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COLORADO DEPARTMENT OF LABOR AND EMPLOYMENT

DIVISION OF OIL AND PUBLIC SAFETY

METHYL TERTIARY BUTYL ETHER GUIDANCE DOCUMENT

May 2005

1.0 Introduction

The Division of Oil and Public Safety (OPS) has developed new regulations, effective May 30, 2005, that incorporate methyl-tertiary butyl ether (MTBE) as a chemical of concern (COC). The regulations are applicable for all leaking petroleum storage tank sites that have not received a "No Further Action" as well as for all future release discoveries. The intent of this guidance document is to supplement, not replace, the OPS *Petroleum Storage Tank Owner/Operator Guidance Document*. At most sites, benzene, toluene, ethylbenzene, xylenes (BTEX) and/or total petroleum hydrocarbons (TPH) will be present, and guidelines contained in the OPS *Petroleum Storage Tank Owner/Operator Guidance Document* will also be applicable.

This guidance document provides background information concerning MTBE use, phase-out, and prevalence in Colorado. The guidance also describes the basic physical and chemical properties of MTBE that affect its transport in the environment to provide an understanding of how site assessment and remediation activities at sites containing MTBE may differ from those being implemented to only address BTEX.

The key elements of this guidance are: (1) the risk-based screening level (20 micrograms per liter (µg/L)), which is based on taste and odor criteria, (2) the evaluation of the potential exposure pathway via groundwater ingestion, and (3) determining the potential points of exposure (POEs), which include water supply wells used for human consumption and surface water features used for human consumption. MTBE will differ from the other COCs in that the property boundary will not be considered a POE.

The primary purpose of this document is to assist owners and/or operators of regulated leaking petroleum storage tank facilities in conducting MTBE investigations. The required time frame for performing site assessments to characterize the plume and define the full extent of MTBE contamination will be determined according to the risk of human exposure posed by the site. For example, the time frame to complete and report assessment activities defining the extent of contamination will be shorter at sites where a POE is located less than 2,500 feet from the source and modeling indicates that the POE will become impacted than at sites where modeling indicates (with OPS concurrence) that the POE will not become impacted.

The level of effort required in performing assessment activities will also be determined according to risk. As already incorporated into the OPS risk-based decision making (RBDM) process, the scope of an investigation is based upon factors such as magnitude of the contamination, distance to receptors, plume status, and flow velocity. Similarly, owners and/or operators are encouraged to use modeling to estimate the placement and number of monitoring wells necessary to characterize the plume and determine the full extent of contamination.

The only POEs considered for this pathway are potential or current water supply wells used for human consumption and potential or current surface water features used for human consumption, therefore it is anticipated that corrective actions will not be required at most sites. In situations where corrective actions are required, careful consideration should be given to the physical and chemical properties of MTBE when designing remediation strategies.

2.0 Historical MTBE Use and Phase Out

In the late 1970s and 1980s, oxygenates such as MTBE and ethanol were added to fuels to improve efficiency while meeting lead phase-out requirements. The use of MTBE became prevalent because of its low cost, ease of production, and favorable transfer and blending characteristics. Other less commonly used oxygenates include methanol, ethyl tertiary-butyl ether (ETBE), tertiary-amyl methyl ether (TAME), diisopropyl ether (DIPE), and tertiary-butyl alcohol (TBA).

In 1987, the Colorado Air Quality Control Commission adopted the first regulations in the country requiring that oxygenated fuels be sold along much of the Colorado Front Range. The purpose of the oxygenated fuels program was to make gasoline burn more cleanly in order to reduce air emissions and smog.

Based in part on the successful oxygenated fuels program that had been ongoing along the Colorado Front Range, the Clean Air Act Amendments of 1990 required that oxygenated fuels be used at service stations and gasoline retail businesses in regions of the United States where ozone or carbon monoxide air quality standards were exceeded. Beginning in 1992, the winter oxygenated fuel program required 2.7% oxygen by weight in gasoline (equivalent to 15% MTBE or 7.3% ethanol by volume) in 40 U.S. metropolitan areas, including those located along the Colorado Front Range. In 1995, the U.S. implemented Reformulated Gasoline Phase I, requiring 2.0% oxygen by weight in gasoline year-round in 28 U.S. metropolitan areas. Reformulated Gasoline Phase II, beginning January 1, 2000, continued to require 2.0% oxygen by weight.

