New Technical Guidance for MTBE Site Characterization

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Abstract

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, 1996) were originally developed to meet regulatory requirements for NAPL and BTEX characterization. However, the chemical properties and subsurface behavior of oxygenated fuel additives are substantially different from those of BTEX or other petroleum hydrocarbons, and so a reevaluation of traditional assessment procedures was warranted. In response to this need, the American Petroleum Institute has produced a technical guidance document, *MTBE Site Characterization Technical Bulletin*, for the appropriate characterization of sites with subsurface releases of fuel oxygenates (API, 1999).

The technical bulletin uses the principles of risk-based decision making to guide the evaluation of sites affected by MTBE or other oxygenates. The publication 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.

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

The guidance reviews the risk factors associated with oxygenate sources, pathways, and receptors. These risk factors are used to develop an initial conceptual model and to tentatively categorize a site as high, medium, or low risk. Various assessment tasks are then conducted to verify the conceptual model, and to confirm whether further investigation or corrective action is needed.

Many of these assessment tasks can take advantage of improved, cost-effective methods for rapid collection and field analysis of soil, soil-gas, and groundwater samples. API (1999) provides an overview of the expedited site assessment approach and provides a detailed guide to current direct-push assessment and monitoring tools, with emphasis on their proper use at MTBE-affected sites.

Introduction

During the past decade, the use of oxygenated fuel additives in gasoline has increased in response to the requirements of the 1990 Clean Air Act. The most widely used oxygenate is methyl tertiary-butyl ether, or MTBE. As oxygenate usage has grown, however, so have concerns regarding the effects of these compounds on groundwater quality. The chemical properties and subsurface behavior of oxygenates differ from those of conventional petroleum hydrocarbons, and so a reevaluation of traditional soil and groundwater assessment approaches is warranted.

The American Petroleum Institute (API) has developed technical guidance for environmental assessment at sites affected by releases of MTBE and other chemically similar ether oxygenates. This bulletin summarizes the guidance presented in API Publication “MTBE Site Characterization Technical Bulletin”, which provides (1) a review of the properties and environmental behavior of MTBE; (2) a decision process that uses risk-based decision-making principles to select an appropriate level of assessment for MTBE-affected sites; and (3) a review of modern assessment tools and techniques for characterizing and monitoring MTBE in the subsurface.

Properties of MTBE and Other Oxygenates

Petroleum fuels consist predominantly of molecules composed of carbon and hydrogen atoms. Familiar examples include benzene, toluene, ethylbenzene, and xylenes (BTEX). Oxygenates contain oxygen atoms, in addition to carbon and hydrogen atoms. Oxygenates are used in petroleum fuels to boost octane ratings and to reduce exhaust emissions. Two kinds of oxygenates are commonly used as fuel additives: alcohols and ethers. Alcohol oxygenates, such as ethanol, are characterized by a carbon-oxygen-hydrogen sequence of atoms; ether oxygenates, such as MTBE, are characterized by a carbon-oxygen-carbon sequence. Modern oxygenated gasoline may contain up to 15 percent MTBE by volume.

The chemical properties of oxygenates differ from those of BTEX compounds in several respects. In general, oxygenates have a stronger affinity for water; they are more likely to dissolve into groundwater and less likely to adsorb to soil or volatilize into soil vapor. An example of the difference in partitioning behavior of benzene and MTBE for a typical soil is shown in Figure 1. This figure assumes a soil with a fraction organic carbon of 0.005, a porosity of 0.38, and a bulk density of 1.7 kg/L.

