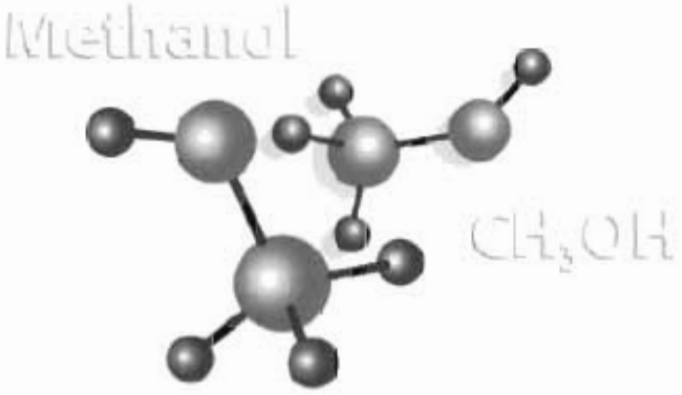

Issues in Methanol Research

Workshop Report

Presented by:
National Water Research Institute

in cooperation with:
American Methanol Institute

October 5-7, 2001

The Hilton Costa Mesa
Costa Mesa, California

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FOREWORD

The use of oxygenates in gasoline was introduced in the 1980s for the purpose of enhancing octane and improving air quality throughout the United States and Europe. Paradoxically, the oxygenate methyl tertiary butyl ether (MTBE) was identified in the 1990s as a contaminant of surface water and groundwater supplies. As a consequence, significant efforts were employed in the late 1990s to address research issues associated with MTBE and its environmental impacts.

Also in the late 1990s, the California MTBE Research Partnership was created by the Association of California Water Agencies, Western States Petroleum Association, and the Oxygenates Fuel Association and managed by the National Water Research Institute (NWRI) to address the issues of MTBE contamination of surface water and groundwater. The results of the program have been the publication of a body of knowledge in the form of a series of 7 reports dealing with treatment technology, economics, and detection methodologies.

Inasmuch as MTBE is being phased-out in California and other states, concerns are being voiced by public and private sector organizations as to what impacts, if any, will emerge if alternative chemicals will be used to meet air-quality standards.

Methanol has been identified as one of the alternative vehicle fuels in the United States; however, as with MTBE, there is a paucity of data and information available as to the potential impact of methanol upon surface water and groundwater resources or its potential interactions with benzene, toluene, ethyl benzene, xylene (BTEX), MTBE, or other chemical plumes.

NWRI invited a group of recognized experts from academia, regulatory agencies, public utilities, and private consulting firms to attend a 2-day Nominal Group Technique (NGT) workshop for the purpose of identifying and prioritizing key research issues that need to be addressed if methanol is to be considered as a fuel substitute. This workshop was the collaborative effort of the American Methanol Institute and NWRI.

This document reports the results of the participants' creative efforts to define the issues that need to be addressed by the nation's research community. Significant efforts were exerted to maintain the integrity of each participant's contribution, and therefore only minor editorial adjustments have been made to ensure readability.

No workshop could be successful without the support provided by the professional staff. Special thanks are extended to Patricia Linsky and Gina Melin, Editors; Tammy Russo, Meeting Coordinator; Joseph Pezely, Graphics Illustrator; Stephen Lyon, Ph.D., Graphics Assistant; Sandra Joy Labbitt, Carol Studley, Tatiana Freitas, Word Processors; and Teresa Taylor, Photographer. Sincere appreciation is extended to William S. Gaither, Ph.D., who, through his masterful facilitating skills, brought the NGT workshop to a successful conclusion.

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

CONTENTS

PARTICIPANTS

Front Row: Jim Davidson, Roy Herndon, J. Michael Davis, Matt Hagemann, Mohsen Mehran, Leslie Smith, Tammy Russo (Meeting Coordinator), Jim Barker, Jim Crowley

Back Row: Stephen Lyon (Graphic Assistant), Rey Rodriguez, Joe Pezely (Graphics), Rula Deeb, Dave Rice, Patricia Linsky (Editor), Walter Weber, Bob Paterek, Ron Hunsinger, Gina Melin (Editor), Mike Kavanaugh, Maria Tikkanen, Bill Gaither (Facilitator), Pedro Alvarez, Roy Spalding, and Ron Linsky (Secretary)

PART 1

WORKING GROUPS' REPORTS

INTRODUCTION

This section contains summary reports that describe each of the 6 highest priority research issues identified by workshop participants. The entire list of 18 priority issues, ranked in descending order of importance, are listed in Part 2 of this report.

Eighteen individuals convened on Friday evening, October 5th, at the Costa Mesa Hilton Hotel in Costa Mesa, California. On the following morning, these recognized experts offered 72 responses to the workshop question: ***What Priority Research Issues Must Be Addressed to Determine Whether Methanol Should Be Considered a Future Drinking-Water Contaminant That Might Require Regulation?***

Working Groups of three individuals were appointed to digest, synthesize, and summarize, in one coherent report, all of the responses to the workshop question that were grouped under 18 major research issue headings. The reader is urged to read Part 2 of this report in which each of the 72 response writeups are presented in the full-text format written by the participants.

The working groups worked Saturday evening and Sunday morning to prepare the following 6 reports. On Sunday morning each working group presented their report to the other participants and enlisted comments. Following each presentation and discussion, usually 20 to 25 minutes, participants were encouraged to offer written comments for the report's improvement. All comments that were submitted appear immediately after each of the working group reports.

Graphics, either PowerPoint or overhead transparencies, used by working groups in their presentations, appear in Appendix E of this report.


WORKING
GROUP

PRIORITY 1

Groundwater Quality Impacts Associated with the Release of Methanol Fuels

WORKING GROUP MEMEBERS:

Alvarez, Crowley, and Kavanaugh

Research Issue Overview:

Since 1965, methanol has been used in the United States as a fuel in certain automotive vehicles, in at least two forms, namely, M85 (containing 85 percent methanol, 15 percent gasoline) and M100 (pure methanol). In 1993, approximately 12 million gallons of methanol were used as a direct fuel in flexible fuel vehicles in California, and another 212 million gallons were used in other fuels and fuel additives. In the future, methanol may be widely used as a fuel for fuel cells in vehicles, or fuel cells used in other applications, such as distributed power sources. The composition of methanol to be used in fuel cells is unknown, but the methanol fuel is likely to include various additives required to ensure safe handling of the fuel, which is highly toxic when ingested. These additives would minimize ingestion (e.g., bitterant), identify the methanol fuel as toxic (e.g., colorant), and provide luminosity or color to a flame when methanol burns. Methanol-powered, micro-fuel cells may also find wide application in various commercial products.

To meet the potential demand for methanol, a nationwide distribution and storage system will have to be constructed. Methanol will be transported around the country in tanker trucks, rail cars, ships or barges, and possibly in pipelines. The methanol is then likely to be stored in underground storage tanks (USTs) located at gas stations that serve as refueling facilities. This increase in production, distribution, and storage of methanol poses a threat to the environment due to potential releases of the methanol fuels during its production, transport, storage, and use.

The release of methanol fuels to the environment has the potential to cause deleterious impacts on water resources, including impacts on human health, ecosystems, and rendering water unsuitable for use, without treatment or remediation. The constituents in the methanol fuel, as well as transformation products of methanol and the additives, may contribute to these deleterious impacts. Knowledge of the environmental fate of methanol, the additives, and transformation byproducts in surface water and groundwater is relatively limited. The extent of the threat of increased methanol use on water quality, both with respect to ecological impacts and impacts on drinking water sources, have not been thoroughly evaluated. Because of its relatively high biodegradability, methanol itself is not expected to be a significant water quality concern.

However, the effects of degradation byproducts and fuel additives could be significant. In addition, we believe that there will be effects on extension of preexisting contaminant plumes due to co-solvent effects and electron acceptor depletion that hinders the natural attenuation of these plumes.

Currently, methanol is an unregulated contaminant in water, and the chemical is not included on the USEPA's contaminant candidate lists. Whether or not methanol should be regulated in the future depends in part on a thorough understanding of the fate and transport of methanol fuels in both surface water and groundwater. This Research Issue addresses the key unknowns related to the impacts of methanol fuel releases on groundwater.

Significant research gaps currently exist regarding the fate and transport of methanol fuels in groundwater. Some of the uncertainties include the following:

- What impacts will methanol fuel releases have on the aesthetic quality of groundwater?
- What are the likely fate, transport, and impacts of methanol fuel additives in the unsaturated and saturated zones?
- What is the likely rate of natural attenuation of methanol fuels under presumed release scenarios?
- Will the release of methanol fuels mobilize minerals and metals that could ultimately impact drinking-water supply wells?
- Will the release of methanol fuels to the groundwater increase the mobility of organic contaminants previously released to the soil?
- What is the fate and transport of degradation byproducts of methanol or fuel additives in the groundwater?
- If methanol or additive compounds were to impact a water supply well, would these compounds represent an aesthetic, as well as an health, impact, and if so, at what levels?

To address these uncertainties, a variety of studies are needed at different scales by using both reductionist and holistic research approaches and disciplines. Response variability, as a function of release scenario and site specificity, will also need to be addressed. In addition, the authors believe that controlled-release experiments are necessary to verify that the processes observed in the laboratory occur at the field scale and to properly calibrate fate and transport predictive models.

The following research issues provide a brief description of broad research topics that will provide the basis to assess the magnitude of the impacts of methanol releases to the soil, and subsequent transport of the methanol to groundwater.

Research Issues:

Research Area 1 - Impacts to Groundwater Quality Resulting from Anaerobic Biotransformation of Methanol

Description:

- Accumulation of volatile fatty acids (VFAs) (e.g., butyric, propionic, acetic, and formic acids) that compromise the taste and odor of drinking water.

- Biofouling of wells and reductive dissolution of oxides (Fe, Mn, As?), which could affect water appearance.

- Mobilization of naturally occurring organic matter from soil.

Importance:

Taste, odor, and color are important drinking water quality parameters that can be affected by anaerobic biotransformations and related biogeochemical interactions. It is important to understand what site-specific conditions (geochemical, microbiological, and hydrogeological) affect the rate and extent of accumulation of undesirable byproducts that could potentially reach water supply wells.

This information is needed to identify indirect consequences inherent in the natural attenuation of methanol releases, such as the identification of the source of chemicals that may reach a water supply well, thus allowing allocation of responsibility between potentially responsible parties. It is also important to identify what additional parameters might have to be included in site characterization protocols.

How Do You Propose to Resolve This Issue?

- Conduct microcosms and column experiments to characterize rate and extent of methanol transformation to undesirable byproducts. The methanol-induced mobilization of minerals and natural organic matter (NOM) should also be considered. Variables should include: electron-accepting conditions, type of aquifer material that serves as bacterial sources, methanol concentration, bicarbonate alkalinity, and trace-metal availability. The literature suggests that high bicarbonate and cobalt concentrations favor the transformation of methanol to VFAs rather than to methane.

- Develop a mathematical model to consider biotransformations, geochemical transitions, microbial growth, and toxicity in both the unsaturated zone and in groundwater.

- Conduct a field study to verify laboratory observations and conclusions.

This is a microbial ecology issue since these aesthetic impacts are partly related to microbial population shifts. Thus, we may have to use molecular biology tools to understand such changes in microbial community structure. This is also a hydrodynamic issue, since no biotransformations are likely to occur until methanol is dispersed and diluted below 1 percent.

Who Are the Individuals Best Able to Address, Resolve (or Dissolve) This Issue?

Multidisciplinary Team. Experience with alcohol oxygenates desirable.

Research Area 2 - Fate and Transport of Additives in Fuel-Cell-Grade-Methanol

Description:

- Identification of additives.
- Characterization of fate and transport properties of additives.
- Identification of transformation products and their ecotoxicological implications under a variety of release scenarios and site-specific conditions.
- Characterization of the functional relationships that control the partitioning and transport in the unsaturated zone.
- Incorporation of degradation rates and partitioning characteristics into fate and transport models for a variety of release scenarios and site-specific conditions for selected additives.

Importance:

Because of concern over additives found in other widely used chemicals, such as certain chlorinated solvents (e.g., 1, 4 – dioxane), widespread use of methanol as a fuel will depend on a comprehensive understanding of the fate and transport of additives specific to use of methanol in fuel cells. Similar to other fuels, various additives will be likely be added to fuel-cell-grade-methanol for a variety of purposes, including performance enhancement, corrosion inhibitors, denaturants, colorants, and providing luminosity. Knowledge of the persistence, mobility, and toxicity of these compounds is needed.

How Do You Propose to Resolve This Issue?

- White paper to identify actual or likely additives; summarize known physical, chemical, and degradation characteristics; summarize known health and ecological impacts of additives; determine likely concentrations of additives following various release scenarios; and determine unknowns regarding fate and transport of additives.

- Microcosm and column experiments to elucidate likely fate and transport of selected additives under various geochemical conditions, and to evaluate the formation of byproducts and fate of byproducts.

- Incorporation of additive fate and transport studies in field studies; include tracking of additives as a component of the field-sampling program.

- Taste and odor studies to determine aesthetic endpoints for those additives posing highest risk of impacting water-supply wells.

Who Are the Individuals Best Able to Address, Resolve (or Dissolve) This Issue?

A multidisciplinary team of researchers in the relevant areas.

Research Area 3 - Field-Based Research: Controlled Releases at Virgin and Former Petroleum Fuel Release Sites

Description:

- Perform controlled releases to characterize the dimensions and stability of neat methanol plumes, co-occurring contaminants, and related transformation byproducts.

- Generate data for model calibration and validation.

- Perform controlled releases to characterize the effect of methanol releases on the dimensions and stability of existing petroleum and oxygenate plumes.

- Test site for improved sampling and refinement of analytical methods. In particular, the use of newly developed molecular probes, quorum, and other biological sensors.

- Improve our understanding of hydrodynamic processes that are required to dilute and disperse methanol to levels that are amenable to biodegradation.

- Provide samples to characterize geochemical transitions and changes in microbial community structure.

- Test site to characterize natural attenuation and engineered remediation strategies.

Importance:

Methanol would likely be stored in USTs or aboveground storage tanks (ASTs) at the location of current gasoline stations and other facilities. We need to understand how releases will affect groundwater resources, preexisting petroleum fuel, and other contamination.

How Do You Propose to Resolve This Issue?

- Plan and prioritize specific research areas and objectives considering budgetary and scheduling constraints (example: $750,000 for 2 years).

- Identify suitable sites. (avoid confounding effects; take advantage of previous site characterization and instrumentation as much as possible).

- Conduct studies.

Who Are the Individuals Best Able to Address, Resolve (or Dissolve) This Issue?

- University of Waterloo, U.C. Davis, Purdue University, University of Florida, Stanford University, University of Michigan, University of Iowa, selected utilities, and consultants.

- A multidisciplinary team of other researchers in the relevant areas.

Comments:

"The report captured the significant issues. Have we identified where we can make use of current/planned research dealing with ethanol?" – ***James Barker***

"The impact of methanol on the fate and transport of co-occurring contaminants is the focus of Priority No. 3. Since Priority No. 1 proposed that research projects are many and are broad in nature, it could be best to remove the emphasis on co-occurring contaminants from this research issue, especially the proposed field component. Such a study is proposed in detail in Priority No. 3." – ***Rula Deeb***

"Do we know what additives will be mixed with methanol? Aren't there additives that we are not aware of? How do we design an efficient research program to address emerging additives?" – ***Mohsen Mehran***

"Effects of methanol on the mobility of inorganic compounds that may be occurring at distributed energy facilities will use methanol-fueled fuel cell reactors. The major users will be factory farms. Enhanced mobility of agribusiness chemicals, such as fertilizers, herbicides, insecticides, etc. Nitrogen and phosphate turnover and mobility may negatively or positively influence groundwater and surface water." – ***J. Robert Paterek***

"Field-based research, along with laboratory research, should be performed in conjunction with the methanol industry (California Fuel Cell Partnership) to adequately be able to address the numerous additives, which may be proprietary and difficult to define." – ***Rey Rodriguez***

"Don't hold up field-based experimentation until there is a better definition of additives. There are significant questions to be addressed that relate to methanol itself, and co-occurring organic contaminants." – ***Leslie Smith***

"I recommend closely working with the California Fuel Cell Partnership, as many of these issues are being addressed, and piggy-backing on the research being funded by the Partnership would be efficient and cost effective." – ***Maria Tikkanen***


WORKING
GROUP 2
WORK SHOP

PRIORITY 2

Develop Sampling and Trace Analytical Methods and Protocols Useful for Assessing the Occurrence of Methanol and Associated Analytes

WORKING GROUP MEMBERS:

Spalding, Hunsinger, Tikkanen

Research Issue Description:

Representative sampling and the precise and accurate analytical procedures to characterize the chemical, biological, and physical characteristics are a prerequisite to any study of occurrence, fate and transport, or drinking-water quality. In the case of the expanding use of methanol as a fuel for either fuel cells or internal combustion engines, the following groups of analytes should be considered: methanol, methanol additives, transformation products, byproducts, and other associated chemical analytes, as well as microorganisms (aerobic and anaerobic).

Both the laboratory and field parameters must be addressed.

Sample Collection. Establish appropriate sample collection methods that include such issues as well purging, holding times, and preservation for each of the analytes listed above.

Establish the appropriate microbial sample collection (including holding times) and preservation methods as determined by redox potentials. Sample collection and preservation methods should be developed for both aerobic and anaerobic bacteria.

Sample collection protocols should ensure that inert materials used do not alter or mask the analytes. Variables, such as casing materials, well construction, sample collection devices, and sampling containers, should be subjected to standard quality assurance/quality control (QA/QC) protocols.

Sampling techniques should be optimized to ensure representative samples are collected.

Development of analytical methodology. The determination of analytical sensitivity should be based on the needs established in preliminary studies of human and ecological toxicology and the chemical and biological dynamics of methanol, additives used with methanol, and methanol byproducts.

The analytical method should optimize sensitivity while maintaining analytical efficiency in a wide spectrum of matrices representative of those occurring in surface water and groundwater. The method will require the analyst to establish reproducible quantitative results. Standard QA/QC methods should be used.

The current detection limit for methanol is inadequate to determine the trace concentrations of this analyte. The development of a robust analytical method capable of quantifying aqueous concentrations of methanol in the low- to sub-part per billion range is required.

The documented analytical procedures should be peer reviewed and acceptable to regulatory authorities.

The methods must conform to standards developed by the USEPA through the National Environmental Laboratory Accreditation Program.

Cost and complexity of analysis should be kept as low as possible without jeopardizing precision, accuracy, or sensitivity.

Importance of Issue:

As the use of methanol expands, the amount of analyses will expand. This preliminary step should be requisite to any expanded use of methanol. The sample collection and analytical protocols would be developed in sufficient time to allow a baseline characterization prior to the introduction of methanol as a generally available fuel.

How Do You Propose to Resolve this Issue?

Develop sample collection and analytical protocols in a timely manner.

Who Are the Individuals Best Able to Address, Resolve this Issue?

Many university, for-profit, and not-for-profit laboratories are well qualified to carry out this work. An external oversight group should be established to evaluate all method development.

