

BEFORE THE POLLUTION CONTROL BOARD
OF THE STATE OF ILLINOIS

RECEIVED
CLERK'S OFFICE

OCT 25 2000

STATE OF ILLINOIS
Pollution Control Board

IN THE MATTER OF:)
)
PROPOSED AMENDMENTS TO)
TIERED APPROACH TO CORRECTIVE)
ACTION OBJECTIVES)
(35 ILL. ADM. CODE 742))
)

R00-19 (B)
(Rulemaking-Land)

P.C.# 9

NOTICE OF FILING

Dorothy M. Gunn, Clerk
Illinois Pollution Control Board
James R. Thompson Center
100 West Randolph Street, Suite 11-500
Chicago, Illinois 60601

Matthew J. Dunn, Chief
Environmental Bureau
Office of the Attorney General
188 W. Randolph, 20th Floor
Chicago, Illinois 60601

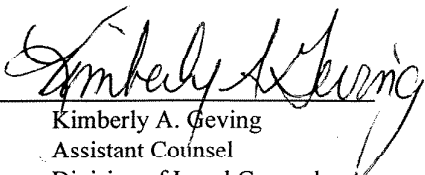
Robert Lawley, Chief Legal Counsel
Dept. of Natural Resources
524 South Second Street
Springfield, Illinois 62701-1787

Amy Jackson, Hearing Officer
IL. Pollution Control Board
500 South Second Street
Springfield, Illinois 62706

Service List

PLEASE TAKE NOTICE that I have filed today with the Illinois Pollution Control Board the Final Comments by the ILLINOIS ENVIRONMENTAL PROTECTION AGENCY, a copy of which is herewith served upon you.

ENVIRONMENTAL PROTECTION AGENCY
OF THE STATE OF ILLINOIS

By: 
Kimberly A. Geving
Assistant Counsel
Division of Legal Counsel

Dated: October 23, 2000

Illinois Environmental Protection Agency
1021 North Grand Avenue East
P.O. Box 19276
Springfield, Illinois 62794-9276
(217) 782-5544

RECEIVED

CLERK'S OFFICE

OCT 25 2000

BEFORE THE ILLINOIS POLLUTION CONTROL BOARD

IN THE MATTER OF:)
)
PROPOSED AMENDMENTS TO)
TIERED APPROACH TO CORRECTIVE)
ACTION OBJECTIVES)
(35 ILL. ADM. CODE 742))

STATE OF ILLINOIS
Pollution Control Board

R00-19
(Rulemaking-Land)

FINAL COMMENTS

NOW COMES the Illinois Environmental Protection Agency ("Illinois EPA"), by and through one of its attorneys, Kimberly A. Geving, and pursuant to 35 Ill. Adm. Code 102.320, respectfully submits these FINAL COMMENTS in the above-captioned matter to the Illinois Pollution Control Board ("Board").

It is the Illinois EPA's contention that the proposed amendments filed in this matter with the Board on May 12, 2000, and the corresponding Errata Sheet filed on August 9, 2000, constitute technically feasible, economically reasonable, and well-supported amendments to Part 742. The Illinois EPA believes that the Board should adopt the proposed amendments in their entirety as submitted by the Illinois EPA, including changes proposed in Errata Sheet Number 1.

A. Background

On May 12, 2000, the Illinois EPA filed its proposed amendments in the above-captioned matter to incorporate changes to the rules that are designed to improve or clarify particular aspects of the Tiered Approach to Corrective Action Objectives ("TACO") methodology. With time, experience, and changes in scientific information on the national level it became necessary to update various elements of Part 742. Over the last three years, the Illinois EPA compiled a list of revisions that evolved into the proposed amendments. Many changes arose from discussions

THIS FILING IS SUBMITTED ON RECYCLED PAPER

the Illinois EPA had with members of the regulated community. Others, such as the addition of MTBE, stemmed from new scientific studies that were published because of increased detections of MTBE in community water supplies.

As always, the Illinois EPA had numerous meetings with the regulated community during the development of the proposed amendments. We believe that their comments and concerns were incorporated into the draft the Board received in May and were further refined through Errata Sheet Number 1.

B. Adoption of the Illinois EPA's Proposal

As stated above, the Illinois EPA believes that it has produced viable amendments that are well supported by the testimony given by Illinois EPA witnesses. In addition, the Illinois EPA would offer its support of the proposed amendments suggested by Gary Zolyak in his pre-filed testimony, including the amendments that he and Georgia Vlahos orally entered into the record at the Springfield hearing. This support is, however, given with a condition. The condition is that all the negotiating parties reach final agreement on the Memorandum of Agreement ("LUC MOA") (attached as Exhibit 1). As of the date of this writing, we are very close to a final agreement. However, the Illinois EPA's Director as well as the appropriate individual at USEPA must still approve the agreement. If the parties fail to reach agreement on the LUC MOA, then the Illinois EPA would be forced to file an amendatory rulemaking with the Board to delete the exemption for federal facilities.

Also attached to these FINAL COMMENTS is a letter from the General Services Administration ("GSA") stating their commitment to install measures to ensure that land use controls are maintained when properties transfer out of federal hands (Exhibit 2). Given their role in the property disposal process and the fact that they are not a party to the LUC MOA, their

THIS FILING IS SUBMITTED ON RECYCLED PAPER

written commitment to ensure that all necessary land use controls and limitations are maintained was a necessary element for the Illinois EPA. We believe that their written confirmation is adequate.

C. Issues of Concern at Hearing

The Illinois EPA believes that there were four main issues that arose at hearing that merit further discussion in these FINAL COMMENTS. Those issues include the following: 1) Environmental Land Use Controls ("ELUC"s)--and two related sub-issues (a. the discussion of the proposed exemption for federal facilities; and b. the use of ELUCs, and TACO in general, by the Illinois EPA's Office of Chemical Safety); 2) slight modification to Section 742.1105(c)(3)(C)(iii); 3) implementation; and 4) the cost and duration of remediation for MTBE.

1. Environmental Land Use Controls

Initially, the Illinois EPA would like to express its opinion that we have presented a strong argument supporting the adoption of our proposed amendments to delete all references to deed restrictions and incorporate the new ELUC provisions. First of all, there is statutory authority and direction to adopt rules for this new institutional control. Second, given the legal complexity and all the related problems associated with deed restrictions, as discussed in my Statement of Reasons and its exhibits, there is a very strong argument for adoption of our proposal, including the changes made in Errata Sheet Number 1. I will not duplicate those arguments here.

a. Federal Exemption from ELUC Recording Provisions

With regard to the proposal by the Department of Defense to include their suggested exemption language, I would reiterate that the Illinois EPA supports their position so long as any

THIS FILING IS SUBMITTED ON RECYCLED PAPER

federal facility that is unable to deed record institutional controls and No Further Remediation determinations enters a LUC MOA with the Illinois EPA. I am also enclosing for the Board's review, as Exhibit 3 to these FINAL COMMENTS, a Policy paper and two guidance documents issued by the Secretary of Defense that should provide the Board with further background and understanding on the issue of land use controls on federally owned lands.

The Illinois EPA believes with reasonable certainty that the terms of the LUC MOA, including all its necessary appendices, offer the same protection of human health and the environment as the provisions in Part 742 from which the federal facilities desire to be exempt. Therefore, the Illinois EPA supports the Department of Defense's proposed amendments under the terms stated above.

b. Use of ELUCs by the Illinois EPA's Office of Chemical Safety

At both hearings on the proposed amendments to TACO the Illinois EPA was asked several questions about the agency's Office of Chemical Safety ("OCS") and its use of ELUCs and other provisions of TACO for spills. On the first day of hearing David Rieser asked whether an ELUC would apply to situations where there had been a release of contaminants in situations under the OCS's oversight of that remediation (ie., remediation not being conducted under the Leaking Underground Storage Tank ("LUST") program, the Site Remediation Program ("SRP"), or RCRA Part B permits and closures.) (See transcript of September 25, 2000 ("TR 1") at p. 30). Additionally, on the second day of hearing, Karen Bernoteit asked a similar line of questions regarding whether an ELUC was available for a site that was not enrolled in a remediation program, but rather was being overseen by OCS. (See transcript of September 11, 2000 ("TR 2") beginning at p. 104.) The line of questioning appeared to challenge the Illinois EPA's

authority to use TACO to determine remediation objectives at sites under the jurisdiction of the OCS.

For the last five years, the Illinois EPA's OCS compliance and enforcement program has focused on the prevention, remediation, and mitigation of releases from contaminants to air, water, and land. OCS's oversight of investigations and remediation of spills to soil and groundwater or surface water comes from authority created under the Illinois Environmental Protection Act ("Act"). That Act, as the Board is well aware, established the Illinois EPA with the charge of protecting human health and the environment and investigating violations of the Act or regulations adopted thereunder. The General Assembly stated in Section 2(c) of the Act that "the terms and provisions of this Act shall be liberally construed so as to effectuate the purposes of this Act." (415 ILCS 5/2)

It is important to note that the authority for all of Illinois EPA's actions is vested in the Director and the agency as a whole, not in any particular Bureau or program. Not all functions of the Illinois EPA fall neatly under a program, such as LUST or SRP. However, that does not release the agency of its charge to protect human health and the environment. Therefore, in order to effectively carries out its duties, the Illinois EPA often must rely upon the direct application of the provisions of the Act and related regulations. Such is the case with the OCS. There are no implementing regulations for the remediation activities that fall under the jurisdiction of the OCS. The OCS's jurisdiction over spills arises as the result of an event, not the status of the facility or site or the nature of the material released. In the context of releases to soil, groundwater, or surface water, the principal legal authorities relied upon by the OCS are provisions prohibiting persons from causing, threatening, or allowing pollution of waters of the State (generally found under Sections 12(a), (d), and (f) and 18(a) of the Act and 35 Ill. Adm.

THIS FILING IS SUBMITTED ON RECYCLED PAPER

Code 620). Those sections enable the Illinois EPA to obtain injunctive relief to investigate and remediate source areas of contamination that cause or threaten to allow water pollution, including groundwater pollution. Actions under these water pollution authorities enable the Illinois EPA to obtain relief against releases of any contaminant. Given the existence of case law defining what constitutes water pollution and the very broad definition of “contaminant” found in the Act, there has, to date, been no necessity to develop extensive implementing regulations.

Because TACO has proved to be an effective approach to determine remediation objectives that protect of human health and the environment based on risk, the OCS compliance and enforcement program has routinely utilized TACO to establish remediation objectives that will apply in matters where injunctive relief may ultimately be sought in a court of equity. There is a strong public policy argument for this approach.

In the interest of maintaining consistency with the Illinois EPA’s overall risk-based approach to clean ups, as well as for the convenience of parties familiar with the TACO approach, the OCS program has relied on TACO, rather than independently developing site-specific remediation objectives.

One of the concerns expressed through Ms. Bernoteit’s line of questioning was how parties would find appeal rights. It is important to note here that OCS has routinely offered parties the opportunity of entry into the SRP as a mechanism for oversight of investigations and remediation. The SRP clearly has established appeal procedures. However, in the event that a party does not elect to use the SRP as a mechanism for oversight and declines to undertake remediation acceptable to the OCS, the Illinois EPA typically has referred such matters for formal enforcement action before courts of equity pursuant to either Section 31 or Section 43 of the Act. If the Illinois EPA and a defendant are unable to negotiate a remediation objective, a

THIS FILING IS SUBMITTED ON RECYCLED PAPER

court of equity clearly has the authority to order an appropriate remedy. Rights of appeal for aggrieved parties exist within the court system of the State of Illinois.

In conclusion, we contend that OCS's use of TACO is acceptable. It is significant to note that the language of Section 742.105(b) does not expressly state that TACO is to be used *exclusively* for Bureau of Land-administered programs. However, in the event that the Board disagrees with this conclusion or feels unsettled on the issue of authority, we would suggest that the Board has the right, under its broad rulemaking authority, to add remediation activities under the OCS to the applicability section of TACO under Section 742.105(b).

2. Modification to Section 742.1105(c)(3)(C)(iii)

At the first hearing, Mr. Rieser asked a line of questions regarding this Section. (See TRI at pp.151-153). It became clear from Mr. Rieser's questions that a clarification of that Section was necessary because of the way that it is currently worded. Therefore, consistent with Mr. Rieser's questions and Mr. Clay and Mr. Nickell's responses, the Illinois EPA would offer the following change to clarify the language: "Are a minimum of ten feet in depth, and contaminants of concern are not within ten feet of any manmade pathway."

3. Implementation

The issue of implementation of the regulations came up quite frequently in the course of the TACO hearings. There were general questions as to the date the amendments as a whole would apply, and there were specific questions with regard to the ELUC provisions and the addition of a remediation objective for MTBE in light of the fact that the Board had not yet received the proposed amendments to the LUST and SRP rules. In response to the general question, the Illinois EPA believes, as is always the case, that the new provisions become effective on the date they are adopted by the Board. Unless another date is clearly specified, the

THIS FILING IS SUBMITTED ON RECYCLED PAPER

Illinois EPA applies the law that is on the books (effective) on the date of its decisions. For instance, if we today received a request for an ELUC approval, it would be reviewed under current law and denied because the ELUC provisions have not yet been adopted. If someone chooses today to file an ELUC on their chain of title, they take the chance that a third party would challenge that as an improper cloud on title. In that scenario, the challenger would probably win because the ELUC provisions have not yet been adopted. The same holds true for each and every other proposed amendment.

The only exception to the implementation issue is regarding the addition of MTBE. Implementation of the MTBE provisions is a bit trickier because it has not yet been proposed as an indicator contaminant under the LUST rules, nor is it referenced in the SRP rules at present. Therefore, the Illinois EPA would suggest that the Board consider adopting the provisions the Illinois EPA has proposed regarding MTBE and include a Board note stating that the MTBE provisions do not become effective until the LUST and SRP amendments are adopted.

Additionally, there was some question as to whether the Illinois EPA intended to reopen sites that have already received their No Further Remediation Letters and require additional clean up of MTBE. Mr. Clay answered that question on the record (TR2 at p. 130) by stating that we would not reopen those sites. However, Mr. Clay expressed that the Illinois EPA would be proposing to allow people that have more than 70 ppb going off-site to conduct remediation and gain access to the UST fund if they have an eligibility determination. Mr. Clay will be testifying more in depth on that issue in the course of the LUST amendment proceedings.

4. Cost and Duration of Remediating MTBE

Near the conclusion of the second day of hearing, Ms. Liu asked Mr. Clay whether he could provide information on the cost and duration of a remediation for MTBE. Mr. Clay stated

THIS FILING IS SUBMITTED ON RECYCLED PAPER

that we would provide some information as part of our final comments. I am attaching three short documents for the Board's review on this issue. They are labeled at Exhibits 4, 5, and 6 and entitled respectively "Remediation Of MTBE Contaminated Soil and Groundwater", "MTBE: Treatability and Remediation", and "Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water". As a side note, we also agreed to attach the IRIS report on MTBE discussed by Dr. Hornshaw. That is attached at Exhibit 7.

D. Special Request

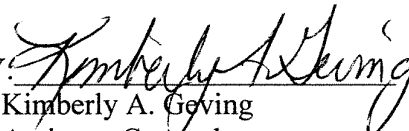
At the second day of hearing the Board inquired whether the Illinois EPA had reviewed a report written by the U.S. Department of Energy ("DOE") on Long-Term Institutional Control Management at DOE sites. The Illinois EPA responded that it had not. In a Hearing Officer Order dated September 19, 2000, the hearing officer requested that Mr. King review and comment on that report in the context of the Illinois EPA proposal in Docket A, involving ELUCs. Unfortunately, we had difficulty in downloading that report and did not receive a hard copy until shortly before these FINAL COMMENTS were due. However, after a cursory review of the report, it is the Illinois EPA's position that the report is not relevant to our proceeding. The focus of the report is DOE's 141 waste sites that are a legacy to U.S. nuclear weapons program. Only one of those sites, Argonne National Laboratory, is in Illinois.

E. Conclusion

The Illinois EPA's position on matters raised in this proceeding is well established in the testimony of its witnesses and in Errata Sheet Number 1. The Illinois EPA has attempted in these FINAL COMMENTS to further clarify and add support to those issues that appeared to be the main topics of concern at hearing.

WHEREFORE, the Illinois EPA submits its FINAL COMMENTS, including the Exhibits, for the Board's consideration and respectfully requests that the Board adopt the Illinois EPA's proposal in its entirety, including Errata Sheet Number 1.

ILLINOIS ENVIRONMENTAL
PROTECTION AGENCY

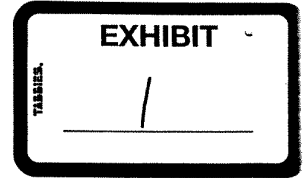
BY: 
Kimberly A. Geving
Assistant Counsel
Division of Legal Counsel

Dated October 23, 2000

1021 North Grand Avenue East
P.O. Box 19276
Springfield, Illinois 62794-9276
(217) 782-5544

Date: 10/19/00

MEMORANDUM OF AGREEMENT
BETWEEN THE
ILLINOIS ENVIRONMENTAL PROTECTION AGENCY
THE
U.S. ENVIRONMENTAL PROTECTION AGENCY
AND THE
U.S. DEPARTMENT OF (NAVY, ARMY, AIR FORCE)



THIS AGREEMENT is entered into this _____ day of _____, by and between the U.S. Environmental Protection Agency ("U.S. EPA"), the Illinois Environmental Protection Agency ("Illinois EPA") and the U.S. Department of the **(Navy, Army or Air Force; Installation Name)** also collectively referred to herein as "the Parties," for the specific purposes hereinafter set forth.

I. BACKGROUND

Environmental investigative activities being undertaken on **(Installation Name)** have revealed and may in the future reveal certain areas of environmental contamination ("Sites") on **(Installation Name)**. These Sites include those subject to regulation under either the Comprehensive Environmental Response, Compensation and Liability Act ("CERCLA") 42 USC 9601 *et. seq.*; the Resource Conservation and Recovery Act ("RCRA"), 42 U.S.C. 6901 *et. seq.*, and/or the provisions of the Illinois Environmental Protection Act, ("the Act") (415 ILCS 5/1 *et. seq.*), where hazardous substances, hazardous wastes or hazardous constituents, or petroleum products or their derivatives were released into the environment as a result of activities conducted over the history of the installation. Such Sites may generally be categorized as follows:

- a. Those that have been fully investigated and specific remedy(ies) previously implemented;
- b. Those that have been fully investigated and remedy(ies) have been selected but have not yet been implemented;
- c. Those that have been fully investigated but final remedy selection decisions have not yet been made; or,
- d. Those in need of initial or further investigative activities before the appropriate final remedy(ies) can be selected and implemented.

(Installation Name) desires that future site remedy determinations take land use into account in order to facilitate the use of risk-based remediation criteria established by U.S. EPA under CERCLA or Illinois EPA under the Act or its corresponding program rules, as may apply to a given Site. The Parties agree that when land use controls ("LUCs") are necessary to ensure the reliability of land

use assumptions, it is essential that appropriate procedures be put in place to ensure such controls will be maintained for as long as necessary to keep the chosen remedy fully protective of human health and the environment. In addition, the Parties agree that it is imperative to ensure that prospective purchasers of the property are fully informed of the existence of such controls and their responsibility to maintain them.

The Parties also recognize that **(Installation Name)** does not have the authority to place land use restrictions in county land records because it would be considered an unauthorized disposal of an interest in federal property (since title is held by the United States and not by **(Installation Name)**). Therefore, this Agreement is designed, in part, to ensure that if **(Installation Name)** desires to undertake a risk-based remediation of any Site falling under the program authorities of the Illinois EPA, that it comply with all applicable LUC requirements of the Act and its corresponding rules.

II. APPLICABILITY

This Agreement applies to each Site where **(Installation Name)** is required to undertake investigative and remedial activities in accordance with CERCLA or applicable Illinois EPA remediation program requirements and where **(Installation Name)** desires to utilize either U.S. EPA CERCLA risk-based Site remediation guidance or Illinois EPA's Tiered Approach to Corrective Action Objectives (TACO) regulations (35 Ill. Adm. Code 742) to undertake a risk-based remediation of the Site. Such Sites shall specifically include those falling under the following Illinois EPA programs:

- a. Leaking Underground Storage Tank ("LUST") Program (35 Ill. Adm. Code 732);
- b. RCRA Part B Permits, corrective action, and Closure Plans (35 Ill. Adm. Code 724 and 725); and,
- c. Site Remediation Program ("SRP") (35 Ill. Adm. Code 740).

Due to the unique nature of ownership interests in the real property at active federal facilities and the inability of **(Installation Name)** to comply with the LUC recording requirements of the Act and corresponding rules of the Illinois EPA, compliance with this Agreement will be deemed to fulfill those requirements until such time as any Site with LUCs on **(Installation Name)** that falls under any of the aforementioned Illinois EPA programs is transferred out of federal ownership. At the time of such transfer, all requirements of the Act and corresponding rules of the Illinois EPA as shall apply to that Site must be met.

III. DEFINITION

For the purposes of this Agreement, the term "Land Use Control" or "LUC" means any restriction or control arising from the need to protect human health and the environment that limits the use of or exposure to environmentally contaminated media (e.g., soils, surface water, groundwater) at any Site on **(Installation Name)**. The term includes controls on access (e.g., engineered barriers, such as caps, and non-engineered mechanisms, such as fences or security guards). Additionally, the term encompasses both affirmative measures to achieve the desired control (e.g., night lighting of an area) and prohibitive directives (e.g., no drilling of drinking water wells). The term also includes "institutional controls." Institutional controls are legal mechanisms for imposing a restriction on land use.

IV. PURPOSE

The Parties intend to accomplish the following specific objectives through execution of this Agreement:

- a. To implement a process to ensure appropriate long-term maintenance of those LUCs that may have already or may hereafter be selected as part of the remedy for any Site on **(Installation Name)**. It is intended such a process will in turn:
 1. Facilitate the application of Federal or State risk-based remediation criteria to Site remediations through consideration of assumed future land usage at those Sites where LUCs will be necessary to make such assumptions reliable;
 2. Elevate the general level of awareness amongst **(Installation Name)** personnel as to the need to maintain such controls in order to ensure long-term protection of human health and the environment.
- b. To implement a process for **(Installation Name)** to periodically advise U.S.EPA and Illinois EPA representatives of the continued maintenance of any LUCs implemented on the **(Installation Name)** and of any planned changes in land use impacting any Site remediated in accordance with risk-based criteria based on the assumption land usage would be controlled, (e.g., restricted to industrial use);
- c. To implement procedures for integrating all Site remedies that include LUCs into the facility land use planning process;
- d. To provide, in part through **(Installation Name's)** good faith compliance with this Agreement, reasonable assurances to U.S. EPA and Illinois EPA those specific pathway and exposure assumptions relied upon in applying a risk-based remediation standard to a given Site will remain valid until

such time as the Parties agree, pursuant to the applicable program procedures under which the Site is conducting remediation, that either different Site controls or unrestricted Site usage would be appropriate; and

- e. To satisfy **(Installation Name's)** obligation to comply with those LUC requirements to be reflected in any NFR determinations (or their equivalent) issued by U.S. EPA or Illinois EPA until such time as **(Installation Name)** and U.S.EPA or Illinois EPA, whichever agency has program authority, determines that those LUCs are no longer necessary for the protection of human health and the environment.

V. APPENDICES

- a. The following Appendices are now or shall hereafter become a part of this Agreement as further specified in paragraphs 1 through 4 below:
 1. The attached Site listing (Appendix A) for those presently known Sites covered under the terms of this Agreement. Appendix A will be updated at on a quarterly basis by **(Installation Name)** to reflect any additions or deletions of Sites as may hereafter be agreed to by the Parties. Copies of all quarterly updates must be promptly distributed to U.S. EPA and Illinois EPA. If no Site additions or deletions have been made during a previous quarter, then no Appendix need be prepared or distributed for that period.
 2. Individual Land Use Control Implementation Plans ("LUCIPs") (Appendix B) for all known Sites to be covered under the terms of this Agreement. These LUCIPs will be developed by **(Installation Name)** within **(insert "thirty (30)" or "sixty (60)" days)** of execution of this Agreement. Each LUCIP will: (1) identify the Site's location by reference to the facility's land use plan or by other means sufficient to enable the Parties to readily locate the Site; (2) identify both the LUC objective for the Site being addressed as well as those particular LUCs to be relied upon to achieve the objective; (3) specify what must be done in order to implement and maintain the specific LUCs required for the Site; and (4) contain a cross-reference to whatever decision document(s) apply to the Site. As future decisions involving LUCs are made at Sites on **(Installation Name)**, these Sites will become covered under this Agreement and listed in Appendix A, and a new LUCIP appropriate to each such newly covered Site will be added to Appendix B. In conjunction with **(Installation Name) (Base Master Plan)**, these plans should serve as a central LUC reference source to assist **(Installation Name)** personnel with completing those periodic Site inspections, review, and certifications required under Paragraph VI of this Agreement.

3. The attached Sample Record of Decision ("ROD") or Decision Document ("DD") language (Appendix C) containing a specific reference to this Agreement; and
 4. The attached listing (Appendix D) of the appropriate agency and facility Points of Contact ("POCs").
- b. Appendix E will contain all future NFR determinations (or their equivalent) as issued by U.S. EPA or Illinois EPA that pertain to Sites covered by this Agreement.

VI. SITE INSPECTION/REVIEW/CERTIFICATION

Within thirty (30) days of finalizing the LUCIP appendices mentioned above or sixty (60) days after execution of this Agreement, whichever occurs first, **(Installation Name)** shall initiate the following specific actions:

- a. Conduct **(insert - quarterly, semi-annual, or annual as negotiated by the Parties)** visual inspections of all Sites where LUCs have previously or may hereafter be implemented at such Sites identified in Appendix A to this Agreement. These inspections will be for the purposes of verifying all necessary LUCs have been implemented and are being properly maintained. The **(Installation Name) (Environmental Program Manager)** will be responsible for: (1) ensuring all required inspections are performed; (2) providing U.S. EPA and Illinois EPA with thirty (30) days advance notice of, and opportunity to participate in, **(insert "one quarterly," one semi-annual" or "the annual")** inspection conducted each calendar year; (3) notifying U.S. EPA and Illinois EPA of any deficiencies noted within thirty (30) days, and; (4) ensuring that corrective measures are undertaken as soon as practicable to correct any such deficiency(ies) with timely notification to U.S. EPA and Illinois EPA detailing corrective actions taken or providing a timetable outlining future remediation activities. If the agency that has program authority for the program under which remediation is taking place declines to concur, then such agency and **(Installation Name)** shall work together to resolve how the noted deficiencies will be corrected.
- b. If **(Installation Name)** has, or hereafter establishes, an environmental compliance board or similar body charged with coordinating and overseeing environmental compliance on the installation, such body shall conduct quarterly reviews to assess the **(Installation Name's)** status in complying with all previously implemented LUCs. Any non-compliance issues will be appropriately resolved with U.S. EPA or Illinois EPA, whichever has program authority over the Site(s) where deficiencies were found.

- c. Prepare and forward an annual report (**insert due date**) to U.S. EPA and Illinois EPA signed by the **(Installation Name) (Commanding Officer)** certifying the continued retention of all implemented LUCs associated with those Sites identified in Appendix A to this Agreement (as last updated).

VII. AGENCY COORDINATION

Effective upon execution of this Agreement, **(Installation Name)** agrees to implement the following agency notification and concurrence procedures:

- a. Except under circumstances reasonably determined by the **(Installation Name)** to be an emergency, the **(Installation Name)** shall provide at least sixty (60) days notice prior to implementation of any Land Use Change (as defined in Section VII.d.) at any Site subject to LUCs. The **(Installation Name)** will provide notification of any such change to U.S. EPA and Illinois EPA. Such notification must be provided for the purpose of obtaining either U.S. EPA or Illinois EPA concurrence (whichever shall have program authority over the affected Site(s)) with the **(Installation Name)** determination as to whether the contemplated change will or will not necessitate the need for re-evaluation of the selected remedy or implementation of specific measures to ensure continued protection of human health and the environment.
- b. Except in the case of an emergency where **(Installation Name)** personnel reasonably believe it is not practicable to wait for U.S. EPA or Illinois EPA concurrence, no Land Use Change should be implemented until U.S. EPA or Illinois EPA concurrence is obtained, consistent with the timeliness requirements set forth in subparagraph (c) below. For Land Use Change(s) affecting LUST or RCRA closure or corrective action Sites over which the State has program authority, although such notifications will be sent to both U.S. EPA and Illinois EPA, the **(Installation Name)** need only obtain Illinois EPA's concurrence with the proposed change. Each notification or request for concurrence must include:
 - 1. An evaluation of whether the anticipated Land Use Change will pose unacceptable risks to human health and the environment or negatively impact the effectiveness of the selected Site remedy;
 - 2. An evaluation of the need for any additional remedial action or LUCs resulting from implementation of the anticipated Land Use Change; and,
 - 3. A proposal for any necessary changes in the selected Site remedy.

Date: 10/19/00

- c. Upon being notified by **(Installation Name)** of an anticipated Land Use Change at a Site, U.S. EPA or Illinois EPA or both shall evaluate the information provided pursuant to paragraph (b) above, and respond in a timely fashion prior to such land use change.
- d. The Parties agree that any of the following will constitute a Land Use Change:
 - 1. Any change in land use (e.g. from industrial to residential) inconsistent with any land use contained in those specific exposure assumptions in the human health or ecological risk assessments that served as the basis for the LUCs implemented at the Site;
 - 2. Any Site activity disrupting the effectiveness of the implemented LUC. Examples include, but are not limited to: excavation at a landfill; groundwater pumping impacting a groundwater pump and treat system; a construction project impacting ecological habitat protected by the remedy; removal of a fence; unlocking of a gate; or removal of warning signs; or,
 - 3. Any Site activity intended to alter or negate the need for the specific LUC(s) implemented at the Site.
- e. The **(Installation Name)** also agrees to immediately notify U.S. EPA and Illinois EPA if, despite its best efforts to ensure compliance with paragraphs (a) and (b) above, any Land Use Change at any Site with an implemented LUC is discovered not having been previously reviewed and concurred in by U.S. EPA or Illinois EPA in accordance with paragraph (a). Such notifications will provide all pertinent information as to the nature and extent of the change and describe any measures implemented or to be implemented (to include a timetable for future completion) to reduce or prevent human health or ecological impacts.

VIII. MOA INTEGRATION

The Parties agree when Site-specific LUCs are to be implemented, an adequate description of the same along with conditions for their use will be included in whatever decision document reflects the selected remedy for a Site as well as in the associated LUCIP. Additionally, Appendix C contains standard language for inclusion in such documents as CERCLA RODs or DDs, Remedial Action Plans (RAPs), closure or post closure plans for RCRA regulated units or formal modifications to a facility's RCRA/HSWA permit, or in separate approval or No Further Remediation (NFR) letters issued by U.S. EPA or Illinois EPA, whichever has oversight authority over the Site in question.

IX. FUTURE PROPERTY CONVEYANCE

Should the decision later be made to transfer to any other agency, private person or entity, either title to, or some lesser form of property interest (e.g., an easement or right of way) in any Site on **(Installation Name)** with an existing LUC(s), then **(Installation Name)** shall ensure:

- a. U.S. EPA and Illinois EPA are provided with notice at least sixty (60) days prior to any such intended conveyance. Such notice must: (1) indicate the mechanism(s) intended to be used to reasonably ensure any LUC(s) needing to remain in place after interest conveyance will be maintained; and (2) include an assurance that **(Installation Name)** has fully advised the property disposal agent who shall prepare the deed(s) or other instruments that will be used to convey the property of the need to include those LUCs that must remain on the property in those documents.
- b. All existing "NFR" determinations (or their equivalent) issued by U.S.EPA or Illinois EPA, have been appended to this Agreement and that a copy of the same is provided to the property disposal agent who will handle the conveyance of any Site with LUCs still in place.
- c. Each LUC is reviewed and incorporated into those property disposal documents (e.g., **Environmental Baseline Survey for Transfer ("EBST") and Finding of Suitability for Transfer ("FOST")**) to meet CERCLA and 40 CFR 373 notice requirements and that copies of the following documents are made available by the property disposal agent to the intended transferee(s) for recordation as may be required by applicable federal or State law:
 - 1) All No-Further-Remediation (NFR) letter(s) or determinations (or their equivalent) issued by U.S.EPA or Illinois EPA as pertain to the property; and,
 - 2) All RODs or similar Site decision documents as pertain to the property.
- d. Each transferee is given adequate notice of existing Site condition(s) and informed of the responsibility that they will be assuming for maintaining any LUCs previously implemented on the property. The notice will indicate that if the LUCs are not maintained, any NFR determination based on the LUCs may no longer be valid.

It is understood the planned conveyance of any Site with LUCs may prompt U.S. EPA or Illinois EPA to re-evaluate the continued appropriateness of any previously agreed upon LUC(s) based upon the level of assurance provided that all necessary LUCs will be adequately maintained.

X. CHANGE IN APPLICABLE STANDARDS

Nothing herein should be construed to preclude **(Installation Name)** from proposing at any time or from the Parties otherwise agreeing to effect the deletion of any Site from coverage under the terms of this Agreement on account of either: (i) a post-remedy implementation change to applicable Federal or State risk-based cleanup standards, or (ii) a change in previously documented contaminant concentration levels allowing for unrestricted use solely as a result of the effects of man induced or naturally occurring bioremediation/attenuation.

XI. FUTURE COMMUNICATIONS

Upon execution of this Agreement each Party shall notify the other Parties as to the name(s), address(es), telephone number(s), electronic mail address(es) and facsimile number(s) of their respective representative(s) who should receive all correspondence and communications on behalf of the Party pertaining to all matters falling under the terms of this Agreement. The listing of agency POCs, which is attached hereto as Appendix D, will be updated by the Parties as appropriate.

XII. SITE ACCESS

(Installation Name) herein agrees to provide U.S. EPA and Illinois EPA representatives, contractors or consultants access to all Sites to be covered by this Agreement at all reasonable times consistent with military mission, national security and health/safety requirements upon presentation of proper credentials. The installation's **(Environmental Program manager)** or his/her designee will coordinate access and escort the regulatory personnel to restricted or controlled access areas, arrange for base passes and coordinate any other access requests that arise. Nothing in this Agreement is intended to be construed to limit in any way the right of entry or inspection, either U.S. EPA or Illinois EPA, may otherwise have by operation of law. U.S. EPA and Illinois EPA representatives will have the authority to enter and move freely around any Site at all reasonable times for purposes including, but not limited to, reviewing the efforts performed by **(Installation Name)** in complying with the terms of this Agreement; conducting such tests as these agencies may deem necessary and verifying all information/data submitted by **(Installation Name)** personnel pursuant to this Agreement.

XIII. DISPUTES

All Parties agree to engage in a good-faith effort to resolve any and all disputes, hereafter arising with regard to the **(Station's)** substantial good-faith compliance with the terms of this Agreement or other matters relating to the Sites addressed hereunder.

XIV. RESERVATION OF RIGHTS

It is agreed and understood U.S. EPA and Illinois EPA reserve all rights and authorities each agency may currently have or hereafter acquire by law to require **(Installation Name)** to comply with those federal and state laws and regulations applicable to the investigation, cleanup and long term maintenance of those Sites to be covered by this Agreement. Moreover, Illinois EPA specifically reserves the right to rescind any NFR letter or determination issued in connection with any Site covered under this Agreement if the LUC(s) associated with that Site(s) are not properly maintained. It is also understood the **(Commanding Officer), (Installation Name)** herein reserves those rights and authorities granted to the Department of Defense (DoD) by federal or state law, regulation, or executive order including, but not limited to, CERCLA, Executive Order 12580 (Superfund Implementation), and the National Contingency Plan (40 CFR Part 300). On behalf of the **Department of the (Navy, Army, Air Force), (the Commanding Officer) (Installation Name)** further reserves the right to put all property under his cognizance to those uses deemed necessary in his discretion for mission accomplishment or otherwise deemed necessary by appropriate military authority to meet the needs of the DoD.

