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Santa Barbara

Determination of the Ecological Risk Associated with a Groundwater Plume of MTBE at Port Hueneme, CA

A Group Project submitted in partial satisfaction
for the requirements for the degree of

Master of Environmental Science and Management

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2000

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Executive Summary

The Donald Bren School of Environmental Science and Management's MTBE2000 project involved performing an Ecological Risk Assessment (ERA) on the subsurface contamination caused by a release of gasoline at the Port Hueneme Naval Facilities Engineering Service Center.

Due to a leaking delivery line/joint fixture between the main underground gasoline storage tank and the distribution module, approximately 11,000 gallons of gasoline was released to the subsurface environment between September 1984 and March 1985 from the Naval Exchange Gasoline Station. This leak produced an extensive 4,600 foot groundwater plume of methyl tertiary butyl ether (MTBE) in the groundwater, which currently covers approximately 45 acres, and a much shorter plume near the source containing benzene, toluene, ethylbenzene, and xylene (BTEX).

Through consultation with an initial Ecological Risk Screening performed on the site in 1998 and the Environmental Protection Agency's Guidelines for Ecological Risk Assessment, Team MTBE2000 determined that soil microorganisms were the most relevant ecological endpoint at risk. A literature review on the effects of MTBE on soil microbial communities indicated that very little research had been conducted on the effects of MTBE on microbes. The Team designed and performed a field experiment aimed at elucidating the relationships between MTBE and BTEX concentrations and toxicity to microbial organisms.

The results of the field experiment indicate that MTBE and BTEX concentrations could not be correlated with toxicity, as measured by the effective concentration at which metabolic activity was decreased by 50 percent, within the plume. Toxicity was measured nearest the source of the release, where MTBE and BTEX were found at very low concentrations during the three-month experimental period. We conclude that either the breakdown products of MTBE and BTEX, or the synergistic relationship between these products, caused the observed toxicity. Further research is needed to better define the source of the toxicity. In addition, the results suggest that natural attenuation rates for BTEX constituents were not retarded by the presence of MTBE.

In concluding the ERA process, Team MTBE2000 has offered recommendations for remediation of the contaminated area. It should be noted, however, that based on the current levels of MTBE and BTEX found, no remediation is

necessary on site, since there is no human health risk and ecological risk is limited to subsurface microbial communities. If remediation is considered in the future, the best remediation alternative, based on both plausibility and cost-benefit analysis, is air stripping.

The Ecological Risk Assessment process is a useful tool for making risk management decisions, however, there are some areas of the process which could be improved. Through our experiences, the Team has developed an extensive critique on the inherent subjectivity of the process, as well as a discussion of alternative methods of addressing risk. One of the most important criticisms is that an ERA is only mandated in response to an event (after it occurs) rather than taking a proactive role to prevent ecological damage.

Project Objectives

The primary objective of this project was to determine the risk associated with a groundwater plume of MTBE located at Port Hueneme. The two most common forms of risk analysis are Ecological Risk Assessments (ERA) and Risk-Based Corrective Actions (RBCA) (RBCA Services 1998). An RBCA is designed to protect human health and environmental resources, but it does not take any of the broader ecosystem concerns into consideration (RBCA Services 1998). In contrast, an ERA estimates the nature and likelihood of effects of human actions on non-human organisms, populations, and ecosystems.

The MTBE2000 Team was charged with performing an ERA, rather than a RBCA, because an ERA, in addition to considering the ecology of the site, is more rigorous in its approach to estimation of effects and uncertainties (RBCA Services 1998). An ecological risk assessment is characterized by a standard paradigm that includes problem formulation, analysis of exposure and effects, risk characterization, and communication with a risk manager. For this assessment, the risk manager is the United States Navy.

The technical scope of the project was defined by the Navy's Three Tiered Ecological Risk Assessment procedure to evaluate the existing groundwater plume of MTBE. Tier One of this procedure consisted of performing an initial risk screening. In completing Tier Two, an Ecological Risk Assessment was performed, as directed by the methodologies outlined in the Environmental Protection Agency (EPA) Guidelines (EPA 1998). Finally, in Tier Three, different remediation technologies were examined and a cost-benefit analysis was created to identify the best available alternative.

In order to complete the ERA, Team MTBE2000 collected data from external sources that was essential to the assessment of ecological risk and, in the Spring and Summer of 1999, developed a field and laboratory experiment to fill gaps in the data. Conducting an independent experiment provided Team members with significant experience in the fields of toxicology and contaminant modeling, experimental design, practical laboratory work, laboratory equipment and procedures, and the use of bioassays. Furthermore, Team MTBE2000 members applied statistics and improved their abilities to interpret experimental results and generate conclusions based on these results.

Team members gained knowledge of various remediation strategies and had an opportunity to interpret cost-benefit analyses. By producing recommendations for future research, Team MTBE2000 members made the important transition from reliance on scientific data to generating management recommendations.

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In performing the Navy's Three Tiered ERA procedure, Team members coordinated extensively with Navy personnel. An initial meeting with interested stakeholders was held in April of 1999 and significant correspondence with experts in the fields of groundwater monitoring, ecotoxicology, and remediation strategies occurred throughout the entire project. In addition, Team members became familiar with the Ecological Risk Assessment Guidelines outlined by the EPA and conducted extensive research and data collection. A model describing the fate and transport of MTBE in the groundwater was developed, using both conceptual and computerized techniques. In addition, a thorough critical analysis of the Ecological Risk Assessment process was generated. Completing the third Tier provided Team members with an interdisciplinary experience within scientific, management, and policy disciplines.

Background Information

In order to understand the relevance of the MTBE2000 project, it is first essential to appreciate the role of MTBE in gasoline and its history in California. Beginning in April of 1996, California Phase 2 Reformulated Gasoline (CaRFG2) was required statewide. CaRFG2 must have an oxygenate content of 1.8 to 2.2 percent by weight (Keller et. al. 1998). Oxygenates are used in gasoline in order to promote more efficient combustion, thereby lowering local carbon monoxide and ozone pollution levels. According to the Vermont Agency of Natural Resources (2000), when compared to conventional gasoline, combustion of reformulated gasoline decreases pollution levels of many atmospheric pollutants: benzene by 24 percent, carbon monoxide by 13 percent, nitrogen oxide by 3 percent, hydrocarbons by 15 percent, and particulates by 15 percent. Although the state mandate requiring the use of oxygenates in gasoline did not specify the use of a particular oxygenate, economic factors led most refiners to select MTBE in order to meet both state and federal oxygenated fuel requirements.

MTBE is also used in reformulated gasoline nationwide. Currently, 30 percent of the gasoline sold in this country is reformulated and 76 percent of this gasoline contains MTBE at approximately 11 percent by volume (Osinski 1998). Prior to the recent controversies surrounding MTBE, use of MTBE had drastically increased since the 1970s (Keller et. al. 1998). In 1990, approximately 100,000 barrels of MTBE were used every day in California (Keller et. al. 1998).

The use of MTBE in gasoline has had unforeseen consequences. Due to its high solubility in water and tendency to resist biodegradation, MTBE migrates with the groundwater and has contaminated many drinking water sources. In a recent study performed by the University of California, it was estimated that, by the year 2010, between 1 and 5 percent (100 to 700 wells) of the public water supply may be impacted by MTBE (Keller et. al. 1998). It is important to note that this estimate ignores the threat to private wells, which have a high risk of contamination and are rarely tested for contaminants.

MTBE significantly alters the taste and odor of water and the EPA has classified it as a potential human carcinogen (U.S. EPA 1993). The California Department of Health Services has established secondary and primary drinking water standards, which are known as Maximum Contaminant Levels (MCLs). Secondary Maximum Contaminant Levels (MCLs) are those levels that are not to be exceeded in drinking water supplied to the public, because they alter the taste, odor, or appearance of drinking water. Title 22 of the California Code of Regulations (22 CCR 64449) identifies the secondary MCL for MTBE at 5 micrograms per liter (µg/L). In addition, primary MCLs are also established for

a contaminant. This level is legally binding and should not be exceeded in the water supplied to the public. The primary MCL is established at a level that is as close as is technically and economically feasible to the public health goal (PHG). While a primary MCL for MTBE has not yet been established, it has been proposed that the value be set at the public health goal for MTBE, 13 μg/L. This public health goal was established by the California Department of Health Services in March of 1999. In response to the threat of drinking water contamination, California Governor Gray Davis recently mandated that MTBE be phased out of California gasoline by December 31, 2002.

However, the primary and secondary drinking water standards apply only to water that is used for, or has the potential to be used for, public water supply. Since the MTBE contaminated aquifer located at Port Hueneme is not a source of public water, it is held to different standards. These standards are determined by the intended use of the water and the potential exposure pathways. The water in the contaminated aquifer will not be pumped or used for any purposes, so there is no required level to remediate to, although political pressures to remediate have increased in recent months (Associated Press 2000).

In addition to the potential human effects associated with MTBE, the chemical may also have measurable effects on plants, animals, and subsurface organisms. Laboratory experiments, which estimate the concentration of a chemical at which 50 percent of experimental rats die (LC50 or LD50), indicate that MTBE has a moderate acute (short term) toxicity from ingestion (U.S. Department of Health and Human Services 1993). Other studies have examined the toxicity of MTBE to freshwater and marine organisms. Mancini et. al. (1999) report preliminary calculations of freshwater concentrations at which no adverse effects are expected for a range of organisms tested. The values for acute and chronic (long term) exposures are 151 and 51 mg MTBE/L, respectively. Calculations of marine concentrations at which no adverse acute and chronic effects occur are 50 and 17 mg MTBE/L, respectively (Mancini et. al. 1999). Therefore, MTBE has the potential to adversely affect both freshwater and marine organisms, depending on the concentration and duration of exposure.

Methods

The methods employed by the MTBE2000 Team to produce the required Ecological Risk Assessment (ERA) were directed by the Naval Policy for Conduction of Ecological Risk Assessments. The procedures defined below have been set forth by the U.S. Navy's Three Tiered approach (Navy 1999).

Tier One: Screening Risk Assessment

A preliminary Ecological Risk Screening was commissioned by the Navy and conducted in August of 1998 (Hunt 1998). This report, which used only existing data, concluded that there was little or no potential ecological risk caused by the MTBE plume at Port Hueneme. This report completed Tier One of the Navy's Ecological Risk Assessment procedure and is included as an appendix to this document (Appendix A).

Tier Two: Baseline Ecological Risk Assessment

An Ecological Risk Assessment serves as the second Tier of this process. Team MTBE2000 completed an ERA by following the Environmental Protection Agency guidelines approved for use by the initiators of the project, the U.S. Navy. The EPA divides the Ecological Risk Assessment procedure into three stages: problem formulation, analysis, and risk characterization. A schematic outline of the ERA process is provided as Figure B-1.

➢ **Stage One: Problem Formulation**

After an Ecological Risk Assessment had been deemed necessary by the Navy, the scale and focus of the project was identified. The goals of the first stage were to identify the assessment endpoints (sensitive ecological receptors) and to create a conceptual model of the ecosystem interactions.

Purpose identification .... Why is a ERA needed?
Problem definition .... What is the scope of the ERA?
Problem characterization .... What are potential pathways / receptors?
Risk characterization and analysis ....
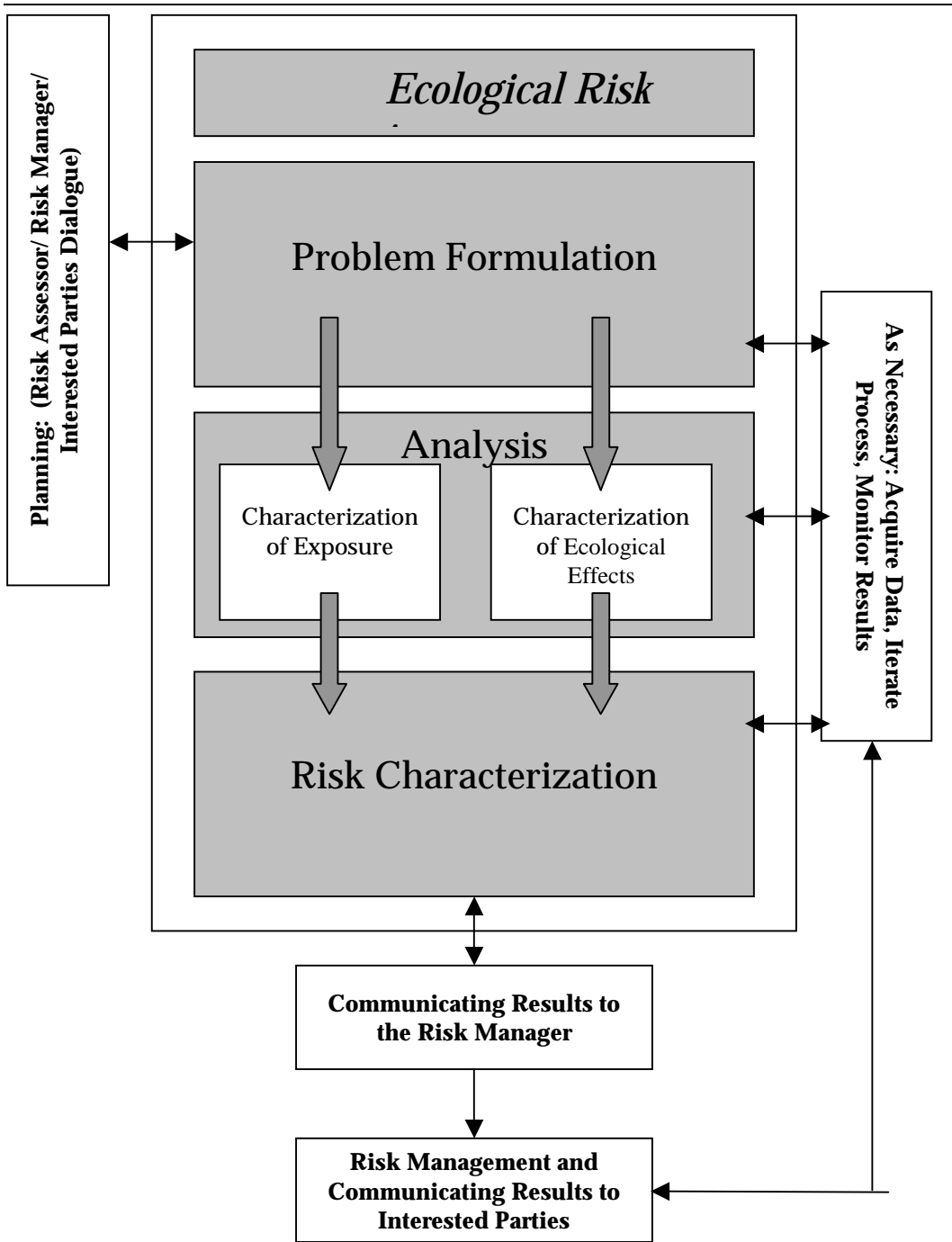
Figure B-1. Framework for Ecological Risk Assessment (adapted from U.S. EPA Guidelines, 1998)

> **Stage Two: Analysis**

During the early stages of performing this Ecological Risk Assessment, soil microbiota were selected as the assessment endpoint to be considered. The details of the selection process can be find in Section 1.6.1 of the ERA document. The MTBE2000 Team compiled published literature relating MTBE levels to the health of soil microbes and found a lack of pertinent data. In an attempt to resolve this issue, Team MTBE2000 developed an independent experimental design and methodology described in detail in the formal report which can be found on pages 81-103 of this document. Generous support from the United States Naval Facilities Engineering Service Center (USNFESC) and the University of California Toxic Substances and Teaching Program's Coastal Contaminant Fund (UC Toxics) facilitated this experiment.

> **Field and Laboratory Experiment**

The primary goal of the experiment was to expand the scope of the ERA to include the existing and potential toxic effects of the presence of MTBE in the groundwater. A bioassay was conducted in order to identify areas of toxicity and extrapolate the toxicity of the groundwater to both aquifer and marine organisms. To fulfill this goal, the MTBE2000 Team used the Microtox™ Acute Toxicity Test to analyze groundwater samples over a three month period.

We felt that a microbial toxicity test should be performed in conjunction with this risk assessment because microorganisms perform a multitude of specific functions within the ecosystem at Port Hueneme. They play an essential role in the geochemical cycling of many nutrients and are indispensable for the elimination of environmental pollutants.

The ecological endpoint selected for this ERA is a microorganism; thus, it was decided that a biological assay using microorganisms would provide the most applicable data. A search of possible microorganism-centered assays was performed by examining the literature to determine which bioassays were appropriate. The Microtox™ bioassay for determining acute toxicity was chosen based on its accessibility, frequency of citations within the literature, and its quantification of the toxicity to microorganisms.

Comparison of the Microtox™ bioassay to other aquatic toxicity bioassays showed that the Microtox™ test produces consistently robust results, although Microtox™ is considered by some to be "more sensitive" to toxicity than traditional bioassays (Qureshi et. al. 1998). In addition, Microtox™ has been identified as the "best available choice" for conducting toxicology screenings and assessments (Qureshi et. al. 1998). Microtox™ is now one of the most thoroughly characterized and validated aquatic bioassays in the world, engendering more than 500 publications, which testify to its place in the arena of toxicity testing (Qureshi et. al. 1998). It has been extensively used worldwide for over 18 years for toxicity screening of chemicals and effluents, water quality and sediment contamination surveys, and environmental risk assessment (Qureshi et. al. 1998).

Team MTBE2000 analyzed the results of this experiment and drew conclusions about the effect of both MTBE and BTEX on microorganisms. After synthesizing the data, we compared the results of this experiment to existing aquatic toxicity data to aid in the interpretation of the data. The experimental design combined the best toxicity analysis tool at our disposal with traditional Gas Chromatography and Mass Spectroscopy so that MTBE and BTEX concentrations, toxicity levels, as well as the spatial and temporal variations of each could be taken into consideration.

➢ **Stage Three: Risk Characterization**

Following the Stage Two assessment, we summarized the assumptions and uncertainties in the conceptual model, as well as in the data itself. A high degree of effort went into illustrating the degree of uncertainty associated with each phase of the ecological risk analysis. Both the error levels associated with current MTBE concentrations and the range of responses and tolerances for organisms were identified, along with information about the site that may potentially change in the future. In addition, the relationships of the data to the risk assessment questions were examined. Finally, the information was related to risk management decisions.

Team MTBE2000 synthesized information from the previous ecological risk screening with current field research, previously published research, and personal communications with the Team's internal and external advisors to complete the Second Tier.

Tier Three: Evaluation of Remediation Alternatives

In order to complete Tier Three, the Team gathered information about available remediation strategies, including techniques currently implemented at Port Hueneme. These alternatives were evaluated based on their potential environmental impacts, costs, and technical merits and benefits, as directed by the Tier Three guidelines. The product of this evaluation can be found on pages 105-119 of this document.

Results—Work Products

Included in this document are the products generated through this group project process.

(1)   The ecological risk assessment created by Team MTBE2000 follows on pages 13-79. Although the introductory material may appear, at times, to be repetitive, the formal document must contain the information when it is submitted to the Navy.

(2)   The experimental write-up is can be found on pages 81-103 of this report.

(3)   The report containing remediation alternatives and their individual merits is included on pages 105-119 and represent completion of the Navy's Tier Three.

Final Report

Ecological Risk Assessment

Evaluation of the Ecological Risk
Associated with a Groundwater
Plume of MTBE at Port Hueneme, CA

March 2000

Presented by:

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1.0   Problem Formulation

Beginning in April of 1996, California Phase 2 Reformulated Gasoline was required statewide. California Phase 2 Reformulated Gasoline must have an oxygenate content of 1.8 to 2.2 percent by weight (Keller et. al. 1998). Oxygenates in gasoline act to promote more efficient combustion, thereby lowering local carbon monoxide and ozone pollution levels. According to the Vermont Agency of Natural Resources (2000), when compared to conventional gasoline, reformulated gasoline results in decreases in pollution levels of benzene by 24 percent, carbon monoxide by 13 percent, nitrogen oxide by 3 percent, hydrocarbons by 15 percent and particulates by 15 percent. Although the state mandate requiring the use of oxygenates in gasoline did not specify the use of a particular oxygenate, most refiners selected MTBE in order to meet both state and federal oxygenated fuel requirements.

MTBE is used in reformulated gasoline nationwide. Currently, 30 percent of the nation's gasoline is reformulated and 76 percent of this gasoline contains MTBE at approximately 11 percent by volume (Osinski 1998). Prior to the recent controversies surrounding MTBE, use of MTBE had drastically increased since the 1970s (Keller et. al. 1998).   In 1990, approximately 100,000 barrels of MTBE were used every day in California (Keller et. al. 1998).

The use of MTBE in gasoline has had unforeseen consequences. Due to its high solubility in water and tendency to resist biodegradation, MTBE migrates with the groundwater and has contaminated many drinking water sources.   In a recent study performed by the University of California, it was estimated that, by the year 2010, between 1 and 5 percent (100 to 700 wells) of the public water supply may be impacted by MTBE (Keller et. al. 1998). This estimate ignores the threat to private wells, which have a high risk of contamination and are rarely tested for contaminants.

Low levels of MTBE can significantly affect the taste and odor of water. The California Department of Health Services has established secondary and primary drinking water standards, which are known as maximum contaminant levels (MCLs). Secondary Maximum Contaminant Levels (MCLs) are those levels which are not to be exceeded in drinking water supplied to the public, because they alter the taste, odor or appearance of drinking water. Title 22 of the California Code of Regulations (22 CCR) 64449 identifies the secondary MCL for MTBE at 5 micrograms per liter

(µg/L). In addition, primary MCLs are also be established for a contaminant. This level is legally binding and should not be exceeded in the water supplied to the public. The primary MCL is established at a level that is as close as is technically and economically feasible to the public health goal (PHG). While a primary MCL for MTBE has not yet been established, it has been proposed at the public health goal for MTBE, which is 13 µg/L. This public health goal was established by the California Department of Health Services in March of 1999. Due to the threat of drinking water contamination, California Governor Gray Davis recently mandated that MTBE be phased out of California gasoline by December 31, 2002.

1.1 Stressor Characteristics

Methyl tertiary butyl ether (MTBE) is highly soluble in water, highly volatile, and does not strongly sorb onto soils. Therefore, upon contact with groundwater, MTBE will mix with the groundwater and will be transported downgradient. Other gasoline components (such as benzene, toluene, ethylbenzene, and xylene [BTEX]) have relatively low solubilities and low vapor pressures. As a result, when BTEX constituents are released into the environment, they will not mix extensively with the groundwater and will remain relatively close to the source of the spill.

When released to the subsurface environment, chemicals can pool together to form a non-aqueous phase liquid (NAPL). Chemicals can partition into and out of the groundwater from the NAPL phase through erratic release events, which can result in the appearance of contaminants in the water column long after the initial leak or spill (EPA 1995). Both MTBE and BTEX are both capable of existing in the NAPL phase.

