Appendix A: CleanUp Review Tiger Team Biographies

CLEANUP REVIEW TIGER TEAM BIOGRAPHIES

Mr. James M. Davidson is a hydrogeologist and the President of Alpine Environmental, Inc. He has led the investigation and remediation of hundreds of hydrocarbon spills since 1988. Mr. Davidson has conducted extensive field and research studies on the transport, remediation and treatment of MTBE and other gasoline additives since 1995. He holds a B.S. degree in geology and an M.S. degree in hydrogeology. Tel: (970) 224-4608, email: jdavidsonalpine@cs.com

Ms. Karla Jenkins Harre is a Technical Services Representative to EFA West and an environmental engineer with NFESC for 6 years. Current work includes providing EFA West with technical assistance and leading the logic development of the cost-to-complete (CTC) environmental budgeting component in NORM. Previous experience includes leading Clean Up Review Tiger Teams (CURTT), BADCAT innovative technology demonstrations and technical evaluations, and the landfill technology application team at NFESC. Before coming to the Navy, Karla worked for Velsicol Chemical Corporation as a project engineer for CERCLA sites. She completed a Bachelor of Engineering degree in Civil and Environmental Engineering from Vanderbilt University and is currently completing a Masters of Business Administration at Pepperdine University. Tel: (805) 982-2636, email: jenkinskj@nfesc.navy.mil.

Mr. James E. Landmeyer is a hydrologist with the U.S. Geological Survey. He is interested in how microbial processes affect the geochemistry of contaminated and pristine ground water systems. He holds a Ph.D. in geology/chemistry from the University of South Carolina. Tel: (803) 750-6128, email: jlandmey@usgs.gov

Mr. Paul Lefebvre recently returned to NFESC after receiving an MBA from the Anderson Graduate School of Management at UCLA. Prior to his graduate studies, he managed the Underground Fuel Pipeline Leak Detection and Location project and led the Constructed Wetlands Technology Application Team for the Environmental Department at NFESC. Paul began his career with the Amphibious and Advanced Base Department at the Naval Civil Engineering Laboratory in 1990, after receiving his bachelor's degree in Mechanical Engineering from the University of Wisconsin, Milwaukee in 1989. Tel: (805) 982-4842, email: lefebvrepf@nfesc.navy.mil

Mr. Michael Martinson is a Senior Consultant with Delta Environmental Consultants, Inc. Mike has over 19 years of consulting and industry experience working in most regulatory settings (UST/LUST, RCRA, TSCA, CERCLA). He contributes to company-wide, multi-site work as well as site-specific efforts in the application of risk-based decision-making, MNA, engineered bioremediation, design and implementation of engineering remedial systems, RBCA and natural attenuation modeling, and senior review of risk assessments. Mike maintains an extensive state-by-state network of contacts to evaluate state regulations, policies, and trends in response to key regulatory issues. He periodically assesses and shares information on state's responses to clean up issues such as MTBE and other oxygenates, MNA, source removal, free-product recovery, GIS-type mapping tools, and long-term management of residual petroleum hydrocarbons for LUST sites beyond "no further action" (NFA) status. Mike continues to closely track the nationwide emergence of MTBE and other oxygenate regulations as well as regulatory program responses for all 50 states. Key interests are LUST and drinking water regulatory program's requirements for enforcement, investigation, cleanup, and regulatory closure/NFA of LUST sites. One contribution from his attention to the MTBE issue has been a national map of clean-up levels that is periodically updated and posted on EPA-OUST's MTBE web-site at http://www.epa.gov/swerust1/mtbe/mtbemap.htm. Tel: (612) 803-0302, email: mmartinson@deltaenv.com

Mr. Michael Pound has worked for Southwest Naval Facilities Engineering Command (SWDIV) for 10 years. He first worked as the Remedial Project Manager for the Point Loma Naval Complex. His responsibilities included development and implementation of CERCLA investigations, UST investigations and removals, air toxic hotspots analyses, and spill prevention and control contingency plans. For the last 8 years, he has been the Technical Manager for the Installation Restoration Program. He is responsible for maintaining technical consistency and regulatory compliance for the Installation Restoration Program among the Navy/Marine Corps facilities in Southwest Division's area of responsibility. Mr. Pound's other responsibilities include development of regional environmental policies, review and evaluation of new regulations and guidance, management of the evaluation and remediation of contaminated sediment at Naval facilities in the San Francisco Bay region, assistance with ESTCP and BADCAT innovative technology demonstrations, development and updating the Department of the Navy's technical guidelines for monitored natural attenuation, and development and implementation of innovative techniques and technologies for the remediation of unexploded ordnance. Additionally he participates in the Navy's Alternative Restoration Technology Team, Remedial Action Optimization/Long-term Management Workgroup, and Human Health/Ecological Risk Forum. Tel: (619) 532-2546; email: poundmj@efdsw.navfac.navy.mil.

Ms. Sonya Webb obtained her B. S. in Civil Engineering at California Polytechnic State University, San Luis Obispo. At NFESC she provides technical support to Southwest Division as a Technical Support Representative, participates in the Phytoremediation Technology Application Team, evaluates innovative technology abstracts and performs alternate COTR duties for Broad Agency Announcement (an alternative contracting method for innovative technologies), and coordinates the Environmental Restoration CD-ROM. Tel: (805) 982-4993, email: webbsm@nfesc.navy.mil.

Ms. Kathryn A. Wurzel, M.P.H., D.A.B.T. is a Diplomate of the American Board of Toxicology with over 20 years experience in public health including assessment and communication of risk from environmental contamination and consumer products. She received a B.S. in Environmental Health from Purdue University and a Master of Public Health in Toxicology from the University of Michigan. Ms. Wurzel began her professional career in local and state government and for the past 13 years has been employed as a pubic health and environmental consultant. Ms. Wurzel has been responsible for the performance of risk assessments and compliance demonstrations for a wide variety of sites ranging from USTs to federal Superfund sites. Ms. Wurzel's broad range of experience as a project manager, lead consultant, risk assessor, and toxicologist has enabled her to develop innovative, holistic, and cost effective strategies for performing risk assessments, demonstrating regulatory compliance, and effectively communicating potential risks to the public. Tel: (404) 347-9050, email: kwurzel@newfields.com.

Appendix B: Toxicological Information and Risk Assessment Considerations: Fuel Oxygenates

TOXICOLOGICAL INFORMATION AND RISK ASSESSMENT CONSIDERATIONS

FUEL OXYGENATES

Cleanup criteria for constituents in soil and groundwater are generally established by determining the health risks associated with potential exposure. Groundwater cleanup criteria may also be established to protect aesthetic quality (taste and odor). The amount and quality of the toxicological data available for each constituent is evaluated by the federal Environmental Protection Agency (EPA) to determine if the data are adequate for establishing health-based criteria. Many states have also developed procedures for determining health-based and/or aesthetic criteria.

There is a hierarchy of toxicity information specified by the EPA in the *Risk Assessment Guidance for Superfund (RAGS).*[1] RAGS states:

> *IRIS is updated monthly, provides verified RfDs and slope factors, and is the Agency's preferred source of toxicity information. Only if values are unavailable in IRIS should other information sources be consulted.*[2]

The *Integrated Risk Information System (IRIS)* is an electronic database accessible via the Internet and maintained by EPA. All toxicity values included in the IRIS database have been reviewed and verified by a group of experts to assure that appropriate consideration is given to the quality of a study and the consistency of results when multiple studies are available. In the event the EPA working group determines that there is 1) insufficient data, 2) the quality of the study (or studies) is inadequate, or 3) the data uncertainties are such that a quantitative estimate of risk using the data would be inappropriate, no numerical toxicity values will be established for use in risk assessments.

As of July 21, 2000, the only fuel oxygenate toxicity value available on *IRIS* is the inhalation Reference Concentration (RfC) for MTBE (methyl *tert*-butyl ether). This is the only potential route of exposure for MTBE that EPA concluded had sufficient information to derive a toxicity value for use in quantitative risk assessments. There is limited data on animal bioassays and relevance of this data to potential human health risks for other routes of exposure to MTBE. The other fuel oxygenates do not appear in the IRIS database.

Toxicological data is generally obtained through conducting animal testing to determine the acute and chronic (non-carcinogenic) effects of exposure to a constituent. Long-term (~ 2 years) studies are conducted to assess the potential carcinogenic effects associated with lifetime exposures.[3] Assays are also conducted to assess the potential mutagenic effects associated with a chemical. There is generally a greater concern for chemicals that induce mutagenesis as well as carcinogenesis due to the relationship of altered genetic material to the induction of cancer.

---

[1] *Risk Assessment Guidance for Superfund*, Volume 1, Human Health Evaluation Manual, U.S. EPA, EPA/540/1-89/002, December 1989, pg. 7-15.

[2] Ibid. Underline appears in *RAGS* document.

[3] The average lifetime of rats and mice is 24 months.

Taste and odor is determined by exposing a panel of humans to varying concentrations of the chemical of interest in water and air. The threshold is the concentration at which a taste or odor is detected by the panel members. An average of the individual thresholds is usually used in the evaluation of concentrations necessary to protect the aesthetic quality of air or water.

MTBE is the current focus of toxicological evaluations because of the widespread presence of MTBE in the nation's groundwater (and to a lesser extent, surface water). The continued use of fuel oxygenates as a means of reducing air pollution increases the impact potential of MTBE and other oxygenates on groundwater and surface water. Regulatory agencies are requesting that water samples be analyzed not only for MTBE but other oxygenates as well. Determining the concentrations of these compounds in water is a laudable effort, but without criteria for comparison based on potential health or aesthetic effects, the significance of detectable concentrations of oxygenates in groundwater or surface water is unknown. Information that cannot be evaluated serves no purpose in furthering the protection of human health and the environment and the mere presence of a compound is often cited as a cause for concern. The available toxicity and aesthetic information on the following fuel oxygenates is presented herein:

- MTBE
- TBA (*tert*-butyl alcohol)
- TAME (*tert*-amyl methyl ether)
- ETBE (ethyl tertiary butyl ether)
- DIPE (diisopropyl ether).

Prior to analyzing for these oxygenate compounds in water, the use of the data and the criteria for evaluation must be clearly established. Failure to address these issues prior to obtaining concentration data is likely to result in increased future sampling requirements, pressure for additional remedial alternative evaluation and activity, and heightened public concern for health and safety.

MTBE

There is no data available on the effects of human consumption of water containing MTBE. Data from laboratory animal exposure to MTBE have occurred at high levels via inhalation exposure or by introducing MTBE in oil directly to the stomach. Use of these studies to quantitatively assess risks from drinking water exposure has serious limitations.

The estimation of a human equivalent oral dose from animal inhalation data has inherent uncertainties and limitations. Factors that impact the *absorption* of a compound from the lungs (and thus the dose) include: 1) physical properties of the compound (i.e., aerosol or gas, particle size, etc.), 2) respiration rate and minute volume of experimental animal, 3) exposure conditions (continuous or intermittent exposures). Interspecies conversion factors also impact the estimation of human doses from animal experiments. These factors are: 1) allometric scaling between species to compensate for different body sizes (i.e., the volume proportion of the body relative to lung size), 2) differences in respiratory system structure and physiology (for example, rats are obligate nose breathers, they do not breathe through their mouths), and 3) qualitative and quantitative differences in absorption and biotransformation between species (i.e., the metabolism rate of MTBE may be slower in humans than in rats – this could increase the observed effect if MTBE is the active compound or decrease the effect if a metabolite of MTBE is responsible).

It is very important to determine whether it is the parent compound (MTBE) or a metabolite (TBA) that is responsible for the biological activity. The absorbed dose via inhalation does not pass through the same liver metabolism as that via ingestion (inhalation of MTBE allows for direct absorption into the blood before any metabolic activity in the liver occurs). Many chemicals (formaldehyde is an example) produce different toxic effects and carcinogenic effects via different routes of exposure.

Acute exposure (exposures to a compound for less than 24 hours) to MTBE indicates that it is not very toxic. Experimental animals exhibit central nervous system depression (including anesthesia) and labored breathing as a result of acute exposure. Full recovery from the exposure was evident within two hours.

MTBE was once used as a medical treatment for dissolving gallstones. The MTBE was injected directly into the bile duct but some of the MTBE entered the bloodstream and was distributed systemically. Two studies on blood levels of MTBE following biliary tract administration indicated MTBE concentrations from a mean of 40 mg/L to a "did not exceed" 10 mg/L. These concentrations are two to three orders of magnitude greater than those observed in worker studies (taxi drivers, tanker truck drivers, garage workers, etc.).[4] Effects reported in patients treated by this procedure included sedation, perspiration, bradycardia (slow heart beat) and elevation of liver enzymes. These reported effects cannot be attributed totally to MTBE because of the confounding effects of anesthesia, the procedure itself, and the underlying gallbladder disease. The procedure has reportedly been well tolerated in large patient groups.[5]

Human exposure to MTBE has been evaluated for individuals exposed to MTBE-containing fuels but the results have been inconclusive. Neurological effects such as headache, dizziness and emotional distress were assessed as well as gastrointestinal problems (nausea, diarrhea) and respiratory irritation. All the studies used an MTBE-gasoline mixture rather than just MTBE; exposure to gasoline vapors alone has been associated with the symptoms evaluated in the MTBE studies.[6]

Animal studies have been conducted to assess the non-carcinogenic chronic and sub-chronic effects of MTBE exposure. The data indicate that kidney toxicity is of concern after MTBE exposure. EPA performed quantitative estimation of potential adverse effects following exposure to MTBE in 1993 based upon a 90-day study. Significant uncertainties are associated

---

[4] *An Evaluation of the Scientific Peer-Reviewed Research and Literature on the Human Health Effects of MTBE, its Metabolites, Combustion Products and Substitute Compounds*, John R. Froines, Principal Investigator.

[5] *Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl Tertiary-Butyl Ether (MTBE)*, EPA Office of Water, EPA-822-F-97-009, December 1997.

