

# Oxygenate Contamination

## WORKSHOP REPORT

PRESENTED BY  
National Water Research Institute

IN COOPERATION WITH  
California Department of Health Services

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California State Polytechnic University  
Pomona, California

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## FOREWORD

Since the National Water Research Institute (NWRI) was founded in 1991, it has sponsored over 120 projects in 14 states, on 22 university campuses, and in 17 utility and/or industrial laboratories. Those projects represent a total research investment of over \$26 million.

As part of its research development activities, NWRI utilizes the Nominal Group Technique (NGT) method that was created in 1968 by Andre L. Delbecq (University of Santa Clara). NWRI has modified the original method so that, today, the NGT method is an intensive experience that provides a rich and robust opportunity for participants to explore issues and reach consensus.

Under its Center for Groundwater Restoration and Protection, NWRI has managed the California MTBE Research Partnership (Partnership) since 1998. The Partnership has invested nearly \$1 million in its research program, which has addressed the most critical issues facing water utilities regarding oxygenate contamination. The results of this research are published in a series of peer-reviewed documents by NWRI. The Partnership is unique because it has brought together the chemical, petroleum, and water industries in a proactive framework to address the many research issues associated with oxygenate contamination of California's water supplies. Members of the Partnership include the Association of California Water Agencies, Oxygenates Fuels Association, and Western States Petroleum Association.

This document reports the results of the creative efforts of all who participated in the workshop. Significant efforts were exerted to maintain the integrity of each participant's contributions, and only minor editorial adjustments have been made to maintain readability.

The Oxygenate Workshop was accomplished through the combined efforts of many individuals, including the collaborative effort between NWRI, the Partnership, and the California Department of Health Services, to organize and present the workshop. The participants, many of whom traveled considerable distances to attend the workshop, provided the energy required and survived the rigors of a very hot weekend and the loss of air-conditioning.

No workshop could be successful without the support provided by the professional staff. Special thanks are extended to Patricia Linsky, Editor; Gina Melin Co-editor; Tammy Dapkewicz, Meeting Coordinator; Joseph Pezely, Graphics Illustrator; Stephen Lyon, Ph.D., Graphics Assistance; Stacey Haro, Word Processor; Carol Psaute, Word Processor, Teresa Taylor, Photographer; and Laurel Hungerford, Photographer. Sincere appreciation is extended to Dr. William S. Gaither, Ph.D. who, through his masterful facilitating skills, brought the NGT to a successful conclusion.

RONALD B. LINSKY  
*Executive Director*  
*National Water Research Institute*  
*Workshop Secretary*



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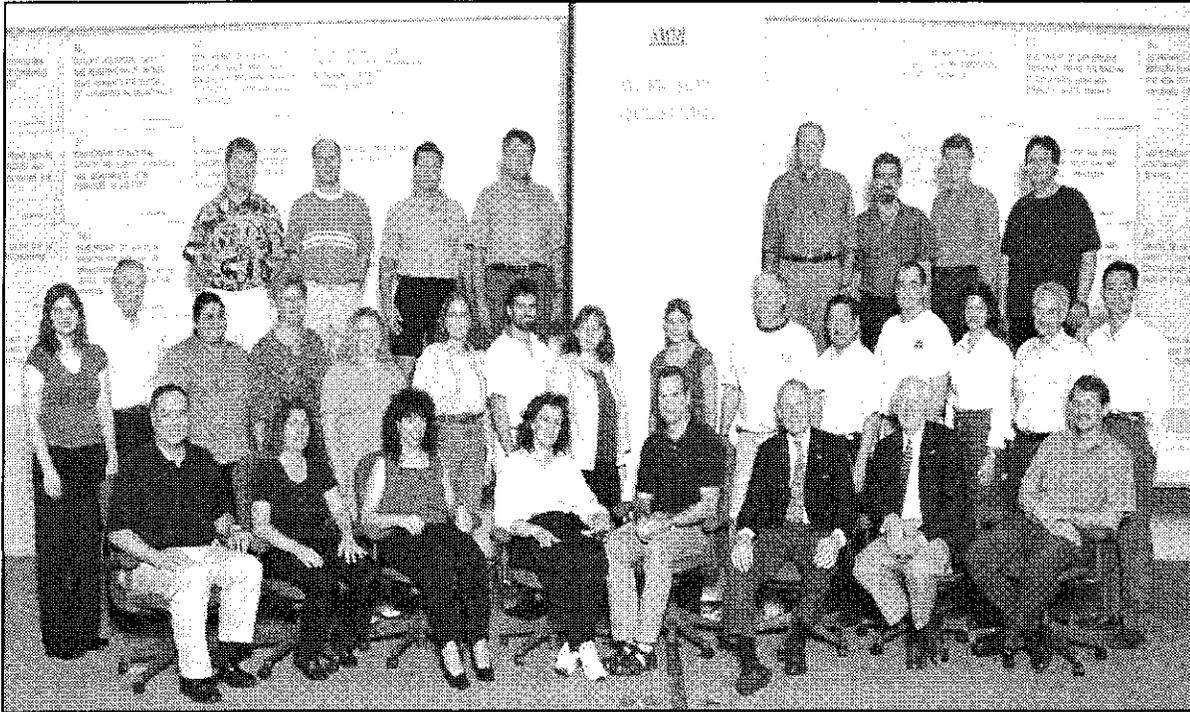
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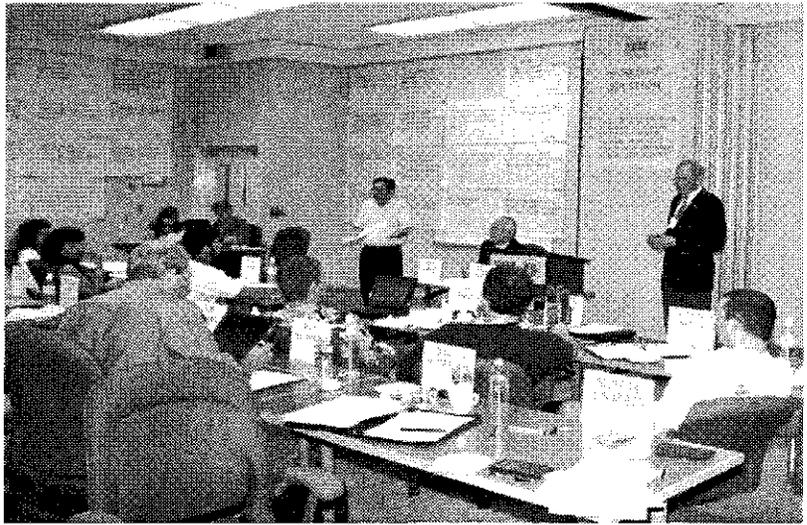
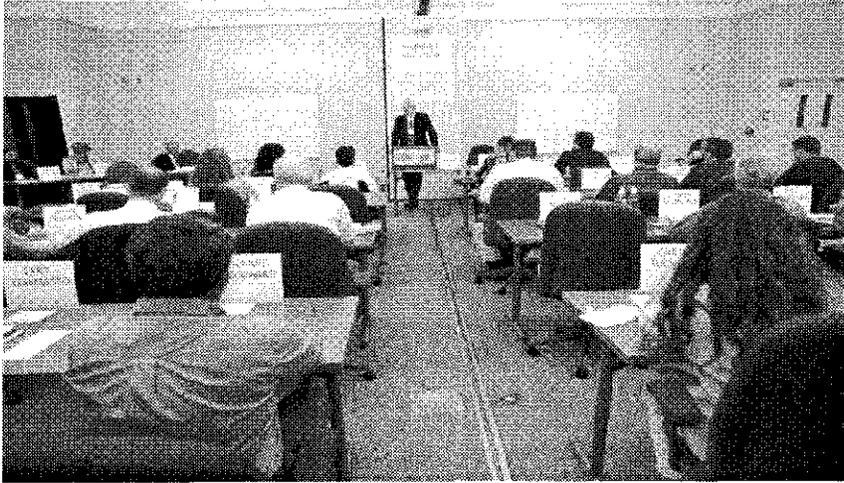
## PARTICIPANTS



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# **Working Groups' Reports**



## **INTRODUCTION**

### **Summary Descriptions of Highest Priority Research Needs to Achieve Cost-effective Treatment and Source Protection of Drinking-water Supplies From Oxygenate Contamination**

Following the completion of the Nominal Group Technique (NGT) Workshop on Saturday evening and the ranking of individual research needs by the participants, the 10 highest priority needs were identified and posted on the workroom wall. Working groups of two or three participants were assigned to examine each of the research needs consolidated under the 10 highest priority major research areas. The task of each working group was to digest, synthesize, and compose a summary research description that included the most important aspects of the individual research needs that had been consolidated under their assigned major research area. The working groups worked late Saturday evening and continued Sunday morning. The following 10 reports are the result of their efforts.

The work groups presented their results on Sunday morning and enlisted comments from the other participants. Each working group took between 15 and 20 minutes for their presentation and the follow-up discussion. All written and signed comments offered by participants are reprinted, verbatim, following each working group report.

If a working group used visuals to illuminate their presentations, copies of those visuals are presented in Appendix E of this report.



# **Optimize Emerging Technologies for Water Treatment of Oxygenates and Their Degradation Products**

## **WORKING GROUP MEMBERS:**

Crowley, Liang, and Suffet

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## **Research Need(s) Description:**

This research will optimize four emerging technologies for water treatment of oxygenates and their degradation products. The technologies are:

- Advanced Oxidation.
- Biological Drinking Water Treatment.
- Sorbents.
- Integrated Membrane Technologies.

These technologies have been initially evaluated by previous studies but will need further laboratory and pilot-plant research to become efficient and viable for use in drinking-water treatment. These technologies are considered to be a research-project step away from being useful for water treatment. The proposed evaluations will consider the cost effectiveness of these technologies versus available technologies. The cost estimates are based upon academic institution grants before overhead (i.e., direct costs only).

## Advanced Oxidation

Ozone/ultraviolet (UV) and ozone peroxide (peroxone) have been shown to remove MTBE and its degradation products in laboratory studies and pilot-plant demonstrations. These processes are effective and can minimize bromate production at ambient pH. This has been piloted with granular activated carbon (GAC) polishing at Charnock. This will be most cost effective at a large treatment facility with low-level concentrations of MTBE, oxygenates, and degradation products, and high flow rates (e.g., 750 mgd). Residual side streams will not occur.

Pulse UV, pulse UV peroxide, and bi-functional aluminum processes are emerging technologies which should be evaluated versus ozone/UV and ozone peroxide for treatment and cost-effectiveness for the water community.

### Recommendations:

1. Optimize pulse UV and pulse UV peroxide processes. Currently, UV is an emerging technology in the water industry for pathogen inactivation. The use of this technology will assist water utilities in achieving both chemical oxidation of MTBE and other oxygenates on pathogen inactivation.

Cost estimate: \$100,000

2. Evaluate the ability of bi-functional aluminum and optimize it, if viable. Bi-functional aluminum is synthesized by acidification of metallic aluminum with strong acids. It has been shown in laboratory studies to have high reactivity and can effectively degrade MTBE in an aqueous solution under ambient conditions. Degradation of MTBE in the parts per million range, using bi-functional aluminum has been completed within hours. The evaluation of bi-functional aluminum at parts per billion concentrations in natural waters under water treatment conditions needs to be carried out for MTBE, oxygenates, and their byproducts.

Cost estimate: \$50,000 for feasibility study; \$50,000 for optimization, if proven feasible.

3. Evaluate different commercial, chemical catalysts and optimize it, if viable.

Cost estimate: \$50,000 for feasibility study; \$50,000 for optimization, if proven feasible.

## Biological Drinking-water Treatment

Pump-and-treat systems for groundwater remediation of difficult-to-degrade compounds (e.g., oxygenates, chlorinated organics) have traditionally used physical/chemical removal techniques (e.g., air stripping, vapor or liquid oxidation, activated carbon sorption). These systems require high initial capital, and significant funding for operation and maintenance expenses. Efficient and reliable *ex situ* biodegradation systems (i.e., bioreactors and biologically-active carbon beds) may have the potential for cost-effective treatment of groundwater containing oxygenates and gasoline range hydrocarbons (GRH) to below maximum contaminant levels (MCL).

Recent data suggest that tertiary-butyl alcohol (TBA) is a common byproduct in the manufacture of MTBE and, therefore, tends to be present in water contaminated with MTBE. The data further suggest that while TBA is present in gasoline in only trace amounts, it can be present in water at 10-100 percent, or more, of the MTBE concentration because it is far more soluble in water and so will partition more to the water phase. Additionally, TBA, acetone, tertiary-butyl formate (TBF), and other oxygenate byproducts may result from degradation of MTBE by other treatment processes (e.g., advanced oxidation). Thus, these processes may benefit from additional polishing for such compounds. TBA, acetone, TBF, and other alcohols (e.g., ethanol) are highly soluble in water and, therefore, are far more difficult to air strip or absorb than even MTBE. Advanced oxidation can further oxidize these compounds, but acetone in particular is recalcitrant to advanced oxidation, so this process may not offer a practical route for treatment in some scenarios.

#### Recommendations:

1. Complete a critical review of biological treatments for removing oxygenates and their byproducts, including naturally-occurring degraders and biologically enhanced activated carbon (BAC) and biologically activated sand (BAS) treatment systems. Include an evaluation of treatment at different concentration levels, reactor types (e.g., column and fluidized bed), temperature (especially between 10 and 20 Celsius), and aerobic and anaerobic treatments. Evaluate regulations in the U.S. and other countries on the use of microbial systems for drinking-water treatment.

Cost estimate: \$30,000

2. Conduct laboratory-scale and pilot-scale evaluations of naturally-occurring oxygenate degraders and normal biological growth in BAC water treatment systems (virgin BAC, or regenerated BAC) and BAS filtration systems of the same empty-bed contact time of oxygenates and their byproducts. The BAS system is used to determine if there is an advantage to using activated carbon. A coconut carbon and a bituminous carbon should also be compared for BAC because of the pore size shape and distribution. For optimum carbon, evaluate at 10 and 20 Celsius.

Cost estimate: \$75,000 for lab-scale feasibility and \$125,000 for pilot, if shown feasible.

## Sorbents

The use of synthetic resin sorbents for the removal of MTBE, TBA, and other oxygenates has been tested under small-scale laboratory conditions and has shown that it can be effective for the removal of oxygenates in drinking water. In addition, small-scale regeneration studies have also been conducted to indicate that resins can be regenerated using steam and can achieve close to the original adsorption capacity; however, the continued loss of capacity over multiple regeneration cycles is still not understood. Laboratory testing is ready to be moved to the field to evaluate both the adsorption and regeneration capacities of resins.

### Recommendation:

1. Conduct laboratory-scale and pilot-scale evaluations of: 1) virgin versus 2) regenerated GAC versus 3) cost-effective synthetic resins for the removal of oxygenates and their byproducts. It has been shown that coconut charcoal is the most effective GAC; however, Rohm and Haas carbonaceous resin 572 should be tested. The resin technology should evaluate regeneration and disposal strategies for cost effectiveness versus regeneration of activated carbon.

Cost estimate: \$75,000 for lab-scale feasibility; \$75,000 for resin regeneration; and \$200,000 for pilot, if shown feasible.

## Integrated Membrane Technologies

Nanofiltration and reverse osmosis membranes have been used for water treatment control of trace organic chemicals, while controlling pathogens and minimizing disinfection byproducts. Membranes have the unique ability of minimizing the change of chemicals while removing them in a concentrated stream for subsequent treatment.

### Recommendations:

1. Bench-scale evaluation of different membranes should be completed to determine the best membranes for removal of oxygenates and should carefully evaluate membrane absorption and diffusion through the membrane for the removal of oxygenates and their byproducts.

Cost estimate: \$75,000

2. Integration of water treatment technologies with membrane system technologies should be considered for the optimum membrane(s) in the above recommendation.

Cost estimate: \$150,000

***Recommended Task Group Members:***

Advanced Oxidation

Sun Liang, Lien Hsing-Lung, Jim Bolton, Jim Malonney

Biological Drinking Water Treatment

Mel Suffet, Rula Deeb, Brigit Arying (UCLA), UC Riverside, UC Davis, Scott Summers,

Sorbents

Mel Suffet, Dennis Clifford, Susan Powers

Integrated Membrane Technologies

Gary Amy, Jim Taylor, Fran Digiano, Sun Liang, Mel Suffet

***Comments:***

“Most of the priority research topics address issues important to very large water utilities, petrochemical industry, and academia. The smaller water utilities (<20,000 people), small rural communities (<2,000 people), and individual private household well owners do not have the financial resources or expertise to:

- Implement research.
- Conduct extensive oxygenate testing programs.
- Perform site investigations to delineate plumes and identify sources and potentially responsible parties (PRPs).
- Pursue litigation against PRPs.

Research is needed that would benefit smaller, unrepresented parties. Such research would include:

- Occurrence studies.
- Small point-of-use and point-of-entry treatment systems.
- Alternate funding strategies to avoid litigation.

This research would have to be funded by government and industry sponsors.” – ***Anthony Brown***

“The use of Power Point was very effective, and the report was comprehensive.” – **Gary Hoffman**

“Resin study should first conduct a paper study on economics to see if the resin process is even competitive with GAC. Resin may only be viable for TBA cleanups if biotreatment is not an option, so at best is likely to be only a niche technology. The resin needs to be cycled several hundred or at least several dozen times to demonstrate it has minimal loss of capacity – otherwise, it won’t be economical. This will greatly increase the cost of the study.

Overall, this whole program looks sound and well constructed.” – **David W. Pierce**

“Cost estimates for field demonstrations are too low. Review of the identified AOP technologies should include cavitation, which was one of the technologies proposed. Some of the technologies suggested that further testing is needed to further evaluate these technologies before they are implemented.

This priority was developed by folding 12 other projects into one newly created priority and new definition. This definition was formulated by the group as an all-encompassing project. Authors who prepared the 12 projects should be identified as the authors of this priority and not just those who combined the projects.” – **Rey Rodriguez**

“AOP using pulsed UV is worth considering. Some questions in my mind still exist about the robustness of AOP in drinking water settings. This is based upon experiences in Santa Monica.

Additional GAC work is not recommended. GAC is well understood and has been validated by the California MTBE Research Partnership.

Good approach for membranes, which hold promise in large Q settings.

Finally, no discussion on emerging, low-cost strategies that might be considered for private or small-water utilities.” – **Scott Tenney**

“Looks fine.” – **Chris Tulloch**

# **Enhance *In Situ* Aerobic and Anaerobic Bioremediation of Oxygenates**

## **WORKING GROUP MEMBERS:**

Deeb and Rodriguez

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### ***Research Needs(s) Description:***

#### **Definition of Enhanced Bioremediation**

Enhanced or engineered *in situ* bioremediation involves the stimulation of microorganisms within a subsurface aquifer to degrade contaminants of concern by active manipulation of physical, chemical, or biological conditions. In most cases, stimulation of indigenous microbial populations requires the addition of electron acceptors, inorganic nutrients, or a primary substrate if the contaminant of concern is not a good source of carbon and energy. In some cases, the addition of exogenous cultures may be needed.

Our current state of knowledge on the biodegradation of ether oxygenates and TBA can be summarized as follows:

- MTBE, ETBE, DIPE, TAME, and TBA have been shown to degrade under aerobic conditions at slow rates relative to other gasoline hydrocarbons.
- The cultures that have been shown to degrade MTBE as the sole source of carbon and energy are relatively slow growing.
- Pilot studies have been done in the field to test intrinsic and enhanced bioremediation. The results from these studies are promising but do not provide compelling indications that the bioattenuation of ether oxygenates and TBA occurs at significant rates in the field.
- While naturally occurring MTBE-degraders may be present at fuel release sites, such microorganisms have yet to be isolated and characterized.
- Limited studies have been done to test the anaerobic biodegradation of ether oxygenates and TBA. However, no cultures with the ability to successfully degrade MTBE and TBA have been identified and the mechanisms for anaerobic MTBE degradation are relatively unknown.

- Unlike ether oxygenates and TBA, ethanol is readily degraded under both aerobic and anaerobic conditions. The discussion here will therefore be limited to enhancing bioremediation schemes of oxygenates excluding ethanol.

### ***Importance:***

#### Lessons Learned From Past Aerobic Studies and Gaps in Aerobic MTBE Remediation Research

Several laboratory studies have shown that MTBE, as well as other ether oxygenates and TBA, can be degraded under aerobic conditions by cultures from diverse environmental sources. Most of these studies were performed in shake-flask experiments under controlled laboratory conditions. While in some instances MTBE and TBA were shown to degrade in laboratory-aquifer microcosms and at gasoline-contaminated sites, there are no compelling indications that the bioattenuation of these compounds is occurring at significant rates in the field. As a result, biological removal of MTBE has yet to be widely applied at gasoline-contaminated sites. In order to increase the feasibility of *in situ* bioremediation for MTBE and TBA, an active engineering approach should be implemented to enhance and optimize biodegradation processes.

The results from past studies are useful for developing engineering approaches for successful bioremediation of MTBE-contaminated aquifers. It is clear that the presence of oxygen is critical for the degradation of MTBE by most of the examined cultures. Therefore, the addition of oxygen to aquifers could be beneficial, especially in the vicinity of gasoline release sources, where rapid consumption of oxygen is typically observed. Next, if the indigenous microbial populations do not possess the ability to use MTBE as a primary substrate, a cometabolic substrate can be introduced to groundwater aquifers in order to support microbial growth and to provide energy. Several compounds, including propane, *iso*-propanol, and *n*-butane, are documented cometabolic substrates for MTBE biodegradation. However, some studies have suggested that even when indigenous MTBE-degrading cultures are present in subsurface environments, their concentrations may be too low to sustain MTBE metabolism. Therefore, aquifer seeding or bioaugmentation with laboratory enriched MTBE-degrading populations may be necessary to promote MTBE degradation at levels required to adequately mitigate contaminant migration. Several pilot-scale field studies are currently being conducted to investigate the feasibility of bioaugmentation at gasoline-contaminated sites. Preliminary results from studies conducted at Port Hueneme, California, suggest that oxygen-amended biobarriers seeded with laboratory cultures may be a promising *in situ* technology for the removal of MTBE from groundwater. Field-scale studies are needed to test the feasibility and cost-effectiveness of such approaches for both plume containment and source zone MTBE and TBA removal. In addition, studies are needed to evaluate the behavior of seeded culture in mixed-contaminant plumes.

One of the objectives of this work would be to develop aerobic bioremediation strategies involving direct metabolism, cometabolism, bioaugmentation, or some combination thereof. A better understanding of the factors limiting MTBE biodegradation in the environment is needed to effectively design such strategies. In addition, field studies are needed to test the effectiveness of such strategies for applications to UST cleanup sites. Finally, when an *in situ* bioremediation strategy is implemented, overlapping lines of evidence should be used to confirm

that the expected biological processes are indeed responsible for MTBE and TBA removal. While conventional techniques may be useful, the development and use of innovative tools such as carbon isotopic fractionation and molecular-based techniques are needed for conclusive evidence of sustained biological activity.

### Lessons Learned From Past Anaerobic Studies and Gaps in Anaerobic MTBE Remediation Research

Limited studies have reported the biodegradation of MTBE under methanogenic conditions. In other studies, TBA was also shown to degrade in soil microcosms. While these studies suggest the possibility of anaerobic MTBE degradation, no microorganisms have been identified with the ability to degrade MTBE in the absence of oxygen. Such cultures are needed in order to determine the mechanisms of anaerobic degradation. Understanding the mechanisms and pathways of anaerobic MTBE and TBA degradation is critical for enhancing the rate and extent of MTBE biotransformation in both laboratory and field settings.

#### ***Approach to Attack this Research Need:***

##### Laboratory Studies

- Need soil and groundwater samples from fuel release sites to determine the prevalence of naturally-occurring MTBE-degraders under controlled laboratory conditions.
- Develop conclusive indicators of *in situ* MTBE and TBA biodegradation. Include innovative tools (molecular-based approaches).
- Need basic scientific laboratory-oriented research to better understand the mechanisms of MTBE and TBA degradation, especially anaerobic biodegradation.
- Identify alternate substrate and nutrients that could optimize growth and sustain the activity of oxygenate-degrading microorganisms in laboratory studies before the results can be extrapolated to field applications.
- Need a better understanding of why the observed cell yields on MTBE and TBA are lower than the theoretical ones.
- Perform laboratory studies to identify anaerobic MTBE-degraders. Once such cultures are identified, scale up studies to determine methods and potential amendments for optimizing degradation rates in the absence of oxygen.

##### Field studies

- Create man-made subsurface biostimulation zones using materials in which delivering and sustaining adequate levels of electron and nutrients is easier than employing aquifer materials (idea of using an infiltration trench with packing material seeded with MTBE-degrading microorganisms through which groundwater is re-circulated)

- Sustain MTBE induction during intermittent MTBE exposure.
- Use inducing agents to decrease acclimation phases in the field.
- Sustain long-term biological activity.
- Combine physical removal technique for removing residual NAPL followed by bioremediation.
- Develop methods for quantifying the extent of bioremediation in source zones (mass balances approach, accumulation of intermediates, etc.).
- Understand the prevalence of naturally-occurring microorganisms at fuel release sites and characterize the environmental conditions to optimize growth and activity of these cultures.
- Maintain and sustain cell populations and microbial activity of relatively slow-growing MTBE-degrading cultures (0.1 – 0.4 g cells/g MTBE). Also, methods to enhance growth of these microorganisms to avoid loss of competitiveness in groundwater biodegradation zones containing other readily degradable substrates such as BTEX compounds.
- Combine physical methods with bioremediation at source zones where residual NAPL may be present.

***Rough Estimate of Costs Needed to Address the Tasks Listed Above:***

Laboratory Studies 1

- Prevalence of indigenous MTBE-degraders.
- Indicators of *in situ* biological activity.
- Optimizing cell growth and sustaining oxygenate activity.

Cost estimate: \$400,000

Laboratory Studies 2

- Anaerobic MTBE degradation (identifying cultures, understanding mechanisms, and optimizing process).  
Cost estimate: \$300,000.

### Field Studies 1

- Seeding laboratory cultures in the field sites near or at source zones to determine performance under expected field conditions, especially at sites impacted by contaminant mixtures (BTEX, MTBE, TBA commingled plumes).

Cost estimate: \$300,000

- Sustaining long-term biological activity in the field, and sustaining MTBE induction during intermittent MTBE exposure.

Cost estimate: \$300,000

### Field Studies 2

- Testing a number of enhanced bioremediation strategies.

Cost estimate: \$300,000/strategy

### Field Studies 3

- Evaluate the biological fate of ethanol in the field and its impact on BTEX biodegradation rates.

Cost estimate: \$350,000

### ***Recommended Task Group Membership:***

- Rula Deeb (Malcolm Pirnie)
- Kate Scow (UC Davis).
- Dick Woodward (Sierra Environmental).
- Lee Newman (University of Washington).
- Joseph Salanitro (Equilon).
- Kirk O'Reilly (Chevron Research & Technology)
- Rob Steffan (Envirogen).
- Rey Rodriguez (H2O R2)
- Lisa Alvarez-Cohen (UC Berkeley).

- Clinton Church (USGS).
- Marc Deshusses (UC Riverside).
- Doug McKay (Waterloo).
- Ellen Moyer (ENSR).
- Murray Einarson (GeoSyntec).
- Pedro Alvarez (University of Iowa).

***Comments:***

“There needs to be more focus on natural attenuation, and this has been lost because of the way the problem has been framed. A better understanding of the significance of natural attenuation would greatly assist designing enhanced *in situ* aerobic/anaerobic bioremediation.” – ***Jim Crowley***

“Too much emphasis on bioaugmentation in field studies.

Because of the efforts to substitute ethanol for MTBE, it is essential to include ethanol aerobic and anaerobic *in situ* bioremediation in this project.

Pilot studies have only been done for aerobic, not anaerobic, MTBE/TBA bioremediation.

Disagree that anaerobic degraders have not been found – microcosms indicate that they are present, although we may not know who they are.

Microcosm evidence of enhanced anaerobic biodegradation using  $\text{Fe}^{+3}$  and humic acid (as an electron shuttling compound). Rates are similar to aerobic rates.” – ***Ellen Moyer***

“Include a statement on the apparent biodegradation of MTBE/TBA under iron-reducing, in addition to methanogenic conditions.” – ***Joseph Salanitro***

“The approach is theoretically sound but seems rather extensive in nature. Recommendation would be to screen and select sites that have shown natural degradation taking place. There may be some value in going to these selected sites and collecting data to support a microbiological evaluation, including the collection of soil and groundwater samples to identify and isolate microorganisms that might be degrading oxygenates at these sites. From this preliminary work, additional activities can be progressed.” – *Scott Tenney*

“Include ethanol in the oxygenates to be studied.” – *Maria Tikkanson*

“This group grew too large, thereby diluting the depth and diversity of important, individual projects – in some cases, eliminating them altogether. The emphasis of this group needs to be redirected to include:

- Anaerobic studies – studies to elucidate oxygenate biodegradation under nitrate reduction, sulfate reduction, iron reduction, and methanogenesis. These investigations have broad application and a high probability for success. Aerobic studies are thoroughly funded and well underway; emphasis needs to shift to passive anaerobic systems.
- Optimization of indigenous consortia, not a continued focus on bioaugmentation.
- Activation/induction of MTBE/TBA degrading enzymes. We must identify compounds that induce the production of MTBE/TBA degrading enzymes in indigenous, *in situ* populations.
- Simple engineering remedies for stimulating indigenous microbes to degrade oxygenate impacted aquifers. This is an inexpensive extension of existing European technology currently in use to remove soluble iron. The potential for success of this approach is high, and the applications are numerous. A simple test demonstration in an existing potable water source impacted by fuel oxygenates would confirm this process (e.g., the Charnock well field).” – *Richard Woodward*





# **Optimize Integrated Water Treatment Systems for Removal of Oxygenates and Degradation Products**

## **WORKING GROUP MEMBERS:**

Drogos, Kavanaugh, Lien

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### *Research Needs(s) Description:*

A number of individual treatment processes have been shown to be effective at removing MTBE from contaminated groundwater. The demonstrated technologies include air stripping and adsorption on granulated activated carbon (GAC). Emerging technologies include advanced oxidation processes (AOPs), adsorption on resins, and certain biological processes. To date, only a few systems are in operation for treating oxygenate-contaminated groundwater for drinking purposes, but a number of communities in California and other parts of the U.S. are now faced with significant treatment challenges for bringing up to standards both groundwater and surface waters containing unacceptable levels of oxygenates, primarily MTBE. The selection of appropriate treatment options has been thwarted in a number of cases (e.g., City of Santa Monica, California, due to various performance, operability, and cost problems).

In addition, pump-and-treat is still the treatment option of choice for controlling plume migration even though the rate of actual cleanup for this technology is slow. Pump-and-treat has been employed in a wide range of MTBE plume settings. The treatment of groundwater containing MTBE at levels ranging from 0.1 to 600 ppm poses significant process challenges. Under these conditions, several individual processes must be combined in series to meet stringent treated-water standards.

The presence of oxygenates other than MTBE also presents treatment challenges that have not yet been resolved. For example, TBA cannot be removed by air stripping and is poorly adsorbed on GAC. Treatment of contaminated water streams at these sites often includes the presence of multiple contaminants (e.g., oxygenates, including MTBE and/or TBA, BTEX, chlorinated solvents, and other organic contaminants). The impact of these various mixtures on treatment system performance is uncertain.

In this context, a number of research data gaps can be identified. The main objective of this research project will be to determine the optimum combination, and integration, of treatment

processes for both drinking water system applications and site cleanup to meet performance, reliability, and cost constraints.

***Importance:***

Current technologies are not able to meet the reliability requirements of drinking water systems. In addition, control of byproduct generation during treatment using some technologies (e.g., advanced oxidation) is uncertain. Also, treatment effectiveness is very complex and site specific. For example, TBA presents significant treatment challenges, and waters high in bromide limit advanced oxidation options due to the potential for bromate formation. The wide range of treatment costs implies the potential for improvements in cost effectiveness. Reported costs for groundwater treatment range over at least one order of magnitude (i.e., \$1-\$10 per 1000 gallons treated for flow rates greater than 500 gpm). Thus, research is needed to reduce uncertainty in selecting optimum treatment process combinations. This research is expected to result in improved system reliability and reduced costs for treating groundwater contaminated with oxygenates and their degradation byproducts. Given predictions that up to 9,000 community water systems in the U.S. may be impacted by oxygenates, the optimization of treatment systems could result in substantial reductions in life-cycle costs for treatment.

***Suggested Approach to Attack this Research Need:***

The following research topics have been identified:

1. Optimization of Individual Processes

- Bio-GAC treatment of oxygenates. Bio-GAC, in which microorganisms are allowed to grow in a bed of GAC, seems a promising option for treating a number of oxygenates and their byproducts. Pilot data at the Santa Monica Charnock site suggested that bio-GAC was a viable option for mixtures of MTBE and TBA to reduce the TBA. MTBE can then be adsorbed by suitable types of traditional GAC. Research needs include optimizing the design of bio-GAC, the impact of water quality on bio-GAC performance, and the assessment of bio-GAC performance reliability.

Laboratory and field-scale studies are recommended.

Cost estimates: \$200,000-\$400,000

- Assess disinfection byproduct and bio-regrowth issues in the distribution systems for advanced oxidation processes/biological treatment of water. AOP and biologically treated water might produce some precursors to form disinfection byproducts, such as aldehydes or ketones. It is important to demonstrate that these byproducts do not present potential toxicity problems. A potential bio-regrowth problem in the distribution systems should also be investigated.

Laboratory and pilot studies recommended.

Cost estimates: \$100,000–\$200,000

- Optimize air-stripping technology. Air stripping of ether oxygenates requires high air/water ratios. However, this technology does not produce byproducts. Also, there is anecdotal evidence that TBA degrades in “packed” towers. Thus, optimizing technology may provide cost/efficiency advantages. Optimization issues include optimum water temperature, tower pressure, and biogrowth on packing.

Pilot and field studies are needed.

Cost estimates: \$100,000-200,000

## 2. Effect of Specific Contaminants on Treatment

- An evaluation of treatment technologies for TBA in groundwater. Evaluate treatment technologies for TBA in groundwater for drinking water treatment.