1.1.1 Physicochemical Properties of Contaminants

The tendency for a chemical to volatilize from water can be accurately estimated by examining the Henry's Law constant. MTBE has a much lower Henry's constant than BTEX constituents, which indicates that it will not easily volatilize once in the water. BTEX constituents have

relatively low Henry's constants, indicating that they will also partition to the water phase and will be slow to transfer to the gas phase.

Soil adsorption coefficients are an indication of how strongly a compound will bind to the organic matter found in soils; the larger the value of the soil adsorption coefficient, the more strongly the contaminant will bind. An examination of soil adsorption coefficients indicates that BTEX constituents will more strongly sorb onto soil sediments than MTBE, which again indicates that BTEX will be confined to a smaller area around the source of contamination.

Table 1 contains the literature values of these properties of MTBE and BTEX for comparison.

1.1.2   Toxicity of MTBE and BTEX to Organisms

Several studies have been performed to determine the acute (short-term) and chronic (long-term) toxicity of both MTBE and BTEX. Estimates based on studies that aim to find the lethal concentration (LC50) or lethal dose (LD50) at which 50 percent of rats die indicate that MTBE has a moderate acute toxicity from ingestion (U.S. Department of Health and Human Services 1993). Similar studies performed on rats, mice, rabbits, and guinea pigs indicate that benzene also has a moderate acute toxicity from ingestion (Agency for Toxic Substances and Disease Registry 1991). In addition, acute animal tests in rats and mice have shown toluene to have low acute toxicity by oral exposure (Agency for Toxic Substances and Disease Registry 1992). Furthermore, laboratory estimates of LC50 and LD50 values for rats and mice orally exposed to ethyl benzene and xylenes indicate moderate toxicity (U.S. Department of Health and Human Services 1993).

In addition, several studies have examined the toxicity of MTBE to freshwater and marine organisms. As reported by Mancini et. al. 1999, preliminary calculations have been conducted to determine the freshwater concentrations of MTBE at which no observable adverse effects (NOAEL) are

expected for a range of organisms. Mancini et. al. (1999) found the NOAEL for acute exposure to be 151 mg/L and 51 mg/L for chronic exposure. Similar tests show that, for MTBE concentrations in marine environments, NOAEL for acute and chronic effects occur are 50 and 17 mg MTBE/L, respectively.

Bioaccumulation occurs when the concentration of a contaminant within an organism is greater than that present in the environment where the organism exists. The bioaccumulation of a substance is determined by considering values for both the bioconcentration factor and the octanol/water partition coefficient. For MTBE, bioconcentration factors range from 0.8 to 1.5 and the octanol/water partition coefficient ranges from 17.2 to 17.5, which indicate a low potential for bioaccumulation (Mancini et. al. 1999). Given these low bioconcentration factors, it is unlikely that MTBE will accumulate in the indigenous microorganism community.

1.1.3 Toxicity of MTBE and BTEX to Humans

Although human responses are not typically included in an Ecological Risk Assessment, human response has been described briefly here because it illustrates general toxicity information and may prove important in the overall findings of the ERA. Humans are sensitive to the presence of MTBE: it can be tasted and smelled at very low levels in drinking water. MTBE significantly alters the taste and odor of water, which makes drinking water contamination an issue. It should also be reinforced at this time that the EPA has classified MTBE as a potential human carcinogen.

As mentioned earlier in this report, the primary and secondary drinking water standards apply only to those waters that are used for, or have the potential to be used for public water supply. Since the MTBE contaminated aquifer located at Port Hueneme will not be used as a source for public water supply, it is held to different standards. These standards are determined by the intended use of the water and the potential exposure pathways. In this case, since the water will not be pumped and used for any purposes, there is no required remediation level.

Benzene is a known human carcinogen and leukemia is the most common form of cancer associated with benzene exposure. Leukemia has been reported in humans exposed to benzene for periods of less than 5 years to over 30 years (EPA 1994b). Due to human health concerns, the EPA has set the maximum acceptable level of benzene in drinking water at 5 μg/L, and the California Department of Heath Services has further restricted this level to 1 μg/L. However, it should be noted that since this is an Ecological Risk Assessment, potential effects on humans will not be considered further.

1.1.4 Degradation of MTBE and BTEX in the Environment

It has been shown that, under aerobic conditions, all components of BTEX can be biodegraded (Salanitro 1993). In addition, research has indicated that, under anaerobic conditions, BTEX constituents can be degraded if iron (III), sulfate, or nitrate are available to serve as electron acceptors. Lovely (1997) asserts that BTEX will first be broken down aerobically, and as oxygen is depleted, microorganisms will begin to break the BTEX down anaerobically by using iron (III) as the electron acceptor. Over time, as the iron (III) is depleted, the microorganisms will then begin using sulfate as the acceptor and, as that becomes depleted, the microorganisms will eventually begin degrading the BTEX through methanogenesis (Lovely 1997).

The results of Borden et. al. (1997) and Davis et. al. (1999) agree with Lovely's description of BTEX biodegradation. Borden et. al. (1997) found that under ambient conditions all BTEX components are degraded during downgradient transport in the aquifer. They found that toluene and ethylbenzene were removed first, followed by removal of m- and p-xylene, which was followed by removal of o-xylene and benzene. Davis et. al. (1999) also found that BTEX degradation will occur in groundwater aquifers. They calculated degradation rates (half-lives) for benzene (over 800 days), toluene (100 to 120 days) and p-xylene (170 to 225 days). Therefore, substantial evidence indicates that significant biodegradation of BTEX will occur within groundwater aquifers either by aerobic or anaerobic metabolic pathways.

In contrast, there is only limited evidence of MTBE biodegradation. A study by Yeh and Novak (1994) found that, in organic-rich soils, MTBE is highly resistant to biodegradation. They further concluded that, in most fuel contaminated sites, biodegradation of MTBE is expected to be difficult. The only situation in which Yeh and Novak reported MTBE biodegradation was under methanogenic (anaerobic) conditions, and this occurred only in soils that contained little organic matter and had a pH between 5.0

and 6.0. However, one limitation of the Yeh and Novak study is that it only measured MTBE breakdown for a 250-day study period, if the study had been extended, significant biodegradation might have been observed.

There is limited evidence that MTBE may biodegrade aerobically. Borden et. al. (1997) found that MTBE biodegrades under aerobic conditions, but that this degradation was limited. They concluded that there was evidence of MTBE degradation near the source, but found no evidence of this degradation in the downgradient aquifer. Furthermore, they determined that MTBE biodegradation was not enhanced by the presence of either BTEX or NH_4. Borden et. al. (1997) also concluded that it is unlikely that the buildup of tert-butyl alcohol (TBA) or other degradation products was inhibiting MTBE biodegradation and that unknown factors were limiting or inhibiting MTBE biodegradation.

To summarize, only limited evidence supporting MTBE biodegradation exists. It is unclear if MTBE is more readily degradable under aerobic or anaerobic conditions, and it is likely that the amount of organic matter in the soil can limit biodegradation. Unknown factors or interactions may inhibit MTBE biodegradation within groundwater aquifers.

1.2 Site Background

The U.S. Naval Construction Battalion Center (CBC) at Port Hueneme, California is located 60 miles northwest of Los Angeles. The harbor was purchased by the U.S. Navy in 1942 for use as a storage facility, training site, and shipping port. The CBC currently encompasses 1,615 acres of land, 29 miles of roads, 10 miles of railroad track, and operates the Port of Hueneme, the only naval deep-water port between San Diego and Seattle. The CBC has a workforce of about 8,900 military personnel and civilians (Port Hueneme Naval Construction Battalion Center 1999). The contaminated portion of the base has been set aside as a National Test Site, where remediation technologies may be implemented to determine their effectiveness in removing existing contaminants from the groundwater. There are more than six

studies currently underway at various locations along the path of the plume.

1.2.1 Source Information

The Naval Exchange Gasoline Station (NEX) is located at the corner of 23rd Avenue and Coats Street between Patterson and Pacific Roads in Port Hueneme. Due to a leaking delivery line and associated coupling between the main underground gasoline storage tank and the distribution module, approximately 4,000 gallons of regular and 6,800 gallons of premium unleaded gasoline were leaked between September 1984 and March 1985 (Hunt 1998). This release resulted in a 4,600 foot long plume of MTBE in the groundwater, which currently covers approximately 45 acres (Hunt 1998). Additional gasoline constituents, such as benzene, toluene, ethylbenzene, and xylene (BTEX), have formed a separate plume from the source and extend approximately 1,200 feet from the source. Figure 1 shows the approximate areas of both the MTBE and BTEX plumes. It has been estimated that the gasoline contained MTBE between 6-11% by volume (Hunt 1998).

1.2.2 Subsurface conditions

The MTBE plume occurs in a semi-perched aquifer at a depth of approximately 10 feet below ground surface (bgs) and reaches a depth of approximately 20 feet bgs (Hunt 1998). Due to the shallowness of this aquifer, it is highly unlikely that this groundwater would ever be used as drinking water supply in the future. Beneath the aquifer is a clay layer with low permeability, beneath which there is an unconfined aquifer at a depth of over 300 feet (Hunt 1998). Figure 2 shows a cross-section of the plume.

The near-surface soils at the NEX Gasoline Station site consist of sands, silts, clays, and gravels (Kram and Lory 1998). Subsurface sediments consist primarily of sand and silty sand, with minor amounts of silt and clay (Kram and

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Lory 1998). The semi-perched aquifer zone consists of fluvial-deltaic sediments that are approximately 25 feet (4.6 meters) thick in the vicinity of the site. The unconfined water table ranges from 8.5 to 12 feet bgs (2.6 to 3.7 meters) and the saturated aquifer thickness is approximately 15 feet (4.6 meters). Hydraulic conductivity ranges from $0.2\text{x}10^{-3}$ to $1.4\text{x}10^{-3}$ meters/second (Kram and Lory 1998). The average linear ground water velocity in the unconfined aquifer ranges from approximately 230 to 1450 feet (70 to 440 meters) per year, assuming a porosity *of 0.3 (Kram and Lory 1998).*

Based on these soil properties, calculations indicate that the velocity of MTBE in the groundwater is approximately 342 feet (104 meters) per year (Hunt 1998; Kram and Lory 1998).

1.3   Organisms present

The initial site inspection of the Port Hueneme MTBE plume revealed few viable exposure pathways. Potential endpoints identified were humans, trees, grasses, waterfowl, soil microbiota, and marine organisms. Due to the overlying urban structures and the fact that the plume is in a shallow semi-perched aquifer that is not used for drinking water, humans can be ruled out as potential endpoints. There is only one tree within the extent of the characterized plume; this pathway was excluded from consideration as a potential endpoint. The selection of on-site grasses as an endpoint was ruled out due to the fact that the roots of grasses do not typically reach the groundwater. Although exposure may occur, the total mass of grasses and the large surface area they cover also eliminated them as potential endpoints. Waterfowl were ruled out due to their migratory nature and short exposure time within the channels, which have not shown MTBE presence. Marine fish were also excluded from consideration because the MTBE has not reached the ocean. Finally, soil microbiota were selected for the following reasons:

- Much of the terrestrial biosphere resides in the soil
- They are central to biogeochemical cycles

- They heavily influence soil properties such as hydrology, aeration, and gaseous composition, all of which are essential for primary production and the decomposition of organic residues and waste materials.

(Brussaard 1997)

Subsurface microbial organisms are the sole endpoints that have had long-term exposure to the plume and therefore are the only organisms considered in this report. In addition, should remediation become required, these microbes will likely be relied upon to remediate the contamination, and their health should be considered within the context of this ecological risk assessment.

1.4   Potential Exposure Pathways

Provided below is a discussion of the potential exposure pathways considered for this Ecological Risk Assessment. A conceptual model generated by this analysis is also included as Figure 3 at the end of this document.

1.4.1   Surface

The MTBE plume is located approximately 8.5 feet below the surface in a shallow aquifer (see Figure 2). Most of the surface above the plume is covered by either asphalt or other man-made structures. These overlying urban systems make it unlikely that surface species have been or will be exposed to the contaminated groundwater.

1.4.2   Aquifers

The potential for fissures or sinks between the perched aquifer and the underlying confined aquifer has not been determined adequately to date, but the potential for subsurface channeling through utility trenches or paleochannels must be considered. The plume occurs almost completely under a mixed industrial and residential setting with little exposed soil or grass areas.

Since much of the land over the MTBE plume is paved with asphalt or concrete, the potential for groundwater recharge is low.

1.4.3   Drainage Channels

MTBE has recently been detected at very low levels in a series of drainage channels along the toe of the plume. The intersection of the plume with the channel has introduced new possibilities for contaminant transport and biological exposure. Organisms residing within these channels may, at some time, be exposed to MTBE. Also, the design of the channels themselves are intended to transport water directly to the harbor. Movement of the groundwater containing MTBE towards the harbor is accelerated due to the presence of this drainage system. However, should MTBE reach this drainage system at any significant concentrations, it would quickly volatilize upon interaction with the atmosphere due to it's propensity to do so once exposed to air.

1.4.4   Harbor

As described in Section 1.2.2, MTBE will quickly volatilize when exposed to the atmosphere due to its high Henry's constant. Potential pathways connecting the groundwater to the harbor are exposed to conditions where volatilization will occur (i.e., through open drainage channels). In addition, concentrations of MTBE in the groundwater at the site are currently measured in the 10^{-6} g/L range; levels that have been found to cause adverse reactions in marine organisms in laboratory studies are on the order of 10^{-3} g/L. Thus, the impact of this MTBE plume to marine biota, should it reach the harbor, is negligible due to the high volatility of MTBE and the relatively low concentrations found on the site.

1.5   Previous Reports Conducted

The preliminary Ecological Risk Screening (Appendix A) that was conducted in 1998 determined that, even if the plume was to reach the ocean or any nearby groundwater sources, it would be unlikely that contaminants from this site would have region-wide effects. However, this screening did not address the effects of the MTBE plume on the subsurface environment. Also, the secondary action standard for MTBE was recently lowered, creating a need for a revised plume delineation map which is currently being created by the Navy.

1.6   Selection of Assessment Endpoints

The problem formulation phase of an Ecological Risk Assessment must have explicit and identifiable endpoints that are specific statements of environmental characteristics to be used as a metric for endpoint assessment. In selecting assessment endpoints, it is useful to consider three distinct criteria: (1) ecological relevance, (2) susceptibility to known or potential stressors, and (3) relevance to management goals (EPA 1998). It should be noted that ecologically relevant endpoints are related to other endpoints through their functions and interactions within the system (EPA 1998).

Potential exposure pathways for the MTBE groundwater plume at Port Hueneme are limited due to geographic and geologic features and observed MTBE concentrations. Other possible exposure pathways include freshwater organisms associated with the drainage channel system near the toe of the plume and marine organisms which could potentially be impacted when the plume reaches the ocean (Figure 1). The potential threat to marine and freshwater organisms was addressed in an ecological risk screening assessment performed in August of 1998 (Appendix A) as discussed below.

The screening assessment compared the MTBE concentrations in wells along the plume to toxicity reference values (TRVs) for acute and chronic effects on freshwater and marine organisms. It was determined by this 1998 report that MTBE levels near the source of the plume could impact the most sensitive of aquatic and freshwater species, but MTBE levels near the toe of the plume were too low to present a risk. MTBE concentration data taken

from more recent testing at the Port Hueneme site found levels well below the freshwater acute TRV threshold of 115 mg/L and the chronic TRV threshold of 66 mg/L (Mancini 1999.). Marine species are more sensitive to the presence of MTBE and no-observed-effects-level (NOEL) benchmarks, which account for chronic impacts on 95% of all aquatic species, have been set at 13 mg/L (Van Leuwen 1992). Hence, freshwater and marine organisms have been eliminated as potential endpoints in this assessment.

1.6.1   Assessment Endpoints

After eliminating all other pathways for contaminant exposure (see Section 1.4), the sole remaining pathway to consider is the subsurface microbial communities whose normal biological activity may involve interactions with MTBE, potentially resulting in biodegradation and/or damage to the microorganism. The limitations created by the geographic and geologic conditions and the existing MTBE concentrations have led to the selection of microbial communities as the assessment enpoint of this investigation.

The ecological assessment endpoint for this ERA has been selected based on ecological importance, policy and societal significance, susceptibility to toxic effects, and appropriateness of scale (Barbour 1997). An endpoint has appropriate scale if potential toxic effects on the site could have a significant impact on the chosen endpoint. For this assessment, the following assessment endpoint was chosen:

- Toxicity to subsurface microorganism communities in four regions of the MTBE plume at Port Hueneme.

Microorganisms are important in ecological systems for many reasons. They are essential in the cycling of nutrients through the ecosystem and in the breakdown of many organic and inorganic substances that occur naturally or are introduced to the system, including gasoline constituents. The presence and activities of

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microorganisms in soils increases soil fertility. In addition, microorganisms utilize available organic compounds or pollutants in both soils and sediments, regardless of whether or not those pollutants may have toxic effects on the microorganisms themselves. Due to their function and ubiquitous presence, microorganisms are an environmentally relevant indicator of pollution (i.e.; MTBE). Microorganisms are now being used to assess the health or state of soil systems and have proven to be a useful tool for policy development (van Beelen and Doelman 1997).

Threats to specific microbial species are not directly addressed in this assessment. Identifying the multitude of individual microbial species present in this ecosystem would be inefficient due to the expansiveness of the contaminated area. Also, the health of the microorganism community in general is significantly more representative of the overall system health and functionality than are individual populations. This analysis is focused on the risk of MTBE to microorganisms and has generalized the ecological risk to the microbial community rather than individual species.

1.7   Conceptual Model

A conceptual model, in the context of an Ecological Risk Assessment, is a graphical representation of the interactions between contaminants, ambient media, and the endpoint biota, which will act as the assessment endpoint of the ERA. Figure 3 shows a conceptual model for the region affected by the gasoline leak at Port Hueneme. The exposure pathways shown represent both (a) potential pathways, which have been ruled out in the preliminary screening, and (b) the pathway selected as the focus of this report.

2.0 Analysis

Soil microbiota have been selected as the relevant assessment endpoint for this ecological risk assessment. These organisms are important in maintaining the natural conditions of the ecosystem, by regulating the concentration of contaminant in the environment through biodegradation. In addition, the importance of bacterial degradation of contaminants at the site makes it valuable to determine if there is any effect of MTBE on ecosystem function. The operational definition of the assessment endpoint for this ERA is the effect of MTBE on the health of subsurface microbial organisms.

2.1   Establish Measurement Endpoints

There are several types of effects data—which establish the quantified effects on an endpoint—potentially available to serve as measurement endpoints for an analysis of the microbial community, which is the assessment endpoint of this analysis. However, an extensive literature review found microorganism endpoint effects data to be very limited. Typically, effects data are results taken from biological surveys, biological indicator analysis, media toxicity analysis, or single chemical toxicity data. It was concluded that the most relevant analysis for understanding the impact of the contaminant release on the microbial community could be attained by examining the toxic effects of relevant

groundwater samples on a well-documented indicator organism. Thus, a set of field and laboratory experiments was performed in order to generate toxicity data directly relevant to the chemical constituents within the plume at Port Hueneme. Results of this experiment can be found on pages 88-91. The findings were later used as a field observation study tool in defining and quantifying ecological risk and presenting the findings to risk assessors.

Soil Microbia

2.1.1   **Biological Survey Data.** No survey data were collected.

2.1.2   **Biological Indicators Data.** No microbial indicator data was available.

2.1.3   **Media Toxicity Data**. No microbally relevant media toxicity information was available.

2.1.4   **Single Chemical Toxicity Data.** Benchmark data not available for microorganisms.

2.1.5   **Groundwater Toxicity Data.** A toxicity experiment was performed. The Microtox™ method of acute toxicity determination was selected based on its accessibility, relative popularity in the literature, and its quantification of the toxicity to microorganisms. The contaminated region was sampled at three different time periods in the Summer of 1999. Water samples were tested as specified by Microtox™ methodologies for the effective concentration at which a sample was toxic enough to adversely affect 50% of the test organisms (EC50). Two samples from each well for each time period were tested in order to provide confirmation of results. Each sample was also tested for the presence of MTBE and BTEX components via Gas Chromatography and Mass Spectroscopy. The relationship between observed EC50 values and the BTEX and MTBE concentrations at each sample location were analyzed and compared as a proxy for the functional assessment endpoint. Any EC50 value that was consistently observed was considered potentially damaging to the microbial community as well as to the ability of microorganisms to break down BTEX and MTBE and their byproducts.

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2.2 Evaluation of Available Data

The U.S. Naval Construction Battalion Center (CBC) at Port Hueneme has been set aside as a National Test Site for the study of the environmental effects of MTBE and as a location where potential remediation alternatives can be tested. On site personnel have installed groundwater monitoring wells near the source of the plume and, guided by field measurements, have extended the spatial range of these sampling wells as the MTBE continues to travel with the groundwater. These wells have been monitored quarterly (or semi-annually, as appropriate) and the data was made available for use in this assessment of ecological risk at the site.

In addition to the contaminant concentration data, information was gathered that provided the NOAEL (No Observable Adverse Effects Level) and the LED (Lethal Effective Dose) of MTBE to marine and freshwater organisms. The data generated by the experimental tests proved to be essential in the assessment endpoint selection process of this ERA, as concentrations measured were much lower than any LED or NOAEL values found in the literature. Contaminant degradation rates were also collected from the literature and utilized in the estimation of the amount of natural attenuation taking place at the site.

2.2.1 Uncertainties in Bioassays

Bioassays, like the one performed within the context of this Ecological Risk Assessment, have been subject to much criticism for their inconsistent results and for using indicators which may be inappropriate for the question at hand. It is important that bioassays be understood in the context to which they are used, and this means understanding the assumptions and subtleties relevant to each particular case. A comparison of the Microtox™ bioassay with other aquatic toxicity bioassays shows that the Microtox™ test produces consistently robust results, although Microtox™ is considered by some to be "more sensitive" to toxicity than traditional bioassays (Qureshi et. al. 1998). In addition, Microtox™ has been identified as the "best available choice" for conducting toxicology

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screenings and assessments (Qureshi et. al. 1998). Most importantly for this Ecological Risk Assessment, the Microtox™ assay also allowed the use of one microbial species as a proxy for the microbial communities of interest at this site, rather than using an unrelated indicator, such as fish or daphnia.

2.2.2 Uncertainties in Toxicity Findings

Uncertainty in the toxicity experiment performed in the Summer of 1999 (reported on pages 81-103) may stem from several possible sources. There are also several assumptions inherent to understanding the groundwater toxicity data obtained from the laboratory work performed.

First, it is possible that the Microtox™ organism (*Vibrio fischeri*) did not respond in the same way that the microorganisms at the site would respond under field conditions. For the purpose of this report, it is assumed that these organisms are representative of the *in situ* microbial organisms.

In the laboratory, Microtox™ procedures require a lengthy and accurate treatment for consistent results; errors that may have occurred in the methods should be viewed as potential sources of uncertainty. Also, the number of samples and replicates examined for each experiment was low and, as a result, very few statistically significant results were observable.