[6] Ibid.

with the use of this study because the study was for only 90 days and not a lifetime and, the dose was extrapolated from a single daily bolus dose in corn oil to a continuous small dose associated with drinking water exposure. It would generally be anticipated that the 90-day exposure would tend to underestimate the toxicity while the bolus dose would be more likely to overestimate the toxic effects. The relative effects of these two factors are unknown and thus make the validity of quantitative evaluation of potential toxic effects questionable.[7]

Lifetime bioassays have been performed on laboratory animals to assess the potential for carcinogenesis. Only one study has been performed via oral MTBE administration; inhalation exposure studies have been conducted. The bioassay via oral exposure to MTBE is the most appropriate to evaluate for potential risks associated with human exposure to MTBE by drinking water ingestion. However, the MTBE was administered to the rats by gavage in olive oil (directly introduced into the stomach daily as one large dose) 4 days per week for two years. A dose-related increase in the incidence of cancer (combined leukemia and lymphomas in female rats and benign testicular tumors in the high-dose male rats) was observed. However, use of this study to quantitatively assess risk from drinking water exposure has limitations: 1) there are potential differences due to the dose delivery (bolus in oil vs. low concentrations in drinking water) and 2) the details of the tumor response data and the histopathological diagnosis (microscopic evaluation of the cell types to determine the type of tumor) were not provided in the study. The National Research Council panel recommended that the findings of this study performed by Belpoggi and his coworkers (1995) not be used in risk estimation until a thorough peer review of the study was performed.[8] Belpoggi published additional information regarding the pathology in a European journal in 1998 but no documentation of a peer review of his findings appears in the literature.[9]

Lifetime inhalation bioassays in the rat indicated that MTBE increased in the incidence of combined renal tubular adenomas and carcinomas as well as testicular tumors in the males. Induction of α-2μ-globulin by MTBE suggested that this protein may have played a role in male rat kidney tumorigenesis. This finding is relevant to the potential carcinogenic risk of human exposure to MTBE. The α-2μ-globulin protein is unique to the male rat. Tumor formation due to the presence of this protein in the male rat urinary tract is not an indication of potential tumor formation in humans because our metabolic processes do not result in the generation of α-2μ-globulin.[10] Until further data is obtained on the involvement of the α-2μ-globulin protein in male rat tumor induction, the EPA policy on establishing if the protein is responsible for the tumorigenesis present cannot be adequately evaluated.

---

[7] Ibid.

[8] Ibid.

[9] *An Evaluation of the Scientific Peer-Reviewed Research and Literature on the Human Health Effects of MTBE, its Metabolites, Combustion Products and Substitute Compounds*, John R. Froines, Principal Investigator.

[10] *Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl Tertiary-Butyl Ether (MTBE)*, EPA Office of Water, EPA-822-F-97-009, December 1997. Referencing the Chun et al. 1992 study.

An 18-month inhalation study was performed on mice and indicated an increase in liver tumors (hepatocellular carcinomas and adenomas).[11] This study cannot be used to quantitatively assess risk in humans due to the lack of a well-developed pharmacokinetic model for converting a chronic inhalation exposure to an equivalent oral exposure. A pharmacokinetic model explains the mechanisms by which a compound is absorbed, distributed and metabolized following exposure via various exposure routes. This information may then be used to develop mathematical models that represents the kinetics and thus allows toxicological data from one route of exposure to be used to estimate the potential toxicological effects via a different route of exposure. In the absence of this type of data, the uncertainties in route-to-route extrapolation are too great to provide reliable estimates of the potential risk of human exposure.

The carcinogencity data support a conclusion that MTBE poses a potential for carcinogenicity to humans at ***high doses***. The data do not support confident quantitative estimation of risk at low exposure concentrations due to the above-described data limitations. The weight of evidence from the available mutagencity data indicates that MTBE is not DNA reactive. The lack of mutagenic activity of MTBE supports a lowered risk of carcinogenesis in humans because the tumorigenic response in animals is therefore not likely to be due to direct-DNA acting phenomena.

It is possible to conclude from reproductive and developmental studies of MTBE exposure in animals that at low concentrations MTBE does not cause developmental or reproductive hazard by inhalation in three different species. This also suggests that humans may not be at risk when exposed to very low concentrations of MTBE. In addition, the chronic oral and inhalation studies support a conclusion that MTBE can pose a hazard on noncancer effects to humans at ***high doses***, but the data do not support confident quantitative estimation of risk at low exposure.

Two metabolites of MTBE (*tertiary*-butyl alcohol and formaldehyde) have indicated carcinogenic effects in animal bioassays. The TBA and formaldehyde bioassays were performed via drinking water exposure and physiological responses similar to MTBE exposure were observed (kidney tumors and leukemia). However, the formaldehyde data is somewhat ambiguous because the study was performed by the same laboratory as the Belpoggi MTBE bioassay and similarly lacks sufficient histopathological data and independent peer review. Another formaldehyde drinking water bioassay in rats showed no evidence of carcinogenicity. Additional information is necessary on MTBE and its metabolites to qualitatively and quantitatively evaluate the potential risk of exposure to humans via drinking water ingestion.

Dermal exposure does not appear to be a significant exposure pathway.[12] The ingestion and inhalation routes of exposure contribute to the potential risks and are therefore the relevant pathways for assessment.

---

[11] Ibid. Referencing the Burleigh-Flayer et al. 1992 study.

[12] *An Evaluation of the Scientific Peer-Reviewed Research and Literature on the Human Health Effects of MTBE, its Metabolites, Combustion Products and Substitute Compounds*, John R. Froines, Principal Investigator.

EPA evaluated the organoleptic effects of MTBE (taste and odor). The studies that have been performed to assess the taste and odor thresholds of MTBE have been performed using small numbers of individuals. Larger numbers of individuals participating in the organoleptic studies might show the full distribution of human sensitivity which as of now remains uncharacterized. However, the existing studies were performed independently and the distributions are consistent with one another. In addition, the presence or absence of other natural or water treatment chemicals can mask or reveal the taste and odor effects. It is EPA's conclusion that the data lends confidence to the conclusion that sensitive individuals respond to taste and odor at about 20-40 μg/L.[13]

EPA recommended in its Drinking Water Advisory that the taste and odor threshold of 20-40 μg/L be used to protect consumer acceptance of the water and to provide a large margin of exposure (safety) from the potential toxic effects of MTBE. EPA further states that:

> *There are over four to five orders of magnitude between the 20-40 mg/L range and concentrations associated with observed cancer and noncancer effects in animals. There is little likelihood that an MTBE concentration of 20-40 mg/L in drinking water would cause adverse health effects in humans, recognizing that some people may detect the chemical below this range. It can be noted that at this range of concentrations, the margins of exposure are about 10 to 100 times greater than would be provided by an EPA reference dose (RfD) for noncancer effects. Additionally, they are in the range of margins of exposure typically provided by National Primary Drinking Water Standards under the Federal Safe Drinking Water Act to protect people from carcinogenic effects.*

Despite the findings of EPA, the California Department of Toxic Substances Control (DTSC) has calculated an MTBE concentration of 13 μg/L in drinking water to be protective of potential carcinogenic effects[14] [15] and a secondary standard (taste and odor) of 5 μg/L.[16] [17]

The chemical properties and taste and odor threshold information is provided in the attached table.

---

[13] *Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl Tertiary-Butyl Ether (MTBE)*, EPA Office of Water, EPA-822-F-97-009, December 1997.

[14] DTSC used the animal bioassay results that EPA determined were inadequate to quantitatively assess the potential human risk of exposure to MTBE.

[15] *Final Statement of Reasons Primary Maximum Contaminant Level for Methyl –tert-Butyl Ether Title 22, California Code of Regulations*, February 2000.

[16] DTSC established the taste and odor threshold using the lowest odor threshold reported in 4 tests (2.5%).

[17] *Final Statement of Reasons Secondary Maximum Contaminant Level for Methyl –tert-Butyl Ether and Revisions to the Unregulated Chemical Monitoring List Title 22, California Code of Regulations.*

Tertiary-Butyl Alcohol (TBA)

MTBE is metabolized to TBA following all routes of exposure. There are indications that TBA is further metabolized to formaldehyde and acetone.

Acute, heavy exposures to TBA lead to irritation of the eyes and mucous membranes, nausea, headache, fatigue and narcosis. Acute exposure has also been reported to cause respiratory tract irritation and can result in a cough and difficulty breathing. The American Conference of Governmental Industrial Hygienists (ACGIH) has established a threshold limit value (TLV) for worker exposure of 303 mg/m^3 for worker exposure over an eight-hour workday. ACGIH states that TBA is not classifiable as to its carcinogenic potential.[18]

Animal studies have been performed for TBA, but the acute health effects were not the focus of the studies. There is very little data on the effects of TBA on reproduction but it appears that effects occur in animal studies only at doses that also cause severe general toxicity. [19]

Four in vitro and two in vivo assays for genotoxicity (mutagenicity) have been performed and all results were clearly negative.[20]

The National Toxicology Program performed a lifetime bioassay on male and female rats and mice via ingestion. The male rats had a significantly increased incidence of tumors in the renal tubules (urinary tract system). There were no cases of renal tumors observed in the female rats. These findings may be related to the induction of the α-2μ-globulin protein in male rats as discussed in the MTBE section. There was equivocal evidence of carcinogenicity in male mice (thyroid tumors) and some evidence in female mice (thyroid tumors).[21] [22]

The chemical properties and taste and odor threshold information is provided in the attached table.

Additional data is necessary in order to more clearly assess the potential carcinogenic activity in animals and to quantitatively evaluate the potential risk of human exposure to TBA. There is currently no health risk-based criterion for evaluation of concentrations of TBA in drinking water.

---

[18] *An Evaluation of the Scientific Peer-Reviewed Research and Literature on the Human Health Effects of MTBE, its Metabolites, Combustion Products and Substitute Compounds*, John R. Froines, Principal Investigator.

[19] Ibid.

[20] Ibid.

[21] Ibid.

[22] *Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl Tertiary-Butyl Ether (MTBE)*, EPA Office of Water, EPA-822-F-97-009, December 1997.

TAME (*tert*-amyl methyl ether)

TAME is a chemically related ether alternative to MTBE. However, even less information on the potential human health effects is available for TAME.

The only human data on TAME identified were from two exposure assessment studies in occupationally exposed gasoline tanker truck drivers. Concurrent exposures occurred to TAME, MTBE and gasoline vapors, so the potential health effects associated with TAME cannot be established. Limited animal study data are also available. A 4-week inhalation study, and a 28-day subchronic genotoxicity study did not identify any pathological effects associated with exposure. It was concluded that the toxic effects induced by TAME were weak.[23]

Exposure to significant concentrations (up to 4000 ppm in air) of TAME resulted in central nervous system depression (sedation, coma, etc.) but the effects were transient (following cessation of exposure, the animals recovered in a matter of hours). A 90-day inhalation study of the *major metabolite of TAME* (tertiary amyl alcohol) indicated increased liver weight and CNS depression at high concentrations (1000 ppm, 6 hours/day, 5 days/week for a total of 90 days).[24]

TAME is not mutagenic. The limited reproductive/developmental toxicity studies via inhalation exposure do not provide sufficient information to assess the potential adverse effects of TAME exposure through drinking water ingestion. A discussion of the issues related to route-to-route extrapolation is presented in the MTBE section.

The taste and odor thresholds in water have been estimated as 128 ppb and 194 ppb respectively. A panel of ten subjects exposed to TAME in water by the Orange County Water District found the odor threshold in tap water to be from 15 to 100 ppb.[25]

The chemical properties and taste and odor threshold information is provided in the attached table.

Additional data is necessary in order to more clearly assess the potential health effects of exposure to TAME. There is currently no health risk-based criterion for evaluation of concentrations of TAME in drinking water.

ETBE (ethyl tertiary butyl ether)

ETBE is a chemically related ether alternative to MTBE. However, even less information on the potential human health effects is available for ETBE.

---

[23] *An Evaluation of the Scientific Peer-Reviewed Research and Literature on the Human Health Effects of MTBE, its Metabolites, Combustion Products and Substitute Compounds*, John R. Froines, Principal Investigator.

[24] Ibid.

[25] Ibid.

A controlled study of eight male volunteers exposed to up to 50 ppm ETBE for two indicated an increasing solvent odor with increasing ETBE concentration and slight decrements in pulmonary function (ability to inhale and exhale). Two animal studies were conducted to evaluate the potential central nervous system effects of inhalation exposure. The studies indicated an increased incidence of sedation and ataxia in animals exposed to concentrations of 4000 ppm and above for 4 or 14 weeks.[26]

ETBE is not mutagenic and there are no reproductive or developmental effect studies available in animals or humans. No animal carcinogenesis bioassays have been performed on ETBE; however, several metabolites of ETBE have demonstrated carcinogenic potential in animals.[27]

The chemical properties and taste and odor threshold information is provided in the attached table.

Additional data is necessary in order to more clearly assess the potential health effects of drinking water exposure to ETBE. The only toxicological data currently available are for the inhalation route of exposure. The issue of route-to-route extrapolation is discussed in the MTBE section. There is currently no health risk-based criterion for evaluation of concentrations of ETBE in drinking water.

DIPE (diisopropyl ether)

DIPE is a chemically related ether alternative to MTBE. However, even less information on the potential human health effects is available for DIPE.

High concentrations (greater than 300 ppm in air) resulted in respiratory irritation to human volunteers. The ACGIH recommended threshold limit value (TLV) is 250 ppm averaged over an 8-hour workday. This concentration was established to protect against irritation effects. Laboratory animals exposed to high concentrations of DIPE in air experienced central nervous system effects such as unsteadiness and excitation followed by depression. It is interesting to note that the 1.0% concentration of a 40% blend of DIPE in gasoline produced the same effect as 1.0% DIPE alone. A subchronic inhalation study in rats up to 7100 ppm DIPE did not show any cellular effects on the lung or nasal turbinates.[28] Concentrations of DIPE vapor between 3% and 6% can be anesthetic and fatal to monkeys. [29]

No mutagenicity studies, reproductive studies or carcinogenicity bioassays are available in the literature for DIPE. The developmental effects DIPE exposure indicates that exposure to high

---

[26] Ibid.

[27] Ibid.

[28] Note: rats are obligate nose breathers so the entire inhalation exposure occurred through the nasal turbinates (similar to our sinus cavities) rather than a portion of the lung exposure being directed through the mouth.

[29] *An Evaluation of the Scientific Peer-Reviewed Research and Literature on the Human Health Effects of MTBE, its Metabolites, Combustion Products and Substitute Compounds*, John R. Froines, Principal Investigator.

concentrations can induce developmental effects, but low dose exposure does not appear to have an adverse effect on the developing fetus.