Comments:

"How is the required limit of detection (LOD) for contaminants that we know very little about to be determined (i.e., how clean is clean for additives?)? Chronological implication must be done after input from toxicology and fate and transport research." – ***Pedro Alvarez***

"Very low-level analysis (ppt) for methanol and byproducts is necessary for research and preliminary screening projects. These analyses would not be used for general monitoring, and a more cost-effective analysis, tailored to address sampling program objectives, can be developed." – ***James Crowley***

"Appropriate sample-collection techniques should be identified, including pump type, purge volume, appropriateness of low flow (?), and well materials." – ***Matt Hagemann***

"In the past, the lowering of detection limits has generally been driven by risk assessments and toxicological studies. What is the rationale for proposing to detect methanol in the low-ppb or sub-ppb levels?" – ***Mohsen Mehran***

"Onsite and real-time analyses would be possible and valuable. A number of techniques are commercially available, such as handheld photo-ionized detector (PID) spectrophotometers and sensors (chemophysically and biologically based). New sensitive and specific methods are being developed. Our laboratory is developing biosensors for specific bacterial groups, including sulfate reducing and methane/methanol utilizing bacteria for corrosion and biofouling use. This can be expanded to include methanol issues." – ***J. Robert Paterek***

"The development of an analytical method should consider the ability of existing laboratories to be able to reproduce the method and the costs to run the analysis (should also be considered in the method selection). Regulatory acceptance and approval is necessary for both drinking water and UST remediation activities. As such, the USEPA and the state agencies should be involved in developing the sample collection and analytical protocols and procedures." – ***Rey Rodriguez***

"Justification for target concentration for maximum daily loads (MDLs) are hazy because toxicology studies for methanol and associated analytes are not complete. The method is necessary to develop prior to initiating environmental toxicology studies. Thus, the regulatory driver to assess MDLs is missing. – ***Roy Spalding***


WORKING
GROUP

PRIORITY 3

Effects of Methanol on the Fate and Transport of Co-occurring Dissolved, Sorbed, Sequestered, and Residualized Organic Contaminants

WORKING GROUP MEMBERS:

Deeb, Paterek, Weber

Research Issue Description:

Identify and evaluate microbiological impacts resulting from the introduction of methanol into subsurface environments.

- Potential elongation of benzene, toluene, ethylbenzene, xylene (BTEX) and methyl tertiary butyl ether (MTBE) plumes at leaking underground fuel tank (LUFT) sites.

  Releases of M85 and/or M100 will likely occur at sites and under similar conditions as "historic" releases of fuel hydrocarbons and oxygenates. The soluble components of gasoline, mainly BTEX compounds and fuel oxygenates, such as MTBE (and its associated compound, tertiary-butyl alcohol [TBA]) and ethanol, can be attenuated by biological reactions at varying rates. In fact, the biological biodegradation of BTEX compounds is the major natural attenuation mechanism for these compounds in subsurface environments. Methanol is expected to biodegrade more readily than BTEX compounds and MTBE, potentially leading to the depletion of the nutrients and electron acceptors needed for the bioattenuation of these latter chemicals. This could potentially result in the elongation of BTEX and MTBE plumes in subsurface environments.

- Impact of high concentrations of methanol on the viability of microorganisms.

  High concentrations of methanol may be encountered at source zones, especially at sites with a shallow water table or a continuous leak of methanol. High aqueous concentrations of methanol may severely restrict the metabolic activity and viability of indigenous microbial populations, at least until dispersive processes reduce concentrations below the inhibition threshold. The rate of recovery of the population is uncertain, but key to the eventual degradation of methanol and co-occurring contaminants in groundwater.

- Impact of methanol on the stability of indigenous microbial communities.

  The introduction of methanol into subsurface environments would likely result in significant changes in the structure and activity of the indigenous microbial community. Methanol can be rapidly biodegraded under most conditions typical of subsurface environments (i.e., aerobic and anaerobic). Because of its ease of biodegradability relative to other organic compounds, methanol could be preferentially utilized. This may disproportionately support the growth of methanol-degrading bacteria that do not commonly degrade a range of co-occurring contaminants.

Identify and evaluate the physicochemical impacts associated with the introduction of methanol to surface and subsurface soils.

Two classes of projects are defined in this priority research area. One class relates to the impacts of methanol on sequestered co-occurring organic contaminants, and the other to impacts on mobile co-occurring contaminants. The term sequestered here defines contaminants that have interacted with soil/sediment organic matter over long periods of time (i.e., they have been historically sorbed and aged or weathered). The term mobile refers to contaminants that exist in the dissolved state, in nonaqueous phase residuals and/or have been recently sorbed. The major difference between these two groups of contaminants is the rate at which they would normally be released to flowing or seeping water that is free of methanol.

- Impact of methanol on sequestered co-occurring contaminants.

  Hydrophobic compounds are known to be sequestered by most types of soils and under a variety of circumstances. M85 and M100 wavefronts could move rapidly under saturated flow conditions and may "sweep" otherwise immobilized contaminants toward water-supply sources. Examples of sequestered co-contaminants of concern include polyaromatic hydrocarbons (PAHs) and chlorinated aromatics in subsurface sites and pesticides in surface soils.

- Impact of methanol on nonsequestered co-occurring contaminants.

  When methanol fuels interact with co-contaminants that exist in the dissolved, nonaqueous phase or recently sorbed states, the enhanced solubility and mobility of these contaminants may take place. This process may have significant impacts on the quality of water in receptor wells that are hundreds of feet away from methanol fuel spill areas.

Importance of Issue:

Releases of methanol fuels will likely occur at the same sites and under similar circumstances as current or prior releases of petroleum-based and/or solvent-related organic contaminants; therefore, following its release, methanol is likely to encounter a range of co-occurring contaminants in the environment.

From a biological viewpoint, the elongation of BTEX and MTBE plumes at LUFT sites due to preferential methanol biodegradation, depletion of nutrients, modification of redox conditions, changes in microbial community structure and activity, and microbial toxification due to initially high concentrations of methanol at the vicinity of spills, could lead to the enhanced migration of these contaminants of concern toward and into public water supplies.

From a physicochemical viewpoint, potential increases in the organic contamination of water sources by hydrophobic compounds, such as PAHs and halogenated aromatics, may result from desequestration reactions in the presence of methanol. Facilitated transport of more mobile contaminants, such as BTEX compounds and chlorinated solvents existing as NAPLs or reversibly sorbed substances, may result from solubilization or co-solubilization by methanol. The lack of information regarding the potential for, and consequences of, such behavior will logically raise concern and may, in turn, lead to misinformed regulation.

How Do You Propose to Resolve This Issue?

Identify and evaluate microbiological impacts resulting from the introduction of methanol into subsurface environments.

- Potential elongation of BTEX and MTBE plumes at LUFT sites.

  Laboratory studies (microcosm and column experiments) are needed to quantify the impact of methanol on BTEX and MTBE biodegradation rates. These studies should be subsequently validated using models.

  Field studies with a possibly simulated release of methanol at a previously BTEX/MTBE-contaminated site are needed to better understand this process in the environment.

- Impact of high concentrations of methanol on the viability of microorganisms.

  Laboratory microcosm and column studies are necessary initially. A field component (pure-phase methanol release into aquifers) may be needed to understand and document the rate of recovery of biotransformation capability following exposure to high concentrations of methanol.

- Impact of methanol on the stability of indigenous microbial communities

  A series of laboratory microcosm experiments should be conducted initially to examine the kinetics and microbial population changes due to the introduction of methanol.

  Molecular approaches, such as gene probes and DNA analysis, can be used as tools.

To evaluate whether laboratory microcosm results and characterization techniques can be extrapolated to the field, a molecular ecology approach should be used to characterize the spatial and temporal changes in subsurface microbial communities as a result of controlled methanol release experiments.

Identify and evaluate physicochemical impacts associated with the introduction of methanol to surface and subsurface soils.

- Impact of methanol on sequestered co-occurring contaminants.

  Critically and strategically designed laboratory investigations of representative soil-contaminant-condition matrices are needed to assess desequestration potentials and related release and transport profiles to serve as basis for migration model(s). These should be determined for an appropriate suite of wave-front conditions (e.g., concentration peak, mass burden, velocity and residence time) and for an appropriate variety of soils having different types of organic matter matrices (e.g., degree of diagenetic alteration, condensation and carbon-oxygen atomic ratios).

- Impact of methanol on non-sequestered co-occurring contaminants.

  Experimental laboratory investigations are required to assess the effects of methanol on the solubilization and co-solubilization processes.

  These experiments are somewhat less complex than those for desequestration because the type of soil organic matrix involved is much less significant.

Who Are the Individuals Best Able to Address and Resolve the Proposed Research Issues?

Collaborations between the various organizations represented by the workshop participants depending on individual areas of expertise are key for the success of any of the proposed research projects.

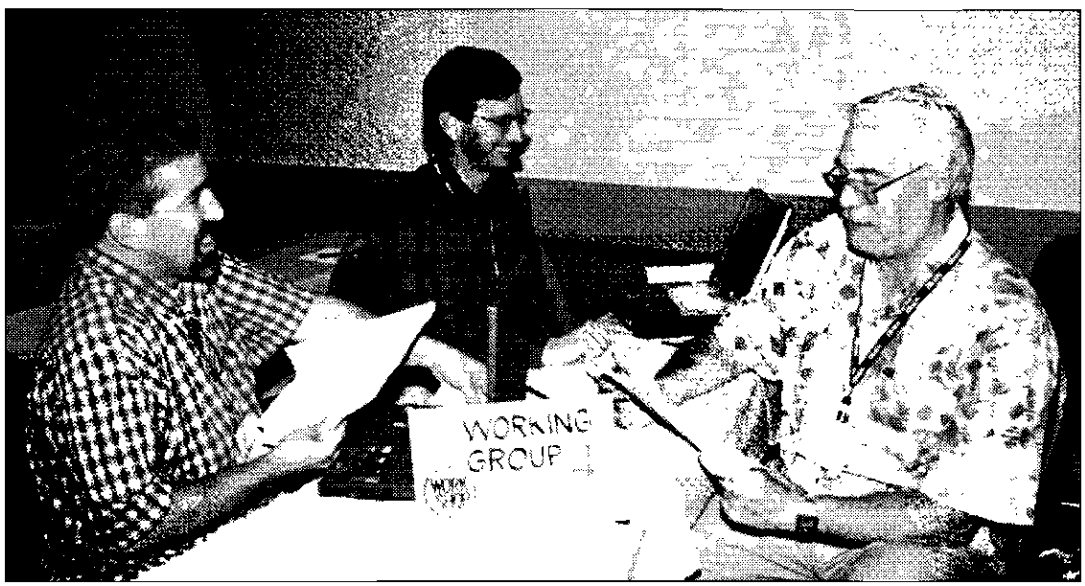
For example, a study involving an evaluation of the extent of BTEX/MTBE plume elongation due to methanol could involve a team comprosed of a consulting company (i.e., Malcolm Pirnie – R. Deeb and M. Kavanaugh), several universities (University of Iowa – P. Alvarez; University of Waterloo – J. Barker; University of Michigan, W. Weber), a national laboratory (Lawrence Livermore – D. Rice) and a private institute (Gas Technology Institute – J.R. Paterek).

Comments:

"Should we consider including the mobilization of toxic inorganic compounds that could be present at the site either due to preexisting contamination or naturally occurring?" – ***Pedro Alvarez***

"This is a critical research need, and the summary is excellent. I would suggest specific focus also on NOM sequestering that could cause deleterious secondary and aesthetic effects on drinking water. This research may also provide valuable information on possible NOM effects at drinking-water treatment plants and in water distribution systems. Additionally, field-based research would be very useful in verifying laboratory findings in this area, and I encourage researchers to work closely with ongoing and planned field-based control release research projects." – ***James Crowley***

"The potential elongation of TBA plumes at LUST sites should also be considered." – ***Rey Rodriguez***


WORKING
GROUP

PRIORITY 4

Human and Ecological Toxicology

Working Group Members:

Barker, Herndon, Rodriguez

Research Issue Description:

The degree of human toxicity of fuel methanol, its byproducts, and additives is critical to determining the level at which methanol should be regulated as a potential drinking-water contaminant. For example, animal studies demonstrate that methanol is a developmental toxicant, and some of these studies suggest that developmental effects can be induced by relatively brief exposure periods during gestation. The relationship between such animal findings and the potential for human developmental hazards for methanol remains uncertain. Both the minimal amount of exposure (concentration and duration) and the time point(s) (critical period) during gestation need to be ascertained in a suitable animal model.

It would be prudent to prioritize the toxicity studies on byproducts and additives that are most likely to be soluble, mobile, and persistent in the environment.

Animal studies demonstrate that methanol can enhance the toxicity of other agents, especially hepatotoxicants. Such effects need to be explored in greater depth to determine which chemicals show synergistic effects and to characterize their dose-response relationships, mechanisms of action, and relevance to environmental exposures.

Once the human toxicity of methanol and associated compounds is assessed, a comparative analysis of available toxicological data on alternative fuels should be performed.

Acute toxicity thresholds to aquatic receptors, due to catastrophic releases of methanol to surface water bodies, are likely understood. However, chronic exposure to methanol byproducts and additives at environmentally relevant levels could pose a risk to aquatic life, thus requiring further research.

Importance of Issue:

If experimental data demonstrate a strong toxicity level for methanol at environmentally relevant concentrations (< 10 mg/L), its byproducts, and additives, then public health risk due to exposure to water containing these constituents could be significant and worthy of regulatory monitoring and compliance. From available evidence, it appears that developmental effects are the most sensitive endpoints for methanol toxicity and, therefore, are likely to drive health reference or advisory values.

The list of compounds showing synergistic toxicity with methanol needs to be better defined. While the synergistic effects of methanol at high concentrations with other compounds have been observed, such effects have not been fully characterized for low-level exposures in the range of environmental relevance.

From an overall risk assessment standpoint, it is important to put into context the toxicity of methanol and associated compounds with that of alternative fuels.

Except for catastrophic releases, ecological impacts of methanol exposure are considered unlikely and, therefore, of lesser importance for assessment. However, additives and byproducts could pose a significant ecological risk and are worthy of toxicity evaluation.

How Do You Propose to Resolve This Issue?

Sound toxicological experiments should be performed to evaluate the short- and long-term exposure thresholds for human toxicity to methanol and associated compounds. The experiments should include environmentally relevant concentrations (<10 mg/L).

A list of priority constituents for toxicological evaluation should be developed based on their relative toxicity (documented or inferred), solubility, mobility, and persistence. Along those lines, because of the inherent cost of mammalian toxicological testing and the expected low probability of human exposure, methanol should be considered a low-priority compound.

Developmental toxicity should be evaluated using nonhuman primates at multiple doses of methanol (preferably in drinking water). The testing needs to be conducted with sufficient numbers of subjects to assure adequate statistical power. This work needs to be conducted so as to be relatable to available pharmacokinetic data on methanol.

Carcinogenicity data for methanol are reportedly unavailable (International Journal of Toxicology, 20:57-85, Suppl. 1 2001), which may suggest the need for focused experiments on health effects from long-term exposure at low concentrations. Data gaps may also exist for other methanol-associated compounds. Therefore, a literature review should be performed to determine if additional toxicity experiments are warranted for these compounds.

Testing of synergistic health effects of methanol should be conducted using rodents with combinations of toxicants administered at several dose-levels (including relatively low, environmentally relevant levels). A sufficient number of animals should be tested to achieve adequate statistical power.

An evaluation of aquatic toxicity of additives and byproducts should be performed through a review of available literature and experiments, as necessary.

Comments:

"Nice overviews. Please also note that methanol might indirectly trigger other health concerns in water treatment and distribution systems. These include microbial growth, trihalomethane (THM) formation during disinfection, and other disinfection byproducts, such as *N*-nitroso dimethyl amine (NDMA)." – ***Pedro Alvarez***

"The comment that the costs of toxicological studies are high and that the priority for further testing of methanol is low needs to be placed in perspective. The value of further toxicity studies (especially focusing on the potential developmental effects of methanol) is that the resulting information reduces the uncertainties in assessing methanol health risks. Uncertainties can modify health reference values (e.g., reference dose [RfD]) by orders of magnitude. Thus, the implications for risk-based corrective actions (e.g., clean-up costs) could be quite substantial and far greater than the cost of a toxicology study." – ***J. Michael Davis***

"There should be an emphasis on evaluating the toxicity of methanol at low concentrations that would be expected in extracted groundwater. Methanol is perceived to be very toxic relative to gasoline, but this is only observed at high concentrations of these chemicals. Comparative evaluations regarding toxicity should focus on environmentally expected concentrations of compounds of interest." – ***Rula A. Deeb***

"Regarding the comment about a spill with methanol that then enters a storm sewer and eventually a waste treatment plant, most wastewater treatment facilities treat 10-250 million gallons per day. Given an initial spill in the open air, there would be a substantial degree of volatilization. Once at the plant, the trickling filter and activated sludge processes would further volatilize the methanol. Once mixed with the large volume of wastewater, the methanol would most likely be an additional carbon source for the bacteria. There would be little likelihood of the methanol making it through the system." – ***Stephen Lyon***

"The literature data indicate that there are no adverse effects of methanol on aquatic organisms (e.g., fathead minnow and rainbow trout) in a concentration range of less than 100 mg/l. A comprehensive review of existing data is needed to focus on the proper range of concentrations tested for aquatic toxicity studies. The potential synergistic effects of additives need to be considered in these studies." – ***Mohsen Mehran***

"The presence of methanol in input water from a sanitation treatment system could increase the production and mobility of sanitation byproducts (e.g., THM). Toxicology, engineering, and chemical effects of methanol into publicly owned treatment works (POTW) should be addressed." – ***J. Robert Paterek***

"The statement that ecological impacts will be limited is inaccurate. A bulk methanol release to surface waters will have significant impacts through direct toxicity as well as eutrophication impacts. 'Ecology' does not stop at the ground surface. There is a complex subsurface microbial ecology that will dominate the processes that assimilate a methanol spill" – ***David Rice***

"Prior to putting out a RFP on any human toxicology study, recommend work with California Office of Environmental Health and Hazard Assessment (OEHHA), to ensure appropriate issues are addressed. California OEHHA establishes health-based goals (Public Health Goals) for contaminants in various matrices. The Public Health Goals for contaminants in water are used as a basis for establishing drinking water standards by the California Department of Health Services, (i.e., Department of Drinking Water and Environmental Monitoring). – ***Maria Tikkanen***

PRIORITY 5

Comprehensive Evaluation of Direct and Indirect Impacts of Methanol

WORKING GROUP MEMBERS:

Davis, Mehran, and Smith

Research Issue Description:

A comprehensive evaluation of the potential health and environmental impacts of methanol fuels needs to consider direct and indirect impacts using a systems-based manner. A life-cycle assessment (LCA) offers a useful approach to accomplishing such a comprehensive evaluation, beginning with feedstock gathering/processing and continuing through production, distribution, storage, use, and disposal. The objective of the LCA would be to identify points in the total life cycle at which significant releases of methanol and/or secondary byproducts could occur. The scope of the LCA needs to be carefully defined to assure that likely conditions that would result in major impacts have been considered, but not so broad as to be unworkable or superficial. An initial, screening-level LCA would rely primarily on existing information and analyses of available data. Modeling and statistical analyses would be used to elucidate issues. To a limited extent, collection of new data might also be undertaken in conjunction with an LCA.

The LCA should include a focus on releases from leaking underground storage tank (LUSTs) and accidental releases during transport and distribution. There are many other potential sources that must be part of the LCA, including catastrophic releases from methanol production facilities, methanol-processing byproducts from stationary fuel cells, byproducts associated with new methanol production technologies, and fuel-cell vehicle crashes. There is also a (probably low) potential for explosive hazard associated with methane derived from methanol degradation in the subsurface. A core part of the LCA is concerned with a risk analysis of the loading of methanol at the terminal, transport to refueling centers, and releases at any of these stages. Development and comparison of release scenarios throughout the distribution and use of methanol are essential components of the LCA. The risk analysis approach identifies environmental vulnerabilities of systems that require infrastructure enhancement prior to increased use of methanol.

