

**NDEP
OXYGENATED FUEL
CORRECTIVE ACTION GUIDANCE
October 1998**

I. BACKGROUND

This Oxygenated Fuel Corrective Action Guidance Document is provided as a tool for NDEP staff and the regulated community to use during assessment through closure of sites where methyl *tert*-butyl ether (MTBE) may be present. This document is intended to articulate the Nevada Division of Environmental Protection (NDEPs) expectations on assessment and remediation projects where MTBE is present and provide consistency in understanding and approach throughout the assessment through corrective action process. This document is to be used in conjunction with existing applicable state and federal regulations and statutes.

The Nevada Division of Environmental Protection (NDEP) oversees a number of projects through the Bureau of Corrective Actions. These projects include: petroleum hydrocarbon releases of various sorts (motor oil, hydraulic fluid, heating oil, diesel fuel, gasoline, etc); heavy metal impacts; various solvent spills; pesticide releases; acid discharges; and antifreeze spills. Assessment of environmental impacts caused by these releases and evaluation of potential human health impacts typically are conducted by the owner/operator [entity legally responsible for the discharge (responsible person/party; RP)] and overseen by an NDEP case officer.

NAC 445A.226 through 445A.22755 (Action Levels for Contaminated Sites); NAC 459.9921 through 459.999 (Storage Tanks); and NAC 590.700 through 590.790 (Clean Up of Discharged Petroleum) are routinely used by NDEP staff during project oversight to help guide the owner/operator through the discovery, assessment, characterization, corrective action, and closure phases of each project. Consistent use of these regulations assures protection of public health & the environment as well as continuity within and between various projects.

Not all contaminants encountered on these projects have established Federal Action Levels [Maximum Contaminant Levels (MCLs)] for groundwater. Recognizing this, the State of Nevada implemented a process to allow determination of action levels applicable to soil and groundwater for these contaminants (reference: "Action Levels for Contaminated Sites"; NAC 445A.226 - 445A.22755). The referenced regulation became effective on October 3, 1996. This NDEP Oxygenated Fuel Corrective Action Guidance is intended to bridge the gap between NAC 459 and NAC 445A and specifically address fuel oxygenates as these compounds have become more wide spread in both their use and their presence in the environment.

II. GUIDANCE DEVELOPMENT

Our knowledge of how MTBE may affect human health, its fate and transport through the environment, and cost effective remedial methods continues to evolve. The NDEP recognizes improvements in our understanding and management of MTBE is an ongoing process. As such, this document is intended to be flexible and may be modified periodically to reflect these changes. Suggested modifications, changes, and/or improvements should be provided in written form and directed to the Chief, Bureau of Corrective Actions at the address given on this letterhead.

III. MTBE CORRECTIVE ACTION GUIDANCE

(1) Corrective Action Statement

The NDEP will require abatement and/or corrective action of petroleum hydrocarbon releases (consistent with NAC 459, NAC 590, NAC 445A, and 40 CFR 280) where public health or the environment are perceived to be at risk of exposure above established numerical values including health based advisories.

(2) Soil Remediation

Soil clean up action levels can be determined in one of the two following ways for sites impacted by petroleum hydrocarbon releases containing MTBE:

1) Use of the existing numerical standard of 100 milligrams per kilogram (mg/kg) total petroleum hydrocarbons (TPH), reference: NAC 459.9973(7).

NOTE (1) -- When using this numerical standard, there is no need to discriminate the occurrence or concentration of MTBE.

NOTE (2) -- To ensure the best possible data are collected, Method 8015 (modified for petroleum hydrocarbons) should be conducted utilizing a "purge & trap" analytical procedure when the source fuel released is gasoline^(6 & 7). Method 8015 (modified) utilizing the "extractable" procedures should be used for diesel, motor oil, hydraulic oil, and other "heavy end" petroleum hydrocarbons^(6 & 7). In some instances (for example, the analyses of soils containing weathered/aged gasoline) the "extractable", "full range", or "fuel fingerprint" procedures may be used.

2) Use of NAC 445A.2272(1)(d) through NAC 445A.2272(3)(d) to develop a site specific and/or pathway specific clean up action level.

NOTE (3) -- Because MTBE can be falsely detected by EPA Method 8020 (as a result of co-elution), EPA Method 8260 is recommended for compound identification and quantitation.

Corrective action (CA) measures utilized on soils impacted by MTBE should be employed as soon as possible after release discovery/confirmation and should focus on immediate source reduction/removal. Rapid response and abatement and use of air-based remedial technologies should reduce the potential for MTBE to migrate to groundwater. The need for implementation of the aforementioned quick response and select CA methods are based upon the various properties which MTBE exhibits. These properties include a tendency not to sorb to soil or aquifer material, a high solubility in water, a high volatility, and low organic carbon and octanol/water partitioning coefficients. These properties contribute to more costly remedial projects if MTBE has migrated to, and significantly impacted, groundwater resources.

Migration through the soil column to first encountered groundwater can be expected where seasonal precipitation (rainfall and/or snowpack) is high; infiltration is great; or where excess water exists due to over-irrigation.