All the available toxicological information available on DIPE is via inhalation exposure. As discussed in the MTBE section, the uncertainties associated with route-to-route extrapolation prevent an assessment of the potential human health effects resulting from DIPE ingestion via drinking water. There is currently no health risk-based criterion for evaluation of concentrations of ETBE in drinking water.

Ecological Effects of Fuel Oxygenates

Studies have been performed to assess the potential ecological effects of MTBE in surface water. The available bioassay data suggests that at the commonly observed environmental MTBE exposure levels found in surface water (below detection to 100 ppb) MTBE should not be toxic to freshwater aquatic life. The negative findings in the developmental assays indicate that developmental toxicity is not likely to occur at environmental MTBE exposure levels. It is interesting to note that tests on "treated" water containing MTBE indicate that the UV/peroxide treatment of MTBE water may be associated with greater toxicity to aquatic organisms that that seen by MTBE itself.[30]

Another University of California-Davis investigator reported that there is little toxicity of MTBE to aquatic organisms with the most sensitive taxonomic group tested being green algae. The most conservative toxicity reference value calculated for rainbow trout is 7000 ppb. It has been estimated that the adverse effects on rainbow trout are not expected until concentrations of MTBE in the water column reach 4600 ppb. These levels are much greater than those associated with adverse taste and odor of MTBE in water and any suggested human health protective water concentration.[31] A toxicity reference value of 66,000 ppb MTBE in surface water was used in an evaluation of management options for water supplies and ecosystems. This value represented the lowest toxicity value to an aquatic organism (fathead minnows) multiplied by safety factors to account for uncertainty.[32]

Regulatory Timetable

EPA is taking steps that could lead to the development of an enforceable National Primary Drinking Water Standard (MCL) for MTBE. In February of 1998, EPA included MTBE on a list of contaminants that may be regulated under the Safe Drinking Water Act. Every five years EPA is required to develop a list of contaminants that may require regulation. Five contaminants from the list must be selected by EPA by August 2001 and determine if they should be regulated.

---

[30] *Toxicity of MTBE to Freshwater Organisms*, Inge Werner and David E. Hinton, UC-Davis, School of Veterinary Medicine via Internet.

[31] *Ecological Risk of MTBE in Surface Waters*, Michael L. Johnson, John Muir Institute of the Environment, UC-Davis via Internet.

[32] *MTBE: Evaluation of Management Options for Water Supply and Ecosystem Impacts*, Orit Kalman and Dr. Jay R. Lund, Department of Civil and Environmental Engineering, UC-Davis, Draft Report October 16, 1998.

The priorities for regulation of compounds on the candidate contaminant list are defined as follows:

- Regulatory determination priorities
- Research priorities
- Occurrence priorities

EPA has placed MTBE on the occurrence priority list for which further data on how widespread the MTBE problem is and the concentrations at which it occurs in water supplies (municipal and private). Health effects research is also a priority due to significant data gaps. It is highly unlikely that EPA would select MTBE in this cycle (August 2001) because of the data gaps.

The additional occurrence data being collected and the ongoing health effects studies will hopefully provide EPA with sufficient information to make a regulatory determination for MTBE. The information will not likely be available until the next 5-year cycle ending August 2006. EPA requires approximately 3½ years for the promulgation of a drinking water regulation. Based on this time schedule, the earliest a drinking water standard could be expected in 2010. [33] While it is possible that the schedule could be shortened, it is unlikely that any health-based Maximum Contaminant Level (MCL) for drinking water standard would be available before 2004, and could be as late as 2010.

The other fuel oxygenates discussed are even more distant from possible regulatory standards. Although some regulatory agencies are currently requesting the quantification of concentrations of these compounds in ground and surface water, there are no standards for comparison of the data. It is not possible at this time to make statements regarding the potential health risks associated with varying concentrations of oxygenates in groundwater. Once the data are available however, the public (and therefore the agencies) will demand to know the consequences of the presence of any detectable levels in the water. The use and value of collecting fuel oxygenate water data at this time, other than MTBE, should be discussed with the appropriate regulatory agency before any data is conducted.

---

[33] *MTBE in Gasoline: Clean Air and Drinking Water Issues*, Congressional Research Service Report for Congress, The Library of Congress, Updated February 25, 2000.

SUMMARY

- EPA Drinking Water Advisory for MTBE is based on protecting the consumer acceptance of the water (adverse taste and odor).
- EPA concluded that the taste and odor threshold currently provided adequate protection of human health based on margins of safety provided for in applicable regulations.
- EPA has concluded that, at the present time, the carcinogenesis bioassay data available for MTBE are not sufficient for quantitative evaluation of the potential human exposure risks to MTBE in drinking water.
- EPA has included MTBE on the candidate list for potential regulation under the Safe Drinking Water Act, but a regulatory standard is unlikely before 2010.
- California established a primary (health-based) water quality standard of 13 μg/L in drinking water based upon the research data that EPA concluded was not sufficient for quantitative risk evaluation.
- California established a secondary (taste and odor) water quality standard of 5 μg/L based on detection in 2.5% of the tests performed using a human odor panel.
- Additional data is needed to evaluate the potential carcinogenic effects of MTBE on exposure via drinking water ingestion because of uncertainties associated with route-to-route extrapolation and the induction of the α-2μ-globulin protein in male rats.
- MTBE is not mutagenic in various assays and thus is not considered to have a direct-DNA effect.
- Data available on the potential carcinogenic effect of TBA is uncertain because of the renal tumor incidence in male rats (α-2μ-globulin protein and its relevance to human metabolism).
- Toxicological data are insufficient for TAME, ETBE and DIPE to assess the potential risk of human exposure to these compounds in drinking water.
- TBA, TAME, ETBE and DIPE are not mutagenic in standard assays.
- No health-based criteria are available for comparison to the fuel oxygenate water concentrations obtained from field sampling.
- Ecological data available for MTBE in freshwater indicate that MTBE exhibits low toxicity to aquatic organisms.
- Fuel oxygenates other than MTBE should not be quantified in water samples until appropriate criteria are available to assess the relevance of any detected concentrations.

Chemical Properties of Selected Compounds[a]

	Benzene[2]	MTBE[2]	Ethanol[3]	ETBE[1]	TAME[1]	TBA[3]
Molecular Weight (g/mol)	78.11	88.2	46.1	102.2	102.2	74.1
Boiling Point (^{0} C)	80.1	55.2	78.5	72.2	86.3	82.4
Vapor Pressure (mm Hg at 20 ^{0} C)	73	240	44	130	75	41
Density (g/L)	0.88	0.74	0.79	0.74	0.77	0.79
Octane Number	94	110	115	112	105	100
Neat Solubility (g/100g H_20)	0.178	4.8	miscible	1.2	1.2	miscible
Solubility into H_20 from Gasoline (g/100g H_20)	<.01	0.55	5.7[b]	0.33	0.24	2.5[b]
Taste Threshold in Water (μg/L)	500	20 to 40	-	47	128	-
Odor Threshold in Water (μg/L)	-	20 to 40	-	35-100	15-100	-
Odor Threshold (ppm)	0.5	0.053	49	0.013	0.027	21

[a] Adapted from USGS. For a detailed discussion of the solubility in water from gasoline mixture containing 2% oxygen, see p. 2-50 - 2-53 of the National Science and Technology Council. *Interagency Assessment of Oxygenated Fuels* (June 1997).

[b] The water solubilities of the alcohols are estimates based on partitioning properties.

Sources:

[1] D.L. Conrad, Texaco Research and Development Department, *The Impacts of Gasoline Oxygenate Releases to the Environment -- A Review of the Literature* (Port Arthur, Texas, 1995).

[2] Donald Mackay, W.Y. Shiu, and K.C. Ma, *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Vol. III, Volatile Organic Compounds* (Boca Raton, FL: Lewis Publishers, Inc, 1993) p. 916.

[3] Donald Mackay, W.Y. Shiu, and K.C. Ma, *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Vol. III, Volatile Organic Compounds* (Boca Raton, FL: Lewis Publishers, Inc, 1993) p. 962.

Key:

" - " signifies "Not Applicable"

g/mol = Grams Per Mole

^{0}C = Degrees Celsius

mm Hg = Millimeters of Mercury

g/L = Grams Per Liter

g/100g H_20 - Grams Per 100 Grams of Water

μg/L = Micrograms Per Liter

ppm = Parts Per Million

Obtained from EPA420-R-99-021, *Achieving Clean Air and Clean Water, The Report of the Blue Ribbon Panel on Oxygenates in Gasoline*, September 15, 1999.

Appendix C: MTBE in Municipal Stormwater

NAWQA VOC National Synthesis

http://wwwsd.cr.usgs.gov/nawqa/vocns/

MTBE IN MUNICIPAL STORMWATER

For release: UPON RECEIPT (Distributed April 15, 1997)

MTBE was detected in some urban stormwater samples collected in 16 cities and metropolitan areas by the USGS, but all detections of MTBE were less than the lower limit of the draft health advisory for drinking water.

At a reporting level of 1.0 µg/L for most samples, USGS scientist Greg Delzer said MTBE was detected in one or more stormwater samples in eight cities--Atlanta, Baton Rouge, Birmingham, Colorado Springs, Denver, Dallas/Fort Worth, San Antonio, and Phoenix. The detection rate in urban stormwater was highest in samples collected during the months of October through March each year of the study (1991-1995). This October-March period corresponds with the expected seasonal use of oxygenated gasoline in areas where carbon monoxide exceeds established air-quality standards.

Concentrations of 62 VOCs and other constituent groups were measured in 592 stormwater samples collected in the 16 cities in 11 states, all of which have a population greater than 100,000. MTBE was the seventh most frequently detected VOC and was detected in 41 of the 592 stormwater samples. In decreasing order, the most frequently detected VOCs were toluene, total xylenes, chloroform, trimethylbenzene, tetrachloroethene, and napthalene. Detections of MTBE ranged from 0.2 to 8.7 µg/L with a median of 1.5 µg/L.

In each of the three cities--Phoenix, Colorado Springs, and Denver--known to use MTBE to abate air pollution, it was detected only in stormwater samples collected during the season when oxygenated gasoline was in use.

MTBE was detected in 40 percent of the samples collected in these cities during October through March.

Detection of MTBE in cities confirmed not to use oxygenated gasoline or reformulated gasoline--Atlanta, Baton Rouge, Birmingham, Dallas/Fort Worth, and San Antonio--may be attributable to the use of MTBE as an octane enhancer.

This USGS work is part of an interagency assessment of the scientific basis and effectiveness of the nation's winter oxygenated fuel program, which is coordinated by the President Office of Science and Technology Policy. It is a compilation of several USGS studies that were done to assist cities in applying for urban stormwater permits. The data were synthesized by the USGS National Water-Quality Assessment Program, one goal of which is to provide a comprehensive assessment of the quality of most of the Nation's water resources.

Appendix D: Technologies Considered for Control and Containment at CBC Pt. Hueneme

Technologies Considered for Control and Containment at NCBC Port Hueneme

Option	Advantages	Limitations
Air Sparging Wells	• Innovative technology with demonstrated effectiveness for MTBE removal • Remediates MTBE plume without requiring groundwater extraction	• Transfers MTBE to the atmosphere • Will require a high air to water flow ratio to strip MTBE from the water • Thin aquifer limits the radius of influence of air sparging around the wells • May require a wide band of wells to provide sufficient residence time in the treatment zone • Capital intensive
Air Sparging Barrier	• Innovative technology with demonstrated effectiveness for MTBE removal • Remediates MTBE plume without requiring groundwater extraction	• Transfers MTBE to the atmosphere • Will require a high air to water flow ratio to strip MTBE from the water • Trench construction increases capital cost and construction complexity particularly with buried utilities • Capital intensive
French Drain (similar to Pump-and-Treat for groundwater extraction and aboveground treatment)	• Conventional technology • Extraction performance independent of aquifer heterogeneity	• High operating cost • Trench construction increases capital cost and construction complexity particularly with buried utilities • Will require a large volume of GAC due to low sorption capacity of MTBE • Fouling and plugging problems • May have air emissions issues • RWQCB is not favorable to GAC • May be required to run it long term (as with pump-and-treat)
Biobarrier (injection of oxygen and bacteria culture)	• Innovative technology with demonstrated effectiveness for MTBE removal • Remediates MTBE plume without requiring groundwater extraction	• May require a wide band of wells to provide sufficient residence time in the treatment zone • May be a lag time of several months before MTBE degradation starts • Low concentrations at leading edge of plume may be insufficient to support a population of MTBE degrading microbes • Will produce recalcitrant by-product, TBA • May require inoculation with

Option	Advantages	Limitations
Biobarrier (continued)		cultured MTBE degrading microorganisms • Oxygen injection will increase operating costs • May only remediate to 15 μg/L, much of the plume has low concentrations
Infiltration Gallery (draws water up, spreads it out, like a fish pond, to activate the microorganisms to remediate it)	• Innovative technology with potential effectiveness for VOC removal • EPA may assist with the design • Oxygenates the water to activate microbial degradation	• May require inoculation with cultured MTBE degrading microorganisms • May be a lag time of several months before MTBE degradation starts • Low concentrations at leading edge of plume may be insufficient to support a population of MTBE degrading microbes • Will produce recalcitrant by-product, TBA • Limited by zone of influence; well could be drawing from one side, but not the other
In-situ Chemical Oxidation	• Innovative technology with potential effectiveness for MTBE removal • Remediates MTBE plume without requiring groundwater extraction	• May require a wide band of wells to provide sufficient residence time in the treatment zone • Difficult to reliably mix the oxidation solution with the groundwater • Oxidation reaction is not selective • By-product production not quantified • Must have good groundwater flow
In-situ Treatment Wall	• Innovative technology with demonstrated effectiveness for VOC removal and high potential for MTBE removal • Remediates MTBE plume without requiring groundwater extraction • Trench design allows flexibility to convert to biotreatment or groundwater extraction, if required	• High capital cost • Trench construction increases capital cost and construction complexity particularly with buried utilities • Will require a large volume of GAC due to low sorption capacity of MTBE • Will require bench-scale testing to determine site specific GAC capacity • Media must be excavated and replaced when exhausted or fouled • MTBE can readily desorb from