Laboratory and field studies are needed.

Cost estimates: \$300,000-\$500,000

- Determine the effect of mixtures of oxygenates on treatment systems. Determine the effect of mixtures of different oxygenates on treatment systems.

Laboratory and field studies are recommended.

Cost estimates: \$300,000-\$500,000

### 3. Integration Optimization

- Integration of technologies for treatment of oxygenates in drinking water. The effectiveness of current available technologies (e.g., GAC, air stripping, and AOP) is still limited for the treatment of MTBE in drinking water. An alternative is to integrate and optimize individual processes for the treatment of oxygenates in drinking water.

Field-scale demonstration projects recommended.

Cost estimate: \$1,000,000

- Combine physical/chemical and biological approaches for achieving time-effective treatment. Optimization of water treatment processes should take advantage of the physical/chemical and biological degradation properties of oxygenates. Treatment combinations should be evaluated that combine an optimum use of the biodegradation and physical/chemical removal of oxygenates. The focus should be on oxygenates or oxygenate mixtures that cannot be easily removed by single treatment options, such as MTBE/TBA mixture.

Laboratory and field studies are recommended.

Cost estimates: \$500,000-\$1,000,000

- Investigate augmentation or optimization of a drinking water treatment for removing low ppb levels of MTBE or other oxygenates. Larger surface water treatment plants using conventional treatment cannot remove MTBE contamination. Research is needed to identify and evaluate treatment options for removing low levels of MTBE (< 20 ppb).

Laboratory studies only.

Cost estimate: \$100,000

### 4. Survey of Existing Systems

- Review of the effectiveness of oxygenate treatment technologies/actual systems throughout the U.S. Develop comparative documentation (including actual data) of the effectiveness of the different types of water treatment systems (both remediation and drinking water treatment) currently in operation nationwide.

Study recommended.

Cost Estimate: \$100,000

## 5. Higher Concentration of Groundwater Contamination Problems

- Develop cost-effective treatment trains for removing oxygenates from groundwater at concentrations greater than 1 mg/L. At LUFT sites, oxygenate concentrations are typically high in the source area (>1 mg/L). Cost effective removal of oxygenates is not available. Effective treatment requires multiple processes to achieve effluent limits. Research is needed to define the optimum treatment combinations to meet stringent treatment standards cost effectively.

Several field studies recommended.

Cost Estimate: \$300,000 per demonstration.

### ***Recommended Task Group Membership:***

Suggested participants could include the following individuals and organizations that have expertise in MTBE water-treatment:

- Water agencies/utilities: Sun Liang (Metropolitan Water District of Southern California), Orange County Water District, Rick Hydrick (South Tahoe Public Utility District), City of Santa Monica, Rey Rodriguez (H<sub>2</sub>O R<sup>2</sup> Consultants)
- Regulatory: Richard Sakaji (California Department of Health Services), Bob Clark (USEPA, Cincinnati Labs)
- Academic/Universities: Mel Suffet (University of California, Los Angeles), Marc Deshusses (University of California, Riverside), Dan Chang (University of California, Davis), Edward Schroeder (University of California, Davis), David Sedlak (University of California, Berkeley), Paul Johnson (Arizona State University), John Crittenden (Michigan Tech), Mark Anderson (University of Wisconsin), Walter Weber, Jr. (University of Michigan)
- Consulting firms: John Gaston (CH2M Hill), Michael Kavanaugh, (Malcolm Pirnie, Inc.), Larry Leong (Kennedy/Jenks Consultants), Issam Najim (Montgomery Watson Americas, Inc.), Daniel Creek (Alpine Environmental, Inc.)
- Equipment manufacturers with research and development (R&D) capabilities: Terry Appleberry (Applied Process Technologies), Representative from Calgon Carbon Corp.

***Comments:***

“Problems, No. 1 and 2 have areas that overlap. These areas relate to emerging versus established technologies. The crossover of similar projects (GACS, AOPs) is necessary where integration of technologies will likely be necessary where optimization of treatment systems is needed in drinking-water sites to achieve effluent goals which meet drinking-water standards and for compliance with Department of Health Service Policy 97-005.

Twelve projects were combined to create one project, which is different from Project 1, in that these are established technologies but not necessarily for treatment of oxygenates but volatile organic compounds.

Also, identify the authors of the individual projects.” - ***Rey Rodriguez***

“Consider a project on treatment of ethanol degradation products from spills. Does formaldehyde, acetone, or any other major product that form, need treatment?” - ***Mel Suffet***

“Optimizing drinking-water treatment is an important element that was identified in previous research plans. Integrated solutions are the next logical step for a detailed evaluation since it is highly likely that an ultimate treatment configuration at affected sites will employ various technologies. The work proposed is a logical build off of work performed and/or evaluated by the California MTBE Research Partnership.” - ***Scott Tenney***

“Include a study of ethanol and its breakdown products in this study of optimized integrated water treatment systems.” - ***Maria Tikkanen***

# **Evaluate Various Reactive Barrier Designs for Enhanced *In Situ* Treatment of MTBE and Other Oxygenates**

## **WORKING GROUP MEMBERS:**

Salanitro and Woodward

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### ***Introduction:***

Permeable Reactive Barriers (PRB) have been used successfully for the treatment of chlorinated hydrocarbon solvents for many years. The reactive barrier can be either a passive or active system that decontaminates the plume as it passes through the reactive barrier. Products of the barrier range from complete mineralization to (as in the case of chlorinated hydrocarbons) chloride, and small molecular weight hydrocarbons. Funnel and gate technology is a variation of the PRB that is beyond the scope of this project.

Examples of other successful reactive barriers include:

- Physical barrier. Activated carbon with iron has been used to sorb organic compounds. The granular activated carbon (GAC) was subsequently regenerated periodically by flushing the loaded GAC with hydrogen peroxide to generate Fenton's reagent. Fenton's reagent oxidizes the organics, thus regenerating the GAC.
- Chemical reactive barrier. Zero-valent iron has been used for remediation of TCE at six installations, including the Borden Aquifer.
- Biological reactive barriers. Oxidative reactive barriers for treatment of MTBE have been successfully installed at four service stations and at Port Hueneme (Salanitro). All five involve bioaugmentation and intermittent oxygen sparging. Oxidative reactive barriers (Regenesis) deliver dissolved oxygen into the water flow to support active biological processing. Oxidative reactive barriers have been used for a wide variety of organic compounds subject to aerobic biodegradation.
- Reductive Reactive Barriers. Peat reactive barriers have been used in California to treat nitrate from fertilizer in groundwater. Nitrate was converted to dinitrogen gas. Nutrient based bio-barriers inject growth-limiting nutrients into the subsurface to stimulate biological

activity. Air-sparging barriers have been used at many sites for the biological oxidation of fuel hydrocarbons.

Reductive dehalogenation is commonly used for the treatment of chlorinated solvents. Bioaugmentation was used to treat carbon tetrachloride in a Michigan aquifer. TCE was treated by Ellis et, Al. (1998) by adding electron donor (lactate) to reduce the redox potential of the aquifer then used indigenous micro flora or bioaugmentation with *Dehalococcus* spp. to achieve complete mineralization of TCE to ethene and chloride. HRC (a lactate-based hydrogen release compound) biobarriers have also been used for reductive dehalogenation of chlorinated solvents.

Laboratory studies have confirmed the effectiveness of biological treatment of MTBE and other oxygenates under both oxidative and reducing conditions. Therefore, similar opportunities exist for the treatment of MTBE and other oxygenates under these conditions.

Because these are low-cost, passive systems (relative to the active remediation systems such as pump-and-treat) they are attractive for the *in situ* treatment of MTBE and fuel oxygenates.

***Research Need(s) Description:***

The spatial distribution of MTBE in the dissolved plume provides a record of the temporal variation in MTBE mass dissolution from the source. Biobarriers can be used for long-term plume treatment to manage the plume in situations where intrinsic bioremediation or monitored natural attenuation may take extended periods for treatment.

Types of PRBs for treatment of MTBE include the following:

- Catalytic conversion of MTBE to TBA by commercial industrial catalysts similar to those used to produce MTBE.
- Fenton's reagent has been successfully used to treat MTBE *in situ*. Chemical oxidation by hydroxyl radicals generated from Pseudo-Fenton's reagent using ferric iron with hydrogen peroxide has been employed at near-neutral groundwater pHs. Three different methods of hydrogen peroxide delivery ought to be evaluated: direct solution injection, *in situ* electrolysis, and hydrogen peroxide pellets.
- Chemical oxidation/reduction with bi-functional aluminum. (Lien)
- Biological reduction using ferric iron and humic acids. (Lovely)
- Biological oxidation using oxygen sparging with or without bioaugmentation. (Salanitro)

While all five approaches have been successfully demonstrated in the laboratory, the first four remain to be demonstrated in the field as PRBs for the treatment of fuel oxygenates. If these approaches can be successfully demonstrated individually, they will form the basis for a blended-

approach application of a proactive-reactive barrier. This blend would replace the pea-gravel backfill around a new tank installation.

In addition, the long-term reliability of each approach needs to be assessed in the field.

***Importance:***

- PRBs have the potential to control the migration of the oxygenate plume.
- PRBs represent a significant cost savings compared to more traditional, active approaches like pump-and-treat,
- PRBs destroy contaminants *in situ* whereas pump-and-treat represents a place/phase transfer.
- PRBs have the potential for reliable, long-term performance.

***Approach and Budget:***

- Conduct a thorough literature review and summary of PRB applications (case studies) and limitations. With particular emphasis on the successes/failures of the many chlorinated-solvent treatment installations.

Cost estimate: \$5,000

- Conduct a series of column studies to define operational parameters for numerical modeling and field implementation, such as groundwater flow, loading capacity, composition of PRB material, degradation products, confirmation of treatment, hydraulic residence time, competing reactions or interferences from gasoline range hydrocarbons (GRHs) groundwater geochemistry, temperature, etc.

Cost estimate: \$30,000 for each approach, four approaches proposed.

- Use operational parameters defined above; conduct model simulations useful for evaluating scaled-up PRBs.

Cost estimate: \$5,000 for each approach.

- Pilot field test of the PRB at an identified, well-characterized, fuel oxygenate plume site near the, source such that the treatment area contains BTEX as well as oxygenate. Pilot scale (potential field application) field parameters (such as groundwater flow through and around barrier) are critical to understanding short- and long-term performance and reliability.

Cost estimate: \$50,000-\$75,000 per approach.

- Conduct a full-scale field demonstration of PRB. Sites for both pilot- and field-scale demonstrations will be selected on the basis of characterization flow oxygenate

concentration, and other parameters identified in the literature review as critical to the success of the PRB operation.

Cost estimate: \$150,000-\$200,000 per approach.

- Install a combination blend for the proactive/reactive barrier to replace the pea-gravel in the backfill of a tank installation.

Cost estimate: \$50,000.

***Recommended Task Group Members:***

- Bob Gilham, Jim Barker, Doug Mackay (University of Waterloo group).
- Rick Devlin (KS geological survey).
- Paul Tradnyek, Rick Johnson (Oregon Graduate Institute).
- Dave Ellis (Dupont).
- Derek Lovley (University of Massachusetts).
- Paul Johnson (Arizona State University).
- Mike Kavanaugh, Rula Deeb (Malcolm Pirnie).
- Kate Scow (University California Davis).
- Clinton Church (United States Geological Survey).
- Murray Einarson (Geo Syntec Consultants).
- Hsing-Lung Lien (Lehigh University).

**Comments:**

“The costs for complete hydrogeologic characterization of sites should be included in the cost estimates for field research on barrier technologies.” –*Jim Crowley*

“Add Kate Scow, University of California, Davis, Rula Deeb, and Mike Kavanaugh of Malcolm Pirnie to the task membership.” – *Rula Deeb*

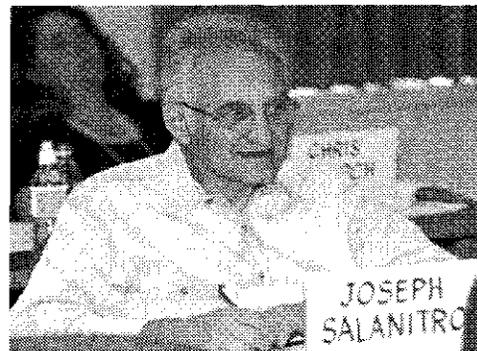
“Literature review should be expanded to include a thorough evaluation of geochemical reactions in any abiotic barrier for MTBE control. Also, hydraulics of barriers should be evaluated from case studies of PRBs with zero valent iron. There are over 100 installations for chlorinated solvents at this time. In addition, literature review should discuss depth and reliability issues associated with the barriers. Increase site review costs to \$50,000.

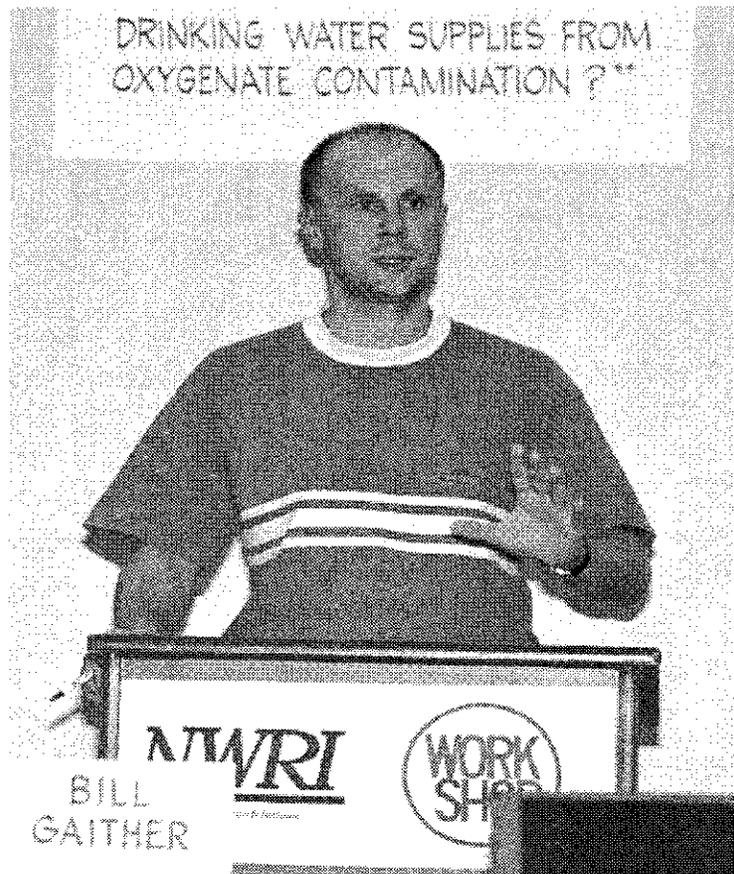
The final outcome of studies should be an evaluation of barrier use at several locations at a site, including barriers under an UST, barrier near the source after release, and barrier at the property boundary.”- *Mike Kavanaugh*

“A statement is made: ‘after installation-reduced/no O&M.’ my understanding is that clogging and O&M costs are not well known with reactive barriers. This would be one of the key things to investigate in this study. In addition, you have to monitor indefinitely.

“Need to often have barriers long-term. This should be mentioned. Also, that they usually do not address the source. How long are pilot studies? Years? Need to look at long-term performance.” –*Ellen Moyer*

“Suggest breaking down costs by technology.”-*Rey Rodriguez*





# **Develop a Comprehensive Understanding of the Fate and Transport of Primary Ether-oxygenates in Representative Hydrogeologic Settings**

## **WORKING GROUP MEMBERS:**

Brown and Tenney

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### *Research Need(s) Description:*

Oxygenates pose a potential threat to drinking-water resources. The fate and transport of MTBE in alluvial settings has been the subject of recent studies. However, most of these studies have focused on homogenous, isotropic settings that do not represent all conditions beneath the entire state. Studies focusing on MTBE releases in such settings are inadequate to assess threats posed by other ether-oxygenates. Additionally, debate still persists regarding the adequacy of this work; in particular, it is unclear whether the quantity and quality of the data were sufficient to support broad conclusions regarding ether-oxygenate fate and transport. In addition, current site characterization and remediation strategies and techniques are primarily based upon fate and transport evaluations for non-oxygenated fuels.

In consideration of this, detailed studies are required to evaluate the fate and transport of the primary ether-oxygenates (e.g., MTBE, ETBE, TBA, DIPE, and TAME) in various hydrogeologic settings. These studies will provide information needed to support decisions regarding:

- Management of oxygenated fuel storage and distributions systems.
- Response to leak and spill events.
- Plume characterization and monitoring.
- Remediation and plume containment.
- Site closure.

***Importance:***

Current site characterization and remediation strategies are based upon the evaluation of fate and transport for non-oxygenated fuels in homogenous, isotropic settings. Such evaluations do not adequately address potential threats that ether-oxygenates pose to drinking water throughout the state. A comprehensive evaluation is needed to address the threats posed by all primary ether-oxygenates in representative hydrogeologic settings.

***Beneficiaries:***

- Water utilities.
- Regulatory officials.
- Petrochemical industry.

***Benefits:***

- To better understand hydraulic, chemical, and biological factors that affect the movement and persistence of ether-oxygenate plumes.
- Establish well-head protection strategies based on understanding the above.
- Guide the establishment or modification of source control, monitoring, and response actions at industrial facilities or potential release sites.
- Prioritize investigation and remediation programs to optimize resource-allocation decisions.
- Improve site characterization techniques.
- Support risk-based decision making.
- Develop more effective remediation or plume control strategies.

***Research Approach:***

1. Review physiochemical and toxicological properties of primary ether-oxygenates.
2. Evaluate hydrogeologic properties and governing relationships affecting multi-phase fate and transport of ether-oxygenates in both vadose and saturated zones.
3. Undertake critical review of existing fate and transport studies (e.g., Port Hueneme, Vandenberg, Borden, Arcadia, East Patchogue, etc.).
4. Develop representative conceptual hydrologic and contaminant fate models.

5. Identify field test sites (~4) in California with representative hydrogeologic conditions and ether-oxygenate releases.
6. Review site-specific information, including release history and characterization.
7. Apply for funding from the State UST Clean-up Fund for fieldwork to characterize the contaminant release at the study sites (see items 8 through 12).
8. Identify the data needs to confirm, revise, or refute conceptual models.
9. Identify techniques for collecting appropriate data of sufficient quality and quantity.
10. Collect and analyze appropriate data.
11. Develop and calibrate numerical models and evaluate model sensitivity to input parameters.
12. Use calibrated models for evaluating fate and transport scenarios.
13. Develop recommendations based upon scenario results.
14. Prepare guidance manual for spill response, site conceptual model development, site characterization (including expedited assessment), risk-based decision making, remediation strategies (including expedited source remediation and plume containment), and closure support.

***Budget:***

Preliminary budget estimates for all phases of this project range from \$0.5 to 3.0 million. The State UST Clean-up Fund, the potentially responsible party (PRP), and the research sponsor would co-fund the field studies at the release sites. In this way, a \$3 million research program might cost the research sponsor only \$500,000.

***Recommended Task Force Members:***

Industry:

- T. Buschek (Chevron).
- C. Stanley (Equilon).
- S. Tenney (Exxon Mobil Oil).

Regulatory:

- C. Tulloch (Santa Clara Valley Water District).
- S. Acree (U.S. Environmental Protection Agency).
- J. Crowley (Santa Clara Valley Water District).
- R. Sakaji (California Department of Health Services).
- C. Voss (U.S. Geological Survey).

Academia:

- M. Anderson (University of Wisconsin).
- S. Neuman (University of Arizona).
- D. Mackay (University of Waterloo/Stanford University).

Consultants:

- M. Einarson (Geo Syntec).
- A Brown (Komex).
- S. Feenstra (Applied Hydrogeologic).

***Comments:***

“Complete approach identified to develop projects for understanding the fate and transport with the available data.” –***Rey Rodriguez***

“The study will add much needed information and significance by identifying the long-term impacts (50-100 years) to source water of low-concentration dissolve plumes left in place.” –***Chris Tulloch***



# **Improve UST Monitoring Equipment and Develop Effective Subsurface Monitoring Systems to Detect Liquid and Vapor Releases of Oxygenates at UST Facilities**

## **WORKING GROUP MEMBERS:**

Davidson and Tulloch

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### ***Research Needs(s) Description:***

There is significant evidence that liquid and vapor-phase fuel and oxygenates are being released from UST systems without being detected by the UST monitoring systems. Most of these leaks are being discovered during tank replacements and site assessments. Unfortunately, the UST leak detection systems have failed to adequately detect leaks early enough to allow rapid response for effective remediation. In many cases, the releases appear to be small. However, due to the chemical characteristics of persistent chemicals (such as fuel oxygenates), these undetected releases are threatening and impacting drinking water sources and drinking water wells. Studies indicate that subsurface environmental monitoring is the most definitive technique to detect these releases and the resulting contamination.

This research should focus on designing cost-effective environmental monitoring systems and identifying improvements to existing UST system monitoring components.

### ***Importance:***

Without a mechanism to effectively detect releases of fuel oxygenates, ongoing efforts of source water protection programs will be significantly less effective. Drinking water will continue to be threatened and impacted by fuel oxygenates, and the cost of addressing contaminated sites will increase.

*How do you propose attacking this research need?*

Task 1: Create Lists of Potentially Leaking Components and Categorize

- Use existing documents of UST system components to, create lists of all UST system components that might potentially leak liquid gasoline, gasoline vapors, or both.
- Categorize each component as to potential loss (liquid, vapor, or both) and as to whether that loss is typically monitored in these systems. Categories include: not currently monitored; monitored adequately; monitored, but ineffectively (threshold too high, system readily fails, system modified or disabled, etc.)

Cost estimate: \$5,000.

Task 2: Estimate Potential Vapor Loss Masses and Possible Subsurface Impacts

- Use a range of values to estimate how much gasoline and MTBE might escape from several of the potential vapor loss locales.
- Use these mass-loss estimates to conduct simple one- or two-dimensional modeling to estimate what groundwater concentrations might result from these potential vapor loss mechanisms (either directly from vapor-phase to dissolved phase, or indirectly via vapor, to soil, and eventually to dissolved phase).
- Evaluate potential vapor loss mechanisms that may cause significant MTBE concentrations in groundwater (i.e., more than 10 µg/L). These should be noted as worthy of field monitoring and will be a priority for further study. Loss mechanisms, which are estimated to be so small as to not produce significant MTBE concentrations in groundwater, will be noted but labeled as low priority for further study and monitoring.
- Conduct if possible (i.e., reasonable effort), similar mass-load determinations for potential liquid-loss pathways.

Cost estimates: \$10,000-\$25,000.

Task 3: Identify Improvements to UST Monitoring System Components Currently in Use

Based on the identification of release locations identified in Task 1, and relative importance of loss volumes in Task 2, perform the following:

- Identify improvements that can be made to lower the leak-detection thresholds for individual monitoring components.
- Identify improvements that can be made to field-test equipment for improved UST system testing (e.g., integrity tests, tracer tests, etc.).

- Identify best management practices or facility management practices that will result in improved leak-detection monitoring, including visual inspections.
- Identify visual-inspection needs and make recommendations of how to implement visual inspections. The recommendations should focus on increasing the likelihood of observing product in secondary-containment components and detecting releases.
- Identify effectiveness of, and improvements to, inventory reconciliation methods in the use of leak detection.
- Identify portions of the UST system that do not currently have sensors, but where leak detection would benefit from their use. Recommend additional vapor and liquid sensors for secondary-containment equipment.
- Identify best available technologies to test the integrity of secondary containment components (i.e., sumps, dispenser pans, secondary piping and tank walls, lined trenches, etc.)
- Identify other improvements to leak-detection equipment or technologies based on a review of existing methods employed in Europe and those in the United States, such as for above-ground tanks (American Petroleum Institute document 653.)
- Identify, if possible, new, enhanced, or innovative UST system monitoring equipment to improve leak detection (e.g., electronic/optical/mechanical, etc.)

Cost estimates: \$10,000-\$25,000.

#### Task 4: Identify New UST Monitoring System Equipment That Can Be Used or Implemented to Increase Leak Detection

- Identify environmental monitoring technologies able to detect low-volume releases of vapor in the subsurface, based on the identification of leaking components described in Tasks 1 and 2.
- Identify the environmental monitoring technologies able to detect low-volume releases of liquid product in the subsurface, based on the identification of leaking components described in Tasks 1 and 2.

Cost estimate: \$10,000-\$15,000.

#### Task 5: Identify and Promote Incentives For Operators/Owners That Will Result in Reduced Releases

Define and promote socio-political changes/steps that would provide incentives to further reduce gasoline/oxygenate losses from USTs, such as:

- Increased regulatory authority available to regulators, etc.
- Tax changes such as the gasoline retailer paying taxes when the product is delivered.
- Other monetary or regulatory incentives.
- Better training and oversight of UST management personnel.

Cost estimate: \$5,000.

#### Task 6: Report

Prepare draft and final report that will summarize the findings and recommendations from Tasks 1-5. The report should be oriented towards educating UST owner/operators, UST construction/maintenance/operation personnel, regulators, consultants, etc. The report should be published and distributed through the research sponsor.

Cost estimate: \$10,000

#### ***Recommended task group membership:***

Convene subject matter experts from regulatory agencies and industry to form a technical advisory committee (TAC). Depending on the research sponsors' needs, the TAC could either conduct this work in its entirety or, if a consultant is hired to do this work, the TAC could oversee and direct the consultant's work.

Possible TAC members (individuals and organizations):

- Shahla Farahnak (Source Water Resources Control Board).
- Jim Crowley, Chris Tulloch: (Santa Clara Valley Water District).
- Local permitting agencies.
- Dave Camille (Tosco), others in Industry.
- Jim Davidson, Murray Einarson, Marcel Moreau in consulting.

- Matt Small: (USEPA).
- Local oversight programs.

***Comments:***

“Control of releases from USTs is the first and most cost-effective defense against soil and groundwater contamination. Research monies should be invested in development of 21<sup>st</sup> century monitoring systems that will provide an early warning of significant releases.

Research should also be conducted to evaluate European tank experience to determine if fewer releases are occurring and determine how this is being achieved.

Finally, research should be conducted to develop an effective emergency response program for assuring that early mitigation measures can be implemented at UST locations within highly vulnerable aquifer systems. Petroleum releases in these areas must be mitigated quickly (within weeks) to avoid unacceptable impacts on community water systems.” – ***Mike Kavanaugh***

“Tank-pit vapor, monitoring wells, and wells close to pipes and dispensers may be an excellent approach to detecting smaller leaks. It would be good to try this at some sites and increase the budget accordingly.” –***Ellen Moyer***

“Suggest increasing the budget because this issue must be resolved; otherwise, the MTBE problems will continue. This priority problem should be moved higher up, closer to number 2.”  
–***Rey Rodriguez***

“Develop a remote-sensing technology to alarm a responsible government agency and the appropriate oil company that a spill has occurred.”–***Mel Suffet***

“Do the field study, rather than just generating a review of existing systems. Adjust budget appropriately”–***Maria Tikkanen***



## **Develop Widely Usable Analytical Methods to Detect MTBE and Its Breakdown Products at Sub-ppb Levels**

### **WORKING GROUP MEMBERS:**

Church and Newman

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#### ***Research Need(s) Description:***

Due to the large quantities of MTBE that have been released (thereby resulting in detectable concentrations in urban air, surface waters, and some shallow groundwater), there is considerable interest in its environmental fate. The major product of all MTBE degradation pathways (biotic and abiotic) is TBA. To date, the use of TBA as an indicator of MTBE degradation has been limited because TBA is difficult to measure at low concentrations. To overcome this difficulty, analytical methods are needed that give rapid and sensitive detection of MTBE and TBA as well as the other likely degradation products (such as TBF, acetaldehyde, methyl acetate, isopropanol, and acetone). It would also be beneficial if these analytical techniques could be used for other compounds that may be used as fuel oxygenates in the future, such as ethanol.

These goals have been partially achieved by the use of various methods; however, these methods are, unfortunately, laboratory specific and often require specialized equipment. The problem, therefore, is to develop analytical techniques for the detection of these compounds at environmentally relevant levels that can be used routinely on typical laboratory equipment.

Additionally, a useful option would be to explore an *in situ* analytical system that eliminates the need to move samples back to a laboratory, where contamination of the sample can occur either in shipment or during analysis in situations where MTBE is routinely used as an extractant in other methods.

#### ***Importance:***

The regulatory limits of MTBE and TBA are currently in the low microgram-per-liter range; thus, developing technologies that can routinely be used to analyze samples to this level are important and necessary. The validation of new methods to remediate or remove MTBE and degradation products from drinking-water sources depends on being able to document removal. Thus, the need exists to develop methods for the analysis of samples that are more complex than routine aqueous samples (i.e., small volume tissue samples).

***How do you propose attacking this research need?***

- Conduct cross-disciplinary communication between biologists, water quality specialists, and analytical chemists to define the likely sample matrixes.
- Examine existing methodologies that can be modified to meet this purpose, including solid-phase micro-extraction, direct aqueous injection, or heated purge and trap.
- Develop new technologies that will address this need in innovative ways.
- Perform method detection limit (MDL) studies to evaluate the ability of the modified or new methods to detect TBA and other degradation products. These methods also need to be approved by the Department of Health Services Office of Drinking Water.

We recommend achieving these goals through a three-tiered approach. This would involve funding three independent research proposals that would benefit from the knowledge gained in the other proposals. Thus, good communication between the research teams is critical. The attached budget would represent an individual budget for each of the proposals. The three projects would be broken down into the following tasks:

- Develop a widely usable analytical method that can be used in a typical laboratory without the need for specialized equipment. This method needs to be sensitive to microgram-per-liter levels and easily modified to examine a wide range of sample matrixes (e.g., water, soil, and bacterial or plant tissue).
- Develop a specialized, ultra-sensitive method capable of analyzing for MTBE and its degradation products at nanogram-per-liter levels in aqueous samples. This method needs to be validated for use in drinking water analyses.
- Develop *in situ* sampling and analysis equipment and methods to eliminate the need for sample transport. The goal will be to develop a method that can analyze aqueous samples to microgram-per-liter levels, but this may not be achievable with field-based equipment.

***Recommended Task Group Membership:***

- Clinton D. Church (USGS).
- Andy Eaton
- B. Ekwurzel
- Gabe Kaplan (GGC Analytical).
- Joel Kiff (Kiff Analytical).
- Lee Newman (College of Forest Resources, University of Washington).
- James F. Pankow (Dept. of Environmental Science, Oregon Graduate Institute).
- Rey Rodriguez (H<sub>2</sub>O R<sup>2</sup> Consultants).
- Mel Suffet (UCLA, Environmental Science & Engineering Program).
- Roy F. Spalding (Water Science Laboratory, University of Nebraska).
- Maria Tikkanen (East Bay Municipal Utility District)
- Gary Yamamoto (California Department of Health Service)

***Proposed budget for Analytical Method Development  
(per task)***

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Salaries and benefits	\$85,000
This would include salaries for faculty (8%), technical support (50%) and a graduate student (100% plus tuition).	
Capitol equipment	40,000
Analytical equipment	
Supplies	20,000
Support	3,000
<hr/>	
Subtotal	\$148,000
Overhead (40%)	59,200
Total	\$207,200

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***Comments***

“Could include AI Verstuyft of Chevron in the task group, (510) 242-3403 or  
awve@chevron.com” - ***David Pierce***

“ Include, Sloana Rhodes, Equilon Enterprises in the working group” – ***Joseph Salanitro***

# **Investigate Ethanol Data Gaps Prior to Increased Ethanol Use**

## **WORKING GROUP MEMBERS:**

Moyer and Pierce, with contribution from Davidson

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### ***Research Need(s) Description:***

A variety of regulatory agencies have mandated substituting ethanol for MTBE in gasoline within a relatively short period of time. However, the consequences of this substitution have not been thoroughly evaluated. A number of data gaps are apparent, including:

- Compatibility with UST components, such as gaskets and seals.
- Trace contaminants present in fuel grade ethanol.
- Effects of ethanol releases to groundwater on BTEX fate and transport.

### ***Importance:***

- If compatibility is a problem, even upgraded UST systems compliant with existing regulations may fail and allow releases.
- Trace contaminants that we are unaware of today may pose unforeseen treatment and remediation problems later, as TBA has with respect to MTBE releases.
- Preferential biodegradation and/or phytoremediation of ethanol could inhibit BTEX degradation and lead to longer BTEX plumes.
- Potential co-solvent impacts of heat ethanol may release BTEX adsorbed from soil or increase BTEX solution into groundwater from free-phase gasoline.

### *Approaches to Attack These Research Needs:*

- Compatibility.

Phase I: Survey UST-system specifications to understand what materials of construction are and have been used; survey literature and vendor information to ascertain current understanding of compatibility; survey tank owners, contractors, and regulators who may have knowledge of compatibility problems, especially in the Midwest where ethanol has been used extensively in gasoline.

Phase II: If information from Phase I indicates a need, perform laboratory compatibility studies on old and new UST system gaskets, seals, and other components. Subject them to gasoline plus ethanol; water plus ethanol; gasoline plus ethanol plus MTBE plus TAB; and air, as appropriate, to mimic actual field conditions at appropriate temperatures over appropriately long periods of time (on the order of one year). Analyze mass loss, constituents leached into the liquids used, and changes in material properties, such as elasticity.

- Trace contaminants. Use suitable analytical methods, including GC-MS, analyze neat samples of fuel-grade ethanol from several major suppliers. If possible, develop a list of target compounds in advance. These would include other alcohols and biodegradation breakdown products, such as aldehydes.
- Impact on BTEX plumes: Review data on ethanol concentrations in groundwater at existing sites. Release gasoline with ethanol, gasoline with MTBE, and unoxygenated gasoline in parallel test plots at a well-characterized site in an area with little or no prior contamination. Test plots would have a phytoremediation area some distance downgradient of the release area. Monitor groundwater and vapor concentrations and biological parameters over time in the parallel plots and compare the fate and transport of gasoline constituents.