(3) Groundwater Remediation

Groundwater clean-up action levels for MTBE vary dependent upon the potential for human health exposure, potential for exposure of other fauna, and proximity to sensitive environments. The interim action level(s) established by NDEP for the occurrence of MTBE in groundwater are based upon health advisories established by the US EPA in conjunction with the US Department of Health & Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. These values are reinforced through use of NAC 445A.22735(1)(d)(2) through NAC 445A.22735(4). The difference between the interim action level applied at a site in close proximity to a "sensitive environment" and an interim action level applied at a site where a "completed exposure pathway" to humans and/or other fauna is unlikely varies by one order of magnitude. **Therefore, the NDEP interim action level for MTBE in groundwater is:**

- 1) 20 micrograms per liter (ug/L) for sites in close proximity to receptors and/or sensitive environments; or**
- 2) 200 ug/L for sites with incomplete exposure pathways.**

Once again, corrective action measures should be implemented on MTBE-impacted groundwater as soon as possible after release confirmation. Left unchecked, an MTBE plume can be expected to migrate through the environment quicker and the resultant contaminant plume in groundwater can be expected to be one to three times longer than unchecked BTEX plumes given the same environmental conditions and with the source (leak and source soils) removed. As such, **expedited site characterization, followed by early implementation of one or more viable groundwater remedial methods, can be expected to reduce overall project costs by abating/correcting the problem prior to plume enlargement.**

(4) Soil & Groundwater Remedial Action Summary

The following table presents the numerical standards associated with management of MTBE in the environment. Please note, only the 100 mg/kg numerical standard for TPH is a codified action level. Other numerical standards are either "interim action levels", or, are derived based upon site specific conditions.

| MEDIA | NUMERICAL STANDARD | ANALYTICAL METHOD |
|------------------------|----------------------------------|-------------------|
| Soil: | | |
| NAC 459.9973(7) - TPH | 100 [†] mg/kg | 8015 M P&T |
| NAC 445A. ----- MTBE | 325 [*] mg/kg | EPA Method 8260 |
| Groundwater ----- MTBE | 20 [*] ug/L (200 ug/L) | EPA Method 8260 |

NOTE [†] Indicates value is not MTBE specific. Rather, this numerical standard is based upon the presence of petroleum hydrocarbons as determined by analytical method 8015, modified for petroleum hydrocarbons. The Purge & Trap technique is recommended for use in this application.

^{*} Indicates value derived from IRIS. This value is based upon a Residential PRG.

^{*} Indicates numerical standard applicable to drinking water, NPDES permitted discharges, and sensitive environments (i.e. The release is in close proximity to a drinking water well, aquifer recharge zone, or surface water body). A numerical standard of 200 ug/L is applicable to sites with incomplete exposure pathways. Therefore, the NDEP interim action level for MTBE in groundwater is either 20 micrograms per liter (ug/L) or 200 ug/L, dependent upon the likelihood of impact to a receptor and/or "sensitive environment".

Action Level in Groundwater for Sites in Close Proximity to Receptors and/or Sensitive Environments:

The interim action level for the occurrence of MTBE in groundwater at sites with any of the following conditions is 20 ug/L (ppb):

! where there is a completed pathway for human exposure;

! water wells (receptors) are located in close proximity (within 1,000 feet) to any portion of the groundwater contaminant plume or facility boundary. As used herein, water wells are any well where water is extracted for: human consumption, bathing, swimming, or recreation; irrigation; application to crops; livestock; and/or industrial use;

! surface water intakes for potable water supplies and/or other beneficial uses are located within one half mile (1/2 mile) of any portion of the groundwater contaminant plume; facility boundary; or spill location;

! construction dewatering (with discharge to a sensitive environment) is occurring or is planned in close proximity (within 1,000 feet) to any portion of the groundwater contaminant plume or facility boundary; and

! a "sensitive environment(s)" is located in close proximity (within 1,000 feet) to the contaminant plume or facility boundary. As used herein, "sensitive environment(s)" include: all surface water bodies including washes that drain to surface water bodies; all wetlands; aquifer recharge zones; and well fields where groundwater is extracted for municipal or other beneficial use.

Additionally, all conveyance of surface water run-off (i.e. culverts, box culverts, storm drains, lined and/or unlined open channels, etc.) that eventually drain or empty to a sensitive environment are considered an extension of that sensitive environment if the conveyance is to be used to manage waste water discharges (i.e. NPDES permitted discharges). As such, NPDES discharges to these conveyances will be managed as a discharge to a sensitive environment.

This numerical standard (20 ug/L) is derived from the lower limit of the lifetime health advisory for consumption of water by an adult; reference US EPA Office of Water⁽¹⁴⁾.

Action Level in Groundwater for Sites with Incomplete Exposure Pathway:

The interim action level for the occurrence of MTBE in groundwater at sites where there is not a completed pathway for human exposure is 200 ug/L (ppb). This numerical standard (200 ug/L) is derived from the upper limit of the lifetime health advisory for consumption of water by an adult; reference US EPA Office of Water⁽¹⁴⁾.