As a result of concerns regarding MTBE (Section 3.0), efforts have been made in several States to discontinue the use of MTBE in gasoline. As of June 2004, legislation that would partially or completely ban or restrict the use of MTBE in gasoline has been passed in 19 states. Colorado Senate Bill 190 was signed into law on May 23, 2000 ordering the phase-out of MTBE as a fuel component or additive by April 30, 2002. This legislation declared “it is the intent of the general assembly…to halt further contamination and pollution of this state’s groundwater supplies by MTBE”.

3.0 MTBE in the Environment

The large scale use of gasoline containing MTBE has led to the inadvertent introduction of MTBE to surface water and groundwater. Because of the high concentrations of MTBE in gasoline, and because of its high solubility, mobility and persistence in water, MTBE has been found in numerous water supplies nationwide. MTBE has been found to be prevalent in petroleum contaminated groundwater statewide in Colorado. An evaluation of groundwater data collected through the OPS Remedial System Inspection Program (RSIP) in 2003 identified that of the 214 monitoring wells sampled, 135 had detectable concentrations of MTBE (63%).

In December 1997, EPA issued a Drinking Water Advisory stating that concentrations of MTBE in the range of 20 to 40 µg/L or below will probably not cause unpleasant taste or odor for most people, recognizing that human sensitivity to taste and odor varies widely. The advisory is a guidance that recommends keeping concentrations below that range. EPA is continuing to study both the potential health effects and the occurrence of MTBE, and it is on the list of contaminants for which EPA is considering setting health standards. As part of an information gathering process, EPA requires that all large drinking water systems and a representative sample of small systems monitor and report the presence of MTBE.

More than 40 States across the country have developed Drinking Water Standards, Guidelines and Action Levels for MTBE. In general the Standards, Guidelines, and Action Levels have been based on aesthetic criteria because estimates of human-health based criteria (using EPA guidelines) have exceeded the aesthetic criteria, to date. However, EPA is continuing to study the toxicity of the chemical and several States have implemented health-based standards.

4.0 Physical and Chemical Properties of MTBE

It is important to be familiar with the chemical and physical properties of MTBE in order to understand how it will behave in the subsurface environment. Knowledge of these properties may also assist in determining which remedial technologies will be suitable at sites with MTBE contamination. Appendix A lists the physical properties of MTBE as well as other commonly used oxygenates. This document will not specifically address MTBE biodegradation. A listing of biodegradation resources and website addresses is provided on the OPS website at http://oil.cdle.state.co.us.

4.1 Solubility

The ability of a chemical to dissolve in water is measured by its solubility. If fuel is released to the subsurface, compounds with high solubility are more likely to dissolve into groundwater and become more mobile. The solubility of MTBE in water is approximately 50,000 mg/L, which is about 30 times more soluble than benzene in water. Since a gasoline mixture typically was comprised of approximately 15% MTBE and only 1% benzene, the effective solubility of MTBE would commonly have been much higher than that of benzene (roughly 7,500 mg/L for MTBE and 17.5 mg/L for benzene).

4.2 Adsorption

Adsorption is the tendency of dissolved compounds in groundwater to partition onto soil particles. For organic chemicals, it is usually assumed that naturally occurring organic matter in soil is the major predictor of adsorption. The tendency of an organic chemical to adsorb to soil is therefore related to the chemical-specific carbon partition coefficient (K_{oc}). The degree of adsorption is used to predict retardation rates for chemicals dissolved in groundwater.

The chemical-specific organic carbon partition coefficient, 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, the value is usually expressed as log K_{oc}. For organic chemicals 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. The log K_{oc} value for MTBE (1.1) is very low, indicating that its movement in groundwater is not significantly retarded.