The loss of MTBE and other potentially toxic chemicals through volatilization during sampling and experimentation may have affected the observed toxicity findings. MTBE, as was discussed earlier, is a very volatile chemical and precautions were taken to limit the loss of MTBE from samples to the atmosphere. However, further examination suggests that volatilization likely occured, possibly resulting in a 4–19% loss of MTBE from groundwater samples during laboratory testing (see Appendix B for calculations). These losses were not

incorporated into the toxicity findings because it is impossible to establish how much of the existing toxicity was a result of MTBE effects.

2.2.3 Uncertainty in Laboratory Analysis

Transfer of the groundwater samples during chemical analysis is another potential source of uncertainty. Samples were stored and transported according to standard methodologies, maintaining low temperatures in order to limit the potential for loss due to volatilization. The Gas Chromatograph and Mass Spectrophotometer apparatus used to determine contaminant concentrations were calibrated with a sensitivity of ±1% of measured value.

2.3 Characterization of Exposure

The original source of contamination, an underground storage tank, released approximately 11,000 gallons of gasoline containing between 6-11% MTBE by volume into an aquifer lying between 8.5 to 12 feet below the surface. Since the source of the contamination lies below the surface, the contaminant has not been exposed to any surface, freshwater, or marine organisms, nor is it expected to in the future under normal conditions. The subsurface microbial community, however, has been exposed to this contaminant; in the near-source zone, the exposure has continued since 1984.

MTBE is a persistent chemical in the environment; it has a high solubility and low sorption coefficient that allows it to remain in the groundwater, and various studies have shown that MTBE is not readily biodegraded. At this time, the exposure of MTBE is confined to *in situ* microorganisms, however, there are potential pathways for distribution into the Port Hueneme harbor that may affect marine organisms in the future.

Geologic factors strongly influence the migration of the plume. Paleochannels appear to be directing the groundwater, and the MTBE, through the subsurface environment. The behavior of the

plume is constantly being monitored, and previous investigations have shown that these channels appear to play a significant role in MTBE movement. A satellite image of the site in 1929 is overlain with the extent of the existing plume for reference and shows these probable pathways for contaminant transport in the future (Figure 4).

2.4 Characterization of Ecological Effects

Investigation of toxicity to individual microbial species ignores potential large-scale community effects. The presence of a toxic substance may have impacts on the greater ecological community that cannot be observed when analyzing a single species. For example, prolonged exposure to a pollutant can induce resistance in microorganism specie potentially resulting in a "resistant" community which may or may not perform similar functions within the ecosystem. It is also possible that sensitive members of the community will be replaced (1) by resistant daughter cells or (2) by unrelated species with potentially different properties. This report does not address these complexities, focusing, instead, on the health of the entire community.

3.0 Risk Characterization

Prior to determining ecological risk at this site, an evaluation of methodologies (included as Risk Estimation below) has been undertaken. Following this section, risks to specific endpoints and organisms has been worked through.

3.1 Risk Estimation

Risk estimation is a process which integrates effects data, exposure data, and information on uncertainties in order to approximation the level of hazard associated with a given contaminant. According to the EPA Guidelines on Ecological Risk Assessment there are five techniques used in risk estimation. They are:

- Categorical rankings
- Comparisons of single-point exposure and effects estimates
- Comparisons incorporating the entire stressor-response relationship
- Incorporation of variability in exposure and/or effects estimates
- Process models that rely partially or entirely on theoretical approximations of exposure and effects
- Field observational studies

Categorical rankings are most appropriate when one risk is being compared with a set of potential risks so that they can be sorted by overall threat. Therefore, this analysis method was not viable for the needs of this ERA. *Single-point exposure and effects comparisons* are most valuable when sufficient exposure and effects estimates data is available. No information was found prior to the experiment that was conducted for this ERA that related the toxicity of MTBE on microorganisms making this analysis method inappropriate for risk estimation. *Comparisons incorporating the entire stressor-response relationship* are only applicable when a curve relating the stressor level to the magnitude of response is available, and this information was not available. *Comparisons incorporating variability in exposure and/or effects* also require exposure and stressor-response profiles and could not provide a useful risk estimation technique here. *Process models* require known mathematical expressions that represent the understanding of the mechanisms behind exposure and response behavior, and did not provide an option for risk estimation.

Field observational studies operate on empirical evidence linking exposure to effects. Often times they measure biological changes within natural settings based on data collected for receptor organisms observed in the problem formulation phase. Field observational studies do not require an existing data base for risk estimation and they also provide a direct means in which to establish causal relations between contaminants and receptors.

There is no analysis for estimation of risk associated with field observational studies beyond the correlation's developed within the study itself. Unlike the comparisons which explore stressor-response relationships with probability curves and frequency charts, the field observational studies are limited to the data, charts and graphs produced for any given experiment.

A literature search and examination of the existing Oak Ridge National Laboratory (ORNL) Benchmarks did not provide adequate information on the effects of MTBE on microorganisms. The Microtox™ bioassay and available Gas Chromatography and Mass Spectroscopy methods were chosen to acquire this data through field observational studies. Sampling design was impacted by the physical inaccessibility of wells to non-Navy personnel as well as time constraints. It was determined that a statistically significant analysis could be performed addressing MTBE, BTEX, and toxicity contamination of the site by using available data and the findings of the field observational study. A discussion of these correlations can be found in the following section.

3.2   Risk Description

The narrow scope of this Ecological Risk Assessment is explained in Sections 1.4 and 1.7 of this ERA. Potential pathways of contamination as well as at-risk organisms for which adequate data existed were both ruled out in the risk screening and assessment endpoint phases. Geologic and geographic characteristics of the site are believed to be channeling the plume away from sensitive regions. This is illustrated by the fact that the observed MTBE and BTEX concentrations throughout the plume are not high enough to pose a direct acute or chronic effect to organisms. Risk related to potential daughter products in the subsurface environment at Port Hueneme may have some influence on this assessment of ecological risk. However, effects of this risk are not included in this investigation in much detail due to a lack of information about the concentrations of these metabolites on site.

The Microtox™ bioassay and the Gas Chromatograph and Mass Spectroscopy tools, which were used for the examination of

toxicity on microorganisms, are capable of producing high quality data. The experiment performed on the groundwater at this site was limited by temporal constraints which affected the quality and adequacy of the data as a result of limited data collection. Statistical significance was also difficult to achieve due to the low number of samples. Additional data quality concerns may result from errors in sampling technique, storage, experimentation methods, and MTBE volatilization as discussed earlier in the ERA, but low replication appears to be the largest limitation to achieving statistical significance. However, the value of the experimental findings should not be completely overlooked. EPA guidelines suggest that any experimental findings and observations should be considered and incorporated into risk assessment when no other information is available.

In order to compensate for low replication of sampled wells, similar wells were grouped into four zones (Figure 5) for the purpose of analysis.

- Zone 1 represents the area within the BTEX zone of the plume and corresponds to wells CBC10, CBC15, CBC17, and CBC19.

- Zone 2 is the area of the plume just beyond the BTEX zone and is characterized by an MTBE presence. Wells CBC24, CBC35, CBC42, and CBC45a comprise Zone 2.

- Zone 3 represents the farthest reaches of the plume; it is also called the toe of the plume. Wells CBC47, CBC49, CBC51, and CBC54 have been grouped into Zone 3.

- The potential transport of MTBE out of the groundwater and along a drainage pipe and ditch near the toe of the plume led to the creation of a fourth zone called the Drainage Channel (DC). Three points along the drainage channel were sampled, these locations were labeled DC1, DC2, and DC3, where DC3 is the farthest from the plume and closest to the ocean.

Several questions were asked in an effort to characterize the relationships between MTBE and BTEX concentrations and measured toxicity, as well as the spatial and temporal distributions of each, thereby addressing the assessment endpoints of this ERA. Specifically, the relationships between toxicity and spatial distribution, MTBE concentration and toxicity, BTEX concentration and toxicity, MTBE concentration and spatial

distribution, temporal changes in MTBE concentration, temporal changes in BTEX concentration, MTBE impacts on BTEX attenuation, and an MTBE mass balance, or pathway analysis, are all developed. The findings discussed in this section are based on a synthesis of literature, monitoring data provided by the Navy, and results from the field experiment performed during the Summer of 1999 (found on pages 81-103 of this document). Uncertainties, ambiguities, and statistical analyses are discussed and developed where possible.

3.2.1   Toxicity in Space and Time

An initial examination of the ecological risk created by the presence of gasoline constituents in the groundwater at Port Hueneme should begin with a discussion of toxicity levels observed within the contaminated region. Zones 1, 2, and 3 were compared based on observed toxicity defined in toxicity units (TU).   Toxicity Units were determined using the equation: $TU = 100/EC_{50}$. Effective Concentration (EC_{50}) is the amount of sample that negatively affects 50% of the test organisms. The toxicity data were collected during July, August, and September 1999. Findings from the Microtox™ bioassay indicate that toxicity levels in Zone 1 were greater than the other two zones (Table 2).

A traditional T-test using 95% confidence revealed that Zones 2 and 3 could not be differentiated with respect to toxicity, i.e., neither was very toxic and there was no noticeable difference between the two zones. It was found with 95% confidence that Zone 1 was statistically different from Zones 2 and 3, indicating the presence of greater toxicity levels. This result is consistent with the fact that Zone 1 lies nearest the source of contamination and has been exposed to aromatic constituents with potentially toxic properties since the leak began over 15 years ago.

3.2.2   MTBE and Toxicity Correlation

The ecological risk associated with the plume is related, at least in part, to the toxicity observed within the system, and the importance of MTBE is directly related to how its presence parallels toxicity. Attempts to correlate MTBE

concentrations with toxicity within the plume were hindered by the fact that the toxicity data was restricted to the Summer of 1999. Results of an ANOVA analysis indicated that there was no significant correlation between MTBE concentrations and toxicity at a 75% level of certainty. Areas of high MTBE concentration often showed no toxicity and wells free of MTBE would sometimes show relatively high toxicity levels (Table 3).

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3.2.3 BTEX and Toxicity Correlation

Analysis of BTEX and toxicity measurements over spatial and temporal scales yielded unexpected results. It was discovered that the presence of BTEX components and measured toxicity were not directly correlated. The lack of correlation can be attributed to the fact that BTEX components were not observed during the sampling period. However, there may be a correlation between toxicity and regions where benzene was detected during sampling events prior to July 1999. In December 1998, the groundwater in well CBC10 contained 3300 µg/L benzene and had unknown toxicity. In the Summer of 1999, no benzene was detected, however, toxicity was observed. It is possible that a volume of non-aqueous phase liquid (NAPL)—a pool of contaminant not integrated into the water phase—containing benzene, MTBE and other BTEX components exists in the environment. Periodic releases from such a source may influence toxicity; however, no evidence to confirm the existence of a NAPL was found during the Gas Chromatography and Mass Spectroscopy analyses of the samples.

3.2.4 MTBE effects on BTEX Attenuation

It was theorized that the presence of MTBE could affect microbial communities and reduce their ability to aid in the natural attenuation of BTEX components. However, the apparent absence of these contaminants throughout the three-month sampling period made it impossible to quantitatively determine how concentrations of the BTEX

changed down-gradient of the source region and difficult to examine attenuation rates. In order to qualitatively establish the cause(s) of BTEX attenuation within the plume, all of the processes that can influence reduction must be considered. Then—if the processes of advection and dispersion, sorption, volatilization, water table fluctuations, and non-biological transformations are accounted for—the remaining attenuation can be attributed to microbial activity.

When these process occur in a situation that is free from human intervention the net reduction is called "natural attenuation" (EPA 1994). The chemical properties of benzene suggest that, when released into soil, it will either volatilize or leach into groundwater where it will be broken down by microbes (EPA 1998). Unlike MTBE, benzene is not highly soluble; it is more likely to sorb to soil particles and be transformed/attenuated in place (Borden et. al. 1997; Davis et. al. 1999). Therefore, an analysis of benzene reduction rates should focus on the processes of volatility and microbial degradation.

Under normal conditions, benzene has a half life of 800 days, which would suggest that, as of the year 2000, benzene levels should be approximately 1% of what they were at initial release, based on natural attenuation alone (Table 4). Aromatic hydrocarbons make up 30% of the volume of conventional gasoline, of which benzene is only 1.6% by volume (EPA 1995). This information is insufficient to establish the original concentration of BTEX released to the environment at Port Hueneme since it is not known exactly what percent of the gasoline constituents exist at this site as a non-aqueous phase liquid (NAPL). Without this information, it is difficult to calculate with high certainty what concentrations should be expected after 15 years of natural attenuation.

It is possible, however, to draw some conclusions about contaminant activities based on the available data collected over the last four years, but it should be stressed that continuous data were only available for a single well location (CBC10) within Zone 1; this well will represent Zone 1 in this analysis. Benzene concentrations detected in

CBC10 have fallen from 10,000 $\mu g/L$ in December 1996 to undetectable levels in the Summer of 1999 (Figure 6). Thus, in the period between December of 1996 and July of 1999 the rate of attenuation exceeded those predicted by the literature by a factor of 10, assuming attenuation is the primary process removing benzene from the region.

An examination of potential benzene volatility rates from the Port Hueneme site displayed interesting results. Though natural attenuation rates based on literature values were exceeded according to available data for CBC10, modeled volatility rates suggest that benzene could naturally partition out of the groundwater and soil and into the air in short time periods.

It is not possible to determine the role played by MTBE in the microbial attenuation of benzene given the limited data set and high potential for volatility.

Under normal conditions, p-xylene and toluene should have had sufficient time to degrade to concentrations of far less than 1% of their original concentrations, even by the 1996 sampling period (Table 4). However, December 1996 samples at CBC10 found detectable concentrations of both toluene and xylene in the groundwater in Zone 1, which suggests that there may be some method of contaminant reintroduction to the subsurface environment, and the groundwater, occurring at irregular intervals. The detection of these typically short-lived chemicals may indicate some retardation of attenuation processes or a pulse of chemicals from the original NAPL.

Degradation data suggests that both toluene and xylene were attenuated quickly after the December 1996 release (Figure 7), at 1.5 and 3 fold normal "natural attenuation" rates respectively. As with benzene, the accelerated removal rates of xylene and toluene may be explained by volatility, re-sorption to soil particles, changes in the height of the water table, or other transformation processes that were under-emphasized by the values found in the literature.

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Attenuation rates are especially difficult to quantify because (a) the constituents appear only at a few wells in the source region (Zone 1) and (b) the presence of these constituents is erratic. However, based on the data currently available, the aromatics are removed at rates which exceed those predicted by normal rates of attenuation. These accelerated rates of attenuation, and the lack of observed aromatics in down gradient wells, suggests that natural attenuation at Port Hueneme is not negatively impacted by the presence of other chemicals that were currently or historically detected in the groundwater. That is, it would appear that MTBE has not negatively impacted the attenuation of the aromatics in the source region. This finding is consistent with findings presented by a study conducted by the American Petroleum Institute which suggest that MTBE concentrations do not impact BTEX attenuation (Bauman 1997).

3.2.5 MTBE in Space and Time

When considering the changes in MTBE concentrations in space and time, it is important to perform a detailed analysis of the recent monitoring data as well as a more robust observation of variability focusing on changes since December of 1996.

Three Month Trend

Statistical analysis of the data representing the spatial and temporal distribution of MTBE levels during the months of July, August, and September 1999 were inconclusive. Only one portion of the drainage channel showed a significant variation in MTBE levels during the experimental period, suggesting a 75% chance of correlation according to a one-tailed variance ratio test. No statistical significance could be attributed to any of the other wells suggesting that (a) the analysis was hindered by the low number of samples retrieved or (b) there was a lack of appreciable concentration changes during the experimental period. The data set indicates that, for many wells, MTBE levels actually increased during the month of August before falling to pre-July levels in September, however this could

not be verified statistically. The absence of a consistent trend among zones or wells makes it difficult to draw conclusions about the down-gradient transport of contaminants during this period, especially given the lack of statistical significance with regard to the spatial distribution of MTBE.

An analysis of the Summer 1999 data found no significant correlation between MTBE concentration and distance from the source according to an ANOVA analysis with 95% confidence. Thus, it is not possible to confirm statistically which zone of the plume is more or less contaminated by MTBE or whether or not the MTBE is truly moving with the groundwater in a quantifiable way over the three month period. However, an analysis of changes over the past three and a half years provided significant results.

Three Year Trend

As stated previously, wells CBC10, CBC42, and CBC49 were chosen to represent Zones 1, 2, and 3 respectively to identify the temporal variation in MTBE content beginning in December of 1996.

All three wells showed a statistically significant trend in MTBE behavior over the four year period, based on a 95% certainty ANOVA analysis. The Zone 1 well, CBC10, showed significant MTBE reduction since December 1996 (Figures 8). CBC42 also showed significant MTBE reduction while MTBE concentrations at CBC49 increased over the same time period (Figures 9 and 10). Therefore, assuming the wells chosen are an accurate representation of the groundwater transport that is occurring within the plume, then the MTBE has been moving out of Zones 1 and 2 and into Zone 3 over the past four years.

In order to explore the net flux of MTBE through the system, a separate analysis was performed in which the average MTBE concentration for each zone was determined based on an overall average for all the wells each zone. According to the averaged data set, the mass of MTBE moving out of the first two zones is much larger

than the concentrations measured moving through Zones 2 and 3. Therefore, it seems that much of the MTBE is unaccounted for by advective and dispersive processes alone. The spatial and temporal variation in MTBE concentrations between Winter 1996 and Summer 1999 produced results that led to an unexpected finding.

3.2.6 MTBE Mass Balance

A more quantitative analysis of the processes which impact the distribution of MTBE in the environment at Port Hueneme will provide a valuable tool in long-term risk assessment. This mass balance will include an examination of biotic and abiotic processes that affected groundwater concentrations of MTBE over a three year period.

In December of 1996, the source region (Zone 1), contained an average of 35,000 µg/L MTBE in the groundwater. In the Summer of 1999 the average MTBE concentration in Zone 1 had decreased to approximately 1200 µg/L, a factor of 30 reduction (Table 5). An examination of MTBE concentration changes over the entire plume yields similar results. In December of 1996, MTBE levels integrated over the entire volume of the plume accounted for 43,000 µg/L. By the Summer of 1999, this total was down to 2,800 µg/L MTBE—a factor of 14 reduction (Figure 11).

Several processes—including advection, dispersion, transformation (including biological attenuation, hydrolysis and redox reactions), volatility, sorption, changes in the shape/size of the plume, and fluctuations in groundwater volume—could possibly explain some of this reduction. Each process is explored in detail below in order to characterize current and future concerns about the fate and transport of the MTBE plume.

Advection and Dispersion

A traditional fate and transport model for advection and dispersion indicated that, given the Zone 1 concentrations

observed in December of 1996, MTBE would not be expected to have traveled as far as the drainage channel under normal conditions. Therefore, advection and dispersion do not appear to account for any of the MTBE reduction.

A model was also developed from the following equations, in an effort to determine the influence of MTBE advection and dispersion at Port Hueneme.

Equation 1—Advection-Dispersion

$$Vx = (K * dh)/(n * dl)$$

Vx	= pore water velocity	(m/day)
K	= hydraulic conductivity	(m/day)
n	= porosity	(m/m)
dh	= change in height	(m)
dl	= change in length	(m)

Equation 2—Advection-Dispersion

$$C(x,t) = (Co/2) * [erfc ((X-Vxt) / (2sqrt(Dxt))]$$

C(x,t)	= concentration at distance x, t	(g/m³)
x	= distance from source	(m)
t	= time	(days)
Co	= initial concentration	(g/m³)
erfc	= complimentary error function	(table value)
Vx	= pore water velocity	(m/day)
Dx	= groundwater dispersion coefficient	(m²/day)

Water sampling at Port Hueneme indicates that MTBE has traveled with the groundwater out of the source zone and into Zones 2 and 3, transporting the MTBE via advection over approximately 45 acres, but not into the drainage channel (Figure 1). If advection processes were responsible for a large portion of the reduction in MTBE concentration, higher levels of MTBE would be present in

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wells near the toe of the plume, thereby marking the passage of MTBE out of the region.

Furthermore, the shape of the relationship between Zone 1 and Zones 2 and 3 appears suspiciously sharp, suggesting that MTBE levels are not distributed normally down gradient of the source region (Figure 11). An analysis of the data gathered since December 1996 at Port Hueneme does not support this behavior, indicating the advection is not responsible for the variations in MTBE concentration over time. In addition, the MTBE plume has also maintained a relatively stable shape and has not dispersed horizontally as it moves toward the ocean. Thus, it would appear that neither advection nor diffusion processes play a significant role in decreasing MTBE concentration within the plume.

The distribution of MTBE and BTEX constituents at the site is further complicated by a recent discovery which suggests that the location of wells used to sample the plume may have been inaccurately reported. The plume was recently surveyed by the Navy in an effort to satisfy this concern, and though the new findings could not be included here, the potential risk of such uncertainties is addressed.

Sorption

Another parameter that is important in characterizing chemical pathways is sorption to the soil. MTBE does not readily sorb to soils due to its low octanol-water partition coefficient (K_{ow}). Due to the fact that some parameters of site characterization were not available, sorption levels were explored for several different soil types and organic concentrations and in each case far less than 1% of the original MTBE concentrations was removed from the water column via sorption. The model used to characterize sorption is outlined below.

Equation 3—Sorption

$$Kd = (Cs/Ce) = Koc * foc$$
$$\mathbf{Cr = Ce*Cs}$$

Kd   = sorbed content   (mL/g)
Cs   = concentration sorbed on soil   (dimensionless)
Ce   = concentration in solution at equilibrium   (g/ml)
Cr   = MTBE removed by sorption   (g/ml)
Koc = soil adsorption coefficient   (mL/g)
Foc = soil organic content   (g/g)

Transformation

Transformation—the conversion of MTBE into other products by physical and biological processes—may also account for a portion of the observed MTBE reduction over the three year period. The two processes of concern for MTBE within groundwater are hydrolysis and microbial consumption. Though biodegradation of MTBE has been observed in certain lab settings, this process is known to occur only occasionally in both anaerobic and aerobic conditions (Bauman 1997).

Hydrolysis is only a factor in waters with low pH values. pH values, taken at the time of well sampling, indicate that pH levels were always basic in nature and varied only slightly from a value 8 (Tables 6-8). This suggests that the most common transformation processes can only account for a small portion of the observed MTBE reduction.

Water Table Fluctuations

Fluctuations in the amount of groundwater present in the system will also impact MTBE concentrations. Contaminant levels will appear more dilute when more water is present and it will appear more concentrated when water levels are down. This three year period of time is not associated with dry climactic conditions, nor do the Summer 1996 represent a time of high precipitation for southern California. However, without actual groundwater depth measurements for 1996 it is impossible to be certain how large a role water table fluctuations has

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played. Realistically, there is no reason to believe that fluctuations in this parameter are responsible for more than very small changes in observed MTBE concentrations.