Action Level in Groundwater for UIC permitted sites:

The interim action level for the occurrence of MTBE in groundwater at sites with existing Underground Injection Control (UIC) permits or for sites applying for an UIC permit will be either 20 ug/L or 200 ug/L depending upon site specific conditions. Establishment of a site specific interim action level for MTBE at sites with existing or planned UIC permits is at the discretion of the Bureau of Water Pollution Control.

(5) **Applicability**

This NDEP Oxygenated Fuel Guidance Document, and the associated interim action levels of 20 ug/L and 200 ug/L, are applicable to all Existing UST systems within the state of Nevada. Releases from existing gasoline UST systems to soil, surface waters, and/or groundwater that are found or reported to the NDEP after October 1998 must incorporate MTBE into their assessment, monitoring, and corrective action processes. At a minimum, EPA Method 8260 (or other comparable GC/MS method) and modified 8015 utilizing purge & trap must be used to evaluate the potential presence and concentration of various VOCs in groundwater. **The interim action levels of 20 ug/L and 200 ug/L will apply to these sites and is dependent upon site specific conditions.**

The determination of whether Corrective Action is necessary and the evaluation of whether the situation warrants an aggressive remedial approach will continue to be made by NDEP staff on a case by case basis following the existing framework provided by NAC 459. **The need to evaluate each site with respect to site specific conditions is particularly important recognizing that fuel composition varies widely from distributor to distributor; between different geographic areas; and between seasons.** Fuel releases that occur at different times of the year, or within different years, may contain: (1) no MTBE, (2) as little as 1% by volume MTBE, or (3) as much as 15% by volume MTBE. **Additionally, more recent experience has shown that the "hydrogeologic conditions may contribute more significantly to the distribution of MTBE than BTEX in groundwater"⁽⁹⁾.** As such, owners/operators of existing UST systems and their consultants involved with assessment through corrective action **should work closely with their NDEP case officer when evaluating the particulars of their case and to determine the applicability of the MTBE interim action levels of 20 ug/L and 200 ug/L to their specific situation.**

Criteria to be used in determining whether corrective action is required and which interim action level is to be used at a particular site include the following:

- ! The presence or absence of a completed pathway for human exposure;
- ! The depth to groundwater beneath the site and, if different, within the site vicinity; (If groundwater monitoring is required, all groundwater measurements are to be referenced to mean sea level (MSL) via an accurate elevation survey conducted by a land surveyor, registered in the state of Nevada.)
- ! The location of and distance to all water wells (receptors) within 1,000 feet of the contaminant plume; (Plan view map(s), drawn to scale, are required for portrayal of water well and plume locations.)
- ! The location of and distance to all proposed and/or active "dewatering projects" within 1,000 feet of the contaminant plume if the dewatering discharge is directed to a sensitive environment; (Dewatering projects, as used herein, encompass short term construction dewatering, longer term construction dewatering, and facilities/structures with routine discharges from sump pumps or similar equipment. Accurately prepared and scaled plan view map(s) are required.)

! The presence of any preferred routes of migration for liquid or vapor phase contaminants; [Potential routes of accelerated migration include: utility corridors (the utility and/or the backfilled material); lithologically or structurally controlled hydrogeology (faults, fissures, fractures, bedding planes, solution cavities, paleo-channels); vertical and/or angled conduits including open [or not properly plugged (sealed)] water wells, monitoring wells, and soil borings (boreholes); and other subsurface anomalous features.]

! The lateral and vertical extent of contamination in the soil column (vadose zone); either based upon total petroleum hydrocarbons (TPH), or, analyte specific volatile organic compounds (VOC) analyses; (Plan view map(s) and cross-sections, drawn to scale, are required for portrayal of contaminant location and shape.)

! The lateral extent of groundwater impacts; (Plan view map(s), drawn to scale, are required for portrayal of groundwater impacts, monitoring well locations, potentiometric surface, and groundwater gradient information.)

! The nature of waste water management for all waste water associated with the release site; (Is waste water currently managed or proposed for management via an NPDES or UIC permit? If so, provide the appropriate permit number(s) on all submittals. Additionally, plan view map(s), drawn to scale, are required for portrayal of the NPDES discharge location and/or UIC injection location, and the associated groundwater impacts, monitoring well locations, potentiometric surface, and groundwater gradient information.)

! The location of and distance to all surface water intakes for potable water supplies and other beneficial uses within 1/2 mile (2,640 feet) of the plume location or facility boundary;

! The location of and distance to all "sensitive environments" within 1,000 feet of the plume location or facility boundary; [Provide a named listing of, location of, and distance to all "sensitive environments" (including various surface water bodies; washes and/or other storm water conveyances that drain to the sensitive environment; wetlands; aquifer recharge zones; and well fields) within 1,000 feet of the contaminant plume. Plan view map(s), drawn to scale, are required for portrayal of the locations of groundwater impacts and sensitive environments.]

! The average annual precipitation at or near the release site; and

! The extent of abatement and/or corrective action that may have occurred during facility upgrades; facility or UST closures; or other site work; (Has any abatement occurred or corrective actions been implemented with regard to this release? If so, what abatement occurred and/or what corrective action was conducted, when, and by whom? How was success measured with regard to the abatement or corrective action?)