Option	Advantages	Limitations
In-situ Treatment Wall (continued)		GAC when input level declines, which almost necessitates changing out the buried GAC wall when MTBE level declines, even if there is some unused adsorption capacity in the GAC.
In-well Air Stripping Wells	• Remediates MTBE plume without requiring groundwater extraction	• Transfers MTBE to the atmosphere • High airflow rate needed to strip MTBE may dry out well • Small bubbles needed to optimize stripping limit air lift pumping effect • Thin aquifer limits the radius of influence of circulation around the wells • May require a wide band of wells to provide sufficient residence time in the treatment zone • If located near utilities SVE must be added (for public perception) to prevent potential vapors in sewers • RWQCB would not permit any GAC to capture VOCs • Requires higher concentrations of MTBE
Monitored Natural Attenuation (MNA)	• Low capital and operating costs	• Conflicting perspectives on whether this alternative works at NCBC • MTBE plume may expand into unacceptable areas or surface water bodies before the MTBE plume stabilizes • Have to show stabilization and why it is stabilizing • May have poor public perception
Oxygen Release Compounds (ORC)	• Innovative technology with demonstrated effectiveness for MTBE removal • Remediates MTBE plume without requiring groundwater extraction • Makes water aerobic	• May require a wide band of wells to provide sufficient residence time in the treatment zone • May be a lag time of several months before MTBE degradation starts • Low concentrations at leading edge of plume may be insufficient to support a population of MTBE degrading microbes • Will produce recalcitrant by-product, TBA

Option	**Advantages**	**Limitations**
ORC (continued)		• May require inoculation with cultured MTBE degrading microorganisms • Periodic ORC replacement will increase operating costs
Phytoremediation	• Innovative technology with demonstrated effectiveness for establishing hydraulic control and may provide some MTBE degradation • Remediates MTBE plume without requiring groundwater extraction • Low capital and operating cost • Can be a positive public involvement project when planting on earth day • NCBC site conditions, high groundwater and asphalt, provide ideal implementation conditions	• Transfers some of the MTBE to the atmosphere • Several months will be required for plants to become established, so interim measures may be needed to provide hydraulic control initially • Degree of hydraulic control unknown during seasonal dormancy of trees
Pump-and-Treat	• RWQCB Prefers this method • Conventional technology • Pumping rate can be adjusted to ensure plume capture • Low capital cost	• High operating cost • May be required to run it long term • Will require a large volume of GAC due to low sorption capacity of MTBE • Fouling and plugging problems

Appendix E: Preliminary Calculations of Freshwater and Marine Water Quality Criteria for MTBE

Preliminary Calculations of Freshwater and Marine Water Quality Criteria for MTBE

E. R. Mancini, ARCO; A. Steen, API; G.A. Rausina, Chevron; D. C. L. Wong, Equilon; W. R. Arnold, Exxon; F. E. Gostomski, USEPA; T. Davies, USEPA; J. R. Hockett and W. A. Stubblefield, ENSR; K. R. Drottar and T. A. Springer, Wildlife International, Ltd.; P. Errico, QualTech

Abstract

A public/private partnership was established in 1997, under the oversight of the American Petroleum Institute (API), to develop aquatic toxicity databases sufficient to calculate ambient water quality criteria for methyl tertiary-butyl ether (MTBE), a gasoline oxygenate. Existing toxicity data were evaluated, consistent with USEPA guidance, resulting in a proposal to conduct 19 additional freshwater and marine tests to satisfy the federal database requirements. Commercial aquatic toxicology laboratories and GLP auditors were competitively selected to develop and report definitive test data under the oversight of industry study monitors; USEPA scientists participated in a critical review role. Freshwater acute toxicity (LC_{50}/EC_{50}) data ranged from 340 to 1742 mg MTBE/L; chronic data (IC_{20}) ranged from 42 to 289 mg MTBE/L. Marine acute data ranged from 136 to 1341 mg MTBE/L while the chronic exposure datum (IC_{20}) was 36 mg MTBE/L. Acute-to-chronic ratios varied from 3.4 to 11.3 with a geometric mean of 5.9. Preliminary calculations of freshwater criteria for acute and chronic exposure effect protection are 151 and 51 mg MTBE/L, respectively. Preliminary calculations of marine criteria for acute and chronic exposure effect protection are 53 and 18 mg MTBE/L, respectively.

Introduction

Methyl tertiary-butyl ether (MTBE) is a five carbon, alkyl ether used for a variety of purposes in many modern gasoline formulations. Concern regarding its occurrence in surface and ground waters of the United States and its potential impact on aquatic resources resulted in the formation of the MTBE Water Quality Criteria Work Group in 1997. The Work Group's objective was the development of freshwater and marine aquatic toxicity

---

Poster presented at the 20th Annual Meeting of the Society of Environmental Toxicology and Chemistry (SETAC), 14-18 November, 1999, Philadelphia, PA.

databases, consistent with USEPA guidance, sufficient to calculate acute and chronic water quality criteria for the protection of aquatic life.

Methods

The MTBE Water Quality Criteria Work Group was convened within the American Petroleum Institute (API) and includes the following, additional institutional members;

Oxygenated Fuels Association (OFA),
Western States Petroleum Association (WSPA),
various member companies of the API, and
USEPA in an advisory/review role (non-funding).

ENSR (Ft. Collins, CO) and Wildlife International, Ltd. (Easton, MD) were competitively selected to conduct the freshwater and marine aquatic toxicity testing program and QualTech was chosen to provide relevant GLP auditing services. Nineteen acute and chronic tests with eight freshwater and nine marine species were conducted under the oversight of industry Study Monitors. ASTM/USEPA standardized protocols and flow-through exposures were used to the maximum extent practicable. Toxicological data and individual study reports were subjected to several levels of QA/QC review provided by the laboratories, Study Monitors, independent third-party auditors, USEPA scientists and Work Group participants. Although final QA/QC reviews are currently in progress for a few of the test data, preliminary calculations of ambient water quality criteria were conducted consistent with relevant guidelines (USEPA, 1985) and current USEPA policy.

Results & Discussion

Tables 1 and 2 present the provisional water quality criteria databases for freshwater and marine species, respectively. The Tables include Work Group-sponsored data as well as other relevant, screened aquatic toxicity data included in the preliminary criteria calculations. The available data and related observational information from laboratory scientists suggest that MTBE exhibits low toxicity to aquatic organisms and that it behaves as a nonspecific narcotic, like many petroleum hydrocarbons.

While USEPA maintains statutory authority for developing and publishing federal ambient water quality criteria, it is possible to follow the available guidance (USEPA, 1985) for the purpose of calculating such criteria where aquatic toxicity databases are adequate. Pertinent calculational values derived from Tables 1 and 2 data are presented below; Table 3 presents the preliminary freshwater and marine ambient water quality criteria for MTBE.

<u>Fresh water</u>
Final Acute Value = 301.8 mg/L
Criterion Maximum Concentration = (301.8 mg/L) / 2 = 150.9 mg/L
Final Acute-Chronic Ratio = 5.866 (geometric mean of values shown in Tables 1 & 2)
Final Chronic Value = (301.8 mg/L) / 5.866 = 51.45 mg/L

<u>Marine</u>
Final Acute Value = 105.17 mg/L
Criterion Maximum Concentration = (105.17 mg/L) / 2 = 52.59 mg/L
Final Acute-Chronic Ratio = 5.866 (geometric mean of values shown in Tables 1 & 2)
Final Chronic Value = (105.17 mg/L) / 5.866 = 17.93 mg/L

Table 4 presents screened, freshwater and marine algal data although, consistent with USEPA guidance, none was sufficient to influence the criteria calculations. Empirically derived bioconcentration factors for MTBE range from 0.8 to 1.5 and octanol/water partition coefficients range from 17.2 to 17.5 indicating a low potential for bioaccumulation (Fujiwara, et al., 1984).

Summary and Conclusions

The MTBE Water Quality Criteria Work Group was convened in 1997 to develop aquatic toxicity databases sufficient to calculate ambient water quality criteria for MTBE. In order to achieve this objective, a total of nineteen freshwater and marine aquatic toxicity tests have been completed and multiple levels of technical data review are nearly complete.

- Preliminary calculations of freshwater criteria for acute and chronic exposure effect protection are 151 and 51 mg MTBE/L, respectively.

- Preliminary calculations of marine criteria for acute and chronic exposure effect protection are 53 and 18 mg MTBE/L, respectively.

- This public/private partnership project constituted a cost-effective and efficient process for generating the toxicity databases necessary for calculating ambient water quality criteria.

Table 1. Provisional, freshwater ambient water quality criteria database for MTBE.

Species	Effect Concentration (mg MTBE/L)	Genus Mean Acute Value (mg MTBE/L)
Acute Exposure (EC_{50}/LC_{50})		
Ceriodaphnia dubia (water flea)	340	340
Hyalella azteca (amphipod)	**473***	473
Daphnia magna (water flea)	**472**	555
	542	
	681	
Physa gyrina (snail)	**559**	559
Hexagenia limbata (mayfly)	**581**	581
Pimephales promelas (fathead minnow)	672	811
	706	
	929	
	980	
Oncorhynchus mykiss (rainbow trout)	887	1047
	1237	
Lepomis macrochirus (sunfish)	**1054**	1054
Chironomus tentans (midge)	**1742**	1742
Chronic Exposure (IC_{20})		
Daphnia magna (water flea)	**42**[1]	
Pimephales promelas (minnow)	**289**[2]	

* Highlighted entries represent Work Group-sponsored data.

[1] Acute-to-chronic ratio for this species was 11.3.

[2] Acute-to-chronic ratio for this species was 3.4.

Table 2. Provisional, marine ambient water quality criteria database for MTBE.

Species	Effect Concentration (mg MTBE/L)	Genus Mean Acute Value (mg MTBE/L)
Acute Exposure(EC$_{50}$/LC$_{50}$)		
Grandidierella japonica (amphipod)	155	155
Americamysis bahia (mysid shrimp)	**187*** 136	159
Palaemonetes pugio (grass shrimp)	**166**	166
Gasterosteus aculeatus (stickleback)	**297**	297
Callinectes sapidus (bluecrab)	**306**	306
Menidia beryllina (silverside)	606	606
Cyprinodon variegatus (sheepshead minnow)	**663**	663
Strongylocentrotus purpuratus (sea urchin)	1341	1341
Mytilus galloprovincialis (mussel)	range finding, nominal **1309**	1309
Rhepoxynius abronius (amphipod)	range finding, nominal **412**	412
Chronic Exposure(IC$_{20}$)		
Americamysis bahia (mysid shrimp)	**36**[1]	

* Highlighted entries represent Work Group-sponsored data.

[1] Acute-to-chronic ratio for this species was 5.3.

Table 3. Preliminary ambient water quality criteria for MTBE.

Water Quality Protection Objective	**Criteria (mg MTBE/L)**
Freshwater Acute Effects (CMC)	**151**
Chronic Effects (CCC)	**51**
Marine Acute Effects (CMC)	**53**
Chronic Effects (CCC)	**18**

Table 4. Freshwater and marine algal toxicity data for MTBE. These data were developed by the Work Group, BenKinney, et al. (1994), Rousch and Sommerfeld (1998) and Bay (personal communication, 1999).

Species	**Measured Effect Concentration (mg MTBE/L)**	**Measured No Effect Concentration (NOEC, mg MTBE/L)**
Freshwater *Selenastrum capricornutum* (green alga)	195 (EC$_{50}$) **491** (EC$_{50}$)*	2462
Synechococcus leopoliensis (blue-green alga)		1976
Navicula pelliculosa (diatom)		2252
Marine *Skeletonema costatum* (diatom)	**114** (EC$_{50}$, cell density) **185** (EC$_{50}$, growth)	
Macrocystis pyrifera (kelp)	616 (IC$_{25}$)	

* Highlighted entries represent Work Group-sponsored data.

Citations

USEPA, 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. PB85-227049. Office of Water, Washington, DC, USA. 98pp.

BenKinney, M.T., J.F. Barbieri, J.S. Gross and P. A. Naro, 1994. Aquatic toxicity of methyl tertiary-butyl ether (MTBE) to aquatic organisms. Presented at the 15th Annual SETAC meeting, 30 October-3 November 1994, Denver, CO.

Rousch, J. M. and M. R. Sommerfeld, 1998. Liquid-gas partitioning of the gasoline oxygenate methyl *tert*-butyl ether (MTBE)under laboratory conditions and its effect on growth of selected algae, *Archives of Environmental Contamination and Toxicology* (34): 6-11.

Bay, Steve. 1999. Southern California Coastal Water Research Project; CA Water Resources Control Board MTBE Project; preliminary data.

Fujiwara, Y., et al., 1984. Biodegradation and bioconcentration of alkyl ethers. *Yukayaken* (33): 111-114.

Appendix F: Lowney Update: Senate Bill 162 Requires School Districts Requesting State Funding for Acquisition or Construction to Prepare a Phase I Environmental Site Assessment

LOWNEYUPDATE

NEWS OF THE LATEST DEVELOPMENTS IN GEOTECHNICAL AND ENVIRONMENTAL ENGINEERING TECHNOLOGIES

THE PROBLEM:

Senate Bill 162 requires that school districts seeking state funding under the School Facilities Program (1998) must contract with a qualified environmental site assessor to prepare a Phase I Environmental Site Assessment. Very few environmental professionals in California have the required registration.

THE SOLUTION:

Either a class 11 environmental assessor or a licensed hazardous waste contractor with appropriate experience must perform the assessment. Lowney Associates meets these qualifications.

THE BENEFITS:

- Contracting with environmental professionals that meet the requirements of Senate Bill 162 will expedite regulatory approval for site acquisition or construction.
- Working with environmental professionals who abide by Senate Bill 162 will expedite state funding.

Senate Bill 162 Requires School Districts Requesting State Funding for Acquisition or Construction to Prepare a Phase I Environmental Site Assessment

By Ron L. Helm, C.E.G. ,R.E.A.

Effective January 1, 2000, Senate Bill 162 prohibits a school district governing board from approving the acquisition of a school site or the construction of a school by a school district, unless an environmental assessment of the site' is performed. The environmental assessment must be prepared in accordance with ASTM E1527-97 and be conducted prior to site acquisition or construction.