Importance of Issue:

Unless a comprehensive approach to an LCA for methanol is taken, problems similar to issues surrounding MTBE use may arise. An important value of an LCA is not just to weigh possible risks and benefits of methanol fuels but to recognize, in advance, potential problems that can be mitigated by applying, improving, or developing suitable control measures. A screening LCA would also help identify critical information gaps and research needs.

How Do You Propose to Resolve This Issue?

An LCA should be conducted for methanol fuels under various scenarios of production and use. Although the initial effort could be limited to screening-level analyses, the assessments should strive to be comprehensive in scope (i.e., "wider than deep"). A wide range of expertise is needed to determine the scope of the LCA, but this does not imply that every conceivable issue needs to be included in the scope of the screening LCA. Judgments about the priority of different issues must be made. Nevertheless, it is important to consider a range of conditions (e.g., various hydrogeological conditions and various release conditions, such as chronic, low-level to acute, high-level). The screening LCA should attempt to refine the identification of key issues and information gaps, with the objective of laying the foundation for more intensive investigation where appropriate. An LCA could also consider methods for site management and remediation following releases.

Who Are the Individuals Best Able to Address, Resolve (or Dissolve) This Issue?

Collaborative efforts involving industry, academia, government, and nongovernmental organizations are proposed to initiate and carry out the proposed projects.

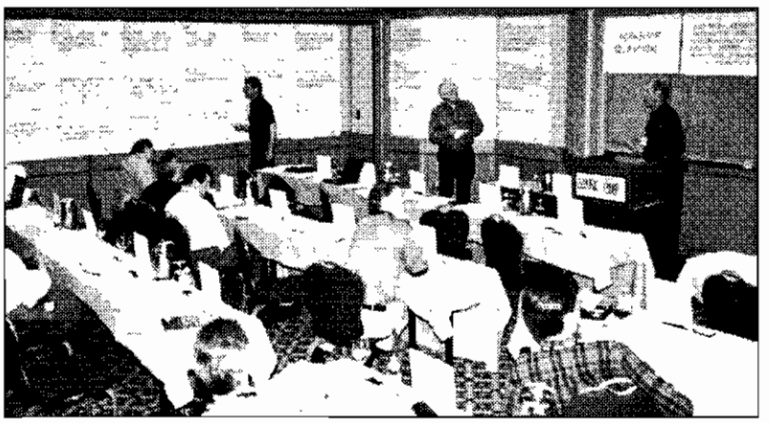
Comments:

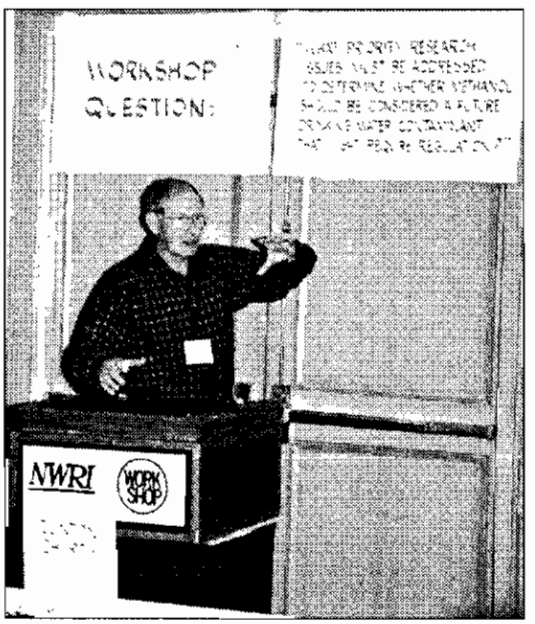
"Nice overview. Please also note that methanol might indirectly trigger other health concerns in water treatment and distribution systems. These include microbial growth, tri halomethane formation during disinfection, and other disinfection byproducts, such as NDMA." – ***Pedro Alvarez***

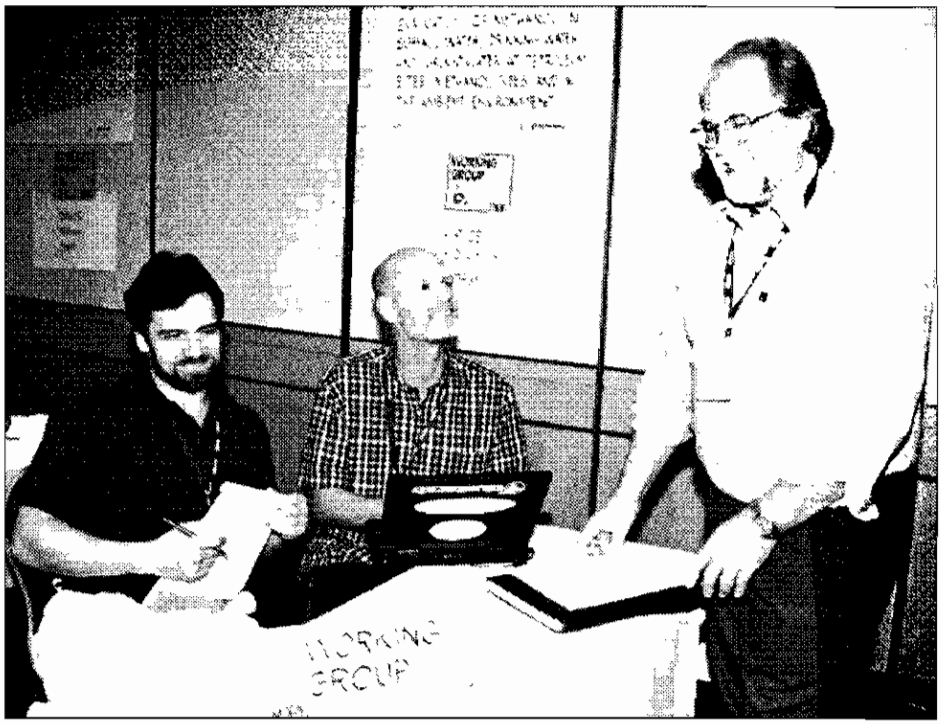
"LCAs should include drinking-water treatment/distribution and wastewater collection/treatment. A workshop should be organized to initially develop a preliminary LCA of methanol. This is a preliminary step in the assessment of methanol and should be conducted as soon as possible." – ***Ron Hunsinger***

"If possible, advantage should be taken of the existing LCAs that have been carried out for the current production and use of methanol. – ***Leslie Smith***

"I recommend closely working with the California Fuel Cell Partnership, as many of these issues are being addressed, and piggy-backing on the research being funded by the Partnership would be efficient and cost effective." – ***Maria Tikkanen***






WORKING
GROUP

PRIORITY 6

Evaluate Methanol in Surface Water, Drinking Water, and Groundwater at Petroleum Sites, Methanol Sites, and in the Ambient Environment

Working Group Members:

Davidson, Hagemann, and Rice

***Research Issue Description*:**

There is no comprehensive evaluation of compiled historical methanol release data and impacts. Little is known regarding the frequency of occurrence, extent, duration, and concentrations of past methanol releases. Further, little is known regarding the lasting secondary impacts of methanol releases to the subsurface or groundwater resources. A database needs to be established and maintained so manufacturers and other stakeholders can share historical case data and support a comprehensive evaluation of potential methanol impacts to surface water and groundwater at methanol sites, petroleum sites, and the ambient environment.

This database will facilitate a better understanding of the analytic and sampling methods for methanol, and secondary impacts (e.g., depleted electron acceptors, lowered pH, changes in BTEX transport, additives of concern, etc.) that need to be assessed.

Importance of Issue:

The information complied in this database will be valuable in assessing the potential future risk of methanol releases and identifying realistic release scenarios that may be expected. This information can also be used to calibrate and validate predictive modeling efforts.

Types of questions that the database could be used to answer include:

- What may be the dimensions, stability, and duration of methanol plumes in groundwater? The data collected can be used to improve our ability to predict the fate and transport of methanol and associated groundwater secondary impacts under different release scenarios.

- What are the background levels of methanol in the subsurface and groundwater? This assessment should include the evaluation of the potential for transient methanol production during fuel hydrocarbon degradation under a variety of subsurface conditions (e.g., high total organic carbon [TOC]).

- What data should be collected at a methanol release site? The database will also serve to identify the key parameters that need to be collected to evaluate methanol impacts. This will establish protocols and educate stakeholders regarding the needed measurements during future investigations.

How Do You Propose to Resolve This Issue?

A working task force comprising methanol industry stakeholders and groundwater experts familiar with the potential impacts of methanol should be formed to prepare the criteria that would qualify a site for inclusion into the database and direct the collection and analysis of the data. This working task force would establish:

- A list of sampling and analytical protocols based on the recommendations of Priority Group 2. Lessons learned from previous historical case analysis studies should be used to help establish the protocol for this investigation.

- A process to identify types of sites to be included in the database, as well as a screening checklist to identify the minimum data requirements that a site must meet in order to be included in the database. This will aid in providing data of known quality. For example, the types of sites that may provide useful information include:
  - fuel-cell-grade-methanol
  - M100
  - M85 petroleum sites
  - MTBE manufacturers

- A database structure. An appropriate basic information model needs to be developed that will allow future integration into large, existing, more-comprehensive databases. (Geotracker/GEMS).

- A case "hunter/gatherer team." This team will acquire site data that meet the screening checklist requirements and enter the information into the database.

A separate investigation of background, including transient in situ methanol production at gasoline release sites, may be needed. The evaluation of in situ methanol production may require the identification of a series of petroleum release sites that need to be sampled for methanol. Prior to this sampling, a series of hypotheses need to be developed based on the likely microbial conditions that could produce methanol during petroleum degradation. The sampling effort would then be focused to address these hypotheses.

In addition, representative surface water samples and drinking water samples (both surface water and groundwater sources) need to be collected and analyzed for methanol and secondary impacts.

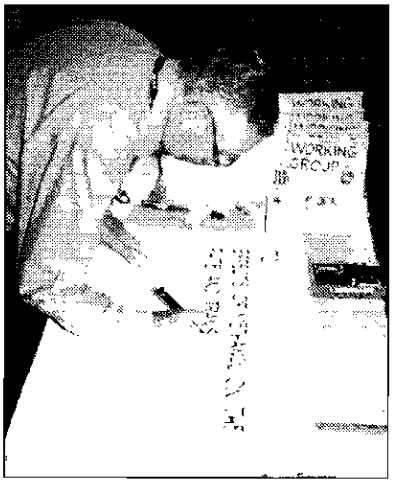
Who Are the Individuals Best Able to Address, Resolve (or Dissolve) This Issue?

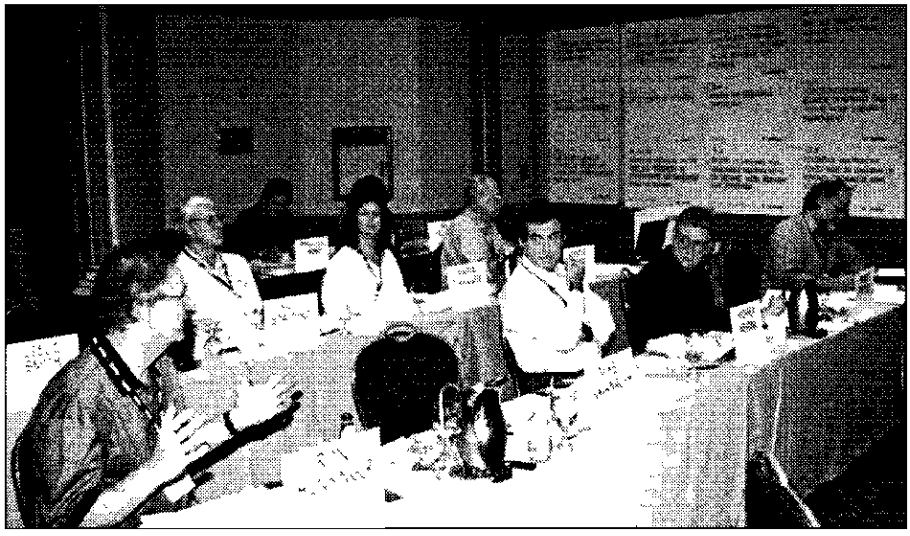
This effort needs to be a partnership among methanol producers and users and scientific experts familiar with historical case analysis. Since this will likely involve a statistical analysis of the data, individuals familiar with the storage, analysis, and manipulation of large amounts of data are required. A good model for this process may be the Chlorinated Solvent Historical Case Analysis Study working task force sponsored by the United States Department of Energy and conducted in collaboration with the Interstate Technology Regulatory Cooperation Working Group.

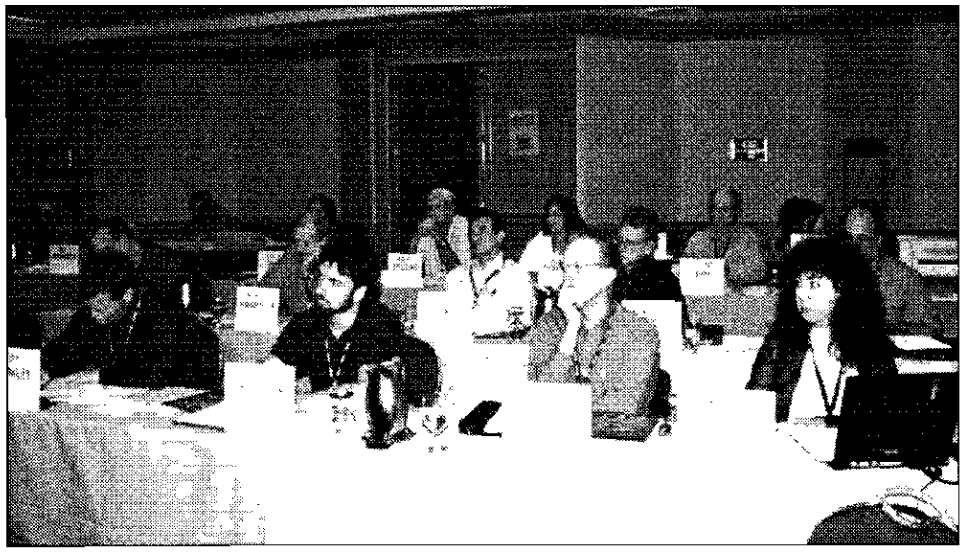
Comments:

"Funding and initiation of this project should begin immediately. This information could well be a driver for the other research areas. Others need to be engaged to provide data on specific sites and to incorporate database information into a larger, more comprehensive database." – ***James Crowley***

"I recommend closely working with the California Fuel Cell Partnership, as many of these issues are being addressed, and piggy-backing on the research being funded by the Partnership would be efficient and cost effective." – ***Maria Tikkanen***

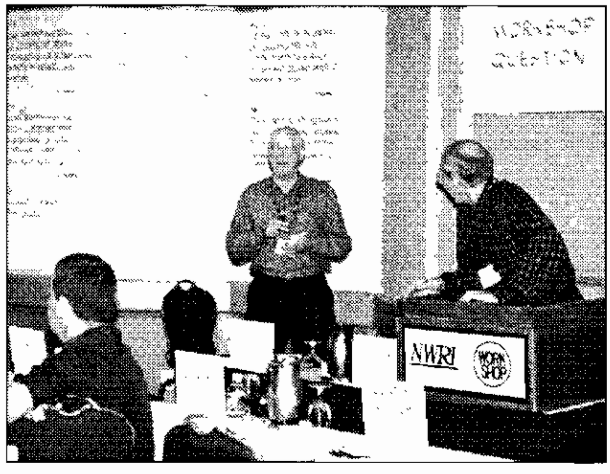






PART 2

NGT WORKSHOP


NWRI

INTRODUCTION

Several University of Wisconsin professors, led by Dr. Andre Delbecq, decided in the mid-60s that business and professional meetings were often inefficient and did not produce the results that the individuals assembled were capable of producing. The result of their work was, among other accomplishments, the conceptualization of the Nominal Group Technique (NGT). The name derived from the notion that any meeting comprises a "nominal group" of participants convened for a particular purpose. The essence of the process required that the participants meet and immediately write their most perceptive and penetrating responses to a prepared question. No discussion was allowed. This avoided the domination of the meeting by one or more vocal individuals and gave each participant the opportunity to have an equal voice in response to the question.

Over three decades have passed since the NGT process was devised. During that time it has been modified and enhanced by Dr. William S. Gaither, working during the last ten years with the National Water Research Institute.

Prior to arriving at the workshop, participants were asked to consider the question: ***What Priority Research Issues Must Be Addressed to Determine Whether Methanol Should Be Considered a Future Drinking-Water Contaminant That Might Require Regulation?*** Issue Identification Forms were also distributed to participants. These forms asked that responses to the workshop question include: a title of 20 words or fewer; a research issue description; the importance of the issue; and a proposed resolution of the issue. The NGT Workshop comprised three distinct steps:

- Identification of research issues.
- Consolidation of research issues into major research issue areas, taking care to minimize overlap between research issue areas.
- Ranking of major research issue areas in descending order of importance by each participant.

The 18 participants identified 72 research issues during the course of the morning. Titles of these research issues were hand-lettered on large sheets of paper and posted on the workroom wall. Each issue was numbered, and the author was identified on the sheet. After lunch, participants were guided through a systematic discussion in which they consolidated the 72 individual research issues into 18 major research areas. At the conclusion of the consolidation step, each participant ranked in descending order of importance, their ten highest priority responses to the workshop question.


REY
RODRIGUEZ

PRIORITY 1

Groundwater Quality Impacts Associated with the Use of Methanol Fuels

Originators:

Alvarez on behalf of himself, Barker, Crowley, Deeb, Kavanaugh, Mehran, Rodriguez, and Tikkanen

The following research issues were consolidated under the above title:

Title: **Aesthetic Impacts to Groundwater Quality Resulting from Anaerobic Biotransformation of Methanol Releases**

Originator: Alvarez

Research Issue Description:

Some undesirable metabolites are likely to accumulate under the anaerobic conditions that would prevail at methanol-contaminated sites. These include butyric and other VFAs that would compromise taste and odor. In addition, methanol would promote the reductive dissolution of oxides and mobilize soil organic matter and other substances that could affect color. However, the geochemical and hydrogeological factors that are conducive to the accumulation of undesirable products are not well understood.

Importance of Issue:

It is important to understand how site-specific conditions will affect the fate of methanol and what constraints may be inherent in its natural attenuation. It is also important to identify what additional parameters might have to be included in site characterization protocols.

How Do You Propose Resolving This Issue?

Conduct microcosms and column experiments to characterize the rate and extent of methanol transformation to undesirable byproducts. Variables should include: electron-accepting conditions, type of aquifer material that serves are bacterial sources, methanol concentration, bicarbonate alkalinity, and trace metal availability. The literature suggests that high bicarbonate and cobalt concentrations favor the transformation of methanol to VFAs rather than to methane.

Note that this is a microbial ecology issue since these aesthetic impacts are partly related to microbial population shifts. Thus, we may have to use molecular biology tools to understand such changes in microbial community structure. This is also a hydrodynamic issue, since no biotransformations are likely to occur until methanol is dispersed and diluted below 1 percent.

Title: **Dimensions and Stability of Methanol Plumes in Groundwater**

Originator: Alvarez

Research Issue Description:

We need to improve our ability to predict the transport and fate of methanol (and its corollary pollutants) under different release scenarios and to assess what is the region and duration of influence of methanol releases on several processes and issues discussed earlier.

Importance of Issue:

Plume stability and dimensions are critical factors for risk assessment since they determine the likelihood and duration of exposure.

How Do You Propose Resolving This Issue?

- Combine laboratory modeling and field studies to assess the variability of plume length and longevity.