XV. ANTI-DEFICIENCY ACT

Nothing in this Agreement will be construed as obligating the **(Navy, Army, Air Force)** or U.S. EPA, their officers, employees, or agents to expend any funds in excess of appropriations authorized for such purposes in violation of the federal Anti-Deficiency Act (31 U.S.C. Section 1341).

XVI. AMENDMENT

Any amendments to this Agreement shall be in writing, executed by the undersigned signatories or their duly authorized designees or successors and attached to this original Agreement.

XVII. TERMINATION

This Agreement will terminate at such time as the undersigned representatives of the Parties or their successors, mutually concur the aforesaid objectives of the Parties have been fulfilled and the need for such an Agreement no longer exists. Alternatively, any Party may unilaterally withdraw from this Agreement upon sixty (60) days written notice to the other Parties but only after reasonable efforts have first been made by all Parties to resolve the dispute(s) leading to the taking of such action. If any Party decides to unilaterally withdraw, the Parties shall nonetheless work towards resolving any outstanding issues as may exist between them. It is understood should the **(Navy, Army, Air Force)** choose to unilaterally withdraw from this Agreement, U.S. EPA and Illinois EPA may choose to

Date: 10/19/00

reconsider any remedy(ies) associated with any Site with a LUC still in place at the time of such withdrawal.

XVIII. REPRESENTATIVE AUTHORITY

Each undersigned representative of the Parties to this Agreement certifies she or he is fully authorized to enter into the terms and conditions of this Agreement and to execute the same so as to effectively bind each Party to its terms.

XIX. EXECUTION

This Agreement shall become effective on the date the last of the authorized representatives of the Parties signs.

FOR THE ILLINOIS ENVIRONMENTAL PROTECTION AGENCY

By: _____ Title: _____

Date: _____

FOR THE U.S. ENVIRONMENTAL PROTECTION AGENCY, REGION 5

By: _____ Title: _____

Date: _____

FOR THE **DEPARTMENT OF THE (NAVY, ARMY, AIR FORCE)**

By: _____ Title: _____

Date: _____

Date: 10/19/00

APPENDIX A
LAND USE CONTROL
SITE LISTING

Date last updated: _____

Site:

LUCIP #:

- 1.
- 2.
- 3.
- 4.
- 5.
- 6.
- 7.
- 8.
- 9.
- 10.

Date: 10/19/00

APPENDIX B

LAND USE CONTROL
IMPLEMENTATION PLAN
FOR SITE _____

1. Site Description: (e.g., former fire fighting training area, approx. size 150' x 200' and contaminants of concern)

2. Site Location: (e.g., northeast corner of the Station between buildings 250 and 260 as reflected on BMP page ____/GIS index under IR Site or GPS information provided in decimal degrees to the nearest sixth digit).

3. LUC Objectives(s): (e.g., to restrict public access to an area for recreational use).

4. LUC(s) Implemented to Achieve Objective(s): (e.g., installation of a fence, warning signs, etc. . . , or BMP notations restricting residential or recreational usage).

5. Decision Document: (e.g., RoD/DD dated _____ or No Further Remediation (NFR) letter dated _____).

6. Other Pertinent Information:

APPENDIX C

SAMPLE ROD/DD
MOA INCORPORATION LANGUAGE

(Insert the following language in those RODs/DDs providing for the use of LUC(s).

By separate Memorandum of Agreement ("MOA") dated _____, with U.S. Environmental Protection Agency ("U.S. EPA"), the Illinois Environmental Protection Agency ("Illinois EPA"), and **(Installation Name)**, on behalf of the **Department of the (Navy, Army, Air Force)**, agreed to implement base-wide, certain periodic Site inspection, condition certification and agency notification procedure designed to ensure the maintenance by **(Installation Name)** personnel of any Site-specific Land Use Controls ("LUCs") deemed necessary for present and future protection of human health and the environment. A fundamental premise underlying execution of this agreement was through the **(Branch of Services)** substantial good-faith compliance with the procedures called for therein, reasonable assurances would be provided to U.S. EPA and Illinois EPA as to the permanency of those remedies that included the use of specific LUCs.

Although the terms and conditions of the MOA are not specifically incorporated or made enforceable herein by reference, it is understood and agreed by the **(Navy, Army, Air Force)**, U.S. EPA and the Illinois EPA that the contemplated permanence of the remedy reflected herein will be dependent upon the **(Installation Name)** substantial good-faith compliance with the specific LUC maintenance commitments reflected therein. Should such compliance not occur or should the MOA be terminated, it is understood the protectiveness of the remedy concurred in may be reconsidered and additional measures may need to be taken to adequately ensure necessary future protection of human health and the environment.

APPENDIX D

AGENCY AND FACILITY POINTS OF CONTACT

ILLINOIS EPA

Name:

Address:

Phone:

U.S.EPA

Name:

Address:

Phone:

(INSTALLATION NAME)

Name:

Address:

Phone:

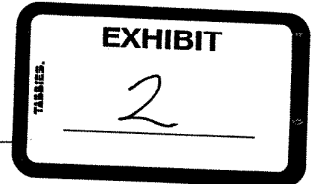
Date: 10/19/00

APPENDIX E

SITE NFR DETERMINATIONS



U.S. GENERAL SERVICES ADMINISTRATION
Office of General Counsel



October 20, 2000

Kimberly A. Geving, Esq.
Assistant Counsel
Division of Legal Counsel
Illinois Environmental Protection Agency
1021 North Grand Avenue East
P.O. Box 19276
Springfield, Illinois 62794-9276

Re: Continuation of Land Use Controls upon Conveyance of Federally
Owned Real Properties by the General Services Administration

Dear Ms. Geving:

I am writing to follow-up on our discussions last week regarding GSA's position on the continuation of any land use controls ("LUCs" or "controls") previously implemented at contaminated sites on federal properties later turned over to GSA for disposal. I would like to take this opportunity to confirm for you GSA's position on that issue.

Generally speaking, if a federal landholding agency were to implement, with either U.S. EPA or State regulatory agency concurrence, a LUC on property which is thereafter turned over to GSA for disposal, GSA would act to ensure that the control in question was carried forward and made binding upon the new owner(s) of the property as necessary to ensure future protection of human health and the environment. Consistent with GSA policy, prior to effecting such a transfer GSA would consult with U.S. EPA or appropriate State regulatory agency representatives concerning whether the control was still required and if so, how best to ensure that it be maintained consistent with the terms of whatever no-further-remediation (NFR) or equivalent regulatory agency determinations may apply to the site(s) on the property.

If, in the course of marketing a parcel of surplus federal property, GSA determines that an existing LUC was effectively impairing the government's ability to dispose of the property, GSA would engage the appropriate landholding agency in discussions concerning the need to complete whatever additional remedial measures (if any) might be necessary to eliminate the need for that site control. Alternatively, there may be instances where a prospective buyer indicates a willingness to accept responsibility for undertaking any additional

1800 F Street, NW, Washington, DC 20405-0002

Federal Recycling Program



Printed on Recycled Paper

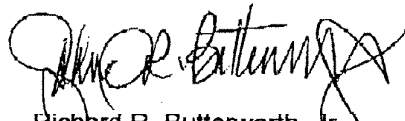
measures required for the release of such a control in order to further their specific redevelopment plans for the property. In either instance, GSA would coordinate all LUC related issues with the appropriate environmental regulatory agency.

Please be assured that with regard to federal properties in the State of Illinois, GSA is fully cognizant of the need for us to obtain your agency's buy-in for the extinguishment or modification of any site remedy-based LUC previously approved by IEPA. Similarly, GSA understands that if such were not done, it would jeopardize the continued validity of any prior site-close-out determination made by IEPA and could well subject the federal landholding agency that agreed to implement and maintain any LUC reflected therein to enforcement action.

Finally, be advised that GSA concurs with the position previously relayed to you by Department of Defense ("DoD") representatives regarding the linkage between the Federal Government's ability to lawfully convey properties with any hazardous substance contaminated sites and the continued validity of any NFR or similar regulatory agency determinations which may have previously been issued in connection with those sites. In this regard, like the DoD we view CERCLA's deed covenant requirement as obligating us to ensure, prior to deed execution, that there are no outstanding regulatory agency concerns regarding whether all necessary remedial measures have been taken to address such contamination. Therefore, GSA likewise is willing to acknowledge that CERCLA essentially dictates that we ensure full regulatory agency coordination prior to transferring such properties out of federal hands.

I hope this letter helps address any questions or concerns IEPA staff or any member of the Illinois Pollution Control Board may have in this matter. Should you have any additional questions, please feel free to call me at (202) 501-4436.

Sincerely,



Richard R. Butterworth, Jr.
Senior Assistant General Counsel

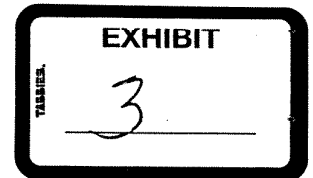
cc:
Mr. Gary Zolyak, DoD REC Counsel



ACQUISITION AND
TECHNOLOGY

OFFICE OF THE UNDER SECRETARY OF DEFENSE

3000 DEFENSE PENTAGON
WASHINGTON DC 20301-3000



AUG. 31 2000

DUSD(ES/CL)

MEMORANDUM FOR ASSISTANT SECRETARY OF THE ARMY
(INSTALLATIONS AND ENVIRONMENT)
ASSISTANT SECRETARY OF THE NAVY
(INSTALLATIONS AND ENVIRONMENT)
ASSISTANT SECRETARY OF THE AIR FORCE
(MANPOWER, RESERVE AFFAIRS, INSTALLATIONS AND
ENVIRONMENT)
DIRECTOR, DEFENSE LOGISTICS AGENCY (D)

SUBJECT: Interim Policy on Land Use Controls Associated with Environmental Restoration
Activities

1. PURPOSE AND SCOPE.

This policy provides an overall DoD framework for implementing, documenting, and managing land use controls (LUCs) for real property being transferred out of Federal control and for active installations. The following two attached documents amplify the policy in this memorandum:

- ◆ DoD Guidance on Land Use Controls Associated with Environmental Restoration Activities for Property Planned for Transfer Out of Federal Control.
- ◆ DoD Guidance on Land Use Controls Associated with Environmental Restoration Activities for Active Installations.

2. DEFINITION.

LUCs include any type of physical, legal, or administrative mechanism that restricts the use of, or limits access to, real property to prevent or reduce risks to human health and the environment. Physical mechanisms encompass a variety of engineered remedies to contain or reduce contamination and/or physical barriers intended to limit access to property, such as fences or signs. Legal mechanisms include restrictive covenants, equitable servitudes, and deed notices. Administrative mechanisms include notices and existing construction permitting or land use management systems that may be used to ensure compliance with use restrictions.

The legal mechanisms used for LUCs are generally the same as those used for institutional controls (ICs) as discussed in the National Contingency Plan (NCP). ICs are primarily legal mechanisms imposed to ensure that restrictions on land use developed as part of a remedy decision stay in place. The term land use controls includes institutional controls.



3. BACKGROUND.

DoD and EPA have issued guidance on how to incorporate future land use into the environmental restoration process (see DoD's July 25, 1997, policy memorandum, *Responsibility for Additional Environmental Cleanup after Transfer of Real Property* and EPA's May 25, 1995, directive, *Land Use in the CERCLA Remedy Selection Process*). Reasonably anticipated future land use assumptions are typically made before completing any CERCLA investigation and may be based on various factors, including statutory land use designations, contractual arrangements for transfer of property, zoning, community reuse plans, and installation master plans. The application of reasonably anticipated future land use assumptions may, in general, result in a remedy decision and remedial action under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) that does not require a physical action to be taken. The decision and action may require restrictions on the use of the property, implemented by LUCs, to ensure that future activity remains consistent with the reasonably anticipated future land use.

LUCs may be needed where containment or treatment of contaminants is not necessary to protect human health and the environment. A determination that there is no unacceptable risk or that a particular response action is not needed may be made by comparing sampling data with appropriate screening levels developed for various land use scenarios, or through a baseline risk assessment using exposure assumptions appropriate for the reasonably anticipated land use.

Restrictions or controls on land use, in some cases, may also be needed while conducting environmental restoration investigations before making an environmental restoration decision, or during implementation of cleanup activities. Reasons for such restrictions may range from site security for property and equipment, to safety concerns typical for a construction or industrial area, to concerns about health or potential exposure to possible contamination. Mechanisms used to ensure the viability of such restrictions or controls required for a specified period of time or necessary until completion of specific environmental restoration activities are often called cleanup LUCs or interim LUCs.

As land use planning and management are typically local functions, this policy and the attached guidance documents focus on how to implement and manage LUCs through applicable land use planning tools in order to ensure the efficacy of the use restrictions. The policy assumes that an appropriate environmental decision has been made and does not reopen those environmental restoration decisions, but provides mechanisms for implementing, in the most effective way possible, those decisions through use of LUCs.

4. POLICY.

The intent of this policy is to ensure that land use activities in the future remain compatible with the land use restrictions imposed on the property during the environmental restoration process. The attached guidance documents provide more detail on implementing the concepts stated below throughout the pre-transfer, transfer, and post-transfer stages of the property transfer process, or, for active installations, the installation land use management process. This policy and implementing guidance are effective immediately. Neither the policy

nor the guidance documents require or suggest that previously concluded decisions be reopened. This policy and guidance will be incorporated into the next revision of appropriate DoD directives, instructions, and other implementing documents. Components need to plan, program, and budget for necessary funding in appropriate accounts to implement this policy and supporting guidance.

a. Requirements applying to both *Transferring Property and Active Installations*.

(1) *Feasibility Studies*. Feasibility Studies that consider a remedy requiring a land use restriction shall include the costs of implementing and maintaining the LUC, as well as an evaluation of an “unrestricted use” alternative. This will enable decision makers to appropriately consider cost in the remedy selection process. Feasibility Studies already in progress on the date of this policy should attempt to conform to this requirement where practicable. Feasibility Studies started after 60 days from the date of this policy shall conform to this requirement.

(2) *Decision Documents*.

- ◆ Environmental restoration decision documents (e.g., RODs) for remedies with LUCs shall describe the exposure scenario that was used to select the remedy, including the assumptions made concerning current and reasonably anticipated future land use(s), and specify the uses that may be made of the property or the activities that are to be prohibited.
- ◆ Decisions to take no further action shall be documented in a decision document. This decision document should set forth the rationale behind the finding and include the relevant exposure assumptions and documentation of the reasonably anticipated future land use. Any currently existing restrictions on land use that were part of the determination of reasonably anticipated future land use should also be described.

(3) *LUC Implementation*. Components shall put appropriate control mechanisms (discussed in the attached guidance documents) in place to manage LUCs and shall incorporate LUCs into the existing land use management processes of the locality (for property being transferred out of Federal control) or the installation (for DoD-controlled property).

- ◆ Components should use a layering strategy or a system of mutually reinforcing controls, as described in the attached guidance documents, to effectively implement LUCs.
- ◆ Components should consider describing the LUC strategy delineating the responsibilities of all parties involved in implementing the LUCs. The level of detail should be commensurate with the size of the parcel and controls needed, and can be part of an existing land use management document or process. This strategy or plan is an internal management tool and does not impose any additional legal obligations.

(4) *LUC Database*. Components should maintain a central database of properties restricted by LUCs. The database should include information on the types of LUCs established and any DoD land use monitoring and management responsibilities.

(5) *LUC Modification/Termination*. LUCs should be modified or terminated through the same process used to establish the LUC, and if terminated, deleted from the mechanisms discussed in the attached guidance documents. Upon modification or termination of a LUC, Components shall undo the layering mechanism, if one was put in place, to avoid future confusion about the

status of the property. If the decision document needs to be amended, Components need to obtain the same general level of applicable regulatory comment and review as the original decision document.

(6) Memorandums of Agreement/Understanding (MOA/MOU). The policy preference is to use existing processes and mechanisms in the development, implementation, and management of LUCs. If however, a separate agreement with a regulatory agency is needed to facilitate the use of LUCs, such agreements shall be consistent with existing law and authority and be similar in scope for similar non-Federal property. Such agreements may not abrogate DoD's CERCLA authorities; and will acknowledge DoD's lead agency status, and should explicitly acknowledge such authorities and rights. Mutually acceptable and reciprocal reservation of rights clauses should be used to avoid otherwise irreconcilable conflicts and stalemates in negotiations. Such agreements, which shall be used only in exceptional cases, should be developed in consultation with other Components and the Office of the Secretary of Defense (OSD) and are also subject to a 72-hour OSD and Component review requirement. Agreements that follow all relevant aspects of an accepted model are exempt from this review requirement, provided the Component has validated the consistency with the model; otherwise, all significant deviations from the model are subject to the 72-hour review requirement.

(7) Federal-to-Federal Property Transfers. For Federal-to-Federal agency property transfers (including transfers between Components), the receiving agency generally will be responsible for the maintenance and management of the LUCs.

b. Requirements applying only to Transferring Property.

(1) LUC Responsibility. Because many types of LUCs are solely within the jurisdiction of local governments (e.g., zoning) and because the property owner has the most direct control over transferred property, Components should encourage the local government and the property owner to take responsibility for the management and enforcement of LUCs.

(2) State Land Use Issues.

- ◆ Components should use state LUC registries where available. If possible, Components should grant a property interest to the relevant state or local agency that will allow the state or local agency to maintain and enforce the LUC.
- ◆ As most LUCs ultimately may be memorialized in the deed as deed restrictions, it is essential that the disposal agency consult state property law and state environmental law when drafting the restriction because state law may require the use of a particular type of instrument or operative language.

c. Requirement applying only to Active Installations.

(1) LUC Responsibility. On active installations, Components have the authority over land use planning and can internally restrict and control use of such property.

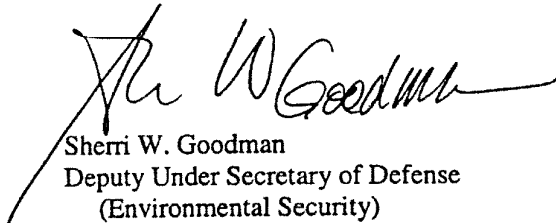
(2) *Land Use Compatibility*. Because the use of property subject to LUCs may change, it is important for the installation to ensure land use activities remain compatible with the restrictions on land use. The installation shall institute a process to review and evaluate the effect on human health and the environment of any proposed land use changes for areas covered by LUCs.

d. Policy Supplementation and Conformity.

The DoD Components may supplement this policy and guidance based on their own specific needs and the land use management tools available at their installations, provided such supplements are determined at the Component Deputy Assistant Secretary level to be consistent with this policy and guidance. Any significant deviation requires prior coordination with the Office of the Deputy Under Secretary of Defense (Environmental Security) [ODUSD(ES)]. Any existing Component policy or guidance must be revised to be consistent with this policy and implementing guidance documents. Component specific supplements must be provided to ODUSD(ES) upon issuance.

5. FOLLOW-UP AND POINT OF CONTACT

DoD is committed to working with all appropriate federal, state, and local agencies and prospective property owners to ensure that LUCs on property being transferred are effective and remain protective. We intend to finalize this policy based on further input from stakeholders and Component experience. The point of contact for this policy is Mr. Shah A. Choudhury at (703) 697-7475.



Sherri W. Goodman
Deputy Under Secretary of Defense
(Environmental Security)

Attachments:
as stated

cc:
DUSD(I)
DGC(E&I)

Department of Defense Guidance on Land Use Controls Associated with Environmental Restoration Activities for Property Planned for Transfer Out of Federal Control

1. PURPOSE.

This document provides guidance to Components, based on Department of Defense (DoD) *Interim Policy on Land Use Controls Associated with Environmental Restoration Activities*, on developing, implementing, recording, and managing land use controls (LUCs) for property planned for transfer from DoD to non-Federal entities. LUCs include any physical, legal, and/or administrative mechanism that restricts the use of, or limits access to, real property to prevent exposure to contaminants above permissible levels. LUCs are employed to protect the integrity of the engineering remedy and human health and the environment after transfer of property.

The objective when implementing LUCs is to develop a system of mutually reinforcing controls to ensure that land use is consistent with restrictions imposed on the property during the environmental restoration process. Implementing LUCs through established real estate and land use management mechanisms provides the best assurance that LUCs will be effective. Beyond establishing the appropriate implementation mechanisms before transfer, DoD may have only limited authority to control the use of property it no longer owns. Because state and local laws govern property transfer and land use, actions to implement and manage LUCs will be governed largely by state and local requirements.

This guidance provides a range of options that may be used separately or collectively for incorporating land use controls into existing land use management processes. It also discusses the roles of the DoD Component environmental office and property disposal agent in the implementation and management processes. The intent of this guidance is to provide an overall framework with a range of available options for use depending on site-specific circumstances.

2. APPLICABILITY AND SCOPE.

a. **Transfers Out of Federal Control.** This guidance applies to real property being transferred out of Federal control where a decision to restrict land use has been made as part of the environmental restoration process. Such property includes early transfers made pursuant to CERCLA section 120(h)(3)(C) and property assigned to another Federal agency solely for the purpose of transfer to a non-Federal entity.

b. **Leased Property.** If Federal real property is put into reuse through a long-term lease before being transferred by deed, the framework described in this guidance is applicable for developing LUCs. Those lease restrictions shall be reflected in the Finding of Suitability to Lease and lease documents as further described in the May 18, 1996, *DoD Policy on the Environmental Review Process to Reach a Finding of Suitability to Lease (FOSL)*.

c. **Exclusions.** This guidance does not apply to property that remains in Federal control, including active installations and property transferred to another Federal agency for its programmatic use. This guidance does not apply to U.S. Army Civil Works property.

3. **GUIDANCE.** The guidance below outlines the process for implementing, documenting, and managing LUCs for property planned for transfer from DoD to non-Federal entities.

a. **Pre-Transfer.**

(1) Consideration of Land Use Controls. In the remedy selection process, uses other than residential or unrestricted use may be considered. For Base Realignment and Closure (BRAC) property, the Local Redevelopment Authority's (LRA's) redevelopment plan (specifically the land use plan) typically will be the basis for land use assumptions. If there is no such redevelopment plan, the supporting property disposal agent or real property management office will develop the reasonably anticipated land use. Development of the reasonably anticipated future land use assumption may entail evaluation of a range of likely land uses taking into account factors such as current land use, current zoning classification, property characteristics, and the land use in the surrounding area. The reasonably anticipated future land use assumptions allow the Component (in conjunction with regulatory agencies) to determine the appropriate remedy and whether LUCs are necessary. The goal is to facilitate community redevelopment efforts; however, this does not imply that reuse alone dictates the selection of the environmental restoration remedy. This remedy must be selected in accordance with the remedy selection criteria established in the NCP that include cost, implementability, and short and long-term effectiveness.

Unlike other activities in the cleanup process, which are the sole responsibility of the environmental office, the development of LUCs is a team effort. Close and continual communication between the supporting environmental office and property disposal agent is essential during the development of LUCs and throughout the entire land use process. Once a decision is made that LUCs are needed, the supporting environmental office, in conjunction with the property disposal agent determines what types of LUCs will be most effective to protect human health and the environment and to facilitate reuse. Typical LUCs include restrictions on residential use, excavation, and ground water use restrictions.

(2) Finding of Suitability to Transfer. After selecting an appropriate use restriction that results in aLUC, the environmental office shall provide sufficient information on the nature and intent of the restrictions to the property disposal agent to ensure that the restrictions are clearly described in property conveyance documents. This information should include a specific description of the LUC; the rationale for the LUC; and the description and location of the affected property. The information should be contained in a Finding of Suitability to Transfer (FOST) or in a functionally equivalent document. The FOST, or equivalent document, functions primarily as a bridge between the environmental process (memorializing the environmental restoration decisions and actions taken) and the real estate process (describing land use planning and management decisions). The FOST should document the specifications of the LUC (e.g., no excavation, no groundwater use) that need to be included in the deed and implemented through

land use management and control mechanisms described later in this document. The property disposal agent will develop the specific deed language.

(3) Implementation of Land Use Controls. Generally, the types of mechanisms that restrict land use are either governmental or proprietary. Governmental mechanisms originate from state or local police power authorities, and include zoning, permitting, and local development ordinances. Proprietary controls are contractual mechanisms, usually established in a deed or contract for sale in the form of covenants or easements. A particular property may require different types of use restrictions. Because many of these mechanisms exist solely within the authority of the state or local government, the property disposal agent should start working closely with the appropriate local or state agencies early in the disposal process.

(a) State Law Issues. The Component environmental office or the property disposal agent, as appropriate, should request that the appropriate state agency specify the types of real estate records, LUC registries, planning and zoning controls, and statutes used in the state to track and enforce LUCs. LUCs shall comply with state LUC management provisions, consistent with Federal law and DoD environmental policy. If possible, the Components should grant a property interest to the relevant state or local agency, which would allow the state or local agency to maintain and enforce the LUC. This will help ensure that real estate rights for the state in which the property is located are enforceable.

(b) Layering Strategy. The most effective method of implementing LUCs is through a layering strategy or system of mutually reinforcing LUCs. When deciding what land management controls may help to reinforce a restriction, the Component shall investigate mechanisms available in the local area, such as the zoning code or a state land use control registry. For example, fully implementing a prohibition on groundwater use may require a deed restriction, a zoning ordinance, a local ordinance restricting use of groundwater, and notice to the local community to ensure that a restriction remains protective and prevents inappropriate uses of the property. Using available state and local real estate mechanisms ensures incorporation of LUCs into the local land use and regulatory processes and continued maintenance of the controls. For further information on tailoring layering mechanisms, see DoD's Environmental Cleanup Web Page at [<http://www.dtic.mil/envirodod/brac/>].

(c) Describing the Land Use Control Strategy. To clearly delineate the responsibilities of all parties involved in implementing the LUCs, Components shall develop a LUC implementation plan. This plan is as an internal management tool and does not impose any additional legal obligations. The Component's plan will reflect the intent of all parties at the time the LUCs are developed and implemented. The level of detail in the plan shall be commensurate with the size of the site, the type of controls needed, and other relevant factors. The plan may be a separate document or part of the property disposal plan. Finalization and implementation of the plan identifying the LUC strategy should occur only after concluding all discussions and coordination with the transferee and local entities. During the five-year review process (discussed later in this document), validation of this plan ensures that LUC mechanisms are still in place. The plan shall also specify the process for

discontinuing the land use controls and layering mechanisms if some or all of the LUCs become unnecessary.

(d) Roles of Other Parties. Other parties critical to the LUC process include the transferee, environmental regulators, and other relevant state and local agencies. The appropriate DoD Component office should identify and establish contact with the transferee and these state and local agencies, which may include local planning agencies, zoning and water boards, tax assessors, and state and Federal environmental regulators. Depending on the function of the state or local agency (i.e., primarily environmental or land use management), the appropriate Component office (environmental or real estate) should coordinate that part of the layering strategy. Once the parties involved in the layering strategy have been identified and after individual discussions have been conducted, both the environmental office and property disposal agent should meet with the parties to discuss the Component's proposed LUC strategy and coordinate a final strategy amenable to all parties.

b. At Transfer.

(1) Deed Restrictions/Transfer Agreements. In accordance with the DoD July 25, 1997, policy memorandum, *Responsibility for Additional Environmental Cleanup after Transfer of Property*, the property disposal agent shall ensure the LUCs are incorporated into the transfer documents for real property. The property disposal agent, with input from the environmental office, will draft the necessary language for the LUCs, as most LUCs ultimately will be memorialized in the deed as deed restrictions. At a minimum, the property disposal agent should verify with the environmental office that the LUC, as drafted, addresses the particular environmental restoration concerns at the site. In drafting the restriction, the property disposal agent should consult both state property and environmental law because it may require the use of a particular type of instrument or operative language. For example, Connecticut environmental law provides a form for drafting the deed restriction and model language to be used in order to create an environmental use restriction recognized in Connecticut.

In addition to the specific language describing the restriction, the transfer documents (such as the contract for sale) shall reference the environmental documents that containing the restriction rationale. At a minimum, these documents should reference the FOST (if BRAC property) or other functionally similar document, the decision document (such as the ROD), and other appropriate environmental documents (e.g., the Environmental Baseline Survey). The transfer documents should also include a reference to the location of the CERCLA Administrative Record. The transfer documents should contain, as appropriate, additional reference information, such as the date of the Proposed Plan and the exposure assumptions used to make the environmental restoration decision or remedy selection. Typically, this type of information is included in the FOST or the Environmental Baseline Survey (EBS) for the transfer. Federal contact information (e.g., a specific Agency office address and telephone number) should be included in the transfer documents in case a problem arises with a LUC, additional contamination is found, or the transferee wishes to modify or terminate a LUC.

In addition, the deed should specifically state the restricted uses of the property beyond the basic categories of residential, commercial, recreational, or industrial. For instance:

“industrial uses permitted include office space and light industrial, but exclude residential housing, playgrounds, nurseries, child-care facilities, and elder-care facilities” or

“the Grantee covenants and agrees that it shall not consume or otherwise use the groundwater underlying the property.”

In developing deed restrictions, the property disposal agent should distinguish the property being restricted from the sections of the property being transferred for unrestricted use. This ensures the identity of the specific parcel with use restrictions is not lost over time and will help ensure deed restrictions survive subsequent property transfers. Suggested ways to describe the restricted portions of property include referencing metes and bounds and/or landmarks. The identification of specific parcels with LUCs in the purchase agreement and deed will also prevent undue loss of value for the entire property and will not burden parcels not requiring LUCs.

Because the property disposal agent drafts the purchase agreement, it should negotiate the responsibilities of the transferee for maintaining LUCs. These responsibilities include, at a minimum, compliance with LUCs, but should also include notifying DoD and other identified stakeholders if a violation of the LUCs occurs. The responsibilities should be memorialized in the purchase agreement and deed. These documents should also state that the transferee’s LUC protections under CERCLA section 120(h)(3) and Section 330 of P.L. 102-484 are tied to these responsibilities to maintain LUCs.

Because some states have statutory limits on the length of time that a covenant or easement can be in effect (e.g., Rhode Island), renewal of such LUCs may be necessary. In negotiating the purchase agreement, the property disposal agent should reach agreement with the transferee on how the restriction is to be renewed. The property disposal agent should memorialize the agreement reached in the deed to provide notice to future purchasers.

(2) Recordation of Land Use Controls. The property disposal agent shall comply with the applicable requirements of state real estate and environmental law governing the implementation of land use restrictions. These requirements may include registering the use control with the state environmental regulatory agency or local land use agency, or using state model language in drafting the use control. The transferee will be responsible for recording the land use restriction. Recordation of the land use restriction must comply with the requirements of state property law for recording deeds, plus any local requirements, as long as they are not inconsistent with Federal law.

At transfer, the property disposal agent should ensure that copies of the deed are provided to appropriate local offices, such as the building permit office, planning office, zoning commission, or the Water Board. This provides an additional source of notice about restrictions. The local agencies may record the restriction on their geographic information system (GIS) or tax

maps or in the subdivision records to formally incorporate the LUC into their existing development review and permitting processes.

c. Post-Transfer.

This section discusses the actions necessary on the part of the Component and what action others (e.g., transferee, state and local governments) should take to ensure LUCs are effectively maintained and, when necessary, modified or terminated.

(1) *Land Use Management Tools.* A number of options, used separately or collectively, can ensure the management and maintenance of land use controls over time and proper incorporation into local land use management systems. The options presented below provide Components with the flexibility to use the tool or tools appropriate to a specific property.

(a) *State Land Use Control Management Systems.* A growing trend in state environmental law is state requirements for managing LUCs that arise because of environmental factors. These requirements mandate methods of developing LUCs and documenting them in state developed registries. Such laws may also require involvement of state regulators to modify and/or enforce LUCs. State environmental laws may resolve state property law issues surrounding enforcement of LUCs by allowing LUCs to be enforced by third parties, including state and local agencies. Where such generally applicable mechanisms exist for managing LUCs, DoD and the transferee will comply with such requirements absent a conflict with Federal law. If such mechanisms exist, Components may not need to employ the additional options specified below. The options below, however, generally provide the same recommendations for LUC management as state laws discussed in this paragraph.

(b) *Notice.* Notifying affected entities of the existence of LUCs is an effective method to prevent inappropriate use of transferred property. Components should not rely solely on recorded real estate records to provide constructive notices on LUCs. The transferee, the Component, or other agencies can provide the notices. A one-time notice should be sent when the LUC is first implemented and annual reminder notices can be generated. The responsibility for and frequency of the notice will depend on the agreement reached between the property disposal agent and the transferee. The property disposal agent should negotiate notice requirements with the future transferee with input, as appropriate, from the environmental regulators and other agencies such as a local planning agency. The notification should be provided to the community, local government officials (e.g., zoning, planning commissions), and transferees through a variety of mechanisms, including public notice or letter.

(c) *Self Certification.* Another type of notice mechanism is self-certification, in which the responsibility for confirming that LUCs remain protective is placed on the transferee (and all subsequent transferees) of the property. For example, on a regular basis, the transferee certifies the land is still being used for the intended purpose, such as industrial or agricultural use. Self-certification can provide a cost-effective means of gaining knowledge on the property use from the person closest to the property. This responsibility should be reflected

in the transfer documents. The parties should also determine which agencies (e.g., state or local regulatory agency, planning or public health agency, Component property disposal agent) will receive the self-certification. Components should negotiate with the transferee to certify to more than one agency (e.g., environmental regulators, local planning agency) as part of the layering strategy. Components should use this mechanism with caution and only in conjunction with a provision for spot-checking self-certification reports, because this mechanism relies on the veracity of the transferee's reporting.

(d) Markings. Where possible, if the area of the property being restricted is sufficiently small, permanent markers may be used to identify restricted use areas. Plaques at the site also may be used to indicate prohibited activities.

(e) Five-Year Reviews and Long Term Monitoring (LTM). Where performed as part of the environmental restoration process and as required by CERCLA, five-year reviews and long-term monitoring of environmental restoration sites may provide convenient opportunities for the Component to concurrently review LUCs. At that time, the integrity of the LUCs or layering mechanism can also be checked (e.g., is zoning still consistent, is land use consistent, are markers/fences still in place?).

(f) Remedial Action Operation. Reviews of on-going remedies during the remedial action operation phase provide opportunities for concurrent review of LUCs. For example, when inspecting a pump-and-treat system, a visual inspection can be made to see that no private well digging has occurred and no irrigation equipment is in evidence.

(2) Preventing Land Use Control Violations. DoD expects the transferee and subsequent owners to abide by the LUCs included in the transfer documents. Local processes, such as overlay zoning, should be used to enforce and manage LUCs. This is necessary because neither DoD nor a Component can enforce LUCs established through the regulatory authority of a state or local government. Because DoD will no longer have ownership of the property, the Component should work with the community and local government to ensure their enforcement of LUCs after the transfer of property. Those entities are in the best position to first become aware of any LUC violation and take action to enforce the use restrictions. They may also have concomitant responsibility for public health and welfare through local land use planning and management processes. In many of these states with established the LUC management systems, as mentioned above (paragraph 3.c.(1)(a)), the state provides LUC enforcement.

(3) Modification/Termination of Land Use Controls. Modification or termination of LUCs may become necessary. This shall be done in accordance with the July 25, 1997, DoD policy memorandum, *Responsibility for Additional Environmental Cleanup After Transfer*, CERCLA, and state law. DoD will participate in the termination or modification of LUCs in two scenarios: (1) if a remedy meets its cleanup goals, the Component will modify or terminate the deed restriction and revise the deed as appropriate; and (2) if a transferee, with the Component's prior approval, has cleaned the property to a stricter cleanup standard, the transferee may request modification or termination of the LUC by the Component. If appropriate, regulatory agencies

need to be involved in amending the environmental restoration decision document to the same extent as they were in the original decision document. The two scenarios are described below:

Scenario #1. Once the Component determines a remedy has attained its cleanup goals, the Component, if warranted, should act to modify or terminate the restriction on the property. This benefits the transferee by making the title more marketable, but also benefits DoD by terminating remaining LUC requirements and associated costs for the property. The Component should seek appropriate involvement from the relevant environmental regulators confirming attainment of the remedial objectives and should then revise the deed restriction accordingly.