The Department of Toxic Substances Control must review the assessment; this agency must determine that the property purchased or to be built upon is not the site of a current or former hazardous waste disposal site, solid waste disposal site, or hazardous waste release site.

The school district must reimburse the Department of Toxic Substances and Control for its response costs; the response costs may be reimbursed under the Leroy F. Greene School Facilities Act of 1998. This bill also states that a school district is not liable in any action filed against the district for making the assessment available for public review.

A qualified environmental site assessor must perform the environmental assessment. This professional must have a class If environmental assessor license as registered by the Office of Environmental Health Hazard Assessment, or a contractor license with the State of California with a hazardous substance certificate. Lowney Associates has several qualified environmental site assessors on staff.

The environmental site assessment is a preliminary review of a property to evaluate whether there has been a release of a hazardous material, or whether a naturally occurring hazardous material is present,, based on reasonably available information about the property and its vicinity (Table 1).

TABLE I. TYPICAL SCOPE OF WORK FOR PHASE I ENVIRONMENTAL SITE ASSESMENT

- Review of public and private records of current and historical land uses
- Review of reported releases of hazardous materials in site vicinity
- Searches of available and relevant databases
- Review of relevant files of federal, state, and local agencies
- Visual surveys of the property and adjacent properties
- Review of historical aerial photographs of the property and the general vicinity

  Interviews with current and previous owners and operators

friends with up-to-date information on standards, policies and federal, state and local regulatory agencies and news of the latest developments in geotechnical and environmental engineering technologies
Lowney Associates © 2000

LOWNEYASSOCIATES
Environmental/Geotechnical/Engineering Services

(continued from front)

The environmental assessment must contain one of the following recommendations:

- A further investigation of the site is not required; or
- A preliminary endangerment assessment is needed, including sampling or testing, to evaluate if.-
  1) a release of hazardous material has occurred and to what extent;
  2) a release of a hazardous material is a threat; and
  3) a naturally occurring hazardous material is present.

If the environmental assessment concludes that further investigation of the site is not required, the assessment and all documentation related to the proposed acquisition or use of the proposed school site must be submitted to the State Department of Education. Within 10 days of receiving the assessment, the Department of Education must forward it to the Department of Toxic Substances Control for review and approval, which must be completed within 30 days.

If the Department of Toxic Substances Control agrees with the conclusion of the environmental assessment that further investigation is not required, the department approves the assessment and notifies the State Department of Education and the school district governing board of the approval.

For more information, please contact Ron Heim at (650) 967-2365, or view the entire bill at http://info.sen.ca.gov.

Mountain View: 405 Clyde Avenue, CA 94043 650.967.2365
Oakland: 129 Filbert Street, CA 94607 510.267.1970
Pasadena: 1785 Locust Street, Suite IO, CA 91106 626.396.1490
Son Ramon: 2258 Camino Ramon, CA 94583 925.275.2550
http://vvww.lowney.com

Appendix G: Emerging Technologies at The National Environmental Technology Test Site

EMERGING TECHNOLOGIES AT THE NATIONAL ENVIRONMENTAL TECHNOLOGY TEST SITE

The Department of Defense (DOD) established the National Environmental Technology Test Sites (NETTSs) to build an infrastructure to validate a number of different types of remediation technologies over a period of time. The Navy's was designated for fuel hydrocarbons, and is funded by DOD, SERDP and ESTCP. The Army's was an explosive site that is now closed. The Air Force possessed a solvent site in Delaware, and an off-gas treatment of chlorinated solvents at McClellan, California. EPA has one in Michigan.

The Port Hueneme NETTS evaluates remediation and characterization technologies for gasoline and fuel oil contaminated soils and groundwater. Due to the increase in concern regarding MTBE's presence in fuel-related sites, and its recalcitrance, it has become the predominant contaminant of concern at the NETTS research platform (see Figure G-1). The technologies that have been evaluated at NETTS should be considered when addressing an MTBE contaminated site. These demonstrations vary form large scale to smaller scale projects.

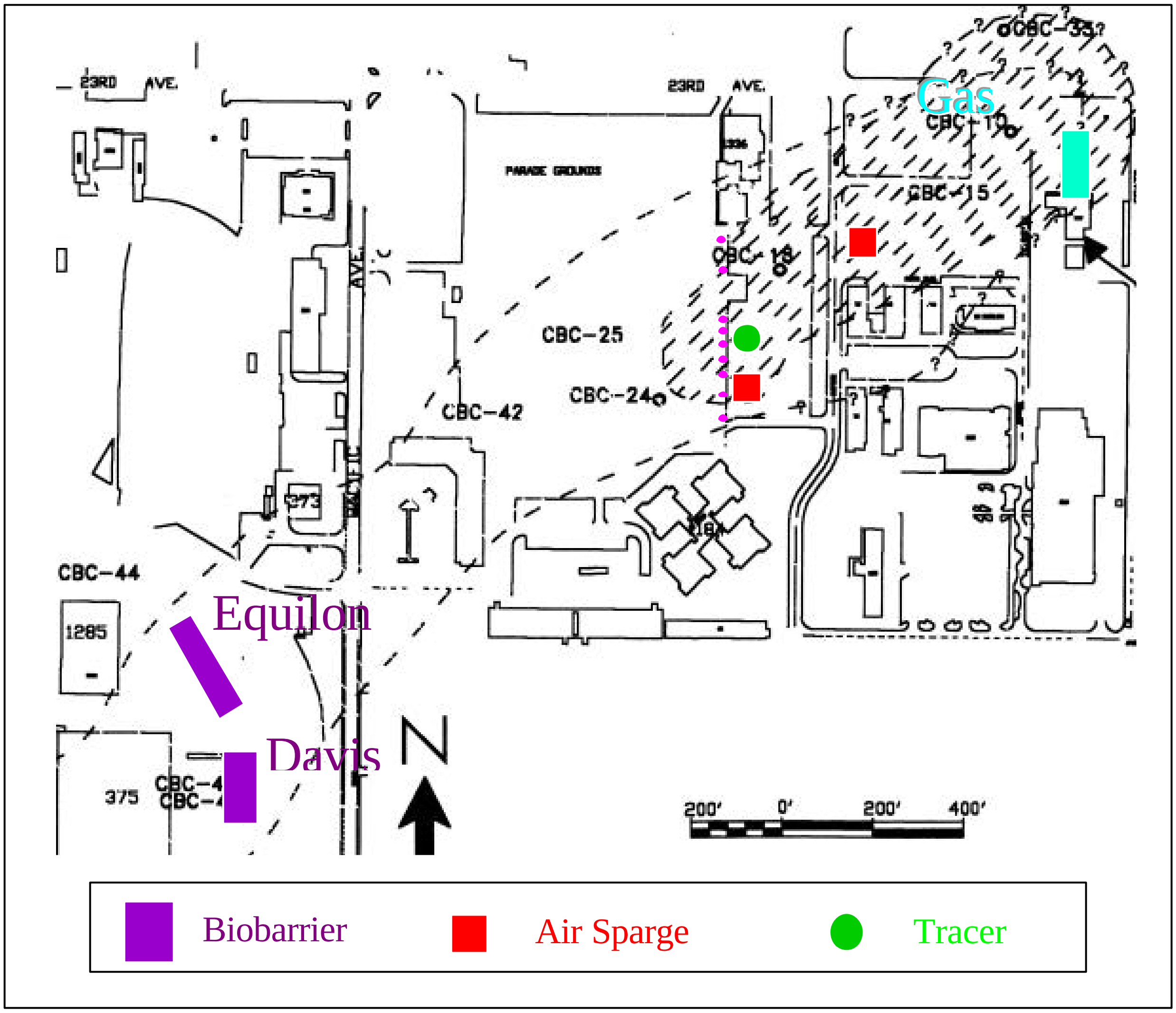

Figure G-1. Emerging Technologies at the Port Hueneme NETTS

AIR SPARGING (2 LOCATIONS)

Air sparging has been utilized to remove of BTEX. Pumps push air through the aquifer into the vadose zone, carrying organic material into the vadose zone encouraging microorganism degradation of BTEX molecules.

NETTS is looking at the ability of air sparging systems to send the air through the aquifer to assist in remediation of MTBE. Although final data has not been published, it appears to eliminate all MTBE within the air sparging unit itself by just pumping air into the aquifer. A paradigm report will be published this summer, presenting air sparging, design, placing of the wells, and how much air to pulse. Since this aquifer is anaerobic and shallow (9'-21' bgs) the microorganisms are encouraged to degrade the MTBE when oxygen is added to the system.

BIOBARRIERS

Equilon

A demonstration is being conducted by Equilon Enterprises and Arizona State University and is the first of its kind to test the treatment of MTBE using isolated ether-degrading microbes, MC-100 (formerly BC-4), as an in-situ biobarrier to downgradient MTBE migration. A biomass slurry suspension (MC-100 culture) has been injected into the dissolved MTBE portion of the NEX plume in an oxygenated aquifer environment. MTBE concentrations in this area of the plume range from 2,000 to 10,000 µg/L and there are no other contaminants present. The demonstration layout includes several 20' x 40' test cells aligned with the direction of groundwater flow (Figure G-2, next page). Each test cell contains thirty-two strategically placed monitoring wells both up and down gradient of the treatment zone to collect groundwater samples for laboratory analysis.

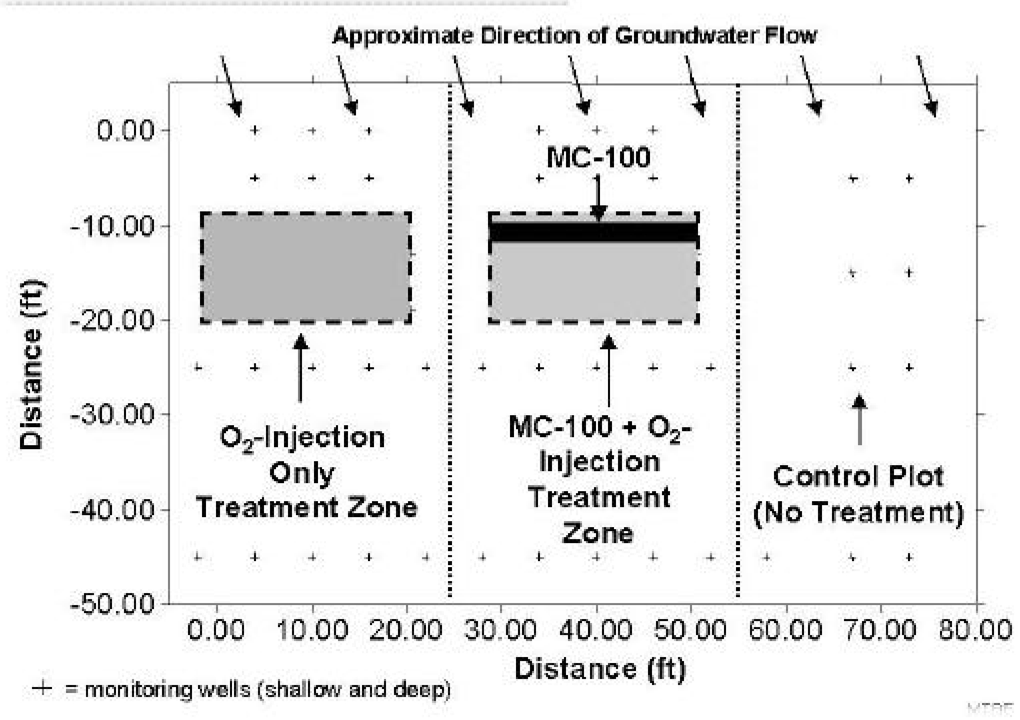

Figure G-2 Biobarrier Field Test Layout

This investigation has led to the future placement of additional bacterial injection test plots in the NEX plume, including one using a pure strain (PC-100) of an isolated ether-degrading microbe from the MC-100 culture. Some of these new plots will be evaluated using injected air, rather than oxygen, to support microbial growth and remediation of MTBE. Some of these new plots will also test various oxygen delivery methods. These new injections occurred last spring.

Bacteria was injected by driving the injector all the way down, close to the aquitard, injecting bacteria, moving up the injection well, injecting more bacteria, moving further up the injection well, injecting more bacteria, and so on until the surface is reached. Approximately one gallon of bacteria is inserted per injection. This attempt to enrich the contaminated aquifer, actually creates a biobarrier.

This demonstration employs bacterial injection in one plot, and an oxygen only plot. The oxygen only plot took about 290 days for the indigenous organisms to start breaking down the MTBE. This demonstrates that there is good microbial breakdown of MTBE under oxygen conditions.

Some downstream monitoring wells contain higher MTBE concentrations than others. This could be due to the pilot test only being 30’ wide rather than 500’ wide (the width of the plume). We are hoping to verify this with a series of monitoring wells. This should also address whether MTBE is remaining at a low µg/L concentrations, with a large enough barrier going across.

UC Davis

University of California Davis ran similar studies to Equilon with the bacterial culture PM-1, oxygen only and air only injections.