- Consider also unsaturated zone transport and source behavior. Variables should include soil type, moisture, spill rate, and electron-acceptor pool.

Title: **Electron Acceptor Depletion in Groundwater**

Originator: Barker

Research Issue Description:

In groundwater, methanol will biodegrade and will not, itself, persist. This will consume electron acceptors or generate an equivalent biochemical oxygen demand (BOD) via fermentation. What impacts will this plume have on drinking-water quality, and how can it be identified and attributed?

Importance of Issue:

When groundwaters are driven anaerobic, certain metals (Fe, Mn, etc.) become mobile and so can be leached from aquifer solids and delivered to wells. Also, organic contaminants, such as BTEX, may become more persistent. The polluter should be responsible for the consequences of the electron acceptor/high BOD plume due to methanol contamination of groundwater. How can the polluter anticipate and define their responsibility? Without information, a polluter could be held responsible for too narrow a range of contaminants (i.e., methanol only) or too broad a range of contaminants (i.e., everything in the well field).

How Do You Propose Resolving This Issue?

- Review redox relationships and identify metals mobilized under anaerobic conditions.
- Develop and use contaminant transport models to assess formation and the persistence of anaerobic plume and metal mobilization (Molson and Barker at the University of Waterloo, and Mayer and Smith at the University of British Columbia, plus others).
- Conduct controlled-release field experiments to demonstrate these processes and evaluate/improve model performance:
  - At Borden, Ontario: Barker at the University of Waterloo; Powers at Clarkson University; and Rice at Lawrence Livermore National Laboratories.
  - At Vandenberg, California: Mackay at the University of California, Davis; and Reinhard at Stanford University.

Title: **Field-Based Research: Controlled Releases at Virgin and Former Gasoline Release Sites**

Originator: Crowley

Research Issue Description:

Perform controlled releases at a variety of field sites to determine the fate and transport of methanol, its additives, and its effects on preexisting petroleum contamination.

Importance of Issue:

High – Methanol would likely be stored in USTs or ASTs at the location of current gasoline stations and other facilities. Need to understand how releases will affect groundwater resources and preexisting petroleum contamination.

How Do You Propose Resolving This Issue?

- Fund research.
- Identify possible additives and byproducts.
- Evaluate studies conducted at the University of Waterloo, McKay; LLNL; U.C. Davis, and elsewhere.
- Bring together a multidisciplinary team with expertise in laboratory, modeling, and field study.

Title: **Environmental Issues Related to In-Tank Flammability of Methanol**

Originator: Deeb

Research Issue Description:

Evaluate the environmental issues associated with the addition of unknown chemicals to M100 to increase the flammable limit.

Importance of Issue:

- Methanol has a very low flammable limit. It can burn at low temperatures if an ignition source is introduced accidentally.
- Additives are being considered to address M100 potential performance and health issues, including luminosity, taste, color, and odor. An additive may be needed to increase the flammable limit.
- How does the risk of M100 change with the use of such additives?

How Do You Propose Resolving This Issue?

Laboratory- and pilot-scale studies may be used to evaluate the environmental fate and transport of these additives.

Studies are also needed to evaluate the toxicity of such additives.

Title: **Fate and Transport of Additives in Fuel-Grade Methanol**

Originator: Kavanaugh

Research Issue Description:

Unknown fate and transport issues regarding additives must be added to methanol because of safety concerns. Issues include:

- Identification of additives.
- Physical/chemical characteristics of additives.
- Biotic/abiotic transformations.
- Byproducts of transformations.
- Ecological effects.
- Human health effects.

Importance of Issue:

With concern over other additives in solvents (e.g, 1, 4 – dioxane), widespread use of methanol as a fuel will depend on a comprehensive understanding of the fate and transport of additives.

How Do You Propose Resolving This Issue?

Conduct a series of specific research projects addressing fate and transport issues for the most widely used additives. Modeling, laboratory- and field studies will be needed.

Title: **Hydrobiogeochemical Behavior of Methanol Gasoline Mixture in the Subsurface Environment**

Originator: Mehran

Research Issue Description:

Hydrogeochemical and biological behavior of methanol/gasoline mixture in the vadose zone and groundwater is complex. Fate and transport parameters would provide a sound basis for extent of investigation, remediation, and regulatory development.

Importance of Issue:

Lack of information may lead to unreasonable regulatory standards and cleanup levels.

How Do You Propose Resolving This Issue?

A literature review to compare the characteristics of known additives/gasoline mixture with methanol/gasoline mixture is the first step.

The second step is to conduct comprehensive bench-scale experiments and pilot tests. The Waterloo Group will be qualified to do the field-scale pilot tests.

Title: **Evaluate Conditions Conducive to the Production of Formic Acid**

Originator: Mehran

Research Issue Description:

Formic acid is the cause of the toxicity of methanol; therefore, the formation of formic acid in the subsurface environment and during various remediation processes is crucial to its production and/or preventing exposure.

Importance of Issue:

The formation of formic acid is important to human health and the environment.

How Do You Propose Resolving This Issue?

Bench-scale and pilot-scale tests can be conducted at facilities that have the monitoring and analytical capabilities. Also, remedial contractors that operate treatment systems can monitor the formation of formic acid.

Title: **Mandate Methanol Monitoring at UST Sites That Store Methanol at Vulnerable Drinking Water Sources**

Originator: Rodriguez

Research Issue Description:

Based on established action levels from health effects studies, the monitoring of methanol should be mandated at sites using and storing methanol at vulnerable receptors (drinking-water sources).

Importance of Issue:

Before the use of methanol was approved as a gasoline additive, analytical methods with sufficiently low detection limits should be in place. The next step would be to have a system in place to require monitoring water supplies.

How Do You Propose Resolving This Issue?

- Review acute and chronic levels.
- Identity analytical methods to achieve health-risk levels.
- Propose detection limits that can be achieved at existing laboratories consistent with health risks.
- Mandate the monitoring of UST sites and vulnerable drinking-water sources.

Title: **Health Effects, Taste, and Odor Considerations of Methanol Additives Should Contamination of a Water Supply Occur with a Methanol Release**

Originator: Tikkanen

Research Issue Description:

Methanol is not sufficiently repugnant to prevent accidental or intentional consumption or exposure (i.e., inhalation/ingestion). Additives may be required to make it so. What are the safety, taste, odor, and health effects of these additives with regard to methanol-based fuel contamination in a water supply?

Importance of Issue:

Health effects, taste, and odor issues must be addressed as water contamination with odor-causing chemicals would be unacceptable to the drinking water consumers. Health effects, taste and odor, and the fate and transport of the additives must be addressed before they can be used.

How Do You Propose Resolving This Issue?

The California Fuel Cell Partnership in Sacramento, California, is a consortium of stakeholders (i.e., producers involved in the development and use of fuel cells, which include such stakeholders as automakers and fuel producers [hydrogen, methanol, gasoline, etc.]). The research suggested could be piggybacked with the research and development being done by the Partnership and the University of California, Davis, which is located nearby. The California Air Resources Board is heavily involved in the Partnership. Money is available.

Title: **Track the Fate and Transport of Methanol Processing (Burning or Reforming) Byproducts and Releases to the Environment, Particularly to Water Supplies**

Originator: Tikkanen

Research Issue Description:

When methanol is used as a fuel in a fuel cell, unless the reforming (processing) process is 100 percent efficient, there may be a waste stream. What will happen to that waste stream? Will it be stored or used for other fueling purposes?

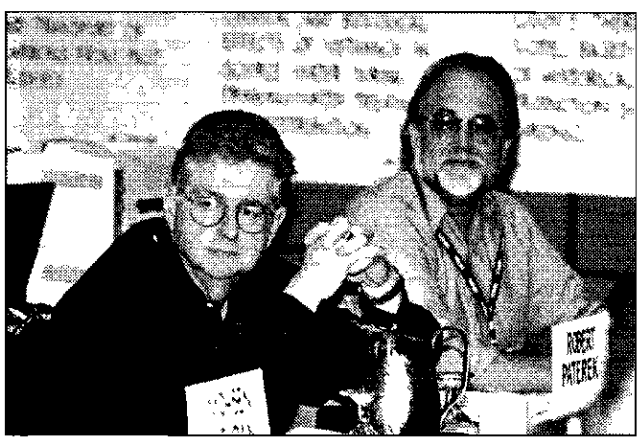
Importance of Issue:

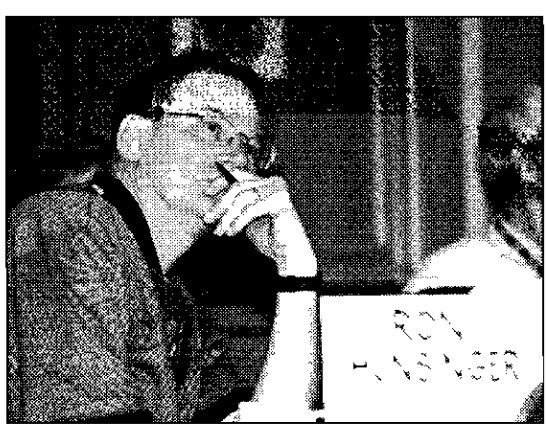
Methanol processing byproducts must be used up, stored up, or disposed of. If stored (e.g., in tanks) or disposed of, there may be releases to the environment (e.g., water, air, soil).

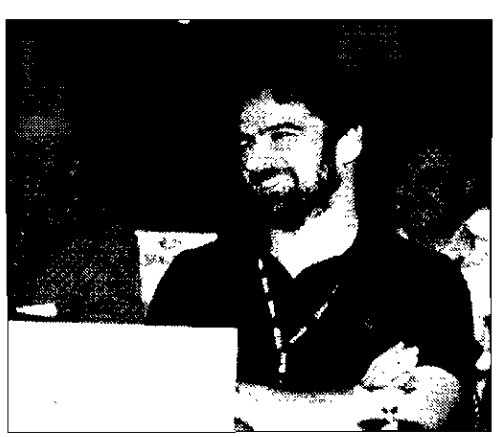
How Do You Propose Resolving This Issue?

- Determine processing byproducts through laboratory studies, field studies, and literature search.
- Do fate and transport studies for the methanol processing byproducts, along with methanol, additives, and degradation byproducts.
- Determine the treatability of these byproducts.
- Work with the California Fuel Cell Partnership and California Air Resource Board to piggyback research efforts.


ROY
HERNDON







PRIORITY 2

Develop Sampling and Trace-Analytical Methods and Protocols Useful for Assessments of the Occurrence of Methanol and Associated Analytes

Originators:

Spalding on behalf of himself, Davidson, Herndon, Hunsinger, Paterek, and Rice

The following research issues were consolidated under the above title:

Title: **Develop Methodologies and Field Sites to Evaluate the Environmental Fate of Methanol and Associated Compounds**

Originator: Spalding

Research Issue Description:

- Analytical development of trace method for methanol in the laboratory.
- Environmental sites are required to test degradation hypothesis in air, surface water, and groundwater.
- Toxicity effects on aquatic ecosystems.

Importance of Issue:

Anaerobic conditions can liberate metals into aqueous solution; however, the same condition can improve groundwater in high-nitrate regions through denitrification.

How Do You Propose Resolving This Issue?

Groundwater:

- Install LUSTs in shallow groundwater areas or use existing tanks.
- Inject isotopically labeled analytes to detect the breakthrough of methanol and associated compounds

Laboratory: Development may include derivitization, which will complicate the process. Much more literature analysis will be necessary.

Surface Water: Simulated stream and lake studies.

Title: **Review of Monitoring Well and Field Instrument Designs**

Originator: Davidson

Research Issue Description:

We have been using standard well materials for a decade or two, but when we consider M85 or M100, we need to reconsider the compatibility and adequacy of the field monitoring, sampling, and measurement devices. Do our physical, electrical, and chemical devices still work effectively?

Importance of Issue:

- It is an echo back to 15 years ago: Poly vinyl chloride (PVC) versus stainless steel for monitoring wells.
- Sample vial septums, photo ionization detectors (PIDs), field gas chromatographs (GCs), well materials, bentonite seals, bailers, gloves, and personal protective equipment – all these need to be considered for compatibility with methanol.

How Do You Propose Resolving This Issue?

- Review available literature on this topic.
- Contact instrument device manufacturers and well materials manufacturers and ask them to consider methanol compatibility with their products.

Title: **Cost Implications of Implementing Monitoring Programs for Methanol and Associated Compounds**

Originator: Herndon

Research Issue Description:

In considering whether methanol and its associated additives and potential byproducts should be regulated in drinking water, the practicality and cost impacts of implementing appropriate sampling and analysis protocols should be assessed.

Importance of Issue:

The question of whether methanol and associated potential contaminants should be regulated should be evaluated as to whether it is technically feasible to perform effective monitoring of these compounds across a broad range of water-supply systems nationwide. The degree of technical feasibility of implementing monitoring programs is directly related to cost.

How Do You Propose Resolving This Issue?

Through research studies proposed in other issues, sampling and analysis protocols and estimated costs can be developed and refined. Protocols and techniques that can be widely employed should involve collaboration between environmental data collection experts, water-system operators, regulatory compliance staff, and analytical laboratory personnel.

Title: **Develop and Adopt Valid Sampling and Analysis and Establish a Database to Sbare Information**

Originator: Hunsinger

Research Issue Description:

Establish analytical and sampling methods for methanol, byproducts, and associated chemical and biological parameters associated with methanol fuels contamination of water. The method adopted must reflect health, aesthetic, and process concerns.

The data should be stored in a comprehensive database that allows sharing a valid data.

Importance of Issue:

Inaccurate data and unshared or unsharable data make progress in knowledge difficult.

How Do You Propose Resolving This Issue?

Coordinate and support (financial and technical) methods and database by an umbrella organization.

Title: **Ultrasensitive Molecular Tools to Determine the Presence and Bioimpact of Methanol-Contaminated Matrices (Vadose, Unsaturated, Surface Water)**

Originator: Paterek

Research Issue Description:

- Methylotrophic bacteria detection and activity:
  - aerobic: methylotrophic bacteria
  - anaerobic: methanogens

- Tools:
  - quorum-sensing compounds
  - specific cofactors or enzymes: F_{420} or coenzyme (C_oM) in methanogens; and methane monooxygenase

Importance of Issue:

Real-time sensors for presence and biological transformation.

How Do You Propose Resolving This Issue?

- Identify molecular tools for key microorganisms.
- Evaluate sensors in the lab and field.
- Engineer continuous and event biosensors.

Title: **Molecular Tools to Characterize Changes in Subsurface Microbial Community Ecology Associated with a Methanol Release**

Originator: Rice

Research Issue Description:

Methanol could decrease the relative populations of anaerobic hydrocarbon-degrading bacteria. Laboratory research with ethanol indicate that methanol, which is generally more degradable than BTEX compounds under anaerobic conditions, may disproportionately support the growth of bacteria that are not anaerobic hydrocarbon degraders.

Importance of Issue:

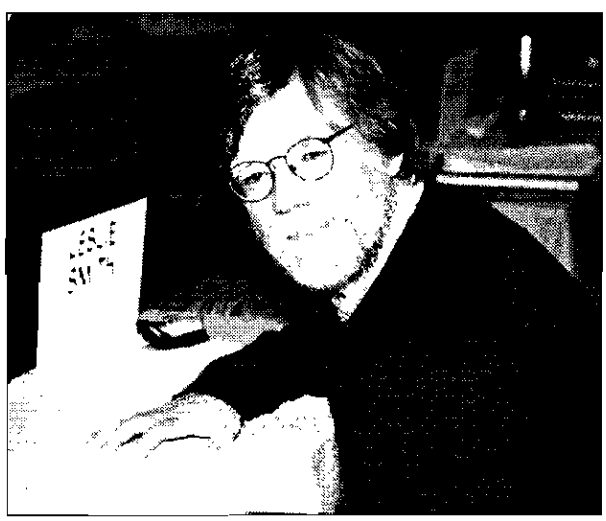
It may be anticipated that methanol may be dispensed at typical gas stations that are still serving conventional gasoline and that there will likely be fuel hydrocarbons present in the subsurface at these fueling stations. Microbially mediated processes will likely dominate the fate and transport of methanol and gasoline components in the presence of methanol. Changes in microbial ecology may change the biodegradation rates of both methanol and any associated fuel hydrocarbons. These changes could increase fuel hydrocarbon plume sizes and/or result in the degradation of water quality through increased taste and odor problems.

How Do You Propose Resolving This Issue?

First, conduct a series of laboratory microcosm experiments, similar to those conducted for ethanol. These experiments should examine kinetics and microbial population changes using molecular approaches, such as gene probes and DNA analysis.

Second, to evaluate whether laboratory microcosm results and characterization techniques can be extrapolated to actual releases, a molecular ecology approach should be used to characterize the spatial and temporal changes in subsurface microbial communities as a result of controlled methanol release experiments.

Dr. Harry Beller and Dr. Staci Kane, LLNL, have demonstrated the utility of using novel DNA-based methods to address the key factors that influence populations of subsurface microbial communities.



PRIORITY 3

Effects of Methanol on the Fate and Transport of Co-occurring Organic Contaminants: Dissolved, Sorbed, Sequestered, and Risidualized

Originators:

Weber/Deeb on behalf of themselves, Barker, Crowley, Rice, Smith, and Spalding

The following research issues were consolidated under the above title:

Title: **Desequestration and Mobilization of Previously Immobilized Hydrophobic Contaminants**

Originator: Weber

Research Issue Description:

Releases of M85 and/or M100 will likely occur at the same sites and under similar circumstances as prior (historic) releases of petroleum-based and/or solvent-related contaminants. The more hydrophobic of such compounds are known to be sequestered by certain types of soils and under certain types of circumstances. M85 and M100 wavefronts will move rapidly under saturated flow conditions and may "sweep" otherwise immobilized contaminants toward water-supply sources.

Importance of Issue:

Potential increases in the organic contamination of water sources by such hydrophobic families of compounds as PAHs and halogenated aromatics may result from their desequestration by methanol. The lack of information regarding the potential for, and consequences of, such behavior will logically raise concern and may, in turn, lead to regulation.

How Do You Propose Resolving This Issue?

Critically and strategically designed laboratory investigations of representative soil-contaminant-condition matrices to assess desequestration potentials and related release and transport profiles to serve as bases for migration model(s) are required. These should be determined for an appropriate suite of wavefront conditions (e.g., concentration peak, mass burden, velocity, and residence time) and for an appropriate variety of soils having different types of organic matter matrices (e.g., degree of diagenetic alteration, condensation, and carbon-oxygen atomic ratios). There are two or three research groups in the United States having particularly suitable experience and qualifications.

Title: **Impact of Methanol on the Subsurface Fate and Transport of Hydrocarbons from Past Fuel Releases**

Originator: Deeb

Research Issue Description:

Evaluate the impact of methanol on the subsurface behavior of other hydrocarbons at fuel spill sites, mainly BTEX compounds and MTBE.

Importance of Issue:

Methanol fuel will most probably be sold at conventional gasoline stations. Methanol is extremely biodegradable under a range of environmental conditions (aerobic and anaerobic). Since methanol is rapidly biodegraded, electron acceptors may become depleted at source zones, leading to anaerobic conditions. This, in turn, may lead to the elongation of BTEX and MTBE plumes since both BTEX and MTBE are most rapidly and efficiently degraded in the presence of oxygen.

How Do You Propose Resolving This Issue?

Laboratory studies are needed to quantify the impact of methanol on BTEX and MTBE biodegradation rates.

Laboratory studies should be followed by modeling studies, as well as field studies to better understand this process in the environment.