Parameters might include: hydrocarbon fractions, BTEX, ethanol, MTBE, TBA, formaldehyde, acetone, organic acids (acetic, etc.), dissolved oxygen, redox potential, pH, iron, sulfate, nitrate/nitrite, ammonia, phosphate, methane, carbon dioxide, oxygen, and plate counts, among others.

- Identify a site where a release of neat ethanol has occurred over a site previously contaminated with a gasoline release, and study the impact of neat ethanol on plume migration and biodegradation of the gasoline components. If possible, identify a site where a controlled release of ethanol could be made, so that parallel studies of plume dynamics with and without ethanol impacts can be made.

Additionally, if no such site is available, conduct column studies in the laboratory. Experiments would study parallel columns contaminated with non-oxygen gasoline. These columns would be leached with spills of new materials, including neat ethanol, gasoline containing MTBE, non-oxy gasoline, and a suitable control material.

- Consider a proposal similar to that of Barker et. al. (5/23/00), who have proposed a strategy to assess a plume of gasoline containing 22% ethanol in Brazil. This plume has already been characterized to some degree and appears very suitable for this investigation. Their approach includes field activities (including additional monitoring wells and improved hydrogeological characterization) and laboratory microcosm experiments.

***Budgets:***

- Compatibility: Phase I at \$40,000 and Phase II at \$300,000-\$400,000, assuming prior compatibility testing has been minimal or none. The American Petroleum Institute may be performing a version of Phase I in the next 6 months.
- Trace Contaminants: \$40,000.
- Impact on BTEX Plumes:
  - Parallel studies with ethanol, MTBE, and oxy-free gasoline: \$300,000-\$500,000.
  - Site study of a neat ethanol spill: \$300,000.
  - Barker et al. study in Brazil: \$150,000 over 3 years.

***Recommended Task Group Members:***

- Compatibility testing. The organization directing the project should be knowledgeable of USTs, gasoline, and analytical issues. Underwriters Laboratory or a similar organization may be best to carry out the actual testing.
- Impact on Plumes. The research organization could be a university or a large environmental consulting firm with expertise in gasoline, *in situ* bioremediation and phytoremediation, natural attenuation, fate and transport, subsurface delivery systems, and analytical.

The task group would probably include Pedro Alvarez, University of Iowa; Roy Spalding and others, University of Nebraska; Barker and others, University of Waterloo; and the Nebraska Ethanol Board.

***Comments:***

“The research on ethanol fate and transport (F&T) should be combined with field studies on F&T for the other oxygenates (Priority 5).

Ethanol has been widely used in many areas of the U.S. (Midwest) and there should be an effort to collect monitoring data for ethanol at these sites, before any major work on field studies begins.

Cost sharing with the Midwest states (e.g., Nebraska) on these projects should be considered.

The effect of temperature should be considered in F&T studies. Biodegradation rates decline significantly at low temperatures (e.g., Lake Tahoe, Great Lakes, and Northern States)” –***Jim Crowley***

“Need to add ‘field Concentrations of ethanol’ from field sites that have ethanol in groundwater to your list. We have almost no data, and so we do not really know which model input/output to use.

On study of pre-existing contaminated sites, also consider ‘release’ of residual hydrocarbons from soil (due to surfactant).” –***Jim Davidson***



## **Develop a Protocol for Multimedia Review of New Oxygenates for Use in Fuels (How Can We Prevent Another MTBE Contamination Catastrophe?)**

### **WORK GROUP MEMBERS:**

Hoffmann and Tikkanen

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### *Research Need(s) Description:*

Often, changes in reformulated fuels to meet regulatory mandates are developed with a limited scope. For example, changes in the specifications of reformulated fuels, as a consequence of the 1990 Clean Air Act Amendments, included an oxygenate requirement which apparently took into consideration only air-quality issues. As a result, potential adverse impacts to soil and water resources were not adequately reviewed and addressed. Upon introduction of MTBE in gasoline, contamination of ground- and surface-waters was observed. Much of this contamination came as a consequence of leaking underground storage tanks (LUSTs) that contaminated groundwater aquifers and gasoline-fueled motorized-boating contamination of drinking-water reservoirs.

It is important to consider both the beneficial and adverse impacts to all environmental phases (e.g., air, water, and soil) when revising fuel-composition specifications to meet legislative and/or regulatory mandates.

### *How do you propose attacking this research need?*

Establish a task force composed of appropriate stakeholders to develop the protocol for multimedia review of new compounds proposed to be added to reformulated fuel. This protocol will be the format used to review available information regarding such issues as environmental fate and transport and the physical properties of oxygenates being considered for use in fuel. Additionally, any necessary data gaps would be identified.

Hold a workshop to bring the stakeholders together to develop the protocol. A Nominal Group Technique workshop may be an effective method of developing this necessary protocol. A

component of the workshop would be to draft a protocol. Subsequent teleconferences and meetings would be used to finalize the protocol.

***Recommended Task Force Membership:***

The task force should include, as a minimum:

- Representatives of petroleum refiners.
- Water utilities that use either groundwater or surface water supplies.
- Association of California Water Agencies.
- American Water Works Association Cal-Nevada.
- Environmental advocacy groups.
- California Air Resources Board.
- State Water Resources Control Board.
- Department of Health Services, State of California.
- California Environmental Protection Agency.
- U.S. Environmental Protection Agency.

***Comments:***

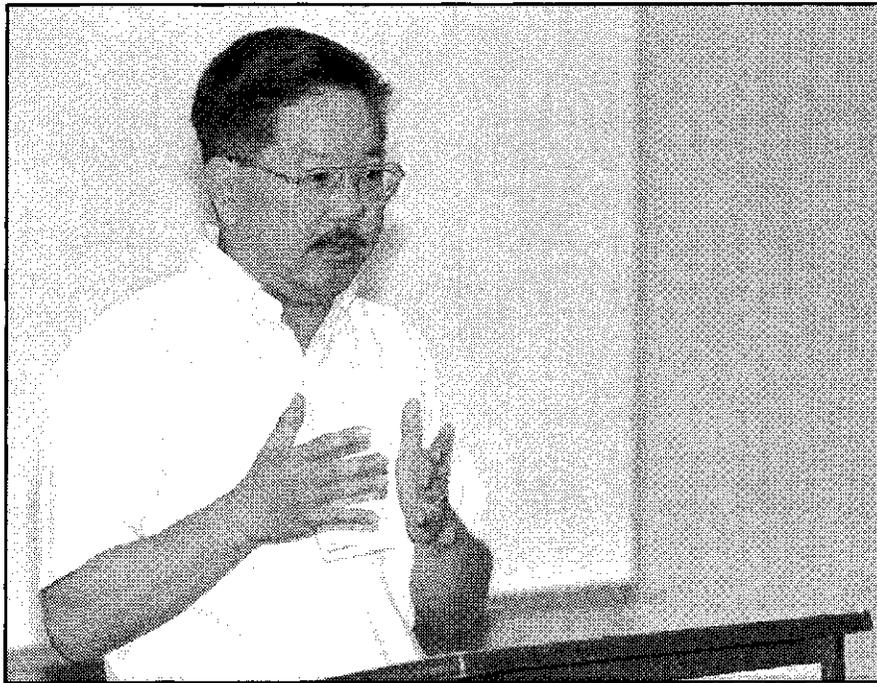
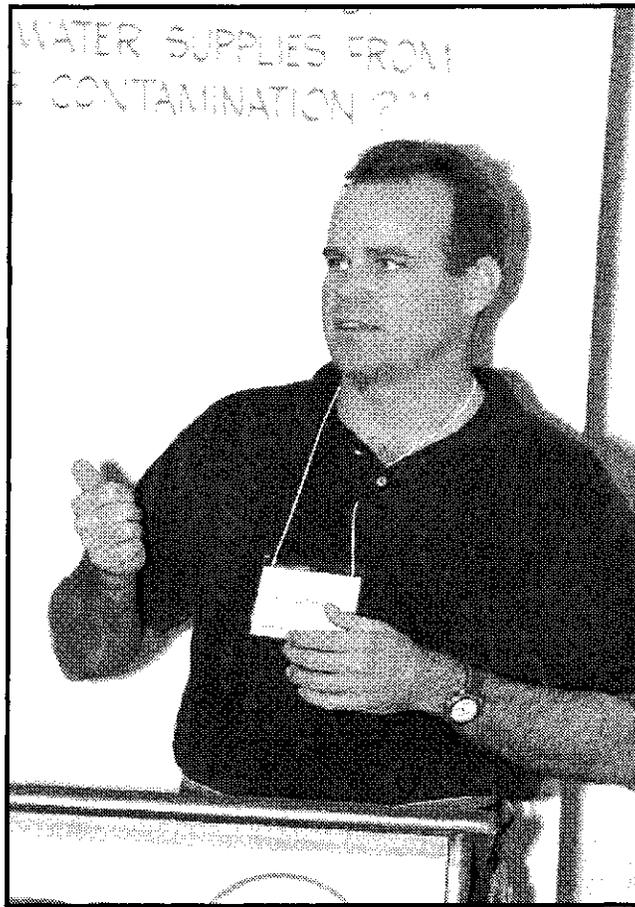
“Learn from other ‘life-cycle analysis’ efforts to see what points should be considered (e.g., automotive manufacturing industry).

Early in the process, bring in different people who were involved in early MTBE approvals and use decisions. Bring in scientific experts from several different disciplines (learn from their experiences in a ‘mini-EPA Blue Ribbon Panel’ manner.” – ***James Davidson***

“Expand stakeholder group to include air quality experts and air quality regulators, and air quality advocacy groups (e.g., American Lung Association). Because this is a national issue, need to include TSCA experts, as well. I would also include EPA experts from the EPA/ORD. Suggest a format that includes a two-day workshop on facts/issues/science/history. Budget should be \$100,000.” – ***Mike Kavanaugh***

“I think that it is important to emphasize that the protocol would identify data gaps, and that it is highly unlikely that all the necessary data would already exist.” – *Ellen Moyer*





# **Predict Maximum MTBE Concentrations in Water-supply Wells**

## **WORKING GROUP MEMBERS:**

Einarson and Yamamoto

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### *Research Need(s) Description:*

In many cases, defining the mass discharge (or total mass flux) of dissolved contaminants emanating from LUFT sites may facilitate estimating the concentration of the contaminants in a water-supply well that eventually captures those plumes. Published values of MTBE mass discharge range from 0.3 to 7 grams per day. This suggests that many dissolved plumes of MTBE will result in relatively minor impacts to large municipal supply wells. For example, at steady-state conditions, a supply well pumping at 250 gpm that captures a 7 gram-per-day plume will contain MTBE at a concentration of approximately 5 ppb. At higher pumping rates, the concentration of the contaminant in the well can be expected to decrease due to the extraction of cleaner groundwater that will further dilute the contaminant in the supply well.

Many additional values of MTBE mass discharge will need to be compiled to define the range of MTBE mass discharge is typical of most fuel-release sites. Also, because MTBE dissolves rapidly from the source-zone NAPL, estimating the mass discharge immediately downgradient of source zones today may understate the MTBE mass discharge already flowing in the distal portion of the dissolved plumes. Additional work is needed to evaluate the temporal evolution of dissolved MTBE plumes and the resulting spatial distribution of MTBE mass in dissolved plumes.

### *Importance:*

Addressing this topic will help California's groundwater managers to:

- Understand the magnitude of the "MTBE Threat."
- Judge whether we will continue to detect only low levels of MTBE in municipal supply wells.
- Design appropriate wellhead treatment systems.

- Understand the “lifespan” of MTBE fuel releases. How long will we need to deal with MTBE contamination in California’s drinking-water wells?
- Identify what types of water-supply wells (e.g., large municipal systems or small domestic wells) are most at risk.
- Estimate the timing of future impacts in order to minimize wellhead-monitoring costs.
- Prioritize site investigation and cleanup efforts.

***Suggested Approach (and estimated budgets):***

- Compile additional estimates of MTBE mass discharge from fuel release sites in California. Use data from conventional site assessments and sites instrumented with transects of multi-level monitoring wells. Calculate the mass discharge values using reliable data from existing pump-and-treat systems (e.g., extraction rate and average MTBE concentration in effluent). Use this information to identify which types of supply wells are most at risk, prioritize site cleanup efforts, and develop programs for cost-effective wellhead monitoring of groundwater quality.

Cost estimate: \$100,000.

- Apply the mass discharge approach at several locations in California where municipal water-supply wells have been impacted by MTBE releases. Identify suspected MTBE source zones and estimate the cumulative MTBE mass discharge emanating from those sites. Use this information to estimate the maximum concentrations of MTBE that will be present in those wells. Monitor MTBE concentrations in samples from the supply wells over time to assess the accuracy of the method. Use the information to design appropriate wellhead treatment systems.

Cost estimate: \$200,000.

- Explore the temporal variations in MTBE mass discharge. This can be accomplished by monitoring the mass discharge in transects of multi-level wells immediately downgradient of source zones. Also, past variations in source-zone MTBE-dissolution rates can be inferred by defining the spatial distribution of MTBE mass in dissolved plumes (MTBE mass discharge in the distal end of a dissolved plume reflects the rate of MTBE dissolution immediately after the release occurred when MTBE in the NAPL was most soluble). Empirical data from this task should be used to validate existing and new numerical-source dissolution models in order to develop tools that can help predict MTBE plume life-spans in a variety of hydrogeologic settings.

Cost estimate: \$500,000.

***Recommended Task Group Membership:***

- California Department of Health Services.
- California Environmental Protection Agency.
- Appropriate county agencies.
- Douglas Mackay (University of Waterloo).
- Graham Fogg (University of California, Davis).
- Bill Rixey (University of Houston).
- Murray Einarson (Geo Syntec Consultants).
- Representatives of major oil companies.
- Representatives from water suppliers.

***Comments:***

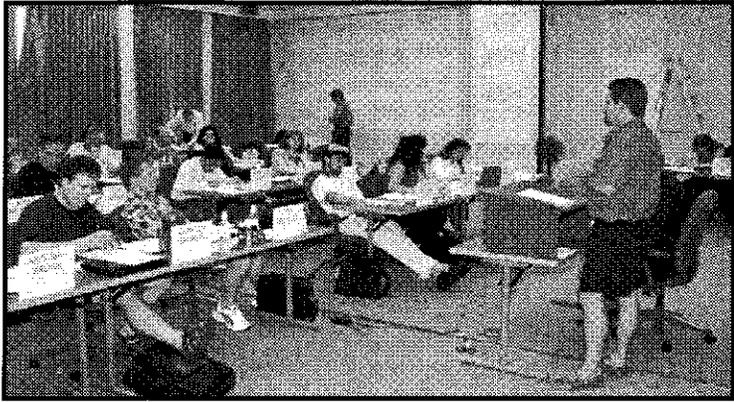
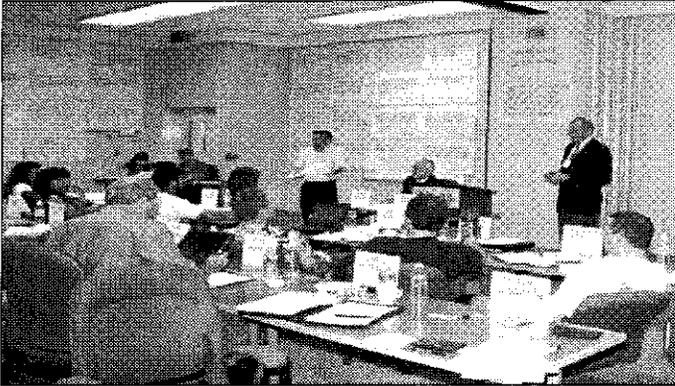
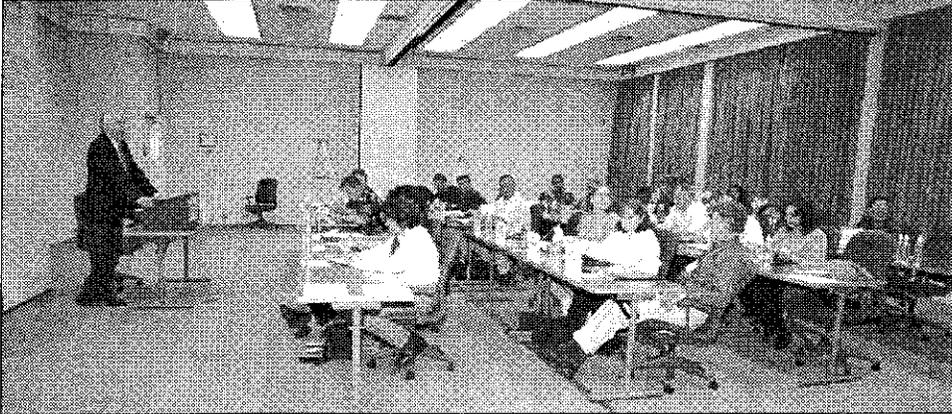
“A study similar to that described in this research priority is currently being conducted by the U.K. Environment Agency. The results of this study, done before the end of the year, will help in the development of this research program.

Komex is conducting the study for the U.K. Environment Agency. We would be able to assist with a similar study in California.

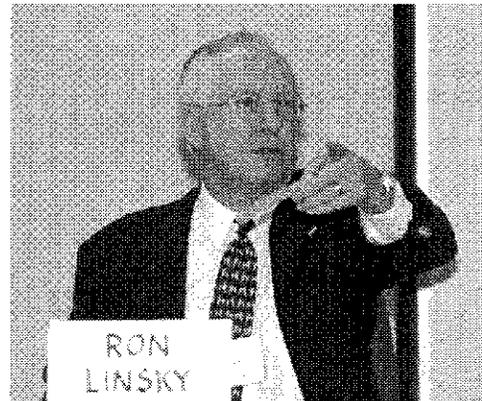
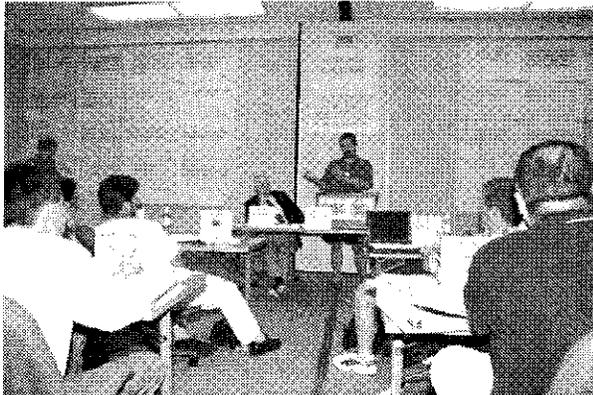
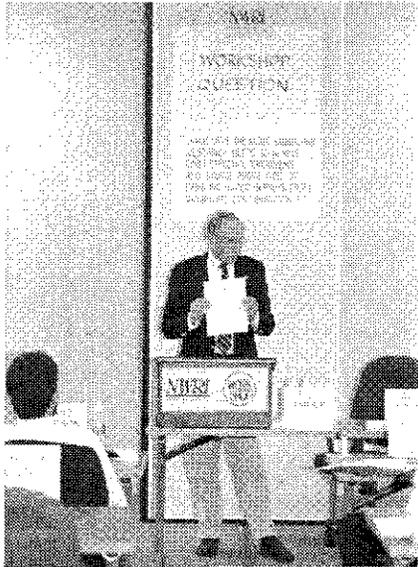
The position of DHS and the water utilities is that the receptor is the resource – the aquifer, not the well. A well is a point in space where water is drawn from the resource. I agree that well-specific concentrations are important in evaluating well-head treatment options; however, they should not be used to prioritize site remediation or as a significant factor in source water assessment and protection programs (SWAPP). We do SWAPPs, not wellhead protection programs as in the 1970-80’s. The water utility should be able to withdraw water from any point within the resource.”-***Anthony Brown***

“The presentation talks about existing wells and seems to assume no new drinking water wells will be installed (e.g., in the middle of the plume or near the source). This could especially be a problem for private wells and/or bedrock wells.” -***Ellen Moyer***

“One caution is that this approach will certainly help estimate concentrations at the drinking-water wellhead. Water utilities must be able to pump from any area in the contaminated aquifer. In southern California, water supplies are dependant on groundwater resources.” - *Key Rodriguez*



# **NGT Workshop**



## INTRODUCTION

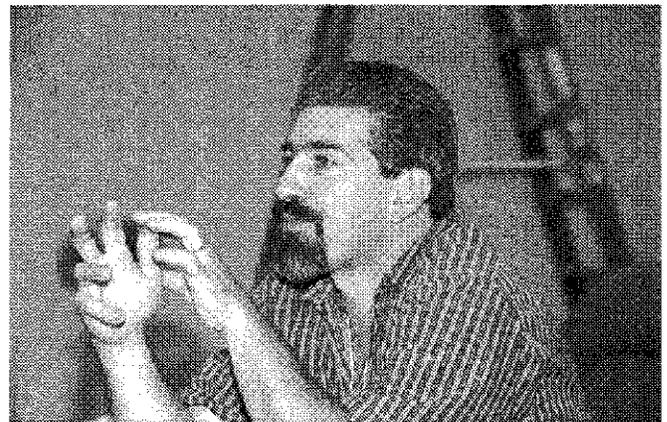
Professors Delbecq and Van de Ven developed the NGT process in the late 1960s at the University of Wisconsin. Their goal was to design a process that would encourage a group of individuals to meet and quickly come to consensus without the usual delays that occur when each participant takes time to establish his or her own credentials before the group, or the dominance of the meeting by one or more highly vocal individual(s). The technique also permits a group of individuals to address a question that cannot be resolved satisfactorily by a single individual. This technique has been improved and refined over the past three decades by Dr. William S. Gaither, who facilitates NGT workshops for NWRI.

Leaders in the field of oxygenate research, remediation, and regulation were identified by NWRI, the California Department of Health Services, and the California MTBE Research to attend the NGT workshop (See Appendix D for Participant List).

Participants were asked in advance to consider the question: *What are the most significant research needs to achieve cost-effective treatment and source protection of drinking-water supplies from oxygenate contamination?* Participants arrived at the Kellogg West Conference Center on the first evening for dinner and orientation, where the workshop guidelines and procedures were reviewed. Early the next morning, the workshop was conducted. It comprised three distinct steps:

1. Identification of research needs.
2. Consolidation of research needs into major research areas, taking care to minimize overlap between research areas.
3. Ranking of research needs in descending order of importance by each participant.

The 22 participants identified 113 research needs during the course of the morning. The titles of these research needs were lettered on large sheets of paper and posted on the workroom wall. After lunch, participants were guided through a systematic discussion in which they consolidated the 113 needs into 29 major research areas. At the conclusion of the consolidation process, each participant completed a ranking sheet on which he or she listed, in descending order of importance, the 10 most important research needs. Participants continually edited and improved the individual research-need write-ups they had presented during the morning session until they departed mid-day on Sunday. They approved each revised write-up prior to leaving the venue.



# **Optimize Emerging Technologies for Water Treatment of Oxygenates and Their Degradation Products**

## **ORIGINATORS:**

Suffet on behalf of himself, Liang, Lien, Pierce, Rodriguez, Salanitro, Tenney, Woodward, and Yamamoto

*The following research needs were consolidated under the above title:*

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**Title:**           **Optimize Emerging Technologies for Water Treatment of Oxygenates and Their Degradation Products**

**Originator:**   Suffet

### ***Research Need Description:***

Many emerging technologies need to be evaluated to be actually used in the remediation of oxygenates and their degradation products.

### ***Importance:***

At present, we do not have the actual data to use the methodology properly.

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**Title:**           **Critical Review of Biological Treatment for Removing Oxygenate Contamination and Their Byproducts in a Drinking Water Treatment Plant**

**Originator:**   Liang

### ***Research Need Description:***

- No clear and full understanding of how to apply biological treatment to produce potable water and meet all drinking-water regulations.
- What are the factors impacting the implementation of this technology?

***Importance:***

It is important to set up a foundation to investigate the biological treatment in the drinking water industry.

***How do you propose attacking this research need?***

Any university professor working on water treatment-related issues can do this work.

---

***Title:***            **Investigate Integrated Membrane Technologies to Remove MTBE and Other Oxygenates**

***Originator:***    Liang

***Research Need Description:***

Very limited information is available on membrane technologies for removing MTBE and other oxygenates. Based on the preliminary research results, reverse osmosis (RO) and nanofiltration (NF) can effectively remove MTBE, but long-term impacts on membrane integrity are unknown.

***Importance:***

Membrane technologies are emerging technologies in the industry. The information collected through this proposed project can provide additional information to employ these technologies.

***How do you propose attacking this research need?***

- Conduct bench-, pilot-, or full-scale studies to approach these challenges.
  - Any researchers currently working on membrane technology can do the work.
- 

***Title:***            **Treatment of MTBE and Other Oxygenates by Pulsed-UV and Pulsed-UV/H<sub>2</sub>O<sub>2</sub> Processes**

***Originator:***    Liang

***Research Need Description:***

Conventional UV, alone, at 254 nm cannot remove MTBE, but pulsed-UV can remove MTBE through direct photolysis. Currently, UV is an emerging technology in the water industry for pathogen inactivation.

The use of this technology will assist water utilities in achieving both chemical oxidation of MTBE and other oxygenates and pathogen inactivation.

***Importance:***

To provide more information and understanding of employing pulsed-UV and pulsed-UV/H<sub>2</sub>O<sub>2</sub> (hydrogen peroxide) technologies in the water industry.

***How do you propose attacking this research need?***

Researchers currently working on UV technologies can do this work. Bench-, pilot-, and full-scale studies are required.

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***Title:***            **Develop Environmental Catalytic Technology for the Treatment of Oxygenates in Drinking-Water Systems Using Bi-functional Aluminum as an Example**

***Originator:***    Lien

***Research Need Description:***

In practice, catalysis is primarily a technology that draws on many fields, such as organic and surface chemistry, and has been widely used in industry for several decades. However, in a conventional water-treatment plant, catalysis seems to be too luxurious to be used. This is because, in part, the goal of the modern water plant has been set only for the treatment of common contaminants using conventional treatment processes. Now, because of oxygenate contamination, it is about time to reconsider the prospective of catalytic technology in water treatment.

***Importance:***

Mainly, two key factors have to be considered in order to design a cost-effective treatment of oxygenates, specifically for drinking-water treatment. One is reactivity. The other is feasibility. Although homogeneous advanced oxidation methods, such as photocatalysis (ozone, ozone/UV, hydrogen peroxide, and ultrasound) have been suggested for effective treatment of oxygenates, these methods are relatively expensive. Various chemical reagents are often needed and may limit their usefulness in water and wastewater treatment. Biodegradation of oxygenates is also being studied in many laboratories. Reported results show that some biodegradation can occur under natural conditions, but the rate is generally slow.

***How do you propose attacking this research need?***

Bi-functional aluminum, as an effective catalyst, is specifically designed to treat oxygenate-contaminated drinking water. Bi-functional aluminum is synthesized by acidification of metallic

aluminum with strong acids. As a newly developed material, bi-functional aluminum could become one of the most promising solutions for the treatment of oxygenates because of its high reactivity and feasibility. It has a high reactivity to effectively degrade MTBE in the aqueous solution under ambient conditions. Degradation of MTBE in the ppm-range using bi-functional aluminum was completed within hours. A heterogeneous reaction occurring in the transformation of MTBE by bi-functional aluminum strongly benefits the feasibility of the bi-functional aluminum technology in drinking-water treatment processes.

A proposal related to this technology has been accepted by the USEPA and will be sponsored by the National Research Council.

---

***Title:***            **Bio-GAC Treatment of Oxygenates**

***Originator:***    Pierce

***Research Need Description:***

Recent data suggest that tertiary-butyl alcohol (TBA) is a common byproduct in MTBE manufacture and, therefore, tends to be present in water contaminated with MTBE. Data suggest that while TBA is present in gasoline in only trace amounts, it can be present in water at 10-100 percent or more of the MTBE concentration because it is far more soluble in water and will partition more to the water phase.

Additionally, TBA, acetone, tertiary-butyl formate (TBF), and other oxygenate byproducts may result from degradation of MTBE by other treatment processes (e.g., advanced oxidation). Thus, these processes may benefit from additional polishing for such compounds.

TBA, acetone, TBF, and other alcohols (e.g., ethanol) are highly soluble in water and, therefore, are far more difficult to air strip or absorb than even MTBE. Advanced oxidation can further oxidize these compounds, but acetone, in particular, is recalcitrant to advanced oxidation, so this process may not be a practical route for treatment in some scenarios.

***Importance:***

Little is currently known about biological degradation of these compounds in mixtures where more biodegradable compounds (e.g., ethanol, BTEX) may compete too well with microorganisms suited to degrade tertiary carbon molecules. Efficacy and design data are needed.

***How do you propose attacking this research need?***

Bio-granular activated carbon (GAC), in which microorganisms are allowed to grow in a bed of granular activated carbon, seems a promising option for treatment of these problem compounds. Pilot data at the Santa Monica Charnock site suggested that bio-GAC was a viable option for

mixtures of MTBE and TBA to reduce the TBA. MTBE can then be absorbed by suitable types of traditional GAC. GAC was not a practical option for TBA because it is so weakly adsorbed and is preferentially displaced from the GAC by MTBE.

A system of bio-GAC (or any suitable fixed film biological reactor) and traditional GAC should be piloted to reduce mixtures of TBA, MTBE, BTEX, and other possible compounds. A side benefit of bio-GAC is that to the extent that it also degrades BTEX, BTEX will not displace MTBE adsorbed on downstream GAC beds.

Organizations that perform this work: Malcolm-Pirnie, Kennedy-Jenks, and other consultants with a background in the treatment of oxygenates and with a process engineering staff.

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**Title:** Evaluate Adsorption Capacity and Regeneration of Synthetic Resin Sorbents for the Removal of Oxygenates in Groundwater

**Originator:** Rodriguez

***Research Need Description:***

The use of synthetic resin sorbents for the removal of MTBE, TBA, and other oxygenates has been tested under small-scale laboratory conditions and has shown that it can be effective for the removal of oxygenates in drinking water. In addition, small-scale regeneration studies have also been conducted to indicate that resins can be regenerated using steam and achieve close to the original adsorption capacity, but an understanding as to the continued loss of capacity over multiple regeneration cycles is still not understood. Laboratory testing is ready to be moved to the field to evaluate both the adsorption and regeneration capacities of resins.

***Importance:***

Full-scale demonstration of this technology is necessary to understand the effectiveness and costs of utilizing this technology. Because of the perceived high costs of resins, limited testing, and the lack of active systems treating MTBE, there has been limited pursuit of this technology over other more established technologies like GAC and air stripping.

***How do you propose attacking this research need?***

- Develop a work plan for the field demonstration testing of synthetic resin sorbents and regeneration alternatives in removing drinking water contaminated with MTBE, TBA, and, potentially, other oxygenates.
- Perform economic analyses of the treatment process.

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**Title:** Are Advanced Oxidation Processes (AOPs) Viable Alternatives for Removing Oxygenates from Drinking Water?

**Originator:** Rodriguez

***Research Need Description:***

Numerous small pilot-scale and laboratory studies have been performed to evaluate the effectiveness of AOPs for underground storage tank (UST) cleanup sites; however, full-scale studies geared toward drinking-water applications have not been conducted. There is a lack of knowledge in:

- The understanding of the potential toxicity of byproduct formations (e.g., aldehydes or ketones, alcohols).
- The understanding of the potential toxicity of process in organic byproduct formation (e.g., bromate from bromide-laden waters).
- The presence of competing organics that may require pre-treatment.
- The understanding of the residual products of AOPs and their impacts on microbial growth in distribution systems.
- Investigating other interference (such as nitrate absorbed by UV, different pH and alkalinity levels changing the formation of hydroxyl radicals) impacting oxygenate reduction.
- Investigating hybrid systems, such as biologically activated carbon systems or others, for the destruction of process byproducts for polishing effluent.

***Importance:***

The uncertainty of the effectiveness and costs of AOP technologies, the analytical methods for some oxygenates (TBA), and the byproducts formed as a result of the breakdown of MTBE, TBA, and other oxygenates have hampered full-scale testing of what appears to be a cost-effective technology in breaking down oxygenates under large- and low-flow rate applications. The cost of performing full-scale demonstration studies has further hampered the development and understanding of AOPs. AOP technologies may be cost effective in treating oxygenates as part of a treatment train with GAC, bio-GAC, and air stripping.

***How do you propose attacking this research need?***

A sufficient number of laboratory testing and small-scale field tests have been performed that identified the types of AOPs that appear to be most effective in breaking down oxygenates. Full-scale pilot studies will be performed using these technologies (UV/hydrogen peroxide, pulsed

UV/hydrogen peroxide, ozone/hydrogen peroxide, cavitation/hydrogen peroxide) to address the uncertainties identified above and to perform an economic analyses on the treatment costs.

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**Title:**           **Optimize *Ex Situ* Biotreatment of Concentration Levels of Oxygenate and Gasoline Range Hydrocarbons (GRH)**

**Originator:**    Salanitro

***Research Need Description:***

Pump-and-treat systems for groundwater remediation of difficult-to-degrade compounds (e.g., oxygenates, chlorinated organics) have traditionally used physical/chemical removal techniques (e.g., air stripping, vapor or liquid oxidation, activated carbon sorption). Such systems require high initial capital and funding for significant operation and maintenance (O&M) expenses.

***Importance:***

Efficient and reliable *ex situ* biodegradation systems (bioreactors and biologically active carbon beds) may have the potential for cost-effective treatment of groundwater containing oxygenates and GRH to below maximum contaminant levels (MCL).

***How do you propose attacking this research need?***

Develop modified, improved, high-solids retention bioreactors and biofilmed carbon beds that can consistently and reliably:

- Achieve  $\geq 99$  percent removal of oxygenate/GRH.
- Operate at varying hydraulic flow regimes (e.g., few to 20 or 30 gpm) with concentrations of oxygenate/GRH in the range of 10 ppm and 100 ppb.
- Biodegrade contaminants at 10° and 20° Celsius.
- Operate with minimal maintenance.

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**Title:** Use Naturally Occurring Oxygenate Degraders in the Remediation of Public and Private Potable Water Supplies

**Originator:** Salanitro

***Research Need Description:***

Current regulatory statutes prohibit the use of microbes in the removal of oxygenates from drinking water. Although naturally occurring soil microorganisms are ubiquitous in groundwater and colonize activated carbon and ion-exchange resins and filtration units, bioaugmentation of existing water-treatment units is not permitted.