Volatilization

The volatilization of MTBE from the groundwater through the vadose, or soil, zone was estimated using a fate and transport model illustrated below:

Equation 4—Volatilization

$$F = [Sa * ((1-H)/Bl)]/[(1/Dc) + (Hv^2 * Sa * mw)/(Ta * gc * T^2)]$$

F	= flux out	(g/(cm² sec))
Sa	= contaminant saturation in air	(g/cm³)
H	= relative humidity	(%)
Bl	= boundary layer	(cm)
mw	= contaminant molecular weight	(g/mole)
Dc	= diffusion coefficient in air	(cm²/s)
Hv	= latent heat of vaporization	(cal/g)
Ta	= thermal conductivity of air	(cal/(sec cm K))
gc	= gas constant	(cal/(mole K))
T	= temperature	(K)

The loss of MTBE to the atmosphere is controlled by the physical characteristics of the site and the chemical properties of MTBE. Since the contaminated area is covered with asphalt, the original analysis of loss processes may not have significantly addressed the importance of the amount of MTBE to soil gas pathway. An analysis of the findings from the fate and transport model suggest that volatilization is capable of accounting for several times more loss than was observed during the four year period. The asphalt roof, which covers most of the plume, is likely impeding complete volatilization to the atmosphere, keeping the MTBE trapped in pore spaces.

3.3 Possible Risks

The risks associated with the MTBE groundwater contamination at Port Hueneme revolve predominantly around unknowns. The delineation and boundaries of the true plume and the geologic properties of the perched aquifer are not fully understood and could present a moderate amount of risk in certain situations. The unknown effects of changes in groundwater volume and velocity and the lack of MTBE and BTEX daughter product concentration data constitute two more possible risks.

- There is some evidence that the plume may actually be moving in a different manner than data provided by the Navy originally suggested. This evidence could have some impact on the assessment of ecological risk. This problem necessitates a re-survey of the location of current wells and reexamination of the true path of the plume, which should be completed in the near future.

- Groundwater may travel through fractures in the perched aquifer, creating previously undetected exposure pathways and more extensive contamination of groundwater. This could have significant implications if the contaminated waters find their way into a drinking water source.

- The likelihood of a large MTBE surge out of the groundwater and into the drainage channel and marine system is small because there is little evidence to suggest that MTBE levels are moving forward with a concentration elevated enough to influence the assessment endpoints.

- It was not possible to fully correlate toxicity information with chemical constituents in the groundwater at Port Hueneme. However, data was not available for the location or concentration of daughter products. MTBE and BTEX both have toxic daughter products, including tert-butyl alcohol (TBA) and trichloroethylene (TCE) which forms in the presence of chlorine. Without this information it is not possible to fully characterize the risk to organisms and the ecosystem. Information about the pervasiveness of these metabolites is also important because the microbial community may be negatively impacted by the presence of

some MTBE and BTEX degradation chemicals, thereby having important feedback effects.

It should be reemphasized at this time that, as the plume is currently characterized, there is no evidence to suggest that risk to the ecological community—whether terrestrial, aquatic, marine, or microbial—should be expected. However, a redefinition of the above-mentioned uncertainties in plume characterization could introduce some potentially adverse impacts to the terrestrial, aquatic, marine, and/or microbial communities.

3.4   Relate Information to Risk Management Decisions

Before any successful management practice can be initiated, the true nature of the plume must be discerned. If the assumptions utilized for the purpose of this risk assessment prove valid, there is little management required beyond continued monitoring efforts. However, if the MTBE or BTEX concentrations are found to be higher or in more ecologically sensitive regions, remediation strategies may be required.

Should the contaminated groundwater be found to permeate other subsurface features, the risk manager may also need to investigate the actions of deeper aquifers, including relations to drinking water wells and other subsurface pathways. In addition, it should be noted that the toxicity experiment was conducted during the relatively dry summer months and results may differ when the water table varies due to heavy rainfall.

If the volatilization analysis is found to be flawed in some way, then the possibility that MTBE may be lost via other pathways will need to be explored further. This is especially true because the spatial distribution of MTBE down the plume exceeds the secondary MCL for California at almost all locations, which suggests that if drinking water supplies or other human related reservoirs are eventually impacted, the entire plume might require remediation (Figure 12).

3.5   Critical data gaps

Upon completion of this ecological risk assessment, the following have been identified as important gaps in the available data:

- *Delineation of Existing MTBE Plume*—The Navy is currently re-surveying the wells and the plume region so that the true plume progression can be accounted for. Once the extent of the plume has been reestablished, further examination of MTBE and BTEX concentrations should be conducted and additional toxicity information should be generated.

- *Consideration of Metabolites*—Both BTEX and MTBE have toxic daughter products. A quantification of the presence of these metabolites should also be undertaken since these products may have a different effect on organisms, communities, and ecosystems than would be expected from the original contaminants themselves.

- *Increased Scope of Toxicity Quantification*—Risk analysis could also benefit from a more robust analysis of plume toxicity correlated to MTBE, BTEX, and daughter product concentrations.

- *Geotechnical Survey of Subsurface*—An accurate characterization of subsurface features and groundwater movement rates and direction would also assist in the risk management decisions. Potential vertical movement through the subsurface could affect the outcome of the MTBE mass balance estimation.

3.5   Monitoring

Because the movement of MTBE, BTEX, and other constituents appear to be moving from the source region in a dynamic and inconsistent fashion it is imperative that monitoring efforts continue so that potential changes in the behavior of the plume can be addressed prior to exposure and increased risk. Monitoring the groundwater in the deeper unconfined aquifer would also allow for a more complete understanding of the ecological risk associated with this contamination.

Figures and Tables—Ecological Risk Assessment

Figure 1. Graphical representation of areal extent of groundwater contamination as May 1999 at Port Hueneme Naval Facilities Engineering Service Center. Red area represents ~45-acre MTBE plume; green represents BTEX plume. (*Source: NFESC*)

Figure 2. Side view of MTBE plume based on Geoprobe groundwater sampling, May 1999. (*Source: NFESC*)
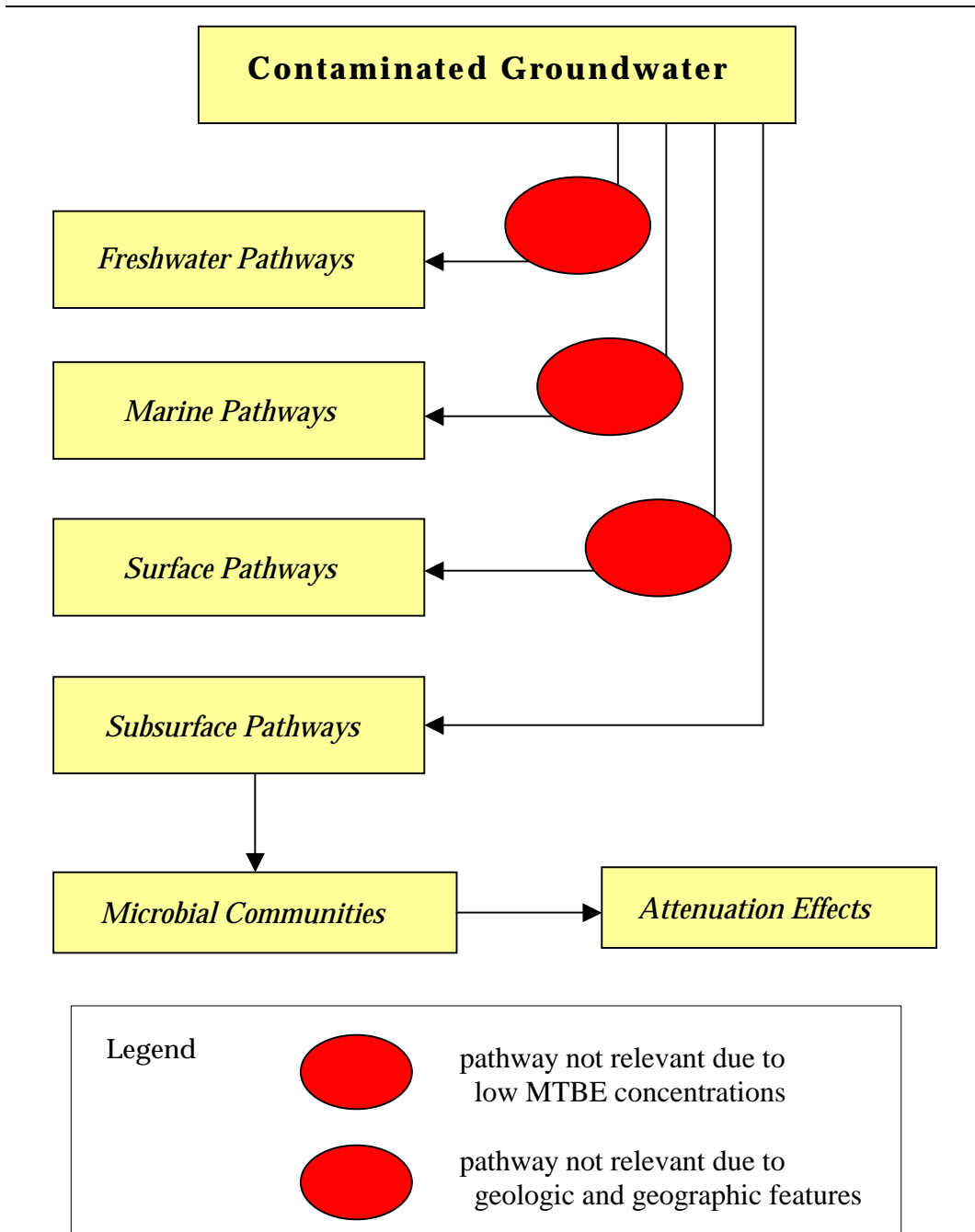
Figure 3: Conceptual model of the mechanisms of transport and exposure pathways by which ecological receptors are exposed to groundwater contaminants at the Port Hueneme site.
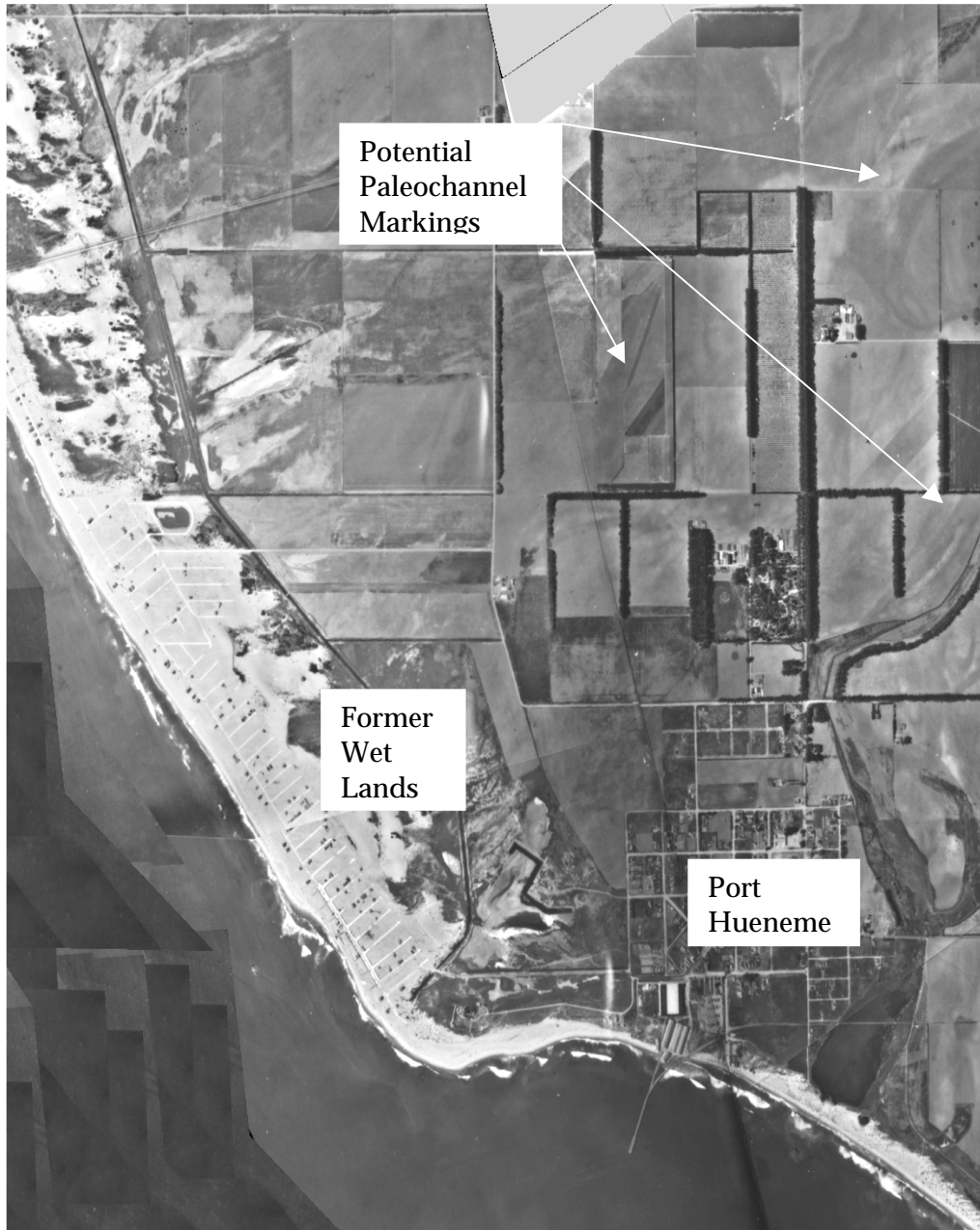
Figure 4: A 1929 aerial photograph of the Port Hueneme area, including potential paleochannels and former wetland areas. (*Source: NFESC*)

Figure 5: Map showing location of wells used for groundwater sampling as well as delineation of zones.

Zone 1 Well CBC10 Benzene Concentration
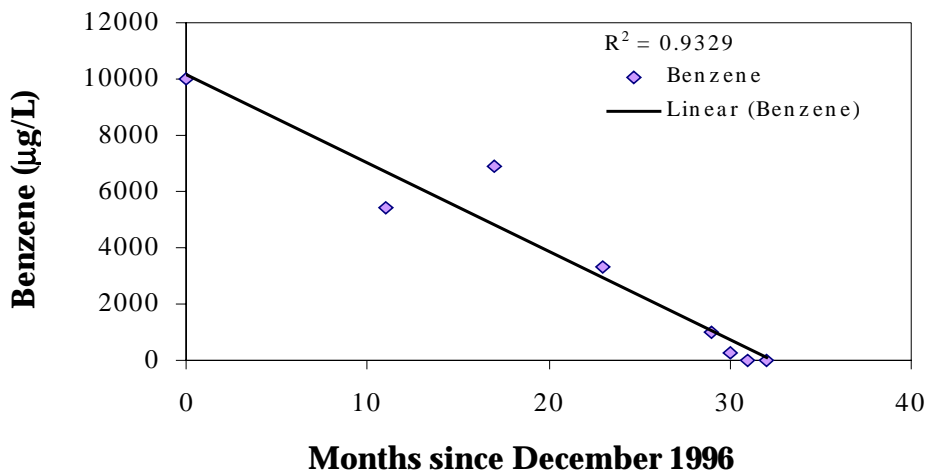
Figure 6. Changes in benzene concentration at CBC 10, for all data since December 1996.

Well CBC10 Toluene and Xylene
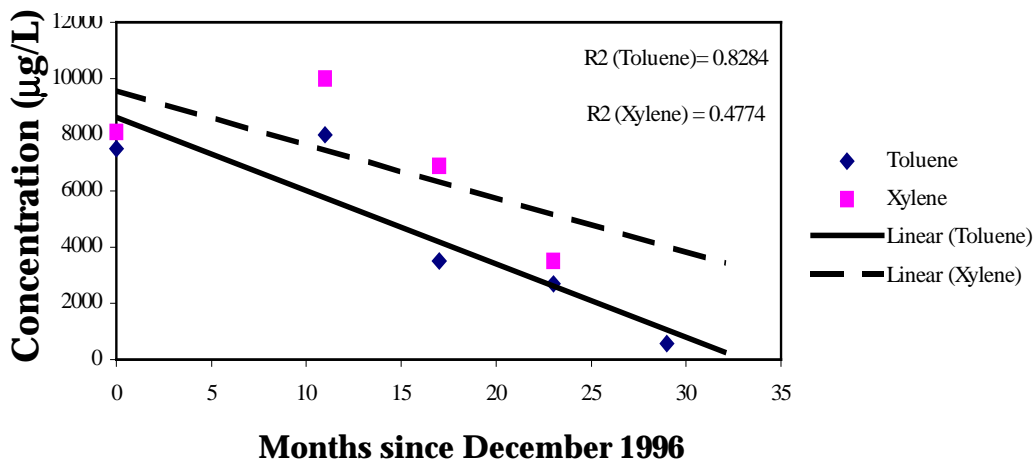
Figure 7. Changes in toluene and xylene concentrations at CBC 10, for all data since December 1996.

Zone 1 — Well CBC10
MTBE Concentration
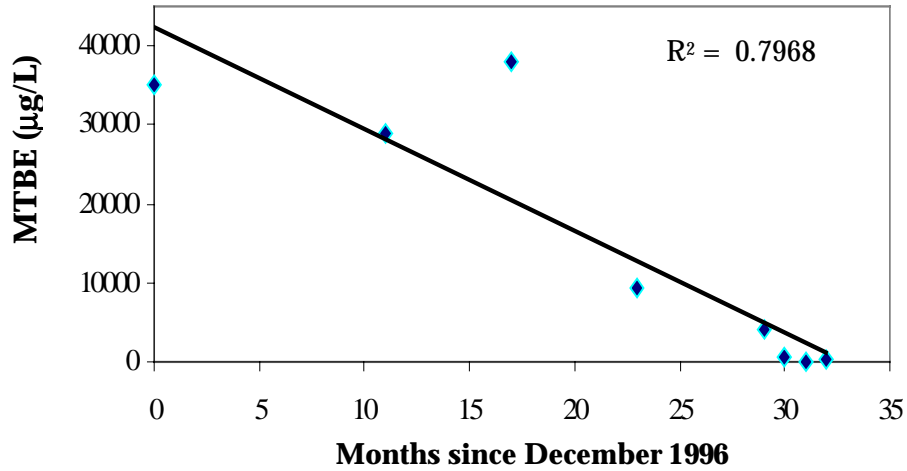
Figure 8. MTBE concentration change for Zone 1, as represented by well CBC 10, for all data dating back to December 1996.

Zone 2 — Well CBC42
MTBE Concentration
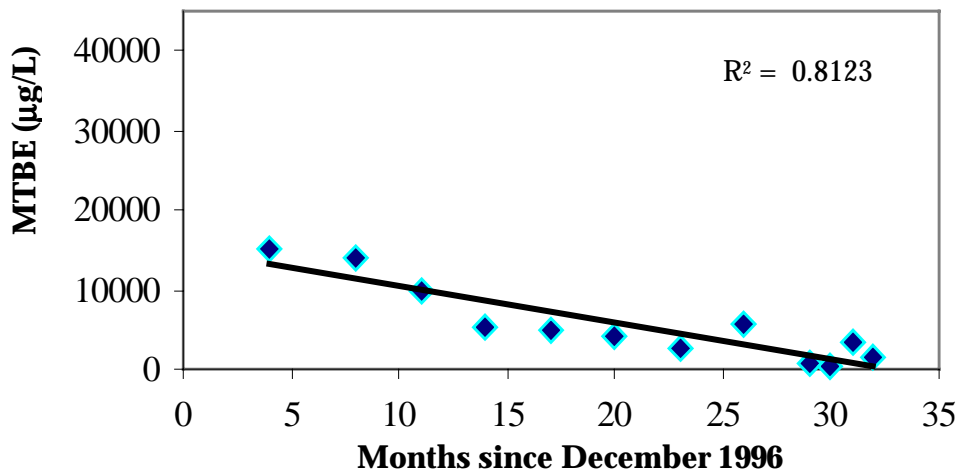
Figure 9. MTBE concentration change for Zone 2, as represented by well CBC42, for all data dating back to December 1996.

Zone 3 — Well CBC49
MTBE Concentration

$R^2 = 0.4357$

MTBE (µg/L)

Months since December 1996
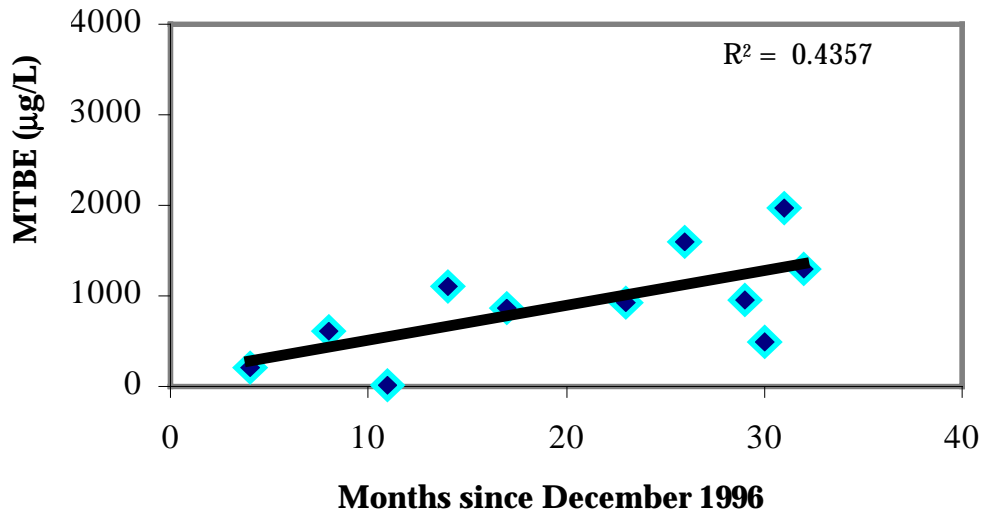
Figure 10. MTBE concentration change for Zone 3, as represented by well CBC49, for all data dating back to December 1996.