Scenario #2. If a transferee desires to clean up property to a higher standard that allows more uses of the property, the transferee must pay for any needed additional studies or environmental restoration actions. The Component shall also require the transferee to post a surety bond or some other form of financial assurance to ensure the additional cleanup will be completed once undertaken by the transferee without the Component needing to pay for it. After reaching the appropriate cleanup level, the transferee (at its expense) would seek the necessary involvement from the appropriate environmental regulators confirming the attainment of the cleanup objectives. Upon providing the property disposal agent with proof of this regulator's concurrence, the transferee would prepare a quitclaim deed for the property disposal agent's signature, which would relinquish the LUC (i.e., the deed restriction).

Upon termination of a LUC, it is important to undo the LUC layering put in place, to avoid future confusion about the status of the property. This will usually require the property disposal agent to provide a one-time notice and direction to all entities involved in the layering scheme.

d. Records Management.

Establishing LUCs is a team effort between the environmental office and property disposal agent. Tracing the history of LUCs, if questions arise, requires reference to a combination of environmental and real estate records. The property disposal agent should maintain a central database of properties with LUCs (transferred or leased property) that includes information on the type of LUCs established, land use monitoring and management responsibilities, and the location of real estate records.

To address any future concerns about a property, the Component should retain the following types of real estate related records:

- ◆ Finding of Suitability for Transfer (FOST)
- ◆ Environmental Baseline Study (EBS) (the applicable portion is generally included in the FOST)
- ◆ Purchase Agreement
- ◆ Deed
- ◆ Cooperative Agreement, or similar documents that specify LUC management responsibilities.

The environmental restoration information that may be required will be contained in the Administrative Record required by CERCLA. However, Component environmental offices need to modify their central program management database of environmental restoration sites to track any continuing environmental restoration responsibilities (e.g., five-year reviews and long term monitoring) and relevant information such as the cleanup level and risk assumption scenario (e.g., industrial, commercial, recreational).

Department of Defense Guidance on Land Use Controls Associated with Environmental Restoration Activities for Active Installations

1. PURPOSE.

This document provides guidance to Components, based on Department of Defense (DOD) *Interim Policy on Land Use Controls Associated with Environmental Restoration Activities*, on the use of available installation land use planning and management tools for implementing, documenting, and managing land use controls (LUCs) for real property at active installations. LUCs include any physical, legal, or administrative mechanism that places restrictions on the use of, or limit access to, real property to prevent exposure to contaminants above permissible levels. The intent of using these controls is to protect the integrity of the engineering remedy (if present) and human health and the environment by limiting the activities that may occur at a particular site.

DoD controls land use at active installations and can internally restrict the use of such property. Consequently, this guidance provides different mechanisms to implement and manage LUCs than those used for property being transferred out of DoD control. For example, this guidance does not provide for the use of deed restrictions to restrict property because deed restrictions cannot be created without a conveyance and property is not being transferred at active installations. Furthermore, Federal real property policy generally does not permit creation of deed restrictions by a land holding agency, such as a DoD Component. As a practical matter, even if deed restrictions could be placed on active installation property, deed restrictions would not be effective for notifying installation personnel of the existence of land use controls because deed restrictions are recorded in the local land records office and title searches are typically not performed when making land use decisions at active installations. Therefore, for Federal land remaining under Federal ownership and control, alternative methods for institutionalizing LUCs are required.

The intent of this guidance is to provide for the protection of human health and the environment by ensuring the compatibility of land use at active installations with any restrictions imposed on the property during the environmental restoration process. This guidance permits flexibility in tailoring and using specific tools and processes at the installation-level, rather than dictating a specific set of measures for use.

2. APPLICABILITY AND SCOPE.

a. Active Installations. This guidance applies to real property at active installations in the United States and U.S. territories. The guidance applies whenever a decision to restrict land is made as part of the environmental restoration process.

b. Leased Property. This guidance also applies to installation property leased to third parties. (In such a situation, in addition to the process outlined below, the Component should inform the

lessee of the existence of the LUCs and make the lessee's compliance with the LUCs a binding condition of the lease.)

c. Exclusions.

(1) *Civil Works Property.* This guidance does not apply to U.S. Army Civil Works properties.

(2) *Federal-to-Federal Transfers.* For Federal-to-Federal agency transfers (including transfers between Components), the receiving agency will generally be responsible for the maintenance and management of LUCs.

(3) *Transferring Property.* For guidance on implementing land use controls for surplus property being transferring out of Federal control, refer to *DoD's Guidance on Land Use Controls Associated with Environmental Restoration Activities for Property Planned for Transfer Out of Federal Control.*

3. GUIDANCE. The guidance below outlines the process for implementing, documenting, managing, and terminating LUCs at active installations.

a. Implementing Land Use Controls. Once a decision has been made in consultation with the supporting land use planning/management office to place limitations on the use of DoD real property due to environmental restoration concerns, the installation shall develop an implementation plan for LUCs. The implementation plan is an internal management tool that explains how LUCs will be established and documented and defines who will be responsible for maintaining and managing them. The implementation plan should be incorporated into the Installation Master Plan or its equivalent. At a minimum, the implementation plan shall describe the location of the land subject to the LUC; explain the LUC (e.g., restrictions on excavation, use of groundwater) and generally allowed uses (e.g., equipment storage, recreation); and specify the duration of the LUC. The plan shall also provide for modifications to the LUC as site conditions change (e.g., if the remedial action improves the groundwater quality). The plan should specify the frequency and requirements of LUC inspections and indicate whether any of these inspections are part of the inspection process for other environmental programs (e.g., internal or external environmental audits).

Implementation of LUCs also involves coordination among the installation personnel responsible for maintaining certain resources. The office that drafts the land use control implementation plan should coordinate with the other affected entities. For example, if the LUCs involve a prohibition on the use of groundwater, then the office that manages groundwater resources should be informed of the LUC; or if the LUCs include a restriction on soil use in a particular area on the installation, construction and maintenance personnel should be informed.

b. Documenting Land Use Controls. Whenever a decision has been made to restrict land use at active installations, the decision document, such as a Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Record of Decision (ROD) or Action Memorandum, should generally explain the restricted uses of the property.

Because LUCs on active installations are not recorded in deeds, Components must use their own systems and processes for recording LUCs. The installation shall incorporate LUCs into the existing land use planning and management systems routinely used at the installation for planning and construction decisions. A combination of common mechanisms, discussed below, and other available tools should be used to effectively track and manage LUCs at the installation.

(1) Installation Master Plan. The Installation Master Plan (sometimes called the Base Comprehensive Plan or General Plan) is used for land use and construction project planning. The installation should incorporate LUCs into appropriate sections of the Master Plan to allow for routine consideration of LUCs in making land use and planning decisions. If the Master Plan is GIS-based, a separate layer should be specifically created for LUC information. In addition, the LUC should be recorded on any installation plat.

(2) Geographic Information Systems (GIS)/Overlay Maps. Computerized maps can depict an installation's historic structures, wetlands, utility systems, and other information as layers for purposes of visual display and analysis. LUCs should be appropriately incorporated into these systems.

(3) Installation Offices. LUCs should also be filed with the installation offices that are responsible for managing the buildings and grounds, utility systems, and construction. The installation contract and real estate/real property offices should also have LUCs on file so that contracts and outgrants can reflect LUCs as appropriate.

c. Maintaining Land Use Controls. The effectiveness of LUCs depends on routine maintenance activities, such as mowing the grass to keep site markers visible and maintaining fences around controlled access areas. It is also dependent on incorporating the maintenance of the LUC into the existing processes of the installation. Some LUCs may be short-term and last only as long as an ongoing environmental restoration system is in place; other LUCs may need to remain in place for a longer period. To ensure that LUCs remain effective and to provide flexibility, this section provides a range of options to use separately or collectively, depending on the type of LUCs, site conditions, and installation processes available.

(1) Site Approval Process. The site approval process is the process for reviewing and approving excavation and construction projects, as well as other land use changes at the installation. To ensure the integrity of the controls and to prevent violations, consideration of LUCs should be incorporated into this process. This could involve reviewing the GIS layer that depicts the LUCs as part of a site/construction approval process.

(2) Markers. Installations may identify areas of restricted use by placing permanent markers around the perimeter of the restricted area. The offices (and/or contractor personnel) responsible for grounds maintenance, construction, and safety should be notified of the existence of these markers, instructed as to their purpose, and directed to inform appropriate officials if the markers are displaced or unauthorized use occurs.

(3) **Inspections.** The inspection of LUCs should become part of existing inspections conducted at the installation. Depending on the type of LUCs, these inspections could include a visual check to ensure that proper maintenance of LUCs is taking place.

(4) **Environmental Self-Audit.** Evaluating and verifying LUCs should be part of the Component's environmental audit and self-inspection program, and should be incorporated into the self-audit checklist and required report.

(5) **Training.** Installations should provide training to personnel, such as grounds, maintenance, real estate/real property, and contractor personnel, regarding the physical location of LUCs and how to care for property subject to LUCs. These personnel should also be informed of allowed and restricted activities.

(6) **Internal Notice.** The relevant office (e.g., Planning, Facilities, Engineering) should periodically send out a notice to other affected offices to serve as a reminder of the existence of LUCs.

(7) **Five-Year Reviews and Remedial Actions.** Where performed as part of the environmental restoration process and as required by CERCLA, five-year reviews and long-term monitoring of environmental restoration sites conducted to assess remedy effectiveness may provide a convenient opportunity for the installation to concurrently review LUCs.

In addition, the installation should inspect LUCs as part of a review of ongoing CERCLA remedial actions. For example, when inspecting a pump-and-treat system, checks can be made to see that that no well digging and/or irrigation equipment is present.

d. **Addressing Land Use Control Non-Compliance.** If, during an installation inspection or through some other process, it becomes apparent that a LUC is being violated, appropriate installation officials should be notified immediately. These officials should take steps to ensure the integrity of the LUC is restored, including any required notifications and corrective actions. In addition, it may be useful to coordinate responsibility for LUC management with installation occupational safety and public safety offices to include LUCs in their regular inspections of, and patrols on, the installation property and activities.

e. **Land Use Compatibility.** At active installations, use of an area containing LUCs may change. The installation must ensure land use remains compatible with the LUC. The installation should institute a process to review and evaluate the effect on human health and the environment of any proposed land use changes. This process, conducted in consultation with the appropriate environmental restoration office, should seek to answer the following questions:

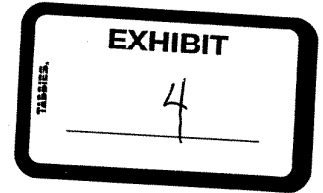
- ◆ Is the proposed land use inconsistent with the exposure scenario outlined in the risk assessment?
- ◆ Will the land use change adversely affect the effectiveness of the selected site remedy?
- ◆ Will the need for any additional remedial actions arise as a result of the implementation of the land use change?

If the answer to any of the above questions is yes, the appropriate process required by environmental regulations and guidance to revise the site remedy, which may require consultation with environmental regulatory agencies, must be followed. This includes reassessing the decision document to determine if an amendment is required for the proposed land use change.

f. Modifying/Terminating Land Use Controls. When the remedy meets the cleanup goals, the installation may need to modify or terminate the LUCs. If, upon meeting the cleanup goal, land use may be unrestricted, the LUC shall be terminated. If some LUCs no longer apply and some are still required, the LUC implementation plan shall be modified to reflect what restrictions still apply.

LUCs at active installations should be modified or terminated through the same process used to establish the LUC, and if terminated, deleted from the documentation mechanisms discussed in this guidance. Installation personnel should refer to the land use control implementation plan, which identifies where LUCs are documented. Additionally, decision documents should be assessed to determine if amendments to decision documents are required by modification/termination of LUCs. Regulatory agencies generally need to be involved in amending the environmental restoration decision document to the same extent as they were in the original decision document.

g. Records Management. LUCs are established and implemented through environmental and land use management processes; consequently, tracing the origin of LUCs requires a combination of these records. LUC records need to be retained by the installation so it will have sufficient information to determine if land use changes can be made in the future. The LUC implementation plan (discussed above) should reference the location of the pertinent LUC records including, but not limited to, the Record of Decision, Feasibility Study, Installation Master Plan, or any of the other systems used to record LUCs.



United States
Environmental Protection
Agency

Office Of Solid Waste And
Emergency Response
(5401G)

EPA 510-F-97-015
January 1998
www.epa.gov/OUST/mtbe/

Office Of Underground Storage Tanks



MTBE Fact Sheet #2

Remediation Of MTBE Contaminated Soil And Groundwater

Background

Methyl tertiary-butyl ether (MTBE) is a fuel additive made, in part, from natural gas. Since 1979, it has been used in the United States as an octane enhancing replacement for lead, primarily in mid- and high-grade gasoline at concentrations as high as 8 percent (by volume). Since the mid-1980s, it has been widely used throughout the country for this purpose. It is also used as a fuel oxygenate at higher concentrations (11 to 15 percent by volume) as part of two U.S. EPA programs to reduce ozone and carbon monoxide levels in the most polluted areas of the country.

Physical And Chemical Characteristics Of MTBE

The effectiveness of remediation methods is directly linked to the physical and chemical characteristics of the constituent of interest. Because MTBE behaves differently in soil, air, and water than other petroleum constituents, the choice of an effective remediation technology may be different when

MTBE is present at a site. Benzene is most often the contaminant of concern in gasoline because of its relatively high solubility and its known carcinogenicity. As a result, comparing the characteristics of MTBE with benzene is helpful in showing how remediation technologies may differ when MTBE is added to gasoline.

- MTBE is about 30 times more soluble than benzene in water. Pure MTBE can reach an equilibrium concentration in water of approximately 5 percent (*i.e.*, 48,000 mg/L).
- When moving from the liquid phase (*i.e.*, free product) to the vapor phase, MTBE is three times more volatile than benzene (*i.e.*, the vapor pressure of MTBE is three times the vapor pressure for benzene).
- When moving from the dissolved phase (in water) to the vapor phase, MTBE is about ten times less volatile than benzene (*i.e.*, its Henry's law constant is 1/10th benzene).

- MTBE is much less likely than benzene to adsorb to soil or organic carbon.
- MTBE is more resistant to biodegradation than benzene.

When MTBE is in the soil as the result of a petroleum release, it may separate from the rest of the petroleum, reaching the groundwater first and dissolving rapidly. Once in the groundwater, MTBE travels at about the same rate as the groundwater whereas benzene and other petroleum constituents tend to biodegrade and adsorb to soil particles.

Soil Remediation

Because it has a very high vapor pressure and a low affinity for sorption to soil, MTBE can be effectively remediated by two soil treatment technologies, typically without any costs beyond those needed for remediating other petroleum constituents. Soil vapor extraction (SVE) is an *in situ* soil treatment technology that removes volatile contaminants from soil in the unsaturated zone above groundwater by extracting the contaminant vapors with a vacuum that is applied to the subsurface. Low-temperature thermal desorption (LTTD) is an *ex situ* soil treatment technology that uses temperatures below ignition levels to separate volatile contaminants from soil. Because of its high vapor pressure, both methods are very effective in removing MTBE from soil. However, SVE and LTTD must be used soon after a release, before most of the MTBE moves from the soil into the groundwater.

Bioremediation methods for soil treatment (e.g., land-farming, bioventing, biopiles) are currently not recommended for removing MTBE because it is

considered recalcitrant to biodegradation. This recommendation may change in the future as new research examines the efficacy of specific strains of bacteria and/or improved methods of biodegrading MTBE.

Groundwater Investigations And Monitoring

Because MTBE behaves differently from petroleum hydrocarbons when released into the environment, a remedial investigation may need to be modified to properly characterize the area of MTBE contamination. Many regulators of UST programs have observed that MTBE's relatively high solubility allows it to dissolve into the groundwater in "pulses" that result in rapid orders of magnitude changes in groundwater concentrations. Pulses, which may be caused by the infiltration of rain water or rising groundwater levels, may necessitate frequent groundwater sampling to determine actual MTBE concentrations and levels of risk to down-gradient receptors. The frequency of sampling should be determined based on the velocity of the groundwater and the number of monitoring wells. Determining the impact of the selected remediation method may be difficult without accurate historical sampling data.

Groundwater Remediation

Pump-And-Treat

In contrast with the preferred remediation techniques for petroleum hydrocarbons such as benzene (e.g., bioremediation), pumping contaminated groundwater and treating it above

ground (*i.e.*, pump-and-treat) may more often be an effective remediation technology for MTBE because MTBE does not adsorb significantly to soil. As a result, fewer aquifer volumes are required to remove all of the MTBE than are required to remove the slowly desorbing petroleum hydrocarbons. In addition, because it is highly soluble, most of the MTBE mass may quickly dissolve into groundwater, making pumping an efficient method for removing large quantities of the contaminant.

As with petroleum hydrocarbons, however, diffusion is also a factor controlling the remediation timeframe. If micropores exist within the aquifer that are not readily influenced by groundwater flow, transfer of a contaminant from the micropores to the macropores will occur through the slow process of diffusion. Hence, in spite of some favorable characteristics, pump-and-treat may not always be an efficient remediation method for MTBE contamination. Aquifers with high total porosity but with low effective porosity remain troublesome in treating any contaminant.

The physical and chemical properties of MTBE are also important in the treatment of MTBE above ground. Because it does not adsorb significantly to carbon, MTBE is not a good candidate for using granular-activated carbon (GAC) to remove it from water. GAC is about 1/3 to 1/8 as effective in removing MTBE as it is in removing benzene. In addition, because MTBE "prefers" to remain in water, air strippers must use a higher volume of air than is required for benzene. Initial field experience indicates that two to five times more air is needed to treat the same volume of water if MTBE

concentrations are less than 5,000 ppb. An additional expense associated with MTBE remediation is that more extraction wells and associated equipment (*e.g.*, pumps, lines) may be required than for benzene because MTBE travels farther and faster than the rest of the plume, resulting in a larger plume size.

The cost of treating an MTBE groundwater plume can be significant, however, cost effective methods do exist. A 1991 American Petroleum Institute study (API Publication No. 4497) determined that air stripping alone was the most cost effective technology for remediating water containing 20-ppm MTBE down to a level of 10 ppb. A 25-gallon per minute air stripping system could achieve this level of remediation for \$9 per 1000 gallons (in 1990 dollars). If off-gas emissions were also a concern, they could be treated for an incremental cost increase of \$7 per 1000 gallons (*i.e.*, \$16 per 1000 gallons total cost). As an alternative, UV-catalyzed oxidation using hydrogen peroxide could be used to treat water and off-gases at a total cost of \$15 per 1000 gallons.

Air Sparging

Air sparging is another groundwater remediation technology that has shown some promise. It accomplishes remediation goals by injecting air directly into the groundwater to volatilize the contaminants *in situ*. A few case studies have shown that reductions in MTBE levels from above 1000 ppb to less than 10 ppb are possible in less than 2 years. However, regardless of the contaminant, air sparging is typically only appropriate in homogeneous sands because heterogeneous sediments may cause dispersion of contaminants and

channeling of air flow. In addition, air sparging should be less effective for MTBE than for benzene because more air is needed to volatilize the MTBE. The addition of dissolved oxygen in the groundwater from air sparging may not significantly increase the biodegradation of MTBE as it would for benzene.

Bioremediation

Although MTBE is generally believed to be resistant to biodegradation, preliminary research has shown that biodegradation may be an effective remediation option under specific conditions. Bioreactors, an *ex situ* form of bioremediation, have shown some initial promise. Additional research and development are continuing to make them more reliable and cost effective. New research is also showing that *in situ* biodegradation may be an effective remediation alternative; however, more information is required to determine the specific environmental conditions that enable significant rates of biodegradation to occur.

Point-Of-Use Treatment

Because MTBE groundwater plumes commonly travel farther than benzene plumes, MTBE may be more likely than the remainder of the petroleum release to impact drinking water wells. As a result, many states have been treating contaminated groundwater at the point of exposure and at the source area of the plume. In New Jersey, regulators have found that GAC is effective in treating low-volume potable wells (*e.g.*, for single-family homes) with contamination levels below 300 ppb. If high-volume potable wells are involved (*e.g.*, for restaurants,

industrial sites) or if concentrations exceed 300 ppb, miniature air strippers may be a more cost-effective option. Manufacturer specifications should be consulted for any treatment unit and followed up with adequate levels of influent and effluent monitoring.

Incremental Cost Increase Of MTBE Groundwater Remediation

The incremental cost increases for UST corrective action activities that involve MTBE versus ones that do not contain MTBE vary widely depending on the history of the release (*e.g.*, how long the release has been occurring, whether MTBE was contained in the initial release, the concentration of MTBE) and the goals of the cleanup. At many sites, the initial concentrations may be low enough that MTBE may not be a greater concern than the remediation of benzene, resulting in no cost increase. But, when an MTBE plume is much larger than the benzene plume and impacts drinking water wells ahead of it, MTBE will be the driving force in remediation efforts, potentially resulting in a very high incremental cost increase.

Based on limited research and anecdotal information, the U.S. EPA's Office of Underground Storage Tanks estimates that at approximately 75 percent of MTBE-contaminated sites, the incremental cost increase of remediation will be less than 50 percent above the cost of remediating the same petroleum release without MTBE. At many of these sites, costs would actually not increase because benzene might still pose the greatest risk, thus driving the remediation effort. At 20 percent of the sites, the incremental cost increase would be between 50

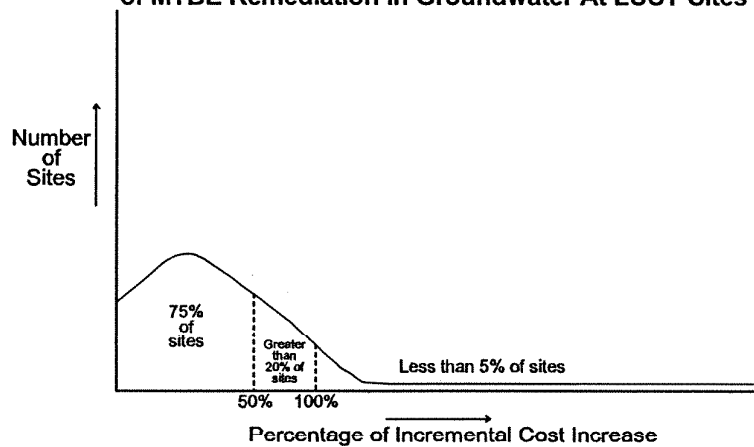
percent and 100 percent. At the remainder (approximately 5 percent) of the sites, the additional cost of remediating MTBE contamination may be an unknown quantity that is greater than 100-percent more. This situation results when benzene has attenuated and poses no further risk, but significant concentrations of MTBE continue to migrate down-gradient and contaminate drinking water supplies. A graph of this distribution is presented in Exhibit 1.

Conclusion

Remediation of MTBE-contaminated soil generally does not pose an additional concern when a petroleum release has occurred because MTBE can often be removed from soil with-

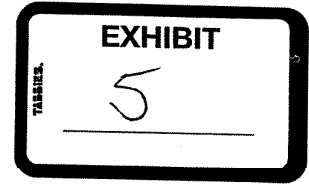
out additional time or expense. But remediating MTBE-contaminated groundwater can be problematic. MTBE's high solubility in water, low rate of adsorption to soil, and low rate of biodegradation can make treating groundwater contaminated with MTBE more expensive than treating groundwater contaminated with petroleum that does not contain MTBE. Fortunately, there are proven treatment technologies available. Pump-and-treat is usually the most cost effective method, but in some cases air sparging may be appropriate. Other existing technologies may also prove effective as more case studies are reported. The potential for *in situ* biodegradation of MTBE is widely believed to be low, but new research may clarify our understanding of conditions that may make it an effective option. In addition to remediation of the source area, point-of-use treatment appears to be a common approach to addressing MTBE when contamination is limited to individual homes or private wells.

Exhibit 1. Preliminary Estimate Of The Incremental Cost Increase of MTBE Remediation in Groundwater At LUST Sites



MTBE: Treatability and Remediation

Oxygenated Fuels Association
Arlington, Virginia
June 1999

**Summary**

Releases of gasoline to the environment can adversely impact drinking water resources, and must be quickly addressed. The presence of MTBE in gasoline raises the focus on leak prevention and increases the need for rapid response. However, remediation efforts can be effectively managed with strategies and treatment technologies commercially available today. Air stripping, advanced oxidation and granulated activated carbon processes can be used to effectively and economically remove MTBE from impacted water resources. Post treatment MTBE levels below taste and odor threshold levels have been demonstrated. Combinations of treatment processes, and emerging technologies can provide even more effective remediation methods for drinking water supplies. The costs for applying these technologies are generally well below alternative water supply and/or replacement costs.

Background

Methyl tertiary butyl ether (MTBE) is an oxygenate compound blended in gasoline as an octane enhancer and to reduce automotive emissions in cleaner-burning reformulated gasoline (RFG) programs in the worst air polluted areas in the nation. When gasoline is released into the environment during transport, production, storage or use, a variety of its constituents, including MTBE, can be transferred into the air or water. Due to its physio-chemical properties, higher concentrations and longer subsurface plumes can be observed with MTBE than are seen with other gasoline compounds. Gasoline releases from underground storage tanks and emissions of uncombusted fuel into lakes and reservoirs by boat engines and jet skis have raised concerns over the potential drinking water impacts. The discussion below highlights various treatment technologies and remediation strategies available today to restore water resources impacted by MTBE's presence.

Discussion

The cost of treating drinking water containing MTBE varies depending on the flow rate of the system, the influent concentration of MTBE in the water, and the level to which MTBE must be treated in the delivered water. The MTBE Research Partnership (a collaborative effort by the Association of California Water Agencies, Western States Petroleum Association, and OFA) has reported on available and most widely used technologies for treatment of water supplies. Three treatment technologies - air stripping, advanced oxidation and adsorption - have been proven effective in removing organic hydrocarbons and MTBE. State regulators and remediation firms have found these technologies acceptable for treating drinking water. The Partnership's detailed examination shows that removing MTBE from drinking water supplies can be accomplished in a cost-effective manner. Moreover, research continues to further optimize these technologies for MTBE removal.

Air-Stripping and Off-Gas Treatment

Air stripping is a proven technology that has been successfully used to remove MTBE from drinking water. This technology has been used for public systems in La Crosse, Kansas, and Rockaway Township, New Jersey. These systems typically use reverse airflow through a column of water to remove the MTBE (exchange from water into the air). Specific system technologies include packed towers, low profile air strippers, bubble diffusion strippers, spray towers and aspiration air strippers. Packed towers are the most cost-effective for MTBE removal. The air stream leaving the treatment system may require off-gas treatment if contaminant levels exceed regulatory emissions standards. Several processes, such as vapor-phase carbon adsorption and thermal oxidation, were found to be the most cost-effective for treating the off-gas emissions. The costs for air-stripping processes to achieve

99 % or greater MTBE removal varies from \$0.10/1000 gallons to \$0.54/1000 gallons treated, depending on conditions.

Advanced Oxidation

Advanced oxidation processes (AOPs) employ ozone, hydrogen peroxide, ultraviolet light, ultrasonic vibration, chemical reactions, and/or high-energy electron beams to remove MTBE from water. AOP's have been used successfully for drinking water applications, primarily in the areas of disinfection and in some cases for VOC removal. The effects of background water chemistry (i.e., other contaminants present) can impact the application of these technologies. The cost estimates for 99% removal of MTBE for these systems ranges from \$0.37/1000 gallons to \$2.62/1000 gallons treated. Future research efforts will focus on cost-efficiencies and range of application for scaled-up systems.

Granulated Activated Carbon

Carbon adsorption is widely used for the removal of synthetic organic compounds, including MTBE, from water. Granulated activated carbon (GAC) vendors also typically supply treatment systems. The type and source of the carbon, as well as the presence of other contaminants in the water, significantly impact the efficiency and cost-effectiveness for most MTBE applications. The GAC systems are often used to polish the treated water from either air stripping or AOP systems. Individual homeowners use small carbon canisters to remove a variety of contaminants, including MTBE, from private wells. The cost estimates for 99% removal of MTBE for GAC systems varies from \$2.00/1000 gallons to \$2.80/1000 gallons treated.

Emerging Treatment Technologies

Several emerging technologies show promise in removing MTBE from drinking water, including membranes, biological degradation and resin adsorption. Depending upon site-specific conditions, these treatment systems may prove cost-effective for remediation of drinking water supplies, particularly when treatment of smaller water volumes is required. Extensive research is underway to define optimal conditions for these emerging technologies.

References

1. MTBE Research Partnership. Treatment Technologies for Removal of Methyl Tertiary Butyl Ether (MTBE) from Drinking Water. December 1998.



Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

Arturo A. Keller¹, Orville C. Sandall², Robert G. Rinker²,
Marie M. Mitani¹, Britta Bierwagen¹, and Michael J. Snodgrass²

¹Bren School of Environmental Science and Management, UCSB, Santa Barbara, CA

²Dept. of Chemical Engineering, UCSB, Santa Barbara, CA

Abstract

Treatment of Methyl Tert-Butyl Ether (MTBE) from contaminated surface and groundwater supplies presents specific challenges due to the physicochemical properties of MTBE which depend strongly on its hydrophilic nature, and translate into a high solubility in water, very low Henry's constant and very low affinity for common adsorbents. In this study we evaluate two common treatment technologies, air stripping and granular activated carbon (GAC), as well as two innovative treatment technologies, hydrophobic hollow fiber membranes and advanced oxidation (AOP) using ozone or ozone/hydrogen peroxide. Where available, we used design parameters from published literature, but in several instances we conducted experimental studies to determine the parameter values or corroborate the literature information. Ten different flow rates/concentration combinations were evaluated in our designs, to cover the range from high flow rate/low concentration typical of surface waters and groundwater drinking water supplies, to low flow rate/high concentration typical of groundwater remediation sites. For all cases, the processes were designed to produce an effluent water of 5 ug/L or less. Capital costs and operating and maintenance costs were determined at the feasibility level, using standard engineering estimating practices.

Air stripping is the lowest cost technology for high flow rates (100 to 1000 gpm), if no air treatment is required. Air treatment can be required depending on the local or Regional Air Quality Board stipulations. Hollow fiber membranes are the lowest cost technology for flow rates of 10 to 100 gpm if no air treatment is required, which is typical at these low flow rates. GAC will be most cost-effective at all flow rates if air treatment is required and the influent water has low levels of other organic compounds. If air treatment is required and the influent has high levels of organics, air stripping is more cost effective than GAC at flow rates of 100 gpm and greater. AOP is in all cases more expensive than the alternative technologies, and there are sufficient uncertainties at this point with respect to by-products of AOP to warrant further study of this technology. It has the potential of being cost-competitive at high flow rates, provided it is fully tested at the field scale. Given that air stripping and GAC are proven technologies in the field, innovative technologies such as hollow fiber membranes and AOP should be compared on a case-by-case basis against these treatment options.

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

The cost of treating MTBE-contaminated water is 40 to 80% higher than treating water contaminated only with other hydrocarbons such as benzene, for conventional technologies such as air stripping and GAC.

1. INTRODUCTION

1.1 MTBE in Water Supplies

Methyl tertiary butyl ether (MTBE) was first added to gasoline in the late 1970's to replace lead as an anti-knocking agent (NSTC, 1997). To reduce pollutant emissions from motor vehicles in parts of California and other air quality non-attainment areas around the U.S., oil companies developed "oxygenated" gasoline formulations (SAE, 1992), which contain up to 15% MTBE by volume and/or other oxygenates such as ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME), tertiary amyl ethyl ether (TAEE), dimethyl ether (DME), diisopropyl ether (DIPE), tertiary butyl alcohol (TBA), ethanol or methanol. The 1990 Federal Clean Air Act mandated the incorporation of oxygenates to gasoline in ozone and carbon monoxide non-attainment areas. The State of California followed with the requirement that gasoline sold in the state meet specific requirements, including an oxygen content (CARB, 1991). MTBE has been the oxygenate of choice due to economic and supply considerations.

Despite federal and state programs to improve handling of gasoline and other fuels in pipelines, underground and above ground storage tanks and other transport modes, gasoline spills and leaks are still relatively common place (Keller et al., 1998; Happel et al., 1998; Doohar, 1998). In addition, uncombusted gasoline is also spilled from boats and recreational equipment directly to surface waters, which may be water supply reservoirs (Keller et al., 1998). The result is that MTBE is the second most frequently detected volatile organic compound in shallow groundwater (Squillace et al., 1996), based on the National Water Quality Assessment program of the USGS. Data from the five major oil companies in California indicates that as of June 1996, out of 412 sites in California tested, 77% had detectable levels of MTBE (Buscheck et al., 1998). Thousands of Underground Storage Tank (UST) sites have detectable levels of MTBE and in a large number of cases groundwater has been impacted at levels which require treatment (Keller et al., 1998). In addition, out of 3,173 drinking water sources tested in California by July 16, 1998, 46 sources had detectable levels of MTBE (CAL-DHS, 1998). Twenty of the 46 water sources with MTBE were surface water reservoirs, with seven presenting concentrations greater than 5 ug/L. Ten groundwater source wells for large public water systems have concentrations above 5 ug/L. Some communities, such as the City of Santa Monica, CA, have been forced to use alternative sources of drinking water due to the contamination of a significant fraction of their regular water supply.

There is concern that MTBE can have deleterious health effects (CAL-EPA, 1998), and may cause ecological damage. Studies by Kalman and Lund (1998) indicate that if water supplies are not treated, a significant percentage of the population may be exposed to levels which can have health effects. However, the main driver for treating contaminated water is the fact that sensitive individuals can detect MTBE in water at very low levels. CAL-DHS proposed on July 24, 1998,

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

a secondary Maximum Contaminant Level (MCL) of 5 ug/L for MTBE (CAL-EPA, 1998). As part of the process by which regulations are adopted under California's Administrative Procedure Act, a proposed regulation is available for a 45-day public comment period. The comment period for the secondary MCL closed on September 7, 1998. It is expected that MTBE contaminated drinking water supplies in California will be required to treat down to the 5 ug/L level. This may in effect become the *de facto* drinking water standard, since this level is below that which can cause acute or chronic human health effects or ecosystem damages.

1.2 Physicochemical properties

The physicochemical properties of MTBE and many of the other oxygenates have increased the magnitude of the problem, when compared to other gasoline constituents. As seen in Table 1, the oxygenates are rather soluble in water, with significantly larger solubility than benzene, toluene, xylenes and other petroleum hydrocarbons (e.g. pentanes, hexanes, etc.). This presents significant issues when considering the fate and transport of these pollutants in the environment and as well as treatment options.

Table 1. Literature values of physicochemical properties of several oxygenates¹

<i>Properties at 25°C</i>	<i>MTBE</i>	<i>ETBE</i>	<i>TAME</i>	<i>TBA</i>	<i>Ethanol</i>
Vapor Pressure (atm)	0.330	0.200	0.090	0.054	0.069
Aqueous solubility (mg/L)	43,000 to 54,300	26,000	20,000	☉	☉
Henry's Law Constant (Mol L Mol ⁻¹ L ⁻¹)	0.024 to 0.123	0.109	0.052	4.3x10 ⁻⁴ to 5.9x10 ⁻⁴	2.1x10 ⁻⁴ to 2.6x10 ⁻⁴
Octanol-Water Partitioning Coefficient, K _{ow} (-)	10 ^{1.2}	10 ^{1.74}	No data	10 ^{0.35}	10 ^{-0.16} to 10 ^{-0.31}
Boiling Point (°C)	55.2	67	86.3	82.9	78.5
Density (g/mL)	0.74	0.73	0.77	0.79	0.79
Molecular Weight (g/mole)	88.15	102.18	102.18	74.12	46.07
CAS Number	1634-04-4	637-92-3	994-05-8	75-65-0	64-17-5

¹Multiple sources, compiled by NSTC, 1997

Given their high solubility, MTBE and the other oxygenates are quite mobile in the environment. They partition weakly to the organic fraction in soils, sediments and suspended particles, preferentially remaining in the aqueous phase. These compounds are expected to move essentially at the same rate as groundwater flow, with practically no retardation due to sorption. Initial studies indicate that biodegradation in the environment is slow (Borden et al., 1997; Mormile et al., 1994; Suflita and Mormile, 1993), but these results may depend on soil and groundwater conditions. However, the relatively rapid detection of MTBE contamination at many monitoring and water supply sites since its widespread introduction indicates that MTBE

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

is relatively persistent under normal environmental conditions, and natural biodegradation is unlikely to be a major process. Thus, MTBE behaves in many respects like a conservative tracer in the environment.

