in drinking water.

Appendix B

SUMMARY OF TIERED RISK-BASED DECISION MAKING

B.1 RISK-BASED DECISION FRAMEWORK

One example of a risk-based decision making framework is the American Society for Testing and Materials (ASTM) three-tiered framework for risk-based decision making applied to petroleum releases, known as the *Standard Guide for Risk-Based Corrective Action (RBCA) Applied at Petroleum Release Sites* (ASTM 1995a). Subsequently, a companion standard guide was drafted that expands the tiered framework to corrective action decisions for releases of a wider range of sites and chemicals of concern (ASTM 1998a). The framework described in these standard guides (ASTM 1995a; ASTM 1998a) has formed the basis of regulatory programs for subsurface chemical releases in many states.

The risk-based decision making framework includes provisions for classifying sites according to immediacy of impact, and a tiered process for developing site-specific remedial goals that comply with state-specific objectives. The risk-based decision making framework can be developed into agency-specific regulatory policy and guidance through the use of a stakeholder group developing technical policy decisions that support agency-specific objectives. These agency-specific objectives may be based on a variety of considerations, including:

- Protection of human health or other ecological receptors;
- Aesthetic criteria, such as taste or odor thresholds for drinking water; and
- Resource conservation objectives, such as groundwater anti-degradation, and preservation or restoration of future beneficial uses of groundwater.

At higher tiers, site-specific estimates of chemical migration and attenuation may be used to evaluate the potential for future chemical exposures, and to refine site-specific (and pathway specific) remedial goals.

It is particularly important to draw a distinction between the use of natural attenuation and risk-based decision making. Natural attenuation processes, including biodegradation, which is usually the most significant process (API, 1996b), affect risk-based corrective action decisions in two ways. First, some regulatory frameworks allow natural attenuation processes to be considered in the selection of remedial goals. For example, under certain conditions, a state may allow the point of compliance in groundwater to be moved away from the point of original release. In this case, natural attenuation processes are considered in order to estimate the magnitude and extent of released chemical that can safely remain near the original source. Secondly, under certain conditions, natural attenuation may be an acceptable corrective action measure in order to achieve remedial goals (ASTM, 1998b; USEPA, 1999). The choice of remedy, whether it is natural attenuation or any other remedy, is not dictated by the risk-based decision making framework. Therefore, chemicals need not biodegrade readily in order to be evaluated using a risk-based decision making framework.

Another important point is that a chemical does not have to have an established toxicity value in order to be used in a tiered risk-based framework. Other relevant, measurable criteria can be used in place of risk-based concentration targets (see the “Non-Risk Considerations” discussion in Section 3.1.2). Non-risk-based goals (resource protection, aesthetic criteria, etc.) can be addressed within a tiered risk-based framework. For example, California has adopted an enforceable Secondary Maximum Contaminant Level for MTBE based on aesthetic (taste and odor) criteria of 5 µg/l. In such cases, the tiered process provides a structured way of making assessment and corrective action decisions, even where health risk is not the primary criterion.

B.2 THE TIERED APPROACH TO RISK EVALUATION AND CORRECTIVE ACTION

A risk evaluation may take the form of a simple screening-level approach that uses conservative, simplifying assumptions regarding sources, pathways, and receptors. Alternatively, a risk evaluation may be very site-specific and detailed. Site-specific refinements usually take the form of more detailed and realistic assumptions about the source concentrations, transport factors, exposure locations, or exposure factors. The objective of a detailed risk evaluation is to reduce uncertainty, which allows and justifies lower levels of conservatism. As additional information or analysis is used to refine the risk evaluation, the level of conservatism at the particular step can usually be reduced, which often (but not always) results in less stringent target cleanup levels. In other words, as a site setting becomes better understood and/or better managed, higher amounts of residual chemicals can often be safely left in place.

A tiered approach is a logical means of making risk-based cleanup decisions while striking a balance between uncertainty and available resources. The concept of a tiered framework can be applied to many risk-based regulatory programs. A tiered approach involves increasingly detailed levels of data collection and human health/environmental risk evaluation. The process starts with a simple, yet conservative, screening approach (Tier 1), and progresses to more site-specific methods (Tiers 2 and 3) only when it is cost-effective and/or necessary to reach a satisfactory remedy. If available information indicates that site concentrations exceed the default screening values provided by the implementing agency, then the party responsible for cleanup has a choice. Either a remedy can be implemented that allows the site to achieve the screening levels, or the screening levels can be refined using site-specific information (Tier 2). The choice is primarily an economic decision made by the responsible party, except in situations where the overall site conditions are likely to result in greater exposures than the conditions assumed by the default screening criteria.

Typically, Tier 2 involves calculations that are similar to those used to derive the Tier 1 screening levels, except that site-specific information is selectively substituted for the non-site-specific, conservative parameters used in Tier 1. Typically, certain transport factors can be modified at Tier 2, such as soil properties, depths to sources or to groundwater, or distances to receptors (or to points of compliance). Most regulatory programs do not allow exposure factors or toxicity factors to be refined at Tier 2.

At Tier 3, greater departures from the default methods and models are acceptable. At Tier 3, typically any site-specific refinement can be made that is properly justified and is acceptable to the regulatory agency. Because Tier 3 can encompass a wide range of site-specific refinements (e.g., highly detailed transport modeling, probabilistic assessments), it is usually not possible to stipulate in detail the specific methods allowed in Tier 3. Most regulatory programs that have adopted a tiered risk-based approach allow site-specific refinements to transport or exposure factors at Tier 3. Because of the wide range of possibilities, Tier 3 usually requires a much larger commitment of resources, both to produce and to review.

To be most effective and to ensure consistency, a regulatory agency must provide clear guidance regarding what types of site-specific methods can be used, particularly for Tier 2.

Note that tiers, as defined in a risk-based decision making framework, are not identical to the levels of assessment described in this document in Section 3.3. The level of assessment (limited, standard, or detailed) is chosen based on the risk factors present at the site, and by the information necessary to reach a protective remedy decision. For example, a standard level of assessment may be used to collect sufficient information to conduct a Tier 1 evaluation, or a Tier 2 evaluation. A detailed level of assessment is more likely to be conducted during a Tier 3 evaluation.

B.3 NON-RISK CONSIDERATIONS AND POLICY CONSTRAINTS

In some situations, non-health-based criteria may also prove important in establishing final site cleanup criteria. For example, other relevant, measurable criteria may include aesthetic considerations (e.g., odor, taste, discoloration) that may affect the future use of a site or resource, even after chemical concentrations have been reduced to levels posing no further health or environmental concern. Resource protection may be a policy objective, and may have associated criteria, even if the resource has no current beneficial use. In addition, other factors, such as legal and economic value considerations, may affect the selection of the remedy(s). These factors can be included in the decision process, usually after health-risk-based cleanup levels have been identified.

The guidance provided in this document is not intended to supercede any local, state or federal policies regarding the assessment of oxygenate releases. Rather, it provides a framework for making assessment decisions to supplement existing policies and procedures, and to provide a framework where agency-specific guidance does not exist.

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