Title: **Cosolubilization of Petroleum Hydrocarbons**

Originator: Barker

Research Issue Description:

When neat methanol is spilled into residual hydrocarbon contamination (residual and free product), the enhanced solubility and mobility of hydrocarbons may occur at least locally in the source zone. Is this process significant for receptor wells some hundreds of feet away?

Importance of Issue:

Alcohol cosolubilization is well understood and well documented. What is not understood is how significant this is in real porous media at real sites. Further, given the short persistence of methanol in groundwater, this cosolubilization may have only a local impact and may not significantly increase the risk of BTEX showing up in wells. Rather, the creation of anaerobic conditions may be a bigger risk factor in BETX persistence. How significant is cosolubilization near sources, and is it significant relative to the persistence of BTEX in plumes driven anaerobic by methanol and its fermentation products? The lack of information will most likely only result in an ineffective direction of the research efforts, but may raise the need for additional site monitoring (good?).

How Do You Propose Resolving This Issue?

Conduct controlled-release experiments and methanol release at existing sites of gasoline contamination. Combination of Borden (Powers, Rixey, Chatziz and Barker, University of Waterloo), with quantifiable mass balances, as well as less-controlled experiments in large-scale lab systems (Paul Johnston, Arizona; Traytnek, Oregon Graduate Institute; and field sites (Mckay, Powers, and perhaps others). Also follow the plumes!

Title: **Field-Based Research: Controlled Releases at Virgin and Former Gasoline Release Sites**

Originator: Crowley

Research Issue Description:

Perform controlled releases at a variety of field sites to determine the fate and transport of methanol, its additives, and its effects on preexisting petroleum contamination.

Importance of Issue:

High – Methanol would likely be stored in USTs or ASTs at the location of current gasoline stations and other facilities. Need to understand how releases will affect groundwater resources and preexisting petroleum contamination.

How Do You Propose Resolving This Issue?

- Fund research.
- Identify possible additives and byproducts.
- Evaluate studies conducted at the University of Waterloo, McKay; LLNL; U.C. Davis, and elsewhere.
- Bring together a multidisciplinary team with expertise in laboratory, modeling, and field study.

Title: **Molecular Tools to Characterize Changes in Subsurface Microbial Community Ecology Associated with a Methanol Release**

Originator: Rice

Research Issue Description:

Methanol could decrease the relative populations of anaerobic hydrocarbon-degrading bacteria. Laboratory research with ethanol indicate that methanol, which is generally more degradable than BTEX compounds under anaerobic conditions, may disproportionately support the growth of bacteria that are not anaerobic hydrocarbon degraders.

Importance of Issue:

It may be anticipated that methanol may be dispensed at typical gas stations that are still serving conventional gasoline and that there will likely be fuel hydrocarbons present in the subsurface at these fueling stations. Microbially mediated processes will likely dominate the fate and transport of methanol and gasoline components in the presence of methanol. Changes in microbial ecology may change the biodegradation rates of both methanol and any associated fuel hydrocarbons. These changes could increase fuel hydrocarbon plume sizes and/or result in the degradation of water quality through increased taste and odor problems.

How Do You Propose Resolving This Issue?

First, conduct a series of laboratory microcosm experiments, similar to those conducted for ethanol. These experiments should examine kinetics and microbial population changes using molecular approaches, such as gene probes and DNA analysis.

Second, to evaluate whether laboratory microcosm results and characterization techniques can be extrapolated to actual releases, a molecular ecology approach should be used to characterize the spatial and temporal changes in subsurface microbial communities as a result of controlled methanol release experiments.

Dr. Harry Beller and Dr. Staci Kane, LLNL, have demonstrated the utility of using novel DNA-based methods to address the key factors that influence populations of subsurface microbial communities.

Title: **Time-Rate of Recovery of Microbial Biotransformation of Methanol/BTEX Following Exposure to High Methanol Concentrations**

Originator: Smith

Research Issue Description:

At sites with shallow water table or a continuous leak of methanol, high-aqueous phase concentrations of methanol seem possible. Metabolic activity and the viability of the microbial population will be severely restricted until dispersive processes reduce concentrations below the inhibition threshold. The rate of recovery of the population is uncertain, but key to the eventual degradation of methanol in groundwater.

Importance of Issue:

Recovery of the microbial population will be a key factor in reducing methanol concentrations to a nominal drinking-water standard.

How Do You Propose Resolving This Issue?

Column experiments are necessary initially, but we will need field experiments (pure-phase methanol release into aquifers) to understand and document the rate of recovery of biotransformation capability.

Title: **Degree to Which BTEX Site Management/Remediation Is Complicated by Methanol Leaks**

Originator: **Smith**

Research Issue Description:

Cosolubilization may increase benzene concentrations from tens of milligrams per liter (mg/L) to hundreds of mg/L in the core of the BTEX plume.

Importance of Issue:

Contaminated site management.

How Do You Propose Resolving This Issue?

Incorporate this issue within the framework of risk assessment for site management.

Title: **Methanol Impacts on Leaching of Herbicides and Soil Contaminants to Surface Waters and Groundwater at Distribution Sites**

Originator: Spalding

Research Issue Description:

Test the acute/chronic toxicity of methanol and associated leaches on surface water. How is toxicity affected by other stream contaminants – atrazine, pesticide degradates in uptake, and toxicity?

Importance of Issue:

May be important if releases occur with drainage to surface water or in areas where groundwater contaminants enter gaining streams. This is an important issue during spring flush.

How Do You Propose Resolving This Issue?

Use simulated streams where different species can be introduced and changes in their life cycle can be interpreted under methanol/acetamide/triazine mixtures.

PRIORITY 6

Evaluate Methanol in Surface Water, Drinking Water, and Groundwater at Petroleum Sites, Methanol Sites, and in the Ambient Environment

Originators:

Davidson on behalf of himself, Alvarez, Crowley, Hunsinger, and Spalding

The following research issues were consolidated under the following title:

Title: **Compile Field Data on Methanol Spills**

Originator: Davidson

Research Issue Description:

- We need to know what concentrations of methanol occur in the groundwater and soil (if, indeed, we can find any methanol in the field), and how those methanol concentrations change with time.
- We need to document methanol's impact on inorganic parameters (dissolved oxygen, etc.).

Importance of Issue:

There seems to be very little field knowledge or data publicly available about accidental methanol releases.

How Do You Propose Resolving This Issue?

- Identify any and all known spills of M85 and M100 methanol by manufacturers and users; review their data set; and consider additional field data collection at those sites.

- Investigate subsurface at M85 and M100 UST and AST sites (there are some out there, e.g., Fortier, Louisiana, site) by collecting soil and groundwater samples and analyzing them for methanol concentrations and related inorganics.

Title: **Dimensions and Stability of Methanol Plumes in Groundwater**

Originator: Alvarez

Research Issue Description:

We need to improve our ability to predict the transport and fate of methanol (and its corollary pollutants) under different release scenarios and to assess what is the region and duration of influence of methanol releases on several processes and issues discussed earlier.

Importance of Issue:

Plume stability and dimensions are critical factors for risk assessment since they determine the likelihood and duration of exposure.

How Do You Propose Resolving This Issue?

- Combine laboratory modeling and field studies to assess the variability of plume length and longevity.

- Consider also unsaturated zone transport and source behavior. Variables should include soil type, moisture, spill rate, and electron-acceptor pool.

Title: **Understand the Transient Production of Methanol at Existing Fuel Release Sites**

Originator: Crowley

Research Issue Description:

Methanol has been sporadically observed at high concentrations at existing fuel release sites. An evaluation of possible pathways for methanol production from BTEX and hydrocarbon degradation may shed light on the background concentrations that can be expected at sites. In addition, such an understanding of the subsurface geochemistry may prove useful in determining ambient natural conditions for lab and bench tests. It would also help in understanding results at field methanol release sites.

Importance of Issue:

High.

How Do You Propose Resolving This Issue?

- Evaluate existing methanol occurrence data at fuel sites.
- Perform additional methanol testing at a variety of sites.
- Gain an understanding of site geochemical conditions.
- Evaluate biological pathways for methanol production from BTEX and hydrocarbon degradation.

Title: **Develop and Adopt Valid Sampling and Analysis and Establish of a Database to Share Information**

Originator: Hunsinger

Research Issue Description:

Establish analytical and sampling methods for methanol, byproducts, and associated chemical and biological parameters associated with methanol fuels contamination of water. The method adopted must reflect health, aesthetic, and process concerns.

The data should be stored in a comprehensive database that allows sharing a valid data.

Importance of Issue:

Inaccurate data and unshared or unsharable data make progress in knowledge difficult.

How Do You Propose Resolving This Issue?

Coordinate and support (financial and technical) methods and database by an umbrella organization.

Title: **Background Levels of Methanol in Surface Water and Groundwater**

Originator: Spalding

Research Issue Description:

With trace methods, determine trace concentrations of methanol in pristine environments.

Importance of Issue:

This is the starting point in most investigations.

How Do You Propose Resolving This Issue?

Test for methanol levels in differently constructed statewide monitoring wells in several regions of the country. May need to employ specialized extraction techniques to determine ambient levels in groundwater, surface water, and municipal waters

PRIORITY 7

Surface Water Quality Impacts Associated with the Use of Methanol Fuels

Originators:

Tikkanen on behalf of herself, Deeb, and Kavanaugh

The following research issues were consolidated under the following title:

Title: **Aesthetic Impacts to Surface Water Quality Resulting from Methanol-Based Fuel Releases**

Originator: Tikkanen

Research Issue Description:

Some undesirable methanol fuel-based byproducts or additives are likely to accumulate under conditions that would prevail at methanol-contaminated sites. These could include noticeable taste and odor chemicals that could contaminate surface water.

Importance of Issue:

It is important to understand how site-specific conditions will affect the fate of these chemicals and what constraints may be inherent in their natural attenuation.

How Do You Propose Resolving This Issue?

- Laboratory studies, field studies, occurrence studies in surface-water supplies (reservoirs).
- Work with existing groups, such as the California Fuel Cell Partnership and California Air Resources Board.

Title: **Impacts of Methanol on Surface Drinking-Water Resources**

Originator: Deeb

Research Issue Description:

Evaluate and model the fate of methanol in surface water (rivers, lakes, reservoirs) and its impact on water quality in these bodies.

Importance of Issue:

The expected growth/demand for methanol as a fuel in fuel-cell vehicles will result in its increased transportation by barge and rail. The major loss mechanisms of methanol in surface water bodies are most likely volatilization and biodegradation.

It is critical to evaluate the impact of a large volume of methanol on the water quality of a surface water body (especially a closed aquatic system, such as a lake). Mainly, the rapid biodegradation rate of methanol could lead to the depletion of oxygen in an aquatic system and the rapid growth of microorganisms and algae. The depletion of oxygen from these processes could lead to fish kills, as well as bad taste and odor problems, and the potential accumulation of potentially harmful metabolic byproducts (e.g., formate, formaldehyde).

How Do You Propose Resolving This Issue?

- Lab and modeling studies quantifying oxygen demand, biodegradation rates, volatilization rates, etc. are needed.
- Past studies involving releases of alcohols (in general) in the environment should be researched.
- Bench-scale and field-scale studies to evaluate the long-term impacts on aquatic systems are needed.

Title: **Fate and Transport of Additives in Fuel-Grade Methanol**

Originator: Kavanaugh

Research Issue Description:

Unknown fate and transport issues regarding additives must be added to methanol because of safety concerns. Issues include:

- Identification of additives.
- Physical/chemical characteristics of additives.
- Biotic/abiotic transformations.
- Byproducts of transformations.
- Ecological effects.
- Human health effects.

Importance of Issue:

With concern over other additives in solvents (e.g, 1, 4 – dioxane), widespread use of methanol as a fuel will depend on a comprehensive understanding of the fate and transport of additives.

How Do You Propose Resolving This Issue?

Conduct a series of specific research projects addressing fate and transport issues for the most widely used additives. Modeling, laboratory- and field studies will be needed.

Title: **Health Effects, Taste, and Odor Considerations of Methanol Additives Should Contamination of a Water Supply Occur with a Methanol Release**

Originator: Tikkanen

Research Issue Description:

Methanol is not sufficiently repugnant to prevent accidental or intentional consumption or exposure (i.e., inhalation/ingestion). Additives may be required to make it so. What are the safety, taste, odor, and health effects of these additives with regard to methanol-based fuel contamination in a water supply?

Importance of Issue:

Health effects, taste, and odor issues must be addressed as water contamination with odor-causing chemicals would be unacceptable to the drinking water consumers. Health effects, taste and odor, and the fate and transport of the additives must be addressed before they can be used.

How Do You Propose Resolving This Issue?

The California Fuel Cell Partnership in Sacramento, California, is a consortium of stakeholders (i.e., producers involved in the development and use of fuel cells, which include such stakeholders as automakers and fuel producers [hydrogen, methanol, gasoline, etc.]). The research suggested could be piggybacked with the research and development being done by the Partnership and the University of California, Davis, which is located nearby. The California Air Resources Board is heavily involved in the Partnership. Money is available.

Title: **Track the Fate and Transport of Methanol Processing (Burning or Reforming) Byproducts and Releases to the Environment, Particularly to Water Supplies**

Originator: Tikkanen

Research Issue Description:

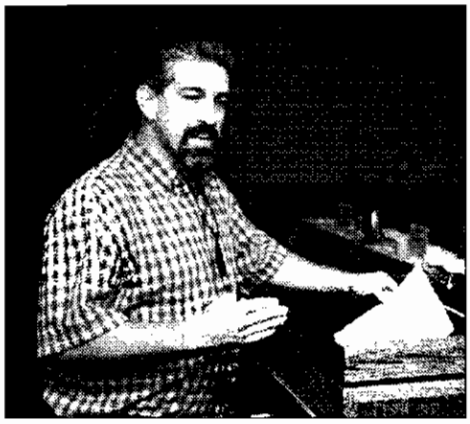
When methanol is used as a fuel in a fuel cell, unless the reforming (processing) process is 100 percent efficient, there may be a waste stream. What will happen to that waste stream? Will it be stored or used for other fueling purposes?

Importance of Issue:

Methanol processing byproducts must be used up, stored up, or disposed of. If stored (e.g., in tanks) or disposed of, there may be releases to the environment (e.g., water, air, soil).

How Do You Propose Resolving This Issue?

- Determine processing byproducts through laboratory studies, field studies, and literature search.
- Do fate and transport studies for the methanol processing byproducts, along with methanol, additives, and degradation byproducts.
- Determine the treatability of these byproducts.
- Work with the California Fuel Cell Partnership and California Air Resource Board to piggyback research efforts

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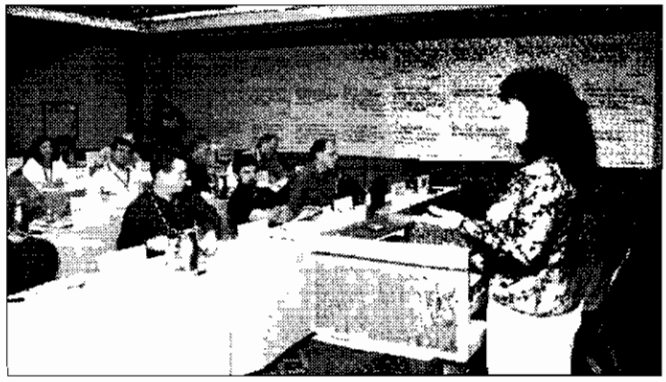


PRIORITY 8

Effects of Methanol Fuel Components and Byproducts on Drinking-Water Treatment and Distribution

Originators:

Hunsinger on behalf of himself, Alvarez, Crowley, Deeb, and Rodriguez

The following research issues were consolidated under the following title:

Title: **Chemical and Biological Effects of Methanol Fuels Contamination in Drinking-Water Treatment and Distribution**

Originator: Hunsinger

Research Issue Description:

Explore the health-related, aesthetic, and process-related effects of methanol fuels and byproducts as contaminants on water quality, including:

- Methanol byproducts.
- Byproducts produced during the disinfection/oxidation process.
- Biological effects on filters.
- Nutrients for distribution-system bacteria.
- Interaction with the nitrification processes in the distribution system.

Importance of Issue:

Drinking water is the primary pathway for the ingestion of methanol fuel components.

How Do You Propose Resolving This Issue?

Conduct literature surveys, monitoring, bench studies, and pilot-plant studies.

Title: **Effects of Methanol on the Biological Stability of Drinking Water**

Originator: Alvarez

Research Issue Description:

Methanol is likely to stimulate microbial growth and related biofouling problems. Is there a greater need for disinfection? Could residual methanol or its byproducts contribute to THM formation during chlorination? Are there any ties to NDMA formation in distribution systems?

Importance of Issue:

One concern is the increased difficulty to treat and distribute high-quality drinking water over the long term.

How Do You Propose Resolving This Issue?

Conduct pilot studies with small water treatment systems.

Title: **Effects of Methanol on Existing Drinking-Water Treatment Processes/Systems**

Originator: Crowley

Research Issue Description:

Methanol fuels and additives at low levels could affect existing drinking-water treatment processes and create undesirable byproducts or negatively affect existing processes. These low levels may be acceptable from a health standpoint, but could cause other undesirable effects in drinking-water treatment process.

Importance of Issue:

High.

How Do You Propose Resolving This Issue?

- Literature study.
- Pilot testing.
- Testing at existing water-treatment plants.

Title: **Taste and Odor Studies for Methanol, Additives, and Expected Byproducts**

Originator: Crowley

Research Issue Description:

Need to have definitive taste and odor studies of methanol in drinking water and its additives and byproducts. Taste and odor could be a big issue, particularly for organic byproducts.

Importance of Issue:

High.

How Do You Propose Resolving This Issue?

Municipal water districts and other water districts could coordinate these studies in accordance with standard methods.

Title: **Impacts of Methanol on Surface Drinking-Water Resources**

Originator: Deeb

Research Issue Description:

Evaluate and model the fate of methanol in surface water (rivers, lakes, reservoirs) and its impact on water quality in these bodies.

Importance of Issue:

The expected growth/demand for methanol as a fuel in fuel-cell vehicles will result in its increased transportation by barge and rail. The major loss mechanisms of methanol in surface water bodies are most likely volatilization and biodegradation.

It is critical to evaluate the impact of a large volume of methanol on the water quality of a surface water body (especially a closed aquatic system, such as a lake). Mainly, the rapid biodegradation rate of methanol could lead to the depletion of oxygen in an aquatic system and the rapid growth of microorganisms and algae. The depletion of oxygen from these processes could lead to fish kills, as well as bad taste and odor problems, and the potential accumulation of potentially harmful metabolic byproducts (e.g., formate, formaldehyde).

How Do You Propose Resolving This Issue?

- Lab and modeling studies quantifying oxygen demand, biodegradation rates, volatilization rates, etc. are needed.
- Past studies involving releases of alcohols (in general) in the environment should be researched.
- Bench-scale and field-scale studies to evaluate the long-term impacts on aquatic systems are needed.

Title: **Cost-Effective Treatment of Large Volumes of Water Contaminated with Low Levels of Methanol**

Originator: Deeb

Research Issue Description:

Evaluate conventional and innovative technologies for the removal of low levels of methanol from large volumes of water in a cost-effective manner.

Importance of Issue:

- Low levels of methanol may reach drinking-water supply wells. Methanol is not currently regulated as a drinking-water contaminant.
- Analytical techniques cannot accurately or cost effectively detect methanol at levels below 50 ppb.

How Do You Propose Resolving This Issue?

- Technologies that are not traditionally used for the treatment of water contaminated with gasoline should be evaluated, such as advanced oxidation processes, biofilters, etc. Pilot-scale studies are needed to evaluate a range of technologies.
- Public acceptance of nontraditional treatment methods for drinking-water applications should be evaluated.