MTBE is a persistent molecule in the environment for several reasons: (1) the ether bond is stable and requires acidic conditions to cleave it; (2) the bulky tert-butyl group does not allow easy access to the ether linkage; and (3) it has only been in the environment for a relatively short time, so indigenous microbes have not had time to develop enzymatic systems to transform MTBE. Initial studies indicated that MTBE was not biodegradable at an appreciable rate under aerobic conditions (Fujiwara et al., 1984; Jensen and Arvin, 1990). More recent studies have found that MTBE is very slowly degraded under aerobic (Steffan et al., 1997; Salanitro et al., 1994; Mo et al., 1997) and anaerobic conditions (Yeh and Novak, 1994). Anaerobic studies have shown that MTBE is degraded only under specific conditions: low organic content in the soils and pH around 5.5 (Yeh and Novak, 1994). MTBE degradation did not proceed in rich soils, possibly due to the abundant availability of other substrates for microbial activity. This was tentatively corroborated by adding easily degradable organic compounds to poor soils at pH 5.5, which inhibited MTBE degradation. It was also observed that under those conditions where MTBE is degraded, there is a considerable time lag before there is any appreciable biodegradation.

Although these results are encouraging to develop *in-situ* bioremediation processes, it is likely that in the next few years the best option is to pump the contaminated water and treat above-ground. Most sites will require Soil Vapor Extraction at the source of the contamination to remove the gasoline residuals which are a continuous source of groundwater contamination. The cost of treating MTBE contaminated water is expected to be higher for traditional above-ground water treatment processes for volatile organic compounds (VOC's), namely air stripping and activated carbon. Preliminary studies by Kavanaugh (1997) indicate that removal costs of MTBE are significantly greater than for benzene and other common pollutants using these technologies.

The high solubility of the oxygenates requires the construction of much larger air stripping units than for conventional VOC's, with higher capital and operating costs. There is significant uncertainty in the design of air stripping units for MTBE and other oxygenates, since the few reported values of Henry's constant vary over a significant range, at the same temperature (c.f. Table 1). Since the boiling point of most oxygenates is relatively low, increasing temperature is likely to have a significant impact on stripping. The stripping factor is a function of the mass transfer coefficient and Henry's constant, which are functions of temperature. The size of the air stripping unit can be reduced significantly if the operating temperature can be increased, although with a corresponding increase in operating cost.

In the case of granular activated carbon (GAC), the relatively low sorption of MTBE results in relatively fast breakthrough, and a high GAC utilization rate. The rate of GAC utilization for MTBE removal is thus more than 20 times greater than for TCE removal. McKinnon and Dyksen (1984) proposed that GAC is not cost effective for the removal of MTBE except at low MTBE concentrations. In addition, since MTBE is only weakly sorbed by GAC, other VOC's in the contaminated groundwater will tend to displace MTBE from sorption sites on the GAC.

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

Such "chromatographic" separation in the GAC unit can be expected once the initial wave of MTBE has been sorbed and then other gasoline constituents such as benzene and toluene arrive to the treatment well, displacing MTBE from the GAC, with a sudden release of large amounts of MTBE.

There is a need for other innovative solutions to remove MTBE and the other oxygenates from contaminated water, whether for direct water supply or for protection of water supply (e.g. remediation of contaminant plumes). Several alternative processes have been proposed. Advanced Oxidation Processes (AOP), which are based on the generation of the hydroxyl radical (OH•) via ultraviolet light, ozone or hydrogen peroxide. OH• effectively oxidizes organic compounds. Several investigators (Raupp and Junio, 1993; Barreto et al., 1995; Venkatadri and Peters, 1993) have reported MTBE oxidation using these processes, and Calgon Carbon Corporation (Reko, 1996) has conducted pilot scale studies that indicate removal efficiencies of 88 to 99.9%, depending on influent conditions. AOPs may be an effective process for treating MTBE contaminated water. There are however some concerns with respect to the generation of by-products.

Membrane technologies have not been studied in connection with the removal of MTBE from water, since most membrane processes are not applicable to VOC's. Hydrophobic hollow fiber membranes present a unique opportunity to remove MTBE and other highly soluble organic compounds from contaminated water. Hollow fiber membranes have been developed to efficiently deliver oxygen to aeration treatment systems (Pankhania et al., 1994; Ahmed and Semmens, 1996) and to strip VOCs from water (Sarti et al., 1993; Semmens et al., 1989). The fiber is made of a hydrophobic polymer, typically polypropylene or polyethylene. In addition to being hollow, the fiber is porous, allowing the movement of molecules across the membrane. In some applications, air or oxygen is delivered through the center of the membrane and is allowed to diffuse out into the water phase surrounding the fiber on the outside. Semmens et al. (1989) developed a process to remove volatile organics from water by passing the contaminated water through the inside of the fiber and passing clean air on the outside of the fiber, which becomes laden with VOC's. Hydrophobic VOC molecules diffuse out of the water, through the membrane and into the flowing air phase, where they can be adsorbed or destroyed through a variety of processes.

As long as MTBE and other oxygenates are used as gasoline additives, there is a potential for their release into the environment. The treatment processes described above present the most applicable technologies for removing the oxygenates from contaminated water. Studies by Converse and Schroeder (1998) and Couch and Young (1998) related to the SB 521 program evaluate the use of two other technologies, UV/hydrogen peroxide and liquid-phase biofiltration. The uncertainty in the physicochemical properties of these compounds requires some additional research to determine which is the most applicable technology at various contaminant concentrations and volumetric flow rates, in terms of cost and removal performance.

1.3 Design Basis

Based on a review of data on the typical MTBE concentrations and flow rates required to treat, available from USGS studies (Squillace et al., 1996; Delzer, 1996), and CAL-DHS (1998) information, two general cases have been identified: (1) low concentration (30-100 ug/L) levels and high flow rates, in the range of 500-1000 gpm (gallons per minute), which are typical of contaminated drinking water supplies, whether from surface waters or from groundwater pumping wells; and (2) high concentration (100-5000 ug/L) and low flow rates, in the range of 10-500 gpm, typical of groundwater wells near the source of contamination, usually a leaking underground storage tank. Ten combinations of flow rate and concentration were selected as the influent characteristics, as indicated in Table 2.

Table 2. Combinations of MTBE Concentration and Flow rate Used for Design

<i>Case</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>	<i>8</i>	<i>9</i>	<i>10</i>
Concentration (ug/L)	100	100	100	500	1000	5000	100	500	1000	5000
Flow rate (gpm)	1000	500	100	100	100	100	10	10	10	10

Although USEPA has in effect a 35 ug/L advisory level, we consider the CAL-DHS secondary MCL level (5 ug/L) as the treatment goal in our design calculations. For some selected cases we evaluate the cost differential between treatment to a 5 ug/L level and a 35 ug/L level.

Capital costs are amortized over a 20 year horizon, at a 4% discount rate. Operation and Maintenance (O&M) costs include operator(s) for the units, materials and electrical power, as well as fuel for the thermal treatment when considered. The costs estimated here are at the feasibility level (accuracy of at best -30% to +50%). For all the technologies considered, additional costs may be required for pretreatment, depending on influent conditions, and post-treatment polishing or storage.

Equipment costs are calculated using the CapCost software (Turton et al., 1998). To estimate the total capital costs, the following factors are applied:

- (1) piping, electrical and valves (30% of equipment);
- (2) site work (10% of equipment);
- (3) contractor fees (15% of equipment plus items 1 and 2);
- (4) engineering costs (15% on top of equipment plus items 1, 2, and 3);
- (5) contingency (20% on top of all previous costs).

O&M costs are calculated based on electrical power requirements (at \$0.08/kW-h), fuel (at \$1.6/million BTU and 3 BTU/scfm), labor (at \$30/hr), materials considering 3% of equipment per year, and contingency plus administrative of 15% on top of all other O&M costs.

The following sections present design considerations and cost estimates for air stripping, granular activated carbon, ozone/hydrogen peroxide oxidation, and hollow fiber membranes. The advantages and disadvantages of each technology are also discussed. Section 6 summarizes the

cost estimates for the various technologies and provides recommendations for the various cases studied. Experimental studies were conducted to verify parameter values required for the calculations. The results are presented in the relevant sections.

2. AIR STRIPPING

2.1 Description of the process

Air stripping involves continuously contacting the contaminated water with a large volume of air to transfer a significant fraction of the volatile organic compounds (VOCs) to the air phase. Pollutant removal efficiency is a function of the design of the air stripping tower as well as the contaminants' Henry's constant, H . MTBE has a relatively low H at ambient temperatures, which presents a significant challenge to effectively remove it using air stripping. A greater emphasis is placed on a well-designed process to achieve the treatment goals. Since air stripping only involves mass transfer from the water to the air phase, additional treatment of the exiting contaminated air stream may be required, depending on local air emissions regulations. Typically, if more than 0.45 kg/day (1 lb/day) is emitted, vapor phase treatment is required, but it also depends on local regulations based on the air quality conditions. Areas with significant non-attainment with respect to air quality may not allow any VOC emissions to the atmosphere.

Figure 1 presents a simple graphical method for determining the need to have vapor phase treatment. Based on a mass balance, the mass flow rate of MTBE in the off-gases is a function of the difference between the influent and effluent concentrations, and the water flow rate into the air stripping unit:

$$M = Q(C_{in} - C_{out}) \quad (1)$$

where M is the mass flow rate (g/s or lb/day), Q is the volumetric flow rate (m^3/s or gpm) and C_{in} and C_{out} are the influent and effluent water concentrations (g/m^3 or ug/L). In this case, $M = 0.45$ kg/day, and C_{out} is 5 ug/L . For a particular site, C_{in} and Q are determined based on the site characterization and feasibility studies. One can then use the graphical method to find the point where C_{in} and Q intersect; if the point is below the bold line, then it is possible to obtain a waiver for off-gas treatment. In many cases, MTBE is not the only VOC present. Therefore, one needs to consider the mass of other VOCs removed by the air stripping unit. Assuming that MTBE represents at most 50% of the mass of VOC in the contaminated water, one can use the thin line in Figure 1 to determine whether gas phase treatment is required.

Considering the ten cases presented in Table 2, only Cases 1, 5 and 6 exceed the 0.45 kg/day limit. However, Cases 2, 4 and 10 fall within the more conservative approach that considers other possible VOCs present in the contaminated water. For completeness, we have done the cost calculations for all ten cases, but this should be reviewed with local regulators on a case-by-case basis. The same considerations apply to hollow fiber membranes, which transfer MTBE from the water to the gas phase.

In terms of the design of the air stripping tower, there are a number of commercial mass transfer technologies available, including (Liu and Liptak, 1997):

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

- packed tower
- spray tower
- bubble diffusion towers
- aspiration air strippers
- low-profile towers

The cost-effectiveness of these technologies has recently been reviewed (MTBE Research Partnership, 1998). The authors conclude that the packed tower technology is the most cost-effective air stripping device, followed by low-profile towers. One of the important considerations is that only the packed tower and the low-profile towers can achieve high MTBE removal efficiencies in one pass, since the other air stripping technologies cannot achieve the high air to water ratios needed for high removal. Since the low-profile towers are limited to a maximum flow rate of 100 gpm, their costs do not scale beyond that size. Based on this information, the designs considered in this study will be based on packed tower technology. The packing material in a packed tower is designed to maximize the contact area between the counter-current water and air flows, to increase the mass transfer. Packed towers are widely available: off-the-shelf or custom systems can be easily obtained.

To treat air emissions, several technologies are typically considered, including (Liu and Liptak, 1997):

- vapor-phase activated carbon adsorption
- catalytic oxidation
- thermal oxidation
- biofiltration
- vapor-phase oxidation using UV, ozone or UV/ozone

Granular activated carbon (GAC) is commonly used to remove VOCs from the gas stream, by physical adsorption, with very high removal efficiency. The VOC vapors (along with the carrier air stream) are passed through a bed of activated carbon, where they sorb onto the active sites. Given the very high surface area of activated carbon, many sorption sites are available. Once the sites are filled, VOC molecules begin to break through the exhaust end of the bed. Monitoring devices can be used to determine the breakthrough of VOCs. Depending on the mode of operation, single or parallel beds can be used. If parallel beds are used, then typically one bed is being used for sorption while the other is being regenerated or the spent carbon is exchanged. On-site regeneration is typically expensive except for very high carbon usage rates; the spent carbon can be regenerated using either nitrogen or steam (Nattkemper, 1997) at high temperatures. It is common to send the spent carbon to off-site regeneration. There are no well-documented studies of gas-phase sorption of MTBE onto GAC, in particular in the presence of other competing hydrocarbons, such as BTEX, typically present at MTBE sites. Given the relatively low sorption affinity of MTBE for GAC, it is possible that it will be displaced out of the GAC bed by other hydrocarbons, resulting in early breakthrough and increased carbon usage. Adsorption decreases with higher humidity and/or temperature in the gas stream entering the GAC bed.

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water.

Catalytic oxidation involves passing the VOC-laden air stream past a catalyst bed, typically at temperatures above 200 °C (392 °F), to oxidize the organic compounds to CO₂ and H₂O. As with any oxidation process, some products of incomplete oxidation will be formed. These can be minimized by controlling the operating conditions, but may require pre-treatment of the water phase to remove sulfur compounds. Studies are currently under way to determine typical products of incomplete MBTE combustion, as well as the optimal operating conditions. The catalysts used are similar to those employed in the catalytic converters used to control automotive emissions, and are readily available for commercial applications. They must be operated well below the Lower Explosive Limit (LEL) of the vapor mixture. The heating value of the gas stream is typically low and thus contributes marginally to heating the incoming vapors. Heat may be supplied by an electrical resistance or a furnace. Since heating is one of the major operating costs, heat recovery is commonly performed using either a recuperative or a regenerative heat exchanger. In a recuperative oxidizer, an air-to-air heat exchanger is employed, recovering up to 70% of the energy (Liu and Liptak, 1997). In a regenerative system, two parallel ceramic beds are used in cyclical operation, one bed to store the heat from the exiting gas stream and the other to transfer the heat to the entering gas stream. Up to 95% heat recovery can be achieved (Liu and Liptak, 1997), at higher capital costs and operational complexity.

Thermal treatment can be achieved using two different technologies, which commonly span the range of air flow rates. An internal combustion engine (ICE) can be used to oxidize MTBE and all other hydrocarbons, at very high conversion efficiencies to CO₂ and H₂O, typically better than 99.9% (Archabal et al., 1997a). Each ICE can handle up to 4.3 m³/hr (150 scfm) of air flow rate, and may require propane as supplementary fuel. Multiple ICE engines may be used to handle larger air flow rates, but typically the cost-effectiveness relative to other technologies decreases rapidly with air flow rate. Furnaces can be used for higher air flow rates, from 8.5 to 85 m³/hr (300 to 3,000 scfm). In contrast to catalytic oxidizers, furnaces are typically operated at much higher temperatures, typically greater than 750 °C (1,382 °F), which requires considerably greater amounts of supplementary fuel (Archabal et al., 1997b). Higher conversion efficiencies are achieved at higher temperatures. As with catalytic oxidizers, heat recovery is an important design consideration.

Gas-phase biofiltration is another alternative for treating the vapors from the air stripping unit. MTBE can be degraded by a number of bacterial groups. At least a few bacterial species are able to use MTBE as a growth substrate and mineralize the compound. Although development of MTBE degrading cultures in unacclimated systems is very slow, acclimated cultures can be used to inoculate treatment systems and inoculated processes have start-up times similar to processes treating more conventional substrates. Successful biodegradation of MTBE has been observed in at least two field biofilter installations. One is located at the Joint Water Pollution Control Plant of the Los Angeles County Sanitation Districts and the other is operated by Environmental Resolutions, Inc. at a gasoline soil vapor extraction site in Richmond, California (Converse and Schroeder, 1998).

There is insufficient information on vapor phase oxidation of MTBE using AOP systems to determine either the feasibility or the costs associated with this technology. Although it is likely that MTBE can be oxidized in the vapor phase (it has a half-life of 3 days in the atmosphere), it

is expected that oxidation by-products can be an issue, which needs to be resolved with additional research. We do not consider AOP in our cost estimates for vapor phase treatment.

2.2 Design considerations

In this study, conventional countercurrent air stripping towers were designed using the method outlined by Treybal (1980), Roberts et al. (1985), Ball et al. (1984) and Staudinger et al. (1990). The method is similar to the one used in the commercial software model AIRSTRIP. Common design parameter values used in the calculations are shown in Table 3.

Table 3. Design Parameters for Air Stripping Units

	<i>Low Flow rate</i>	<i>Medium Flow rate</i>	<i>High Flow rate</i>	<i>Very High Flow rate</i>
Water Flow rate	6.3x10 ⁻⁴ m ³ /s (10 gpm)	0.0063 m ³ /s (100 gpm)	0.031 m ³ /s (500 gpm)	0.063 m ³ /s (1000 gpm)
Tower Diameter	0.36 m (1.2 ft)	1.13 m (3.7 ft)	2.54 m (8.3 ft)	3.6 m (11.8 ft)
Tower Height	Packing height + 3 m			
Packing Material	1" Intalox Saddles			
Volumetric Air-Water Ratio	150:1			
Planned Operating Schedule	24 hours/day, 7 days/week, 52 weeks/yr			

Given the importance of Henry's constant for the design of both air stripping and membrane stripping systems, considerable effort has been dedicated to obtaining reliable values. Since the oxygenates are quite soluble, precise experimental determination of Henry's constant presents some challenges. Robbins et al. (1993) published their experimental determination of Henry's constant, H , for MTBE as a function of temperature, T , for the range from 25 to 50 °C. The temperature dependence of Henry's constant can be approximated by an equation of the form $H = \exp(A - B/T)$, where A and B are experimentally determined coefficients. Using the data presented in Robbins *et al.* (1993), $A = 21.2$ and $B = 7406$ K, where H is in dimensionless form and T is in K. The static headspace method (Robbins et al., 1993) compares favorably with the well-known EPICS method (Ashworth et al., 1988) for benzene, toluene, ethylbenzene, xylenes, trichloroethane, tetrachloroethene and trichloroethene, with a maximum difference of 7% between methods, and an average difference of just 1% between methods. The EPICS method requires careful weighing of the amount of VOC added to two bottles to make sure they are equal (Lincoff and Gossett, 1984) or even with a modified EPICS method, knowing the precise ratio of masses (Gossett, 1987). The static headspace method does not require that the exact concentration of the VOC nor its matrix be known (Robbins et al., 1993), which significantly simplifies the method.

We evaluated Henry's constant for MTBE using two different methods. The first involves using the method described by Ramachandran et al. (1996), using the SPME/GC/MS method described by Arthur et al. (1992). The second method uses the vapor-pressure data reported by

Krähenbül and Gmehling (1994) for several oxygenates, combined with experimental measurements of the solubility of MTBE at different temperatures, to calculate Henry's constant (in dimensionless form) using the definition of Henry's constant:

$$H = P^{sat} / C_w RT \quad (2)$$

where P^{sat} is the saturation vapor pressure (kPa), C_w is the solubility of the organic compound (mol L^{-1}), and R is the ideal gas constant ($\text{kPa mol L}^{-1} \text{K}^{-1}$). Table 4 presents the coefficients of Antoine's Equation (Antoine, 1888) for vapor-pressure dependence on temperature for MTBE, ETBE, TAME and tert-Amyl Ethyl Ether (TAE), using:

$$P^{sat} = A + \frac{B}{T + C} \quad (3)$$

with P^{sat} in kPa and T in K. Figure 2 presents a comparison of our results to Robbins et al. (1993). Our results indicate that the data from Robbins et al. (1993) may be somewhat conservative, but is adequate for designing gas-liquid mass transfer systems.

Table 4. Coefficients of the Antoine Equation for several oxygenates¹

	<i>MTBE</i>	<i>ETBE</i>	<i>TAME</i>	<i>TAE</i>
A	6.070343	6.073724	6.067822	5.926451
B	-1158.912	-1206.874	-1256.258	-1218.389
C	-43.200	-49.190	-50.100	-63.940

¹from Krähenbül and Gmehling, 1994

Given their low Henry's constants at ambient temperature, air stripping of the oxygenates requires very high air-to-water volumetric flow ratios. In addition, increasing the operating temperature can increase Henry's constant significantly (Truong and Parmele, 1992; Butillo et al., 1994), improving performance, reducing tower dimensions and capital and O&M costs.

Depending on the source of water (surface water, groundwater, stormwater, process water), the influent characteristics with respect to other organic and inorganic contaminants may require pretreatment, such as filtration, particle settling tanks, oil/water separation, etc. It is beyond the scope of the current study to evaluate all the possible influent characteristics and perform a full cost analysis. As in any air stripping operation, the removal of CO_2 that occurs in the tower results in precipitation of carbonates and other mineral precipitates (scaling), which must be controlled through periodic washing of the column with acidic solutions. This is considered in our O&M costs.

As pointed out by Butillo et al. (1994), if the concentrations of MTBE in the influent contaminated water are high ($>1,000$ ppm), it is highly recommended to install a Lower Explosive Limit (LEL) analyzer, to continuously monitor the gas phase concentrations in the tower, and to use this information to either increase the air flow rate or decrease the water flow rate in the

stripping tower to avoid a potential explosion. The stripping unit should be operated below 50% LEL.

2.3 Cost Estimates

Costs for an influent water at 15 °C and an effluent of 5 ug/L are considered for five cases: (1) no vapor treatment; (2) vapor treatment using thermal oxidation with no heat recovery to preheat the influent water; (3) vapor treatment using thermal oxidation with heat recovery to bring the water temperature to 25 °C; (4) vapor treatment using GAC; and (5) vapor treatment using a gas-phase biofilter, as designed and tested at UC Davis (Eweis et al., 1997, 1998). Capital costs considered include the stripping towers, pumping station, fired heater and heat exchanger as required, GAC bed and carbon replacement costs, accessories (instrumentation, piping, valves, electrical), as well as contractor installation and engineering. For comparison, costs for an influent water at 15 °C and an effluent at 35 ug/L are also presented. In addition, a cost analysis of a comparable air stripping tower for benzene was evaluated, with no vapor treatment, to evaluate the relative additional cost of treating MTBE vs. a typical hydrocarbon component of gasoline.

Figures 3 and 4 present the effects of increasing temperature on tower height for the ten cases studied under the two effluent conditions. At low operating temperatures, it becomes increasingly difficult to meet the overall removal efficiency. For the 5 ug/L effluent quality, it is not possible to achieve it at 5 °C under any of the design conditions. As temperature increases, the improvement in the mass transfer coefficient due to a much larger H allows for smaller towers. The temperature effect becomes less important above 25 °C, indicating that there is little additional gain in removal but a correspondingly higher operating cost to heat the influent water.

Table 5 summarizes the resulting treatment costs (in \$/1000 gal) for the ten cases considered. The 5 ug/L effluent design criteria results in the need for significantly greater packing height, all other conditions held equal, than the 35 ug/L effluent criteria. In some cases, this leads to impractical or unacceptable air-stripping tower heights (from a community's perspective). This could be overcome by redesigning the system to have two or more towers in series, or by designing the stripping tower to only remove a certain fraction of the influent MTBE and add a GAC polishing step after the stripping tower. The polishing step may be desirable, in any case, to ensure that no MTBE is discharged in the water effluent, albeit at a higher capital and O&M cost. In general, treating MTBE-contaminated water to the 5 ug/L standard is 20 to 80 % more expensive than treating the same influent to the 35 ug/L, with the largest impact on low flow rate units.

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

Table 5. Amortized Cost, dollars per 1000 gallons treated using Air Stripping

<i>Case</i>	<i>1</i>	<i>2*</i>	<i>3*</i>	<i>4*</i>	<i>5</i>	<i>6</i>	<i>7*</i>	<i>8*</i>	<i>9*</i>	<i>10*</i>
Concentration (ug/L)	100	100	100	500	1000	5000	100	500	1000	5000
Flow rate (gpm)	1000	500	100	100	100	100	10	10	10	10
Effluent at 5 ug/L										
No air treatment	0.23	0.25	0.40	0.59	0.68	0.88	1.54	2.30	2.65	3.55
Thermal Oxidation w/o heat recovery	0.56	0.62	0.93	1.17	1.28	1.54	3.07	3.56	3.96	5.92
Thermal Oxidation with heat recovery	0.50	0.53	0.76	0.84	0.88	0.97	2.35	2.68	2.84	3.22
GAC for air treatment	0.66	0.70	1.08	1.58	1.86	2.81	2.90	4.37	5.14	7.45
Gas Phase Biofilter for air treatment	0.33	0.41	0.73	0.97	1.07	1.33	3.51	4.60	5.11	6.42
Effluent at 35 ug/L										
No air treatment	0.17	0.17	0.28	0.48	0.59	0.87	1.15	2.06	2.58	3.45
Thermal Oxidation w/o heat recovery	0.48	0.51	0.73	0.92	1.04	1.31	2.17	3.08	3.60	4.97
Thermal Oxidation with heat recovery	0.31	0.33	0.46	0.50	0.53	0.60	1.24	1.43	1.53	1.76
GAC for air treatment	0.58	0.59	0.87	1.33	1.62	2.59	2.00	3.29	4.08	5.95
Gas Phase Biofilter for air treatment	0.25	0.30	0.52	0.72	0.83	1.11	2.62	3.53	4.05	4.92
Benzene at 1 ug/L										
Benzene (no air treatment)	0.16	0.17	0.29	0.38	0.42	N.A.	1.08	1.36	1.47	N.A.

*air treatment may not be required for this system.

N.A. = not applicable, since benzene cannot be dissolved at these high concentrations.

If thermal or catalytic oxidation is used to treat the vapors from the air stripping unit, it is more cost effective to use the waste heat to preheat the water flowing into the air stripping unit. This results in a significant reduction in tower height which reduces both capital costs and operating costs in terms of the power requirements. This is valid at all flow rates and concentrations, but is more important to consider in low flow rate units. In the case of high influent concentrations, very high air stripping towers are required. Preheating the influent can reduce in savings large enough to pay for the vapor phase treatment.

At high flow rates (more than 100 gpm), the most cost-effective air treatment system is the gas-phase biofilter. Not included in these cost estimates is the additional land required to site the biofilter, which has a large footprint. For low flow rates (100 gpm or less), the most cost-effective vapor treatment is thermal oxidation with heat recovery to preheat the influent water. GAC is not cost-effective for air treatment under any of the cases studied, given the low MTBE sorption capacity of GAC.

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

Since the Henry's constant for ETBE and TAME are in the same range as MTBE, air stripping costs should be similar to MTBE. Air stripping would not be a suitable technology for TBA or ethanol, given their extremely low H . For comparison, Table 5 presents the costs of treating benzene-contaminated water, at the same influent conditions down to the drinking water MCL of 1 ug/L. Benzene would be representative of the most difficult petroleum hydrocarbon to remove from water, since it has a low H , relatively high solubility and a very strict standard. Even though the effluent is treated to a lower level, the cost of treating MTBE contamination is 50 to 150 % more expensive than treating benzene contamination, using air stripping.

2.4 Advantages and Disadvantages

Advantages: Air stripping is a proven technology, which has been applied commercially to treat MTBE-contaminated water at low and very high flow rates. It can achieve high removal efficiencies, is mechanically reliable and flexible enough to handle some variations in feed stream MTBE concentrations without a significant effect on removal efficiency. If high variations are expected, air stripping may require a post-treatment polishing step using granular activated carbon to meet effluent standards. Packed air stripping units can be designed to treat up to 1,000 gpm, with significant economies of scale. Higher flow rates require multiple units. Several commercial vendors offer the technology and there is ample expertise in their design and operation.

Disadvantages: MTBE is only transferred from water to air, resulting in either air emissions or expensive air treatment. Variations in water flow rate can affect removal efficiency if the tower is operated at high MTBE removal efficiencies. Dissolved iron, calcium and magnesium in the MTBE-contaminated water will eventually deposit scales in the packing material, requiring a brief shut-down period to wash the packing with an acidic solution, or eventually replace the packing material. Biological growth in the packing may also reduce removal efficiency.

3. ADSORPTION PROCESSES

3.1 Description of the process

Adsorption processes rely on the affinity of a solid surface for particular chemicals. For example, activated carbon has a high affinity for organic compounds, and is particularly useful in removing them from contaminated water or gas streams. Activated carbon is prepared from naturally occurring materials with high carbon content, such as coconut shell, various coals, peat or wood. The carbonaceous material is pulverized and then heated to a high temperature. This process greatly increases both the surface area of the carbonaceous material and the affinity for organic chemicals. Other adsorbents have been developed, including polymeric resins and molecular sieves. We only evaluate the cost and performance of activated carbon since it is the only adsorbent for which adsorption isotherm data is readily available.

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

The most important property of an adsorbent/adsorbate pair is their affinity, usually measured in terms of mass of organic adsorbed per unit mass of adsorbent (e.g. mg/g). Sorption capacity and the load of contaminants in the influent water stream determine the service life of an adsorption system. In most cases, the adsorbent can be renewed periodically. Activated carbon can be regenerated using steam. For some operations, it is more cost-effective to ship the spent adsorbent to a regeneration facility off-site, and replace the bed of adsorbent with new or regenerated material. The frequency of regeneration is dictated by the time it takes for the organics to saturate the adsorbent and break through at the outlet. To avoid discharging organics in the effluent, two or more adsorption beds are usually operated in series or in parallel. The first bed is operated until the adsorbent breaks through and then the influent water is routed to the second bed while the first is replaced or regenerated. Once the time to breakthrough is known, the beds can be operated almost automatically, switching from one bed to the other at predetermined intervals.

Laboratory or bench-scale tests are used to determine the adsorption characteristics of an adsorbent/adsorbate pair. Different types of activated carbon have different affinity for MTBE. Given the relatively high affinity of MTBE for water, which results in high solubility, it has a low affinity for activated carbon. Sorption isotherms were obtained from Calgon Carbon Corporation for three types of activated carbon. Information provided by the manufacturer indicates that coconut-based activated carbon (GRC-22) is the most suitable for MTBE adsorption from contaminated water (Cobes, 1998). Figure 5 presents the equilibrium data for GRC-22. The carbon use rate is 0.098 kg/m³ (0.82 lb/1000 gal) and the equilibrium capacity is 10.5 mg/g when in equilibrium with water at 1000 ug/L. The sorption isotherm can be modeled using the Freundlich model (Liu and Liptak, 1997), with decreasing sorption capacity at higher concentrations:

$$C_s = K_f C_w^{(1/n)} \quad (4)$$

where C_s is the sorbed concentration (mg MTBE/g GAC), K_f is the Freundlich sorption coefficient, equal to 11.7 (mg MTBE/g GAC)(L water/mg MTBE)^{1/n} for MTBE sorbing to GRC-22, C_w is the aqueous MTBE concentration in equilibrium with the sorbed concentration and n is an empirical coefficient, equal to 1.4 for MTBE sorbing to GRC-22. Different vendors offer GAC with other sorption capacities for MTBE (MTBE Research Partnership, 1998); it is advisable to determine the type of GAC that will be used for each case. In addition, the sorption isotherms are determined in the laboratory using virgin GAC with spiked distilled water. In practice, MTBE-contaminated water may contain other organic material that will compete for the sorption sites. It has also been observed in several field cases that as the composition of the contaminated water changes, other dissolved VOCs such as benzene can easily displace MTBE from the GAC, releasing a strong pulse of MTBE into the effluent.

3.2 Design considerations

An important parameter in the design of an adsorption system is the Empty Bed Contact Time (*EBCT*). For a system treating contaminated water, *EBCT* should be on the order of several

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

minutes, to allow sufficient contact time between the adsorbate (MTBE) and the adsorbent (GAC). In practice, a minimum EBCT of 10 min is commonly used for water treatment design. To estimate *EBCT*, the superficial velocity, v_s (m/s or ft/s) of the liquid phase through the contacting vessel must be determined, from the flow rate, Q (m³/s or gpm), and the cross-sectional area of the vessel, A (m² or ft²):

$$v_s = Q/A \quad (5)$$

and

$$EBCT = L/v_s \quad (6)$$

where L is the length of the vessel.

Commercial vessel sizes are used in the design. Vendors can provide information on the EBCT for a given flow rate. The minimum EBCT determines the minimum vessel size required. The maximum standard commercial vessel size is 20,000 lb of GAC, based on transportation restrictions. Customized vessels can be constructed, at a higher cost, and are not considered in the design. Table 6 indicates the vessel size chosen for each case, as well as some other operating parameters.

Table 6. GAC Operating Conditions

Case	1	2*	3*	4*	5	6	7*	8*	9*	10*
Concentration (ug/L)	100	100	100	500	1000	5000	100	500	1000	5000
Flow rate (gpm)	1000	500	100	100	100	100	10	10	10	10
Vessel size (lb GAC)	20000	20000	5000	5000	5000	5000	500	500	500	500
Vessel size (kg GAC)	9090	9090	2273	2273	2273	2273	227	227	227	227
Number of vessels ¹	2 + 2	1 + 1	1 + 1	1 + 1	1 + 1	1 + 1	1 + 1	1 + 1	1 + 1	1 + 1
Vessel internal length (m)	2.8	2.8	1.95	1.95	1.95	1.95	0.9	0.9	0.9	0.9
Vessel internal diameter (m)	3.05	3.05	1.82	1.82	1.82	1.82	0.86	0.86	0.86	0.86
Superficial velocity (m/s)	15.6	15.6	8.72	8.72	8.72	8.72	3.95	3.95	3.95	3.95
EBCT (min)	10.7	10.7	13.4	13.4	13.4	13.4	13.5	13.5	13.5	13.5
GAC changes per year ²	2.1	2.1	1.7	3.3	4.4	8.6	1.7	3.3	4.4	8.6

¹in series

²low organics scenario

Another important parameter is the Mass Transfer Zone (MTZ), a region of rapidly changing concentration, which moves as a wave through the sorption vessel (Watts, 1998). Breakthrough of MTBE occurs when the leading edge of the MTZ reaches the outlet of the vessel. The adsorbent is completely spent when the trailing edge of the MTZ reaches the outlet of the vessel. MTZ can be determined either experimentally (Bohart and Adams, 1920; Hutchins, 1973) or estimated using the method developed by Crittenden et al. (1985). The length of the vessel and MTZ determine the service interval for the vessel.

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

Using Equation 4, the sorbed concentration in equilibrium with the influent concentration is estimated. Two influent water characteristics are considered, one with a low level of background organics and one with a high level of background organics. These other organics can be other VOCs (e.g. benzene, toluene, xylenes) or natural organic matter in the influent water. K_f is adjusted to compensate for competitive sorption, by reducing it 20% for the low organics loading scenario, and another 20% for the high organics loading scenario. The total MTBE mass removed annually is estimated from the influent concentration and flow rate specified in the ten cases (Table 1). It is assumed that the effluent exits the treatment units with no MTBE. The GAC required is then calculated using the MTBE mass removed and C_s at equilibrium with the influent water. The frequency of GAC replacement or regeneration is then estimated considering the amount of GAC per vessel. Annual labor costs increase with increasing GAC replacement or regeneration.