4.3 Retardation

The retardation ratio (or retardation coefficient) is simply the movement of water divided by the rate of movement of the contaminant. The retardation rate of MTBE is generally close to 1, which means it will move at a rate similar to groundwater. However, the rate will vary depending on concentrations of organic carbon in the aquifer solids. In general, dissolved-phase MTBE has a low tendency to adsorb to soil or to volatize into soil vapor making it relatively mobile and persistent in the dissolved phase.

4.4 Vapor Pressure

The ability of a chemical to migrate from free product into the vapor phase is measured by the vapor pressure, commonly expressed in millimeters of mercury (mm Hg). The vapor pressure of MTBE at 25ºC is 251 mm Hg which is approximately three times greater than the vapor pressure of benzene. Thus, MTBE has a relatively strong tendency to volatilize from free product.

4.5 Henry's Law Constant

Henry's Law coefficient is used to describe the partitioning of an organic chemical between the dissolved phase and vapor phase. Henry's Law coefficient is simply defined as the ratio of the concentration of the chemical in the vapor phase to the concentration of the chemical dissolved in water. If fuel components are dissolved in groundwater, compounds with higher Henry's Law coefficients are more likely to volatilize into soil vapor, while compounds with lower Henry's Law coefficients are more likely to remain dissolved in groundwater.

The dimensionless Henry's Law coefficient for benzene is approximately 0.22 [(mg benzene/L vapor)/(mg benzene/L water)]. The Henry's Law coefficient for MTBE has been estimated to range from 0.022 to 0.12. Thus, MTBE has a relatively low tendency to volatilize from groundwater.

5.0 Applicability of MTBE Regulations

MTBE will be considered a COC for all leaking petroleum storage tank sites that have not received a "No Further Action" on May 30, 2005, as well as for all future releases. Additionally, if water supply wells used for human consumption and/or surface water features used for human consumption have been impacted by MTBE as a result of contamination from a site that had previously received a "No Further Action", the site will be reactivated.

6.0 Risk-Based Screening Level (RBSL) & Exposure Pathway

The RBSL for MTBE will be 20 μg/L for the groundwater ingestion pathway. This level is based on the lower value of the range established by the US EPA for aesthetic taste and odor threshold.

Groundwater ingestion will be considered the only exposure pathway of concern for MTBE because of the taste and odor criteria as well as its chemical-physical properties. Concentrations of MTBE in soil will tend to be low because it does not readily sorb to soil particles. It is also expected that concentrations of MTBE in soil vapors will also be low because MTBE has a low Henry's Law coefficient indicating that it will not readily partition from the dissolved phase to the vapor phase. Although MTBE will readily volatilize from free product, it is anticipated that the free product portion of a plume will be addressed through the criteria already established for the other COCs. The direct exposure routes and volatilization route from surface soil are not considered due to the aesthetic criteria for MTBE.

7.0 Other Oxygenates and Breakdown Products

Tertiary butyl alcohol (TBA) is often present as a by-product of MTBE production and is also a primary by-product of MTBE degradation. In addition, several ethers, such as ETBE, TAME, and DIPE have been used as oxygenates in gasoline. Although these oxygenates are not considered COCs at this time, owners and/or operators are encouraged to analyze for these chemicals, particularly in situations where remediation strategies are being evaluated.

8.0 Points of Exposure

The point of exposure (POE) is the location at which a person or sensitive environment may be exposed to a COC. For MTBE, the applicable POEs will be water supply wells used for human consumption and surface water features used for human consumption. These water supplies may be currently existing or planned to be developed within five years.

Surface water feature POEs will include water bodies such as ponds, lakes, reservoirs, streams, creeks, and their tributaries that have water withdrawn that is used for human consumption. If the water body is located downgradient and <2,500 feet from a source and the extent of contamination can't be defined upgradient, groundwater sampling is required along the centerline of the plume adjacent to the water body. If the MTBE RBSL is exceeded at this location, the water body will be required to be sampled. The surface water feature may be screened out from further investigation and potential remediation only if it can be demonstrated through four quarters of monitoring that concentrations are below and do not have the potential to exceed the RBSL upgradient of the takeout location of the water used for public consumption.