MTBE Concentration for all Zones—Dec-96 to Sep-99
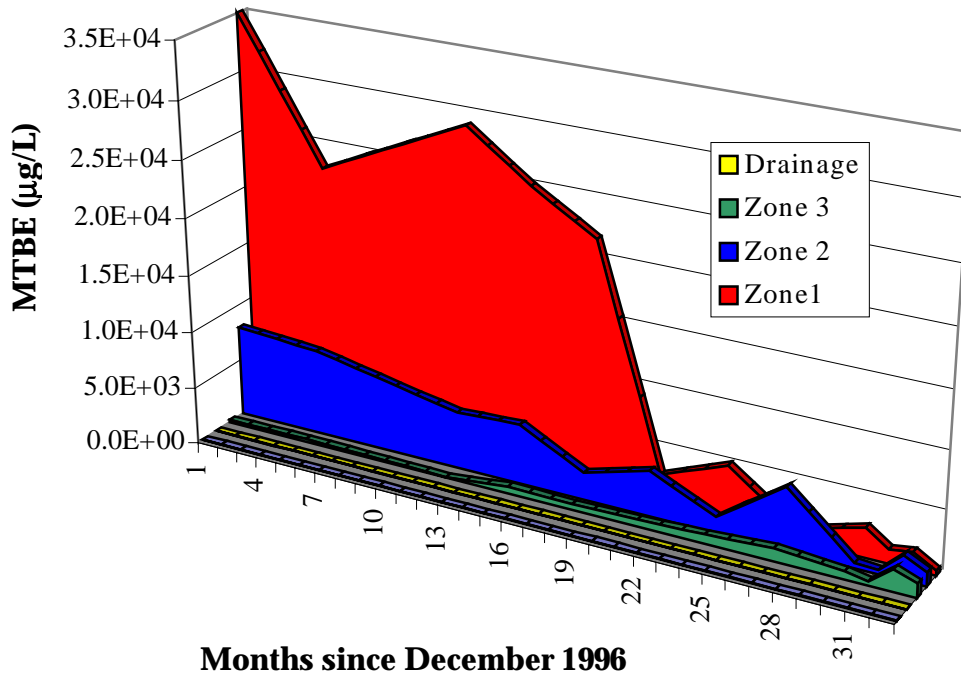
Figure 11. Changes in MTBE concentration averaged for each of the four zones defined in the Experimental Methods section are compared from data back to December 1996. The high concentrations observed in Zone 2 diminish with time, but concentrations in Zone 2 and 3 do not increase to account for this loss.

Average MTBE Concentration for June, July, August and September 1999
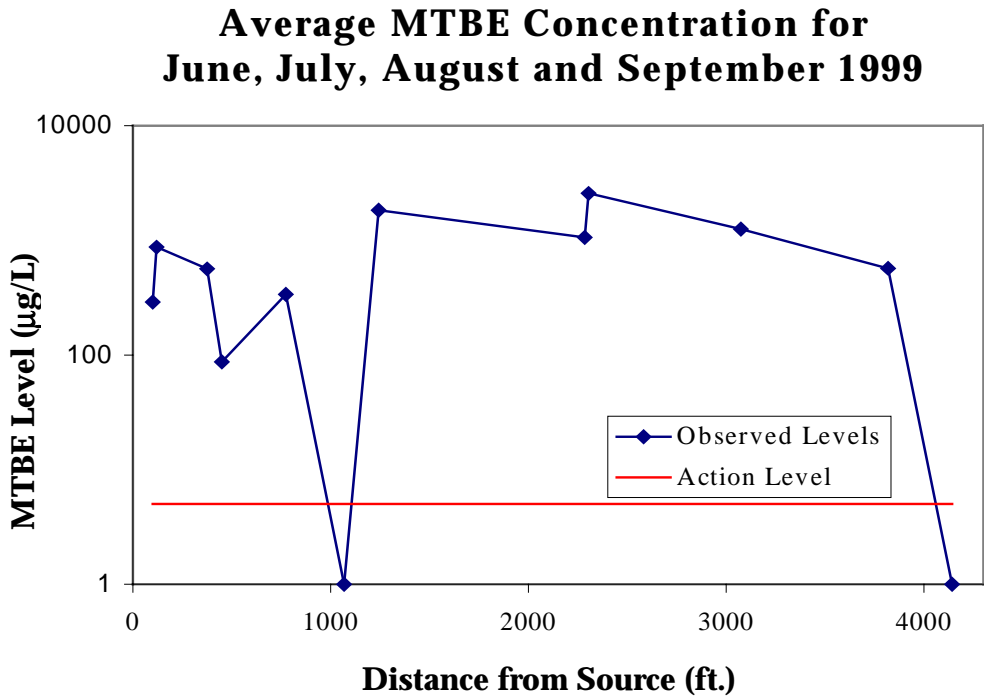
Figure 12. MTBE concentration averaged for the July, August, and September 1999 experimental period is graphed logarithmically against the distance from the NEX station. The current MCL action level is also plotted. Current MTBE levels exceed MCL action levels at almost all locations.

	MTBE	**Benzene**	**Toluene**	**Ethylbenzene**	**Xylenes**
Solubility (mg/L)	50,000	1790	534.8	161	146-175
Vapor Pressure (mm Hg @25°C)	245	76	28.4	9.53	6.6-8.7
Henry's Constant (H/RT)	0.018	0.22	0.24	0.34	0.31
Koc	12.3	80	178	871	56-204

Table 1. Physicochemical properties of on-site contaminants. (*Source: EPA Fact Sheet*)

	Distance	Test 1—Toxicity		Test 2—Toxicity	
	(ft)	5 min	15 min	5 min	15 min
Zone 1	100	5 7 5	4 5 4	2 9 4	2 7 3
	120	4 5 6	5 5 6	4 7 3	4 7 4
	376	— — 4	— — —	— — 1	— — —
	450	7 12 3	8 13 2	8 9 —	12 11 —
Zone 2	772	— — —	— — —	— — —	— — —
	1070	— — —	— — —	— — —	— — —
	1244	— — —	— — —	67 — —	— — —
	2285	— — —	— — —	— — —	— — —
Zone 3	2304	— — 1	— — —	— — —	— — —
	3073	— — —	— — —	— — 2	— — —
	3820	— — —	— — —	— — —	— — —
	4143	2 — —	— — —	— 3 —	— — —

Table 2. Toxicity of groundwater (as Toxicity Units) for groundwater samples collected at Port Hueneme during the Summer of 1999

[MTBE]	Test One		Test Two	
ppb	5 min	15 min	5 min	15 min
4762	—	—	—	—
4158	5	5	7	7
3357	—	—	—	—
2904	1	—	—	—
2861	—	—	—	—
2547	4	5	4	4
1975	—	—	—	—
1638	—	—	—	—
1637	—	—	—	—
1303	—	—	2	—
915	—	—	—	—
913	6	6	3	4
659	—	—	—	—
572	5	4	2	2
572	7	8	8	12
535	—	—	—	—
486	—	—	—	—
478	—	—	—	—
478	—	—	—	—
450	—	—	67	—
380	—	—	—	—
332	—	—	—	—
259	—	—	—	—
195	12	13	9	11
166	5	4	4	3
141	—	—	—	—
133	7	5	9	7
69	—	—	—	—
66	3	2	—	—
33	—	—	—	—
27	—	—	—	—
26	4	—	1	—
16	—	—	—	—
16	—	—	—	—
10	—	—	—	—
0	—	—	—	—
0	2	—	—	—
0	—	—	—	—
0	—	—	—	—
0	—	—	3	—
0	—	—	—	—

Table 3. Concentration of MTBE and toxicity of groundwater at Port Hueneme site

	Benzene	**Toluene**	**p-Xylene**
Attenuation rate (1/yrs)	0.32	2.30	1.26
True Life (yrs)	14	14	14
Remaining from original leak (%)	1.19	1.04E-12	2.04E-06
Concentration in Dec-96 (µg/L)	10000	7500	8100
Concentration in Jun-96 (µg/L)	1	1	1
Time elapsed (yrs)	2.50	2.50	2.50
Observed attenuation rate (1/yrs)	3.7	3.6	3.6

Table 4. Literature decay rate information for the natural attenuation of benzene, toluene and p-xylene is presented with expected percent remaining after 14 years and observed attenuation levels over the last 2.5 years. Calculations performed after Davis et. al., 1999.

Sample Date	Months after Dec-96	MTBE	Benzene	Toluene	Ethyl-benzene	Xylene
		(all concentrations measured in µg/L)				
Dec-96	0	35000	10000	7500	1200	8100
Dec-97	11	29000	5400	8000	2900	10000
Jun-98	17	38000	6900	3500	600	6900
Dec-98	23	9300	3300	2700	1400	3500
Jun-99	29	4000	1000	560	250	—
Jul-99	30	572	243	—	—	—
Aug-99	31	133	—	—	—	—
Sep-99	32	166	—	—	—	—

Table 5. Concentration of contaminants in Zone 1 as represented by well CBC01. This table contains all available data from December 1996 to September 1999.

Well	Water Depth (cm)	Temp (°C)	Dissolved Oxygen (mg/L)	pH	Conductivity (mS/cm)	Redox (mV)
CBC 01	277.5	21.37	0.08	6.75	2.57	-92
CBC 10	259.0	22.81	0.12	6.83	2.42	-75
CBC 15	262.0	22.56	0.10	6.77	2.00	-94
CBC 17	282.0	20.44	0.09	6.70	2.78	-72
CBC 19	268.0	22.51	0.09	6.84	2.02	-155
CBC 24	229.5	23.12	0.08	6.76	2.05	21
CBC 35	224.5	22.07	0.13	6.69	2.98	24
CBC 42	229.5	24.10	0.14	6.68	2.24	37
CBC 45a	215.5	22.18	0.16	6.74	2.44	13
CBC 47	178.5	22.32	0.21	6.79	2.74	22
CBC 49	189.0	22.00	0.23	6.76	2.79	19
CBC 51	182.5	22.07	0.23	6.76	2.76	34
CBC 54	169.5	21.96	0.20	6.91	3.04	-7
DC 01	N/A	20.49	7.51	7.24	2.65	251
DC 02	N/A	21.66	6.57	7.49	2.70	237
DC 03	N/A	21.95	4.43	7.20	2.95	241

Table 6. Physical properties of water samples taken *in situ* during July of 1999. All data recorded on Hydrolab apparatus as directed by Naval procedures.

Well	Water Depth	Temp	Dissolved Oxygen	pH	Conductivity	Redox
	(cm)	(°C)	(mg/L)		(mS/cm)	(mV)
CBC 01	278.5	21.43	0.14	6.27	2.46	-59
CBC 10	260.5	22.82	0.16	6.32	2.28	-79
CBC 15	268.5	22.62	0.12	6.35	2.06	-41
CBC 17	274.0	20.56	0.11	6.24	2.77	-15
CBC 19	270.5	22.66	0.09	6.42	1.98	-66
CBC 24	231.5	22.71	0.12	6.29	2.05	87
CBC 35	220.5	21.52	0.10	6.23	3.01	85
CBC 42	230.5	23.85	0.11	6.23	2.33	89
CBC 45a	144.5	21.68	0.27	6.33	2.45	72
CBC 47	180.5	22.41	0.20	6.38	2.77	132
CBC 49	192.0	22.75	0.24	6.39	2.79	82
CBC 51	185.0	22.48	0.23	6.43	2.76	96
CBC 54	173.0	22.46	0.25	6.62	3.04	44
DC 01	N/A	19.84	7.29	7.09	2.64	327
DC 02	N/A	20.30	8.35	7.21	2.71	315
DC 03	N/A	21.63	4.62	6.81	2.85	331

Table 7. Physical properties of water samples taken *in situ* during August of 1999. All data recorded on Hydrolab apparatus as directed by Naval procedures.

Well	Water Depth (cm)	Temp (°C)	Dissolved Oxygen (mg/L)	pH	Conductivity (mS/cm)	Redox (mV)
CBC 01	281	21.63	0.1	7.07	2.51	87
CBC 10	262.5	22.75	0.21	7.22	2.31	34
CBC 15	—	—	—	—	—	—
CBC 17	284.5	20.73	0.11	7.05	2.74	72
CBC 19	272.2	23.23	0.17	7.25	1.98	45
CBC 24	225.6	22.6	0.12	7.12	2.01	64
CBC 35	262.4	22.32	0.15	7.06	3.01	51
CBC 42	283.2	27.47	0.36	6.95	2.05	189
CBC 45a	178.2	22.12	0.27	7.12	2.47	55
CBC 47	183.5	23.76	0.61	6.97	2.7	155
CBC 49	194.1	27.1	1.17	7.03	2.79	111
CBC 51	187.1	23.27	0.9	6.95	2.7	184
CBC 54	174	22.78	0.24	7.35	3.03	26
DC 01	N/A	19.01	6.48	7.73	2.6	141
DC 02	N/A	20.42	6.57	7.97	2.65	217
DC 03	N/A	21.38	4.92	7.63	2.66	251

Table 8. Physical properties of water samples taken *in situ* during September of 1999. All data recorded on Hydrolab apparatus as directed by Naval procedures. Note: Samples taken from well CBC15 were collected one day after all others from this sampling event and the Hydrolab was unavailable for use.

Appendix A—Ecological Risk Screening

**Ecological Risk Screening of MTBE Plume
at the
Naval Exchange Gasoline Station,
Naval Construction Battalion Center
Port Hueneme, CA**

August 13, 1998

A 4,100 foot long groundwater plume of methyl tertiary-butyl ether (MTBE) covering 39 acres resulted from gasoline leaks in fuel delivery lines at the Naval Exchange (NEX) Gasoline Station at Port Hueneme. Approximately 4,000 gallons of regular gasoline and 6,800 gallons of premium unleaded gasoline leaked between September 1984 and March 1985. The exact percentages of MTBE in the gasoline were unknown, but are estimated to have been between 6% and 11%. The NEX Gasoline Station has operated in the vicinity of Building 797, at the southeast intersection of 23rd Avenue and Dodson Street, since 1950. There is no information available on any releases that may have occurred prior to 1984.

The objective of this screening assessment was to determine whether the MTBE plume poses a potential risk to the ecosystem. Potential exposure pathways and receptors were evaluated, and an ecological effects evaluation was completed.

<u>Environmental Setting</u>
The MTBE plume occurs in a semi-perched aquifer at a depth of approximately 10 feet below ground surface (bgs) and reaches a depth of approximately 20 feet. Because it is a shallow aquifer, it is very unlikely that this groundwater would ever be used as a drinking water supply. Beneath the aquifer is a clay layer with low permeability, and another aquifer at a depth of over 300 feet. The near-surface soils at the NEX Gasoline Station site consist of sands, silts, clays, and gravels. The subsurface sediments consist primarily of sand and silty sand with minor amounts of silt and clay. The current land use is industrial, and much of the area over the MTBE plume is paved with asphalt or concrete.

Most gasoline constituents, such as benzene, toluene, ethylene, and xylene (BTEX), have migrated only a short distance from the source (approximately 1200 feet), and recent data shows that the BTEX plume is receding. In addition, interim removal actions were conducted between 1991 and 1993, in which free product and contaminated soil were removed from the source area. However,

MTBE has migrated a greater distance with the groundwater, due to its chemical properties: it is highly soluble, has low adsorption to soil, and does not readily degrade. A drainage channel is located about 1500 feet down gradient of the leading edge of the MTBE plume. This drainage channel is approximately 8 - 14 feet deep and 15 - 25 feet wide. It is assumed that the semi-perched aquifer daylights into this drainage channel at some point, but it is not known exactly where or by what route.

Contaminant Fate and Transport
The main mechanism of transport of MTBE at this site is as a dissolved constituent in groundwater. Because MTBE is highly soluble in water (51 g/L at 25°C), does not readily degrade in the groundwater environment, and does not adhere to soil or organic matter (estimated organic carbon partitioning coefficients of 10.96 - 12.3), it travels freely with the groundwater (US EPA 1994). Site characterization and groundwater monitoring data indicate that the MTBE is moving only in one direction, resulting in an elongated plume with little outward spreading. A geophysical survey conducted on April 17, 1997 revealed that a paleostream channel acting as a preferential flow pathway was the cause of the elongated MTBE plume.

A 1997 study estimated the time it would take for the leading edge of the MTBE plume to reach the closest section of the drainage channel (TtEMI 1997). Assuming that 1984 was the release date and using conservative calculation parameters, which disregarded absorption or adsorption to sediment or potential down gradient volatilization, the study calculated that MTBE would have traveled down gradient at approximately 340 feet per year. At this conservatively calculated flow rate, the MTBE plume would intersect the nearest surface water drainage ditch in approximately 4.4 years. This ditch is approximately 1,500 feet down gradient of the present lead edge of the MTBE plume.

MTBE is highly volatile when exposed to the atmosphere, so if the groundwater plume daylights into the drainage channel, any MTBE present would be expected to volatilize rapidly. The volatilization half-life of MTBE in streams was estimated to be 2.5 hours. MTBE is not expected to absorb to sediments or suspended particulate matter (US EPA 1994).

MTBE demonstrates a low potential for bioaccumulation (Mancini 1998 and US EPA 1994). Therefore, MTBE bioconcentration in tissue of prey species and subsequent effects to predators is not a concern at this site.
Ecotoxicity of MTBE
The existing aquatic toxicity data for freshwater and marine species indicate that MTBE exhibits a low level of aquatic toxicity by nonspecific narcosis (US EPA

1994). Some marine species tend to be more sensitive than freshwater species to MTBE (Mancini 1998).

Burrowing mammals may be effected by three potential routes of MTBE soil exposure: soil ingestion, dermal contact, and inhalation. The following no-effect MTBE soil concentrations were calculated from existing toxicity data: 1250 mg/kg for incidental ingestion; 500 mg/kg for dermal exposure; and 250 ppmv for inhalation (Mancini 1998).

Exposure Pathways
A potential exposure pathway exists from the impacted groundwater to ecological receptors in the drainage channel. Potential primary receptors include plants, aquatic invertebrates, insects, frogs, etc. Potential secondary receptors include species that feed on primary receptors, such as birds and rodents. At present this exposure pathway is not complete, but using the conservative assumptions described above, it is possible that the MTBE plume will intercept the channel in approximately 4.4 years.

Soil was also impacted by the spill, but the leaks occurred at a depth of at least a few feet, where few ecological receptors are located. Burrowing animals generally reach depths of no more than 4 feet (Lidicker 1989). Earthworms and other soil invertebrates prefer the aerated, biologically active zone in the first 2 - 3 feet. While some plant roots may reach depths of 10 feet or more, at least 90 percent are located in the first 4 - 5 feet (Raven 1986). Therefore, most terrestrial ecological risk assessments consider only the soil in the top 3 - 4 feet.

At this site, it can be assumed that there is no complete exposure pathway from MTBE in the soil to terrestrial receptors. The removal actions completed in 1993 removed free product and highly contaminated soil. While it is possible that there may be some pockets of soil which still contain MTBE, it is likely that they would be located at depths greater than the biologically active zone. The only potentially complete exposure pathway to ecological receptors is from the groundwater into the drainage channel.

Assessment and Measurement Endpoints and Evaluation of Ecological Effects
In this screening assessment, endpoints included any adverse effects to ecological receptors. Because the only potential exposure pathway is to receptors in the drainage channel, the assessment endpoints considered were freshwater aquatic receptors. Conservative screening ecotoxicity benchmarks were used to determine whether a potential risk exists.

The most comprehensive analysis to date of aquatic toxicity reference values (TRVs) was conducted by Mancini (1998). Both freshwater and marine TRVs

were calculated based on a compilation of existing toxicity data. These TRVs were calculated using the guidance for developing federal ambient water quality criteria (AWQC), and are intended to be used in conducting generic as well as site-specific ecological risk assessments. For freshwater aquatic organisms, the TRV for protection of acute effects was calculated to be 115 mg/L. The TRV for protection of chronic effects was calculated as 66 mg/L. (Mancini, 1998).

Since the endpoint for the screening-level assessment was no adverse effects to any receptors, it was most appropriate to apply the most protective effects threshold. The threshold for chronic toxicity is 66 mg/L. Surface water concentrations at or below this level would not be anticipated to cause adverse ecological effects to freshwater organisms (Mancini, 1998).

While this TRV is the best-documented and most relevant screening benchmark for this site, a literature search resulted in two more conservative values. Van Leuwen et. al. (1992) published a no-observed-effects-level (NOEL) for no chronic effects to 95% of aquatic species. The NOEL was calculated as 13 mg/L. However, the toxicity data incorporated marine species, which appear to be more sensitive to MTBE than freshwater species. Also, US EPA (1993) reported a daphnid chronic value of 17 mg/L. This value was not a result of toxicity tests with daphnids, but was extrapolated from fathead minnow bioassays, using Quantitative Structure Activity Relationship (QSAR) calculations. To ensure an additional level of conservatism, these two values were used qualitatively for comparison to groundwater concentrations.

The measurement endpoint was the comparison of MTBE concentrations in groundwater to the ecotoxicity benchmarks of 66 mg/L, 17 mg/L, and 13 mg/L. Groundwater concentrations at various points in the plume are currently well documented, and the leading edge of the plume is monitored regularly. Fate and transport of MTBE from the groundwater to the drainage channel was addressed qualitatively.

Exposure Estimate and Risk Calculation
Data was examined from quarterly groundwater monitoring that took place in 1996, 1997, and 1998. The monitoring involved analyzing samples from 35 wells for MBTE and other constituents of gasoline. Not all wells were analyzed every quarter, but the data available is sufficient to provide a good characterization of the extent of contamination.

All of the groundwater MTBE concentrations analyzed were well below the freshwater aquatic TRV of 66 mg/L. Therefore, even if aquatic receptors were in direct contact with groundwater, no adverse ecological effects would be expected.

If the most conservative benchmark of 13 mg/L is applied, the only wells which have exceeded this value are CBC-10, CBC-155, and CBC-42. All of these wells are close to the original source and far from the drainage channel. The highest MTBE concentrations in these wells were 38 mg/L, 23 mg/L and 15 mg/L, respectively. It can easily be demonstrated, using very conservative fate and transport assumptions, that by the time the plume reaches the drainage channel, MTBE concentrations will be well below 13 mg/L. The highest detected MTBE concentration near the current leading edge of the plume was 1.1 mg/L, at CBC-49 in March 98. Groundwater data along the length of the plume has shown a fairly consistent concentration gradient from the source area to the leading edge. Therefore, it is expected that groundwater will never intercept the drainage channel with MTBE concentrations greater than 13 mg/L, and ecological receptors will not be impacted.

Although the drainage channel eventually empties into the Hueneme Harbor, MBTE volatilizes so quickly that it is expected to be at non-detect levels by the time the water reaches the marine environment. The volatilization half-life of MTBE in streams is approximately 2.5 hours (U.S. EPA 1994).

Results and Recommendations
The results of this screening assessment indicate that the MTBE plume on this site poses little or no ecological risk. Even with the extremely conservative assumptions that were employed in this screening, no adverse effects to ecological receptors are anticipated. Quarterly groundwater monitoring will continue to take place at the site, and movement of the MTBE plume will be closely watched. The MTBE plume is part of a National Test Site, and several studies are taking place there, including phytoremediation and natural attenuation of MTBE. As more data becomes available on the ecotoxicity of MBTE, the ecological effects at this site may be reevaluated.