Once the sorbent in the GAC comes to equilibrium with the influent aqueous concentration, the GAC must be replaced by virgin GAC or regenerated on site using steam. Figure 6 presents a typical flow diagram for steam regeneration, which includes a condenser and a decanter to recover the organic phase. The water from the decanter is passed through a separate GAC bed, since our calculations indicate that this is a less expensive option than passing it through the main GAC beds. Although the recovered MTBE has a value as fuel, given the small amounts of MTBE recovered per year (only 272 kg in the most contaminated case), it is likely that the recovered MTBE will be sent to disposal as a hazardous waste. However, this is easier and less expensive than sending large volumes of MTBE-loaded GAC for regeneration off-site. Since the sorption capacity of GAC decreases after each steam regeneration, the GAC usage rate is increased by a factor of 25%, and the GAC bed is replaced once a year.

3.3 Cost Estimates

Cost estimates for four conditions are evaluated. The two main criteria we considered are: (1) low versus high organic loading in the influent water, since this has a significant effect on GAC usage rate, and (2) GAC replacement every time versus on-site regeneration using steam. GAC costs are \$1.25 per pound. Shipping the spent GAC to an off-site regenerator is estimated to cost \$0.25 per pound. Cost estimates are presented in Table 7.

High organics loading increases the total treatment costs by 10 to 23 %. It is important to characterize the water to be treated before the design of a system, and to run a bench-scale pilot test to determine the expected GAC usage rate for the particular site conditions.

On-site regeneration using steam is more cost-effective than GAC replacement for flow rates of 100 gpm or higher. It is also more cost-effective at 10 gpm when the influent concentration is very high (5000 ug/L). In general, for the smaller systems on-site regeneration involves more labor. Since these systems are likely to be in gas stations and other non-industrial sites, steam regeneration is also not as appropriate, since it involves skilled personnel not readily available on site. For these systems, it is common practice to replace the GAC once it is spent.

A cost comparison between treatment costs for MTBE-contaminated water and benzene-contaminated water indicates that MTBE is 110 to 560% more expensive to treat than benzene,

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

for the low organics case where GAC is always replaced. The lower sorption capacity has a major impact on the economics of the treatment.

Table 7. Amortized Cost, dollars per 1000 gallons treated using GAC

Case	1	2	3	4	5	6	7	8	9	10
Concentration (ug/L)	100	100	100	500	1000	5000	100	500	1000	5000
Flow rate (gpm)	1000	500	100	100	100	100	10	10	10	10
Low organics, replace GAC	0.65	0.66	0.93	1.43	1.77	3.07	1.20	1.81	2.24	3.85
High organics, replace GAC	0.74	0.76	1.03	1.65	2.08	3.77	1.32	2.09	2.62	4.71
Low organics, regenerate GAC	0.34	0.38	0.55	0.81	0.98	1.67	1.98	2.25	2.50	3.29
High organics, regenerate GAC	0.39	0.44	0.61	0.93	1.15	2.05	2.18	2.60	2.92	4.02
Benzene, low or organics, replace GAC	0.17	0.18	0.42	0.43	0.43	N.A.	0.57	0.58	0.59	N.A.

N.A. = not applicable, since benzene cannot be dissolved at these high concentrations.

3.4 Advantages and Disadvantages

Advantages: GAC is a proven technology for treating water contaminated with organics. Very high removal efficiencies are achieved with proper operation. GAC is a simple technology with high mechanical reliability that can handle large variations in influent MTBE concentrations as well as variations in water flow rate. Several commercial vendors offer the technology and there is ample expertise in the design and operation of GAC units.

Disadvantages: Natural organic matter and other dissolved organic chemicals in the influent water have a stronger affinity for GAC than MTBE, so they will displace MTBE from the adsorption sites, reducing even further the removal efficiency and increasing the carbon use rate. An abrupt change in influent concentration of other organics (for example as the benzene plume arrives at the extraction well) can result in sudden desorption of large amounts of MTBE into the effluent; monitoring of the operation is required to reduce the risk of MTBE exposure. GAC units are commercially available in specific sizes, which limits the design options in terms of EBCT and the frequency of GAC replacement, which may not be as cost-effective as if a custom-designed unit was built. The maximum GAC vessel size is typically 20,000 lb, which means that economies of scale are not possible for flow rates above 500 gpm.

4. OZONE/HYDROGEN PEROXIDE OXIDATION PROCESSES

4.1 Description of the process

The process of ozonation is an option for the treatment of wastewater and drinking water. With reduced installation and operating costs, along with the development of large scale ozone generators, there has been increasing interest in using ozone to treat water containing compounds that are difficult or expensive to remove using other methods (Peleg, 1976). In the past 40 years,

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

ozonation reactions in water containing organic and inorganic compounds have been investigated. In some cases, ozone treatment alone has been sufficient to degrade contaminants to meet effluent standards.

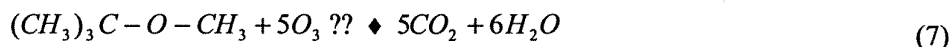
Ozonation involves a large number of reactions, which include molecular ozone, oxygen, and free radical reactions. The hydroxyl radical (OH•) is a product of ozone decomposition. It has been seen to react non-selectively with many organic and inorganic compounds, and is hypothesized to be the most important reactive intermediate in aqueous systems. Hydroxyl radicals have an oxidizing power which ranks behind only that of fluorine and molecular oxygen, and it is twice as strong as an oxidizing reagent as chlorine. Ozone, alone or in combination with hydrogen peroxide, has the potential to fully oxidize organic compounds such as MTBE to carbon dioxide and water.

Since hydroxyl and other radicals can be scavenged by a combination with other radicals or through production of secondary radicals of lower reactivity, it is important to determine the kinetics of oxidation for each compound. The most important scavengers in wastewater are carbonate and bicarbonate (Buxton et al., 1988). Other organics present will also reduce the efficiency of MTBE oxidation

Byproduct formation from the incomplete oxidation in ozonation processes is of great concern due to the potential to create a more toxic compound than the starting reactant. Studies from Vel Leitner et al. (1994) show that ozonating MTBE or ETBE result in the formation of tert-butyl formate (TBF) or tert-butyl acetate, respectively. Tert-butyl alcohol (TBA) was also seen to be a byproduct for MTBE or ETBE. Batch and semi-batch reactors were used to measure the degradation and formation of the reactants and products. The formation of the products identified during the course of the ozonation experiments was explained by a mechanism involving molecular attack of ozone on ethers via a carbonium ion-like transition state followed by the expulsion of hydrogen peroxide. Vel Leitner et al. (1994) also provide the applied ozone dose (mol/mol) for 80% degradation of MTBE or ETBE, at several pH. Because toxicological studies have shown TBF and TBA to be more toxic than MTBE, stoichiometric investigations are necessary before implementing ozonation as a treatment technology that is effective. These intermediates may represent a significant fraction of the reaction products if insufficient time is allowed for complete oxidation.

The process is in principle simple. Hydrogen peroxide (H₂O₂) is added to the influent water, and then ozone (O₃) is mixed in. O₃ is generated from dehydrated air in commercially available ozone generators. O₃ must be bubbled into the solution. A limitation of this process is the solubility of O₃, which decreases with increasing water temperature. As O₃ and H₂O₂ react in the aqueous solution, they generate OH•. The mixture in the reactor is constantly stirred to promote contact between the organic pollutants (e.g. MTBE) and OH•.

Full oxidation of MTBE would require 5 moles of ozone, according to the reaction:



Ozone consumption can be reduced by addition of hydrogen peroxide (H₂O₂). Vel Leitner et al. (1994) studied the oxidation of MTBE and ETBE using ozone and ozone/hydrogen peroxide.

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

Their results indicate that MTBE requires the combination of O₃/H₂O₂ for faster degradation, while ETBE can be degraded at similar rates using either O₃ or O₃/H₂O₂. The second order kinetic constant for MTBE oxidation using O₃/H₂O₂ was determined by Buxton et al. (1988), with $k_{\text{MTBE/OH}} = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Vel Leitner et al. (1994) determined that $k_{\text{ETBE/OH}}/k_{\text{MTBE/OH}} = 1.7$.

4.2 Design considerations

A continuously-stirred flow reactor (CSFR) coupled to an ozone generator is the basis for the design. Based on Equation 7, the reaction is second-order. The kinetics data is used to determine the size of the reactor. The design also evaluates the use of CSFR in series to meet the treatment objectives. The design equation is:

$$\frac{C_{Ao}}{C_{Ai}} = \frac{1}{1 + \frac{Vk_2 C_B}{Q}}^{-1} \quad (8)$$

where C_{Ao} = outlet concentration of reactant A (MTBE), M,

C_{Ai} = inlet concentration of reactant A (MTBE), M,

V = reactor volume, L,

k_2 = second order kinetic rate constant, $\text{M}^{-1} \text{s}^{-1}$,

C_B = average concentration of reactant B (Ozone), M,

Q = water flow rate, L s^{-1} ,

N = number of reactors in series.

We assume that the ozone concentration is the same for all reactors, since ozone is sparged into each one. All reactor volumes are equal. The kinetic constant must be corrected to the influent water temperature. Ozone requirements are based on the stoichiometric ratio, with a safety factor to account for losses due to reaction with other organic compounds, yield factor, and ozone volatilization. For the design of a hydrogen peroxide/ozone system, H₂O₂ requirements are based on the molar ratio determine by Vel Leitner et al. (1994).

4.3 Experimental Studies

The objectives of our experimental studies were to (1) confirm the kinetic rate constants and determine the temperature dependency, (2) evaluate the combined effect of ozone and hydrogen peroxide reacting with MTBE, and (3) carry out a mass balance of the reactants and products of the species involved.

For the kinetic rate constants, we conducted steady state measurements of MTBE degradation under temperature controlled, complete mixing conditions, using ozone and ozone/hydrogen peroxide. Measurements of flow rates and reactant concentration in and out of the reactor were made under steady flow conditions in order to obtain mean residence times and molar fractional conversions, to calculate reaction rates. To determine the stoichiometry, we

measured initial and final concentrations of the reactants and products in a batch reactor as a function of time.

4.3.1 Methods

All aqueous solutions were prepared using milli-Q water. The solutions were buffered at a pH of 7.2 with a phosphate buffer (mono and di basic salts) at a 30mM concentration. The ozone solutions were obtained by sparging the oxygen/ozone gas mixture from a Welsbach Ozone Generator (Model T-408) into water. Ultra high purity oxygen, passed through a Drierite Gas Purifier, was used as the oxygen source for the ozone generator. Gas chromatography/mass spectrometry (GC/MS) was used to analyze for the organic compounds and the indigo dye method (Bader and Hoigne, 1982) was used to measure ozone concentration in aqueous solutions.

A 1000 mL continuous flow stirred tank reactor (CFSTR) system was used to study ozonation kinetics. Both inlet streams were pressure fed into the reactor; the ozone stream used the back pressure available from the ozone generator and the MTBE solution reservoir was pressurized with nitrogen. The flow rates of the inlet streams were controlled with calibrated rotameters. The reactor was placed in a bath for temperature control, with a temperature range of 20°C to 50°C. Inlet and outlet samples were withdrawn using syringes and the samples were analyzed for the organics and for ozone, following Rinker and Sandall's method (1992). Hydrogen peroxide was added to the MTBE reservoir when applicable. Previous studies, as well as work done in our lab, show no appreciable degradation of MTBE when combined with hydrogen peroxide alone (Yeh and Novak, 1995).

The stoichiometric batch reactions were carried out in 40-mL reaction vials, with a known volume and concentration of aqueous MTBE. A known volume and concentration of aqueous ozone was added to the flask and allowed to react within a specified time period. The ozone was then immediately quenched, with an analysis done for the concentration of ozone. The degradation of ozone on its own was also measured, to accurately calculate the moles of ozone that reacted with MTBE. The concentration of the unreacted aqueous MTBE was then measured using GC/MS, to calculate the moles of MTBE consumed by the known moles of ozone initially added.

For the analysis of VOCs, a Hewlett Packard 5890 Gas Chromatograph equipped with a Hewlett Packard 5970 Mass Selective Detector was used to qualitatively and quantitatively analyze the molar concentrations of the MTBE, TBF, and TBA. Solid phase microextraction (SPME) fiber was used to extract the organic components from the aqueous phase, and the fiber was then placed in the GC/MS injection port at 150 °C. A VOCOL (Supelco) capillary column (30m x 0.25mm) with a temperature program from 70 to 140 °C was used. All the analysis were made in duplicates with a reproducibility of $\pm 10\%$.

Hydrogen peroxide was quantitatively measured by adding the samples to potassium iodide in acidic solution to yield iodine. Colorimetric analysis was then carried out using a Hewlett Packard 8452A Diode Array Spectrophotometer. The absorbance at 350 nm was used as the wavelength of analysis.

4.3.2 Results and Discussion

The rate of reaction in $M s^{-1}$ as measured experimentally is:

$$Rate = \frac{(v_i C_i - v_o C_o)}{V_R} \quad (9)$$

where v_i = volumetric flow rate of inlet MTBE stream, $L s^{-1}$,
 v_o = volumetric flow rate of outlet stream, $L s^{-1}$,
 C_i = concentration of MTBE in inlet, M,
 C_o = concentration of MTBE in outlet, M,
 V_R = volume of reactor, L.

The kinetic rate expression is:

$$Rate = k_2 C_{O_3} C_o \quad (10)$$

where k_2 = second order kinetic rate constant, $M^{-1} s^{-1}$,

C_{O_3} = outlet concentration of ozone, M.

k_2 can then be determined from the experimental data from Equations (9) and (10):

$$k_2 = (v_i C_i - v_o C_o) / (V_R C_{O_3} C_o) \quad (11)$$

Table 8 presents the results for ozonation (without hydrogen peroxide). The Arrhenius plot is shown in Figure 7:

Table 8. Experimental values for MTBE ozonation

T (°C)	C_i (ug/L)	C_o (ug/L)	$v_i = v_o$ (mL/sec)	$C_{O_3, out}$ (ppm)	k_2 (L/mol sec)
22.35	1.703	0.4053	0.6	0.595	529.61
22.45	1.824	0.378	0.6	0.76	483.59
30.00	1.824	0.395	0.6	0.595	633.62
33.02	3.249	0.835	0.6	0.349	891.4
41.25	1.824	0.411	0.6	0.238	1502.43

The activation energy (E_a) for the ozonation of MTBE is $10.4 \text{ kcal mol}^{-1} \text{ K}^{-1}$. The temperature dependence of k_2 is:

$$k_2 = 10^{4.333} \exp(-10.4 / RT) \quad (12)$$

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

TBF was produced both during ozonation and ozone/hydrogen peroxide treatment. The yield of TBF ranged from 25 to 63% of the initial MTBE, for the residence time in our experimental flow reactor. Longer residence times will result in higher conversion of TBF to CO₂. TBA was detected in residual amounts only for the ozone/hydrogen peroxide combination. The concentration for TBA was below the detection limit. Depending on operating conditions and residence time, a significant amount of TBF may be produced in the effluent. Adequate design and pilot testing is required for each influent water.

4.3 Cost estimates

The temperature influent water is considered to be 15 °C. The mean ozone concentration in the reactor is estimated to be 5 mg/L. The ozone generator is sized based on Equations 8 and 12, with a safety factor of 100% for ozone requirements (i.e. the ozone demand is doubled). Table 9 presents the design parameters considered for each case.

Table 9. Ozone only Reactor Design

<i>Case</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>	<i>8</i>	<i>9</i>	<i>10</i>
Concentration (ug/L)	100	100	100	500	1000	5000	100	500	1000	5000
Flow rate (gpm)	1000	500	100	100	100	100	10	10	10	10
Reactor Volume (gal)	1000	500	200	500	500	1000	100	100	100	200
Number of Reactors	3	3	2	2	2	3	1	2	2	2
Ozone Production (kg/hr)	0.25	0.12	0.025	0.12	0.25	1.24	0.003	0.012	0.025	0.12

Quotes for commercial ozone generators were obtained. For comparison, we also designed an ozonation system where the reaction of ozone would reduce MTBE concentrations to 35 ug/L, and a subsequent GAC filtering setup would remove all the residual MTBE and by-products. A cost estimate for a comparable UV/H₂O₂ system was prepared using cost estimates from the MTBE Research Partnership (1998) report. Cost estimates are presented in Table 10.

Table 10. Amortized Cost, dollars per 1000 gallons treated using O₃

<i>Case</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>	<i>8</i>	<i>9</i>	<i>10</i>
Concentration (ug/L)	100	100	100	500	1000	5000	100	500	1000	5000
Flow rate (gpm)	1000	500	100	100	100	100	10	10	10	10
Only Ozone	0.29	0.41	1.17	1.52	1.68	3.48	3.55	4.19	4.19	5.78
Ozone + GAC	0.67	0.75	1.44	1.95	2.14	3.45	5.99	6.02	6.05	7.25
UV/Hydrogen Peroxide	0.62	0.65	1.30	1.35	1.40	1.83	3.15	3.20	4.01	4.06

4.4 Advantages and Disadvantages

Advantages: MTBE is destroyed, eliminating the need for air treatment or disposal of hazardous wastes (e.g. spent GAC). Economies of scale can make this a competitive process at higher flow rates. AOPs have been used in Europe for decades for water treatment. Use of AOPs may reduce the cost of chlorination of drinking water treated to remove MTBE.

Disadvantages: The formation of oxidation intermediates as well as other oxidized compounds such as bromate (which has an Maximum Contaminant Level of 10 ug/L) is a significant health concern. There is limited experience with MTBE oxidation in pilot studies, and results have not been favorable. It is important to control ozone and hydrogen peroxide doses, as well as pH and temperature. High organic loading as well as high levels of dissolved minerals in water will reduce MTBE removal efficiency. AOPs can handle small variations in flow rate and concentration, but typically a surge tank is used if large fluctuations are expected. At low flow rates, high capital costs typically limit the applicability of this technology. Few vendors have sufficient technical expertise to implement the technology. More research is needed to determine optimal operating conditions and the limitations of this technology.

5. HOLLOW FIBER MEMBRANES

5.1 Description of the process

A membrane is a semi-permeable thin layer of material separating two fluids, as a function of physical and chemical properties. There are many types of membranes, such as microfiltration (MF), reverse osmosis (RO) and hollow fiber membranes (HFM). MF membranes can remove particulates, RO membranes retain solutes as water permeates the membrane and HFM can be used to degas liquids, taking advantage of the membrane's hydrophobic nature (Mallevalle et al., 1996).

Interest in membrane technology has driven research in various fields, such as environmental engineering, water and wastewater treatment including desalination, biomedical applications and the food industry (Aptel and Buckley, 1996). Membranes have many applications. For example, RO membranes are used in: (1) electronics industry to produce ultrapure water, (2) pharmaceutical industry for dialysis bath makeup, (3) food industry for the preparation of carbonated beverages, and (4) power stations for boiler feed water. There are also various levels of filtration membranes (from nanofiltration to microfiltration) that range from removing calcium and magnesium ions in water softeners to particulates. Membranes can also be used for gas filtration (gas/gas separation, e.g. enriching air with nitrogen or oxygen) and gas diffusion, which uses a porous membrane (Aptel and Buckley, 1996).

Membranes also have different characteristics that enable various separation techniques, such as being porous, nonporous or an ion exchange membrane. They can also be made of either one material (asymmetric) or two different layers (composite) and come in different shapes, such as

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

flat or cylindrical. Cylindrical membranes are divided into two classes: (1) tubular (>3 mm inner diameter) and (2) hollow fiber (<3 mm inner diameter). Membrane materials vary as well. Many types of polymers can be used, with some popular choices being polyacrylonitrile, polysulphone, and polyethersulphone. Common polymers for hydrophobic membranes include polytetrafluoroethylene (PTFE), polyvinylidene fluoride, polyethylene, polycarbonate or isotactic polypropylene (Aptel and Buckley, 1996).

Microporous HFM have been successfully used to strip various compounds from water such as volatile organic compounds (VOC), hydrogen sulfide, sulfur dioxide, oxygen, carbon dioxide, bromine, and ammonia using a sweep gas to remove the gases and vapors from the membrane surface (e.g., Semmens et al., 1989, 1990; Zhang and Cussler 1985a,b; Yang and Cussler, 1986; Sarti et al., 1993).

Pervaporation uses a vacuum sweep to remove gases and vapors from the membrane surface. The activity difference driving this process is maintained with a partial vacuum on the permeate side (Aptel and Buckley, 1996). A large concentration gradient is established between the aqueous phase concentration and the concentration in the gas phase. Uses of pervaporation include the dehydration of alcoholic azeotropes and removal of volatile organic compounds (VOC) from water (Sarti et al., 1993).

HFM is considered in this study to improve the mass transfer rate of MTBE from water to air. Contaminated water is pumped through the lumen side of bundled microporous polypropylene hollow fibers while a vacuum is drawn counter-currently on the outside of the fibers. The hydrophobic membrane allows for efficient transfer of volatile compounds from aqueous to gas phase. While the water is pumped through the hollow fibers, volatile components volatilize and diffuse through the gas-filled pores of the hollow fiber, due to the large concentration gradient. Volatile compounds can then be pulled through by a vacuum, swept away by a sweep gas or reacted with a second solution. Pollutants can be effectively transferred through the gas-filled pores to the gas phase while water does not permeate due to the polymer's hydrophobic nature. Compounds transfer from water to air in response to a concentration gradient maintained by the constant flow of contaminant-free air across the exterior of the fibers. Hollow fibers have a large surface area per unit volume, allowing greater contact between the phases. This provides relatively fast removal of the contaminant. Studies by Semmens et al. (1989) and Zander et al. (1989) showed that mass transfer of volatile organic compounds (VOCs) could be an order of magnitude greater than achievable by packed tower aeration when using HFM with a sweep gas.

There are several advantages of hollow fiber membranes over air-stripping: (1) lower air flow rates can be used, requiring small vapor-phase treatment units, (2) water and air flow rates can be controlled independently to maximize mass transfer because they are separated by the membrane, (3) there is no aqueous flow channeling due to the hollow fiber configuration, and (4) the air stream will contain little water due to the hydrophobic nature of the membrane. This allows more efficient treatment of the contaminant in the gas phase (Zander et al., 1989).

5.2 Design considerations

Gas transfer from the lumen of the hollow fiber membrane through the micropores is driven by a concentration gradient. At equilibrium, the concentration in the water (C_w) is related to the concentration in the air (C_g) by the dimensionless Henry's law constant ($H = C_g/C_w$). Henry's law constant increases with temperature, making diffusion into the gas phase more favorable at higher temperatures.

The constant air flow past the membrane pores effectively keeps the air phase concentration of the contaminant near zero, allowing constant diffusion from the water to the membrane surface and into the air-filled pores. The contaminant's rate of diffusion is limited by three resistances: (1) diffusion through the water to the membrane surface ($1/k_w$), (2) diffusion through the air-filled pores ($1/k_m$), and (3) diffusion from the exterior membrane surface into the bulk air ($1/k_g$) (Castro and Zander, 1995; Costello et al., 1993). The transfer coefficients through the air-filled pores and the bulk air are expressed in terms of water-phase transport by multiplying by H . The overall mass transfer coefficient (K_{oL}) for the contaminant is the reciprocal sum of the individual resistances:

$$\frac{1}{K_{oL}} = \frac{1}{k_L} + \frac{1}{Hk_M} + \frac{1}{Hk_G} \quad (13)$$

The aqueous and gas phase mass transfer coefficients depend on operating conditions, especially water (u_L) and gas (u_G) flow rates, the characteristic length (d_e , inner diameter of the fiber), the kinematic viscosity of the fluid, ν , and the diffusivity of the pollutant in either phase, D . The diffusivity of most volatile and semivolatile compounds is approximately four orders of magnitude smaller in water than air (Cussler, 1997). Therefore, the resistance due to diffusion through the water phase generally controls the overall mass transfer rate, while the membrane has negligible resistance, especially for the thin hollow fibers used in this module (around 10-50 μm in thickness).

Aptel and Semmens (1996) modeled the removal of VOCs from water assuming a plug flow reactor with a constant mass transfer coefficient along the length of the fiber:

$$-u_L \frac{dC_w}{dx} = K_{oL} a (C_w - C^*) \quad (14)$$

where x = linear dimension along the length of HFM unit,

a = interfacial area of membrane per unit volume in module,

C^* = equilibrium concentration of VOC in gas phase.

If the vacuum pressure is sufficiently large, it can be assumed that C^* is negligible. Equation 14 can be solved to find the concentration at the outlet:

$$C = C_o \exp[-K_{oL} a (x/u)] \quad (15)$$

The relationship between the mass transfer coefficients and the operating parameters can be determined from dimensional analysis. A dimensionless correlation between the Sherwood (Sh), Reynolds (Re) and Schmidt (Sc) numbers has been proposed by Yang and Cussler (1986):

$$Sh = q Re^r Sc^t \quad (16)$$

Where $Sh_p = \frac{k_p d_e}{D_p}$, $Re = \frac{u_p d_e}{\nu_p}$, $Sc = \frac{\nu_p}{D_p}$ and q , r , and t are empirical coefficients obtained experimentally for the hollow fibers. The subscript p refers to either the gas or aqueous phase. In these studies the focus was on MTBE removal with existing commercial HFM units, so d_e , D and ν were not varied. One can thus simplify the relationship to:

$$k_w = k_1 u_w^m \quad (17)$$

and

$$k_g = k_2 u_g^n \quad (18)$$

where k_1 , k_2 , m and n are empirical coefficients. Pilot scale studies at various water flow rates, air flow rates and temperatures were used to determine the empirical coefficients. Equations 13, 14, 17 and 18 can then be used as a mathematical model to scale up the experimental results to the field scale.

5.3 Experimental Studies

5.3.1 Method

A hydrophobic hollow fiber membrane module (Liqui-Cel, with Celgard fibers, Hoechst Celanese) was used. The hollow fiber construction is indicated in Figure 8. The membrane module has inlet and outlet ports for the aqueous and gaseous phases. The module has an overall mass transfer area of 1.4 m², and an effective fiber length of 0.203 m. The fibers are made of polypropylene, specially extruded to provide a well-characterized porosity to the fiber, which allows the transport of hydrophobic VOC molecules from the inside of the fiber (aqueous phase) to the outside of the fiber (gas phase), as shown in Figure 9, through pervaporation. Due to the hydrophobic nature of the fiber, only trace amounts of water pass through the membrane to the gas phase. A simplified process sheet is shown in Figure 10. Vacuum is applied to the shell-side of the module, and air is allowed to bleed in to the module at a controlled rate. Water is pumped into the lumen-side of the fibers.

MTBE was added to approximately 200 L of tap water and recirculated for 2 hours to achieve complete mixing. Contaminated water was then pumped through the membrane at various flow rates and sampled directly before and after the hollow fiber unit. The waste stream was collected into a waste tank, not recirculated.

Experiments were performed at two air flow rates, 11.3 L/min (0.4 SCFM) and 39.7 L/min (1.4 SCFM). Water flow rates ranged from 0.2 to 1.8 L/min (0.05 to 0.5 gpm). The experiments

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

were run at 23°C, 30°C, and 40°C (73.4°F, 86°F, and 104°F). The water was heated by passing it through copper tubing in a Fisher Scientific Isotemp 220 water bath.

Water samples were collected before and after the HFM unit using 40 ml vials, sealed with a septum lined cap. Samples were extracted using a 100 µm polydimethyl siloxane (PDMS) solid phase microextraction (SPME) fiber and analyzed in an HP 5890 gas chromatograph with a Supelco VOCOL capillary column coupled to an HP 5970 Mass Spectrometer. Removal was calculated as a percent difference.

5.3.2 Results and Discussion

The results of many combinations of operating parameters were analyzed using Equations 13, 14, 17 and 18. Figure 11 presents a comparison between experimental and theoretical removal efficiency using the following empirical correlations for the mass transfer coefficients:

$$k_w = 3.05u_w^{0.74} \quad (19)$$

and

$$k_g = 0.69u_g^{0.05} \quad (20)$$

Henry's constant is estimated using the results of Robbins et al. (1993).

At low water flow rates (<0.3 L/min), temperature and air flow effects on removal efficiency are not very significant. At these flow rates removal was between 80 and 99%. At higher flow rates, temperature had a significant effect on MTBE removal. The increase in water temperature increased MTBE's Henry's constant, driving the equilibrium partitioning towards the gas phase.

Increase in air flow rate did not significantly affect removal efficiency at any of the three temperatures investigated, and this is reflected in the low value of n . Relatively low air to water volumetric ratio were used, in the range from 6 to 56, with high removal efficiencies even at air to water ratios as low as 22.

5.4 Cost estimates

These results have been used to design a hollow fiber membrane module that can be used in commercial applications. Predicted MTBE removal efficiency is shown in Figure 12. The commercial membrane module (Separel, Pall Corporation) has an interfacial area of 40 m² and an effective length of 0.5 m. The module is designed to handle water flow rates up to 1.3 L/s (21 gpm). Multiple modules can be used in parallel to treat higher flow rates. The air to water volumetric ratio considered for the design is only 30, compared to an air to water ratio of 150 for the air stripping unit. This results in a much smaller off-gas treatment stream, with corresponding capital and O&M cost savings.

For the design, the HFM unit is operated at 0.63 L/s (10 gpm). Costs considered include the membrane module, influent water pump, vacuum pump and instrumentation to monitor pressure and flow rate. Capital costs for a single unit, without vapor treatment, are on the order of \$10,000. Several gas-phase treatment systems were evaluated, following the same considerations

as for the air stripping unit. The most cost-effective combination, if air treatment is required, is HFM followed by gas-phase GAC. A very compact unit can be designed, both in terms of footprint and overall height, compared to an air stripping unit.

As indicated in Table 11, the amortized treatment costs do not scale well, since to treat higher flow rates or concentrations, multiple HFM units are placed in series or parallel. This arrangement is common for water degassing operations. In addition, the cost of removing other VOCs is essentially the same as for MTBE, since the module size cannot be easily modified.

Table 11. Amortized Cost, dollars per 1000 gallons treated using HFM

<i>Case</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>	<i>8</i>	<i>9</i>	<i>10</i>
Concentration (ug/L)	100	100	100	500	1000	5000	100	500	1000	5000
Flow rate (gpm)	1000	500	100	100	100	100	10	10	10	10
MTBE (no air treatment)	0.69	0.72	0.78	0.78	1.16	1.16	1.05	1.05	1.46	1.46
MTBE (with air treatment)	1.05	1.12	1.35	1.66	2.25	3.05	1.91	2.29	2.96	3.96
Benzene (no air treatment)	0.69	0.72	0.78	0.78	1.16	N.A.	1.05	1.05	1.46	N.A.

5.5 Advantages and Disadvantages

Advantages: The membrane module has a very small footprint compared to all the other technologies. High removal efficiencies can be obtained in modular steps. The technology is mechanically reliable, with few moving parts. All the components are off-the-shelf items that can be readily assembled.

Disadvantages: Limited field tests have been performed. Iron, calcium and manganese will precipitate on the fiber surface, plugging the fiber's pores. Acid backwash is effective for cleaning the fibers. The useful life of a unit has not been determined. There are limited economies of scale since multiple membrane modules must be used to treat higher flow rates. A surge tank is required if significant fluctuations in flow rate or MTBE concentration are expected, to achieve the desired removal efficiency.

6. FINAL RECOMMENDATIONS

Table 12. Amortized Cost, Dollars per 1000 gallons treated

	1	2*	3*	4*	5	6	7*	8*	9*	10*
Concentration (ug/L)	100	100	100	500	1000	5000	100	500	1000	5000
Flow rate (gpm)	1000	500	100	100	100	100	10	10	10	10
Air Stripping										
MTBE (no air treatment)	0.23	0.25	0.40	0.59	0.68	0.88	1.54	2.30	2.65	3.55
MTBE (with air treatment)	0.33	0.41	0.76	0.84	0.88	0.97	2.35	2.68	2.84	3.22
GAC										
MTBE w/low organics	0.34	0.38	0.55	0.81	0.98	1.67	1.20	1.81	2.24	3.85
MTBE w/high organics	0.39	0.44	0.61	0.93	1.15	2.05	1.32	2.09	2.62	4.71
AOP										
Ozone only	0.29	0.41	1.17	1.52	1.68	3.48	3.55	4.19	4.19	5.78
Ozone + GAC	0.67	0.75	1.44	1.95	2.14	3.45	5.99	6.02	6.05	7.25
UV/Hydrogen Peroxide	0.62	0.65	1.30	1.35	1.40	1.83	3.15	3.20	4.01	4.06
Hollow Fiber Membrane										
MTBE (no air treatment)	0.69	0.72	0.78	0.78	1.16	1.16	1.05	1.05	1.46	1.46
MTBE (with air treatment)	1.05	1.12	1.35	1.66	2.25	3.05	1.91	2.29	2.96	3.96

*air treatment may not be required for this system.

A cost comparison of the four technologies evaluated is presented in Table 12. Air stripping is the lowest cost technology for high flow rates (100 to 1000 gpm), if no air treatment is required. Air treatment can be required depending on the local or Regional Air Quality Board stipulations. Hollow fiber membranes are the lowest cost technology for flow rates of 10 to 100 gpm if no air treatment is required, which is typical at these low flow rates. GAC will be most cost-effective at all flow rates if air treatment is required and the influent water has low levels of other organic compounds. If air treatment is required and the influent has high levels of organics, air stripping is more cost effective than GAC at flow rates of 100 gpm and greater. AOP is in all cases more expensive than the alternative technologies, and there are sufficient uncertainties at this point with respect to by-products of AOP to warrant further study of this technology. It has the potential of being cost-competitive at high flow rates, provided it is fully tested at the field scale. Given that air stripping and GAC are proven technologies in the field, innovative technologies such as hollow fiber membranes and AOP should be compared on a case-by-case basis against these treatment options.

The cost of treating MTBE-contaminated water is 40 to 80% higher than treating water contaminated only with other hydrocarbons such as benzene, for conventional technologies such as air stripping and GAC.