Because the MTBE RBSL is based upon aesthetic criteria and the threats from vapors are anticipated to be minimal, the additional POEs specified in OPS regulations for other COCs will not be utilized. These POEs include subsurface utilities, structures, sensitive environments, and groundwater wells and surface waters that are not used for human consumption. The property boundary will also not be considered a POE for MTBE due to the potentially extensive size of

MTBE plumes and the resistance of MTBE to volatilize and biodegrade. The cost to cleanup MTBE concentrations in groundwater to meet aesthetic criteria at the property boundary at sites where human exposure is not occurring is not economically feasible. If future studies identify MTBE as a human carcinogen, this policy will be reevaluated.

9.0 Point of Compliance

Point of compliance (POC) wells must be placed downgradient of the source area, beyond the limits of the defined extent of contamination, and between the defined extent of contamination and any POEs. The POC should be located no closer to the POE than a one-year travel time, if possible. The concept of the POC for MTBE investigations is the same as is used for other COCs. The POC wells must be spaced such that contaminant migration will be detected across the leading edge of the plume to insure that all POEs are protected. If the POC has concentrations that exceed RBSLs, remediation must bring the POC into compliance. At sites that have both BTEX and MTBE RBSL exceedences, it is likely that there will be two different locations where compliance is required to be achieved; a location upgradient of the property boundary for BTEX, and a location upgradient of a water supply well used for human consumption and/or a surface water feature used for human consumption for MTBE.

POEs will not be considered as POCs when pathway elimination is requested. For example, if a water supply well that was formerly impacted comes into compliance, a monitoring well that will serve as a POC must be installed between the source and the water supply well. Similarly, modeling (without the actual installation of a POC well) may not be used to determine the location where compliance is achieved.

Careful consideration should be given during the MTBE investigation to determine lateral and vertical placements of POC wells. In many instances, POEs will be pumping water supply wells that will cause plumes to dive. Due to potential hydraulic influences of the pumping water supply wells, the POCs may be required to be placed upgradient and/or cross-gradient and screened appropriately to intercept MTBE contamination if present.

10.0 Laboratory Analytical

Conventional analytical procedures designed for BTEX can also be used to quantify MTBE and other ether concentrations when the procedures are specifically calibrated for those chemicals. The SW-846 Methods 8260 (by Gas Chromatography/Mass Spectrometry (GC/MS)) and 8021 (by PID detector (GC/PID)) are the most commonly used analytical methods for MTBE.

Method 8021 GC/PID will be allowed for analysis of MTBE when samples collected from key locations are verified using Method 8260 GC/MS. Key locations for verification sampling include:

- The source monitoring well (at sites where no MTBE is detected).
- The POC well(s) (in situations where POC well(s) have not yet been installed, the verification sampling will be performed on samples from the most downgradient monitoring well).

- The monitoring well with the highest concentration of MTBE.
- All impacted or potentially impacted POEs.

Verification sampling utilizing Method 8260 GC/MS is required because Method 8021 GC/PID is susceptible to both false positives (misidentifying the presence of an oxygenate) and false negatives (failing to identify the presence of an oxygenate). Methods using MS for compound identification, following initial assessment by GC, provide a higher level of assurance that MTBE has been identified correctly and quantified adequately.

If the calibration curve for Method 8021 GC/PID is not current, the method can return false negatives for MTBE. Method 8021 GC/PID uses a specialized light bulb (lamp) to ionize analytes of concern. The lamps typically used in a PID operate at a maximum potential of 10 electron volts (eV). The potential required to ionize MTBE is 10eV, which is often the maximum potential of these lamps. Although the PID may respond to MTBE when the lamp is new, the response becomes weaker as the lamp ages with use. False positive results may be obtained because Method 8021 GC/PID may be subject to coelution interferences when samples contain significant concentrations of petroleum hydrocarbons.

Method 8260 GCMS has a higher degree of accuracy in detecting MTBE and may be used in lieu of Method 8021 GC/PID for all samples collected. The cost for Method 8260 GC/MS analysis is comparable to Method 8021 GC/PID analysis if the reports are limited to BTEX and MTBE. Reimbursement from the Petroleum Storage Tank Fund (PSTF) will be made in accordance with the Reasonable Cost Guidelines and will not vary by method.