Open cases: [facilities with a reported release that have not yet secured a "No Further Action (NFA) determination from NDEP] must incorporate MTBE into their assessment, monitoring, and corrective action processes immediately. At a minimum, EPA Method 8260 (or other comparable GC/MS method) and modified 8015 utilizing purge & trap must be used to evaluate the potential presence and concentration of various VOCs in groundwater. When MTBE is found to be present as a component of the release, future site related monitoring must incorporate MTBE into the list of analytes routinely measured. MTBE must remain on this list of analytes routinely measured at this site through case closure. If MTBE is shown not to be present through analyses of groundwater from all site related monitoring wells via a GC/MS method and this facility no longer stores and dispenses fuel, future monitoring may suspend analyses for MTBE and by GC/MS methods. If MTBE is shown not to be present through analyses of groundwater from all site related monitoring wells via a GC/MS method

but the facility operates a registered UST system, future site related monitoring must incorporate MTBE into the list of analytes routinely measured. **The need to incorporate MTBE into the corrective action components of the project will be evaluated and determined on a case by case basis.**

Closed cases: (facilities with a release that have secured an NFA determination from NDEP) will not be required to immediately: (1) reopen their case; (2) conduct an assessment for the potential presence of MTBE; or (3) conduct corrective action regarding MTBE. If new information is provided to NDEP, now or in the future, that reveals the presence of MTBE in groundwater at actionable levels and provides evidence suggesting the "closed facility" is the source, NDEP will consider whether the information presented warrants further action⁽¹³⁾. The current property owner will be contacted by NDEP and requested to "assess the extent and magnitude of the recently discovered contaminant" if the information provided warrants action to protect public health & the environment.

In all cases, soil samples collected from facilities where the known or suspected release is comprised of gasoline must analyze these samples for the potential presence and concentration of petroleum hydrocarbons by modified method 8015 using purge & trap methods.

Other variations of method 8015 modified (the extractable procedure) are designed for, and work best on, heavier fuels (diesel, kerosine, JP-4, motor oil, etc). "Fuel Fingerprints" and "Full Range" nomenclatures typically entail use of the extractable procedure followed by comparison of sample data GC analyses to a number of known standards of gasoline, diesel, oil, etc. These variations are acceptable for "screening" a site or set of samples to determine which fuel(s) are present. Because the preparatory portion of the extractable procedure involves heating of the sample with an open top, many of the lighter [more volatile (C₆ and less)] end components are lost (evaporated) from the sample prior to GC analysis. These procedures, therefore, are not acceptable for quantifying the concentration of petroleum hydrocarbons in the gasoline range as the resultant data are biased to the low end.

IV. REGULATORY AUTHORITY

The Department of Conservation and Natural Resources (DCNR), Division of Environmental Protection is statutorily charged with protection of public health and the environment. Various State regulations have been promulgated to address this mission. These include the following:

- | NAC 445A - Water pollution control regulations;
- | NAC 444 - Hazardous waste regulations;
- | NAC 459 - Storage tank regulations; and
- | NAC 590 - Clean up of discharged petroleum.

The NDEP is required to enforce the regulations adopted by the State Environmental Commission ("Commission"). The Commission periodically revises these regulations to accommodate adjustments in contaminant action levels and/or remediation requirements as scientific evidence and experience accumulate⁽¹³⁾.

Lacking a codified MCL, most agencies that have established a numerical standard for MTBE in water have done so based upon odor, taste, and/or health advisors. The MTBE related advisory information released to date include:

- | US EPA (Office of Water) Taste & Odor Advisory; December 1997; 20-40 ug/L;
- | US EPA (ATSDR) Lifetime Health Advisory; 1995; 20 ug/L; and
- | US EPA (ATSDR) Health Advisory; 1995; 200 ug/L.

Given the body of information presently available, NDEP has set interim action levels for the occurrence of MTBE in surface water or ground water at 20 ug/L or 200 ug/L; dependent upon the proximity to sensitive environments and/or the potential for exposure by a receptor (humans or other fauna). As such, this guidance document presents a framework, criteria, and rationale for facility owners, consultants, contractors, local government agencies, state government agencies, and the general public to use when evaluating potential risks associated with fuel releases which may contain MTBE; mechanism to abate the hazards and lessen the risks; and action levels applicable to their site.

V. PROPERTIES & CHARACTERISTICS OF MTBE

(1) Properties

MTBE is the common name for methyl *tert*-butyl ether. It is an ether with the following chemical formula $\text{CH}_3\text{OC}(\text{CH}_3)_3$ ⁽¹⁰⁾. Ethers are compounds containing an oxygen atom bonded to two carbon atoms⁽²⁾.

Typically, MTBE is produced by reacting liquid isobutylene with a small amount of methanol (from natural gas) in the presence of ion-exchange resin catalysts at 100° C^(2, 9, & 14). The isobutylene is produced from butane derived from the petroleum cracking & distillation process⁽²⁾. Several other process variations are also commercially available.