7. REFERENCES

- Aptel, P., Buckley, C.A., 1996. Categories of membrane operations, in *Water Treatment: Membrane Processes* (eds. Mallavialle, J., Odendaal, P.E., Wiesner, M.R.). McGraw-Hill, New York.
- Aptel, P., Semmens, M.J., 1996. Multiphase membrane processes, in *Water Treatment: Membrane Processes* (eds. Mallavialle, J., Odendaal, P.E., Wiesner, M.R.). McGraw-Hill, New York.
- Ahmed, T., Semmens, M.J., 1996. Use of transverse flow hollow fibers for bubbleless membrane aeration, *Water Res.* 30(2):440-446
- Antoine, C., 1888. *C. R. Acad. Sci.* 107:681-684
- Archabal, S.R., Downey, D. C., Guest, P.R., Plaehn, W.A., Vessely, M.J., Marchand, E.G., 1997a. The Internal Combustion Engine as a low-cost soil vapor treatment technology. Paper presented at the *2nd Tri-Service Environmental Technology Workshop*, St. Louis Missouri, June 10-12.
- Archabal, S.R., Guest, P.R., Cyr, G., Downey, D. C., Vessely, M.J., Brown, D., Gonzales, J., Kraft, D., 1997b. Performance and cost evaluation of flameless thermal oxidation for vapor-phase VOC treatment. Paper presented at the *2nd Tri-Service Environmental Technology Workshop*, St. Louis Missouri, June 10-12.
- Arthur, C.L., Killam, L.M., Motlagh, S., Lim, M. Potter, D.W., Pawliszyn, J., 1992. Analysis of substituted benzene compounds in groundwater using solid-phase microextraction. *Enviro. Sci. Technol.*, 26, 979-983.
- Ashworth, R. A., Howe, G. B., Mullins, M. E., Rogers, T. N., 1988. Air-water partitioning coefficients of organics in dilute aqueous solutions, *J. Hazardous Materials* 18:25-36
- Bader, H., Hoigne, J., 1982. *Ozone: Science and Engineering*, vol 4:4, pp 169-176.
- Ball, W., Jones, Kavanaugh, M., 1984. Mass transfer of volatile organic compounds in packed tower aeration, *JWPCF* 56:126-136
- Barreto, R. D., Gray, K. A., Anders, K., 1995. Photocatalytic degradation of Methyl tert-Butyl Ether in TiO₂ slurries, a proposed reaction scheme, *Water Res.* 29(5):1243-1248
- Bohart, G.S., Adams, E.Q., 1920. Some aspects of the behavior of charcoal with respect to chlorine. *J. Am. Chem. Soc.*, 42:523-544.
- Borden, R.C., Daniel, R. A., LeBrun, L. E. IV, Davis, C. W., 1997. Intrinsic biodegradation of MTBE and BTEX in a gasoline-contaminated aquifer. *Water Resources Res.* 33:1105-1115
- Buscheck, T.E., Gallagher, D. J., Kuehne, D. L., Zuspan, C.R., 1998. *Southwest Focused Conference, National Groundwater Association*, June 3-4.
- Buttillo, J.V., Pulido, A. D., Reese, N.M., Lowe, M. A., 1994. Removal efficiency of MTBE in water: Confirmation of a predictive model through applied technology, in *Proceedings of the API/NGWA Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection and Remediation*, Nov 2-4, Houston, Texas, 91-105
- Buxton, G.V., Greenstock, C. L., Helman, W. P., Ross, A. B., 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radical in aqueous solutions, *J. Phys. Chem. Ref. Data* 17:513-886

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

- CAL-DHS, 1998. Summary of sampling of public drinking water systems for methyl tertiary butyl ether (MTBE): covers data through July 16, 1998. *California Department of Health Services, Prevention Services, Division of Drinking Water and Environmental Management*. (<http://www.dhs.cahwnet.gov/ps/ddwem/chemicals/MTBE/mtbesummary.htm>).
- CAL-EPA, 1998. *Draft Public Health Goal for Methyl Tertiary Butyl Ether (MTBE) in Drinking Water*. Pesticide and Environmental Toxicology Section, Office of Environmental Health Hazard Assessment, California Environmental Protection Agency, Sacramento, CA.
- CARB, 1991. *Proposed Regulations for California Phase 2 Reformulated Gasoline*, California Air Resources Board, Staff Report, Stationary Source Division.
- Castro, K., Zander, A.K., 1995. Membrane air-stripping: effects of pretreatment. *Jour. AWWA*, 87:3:50.
- Cobes, E.R., 1998. MTBE Isotherm Results – TSR No. 19971149. Communication from *Calgon Carbon Corporation*, Pittsburgh, PA
- Converse, B., Schroeder, E.D., 1998. Estimated costs associated with biodegradation of MTBE, in *Health and environmental assessment of MTBE, vol. 3*. UC Toxics Research and Teaching Program, UC Davis.
- Costello, M. J., Fane, A. G., Hogan, P. A., Schofield, R. W., 1993. The effect of shell-side hydrodynamics on the performance of hollow fiber modules, *J. Membrane Sci.* 80:1-11
- Chang, P., Young, T., 1998. Reactivity and by-products of Methyl Tertiary Butyl Ether resulting from water treatment processes, in *Health and environmental assessment of MTBE, vol. 3*. UC Toxics Research and Teaching Program, UC Davis, CA.
- Crittenden, J.C., Luft, P., Hand, D.W., Oravitz, J.L., Loper, S.W., Arl, M., 1985. Prediction of multicomponent adsorption equilibrium using ideal adsorbed solution theory. *Environ. Sci. Technol.*, 19, 1037-1043.
- Cussler, E.L., 1997. *Diffusion, mass transfer in fluid systems*. Cambridge University Press, Cambridge, 1997.
- Delzer, G. C., Zogorski, J. S., Lopez, T. J., Bosshart, R. L., 1996. Occurrence of the gasoline oxygenate MTBE and BTEX compounds in urban stormwater in the United States, 1991-95. Water Resources Investigations Report 96-4145, *United States Geological Survey*.
- Doohar, B.P., 1998. Making risk-based management decisions at fuel hydrocarbon impacted sites under sparse data conditions. Ph.D. dissertation, *Univ. of California, Los Angeles*.
- Eweis, J.B., N. Watanabe, E. D. Schroeder, D. P.Y. Chang, K. M. Scow., 1998. MTBE biodegradation in the presence of other gasoline compounds. *National Ground Water Association Conference on MTBE and Perchlorate*, Anaheim, CA, June 3-4.
- Eweis, J., Schroeder, E., Chang, D., Scow, K., Morton, R., and Caballero, R., 1997. Meeting the Challenge of MTBE Biodegradation. *Proceedings of the 90th Annual Meeting & Exhibition, Air & Waste Management Association*, Toronto, Canada, June 8-13.
- Fujiwara, Y., Kinoshita, T., Sato, H., Kojima, I., 1984. Biodegradation and bioconcentration of alkylethers. *Yukagaku* 33:111-114.
- Happel, A.M., Beckenbach, E.H., and Halden, R.U., 1998. *An evaluation of MTBE impacts on California groundwater resources*. LLNL Report UCRL-AR-130897, Lawrence Livermore National Laboratory, Livermore, CA

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

- Hutchins, R.A., 1993. New method simplifies design of activated carbon systems. *Chem. Eng.* 80, 133-138.
- Gossett, J. M., 1987. Measurement of Henry's law constants for C₁ and C₂ chlorinated hydrocarbons, *Environ. Sci. Technol.* 21:202-208
- Jensen, M.H., Arvin, E., 1990. Solubility and degradability of the gasoline additive MTBE and gasoline compounds in water. In *Contaminated soil* (eds. Arendt, F., Hinsenveld, M., Van den Brink, W.J.), Kluwer, Dordrecht, pp 445-448.
- Kalman, O., Lund J., 1998. MTBE: Evaluation of management options for water supply and ecosystem impacts, in *Health and environmental assessment of MTBE, vol. 3*. UC Toxics Research and Teaching Program, UC Davis.
- Keller, A.A., Froines, J., Koshland, C., Reuter, J., Suffet, I.H., Last, J., 1998. *Health and environmental assessment of MTBE, vol. 1*. UC Toxics Research and Teaching Program, UC Davis.
- Kavanaugh, M., 1997. *Estimates of annual costs to remove MTBE from water for potable uses*. Malcolm Pirnie Report 3195-001. Malcolm Pirnie, Oakland, CA.
- Krähenbül, M. A., Gmehling, J., 1994. Vapor pressures of Methyl *tert*-Butyl Ether, Ethyl *tert*-Butyl Ether, Isopropyl *tert*-Butyl Ether, *tert*-Amyl Methyl Ether and *tert*-Amyl Ethyl Ether. *J. Chem Eng. Data* 39:759-762
- Lincoff, A. H., Gossett, J. M., 1984. In *Gas Transfer at Water Surfaces*, (eds. Brutsaert, W. Jirka, G. H.) Reidel, Dordrecht, The Netherlands.
- Liu and Liptak, 1987. *Environmental Engineer's Handbook, 2nd Edition*. Lewis Publishers, Boca Raton, Florida.
- Mallevalle, J., Odendaal, P.E., Wiesner, M.R. The emergence of membranes in water and wastewater treatment, in *Water Treatment: Membrane Processes* (eds. Mallavialle, J., Odendaal, P.E., Wiesner, M.R.). McGraw-Hill, New York, 1996.
- Mo, K., Lora, C.O., Wanken, A.E., Javanmardian, M., Yang, N., Kulpa, C.F., 1997. Biodegradation of ethyl *tert*-Butyl Ether by pure bacterial cultures. *Appl. Microbiol. Biotechnol.*, 47:69-72.
- Mormile, M. R., Liu, S., Sufflita, J. M., 1994. Anaerobic biodegradation of gasoline oxygenates: extrapolation of information to multiple sites and redox conditions. *Environ. Sci. Technol.* 28:1727-1732
- McKinnon, R. J. and Dyksen, J. E., 1984. Removing organics from groundwater through aeration plus GAC. *J. Am. Water Works Assoc.* 76:42-47
- MTBE Research Partnership, 1998. *Evaluation of Treatment Technologies for Removal of Methyl tertiary-Butyl Ether (MTBE) from Drinking Water: Air stripping, Advanced Oxidation Processes (AOP), Granular Activated Carbon (GAC)*. Association of California Water Agencies, 910 K Street, Suite 100, Sacramento, CA 95814-3577.
- Nattkemper, R.C., 1997. Cost and performance differences between steam and nitrogen desorption of activated carbon. *23rd Biennial Conference on Carbon*, Pennsylvania State University, July 13-18.
- NTSC, 1997. *Interagency assessment of oxygenated fuels*. Executive Office of the President of the United States, National Science and Technology Council, Committee on Environment and Natural Resources.

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

- Pankhania, M., Stephenson, T., Semmens, M. J., 1994. Hollow fiber bioreactor for wastewater treatment using bubbleless membrane aeration, *Water Res.*, 28(10):2233-2236
- Peleg, M., 1976. *Water Research*, vol 10, pp361-365.
- Ramachandran, B.R., Allen, J. M., Halpern A. M., 1996. Air-water partitioning of environmentally important organic compounds. *J. Chem. Educ.*, 73, 1058-1061.
- Raup, G. B. and Junio, C. T., 1993. Photocatalytic oxidation of oxygenated air toxics. *Applied Surface Science*, 72:321-327
- Reko, P., 1996. Personal communication, Applications Engineer for *Calgon Carbon Oxidation Technologies*, Tucson, AZ.
- Rinker, R. G., Sandall, O. C., 1992. *Kinetics of the Reaction of Ozone with Several Toxic Organic Compounds*. Final Report on Research Sponsored by East Bay Municipal Utilities District.
- Rinker, E.B., Ashour, S.S., Johnson, M. C., Kott, G.J., Rinker, R.G., Sandall, O.C., 1995. Effect of temperature and pH on the kinetics of the aqueous phase reaction between ozone and 2,4,6-Trichlorophenol. Presented at the *1995 AIChE Meeting*, November 12-17, Miami Beach, FL.
- Robbins, G. A., Wang, S., Stuart, J. D., 1993. Using the static headspace method to determine Henry's law constants, *Anal. Chem.* 65:3113-3118
- Roberts, P. V., Hopkins, G.D., Munz, C., Riojas, A.H., 1985. Evaluating two-resistance models for air stripping of volatile organic contaminants in a countercurrent packed column, *Environ. Sci. Technol.* 19:164-173
- SAE, 1992. *Auto/Oil Air Quality Improvement Research Program, SAE report SP-920*. Society of Automotive Engineers, Dearborn, MI.
- Salanitro, J.P., Diaz, L.A., Williams, M.P., Wisniewski, H.L., 1994. Isolation of a bacterial culture that degrades MTBE. *Applied Environ. Microbiology*, 60:2593-2596.
- Sarti, G.C., Gostoli, C., Bandini, S., 1993. Extraction of organic components from aqueous streams by vacuum membrane distillation. *J. Membr. Sci.*, 80:21.
- Semmens, MJ, Foster, DM, Cussler, EL., 1990. Ammonia removal from water using microporous hollow fibers. *J. Membr. Sci.* 51:127-140
- Semmens, M.J., Qin, R., Zander, A., 1989. Using a microporous Hollow-Fiber Membrane to separate VOCs from water. *J. AWWA*, 81:4:162.
- Squillace, P. J., Zogorski, J. S., Wilber, W. G., Price, C. V., 1996. Preliminary assessment of the occurrence and possible sources of MTBE in groundwater in the United States, 1993-1995. *Environ. Sci. Technol.* 30:1721-1730.
- Staudinger, J., Knocke, W.R., Randall, C.W., 1990. Evaluating the Onda mass transfer correlation for the design of packed-column air stripping. *J. AWWA* 72-79.
- Steffan, R.J., McClay, K., Vaiberg, S., Condee, C.W., Zhang, D., 1997. Biodegradation of the gasoline oxygenates Methyl tert-Butyl Ether, Ethyl tert-Butyl Ether, tert-Amyl Ethyl Ether by propane-oxidizing bacteria. *Applied Environ. Microbiology*, 63(11):4216-4222.
- Suflita, J. M. and Mormille, M. R., 1993. Anaerobic biodegradation of known and potential gasoline oxygenates in the terrestrial subsurface. *Environ. Sci. Technol.* 27: 967-978
- Treybal, 1980. *Mass Transfer Operations*, McGraw-Hill, New York.
- Truong, K., Parmele, C. S., 1992. Cost effective alternative treatment technologies for reducing concentrations of Methyl tertiary -Butyl Ether and Methanol in groundwater, in *Hydrocarbon*

Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water

Contaminated Soils and Groundwater, vol.2, (eds. E. J. Calabrese and P. T. Kostecki), Lewis Publishers, Inc., Chelsea, MI

- Turton, R., Bailie, R., Whiting, W.B., Shaeiwitz, J.A., 1998. *Analysis, synthesis and design of chemical processes*. Prentice Hall, New York, NY.
- Vel Leitner, N. K., Papailhou, A. L., Croue, J. P., Peyrot, J., Dore, M., 1994. Oxidation of Methyl tert-Butyl Ether (MTBE) and Ethyl tert-Butyl Ether (ETBE) by ozone and combined ozone/hydrogen peroxide. *Ozone Science and Eng.*, 16:41-54
- Venkatadri, R. and Peters, R. W., 1993. Chemical oxidation technologies: Ultraviolet light/hydrogen peroxide, Fenton's reagent and titanium dioxide assisted photocatalysis. *Hazardous Waste and Hazardous Materials*, 10(2):107-149.
- Watts, R., 1998. *Hazardous Wastes: Sources, Pathways, Receptors*. John Wiley and Sons, Inc., New York, NY.
- Yang, M-C., Cussler, E. L., 1986. Designing hollow fiber membrane contactors. *J AIChE* 32(11):1910-1916.
- Yeh, C.K., Novak, J.T., 1994. Anaerobic biodegradation of gasoline oxygenates in soils. *Water Environment Research*, 66(5):744-752.
- Yeh, C. K., Novak, J. T., 1995. *Water Environmental Research*, vol 67, no.5, pp 828-834.
- Zander, AK, Semmens, MJ, Narbaitz, RM., 1989. Removing VOC's by membrane stripping. *J. Am. Water Works Assoc.* 81(11):76-81.
- Zhang, Q., Cussler, E.L., 1985a. Microporous hollow fibers for gas adsorption. *Jour. Membrane Sci.*, 23:321.
- Zhang, Q., Cussler, E.L., 1985b. Bromine recovery with hollow fiber gas membranes. *Jour. Membrane Sci.*, 24:43.

Figure 1. Graphical Determination of Off-gas Treatment

assuming a 1 lb/day (0.45 kg/day) cap on VOC emissions

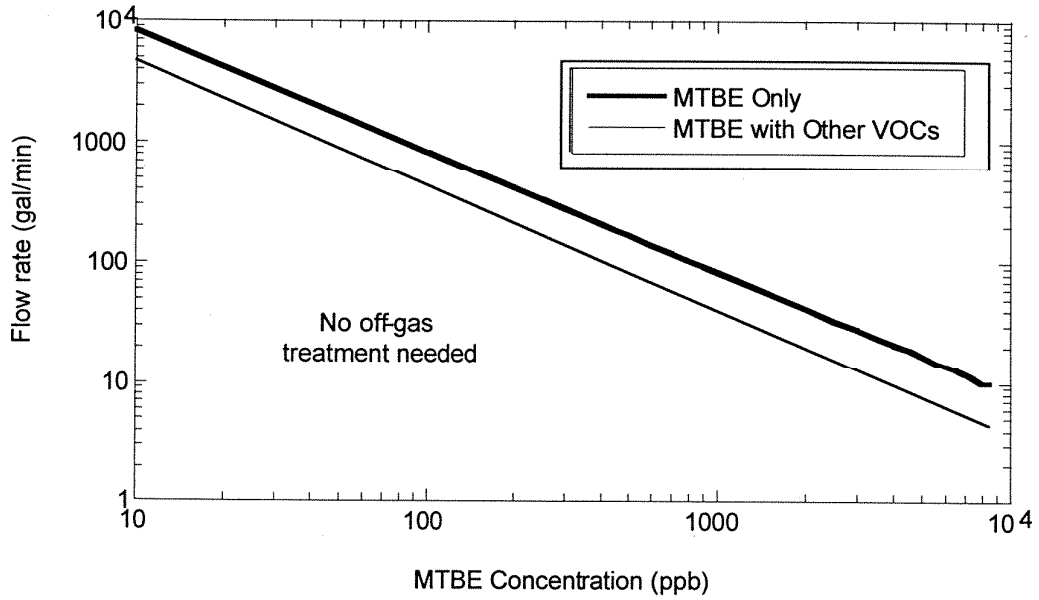


Figure 2. Temperature Dependence of MTBE's Henry's Constant

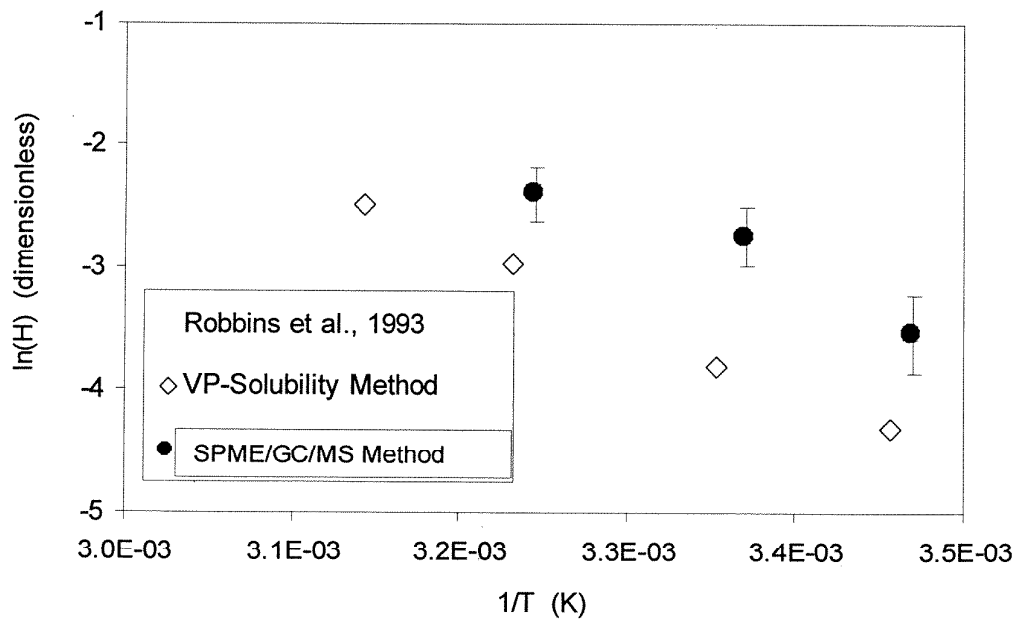


Figure 3. Packing Height as a Function of Temperature, 5 ug/L effluent

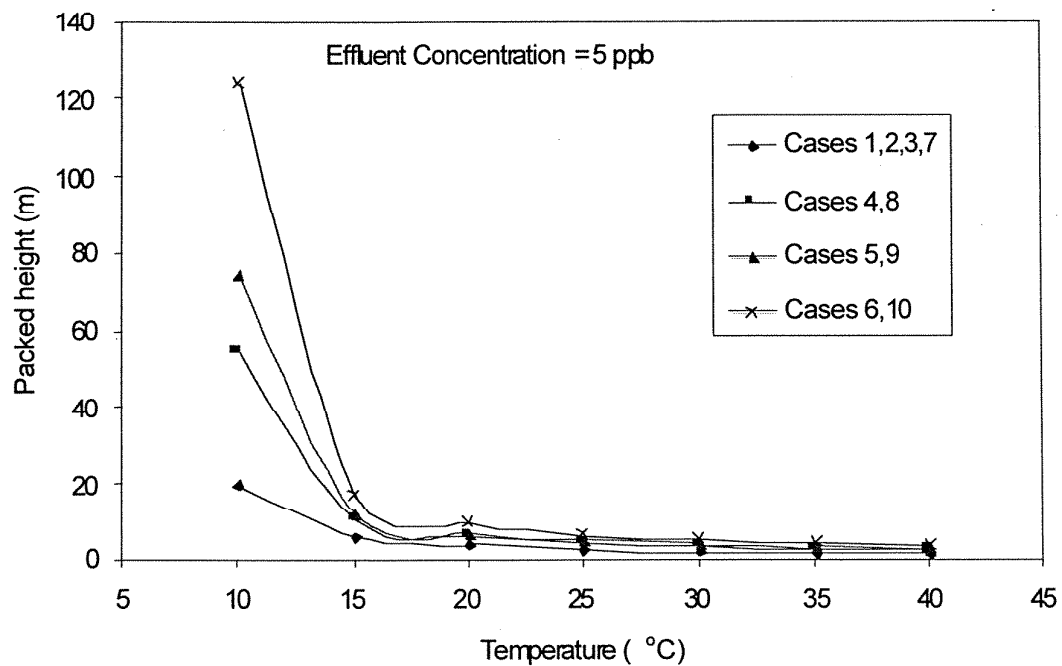


Figure 4. Packing Height as a Function of Temperature, 35 ug/L effluent

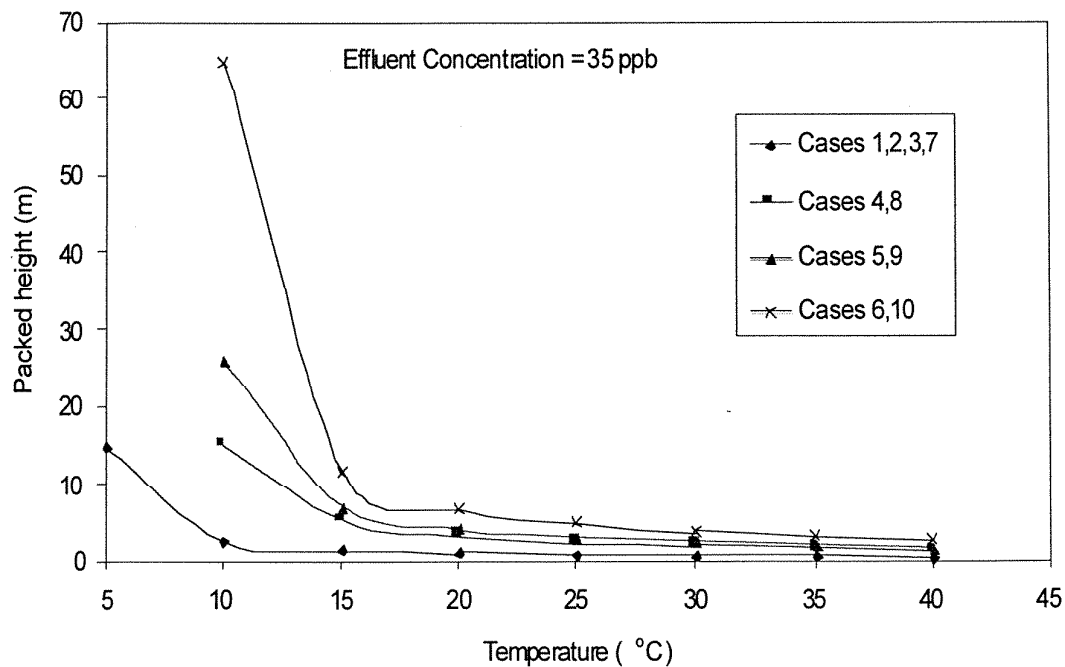


Figure 5. Equilibrium Adsorption Isotherm for MTBE on GRC-22

data from Calgon Carbon Corporation, 1998

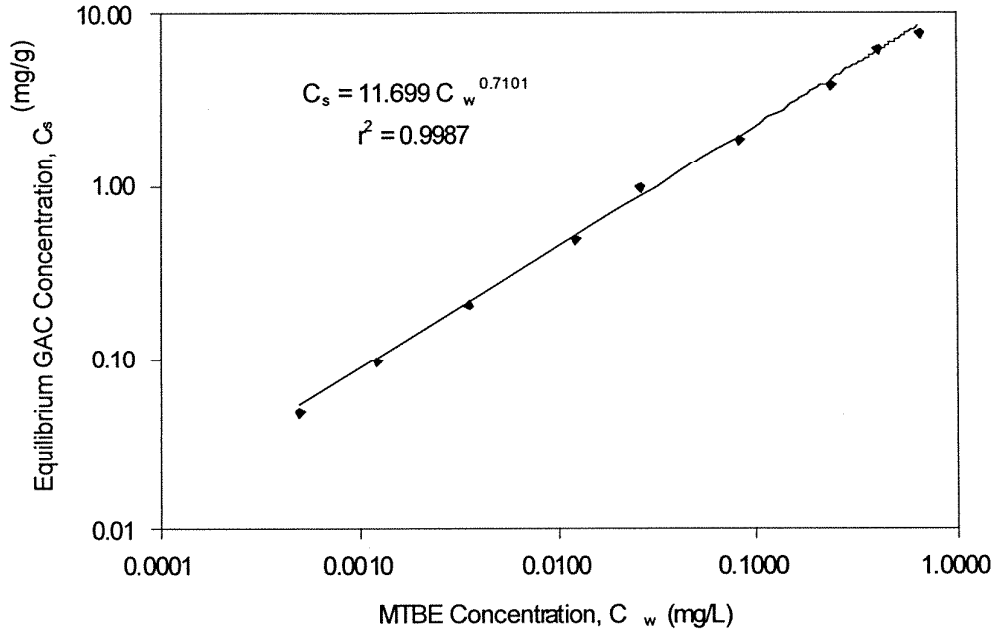


Figure 6. Flow Diagram for GAC with Steam Regeneration

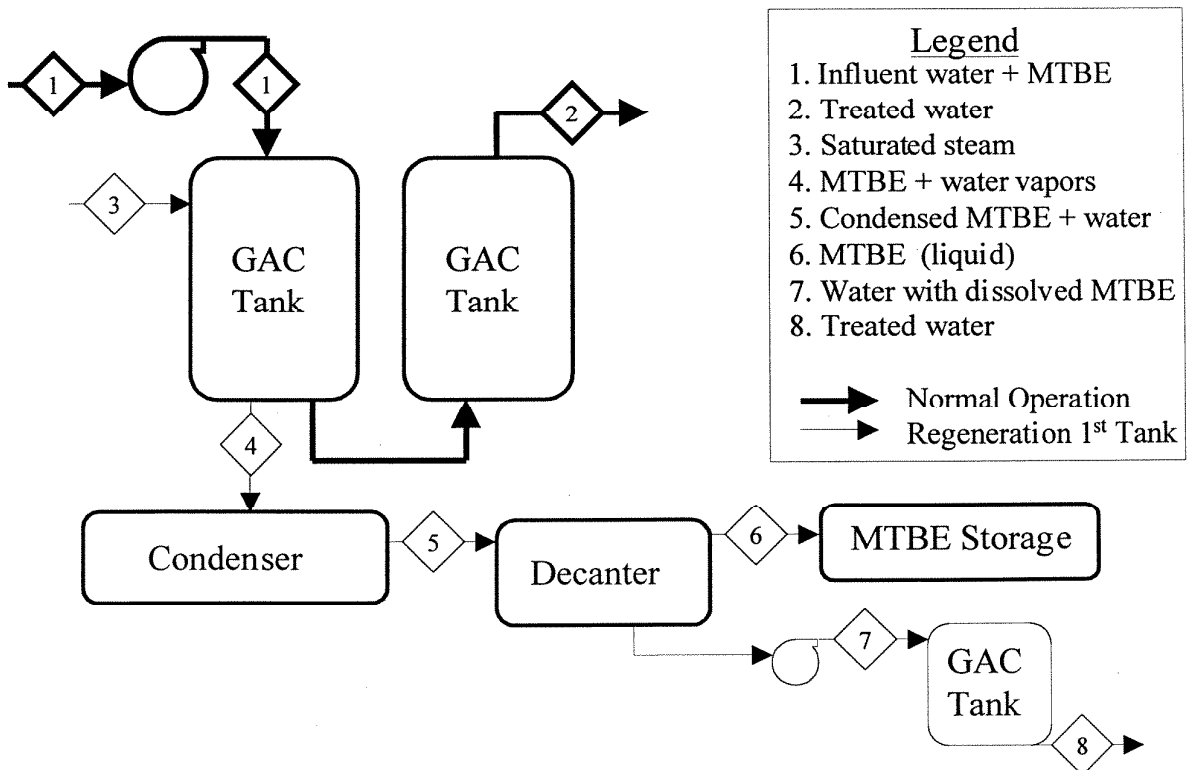


Figure 7. Temperature Dependence of MTBE Oxidation with Ozone

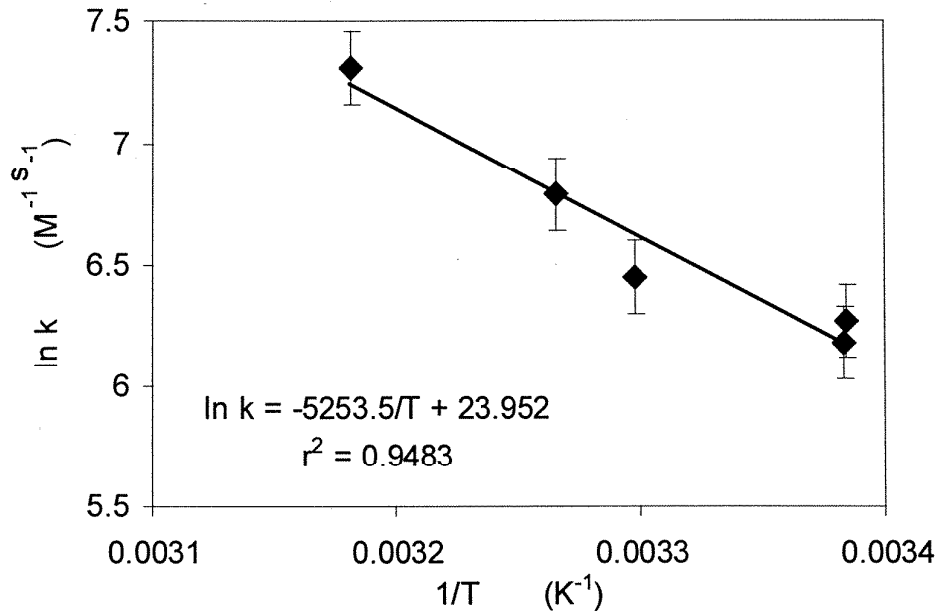


Figure 8. Typical Hollow Fiber Membrane Model Construction

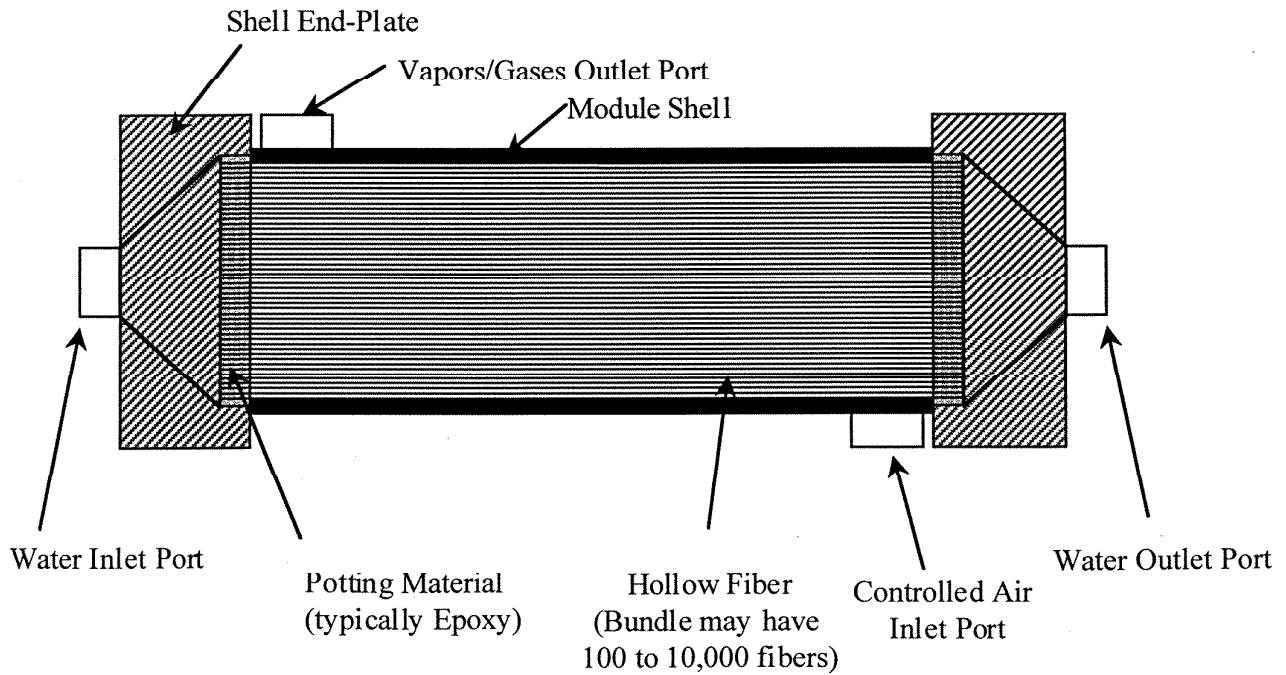


Figure 9. Hollow Fiber cross-sectional view

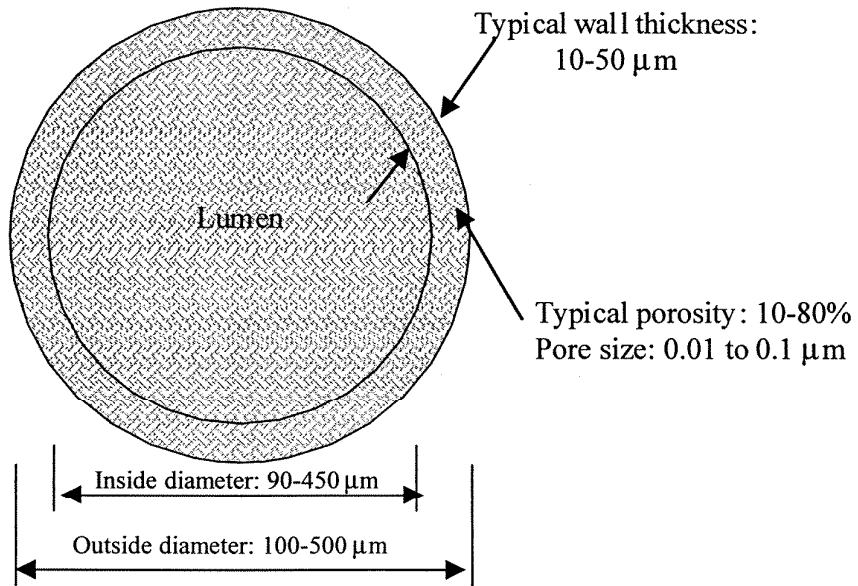


Figure 10. Hollow Fiber Membrane Process Diagram

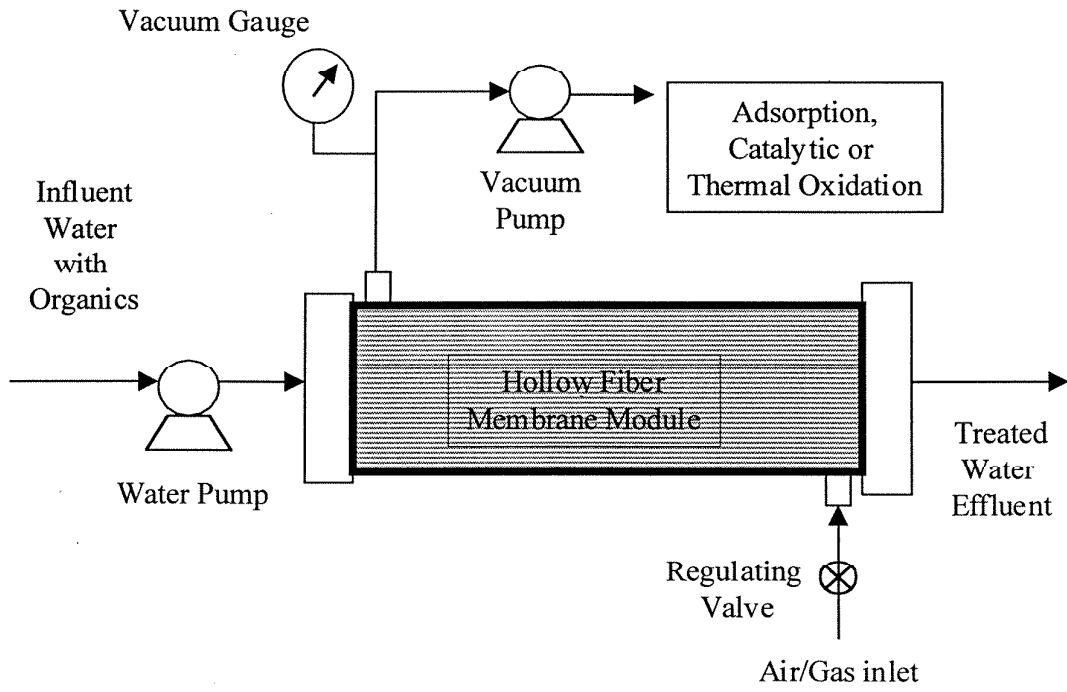


Figure 11. Comparison between theoretical and experimental removal efficiency for Hollow Fiber Membrane