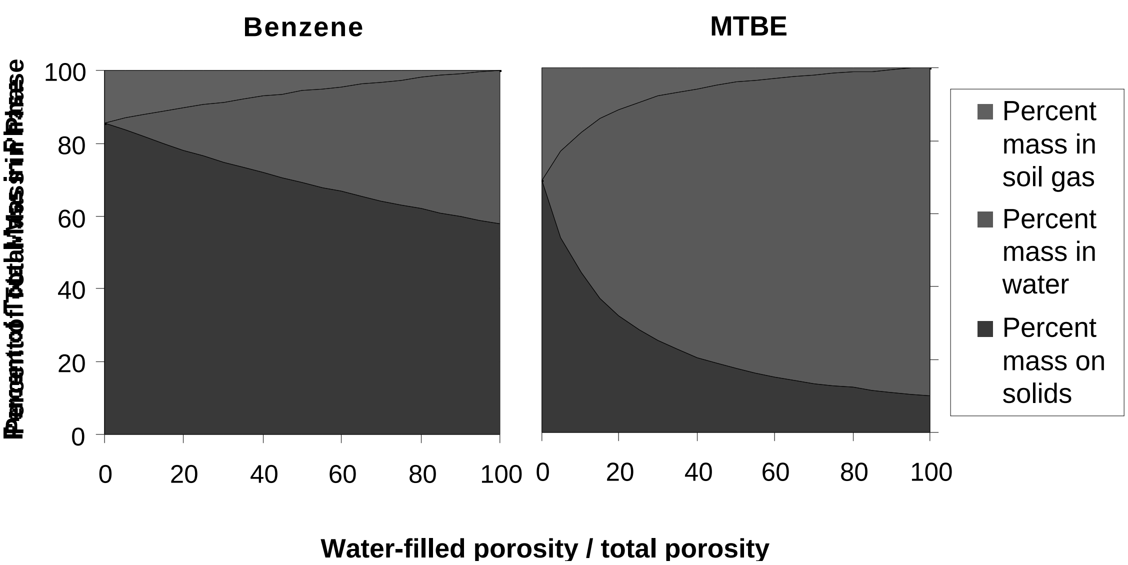

Figure 1. Comparison of phase distribution for benzene and MTBE in a typical soil.

Thus, an accidental release of oxygenated fuel is more likely to affect groundwater than a comparable release of conventional fuel. In the case of alcohol oxygenates, this potential appears to be mitigated by relatively high biodegradation rates. However, MTBE and other ether oxygenates appear to be relatively resistant to biodegradation in many subsurface environments. Dissolved-phase MTBE plumes in groundwater tend to be more mobile and persistent than associated BTEX plumes, and may extend further downgradient. These potential differences in partitioning and mobility may require different assessment strategies than have been commonly used for BTEX plumes.

Risk-Based Decision-Making and MTBE Assessment

Risk-based decision making can be used to evaluate and address a variety of environmental concerns, including those related to subsurface releases of oxygenates. In API (1999), the principles of risk-based decision making are discussed and applied to MTBE site characterization.

The level of assessment at an MTBE release site is determined by risk factors associated with the sources of oxygenate release, the pathways of migration and exposure, and receptors that may be potentially exposed to the released chemical. For example, a site affected by a large release, underlain by shallow groundwater, and located near shallow water-supply wells would warrant a high level of assessment. Conversely, a site affected by a small release, underlain by deep groundwater, with no nearby supply wells would likely warrant a lower level of assessment.

The guidance reviews the risk factors associated with oxygenate sources, pathways, and receptors. Certain risk factors are usually known earlier in the assessment process, such as whether groundwater is currently used for potable purposes. The risk factors that are known (or assumed) early in the site characterization are used to develop an initial conceptual model of the site, and are used to tentatively categorize a site as high, medium, or low risk. Various assessment tasks are then conducted to verify the conceptual model, and to confirm whether further investigation or corrective action is needed. The level of effort expended on each assessment task depends on whether a site is categorized as high, medium, or low risk. The risk category and the associated level of effort for each task may change as new information is obtained during the site characterization.

API (1999) includes a series of decision matrices to help determine the appropriate overall level of assessment, and to suggest an appropriate level of effort for each assessment task. Three general levels of assessment are outlined: the standard level, the limited level, and the detailed level. The standard level of assessment would be appropriate for the greatest number of sites; it involves moderate sample spacing with some vertical characterization, as well as horizontal characterization. It also includes The limited level of assessment is appropriate at sites with unusually low risk factors, or as the first stage of data collection; it involves relatively large sample spacing with an emphasis on horizontal characterization. A detailed level of assessment requires the highest level of effort for each characterization task. This would be warranted at sites with unusually high risk factors; it includes relatively close sample spacing and extensive vertical characterization of chemical concentrations and hydraulic properties. It would also include an extensive survey of potential nearby conduits for subsurface migration, and a wider-ranging inventory of nearby water wells.

Although particular conditions may warrant a more detailed level of assessment (e.g., groundwater that is currently used for potable purposes has been affected by MTBE), in many cases there will be no simple “bright lines” or “litmus tests” to indicate when a more detailed characterization is necessary. The decision to increase of decrease the level of effort and detail should be based on whether the available information is sufficient to make a protective site management decision. As an example, consider a site where released MTBE has affected a nearby potable-use well. At this particular site, the data collected to date indicate that the hydrogeologic setting is well understood, and the MTBE in the potable well is readily attributed to the release at the nearby site. Although the situation may fulfill the criteria for a detailed level of assessment, a protective remedy (such as source removal, combined with wellhead treatment and hydraulic containment) could be implemented with the existing assessment information, so a more detailed level of assessment would not be necessary.

MTBE Assessment and Monitoring

In recent years, a variety of innovative new tools and techniques has been developed for subsurface characterization. These approaches have proven to be of great value to environmental assessment in general, and to the evaluation of MTBE releases in particular.

MTBE release sites are commonly characterized by relatively small source zones and long, thin, dissolved-phase plumes (Figure 2). Such sites can be delineated most cost-effectively when samples can be rapidly collected and analyzed in the field, thereby allowing the site investigator to "chase the plume" based on the most recent sampling results. This approach, known as expedited site assessment (ESA), has been recognized by ASTM (ASTM, 1999) and the U.S. Environmental Protection Agency (U.S. EPA, 1997).