MTBE is a volatile organic compound (VOC) added to gasoline to both increase the octane number and as an oxygenating agent in both reformulated gasoline (RFG) and oxygenated fuel⁽¹⁰⁾. The addition of MTBE to fuel is intended to reduce carbon monoxide emissions (and atmospheric concentrations of carbon monoxide and ozone) associated with combustion⁽¹⁰⁾. A number of other VOCs can be present as oxygenating compounds including: methanol, ethanol, tertiary butanol, di-isopropyl ether (DIPE), ethyl tertiary butyl ether (ETBE), and tertiary amyl methyl ether (TAME)⁽¹⁾. MTBE is by far the most common of these fuel oxygenates because of its low cost, ease of production, and favorable blending characteristics⁽¹⁰⁾.

Tables 3-1 and 3-2 (Appendix A) provide a listing of physical and chemical properties associated with MTBE⁽¹⁴⁾. A summary of these and other references reveals the following characteristics:

| | |
|---------------------------|---|
| <u>Chemical Structure</u> | ! MTBE is a hydrocarbon with the following chemical formula $(\text{C}_5\text{H}_{12}\text{O})$ ⁽¹⁴⁾ ; |
| <u>Use</u> | ! MTBE is routinely blended into gasoline to meet reformulated gasoline (RFG) standards (11% MTBE by volume) and oxygenated fuel requirements (15% MTBE by volume) ⁽¹⁰⁾ ; |
| <u>Odor</u> | ! MTBE (and gasoline containing MTBE) has a pungent odor; the odor detection threshold is ~680 ug/L when included in a liquid mixture; Terpene-like odor ⁽¹⁰⁾ . |
| <u>Flammability</u> | ! MTBE is flammable and is a moderate fire risk; |
| <u>Solubility</u> | ! MTBE is highly soluble in water ranging between 4 and 5% ⁽¹⁴⁾ ; the solubility in water is 42,000 mg/L (23.2 to 54.4 g/L at 25 degrees C ⁽¹⁰⁾ ; (NOTE: this solubility is ~XXX times greater than the solubility of benzene in water) |

Volatility † MTBE has a high vapor pressure of 245 mm Hg and a Henry's Law Constant of $\sim 5.87 \times 10^{-4}$ atm-m³/mole which promotes rapid volatilization from surface water or soil surfaces;

Vapor Pressure † MTBE has a relatively high vapor pressure of 3.27 to 3.35 X 10⁴ Pa at 25 degrees C⁽¹⁰⁾.

Density † The density for MTBE is 0.7405 g/cc⁽¹⁴⁾ [0.74 g/mL⁽²⁾];

Boiling Point † MTBE has a boiling point of 55° C⁽²⁾;

Organic Carbon

Partitioning

Coefficient † The K_{oc} for MTBE is ~ 11.2 . This low value indicates little tendency to sorb to soil particles⁽¹⁴⁾.

Octanol/Water

Partition

Coefficient † The relatively low octanol/water partition coefficient (log of K_{ow}) is 0.94 to 1.16⁽¹⁰⁾.

Henry's Law

Constant

† Reported Henry's Law Constant varies from 59 to 305 Pa m³/mol⁽¹⁰⁾ but is generally assumed to be less than 100 Pa m³/mol⁽¹⁰⁾.

Air Pollution

† MTBE is on the Hazardous Air Pollutants (HAPs) List⁽¹⁰⁾.

EPA Cancer

Classification

† MTBE is considered a possible human carcinogen by the U.S. EPA⁽¹⁴⁾.

(2) Use

MTBE was first synthesized by ARCO in the 1960s⁽⁸⁾. Its use as an octane enhancer in gasoline started in the late 1970s⁽¹⁾. Increased production and widespread use as an oxygenate in gasoline increased rapidly in the late 1980s to address air quality issues in some geographic areas^(1 & 14). The 1990 Clean Air Act Amendments require the addition of fuel oxygenates to gasoline used in some metropolitan areas⁽¹⁰⁾. Since the late 1980s, MTBE and ethanol have been the two preferred oxygenates used in reformulated gasoline⁽¹⁴⁾; one or the other may be used at a time. Since 1979, the U.S. EPA has allowed progressively higher percentages of MTBE in reformulated gasolines⁽¹⁴⁾. The percentage has risen from 7% (by volume) in 1979 to 11% (by volume) in 1981 to 15% (by volume) in 1988⁽¹⁴⁾.

Gasoline must contain no less than 2.7% oxygen by weight (15% MTBE by volume) to meet the 1990 Clean Air Act Amendment fuel oxygenate requirements⁽¹⁰⁾. Although select metropolitan areas were required to use oxygenated fuels by November 1, 1992, some areas were using fuel oxygenates since 1988 to improve air quality⁽¹⁰⁾.

Many other geographic areas are either required to use, or have elected to participate in, the reformulated gasoline program on a year-round basis since 1995⁽¹⁰⁾. Reformulated gasoline must contain at least 2.0% oxygen by weight, a maximum of 1.0% benzene by volume, and a maximum of 25% aromatic hydrocarbons by volume⁽¹⁰⁾. Reformulated gasoline would contain at least 11% MTBE by volume to meet this requirement⁽¹⁰⁾.