If TBA or the other oxygenates are being analyzed, Method 8260 GC/MS should be used. The lamps typically used in a PID for Method 8021 GC/PID operate at a maximum potential below the ionization potentials of ethanol (10.2 eV) and TBA (10.25 eV) thereby potentially missing these chemicals when a PID method is used.

When using either Method 8021 GC/PID or Method 8260 GC/MS, proper sample preparation procedures are required. The two most common sample preparation procedures are 5030 (purge-and-trap) and 5021 (headspace). If both ethers and BTEX are target analytes of interest, then using Method 5030 at ambient temperature (rather than heated) is adequate to determine concentrations of oxygenates that are greater then 5 ug/L. If TBA is being analyzed at the same time as MTBE, precautions should be taken during extraction of the TBA. Due to TBA's high solubility in water, samples are often heated to 80° C for the extraction. Heating an MTBE sample preserved with acid can cause hydrolysis to occur. During hydrolysis, MTBE can be converted to TBA, which will give false results for both analytes. Contact should be made with the laboratory to discuss sampling preparation methodologies and the use of preservatives in these situations.

11.0 Initial MTBE Analysis, Reporting & Pathway Evaluation

11.1 MTBE Analysis

MTBE analysis is required for all groundwater samples collected on or after May 30, 2005. At existing sites, **sampling and analysis for MTBE will be performed within 3 months** of May 30, 2005. Since the OPS has requested that MTBE be analyzed since 1999 (*Petroleum Storage Tank Owner/Operator Guidance Document*), it is expected that this quarterly analysis will already be occurring at most petroleum release sites.

11.2 Receptor Survey

A receptor survey will be performed to identify all current and planned (within five years) surface water features located potentially downgradient and within 2,500 feet (ft) of the source and all current and planned (within five years) water supply wells located potentially downgradient and with a radius of influence within 2,500 ft of the source. For existing sites, this data should have already been collected and reported in the Site Characterization Report for receptors within 1,320 ft of the release. The additional distance required in the receptor survey (2,500 vs. 1,320 ft) is due to the high mobility and persistence of MTBE in comparison to the BTEX chemicals. Although the intent is to protect only those locations that pose a threat through human consumption, all water supply wells and surface water features that are located potentially downgradient of the source should initially be identified. Resources used to identify the POEs should be readily available and include records from local planning and zoning offices, the Department of Natural Resources, and local water districts.

The receptor survey will include a detailed map with each potential POE clearly identified (including the radius of influence of the well) and a table that lists details concerning the POE. In the case of the POE being a current pumping well, the pertinent information will be the pumping rate, depth of the well, screened interval and the calculated radius of influence. A well completion diagram will be included in the report.

11.3 Initial Reporting

For existing sites, the owner and/or operator will incorporate the MTBE concentrations and the results of the receptor survey into the next Quarterly Monitoring report. This report will be submitted to the OPS within **6 months** of MTBE regulation implementation (May 30, 2005). The Quarterly Monitoring report will also include an evaluation of whether the groundwater ingestion pathway is complete and a determination of the appropriate site priority classification, as discussed in Section 12.

For new release sites, the owner and/or operator will incorporate the MTBE concentrations and the results of the receptor survey into the Site Characterization Report (SCR), which must be submitted within 90 days of the date of the release.

The groundwater ingestion pathway will be considered incomplete and no further analysis for MTBE will be required if the results obtained during the initial monitoring event indicate either of the scenarios identified below:

- MTBE is not detected during quarterly groundwater sampling. This scenario is appropriate only if it is confirmed by OPS that the monitoring wells were located such that MTBE would be detected, if present.

- Four quarters of MTBE laboratory data indicates that MTBE concentrations are stable or declining, the extent of the contamination has been defined and it can be demonstrated that there are no threats to POEs. This scenario is appropriate only if MTBE laboratory analysis has been ongoing and at least four consecutive quarters of groundwater data is available at the site.

12.0 Prioritizing MTBE Investigations

This section outlines a priority classification for performing site characterization activities including defining the extent of MTBE contamination. OPS will classify sites according to the potential threats to water supplies. This will allow owner and/or operators to prioritize assessments at their sites and will allow OPS to give greatest oversight to those sites that pose the greatest risk. Sites where there are known MTBE impacts to water supplies and those that are situated close to current water supplies are given the highest priorities.

