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Strategies for Characterizing Subsurface Releases of Gasoline Containing MTBE

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A summary of research results from API's Soil & Groundwater Technical Task Force

The American Petroleum Institute (API) has developed guidelines for evaluating subsurface releases of gasoline containing methyl tertiary-butyl ether (MTBE) or other oxygenated fuel additives. These guidelines are presented in API Publication 4699, "Strategies for Characterizing Subsurface Releases of MTBE" (Nichols *et al.*, 2000), and are briefly outlined in this research bulletin.

API Publication 4699 applies the principles of risk-informed decision making to the evaluation of MTBE-affected sites; in other words, it adds exposure and risk considerations to the traditional components of the corrective action process. The risk factors at a given site are evaluated through a "Conceptual Site Model", which is an inventory of all known or potential oxygenate sources, pathways, and receptors. Based on these risk factors, three levels of assessment are defined: standard, limited, and detailed. The appropriate level of assessment is initially determined based on receptor data, which can typically be obtained from a survey of nearby wells and land uses. A subsurface investigation may then be conducted to obtain information on sources and pathways. The level of assessment can be "upgraded" or "downgraded" as warranted by the resulting source and pathway information.

API Publication 4699 includes a review of the chemical properties and subsurface behavior of MTBE and other oxygenated fuel additives. It also provides an overview of characterization and monitoring issues at oxygenate release sites, as well as a detailed review of the tools and techniques used for subsurface assessment. The expedited site assessment process and the use of modern direct-push tools are particularly emphasized, since these approaches are especially well-suited for use at MTBE-affected sites.

The 1990 Federal Clean Air Act Amendments 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), to reduce motor vehicle emissions and improve air quality. 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 soil and 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 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. MTBE in particular has a relatively strong affinity for water (Figure 1), and biodegrades more slowly than BTEX.

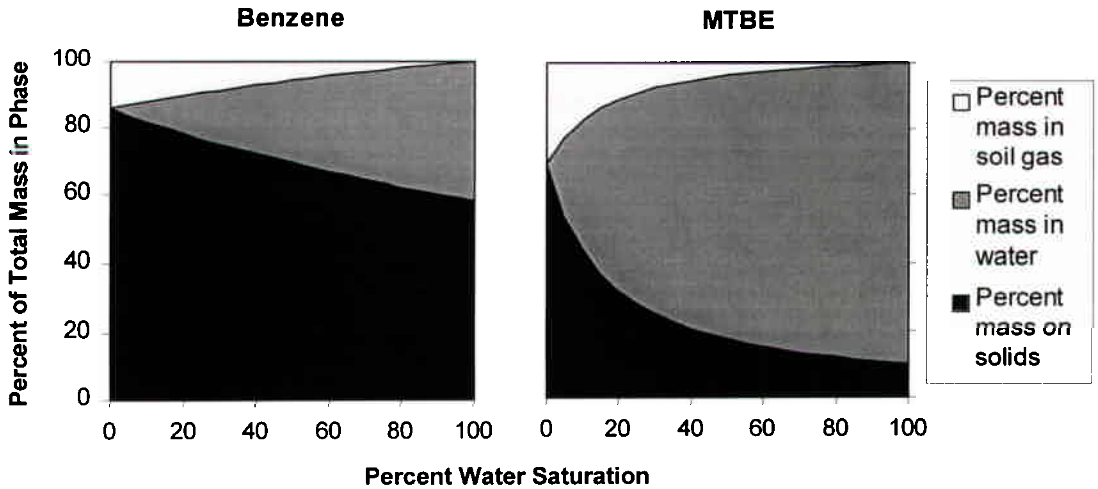

Figure 1: Equilibrium Partitioning of Benzene and MTBE in an Example Soil

In light of these differences, a reevaluation of traditional assessment procedures is warranted. The American Petroleum Institute (API) has therefore developed guidelines for evaluating subsurface releases of gasoline containing MTBE or other oxygenated fuel additives. These guidelines are described in API Publication 4699, "Strategies for Characterizing Subsurface Releases of MTBE", and are summarized in this research bulletin.

RISK-INFORMED DECISION MAKING AND MTBE

API Publication 4699 applies the principles of risk-informed decision making to the evaluation of MTBE-affected sites, by adding exposure and risk considerations to the traditional components of the corrective action process. These issues are evaluated using a **Conceptual Site Model** (CSM), which is an inventory of known and potential sources, pathways, and receptors associated with a particular release (Figure 2).