Nearly all of the MTBE produced in the United States is produced for use in reformulated gasolines⁽¹⁴⁾. Approximately 70% of the saleable production capacity is concentrated along the Texas Gulf Coast⁽¹⁴⁾. Four states (California, Louisiana, Michigan, and Texas) account for over 50% of its use⁽¹⁴⁾.

Oxygenated fuels (which include MTBE or other oxygenates such as ethanol) have been used in the winter in Reno and Las Vegas since 1989⁽¹⁰⁾. Additionally, MTBE has been added to premium fuels in some geographic areas since 1979⁽¹⁰⁾. As a result of this usage since the late 1970's, possible point sources of MTBE include leaking USTs; leaking ASTs; leaks in refueling facility pipelines; spills/leaks related to fuel conveyance pipelines; spills/leaks at loading racks and fuel transfer facilities; and releases related to permitted and/or unpermitted underground injection or surface water discharges⁽¹⁰⁾.

(3) Exposure Potential

The risk for human exposure was generally low when MTBE production was low; i.e., prior to 1970⁽¹⁴⁾. The current widespread use of MTBE in reformulated gasoline significantly increases the possibility of the general public being exposed to MTBE at low levels⁽¹⁴⁾. Opportunities for exposure closely parallel those for other organic hydrocarbon gasoline additives such as benzene or toluene⁽¹⁴⁾. General population exposure to MTBE can occur through three routes: inhalation, dermal contact, and ingestion of contaminated groundwater⁽¹⁴⁾.

Inhalation exposures can occur during vehicle refueling, as a direct result of inhalation of vehicle emissions, and due to pre-combustion volatilization into the ambient air. MTBE is listed as a hazardous air pollutant within the 1990 Clean Air Act Amendments^(10 & 14).

Another more localized risk is groundwater contamination, especially in shallow groundwater aquifers⁽¹⁴⁾. MTBE tends not to sorb to soil particles. The low organic carbon partitioning coefficient suggests MTBE will likely exhibit considerable mobility and readily leach to groundwater⁽¹⁴⁾. When introduced to subsurface soils or groundwater, MTBE may be fairly persistent because volatilization to the atmosphere is significantly reduced⁽¹⁴⁾. Because MTBE is persistent and mobile in groundwater, it can move from shallow to deeper aquifers with time⁽¹⁰⁾.

Leaking USTs are a documented source of groundwater contamination. As much as 20% of regulated USTs may either be leaking now or can be expected to leak in the near future^(10 & 14). Some number of UST leaks would have been, or will be, comprised of reformulated gasoline or other gasolines containing MTBE.

(4) Environmental Fate

MTBE can be emitted to any or all environmental media (air, surface water, groundwater, and soil) depending on the source of the release, formulation mixture, and prevailing environmental conditions⁽¹⁴⁾. Prior to the 1990s, there has been limited routine monitoring for MTBE in all environmental media; consequently, there are very limited historical data available⁽¹⁴⁾. Most conclusions on environmental fate, therefore, tend to depend heavily on the results of models⁽¹⁴⁾.

MTBE is expected to undergo destruction once released into the atmosphere from fairly rapid reactions with hydroxyl radicals⁽¹⁴⁾. MTBE has been estimated to exhibit a relatively short half-life in the atmosphere of one (1) to eleven (11) days⁽¹⁰⁾. There are two main decomposition pathways: the first results in final products such as acetone and *tert*-butyl formate, the latter of which may reside in the atmosphere for up to 15 days; the second decomposition pathway results in final products that can include 2-methoxyl-2-methyl propanol, acetone, acetaldehyde, peroxyacetyl nitrate (PAN), formaldehyde, and methyl acetate⁽¹⁴⁾.

Possible non-point sources of MTBE include atmospheric deposition⁽¹⁰⁾. Once in the atmosphere, MTBE can partition into precipitation⁽¹⁰⁾. Atmospheric concentrations of MTBE would be significantly greater during the winter months as a result of increased use of oxygenated fuels. Based upon work conducted by Robins and others (1993) and given a constant atmospheric concentration of MTBE, the lower the temperature, the greater the resultant concentration of MTBE in precipitation⁽¹⁰⁾.

Where MTBE is introduced into the environment as part of a gasoline release from a leaking UST, its relatively high water solubility and propensity not to sorb to soil particles can be expected to encourage migration to local groundwater supplies⁽¹⁴⁾. In groundwater, MTBE can be fairly persistent as it shows limited susceptibility to either anaerobic or aerobic biodegradation⁽¹⁴⁾.

In non-oxygenated gasoline, the BTEX compounds are the most soluble and most mobile components⁽¹⁰⁾. In oxygenated gasoline, MTBE is even more soluble and more mobile than any of the BTEX compounds⁽¹⁰⁾. Therefore, hydrogeologic conditions may contribute more significantly to the distribution of MTBE than BTEX in groundwater⁽⁹⁾.