Title: **How Will Methanol Affect Existing Groundwater or Surface-Water Treatment Systems?**

Originator: Rodriguez

Research Issue Description:

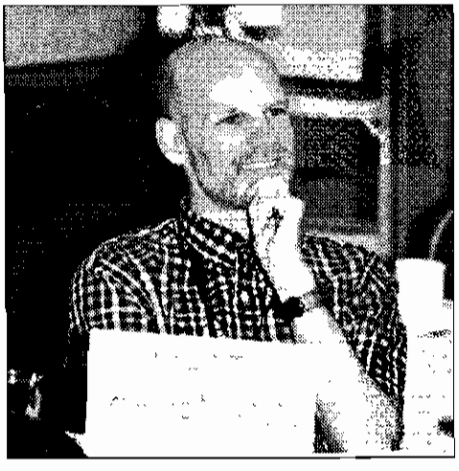
Existing systems that rely on enhanced biodegradation may be affected by the preferential breakdown of methanol over ethers, BTEX, or other alcohols. The impacts may be evaluated through laboratory or field research.

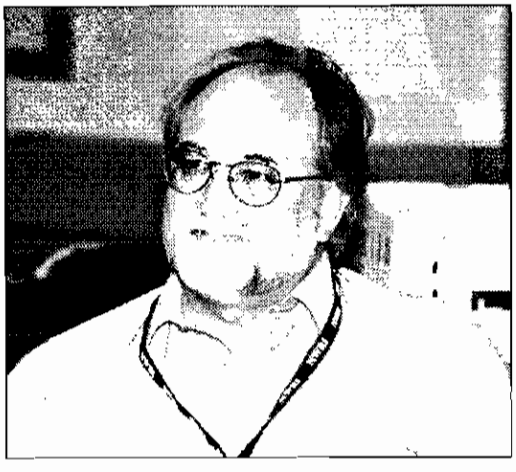
Importance of Issue:

Potential impacts to existing treatment systems may lead to the replacement of the treatment process due to methanol effects.

How Do You Propose Resolving This Issue?

- Microcosm studies.
- Pilot testing.





PRIORITY 9

Methanol As a Potential Groundwater Contaminant: A Compendium of the History of Use, Regulation, and Research

Originators:

Hagemann on behalf of himself, Barker, and Rice

The following research issues were consolidated under the following titles:

Title: **Methanol as a Potential Groundwater Contaminant: A Compendium of the History of Use, Regulation, and Research**

Originator: Hagemann

Research Issue Description:

Comprehensive review of methanol/groundwater issue. Include production (past and projected), distribution infrastructure, regulatory, research (fate and transport), major spill incidents, and the need for further research.

Importance of Issue:

Must learn from history. Think of how different the MTBE/groundwater issue would be today if we had conducted joint research efforts in the late 1970's.

How Do You Propose Resolving This Issue?

Use the participants at this workshop!

Title **Prioritize Groundwater Research**

Originator: Barker

Research Issue Description:

Given some process understanding, some experience at "real" sites, and limited controlled-field experience, how can we effectively design research?

Importance of Issue:

If controlled field tests are to be undertaken, they must be effectively designed. They should include as many issues as possible, but the issues must be of high priority. They may also be used to demonstrate understanding and remedial technologies.

How Do You Propose Resolving This Issue?

Form research teams integrated through real-world experience, theory/lab experts, and controlled field testers. Focus the design of controlled field experiments to best use this intensive research. Involve the research team throughout.

Title: **Comparative Evaluation of Ethanol and Methanol Environmental Impacts**

Originator: Rice

Research Issue Description:

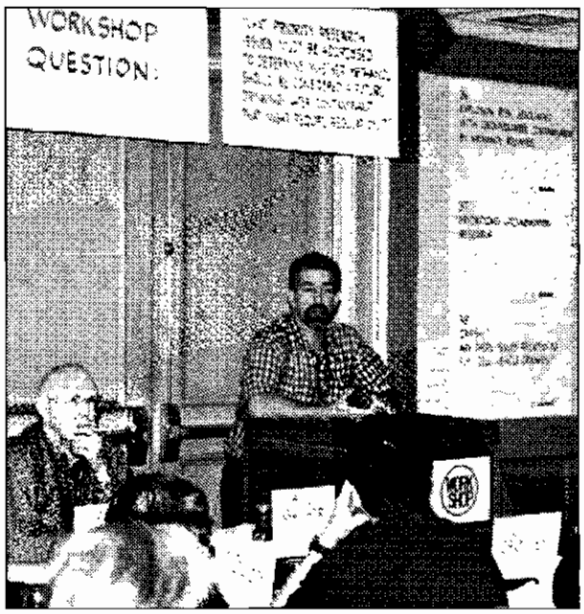
The research on ethanol groundwater impacts seems to be more advanced than for methanol. A cross-mapping study is needed that identifies areas where ethanol research can be confidently used to reduce uncertainty regarding methanol impacts and where methanol release scenarios may be significantly different and need new research.

Importance of Issue:

The information resulting from ethanol research can be cost effectively leveraged into methanol conceptual model development.

How Do You Propose Resolving This Issue?

Use comparative life cycle approaches that consider physio/chemical processes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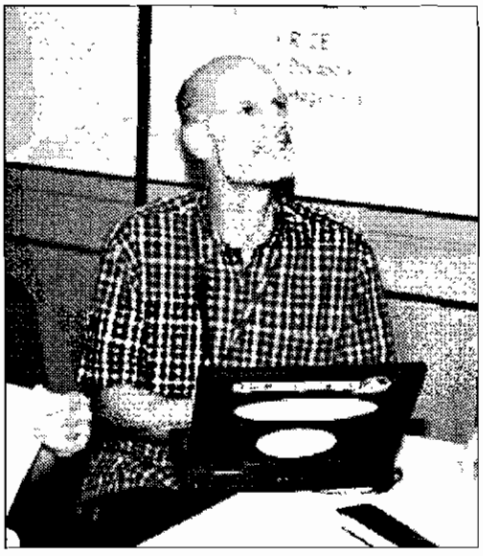


PRIORITY 10

Vulnerability Assessment of Public and Private Water Supplies (Both Wells and Surface Water) from Methanol Releases

Originators:

Rodriguez on behalf of himself, Alvarez, and Hagemann

The following research issues were consolidated under the following titles:

Title: **Determine the Range of Methanol Concentrations That Can Be Expected in Drinking-Water Sources Near USTs That Contain Methanol**

Originator: Rodriguez

Research Issue Description:

Understanding of the fate and transport of methanol is necessary to be able to predict the behavior of methanol plumes. This will lead to a better understanding of wells that are more susceptible to being impacted with a resulting vulnerability assessment of drinking-water sources.

Importance of Issue:

Identifying wells at high risk provides increased monitoring of wells more susceptible to being impacted.

How Do You Propose Resolving This Issue?

Two step approach: First, perform field-based research coupled with modeling to understand the fate and transport of methanol. Second, apply this understanding to determine which wells are at highest risk. The result is a vulnerability assessment of drinking-water sources.

Title: **Dimensions and Stability of Methanol Plumes in Groundwater**

Originator: Alvarez

Research Issue Description:

We need to improve our ability to predict the transport and fate of methanol (and its corollary pollutants) under different release scenarios and to assess what is the region and duration of influence of methanol releases on several processes and issues discussed earlier.

Importance of Issue:

Plume stability and dimensions are critical factors for risk assessment since they determine the likelihood and duration of exposure.

How Do You Propose Resolving This Issue?

- Combine laboratory modeling and field studies to assess the variability of plume length and longevity.
- Consider also unsaturated zone transport and source behavior. Variables should include soil type, moisture, spill rate, and electron-acceptor pool.

Title: **A Preliminary Assessment of the Vulnerability of Drinking-Water Supplies from Methanol Releases**

Originator: Hagemann

Research Issue Description:

Use the analytical tools of source water protection to:

- Map drinking water sources.
- Assume hydrological and fate and transport properties.
- Determine wells and sources that are vulnerable.

Importance of Issue:

Will allow a comparison of the benefits and costs (contamination) with the use of methanol as a fuel.

How Do You Propose Resolving This Issue?

Use the tools developed for MTBE vulnerability assessments:

- USEPA Ada Laboratory (Oklahoma).
- Lawrence Livermore National Laboratory (LLNL).
- Oregon Graduate Institute.

Title: **Assess Impacts on Small Private Water-Supply Wells**

Originator: Rodriguez

Research Issue Description:

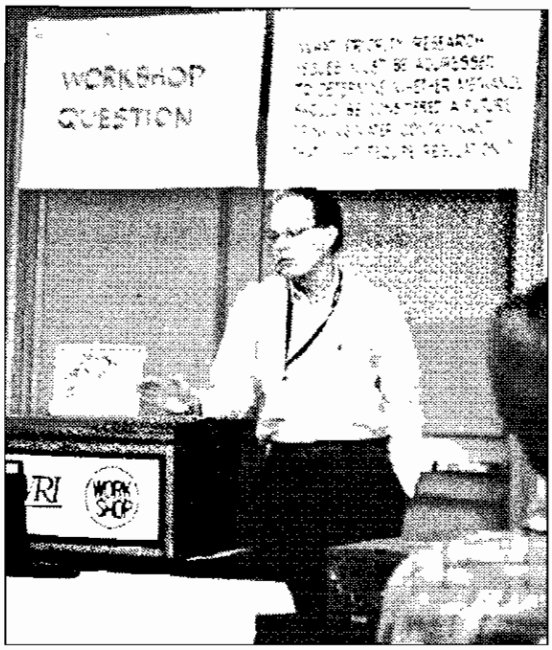
Evaluate the potential impacts and threats to private water-supply wells (home wells).

Importance of Issue:

Private water well owners may be more susceptible to drinking contaminated water. As such, a vulnerability assessment is necessary to provide guidance to local health agencies and private well owners.

How Do You Propose Resolving This Issue?

- Monitoring by a regulatory agency funded by methanol producers (both sources and receptors).
- Understanding the fate and transport mechanism through other research.
- Developing a vulnerability assessment on private wells.


WORKSHOP
QUESTION


MARIA
TIKKANEN

PRIORITY 11

Total Exposure Potential

Originators:

Davis on behalf of himself, Hagemann, and Tikkanen

The following research issues were consolidated under the following title:

Title: **Methanol Total Exposure Potential**

Originator: Davis

Research Issue Description:

High-end total exposure potential for methanol needs to be determined not only for the ingestion of drinking water, but also for dermal contact (e.g., bathing), inhalation (e.g., showering), and for nondrinking-water sources (e.g., the inhalation of vapors during refueling), as well as endogenous levels (e.g., aspartame, fruits, etc.). The focus needs to be on exposure scenarios that would pose the greatest exposure potential, even if unlikely (i.e., including accidental exposures, such as dermal contact from spillage during refueling). Also, attention needs to be given to characterizing the temporal pattern of exposures (i.e., focusing on short-term peaks as well as longer-term averages). A parallel effort needs to be devoted to aquatic and terrestrial ecosystems.

Importance of Issue:

If even "worst-case" exposure estimates (that have objective scientific consensus) do not suggest that adverse health effects are likely (e.g., in relation to an oral RfD), then public health officials can have greater confidence that methanol poses less of a health risk. (However, this assumes that health effects are adequately characterized [e.g., a high-confidence RfD would exist for methanol]). A similar argument applies to ecosystems.

How Do You Propose Resolving This Issue?

This issue can be addressed in stages. First, by using conventional assumptions and empirical measurements, exposures can be estimated for various scenarios that would likely represent conditions constituting the upper tail of a distribution of exposure levels. New work might be necessary to obtain empirical measurements (e.g., methanol vapor concentrations in showers under different conditions of concentration, temperature, flow-rate, etc.).

Second, to achieve greater confidence (e.g., if the "worst-case" estimates are close to a health reference value), actual personal measurements could be obtained to determine whether the estimated exposure levels need to be adjusted up or down.

If concern still exists, more extensive work, possibly using biomarkers of exposure, might be needed. For ecosystems, attention could focus first on freshwater and estuarine ecosystems. All exposure estimates should be considered in relation to a contemporary, evolving understanding of methanol fate and transport.

Title: **Potential for Drinking-Water Contamination from Catastrophic Releases at Methanol Facilities**

Originator: Hagemann

Research Issue Description:

The September 11, 2001, disaster raises many questions that, previously, we could not fathom. Catastrophic releases could be caused by intentional or unintentional activities.

Importance of Issue:

Drinking water is at risk from a number of catastrophic scenarios. Would a reliance on methanol pose additional risk?

How Do You Propose Resolving This Issue?

Analyze with an Emergency Planning Group.

Title: **Track the Fate and Transport of Methanol Processing (Burning or Reforming) Byproducts and Releases to the Environment, Particularly to Water Supplies**

Originator: Tikkanen

Research Issue Description:

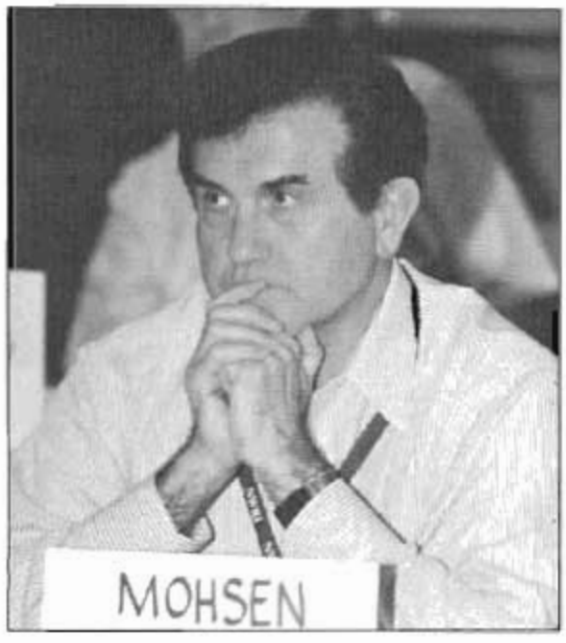
When methanol is used as a fuel in a fuel cell, unless the reforming (processing) process is 100 percent efficient, there may be a waste stream. What will happen to that waste stream? Will it be stored or used for other fueling purposes?

Importance of Issue:

Methanol processing byproducts must be used up, stored up, or disposed of. If stored (e.g., in tanks) or disposed of, there may be releases to the environment (e.g., water, air, soil).

How Do You Propose Resolving This Issue?

- Determine processing byproducts through laboratory studies, field studies, and literature search.
- Do fate and transport studies for the methanol processing byproducts, along with methanol, additives, and degradation byproducts.
- Determine the treatability of these byproducts.
- Work with the California Fuel Cell Partnership and California Air Resource Board to piggyback research efforts.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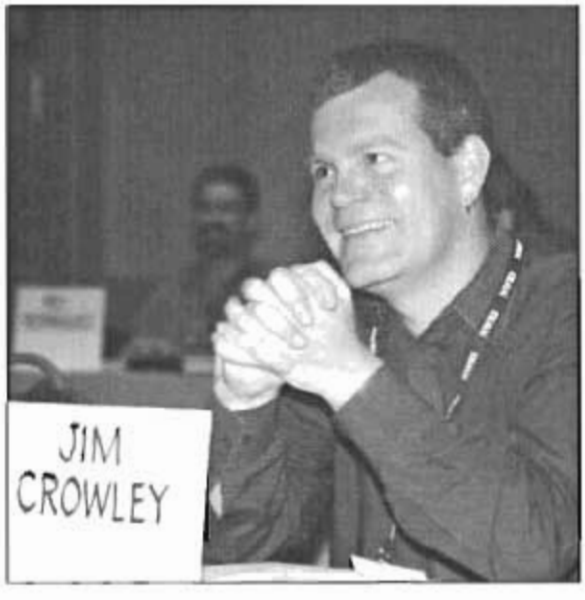

JIM
CROWLEY

PRIORITY 12

Laboratory and Field Investigations of Cost-Effective Treatment Technologies for Groundwater Impacted by Methanol/Gasoline Mixtures

Originators:

Mehran on behalf of himself and Crowley

The following research issues were consolidated under the above title:

Title: **Laboratory and Field Investigations of Cost-Effective Treatment Technologies for Groundwater Impacted by Methanol/Gasoline Mixtures**

Originator: Mehran

Research Issue Description:

Conventional treatment techniques, such as air stripping and carbon adsorption, are not capable of treating groundwater impacted by methanol. Evaluating cost-effective treatment techniques in the presence of gasoline is crucial.

Importance of Issue:

Removal efficiency of methanol would have a significant effect on regulatory standards. The evaluation can also be directed by any existing regulatory standards or clean-up levels.

How Do You Propose Resolving This Issue?

Perform bench-scale and pilot tests using various mixtures. Most research organizations with equipment and laboratories can do the work.

Title: **Bioaugmentation of Existing Fields Sites to Address a Range of Contaminants, Including Methanol**

Originator: Crowley

Research Issue Description:

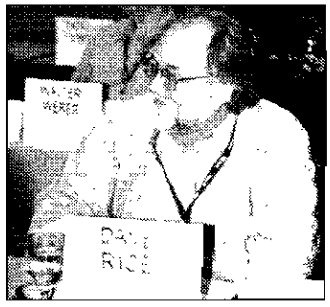
We need a thorough understanding of the geochemical environment in the subsurface and what changes could allow the degradation of contaminants. This would allow us to bioaugment/engineer sites so that methanol and a range of contaminants could be naturally remediated.

Importance of Issue:

Medium.

How Do You Propose Resolving This Issue?

- Bring together all aspects of site geochemistry that affect the fate and transport of contaminants.
- Evaluate how site conditions and geochemistry change with time.
- Determine biodegradation pathways and mechanisms.
- Develop strategies to bioaugment/stimulate site conditions to allow the degradation of contaminants.
- Establish a research partnership to focus research and coordinate projects.



PRIORITY 13

Behavior of Methanol and Fuel Hydrocarbon in the Presence of Methanol during Vadose Infiltration

Originators:

Rice on behalf of himself and Smith

The following research issues were consolidated under the above title:

Title: **Behavior of Methanol As It Infiltrates the Vadose Zone**

Originator: Rice

Research Issue Description:

The functional relationships that control the retention of methanol in the unsaturated zone are not well known, especially in the presence of fuel hydrocarbons. Methanol can be expected to partition into any vadose pore water either through direct contact or vapor transport. Methanol will alter the retention of fluids in the vadose zone. Initial results of research on ethanol indicate that there is a possibility for a reversal from water wetting to light nonaqueous phase liquid (LNAPL) wetting in the presence of methanol.

Importance of Issue:

It may be anticipated that methanol may be dispensed at typical gas stations that are still serving conventional gasoline and that there will likely be fuel hydrocarbons present in the subsurface at these fueling stations. Understanding the mobility of methanol through the vadose zone is key to assessing groundwater vulnerabilities, particularly if fuel hydrocarbons are present at the release site.

How Do You Propose Resolving This Issue?

- Laboratory studies to better quantify the functional relationships that control the retention of methanol in the unsaturated zone. These studies should examine the retention of ethanol as a function of soil type, moisture content, and spill rate, and should include laboratory tests to better define the significance of the observed reversal from water wetting to LNAPL wetting.

- Numerical modeling. Improved modeling efforts are needed to better represent the complex behavior of gasoline-free product in the presence of methanol. This modeling should include the partitioning of ethanol into the aqueous phase of the unsaturated zone, as well as the resulting change in interfacial properties, flow characteristics, and co-solvency.

- A field-scale test that includes the release of methanol-blended gasoline under unsaturated conditions. A field-scale controlled release is needed to validate the field processes observed in the laboratory and to calibrate predictive models of the long-term net flux of methanol and methanol plus fuel hydrocarbons into groundwater.