The guidelines include a detailed review of risk factors associated with sources, pathways, and receptors at sites affected by releases of oxygenated fuel. Based on these risk factors, three levels of assessment are defined: the **standard**, **limited**, and **detailed** levels. Example conditions associated with these levels of assessment are summarized qualitatively in Table 1. Note that these conditions are presented as examples only; they are notintended to encompass all possible site considerations. Other relevant criteria or risk factors could be evaluated as well.

The level of effort is lowest with the limited level of assessment, and increases with the standard and detailed levels. The limited level of assessment involves relatively large sample spacing, with an emphasis on horizontal (rather than vertical) characterization. Higher levels of assessment involve closer sample spacing, increasing emphasis on vertical characterization, and more frequent use of depth-discrete soil sampling techniques and multi-level groundwater sampling methods.

API Publication 4699 suggests the following sequence of site characterization tasks:

1. **Gather data about receptors.** In most cases, detailed information about potential receptors can be readily collected through a survey of nearby wells and land uses (Table 2).

2. **Use the receptor data to determine the initial level of assessment.** Site-specific receptor data can typically be obtained more easily than site-specific data about pathways or sources. Receptor information should therefore be used initially to determine which level of assessment – standard, limited, or detailed – is warranted.

Table 1. 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

3. **Conduct a subsurface investigation to obtain source and pathway data.** The initial level of effort should follow the determination made in Step 2. The CSM should be verified and updated using all available data as characterization proceeds. Specific source and pathway characterization tasks are listed in Tables 3 and 4.

4. **If warranted by the source and pathway data, revise the initial level of assessment.** If the source and pathway data show that the potential for risk is higher or lower than previously assumed, then the level of assessment should be revised upward or downward accordingly.