The initial site priority classification determination will consider only the distance to a POE. As site characterizations are being performed and more information is obtained the site's initial priority classification may change, with concurrence by the OPS. For example, if it can be determined (with concurrence by OPS) that there are no threats to POEs during the preliminary data collection phase of a Priority Classification II site, the site may be reclassified as a III. Section 13 outlines the level of effort requirements based on site priority classifications.

Priority for assessment activities will be in order from Priority Classification I to Priority Classification III, with Priority Classification I sites having the most severe threats and Priority Classification III having the least. The appropriate pace and degree of the characterization required for the different classes are addressed in the following text as well as in Section 13 of this document. For existing sites, the time frames identified below commence with the date of rule promulgation. For new sites, the time frames identified below commence with the date of release discovery. If documented issues arise that prohibit the achievement of these time frames, the OPS will grant extensions on a site-by-site basis.

12.1 Priority Classification I

- **Impacted POE**

1. Requires **timely** mitigation of the water supply.
2. Requires **timely** sampling and analysis of POEs.
3. May require timely initiation of the remediation of the core portion of the groundwater plume. Timeframe and action must receive prior approval of OPS.
4. May require soil sampling, if it appears that soil is acting as a secondary source. If it appears that initial abatement is necessary, timeframe and action must receive prior

approval of OPS.

5. Requires quarterly groundwater monitoring.
6. Requires definition of the lateral extent of the plume to 20 µg/l within **9 months**. See Section 13 for plume definition requirements.
7. Requires definition of the vertical extent of the plume within **9 months**. See Section 13 for plume definition requirements.
8. Requires submittal of MTBE Assessment Report (as outlined in Section 13) within **12 months**.

12.2 Priority Classification II

- **Existing or planned POE located <2,500 feet from source, and**
- **Potential of impacts is unknown, or**
- **Contamination has the potential to impact a POE.**

1. Requires sampling and analysis of POEs within **9 months**.
2. Requires computer modeling to predict timeframe and magnitude of potential impacts to receptor within **9 months** (model will be updated as additional data is collected).
3. May require timely initiation of the remediation of the core portion of the groundwater plume if modeling results indicate imminent threat to receptor. Timeframe and action must receive prior approval of OPS.
4. May require soil sampling if modeling results indicate imminent threat and it appears that soil is acting as a secondary source. If it appears that initial abatement is necessary, timeframe and action must receive prior approval of OPS.
5. Requires quarterly groundwater monitoring.
6. Requires definition of the lateral extent of the plume to 20 µg/l within **12 months**. See Section 13 for plume definition requirements.
7. Requires definition of the vertical extent of the plume within **12 months**, if warranted (i.e. pumping well, infiltration). See Section 13 for plume definition requirements.
8. Requires submittal of MTBE Assessment Report (as outlined in Section 13) within **15 months**.

12.3 Priority Classification III

- **Existing or planned POE located <2,500 feet from source, and it has been demonstrated (with OPS concurrence) that contamination does not have the potential to impact a POE, or**
- **Existing or planned POE located >2,500 feet from source, and modeling indicates that the plume would migrate beyond 2,500 feet.**

1. Requires computer modeling to predict plume migration to a distance of 2,500 feet from the source within **9 months** (model will be updated as additional data is collected).
2. Requires quarterly groundwater monitoring.
3. Requires definition of the lateral extent of the plume to 20 µg/l within **15 months**. See Section 13 for plume definition requirements.
4. Requires submittal of MTBE Assessment Report (as outlined in Section 13) within **18 months**.

12.4 Time Frame Summary

This Section summarizes, by Priority Classification, the time frames to perform the activities described in Sections 11.1, 11.2, 11.3, 12.1, 12.2, and 12.3 and submit the reports to OPS.