Title: **Dilution of Pure-Phase Methanol into Soil Water during Infiltration through the Unsaturated Zone**

Originator: Smith

Research Issue Description:

For a methanol spill, assessing potential groundwater impacts depends upon having available reliable values for methanol concentrations that reach the water table. To what extent does mixing and dilution in the unsaturated zone drive concentrations down towards/below an inhibition threshold for the onset of biotransformation?

Importance of Issue:

Key data for input for the predictive analysis of groundwater impacts.

How Do You Propose Resolving This Issue?

Large-diameter column infiltration experiments with the release of pure-phase methanol into porous media with different water contents.

PRIORITY 14

Impacts on Infrastructure and the Environment from Methanol Production Technologies (Existing and Novel) and Distribution Systems

Originator:

Paterek

The following research issues were consolidated under the above title:

Title: **Methanol and Its Impacts on Infrastructure: Enhanced Corrosion and Deterioration from Release of Methanol into Water**

Originator: Paterek

Research Issue Description:

- Material reaction(s) in chemical engineering data/technology transferred to "environmental" conditions.
- Risk engineering and failure engineering combined.

Importance of Issue:

- Methanol could increase the capital costs during manufacturing, distribution, and transport.
- Methanol could disrupt water, sewage, natural gas pipelines, and storage tanks.

How Do You Propose Resolving This Issue?

- Material chemistry and the engineering of methanol on chemical, water, wastewater, natural gas, fuel (crude oil and refined hydrocarbons).
- Corrosion and biodegradations effects with methanol in ground or facilities.

Title: **Environmental Pressures of "New" Methanol Production Technologies**

Originator: Paterek

Research Issue Description:

Identify the competing technologies:

- Feedstocks: natural gas, biomass, and coal.
- Byproducts.
- Catalysts.
- Wastes.

Importance of Issue:

As a market grows for methanol, new technologies and "improvements" to existing stream reformation of synthetic gas (natural gas, coal, biomass) will come online.

How Do You Propose Resolving This Issue?

Evaluate the existing production system as well as proposed methods, including:

- Reduced metal (copper or titanium) catalyzed reformation of natural gas.
  - coal
  - biomass or wastes
- Countercurrent Moving Bed Chromatographic Reactor.
- Ceramic catalysts.
- Enzymatic: formate dehydrogenase (DH) → formaldehyde DH → alcohol DH.

PRIORITY 15

Verify Tightness (Leak Prevention) and Compatibility of Storage, Pumping, and Distribution Systems

Originators:

Davidson on behalf of himself, Crowley, Kavanaugh, Paterek, and Rodriguez

The following research issues were consolidated under the above title:

Title: **Verify Tightness (Leak Prevention) and Compatibility of Storage, Pumping, and Distribution Systems**

Originator: Davidson

Research Issue Description:

Considering methanol's aggressiveness, and the obvious importance of preventing leaks, we need a careful and thorough review of tightness and, especially, the compatibility of the major and minor components used in methanol storage, pumping, and distribution equipment.

Importance of Issue:

- Avoid liquid and vapor losses of neat methanol, and/or methanol-blended fuels.
- Recognize methanol's known aggressive tendencies towards certain fuel distribution components.

How Do You Propose Resolving This Issue?

- Understand existing and proposed methanol storage, pumping, and distribution systems.
- Review existing compatibility knowledge.
- As needed, conduct long-term (months) emersion compatibility testing in the laboratories of samples and coupons of key materials with M100 and M85.

Title: **BMPs for Storage and Distribution of Methanol**

Originator: Crowley

Research Issue Description:

Best Management Practices (BMPs) for the storage and distribution of methanol should be developed to reduce the occurrence of incidental spills and small releases.

Importance of Issue:

Very high.

How Do You Propose Resolving This Issue?

- Take what is used in the petroleum industry as a start.
- Identify methanol-specific storage and product management issues.
- Develop draft BMPs with industry and stakeholders.
- Voluntary implementation versus regulation?

Title: **Develop a Fail-Safe Storage System for Methanol**

Originator: Kavanaugh

Research Issue Description:

Methanol could be stored in an UST or AST with appropriate structural and monitoring systems to minimize releases. Eliminating releases by developing a fail-safe system could eliminate the need to regulate methanol as a drinking water contaminant. An analysis of trade-offs between cost, implementation, and effectiveness could lead to the development of a new and improved storage system at fuel distribution sites.

Importance of Issue:

It is essential to reduce the risks of chronic releases from storage systems.

How Do You Propose Resolving This Issue?

Encourage competition between tank manufacturers with a prize for the winner(s).

Title: **Methanol Runoff from Fueling and Storage Facilities**

Originator: Paterek

Research Issue Description:

- Review effects where industrial methanol is used (e.g., road antifreeze).
- Reactions with infrastructure (e.g., road bed [asphalt]) that mobilizes chemicals and contaminants.
- Photochemical and biotransformation.
- Stormwater transport contaminants, including methanol to surface water or groundwater.

Importance of Issue:

Runoff effects on treatment systems.

How Do You Propose Resolving This Issue?

- Evaluate methanol reaction to contacts with stormwater, such as paving materials, pipelines.
- Study transforms of methanol and any mobilized by methanol.
- Study the effects of runoff on surface water and groundwater quality.
- Methods/technology to control/treat storm runoff.

Title: **Develop Effective Monitoring Systems to Detect Liquid and Vapor Releases of Methanol**

Originator: Rodriguez

Research Issue Description:

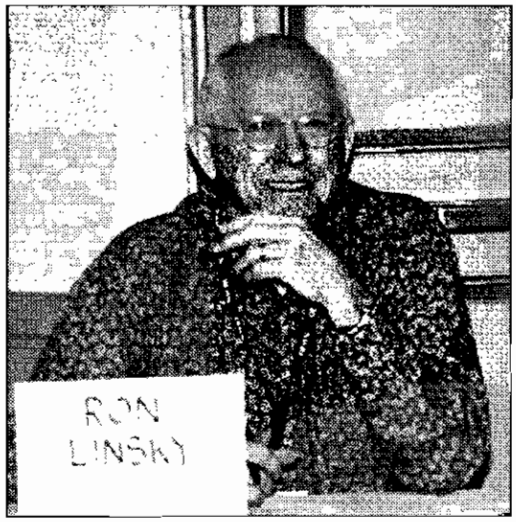
- Review existing leak detection systems and provide recommendations as to their applicability to detect methanol releases.
- Develop devices or systems to detect methanol releases.

Importance of Issue:

Early detection of contaminants is critical in the rapid characterization and cleanup of the release to reduce the risk of impact to drinking-water supplies.

How Do You Propose Resolving This Issue?

- Identify leak detection systems.
- Review compatibility issues with methanol.
- Evaluate the effectiveness of existing leak detection systems.
- Work with manufacturer groups and UST researchers to develop appropriate leak detection systems.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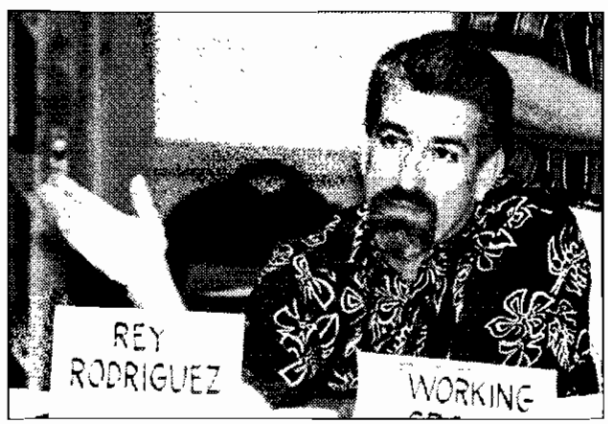

REY
RODRIGUEZ
WORKING

PRIORITY 16

Need to Translate Research Results into the Public-Policy Process

Originator:

Linsky

Research Issue Description:

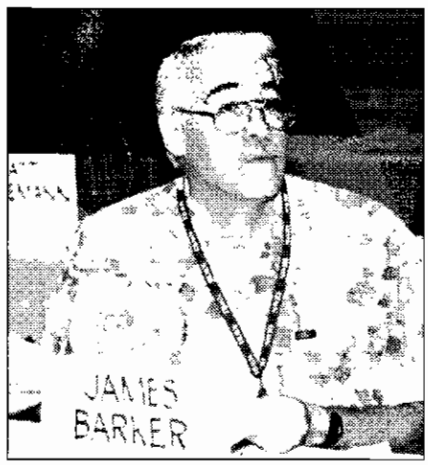
To be most effective, research results need to serve as the foundation for public-policy development.

Importance of Issue:

Public policy is the developmental endpoint of research that focuses on environmental-quality issues.

How Do You Propose Resolving This Issue?

Establish a project that would translate the results of methanol research into the language of public-policy development and at a level of sophistication for policy makers.


JAMES
BARKER

PRIORITY 17

Need for Descriptive and Predictive Models Based on the Evaluation of Methanol-Contaminated Sites: Acute and Chronic

Originators:

Paterek on behalf of himself, Crowley, Hagemann, and Smith

The following research issues were consolidated under the above title:

Title: **Odum's Thermodynamic Model Based on the Evaluations of Historically Contaminated Production Sites: Acute and Chronic**

Originator: Paterek

Research Issue Description:

- Identify and characterize sites: chronic and acute.
- Evaluate:
  - chemistry, geology, microbiology
  - toxicology: human routes and ecological
- Perform laboratory or field-scale model evaluations.

Importance of Issue:

Regulations without this data will be "guesswork."

How Do You Propose Resolving This Issue?

Research Consortia:

- Evaluate model parameters.
- Correlate to "real world" sites.
- Model testing and refinements.
- Lab-scale microcosms.
- Model refined.

Title: **BMPs for Storage and Distribution of Methanol**

Originator: Crowley

Research Issue Description:

Best Management Practices (BMPs) for the storage and distribution of methanol should be developed to reduce the occurrence of incidental spills and small releases.

Importance of Issue:

Very high.

How Do You Propose Resolving This Issue?

- Take what is used in the petroleum industry as a start.
- Identify methanol-specific storage and product management issues.
- Develop draft BMPs with industry and stakeholders.
- Voluntary implementation versus regulation?

Title: **Methanol as a Potential Groundwater Contaminant: A Compendium of the History of Use, Regulation, and Research**

Originator: Hagemann

Research Issue Description:

Comprehensive review of methanol/groundwater issue. Include production (past and projected), distribution infrastructure, regulatory, research (fate and transport), major spill incidents, and the need for further research.

Importance of Issue:

Must learn from history. Think of how different the MTBE/groundwater issue would be today if we had conducted joint research efforts in the late 1970's.

How Do You Propose Resolving This Issue?

Use the participants at this workshop!

Title: **Ultrasensitive Molecular Tools to Determine the Presence and Bioimpact of Methanol-Contaminated Matrices (Vadose, Unsaturated, Surface Water)**

Originator: Paterek

Research Issue Description:

- Methylotrophic bacteria detection and activity:
  - aerobic: methylotrophic bacteria
  - anaerobic: methanogens
- Tools:
  - quorum-sensing compounds
  - specific cofactors or enzymes: F_{420} or coenzyme (C_oM) in methanogens; and methane monooxygenase

Importance of Issue:

Real-time sensors for presence and biological transformation.

How Do You Propose Resolving This Issue?

- Identify molecular tools for key microorganisms.
- Evaluate sensors in the lab and field.
- Engineer continuous and event biosensors.

Title: **Dilution of Pure-Phase Methanol into Soil Water during Infiltration through the Unsaturated Zone**

Originator: Smith

Research Issue Description:

For a methanol spill, assessing potential groundwater impacts depends upon having available reliable values for methanol concentrations that reach the water table. To what extent does mixing and dilution in the unsaturated zone drive concentrations down towards/below an inhibition threshold for the onset of biotransformation?

Importance of Issue:

Key data for input for the predictive analysis of groundwater impacts.

How Do You Propose Resolving This Issue?

Large-diameter column infiltration experiments with the release of pure-phase methanol into porous media with different water contents.

PRIORITY 18

Use of Methanol for Soil and Groundwater Remediation

Originator

Barker

Research Issue Description:

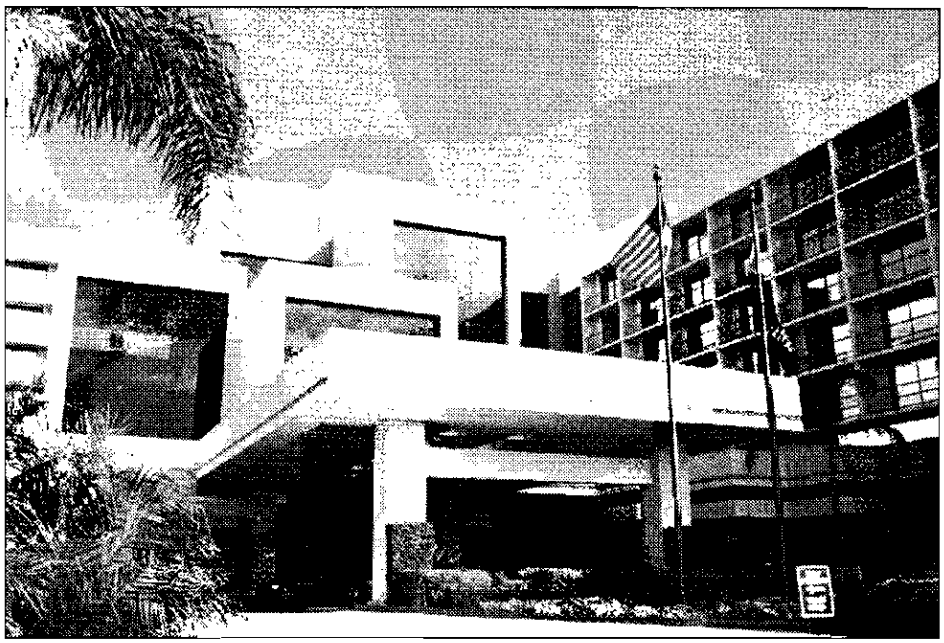
Methanol can be used in the remediation of groundwater and soil. Should its use be restricted because of drinking-water concerns?

Importance of Issue:

Uncertain. Perhaps the beneficial use of methanol could be unreasonably restricted.

How Do You Propose Resolving This Issue?

Carry on with the current program to provide remedial technology companies with insight into acceptable levels of residual methanol following remediation.



STRENGTH OF FEELING ANALYSES OF PARTICIPANTS AND SUBGROUPS OF PARTICIPANTS

The following 4 tables give a quantitative sense of the degree of agreement (or disagreement) among the workshop participants regarding the importance of each identified and prioritized research issue. Table 1 is organized according to the priority ranking by all 18-workshop participants of all 18 major research issue areas on which they voted.

Tables 2, 3, and 4 show how each of the three subgroups of participants ranked the 18 major research issue areas. The three subgroups comprised: consultants, university researchers, and water district employees.

To create these tables, each of the 18 participants voted individually for the ten highest priority responses to the workshop question: ***What Priority Research Issues Must Be Addressed to Determine Whether Methanol Should Be Considered a Future Drinking-Water Contaminant That Might Require Regulation?*** Before tallying the results of the balloting, each participant was assigned to a subgroup that best described his or her occupation.

Each table lists the research issues in descending order of importance, the issue title, the times it was voted for (picked), the total number of points received from the balloting, and finally, the strength of the group's feeling, expressed as a percentage.

For example, if all 18 participants had given their first priority vote for Table 1, item 1, it would have received 180 points; the Times Picked/Pts. would have shown 18/180; and the Strength of Feeling column would have shown 100%. Actually, only 16 of the 18 participants voted for the number one priority research issue, and they assigned it a total of 117 points. Thus, the Strength of Feeling of 65.0% was calculated as 117/180 x 100 = 65.

Examining Tables 1, 2, and 4 it can be seen that the seven consultant participants and the four water district participants agreed fairly closely. By contrast, the seven university researcher participants, after agreeing with the other 11 participants on the first three issues, registered some very different perceptions of what research areas ought to be tackled after that. For example, they raised to their next highest priorities (priority 4 and priority 5) the seventh and thirteenth priority issues of all participants. Further, after they went below their first three priority issues, on which they were in good agreement (in the 70+ percent range), they showed little agreement beyond that point, dropping into the thirty percent area and below for all the rest of the issues.

In establishing research-funding priorities, it may be important to reconcile the kinds of dramatic differences in opinion shown in the following tables, at least below the top three priority issues.

Table 1

Research Issues (18) Ranked by All Participants (18)

Rank	Title	Times Picked/Pts.	Strength of Feeling
1.	Groundwater Quality Impacts Associated with the Use of Methanol Fuels	16/117	65.0%
2.	Develop Sampling and Trace-Analytical Methods and Protocols Useful for Assessments of the Occurrence of Methanol and Associated Analytes	16/117	65.0%
3.	Effects of Methanol on the Fate and Transport of Co-occurring Organic Contaminants: Dissolved, Sorbed, Sequestered, and Residualized	17/116	64.4%
4.	Human and Ecological Toxicology	14/85	47.2%
5.	Comprehensive Evaluation of Direct and Indirect Impacts of Methanol	14/69	38.3%
6.	Evaluate Methanol in Surface Water, Drinking Water, and Groundwater at Petroleum Sites, Methanol Sites, and in the Ambient Environment	11/64	35.6%
7.	Surface Water Quality Impacts Associated with the Use of Methanol Fuels	12/62	34.4%
8.	Effects of Methanol Fuel Components and Byproducts on Drinking-Water Treatment and Distribution	13/60	33.3%
9.	Methanol As a Potential Groundwater Contaminant: A Compendium of the History of Use, Regulation, and Research	9/48	26.7%
10.	Vulnerability Assessment of Public and Private Water Supplies (Both Wells and Surface Water) from Methanol Releases	11/44	24.4%
11.	Total Exposure Potential	6/41	22.8%

Rank	Title	Times Picked/Pts.	Strength of Feeling
12.	Laboratory and Field Investigations of Cost-Effective Treatment Technologies for Groundwater Impacted by Methanol/Gasoline Mixtures	8/40	22.2%
13.	Behavior of Methanol and Fuel Hydrocarbons in the Presence of Methanol during Infiltration	8/39	21.7%
14.	Impacts on Infrastructure and the Environment from Methanol Production Technologies (Existing and Novel) and Distribution Systems	7/28	15.6%
15.	Verify Tightness (Leak Prevention) and Compatibility of Storage, Pumping, and Distribution Systems	7/22	12.2%
16.	Need to Translate Research Results into the Public Policy Process	5/22	12.2%
17.	Need for Descriptive and Predictive Models Based on the Evaluation of Methanol-Contaminated Sites: Acute and Chronic	5/15	8.3%
18.	Use of Methanol for Soil and Groundwater Remediation	1/1	0.6%

Table 2

Research Issues (18) Ranked by Consultant Participants (7)