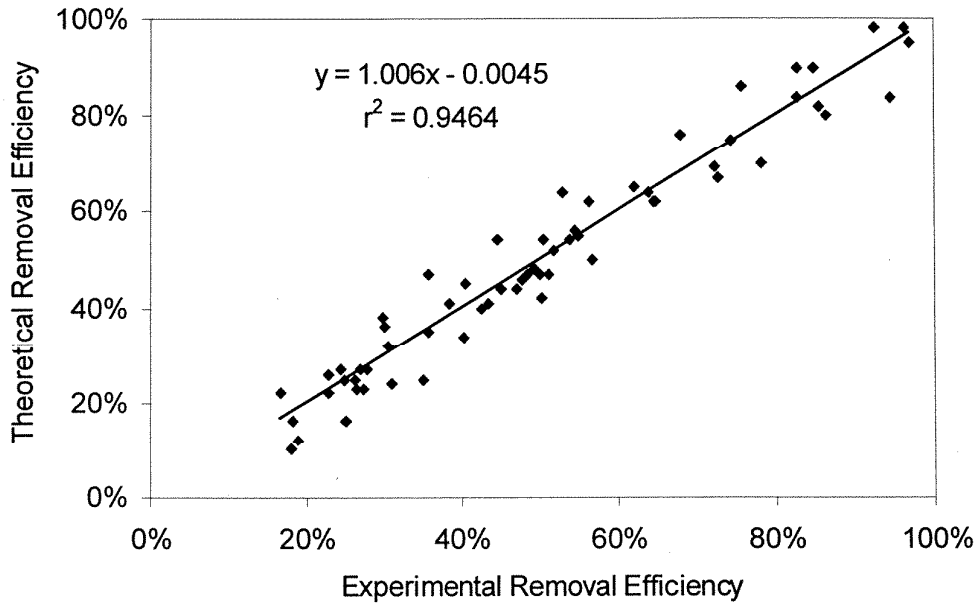
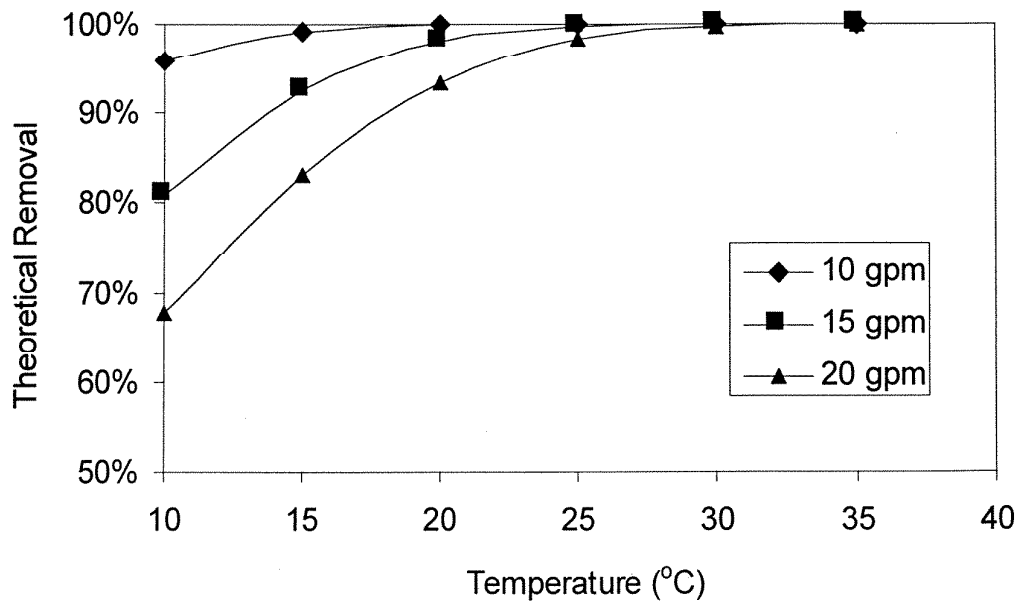
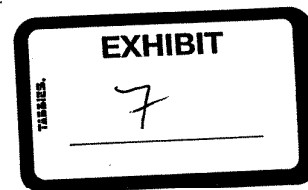


Figure 12. Predicted performance for commercial membrane





Methyl tert-butyl ether (MTBE)
CASRN 1634-04-4

Contents

- I.A. REFERENCE DOSE FOR CHRONIC ORAL EXPOSURE (RfD)
- I.B. REFERENCE CONCENTRATION FOR CHRONIC INHALATION EXPOSURE (RfC)
- II. CARCINOGENICITY ASSESSMENT FOR LIFETIME EXPOSURE
- VI. BIBLIOGRAPHY
- VII. REVISION HISTORY
- VIII. SYNONYMS

0545
Methyl tert-butyl ether (MTBE); CASRN 1634-04-4

Health assessment information on a chemical substance is included in IRIS only after a comprehensive review of chronic toxicity data by U.S. EPA health scientists from several Program Offices and the Office of Research and Development. The summaries presented in Sections I and II represent a consensus reached in the review process. Background information and explanations of the methods used to derive the values given in IRIS are provided in the Background Documents.

STATUS OF DATA FOR MTBE

File On-Line 12/01/1991

Category (section)	Status	Last Revised
Oral RfD Assessment (I.A.)	no data	03/01/1993
Inhalation RfC Assessment (I.B.)	on-line	09/01/1993
Carcinogenicity Assessment (II.)	no data	

I. CHRONIC HEALTH HAZARD ASSESSMENTS FOR NONCARCINOGENIC EFFECTS

I.A. REFERENCE DOSE FOR CHRONIC ORAL EXPOSURE (RfD)

Substance Name -- Methyl tert-butyl ether (MTBE)
 CASRN -- 1634-04-4

Not available at this time.

I.B. REFERENCE CONCENTRATION FOR CHRONIC INHALATION EXPOSURE (RfC)

Substance Name -- Methyl tert-butyl ether (MTBE)
 CASRN -- 1634-04-4
 Last Revised -- 09/01/1993

The inhalation Reference Concentration (RfC) is analogous to the oral RfD and is likewise based on the assumption that thresholds exist for certain toxic effects such as cellular necrosis. The inhalation RfC considers toxic effects for both the respiratory system (portal-of-entry) and for effects peripheral to the respiratory system (extrarespiratory effects). It is expressed in units of mg/cu.m. In general, the RfC is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily inhalation exposure of the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. Inhalation RfCs were derived according to the Interim Methods for Development of Inhalation Reference Doses (EPA/600/8-88/066F August 1989) and subsequently, according to Methods for Derivation of Inhalation Reference Concentrations and Application of Inhalation Dosimetry (EPA/600/8-90/066F October 1994). RfCs can also be derived for the noncarcinogenic health effects of substances that are carcinogens. Therefore, it is essential to refer to other sources of information concerning the carcinogenicity of this substance. If the U.S. EPA has evaluated this substance for potential human carcinogenicity, a summary of that evaluation will be contained in Section II of this file.

I.B.1. INHALATION RfC SUMMARY

Critical Effect	Exposures*	UF	MF	RfC
Increased absolute and relative liver and kidney weights and increased severity of spontaneous renal lesions (females),	NOAEL: 1453 mg/cu.m (403 ppm) NOAEL(ADJ): 259 mg/cu.m NOAEL(HEC): 259 mg/cu.m LOAEL: 10899 mg/cu.m (3023 ppm) LOAEL(ADJ): 1946 mg/cu.m	100	1	3E+0 mg/cu.m

increased prostration (females), and swollen periocular tissue (males and females) LOEL(HEC): 1946 mg/cu.m

Chronic Rat 24-Month
Inhalation Study

Chun et al., 1992

*Conversion Factors and Assumptions -- MW = 88.15. Assuming 25 C and 760 mmHg, NOAEL(mg/cu.m) = 403 ppm x 88.15/24.45 = 1453. NOAEL(ADJ) = 1453 x 6 hours/24 hours x 5 days/7 days = 259 mg/cu.m. The NOAEL(HEC) was calculated for a gas:extrarespiratory effect in rats assuming periodicity was attained. Because the b:a lambda values are unknown for the experimental species (a) and humans (h), a default value of 1.0 is used for this ratio. NOAEL(HEC) = NOAEL(ADJ) x [b:a lambda(a)/b:a lambda(h)] = 259 mg/cu.m.

I.B.2. PRINCIPAL AND SUPPORTING STUDIES (INHALATION RfC)

Chun, J.S., H.D. Burleigh-Flayer, and W.J. Kintigh. 1992. Methyl tertiary butyl ether: vapor inhalation oncogenicity study in Fischer 344 rats (unpublished material). Prepared for the MTBE Committee by Bushy Run Research Center, Union Carbide Chemicals and Plastics Company Inc. Docket No. OPTS-42098.

In a chronic inhalation study (Chun et al., 1992), Fischer 344 rats (50 males, 50 females/group) were exposed to analytical mean concentrations of 403, 3023, or 7977 ppm methyl tertiary-butyl ether (MTBE) vapors (1453, 10,899, or 28,760 mg/cu.m) 6 hours/day, 5 days/week for 24 months (duration-adjusted values are 259, 1946, and 5136 mg/cu.m, respectively). The control animals breathed air. Hematology (all rats) was performed halfway through the experiment (control and high-concentration groups) and prior to final sacrifice (all groups). Blood and urine samples were collected and stored, but complete serum chemistry and urinalysis were not performed. Corticosterone levels were measured on 10 rats/sex/group prior to sacrifice. Clinical signs, body weights, organ weights, and food consumption were monitored. Complete necropsy and histopathology, including examination of the nasal turbinates and lower respiratory tract, were performed on all animals.

Survival times for females were not significantly different between exposed and control rats. A slight decrease in mean survival time was observed in the males exposed to the low concentration (controls, 632 days; low-concentration group, 617 days; $p < 0.05$). Survival time clearly decreased in males exposed to both the mid and high concentrations (mid-concentration group, 587 days; high-concentration group, 516 days; $p < 0.01$), leading to earlier sacrifice times at 97 and 82 weeks, respectively. According to study pathologists, chronic, progressive nephropathy was the main cause of death in the higher concentration groups and also contributed to a slight increase in mortality in the males exposed to the low concentration (Garman, 1993a,b). In NTP oral and inhalation 2-year studies of other compounds that exacerbate rat chronic, progressive nephropathy (e.g., 1,4-dichlorobenzene, dimethyl methylphosphonate, hexachloroethane, isophorone, pentachloroethane, tetrachloroethylene, chloroethalonil, and trichloroethylene), survival rates in male rats have been low, particularly in the high-dose groups (U.S. EPA, 1991). As with MTBE, decreased survival of male rats exposed to dimethyl methylphosphonate was attributed, at least in part, to chemically related kidney toxicity (i.e., nephropathy) (NTP, 1987).

For animals exposed to the high concentration, clinical signs that were markedly increased over controls were ataxia (2-4% of controls at end of study vs. 100% of males and females at high-exposure level starting day 2) and

earlier onset and increased incidence of swollen periorbital tissue (<50% of controls at end of study vs. 84% of males and 100% of females starting day 12). The observation of ataxia at this exposure level is consistent with findings from the subchronic study discussed below (Dodd and Kintigh, 1989). Increased salivation was observed in males only at the high-exposure level. At the mid-concentration level, the authors did not report increased ataxia, but an increase in incidence of prostration was observed in females (6/50 controls vs. 15/50 at the mid concentration). Early onset and increased incidence of swollen periorbital tissue were also reported at the mid-concentration level (68% of males and 100% of females starting days 12 and 19, respectively). Swollen periorbital tissue, salivation, and prostration were not reported at any exposure level in the subchronic study (Dodd and Kintigh, 1989).

As is discussed in Section I.B.4., the corresponding subchronic study by Dodd and Kintigh (1989) assessed several neurological endpoints, including pathological examinations, brain size parameters, and functional observational batteries (FOBs). The only CNS effect found in the subchronic study at the 4000-ppm level was a slight decrease in brain length of the male rats ($p < 0.05$). Significant ($p < 0.05$) decreases in absolute brain weights of 8000-ppm males and females supported the use of this endpoint as a critical effect for derivation of the previously reported MTBE RfC, which was based on these 90 day study data. The chronic study did not measure brain length as a parameter, but did assess brain weight. The lack of brain length measurements in the chronic study is not considered a major study deficit because no significant differences in male or female brain weights were observed at any chronic exposure level.

As was observed in the subchronic study (Dodd and Kintigh, 1989), body weight gain and absolute body weight were decreased in both sexes of the high-concentration group. Just prior to sacrifice at week 81, body weight gain and absolute body weight in males were decreased 29 and 19%, respectively. Body weight gain and absolute body weight in females were decreased 22 and 13%, respectively, at the end of the study. Exposure-related, 18-25% increases in kidney and liver weights (absolute and relative to body and brain weights) were reported in females in the mid- and high-exposure groups ($p < 0.01$). No significant increases in liver or kidney weights were observed in the male rats.

No concentration-related histopathologic findings were reported in the livers of either sex. Increased incidence of hepatocellular hypertrophy (males) and degeneration (females) were observed in animals exposed to the mid concentration, but not the high concentration. No treatment-related lesions were observed in the respiratory tract in any group. Similarly, no pathologic changes were reported in the corresponding subchronic study by Dodd and Kintigh (1989).

Increases in microscopic kidney changes indicative of chronic nephropathy were seen in a concentration related manner in all groups of exposed male rats and, to a lesser extent, in females exposed to the mid and high MTBE concentrations. Increases in the severity of mineralization and interstitial fibrosis were observed at all chronic-exposure concentrations in the male rats. Increased mineralization was not observed in females, but increases in mild to moderate glomerulosclerosis and interstitial fibrosis and tubular proteinosis were observed at the mid- and high-exposure levels in the female rats.

U.S. EPA (1991) clearly indicates that nephropathy in male rats associated with the induction of alpha-2u-globulin (a male-rat-specific protein) accumulation in hyaline droplets (located in the P2 segment of the proximal tubule cells of the kidneys) "is not an appropriate endpoint to determine noncancer (systemic) effects potentially occurring in humans." U.S. EPA (1991) further outlines the following criteria for identification of an alpha-2u-globulin toxicant: (1) increased number and size of hyaline droplets in renal proximal tubule cells of treated male rats, (2) the accumulating protein in the hyaline droplets is alpha 2u globulin, and (3) additional aspects of

pathological sequence of lesions associated with alpha-2u-globulin nephropathy are present, as described in U.S. EPA (1991). For reasons discussed below, the nephropathy in the male rats (and the associated decreased survival time) is thought to be at least partially due to alpha-2u-globulin accumulation, confounding the results of the male rat chronic bioassay and precluding its use as a basis for a quantitative determination of human noncancer risk.

The first criterium listed above was addressed in the subchronic study by Dodd and Kintigh (1989). They reported that slides of kidney sections from five male rats in each treatment group and from five female rats from the high-level (7977-ppm) treatment group were independently "blind" evaluated by three pathologists for treatment-related differences in hyaline droplet formation. The average grades for extent of hyaline droplet formation based on a scale ranging from 0 (no findings) to 5 (severe) were 0 for the female rats exposed to 7977 ppm and 2.56, 1.94, 3.06, and 3.66 for the control and 800-, 4000-, and 7977-ppm males, respectively. Thus, these results indicate no hyaline droplet formation in female rats and a moderate (one-grade) increase in hyaline droplet formation for male rats at the high-exposure level. Further, hyaline droplet increases at the high dose were observed in a subchronic gavage study (Robinson et al., 1990) and in a subchronic drinking-water study (Lindamood et al., 1992) of male Fischer 344 rats exposed to tert-butyl alcohol (TBA), the principal metabolite of MTBE.

The second criterium, alpha-2u-globulin levels in the hyaline droplets, was addressed in a separate analysis of male rats from the subject subchronic study (Swenberg and Dietrich, 1991). Although they were not increased in a concentration-related manner, Swenberg and Dietrich (1991) observed an approximate doubling in the percentage of renal cortex staining for alpha 2u globulin in all male rat exposure groups of the subchronic study. Although the pattern of alpha-2u-globulin accumulation is not consistent with other known alpha-2u-globulin toxicants (e.g., limonene), these results suggest that the aforementioned increase in hyaline droplet formation could, at least partially, be due to the accumulation of this male-rat-specific protein.

Finally, subchronic and chronic inhalation studies reveal that MTBE does induce most of the pathologic progression (from hyaline droplet formation to acceleration of chronic progressive nephropathy to renal tubular cell tumors) identified as characteristic of alpha-2u-globulin-type toxicity (U.S. EPA 1991). Swenberg and Dietrich (1991) reported that alpha-2u-globulin-positive proteinaceous casts at the junction of the proximal tubules and the thin limb of Henle were not observed. However, Robinson et al. (1990) found that 50% of male Sprague-Dawley rats orally dosed with 1200 mg MTBE/kg displayed "small numbers of tubules which were plugged with granular casts." Further, granular casts at this part of the nephron can lead to subsequent tubular dilation (U.S. EPA, 1991), an effect that was noted in the chronically exposed male (1/50, 13/50, 14/50, and 11/50 in control and low-, mid-, and high-exposure groups, respectively), but not female (2/50, 0/50, 3/50, and 3/50 in control, low-, mid-, and high-exposure groups, respectively) rats (Chun et al., 1992). The reason this pathology was not observed following the 90-day study is not known at this time but may be related to differences in test species strain or due to differences resulting from differing administration routes.

Another indication that MTBE exacerbation of chronic progressive nephropathy (CPN) may be related to alpha 2u globulin is that MTBE accelerates CPN to a much lesser degree in animals that can not produce alpha 2u globulin (i.e., female rats, all mice). The graded kidney lesion responses observed in male and female rats (Tables 40 and 45) were analyzed by logistic regression models to determine the extent to which MTBE impacted male and female kidneys differently. Males and females differed significantly with respect to concentration-response slopes for interstitial nephritis ($p < 0.025$), interstitial fibrosis ($p < 0.005$), and mineralization ($p < 0.005$), but not with respect to tubular proteinosis ($p > 0.1$) and glomerulosclerosis ($p > 0.1$) (Allen, 1993). In all cases where the slopes differed significantly, the slope for males was greater than the slope for females.

As with the male rats, the nephropathy present in the female MTBE-exposed

rats did not differ histologically from the "spontaneous" nephropathy common in older Fischer 344 rats. The heightened degrees of nephropathy seen in relation to the MTBE exposures represent an exacerbation of this spontaneous rat nephropathy (Garman, 1993a). Of the observed kidney lesions, the study pathologist's diagnosis of tubular proteinosis was considered most representative of overall nephropathy (Garman, 1993b). An analysis of the average severity grade for these lesions in the different exposure groups (where 1 = minimal, 2 = mild, 3 = moderate, 4 = marked, and 5 = severe) revealed scores of 2.8, 2.8, 3.8, and 3.5 for females sacrificed at 24 months in the control group and 403-, 3023-, and 7977-ppm exposure groups, respectively (Eldridge, 1993). Trend analyses (using methods described by Tukey et al., 1985) of this and other kidney lesions confirm the 403-ppm NOAEL and 3023-ppm LOAEL with respect to renal effects in the female rats (Allen, 1993). In males, 403-ppm was determined to be a NOAEL for interstitial nephritis, tubular proteinosis, and glomerulosclerosis, and a LOAEL for mineralization and interstitial fibrosis. The 403-ppm NOAEL for renal effects in the female rats was also confirmed via a blinded reevaluation of the original kidney slides by a second pathologist (Busey, 1993).

In summary, there is some evidence for alpha-2u-globulin nephropathy in male rats. This limited evidence, however, is sufficient to eliminate male rat kidney nephropathy as a possible critical endpoint for use in the derivation of an RfC. Also, the induction of nephropathy in females indicates that MTBE induces renal pathology by more than one mechanism. Because the female rat lacks alpha 2u globulin, the mechanism of pathologic induction is not considered to be unique, and renal pathology in females is thus considered to be suitable for use in the development of an RfC.

Exposure to MTBE vapor for 24 months produced various signs of toxicity in female rats exposed to 3023 ppm MTBE, including prostration, swollen periocular tissue, increased relative and absolute liver and kidney weights, and increased severity of certain renal lesions. Thus, 3023 ppm was a LOAEL [LOAEL(HEC) = 1946 mg/cu.m], and 403 ppm [NOAEL(HEC) = 259 mg/cu.m] was a NOAEL for chronic exposure to female rats.

A two-generation reproduction study (Neeper-Bradley, 1991) of Sprague-Dawley rats lends support to the NOAEL level determined in the Chun et al. (1992) chronic study. In accordance with current U.S. EPA risk assessment policy, no adjustment is made to approximate an equivalent continuous exposure level for developmental endpoints (U.S. EPA, 1989a). As a result, the NOAEL(HEC) for this developmental endpoint is higher than the NOAEL(HEC) derived from the Chun et al. (1992) study.

Neeper-Bradley (1991) conducted a two-generation reproduction study in CD (Sprague-Dawley) rats. Male and female rats were exposed to mean MTBE concentrations of 0, 402, 3019, and 8007 ppm over two generations. F0 animals, 25/sex/concentration, were exposed for 10 weeks and then bred once to produce F1 litters. Twenty-five pups/sex/group from the F1 generation were selected randomly to be parents of the F2 generation and were exposed for at least 8 weeks prior to mating. Exposures continued through mating, through day 19 of gestation, and from lactation days 5-28 for both generations of parents. The rats were exposed for 6 hours/day, 5 days/week during the prebreeding exposure period and for 7 days/week during mating, gestation, and postnatal periods. The approximate age of the F0 animals at the start of prebreeding exposures was 6 weeks. Prebreeding exposures for the selected F1 weanlings began 29-31 days from birth. Parental animals were monitored for clinical signs of toxicity, food consumption, and body weight. All F0 and F1 parents were necropsied and examined for gross lesions; liver weights of F1 parents were measured at necropsy. Upper and lower respiratory tracts and selected reproductive tissues from the high-concentration and control groups were examined histologically, as were tissues with gross lesions. Offspring were evaluated for viability, survival, body weight, and sex distribution.

Prebreeding exposures¹ of 7977 ppm resulted in reduced food consumption during the first 2-3 weeks (F0 and F1 males) and body weight and body weight gain reductions throughout the exposure period (F0 and F1 males and F1

females). Other signs of parental toxicity at 7977 ppm included perioral wetness, hypoactivity, lack of startle reflex, ataxia, blepharospasm, and increased relative liver weights (F1 generation only). At 3023 ppm, adult effects included hypoactivity, lack of startle reflex, blepharospasm, increased relative liver weights (F1 males only), and transient reductions in body weight (F1 males and females). The histopathologic evaluation revealed no exposure-related lesions in the organs examined from males and females of either parental generation. The NOAEL and LOAEL for paternal effects in this study were 403 and 3023 ppm, respectively, which support the effect levels designated for the principal study (Chun et al., 1992).

Mating, fertility, and gestational indices were not adversely affected in either of the two parental generations. Body weights, weight gains, and food consumption were similar for treated and control groups throughout gestation. However, maternal exposure to 3023 and 7977 ppm resulted in statistically significant reduced body weights and reduced body weight gains in F1 pups ($p < 0.05$ at 3023 ppm; $p < 0.01$ at 7977 ppm) and F2 pups ($p < 0.01$ for both exposure groups), principally during the latter periods of lactation. A significant ($p < 0.01$) decrease in pup survival in the F1 litter on lactation days 0-4 (pre-cull) for the 7977-ppm exposure group (91.5% survival, 259/283) compared with controls (98.6%, 289/293) was attributed to the loss of an entire litter (16 pups). The authors state that this loss was not related to MTBE toxicity, but no further explanation is provided. In the 7977-ppm F2 litters, pup survival was reduced on postnatal day 4 (93.5% survival, 275/294) compared with controls (98.1%, 305/311). A NOAEL of 403 ppm [1442 mg/cu.m; NOAEL (NEC) - 1442 mg/cu.m] and a LOAEL of 3023 ppm (10,816 mg/cu.m) for reduced body weight and body weight gain in both F1 and F2 pups during postnatal development (lactation period) were determined.

Biles et al. (1987) conducted a one-generation reproductive toxicity investigation. Sprague-Dawley rats (15 males, 30 females/group) were exposed to MTBE concentrations of 0, 290, 1180, and 2860 ppm (0, 1046, 4254, and 10,311 mg/cu.m) (males) and 0, 300, 1240, and 2980 ppm (0, 1082, 4470, and 10,743 mg/cu.m) (females), 6 hours/day, 5 days/week, during the premating interval (12 weeks for males, 3 weeks for females). There were two 5-day mating intervals (two females for every male). Males (F0 generation) continued to be exposed during and between matings, whereas F0 females were exposed 7 days/week on days 0-21 of gestation and 5 days/week on days 5-20 of lactation. After unexposed litters (Fla) were weaned, the F0 males and F0 females underwent another mating period with the same exposure regimen to produce a second litter (Flb). F0 males were sacrificed after this mating period, and females were sacrificed after the end of Flb weaning. Thus, F0 males were exposed overall to MTBE for approximately 28 weeks, and F0 females were exposed for 16 weeks. These animals were examined for gross changes, especially in their reproductive organs. Histopathologic examination revealed an increased incidence of dilated renal pelvis in females exposed to 300 (4/30, 13%) and 2980 ppm (5/30, 17%) compared with controls (1/30, 3%). However, this finding was not observed at the mid concentration of 1240 ppm (0/30, 0%), which preclude establishing an unequivocal concentration-response relationship. The pregnancy rate was not significantly affected in either mating interval (Fla and Flb), although the Flb matings were slightly reduced in the high-exposure group (18/25, 76%) compared with controls (22/25, 88%). On day 4 of lactation, each litter with greater than 10 pups was culled. Pups were sacrificed on day 21 of lactation. The pup viability indices at birth were slightly, but significantly, decreased ($p < 0.05$) in the Flb litters of the dams exposed to 1240 (95.5% viability, 278/291) and 2980 ppm (95.5% viability, 234/245) compared with litters of controls (99% viability, 292/295). The Fla litter's pup viability indices did not differ from controls. Pup survival in the Fla litter was significantly decreased ($p < 0.01$) on lactation days 0-4 (pre-cull) for the 300- (91.4% survival, 317/347) and 1240-ppm (89.1% survival, 205/230) exposure groups compared with controls (98.2% survival, 324/330). However, the Fla high-exposure group displayed no reduction in pup survival when compared to controls, and no reduction in pup survival was seen in the Flb litters. Further, pup survival indices for lactation days 4-21 (post-cull) were not increased over controls. Consequently, the reduced pup survival in the Fla low- and mid-exposure groups

is not believed to be a treatment-related effect. A NOAEL of 300 ppm [1082 mg/cu.m; NOAEL(HEC) = 1082 mg/cu.m] and a LOAEL of 1240 ppm (4470 mg/cu.m) (female rats) for decreased pup viability in Flb litters were determined.

I.B.3. UNCERTAINTY AND MODIFYING FACTORS (INHALATION RfC)

UF -- An uncertainty factor of 10 is applied to account for extrapolation to sensitive human subpopulations. An additional factor of 3 is used to account for interspecies extrapolation. A full 10-fold adjustment for interspecies extrapolation is not deemed necessary due to the use of dosimetric adjustments. An uncertainty factor of 3 is applied for data base deficiencies because of the lack of certain information from the chronic exposure bioassay (e.g., urinalysis results, serum chemistry, and limited reporting of motor activity/clinical signs during exposure).

MF -- None

I.B.4. ADDITIONAL STUDIES / COMMENTS (INHALATION RfC)

Information on human exposure to MTBE is limited. Humans are acutely exposed to MTBE as a part of a medical treatment to dissolve cholesterol gallstones (Thistle, 1992). Injection of the gall bladder with a high dose of MTBE can be associated with several types of health effects (e.g., nausea, vomiting, sleepiness). Minor transient mucosal damage in the gallbladder has been demonstrated with extensive exposure, but no clinically significant consequences have been reported. One patient has been reported to have developed intravascular hemolysis and renal failure following inadvertent extravasation of a large bolus of MTBE (Ponchon et al., 1988). Reliable data from epidemiology studies of human exposure to airborne MTBE are not currently available.

In a chronic inhalation study (Burleigh-Flayer et al., 1992), CD-1 mice (50 males, 50 females/group) were exposed to mean concentrations of 402, 3014, or 7973 ppm MTBE vapors (1442, 10,816, or 28,843 mg/cu.m) for 6 hours/day, 5 days/week (duration-adjusted values are 258, 1288, and 2575 mg/cu.m, respectively) for 18 months. The control animals breathed air. Hematology (all mice) and urinalysis (20 mice/sex) were performed halfway through the experiment (control and high-concentration groups) and prior to final sacrifice (all groups). In addition, corticosterone was measured on 10 mice/sex/group prior to sacrifice. Clinical signs, body weights, organ weights, and food consumption were monitored. A complete necropsy and histopathology, which included examination of the nasal turbinates and the lower respiratory tract, was performed on all animals.

Male mice from the high-exposure group exhibited an increased mortality rate, probably due to a slightly increased frequency of obstructive uropathy. However, the frequency of death due to this disease in the high-concentration group was still within the range noted for historical controls (Maita et al., 1988). Ataxia was observed in 50/50 animals (both sexes) exposed to the high MTBE concentration. In addition, prostration was noted between days 25 and 522 in 8/50 female mice exposed to the highest concentration (vs. 1/50 controls). Other effects reported in both sexes of the high-concentration group included decreased body weight gain and absolute body weight (not statistically significant for females), and a slight decrease in urinary pH. No concentration-related hematologic effects were reported.

Concentration-related increases in liver weight (absolute and relative to body and brain weights) were reported in both male and female mice. In the

females, the liver weight increases were statistically significant at all but the lowest exposure level ($p < 0.01$). In males, significant increases in liver weights were observed at the lowest exposure level ($p < 0.05$), but the only measure that indicated a concentration response was liver weight relative to brain weight ($p < 0.05$).

Absolute and relative male kidney weights were significantly increased in the lowest ($p < 0.01$) and mid-exposure groups ($p < 0.05$), but, as with the male liver weights, the increases were less than 10%, and a concentration-response relationship was not apparent (i.e., there was no statistical difference at the high-exposure level and significance at the mid-exposure level was less than at the low-exposure level). Female kidney weights were only increased significantly ($p < 0.01$) relative to body weight for animals exposed to the highest concentration.

Decreases in absolute brain weight were also reported in both sexes of the high-concentration group (6% for both sexes; $p < 0.01$). Absolute and relative spleen weights were increased for the high-exposure group females ($p < 0.01$), and absolute and relative adrenal weights were increased for the high-exposure group males ($p < 0.01$).

Histopathologic evaluation revealed no lesions in any organ except the liver. An increased incidence of hepatocellular hypertrophy was seen at the highest exposure level in both sexes, but was only significant ($p < 0.05$) in the male mice.

The increased liver, kidney, and adrenal weights, as well as the decreased brain weights, reported in this study at the highest exposure level are consistent with the subchronic rat study (Dodd and Kintigh, 1989). Although statistically significant ($p < 0.05$) increases in both absolute and relative liver and kidney weights were observed in the low- and mid-concentration groups, the male liver and kidney weights did not tend to increase with increasing exposure concentration, and the female liver and kidney weight increases (both absolute and relative) at the low- and mid-concentration levels were only 9% or less over controls. The high-exposure level is considered a LOAEL [LOAEL(HEC) = 2575 mg/cu.m] based on the significant increase in absolute (females only) and relative liver weights (around 30%; $p < 0.01$), the increased incidence of anesthetic effects, and the significant (as much as 24%) decrease in body weight. The decreased survival time in the male mice may suggest that the highest concentration exceeded the MTD, but it may also be due to increased frequency of a spontaneous obstructive uropathy common in this strain of male mice. The mid-exposure level is considered a NOAEL [NOAEL(HEC) = 1288 mg/cu.m] for this study.

In a subchronic inhalation study (Dodd and Kintigh, 1989), Fischer 344 rats (25/sex/group) were exposed to mean concentrations of 797, 3920, or 8043 ppm MTBE vapors (2873, 14,133, or 28,998 mg/cu.m) for 6 hours/day, 5 days/week (duration-adjusted values are 513, 2524, and 5178 mg/cu.m, respectively) for 13 weeks. The control animals breathed air. The high-exposure concentration was set at 50% of the LEL. Hematologic tests were performed before exposure (5/sex/group) and during weeks 5 and 14 (10/sex/group) of the study. Clinical observations were made of the groups; ophthalmic observations were made prior to the first exposure and at study end; and body weights, organ weights (15/sex/group), and food consumption were monitored. Ten rats/sex/group were perfusion-fixed for microscopic evaluation of the nervous system tissues. Brain weights and measurements were taken on all perfusion-fixed rats, and light microscopic evaluations were performed on the nervous system of 6/sex/group. The remaining 15 rats/sex/group received complete necropsy evaluations. Nasal turbinates (four sections), trachea, and lung (three sections) were examined in the control and high-exposure groups and the lung only in the low- and mid-concentration groups. A battery of neurobehavioral tests was performed on 15 rats/sex/group prior to first exposure and at exposure weeks 1, 2, 4, 8, and 13, and motor activity was determined prior to first exposure and at exposure weeks 4, 8, and 13.

No treatment-related findings were noted for the respiratory tract.

Lymphoid hyperplasia within the submandibular lymph nodes of the males in the high-exposure group was noted, but no reason was found for its occurrence.

Necropsy examination of nervous system tissue (10/sex/group) showed no evidence of treatment-related changes in exposed animals compared with the controls. However, at both the mid- and high-exposure levels, an absolute decrease in brain length was observed in male rats. Reductions in absolute brain weight in both sexes were noted at the high-exposure level, but not at the mid concentration. The authors observed no statistically significant changes in brain weight, expressed as a percentage of body weight, nor in brain width. Nevertheless, the effect on brain length was statistically significant ($p < 0.05$) and concentration related. Thus, this effect was felt to be consistent with the toxicity observed in other organ systems.

Dodd and Kintigh (1989) also evaluated the neurotoxic effects of MTBE using an FOB for 10 rats/sex/group and a motor activity test for the remaining 30 animals from each group. The mid- and high-concentration groups deviated from controls with respect to several FOB endpoints. The authors cite elevated body temperature in the high-exposure group males (day 7) and in the mid- and high-exposure group females (day 91). However, the overall downward trend in body temperature across control and exposure groups suggests an anomaly in the test procedure and calls to question the validity of these data. The authors note a decreased mean latency to rotate on the inclined screen in low- (days 14 and 28) and mid-concentration (days 7, 14, and 28) males. However, the data reported for this procedure are highly variable across groups and over time. Decreased hind limb grip strength was observed in mid-concentration males (days 28 and 91), but increased hind-limb grip strength was observed in mid-concentration females (day 91). Cumulative test-session motor activity was decreased for males exposed to the highest MTBE concentration (28% at day 55) and increased for females exposed to the lowest (20% at day 55) and mid concentrations (36% at day 55). The lack of a clearly defined concentration-response relationship calls into question the toxicological significance of these data.