Activity	Priority Class I	Priority Class II	Priority Class III
Sampling & Analysis of Existing Wells for MTBE	3 Months	3 Months	3 Months
Submit Monitoring Report with MTBE Analysis & Receptor Survey	6 Months	6 Months	6 Months
Mitigation of Water Supply	Timely	NA	NA
Sampling & Analysis of POEs	Timely	9 Months	NA
Computer Modeling	NA	9 Months	9 Months
Remediation of Core Portion of Plume	As Necessary/ Upon OPS Approval	As Necessary/ Upon OPS Approval	NA
Soil Sampling	As Necessary	As Necessary	NA
Groundwater Monitoring	Quarterly	Quarterly	Quarterly
Lateral Extent Definition	9 Months	12 Months	15 Months
Vertical Extent Definition	9 Months	12 Months/As Necessary	NA
MTBE Assessment Report Submittal	12 Months	15 Months	18 Months

13.0 MTBE Site Assessment

The purpose of this section is to guide owner and/or operators in the level of assessment required to evaluate MTBE contamination in groundwater. The information required to characterize a site where a petroleum release has occurred is provided in the *Petroleum Storage Tank Owner/Operator Guidance Document*. In most situations where MTBE contamination is identified, BTEX contamination will also be present, and this MTBE guidance should be used in conjunction with the *Petroleum Storage Tank Owner/Operator Guidance Document* to complete all required assessment tasks.

As discussed in Section 12, the site is classified into one of three priority levels. The priority classifications are determined based on the degree of actual or potential threat that the site poses to a POE. The three Priority Classifications, I, II, and III, require different levels of site assessment. A Priority Classification I site requires a Detailed Level Assessment. A Detailed Level Assessment is a comprehensive assessment and it requires the highest level of effort. A Priority Classification II site requires a Standard Level Assessment. A Priority Classification III site requires a Limited Level Assessment, which is a screening-level assessment requiring a relatively low level of effort. These three site assessment levels are defined in the following paragraphs.

13.1 Detailed Level Assessment

A Detailed Level Assessment will involve performing the following tasks:

1. Obtain water level measurements and construct potentiometric maps to determine the horizontal groundwater gradient. (This may have been completed previously.)
2. Conduct hydraulic testing to calculate velocity of vertical and horizontal flow.
3. Identify the geological controls on groundwater movement (may have been completed previously).
4. Generate geologic cross-sections using monitoring well and water supply logs.
5. Define horizontal extent of the MTBE plume. The use of modeling to estimate the placement and number of monitoring wells necessary to characterize the plume is encouraged.
6. Define vertical extent of MTBE using extensive depth discrete soil (if appropriate), and groundwater sampling methods.
7. Plot concentration versus time for individual wells to assess source depletion and hydraulic influences.
8. Plot concentrations versus distance for centerline wells over multiple time periods to assess plume stability.

13.2 Standard Level Assessment

A Standard Level Assessment will involve performing the following tasks:

1. Obtain water level measurements and construct potentiometric maps to determine the horizontal groundwater gradient. (This may have been completed previously.)
2. Conduct hydraulic testing to calculate velocity of horizontal flow, and in site-specific cases vertical flow (may have been completed previously).
3. Update computer simulations of groundwater flow and transport using current site-specific data to estimate the potential for migration to receptors. Include the effects of groundwater pumping (if appropriate).
4. Identify the geological controls on groundwater movement (may have been completed previously).
5. Generate geologic cross-sections using monitoring well and water supply well logs.
6. Define horizontal extent of the MTBE plume. The use of modeling to estimate the placement and number of monitoring wells necessary to characterize the plume is encouraged.
7. Define vertical extent of MTBE using depth discrete groundwater sampling methods. (This requirement will be evaluated on a site-by-site basis.)
8. Plot concentration versus time for individual wells to assess source depletion and hydraulic influences.
9. Plot concentrations versus distance for centerline wells over multiple time periods to assess plume stability.

13.3 Limited Level Assessment

A Limited Level Assessment will involve performing the following tasks:

1. Obtain water level measurements and construct potentiometric maps to determine the horizontal groundwater gradient. (This may have been completed previously.)
2. Estimate velocity of horizontal flow. (This may have been completed previously.)
3. Identify the geological controls on groundwater movement. (This may have been completed previously.)
4. Define horizontal extent of the MTBE plume. The use of modeling to estimate the placement and number of monitoring wells necessary to characterize the plume is encouraged.