***Importance:***

The inclusion of biotreatment (using non-pathogenic, naturally occurring microbes) as an additional remedial technology for potable-water supplies could reduce the cost of physical and chemical treatment. For example, oxygenates are poorly sorbed by activated carbon, but filtration systems inoculated with actively degrading organisms could reduce replacement costs and improve the O&M costs of carbon beds.

***How do you propose attacking this research need?***

- Evaluate the potential for drinking-water biotreatment in conjunction with existing technologies (physical/chemical).
- Determine requirements for bioaugmenting GAC beds and limits to treating oxygenates (concentrations, hydrolic residence time [HRT], reliability) in simulated pilot tests.
- Determine potential toxicity of microbes intended for water biotreatment using standardized pharmacological and pathogenicity tests in animals (mice/rats/rabbits).

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**Title:** Evaluate and Develop Cost-effective Synthetic Resin Regenerate Disposal Strategies

**Originator:** Tenney

***Research Need Description:***

Synthetic resin adsorbents are viable for removing MTBEs in the presence of competing synthetic organic compounds (SOCs), such as TBA. Resin treatment systems, however, have high-capital costs, especially when compared to similar treatment technologies, such as GAC. In spite of high-capital costs, resin treatment systems may be promising if long-term costs (e.g., O&M costs) can be demonstrated to be lower than those for similar technologies. The key

to minimizing long-term O&M costs is the development of low-cost strategies to manage resin regenerant streams.

***Importance:***

Fixed bed adsorbents, such as GAC and synthetic resins, are attractive because of their ready acceptance by regulatory agency officials and their ease of use. GAC is a viable technology for MTBE removal, but its performance declines in the presence of increased natural organic matter (NOM) content and SOCs. In addition, GAC is known to have relatively high O&M costs for MTBE removal. Resin systems are effective at MTBE removal and have been shown to be effective at removing TBA.

***How do you propose attacking this research need?***

Evaluate various resin regenerant management options at both bench- and pilot-scale studies for various resins and source waters.

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***Title:***           **Chemical Catalyst for *Ex Situ* Degradation of Ether Oxygenates or for *In Situ* Abiotic Barriers**

***Originator:***   Woodward

***Research Need Description:***

MTBE is synthesized using a catalyst. However, if reactive conditions of pH and water content are off target, MTBE is converted to TBA.

***Importance:***

We need to explore commercial synthetic catalysts to define the conditions for optimizing catalysts for the degradation of ether oxygenates.

***How do you propose attacking this research need?***

Art Diaz's group on basic stability of ethers with pH and catalysts ETBE/MTBE producers and process chemistry would also be sources for this strategy.

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**Title:** Investigate Use of Regenerated Granular Activated Carbon (GAC) for MTBE Treatment

**Originator:** Yamamoto

***Research Need Description:***

Use of regenerated GAC for volatile organic compounds (VOCs) has resulted in water quality problems, like sulfide odors, and much shorter bed life than predicted.

***Importance:***

Should only virgin GAC be used, or can regenerated GAC be used without problems? It will probably be a question that the Department of Health Services will need to answer in the future.

***How do you propose attacking this research need?***

Fenton's regeneration system may be a way to produce a safe regenerated GAC system. Evaluate GAC that has been used to remove MTBE/TBA through several regenerations.

# **Conduct Laboratory and Field Tests of Enhanced *In Situ* Anaerobic and Aerobic Bioremediation of Oxygenates**

## **ORIGINATORS:**

Moyer on behalf of herself, Church, Deeb, Einarson, Newman, Rodriguez, Salanitro, and Woodward

*The following research needs were consolidated under the above title:*

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**Title:** Field Testing of Enhanced *In Situ* Anaerobic Bioremediation of MTBE/TBA

**Originator:** Moyer

### ***Research Need Description:***

Unenhanced anaerobic biodegradation of MTBE/TBA is usually too slow to adequately address source and near-source zones in the subsurface. Making these zones aerobic (i.e., by adding sufficient oxygen) is often difficult (i.e., resulting in clogging) and expensive.

### ***Importance:***

If ways could be found to accelerate *in situ* anaerobic biodegradation, timely cost-effective *in situ* destruction of high MTBE/TBA concentrations in soil and groundwater could be achieved. Acceleration of anaerobic MTBE/TBA biodegradation by the addition of humic acid and ferric iron has been demonstrated in laboratory microcosms. Acceleration of anaerobic benzene biodegradation by the addition of sulfate and by the addition of humic acid (an electron shuttle) and ferric iron has been demonstrated in the field. Field demonstrations of enhanced MTBE/TBA anaerobic biodegradation are needed.

### ***How do you propose attacking this research need?***

Pilot test several anaerobic enhancements at a suitable well-characterized field site in a near-source zone that is anoxic but free of separate-phase hydrocarbons. Set up three test plots for: a control; ferric iron and humic acid addition; and sulfate addition. Monitor baseline, pilot testing, and rebound groundwater samples from up- and down-gradient wells. Dr. Derek Lovley at the University of Massachusetts conducted the above-referenced research.

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**Title:**           **How Effective is Bio-enhancement of Native Microorganisms for the Treatment of MTBE *In Situ* (Source and Non-source Zones)?**

**Originator:**   Church

***Research Need Description:***

A number of studies (Mackay, Salanitro, Church) have indicated the existence of native microorganisms capable of degrading MTBE, if they are stimulated with oxygen.

We need to find out how common this occurrence is and how effective enhancement is for degrading MTBE *in situ*.

***Importance:***

Theoretically, the most effective way to protect sources is to stop the problem at or near its source. Unfortunately, we have no cost-effective way of doing this at present. Enhanced biotreated permeable “barriers” could solve this problem *if* we can figure out how to make this work.

***How do you propose attacking this research need?***

Salanitro, Mackay, Church

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**Title:**           **Understanding the Limitations, Mechanisms, and Implications of Anaerobic Oxygenate Biodegradation in Source Zones**

**Originator:**   Deeb

***Research Need Description:***

Source zones are typically oxygen-limited due to the presence of high concentrations of hydrocarbons. We know very little about anaerobic MTBE and TBA biodegradability, and even less about the biodegradation of ETBE, tertiary amyl methyl ether (TAME), and diisopropyl ether (DIPE) under anaerobic conditions. However, we know that ethanol is readily degraded anaerobically. The degradation of ethanol under methanogenic conditions in source zones and the accumulation of methane under gasoline stations could be problematic. Field studies are needed to investigate this.

***Importance:***

- No field studies have investigated the fate and transport (F&T) of ethanol-blended gasoline from leaking underground storage tank (LUST) releases in the U.S.
- No information/speculation is available on the degradation pathways of MTBE, other ether oxygenates, and TBA under anaerobic conditions.

***How do you propose attacking this research need?***

Laboratory studies are needed to understand the mechanisms of anaerobic MTBE, other ether oxygenates, and TBA degradation. Field studies are needed to understand the fate and transport of ethanol-blended gasoline plumes in subsurface environments.

---

***Title:***           **How Ubiquitous Are Indigenous, Naturally Occurring, MTBE-degrading Microorganisms at Fuel Release Sites?**

***Originator:***   Einarson

***Research Need Description:***

Naturally occurring MTBE-degrading microorganisms have been discovered at a number of fuel-release sites in California. These microbes can be stimulated to degrade dissolved plumes of MTBE *in situ*. California has many diverse climates and hydrologic terrains. We need to understand how ubiquitous these microbes are throughout the state.

***Importance:***

Low-cost, *in situ* treatment of MTBE plumes may be possible by stimulating the growth of naturally-occurring microbes.

***How do you propose attacking this research need?***

- Collect soil and groundwater samples from dozens of fuel-release sites throughout the state.
- Set up microcosms to see if MTBE degraders are present and determine the environmental conditions that enhance their growth.

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**Title:** Determine the Interaction Between Plants and Microbes and How This Interaction Can Enhance Oxygenate Metabolism

**Originator:** Newman

***Research Need Description:***

No biological system works independently. There are always interactions between complete biotic/abiotic ecosystems. Microbiologists and botanists tend to look at their systems independently, and there is a need for more integration of research.

***Importance:***

Different plants can have varying impacts on soil microbial populations, and the same plants can have significant seasonal variation in their impact on the microbes. If we can identify these interactions and how they affect oxygenate metabolism, we can design optimal plant/microbial systems.

***How do you propose attacking this research need?***

Studies that look at the system interactions and how each can enhance the effectiveness and cost-effectiveness of the technologies.

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**Title:** Develop a Better Understanding of the Biological Metabolism of MTBE at the Biochemical and Molecular Levels

**Originator:** Newman

***Research Need Description:***

We really do not know or understand the enzyme systems involved in MTBE degradation or the genetic systems that produce these enzymes. Thus, we do not have the necessary knowledge to make informed choices when we want to enhance these systems.

***Importance:***

Understanding co-factors or inhibitors to enzyme systems can enhance enzyme efficiency, and understanding the genetic system can give us probes to identify new organisms as well as ways to increase enzyme production in the organisms.

*How do you propose attacking this research need?*

Willingness to fund “basic science” research to better understand the systems.

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**Title:** Perform a Field Demonstration of *In Situ* Trickling Filtration for the Removal of Oxygenates with Particular Emphasis on Ethers

**Originator:** Rodriguez

***Research Need Description:***

Treatment alternatives for oxygenates are broken down into the *in situ* and pump-and-treat categories. Generally, pump-and-treat is more costly but has, for the most part, proven to remove contamination at a faster rate than *in situ* technologies. The application of a pump-and-treat technology bio-filter has been proven to work successfully in the laboratory, but the application for using pea-gravel in the ground as the media to trickle the water and percolate back to the source has not been pursued.

***Importance:***

If this technology is successful, the applications where pump-and-treat systems are necessary would allow for an alternative whereby the pumped water is returned to the aquifer for beneficial use as opposed to being discharged into sewers or surface bodies.

***How do you propose attacking this research need?***

Perform a field demonstration project. The contaminated groundwater is pumped from the aquifer via a pumping well and re-injected into an infiltration trench packed with a porous material, such as perlite or lava rock seeded with MTBE-degrading microorganisms. The groundwater trickles through the packed bed and is detoxified by the attached organisms. The objective of the research is to evaluate the effectiveness of this system for practical cleanup applications.

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**Title:** Enhance Microbial Growth and Activity of Indigenous and Bioaugmented MTBE-degraders in Aquifers

**Originator:** Salanitro

***Research Need Description:***

Ethers (MTBE) and branched alcohols (BA) (e.g., TBA) do not support good growth of bacteria present in soil and biosludge systems. Actual estimates of cell yields of enrichment cultures and single-culture isolates range from 0.05 – 0.2 g cells dry wt./g compound. Theoretical calculations of cell yields on these compounds indicate these yields should be >1 g/g. Therefore, ethers and BA appear to have an adverse effect on the energy metabolism of microbial cells during biodegradation.

***Importance:***

Microbes, which cannot grow well on substrates such as MTBE and TBA, are difficult to maintain and sustain cell populations and consistent biodegradative activity. Such systems are also sensitive to pH, temperature, dissolved oxygen, redox conditions, and substrate concentrations, and are difficult to isolate and recover from mixed populations. Also, these slow-growing systems may lose their competitiveness in groundwater treatment systems containing other more readily utilizable substrates (e.g., BTEX).

***How do you propose attacking this research need?***

- Identify alternate substrates and/or nutrients (e.g., oxygen or nitrogen) that may improve cell growth and sustain activity of oxygenate-degraders in biobarriers.
- Screen natural occurring ether and BA degraders, which grow more efficiently on these compounds.
- Understand the mechanism(s) by which ethers and BA do not support good microbial growth.

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**Title:** *In Situ* Bioremediation of Source Zone Oxygenates and Gasoline Range Hydrocarbons (GRH)

**Originator:** Salanitro

***Research Need Description:***

High concentrations of oxygenate and GRH are trapped in NAPL and soil-pore phases of unsaturated and saturated subsoils from fuel releases. Source leaching of soluble organics (BTEX) and oxygenate (MTBE/TBA) with water table fluctuations and rainfall events may continue to expand the horizontal and vertical spreading of oxygenate plumes.

***Importance:***

The bioremediation or combined physical (sparging/soil vapor extraction [SVE]) and biological degradation of source levels of oxygenate and GRH could significantly reduce the growth and longevity of oxygenates plumes. Improved techniques are also needed to delineate source-zone mass amounts and dissolution rates of fuel components.

***How do you propose attacking this research need?***

- Determine optimum conditions and limitations (nutrients, microbial-seed distribution, and oxygenate/GRH concentrations) for enhancing oxygenate degradation in the presence of NAPL and soil-pore phases of oxygenates and GRH.
- Understand dissolution rates of oxygenates and GRH with water table fluctuations from sources and its effect on bioremediation.
- Develop methods for quantifying the extent of bioremediation of source contaminants (e.g., sampling, analysis, mass balance, microbial intermediates).

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**Title:** Improve Drinking Water Quality by *In Situ* Oxygenation Prior to Water Production

**Originator:** Woodward

***Research Need Description:***

Oxygen appears to be the limiting factor for *in situ* biological treatment of ethers by indigenous microorganisms. Inject oxygen, as air, into the aquifer to stimulate *in situ* biological treatment before drinking water is pumped to the surface.

***Importance:***

While the process was routinely used in Europe to address soluble-iron problems in drinking water, it remains to be demonstrated for *in situ* stimulation of biodegradation of organic compounds.

***How do you propose attacking this research need?***

- Review the European experience with aeration-ringed production wells for precipitation of soluble iron.
- Install, operate, and monitor an aeration ring at a production well in a fuel oxygenate-impacted aquifer – e.g., Charnock

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***Title:***            **Rapid Induction of Ether-, 3°/4° Alcohol-, and Alkylate-degrading Enzymes by Identifying Enzyme-inducing Compounds**

***Originator:***    Woodward

***Research Need Description:***

Indigenous microorganisms have a long lag phase before degradation begins. We need to find the induction agent to stimulate indigenous organisms to recognize ethers, 3°/4° alcohols, and alkylates as a substrate to facilitate their subsequent biodegradation. Indeed, inducing agents could even be formulated into new reformulated gasolines.

***Importance:***

Absence of this inducing agent delays *in situ* biodegradation so plumes enlarge before the biological process becomes effective. Identified inducing agents could be injected into plumes, releases, or spills to accelerate *in situ* bioremediation.

***How do you propose attacking this research need?***

- Survey ethers and ether analogs (e.g., thio ethers) for the ability to induce enzyme production to stimulate MTBE degradation.
- Use Query on Structure Activity Relationships (QSAR) to find promising analogs for oxygenate ethers that would serve as enzyme-inducing agents.

# **Optimize Integrated Water-treatment Systems for Oxygenates and Degradation Products**

## **ORIGINATORS:**

Suffet on behalf of himself, Brown, Deeb, Drogos, Hoffmann, Kavanaugh, Liang, Lien, Pierce, Rodriguez, and Yamamoto

*The following research needs were consolidated under the above title:*

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**Title:** Optimizing Integrated Water-treatment Systems for Oxygenates and Degradation Products (e.g., Hydroxy Radical/GAC)

**Originator:** Suffet

### ***Research Need Description:***

Individual systems have been studied for individual oxygenates or degradation products; what is needed is an optimized integrated approach. Oxygenates and degradation products include MTBE and its byproducts, ethanol and its byproducts, and product (Oxygenate X) and its byproduct. Other methods besides hydroxy/GAC include: biodegradation/GAC, aeration/GAC, bi-functional aluminum/GAC, and GAC/resins.

### ***Importance:***

- Cost control.
- Minimize public exposure.
- Two different types of systems can be evaluated: high concentration systems where bio-GAC is best, and low-level concentration systems where hydroxy/GAC may be best.

### ***How do you propose attacking this research need?***

Lab studies to pilot studies at different sources.

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**Title:** Evaluate Treatment Technologies for TBA in Groundwater

**Originator:** Brown

**Research Need Description:**

Evaluate treatment technologies for TBA in groundwater, for both:

- Site remediation.
- Drinking water treatment.

There is little available information on the treatment of TBA in groundwater. TBA is difficult to treat using air stripping (Henry's constant = 0.00048) and GAC. However, it is susceptible to *ex situ* biological degradation.

**Importance:**

- TBA is present in fuel grade MTBE at 1 to 5 percent by volume.
- TBA is usually present where MTBE is detected.
- TBA is a degradation product of MTBE.

**How do you propose attacking this research need?**

- Initial desk study – collate existing information on TBA treatment at LUST sites and impacted drinking-water supplies.
- Field and laboratory testing of selected promising technologies.

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**Title:** Combine Physical/Chemical and Biological Approaches for Achieving Time-effective Treatment

**Originator:** Deeb

**Research Need Description:**

The use of bioremediation at MTBE-impacted sites may not be effective from a time perspective due to low-observed degradation rates of MTBE in the field and the slow growth of MTBE-degraders. Consider a combination of physical/chemical technologies followed by *in situ* bioremediation (the bioattenuation) as a polishing step.

Example of technology integration with *in situ* bioremediation: Steam injection/vacuum extraction for non-aqueous phase liquid (NAPL) removal in a fractured bedrock environment. This could remove the majority of NAPL but may leave residual contamination. Steam injection/vacuum extraction may re-oxygenate anaerobic environments, decrease the numbers of “predators” in subsurface environments, and increase temperature, thereby enhancing biological activity (up to an optimum temperature).

***Importance:***

The combination of technologies from a time and cost perspective may be critical. In addition, it could help in reaching regulatory standards. Integration of biotechnologies with a physical/chemical technology can be used in *ex situ* and *in situ* approaches.

***How do you propose attacking this research need?***

Research on laboratory and pilot-scale levels is needed before scaling such efforts to the field.

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***Title:***            **Determine the Effect of Mixtures of Oxygenates in Plumes and Potential Effects on Treatment Systems**

***Originator:***    Drogos

***Research Need Description:***

Determine the effect of mixtures of different oxygenates in plumes, such as ethanol added to an existing MTBE/BTEX plume (see elongation of various constituents in plume), or the effect of ETBE on an existing MTBE plume (increase in TBA occurrence), etc.

***Importance:***

The effects of MTBE alternatives (and new diesel fuel compounds?) on existing MTBE plumes are postulated in some cases, but not currently well known. What is the actual data? It is important to understand potential changes in plume behavior and the ramifications to treatment systems.

***How do you propose attacking this research need?***

Perform bench-top and field studies of interactions of oxygenates in plumes. Perform a detailed review of data on monitoring of existing plumes with oxygenate mixtures.

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**Title:** Review the Effectiveness of Oxygenate Treatment Technologies/Actual Systems Throughout the U.S.

**Originator:** Drogos

**Research Need Description:**

Develop comparative documentation (including actual data) of the effectiveness of the different types of water-treatment systems (both remediation and drinking-water treatment) currently in operation nationwide.

**Importance:**

There are numerous operating treatment systems throughout the U.S. Much data is being collected regarding the success or lack thereof of these systems. Also, the systems are treating a mix of contaminants generating data that would prove useful for water retailers (e.g., Manter, Kansas, has a GAC system for MTBE, BTEX, ethylene dibromide [EDB], and ethylene dichloride [EDC] treatment).

**How do you propose attacking this research need?**

Develop a collaborative effort to share and analyze data from the various systems. Involve the agencies (with the systems), universities, and California agency experts to evaluate the data. It is appropriate to collaborate nationwide, especially among public agencies.

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**Title:** Develop Cost-effective “Complete” Oxygenate Treatment Trains That Address the Handling of all Contaminant Byproducts and Waste Streams

**Originator:** Hoffman

**Research Need Description:**

“Real World” total costs that address all treatment and associated costs of oxygenate contamination have not been fully evaluated.

**Importance:**

The availability of total treatment costs to water suppliers is critical for decision making regarding technology selections and budgeting.

*How do you propose attacking this research need?*

- Conduct a comprehensive evaluation of existing treatment technologies and the identified capital and O&M costs for oxygenates and byproducts.
  - Deliverables: treatment train cost and byproduct matrix.
- 

**Title:**           **Development of Cost-effective Treatment Trains for the Removal of Oxygenates From High Strength (>1 mg/L) Waste Streams**

**Originator:**   Kavanaugh

***Research Need Description:***

At LUFT sites, oxygenate concentrations are typically high in the source area (>1 mg/L). Cost-effective removal of oxygenates are not available. Effective treatment requires multiple processes to achieve effluent limits.

***Importance:***

GAC/air stripping/AOP are effective for treatment of groundwater with oxygenate levels < 1 mg/L (1000 ppb). This requires 99.5 percent removal. Above this level, several processes operated in series are needed to meet treatment standards. Costs are quite high. Must consider achieving cost reduction by optimization of processes or development of new techniques.

*How do you propose attacking this research need?*

- Paper study of existing treatment systems from UST sites - compile information.
  - Partnering with responsible parties, Department of Defense (DOD), USEPA for field demonstration.
- 

**Title:**           **Optimize Air Stripping Technology**

**Originator:**   Kavanaugh

***Research Need Description:***

Stripping of oxygenates requires high air/water ratios. However, this technology does not produce byproducts. Also, evidence suggests that TBA degrades in “packed” towers. Thus, optimizing this technology may provide cost-efficient advantages. Optimization issues include optimum water temperature, tower pressure, and biogrowth on packing.

***Importance:***

Air stripping will continue to be a core *ex situ* technology for groundwater treatment. Under vacuum, stripping of low Henry's constant compounds like MTBE and can be quite effective. This technology could provide cost advantages if TBA is an issue.

***How do you propose attacking this research need?***

- Consultant study of feasibility of low vacuum air stripping.
- Study to evaluate biodegradation of TBA in packed towers.

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***Title:*** Assess Disinfection Byproduct and Bio-regrowth Issues in the Distribution Systems for AOP/Biological Treatment of Water

***Originator:*** Liang

***Research Need Description:***

- AOP and biologically treated water might produce some precursors to form disinfection byproducts, such as *N*-nitroso dimethyl amine (NDMA) and others.
- It is important to demonstrate no potential toxicity of disinfection byproducts for AOP/biologically treated water.
- A potential bio-regrowth problem in the distribution systems could be a problem in not meeting drinking water quality regulations.

***Importance:***

It is essential to get a regulatory permit to implement and operate the AOP/biological processes.

***How do you propose attacking this research need?***

- Apply for AWWARF, NWRI, and DHS research grants.
- Recognize that any researchers with a good understanding of these issues can do the work.
- Conduct bench-scale and pilot-scale studies.

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**Title:** Investigate Augmentation or Optimization of Drinking-water Treatment for Removing Low PPB Levels of MTBE or Other Oxygenates

**Originator:** Liang

**Research Need Description:**

Large-surface water treatment using conventional treatment cannot remove MTBE contamination. Therefore, it is important to assist water utilities in reducing MTBE and other oxygenates to meet regulatory requirements.

**Importance:**

It is important to assist the water utilities, which have no other alternative source of water supplies, in solving their MTBE and other oxygenate contamination problems in a cost-effective manner.

**How do you propose attacking this research need?**

- Consider AWWARF, NWRI, and DHS for funding.
- Conduct pilot- and full-scale studies.
- Recognize that any researcher who understands conventional drinking-water treatment and MTBE contamination problems can do the work.

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**Title:** Integrate Technologies for Treatment of Oxygenates in Drinking Water

**Originator:** Lien

**Research Need Description:**

The effectiveness of current available technologies (i.e., GAC, air stripping, and AOP) is still limited for treatment of MTBE in drinking water. An alternative is to integrate and optimize individual processes for the treatment of oxygenates in drinking water.

**Importance:**

One of the best and most effective strategies of the MTBE problem in drinking water is the integration of technologies.

*How do you propose attacking this research need?*

- Determine the advantages and disadvantages of current available technologies.
- Optimize the technologies. For example: combinations of GAC and AOP, bi-functional aluminum and GAC, bi-functional aluminum and synthetic resins may take advantage of these technologies and avoid the disadvantages.

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**Title: Optimize Technologies for Treatment of MTBE Byproducts in Drinking Water**

**Originator:** Lien

***Research Need Description:***

MTBE byproducts, such as TBA, is, on a certain degree, much more difficult to treat than MTBE. This is why TBA becomes the byproduct in the treatment of MTBE by AOP. Optimization of current available technologies may provide a promising direction to cleanup the MTBE byproducts.

***Importance:***

If we can develop a suitable technology for the treatment of MTBE and its degradation byproducts, then the integration of technologies becomes promising.

***How do you propose attacking this research need?***

An evaluation of the current available technologies should be the first step in the investigation of the TBA sorption capacity of synthetic resins.

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**Title: Bio-GAC Treatment of Oxygenates**

**Originator:** Pierce

***Research Need Description:***

Recent data suggests that TBA is a common byproduct in MTBE manufacture and, therefore, tends to be present in water contaminated with MTBE. Data suggests that while TBA is present in gasoline in only trace amounts, it can be present in water at 10-100 percent or more of the MTBE concentration because it is far more soluble in water and will partition more to the water phase.

Additionally, TBA, acetone, TBF, and other oxygenate byproducts may result from the degradation of MTBE by other treatment processes (i.e., advanced oxidation). Thus, these processes may benefit from additional polishing for such compounds.

TBA, acetone, TBF, and other alcohols (i.e., ethanol) are highly soluble in water and, therefore, are far more difficult to air strip or absorb than even MTBE. Advanced oxidation can further oxidize these compounds, but acetone in particular is recalcitrant to advanced oxidation, so this process may not be a practical route for treatment in some scenarios.

***Importance:***

Little is currently known about biological degradation of these compounds in mixtures where more biodegradable compounds (ethanol, BTEX) may compete too well with microorganisms suited to degrade tertiary carbon molecules. Efficacy and design data are needed.

***How do you propose attacking this research need?***

Bio-GAC, in which microorganisms are allowed to grow in a bed of GAC, seems a promising option for treatment of these problem compounds. Pilot data at the Santa Monica Charnock site suggested that bio-GAC was a viable option for mixtures of MTBE and TBA to reduce the TBA. MTBE can then be absorbed by suitable types of traditional GAC. GAC was not a practical option for TBA because it is so weakly adsorbed and is preferentially displaced from the GAC by MTBE.

A system of bio-GAC (or any suitable fixed film biological reactor) and traditional GAC should be piloted to reduce mixtures of TBA, MTBE, BTEX, and other possible compounds. A side benefit of bio-GAC is that to the extent that it also degrades BTEX, BTEX will not displace MTBE adsorbed on downstream GAC beds.

Organizations who perform this work: Malcolm-Pirnie, Kennedy-Jenks, and other consultants with a background in the treatment of oxygenates and with a process engineering staff.

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***Title:***            **Evaluate the Effectiveness and Applicability of the Biological Process in Activated Carbon Media for Removal of Oxygenates with Emphasis on Alcohols (TBA)**

***Originator:***    Rodriguez

***Research Need Description:***

The detection of MTBE with TBA in drinking water has become more pervasive, which makes removal even more difficult due to the properties of TBA, which is more difficult to strip and has less adsorption capacity to carbon. However, TBA and other alcohols can degrade with rapid acclimation periods under the favorable aerobic conditions, which occur in carbon vessels. TBA

removals in field carbon study systems and other media have shown excellent breakdown capabilities with rapid result.

***Importance:***

Full-scale demonstration of this technology is necessary to understand the effectiveness, acclimation period, sensitivity, applicability, and costs of utilizing this technology. Because of the limited testing and perceived problems with biological approach to drinking-water applications, this viable and cost-effective technology has not been pursued in favor of the more traditional approaches.

***How do you propose attacking this research need?***

Develop a work plan for the field demonstration testing of bio-GAC for removing drinking water contaminated with TBA, MTBE, and potentially other gasoline compounds. The evaluation will include an understanding of the acclimation process, ability of natural occurring bacteria to breakdown TBA, reliability, and sensitivity analyses. Then perform an economic analysis of the treatment process.

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***Title:***            **Water Quality Parameters Affecting Full-scale GAC Treatment of MTBE and TBA**

***Originator:***    Yamamoto

***Research Need Description:***

Water contains many organic compounds that may affect the bed life of GAC, (i.e., reduce the expected bed life of the GAC treatment system before regeneration/replacement is needed).

***Importance:***

More accurate determinations of GAC bed life are needed to determine the most cost effective alternative. In most instances, the bed life of the GAC has been overestimated.

***How do you propose attacking this research need?***

Gather data while Santa Monica, California, operates its full-scale GAC system.

# **Evaluate Various Reactive Barrier Designs for Enhanced *In Situ* Treatment of MTBE and Other Oxygenates**

## **ORIGINATORS:**

Einarson on behalf of himself, Church, Kavanaugh, Lien, and Woodward

*The following research needs were consolidated under the above title:*

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***Title:* Evaluate Various Reactive Barrier Designs for Enhanced *In Situ* Treatment of Plumes of Dissolved MTBE and Other Oxygenates**

***Originator:* Einarson**

### ***Research Need Description:***

Effective *in situ* biotreatment of dissolved MTBE plumes requires intimate contact between the contaminant, nutrients, electron acceptors, and microbial community. The subsurface environment is notoriously heterogeneous, which impedes the thorough mixing of these ingredients, potentially leading to incomplete treatment of the dissolved plume. Several technologies are widely used in the environmental industry to manipulate the subsurface geochemical environment. These technologies include injection of liquid reactants, diffusion and sparging of gaseous compounds, reactive walls, recirculation systems, and funnel-and-gate treatment systems.

### ***Importance:***

Effective enhanced *in situ* treatment of oxygenate plumes requires the effective manipulation of the subsurface geochemical environment.

### ***How do you propose attacking this research need?***

A wide spectrum of existing and innovative reactive barriers should be evaluated to identify the best designs for low-cost *in situ* treatment of dissolved contaminant plumes emanating from LUFT sites. A wide body of literature and case studies exists, which should be thoroughly reviewed and summarized. Much of this information was developed for the *in situ* treatment of chlorinated VOC plumes. A short list of preferred designs should be prepared, and the preferred

designs should be evaluated further using numerical simulations and controlled pilot-scale installations at actual release sites.

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**Title:** Investigate the Potential of Using Psuedo-Fenton Chemistry ( $\text{H}_2\text{O}_2$  Plus Mineral  $\text{Fe}^{+3}$ ) in an *In Situ* Permeable Reactive Barrier Mode

**Originator:** Church

***Research Need Description:***

Various AOP processes rely on degrading MTBE through the generation of hydroxyl radicals. However, few of these have been applied *in situ* due to cost and technical limitations. Pseudo-Fenton chemistry ( $\text{H}_2\text{O}_2$  plus mineral  $\text{Fe}^{+3}$ ) has the potential to generate hydroxyl radical *in situ* at typical groundwater pH values.

***Importance:***

Permeable reactive barriers, which generate hydroxyl radicals, have the potential to stop plumes (MTBE or BTEX) “in their tracks.”

***How do you propose attacking this research need?***

*In situ* tests of delivery systems:

- Solution (injection well).
- Electrolysis.
- Peroxide pellets.

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**Title:** Complexity of VOC Contamination in Sub-surface Remediation

**Originator:** Kavanaugh

***Research Need Description:***

The occurrence of MTBE and chlorinated organic solvents in contaminated groundwater has been frequently discovered in the same urban aquifers. According to USGS, chloroform and MTBE were the first and second most frequently detected VOCs in shallow groundwater from selected urban areas.

***Importance:***

The co-existence of MTBE and chlorinated organic compounds tends to complicate remediation strategies because MTBE is more favorably inclined to undergo the oxidation reaction while many of the chlorinated organic compounds tend to undergo the reduction reaction. For example, the advanced oxidation reactions of MTBE, using Fenton's reagent and reductive dechlorination of chlorinated organic compounds using zero-valent iron, have been studied. There is an urgent need to develop and integrate technologies in order to treat both oxidized and reduced contaminants in the subsurface. I report here a novel material, bi-functional aluminum, that was developed as a heterogeneous oxidative catalyst and a reductant for the simultaneous transformation of MTBE and chlorinated organic compounds.

***How do you propose attacking this research need?***

Bi-functional aluminum, with both reductive and oxidative catalytic functionality, could serve as a potential remediation agent to clean up a variety of VOC contamination in groundwater. Reactive barrier technology, such as iron wall, has been successful for *in situ* remediation. A combination of both bi-functional aluminum and reactive barrier technology could be a very promising method to remediate VOCs in subsurface. The USEPA may be a possible source to support this project.

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**Title:** Develop Barrier Technologies for Long-term Containment of Low and High Strength Oxygenate Plumes

**Originator:** Lien

***Research Need Description:***

Active remediation of oxygenate plumes will likely not be effective at achieving low (<MCL) levels of oxygenates, and plume contaminant on some scale is likely to be part of the long-term solution. Barriers can be active (sparging) or passive (biobarrier), and uncertainties persist as to long-term reliability.

***Importance:***

Barriers offer significant cost savings relative to active remediation systems, such as pump-and-treat.

***How do you propose attacking this research need?***

- Academic research on the long-term reliability of barriers.
- Academic research on abiotic barriers.
- Collaboration/partnerships to support careful monitoring for long-term evaluation.

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***Title:***            **Proactive/Reactive Barrier**

***Originator:***    Woodward

***Research Need Description:***

We can make the assumption that all tanks, sooner or later, will leak. Stored liquids will get away. We need an *in situ* process to contain and initiate remediation as soon as a leak occurs: proactive reactive barriers. We need to replace the pea gravel backfill in a tank installation. The barrier should sorb gasoline constituents and degrade them – both chemical and biological processes are needed.

***Importance:***

- Sorbent, reactive material needs to be developed.
- Bench-scale selection/development.
- Potential for amplifying of leak/spill sensor sensitivity.

***How do you propose attacking this research need?***

Interdisciplinary approach of chemists, physical scientists, and microbiologists will produce a backfill material that contains leak/spill by adsorption; reacts chemically to degrade gasoline constituents; and initiates biodegradation process from encapsulated biodegradation materials. The process would be optimized by column studies of blended sorbent, chemical reactant, and biological seed.