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Appendix B—Stagnant Two-Film Model

The Stagnant Two-film Model is used to establish flux of a chemical through a given interface. In this case we are solving for the flux of MTBE out of a small cuvette containing our water sample and into the air during our toxicity analysis. The loss of MTBE via this volatilization process could potentially impact our toxicity findings and is therefore worth investigating. Fate and transport chemistry dictates that chemicals typically move across an interface based on the following equations:

F　　**=**　　**Vtot(Cw – Ca/Kh)**
Vtot　**=**　　**(1/(Zw/Dw)+(Za/DaKh))**

Description of Values

F	=	Flux out of the cuvette
Vtot	***=***	***Total Volatilization***
Ca	=	Concentration of contaminant (MTBE) in the air
Cw	=	Concentration of contaminant (MTBE) in the water
Da	=	Rate of diffusion through the air layer
Dw	=	Rate of diffusion through the water layer
Za	=	Size of the air interface layer
Zw	=	Size of the water interface layer
Kh	=	Henry's constant, represents overall trend toward volatilization

Corresponding Values

Ca	=	0
Cw	=	500ppb
Dw	=	1.123E-5 cm^2/s　(from MW MTBE = 88.15)
Da	=	0.084 cm^2/s　　(from MW MTBE = 88.15)

In order to estimate the potential impact of volatilization on our sample, liberal numbers for the range of Zw and Za were used.

Zw	=	something in range of .05-.5 mm
Za	=	something in range of 1-10 mm

In order to estimate the impact of volatilization on our sample liberal Kh values were also used. All estimates are based on the 1.2E-1 approximation.

| Kh | = | 5.5 E-4 atm m^3/mol at 25C |
| | = | 2.2E-2 - 1.2E-1 unitless |

Solving Vtot

Vtot = (1/[(.005(cm)/1.123E-5(cm^2/s))

+(.1(cm)/(.084(cm^2/s)*1.2E-1(unitless)]

Vtot = 2.2E-3 cm/s   when Zw = .05 and Za = .1

Based on ppb to g/ml Conversion

Cw = 500 ppb MTBE = 2.45 E-6 g/ml
Ca = 0

Ca/Kh = 0/Kh = 0

Solving for F

F = 2.2E-3 cm/s (2.45E-6 g/cm^3 - 0/Kh)
= 2.2E-3 * 2.45E-6 (g/cm^2 per s)
= 5.5E-9g MTBE lost per square centimeter of surface per second.

Solving for MTBE Concentration in Vial

Sample vial size was estimated at 3.5ml, with a surface of 1 cm^2.
                The total MTBE in the vial is 2.45E-6 g/ml; *3.5 ml = 8.6 E-6 g MTBE

Solving for Volatility Rate

5.5E-9g MTBE * (X)seconds = 8.6 E-6 g MTBE

= 1.55E3 seconds = 26 minutes

Recall that all of the assumptions were made by taking only the most liberal values into consideration. A more conservative account, taking into account the cooler temperatures of the test mechanisms would undoubtedly yield a much reduced rate of volatilization.

Solving with a less conservative interface

If Za and Zw are more near the middle of the range, say .25 and .5 respectively we find.

Vtot   =   4.4E-4 cm/s

F   =   4.4E-4 cm/s (2.45E-6 g/cm^3 - 0/Kh)
    =   4.4E-4 * 2.45E-6   (g/cm^2 per s)
    =   1.1E-9 g MTBE lost per square centimeter of surface per second

Considering the sample vials are roughly 3.5ml with surface of 1 cm^2, the total MTBE in the vial is 2.45E-6 g/ml; *3.5 ml = 8.6 E-6 g MTBE

Solving for Volatilization Rate (less conservative)

Vtot   =   1.1E-9g MTBE * (X)seconds = 8.6 E-6 g MTBE
X   =   7.8E3 seconds
    =   2 hours 12 minutes

If we assume that the samples were exposed to the air for approximately 5 and 15 minutes each during toxicity analysis we find:

Maximum loss by end of experiment (Liberal)

5minutes/26 minutes = 19% loss by 5 minute analysis

15minutes/26 minutes = 57% loss by 15 minute analysis

Maximum loss by end of experiment (Moderately Conservative)

5min/132mins = 4% loss by 5 minute analysis

15min/132mins = 11% loss by 15 minute analysis

These values should still be considered liberal estimates. Real volatilization rates would in all likelihood be smaller.

We did not observe differences between our 5 and 15 minute analysis, which suggests that the loss of MTBE via volatilization didn't significantly alter our toxicity findings. Review of this examination by Arturo Keller Ph.D. suggested that these findings were all very conservative and that a smaller percent loss would actually be expected under the given conditions.

Experimental Write-Up

Determination of the Toxicity Associated with a Release of MTBE and BTEX into the Groundwater

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Between September 1984 and March of 1985 an underground storage tank at Port Hueneme, released approximately 4,000 gallons of regular and 6,800 gallons of premium unleaded gasoline into the ground. An experiment was performed in July, August, and September of 1999 in order to assess the ecological risk to underground microorganism communities created by BTEX and MTBE contaminants associated with the 1984 release. Microtox™ analysis and Gas Chromatography and Mass Spectroscopy tests were completed in order to correlate the relationship between MTBE, BTEX, toxicity, temporal variability, and spatial deviation down gradient of the plume. The experimental findings suggest that the plume is not easily differentiable with regard to space or time during this three month period and that MTBE, BTEX, and toxicity levels are not directly correlated. In regions where MTBE and BTEX concentrations have dropped over the past three years, toxicity was detected; however, the source(s) of the toxicity cannot be isolated using available data.

Introduction

Methyl tert-butyl ether (MTBE) is added to gasoline in order to promote more efficient combustion. The extra oxygen that MTBE provides converts carbon monoxide, which is produced as a result of incomplete combustion, to carbon dioxide (Keller et. al. 1998). Effective April 1996, the California Air Resources Board enacted a regulation that mandated the statewide use of California Phase 2 Reformulated Gasoline (Keller et. al. 1998). Although CaRFG2 does not specify MTBE as the required oxygenate, most refineries selected it due to economic reasons. California gasoline currently contains 11% MTBE by volume (Kirchstetter et. al. 1998).

Since the late 1970s, MTBE has been added to gasoline on the base to reduce toxic air emissions and to enhance the octane of conventional gasoline mixtures. Due to a leaking delivery line/joint fixture between the main underground gasoline storage tank and the distribution module, approximately 4,000 gallons of regular and 6,800 gallons of premium unleaded gasoline was released between September of 1984 and March of 1985. This incident produced a 4,100-foot long plume of MTBE in the groundwater, which covers almost 39 acres. MTBE concentrations in the most downgradient monitoring wells were identified to be as high as 16,000 µg/L (Lorenzana 1999).

When released to the environment through a gasoline spill or underground storage tank (UST) leak, MTBE can migrate extensively due to its high solubility in water and tendency to resist biodegradation. Once it has entered the subsurface, it can reach surface or coastal waters and eventually impact aquatic organisms. The MTBE2000 Group Project was created in an attempt to quantify the ecological risk associated with such a release at the U.S. Naval Construction Battalion Center (CBC), Port Hueneme, California.

Recent research has suggested that invertebrate species, in general, are more sensitive to MTBE than fish or amphibian species (Stubblefield et. al. 1998). It is estimated that levels as high as 66 mg/L may have no significant ecological effects on freshwater organisms (Mancini et. al. 1999). In 1998, an ecological risk screening performed on the plume at Port Hueneme determined that the groundwater concentrations of MTBE were well below this freshwater aquatic guideline (Hunt 1998). However, due to the unpredictable nature of the plume's movement, groundwater wells continue to be monitored at the site.

The toxicity of the contaminated groundwater to microorganisms has not yet been determined. A Microtox™ bioassay will provide the effective concentration of a sample that will affect the test organism by either causing its death or

inhibiting its metabolic processes. The information attained through this study will facilitate future research efforts by lending a better understanding of the extent of toxicity associated with the current plume as well as the potential movement and expansion of the MTBE plume over time. It has been shown through background monitoring well data that MTBE concentrations in areas not in the path of the plume are currently at below detectable levels (Lorenzana 1999).

MTBE is not the only chemical present in the ground water at Port Hueneme. The source region of the plume is known to be contaminated with the gasoline byproducts benzene, toluene, xylene, and ethylbenzene (BTEX) which are residuals from the original leak. MTBE and BTEX degradation products may also be expected to be present in various concentrations throughout the entire MTBE contaminated region. The degradation of organics, like MTBE, by abiotic and biotic reactions normally leads to the formation of other organic compounds or daughter products. The mineralization, or complete breakdown, of an organic compound to carbon dioxide and water can involve many reactions over an extended length of time. MTBE degradation can occur in both aquatic environments or in the atmosphere to produce a range of both inert and toxic daughter products (HSDB 1994; U.S. EPA 1993).

The degradation of MTBE in groundwater can lead to the formation of tertiary-butyl alcohol (TBA), a carcinogen (Borden et. al. 1997). Other secondary degradation products that may be formed include methyl acetate, acetone, and formaldehyde (U.S. EPA 1993). The majority of these byproducts will not be an important concern to at this site, since their presence and concentration is expected to be insignificant in the groundwater or as deposition products. Several of the MTBE metabolites may be toxic to microorganisms, but little information exists on this type of toxicity affect. Furthermore, evaluating the ratio or concentration of metabolites, and other petroleum byproducts is beyond the scope of this examination. However, outlier toxicity findings may indicate the presence of these chemicals and be useful for further analysis.

Experimental Design

In order to acquire a full understanding of the toxicity associated with the MTBE contaminated groundwater at Port Hueneme we have divided the plume into four distinct zones (Figure E1). The first zone is the area near the head of the plume where the leak originally occurred. This region has historically (a) shown the highest MTBE concentrations and (b) been contaminated with BTEX components. The second zone includes the middle section of the plume. MTBE concentrations in this region have shifted over time—levels have recently begun to decrease—as the contaminant travels with the groundwater. The third zone includes the toe of the plume which is currently under scrutiny as the plume has been moving into this area. The fourth zone is a storm drain system where MTBE has been recently detected, potentially accelerating the transport of MTBE toward the ocean. Findings in this region will provide knowledge about the most eminent toxicity risk to the oceanic community.

Four wells from Zones 1 through 3, three locations within the storm drain system, and one background well were sampled. The wells were selected based upon accessibility and general representation of the plume. Figure 2 shows the location of each sampling point along with well CBC1, which is outside the influence of MTBE on site and is typically used to represent background concentrations.

At each well, three samples were extracted. Two water samples taken from each well were analyzed using the Microtox™ analysis in order to provide duplication of results. These samples were stored at 2–8ºC and used within 48 hours in order to maintain viability. The third sample was placed in a separate cooler for transportation to a gas chromatograph/mass spectrometry testing facility at the University of California, Santa Barbara (Keller Lab). Thus, for each of our three experiments we collected a total of 16 water samples and conducted a total of 32 Microtox tests.

Sample Collection and In Situ Testing

The sample collection protocol utilized in this experiment was adapted from the Micro Well Groundwater Sampling Procedure provided by the personnel from the National Test Site at Port Hueneme. Details of the Hydrolab preparation methods were acquired from personal communications with Dale Lorenzana, who assisted in the collection of samples on site.

In order to eliminate the possibility of cross contamination of water samples, a separate tube assembly was created for each well. Sample tube assemblies were created by taking a six inch piece of 6402-15 NORPRENE® pump tubing, inserting an 18 ft length of Poly Tubing into one end of the pump tubing and a six inch piece of Poly Tubing into the other. The sample/pump tubing can be cut and assembled prior to or during the sampling event. The assembly was then attached to the Hydrolab and to a pump that draws the water out of the well.

The Hydrolab allowed for in situ testing of the well waters. Prior to use, the Hydrolab batteries were checked and the multiprobe cleaned and calibrated, per standard practices as outlined in manual. The Hydrolab was attached and measurements taken prior to the drawing of the water sample. An effluent pump tube was also connected by a length of polyethylene tubing that ran to a wastewater container to collect excess groundwater.

A basic sampling procedure is outlined below:

1. Using a battery-powered measuring device, record depth to water measurements before sampling begins and measurements in field logbook.

2. Insert polyethylene tubing sample tube assembly into well and the other end into the influent tubing of the Hydrolab flow through cell (FTC).

3. Start peristolic pump and run pump at approximately 500 mL per minute.

4. After the FTC is full and effluent is running into the wastewater container, turn on Hydrolab Display Logger.

5. Continue to run pump at approximately 500 mL per minute until the dissolved oxygen (DO) reading stabilizes.

6. Record Display Logger readings (water temperature, pH, conductivity, and redox potential) in field logbook.

7. Turn pump speed to zero.

8. Close influent valve to FTC.

9. Pull polyethylene tubing from influent tubing for FTC. (This is the sampling point)

10. Slowly turn the pump speed up to fill sample bottle. Tilt bottle slightly to allow the water to flow down the inside wall of the sample bottle. When the bottle is full, zero the pump speed and cap the sample bottle.

11. Label samples with date/time and well number and store on ice for analysis.

Three 150 mL groundwater samples were transferred into Teflon lined screw cap borosilicate containers filled to capacity, leaving no air space, and stored at approximately 4°C.

Note: Toxicological samples must be used within 48 hours after sampling event. Remaining samples may be stored and further analyzed for contaminant concentrations within 14 days of sampling events.

Microtox™ Bioassay

The following method protocol was derived from the Microtox™ Basic Test Protocol manual (Microbics Corporation 1992). The procedures described are for a single sample and were repeated in order to test three samples consecutively, as directed by the manual.

Introductory Steps

1.   Prepare phenol standard:
   a) Add 50 mg crystalline phenol to 500 mL volumetric flask.
   b) Add distilled water up to the 500 mL mark on the flask and seal.
   c) Mix well.
2. Perform complete basic test protocol using phenol standard (prior to each test session).
3. Record pH measurements during sampling events using Hydrolab software.

Preparation of the Analyzer

1. Place clean cuvettes in wells (rows A and B, and in Reagent well).
2. Pipette 1000 μL Microtox™ Reconstitution Solution (Recon Solution) into cuvette in Reagent well.
3. Pipette 500 μL Microtox™ Diluent into wells B1-B5.

4. Pipette 1000 μL Microtox™ Diluent into wells A1-A4.

Preparation of Sample

1. Pipette 250 μL Microtox™ Osmotic Adjustment Solution (MOAS) into well A5.
2. Add 2500 μL of sample to well A5. Mix using pipettor, by filling and dispensing the pipettor 3-4 times.
3. Create 1:2 serial dilutions:
a) Transfer 1000 μL from A5 to A4. Mix as before.
b) Transfer 1000 μL from A4 to A3. Mix as before.
c) Transfer 1000 μL from A3 to A2. Mix as before.
4. Discard 1000 μL from A2.
5. Discard 750 μL from A5.
6. Wait 5 minutes for temperature equilibration.

Preparation of Reagent

1. Take a vial of Microtox™ Reagent from freezer.
2. Take the cuvette from the Reagent well. Dump the reconstitution solution into the reagent vial as quickly as possible.
3. Swirl the reagent vial 3 – 4 times, pour the reagent into the cuvette, and place cuvette into the Reagent well.
4. Mix the reconstituted reagent with a 500 μL pipettor (using a new pipettor tip) by filling and dispersing the pipettor 20 times.
5. Pipette 10 μL reconstituted reagent into wells B1-B5.
6. Mix the reagent in each cuvette (B1-B5), using a 250 μL pipettor (or by hand) 2 – 3 times.
7. Wait 15 minutes after reagent dilution for reagent stabilization.

Preparation of Computer

1. Call up the Basic Test program. Select Start Testing to begin entering parameters.
2. Set number of tests (1), enter a unique file name for each test, enter description: well number, pH, and date.

3.	Set current test parameters: enter number of controls, number of dilutions, initial concentration, dilution factor, and times (set to analyze at 5 minutes and 15 minutes as per standard Microtox™ procedure).

Test Protocol

1.	Place B1 cuvette in READ well. Press the SET button.
2.	Touch the computer space bar.
3.	READ zero time l_o light levels as prompted by the computer screen.
4.	Immediately make the following 500 µL transfers, mixing after each transfer: A1 to B1, A2 to B2, A3 to B3, A4 to B4, A5 to B5.
5.	Touch the computer space bar.
6.	When the timer sounds, READ (5 & 15 minute) light levels as prompted by "ENTER" on the computer screen. The computer automatically records data from the Microtox™ unit.

Gas Chromatography and Mass Spectrometry

As noted in the experimental design section of this report, contaminant concentrations were determined using Gas Chromatography and Mass Spectrometry in a laboratory facility at the University of California, Santa Barbara. The methods employed were adapted from the EPA method, but instead of purge and trap, a Solid Phase Micro-Extraction (SPME) technique was used. In this analysis, Polydimethyl Siloxane Carboxen fiber was used to extract MTBE and BTEX from a liquid phase, and the fiber then placed in the GC injection port for desorption at 250ºC. The analyses were done by using a Hewlett Packard 5890 Gas Chromatography equipped with a Flame Ionization Detector (FID). The temperature of the detector was set at 250ºC. A VOLCOL (Supelco) capillary column (30m x 0.25 mm with 0.25 m film) was used. The column temperature was programmed from 100 to 120ºC at an increasing rate of 12.0ºC/min. Sample variation upon duplicate analyses was accurate to ± 1% of measured value.

Results

Benzene concentrations were observed at irregular intervals at two locations in the source region (Zone 1) over the course of the experiment.   Benzene with enough consistency to draw a significant correlation with toxicity, MTBE concentration, or spatial and temporal distribution (see Table E1).   High toxicity levels were often

associated with low MTBE concentrations, and high MTBE concentrations were often associated with low toxicity levels; MTBE and toxicity could not be correlated (Figure E2). MTBE concentrations varied greatly in all three zones over the experimental period (Table E2) and did not appear to increase or decrease with distance from the source of the initial contamination (Figure E3). Toxicity levels were highest in Zone 1 and low in all wells 500 feet or more from the source (Figure E4). Most wells located outside the source zone were found to have no toxicity. Comparisons of MTBE concentrations between the July, August, and September 1999 sampling events indicate that concentrations were highest for all zones in August (Figure E5). Toxicity levels during the July, August, and September experimental periods indicate that toxicity was the only region to display appreciable toxicity within each time period (Figure E6).

Discussion

The data acquired during the experimental period provide MTBE, BTEX, and toxicity information that incorporates complete spatial representation over a three month period. In an effort to better characterize the toxicity of the plume and the relationship between toxicity, BTEX levels, MTBE levels, and spatial and temporal distribution, a suite of potential corollary relationships were examined.

Correlation of [BTEX] and Toxicity

Analysis of BTEX and toxicity measurements over spatial and temporal scales yielded unexpected results: BTEX and toxicity data were not directly correlated. However, there may be a correlation with regions where benzene was found in previous sampling events, with current toxicity findings. In December 1998, the groundwater in well CBC10 contained 3300 ppb benzene and had unknown toxicity. In the Summer of 1999 no benzene was detected yet toxicity was observed. The apparent absence of BTEX during the three-month sampling period also made it impossible to explore how the concentration of the products changed down-gradient of the source region and difficult to examine attenuation rates.

Correlation of [MTBE] and Toxicity

Experimental findings indicate that there is no significant correlation between MTBE concentrations and toxicity, according to an ANOVA F-test at a confidence of 75%. Areas of high MTBE concentration often showed no toxicity, whereas wells free of MTBE would sometimes show relatively high toxicity levels (Table E3).

Toxicity/Contaminant Concentration

Attempts to correlate MTBE concentrations with toxicity indicated that there is no significant direct correlation (Appendix B). Areas of high MTBE concentration often showed no toxicity whereas wells free of MTBE would sometimes show relatively high toxicity levels (Table E3).

Implications of MTBE Presence on Contaminant Degradation

It was theorized that the presence of MTBE could affect microbial communities and reduce their ability to aid in the natural attenuation of the BTEX products. Under normal conditions benzene has half-life of 800 days, xylene 200 days, and toluene 100 days (Davis, 1998). This suggests that, at the time this experiment was conducted, benzene levels should have degraded by 12% over the experimental period (Table E4). The chemicals p-xylene and toluene should have had time to degrade to concentrations of 60 and 40% respectively of the July concentrations, as is shown in Figure E7. Benzene, toluene, and xylene were not observed with any regularity during our experimental period, thus an analysis of attenuation levels could not be undertaken. However, an examination of attenuation rates for the plume can be found in the Ecological Risk Assessment performed concurrently with this experiment, which included an examination of degradation rates based on changes in these chemicals over a four-year period beginning in 1996.

Correlation of Toxicity to Spatial Distribution

One of the most significant findings from this experiment was the correlation between toxicity levels and spatial distribution (Figure E6). The toxicity data generated from July, August, and September 1999 groundwater samples, indicated that toxicity levels in Zone 1 were greater than the other two zones (Table E1). Statistical analysis, using a traditional T-test using 95% confidence, revealed that Zones 2 and 3 could not be differentiated with respect to toxicity—i.e., neither was very toxic and there was no noticeable difference between the two zones. Another 95% confidence T-test revealed that Zone 1 was statistically different than the other two, with respect to toxicity. This result is not surprising considering that Zone 1, the area nearest the source, has been exposed to aromatic constituents, some of which are known carcinogens, for over 15 years. It is unclear to what extent BTEX compounds and degradation products have moved within the plume, however, toxicity observations and BTEX concentration analyses indicate that these products are still restricted to the source region.

Correlation of [MTBE] to Spatial Distribution

Attempts to isolate the location of MTBE along the plume spatially proved to be difficult (Figure E3). None of the three experimental sample periods found a significant correlation between MTBE concentration and distance from the source, not even to 75% confidence using a traditional ANOVA F-test. Thus, it is not possible to suggest which zone of the plume is more or less contaminated by MTBE or whether or not the MTBE is truly flowing with the groundwater in a quantifiable way. However, a more comprehensive temporal analysis of MTBE migration can be found in the MTBE2000 ERA document and appendices which outline a model of the plume migration..

Correlation of [MTBE] over Time

An examination of changes in MTBE concentration over the three-month period found similar results to the spatial analysis (Figure E5). However, MTBE concentrations increased in August for all zones, suggesting either (a) a shift in the water table that could potentially increase concentrations or (b) an unknown release of MTBE to the aquifer from a non aqueous phase source or new release. The data and replications proved to be too sparse and the action of MTBE contaminated groundwater too erratic to draw noteworthy conclusions. One well and one portion of the drainage channel showed a significant variation in MTBE levels during the experimental period, yielding a 75% chance of correlation with a 1-tailed variance ratio test. The lack of a more consistent trend among zones or wells makes it difficult to draw any conclusions about flow through the plume, especially considering the unclear spatial findings on MTBE distribution.