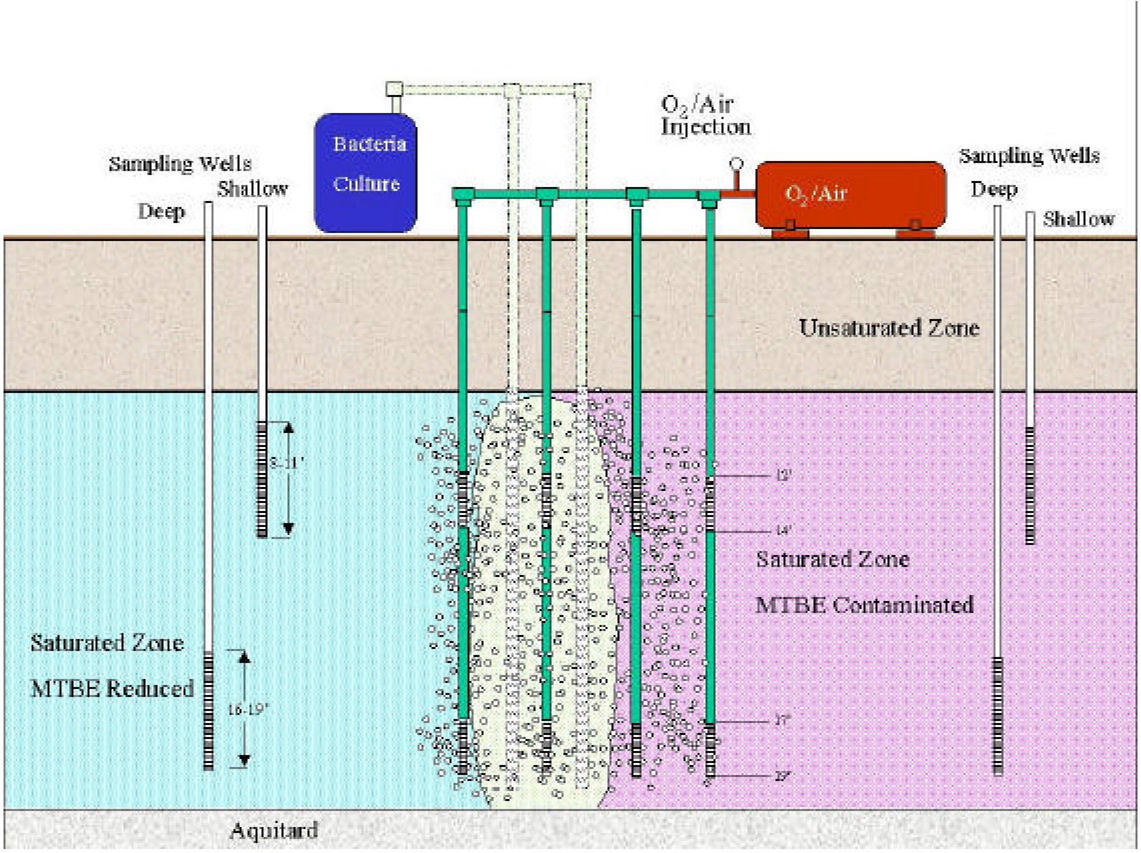

Figure G-3. Bacterial Injection

The University of California (UC) at Davis and the University of Waterloo are conducting a field study in the NEX plume to investigate the feasibility of using in-situ bioaugmentation with a pure bacterial culture to reduce concentrations of MTBE. UC Davis isolated the bacterial culture, PM1, from a field-operated biofilter at the Joint Water Pollution Control Plant of the Los Angeles County Sanitation District. PM1 is able to utilize MTBE as its sole carbon and energy source.

Three test plots have been installed at the PM1 injection site as follows: (1) PM1 culture injection with oxygen sparging, (2) oxygen sparging only, and (3) air sparging only. Each plot is 9’ by 4.5’ and perpendicular to groundwater flow. Separation distances between each plot are sufficient to prevent cross-contamination. Thirty monitoring wells have been installed within each test plot up and down gradient of the injection locations to determine changes to the water once it has passed through the test area.

The main objective of this study is to determine if a bacterial culture injected into groundwater can effectively degrade MTBE under field conditions. Also analyzed will be the differences between the injected MTBE biodegrading culture and the indigenous microorganisms in the anaerobic aquifer environment of the NEX plume once they are given either oxygen or air for growth enhancement.

MONITORED NATURAL ATTENUATION TRACER TESTS

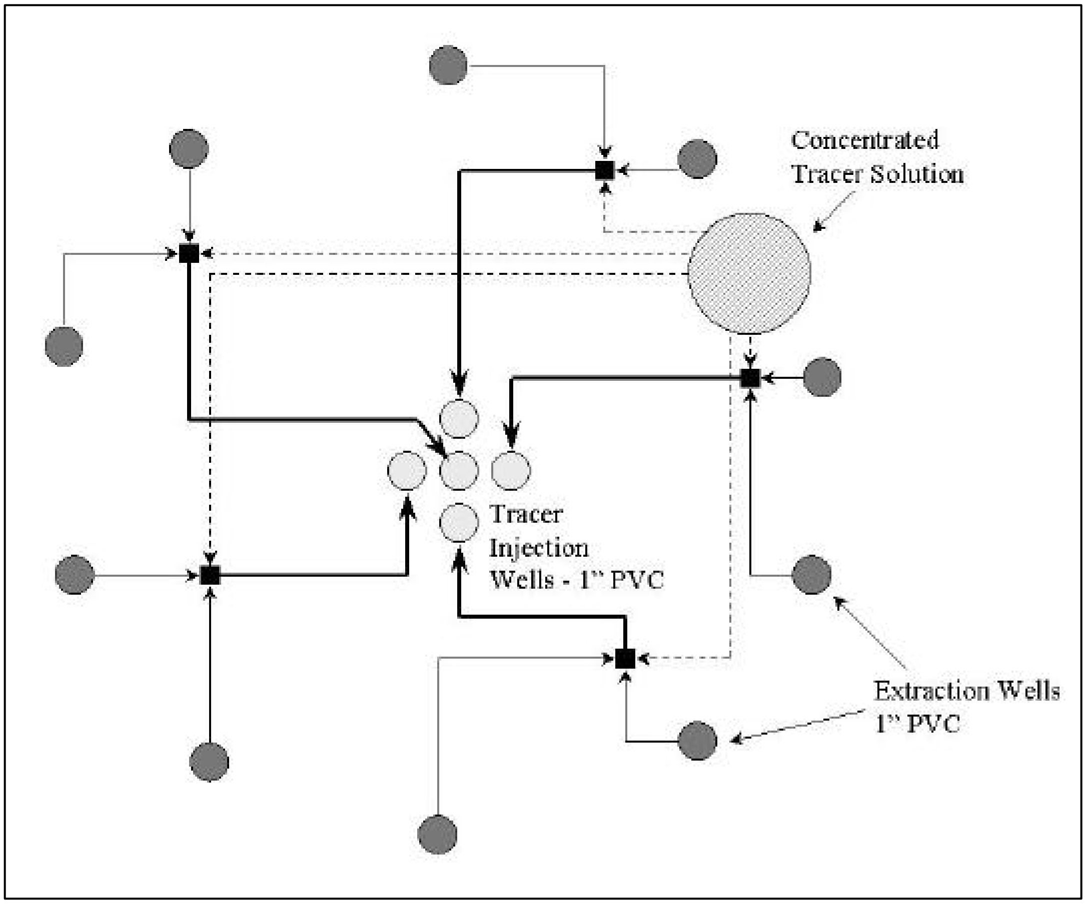

Figure G-4. Tracer Test Injection Well Configuration

To measure natural attenuation of MTBE in the NEX plume, the Oregon Graduate Institute and Arizona State University are conducting a study which employs a custom chemical solution of deuterated MTBE (2H12 –MTBE) as a tracer in the existing fuel hydrocarbon plume. The target concentration of 2H12-MTBE within the tracer plume was 1 mg/L, see Figure G-4. Because deuterated molecules are slightly heavier than normal molecules, the tracer and its degradation products can be distinguished from existing MTBE (1H12-MTBE) molecules in the plume by differences in their weight using a gas chromatograph with a mass selective detector. Bromide (NaBr), which has water solubility similar to MTBE, was added at a concentration similar to the concentration of the tracer, but as a conservative tracer (non-volatile, non-biodegradable) compound with which the measurable mass of tracer MTBE could be compared. Fluorescein dye was added to provide an indication that 2H12-MTBE and NaBr might be present in the groundwater.

The distribution and concentration of the 2H12-MTBE and bromide within the MTBE plume were characterized using temporary sampling points after four months, eight months, one year, and two years of plume migration. At each sampling point, samples have been collected at a minimum of five discrete depths to determine the vertical distribution of the tracer plume. Results of the bromide analysis and any presence of fluorescein are being used to further refine the sampling density within the plume. Figure G-5 shows the movement of the tracer over a 15-month time period.

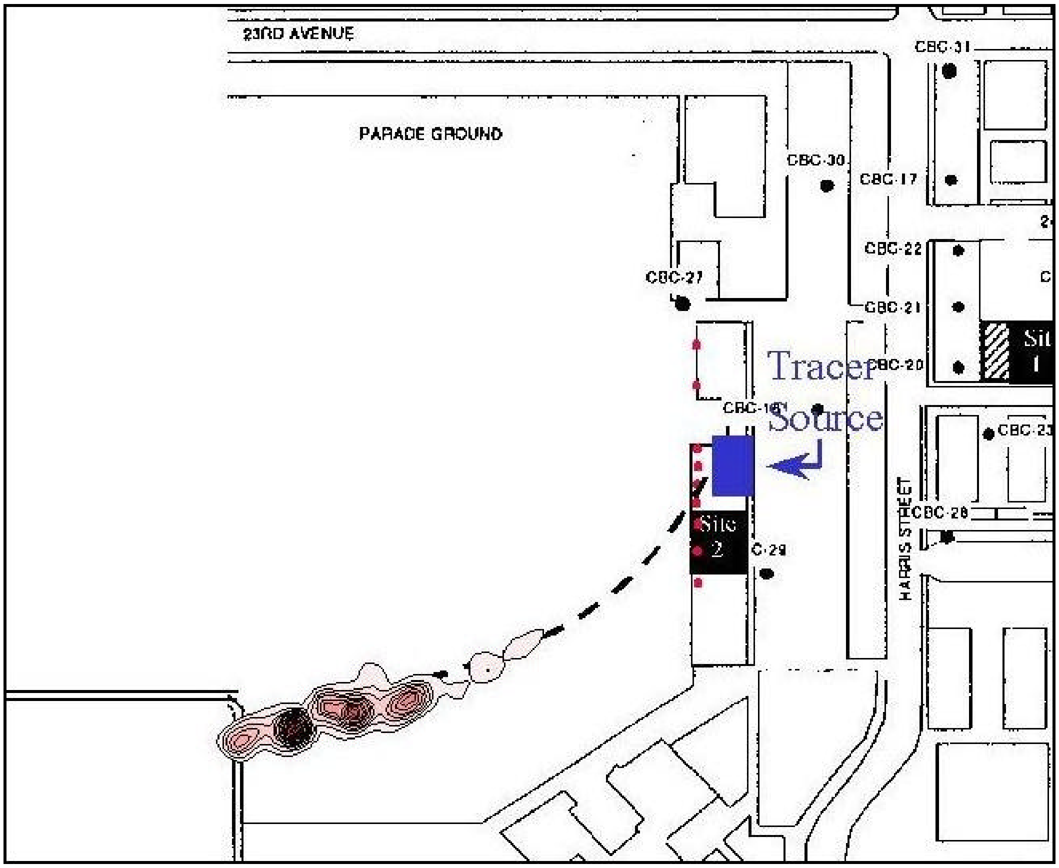

Figure G-5. Pathway of MTBE

When samples were taken, perdeuterated TBA, metabolic product, as well as bacteria cells with deuterated molecules were not recovered. Because of their findings it was determined that MTBE was not naturally attenuating in the aquifer at that time. However, Dr. John Wilson, US EPA came through and performed a number of pushes and collected water samples to evaluate whether methanogenic breakdown of the MTBE was occurring. He found that indigenous microorganisms would breakdown MTBE molecules to a certain point. Then the methane producing bacteria would take it down the rest of the way to water. He felt there was some methanogenic breakdown of the MTBE.

PHYTOREMEDIATION

Lab studies performed by the University of Washington show that eucalyptus uptake and transpire MTBE. The eucalyptus tree within the NETTS MTBE plume is located near the NEX Gas Station. Groundwater samples verify that the tree is located within the MTBE plume, and indicate that MTBE concentrations are lower on the downstream side of the tree. Leaf bag analysis (transpiration measurements), leaf and branch tissue analysis, and plant tissue coring samples yield no findings of MTBE or its break down products. Subsequently, it appears that the tree is either remediating MTBE in the rhizosphere, as the MTBE concentrations are affected in the groundwater, or that the size and maturity of the tree, with the low concentrations of MTBE in groundwater, allow the tree to break down the MTBE to untraceable levels.

Appendix H: MTBE and BTEX in Trees Above Gasoline-Contaminated Groundwater

*Preprint of Paper to be published in Proceedings of the "Remediation of Chlorinated and Recalcitrant Compounds"
Battelle Conference, May 22-25, 2000, Monterey, CA.*

MTBE AND BTEX IN TREES ABOVE GASOLINE-CONTAMINATED GROUND WATER

James E. Landmeyer (U.S. Geological Survey, Columbia, SC)
Don A. Vroblesky and Paul M. Bradley (U.S. Geological Survey, Columbia, SC)

ABSTRACT: The fuel oxygenate compound methyl *tert*-butyl ether (MTBE) and the conventional gasoline compounds benzene, toluene, ethylbenzene, and the isomers of xylene and trimethylbenzene were detected and identified using purge-and-trap gas chromatography/mass spectrometry methods in core material of mature live oak trees (*Quercus* virginiana) located above a gasoline-contaminated shallow aquifer. Conversely, these gasoline compounds were not detected in core material of oaks located outside of the gasoline plume. This detection of gasoline compounds in trees at a contaminated field site is important, particularly for the more soluble and less biodegradable compounds MTBE and benzene, because it provides unequivocal field evidence that trees can act as sinks to remove contaminants from ground-water systems.

INTRODUCTION

Results of laboratory-scale studies have suggested that herbaceous and woody plants have the potential to take up a variety of dissolved petroleum-derived compounds during transpiration. For example, it has been recognized for some time that pesticide uptake can occur in a wide variety of non-woody plants, including barley (Schone and Wood, 1972; Donaldson et al., 1973; Briggs and Bromilow, 1982), bean (Lichtner, 1983), corn (Darmstadt et al., 1983; Leroux and Gredt, 1977; Upadhyaya and Nooden, 1980), peanuts (Hawxby et al., 1972), and soybeans (Moody et al., 1970; McFarlane et al., 1987; McCrady et al., 1987). For woody plants, Burken and Schnoor (1997) demonstrated the uptake and metabolism of the widely used herbicide atrazine by poplar trees (*Populus deltoides*). Additionally, a preliminary report (Newman et al., 1999) indicated that poplar (*Populus spp.*) and eucalyptus (*Eucalyptus spp.*) could take up the fuel oxygenate compound methyl *tert*-butyl ether (MTBE) under laboratory conditions. More recently, Burken and Schnoor (1998) reported the uptake, translocation, and volatilization of the common ground-water contaminants benzene, toluene, ethylbenzene, and xylene (BTEX) by poplar cuttings in short-term hydroponic experiments in the lab. Their results confirm that the relative ease of compound uptake is related to the logarithm of the octanol-water partition coefficient (log K_{ow}), as stated initially by Briggs et al. (1982). Essentially, compounds having log K_{ow}'s between 0.5-3.0 are preferentially taken up by roots. Because the log K_{ow}'s of the ground-water contaminants MTBE, benzene, toluene, ethylbenzene, o-xylene, m-xylene, and p-xylene are within this range (1.20, 2.13, 2.65, 3.13, 2.95, 3.20, and 3.18, respectively), their uptake during laboratory transpiration studies is not surprising.