13.4 Modeling

The OPS encourages the use of modeling as a key tool to predict potential impacts to POEs, to determine the location and spacing of monitoring wells, and to estimate time to achieve cleanup goals for the current COCs. Due to the tendency of MTBE to move faster and further than BTEX in groundwater, it is especially important that modeling be performed. Modeling is not a substitute for site data. All required site data must be collected for the appropriate level of assessment. Some of the more common models are listed below:

Mass Flux Estimates
The contaminant mass flux is the mass moving across a control area over time. The units of mass flux are mass per time. This is also called the mass flow rate or the mass discharge rate. To calculate mass flux, groundwater flow and contaminant concentration data are combined to estimate the rate of contaminant mass transfer (e.g., grams per day) past selected transects through an affected groundwater plume. Mass flux results from one or more transects can be used to evaluate:

- The potential water quality impacts on downgradient water supply sources.
- The natural attenuation of the contaminant mass with distance downgradient of the source.
- The relative benefits of various remedial actions based on their anticipated reductions in mass flux from the source to the receptor.

Contaminant Fate and Transport Modeling
Computer fate and transport modeling can be performed to determine the placement of downgradient POC wells, appropriate well spacing, and time until site closure. Several commercial fate and transport models are available, such as RISC and Bioscreen. These models are not difficult to use and can be run with minimal site-specific data. However, as more data is available throughout the assessment it is advisable to rerun the model to obtain better estimates of contaminant transport.

If it is necessary to define a plume vertically, due to the location of the plume being within the zone of influence of a water supply well, a groundwater flow model such as Quick Flow should be used. Quick Flow can estimate the depth of the plume and minimize the number of deep wells that will need to be installed.

Models that consider recharge and accretion rates should be used to estimate the depth of wells in recharge areas to avoid installing monitoring wells with screen intervals above the zone of contamination.

14.0 Remediation of MTBE Contaminated Groundwater

Sites that require remediation of MTBE plumes commonly have BTEX present as well. If remediation is being performed for BTEX contamination, it may also be effective for remediating MTBE. The remedial method selection for a site must consider all of the physical and chemical properties of the COCs, the ability of the method to achieve the cleanup goals, and the cost effectiveness of the remedial method.

If both BTEX and MTBE are present, initial remedial costs for pilot testing, Corrective Action Plan (CAP) preparation and remedial design should not significantly increase due to the presence of MTBE. The effect that MTBE has on remedial technology implementation costs will be site-specific. It should be noted that early detection and expeditious response to releases generally lowers costs considerably. MTBE remediation is required at sites where one or more of the following conditions exist:

- One or more POEs or POCs have been impacted by MTBE contamination exceeding 20 µg/l.
- There is free product in groundwater or a soil source contributing to high concentrations of MTBE.
- The plume is expanding and/or migrating, and there is a POE within 2,500 ft of the source.
- Modeling indicates that a POE or a POC may become impacted.
- Future use of an impacted water source has been planned.

Remedial technologies for the removal of MTBE from groundwater have had varying degrees of success. The costs associated with each technique depend upon level of contamination and removal efficiency. A listing of remediation resources and website addresses is provided on the OPS website at http://oil.cdle.state.co.us.

15.0 Pathway Elimination/No Further Action

Pathway elimination for MTBE contamination will be considered in the following situations:

- MTBE concentrations are below 20 µg/l.
- MTBE concentrations exceed 20 µg/l but the plume is defined, POC wells are below 20 µg/l, and modeling indicates that the POC will not become impacted above 20 µg/l in the future.
- There are no POEs located downgradient within 2,500 feet of the source, and modeling indicates that the plume will not migrate beyond 2,500 feet.

Appendix A

Physical Properties of BTEX and Fuel Oxygenates

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

Notes:

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

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

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

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

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

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

6 = Soil Condition A: foc=0.001 mg/mg, bulk density=1.75 kg/L, porosity=0.25

7 = Soil Condition B: foc=0.004 mg/mg, bulk density=1.75 kg/L, porosity=0.25