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**Title:**            **Chemical Catalyst for *Ex Situ* Degradation of Ether Oxygenates or for *In Situ* Abiotic Barriers**

**Originator:**    Woodward

***Research Need Description:***

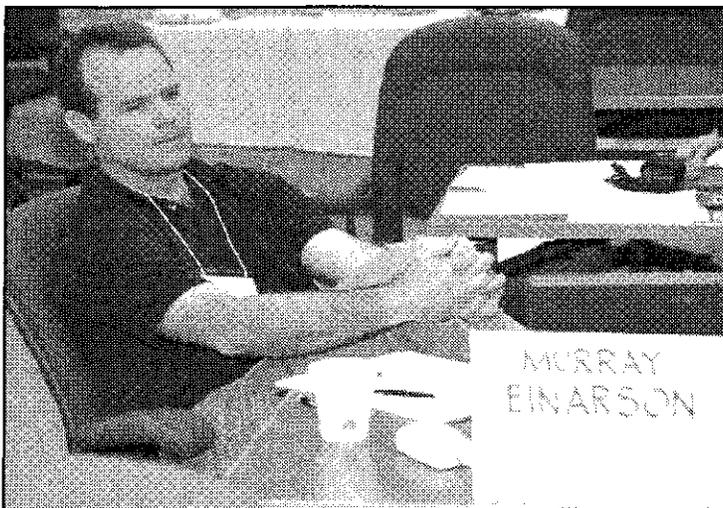
MTBE is synthesized using a catalyst. However, if reactive conditions of pH and water content are off target, MTBE is converted to TBA.

***Importance:***

We need to explore commercial synthetic catalysts to define the conditions for optimizing catalysts for the degradation of ether oxygenates.

***How do you propose attacking this research need?***

- Art Diaz's group on basic stability of ethers with pH and catalysts.
- ETBE/MTBE producers.
- Process chemists.



# **Develop a Comprehensive Understanding of MTBE and Oxygenate Fate and Transport Based on Accurate Data**

## **ORIGINATORS:**

Tulloch on behalf of herself, Brown, Church, Crowley, and Einarson

*The following research needs were consolidated under the above title:*

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***Title:*            Develop a Comprehensive Understanding of MTBE and Oxygenate F&T, Based on Real Data**

***Originator:***    Tulloch

### ***Research Need Description:***

Limited scope plume studies have been conducted in California, Texas, and possibly elsewhere. These studies suffered from a lack of data or inadequate monitoring well networks. These studies have not resulted in a better understanding of F&T. Since prior plume studies, detailed investigations and monitoring has been performed; however, the resulting data has not been tracked.

### ***Importance:***

Without a comprehensive understanding of MTBE plumes and the fate and transport of MTBE, source water protection efforts will be limited. Better understanding of plumes can help reduce investigation costs and allow for more effective cleanup.

### ***How do you propose attacking this research need?***

- Survey local oversight agencies to find MTBE cases with adequate monitoring well networks.
- Develop a database to collect site specific data, including geology, hydrogeology, and concentrations in wells over time.

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**Title:** Evaluate and Demonstrate Field Methods to Characterize Oxygenate Presence, Fate, and Transport in Fractured Rock

**Originator:** Brown

***Research Need Description:***

The contaminant hydrogeology of fractured rock is very different and far more complex than that of alluvial deposits. Groundwater presence, flow, and geochemistry are difficult to characterize. The addition of contaminants further complicates this characterization. Field characterization methods currently focus on investigations in alluvial deposits. These methods will not work in fractured rock and may make the problem worse.

***Importance:***

More than 50 percent of the U.S. is directly underlain (less than 50 feet below ground surface) by fractured rock. Numerous small, private water-supply wells are completed in fractured rock. Small spills in fractured rock can impact a large volume of subsurface and can travel great distances in a short time, potentially impacting water-supply wells.

***How do you propose attacking this research need?***

- Develop a field guidance manual.
- Review techniques currently being used, particularly those applied to characterize chlorinated solvent and radionuclide contamination in fractured rock.
- Review and promote innovative techniques.
- Evaluate the applicability of existing and innovative techniques to sites with oxygenate contamination.
- Conduct field demonstrations to further evaluate and develop the promising/applicable techniques.

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**Title:**            **What is the Environmental Fate and Human Health Effects of TBA Resulting from the Use of MTBE?**

**Originator:**    Church

***Research Need Description:***

MTBE degradation, whether through biological or advanced oxidation processes, produce similar degradation products. These products are TBA, possibly TBF, acetone, isopropanol, etc. Of these products, TBA and TBF have known deleterious health effects. TBF has a rapid hydrolysis rate that produces TBA. TBA, which appears to be at least as recalcitrant as MTBE, is a known human carcinogen, yet little emphasis to date has been placed on: 1) its occurrence, 2) its health effects, or 3) its treatment in drinking water.

***Importance:***

At present, little effort is being focused on its occurrence, let alone its removal.

***How do you propose attacking this research need?***

Numerous researchers are well equipped to attack these problems:

- Microbial Degradation of TBA: Salanitro, Scow, Dochusses, etc.
- Fate: Church, Einarson, MacKay, Amerson-Treat, Johnson, etc.
- AOP: Sun Liang, Hoffman, Brown, Malcolm Pirnie, Inc., etc.

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**Title:**            **MTBE and Fuel Oxygenate F&T - Field Studies**

**Originator:**    Crowley

***Research Need Description:***

At least four large field studies relative to the F&T of MTBE and oxygenates are necessary to verify theoretical assumptions and to gain a more thorough understanding of the behavior of plumes in real-world settings.

In particular, our understanding of mass transfer from the source in a varying flow field and the influence of biotic and abiotic process on the plume would greatly benefit from field studies.

***Importance:***

Better understanding of plumes leads to saving money in investigations and, particularly, in the cleanup phase. It also allows for a better assessment of the risk to receptors.

***How do you propose attacking this research need?***

American Petroleum Institute (API) – Various oil companies, universities, and individuals

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***Title:***            **Drinking-water Well Mixing Studies/Modeling – Significance of MTBE and Oxygenate Mass Flux (Plume Discharge Rates)**

***Originator:***    Crowley

***Research Need Description:***

The significance of MTBE and oxygenate mass discharged to a public water well needs to be investigated. Processes occurring in the well and in the immediate vicinity of the well can seriously reduce the maximum concentration that can be discharged from the well. A better understanding of the mixing processes in and near the well will allow us to better understand the ultimate level of exposure to receptors when oxygenates are present in the groundwater resource.

***Importance:***

Saving funds relative to cleanup cost.

***How do you propose attacking this research need?***

Department of Health Services (DHS), Source Water Assessment Program (SWAP), National Groundwater Association (NGWA), Groundwater Resources Association (GRA), and water retailers.

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***Title***            **How Quickly Will Unmitigated MTBE Releases Naturally Attenuate Due to Source Depletion?**

***Originator:***    Einarson

***Research Need Description:***

Due to its high solubility, MTBE is preferentially leached from residual NAPL. Early conceptual models suggested that MTBE source zones would be quickly depleted, and the resulting plumes would soon become detached from the source zones. This has generally not

been the case. Rapid depletion of MTBE in source zones is hampered by ever-decreasing effective solubilities, diffusion-limited mass transfer in NAPL, low surface area to mass ratios, and diffusion into/out of low permeability units.

***Importance:***

We need to understand how long, unmitigated MTBE release sites will pose a threat to our groundwater resources.

***How do you propose attacking this research need?***

- Theoretical (look to chlorinated volatile organic compounds [CVOC] experience!).
- Modeling.
- Field monitoring of plumes in stable flow fields.
  - Temporal monitoring down-gradient of source zones
  - Define contaminant mass discharge as a function of plume length (a plume is a record of the dissolution history of the source zone)

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***Title:***            **Determine Source Water Vulnerability from Undetected Low Volume Releases of Fuel Oxygenates**

***Originator:***    Tulloch

***Research Need Description:***

There is significant evidence that shows liquid- and vapor-phase fuel and oxygenates are being released from UST systems without being detected by the UST monitoring systems. In addition, many non-point releases, such as backyard spills and dumping, occur and can impact drinking water sources. In many cases, the releases appear to be small. However, due to the chemical characteristics of persistent chemicals, such as fuel oxygenates, these undetected releases are threatening and impacting drinking-water sources and drinking-water wells.

This research should focus on determining the overall and regional vulnerability of source water from these releases.

***Importance:***

Without an understanding of the vulnerability of source water from small releases, ongoing efforts of source water protection programs may not be able to prioritize their efforts, and drinking water will continue to be threatened and impacted by fuel oxygenates.

*How do you propose attacking this research need?*

- Convene subject matter experts from regulatory agencies and industry to form a technical advisory committee (TAC).
- The TAC should develop effective approaches to modeling groundwater impacts from low-volume releases using region-specific information.
- Water agencies.
- Industry.
- Consulting, Murray Einerson, Doug Mackay.
- USEPA, Matt Small?

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**Title:** Long-term Source Water Impacts Resulting from Residual Low Concentration Oxygenate Plumes

**Originator:** Tulloch

**Research Need Description:**

There are thousands of MTBE plumes in California. It is unlikely that they will be remediated to non-detectable concentrations or MCLs. The result will be that thousands of plumes of MTBE or other oxygenates will remain for decades to come. The long-term impacts of these residual plumes are not well understood. This research should focus on determining the long-term (50-100 years) impacts to future drinking-water sources.

**Importance:**

Current source water protection research and programs do not adequately address the long-term impacts of residual oxygenate plumes. It is necessary for this to be understood so that cleanup, risk management, and long-term source water management program can be effective.

*How do you propose attacking this research need?*

- Convene a TAC.
- Develop an economic model.
- Develop an F&T model.
- Verify F&T results by comparing to other long-term impact research of persistent chemicals.

# **Develop Effective Subsurface Monitoring Systems and Improve UST Monitoring Equipment to Detect Liquid and Vapor Releases of Oxygenates at UST**

## **ORIGINATORS:**

Tulloch on behalf of herself, Davidson, Kavanaugh, Rodriguez, Tenney, and Woodward

*The following research needs were consolidated under the above title:*

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**Title:**            **Develop Effective Subsurface Environmental Monitoring Systems to Detect Liquid and Vapor-phase Releases of Oxygenates from UST Systems**

**Originator:**    Tulloch

### ***Research Need Description:***

There is significant evidence that shows liquid and vapor-phase fuel and oxygenates are being released from UST systems without being detected by the UST monitoring systems. In many cases, the releases appear to be small. However, due to the chemical characteristics of persistent chemicals (such as fuel oxygenates), these undetected releases are threatening and impacting drinking-water sources and drinking-water wells. Studies indicate that subsurface environmental monitoring is the most definitive technique to detect these releases and the resulting contamination.

This research should focus on designing cost-effective environmental monitoring systems.

### ***Importance:***

Without a mechanism to effectively detect releases of fuel oxygenates, ongoing efforts of source water protection programs will be significantly less effective, and drinking water will continue to be threatened and impacted by fuel oxygenates.

*How do you propose attacking this research need?*

- Convene subject matter experts from regulatory agencies and industry to form a TAC.
- The TAC should develop effective approaches to environmental monitoring given their understanding of how and where these small releases occur.
- Individuals/Organizations:
  - State Water Resources Control Board (SWRCB): Shahla Farahnak
  - Santa Clara Valley Water District (SCVWD): Jim Crowley/Christine Tulloch
  - Local permitting agencies
  - Industry: Dave Camille of Tosco
  - Consulting: Marcel Moreau, Murray Einarson
  - USEPA: Matt Small
  - Local oversight programs

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**Title:**            **Establish the Occurrence and Environmental Significance of MTBE Vapor Losses from UST Systems**

**Originator:**    Davidson

***Research Need Description:***

It is difficult enough to prevent small-scale liquid gasoline losses from UST systems. Preventing and detecting vapor losses are even more difficult. Due to its high vapor pressure, MTBE will comprise a large portion of the vapors in the vapor recovery lines, the vent lines, and the headspace of a UST. Thus, there may commonly be MTBE vapor losses occurring at several places along the UST system.

***Importance:***

This potential loss mechanism has been hinted at, or tentatively identified, in several previous studies and literature reviews. A certain portion of contaminated sites seem to have odd “MTBE only” contamination that could readily be explained this way. Vapor tightness from liquid-containment UST systems does not get much focus, so this potential source may be overlooked.

***How do you propose attacking this research need?***

- Literature review.
- Conduct theoretical vapor loss and vapor-phase transport and transfer mass calculations.
- If possible, conduct lab-scale experiments and/or field tests to determine actual occurrence and significance.

Who could do it: UST design and UST loss experts from academia, USEPA, consultants, industry, and government.

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**Title:** Development of Rapid Response Technologies for LUFT Cleanups

**Originator:** Kavanaugh

***Research Need Description:***

Because of oxygenate recalcitrance, rapid response after a spill or continual release from an underground storage tank is essential. The problem is that evidence of a spill/release usually occurs well after the event. Many delays occur even after a release is detected. In vulnerable groundwater areas, rapid response is essential. A comprehensive approach is needed.

***Importance:***

Current monitoring and response strategies are either too insensitive or too slow, or both. Rapid response is cost effective because the costs of delay are significant. Why do European nations not have this problem?

***How do you propose attacking this research need?***

- Develop a contingency planning guidance manual for LUFT owners.
  - Study the European experience.
  - Fund innovative technologies for spill monitoring at UST sites.
- 

**Title:** Identify, Evaluate, and Field Test Technologies Available for Detecting Vapor and Liquid Releases from USTS

**Originator:** Rodriguez

***Research Need Description:***

Most gasoline leaks from USTs are being detected during tank replacements, and leak detection systems have failed to adequately detect leaks early enough to allow rapid response for effective remediation.

***Importance:***

The use of inadequate leak detection systems will continue to threaten drinking water supplies and increase the costs of the ultimate cleanup of contaminated groundwater if we do not identify releases when they initially occur.

***How do you propose attacking this research need?***

Call on industry, regulators, and consultants to identify, develop, and field test equipment that can be used to accurately detect low-levels of releases from both vapor and liquid releases.

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***Title:***            **Evaluate and Develop Smart Tools for Monitoring Fuel Storage and Distribution Systems**

***Originator:***    Tenney

***Research Need Description:***

Fuel releases from UST systems often go undetected. Furthermore, once released, such compounds are often not observed until they reach the shallow saturated zone beneath the site. Better product inventory, reconciliation systems, advanced environmental monitoring systems are needed.

***Importance:***

USTs are a significant source of shallow groundwater contamination throughout the U.S. Monitoring improvements that provide advanced warning of “trouble on the horizon” are significant to drive down long-term threats and reduce costs.

***How do you propose attacking this research need?***

- Establish a workshop/planning group of industry, academia, regulatory, subject-matter experts to review the current state of technology.
- Evaluate existing industry construction, maintenance guidelines (e.g., American Petroleum Institute 653 for above-ground storage tanks).
- Evaluate and select appropriate advanced technologies for field demonstration studies (e.g., tracer technology, acoustic emission testing, etc.).

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**Title:**        **Monitor Incentives for Detection and Reduction of Gasoline Contamination**

**Originator:**    Woodward

***Research Need Description:***

In the U.S., gasoline at the wholesale/retail level has little pre-tax value (compared to after-tax value). Increasing the value at the retailer's level by putting the tax here would provide a greater incentive for monitoring and action. Leaks/releases would thus be a taxed product, and the retailer would have a strong incentive to monitor and act. Indeed, this is the European experience.

***Importance:***

We need active, sensitive monitoring systems, better than 0.2 gal/hr, and the incentives to watch these closely.

***How do you propose attacking this research need?***

- Survey sensing systems and monitoring tools that are currently available.
- Improve existing or develop new sensors for ethers, alcohols, and alkalytes.
- Adopt legislation that forces the retailers to pay the tax when the product is delivered rather than when it is dispensed.
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# **Develop Analytical Methods for MTBE and Its Breakdown Products at Ppt/ppb Levels**

## **ORIGINATORS:**

Suffet on behalf of himself, Church, Newman, Rodriguez, Tikkanen, and Yamamoto

*The following research needs were consolidated under the above title:*

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**Title:**            **Development of Analytical Methods for MTBE and Its Breakdown Products at Ppt-ppb Levels, Especially Small-volume Samples**

**Originator:**    Suffet

### ***Research Need Description:***

Small-volume samples are developed in research studies from the fate of pollutants and treatment studies, (e.g., phytoremediation, natural biodegradation, lab treatment studies, etc.).

### ***Importance:***

Researchers cannot determine concentrations to evaluate for levels to confirm mechanisms and understand natural processes.

### ***How do you propose attacking this research need?***

One specific example of a method that could be tried is solid-phase microextraction (SPME) approaches.

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**Title:**            **Develop Widely Usable Analytical Techniques Capable of the Simultaneous Measurement of MTBE and Its Primary Degradation Products in Water at Sub-ppb Levels**

**Originator:**    Church

***Research Need Description:***

Various analytical techniques have been developed that can perform simultaneous analyses of MTBE and its degradation products at sub-ppb levels. Unfortunately, these techniques tend to be laboratory-specific and require the use of specialized equipment. We need a widespread analytical technique that can be used in all labs.

***Importance:***

- California now has a “regulatory limit” for TBA of 12 ppb. Most currently used analytical techniques cannot measure this low reliably.
- The most sensitive measure (and unequivocal proof), if you evaluate mass rather than concentration of MTBE degradation is documenting the existence of degradation products.

***How do you propose attacking this research need?***

- Through solid phase micro extraction (SPME), direct aqueous injection, or heated purge and trap/carbotrap.
- Individuals: Church, Pankow-Luo, Kaplan, Rodriguez, Ekwurzel.
- NWRI/SPME-method adaptation.

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**Title:**            **Develop New Biological Technologies for the Treatment of Oxygenates: The Need for Improved Analytical Methods**

**Originator:**    Newman

***Research Need Description:***

The goal is to validate biological treatment technologies. To do this, we need to be able to trace both the movement of the parent compound and metabolites of the compound. One of the major problems is the development of analytical methods that work with biological systems and are sensitive to regulatory limits. The most current research is being done at current limits of detection, which can be 100-1000 fold higher.

***Importance:***

In order to develop these technologies, we need to be able to analyze their effectiveness. Biological treatment technologies, phytoremediation in particular, have great potential for the treatment of oxygenates in groundwater, but they can only be fully accepted when their effectiveness is proven.

***How do you propose attacking this research need?***

Cross-disciplinary research between biologists and analytical chemists to develop the methodology needed.

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**Title:            Develop an Analytical Method or Modify an Existing Method with  
Regulatory Approval for TBA for Drinking Water Applications**

**Originator:**    Rodriguez

***Research Need Description:***

In California, there is an action level of 12 µg/L in drinking water for TBA. The current analytical method using gas chromatography/mass spectrometry (524.2) does not include TBA as an analyte, but the method can be used at detection limits that are near the action level. Simple modifications of the method will allow for standard methods in drinking water analyses (524.2), to be utilized as part of the routine VOC analysis.

***Importance:***

The uncertainty of regulatory approval of the available methods and modifications to existing drinking water methods have hampered the understanding of the extent of TBA impacts and effectiveness in removing of TBA in treatment systems without regulatory support and approval of the available methods.

Existing analytical data collected may be questionable in treatment system effluent, site remediation data, and drinking-water wells, which have been analyzed using modifications of standard methods or may not be usable data due to the high reporting limits employed.

***How do you propose attacking this research need?***

MDL studies can be performed to evaluate the ability and modification of the method to detect TBA and to document modifications of the existing 524.2 method for approval by the DHS's Office of Drinking Water.

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**Title:**           **Develop an Analytical Technique That Can Be Installed and Remotely Accessed in Field in a Water Body (Lake, Reservoir, River) to Monitor MTBE and Other Oxygenates at Low-level Concentrations (0.5 – 50 ppb)**

**Originator:**   Tikkanen

***Research Need Description:***

There is a need for monitoring a water body *in situ* because, many times (particularly if the water body is a reservoir), there are high probabilities of contamination of grab monitoring samples from the motorized boat used to transport the sampler to the site of sampling.

***Importance:***

Much of the monitoring data is lost because, in the sampling process, contamination is introduced. This *in situ* monitoring would eliminate self-contamination as well as allow for real-time monitoring of the water quality of a lake, reservoir, or river.

***How do you propose attacking this research need?***

- Develop a request for proposals (RFP) and publish it.
- Choose a research proposal and award it.
- Funding from the American Water Works Association Research Foundation (AWWARF), and/or the State Water Resources Control Board (SWRCB).

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**Title:**           **Develop Analytical Methods for AOP Byproducts in the Ppt Levels**

**Originator:**   Yamamoto

***Research Need Description:***

If the AOP process does not completely destroy MTBE, then other compounds are formed. At what levels are these compounds present? Will these be harmful? What compounds are present?

***Importance:***

DHS needs this information to decide whether to approve the technology. For example, a new disinfection byproduct at ppt levels has been recently found. Will AOP create something at ppt that will be of concern?

*How do you propose attacking this research need?*

Work with USEPA, USGS, Lawrence Livermore National Laboratory, commercial laboratories, or the DHS lab to develop methodologies.



# **Investigate Ethanol Data Gaps Prior to Increased Ethanol Use**

## **ORIGINATORS:**

Davidson on behalf of himself, Moyer, and Pierce

*The following research needs were consolidated under the above title:*

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**Title:**            **Field Data Collection from Ethanol Releases: Fate, Transport, Remediation, and Treatment**

**Originator:**    Davidson

### ***Research Need Description:***

While there are numerous literature and theoretical studies of ethanol's environmental behavior, there is almost no field data whatsoever to support or refute the theories and models.

This is a big knowledge gap.

### ***Importance:***

Since California is switching primarily to ethanol-blended gasoline, and as the nation might, it is critical that we be able to confirm/refute/adapt our assumed knowledge about ethanol's fate, transport, remediation, and treatment, including ethanol's impact on pre-existing hydrocarbon contamination and pre-existing MTBE contamination.

### ***How do you propose attacking this research need?***

- Extensive search for existing sites (consultant or university effort led by DHS, NWRI, API, USEPA, or others).
- Conduct controlled field releases or large-scale lab releases of ethanol-blended gasoline (Western Michigan University, Oregon Graduate Institute, or Waterloo).

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**Title:** Determine the Compatibility of Common UST System Components with Ethanol-blended Gasoline

**Originator:** Davidson

**Research Need Description:**

Previous experience and studies have shown slight incompatibility between select UST components and MTBE, and serious incompatibility between methanol and certain UST components. There seems to be a potential for ethanol incompatibility with some UST system components (e.g., tanks, pipes, gaskets, glues, bushings, etc.).

**Importance:**

If we are switching primarily to ethanol-blended gasoline statewide in December 2002, and perhaps nationwide, then we need to establish any ethanol-UST incompatibilities beforehand.

**How do you propose attacking this research need?**

- Review existing ethanol-UST component literature by a UST compatibility work team (e.g., consultants, DHS, NWRI, and API). Note: API project will start soon.
- Laboratory compatibility testing (while we still have some lead time) by university labs, industry organizations, USEPA, etc.

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**Title:** Field Investigation of the Effect of *In Situ* Ethanol Biodegradation and Phytoremediation on Benzene F&T

**Originator:** Moyer

**Research Need Description:**

Modeling of the F&T of gasoline in the subsurface predicts that preferential ethanol biodegradation will result in longer benzene plumes. Confirmation of this phenomenon in the field has been minimal or non-existent.

**Importance:**

Switching from MTBE to ethanol as an oxygenate may exacerbate groundwater contamination by benzene. Field data is needed to evaluate the magnitude of this potential problem. Field data could indicate that substituting ethanol for MTBE could jeopardize source protection relative to benzene, a known human carcinogen.

*How do you propose attacking this research need?*

- Release gasoline with ethanol, gasoline with MTBE, and unoxygenated gasoline in parallel test plots at a well-characterized site in an area with little or no prior contamination.
- Monitor groundwater, vapor concentrations, biological parameters over time in the parallel plots and compare F&T of gasoline constituents.

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**Title:** A Field Assessment of the Impact of Ethanol in Gasoline on BTEX Plumes in Groundwater

**Originator:** Pierce

**Research Need Description:**

Aqueous ethanol is relatively non-toxic, but two groundwater concerns persist:

- Ethanol at high concentrations in groundwater can enhance the solubility of mobile, aromatic hydrocarbons (BTEX) from gasoline.
- Ethanol may decrease the rate of BTEX biodegradation in groundwater mainly because ethanol may have preferential access to electron acceptors, particularly oxygen.

**Importance:**

“The lack of BTEX and ethanol concentration data at gasohol leak sites is a major knowledge gap.” (Rice et al., 1999) The most pressing need appears to be gaining field experience with ethanol/gasohol releases so that the most significant issues can be identified and appropriate research conducted. The requirements of a desirable field site include:

- Ethanol/gasohol has impacted groundwater.
- The distribution of organic contaminants, electron acceptors, etc. is either well known or easily characterized.
- The source history is sufficiently understood so that the evolution of the groundwater situation can be reliably inferred from current distributions and historic data.

***How do you propose attacking this research need?***

Barker et al. of the University of Waterloo have proposed a strategy to API to assess an ethanol plume in Brazil. Their approach includes field activities (additional monitoring wells and improved hydro geological studies) and laboratory microcosm experiments.<sup>1</sup>

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***Title:*** Investigation of Trace Contaminants in Fuel-grade Ethanol

***Originator:*** Pierce

***Research Need Description:***

With MTBE, we were surprised by TBA trace contaminants. Want to avoid the elements of surprise with other oxygenate additives.

***Importance:***

Avoid unexpected compounds associated with gasoline/ethanol spills.

***How do you propose attacking this research need?***

Analyze commonly available fuel-grade ethanol sources for trace contaminants and biodegradation byproducts, such as formaldehyde.

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<sup>1</sup> Barker, J.F., B.J. Butler, E. de Oliveira, and P.J.J. Alvarez. May 23, 2000, "A Field Assessment of the Impact of Ethanol in Gasoline on BTEX plumes in Groundwater Using a Brazilian E22 Plume." A Research Proposal submitted to the American Petroleum Institute.<sup>1</sup>

# **Develop Protocol for Multimedia Review of New Compounds for Use in Fuels (How Can We Prevent Another MTBE Contamination Catastrophe?)**

## **ORIGINATORS:**

Tikkanen on behalf of herself, Church, Drogos, and Yamamoto

*The following research needs were consolidated under the above title:*

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**Title:**            **Develop Protocol for Multimedia Review of Fuel Additives/Enhancers to Gasoline, or Other Fuels Used in Automobiles**

**Originator:**    Tikkanen

### ***Research Need Description:***

Typically, changes in reformulated fuels are developed with a limited scope (e.g., reduction of specified hydrocarbons that come from mass automobile use). The consequences of what happens if the reformulated fuel contaminates a surrounding media (e.g., soil, water) were not adequately reviewed or addressed. For example, MTBE was added to gasoline to improve air quality, but negatively impacted water quality.

### ***Importance:***

Prevent future contamination of all environmental phases (media) when mandating new fuel composition for automotive use through a multimedia review of proposed fuel changes.

***How do you propose attacking this research need?***

Put together a task force composed of the appropriate stakeholders to develop a protocol for reviewing the multimedia effects of proposed fuel composition changes. Include representatives from petroleum processors, the Air Resources Board, water utilities (with groundwater and surface water sources), DHS (including drinking water and The Office of Environmental Health Hazard Assessment), State Water Resources Control Board, and USEPA.

- Conduct an NGT Workshop for a first draft of these protocols.
- Determine if AWWARF funds would be available.

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***Title:***           **How Do We Keep From Making Stupid Mistakes Again?**

***Originator:***   Church

***Research Need Description:***

Do we need oxygenates? Are they effective? In choosing a “new” oxygenate, we need to learn from the past. MTBE was a bad choice. ETBE or TAME are only slightly better. Ethanol is likely to increase the extent of the BTEX plumes as would methanol by creating formaldehyde as a degradation product.

***Importance:***

We need to be proactive rather than retroactive.

***How do you propose attacking this research need?***

Asking the right questions and doing the research *before* millions of gallons of oxygenates are put into use would prevent expending millions of dollars in future cleanup. We can learn much by looking outside our frame of reference, (e.g., Brazil has used ethanol in gasoline for many years).

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**Title:** Determine the Physical Properties and Environmental F&T of Oxygenates Available for Use, and Being Developed for Use, in Fuels

**Originator:** Drogos

***Research Need Description:***

Measure the physical properties and environmental F&T of the various oxygenates.

***Importance:***

Alternatives to MTBE are being proposed and/or their use increased. Senator Kerry recently proposed adding up to 22 percent ETBE in U.S. fuels (approximately 17 percent would be equivalent to 11 percent MTBE). Ethanol is being used in increasing amounts. What are its effects on existing plumes? Changes in diesel formulations are currently being promulgated. Diesel regulations today are where gasoline regulations were in 1990. The potential exists for not only MTBE replacements for gasoline, but also for potential new contaminants in diesel. New oxygenates are being developed in Europe for introduction to worldwide markets, and some of these have been extensively studied by U.S. oil companies. It is important to be able to anticipate the behavior of these compounds so that we will know how to handle a new contaminant when it appears in the environment and be able to influence the decision-making process regarding what compounds are added to fuels. Also, there is much variation in the reported values for the physical properties of fuel oxygenates.

***How do you propose attacking this research need?***

- Perform laboratory studies at universities to measure the physical properties of oxygenates, as much variation currently exists in measured physical properties to date.
- Fund field studies of existing plumes, laboratory plumes, or created plumes (e.g., Borden).
- Review field data of existing plumes; collaborate on ethanol monitoring/data sharing in areas of heavy use (U.S. Midwest), including an extensive plume study performed in Brazil. I would like to challenge the group to look beyond California to the available information worldwide.
- Develop an international network of interested parties to share data and valuable information on oxygenates behavior available from sources in Europe.

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**Title:** How Can We Prevent Another MTBE?

**Originator:** Yamamoto

***Research Need Description:***

MTBE will be phased out from gasoline and replaced by another oxygenate. MTBE was added to gasoline to have cleaner air but was not evaluated adequately on its possible effect on the environment. We need to do that for MTBE's replacement. If the replacement for MTBE will cause a water quality problem, it should not be approved.

***Importance:***

Prevent future water-quality problems that will need to be remediated or will result in the loss of drinking-water sources.

***How do you propose attacking this research need?***

Establish a management committee consisting of representatives from the Air Quality Board, the Water Board, DHS, petroleum industry, and Association of California Water Agencies. The committee should identify issues and research needs that need to be addressed.



# **Determine Range of MTBE Concentration That Can Be Expected in Supply Wells That Capture MTBE Plumes Emanating from LUFTs. What Types of Supply Wells Are Most at Risk?**

## **ORIGINATORS:**

Einarson on behalf of himself, Crowley, and Yamamoto

*The following research needs were consolidated under the above title:*

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**Title:**           **What Range of MTBE Concentrations Can Be Expected in Supply Wells That Captured MTBE Plumes Emanating From LUFTS? What Types of Supply Wells Are Most at Risk?**

**Originator:**   Einarson

### ***Research Need Description:***

In many cases, defining the mass discharge (total mass flux) of dissolved contaminants emanating from LUFT sites may facilitate estimation of the concentration of the contaminants in a water-supply well that eventually captures those plumes. Our analysis suggests that many dissolved plumes of MTBE will result in relatively minor impacts to large-municipal supply wells. Published values of MTBE mass flux range from 0.3 to 7 grams per day. At steady-state conditions, a supply well – pumping at 250 gpm – that captures a 7 gram-per-day plume will contain MTBE at a concentration of approximately 5 ppb. At higher pumping rates, the concentration of the contaminant in the well can be expected to decrease due to increased dilution of the contaminant in the supply well.

### ***Importance:***

We do not yet know the magnitude of the “MTBE Threat.” Will it cause widespread shut downs of municipal water-supply wells or will concentrations hover around current detection limits?

*How do you propose attacking this research need?*

To assess the significance of MTBE releases, we must define the range of mass discharge values that are typical of LUFT sites. This can be done by monitoring dissolved plumes in a way that the discharge of contaminant mass can be estimated. Operating records from existing pump and treat remediation can also be used to estimate the mass discharge of dissolved contaminants emanating from source zones. However, these values may overestimate the mass flux due to increased groundwater velocities induced by pumping of the well(s).

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**Title:**            **Drinking-water Well Mixing Studies/Modeling – Significance of MTBE and Oxygenate Mass Flux (Plume Discharge Rates)**

**Originator:**    Crowley

**Research Need Description:**

The significance of MTBE and oxygenate mass discharged to a public drinking-water well needs to be investigated. Processes occurring in the well, and in the immediate vicinity of the well, can seriously reduce the maximum concentration that can be discharged from the well. A better understanding of the mixing processes in and near the well will allow us to better understand the ultimate level of exposure to receptors when oxygenates are present in the groundwater resource.

**Importance:**

Saving of funds relative to cleanup costs.

*How do you propose attacking this research need?*

DHS, SWAP, NGWA, GRA, water retailers.

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**Title:**            **Predicting Maximum Oxygenate Concentrations in Groundwater to Enable Cost-effective Drinking-water Treatment Design**

**Originator:**    Yamamoto

**Research Need Description:**

The design of a treatment system is dependent upon the anticipated oxygenate levels in the groundwater. The oxygenate concentration at a spill/leak site may be in the thousands of ppm. What level will occur at a drinking-water well?

***Importance:***

If the predicted oxygenate levels are not close to actual levels, then the treatment system will be oversized or undersized. If the treatment system is seriously undersized, then standards may not be met. This is especially critical for the design of aeration systems and will affect the level of funding approved by DHS.

***How do you propose attacking this research need?***

- Use existing studies on retardation and biodegradation.
- Set up more field studies to track oxygenate levels.