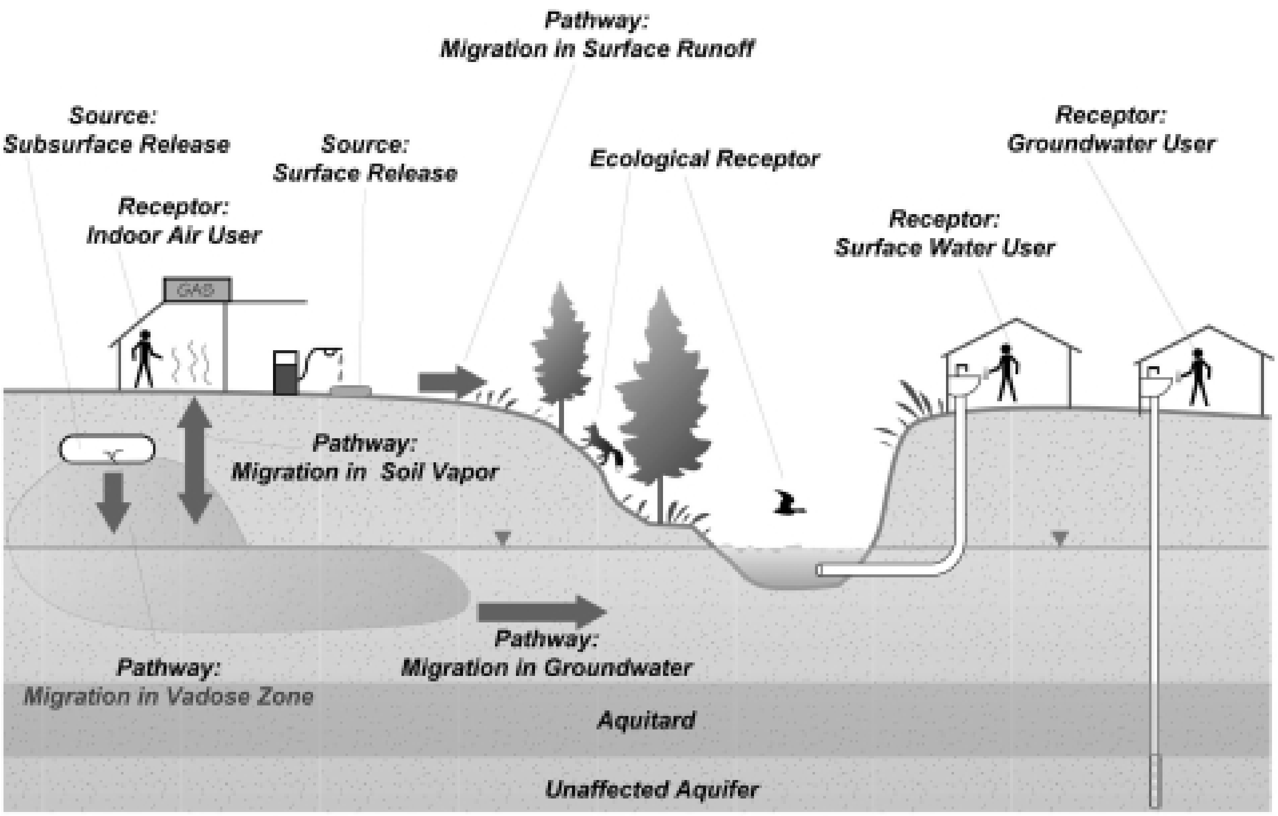

Figure 2: Example of Conceptual Site Model

5. **Continue assessment and monitoring** until sufficient information has been collected to verify the validity of the CSM and to Make an acceptable interim or final remedy decision. Specific monitoring tasks are listed in Table 4.

PRACTICAL ASSESSMENT OF MTBE RELEASES

API Publication 4699 reviews the chemical properties and subsurface behavior of MTBE and other oxygenated fuel additives. It also discusses the practical issues

Table 2. Receptor Identification Tasks

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.

Table 3. Pathway Characterization Tasks

Investigation Tasks		Level of Assessment		
		Detailed	**Standard**	**Limited**
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
	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

Table 3. Pathway Characterization Tasks (continued)

Investigation Tasks		Level of Assessment		
		Detailed	**Standard**	**Limited**
Pathway Characterization	**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

specifically associated with MTBE-affected sites, such as the following:

- **Receptor characterization**, including surveys of local wells, surface-water bodies, ecological receptors, and present and future land uses.
- **Pathway characterization**, including assessment of geology, flow systems (e.g., Figure 3), plume boundaries, plume stability, and artificial conduits.
- **Source characterization**, including evaluation of source zones, source depletion, oxygenate vapors, and oxygenated fuel NAPL.
- **MTBE vs. BTEX characterization,** including source differences, plume geometry differences, relative biodegradability, and sample media biases.

API Publication 4699 includes a review of the tools and techniques used for subsurface assessment at MTBE-affected sites. It particularly emphasizes expedited site assessment techniques and modern direct-push sampling tools, as these are especially well-suited for use at MTBE affected sites. A variety of innovative technologies, including surface geophysical surveys, active and passive soil gas sampling tools, direct-push soil

Table 4. Source Characterization Tasks and Verification Monitoring Tasks

Investigation Tasks		Level of Assessment		
		Detailed	**Standard**	**Limited**
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
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

sampling tools, well points, sealed-screen samplers, vertical profilers, single-interval and multi-level monitoring wells, cone penetrometers, and other specialized instruments are discussed and ranked based on their suitability for different assessment tasks.

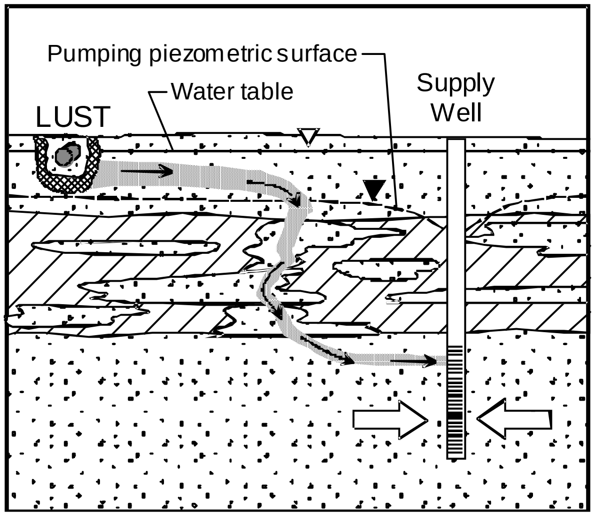

Figure 3: MTBE Plume Migrating Through a Leaky Aquitard

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