However, the uptake of these gasoline compounds by mature trees has not been documented under field conditions. For example, in the study cited above (Burken and Schnoor, 1998) that indicated uptake of MTBE by poplar (*Populus spp.*) and eucalyptus (*Eucalyptus spp.*) cuttings under laboratory conditions, no MTBE uptake was measured in mature trees at an MTBE contaminated site. This current study was undertaken, therefore, to determine if the soluble fuel compounds MTBE, benzene, toluene, ethylbenzene, and o-, m-, and p-xylenes shown to be taken up under laboratory conditions are present in mature live oaks growing above gasoline-contaminated ground water.

Study Site. The study site is a gasoline station (Figure 1) near Beaufort, South Carolina (SC). Fuel-oxygenated gasoline from a leaking underground storage tank was detected in the shallow, water-table aquifer in late 1991(Landmeyer et al., 1996). The water-table aquifer is comprised of well-sorted sand grains of Pleistocene to Holocene age. The water-table aquifer is underlain by a regional clay-rich confining unit at around 45 feet (ft) (13.7 m). There is less than 0.01% natural sedimentary organic matter in the sandy aquifer. The depth to water is about 13 ft (3.9 m) near the release area, and from 9 to 2 ft (2.7 to 0.6 m) near a drainage ditch approximately 700 ft (215 m) downgradient (Figure 1) of the release area. Recharge to the water-table aquifer is by rainwater infiltration, with precipitation approaching 60 inches per year (in/yr) (132 cm/yr).

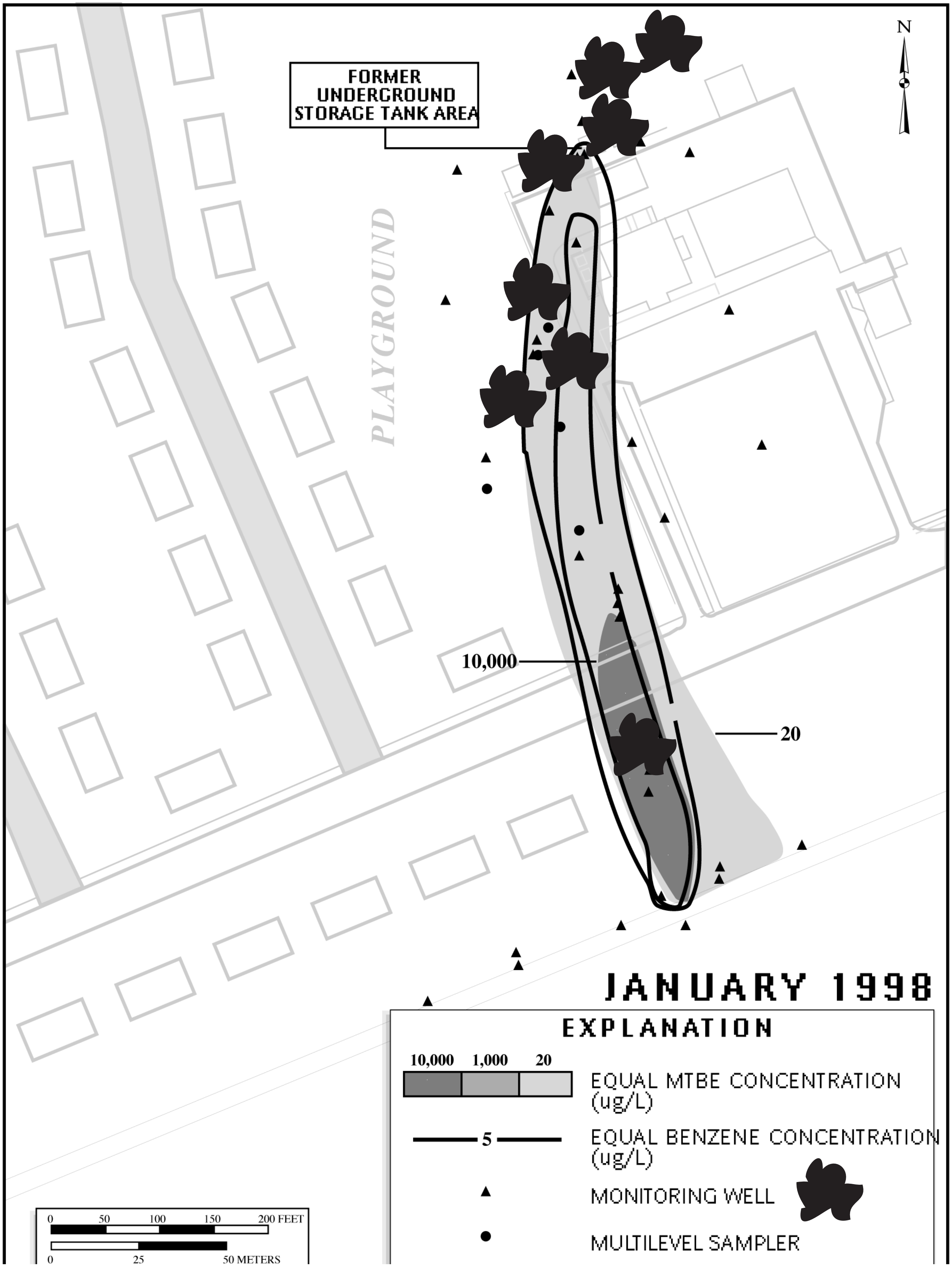

FIGURE 1. Study site near Beaufort, South Carolina, indicating location and reference number of tree samples, monitoring wells mentioned in text, and isoconcentration contours of MTBE and benzene in ground water (collected January 1998).

The study site is characterized by a dense stand of mature (>40 years old) live oak trees (*Quercus* virginiana) (Figure 1). Live oaks derive their common name from their ability to maintain leaves throughout winter, even though they are deciduous. As a result, live oaks transpire water continually throughout the year, and therefore are an excellent genus to study transpiration-related processes. The trees at the site have well-developed and extensive networks of horizontal and vertical roots, as evidenced by conspicuous root material at land surface some distance from tree trunks, and the presence of observable root material at the water table in boreholes completed near trees.

METHODS

Ground-Water Geochemistry. The distribution of gasoline compounds as well as geochemical parameters that indicate the redox zonations at the site have been documented over seven sampling events between 1993 and 1998 (Landmeyer et al., 1996; Landmeyer et al., 1998). However, only the gasoline compound distribution will be discussed here. Conventional poly-vinyl chloride (PVC) monitoring wells (2-inch [4.4 cm] diameter, screened across or below the water table with 12.5 ft [3.8 m] screens) and multi-level sampling wells (1-inch [2.2 cm] diameter, with variably spaced screened intervals) were analyzed for MTBE and BTEX at each sampling event. Before sampling, each well was purged until stable measurements of water temperature (in°Celsius) and pH (in standard units) were obtained. MTBE and BTEX samples were collected in 40-mL glass vials using a peristaltic pump at a low flow rate, preserved with 3 drops of concentrated HCl, and capped using Teflon-lined septa. BTEX compounds were quantified using purge-and-trap gas chromatography with flame-ionization detection. MTBE was quantified using direct-aqueous injection gas chromatography with mass spectrometry detection by the Oregon Graduate Institute (Church et al., 1997).

Tree-Core Sample Collection and Analysis. Cores of tree tissue were obtained from trees located in uncontaminated areas upgradient of the ground-water source area and plume, and from trees growing in the area delineated by dissolved-phase ground-water contamination (Figure 1) using an increment borer in mid-June 1999. Tree coring methods have been used previously to determine the presence of chlorinated solvents (Vroblesky et al., 1999) and metals (Forget and Zayed, 1995) in tree rings. Cores were collected at a height of 1 ft (0.3 m) above ground on the northeast side of each tree. Replicate cores about 2 inches apart were taken at each tree sampled. The average core collected was about 2.0 inches by 1/4 inch (volume of 0.09 in^3) (4 cm by 0.5 cm; volume of 0.72 cm^3), and consisted of the most recent growth rings, which contain the water-conducting xylem in ring-porous trees such as oaks. Each core was immediately placed into a 40 mL glass vial and capped with a Teflon stopper. At the time of sampling, the air temperature was about 85°F, skies were sunny, winds were from the West at 5 miles per hour (mph) and low relative humidity (<60%). Because the site is an active gas station, air samples for gasoline compound detection were also collected in 40 mL glass vials, after waving an open vial for a few seconds near the contaminated area downgradient of the fuel release.

In the laboratory, the volatile organic compounds in the tree core were separated and identified using a purge-and-trap GC/MS method similar to U.S. EPA method 8260. Prior to purging of each sample, 5 mL of pesticide-grade methanol was added to each 40-mL vial containing core material, and brought to a final volume of 25 mL using organic-free reagent water. Each vial was then purged with helium, the volatile compounds trapped in a tube containing sorbent material, and manually injected onto a 30 m, 0.25 mm inside diameter capillary column coated with Rtx 502.2 (RESTEK) at a 1.4 µm film thickness. Identification of target gasoline compounds was confirmed by comparing sample mass spectra to the mass spectra of reference material from the National Institute of Standards and Technology under identical run conditions. Three internal standards (fluorobenzene, 2-bromo-1-chloropropane, and 1,4-dichlorobutane) and three surrogate standards (1,4-difluorobenzene, d_8-toluene, 4-bromofluorobenzene) were used. Surrogate recoveries ranged between 93 and 100%. Target compound concentrations are reported as concentrations in µg/L in the headspace of vials containing core material.

RESULTS AND DISCUSSION

MTBE and BTEX Detection in Tree Cores. MTBE, benzene, toluene, ethylbenzene, and the xylene isomers were not detected in the headspace samples of core material collected from oaks growing hydrologically upgradient of the release area (Table 1, Trees 1 and 2; Figure 1). Trees 1 and 2 are located about 146 ft (46 m) and 136 ft (45 m) north of well 5, respectively (Figure 1). Well 5 is located about 75 ft (35 m) upgradient of the release area, screened across the water table, and MTBE and BTEX concentrations there have remained below detection since monitoring activities began at the site in 1993 (Landmeyer et al., 1998).

However, MTBE, benzene, toluene, ethylbenzene, and the xylene isomers were detected in the headspace of core samples taken from trees growing above the former source area (Table 1, Trees 3 and 4; Figure 1) and the delineated plume of ground-water contamination (Table 1, Trees 5 and 6; Figure 1). Headspace samples of core material from Tree 3 had detections for toluene at 5.4 µg/L, and Tree 4 had no toluene but m-,p-xylene (5 µg/L total), and o-xylene (6.3 µg/L) were detected. These detections in Trees 3 and 4 are related to the residual contamination in the former source area due to incomplete removal of contaminated sediments in 1993 (Landmeyer et al., 1998). This incomplete removal of source-area material has also caused a “wake” of dissolved-phase contamination to continue to be observed between the source area and downgradient wells in the direction of ground-water flow even 6 years after source removal activities (Figure 1).

Headspace samples of core material from live oaks sampled in the area delineated by gasoline compounds downgradient of the former source area contained chromatographic peaks confirmed by MS to be MTBE, benzene, toluene, ethylbenzene, and the xylene and TMB isomers (Table 1, Trees 5 and 6; Figure 1). For example, headspace samples of core material from Tree 6, located about 11 ft (4 m) east of well 8 (Figure 1), had 54.0 µg/L MTBE, 4.8 µg/L benzene, 10.1 µg/L toluene, 8.5 µg/L ethylbenzene, 10.8 µg/L m and p-xylene, 7.4 µg/L o-xylene, 6.1 µg/L 1,3,5-TMB, and 5.4 µg/L 1,2,4-TMB. The concentration of MTBE in Tree 6 was the highest detected of all trees cored. Tree 5 adjacent to Tree 6 had the highest detection of toluene (26.2 µg/L). In August 1998, samples of ground water from well 8, which is screened across the water table in the area where root penetration has been observed, had 5,800 µg/L MTBE, 508 µg/L benzene, 674 µg/L toluene, 149 µg/L ethylbenzene, and 580 µg/L total xylenes (author, unpublished data). This detection of MTBE and benzene in transpiration-stream water of a mature tree at a contaminated field site is to our knowledge the first field-scale confirmation of laboratory-scale experimental data. Headspace samples of air collected from this area did not contain peak responses representative of MTBE, benzene, toluene, ethylbenzene, or the isomers of xylene or TMB (data not shown).

TABLE 1. Concentrations (in µg/L) of the gasoline compounds MTBE, benzene, toluene, ethylbenzene, and the isomers of xylene and trimethylbenzene (TMB) in the headspace of vials containing tree cores collected at a field site near Beaufort, South Carolina, June 1999. Non detection is represented by nd, not analyzed by na.

Compound	**Upgradient of Former Source Area**		**Former Source Area**		**Dissolved-Phase Plume**		**Vertical Flow Area**	
	Tree 1	**Tree 2**	**Tree 3**	**Tree 4**	**Tree 5**	**Tree 6**	**Well 8**	**Tree 7**
MTBE nd	nd	nd	nd	nd	9.4	54	5,800	nd
Benzene	nd	nd	nd	nd	7.2	4.8	508	nd
Toluene	nd	nd	5.4	nd	26.2	10.1	674	nd
Ethylbenzene	nd	nd	nd	nd	nd	8.5	149	nd
m,p-Xylene	nd	nd	nd	5.0	10.1	10.8	580	nd
o-Xylene	nd	nd	nd	6.3	5.6	7.4		nd
1,3,5-TMB	nd	nd	nd	nd	7.8	6.1	na	nd
1,2,4-TMB	nd	nd	6.0	19.6	5.3	5.4	na	nd

No compound detection for MTBE and BTEX were seen in headspace samples of core material from Tree 7 (Table 1), even though this tree is located downgradient of the release area. This lack of compound detection can be explained by the location of Tree 7 being (1) at the edge of the delineated plume boundary (Figure 1), which probably results in the majority of transpiration water being derived from uncontaminated ground water, and (2) in an area where dissovled-phase contamination originally near the water-table surface is pushed deeper into the aquifer by vertical recharge of percolating rainwater (Landmeyer et al., 1998). This vertical displacement of the dissolved-phase plume deeper into the aquifer away from root interaction is why no trees were cored downgradient of Tree 7.