Conclusions

The experimental findings suggest several things. First, they suggest that the nature of the plume is not easily differentiable with regard to space or time and that MTBE, BTEX and toxicity levels do not appear to be directly correlated. The evidence here indicates that regions currently associated with MTBE contamination have no statistical relationship with observed toxicity, even at high MTBE concentrations. Regions where MTBE and BTEX chemicals have been in the past and have either (a) moved out of the region or (b) been degraded into other products, appear to display features of toxicity; however, this observation could not be supported by the statistics. Future experiments, which focus on the degradation products and the contaminant pathways, may better explain the observed patterns in toxicity.
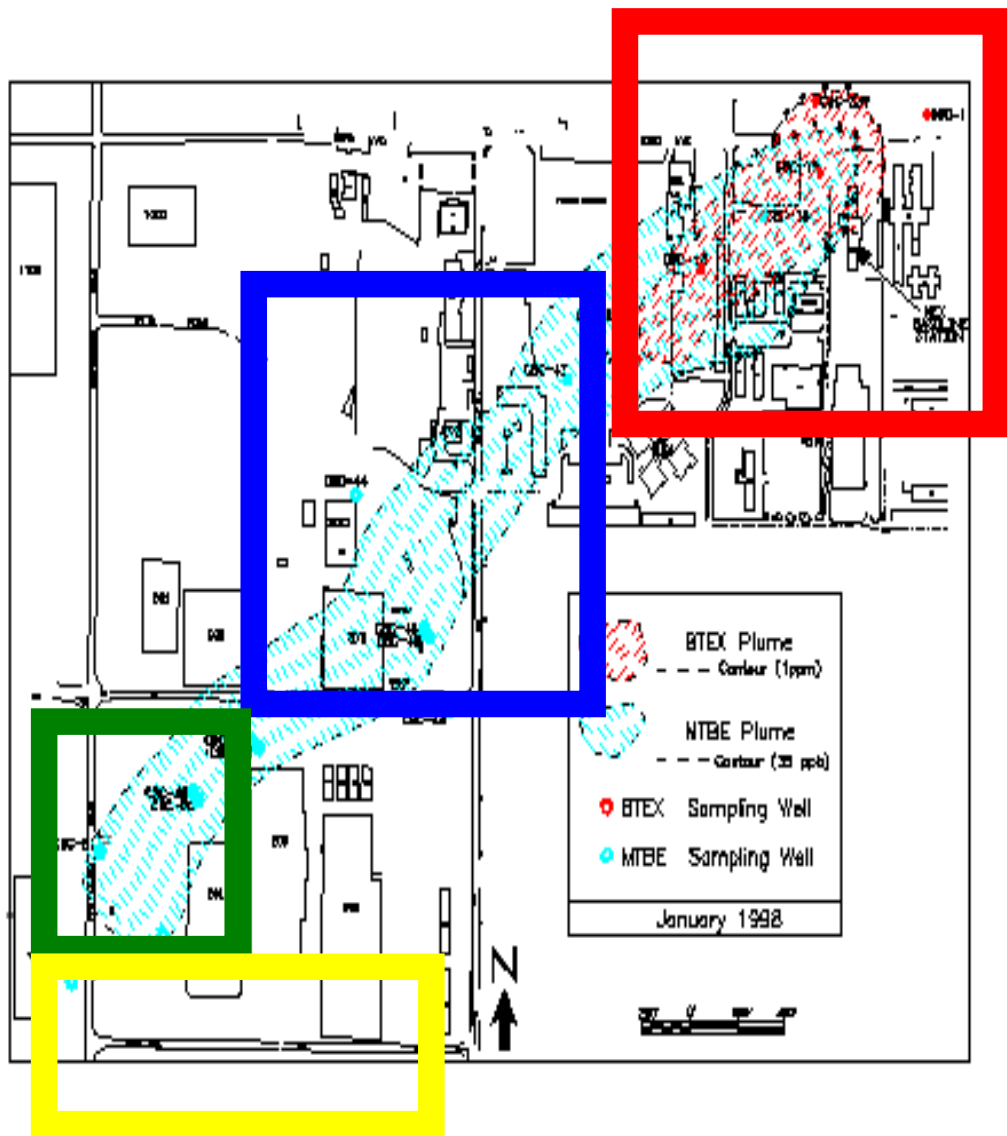
Figures and Tables—Ecological Risk Assessment

Legend:
- 🟥 Region One—Source
- 🟦 Region Two—Middle of Plume
- 🟩 Region Three—Toe of Plume
- 🟨 Drainage Channels

Figure E1. Map showing the delineation of the Port Hueneme site.

Toxicity vs. MTBE
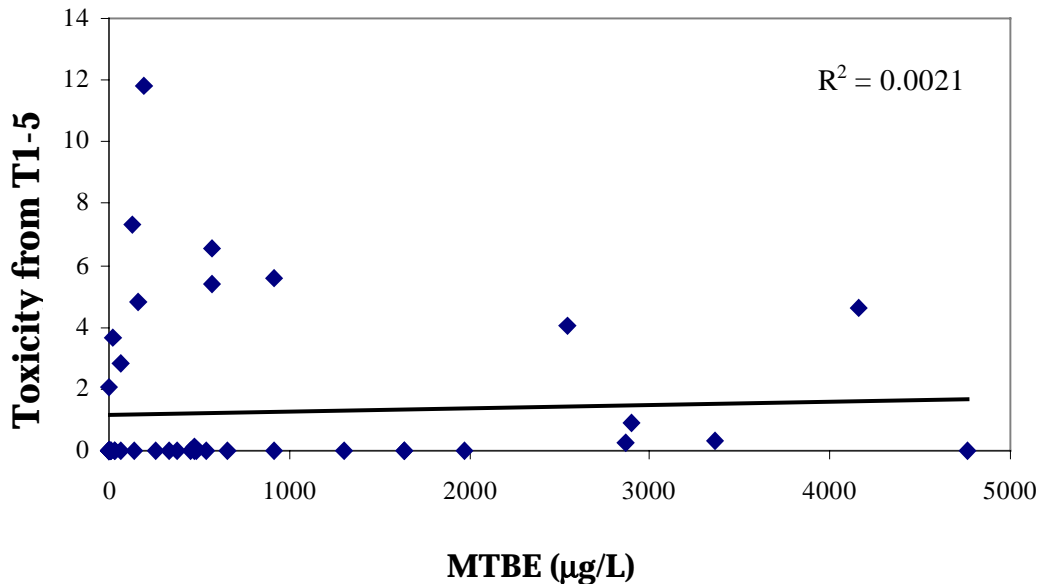## July, August, and September 1999

Figure E2. Concentration of MTBE and toxicity units compared for the three-month experimental period (July, August, September 1999).

MTBE vs. Distance from Source

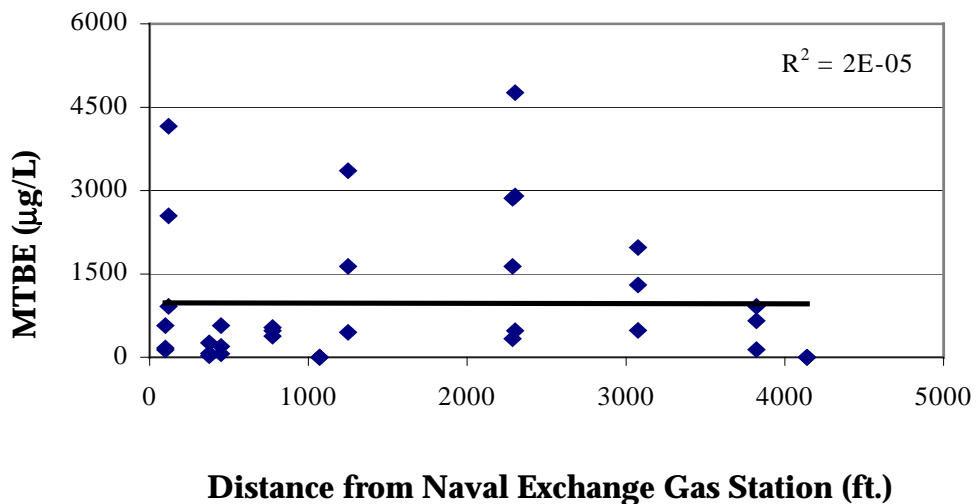**Distance from Naval Exchange Gas Station (ft.)**

Figure E3. Concentration of MTBE and distance from the source of contamination (NEX Station), averaged over the three month sampling period (June, July, August 1999).

Toxicity vs. Distance from Source

Distance from Naval Exchange Gas Station (ft.)
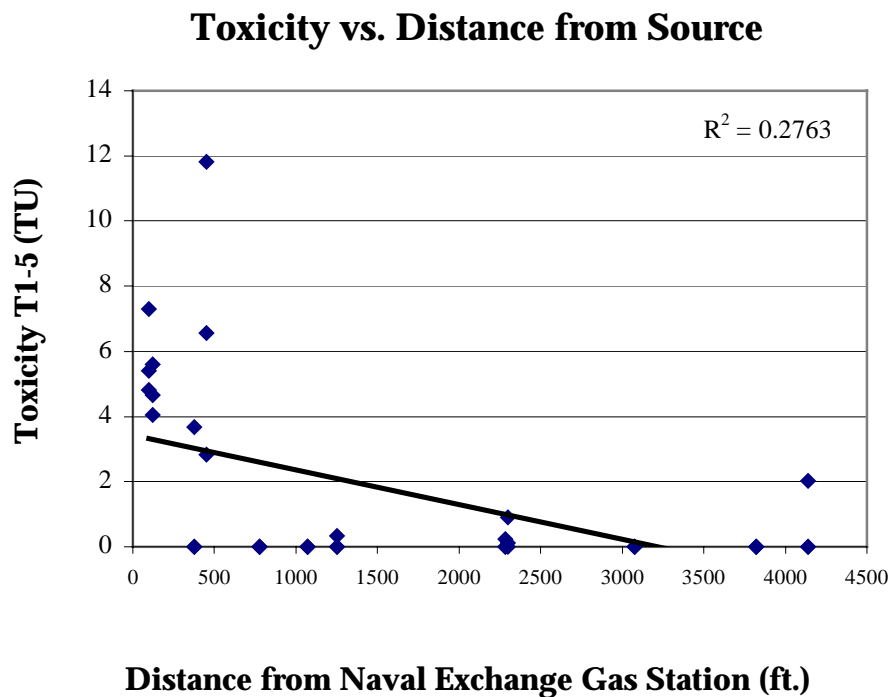
Figure E4. Groundwater toxicity plotted versus the distance of the well from the source of contamination (NEX Station) compared over the three-month experimental period (July, August, September 1999). Toxicity units are defined as TU = $EC_{50}/100$. Toxicity data provided are for the one set of samples from at one testing time (5 minute) that best represented the entire data set.

Average MTBE Concentrations

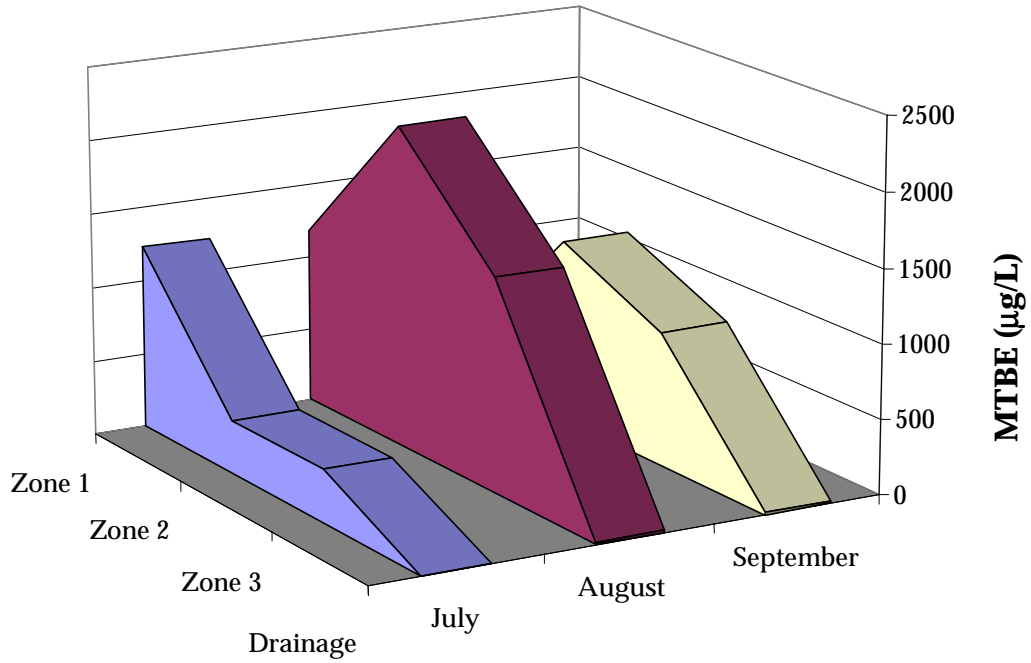**Figure E5**. Changes in MTBE concentration averaged for each of the four zones defined in the Experimental Methods section are compared for the duration of the three-month experiment. Highest concentrations are found in August of 1999 in Zone 2.
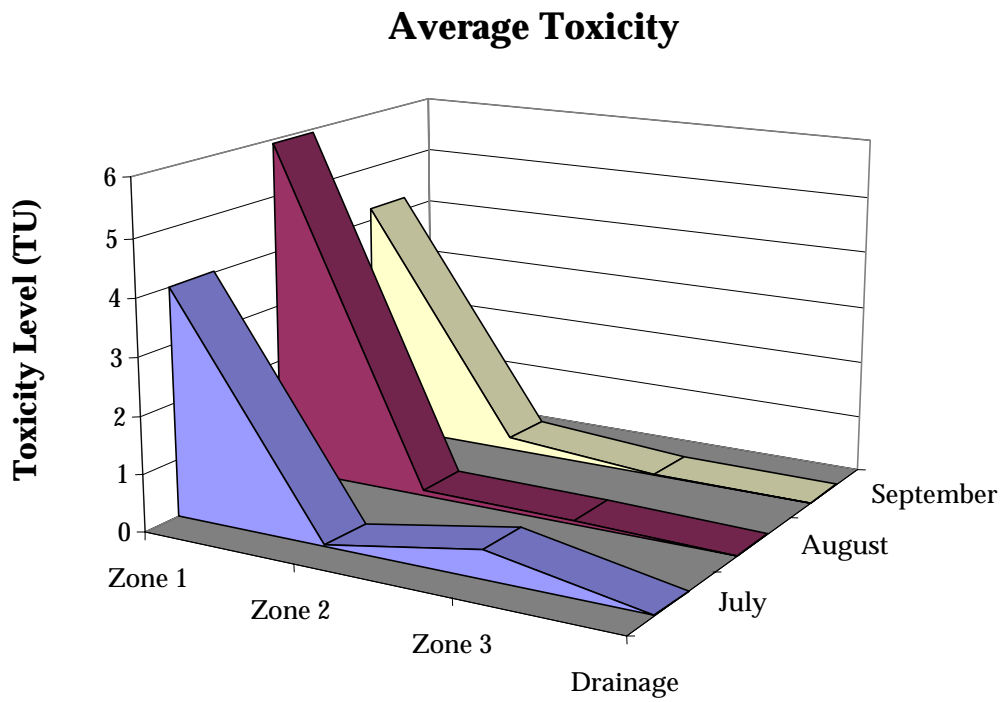
Average Toxicity

Figure E6. Average toxicity unit values are compared for the three month experimental period (June, July, and August 1999).

Well CBC10 Toluene and Xylene Concentrations

R2 (Toluene)= 0.8284

R2 (Xylene) = 0.4774

Concentration (µg/L) — vertical axis, values: 0, 2000, 4000, 6000, 8000, 10000, 12000

Months since December 1996 — horizontal axis, values: 0, 5, 10, 15, 20, 25, 30, 35

◆ Toluene ■ Xylene ——— Linear (Toluene) — — Linear (Xylene)

Figure E7. Changes in toluene and xylene concentrations at CBC10, for all data since December 1996.

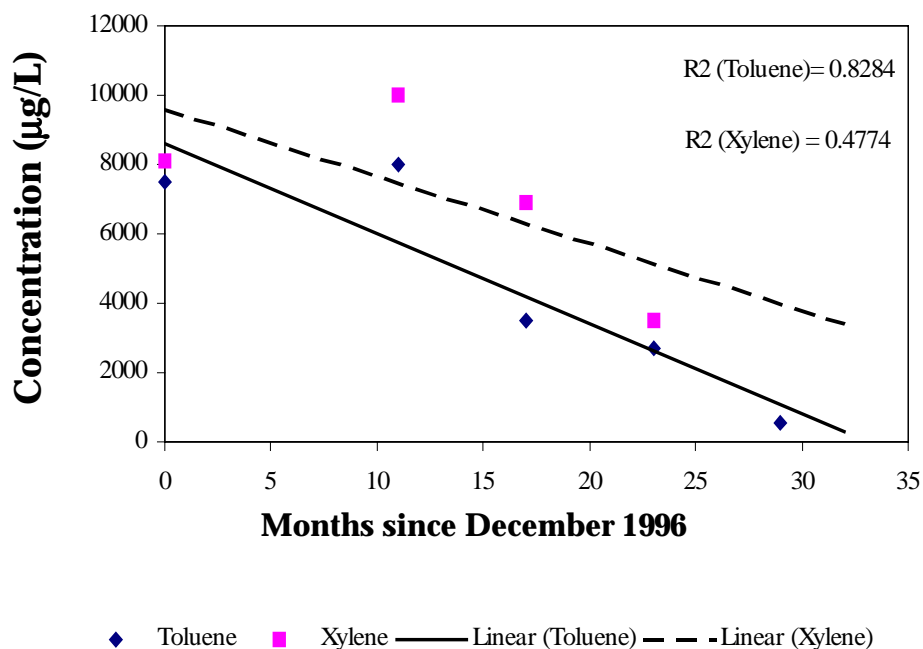|	Distance	[benzene]	[MTBE]	Toxicity (TU)		Toxicity (TU)	
	ft	ppb	ppb	5 min	15 min	5 min	15 min
Zone 1	100	246	572	5	4	2	2
	450	15	572	7	8	8	12
	100	—	133	7	5	9	7
	100	—	166	5	4	4	3
	120	—	2547	4	5	4	4
	120	—	4158	5	5	7	7
	120	—	913	6	6	3	4
	376	—	69	—	—	—	—
	376	—	259	—	—	—	—
	376	—	26	4	—	1	—
	450	—	195	12	13	9	11
	450	—	66	3	2	—	—
Zone 2	772	—	478	—	—	—	—
	772	—	535	—	—	—	—
	772	—	380	—	—	—	—
	1070	—	0	—	—	—	—
	1070	—	0	—	—	—	—
	1070	—	0	—	—	—	—
	1244	—	450	—	—	67	—
	1244	—	3357	—	—	—	—
	1244	—	1637	—	—	—	—
	2304	—	478	—	—	—	—
	2304	—	4762	—	—	—	—
	2304	—	2904	1	—	—	—
Zone 3	2285	—	332	—	—	—	—
	2285	—	2861	—	—	—	—
	2285	—	1638	—	—	—	—
	3073	—	486	—	—	—	—
	3073	—	1975	—	—	—	—
	3073	—	1303	—	—	2	—
	3820	—	141	—	—	—	—
	3820	—	915	—	—	—	—
	3820	—	659	—	—	—	—
	4143	—	—	2	—	—	—
	4143	—	—	—	—	3	—
	4143	—	—	—	—	—	—

Table E1. Contaminant concentration and toxicity of groundwater at Port Hueneme for samples collected during Summer of 1999.

Zone	Distance ft	[MTBE] ppb
2	2304	4762
1	120	4158
2	1244	3357
2	2304	2904
3	2285	2861
1	120	2547
3	3073	1975
3	2285	1638
2	1244	1637
3	3073	1303
3	3820	915
1	120	913
3	3820	659
1	100	572
1	450	572
2	772	535
3	3073	486
2	772	478
2	2304	478
2	1244	450
2	772	380
3	2285	332
1	376	259
1	450	195
1	100	166
3	3820	141
1	100	133
1	376	69
1	450	66
1	376	26
2	1070	0
2	1070	0
2	1070	0
3	4143	—
3	4143	—
3	4143	—

Table E2. Concentration of MTBE with consideration of Zone and distance from source (NEX Station, Port Hueneme).

[MTBE]	Test One		Test Two	
ppb	5 min	15 min	5 min	15 min
4762	—	—	—	—
4158	5	5	7	7
3357	—	—	—	—
2904	1	—	—	—
2861	—	—	—	—
2547	4	5	4	4
1975	—	—	—	—
1638	—	—	—	—
1637	—	—	—	—
1303	—	—	2	—
915	—	—	—	—
913	6	6	3	4
659	—	—	—	—
572	5	4	2	2
572	7	8	8	12
535	—	—	—	—
486	—	—	—	—
478	—	—	—	—
478	—	—	—	—
450	—	—	67	—
380	—	—	—	—
332	—	—	—	—
259	—	—	—	—
195	12	13	9	11
166	5	4	4	3
141	—	—	—	—
133	7	5	9	7
69	—	—	—	—
66	3	2	—	—
33	—	—	—	—
27	—	—	—	—
26	4	—	1	—
16	—	—	—	—
16	—	—	—	—
10	—	—	—	—
0	2	—	—	—
0	—	—	—	—
0	—	—	3	—
0	—	—	—	—

Table E3. Toxicity as a function of MTBE concentration.

	Benzene	**Toluene**	**p-Xylene**
Attenuation rate (1/yrs)	0.32	2.30	1.26
True Life (yrs)	14	14	14
Remaining from original leak (%)	1.19	1.04E-12	2.04E-06
Concentration in Dec-96 (µg/L)	10000	7500	8100
Concentration in Jun-96 (µg/L)	1	1	1
Time elapsed (yrs)	2.50	2.50	2.50
Observed attenuation rate (1/yrs)	3.7	3.6	3.6

Table E4. Literature decay rate information for the natural attenuation of benzene, toluene and p-xylene is presented with expected percent remaining after 14 years and observed attenuation levels over the last 2.5 years. Calculations performed after Davis et. al., 1999.

Tier Three Report

Under guidelines specified by the U.S. Navy, an environmental contamination event that may have detrimental effects to the ecology of the site must be evaluated using a three-tiered approach (U.S. Navy 1999). Producing the first and second tiers involved quantifying the ecological risk associated with the contamination. The third tier offers recommendations that will minimize the effects of contamination through defining available remediation strategies, determining the costs and benefits of these options, and narrowing down the possibilities to the best environmental and cost-effective solutions.

Following the completion of the second Tier, Team MTBE2000 gathered information about a multitude of remediation techniques from the literature, focusing on techniques that are currently being implemented at the site. The Naval Facilities Engineering Service Center (NFESC) at Port Hueneme has offered universities and private companies professional assistance in complying with environmental regulations. There are currently six technologies being tested at the site. All of the remediation alternatives considered in this report were evaluated based on their potential environmental impacts, cost, and technical merits and benefits, as directed by the Naval guidelines.

Although a detailed inventory of the chemical properties of the contaminants of concern may be unnecessary in a Tier Three report, it is imperative to consider the special circumstances of both the contaminant and the site to provide a groundwork for forming recommendations. Approximately 11,000 gallons of gasoline containing methyl tertiary butyl ether (MTBE) were released to the subsurface environment in 1984 from a leaking underground storage tank (UST). MTBE is extremely soluble in water and resistant to degradation (Yeh and Novak 1994), especially when compared to other gasoline components like benzene, toluene, ethylbenzene, and xylene (BTEX). Although the extent of BTEX contamination is limited to a small area surrounding the UST, the groundwater plume of MTBE currently extends 45 acres from the source. For more specific information regarding the specifics of the environmental disturbance, consult the Tier Two Report.