# **Evaluate Environmental Information Management Systems, Decision-making Processes, and Conduct a Critical Review of the Cost-effectiveness of the California UST Program and Existing Resource Protection Programs**

## **ORIGINATORS:**

Tenney on behalf of himself, Crowley, Drogos, Newman, and Tulloch

*The following research needs were consolidated under the above title:*

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**Title:** Evaluate and Develop a Comprehensive, Prototype, Statewide Environmental Information Management System and Programs

**Originator:** Tenney

### ***Research Need Description:***

Critical information needed to make key decisions regarding groundwater resource protection issues is not readily available to the various stakeholders that could benefit from access to the data. In spite of the fact that several efforts to establish an information management system have been initiated during the past few years (e.g., Multi-Agency Data Management Advisory Committee[MADMAC], GeoTracker), high-volume/high-quality data is still not readily available to those who would benefit from it. Critical information is found in a variety of locations and in a variety of formats, which has impeded the efficiency of performing important analyses at the local, regional, and state levels. Such analyses would be valuable to public policy makers who are involved in developing strategies that protect domestic drinking-water supplies. Additionally, information that is generated at ongoing groundwater investigation programs (e.g., UST programs) is not collected and managed in a standardized manner. Finally, quantitative decision making (e.g., Risk-Based Vulnerability Analyses), based on valid data and sound analytical approaches, offer promise in highlighting vulnerable areas so that adequate resources can be focused toward these areas. In light of all this, it is recommended that the State of California (State) consider the following:

- Develop and stream an Environmental Information Management System (EIMS) that bundles critical groundwater resource information and makes the same available through the Internet.
- Develop standard procedures for collecting and managing groundwater data.
- Work with SWRCB and local regions to implement standardization so that data at ongoing programs is collected and ported to the EIMS.

Additionally, it is advised that the State empower a third-party audit firm to perform detailed analyses of the cost effectiveness of the UST Program and develop recommendations to improve its effectiveness using real data that is readily available.

Finally, the State should fund the evaluation of available risk-based screening tools that could be adapted for use at planning-level evaluations of proposed and existing facilities.

***Importance:***

- Standardized collection, reporting, and management protocols will empower decision makers by allowing focused analyses using actual data, if the data is readily available.
- Integrating and standardizing the data into one comprehensive application provides opportunities for state and industry officials to evaluate areas of vulnerability.
- Integrating information needed for detailed risk analyses will increase the use of such tools, which will improve planning for improvements at affected facilities.
- Adopting standardized risk-analysis procedures based on solid, readily-available data will encourage industry and regulatory officials to use these tools for evaluating proposed projects and/or corrective actions.

***How do you propose attacking this research need?***

- Convene a working group of subject matter experts to assess environmental information and management needs and to evaluate existing state of systems/technology. Who will use this information and how it will be manipulated?
- Establish a workgroup to compile data, information, and research reference materials that would be posted to an interactive Web Site that would host the EIMS and relevant reference information.
- Integrate quantitative information into the EIMS.
- Select risk/vulnerability screening tools that might be used to evaluate potential threats to sources of drinking water.

- Establish a working group to identify systems, infrastructure, management systems, and data pathways that would be needed to stream a comprehensive EIMS.
- Perform detailed cost-analysis and highlight benefits that such a program would produce.
- Work with SWRCB and local Certified Unified Program Agencies (CUPAs) to develop standardized data management protocols for sites with ongoing monitoring programs.

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**Title:**            **Comprehensive Economic Evaluation/Review of California’s UST Cleanup Programs**

**Originator:**    Crowley

***Research Need Description:***

California’s UST program is fraught with inefficiencies that result in a waste of resources and sometimes inadequate protection of water resources. The widespread occurrence of MTBE and fuel oxygenates at gasoline stations and fuel leak sites is testimony to these problems. A thorough review of both the cleanup fund and the UST program structure is needed to evaluate if the most cost-effective management strategy is being employed.

***Importance:***

Program inefficiencies, inadequate cleanup, and inappropriate poor guidance, etc. result in millions of dollars wasted each year. This money could be used to provide greater protection to those water resources that are most vulnerable to oxygenate contamination.

***How do you propose attacking this research need?***

Economic audit and evaluation by a private third-party auditor.

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**Title:**            **Develop Site Cleanup Requirements for MTBE and Oxygenates – Combined Use of Risk Assessment and Resource Protection Tools**

**Originator:**    Crowley

***Research Need Description:***

The cleanup requirements for MTBE and oxygenates at gasoline release sites are not very well understood by regulators, consultants, and responsible parties. The development of a comprehensive framework combining risk assessment with resource protection strategies for

various common site scenarios would greatly benefit all parties. In addition, it would both clarify the site-decision process and result in less-expensive site cleanup and management.

***Importance:***

Considerable state and private funds are currently wasted on inappropriate, and sometimes inadequate, investigation and cleanup because there is no clear understanding of the cleanup requirements.

***How do you propose attacking this research need?***

Develop a framework for determining cleanup requirements using risk assessment and resource protection tools.

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***Title:***            **Establish a Workgroup to Compile Data, Information, Research, etc., on Fuel Oxygenates**

***Originator:***    Drogos

***Research Need Description:***

- Establish a research workgroup/committee to pull together the existing data and studies on oxygenates.
- Compile and index the data.

***Importance:***

There is much useful data available on oxygenates (e.g., Brazil ethanol studies, ETBE studies in the Midwest, data on effectiveness of drinking-water treatment systems worldwide, etc.) that were maintained or compiled by many sources. The data is not easily or readily available. The latest data, particularly on recent research, is extremely valuable to those managing the problem of oxygenate contamination.

***How do you propose attacking this research need?***

- Establish a workgroup/committee of agencies, university researchers, petroleum industry, and environmental professionals (with ongoing projects) that would be large enough to research data, on a large scale, and report on a quarterly basis the latest developments, research, studies, etc., regarding oxygenates. Specific subjects/areas would be divided among members to research.
- Develop an interactive website where the group can post oxygenate information, web links, etc. The goal is to establish a readily-accessible clearing house of all available data.

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**Title:**            **Development of International Databases**

**Originator:**   Newman

***Research Need Description:***

Many countries in the European Union (EU) and Asia followed the United State's lead and added MTBE to gasoline. In the EU, they are just beginning to face the problems of tank leakage and groundwater contamination.

***Importance:***

While the EU is behind us in facing this problem, it is becoming an important issue. Research is starting in many areas, and it will be important for researchers and regulators to keep abreast with developments, both in site characteristics and in treatment.

***How do you propose attacking this research need?***

- Reach out to EU regulators to open channels of communication in this area.
- Fund international meetings and workshops to bring people together.

---

**Title:**            **Establish a Formal Communication Pathway to Convey Key Research Results to State and Federal Policy Makers**

**Originator:**   Tenney

***Research Need Description:***

Controversies surrounding MTBE in the last several years created an outrage response from the general public. Regulatory agency officials and the California Legislature reacted to the outrage by establishing additional regulations and forcing the phase out of the fuel additive by 2003, despite the fact that federal oxygenate requirements still exist. The phase out of MTBE has raised a number of questions regarding oxygenate substitution.

Interesting cultural and social dynamics are established when outraged individuals are pressuring decision makers. In such a climate, it is desirable to provide decision makers with up-to-date information so that informed decisions, driven by logic, can be made.

***Importance:***

Effective pathways are needed to rapidly convey current information regarding oxygenate issues to decision makers. This will allow public policy makers to make better-informed decisions or address the public in ongoing dialogues. Information generated during the next several months to years will be important for public policy makers as they consider additional drinking-water protection strategies.

***How do you propose attacking this research need?***

- Identify key legislative personnel, regulatory agency personnel, and citizen action group representatives who would benefit from updated information that would be provided on a regular basis.
- Establish a regularly scheduled meeting with key personnel to communicate critical issues as they are developed.

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***Title:***            **Develop a Comprehensive Understanding of MTBE and Oxygenate F&T Based on Real Data**

***Originator:***    Tulloch

***Research Need Description:***

Limited-scope plume studies have been conducted in California and Texas, and possibly elsewhere. These studies suffered from a lack of data or inadequate monitoring-well networks. These studies have not resulted in better understanding of F&T. Many LUST sites have performed detailed investigations and monitoring since prior plume studies, and the resulting data is not being tracked.

***Importance:***

Without a comprehensive understanding of MTBE plumes and the F&T of MTBE, source-water protection efforts will be limited. Better understanding of plumes can help reduce investigation costs and allow for more effective cleanup.

***How do you propose attacking this research need?***

- Survey local oversight agencies to find MTBE cases with adequate monitoring well networks.
- Develop database to collect site-specific data, including geology, hydrogeology, and concentrations in wells over time.

# **Monitor Natural Attenuation for MTBE: Use Lessons Learned, Develop Innovative Assessment Tools, and Provide Guidance**

## **ORIGINATORS:**

Davidson on behalf of himself, Crowley, Deeb, Newman, Salanitro, and Tulloch

*The following research needs were consolidated under the above title:*

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**Title:**           **Develop Guidance for Assessing the Natural Attenuation of MTBE**

**Originator:**   Davidson

### ***Research Need Description:***

With the increased use of monitored natural attenuation (MNA) and the recognition that MTBE is sometimes naturally biodegrading, people are looking to natural attenuation for addressing MTBE plumes. However, the existing data has not been thoroughly compiled or analyzed. People are often not collecting the right field data to review their site's appropriateness of using MNA for MTBE.

### ***Importance:***

People are considering MNA to address an entire MTBE plume or to address the residual MTBE plume after source area remediation by some other technology. Indeed, the initial remediation technology does not matter; essentially all MTBE-impacted sites will eventually use MNA. We need to provide an accurate summary of pertinent MNA.

### ***How do you propose attacking this research need?***

- Compile all existing natural attenuation data.
- Develop guidance for collecting the right data to determine whether or not natural attenuation can be expected to reasonably handle MTBE plume at a given site.

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**Title:** Proving Biodegradation of MTBE and Fuel Oxygenates at Fuel Release Sites

**Originator:** Crowley

***Research Need Description:***

Very little information is available regarding the demonstration of biodegradation of MTBE in the field. For example, what lines of evidence are considered appropriate for gasoline release sites? What level of monitoring and verification is necessary before regulatory buy-off?

Such questions must be answered before MNA can be considered appropriate as part of the site cleanup strategy for MTBE plumes.

Bring theory into field as soon as possible. A protocol is needed.

***Importance:***

Any level of biodegradation will make a significant difference in the ultimate risk posed by MTBE and oxygenate plumes to receptors. State cleanup funds spend a considerable amount of resources on sites where MNA would be a more cost-effective alternative for cleanup.

***How do you propose attacking this research need?***

- Develop MNA protocol for MTBE and oxygenates.
- Develop models to evaluate alternatives with MNA.
- Verify MNA effectiveness through F&T studies.

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**Title:** Molecular-based Tools to Investigate MTBE-degradation Potential in the Field

**Originator:** Deeb

***Research Need Description:***

Laboratory-studied MTBE-degraders have been characterized at the genus level and, in some cases, at the species level (Rob Steffan, Envirogen; Salanitro, Equilon; Deeb, Scow and Alvarez-Cohen, UC Berkeley and UC Davis). These pure cultures have nothing in common phylogenetically. In addition, the response of these cultures to environmental conditions has been shown to vary. What is the common link at the molecular level between the organisms that facilitate MTBE biodegradation? When is it appropriate to extrapolate laboratory observations

to the field? How feasible is the use of molecular probes (and other non-conventional innovative tools) to look for MTBE-degrading microorganisms in soil and groundwater?

***Importance:***

A better understanding of MTBE-degraders at the molecular level, using both laboratory and field-derived microorganisms, can be useful to evaluate the potential for MTBE bio-attenuation in the field. Molecular-based tools can be used to prove that MTBE “disappearance” is due to the activity of microbial communities in the subsurface.

***How do you propose attacking this research need?***

Basic and fundamental studies, such as the one proposed above, can be performed by universities (UC Davis, UC Berkeley, Oregon Graduate Institute, etc.) in collaboration with consultants and site managers at MTBE-impacted sites.

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***Title:***           **Innovative Tools for Assessing MNA at Oxygenate-contaminated Sites**

***Originator:***   Deeb

***Research Need Description:***

Develop tools to assess MNA approaches for use at oxygenate-impacted sites. There is a need for quick and conclusive methods to understand the mechanisms responsible for oxygenate removal. One potentially useful tool is carbon isotopic fractionation ratios ( $^{13}\text{C}/^{12}\text{C}$ ). This tool, should it work for MTBE and TBA, may also be useful in tracing the source of TBA (i.e., whether TBA was introduced to the subsurface environment as a component of gasoline *or* whether it was produced as a byproduct of MTBE biodegradation).

***Importance:***

Fast and powerful techniques to understand field observations are needed.

***How do you propose attacking this research need?***

Laboratory studies are needed to determine whether isotopic fractionation of MTBE, other oxygenates, and their biodegradation byproducts are possible. Field studies are needed to establish the success and applicability of such tools in the field.

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**Title:**            **Develop a Better Understanding of the Biological Metabolism of MTBE at the Biochemical and Molecular Levels**

**Originator:**   Newman

***Research Need Description:***

We really do not know or understand the enzyme systems involved in MTBE degradation or the genetic systems that produce these enzymes. Thus, we do not have the necessary knowledge to make informed choices when we want to enhance these systems.

***Importance:***

Understanding co-factors or inhibitors to enzyme systems can enhance enzyme efficiency, and understanding the genetic system can give us probes to identify new organisms as well as ways to increase enzyme production in the organisms.

***How do you propose attacking this research need?***

Willingness to fund “basic science” research to better understand the systems.

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**Title:**            **Does Natural Bioattenuation of Oxygenates Occur in Aquifers?**

**Originator:**   Salanitro

***Research Need Description:***

Natural attenuation of ethers and branched alcohols (BA) may occur in some aquifers due to groundwater dispersion/dilution effects along flow paths and heterogeneous subsurface lithologies. Some lab microcosm studies suggest that ethers and BA biodegrade after a lag period. However, lab systems can only suggest the potential for biodegradation mechanisms, but cannot be used to infer actual field bioattenuation rates. The contribution of biodegradation components of oxygenate attenuation needs to be adequately quantified from field observation and modeling.

***Importance:***

Determination of the existence of *in situ* biodegradation of plume oxygenates (rate constants) may be used in MNA and RBCA models to predict the extent of plume migration, potential impacts to receptor wells (longevity of plumes and sources), and to demonstrate intrinsic containment.

*How do you propose attacking this research need?*

- Study some oxygenate plumes in more detail (e.g., discrete depth sampling, more monitoring wells, encompassing plume and source zones, and integration of plume mass in accounting for dispersion dilution decreases from losses due to biodecay).
- Identify geochemical (redox species) conditions in aquifers and “footprint” indicators (intermediates, stable isotope enrichment).
- Obtain definitive aerobic and/or anaerobic biodegradation evidence on the extent and rates of biotransformation possible in lab assays of aquifer material relative to readily degradable compounds (BTEX).

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**Title: Long-term Source Water Impacts Resulting From Residual Low Concentration Oxygenate Plumes**

**Originator:** Tulloch

***Research Need Description:***

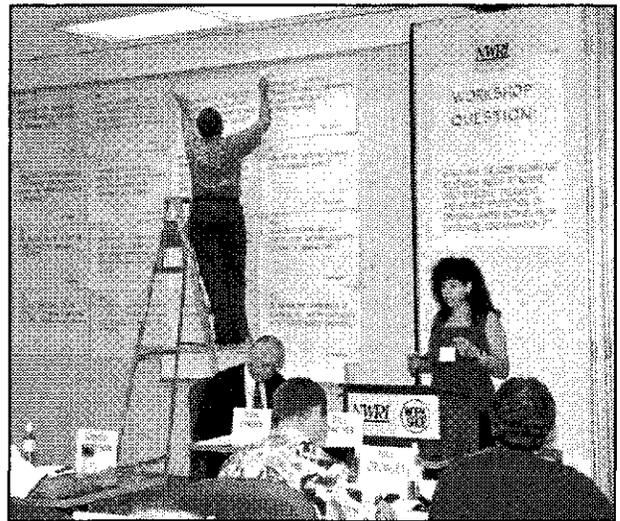
There are thousands of MTBE plumes in California. It is unlikely that they will be remediated to non-detectable concentrations or MCLs. The result will be that thousands of plumes of MTBE or other oxygenates will remain for decades to come. The long-term impacts of these residual plumes are not well understood. This research should focus on determining the long-term (50-100 years) impacts to future drinking-water sources.

***Importance:***

Current source water protection research and programs do not adequately address the long-term impacts of residual oxygenate plumes. It is necessary for this to be understood so that cleanup, risk management, and a long-term source water management program can be effective.

***How do you propose attacking this research need?***

- Convene a TAC.
- Develop an economic model.
- Develop a F&T model.
- Verify F&T results by comparing to other long-term impact research of persistent chemicals.



# **Develop and Optimize Chemical/Physical *In Situ* Technologies to Enhance Source and Plume Cleanup**

## **ORIGINATORS:**

Kavanaugh on behalf of himself, Deeb, Drogos, Einarson, and Hoffmann

*The following research needs were consolidated under the above title:*

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**Title:**            **Develop Cost-effective Techniques to Remove Free and Residual Light Non-aqueous Phase Liquid (LNAPL) at any Depth**

**Originator:**    Kavanaugh

### ***Research Need Description:***

Current technologies only remove 20-40 percent of LNAPL at LUFT sites. The remaining residual product is a continuing source of petroleum hydrocarbons to groundwater.

### ***Importance:***

Residual LNAPL with oxygenates is a continuous source of oxygenates to groundwater. Because oxygenates have a slow biodegradation rate, long plumes can occur and continue to impact receptors. Because of limitations on the use of natural attenuation with oxygenates, increased removal efficiency is needed for LNAPL removal.

### ***How do you propose attacking this research need?***

- Critical review of LNAPL removal technologies.
- University research on mechanistic aspects.
- At least two field studies; joint-partnership between responsible parties, vendors, and consultants.

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**Title: Combine Physical/Chemical and Biological Approaches for Achieving Time-effective Treatment**

**Originator:** Deeb

**Research Need Description:**

The use of bioremediation at MTBE-impacted sites may not be effective from a time perspective due to low observed degradation rates of MTBE in the field and the slow growth of MTBE-degraders. Consider a combination of physical/chemical technologies followed by *in situ* bioremediation (the bioattenuation) as a polishing step.

An example of technology integration with *in situ* bioremediation: Steam injection/vacuum extraction for NAPL removal in a fractured bedrock environment. This could remove the majority of NAPL, but may leave residual contamination. Steam injection/vacuum extraction may re-oxygenate anaerobic environments, decrease the numbers of “predators” in subsurface environments, and increase temperature, thereby enhancing biological activity (up to an optimum temperature).

**Importance:**

The combination of technologies from a time and cost perspective may be critical. In addition, it could help in reaching regulatory standards. Integration of biotechnologies with a physical/chemical technology can be used in *ex situ* and *in situ* approaches.

**How do you propose attacking this research need?**

Research on laboratory- and pilot-scale levels is needed before scaling such efforts to the field.

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**Title: Review the Effectiveness of Oxygenate Treatment Technologies/Actual Systems Throughout the U.S.**

**Originator:** Drogos

**Research Need Description:**

Develop comparative documentation (including actual data) of the effectiveness of the different types of water treatment systems (both remediation and drinking-water treatment) currently in operation nationwide.

***Importance:***

There are numerous operating treatment systems throughout the U.S. Much data is being collected regarding the success or lack thereof of these systems. In addition, the systems are treating many contaminants that are generating data that maybe useful for water retailers (e.g., Manter, Kansas, has a GAC system for MTBE, BTEX, EDB, and EDC treatment.)

***How do you propose attacking this research need?***

Develop a collaborative effort to share and analyze data from the various systems. Involve the agencies with the systems, universities, and California agency experts to evaluate the data. It would be appropriate to collaborate nationwide, especially among public agencies.

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***Title***            **How Quickly Will Unmitigated MTBE Releases Naturally Attenuate Due to Source Depletion?**

***Originator:***    Einarson

***Research Need Description:***

Due to its high solubility, MTBE is preferentially leached from residual NAPL. Early conceptual models suggested that MTBE source zones would be quickly depleted, and the resulting plumes would be soon become detached from the source zones. This has generally not been the case. Rapid depletion of MTBE in source zones is hampered by ever-decreasing effective solubilities, diffusion-limited mass transfer in NAPL, low surface area to mass ratios, and diffusion into/out of low permeability units.

***Importance:***

We need to understand how long unmitigated MTBE release sites will pose a threat to our groundwater resources.

***How do you propose attacking this research need?***

- Theoretical (CVOC experience!).
- Modeling.
- Field monitoring of plumes in stable flow fields.
  - Temporal monitoring down-gradient of source zones
  - Define contaminant mass discharge as a function of plume length (a plume is a record of the dissolution history of the source zone).

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***Title:***            **Development of *In Situ* Technologies for Plume Concentration of Oxygenate Contamination to Enhance the Efficiency of Pump-and-Treat Remediation Projects**

***Originator:***    Hoffmann

***Research Need Description:***

Current remediation methods do not effectively contain contamination plumes, and pumping groundwater is being used as an inefficient method to attract oxygenate plumes for extraction and treatment.

***Importance:***

Plume containment and oxygenate plume concentrations are critical for efficient pump-and-treatment projects.

***How do you propose attacking this research need?***

Adapt existing resin and barrier technologies in laboratory testing.

# **Evaluate Current Gasoline Containment Practices and Needs and Opportunities for Improvement and Development of Best Management Practices (BMPs) (UST & Marina Refueling)**

## **ORIGINATORS:**

Moyer on behalf of herself, Tikkanen, and Drogos

*The following research needs were consolidated under the above title:*

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**Title:** Evaluate Current Gasoline Containment Practices and Needs and Opportunities for Improvement

**Originator:** Moyer

### ***Research Need Description:***

It was thought that the 1988 federal UST requirements would largely solve the problem of releases associated with USTs. However, expectations have not been fully realized, and there is significant contamination associated with USTs. However, we do not know specifics:

- How well do various types of UST and leak detection systems and components work in the field?
- How well is this equipment installed, operated, and maintained?
- How much is old contamination that was never addressed?
- How much is due to spills and overfills?
- What USTs are still out of compliance, in what ways, and why?

***Importance:***

Until we identify and prioritize the weak points in gasoline containment systems, we will not know how to most cost-effectively improve these systems. The above questions will be difficult to answer, but it is probably worth the effort because preventing releases, or detecting them earlier, may well be easier than remediating them.

***How do you propose attacking this research need?***

A variety of activities will be necessary, including those listed below:

- Review existing documentation and interview UST owners, contractors, regulators, and experts relative to the above questions.
- Inspect malfunctioning equipment on removal and determine the cause of the malfunction.
- Install/monitor tank-pit groundwater and/or vapor-monitoring wells and, when contamination is detected, pinpoint the source. If necessary, dig up the entire UST system and delineate soil contamination.
- Inspect new and existing UST and leak detection system installations.
- Determine training, inspection, and certification practices.

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***Title:***            **Develop BMPs for O&M of Refueling Facilities at Marinas on Drinking-water Reservoirs**

***Originator:***    Tikkanen

***Research Need Description:***

MTBE (and other gasoline components) has been found in water from reservoirs, which permit use of motorized recreational vehicles and serve as drinking-water sources. One source of MTBE (and other gasoline components) is the refueling activity on that reservoir.

Reasons for this refueling contamination include failure of the storage container and its components, spillage during the refueling of storage tank, and dispensing of fuel from the tank.

***Importance:***

Many reservoirs that serve as a drinking water source permit motorized recreation in the reservoir. Restriction or elimination of this activity is *not* an option. Therefore, a cleaner use of the fueling facilities is needed to prevent contamination of the reservoir by this activity.

How do you propose attacking this research need?

- Literature research.
- Review of “Report of the State Water Resources Control Board’s Advisory Panel on Fueling and Refueling Practices at California Marinas”, January 1999.
- Expand on recommendations of the SWRCB report.
- Use SWRCB as a resource for staff and money.
- Use Department of Boating and Waterways as a resource for staff and money.
- Possible investigator: J. Reuter, University of California, Davis, is a researcher currently involved in oxygenate contamination/F&T/etc. of drinking-water reservoirs/lakes.

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***Title:***            **Perform a Forensic Analysis of an Upgraded UST System Exhibiting Signs of a Recent MTBE Release**

***Originator:***    Drogos

***Research Need Description:***

Perform a forensic excavation of an entire upgraded UST system. Start capturing data indicative of a release during removal of the tank system; trace the leak.

***Importance:***

There is strong evidence suggesting that releases are occurring from upgraded UST systems, but little work to establish how the releases are occurring. Identify the cause of releases from upgraded UST systems is important to halt the continued release of MTBE (and MTBE alternatives) to groundwater supplies.

***How do you propose attacking this research need?***

Provide funds and a project team to perform a detailed excavation and forensic analysis of an upgraded UST system at a public agency facility or a major oil company gas station.



# **Conduct a Critical Review of the Potential Threat to Groundwater Contamination From Leaking Gasoline and Oil Pipelines**

**ORIGINATOR:**

Rodriguez

***Problem Description:***

In California, there are thousands of miles of pipelines that convey gasoline throughout the state. These pipelines threaten the groundwater drinking-water supplies. Regulations to ensure their safety are focused on catastrophic releases, which are based on antiquated regulations, and need to be updated with stricter testing and monitoring requirements.

***Importance:***

Product pipelines are suspected of releasing gasoline and other contaminants throughout the state; however, it is difficult to identify releases without the adequate monitoring and ongoing assessment of these pipelines.

***How do you propose attacking this research need?***

Conduct an NGT workshop with regulatory agencies, pipeline owners, operators, maintenance personnel, equipment manufacturers, and engineering consultants to develop:

- An understanding of the potential threat of drinking-water supplies from small leaks in pipelines.
- Guidelines for designing, testing, and maintaining of pipelines that convey gasoline containing oxygenates.



# **Conduct Long-term Human Health Effects Study of MTBE/Oxygenate Exposure in Drinking Water**

## **ORIGINATORS:**

Crowley on behalf of himself and Church

*The following research needs were consolidated under the above title:*

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**Title:** Long-term Human Health Effects Study of MTBE/Oxygenate Exposure in Drinking Water

**Originator:** Crowley

### ***Research Need Description:***

There is a lack of definitive research related to the ingestion of MTBE and other oxygenates at low concentrations in drinking water. Consumer acceptability relative to low levels of oxygenates in drinking water is a significant issue for the water community. Specific health effect studies are needed to allow the water community to demonstrate the potability of water, even at concentrations significantly below established MCLs.

### ***Importance:***

- Public acceptability.
- Cost of treatment.

### ***How do you propose attacking this research need?***

NWRI, DHS, Water Environment Federation (WEF), AWWARF.

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**Title:**            **What is the Environmental Fate and Human Health Effects of TBA Resulting From the Use of MTBE?**

**Originator:**   Church

***Research Need Description:***

MTBE degradation, whether through biological or advanced oxidation processes, have commonalities in that they produce similar degradation products. These products are TBA, possibly TBF, acetone, isopropanol, etc. Of these products, TBA and TBF have known deleterious health effects. TBF has a rapid hydrolysis rate that produces TBA. TBA, which appears to be at least as recalcitrant as MTBE, is a known human carcinogen, yet little emphasis to date has been placed on either its occurrence, its health effects, or its treatment in drinking water.

***Importance:***

At present, little effort is being focused on its occurrence, let alone its removal.

***How do you propose attacking this research need?***

Numerous researchers are well equipped to attack these problems:

- Microbial degradation of TBA: Salanitro, Scow, Dochusses, etc.
- Fate: Church, Einarson, MacKay, Amerson-Treat, Johnson, etc.
- AOP: Sun Liang, Hoffman, Brown, Malcolm Pirnie, Inc., etc.

# **Design, Construct, and Operate a High-tech Service Station That Implements Proactive Detection, Monitoring, and Remediation Technologies to Prevent Groundwater Contamination**

## **ORIGINATORS:**

Rodriguez on behalf of himself, Tenney, and Woodward

*The following research needs were consolidated under the above title:*

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***Title:* Design, Build, Construct, and Operate a High-tech Service Station That Implements Pro-active Leak Detection, Monitoring, and Remediation Technologies to Prevent Impacts to Surrounding Soil and Groundwater**

***Originator:*** Rodriguez

## ***Research Need Description:***

USTsystems leak. It is not clear where the leaks are coming from. The obvious suspects are the tanks, distribution lines, vapor recovery system, etc., but it does not appear to be a common source of the release.

## ***Importance:***

Leaks from USTs will continue from UST facilities. Without stopping the leaks, efforts and funds will focus on cleanup as opposed to stopping the leaks. Both need to be addressed.

## ***How do you propose attacking this research need?***

Convene representatives from the oil industry, water utilities, academia, and consultants to develop design criteria, construction, operation, and monitoring of high-tech gasoline dispensing facilities.

---

**Title:** Evaluate UST Operational Characteristics Using Reality-based Approaches

**Originator:** Tenney

***Research Need Description:***

Public impression suggests that existing UST programs are not cost and environmentally effective. Improving both environmental performance and cost-effectiveness of UST programs will require information concerning:

- Root causes of site-specific malfunction mechanisms leading to potential release scenarios.
- Identification of areas/equipment that offer improvement opportunities.

Reliability approaches hold promise in that they use existing event-frequency information to identify areas of vulnerability. In doing so, critical and non-critical activities can be utilized, and management strategies can be improved.

***Importance:***

USTs are a significant potential source of shallow groundwater contamination. Identifying problem areas and focusing resources toward these areas may reduce long-term threats to groundwater.

***How do you propose attacking this research need?***

- Convene a group to select operating UST systems that would participate in a study.
- Develop a data management and reporting system in which event information would be populated.
- Use a detailed data set to evaluate the occurrence and distribution of events.
- Develop recommendations based on data conclusions.

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**Title:** Proactive/Reactive Barrier

**Originator:** Woodward

***Research Need Description:***

We can make the assumption that all tanks, sooner or later, will leak. Stored liquids will get away. We need an *in situ* process to contain and initiate remediation as soon as a leak occurs: proactive reactive barriers. We need to replace the pea gravel backfill in a tank installation. The barrier should sorb gasoline constituents and degrade them – both chemical and biological processes are needed.

***Importance:***

- Sorbent, reactive material needs to be developed.
- Bench-scale selection/development.
- Potential for amplification of leak/spill sensor sensitivity.

***How do you propose attacking this research need?***

Interdisciplinary approach of chemists, physical scientists, and microbiologists will produce a backfill material that contains leak/spill by adsorption, reacts chemically to degrade gasoline constituents, and initiates biodegradation process from encapsulated biodegradation materials. The process would be optimized by column studies of blended sorbent, chemical reactant, and biological seed.



## **Quantify and Model the Effect of Co-contaminants on the Biodegradation Rates of Ether Oxygenates in the Field**

**ORIGINATOR:**

Deeb

***Problem Description:***

MTBE and other oxygenates are most often found at sites that are impacted by complex mixtures of gasoline hydrocarbons. Some gasoline components have been shown to stimulate cometabolic MTBE biodegradation (e.g., n-alkanes, propane). Alternatively, MTBE biodegradation may be inhibited in the presence of more easily biodegradable compounds. This can occur when MTBE-degrading cultures preferentially utilize easily degradable hydrocarbons, such as BTEX. Inhibition can also occur when preferential hydrocarbon use in mixed contaminant plumes results in the depletion of oxygen, other electron acceptors, and nutrients necessary for the biodegradation of MTBE and ether oxygenates.

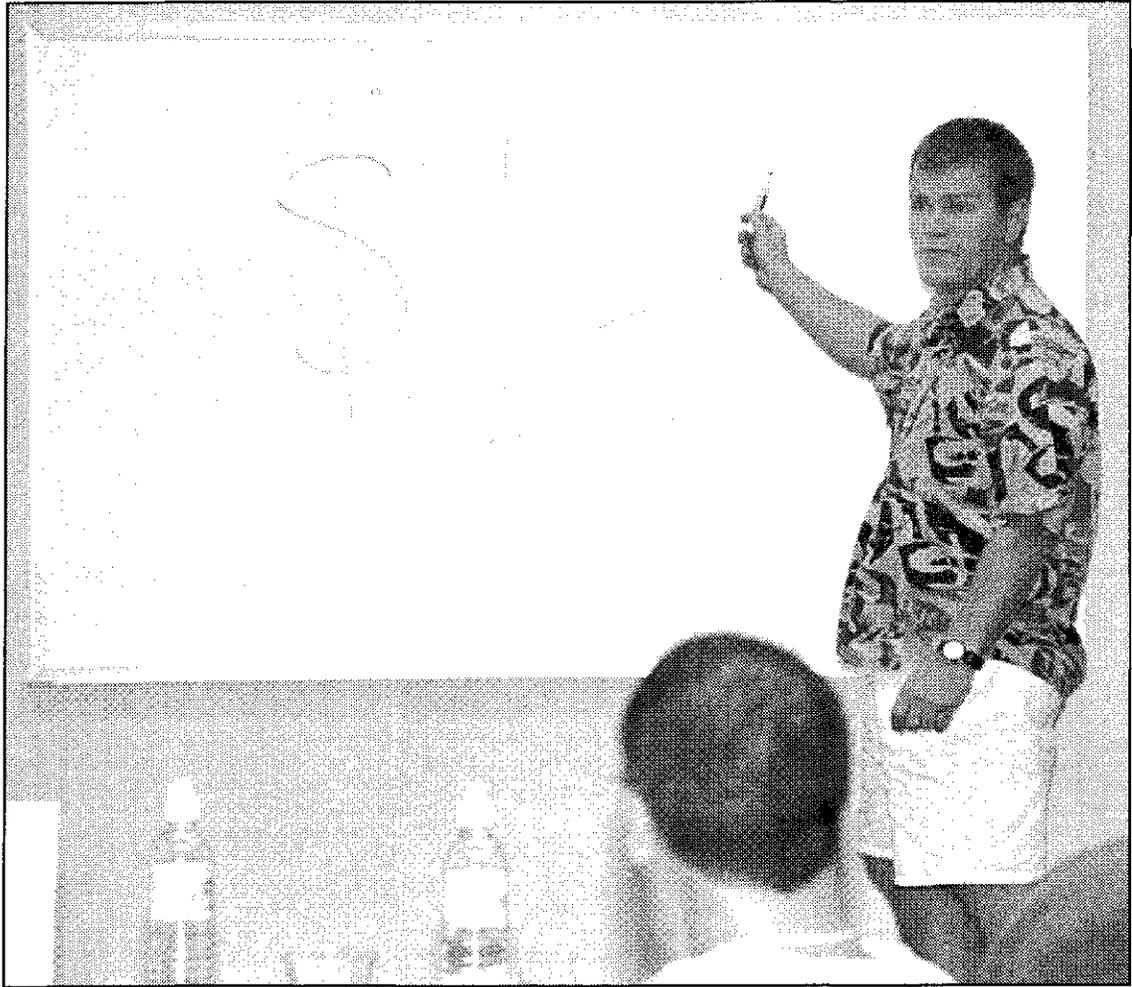
***Importance:***

While some laboratory studies have been done to elucidate possible mechanisms of inhibition of MTBE biodegradation in contaminant mixtures, field studies are needed to understand co-substrate interactions in complex environments.