Rank	Title	Times Picked/Pts.	Strength of Feeling
1.	Effects of Methanol on the Fate and Transport of Co-occurring Organic Contaminants: Dissolved, Sorbed, Sequestered, and Residualized	7/48	68.6%
2.	Human and Ecological Toxicology	7/42	60.0%
3.	Groundwater Quality Impacts Associated with the Use of Methanol Fuels	6/39	55.7%
4.	Develop Sampling and Trace-Analytical Methods and Protocols Useful for Assessments of the Occurrence of Methanol and Associated Analytes	6/39	55.7%
5.	Comprehensive Evaluation of Direct and Indirect Impacts of Methanol	6/36	51.4%
6.	Evaluate Methanol in Surface Water, Drinking Water, and Groundwater at Petroleum Sites, Methanol Sites, and in the Ambient Environment	5/31	44.3%
7.	Surface Water Quality Impacts Associated with the Use of Methanol Fuels	6/28	40.0%
8.	Effects of Methanol Fuel Components and Byproducts on Drinking Water Treatment and Distribution	6/24	34.3%
9.	Total Exposure Potential	3/21	30.0%
10.	Methanol As a Potential Groundwater Contaminant: A Compendium of the History of Use, Regulation, and Research	3/16	22.9%
11.	Vulnerability Assessment of Public and Private Water Supplies (Both Wells and Surface Water) from Methanol Releases	2/16	22.9%

Rank	Title	Times Picked/Pts.	Strength of Feeling
12.	Laboratory and Field Investigations of Cost-Effective Treatment Technologies for Groundwater Impacted by Methanol/Gasoline Mixtures	2/13	18.6%
13.	Need to Translate Research Results into the Public-Policy Process	3/11	15.7%
14.	Verify Tightness (Leak Prevention) and Compatibility of Storage, Pumping, and Distribution Systems	3/10	14.3%
15.	Behavior of Methanol and Fuel Hydrocarbons in the Presence of Methanol during Infiltration	3/9	12.9%
16.	Impacts on Infrastructure and the Environment from Methanol Production Technologies (Existing and Novel) and Distribution Systems	1/1	1.4%
17.	Use of Methanol for Soil and Groundwater Remediation	1/1	1.4%

Table 3

Research Issues (18) Ranked by University Researcher Participants (7)

Rank	Title	Times Picked/Pts.	Strength of Feeling
1.	Groundwater Quality Impacts Associated with the Use of Methanol Fuels	6/52	74.3%
2.	Develop Sampling and Trace-Analytical Methods and Protocols Useful for Assessments of the Occurrence of Methanol and Associated Analytes	7/51	72.9%
3.	Effects of Methanol on the Fate and Transport of Co-occurring Organic Contaminants: Dissolved, Sorbed, Sequestered, and Residualized	7/50	71.4%
4.	Surface Water Quality Impacts Associated with the Use of Methanol Fuels	4/27	38.6%
5.	Behavior of Methanol and Fuel Hydrocarbons in the Presence of Methanol during Infiltration	4/25	35.7%
6.	Methanol As a Potential Groundwater Contaminant: A Compendium of the History of Use, Regulation, and Research	4/24	34.3%
7.	Evaluate Methanol in Surface Water, Drinking Water, and Groundwater at Petroleum Sites, Methanol Sites, and in the Ambient Environment	4/23	32.9%
8.	Effects of Methanol Fuel Components and Byproducts on Drinking-Water Treatment and Distribution	4/22	31.4%
9.	Impacts on Infrastructure and the Environment from Methanol Production Technologies (Existing and Novel) and Distribution Systems	5/22	31.4%
10.	Laboratory and Field Investigations of Cost-Effective Treatment Technologies for Groundwater Impacted by Methanol/Gasoline Mixtures	4/21	30.0%
11.	Human and Ecological Toxicology	4/17	24.3%

Rank	Title	Times Picked/Pts.	Strength of Feeling
12.	Comprehensive Evaluation of Direct and Indirect Impacts of Methanol	5/16	22.9%
13.	Vulnerability Assessment of Public and Private Water Supplies (Both Wells and Surface Water) from Methanol Releases	5/14	20.0%
14.	Need for Descriptive and Predictive Models Based on the Evaluation of Methanol-Contaminated Sites: Acute and Chronic	4/12	17.1%
15.	Need to Translate Research Results into the Public-Policy Process	1/5	7.1%
16.	Total Exposure Potential	1/3	4.3%
17.	Verify Tightness (Leak Prevention) and Compatibility of Storage, Pumping, and Distribution Systems	1/1	1.4%

Table 4

Research Issues (18) Ranked by Water District Participants (4)

Rank	Title	Times Picked/Pts.	Strength of Feeling
1.	Develop Sampling and Trace-Analytical Methods and Protocols Useful for Assessments of the Occurrence of Methanol and Associated Analytes	3/27	67.5%
2.	Groundwater Quality Impacts Associated with the Use of Methanol Fuels	4/26	65.0%
3.	Human and Ecological Toxicology	3/26	65.0%
4.	Effects of Methanol on the Fate and Transport of Co-occurring Organic Contaminants: Dissolved, Sorbed, Sequestered, and Residualized	3/18	45.0%
5.	Total Exposure Potential	2/17	42.5%
6.	Comprehensive Evaluation of Direct and Indirect Impacts of Methanol	3/17	42.5%
7.	Effects of Methanol Fuel Components and Byproducts on Drinking-Water Treatment and Distribution	3/14	35.0%
8.	Vulnerability Assessment of Public and Private Water Supplies (Both Wells and Surface Water) from Methanol Releases	4/14	35.0%
9.	Verify Tightness (Leak Prevention) and Compatibility of Storage, Pumping, and Distribution Systems	3/11	27.5%
10.	Evaluate Methanol in Surface Water, Drinking Water, and Groundwater at Petroleum Sites, Methanol Sites, and in the Ambient Environment	2/10	25.0%
11.	Methanol As a Potential Groundwater Contaminant: A Compendium of the History of Use, Regulation, and Research	2/8	20.0%

Rank	Title	Times Picked/Pts.	Strength of Feeling
12.	Surface Water Quality Impacts Associated with the Use of Methanol Fuels	2/7	17.5%
13.	Laboratory and Field Investigations of Cost-Effective Treatment Technologies for Groundwater Impacted by Methanol/Gasoline Mixtures	2/6	15.0%
14.	Need to Translate Research Results into the Public Policy Process	1/6	15.0%
15.	Behavior of Methanol and Fuel Hydrocarbons in the Presence of Methanol during Infiltration	1/5	12.5%
16.	Impacts on Infrastructure and the Environment from Methanol Production Technologies (Existing and Novel) and Distribution Systems	1/5	12.5%
17.	Need for Descriptive and Predictive Models Based on the Evaluation of Methanol-Contaminated Sites: Acute and Chronic	1/3	7.5%

APPENDICES

APPENDIX A

ACRONYMS

AST	aboveground storage tank
BMP	Best Management Practices
BOD	biochemical oxygen demand
BTEX	benzene, toluene, ethylbenzene, xylene
DH	dehydrogenase
GC	gas chromatographs
LCA	life cycle assessment
LLNL	Lawrence Livermore National Laboratory
LNAPL	light nonaqueous phase liquid
LOD	limit of detection
LUFT	leaking underground fuel tank
LUST	leaking underground storage tank
MDL	maximum daily load
MTBE	methyl tertiary butyl ether
NAPL	nonaqueous phase liquid
NDMA	N-nitroso dimethyl amine
NOM	natural organic matter
NWRI	National Water Research Institute
PAH	polyaromatic hydrocarbon
PID	photo ionization detector
POTW	publicly owned treatment works
ppb	parts per billion
PVC	poly vinyl chloride
QA/QC	quality assurance/quality control
RfD	reference dose
TBA	tertiary-butyl alcohol
THM	trihalomethane
TOC	total organic carbon
USEPA	United States Environmental Protection Agency
UST	underground storage tank
VFA	volatile fatty acid

APPENDIX B

PREVIOUS NGT WORKSHOPS CONDUCTED BY NWRI

Chino Basin Organics Management. Report of a workshop sponsored by NWRI in cooperation with the Inland Empire Utilities Agency, and the Southern California Alliance of Publicly Owned Treatment Plants. Kellogg West Conference Center/Hotel, California State Polytechnic University, Pomona, CA, April 18-20, 2001. NWRI Report No. NWRI-01-03, 205p.

Desalination Research & Development. Report of a workshop sponsored by NWRI in cooperation with the United States Bureau of Reclamation. Kellogg West Conference Center/Hotel, California State Polytechnic University, Pomona, CA, January 19-21, 2001. NWRI Report No. NWRI-01-02, 185p.

Knowledge Management. Report of a workshop sponsored by NWRI. Kellogg West Conference Center/Hotel, California State Polytechnic University, Pomona, CA January 5-7, 2001. NWRI Report No. NWRI-01-01, 169 p.

Oxygenate Contamination. Report of a workshop sponsored by NWRI in cooperation with the United States Bureau of Reclamation. Kellogg West Conference Center/Hotel, California State Polytechnic University, Pomona, CA, September 15-17, 2001. NWRI Report No. NWRI-00-02, 258p.

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. NWRI Report No. NWRI-99-03, 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. NWRI Report No. NWRI-99-02, 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. NWRI Report No. 98-02, 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. NWRI Report No. NWRI-98-01, 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. NWRI Report No. NWRI-97-4, 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. NWRI Report No. NWRI-97-2, 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. NWRI Report No. NWRI-97-1, 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. NWRI Report No. NWRI-97-3, 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. NWRI Report No. NWRI-95-2, 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. NWRI Report No. NWRI-95-1, 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. NWRI Report No. NWRI-94-2, 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. NWRI Report No. NWRI-94-1, 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. NWRI Report No. NWRI-93-3, 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. NWRI Report No. NWRI-1-92, 103p.

APPENDIX C

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APPENDIX D

PARTICIPANTS' BIOGRAPHICAL SKETCHES

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Pedro Alvarez has taught at the University of Iowa since 1993, focusing on the applications and implications of biological treatment processes in Environmental Engineering. His research interests include the bioremediation of contaminated aquifers, fate and transport of hazardous substances, and treatment of contaminated soil, water, or wastewater. In addition, he is also Associate Director of the Center for Biocatalysis and Bioprocessing at the University of Iowa. Among his honors, he is a Diplomate of the American Academy of Environmental Engineers and received a Career Award from the National Science Foundation and Outstanding Achievement Award in Environmental Engineering from the University of Michigan. Alvarez received a B.S. in Civil Engineering from McGill University in Montréal, a certificate in Hazardous Waste Management from the University of California, Riverside, and both an M.S. and Ph.D. in Environmental Engineering from the University of Michigan, Ann Arbor.

James F. Barker, Ph.D.
Professor and Chair, Department of Earth Sciences
University of Waterloo

Jim Barker has been a faculty member of the Earth Sciences Department at the University of Waterloo in Ontario, Canada, since 1980, conducting research on the mitigation, fate, and remediation of organic contaminants in groundwater. His groundwater research involving methanol used natural gradient field studies in the experimental aquifer site at Canadian Forces Base Borden, with supporting lab and modeling studies, to identify the interaction of methanol with pure-phase and dissolved gasoline components as well as the fate of methanol and BTEX in the presence of methanol. Similar studies are currently considering ethanol fuels. Barker received both a B.S. and M.S. in Geology from McMaster University in Ontario and a Ph.D. in Geology from the University of Waterloo.

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 understanding the fate and transport of MTBE and other fuel oxygenates in groundwater. He is also a member of the Research Advisory Committee for the California MTBE Research Partnership. Crowley received a B.S. degree from the University College Cork in Ireland.

James M. Davidson, P.G.
President
Alpine Environmental, Inc.

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.

J. Michael Davis, Ph.D.
Senior Scientist, National Center for Environmental Assessment
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J. Michael Davis has worked with the United States Environmental Protection Agency (USEPA) for more than 20 years, primarily in assessing the health risks associated with lead, manganese, MTBE, alcohols, and other fuels and fuel additives. Over the past several years, he had helped formulate and coordinate research programs on these and other issues, including chairing EPA workshops on oxygenate information and research needs and participating in an EPA Blue Ribbon Panel on oxygenates in gasoline. Davis received a B.A. in Psychology from Concord College in West Virginia and a Ph.D. in Experimental Psychology from Duke University. Postdoctoral work included fellowships at the University of Oxford in England for Zoology and from the University of North Carolina at Chapel Hill in Neurotoxicology.

Rula A. Deeb, Ph.D.
Senior Project Engineer/Bioremediation Specialist
Malcolm Pirnie, Inc.

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.

Matt Hagemann
Hydrogeologist
Komex H_2O Science, Inc.

Matt Hagemann specializes in developing strategies to achieve compliance in site assessment and remediation. He spent ten years with the USEPA where he served as the Senior Science Advisor. During his career, Hagemann has worked as a hydrogeologist with the National Park Service, Hawaii, and has taught extensively at the university level. He received a B.S. in geology from Humboldt State University and a M.S. in geology from California State University, Los Angeles.

Roy L. Herndon, P.G.
District Hydrogeologist
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Roy Herndon has 16 years experience in hydrogeologic investigations pertaining to environmental and water supply projects in California, Nevada, and Arizona. Since 1992, he has managed the Hydrogeology Department at the Orange County Water District (California), overseeing activities such as constructing a basin-wide numerical groundwater flow model, developing a comprehensive data management and geographic information system, and designing/constructing monitoring and municipal water wells. He also has directed hydrogeologic studies that, collectively, entailed the construction of over 100 monitoring wells, 50 of which exceed 1,000 feet in depth. Herndon received a B.A. in Geology from Colorado College and an M.S. in Hydrology and Water Resources from the University of Arizona.

Ron Hunsinger
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Ron Hunsinger is the Manager of Water Quality for East Bay Municipal Utility District, a utility serving 1.3 million people in Oakland, Berkeley, and East Bay Area, California. He has authored and co-authored over 80 research papers, book chapters, technical reports, and conference presentations, and he has in the past worked as a researcher, regulator, and research-grant administrator. Research has included work on pilot plants, emerging contaminants (asbestos, dioxin, MTBE, NDMA, etc.), and treatment plant optimization. His current position involves overseeing water-quality legislation and regulation activities, monitoring, research, capital and operating programs, and policies within the utility addressing source, treatment, and distribution. Hunsinger is a graduate of Waterloo University College.

Michael C. Kavanaugh, Ph.D., P.E., D.E.E.
Vice President
Malcolm Pirnie, Inc.

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. 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 (D.E.E.) of the American Academy of Environmental Engineers and a consulting professor of Environmental Engineering at Stanford University. He was 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.

Mohsen Mehran, Ph.D.
Chief Executive Officer
England Geosystem, Inc.

For the past 30 years, Mohsen Mehran's research has focused on groundwater flow and the migration of chemical constituents in porous/fractured media, with particular emphasis on remediation, water resources management, and groundwater/contaminant transport modeling. He has been a faculty member at Tehran Polytechnic in Iran and the Universities of California, Davis and Berkeley. He is the Chief Executive Officer and principal hydrogeologist for England Geosystem, which provides environmental and geotechnical consulting services. He has published more than 50 articles related to soil and groundwater investigation/remediation. Mehran received a B.S. in Agricultural Engineering from Tehran University and both an M.S. in Soil Physics and Ph.D. in Civil Engineering from the University of California, Davis.

J. Robert Paterek, Ph.D.
Manager, Environmental Biotechnology
Gas Technology Institute

Bob Paterek has almost 20 years experience in the fields of microbial biotechnology and environmental chemistry. This experience includes tenure as a Senior Analytical Chemist with a pharmaceutical company in South Carolina, Director of Microbiology with a commercial research and development firm in New Jersey, Vice President/Lab Director/Co-owner of an environmental analysis lab and bioremediation lab in New Orleans, and Manager of an environmental chemistry research group in San Diego. Currently, he is Manager of the Environmental Biotechnology Department at the Gas Research Institute in Des Plaines, Illinois. Paterek received his B.S. and M.S. in Microbiology from Clemson University and a Ph.D. from the Microbiology and Cell Science Department at the University of Florida.

David W. Rice, Jr.
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Lawrence Livermore National Laboratory

David Rice has worked at the Lawrence Livermore National Laboratory (LLNL) in California since 1976, focusing his research on the environmental impacts of transportation fuels, fate and transport of subsurface contaminants, environmental remediation, and toxicology of the early life and reproduction of fish. For the past four years, he has been the Group Leader of the Environmental Chemistry and Biology Group for the Environmental Restoration Division of LLNL. In addition, since 1999, he has been the Project Director for evaluating the potential surface and groundwater impacts that may result from the use of ethanol as a replacement for MTBE in gasoline. Rice received a B.A. in Life/Physical Sciences at California State University, San Jose and an M.A. in Biology from California State University, Hayward.

Rey Rodriguez
President
$H_2O \bullet R^2$ Consulting Engineers, Inc.

Rey Rodriguez has over 16 years of civil engineering experience in the public and private sectors, 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, California. He is also Sub-committee Chair of the Source Water Protection Committee for the California MTBE Research Partnership (Partnership), which he helped co-found in 1997. Mr. Rodriguez also teaches a class throughout North America on the design and implementation of treatment technologies for MTBE, TBA, and other oxygenates. 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.

Leslie Smith, Ph.D.
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Leslie Smith has taught at the University of British Columbia since 1981 and has been the Cominco Chair in Minerals and the Environment since 1997. His research field largely focuses on contaminant transport processes in groundwater systems, both in heterogeneous porous media and fractured crystalline rock. Over the past year, he has worked with Methanex to more fully understand and quantify the potential impacts on groundwater of methanol releases to aquifers. Among his current activities, he is a member of the Committee on Remediation Science and Technology at the Hanford Site for the U.S. National Academy of Sciences, and he is President-elect of the Hydrology Section for the American Geophysical Union (2000-2002). Smith received a B.S. in Geology from the University of Alberta and a Ph.D. in Geological Sciences from the University of British Columbia.

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Roy Spalding has been Associate Director of the Water Center and Director of the Water Sciences Laboratory at the University of Nebraska, Lincoln, since 1988. He has also served as President of Hydro-Trace, Inc., an environmental consulting firm, since 1981. His research interests are in the field of water quality as it relates to the fate and transport of agrichemicals, the cost-effective remediation of agrichemicals and industrial solvents, and the pragmatic use of radioactive and stable isotopes in environmental applications. Recently, he was co-author of *Trace Analysis of Ethanol and MTBE in Water Using Solid Phase /Microextraction and GC/MS*, published by NWRI for the California MTBE Research Partnership in 1999. Spalding earned a B.A. in chemistry at Kenyon College, an M.S. in Environmental Science and Engineering at the University of North Carolina, and a Ph.D. in Geochemical Oceanography at Texas A&M University.

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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. In Spring 2001, Tikkanen became Senior Scientist at Kennedy/Jenks Consultants in Sacramento. Prior, she managed the MTBE Reservoir Monitoring and Management Program as Senior Scientist 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.

Walter J. Weber, Jr., Ph.D., P.E., D.E.E.
Gordon Maskew Fair and Earnest Boyce Distinguished University Professor
University of Michigan, Ann Arbor

Walter Weber is an environmental scientist, engineer, and professor recognized for developing technologies for water treatment, water pollution control, reclamation, and reuse. In 1972, he wrote the textbook *Physiochemical Processes for Water Quality Control*, which is still the principle text in its field and has since written three other textbooks. He founded the Great Lakes and Mid-Atlantic Hazardous Substance Research Center and the National Center for Integrated Bioremediation Research and Development, which both are supported by the U.S. Environmental Protection Agency, U.S. Department of Defense, U.S. Department of Energy, and several major industrial firms. He was named a Diplomate in the American Academy of Engineers in 1975 and elected to the National Academy of Engineering in 1985. In 1996, Weber was honored with The Clarke Prize for his many achievements. Currently, he serves a Chair of the Research Advisory Committee for the California MTBE Research Partnership. He received his Sc.B. in Chemical Engineering from Brown University, M.S.E. in Environmental Engineering from Rutgers, and A.M. in Environmental Chemistry and Ph.D. in Water Resources Engineering from Harvard University.

APPENDIX E

WORKING GROUPS' VISUAL PRESENTATIONS