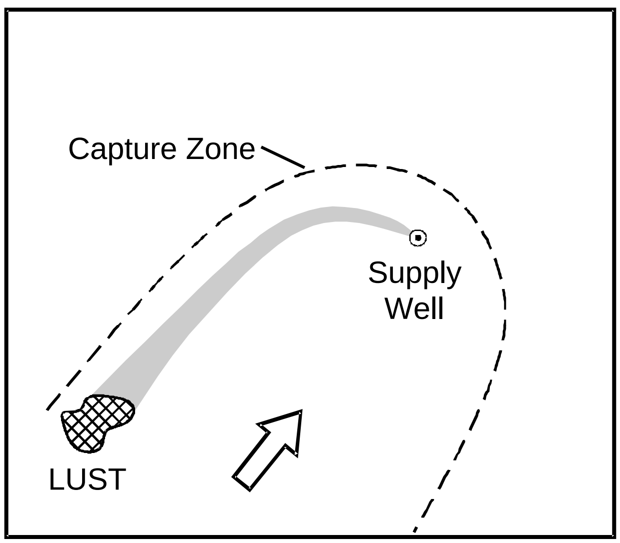

Figure 2. Example MTBE plume geometry, showing plume capture by a supply well.

In ESAs, analytical data are generated and interpreted on-site by whenever possible. The sampling and analysis plan is dynamic; as new data become available, they are used to direct the assessment. Additional sampling depths and locations are chosen to test specific aspects of the conceptual site model, and the assessment proceeds until the model no longer changes significantly. An ESA may be completed in a single intensive phase of investigation, which typically lasts several days. In contrast, a conventional site assessment might require multiple phases of field work, each separated by weeks or months of laboratory analysis and data review, which could delay corrective action decisions by months or even years.

The ESA approach has been made possible by the development of improved, cost-effective methods for rapid collection and field analysis of soil, soil-gas, and groundwater samples. Direct push methods have replaced 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 samples at economical prices. API (1999) provides an overview of the ESA approach and a detailed guide to current direct-push assessment and monitoring tools, with emphasis on their proper use at MTBE-affected sites. An example direct-push multilevel well installed using a large-diameter direct-push drive casing is shown in Figure 3. The figure also shows an example of the data that can be obtained from such a tool (Einarson et al., 1999).

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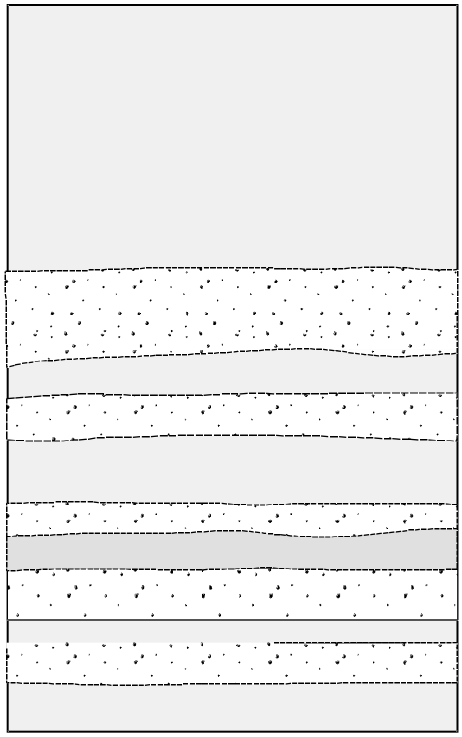

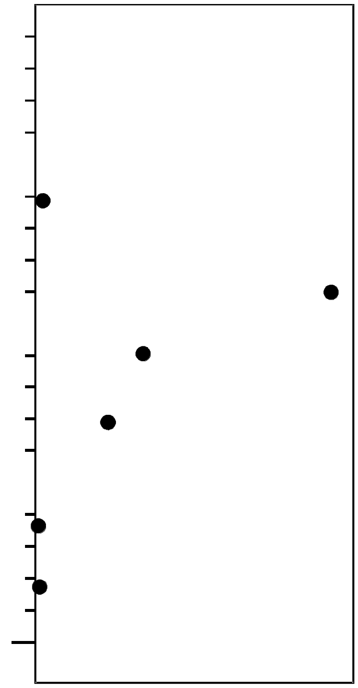

Biographical Sketches

Eric M. Nichols, PE, is Senior Associate Engineer with LFR/Levine·Fricke. Mr. Nichols provides senior review for modeling and exposure assessment on a variety of federal and private-sector environmental restoration and water resources projects. He teaches courses in modeling, risk assessment, groundwater hydrology, and site assessment. Mr. Nichols has a B.S. from U.C. Berkeley and an M.S. from MIT. Eric is also LFR's Manager of Quantitative Services. He is a certified American Society of Testing and Materials (ASTM) trainer in the standards for Risk-Based Corrective Action (RBCA) and Remediation by Natural Attenuation (RNA).

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