***How do you propose attacking this research need?***

Seek funding for controlled field studies from:

- USEPA
- Oil Companies
- Western States Petroleum Association



# **Develop Strategies to Control MTBE and Oxygenate Plume Migration**

**ORIGINATOR:**

Crowley

***Problem Description:***

The migration of MTBE and oxygenate plumes in groundwater is not actively controlled at most fuel-release sites. At many of these sites, significant lateral and vertical movement of plumes occurs because the pace of investigation is slow, and considerable time may elapse prior to the implementation of treatment. The increased plume size and associated nuisance result in significantly higher costs for investigation, treatment, and third-party liability.

***Importance:***

- Increased plume size = increased cost and delay in ultimate cleanup.
- Wells and water resources are at greater risk of contamination.

***How do you propose attacking this research need?***

- Development of a guidance document that outlines migration control strategies for MTBE and oxygenate plumes and provides numerous case examples.
- Modeling to demonstrate the need for migration control and to demonstrate the effectiveness of various alternatives.
- Participation by API, WSPA, and others.



# **Examine Living-plant-based Remediation Systems Including Uptake Rates, Metabolism, and Evaluation of Prototype Treatment Systems**

## **ORIGINATORS:**

Newman on behalf of herself, Brown, Hoffmann, and Moyer

*The following research needs were consolidated under the above title:*

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**Title:** Determine the Fate of MTBE and Other Oxygenates in Plants

**Originator:** Newman

### ***Problem Description:***

At this time, we know that plants readily take up MTBE from soil or water. What we do not know is the fate of MTBE after uptake. Laboratory work has suggested that transpiration (release into the air) is the primary fate, but studies with other compounds have shown us that the metabolic activity of plants differs dramatically between the lab and field.

### ***Importance:***

The best treatment technologies are those that remove/degrade the metabolite, not simply transfer from one media to another (i.e., water to air). Several phytoremediation sites are already being or have been installed; thus, it is critical that we better understand what is happening in these systems.

### ***How do you propose attacking this research need?***

There is a need for long-term funding of fieldwork to determine the fate of MTBE under “Real World” conditions as opposed to only laboratory/chamber studies.

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**Title:** Evaluate the Use of Engineered Wetlands to Treat Low Levels of Oxygenates in Surface Waters (Including Reservoirs) and Sewage Discharges (Industrial and Municipal)

**Originator:** Brown

**Problem Description:**

MTBE and other oxygenates are present at low levels in surface runoff and in many surface water supplies and sewage discharges. To remove MTBE, very large volumes of water will need to be treated.

**Importance:**

Conventional systems (e.g., air stripping and GAC) will be large and costly.

**How do you propose attacking this research need?**

Spike influent water at a gravel-based treatment wetland cell (e.g., Chino Basin). This provides surfaces for adsorption and degradation in a mixed aerobic and anaerobic environment. Conduct detailed in-cell monitoring (surface and subsurface, water, soil, air, and organic matter) of contaminant fate.

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**Title:** Evaluate the Impact of Stormwater Runoff Contribution to Oxygenate Contamination of Drinking Water Sources

**Originator:** Hoffmann

**Problem Description:**

Oxygenates are present in stormwater runoff, which ultimately enters groundwater and surface waters.

**Importance:**

The contribution of oxygenate contamination resulting from stormwater runoff needs to be addressed.

**How do you propose attacking this research need?**

Field study of oxygenates in stormwater runoff.

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**Title:** Evaluate Biological (Plant) Methods for the Removal/Reduction of Oxygenates in Stormwater Runoff to Develop Stormwater Collection and Disposal Design Criteria

**Originator:** Hoffmann

***Problem Description:***

The oxygenate contribution from runoff to groundwater and surface water has not been addressed in existing source water protection strategies.

***Importance:***

The oxygenate contribution in storm water possesses a potential significant impact to drinking-water sources. The treatment of storm water prior to entering drinking-water sources could reduce the contaminant load on groundwater and surface water.

***How do you propose attacking this research need?***

Conduct field-pilot studies of oxygenated contaminated runoff to determine the effectiveness of a variety of plant species regarding oxygenate uptake from overland flow and catch basins.

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**Title:** Phyto-GAC for MTBE/TBA Water Treatment

**Originator:** Moyer

***Problem Description:***

Problems with regenerating GAC used for MTBE have been documented. Bio-GAC is one approach to this problem. Phyto-GAC would possibly further enhance carbon regeneration by supporting microbial populations on root hairs and providing plant exudates and oxygen. In addition, the plants themselves may break down MTBE/TBA. Furthermore, the plants' transpiration could be exploited to reduce effluent volume, if desired.

***Importance:***

This approach could reduce treatment costs.

***How do you propose attacking this research need?***

Laboratory-test treatment of MTBE/TBA/gasoline-contaminated water using GAC, bio-GAC, and phyto-GAC and compare effluent concentrations and carbon bed life.



# **Develop Small, Low-cost Packaged Point-of-Use and Point-of-Entry Treatment Systems**

## **ORIGINATORS:**

Brown on behalf of himself and Tikkanen

*The following research needs were consolidated under the above title:*

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***Title:*            Develop Small, Low-cost Packaged Point-of-Use and Point-of-Entry Treatment Systems for Oxygenate Contamination in Individual Households and Small-community Water Supplies**

***Originator:***    Brown

### ***Problem Description:***

Need systems for private-well owners (< 1gpm) and small communities (< 25gpm) that are:

- Small.
- Modular.
- Robust.
- Low maintenance.
- Consistent.
- Foolproof.
- Long lasting.
- Compliant with drinking water standards.
- Free?

***Importance:***

There are thousands of small private water-supply wells in California and many small-community water supplies. These systems are not monitored for oxygenates on the same regular basis as at larger public utilities. In the event of oxygenate contamination, individuals and small communities cannot afford expensive investigation programs to determine “who did it?” They cannot afford complicated treatability feasibility studies, designs, and construction programs. In addition, they do not have the technical ability to operate complex systems. They are also not represented by associations with financial/political donations.

***How do you propose attacking this research need?***

- Initial paper study looking at existing systems used for household water treatment (can they handle oxygenates?).
- Low-flow groundwater remediation systems (can they meet drinking-water standards?).
- Field demonstration at selected promising systems.

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***Title:***            **Develop a Small, Cost-effective, Low to Medium Flow, Stand-alone Water Treatment System to Treat Water Contaminated with Low-Level Concentrations (<50ppb) of Oxygenates (Particularly MTBE)**

***Originator:***    Tikkanen

***Problem Description:***

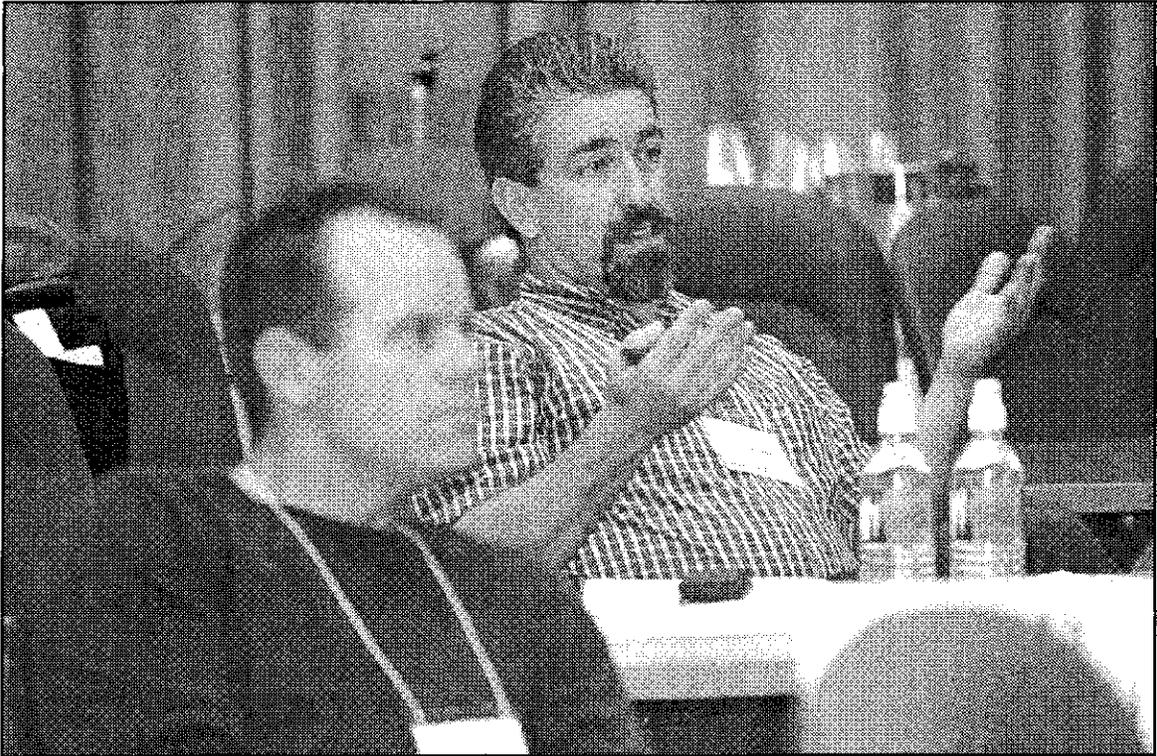
Many current drinking-water treatment technologies do not effectively remove MTBE (and other oxygenates) at the low concentrations found in surface water, which is used as a source for drinking water. Effectively, MTBE concentrations found in influent to the conventional water-treatment plant are equal to effluent concentrations from the plant. Many small drinking-water systems have only one source of water. That source of water may be a lake contaminated with MTBE or a groundwater well. Treatment of this contaminated source water is needed.

***Importance:***

Many lakes (reservoirs) serve as the source of drinking water for small communities that are located around the reservoir. Motorized recreational boating on the lake has contaminated this water source with gasoline components. This water must be treated for these contaminants prior to delivery to customers. There is neither the money, land, nor personnel resources to build and maintain a large, highly complex water treatment facility. There is critical need to cost-effectively remove oxygenates from this water using a small, low to medium flow, stand-alone, water-treatment system.

*How do you propose attacking this research need?*

- Literature search: Expansion on “*Treatment Technologies for Removal of MTBE from Drinking Water.*” February 2000.
- Bench scale testing: Pilot plant testing.
- Consulting firms could be used to do the study.
- AWWARF funding should be sought.



# **Assess Oxygenate Impacts on Small, Private Water-supply Wells in California**

**ORIGINATOR:**

Einarson

***Problem Description:***

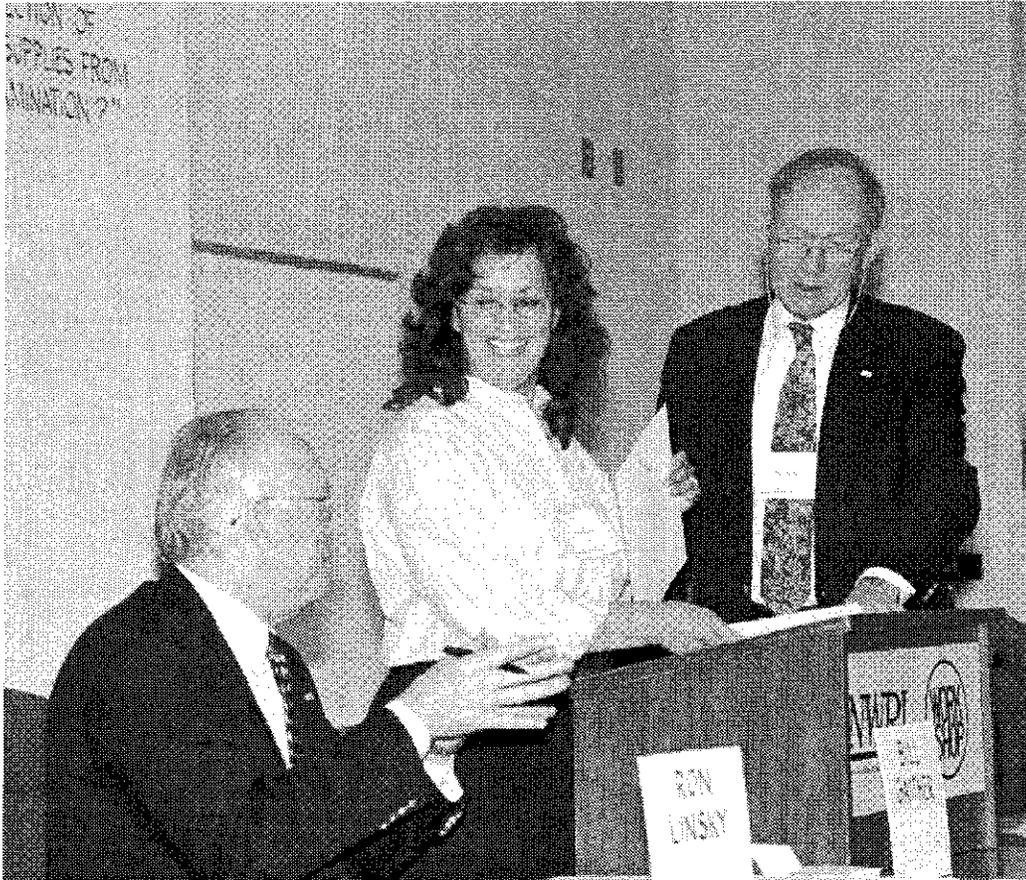
Small, private water-supply wells may be at greater risk of contamination than large municipal water-supply wells. Ironically, small water systems are exempt from mandatory testing for MTBE and other oxygenates.

***Importance:***

We need to better understand the threat of groundwater contamination in rural communities.

***How do you propose attacking this research need?***

Test groundwater samples from a subset of small domestic wells throughout the state.



# **Review and Assess Needs When Electric-powered Motors Are Used on Recreational Boats Exclusively on a Drinking-water Reservoir**

**ORIGINATOR:**

Tikkanen

***Problem Description:***

If gasoline-powered recreational boats are eliminated on certain reservoirs, other options for general recreational use must be considered. Electric-powered boats have been suggested as a replacement for gasoline-powered boats.

***Importance:***

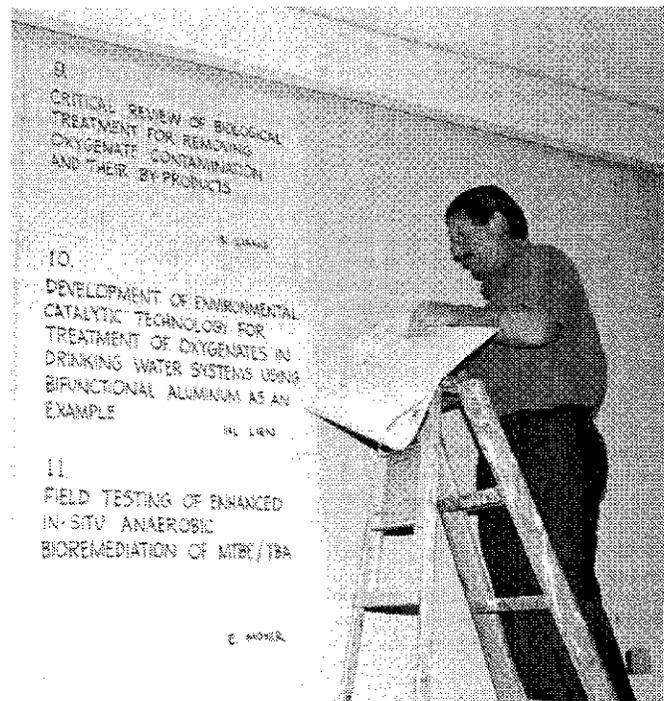
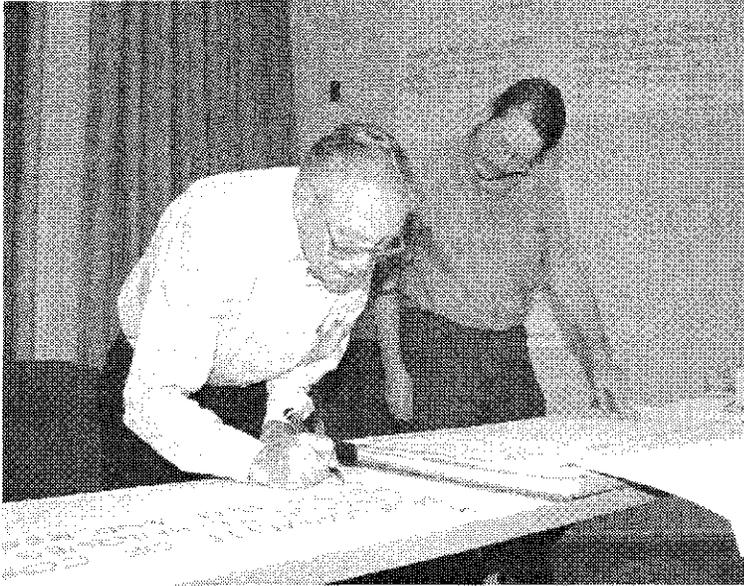
As gasoline contamination of drinking-water reservoirs has been observed when gasoline-powered boating is permitted on a reservoir, there has been a public call to remove any gasoline-emitting vehicle from use on the reservoir. Electric-powered boats have been suggested as an alternative. The electric-powered motors would emit no hydrocarbon pollution to the reservoir.

***How do you propose attacking this research need?***

The issues that must be considered include:

- Are electric-powered boats feasible for recreational use?
- What are the safety issues?
- What infrastructures must be set in place?
- Have electric-powered boats been used on other reservoirs?
- What have been the consequences, if any?

Studies could be conducted with grants from the Department of Boating and Waterways as well as the Air Resources Board.



# **Evaluate Ways to Reduce Gasoline and Water Consumption**

**ORIGINATOR:**

Moyer

***Problem Description:***

One root to the problem of oxygenates in groundwater is the vast quantities of gasoline and potable water that are currently used. If we could reduce gasoline and potable water use, groundwater contamination by oxygenates, as well as a host of other environmental problems, would be reduced accordingly.

***Importance:***

We need to identify the barriers (e.g., technical, political, social, institutional, economic) to reduce the consumption of gasoline and water by organizations and individuals.

Possible strategies include:

- Improving internal-combustion engine efficiency.
- Increasing the use of vehicles using alternative energy sources (e.g., electric).
- Increasing the use of public transportation.
- Using and reusing water more effectively.

Once identified, perhaps some of these barriers can be overcome.

***How do you propose attacking this research need?***

Establish a multi-disciplinary task force incorporating many perspectives to study the various aspects of these problems, and recommend practical ways to overcome these barriers.



# **Assess the Applicability of Market-share Liability to Pay for the Cleanup of Oxygenate Contamination of Aquifers and Wells**

## **ORIGINATORS:**

Brown on behalf of himself and Kavanaugh

*The following research needs were consolidated under the above title:*

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***Title:***            **Assess the Applicability of Market-share Liability to Pay for the Cleanup of Oxygenate Contamination That Impacts Regional Aquifers and/or Water Supply Wells**

***Originator:***    Brown

### ***Problem Description:***

Oxygenate plumes in regional aquifer systems, especially those that impact water-supply wells, may be the result of numerous releases at multiple sites. Even shallow plumes that extend off-site may be a mix of contaminants from more than one site. Oxygenate contamination cannot be geochemically fingerprinted to the degree needed to specify the source. We have to rely on contaminant hydrogeology to define the source(s), and the data needed is expensive to collect and open to interpretation.

### ***Importance:***

Regional aquifers and water-supply wells are not being cleaned up due to disagreements over responsibility.

### ***How do you propose attacking this research need?***

Develop a groundwater risk matrix that considers the following for each oil company:

- Number of LUST sites.
- The concentration at these LUST sites.
- The proximity to water-supply wells and others.

- Other factors to be determined from a needs assessment.

If the matrix indicates that the cumulative risk to groundwater for each oil company is comparable to their market share, then the market-share liability approach would be applicable.

If the approach is applicable, the state UST fund could pay for cleanup of aquifers and water-supply wells operated by water utilities.

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***Title:***            **How Can Alternative Dispute Resolution (ADR) Techniques Be Used to Accelerate Cleanup of Oxygenate Sites?**

***Originator:***    Kavanaugh

***Problem Description:***

Current remediation of LUFT sites with oxygenates is stalled due to litigation. ADR offers a potential dispute resolution technique to break the log jam.

***Importance:***

Rapid remediation is critical to minimizing impacts and remediation costs.

***How do you propose attacking this research need?***

Set up an expert working panel to prepare a report on the suitability/implementation of an ADR approach to accelerating cleanup.

# **Conduct Cost-benefit Analysis of Treating Oxygenate Contamination in Drinking Water to Different Standards**

**ORIGINATOR:**

Brown

*Problem Description:*

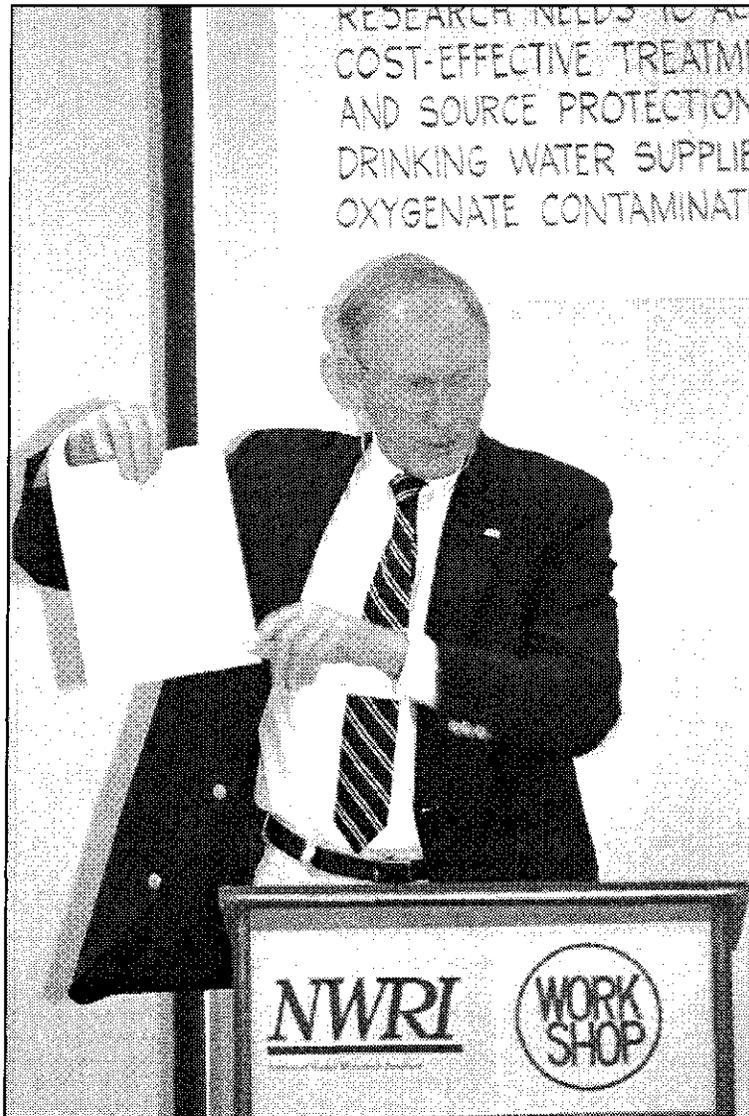
There are four potential standards that drinking water could be treated to: health, aesthetic, those the public will accept, and non-detect. There is a lot of debate between water utilities and potentially responsible parties as to what is the appropriate end point. However, no one has evaluated the incremental cost of treatment to various stringent standards using different techniques. No one has asked the public for their opinion as to the level they feel is acceptable given that the incremental costs will ultimately be passed on to the public. No one has evaluated the actual or perceived benefit of treating to a more stringent standard.

*Importance:*

Incremental costs may or may not be large. If not, then why all the debate over the end point? If they are, then is the public prepared to accept the increase in costs for a certain level of benefit?

*How do you propose attacking this research need?*

- Review existing treatment systems and conduct engineering feasibility evaluations (including cost estimates) for various technologies used to treat drinking-water to different end points.
- Conduct a public acceptance survey in areas with and without MTBE in drinking water.
- Quantify actual and perceived benefits.



# **Review MTBE Synthesizing Methods to Provide Insight for Developing MTBE Treatment Technologies**

**ORIGINATOR:**

Lien

***Problem Description:***

Figuring out the synthetic methods of MTBE may provide insight for developing MTBE treatment technologies. Since the chemical reaction is reversible, it is possible to control the operation conditions in order to reverse the reaction direction from the formation of MTBE to decomposition of MTBE.

***Importance:***

Developing of a new technology often takes a lot of time and effort. However, there is an urgent need to develop cost-effective treatment processes for MTBE removal in drinking-water systems. Therefore, it is important to shorten time consumption during the development stage.

***How do you propose attacking this research need?***

- Review all MTBE synthetic methods.
- Evaluate the possibility of enhancing reversed reaction by adjusting operation conditions.
- Conduct laboratory tests.



# **Conduct a Critical Review of California's Wellhead Protection Program**

## **ORIGINATORS:**

Einarson on behalf of himself and Crowley

*The following research needs were consolidated under the above title:*

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***Title:* Critical Review of California's Wellhead Protection Program**

***Originator:* Einarson**

### ***Problem Description:***

California lags behind many states in implementing a wellhead protection program. Continued rapid urbanization of the state will increase the risk of contamination to groundwater. Potential sources of groundwater contamination should be kept, as much as possible, out of the capture zones of water-supply wells.

### ***Importance:***

A statewide wellhead protection program will help protect dwindling California groundwater resources from further contamination.

### ***How do you propose attacking this research need?***

- Assess the state's current efforts.
- Compare to similar programs in other states and countries.
- Provide recommendations to the state.

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***Title: Strategies to Reduce MTBE and Oxygenate Contamination in Drinking-water Wells  
– A Guide for Water Retailers and Well Owners.***

***Originator:*** Crowley

***Problem Description:***

Well owners and water retailers are generally unaware that their actions can exacerbate conditions for the migration of oxygenates associated with nearby gasoline (fuel) storage facilities. Educational materials must be developed to inform well owners of the significance of their actions in contributing to the threat of contamination by oxygenates in their wells.

***Importance:***

- Prevent exposure to public.
- Coordinate the actions to reduce impacts to receptors.

***How do you propose attacking this research need?***

- Guidance materials – Educational/public outreach.
- NGWA, GRA.

## **Identify Scientists, Engineers, Regulators, and Politicians Who Developed, Advocated, and Adopted MTBE and Determine Why They Did Not Foresee Present Problems**

### **ORIGINATOR:**

Gaither

### ***Problem Description:***

Efforts to solve environmental problems often result in creating serious unforeseen consequences. Complex chemical solutions to environmental problems will increasingly cause serious unforeseen consequences.

### ***Importance:***

Implementation of complex chemical solutions to environmental problems can result in more costly rectification measures than the cost of ignoring (or deferring) corrective measures.

### ***How do you propose attacking this research need?***

- Employ an analysis team comprising of forensic scientists, engineers, political scientists, and risk analysts to review the introduction on MTBE.
- Prepare a case study and make recommendations to avoid similar future unforeseen consequences.



## STRENGTH OF FEELING ANALYSIS

The following tables provide a quantitative sense of the degree of agreement or lack of agreement between the workshop participants regarding the importance of each identified and prioritized research need. Table 1 depicts how all 22 workshop participants ranked the 29 research needs that they proposed, and on which they voted. Part 2 of this report lists the complete set of 113 research needs presented by the participants during the NGT workshop. All 113 research-need write-ups either stood alone or were consolidated under one of the 29 major research areas that were ranked by the participants.

The five subsequent tables (2 through 6) illustrate how each of five subgroups of participants ranked the 29 priority research needs. Subgroups membership represented university researchers, consulting practitioners, regulators, water utilities, and the petroleum industry.

Each table lists in descending order the priority ranking of the 29 major research needs. Participants voted independently for their 10 highest priority research needs. In addition to the title of each research need, the tables include the number of times a need was selected, the total number of points it received, and the strength of the group's feeling expressed as a percentage. For example, if all 22 participants had voted for the same research need as their highest priority, it would have received  $22 \times 10 = 220$  points and its Strength of Feeling would have been 100 percent. In fact, 18 of the 22 participants selected research need No. 113 as one of their priority research needs (not necessarily their highest priority) and gave it a total of 112 votes. Thus, the Strength of Feeling of 50.9 percent was calculated as  $112/220 \times 100 = 50.9$ . Two of the research needs (28 and 29) received no priority ranking votes; therefore, their Strength of Feeling is shown as zero.

The importance of subgroup rankings can be seen by observing that the entire group of 22 participants had relatively weak agreement (50.9 percent) on the highest-priority research need shown in Table 1. This top ranking was influenced by the relatively high priority assigned it by two subgroups: the academic researchers, whose 80.0 percent ranking is shown in Table 2, and the regulatory participants, whose 75 percent ranking is shown in Table 5. Interestingly, the regulatory participants were in near-unanimous agreement (95.0 percent) on their highest priority research need, which was ranked only sixth (35.0 percent) by water utility participants (see Table 6), fifth (43.3 percent) by petroleum industry participants (see Table 4), and fifth (37.5 percent) by consulting practitioners (see Table 3).

It is important to note that these substantially different perceptions of the most important research need may influence what topics are funded in the future.