The behavior of a plume of MTBE mixed with gasoline and other organic hydrocarbons (such as BTEX) in contact with groundwater can become very complicated⁽¹⁴⁾. The pollution chemistry of a reformulated gasoline plume mixing with fresh groundwater will be driven mostly by the effects from the BTEX components where MTBE is present at less than 5% (by volume)⁽¹⁴⁾. Where MTBE mixture ratios are greater than 10% (by volume), BTEX water solubilities can be increased markedly. Additionally, the MTBE co-solvency can change the sorption/desorption characteristics of other hydrocarbons, thus increasing their mobility⁽¹⁴⁾.

When compared to the BTEX compounds, MTBE plumes will generally occupy a larger portion of the subsurface⁽¹⁰⁾, for the following reasons:

- ! MTBE is persistent in aerobic and anaerobic groundwater⁽¹⁰⁾;
- ! MTBE can occur in large concentrations in gasoline; and
- ! MTBE does not sorb to aquifer material and is more mobile in groundwater than other BTEX compounds based on field data and physical and chemical properties (solubility, vapor pressure, K_{ow} and K_{oc}).

Based upon the work completed to date, MTBE plumes are likely to undergo only dispersive attenuation⁽¹⁰⁾.

The USGS suggests that urban areas with a long history of reformulated gasoline usage may face increased risks of groundwater contamination from MTBE⁽¹⁴⁾.

(5) Monitoring

Until recently, MTBE has not been included ordinarily as a requested analyte in most surface water or groundwater monitoring programs⁽¹⁴⁾. The presence and concentration of MTBE can be identified and reported through many analytical methods including: EPA Method 624, EPA Method 602, EPA Method 8020, EPA Method 8240, and EPA Method 8260. Because various VOCs can co-elute, analytical methods that only rely upon gas chromatography (GC) for compound identification may provide erroneous results. Methods using mass spectrometry (MS) for compound identification, following initial assessment by GC, provide a much higher level of assurance that MTBE has been identified correctly and quantified adequately.

EPA Method 8260 utilizes purge & trap, capillary column, and GC/MS technology to evaluate the presence or absence and concentration of an extensive list of VOCs including MTBE. Use of EPA Method 8260 is encouraged by the NDEP, Bureau of Corrective Actions to evaluate sites for the potential presence and concentration of MTBE⁽¹²⁾.

(6) Data Gaps

A number of unknowns persist with regard to MTBE. A better understanding of the transport of MTBE from land surface to shallow groundwater, and from shallow to deeper aquifers would be used to protect public water supplies and in developing wellhead protection plans for public water supplies⁽¹⁰⁾. Because MTBE is mobile and persists in groundwater, it is reasonable to expect that it will move from shallow to deep groundwater with time, but it is not known how quickly and at what concentrations⁽¹⁰⁾. Additional study and data on the fate of MTBE are needed to determine if MTBE, or its degradation products, will accumulate in groundwater over time⁽¹⁰⁾. There also may be degradation products of MTBE in air, such as *tert*-butyl formate, which enters shallow groundwater with recharge following precipitation events⁽¹⁰⁾.

Groundwater monitoring conducted in areas of relatively high annual precipitation where shallow groundwater is impacted by MTBE should evaluate what effect, if any, the periodic "recharge" has upon the dissolved MTBE plume. Monitoring conducted to date suggests that, in some instances, the dissolved MTBE plume may migrate vertically downward under the effects of uniformly recharged water above the dissolved MTBE plume. If vertical migration downward is detected at a specific site, considerable care should be exercised in: (1) evaluating the suitability of the existing, established monitoring well network; (2) assessing the need for multi-level sampling of groundwater; and (3) evaluating the vulnerability of any nearby potable water well.

(7) **Viability Remedial Methods**

This section of the NDEP Oxygenated Fuel Corrective Action Guidance contains a brief review of corrective action methods suitable for use at sites with fuel releases containing MTBE. Additionally, this section presents a listing of criteria to use when evaluating the suitability of MTBE related treatment technologies. This section is by no means complete! The review of corrective action methods is not exhaustive! This present contents of this section are provided to stimulate thought in the regulated community regarding viable, cost effective, remedial methods and optimization of existing remedial methods. This section will be revised periodically as additional information becomes available. The first such significant revision will likely occur by mid 1999 following public distribution of a report summarizing the effectiveness of various corrective action methods on the remediation of MTBE.

A variety of remedial methods are currently in use treating sites with soil and/or groundwater impacts containing MTBE. Some remedial systems have been designed (and are being operated) specifically to address MTBE. Other existing remedial systems are being optimized to better remediate MTBE containing hydrocarbon releases. Still other remedial systems employ new, emerging technologies. These new technologies may offer cost effective solutions, however, there are limited performance records for review. What seems clear at this point is:

- | air-based technologies work; particularly in source areas;
- | air-based technologies work well in the vadose zone;
- | total project costs are reduced if the release is recognized and aggressively managed early on and while the release (contaminants) is present only in the vadose zone;
- | project costs increase considerably if groundwater is impacted significantly and aggressive corrective action is required; and
- | total project costs can be reduced if the presences, concentration, and mass of MTBE and remedial action goal (numerical standard) are considered during the remedial selection and design phases of the project.