Slight hematologic alterations were observed in both male and female rats exposed to mid- and high-exposure levels. All of these changes, however, were within the range of historical measurements for this species (Charles River Breeding Laboratories, 1984). The most noteworthy biochemical finding, however, was a significant ($p < 0.05$) increase in corticosterone levels for the high-exposure group, which is consistent with the observed increase of relative adrenal weight. The interaction of MTBE with the neuroendocrine system (e.g., at the hypothalamus, pituitary, or adrenal glands) is unknown.

There were no exposure-related alterations in mean body weight for rats exposed to the low concentration. Male rats in the mid-concentration group had reduced body weight gain during the first week, but their mean body weights were similar to controls after week 5. Female rats in the mid-concentration group experienced a slight body weight gain reduction during weeks 3 and 4. Body weight gains were depressed in both male and female rats in the high-exposure group for the first 3 weeks of exposure. There was a concentration-related increase in liver, kidney, and adrenal weights relative to body weight of the treatment groups compared with controls. Absolute weights of these organs were also significantly increased, and relative weights were at least 10% greater ($p < 0.01$) than controls for male and female rats in the 4000- and 8000-ppm groups. In the mid- and high-exposure groups, relative weight increases in the males were 20 and 39% in the liver, 12 and 19% in kidneys, and 18 and 55% in adrenals, whereas increases in the females were 13 and 15% in the liver, 13 and 10% in kidneys, and 13 and 29% in adrenals, respectively. The relative lung weight in the high-concentration group was 3.5-6.5% greater than the controls. An increase in the degree, but not frequency, of hemosiderosis within the spleens of males exposed to the high concentration was observed, and there was also a mild increase in number and/or size of hyaline droplets within renal proximal tubules. Consistent with the chronic studies in rats (Chun et al., 1992) and mice (Burleigh-Flayer et al., 1992), the overall weight of evidence indicates that the mid-exposure level is moderately adverse to several organ systems, as indicated by

decreased brain length and increased relative kidney (females), adrenal, and liver weights. Thus, a NOAEL of 797 ppm (2873 mg/cu.m) and a LOAEL of 3920 ppm (14,133 mg/cu.m) were determined.

CD-1 mice and Fischer 344 rats (5/sex/species/group) were exposed to 0, 2000, 4000, and 8000 ppm (0, 7211, 14,421, and 28,843 mg/cu.m) MTBE for 6 hours/day in the 13-consecutive-day, range-finding study (Dodd and Kintigh, 1989). Duration-adjusted exposure levels are 0, 1288, 2572, and 5150 mg/cu.m, respectively. Body weights, organ weights (brain, liver, kidneys, lungs, and adrenals), and individual clinical signs were monitored. Complete necropsy was performed on each animal, and all gross lesions were submitted to microscopy. Detailed behavioral observations were performed on rats only. A statistically significant depression in body weight gain was observed in male rats at the high-exposure concentration. There were no exposure-related effects on absolute body weight or body weight gain for mice. Relative liver weights (both sexes) and relative kidney weights (males only) were increased in rats at the high- and mid-exposure concentrations. Relative adrenal weights were increased at the high concentration in both sexes. Relative brain weights in the female rats in the 8000-ppm group were also significantly reduced. For mice, relative liver weights were increased at all concentrations (females only at the low- and mid-exposure levels). There were no weight changes in the lungs, brains, adrenals, or testes of mice when compared with control mean weights. No treatment-related macroscopic lesions were observed in either species. Reversible behavioral alterations (ataxia, decreased startle and pain reflexes, and decreased muscle tone) were observed in both sexes of rats exposed to 8000 ppm. These data suggested that 2000 ppm was a minimal effect level based on the relative liver weight changes in the female rats.

Greenough et al. (1980) exposed Sprague-Dawley rats (10/sex/group) to MTBE at 250, 500, or 1000 ppm (901, 1802, or 3605 mg/cu.m) 6 hours/day, 5 days/week for 13 weeks (duration-adjusted concentrations are 161, 322, or 644 mg/cu.m, respectively). Controls inhaled air only. Food and water consumption, body and organ weights, clinical signs, ophthalmoscopy, necropsy, and histopathology of animals were reported. Histopathology included examination of one transverse section through the nasal cavity, a series of transverse sections through the larynx and trachea, and one cut through the left lung (control and high-exposure groups) and cuts through both lungs (low- and mid-exposure groups).

No clinical signs were observed. Mean body weights were inconsistent, and differences were less than 10% compared with controls. The 1000-ppm females had significant ($p < 0.05$) reductions in absolute and relative (27% decrease) lung weights compared with controls. The 500- and 1000-ppm males showed a mean decrease of 8% in relative lung weight compared with controls. However, these findings do not appear to be concentration related, are not associated with adverse histopathologic or functional observations, and are not reproduced in the Dodd and Kintigh (1989) study. Significant ($p < 0.05$) differences in the absolute weights of the heart (male) and thymus (female) of 1000-ppm animals, kidneys of 500-ppm males, and adrenals of 250-ppm females were reported, but were not concentration-related changes. Histopathologic effects observed in the nasal cavity, larynx, trachea, and lungs of treated and control animals included focal inflammatory changes (pulmonary lymphoid vascular cuffing, localized polymorphonuclear leukocytes, and alveolar macrophages), epithelial and goblet cell hyperplasia, and congestion (lung only). Although these changes occurred in control and exposed animals, the changes did not appear to be concentration related and may be indicative of infection due to inadequate description of animal husbandry; any attempt to isolate causative organisms precludes conclusion. The possibility thus remains that respiratory effects of MTBE may have been unfounded by concomitant respiratory infection.

Hematologic and clinical chemistry tests were performed only on the control and 1000-ppm groups. Hemoglobin levels were increased ($p < 0.001$), as were BUN levels ($p < 0.05$) in 1000-ppm male rats compared with control values after 13 weeks of exposure. Female rats in the 1000-ppm group showed a

significant decrease ($p < 0.05$) in LDH levels, as well as an increase in glucose and albumin levels. The mean corpuscular hemoglobin concentration (MCHC) increased significantly in 1000-ppm males ($p < 0.01$) and decreased in females ($p < 0.05$). It could not be determined if any changes were concentration related because the two low-concentration groups were not evaluated. These effects are not corroborated by the Dodd and Kintigh (1989) study at higher concentrations. A free-standing NOAEL of 1000 ppm [3600 mg/cu.m; NOAEL(HEC) = 3600 mg/cu.m] was determined for this study based on the lack of treatment-related effects in any organ or system.

Gill (1989) evaluated neurotoxicity of MTBE in a single acute inhalation study in which Fischer 344 rats (22/sex/group) were exposed to 0, 800, 4000, or 8000 ppm MTBE (0, 2884, 14,421, and 28,843 mg/cu.m) for 6 hours. Transient increases in motor activity were observed for males in the 800- and 4000-ppm exposure groups. After 1 hour of exposure, a significant ($p < 0.01$) increase in the incidence of abnormal gait was observed in the 8000-ppm group. This was evidenced by a concentration-dependent increase in the incidence and severity of ataxia and duck-walk gait in males and females at the two highest concentrations. Labored respiratory pattern, increased lacrimation, decreased muscle tone, decreased mean performance on the treadmill, increased mean latency to tail withdrawal reflex, increased mean forelimb grip strength, and increased hindlimb splay were also observed in the 8000-ppm group ($p < 0.01$) at 1 hour of exposure. None of these motor function changes remained after 6 hours of exposure. Results also show that a 6-hour exposure to 8000 ppm MTBE significantly affected the motor activity of rats, especially during the first 50 minutes of the test session. The NOAEL based on these neurologic effects is 4000 ppm (14,421 mg/cu.m), and the LOAEL is 8000 ppm (28,843 mg/cu.m).

A 9-day inhalation study was performed (Bio/Dynamics, 1984) on Sprague-Dawley rats (20/sex/group) in which fasted and nonfasted animals were exposed to concentrations of 101, 300, 1020, and 2970 ppm MTBE vapors (364, 1082, 3677, and 10,708 mg/cu.m) 6 hours/day, 5 days/week. Lacrimation, conjunctival swelling, and corneal changes were observed in both treated and control animals; however, statistical significance was not reported. Although data were not shown, the authors report that there was a greater incidence of these clinical signs in males. A significant increase in the relative liver weight was evident in the fasted animals at 2970 ppm. Relative adrenal weights were significantly elevated in nonfasted, 300-ppm females and relative kidney weights were increased ($p < 0.05$) in nonfasted females exposed to 300 and 2970 ppm. Because a similar trend was not seen in fasted females at these exposure levels, and because these findings apparently were not concentration related, these observations in the nonfasted females are not considered treatment related. Both the nasal mucosa and the trachea were examined microscopically in controls and rats exposed to 1020 and 2970 ppm. Microscopic examinations revealed a significant increase in incidence of chronic inflammation in the nasal mucosa and the trachea at 1020 and 2970 ppm compared with pretest controls, but lung weight was not different from controls.

Savolainen et al. (1985) exposed 3-month-old male Wistar rats (20/group) to 50, 100, or 300 ppm MTBE vapor (181, 361, or 1082 mg/cu.m) 6 hours/day, 5 days/week for 2-15 weeks (duration-adjusted concentrations are 32, 64, or 193 mg/cu.m., respectively). Five animals from each chamber were weighed and sacrificed after weeks 2, 6, 10, and 15. The rats were bled, and their cerebral hemispheres, livers, kidneys, samples of right gluteal muscle (1 g), and samples of perirenal fat (1 g) were taken at autopsy. Although body weights did not differ significantly between groups early in the study, exposed rats did have higher weights than controls by week 15; mean weights were 365 g, 408 g (12% increase), 420 g (15% increase), and 407 g (12% increase) in animals exposed to 0, 50, 100, and 300 ppm, respectively. A significant ($p < 0.05$) concentration-dependent increase in microsomal uridine diphosphate-glucuronosyltransferase activity in liver and kidney, as well as NADPH cytochrome c-reductase activity in kidney, occurred after 2 weeks of exposure. These effects were not observed after 15 weeks of exposure. The study was limited because histopathology was not conducted and organs were not weighed.

Conaway et al. (1985) exposed pregnant Sprague-Dawley rats (23-25/group) and pregnant CD-1 mice (24-29/group) to 0, 260, 1100, or 3300 ppm MTBE (0, 937, 3965, or 11,897 mg/cu.m) 6 hours/day during gestational days 6-15. Maternal body weights were recorded for both species on days 0, 6, 12, 15, and 18 and on day 20 for rats. Physical examinations for signs of toxicity were performed at the same time as weights were recorded. Food and water consumption was recorded for days 6-9, 9-12, 12-15, and 15-18 and for days 18-20 for rats. Dams were sacrificed on day 20 (rats) or day 18 (mice) by carbon dioxide inhalation. Laparotomies were performed, and dams and pups were examined for gross abnormalities. Each fetus was weighed, and crown-rump distance was recorded. Late and early resorptions were scored. When no uterine implantation sites were observed, the uterus was stained to examine the foci of implantation. One-third of the fetuses in each litter were examined for soft-tissue abnormalities, and two-thirds of the fetuses were examined for skeletal abnormalities.

The pregnancy rate in rats was similar for all groups. Organ weights were not significantly different in exposed animals compared with control values. The mean number of corpora lutea, implantations, resorptions, and live fetuses was not significantly different among groups. Fetuses were weighed and examined for deformities, but no significant incidence of soft-tissue or skeletal anomalies was observed. A free-standing NOAEL of 3300 ppm [11,897 mg/cu.m; NOAEL(HEC) = 11,897 mg/cu.m] for reproductive and developmental toxicity effects was determined for rats with no reported maternal toxicity.

In mice, a slight increase in the incidence of lacrimation was observed among females (groups not specified) during exposure. The number of implantations in treatment groups was not statistically different compared with controls. The numbers of resorptions were 17, 11, and 17.3% in the 260-, 1100-, and 3300-ppm groups, respectively, compared with 9% in controls. These differences are of questionable significance because they do not appear to be concentration dependent, and the high number of resorptions in the low- and high-exposure groups were due to nearly complete resorptions in two females of the low-exposure group and complete resorption in two females of the high-exposure groups. Excluding the data for these four females, resorption data for these groups did not differ from controls. Mean fetal weights in treated animals were not significantly different from the controls. Soft-tissue anomalies per litter or per fetus were not found to be different among groups. Although not statistically significant, concentration-related skeletal variations per litter were found to be 2/27 (7.4%) in the control group and 3/26 (11.5%), 4/25 (16%), and 6/27 (22.2%) in the 260-, 1100-, and 3300-ppm groups, respectively. Cleft palates were noted in control (0.7%, 2/281), 260-ppm (0%, 0/265), 1100-ppm (0.4%, 1/251), and 3300-ppm (0.7%, 2/290) groups. A free-standing NOAEL of 3300 ppm [11,977 mg/cu.m; NOAEL(HEC) = 11,977 mg/cu.m] for developmental effects was determined for mice with minimal indications of maternal toxicity.

Pregnant CD-1 mice (30/group) were exposed to MTBE at concentrations of 0, 1035, 4076, and 8153 ppm (0, 3731, 14,695, and 29,394 mg/cu.m) 6 hours/day from gestational days 6 to 15 (Bushy Run Research Center, 1989a). No animals died and none aborted during the exposure period. Three dams at 0 ppm and two dams at 400 ppm delivered early and were removed from the study. The remaining dams were sacrificed on day 18 of gestation. No signs of maternal toxicity were observed in the dams exposed to 1035 ppm. At 4076 ppm, there were slight, but not statistically significant, indications of reduced maternal body weight and body weight gain. Though the only observation for this exposure group reported was lacrimation in one dam, the authors indicate in the abstract and text of the report that hypoactivity and ataxia were observed in dams at 4076 and 8153 ppm. Clinical signs of maternal toxicity, including hypoactivity, ataxia, prostration, labored respiration, lacrimation, and periocular encrustation, were significantly increased at 8153 ppm. Significant reductions in food consumption, body weight, and body weight gain were also observed in dams exposed to 8153 ppm. A NOAEL of 1035 ppm [3731 mg/cu.m; NOAEL(HEC) = 3731 mg/cu.m] and a LOAEL of 4076 ppm [14,695 mg/cu.m; LOAEL(HEC) = 14,695 mg/cu.m] were determined for maternal toxicity.

MTBE did not affect the number of corpora lutea, total implants, or preimplantation loss per litter in any exposure group. There were significant ($p < 0.01$) increases in the number of nonviable implantations per litter, late resorptions, and dead fetuses; and significant reductions in the number of viable implantations ($p < 0.01$), percent of live fetuses ($p < 0.01$), and percent of male fetuses ($p < 0.05$) in the 8153-ppm group. Fetal body weight per litter (male and female) were significantly ($p < 0.01$) decreased at 4076 and 8153 ppm. A significant reduction in the incidence of partial fetal atelectasis and an increase in fetal atelectasis occurred at 8153 ppm. There were 24 skeletal variations (i.e., defects in cervical, thoracic, and caudal centra, forepaws, hindpaws, sternbrae, and skull plates/bones), all indicative of reduced ossification, that were significantly elevated in fetuses at 8153 ppm. There was a decreased incidence of unossified intermediate phalanges of the hindlimb at the high concentration. At 4076 ppm, there were seven skeletal variations related to reduced ossification (cervical centra, forepaw, hindpaw, and sternbrae) that showed a significantly increased incidence. At 1035 ppm, a significantly increased incidence of poorly ossified intermediate phalanges of the hindlimb was found. This finding was probably not treatment related because the alteration was not seen at the higher concentrations. In general, the effects were significant at the $p < 0.01$ level. A NOAEL of 1035 ppm [3725 mg/cu.m; NOAEL(HEC) = 3725 mg/cu.m] and a LOAEL of 4076 ppm (14,670 mg/cu.m) were determined for mice based on fetal body weight reductions with minimal maternal toxicity.

Developmental toxicity in rabbits was also investigated by Bushy Run Research Center (1989b). Pregnant New Zealand white rabbits (15/group) were exposed to 0, 1021, 4058, and 8021 ppm MTBE (0, 3681, 14,630, and 28,918 mg/cu.m) 6 hours/day, during gestational days 6-18. None of the does died, aborted, delivered early, or had to be removed from the study. There were no differences in maternal body weights among the groups. Reduced maternal body weight gain and food consumption were observed during the major period of organogenesis at 4058 and 8021 ppm. However, there were large standard deviations across the groups for body weight gain measurements. Relative liver weight was significantly increased by 14% ($p < 0.05$), and absolute liver weight was slightly, but not significantly, increased in does exposed to 8021 ppm. No histopathologic examination of the liver was conducted. The number of corpora lutea, resorptions, and viable and nonviable implantations were not significantly different among groups. Fetal body weights per litter were not statistically different among groups. There was no significant difference in the incidence of fetal malformations. This study identifies a free-standing NOAEL for developmental toxicity in rabbits of 8021 ppm [28,918 mg/cu.m; NOAEL(HEC) = 28,918 mg/cu.m].

Groups of male and female rats received a single 6-hour exposure to MTBE vapor in nose-only inhalation chambers at targeted MTBE concentrations of 400 and 8000 ppm and daily repeat 6-hour exposures for 15 days at a targeted MTBE concentration of 400 ppm (Ferdinandi et al., 1990). Four rats/sex/group were then euthanized and examined. Steady-state plasma concentrations were reached at approximately 4 to 6 hours for MTBE and roughly 6.5 hours for TBA, the principal metabolite of MTBE. MTBE-metabolizing enzymes were saturated during high-concentration exposure. The elimination half-life ($t_{1/2}$) of MTBE was approximately the same after single low- and high-concentration exposures (0.52 and 0.63 hours, respectively). After the repeat exposures, the MTBE $t_{1/2}$ was slightly shorter (0.48 and 0.51, respectively). The TBA $t_{1/2}$ ranged from 2.8 to 3.4 hours after the low- and high-concentration single exposures. After the repeat exposure regimen, the TBA $t_{1/2}$ was significantly lower (1.8 and 1.5 hours in the male and female rats, respectively). There was a slight, but statistically significant, sex difference in the pharmacokinetics of MTBE (e.g., plasma clearance was faster in females), but no sex differences in the elimination kinetics of TBA were observed.

I.B.5. CONFIDENCE IN THE INHALATION RfC

Study -- Medium
Data Base -- Medium
RfC -- Medium

Confidence in the study is medium. It was well-designed (e.g., with respect to exposure protocol, number of animals, and exposure duration), identified a consistent LOAEL and NOAEL for a constellation of organ systems, and involved extensive histopathology on both sexes. However, the results of the rat study are confounded by the high mortality in the males, which is presumed to be the result of rat chronic nephropathy. Further, the lack of certain information from the chronic bioassay reduces confidence in the study (e.g., urinalysis results, serum chemistry, and limited reporting of motor activity/clinical signs during exposure). Confidence in the data base is medium to high because of the existence of chronic and subchronic bioassays in more than one species, developmental studies in several different species, and the existence of single- and two-generation reproductive studies in the rat. Medium to high confidence in the RfC follows.

I.B.6. EPA DOCUMENTATION AND REVIEW OF THE INHALATION RfC

Source Document -- This assessment is not presented in any existing U.S. EPA document.

Other EPA Documentation -- U.S. EPA, 1989, 1993

Agency Work Group Review -- 06/13/1991, 04/01/1993, 07/21/1993

Verification Date -- 07/21/1993

I.B.7. EPA CONTACTS (INHALATION RfC)

Please contact the Risk Information Hotline for all questions concerning this assessment or IRIS, in general, at (513)569-7254 (phone), (513)569-7159 (FAX) or RIH.IRIS@EPAMAIL.EPA.GOV (internet address).

II. CARCINOGENICITY ASSESSMENT FOR LIFETIME EXPOSURE

Substance Name -- Methyl tert-butyl ether (MTBE)
CASRN -- 1634-04-4

Not available at this time.

VI. BIBLIOGRAPHY

Substance Name -- Methyl tert-butyl ether (MTBE)
CASRN -- 1634-04-4
Last Revised -- 09/01/1993

VI.A. ORAL RfD REFERENCES

None

VI.B. INHALATION RfD REFERENCES

Allen, B. 1993. ICF Kaiser. Telefaxed communication to Jeffrey S. Gift of U.S. EPA. Description of logistic model: Summary of test for trend (unpublished material), June 23.

Biles, R.W., R.E. Schroeder, and C.E. Holdsworth. 1987. Methyl tertiary butyl ether inhalation in rats: A single generation reproduction study. Toxicol. Indust. Health. 3: 519-534.

Bio/Dynamics Inc. 1984. A nine-day inhalation toxicity study of MTBE in the rat (final report vol. 1) (unpublished material). TSCATS/301698. EPA/OTS No. 86870000264.

Burleigh-Flayer, H.D., J.S. Chun, and W.J. Kintigh. 1992. Methyl tertiary butyl ether: Vapor inhalation oncogenicity study in CD-1 mice (unpublished material). Prepared for the MTBE Committee by Bushy Run Research Center, Union Carbide Chemicals and Plastics Company Inc. Docket No. OPTS-42098.

Busey, W.M. 1993. Histopathologic evaluation of kidneys from male and female rats utilized in a vapor inhalation oncogenicity study of methyl tertiary butyl ether. MTBE Task Force Study No. 91N00138 dated July 19, 1993 (unpublished material).

Bushy Run Research Center, Union Carbide Chemicals and Plastics Company Inc. 1989a. Developmental toxicity study of inhaled methyl tertiary butyl ether in CD-1 mice (final report). TSCATS/403186. EPA/OTS No. FYI-OTS-0889-0689.

Bushy Run Research Center, Union Carbide Chemicals and Plastics Company Inc. 1989b. Developmental toxicity study of inhaled methyl tertiary butyl ether in New Zealand white rabbits (final report). TSCATS/403186. EPA/OTS No. FYI-OTS-0889-0689.

Chun, J.S., H.D. Burleigh-Flayer, and W.J. Kintigh. 1992. Methyl tertiary butyl ether: Vapor inhalation oncogenicity study in Fischer 344 rats (unpublished material). Prepared for the MTBE Committee by Bushy Run Research Center, Union Carbide Chemicals and Plastics Company Inc. Docket No. OPTS-42098.

Conaway, C.C., R.E. Schroeder, and N.K. Synder. 1985. Teratology evaluation of methyl tertiary butyl ether in rats and mice. J. Toxicol. Environ. Health. 16(6): 797-809.

Charles River Breeding Laboratories. 1984. Baseline hematology and clinical chemistry values for Charles River Fischer-344 rats-CDF (F-344)Cr1BR as a function of sex and age. January 1984 Technical Bulletin published by the Charles River Breeding Laboratories, Vol. 8, No. 1.

Dodd, D.E. and W.J. Kintigh. 1989. Methyl tertiary butyl ether (MTBE): Repeated (13-week) vapor inhalation study in rats with neurotoxicity evaluation (unpublished material). Prepared for the MTBE Committee by Bushy Run Research Center, Union Carbide Chemicals and Plastics Company Inc. TSCATS 403187. EPA/OTS No. FYI-OTS-0889-0689.

Eldridge, S.R. 1993. Nephropathy in female F344 rats: A summary of the MTBE oncogenicity study and review of historical findings (unpublished material). Attachment to letter to Mr. John Kneiss (Chair of the Synthetic Organic Chemical Manufacturers Association, MTBE Task Force), May 20.

Ferdinandi, E.S., L. Buchanan, and R.G. Alexander. 1990. Pharmacokinetics of methyl tert-butyl ether (MTBE) and tert-butyl alcohol (TBA) in male and female Fischer-344 rats after single and repeat inhalation nose-only exposures to MTBE (unpublished material). Prepared for the MTBE Committee by Bushy Run Research Center, Union Carbide Chemicals and Plastics Company Inc. Docket No. OPTS-42098.

Garman, R.H. 1993a. Bushy Run Research Center. Correspondence to Larry S. Andrews of ARCO Chemical Company. May 3.

Garman, R.H. 1993b. Bushy Run Research Center. Correspondence to Larry S. Andrews of ARCO Chemical Company. May 15.

Gill, M.W. 1989. Methyl tertiary butyl ether single exposure vapor inhalation neurotoxicity study in rats (unpublished material). Bushy Run Research Center, Union Carbide Chemicals and Plastics Company Inc.

Greenough, R.J., P. McDonald, P. Robinson et al. 1980. Methyl tertiary-butyl ether (Driveron) three-month inhalation toxicity in rats (unpublished material). Prepared for Chemische Werke Huls AG, West Germany, by Inveresk Research International. TSCATS/303353. EPA/OTS No. 86-870000172.

Lindamood, C., III, D.R. Farnell, H.D. Giles et al. 1992. Subchronic toxicity studies of t-butyl alcohol in rats and mice. *Fund. Appl. Toxicol.* 19: 91-100.

Maita, K., M. Hirano, T. Harada et al. 1988. Mortality, major cause of moribundity, and spontaneous tumors in CD-1 mice. *Toxicol. Pathol.* 16: 340-349.

Neeper-Bradley, T.L. 1991. Two-generation reproduction study of inhaled methyl tert-butyl ether in CD Sprague-Dawley rats (unpublished material). Bushy Run Research Center, Union Carbide Chemicals and Plastics Company Inc.

NTP (National Toxicology Program). 1987. Toxicology and carcinogenesis studies of dimethyl methylphosphonate (CAS No. 756-79-6) in F344/N rats and B6C3F1 mice (gavage studies). NIH Publication No. 88-2579.

Ponchon, T., J. Baroud, B. Pugol et al. 1988. Renal failure during dissolution of gallstones by methyl tert-butyl ether. *Lancet.* 2: 276-277.

Robinson, M., R.H. Bruner, and G.R. Olson. 1990. Fourteen- and ninety-day oral toxicity studies of methyl tertiary-butyl ether in Sprague-Dawley rats. *J. Am. Coll. Toxicol.* 9: 525-539.

Savolainen, H., P. Pfaffli, and E. Elovaara. 1985. Biochemical effects of methyl tertiary-butyl ether in extended vapour exposure of rats. *Arch. Toxicol.* 57: 285-288.

Swenberg, J.A. and D.R. Dietrich. 1991. Immunohistochemical localization of alpha-2u-globulin in kidneys of treated and control rats of a 13-week vapor inhalation study undertaken with methy tertiary butyl ether (MTBE). Report to John Kneiss (Manager, MTBE Task Force), July 26, 1991.

Thistle, J.L. 1992. Direct contact dissolution therapy. Clin. Gastroenterol. 6: 715-725.

Tukey, J.W., J.L. Ciminera, and J.F. Heyse. 1985. Testing the statistical certainty of a response to increasing doses of a drug. Biometrics. 41: 295-301.

U.S. EPA. 1989a. Proposed amendments to the guidelines for the health assessment of suspect developmental toxicants. Federal Register. 54: 9386-9403.

U.S. EPA. 1989b. Reportable Quantity Document for Methyl Tertiary Butyl Ether. Prepared by Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office, Cincinnati, OH for the Office of Solid Waste and Emergency Response, Washington, DC.

U.S. EPA. 1991. Alpha-2u-globulin: Association with chemically induced renal toxicity and neoplasia in the male rat. Risk Assessment Forum. EPA/625/3-91/019F.

U.S. EPA. 1993. MTBE-oxygenated gasolines and public health issues. Office of Research and Development, Washington, DC.

VI.C. CARCINOGENICITY ASSESSMENT REFERENCES

None

VII. REVISION HISTORY

Substance Name -- Methyl tert-butyl ether (MTBE)
CASRN -- 1634-04-4

Date	Section	Description
08/01/1991	I.B.	Inhalation RfC now under review
12/01/1991	I.B.	Inhalation RfC on-line
12/01/1991	VI.	Bibliography on-line
03/01/1993	I.A.	Oral RfD now under review
05/01/1993	I.B.	Inhalation RfC noted as pending change
05/01/1993	I.B.6.	Work group review date added
08/01/1993	I.B.	Withdrawn; new RfC verified (in preparation)
08/01/1993	I.B.6.	Work group review date added
08/01/1993	I.B.7.	EPA contact changed
08/01/1993	VI.	Bibliography withdrawn

09/01/1993 I.B. Inhalation RfC replaced; RfC changed
09/01/1993 VI.B. Inhalation RfC references on-line

VIII. SYNONYMS

Substance Name -- Methyl tert-butyl ether (MTBE)
CASRN -- 1634-04-4
Last Revised -- 12/01/1991

1634-04-4
Propane, 2-methoxy-2-methyl-
methyl tert-butyl ether
T-BUTYL METHYL ETHER
Ether methyl tert-butylique [French]
Ether, tert-butyl methyl
HSDB 5847
METHYL 1,1-DIMETHYLETHYL ETHER
METHYL-tert-BUTYL ETHER
Methyl-tert-butylether
Metil-terc-butileter [Spanish]
tert-Butyl methyl ether
2-METHOXY-2-METHYLPROPANE
2-METHYL-2-METHOXYPROPANE

[IRIS Home Page](#)

[Substance File List](#)



**Send
Comments**



Search



**NCEA
Home Page**



**ORD
Home Page**



**EPA
Home Page**

Last updated: 5 May 1998

URL: <http://www.epa.gov/iris/subst/0545.htm>

STATE OF ILLINOIS)
)
COUNTY OF SANGAMON)

PROOF OF SERVICE

I, the undersigned, on oath state that I have served the attached Final Comments upon the person to whom it is directed, by placing a copy in an envelope addressed to:

Dorothy M. Gunn, Clerk
IL. Pollution Control Board
James R. Thompson Center
100 W. Randolph, Ste 11-500
Chicago, Illinois 60601

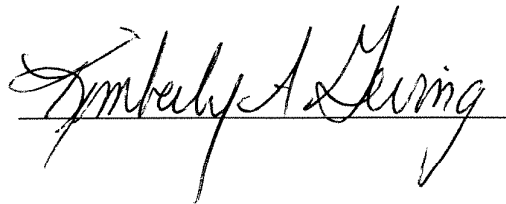
Matthew J. Dunn, Chief
Environmental Bureau
Office of the Attorney General
188 W. Randolph, 20th Floor
Chicago, Illinois 60601

Amy Jackson, Hearing Officer
IL. Pollution Control Board
500 South Second Street
Springfield, Illinois 62706

Robert Lawley, Chief Legal Counsel
Dept. Of Natural Resources
524 South Second Street
Springfield, Illinois 62701-1787

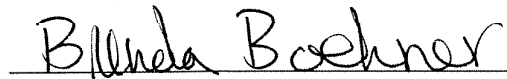
Service List

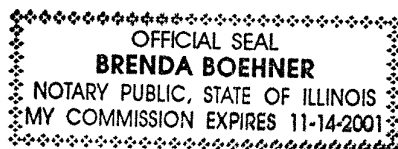
and mailing it from Springfield, Illinois on 10/23/00 with sufficient postage affixed.



SUBSCRIBED AND SWORN TO BEFORE ME

this 23 day of October


Notary Public



SERVICE LIST: R00-19
 PROPOSED AMENDMENTS TO TIERED APPROACH TO CORRECTIVE ACTION OBJECTIVES
 August 28, 2000

lname	fname	company	Address	citystate	zip
Anderson	Joan G.	Joan G. Anderson, Ltd.	PMB #202 4700 Gilbert Road, Suite 47	Western Springs, IL	60558
Anderson	Steve	Admiral Environmental Services, Inc.	2025 S. Arlington Heights Road, Suite 103	Arlington Heights, IL	60005-4141
Bianco Curley	Chris Erin	CICI Environmental Dept. Manager	9801 Higgins Road, Suite 515	Rosemont, IL	60018
Dickett	William G.	Midwest Engineering Services Sidley & Austin	4243 West 166th Street	Oak Forest, IL	60452
Dunn	Matthew J.	Chief, Environmental Bureau	Bank One Plaza 10 South Dearborn	Chicago, IL	60603
Geving	Kimberly A.	Office of the Attorney General EPA, Division of Legal Counsel	188 W. Randolph Street, 20th Floor	Chicago, IL	60601
Gobelman	Steven	IDOT Design & Environment	1021 N. Grand Avenue East P.O. Box 19276	Springfield, IL	62794-9276
Gunn	Dorothy	Clerk of the Board Illinois Pollution Control Board	2300 South Dirksen Parkway	Springfield, IL	62764
Hambley	Douglas F.	Gravis, Antlaly, Schloemer & Associates, Inc.	100 W. Randolph St., Suite 11-500	Chicago, IL	60601
Heyde, Esq.	John M.	Sidley & Austin	8501 W. Higgins Road, Suite 280	Chicago, IL	60631-2801
Hochwarter	John W.	Missman, Stanley & Associates	Bank One Plaza 10 South Dearborn	Chicago, IL	60603
Hodge, Esq.	Katherine D.	Hodge & Dwyer	333 East State Street P.O. Box 4327	Rockford, IL	61110-0827
Jackson Jacobs Jamison Keefer Lawley	Amy Richard George Don Robert T.	Illinois Pollution Control Board Thompson Coburn Hanson Engineers Illinois State Geological Survey Chief Legal Counsel	3150 Roland Avenue P.O. Box 5776	Springfield, IL	62705-5776
Mankowski Marszalek Nienkerk	Bob Mark Monte	Department of Natural Resources EPI Andrews Environmental Engineering Clayton Group Services	600 South Second Street, Suite 402 One Firststar Plaza 3971 Bison Trail 615 East Peabody Drive 524 South Second Street 16650 South Canal Street 3535 Mayflower Blvd. 3140 Finley Road	Springfield, IL St. Louis, MO Rockster, IL Champaign, IL Springfield, IL South Holland, IL Springfield, IL Downers Grove, IL	62704 63101 62563 61820 62701 60473 62707 60515

SERVICE LIST: R00-19
 PROPOSED AMENDMENTS TO TIERED APPROACH TO CORRECTIVE ACTION OBJECTIVES

August 28, 2000

Peterson	IERG	215 East Adams	Springfield, IL	62701
Reed	Jenner & Block	One IBM Plaza, 39th Floor	Chicago, IL	60611
Richardson	Commonwealth Edison	10 South Dearborn	Chicago, IL	60603
Rieser	Environmental Services Department	150 North Michigan, Suite 2500	Chicago, IL	60601
Sargis	Ross & Hardies	19 South LaSalle Street, Suite 1203	Chicago, IL	60603
Schick	Mauck Bellande & Cheely	2300 South Dirksen Parkway	Springfield, IL	62764
	IDOT			
	Legal Department			
Soutter	Conestoga-Rovers & Associates	8615 West Bryn Mawr	Chicago, IL	60631
Steinhour	Weaver, Boos & Gordon	2021 Timberbrook Lane	Springfield, IL	62702
Trivedi	Trivedi Associates, Inc.	2055 Steeplebrook Court	Naperville, IL	60565
Vamos	DAI Environmental, Inc.	5 Revere Drive, Suite 310	Northbrook, IL	60062
Vlahos	Office of Counsel	2601 A Paul Jones St.	Great Lakes, IL	60083
Vogel	Naval Training Center			
Walton	The Stolar Partnership	911 Washington Avenue, 7th Floor	St. Louis, MO	63101
Yonkauski	Site Remediation Advisory Comm.	2520 Brooks Drive	Decatur, IL	62521
Zolyak	Department of Natural Resources	524 South Second Street	Springfield, IL	62701
	Department of Defense Regional	5179 Hoadley Road, Bldg. E-4460	Aberteen, MD	21010-5401
	U.S. Army Env. Center			