**TABLE 1**

Research Needs (29) Ranked by All Participants (22)

<b>Rank</b>	<b>Title</b>	<b>Times Picked/Pts.</b>	<b>Strength of Feeling</b>
1.	Optimize Emerging Technologies for Water Treatment of Oxygenates and Their Degradation Products	18/112	50.9%
2.	Conduct Laboratory and Field Tests of Enhanced <i>In Situ</i> Anaerobic and Aerobic Bioremediation of Oxygenates	17/111	50.5%
3.	Optimize Integrated Water-treatment Systems for Oxygenates and Degradation Products	16/102	46.4%
4.	Evaluate Various Reactive Barrier Designs for Enhanced <i>In Situ</i> Treatment of MTBE and Other Oxygenates	16/96	43.6%
5.	Develop a Comprehensive Understanding of MTBE and Oxygenate Fate and Transport Based on Accurate Data	15/76	34.5%
6.	Develop Effective Subsurface Monitoring Systems and Improve UST Monitoring Equipment to Detect Liquid and Vapor Releases of Oxygenates at UST	11/71	32.3%
7.	Develop Analytical Methods for MTBE and Its Breakdown Products at Ppt/ppb Levels	12/67	30.5%
8.	Investigate Ethanol Data Gaps Prior to Increased Ethanol Use	12/60	27.3%
9.	Develop Protocol for Multimedia Review of New Compounds for Use in Fuels (How Can We Prevent Another MTBE Contamination Catastrophe?)	9/59	26.8%
10.	Determine Range of MTBE Concentration That Can Be Expected in Supply Wells That Capture MTBE Plumes Emanating From LUFTs. What Types of Supply Wells Are Most at Risk?	10/56	25.5%
11.	Evaluate Environmental Information Management Systems, Decision-making Processes, and Conduct a Critical Review of the Cost-effectiveness of the California UST Program and Existing Resource Protection Programs	11/53	24.1%
12.	Monitor Natural Attenuation for MTBE: Use Lessons Learned, Develop Innovative Assessment Tools, and Provide Guidance	8/49	22.3%
13.	Develop and Optimize Chemical/Physical <i>In Situ</i> Technologies to Enhance Source and Plume Cleanup	12/47	21.4%
14.	Evaluate Current Gasoline Containment Practices and Needs and Opportunities for Improvement and Development of Best Management Practices (BMPs) (UST & Marina Refueling)	8/42	19.1%

<b>Rank</b>	<b>Title</b>	<b>Times Picked/Pts.</b>	<b>Strength of Feeling</b>
15	Critical Review on the Potential Threat to Groundwater Contamination From Leaking Gasoline and Oil Pipes	6/30	13.6%
16.	Conduct Long-term Human Health Effects Study of MTBE/Oxygenate Exposure in Drinking Water	6/28	12.7%
17.	Design, Construct, and Operate a High-tech Service Station that Implements Proactive Detection, Monitoring, and Remediation Technologies to Prevent Groundwater Contamination	4/22	10.0%
18.	Quantify and Model Effect of Co-contaminants on the Biodegradation Rates of Ether Oxygenates in the Field	4/19	8.6%
19.	Develop Strategies to Control MTBE and Oxygenate Plume Migration	6/18	8.2%
20.	Examine Living-plant-based Remediation Systems Including Uptake Rates, Metabolism, and Evaluation of Prototype Treatment Systems	3/18	8.2%
21.	Develop Small, Low-cost, Packaged Point-of-Use and Point-of-Entry Treatment Systems	4/18	8.2%
22.	Assess Oxygenate Impacts on Small, Private Water-supply Wells in California	4/18	8.2%
23.	Review and Assess Needs When Use of Electric-powered Motors Are Used on Recreational Boats Exclusively on a Drinking-water Reservoir	2/12	5.5%
24.	Evaluate Ways to Reduce Gasoline and Water Consumption	1/10	4.5%
25.	Assess the Applicability of Market-share Liability to Pay for the Cleanup of Oxygenate Contamination of Aquifers and Wells	1/8	3.6%
26.	Conduct Cost-benefit Analysis of Treating Oxygenate Contamination in Drinking Water to Different Standards	3/7	3.2%
27.	Review MTBE Synthesizing Methods to Provide Insights for Developing MTBE Treatment Technologies	1/1	0.5%
28.	Conduct a Critical Review of California's Wellhead Protection Program	0/0	0.0%
29.	Identify Scientists, Engineers, Regulators, and Politicians Who Developed, Advocated, and Adopted MTBEs and Determine Why They Did Not Foresee Present Problems	0.0	0.0%

**TABLE 2**

## Research Needs (29) Ranked by Academic Participants (3)

Rank	Title	Times Picked/Pts.	Strength of Feeling
1.	Optimize Emerging Technologies for Water Treatment of Oxygenates and Their Degradation Products	3/24	80.0%
2.	Optimize Integrated Water-treatment Systems for Oxygenates and Degradation Products	3/19	63.3%
3.	Conduct Laboratory and Field Tests of Enhanced <i>In Situ</i> Anaerobic and Aerobic Bioremediation of Oxygenates	3/18	60.0%
4.	Develop Analytical Methods for MTBE and Its Breakdown Products at Ppt/ppb Levels	2/18	60.0%
5.	Conduct Long-term Human Health Effects Study of MTBE/Oxygenate Exposure in Drinking Water	3/15	50.0%
6.	Develop and Optimize Chemical/Physical <i>In Situ</i> Technologies to Enhance Source and Plume Cleanup	2/14	46.7%
7.	Evaluate Various Reactive Barrier Designs for Enhanced <i>In Situ</i> Treatment of MTBE and Other Oxygenates	2/10	33.3%
8.	Examine Living-plant-based Remediation Systems Including Uptake Rates, Metabolism, and Evaluation of Prototype Treatment Systems	1/9	30.0%
9.	Conduct Critical Review of Potential Threat to Groundwater Contamination From Leaking Gasoline and Oil Pipelines	1/7	23.3%
10.	Monitor Natural Attenuation for MTBE: Use Lessons Learned, Develop Innovative Assessment Tools, and Provide Guidance	1/6	20.0%
11.	Design, Construct, and Operate a High-tech Service Station That Implements Proactive Detection, Monitoring, and Remediation Technologies to Prevent Groundwater Contamination	1/6	20.0%
12.	Evaluate Environmental Information Management Systems, Decision-making Processes, and Conduct a Critical Review of the Cost-effectiveness of the California UST Program and Existing Resource Protection Programs	2/5	16.7%
13.	Investigate Ethanol Data Gaps Prior to Increased Ethanol Use	1/3	10.0%
14.	Conduct Cost-benefit Analysis of Treating Oxygenate Contamination in Drinking Water to Different Standards	1/3	10.0%
15.	Develop a Comprehensive Understanding of MTBE and Oxygenate Fate and Transport Based on Accurate Data	1/3	10.0%

<b>Rank</b>	<b>Title</b>	<b>Times Picked/Pts.</b>	<b>Strength of Feeling</b>
16.	Determine Range of MTBE Concentration That Can Be Expected in Supply Wells That Capture MTBE Plumes Emanating From LUFTs? What Types of Supply Wells Are Most at Risk?	1/2	6.7%
17.	Develop Small, Low-cost, Packaged Point-of-Use and Point-of-Entry Treatment Systems	1/2	6.7%
18.	Review MTBE Synthesizing Methods to Provide Insights for Developing MTBE Treatment Technologies	1/1	3.3%

**TABLE 3**

Research Needs (29) Ranked by Consultant Participants (8)

<b>Rank</b>	<b>Title</b>	<b>Times Picked/Pts.</b>	<b>Strength of Feeling</b>
1.	Conduct Laboratory and Field Tests of Enhanced <i>In Situ</i> Anaerobic and Aerobic Bioremediation of Oxygenates	7/54	67.5%
2.	Evaluate Various Reactive Barrier Designs for Enhanced <i>In Situ</i> Treatment of MTBE and Other Oxygenates	6/38	47.5%
3.	Develop Effective Subsurface Monitoring Systems and Improve UST Monitoring Equipment to Detect Liquid and Vapor Releases of Oxygenates at UST	6/34	42.5%
4.	Optimize Emerging Technologies for Water Treatment of Oxygenates and Their Degradation Products	5/34	42.5%
5.	Optimize Integrated Water-treatment Systems for Oxygenates and Degradation Products	6/30	37.5%
6.	Investigate Ethanol Data Gaps Prior to Increased Ethanol Use	5/29	36.3%
7.	Monitor Natural Attenuation for MTBE: Use Lessons Learned, Develop Innovative Assessment Tools, and Provide Guidance	4/24	30.0%
8.	Determine Range of MTBE Concentration That Can Be Expected in Supply Wells That Capture MTBE Plumes Emanating From LUFTs. What Types of Supply Wells Are Most at Risk?	4/23	28.8%
9.	Develop Protocol for Multimedia Review of New Compounds for Use in Fuels (How Can We Prevent Another MTBE Contamination Catastrophe?)	3/22	27.5%
10.	Develop a Comprehensive Understanding of MTBE and Oxygenate Fate and Transport Based on Accurate Data	4/19	23.8%
11.	Evaluate Environmental Information Management Systems, Decision-making Processes, and Conduct a Critical Review of the Cost-effectiveness of the California UST Program and Existing Resource Protection Programs	4/17	21.3%
12.	Develop Analytical Methods for MTBE and Its Breakdown Products at Ppt/ppb Levels	5/15	18.8%
13.	Quantify and Model Effect of Co-contaminants on the Biodegradation Rates of Ether Oxygenates in the Field	2/14	17.5%
14.	Conduct Critical Review of Potential Threat to Groundwater Contamination From Leaking Gasoline and Oil Pipelines	3/13	16.3%

<b>Rank</b>	<b>Title</b>	<b>Times Picked/Pts.</b>	<b>Strength of Feeling</b>
15.	Evaluate Current Gasoline Containment Practices and Needs and Opportunities for Improvement and Development of Best Management Practices (BMPs) (UST & Marina Refueling)	2/12	15.0%
16.	Assess Oxygenate Impacts on Small, Private Water-supply Wells in California	2/11	13.8%
17.	Evaluate Ways to Reduce Gasoline and Water Consumption	1/10	12.5%
18.	Examine Living-plant-based Remediation Systems Including Uptake Rates, Metabolism, and Evaluation of Prototype Treatment Systems	2/9	11.3%
19.	Assess the Applicability of Market-share Liability to Pay for the Cleanup of Oxygenate Contamination of Aquifers and Wells	1/8	10.0%
20.	Design, Construct, and Operate a High-tech Service Station That Implements Proactive Detection, Monitoring, and Remediation Technologies to Prevent Groundwater Contamination	2/8	10.0%
21.	Develop and Optimize Chemical/Physical <i>In Situ</i> Technologies to Enhance Source and Plume Cleanup	3/7	8.8%
22.	Develop Small, Low-cost, Packaged Point-of-Use and Point-of-Entry Treatment Systems	1/6	7.5%
23.	Conduct Cost-benefit Analysis of Treating Oxygenate Contamination in Drinking Water to Different Standards	1/2	2.5%
24.	Develop Strategies to Control MTBE and Oxygenate Plume Migration	1/1	1.3%

**TABLE 4**

Research Needs (29) Ranked by Petroleum Participants (3)

<b>Rank</b>	<b>Title</b>	<b>Times Picked/Pts.</b>	<b>Strength of Feeling</b>
1.	Evaluate Various Reactive Barrier Designs for Enhanced <i>In Situ</i> Treatment of MTBE and Other Oxygenates	3/18	60.0%
2.	Investigate Ethanol Data Gaps Prior to Increased Ethanol Use	3/17	56.7%
3.	Develop Effective Subsurface Monitoring Systems and Improve UST Monitoring Equipment to Detect Liquid and Vapor Releases of Oxygenates at UST	2/16	53.3%
4.	Optimize Emerging Technologies for Water Treatment of Oxygenates and Their Degradation Products	3/16	53.3%
5.	Optimize Integrated Water-treatment Systems for Oxygenates and Degradation Products	2/13	43.3%
6.	Develop a Comprehensive Understanding of MTBE and Oxygenate Fate and Transport Based on Accurate Data	3/13	43.3%
7.	Evaluate Current Gasoline Containment Practices and Needs and Opportunities for Improvement and Development of Best Management Practices (BMPs) (UST & Marina Refueling)	2/12	40.0%
8.	Conduct Laboratory and Field Tests of Enhanced <i>In Situ</i> Anaerobic and Aerobic Bioremediation of Oxygenates	2/11	36.7%
9.	Evaluate Environmental Information Management Systems, Decision-making Processes, and Conduct a Critical Review of the Cost-effectiveness of the California UST Program and Existing Resource Protection Programs	1/10	33.3%
10.	Determine Range of MTBE Concentration That Can Be Expected in Supply Wells That Capture MTBE Plumes Emanating From LUFTs. What Types of Supply Wells Are Most at Risk?	1/8	26.7%
11.	Monitor Natural Attenuation for MTBE: Use Lessons Learned, Develop Innovative Assessment Tools, and Provide Guidance	1/8	26.7%
12.	Design, Construct, and Operate a High-tech Service Station That Implements Proactive Detection, Monitoring, and Remediation Technologies to Prevent Groundwater Contamination	1/8	26.7%
13.	Develop and Optimize Chemical/Physical <i>In Situ</i> Technologies to Enhance Source and Plume Cleanup	2/7	23.3%
14.	Develop Strategies to Control MTBE and Oxygenate Plume Migration	2/5	16.7%

<b>Rank</b>	<b>Title</b>	<b>Times Picked/Pts.</b>	<b>Strength of Feeling</b>
15.	Conduct Cost-benefit Analysis of Treating Oxygenate Contamination in Drinking Water to Different Standards	1/2	16.7%
16.	Develop Protocol for Multimedia Review of New Compounds for Use in Fuels (How Can We Prevent Another MTBE Contamination Catastrophe?)	1/1	3.3%



**TABLE 5**

Research Needs (29) Ranked by Regulatory Participants (2)

<b>Rank</b>	<b>Title</b>	<b>Times Picked/Pts.</b>	<b>Strength of Feeling</b>
1.	Optimize Integrated Water-treatment Systems for Oxygenates and Degradation Products	2/19	95.0%
2.	Optimize Emerging Technologies for Water Treatment of Oxygenates and Their Degradation Products	2/15	75.0%
3.	Develop Analytical Methods for MTBE and Its Breakdown Products at Ppt/ppb Levels	2/14	70.0%
4.	Determine Range of MTBE Concentration That Can Be Expected in Supply Wells That Capture MTBE Plumes Emanating From LUFTs. What Types of Supply Wells Are Most at Risk?	2/11	55.0%
5.	Develop Protocol for Multimedia Review of New Compounds for Use in Fuels (How Can We Prevent Another MTBE Contamination Catastrophe?)	1/10	50.0%
6.	Investigate Ethanol Data Gaps Prior to Increased Ethanol Use	2/9	45.0%
7.	Evaluate Various Reactive Barrier Designs for Enhanced <i>In Situ</i> Treatment of MTBE and Other Oxygenates	1/7	35.0%
8.	Review and Assess Needs When Use of Electric-powered Motors Are Used on Recreational Boats Exclusively on a Drinking-water Reservoir	1/6	30.0%
9.	Develop and Optimize Chemical/Physical <i>In Situ</i> Technologies to Enhance Source and Plume Cleanup	1/5	25.0%
10.	Conduct Laboratory and Field Tests of Enhanced <i>In Situ</i> Anaerobic and Aerobic Bioremediation of Oxygenates	1/4	20.0%
11.	Evaluate Current Gasoline Containment Practices and Needs and Opportunities for Improvement and Development of Best Management Practices (BMPs) (UST & Marina Refueling)	1/4	20.0%
12.	Quantify and Model Effect of Co-contaminants on the Biodegradation Rates of Ether Oxygenates in the Field	1/2	10.0%
13.	Develop Small, Low-cost, Packaged Point-of-Use and Point-of-Entry Treatment Systems	1/2	10.0%
14.	Conduct Critical Review of Potential Threat to Groundwater Contamination From Leaking Gasoline and Oil Pipelines	1/1	5.0%
15.	Develop a Comprehensive Understanding of MTBE and Oxygenate Fate and Transport Based on Accurate Data	1/1	5.0%

**TABLE 6**

Research Needs (29) Ranked by Utility Participants (6)

<b>Rank</b>	<b>Title</b>	<b>Times Picked/Pts.</b>	<b>Strength of Feeling</b>
1.	Develop a Comprehensive Understanding of MTBE and Oxygenate Fate and Transport Based on Accurate Data	6/40	66.7%
2.	Conduct Laboratory and Field Tests of Enhanced <i>In Situ</i> Anaerobic and Aerobic Bioremediation of Oxygenates	4/24	40.0%
3.	Develop Protocol for Multimedia Review of New Compounds for Use in Fuels (How Can We Prevent Another MTBE Contamination Catastrophe?)	3/24	40.0%
4.	Evaluate Various Reactive Barrier Designs for Enhanced <i>In Situ</i> Treatment of MTBE and Other Oxygenates	4/23	38.3%
5.	Optimize Emerging Technologies for Water Treatment of Oxygenates and Their Degradation Products	5/23	38.3%
6.	Optimize Integrated Water-treatment Systems for Oxygenates and Degradation Products	3/21	35.0%
7.	Evaluate Environmental Information Management Systems, Decision-making Processes, and Conduct a Critical Review of the Cost-effectiveness of the California UST Program and Existing Resource Protection Programs	4/21	35.0%
8.	Develop Effective Subsurface Monitoring Systems and Improve UST Monitoring Equipment to Detect Liquid and Vapor Releases of Oxygenates at UST	3/21	35.0%
9.	Develop Analytical Methods for MTBE and Its Breakdown Products at Ppt/ppb Levels	3/20	33.3%
10.	Develop and Optimize Chemical/Physical <i>In Situ</i> Technologies to Enhance Source and Plume Cleanup	4/14	23.3%
11.	Determine Range of MTBE Concentration That Can Be Expected in Supply Wells That Capture MTBE Plumes Emanating From LUFTs. What Types of Supply Wells Are Most at Risk?	3/14	23.3%
12.	Evaluate Current Gasoline Containment Practices and Needs and Opportunities for Improvement and Development of Best Management Practices (BMPs) (UST & Marina Refueling)	3/14	23.3%
13.	Conduct Long-term Human Health Effects Study of MTBE/Oxygenate Exposure in Drinking Water	3/13	21.7%
14.	Develop Strategies to Control MTBE and Oxygenate Plume Migration	3/12	20.0%

<b>Rank</b>	<b>Title</b>	<b>Times Picked/Pts.</b>	<b>Strength of Feeling</b>
15.	Monitor Natural Attenuation for MTBE: Use Lessons Learned, Develop Innovative Assessment Tools, and Provide Guidance	2/11	18.3%
16.	Conduct Critical Review of Potential Threat to Groundwater Contamination From Leaking Gasoline and Oil Pipelines	1/9	15.0%
17.	Develop Small, Low-cost, Packaged Point-of-Use and Point-of-Entry Treatment Systems	1/8	13.3%
18.	Assess Oxygenate Impacts on Small, Private-supply Water Wells in California	2/7	11.7%
19.	Review and Assess Needs When Use of Electric-powered Motors Are Used on Recreational Boats Exclusively on a Drinking Water Reservoir	1/6	10.0%
20.	Quantify and Model Effect of Co-contaminants on the Biodegradation Rates of Ether Oxygenates in the Field	1/3	5.0%
21.	Investigate Ethanol Data Gaps Prior to Increased Ethanol Use	1/2	3.3%



## APPENDICES



## APPENDIX A

### ACRONYMS

ADR	alternative dispute resolution
AOP	advanced oxidation process
API	American Petroleum Institute
AWWARF	American Water Works Association Research Foundation
BA	branched alcohols
BTEX	benzene, toluene, ethylbenzene, xylene ( <i>o</i> -, <i>m</i> -, <i>p</i> -xylene)
CUPA	Certified Unified Program Agency
CVOC	chlorinated volatile organic compounds
DHS	(California) Department of Health Services
DIPE	diisopropyl ether
DOD	United States Department of Defense
EDB	ethylene dibromide
EDC	ethylene dichloride
EIMS	Environmental Information Management System
ETBE	ethyl tertiary butyl ether
F&T	fate and transport
Fe <sup>+3</sup>	ferric iron
GAC	granular activated carbon
GC/MS	gas chromatography/mass spectrometry
GRA	Groundwater Resource Association
GRH	gasoline range hydrocarbon
H <sub>2</sub> O <sub>2</sub>	hydrogen peroxide
HRT	hydraulic residence time
LNAPL	light non-aqueous phase liquid
LUFT	leaking underground fuel tank

## ACRONYMS (continued)

LUST	leaking underground storage tank
MADMAC	Multi-agency Data Management Advisory Committee
MCL	maximum contaminant level
MDL	method detection limit
MNA	monitored natural attenuation
MTBE	methyl tertiary butyl ether
NAPL	non-aqueous phase liquid
NDMA	<i>N</i> -nitroso dimethyl amine
NF	nanofiltration
NGT	Nominal Group Techniques
NGWA	National Groundwater Association
nm	nanometer
NOM	natural organic matter
NWRI	National Water Research Institute
O <sub>3</sub>	ozone
O&M	operation and maintenance
OGI	Oregon Graduate Institute
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
PRB	permeable reactive barriers
QSAR	Query on Structure Activity Relationships
R&D	research and development
RFP	Request for Proposals
RO	reverse osmosis
SOC	synthetic organic compound
SCVWD	Santa Clara Valley Water District
SPME	solid-phase microextraction
SVE	soil vapor extraction

ACRONYMS (continued)

SWAP Source Water Assessment Program  
SWRCB State Water Resources Control Board

TAC Technical Advisory Committee  
TAME tertiary amyl methyl ether  
TBA tertiary-butyl alcohol  
TBF tertiary-butyl formate

USEPA Environmental Protection Agency  
USGS United States Geological Survey  
UST underground storage tank  
UV ultraviolet

VOC volatile organic compounds

WEF Water Environment Federation  
WSPA Western States Petroleum Association



## APPENDIX B

### PREVIOUS NGT WORKSHOPS CONDUCTED BY NWRI

*Utility Leadership.* Report of a workshop sponsored by NWRI in cooperation with Malcolm Pirnie, Inc., the University of Southern California, and the University of South Florida. Kellogg West Conference Center/Hotel, California State Polytechnic University, Pomona, CA, October 24-26, 1999: 154p

*Non-potable Water Recycling.* Report of a workshop sponsored by NWRI in cooperation with Irvine Ranch Water District and the Orange County Water District. Kellogg West Conference Center/Hotel, California State Polytechnic University, Pomona, CA, May 23-25, 1999: 174p.

*Conjunctive Use Water Management Program.* Report of a workshop jointly sponsored by NWRI, Association of Ground Water Agencies, and the Metropolitan Water District of Southern California. Kellogg West Conference Center/Hotel, California State Polytechnic University, Pomona, CA, May 27-29, 1998: 157p.

*Barriers to Providing Safe Drinking Water Through Small Systems.* Report of a workshop jointly sponsored by NWRI, Pan American Health Organization, and NSF International/WHO Collaborative Center. Pan American Health Organization Headquarters, Washington, D.C., May 13-15, 1998: English report: 175p., Spanish report: 188p. (Bound in a single volume.)

*Barriers to Harvesting Stormwater.* Report of a workshop jointly sponsored by NWRI, Los Angeles County Department of Public Works, County of Orange Public Facilities & Resources Department, Southern California Coastal Water Project, and the American Oceans Campaign. Kellogg West Conference Center/Hotel, California State Polytechnic University, Pomona, CA, September 22-24, 1997: 159p.

*Groundwater Disinfection Regulations Benefits Conference.* Report of a conference sponsored by NWRI. Arnold and Mabel Beckman Center, National Academies of Sciences and Engineering, Irvine, CA, March 17, 1997: 75p.

*Groundwater Disinfection Regulation.* Report of a workshop jointly sponsored by NWRI and the USEPA. Arnold and Mabel Beckman Center, National Academies of Sciences and Engineering, Irvine, CA, January 6-8, 1997: 209p.

*Membrane Biofouling.* Report of a workshop jointly sponsored by NWRI, UNESCO Centre for Membrane Science and Technology, and CRC for Waste Management and Pollution Control, LTD. UNSW Institute of Administration, Sydney, Australia, November 15-17, 1996: 176p.

*The Santa Ana River Watershed.* Report of a workshop jointly sponsored NWRI and the Santa Ana Watershed Project Authority. Co-sponsors included: City of San Bernardino Water Department, City of Riverside, Western Municipal Water District, and Orange County Water

District. Kellogg West Conference Center/Hotel, California State Polytechnic University, Pomona, CA, August 23-25, 1995: 182p.

*The New River.* Report of a workshop jointly sponsored by NWRI and the County of Imperial, California. Barbara Worth Country Club, Holtville, CA, May 19-21, 1995: English report: 134p., Spanish report: 134p. (Bound in a single volume)

*Establishment of The Middle-East Water and Energy Research and Technology Centre.* Report of a workshop jointly sponsored by NWRI and the Sultanate of Oman through the Worldwide Desalination Research and Technology Survey. Muscat, Oman: September 21, 1994: 29p

*Risk Reduction in Drinking Water Distribution Systems.* Report of a workshop jointly sponsored by NWRI and the Environmental Criteria and Assessment Office of the USEPA. Arnold and Mabel Beckman Center, National Academies of Sciences and Engineering, Irvine, CA, February 27-28, 1994: 142p.

*Fouling and Module Design.* Report of a workshop jointly sponsored by NWRI and the National Science Foundation (NSF). Virden Conference Center of the University of Delaware, Lewes, DE, October 30 – November 1, 1993: 115p.

*Groundwater Disinfection Rule.* Report of a workshop jointly sponsored by NWRI and the USEPA in collaboration with the Weston Institute. Virden Conference Center of the University of Delaware, Lewes, DE. June 7-8, 1992: 103p.

## APPENDIX C

### NGT PARTICIPANT BIOGRAPHICAL SKETCHES

#### **Anthony Brown**

*President and Principal Hydrologist, Komex H<sub>2</sub>O Science, Inc.*

*Director, USA and Latin America for Komex Environmental Limited*

Tony Brown has conducted numerous remedial investigations/site characterization studies for sites contaminated with organic and inorganic chemicals and has extensive experience in the design and implementation of remediation programs. He is a recognized expert in the fate, transport, and remediation of MTBE and the protection of source waters from MTBE contamination, and was co-author of *Treatment Technologies for the Removal of MTBE from Drinking Water* (California MTBE Research Partnership, 1999). He currently teaches at the University of California, Irvine and is a visiting lecturer at Imperial College in London, England. Brown received a B.A. in Physical Geography from King's College at the University of London, a M.Sc. in Engineering Hydrology from Imperial College of Science, Technology, and Medicine at the University of London, and a D.I.C. Postgraduate Diploma in Civil Engineering from Imperial College.

#### **Clinton D. Church, Ph.D.**

*Microbiologist, Water Resources Division*

*United States Geological Survey*

Clint Church joined the U.S. Geological Survey in September 2000 to research the existence and effects of microbial contamination in the Santa Ana River, California, during storm events. For the past 5 years, he conducted research on the environmental fate of MTBE as a research assistant at the Oregon Graduate Institute. Among his research, he developed a GC/MS analytical technique for simultaneous measurement of MTBE and the products of its degradation at the sub ppb level. He is also the author/co-author of 18 publications on MTBE. Church received both a B.A. in Secondary Education and B.S. in Geology from the University of Montana and a Ph.D. in Environmental Science and Engineering from Oregon Graduate Institute.

#### **James S. Crowley, P.E.**

*Engineering Unit Manager for the Leaking Underground Storage Tank Local Oversight Program, Santa Clara Valley Water District*

Jim Crowley has 15 years of experience in civil and environmental engineering. He leads a team of technical professionals who provide regulatory oversight for the 2,250 fuel leak cases reported within Santa Clara County. Currently, his work focuses on assessing the threat posed by fuel oxygenates to the water resources of Santa Clara County. He has been actively involved in promoting changes to ensure the protection of water supplies from contamination and in

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Jim Davidson has extensive experience investigating and remediating petroleum releases and has been involved with more than 400 contamination projects across the United States and internationally since 1984. He is a nationally recognized expert on the subsurface occurrence, movement, and remediation of MTBE and has authored/co-authored 15 publications on a variety of MTBE/fuel oxygenate issues, including *Treatment Technologies for the Removal of MTBE from Drinking Water* (California MTBE Research Partnership, 1999). He has also taught MTBE training sessions on more than 50 occasions for a variety of regulatory agencies and professional organizations. In addition, Davidson is a member of an elite U.S. Navy science panel addressing complex MTBE problems. He received a B.S. degree in Geology from the University of Massachusetts and a M.S. in Hydrogeology from Colorado State University.

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Rula Deeb has over 10 years experience with environmentally related water issues. Over the last 8 years, she has developed and implemented research projects on the use of *in situ* bioremediation at sites impacted by contaminant mixtures, including gasoline aromatics and fuel oxygenates. She has developed educational programs on global environmental issues for the United Nations and has taught at Stanford University. Deeb received B.A. degrees in Mathematics, Chemistry, and Computer Science from Warren Wilson College in North Carolina, and both her M.S. and Ph.D. in Civil/Environmental Engineering from the University of California, Berkeley.

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Murray Einarson has over 16 years of experience as an environmental consultant. He participated in the University of Waterloo MTBE research project at Vandenberg Air Force Base in California, and is now developing a low-cost funnel-and-gate system for enhanced bioremediation of MTBE plumes at gasoline service stations. Among his publications, he co-authored *Expedited Site Assessment Tools for Underground Storage Tanks Sites* (U.S. EPA, 1997) and *Strategies for Characterizing Subsurface Releases of Gasoline Containing MTBE* (American Petroleum Institute [API], 2000). In addition, he is an instructor at the University of Waterloo field school and will teach an upcoming API course on characterizing sites with dissolved MTBE plumes. Einarson received a B.A. in Geology from the University of California, Santa Barbara and an M.Sc. in Hydrogeology from the University of Waterloo.

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Mike Kavanaugh is a chemical and environmental engineer who has provided a broad range of environmental services to private and public sector clients for over 25 years. His expertise lies in hazardous waste management, soil and groundwater remediation, process engineering, industrial waste treatment, water reuse, and water quality, among many others. He has authored/co-authored over 40 technical papers, including *Treatment Technologies for the Removal of MTBE from Drinking Water* (California MTBE Research Partnership, 1999). In addition, Kavanaugh is a Diplomat of Environmental Engineering (DEE) of the American Academy of Environmental Engineers and a consulting professor of Environmental Engineering at Stanford University. He was also elected to the National Academy of Engineering (NAE) in 1998. He received a B.S. and M.S. in Chemical Engineering from Stanford University and the University of California at Berkeley, respectfully, and a Ph.D. in Civil/Environmental Engineering from Berkeley.

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Sun Liang manages the Water Quality Section at the Metropolitan Water District. He has been the project manager and co-principal investigator of several MTBE studies, including a study funded by the American Water Works Association Research Foundation (AWWARF) for removing MTBE by advanced oxidation processes. He has authored over 45 publications (including a half a dozen on MTBE) and also co-authored *Treatment Technologies for the Removal of MTBE from Drinking Water* (California MTBE Research Partnership, 1999). Liang received a B.A. in Agricultural Engineering from National Taiwan University, a M.S. in Civil/Sanitary Engineering from the University of California, Berkeley, and a Ph.D. in Civil/Environmental Engineering from the University of Michigan, Ann Arbor.

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Sam Lien has spent the past year at Lehigh University in Pennsylvania as a Postdoctoral Research Associate, where he designed and implemented the nanoscale iron technology for successful in situ groundwater remediation. He will join the U.S. EPA's National Risk Management Research Laboratories in October 2000 to develop technologies for the treatment of MTBE. He has also written papers and presented on analyzing, measuring, and treating contaminants such as MTBE. Lien received a B.S. in Environmental Science from Tunghai University in Taiwan, a M.S. in Environmental Engineering from National Taiwan University, and a Ph.D. in Environmental Engineering (with a background in Environmental Chemistry) from Lehigh University.

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Ellen Moyer is a program manager in ENSR's Remediation Services Department, specializing in *in situ* and biological treatment. She has researched UST regulations and best management practices to prevent gasoline releases to the environment and has conducted/ presented numerous seminars on MTBE remediation. In addition, she managed an oxygenate project to interface with top environmental regulators in the eight northeastern states to discuss air and water issues relative to MTBE. Moyer received a B.A. in Anthropology from the University of Massachusetts, Boston and both a M.S. and Ph.D. (in Environmental Engineering and Civil Engineering, respectively) from the University of Massachusetts.

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With a background in pathology and biochemistry, Lee Newman has worked with phytoremediation in a variety of trees and wetland plants for the past 7 years. Her work includes the genetic engineering of plants for increased tolerance to heavy metal stress as well as the uptake and degradation of chlorinated solvents, chlorinated aromatics, fuel additives (including MTBE), and pesticides. Newman received an A.A. in Chemistry from Atlantic Community College in New Jersey, a B.S. in Biology (minor in Chemistry) from Stockton College in New Jersey, a M.S. in Microbiology from Rutgers University and Robert Wood Johnson Medical School, and a Ph.D. in Microbiology and Molecular Genetics from Rutgers/Robert Wood.

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With a broad background in wastewater issues (both process and regulatory), Dave Pierce serves with a team of highly experienced water- and waste-process engineers at Chevron. He has dealt with issues for refining, chemical, marketing, shipping, exploration, and production for both Chevron and foreign affiliates. Since joining Chevron in 1972, Pierce has had a broad spectrum of assignments in environmental, refining, and chemical plant processes. He is an active member of the American Petroleum Institute's (API) Water Program Group and is Chair of API's Clean Water Issues Task Force. He is also a member of the Research Advisory Committee for the California MTBE Research Partnership. He received both B.S. and M.S. degrees in Chemical Engineering from Cornell University.

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Rey Rodriguez has over 16 years of civil engineering experience in the public and private sector, specializing in water resources. He has overseen the MTBE groundwater contamination investigation and implementation of the treatment system at Santa Monica's contaminated well fields since the 1996 discovery of MTBE contamination in Santa Monica, CA. He is also Subcommittee Chair of the Source Water Protection Committee for the California MTBE Research Partnership (Partnership), which he helped co-found in 1997. In addition, he has co-authored and presented numerous papers on MTBE, including *Treatment Technologies for the Removal of MTBE from Drinking Water* (Partnership, 1999). Rodriguez received a B.S. degree in Civil Engineering from California State Polytechnic University at Pomona.

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During his 29-year career with Shell/Equilon, Joe Salanitro has been involved in animal health research and in the chemical and oil sectors of environmental technology, including the aerobic and anaerobic biodegradability testing of surfactants, solvents, pesticides, and petrochemical waste effluents and the role of microbes in sour gas formation in oilfield waterfloods. His current interests are biodegradation testing in environmental media, including the biodegradation and bioremediation of fuel oxygenates. He is also the author/co-author of over 35 publications and is the associate editor of *Bioremediation J.* Salanitro earned both B.S. and M.S. degrees in Chemistry and Biology, respectively, from St. John's University in New York and a Ph.D. in Microbiology from Indiana University.

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Mel Suffet has taught Environmental Chemistry at UCLA since 1991. He specializes in aquatic chemistry, hazardous and off-flavor chemicals, drinking water treatment, stormwater runoff, water reclamation, and estuary and sediment chemistry. He has edited six books and has authored more than 90 journal articles. Among his current research, Suffet is investigating the treatment of MTBE by activated carbon water for the California MTBE Research Partnership. He received a B.S. in Chemistry from Brooklyn College, a M.S. in Chemistry from the University of Maryland, and a Ph.D. in Environmental Science from Rutgers University.

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Scott Tenney manages Continuous Improvement Programs for ExxonMobil Corp. at the Torrance, California refinery. This work emphasizes strategic planning to optimize the performance of multi-media environmental compliance programs and provide guidance for resource allocation decisions. Prior to this role, he directed groundwater restoration activities for Mobil Oil Corporation at one of the largest groundwater remediation programs in California. He is the Chair of the Treatability Subcommittee for the California MTBE Research Partnership and is currently active in ongoing discussions between industry and the regulatory community regarding water quality planning issues, including total maximum daily loading (TMDL) issues. Tenney received B.S. degrees in Geology and Geophysics from the University of Wisconsin and was formally trained as a surface water and groundwater hydrologist.

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With over 25 years of experience in chemistry, Maria Tikkanen has authored over 60 publications and is a member of various organizations, such as the American Chemical Society, Society for Applied Spectroscopy, and American Water Works Association. She also Chairs the Environmental Chemistry Symposium, Rocky Mountain Conference. Tikkanen manages the MTBE Reservoir Monitoring and Management Program at the East Bay Municipal Utility District. In addition, she was Chair of the Vessel Emissions Work Group of the Advisory Panel to the State Water Resource Control Board's *Report on the Fueling and Refueling Practice at California Marinas*. Tikkanen received her B.S., M.S., and Ph.D. in Chemistry from the University of New Mexico.

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For 12 years, Chris Tulloch has overseen the investigation and cleanup of several hundred LUST sites as well as developed administrative and technical guidance and reviewed and analyzed regulatory and legislative changes. Her responsibilities include providing regulatory oversight for LUST sites and developing groundwater protection strategies. Tulloch has assisted with the District's MTBE strategy, participated in the Governor's Advisory Panel on Releases from Upgraded Fuel Systems, co-managed the District's pilot study of operating USTs and MTBE occurrence, and performed a detailed study of MTBE occurrence and release scenarios at fuel leak sites with operating USTs. She received a B.S. in Environmental Studies from San Jose State University.

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Dick Woodward has over 26 years experience as a senior scientist as consulting microbiologist managing microbial systems in soils, sludge, and aquifers contaminated with hazardous waste. He has completed hazardous waste bioremediation projects for over 30 industrial clients throughout the United States, treating wastes such as mixed petroleum hydrocarbons, crude oil, BTEX, and chlorinated solvents. Currently, he teaches a class in Hazardous Solid Waste Management at the University of Texas School of Public Health. Woodward received a B.S. in Secondary Education/Biology from Millersville State University and a M.A. in Botany/Plant Physiology from the University of South Florida. Additional graduate work includes soil microbiology and plant pathology at Pennsylvania State University.

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