Criteria to use when evaluating treatment technologies for use in remediating soils and groundwater impacted by MTBE containing fuels include:

- | Cost effectiveness;
- | Applicability;
- | Reliability;
- | Robustness;
- | Regulatory Approval;
- | Simplicity; and
- | Size of footprint.

Remedial methods with demonstrated effectiveness for reduction of MTBE parallel the more widely used and accepted remedial methods typically employed for the reduction of BTEX compounds. These methods include:

- ! Vapor Extraction;
- ! Air Stripping;
- ! Air Sparge / Vapor Extraction;
- ! In Well Air Stripping;
- ! Enhanced In-situ Biodegradation;
- ! Slurping in conjunction w/ Air Stripping & Vapor Extraction; and
- ! Bio-Slurping in conjunction w/ Air Stripping & Vapor Extraction.

With the exception of biodegradation (in-situ or ex-situ), most remedial methods with demonstrated effectiveness remediating fuels with MTBE utilize "air-based technologies". Dependent upon which method is selected and other site specific / geographic specific conditions, the resultant performance can be optimized during the design phase of the project. This optimization can take the form of:

- ! Utilization of "waste heat" from the remedial system to "pre-heat" influent contaminated water to an air stripper. This practice can reduce the air:water ratio required for effective MTBE removal;
- ! Injection of liquid, gaseous, or solid forms of oxygen (or oxygen containing compounds) to assist the biodegradation processes; and
- ! Coupling complimentary technologies together to expedite the remedial time frame and reduce over all project costs. Examples include coupling:
 - = Air sparge and vapor extraction (AS/VE);
 - = GAC (or another off-gas treatment method) with air stripping or vapor extraction particularly during the initial 1 to 6 months of remedial system operation until the extracted vapor load is significantly reduced to allow system operation without off-gas treatment; and
 - = Deployment of hydrogen peroxide through AS, VE, and/or monitoring wells or use of pure oxygen for sparging in conjunction with VE or AS/VE.

VI. REFERENCES

- (1) Analyses Required for Oxygenate Compounds in California Gasoline - EPA Method 8260; California Regional Water Quality Control Board, Central Valley Region, 3443 Router Road, Suite A, Sacramento, CA 95827-3098; July 18, 1997.
- (2) Chemical of the Week;
<http://scifun.chem.wisc.edu/chemweek/MTBE/MTBE.html>;
August 31, 1998.
- (3) Contaminated Soil and Groundwater Remediation Guidance; Nevada Division of Environmental Protection, Bureau of Corrective Actions, 333 W. Nye Lane, Carson City, NV 89710; June 25, 1992; Biaggi, Allen B.
- (4) Controlling UST Cleanup Costs; Fact Sheet #5: Understanding Contractor Code Words; USEPA, Office of Emergency Response; EPA 500-F-92-005; May 1992.
- (5) Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl Tertiary-Butyl Ether (MtBE); U.S. Environmental Protection Agency, Office of Water; EPA-822-F-97-008; December 1997.
- (6) Leaking Underground Fuel Tank (LUFT) Field Manual: Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure; May 1988; State of California, Leaking Underground Fuel Tank Task Force.
- (7) Leaking Underground Fuel Tank (LUFT) Field Manual Revision: Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure; March 1989; State of California, Leaking Underground Fuel Tank Task Force.
- (8) L.U.S.T.LINE; New England Interstate Water Pollution Control Commission, 255 Ballardvale Street, Wilmington, MA 01887-1013; Bulletin 24; July 1996.
- (9) Occurrence and behavior of MTBE in Groundwater; Chevron Research and Technology Company; Buscheck, Tim, Gallagher, Dan, Peargin, Tom, Kuehne, Don, and Zuspan, Chuck; February 1998.
- (10) A Preliminary Assessment of the Occurrence and Possible Sources of MTBE in Ground Water of the United States, 1993-94; U.S. Geological Survey Open-File Report 95-456; Squillace, Paul J., Zogorski, John S., Wilber, William G., and Price, Curtis V.

- (11) Removal Efficiency of MTBE in Water: Confirmation of a Predictive Model Through Applied Technology, (undated); SEACOR & ARCO Terminal Services Corporation, A Subsidiary of Atlantic Richfield Company (ARCO); Buttilo, John V., Pulido, Andrew D., Reese, N. Mark, and Lowe, Mark A.
- (12) Nevada Division of Environmental Protection, Risk Based Corrective Action Program for Petroleum Release Sites: Tier 1 Soil Screening Evaluation User's Guide; Preliminary Draft, (undated); Nevada Division of Environmental Protection, Bureau of Corrective Actions, 333 W. Nye Lane, Carson City, NV 89710.
- (13) State of Nevada, Attorney General Opinion: The Propriety of Reopening Conditionally Closed Sites; State of Nevada; Office of the Attorney General, Environmental Division, 333 W. Nye Lane, Carson City, NV 89710; March 6, 1992.
- (14) Toxicological Profile for Methyl *tert*-Butyl Ether; U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Division of Toxicology/Toxicology Information Branch, 1600 Clifton Road NE, E-29, Atlanta, Georgia 30333; August 1996.