As stated above, the trimethylbenzene isomers 1,3,5-TMB and 1,2,4-TMB were also identified in the cored material in Trees 3, 4, 5, and 6 located above the original source area and delineated dissolved-phase plume (Table 1). The TMB isomers are common components of gasoline, and because their solubility and sorption characteristics are similar to benzene and toluene, these relatively nonbiodegradable isomers are routinely used as conservative tracers to estimate biodegradation rates of aromatic hydrocarbons from field data (Weidemeier et al., 1997). The detection of the TMB isomers in transpiration stream water follows from a log K_{ow} of 3.78 for 1,2,4-TMB. The fact that trees can remove TMB isomers from contaminated ground water needs to be considered if TMB isomers are to be used as conservative tracers in ground-water studies of contaminant transport.

The chlorinated compounds chloroform and methyl chloride were detected in trees cores collected in uncontaminated and contaminated areas. Chloroform concentrations in the headspace of vials containing tree cores ranged from 18.7 to 89.1 µg/L, and methyl chloride concentrations ranged from 20.1 to 63.3 µg/L (data not shown). Chloroform and methyl chloride have log K_{ow}'s that would suggest uptake by trees (1.90 and 0.90, respectively). Their detection in tree cores suggests that the most likely source is chlorinated irrigation water. A nationwide survey of 1501 shallow ground-water samples conducted by the U.S. Geological Survey indicated that chloroform was the most commonly detected volatile organic compound in shallow wells (Squillace et al., 1996).

The detection of the common ground-water contaminants MTBE, BTEX, and the TMB isomers in mature trees that grow above a shallow aquifer characterized by a fuel spill is important, because it extends laboratory-scale observations to real field sites. These results suggest the possible use of trees to remove soluble gasoline-related compounds such as MTBE and benzene from contaminated ground-water systems. The transpiration process of trees requires large volumes of water (up to 53 gal/day for 5-year old trees [Newman et al., 1997]) to balance transpiration losses. Although trees most commonly use recent rainfall to meet short-term water demands, ground water can provide water during times of low precipitation to meet longer-term needs. Because tree-root systems often contact the water-table surface, the potential exists for sources of contaminants containing non-aqueous phase liquids, such as petroleum hydrocarbon compounds and chlorinated solvents dissolved in ground water to come into contact with tree roots, particularly in discharge zones where ground-water flowlines converge to bring even the denser chlorinated compounds to the surface. Results from our study suggest that trees exhibit the potential to uptake synthetic organic compounds dissolved in ground water, particularly those gasoline-related compounds that are accidentally released into the environment. It is not yet clear whether uptake of soluble ground-water contaminants by trees may serve to remove substantial amounts of hydrocarbons from contaminated ground- water systems. However, these results show that contaminant uptake occurs in measurable quantities, and suggest that this phenomenon may have important environmental applications.

ACKNOWLEDGMENTS

This study was supported by the U.S. Geological Survey's Toxic Substances Hydrology Program, the Southern Division, Naval Facilities Engineering Command, and the Marine Corps Air Station Beaufort, South Carolina.

REFERENCES

Briggs, G.G., R.H. Bromilow, and A.A. Evans. 1982. *Pesticide Science*. 13, 495-504.

Burken, J.G. and J.L. Schnoor. 1997. *Environmental Science & Technology*. 31,1399-1406.

Burken, J.G. and J.L. Schnoor. 1998. "Predictive relationships for uptake of organic contaminants by hybrid poplar trees." *Environmental Science & Technology*. 32, 3379-3385.

Church, C.D., L.M. Isabelle, J.F. Pankow, D.L. Rose, and P.G. Tratnyek. 1997. "Method for determination of methyl tert-butyl ether and its degradation products in water." *Environmental Science & Technology*. 31, 3723-3726.

Darmstadt, G.L., N.E. Balke, and L.E. Schrader. 1983. *Pesticide Biochem. Physiology,* 19, 172-183.

Donaldson, T.W., D.E. Bayer, and O.A. Leonard. 1973. *Plant Physiology,* 52, 638-645.

Forget, E. and J. Zayed. 1995. "Tree-ring analysis for monitoring pollution by metals," in *Tree rings as indicators of ecosystem health*, Lewis, T.E., Eds., CRC Press, 157-176.

Hawxby, K., E. Basler, and P.W. Santelmann. 1972. *Weed Science,* 20, 285-289.

Landmeyer, J.E., F.H. Chapelle, and P.M. Bradley. 1996. "Assessment of intrinsic bioremediation of gasoline contamination in the shallow aquifer, Laurel Bay Exchange, Marine Corps Air Station Beaufort, South Carolina." *U.S. Geological Survey Water-Resources Investigations Report 96-4026,* 50 p.

Landmeyer, J.E.; F.H. Chapelle, P.M. Bradley, J.F. Pankow, C.D. Church, and P.G. Tratnyek. 1998. "Fate of MTBE relative to benzene in a gasoline-contaminated aquifer (1993-1998)." *Ground Water Mon. & Remed.* 18, 93-102.

Leroux, P. and M. Gredt. 1977. *Neth. Journal Plant Pathol.* 83, 51-61.

Lichtner, F.T. 1983. *Plant Physiology, 71*, 307-312.

McCrady, J.K., C. McFarlane, and F.T. Lindstrom. 1987. *J. Experimental Botany,* 38, 1875-1890.

McFarlane, J.C., T. Pfleeger, and J. Fletcher. 1987. *J. Environ. Quality*, 16, 372-376.
Moody, K., Kust, C.A., Buchholtz, D.P. 1970. *Weed Science,* 18, 642-647.

Newman, L., S. Strand, J. Duffy, G. Ekuan, M. Raszaj, B. Shurtleff, J. Wilmoth, P. Heilman, and M. Gordon. 1997. *Environmental Science & Technology*. 31,1062-1067.

Newman, L.A., M.P. Gordon, P. Heilman, D.L. Cannon, E. Lory, K. Miller, J. Osgood, and S.E. Strand. 1999. "Phytoremediation of MTBE at a California naval site." *Soil & Groundwater Cleanup*. 42-45.

Schone, M.G.T. and A.V. Wood. 1972. *Weed Research*. 12, 337-347.

Squillace, P.J., J.S. Zogorski, W.G. Wilber, and C.V. Price. 1996. *Environ. Sci. & Tech*. 30, 1721-1730.

Upadhyaya, M.K. and L.D. Nooden. 1980. *Plant Physiology,* 66,1048-1052.

Vroblesky, D.A., C.T. Nietch, and J.T. Morris. 1999. "Chlorinated ethenes from groundwater in tree trunks." *Environ. Science & Technol*. 33,510-515.

Weidemeier, T.H., M.A. Swanson, J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. in *Intrinsic Bioremediation*, Battelle Press. 3(1), 31-51.

Appendix I: Additional References Available Through NFESC

MTBE RERENCES

1. The Presence of MTBE and Other Gasoline Compounds in Maine's Drinking Water: A Preliminary Report Maine Departments of Human Services, Environmental Protection and Conservation. October 13, 1998.

2. Health & Environmental Assessment of MTBE, Volume 1, John Froines, University of California, Davis, Arturo Keller, University of California Santa Barbara, et al. November 1998.

3. Margo T. Oge Director, Office of Mobile Sources, U.S. Environmental Protection Agency, Presentation before the Committee on Energy and Environment of the Committee on Science, U.S. House of Representatives September 14, 1999.

4. Achieving Clean Air and Clean Water: The Report of the Blue Ribbon Panel on Oxygenates in Gasoline (appointed by U.S. EPA Administrator, Carole M. Browner), EPA 420-R-99-021, September 15, 1999.

5. Summary of Dissenting Opinion, Achieving Clean Air and Clean Water: The Report of the Blue Ribbon Panel on Oxygenates in Gasoline, Todd C. Sneller, Member, Blue Ribbon Panel, September 1999.

6. MTBE in Drinking Water: Surface Water Sources/Ground Water Sources (California), California Department of Health Services, May 8, 2000.

7. Acute Testicular Toxicity of MTBE and Breakdown Products in Lab Mice, JE Billitti, BC.Faulkner and BE Wilson, Animal Sciences Department, University of California, Davis

8. Strategies for Characterizing Subsurface Releases of Gasoline Containing MTBE American Petroleum Institute, Regulatory and Scientific Affairs, Publication Number 4699, February 2000.

9. MTBE and BTEX in Trees Above Gasoline-Contaminated Ground Water, James E. Landmeyer, USGS, Preprint of Paper to be published in Proceedings of the "Remediation of Chlorinated and Recalcitrant Compounds" Battelle Conference, May 22-25, 2000.

10. Fate of MTBE Relative to Benzene in a Gasoline-Contaminated Aquifer (1993-98) James E. Landmeyer, USGS, Reprinted from Ground Water Monitoring & Remediation, Vol.18, No. 4, Fall 1998.

11. Aerobic Mineralization of MTBE and *tert*-Butyl Alcohol by Stream-Bed Sediment Microorganisms, Paul M. Bradley, James Landmeyer, Francis Chapelle, USGS, Environmental Science and Technology, Volume 33, pages 1877-1879, 1999.

12. MTBE in Drinking Water, (Fact Sheet) U.S. EPA Office of Water, Office of Ground Water and Drinking Water, http://www.epa.gov/safewater/mtbe.html.

13. MTBE and Drinking Water, (Memorandum from Chuck Fox, Assistant Administrator for Water, U.S.EPA dated 4/3/00) http://www.epa.gov/safewater/protect/pmtbe.html.

14. MTBE and Underground Storage Tanks U.S. EPA Office of Underground Storage Tanks (Fact Sheet), http://www.epa.gov/swerust1/mtbe/.

15. Drinking Water Advisory: *Fact Sheet* Consumer Acceptability Advice and Health Effects Analysis on Methyl Tertiary-Butyl Ether (MtBE), U.S. EPA Office of Water, EPA-822-F-97-009, December 1997.

16. Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl Tertiary-Butyl Ether (MtBE), U.S. EPA Office of Water, EPA-822-F-97-009, December 1997 (support document for Fact Sheet).

17. Congressional Research Service, The Library of Congress (CRS), Report for Congress MTBE in Gasoline: Clean Air and Drinking Water Issues, James E. McCarthy and Mary Tiemann, updated February 25, 2000.

18. Methyl Tertiary-Butyl Ether (MTBE) Overview, Walter Swain, United States Geological Survey, May 2, 2000. http://water.wr.usgs.gov/mtbe/

19. Human health effects from exposure to gasoline containing methyl-tertiary-butyl ether, M.A. Mehlman, Agency for Toxic Substances and Disease Registry (ATSDR), Environmental Journal of Oncology, Volume 3, Number 3, pages 171-189, 1998.

20. An Evaluation of the Scientific Peer-Reviewed Research and Literature on the Human Health Effects of MTBE, its Metabolites, Combustion Products and Substitute Compounds, John R. Froines, Ph.D. et al.

21. Toxicity of MTBE to Freshwater Organisms, Inge Werner and David E. Hinton, School of Veterinary Medicine, University of California, Davis.

22. Ecological Risk of MTBE in Surface Waters, Michael L. Johnson, John Muir Institute of the Environment, University of California, Davis.

23. MTBE: Evaluation of Management Options for Water Supply and Ecosystem Impacts Orit Kalman and Dr, Jay R. Lund, Department of Civil and Environmental Engineering, University of California, Davis, Draft Report October 16, 1998.

24. MTBE Groundwater Clean-up Levels for LUST Sites: Current & Proposed (map) http://www.epa.gov/swerust1/mtbe/mtbemap.htm

25. Final Statement of Reasons, Primary Maximum Containment Level for Methyl tert-Butyl,Title 22, California Code of Regulations, R-8-99, February 2000.

26. Final Statement of Reasons, Secondary Maximum Containment Level for Methyl tert-Butyl Ether and Revisions to the Unregulated Chemical Monitoring List, Title 22, California Code of Regulations, R-44-97.

27. Response to Public Comments on R-44-97 (Final Statement of Reasons, Secondary Maximum Containment Level for Methyl tert-Butyl Ether and Revisions to the Unregulated Chemical Monitoring List), California.

28. Health & Environmental Assessment of MTBE, Report to the Governor and Legislature of the State of California as Sponsored by SB 521, Volume 1, Summary and Recommendations, Arturo Keller, Ph.D., et al., November 1998.

29. Impacts of MTBE on California Groundwater, Graham E. Fogg et al., Hydrologic Sciences, Department of Land, Air and Water Resources, University of California, Davis.

30. An Evaluation of MTBE Impacts to California Groundwater Resources, Lawrence Livermore National Laboratory, University of California, Anne M. Happel et al., Report Submitted to the California State Water Resources Control Board, June 11, 1998.

31. Exposure of Humans to MTBE from Drinking Water, Michael L. Johnson, John Muir Institute of the Environment, University of California, Davis.

32. UC Report: MTBE Fact Sheet, November 12, 1998.

33. MTBE and BTEX in Trees above Gasoline-Contaminated Groundwater; James E. Landmeyer, Don A. Vroblesky, and Paul M. Bradley, USGS, Columbia, SC.

34. An Analysis of Air Sparging for Chlorinated Solvent Sites, Remediation of Chlorinated and Recalcitrant Compounds Volume C1-1, Physical, Chemical, and Thermal Technologies. Richard A. Brown, Fluor Daniel GTI, NJ, USA; David H. Bass, Fluor Daniel GTI, MA, USA, and Wilson Clayton, Fluor Daniel GTI, CO, USA.

35. Assessment of MTBE Discharge Impacts on California Marine Water Quality. Steven M. Bay and Jeffrey S. Brown, Southern California Coastal Water Research Project, Westminster, CA, State Water Resources Control Board California, February 4, 2000.