
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 volatilize 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 Gavvas, 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 ($\mu\text{g/L}$); however, greatly elevated oxygenate detection limits were needed at TPH concentrations of 5,000 and 50,000 $\mu\text{g/L}$ 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.

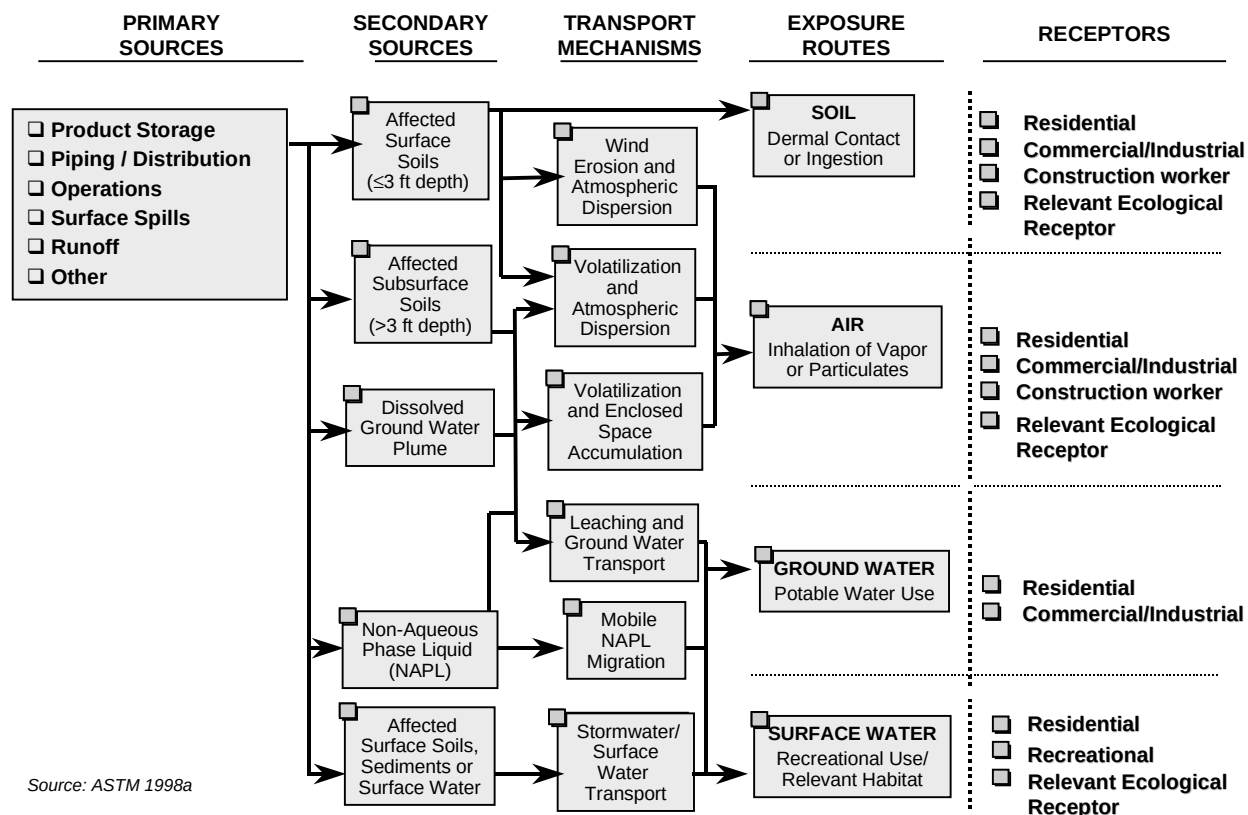


Figure 3-1. Example of an Exposure Pathway Flowchart

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)	Review regional information; develop conceptual model of flow system between site and groundwater receptor(s)	Review regional information; develop conceptual model of flow system between site and groundwater receptor(s)
		Define horizontal and vertical flow system (potentiometric contours)	Define horizontal flow system (potentiometric contours)	Define horizontal flow system (potentiometric contours)
		Evaluate vertical flow potential (use site-specific water level measurements to estimate vertical hydraulic gradients)	Evaluate vertical flow potential (use regional or site-specific water level measurements to evaluate vertical gradients)	Similar in detail to historical BTEX investigation
		Assess hydraulic communication between source and receptor wells	May include hydraulic tests and assessment of vertical hydraulic communication	
		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		

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.