The following list of technologies have been selected as viable options that could be or have been employed at the Port Hueneme site. Portions of information are summarized based upon information from a US DOE database (U.S. Dept. of Energy 1995) that looks at different "possible remediation technologies currently in use", contaminants, and regulations. This database is typically used to quickly identify applicable technologies for waste cleanup. Phytoremediation, natural attenuation, *in-situ* bioremediation, and air stripping are described below since

these remediation technologies are the most appropriate for the Port Hueneme MTBE plume. Additional technology descriptions that were only briefly considered as viable on the site are presented as an appendix exactly as they are described in the US DOE database (U.S. Dept. of Energy 1995).

Remediation Strategies

Phytoremediation

Phytoremediation is one of the innovative treatment technologies being studied at Port Hueneme that employs plants and their associated microbiota, soil amendments, and agronomic techniques to remove, contain or render inert environmental contaminants, like MTBE. At the Port Hueneme site, the University of Purdue is attempting to determine the potential of a wide variety of plants, including indigenous Californian species, for diesel fuel uptake, which may also have applications for MTBE remediation. Contaminated sediments from the Long Beach Naval Shipyard were placed within a self-contained confinement compartment and differing plants were dispersed and propagated in attempt to identify specific plant traits that promote remediation of diesel fuel. This may not be directly applicable to the MTBE plume at Port Hueneme, but this demonstrates the potential wider application of other technologies.

Natural Attenuation

The term "natural attenuation", as defined by U.S. EPA, refers to naturally-occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media. These in-situ processes include biodegradation, dispersion, dilution, adsorption, volatilization, and chemical or biological stabilization or destruction of contaminants (EPA 1994a). The use of "monitored natural attenuation" is used to indicate that natural processes have been incorporated into the site remedy for specified cleanup levels within some reasonable time frame. The site is monitored to show that there is a decline in contaminant concentration. Natural attenuation processes typically occur at all sites, but to varying degrees of effectiveness. This depends on the types of contaminants present and the physical, chemical, and biological characteristics of the soil and groundwater.

It is important to clarify two key points outlined by the EPA:

- Monitored attenuation is recognized by the U.S. EPA as a viable method of remediation for soil and groundwater; however, it should not be considered a default option ("presumptive remedy") (EPA 1994b).

- Natural attenuation is different from "no action" in that "no action" sites pose virtually no risk, allowing regulatory agencies to conclude that no further cleanup activities will be necessary. Sites where monitored natural attenuation is being used are doing so because there is a risk at the site, such as groundwater contaminant concentrations above drinking water standards. Therefore, monitored attenuation is not a "walk away" option because adequate site characterization, monitoring, and analysis must be conducted to determine its viability as a remedy (EPA 1994b).

According to a 1994 report by the EPA, in order for natural attenuation to be used at a specific site, certain criteria must be provided: (1) Data showing a decline of contaminant concentrations over time, (2) Hydrogeologic or chemical data that can indirectly demonstrate the types of natural attenuation processes active at the site, and (3) Quantification of the rates at which those processes are reducing contamination levels. Consideration of this alternative should also include results of laboratory or field studies to demonstrate that native bacteria can biodegrade contaminants of concern under controlled conditions.

Natural attenuation has several advantages that Port Hueneme site managers can utilize. For example, there is an associated lower overall remediation cost. Since the contaminant is left in the ground, there is less generation of remediation wastes and also fewer and less intrusive surface facilities for remediation. Some of the potential disadvantages of natural attenuation are: (a) significantly longer cleanup times than other more active remediation, (b) assumed responsibility of long-term monitoring and its associated costs, (c) costly and complex site characterization, and (d) the potential for continued contamination if natural attenuation does not meet remediation expectations (U.S. Army 1998).

Typically, the use of "monitored natural attenuation" is restricted to sites where the contaminant does not pose unacceptable risks to human or other environmental receptors, with cleanup objectives being achieved

within a reasonable time frame. Port Hueneme is a candidate for the potential use of natural attenuation because the aquifer is not being used for drinking water. It should be noted that natural attenuation would not be acceptable to federal or state agencies if there was a real threat that contaminants would reach sensitive receptors. Although natural attenuation may take longer to achieve than other forms of remediation, remediation time frames for natural attenuation should be and need to be carefully estimated and compared with the remediation alternatives undergoing analysis.

There are several methods used to measure natural attenuation rates. For example, at the NFESC, monitored natural attention has been performed with deuterized (^{2}H) MTBE, which has a slightly higher molecular weight. Once introduced to the groundwater via injection wells at Port Hueneme, it became possible to trace the movement of MTBE and the rate of natural attenuation. This was characterized by measuring deuterized carbon dioxide given off due to microbial actions/influences at corresponding measuring wells. The eventual results of this study will allow managers to evaluate the rate of the in situ processes (biodegradation, dispersion, dilution, volatilization, etc.) going on within the plume.

In-Situ *Bioremediation*

Bioremediation is the incorporation of biological processes that can modify organic contaminants present in the subsurface environment. Microorganisms use the organic contaminants for growth and other biological processes. Equilion's Westhollow Technology Center teamed with Arizona State University is attempting to bioremediate MTBE plume at Port Hueneme. Recent laboratory experiments and limited field studies by this team have demonstrated that MTBE can be aerobically degraded by the Shell Development Company's mixed bacteria culture BC-4. The culture is a mixture of ordinary soil bacteria such as coryneforms, pseudomonads and achromobacter species that have been acclimated to MTBE for more than a year. Additionally, Kate Scow from UC Davis has recently inserted her own cultivated microbes into the soil for bioremediation. Both of these projects should yield valuable degradation rates of MTBE and may prove to be a powerful remediation tool at Port Hueneme.

Air Stripping

Air stripping is the process of removing volatile components from an aqueous stream by contacting it with air. The driving force of the air stripping process is the concentration gradient between the aqueous and gaseous phases. The process works best on contaminants with large Henry's Law constants and high diffusivity in both liquids and gases. The treated aqueous stream is often clean enough to discharge but is sometimes polished with carbon adsorption to removed trace amounts of residual contaminants. The off-gas is either released directly to the atmosphere or treated to remove or destroy the collected volatile contaminants. Air stripping of aqueous streams is typically accomplished by countercurrent extraction in a packed tower equipped with an air blower. The purpose of the packed tower is to create a high level of turbulence and increase the contact surface between air and water. The cleanest air is introduced at the bottom of the stripper where it contacts the cleanest water. This countercurrent flow allows the treated water flowing downward to reach levels of contamination well below 1 ppb. Typically, the tower packing is randomly paced, however, stacked or structured packings have been developed and implemented (U.S. Dept. of Energy, 1995).

In-Situ *Air Sparging*

Air sparging is the process of injecting clean air directly into an aquifer for remediation of contaminated groundwater. It relies on two basic mechanisms working: (1) biodegradation, and (2) volatilization. Air is forced through the contaminated aquifer to provide oxygen for bioremediation and/or to strip contaminants out of the aquifer. *In situ* air sparging is a treatment technology for removing volatile organic compounds (VOCs) from saturated soils and groundwater. Air is injected into the saturated zone below or within the areas of contamination. This causes VOCs that are dissolved in the groundwater and those that are sorbed to the soil to partition into the gaseous phase, and are removed by advection. Air sparging essentially creates a crude air stripper in the subsurface, with the saturated soil acting as the packing (soil). Injected air bubbles pass through the water column over the packing, coming into contact with dissolved/adsorbed phase contaminants in the aquifer and causing the VOCs to volatilize. The "stripped" contaminants are then transported in the gaseous phase to the vadose zone where they can be captured with vapor extraction well(s) and treated using a standard vapor extraction treatment system.

Air sparging is often combined with a vapor extraction system because the compounds mobilized by the air sparging system could discharge near or at the ground surface if not effectively captured in the vadose zone. Application of both traditional soil vapor extraction and air injection would therefore be required to address both the soil and groundwater contamination. Below the water table, air bubbles need to travel vertically through the aquifer in order to strip the VOCs. Above the water table, VOCs can be removed by inducing airflow through areas of contamination by applying a vacuum. Air sparging is generally applicable to those chemicals that are easily removed from contaminated groundwater through traditional air stripping towers, such as lighter petroleum compounds and chlorinated solvents. Less strippable compounds may be remediated with enhancements to the standard sparging process, such as using a combination of air, ozone, and/or hydrogen peroxide as the injected gas. This can provide an increased oxidation potential for semi-volatile organic compounds (SVOCs), making them more amenable to in situ air sparging.

Air sparging is generally suitable for soils that can be effectively remediated with soil vapor extraction. It is most effective in permeable, coarse-grained soil. Permeable soils have lower air entry pressure requirements and provide a medium for more even air distribution, allowing for better mass transfer efficiencies and more effective VOC removal. Less permeable soils (i.e., fine grained sands) require higher air entry pressures and are more likely to cause the formation of significant gas pockets, which may impede air sparging effectiveness (U.S. Dept. of Energy, 1995).

Incorporation of Cost-Benefit Analysis

The remediation strategies outlined above and in the appendix to follow are those that either (a) are currently being employed at the base or (b) are likely to be the most applicable at the Port Hueneme site for remediation efforts on the existing MTBE plume. After selecting the most feasible options, a cost-benefit analysis (CBA) was performed by Cindy Wu, a graduate of the Masters program at the Donald Bren School of Environmental Science and Management, U.C. Santa Barbara, on the four preferred strategies to determine the most efficient and cost effective technology for the Port Hueneme site: Air Stripping, Granulated Active Carbon (GAC), Hollow Fiber Membrane (HFM) and a

Trickling Biofilter. A copy of the CBA can be found as an appendix to this report.

It should be noted that, although the assessment of ecological risk does not take human health risk into consideration, based on the many uncertainties with the plume (distribution of MTBE, direction of plume movement, and possible preferential pathways between subsurface aquifers), it was decided to include human risk for purposes of the cost-benefit analysis.

Conclusions of Tier Three Report

Based on the examination of remediation strategies and the cost-benefit analysis, Team MTBE2000 recommends that air stripping is the best remediation alternative available to treat the MTBE-contaminated groundwater. The total cost for remediating the MTBE plume at Port Hueneme is estimated to be $4.2 million. However, it should be noted that natural attenuation was not considered in the cost-benefit analysis and may, in fact, be a better remediation alternative, due to the low levels of toxicity found on site, low set up and operation costs, and low waste generation. Remediation by natural attenuation is increasingly more accepted as a remedial option for groundwater and soil contamination (EPA 1994b) and may be the most cost effective and beneficial solution.

Tier Three—Cost-Benefit Analysis

With thanks to Cindy Wu

Cost Estimate for Mitigation of the MTBE plume
at Port Hueneme, California

BACKGROUND

MTBE facts

Methyl tertiary butyl ether (MTBE) is a synthetic organic chemical used as a gasoline oxygenate. It promotes more complete burning of gasoline, reducing carbon monoxide and ozone emissions. Since the late 1970's, MTBE had been added to fuel as an octane enhancer. In the Clean Air Act of 1990, congress mandated the use of reformulated gasoline (RFG), that included MTBE, for areas that did not meet the National Ambient Air Quality Standards [3]. In 1992, oil companies began using MTBE extensively in California to meet reformulated gas requirements of the state Air Resources Board. Studies showed that the air quality in areas where the gasoline additive was used exceeded the national emissions standards. The significant decline in air pollutants between 1994 and 1995 was attributed to the use of MTBE enhanced RFG [2].

MTBE contamination was detected in groundwater and surface water throughout California as a result from leaking underground storage tanks (UST). Drinking water wells in Santa Monica, South Lake Tahoe, Santa Clara Valley and Sacramento area were shut down due to MTBE-contaminated groundwater [2]. MTBE is a highly soluble and volatile compound in water. Research indicates that dissolved MTBE is resistant to biodegradation and is highly mobile. In October 1997, the California Department of Health Services (DHS) developed a

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secondary maximum contaminant level (SMCL) of 5 parts per billion (ppb) to ensure no taste nor odor can be detected. However, California DHS has not issued a primary drinking water standard to address protection of human health. The existing health advisory on MTBE is 20-40 ppb, set by the US EPA [2].

Site History
Port Hueneme (pronounced "Why-nee-mee") is located in Ventura County approximately 50 miles east of Santa Barbara. It is the largest commercial deep-water harbor between Los Angeles and San Francisco, and serves as headquarters for the US Naval Construction Battalion Center (USNCBC) [1].

Approximately 11,000 g of leaded and unleaded fuel was released into the soil and groundwater from UST lines between September 1984 and March 1985 [9]. As of fall 1996, the benzene, toluene, ethylbenzene and xylene (BTEX) plume from the UST leakage was delineated. For the hydrogeologic conditions at the site, MTBE is migrating farther and faster than BTEX [9], towards the Pacific Ocean. Recent site characterization showed that the MTBE plume is 46 acres with approximately 20 feet of saturated thickness (~ 300 million gallons) and increasing [9]. The concentration of the plume at the source is 29 parts per million (ppm) [10], which is 5,800 times greater than the 5 ppb SMCL set by the state of California. The concentration at the leading edge of the plume is 600 ppb and increasing as of June 1999. Mark Kram, a hydrogeologist on the naval base, speculated that the concentration at the leading front will reach 1000 ppb. The plume front is 750 feet away from a channel, which can transport the pollutants into the ocean with a single rain event [9]. A satellite photograph of Port Hueneme with overlay of the MTBE plume shows major roads, construction battalion center fence line, harbor outlines, and canals for water drainage. Other characteristics of the aquifer at the naval base are as follow [9]:

> - the groundwater is in a semi-perched unconfined aquifer;
> - the aquifer contains fluvial deltaic sediments with 4.6 m of saturated thickness;
> - the water table ranges from 3 – 4 meters below ground surface (bgs);
> - the groundwater velocity ranges from 70 to 400 meters per year assuming a porosity of 0.3; and
> - the groundwater contains 1,212 mg/L of total dissolved solids.

Human Health Risks and Ecological Risks
Based on the limited array of existing data, MTBE is not known to cause adverse human health effects at typical concentrations in the groundwater [3]. Numerous agencies and research are currently conducting research on the toxicity of MTBE to humankind and other species. In the report to the Governor and legislature of the state of California, Keller et al. (1998) indicate that

combustible byproducts of MTBE could exacerbate or even cause asthma, however, further research is warranted to provide statistically significant data [7]. MTBE is an animal carcinogen with the potential to cause cancer in human at high concentrations (e.g. 8000 ppm). The animals tested have not been exposed through drinking water, thus, there are significant uncertainties about the likelihood that human exposure to low concentrations found in drinking water would cause cancer. Research by Johnson (1998) shows that toxicity of MTBE to aquatic organisms is low. Adverse effect on trout in lakewater not expected to occur until concentration of MTBE in the water column reaches 4,700 ppb [6]. No information is presently available for the effects of MTBE on biota in estuarine environment, such as Port Hueneme.

The plume at Port Hueneme does not pose risk to human health because the groundwater is not used for human ingestion. Most of the naval base is covered with asphalt, therefore, there is no risk from inhaling MTBE fume. There is a wetland on the navy base, and MTBE-contaminated groundwater may sip out and pollut surface water. However, the concentration in the surface is not likely to reach 4,700 ppb, therefore, aquatic organisms such as fish and waterfowls would not be exposed to dangerous levels of MTBE. If the plume reaches the ocean before delineation can be completed, the cost of clean up may increase by many folds because the tides and currents would disperse MTBE. With increase dispersal, higher number of biota populations are exposed to the pollutant leading to possible higher environmental costs. One caveat to keep in mind is that the deduction of no risk to human and wildlife is based on limited and incomplete information. Thus, further research is needed to elucidate the full impact of MTBE. The MTBE plume at Port Hueneme will be remediated to comply with current regulatory standards of 5 ppb in concentration.

A cost-effectiveness analysis will be performed to determine which technology is the optimal choice in remediating the plume. Cost-effectiveness analysis is used because the benefits of the plume remediation can not be easily identified and quantified. Due to the limited amount of toxicity information on MTBE, the impacts and the receptors are not yet fully determined. In addition, it is difficult to estimate the cost to human health and ecological damages. There are methods such as quantifying total health care costs and contingent valuations. However, it is beyond the scope of this paper to valuate the benefits. A cost-effectiveness analysis does not monetize benefits, it measures benefits with levels of effectiveness. Cost-effectiveness (CE) can be calculated in terms of cost per unit of outcome effectiveness [4]. In order to compare different options, the ratios of cost to effectiveness of all the alternatives are calculated.

Cost-effectiveness ratio = Cost/ effectiveness

The higher the CE ratio, the more one measure of effectiveness costs. Therefore, the most cost efficient project has the smallest CE ratio among the alternatives. In this case study, the effectiveness of remediating the plume is assumed to be the same among all treatment technologies. The effectiveness is assigned a measure of 1 to denote completion of the mitigation meeting regulatory standard. The CE ratio is thus equal to the cost of the treatment technology, and the option with the lowest cost is the optimal technology. This paper compares the costs of four remediation options, and presents a recommended treatment technology with the total expenditure for the MTBE plume at Port Hueneme.

REMEDIATION OPTIONS AND COSTS

Myriad of remediation technologies is available to mitigate MTBE plume in groundwater. This paper compares the costs for applicable physical and biological treatments. Physical treatments involve removal of the pollutants from environmental mediums (e.g. water, soil and air) using physiochemical properties of the compounds. Physical treatments have been widely used and commonly accepted. Three physical treatments compared in this paper are air stripping, granular activated carbon (GAC), and hollow fiber membrane (HFM). Biological treatment is the use of living organisms (e.g. microbes, plants) to remove or disintegrate pollutants. Bioremediation is a rapidly developing field because it is more economical than physiochemical treatments while maintaining the same removal efficiency. Trickling biofilter is the only biological treatment discussed in this paper because it is the only technology with successful biodegradation of MTBE and information on costs.

The costs for each MTBE remediation options were obtained from Keller et al. (1998) [8] for the physical treatments, and Converse and Schroeder (1998) [5] for the biological treatment. Table 1 lists the costs for each treatment options, presented in dollars per 1000 gallon. The values include capital costs and operation & maintenance (O&M) costs. The capital costs include the following general items [8]:

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

The O & M costs include the following items [8]:

- ➢ electrical power requirements at $0.08/kW-h;
- ➢ fuel at $1.6/million BTU and 3 BTU/scfm;
- ➢ labor at $30/hr;
- ➢ materials at 3% of equipment cost per year;
- ➢ contingency at 20% of other O&M costs; and
- ➢ administrative cost of 15% on top of all other O&M costs.

The cost estimates in Table 1 were evaluated based on remediation of the groundwater to a target MTBE concentration of 5 ppb. The values were amortized over a 20-year return period, discounted to 1998 dollar with a 4% interest rate [5,8]. The costs are not presented in 1999 dollar value because the discounting was performed in September 1999. It has not been a full year between the time the estimates were devised and the time this paper was written. Therefore, no annual discounting will be performed. The cost estimates have an accuracy of –30% to 50% [8]. Based on available cost data, Table 1 includes four scenarios for treatment parameters: MTBE-contaminated groundwater concentrations at 1000 ppb and 5000 ppb, with flow rates of 10 gallons per minute (gpm) and 100 gpm. The concentration of the leading edge at Port Hueneme is expected to reach 1000 ppb and possibly higher. Therefore, it is necessary to use treatment parameters that are capable of remediating the worst case scenario in plume concentration. In order to treat high groundwater concentration such as 5000 ppb, the flow rates that ensure adequate removal efficiencies are 10 gpm and 100 gpm.

Physical Treatments

Air stripping
Air stripping is one type of pump and treat system, where the groundwater is pumped from the subsurface, treated to remove the contaminants, and recharged back into the ground or discharged to a municipal sewage plant. Large volume of air is continuously bubbled into the contaminated water in order to transfer the pollutants from the water to the air phase. The conventional air stripper configuration used in groundwater treatment is a countercurrent packed column. In this configuration, contaminated groundwater is pumped to the top of a packed column, and simultaneously, clean air is blown from the base of he column, thus maximizing the amount of pollutants transferred from water to air [12]. Additional treatment of the contaminated air stream is required by the California emissions regulations. Among air stream treatment options, the most cost-effective technology for the plume at Port Hueneme (e.g. flow rates at 100 gpm or lower and concentration at 1000 ppb or greater) is thermal oxidation with heat recovery to preheat the influent water[8]. Thermal oxidation is the process where the contaminated air stream is preheated, thoroughly mixed, and

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combusted at high temperatures (1200° F to 1600° F) to form carbon dioxide and water [11].

The air stripping costs listed in Table 1 for the four scenarios include the following specific items:

> stripping tower;
> pumping station;
> fire heater and heat exchanger;
> thermal oxidizer and scrubber;
> injection and extraction wells;
> accessories (e.g. instrumentation, piping, valves, electrical);
> contractor installation and engineering fees; and
> O&M costs including:
  - routine maintenance and cleaning of the equipment;
  - electrical cost; and
  - all other O&M costs listed previously.

The advantage of air stripping is that it is a proven technology and used extensively in the industry. Air stripping has been applied commercially to treat MTBE contaminated groundwater and can achieve high removal efficiencies at low and high flow rates. It can also treat water streams with variable MTBE concentrations without compromising removal efficiency. The disadvantage is that additional air treatment is required for the emissions from the stripping tower. Another disadvantage is that deposits from iron, calcium and magnesium in the groundwater and biological growth in the packing material decrease the removal efficiency. A shut-down period is needed to remove the mineral deposits or replace the packing material.

Granular Activated Carbon
Granular activated carbon (GAC) treatment utilizes the adsorption tendency of the pollutants to surfaces of carbonaceous materials in removing pollutants from water and air. Activated carbon is prepared by pulverizing natural materials, such as coconut shell, coals, peat and wood. Pulverization greatly increases the affinity of the materials for organic chemicals. Therefore, activated carbon has high affinity for MTBE, and can be used to remove the contaminant from the environment [8]. Two conditions were considered in estimating the cost for using GAC: 1) whether the groundwater contains low or high organic content, and 2) whether GAC replacement or on-site regeneration will be used. The groundwater at Port Hueneme is assumed to contain high organic content. Keller et al. (1998)[8] found that GAC replacement is more cost-effective for flow rates less than 100 gpm. The costs Table 1 were estimated for conditions where the influent contains high organic loading and the activate carbon will be replaced. The costs for GAC include the following specific items:

- ➢ installation of sorption vessels;
- ➢ activated carbon;
- ➢ replaceable cassettes;
- ➢ condensers;
- ➢ decanters; and
- ➢ O&M costs.

The advantages of GAC are that it is a proven technology for treating contaminated water, and it has high removal efficiencies with proper operation. In addition, GAC is a simple technology with high mechanical reliability that can handle large variations in MTBE concentrations and water flow rate [8]. One disadvantage of GAC is that natural organic matter and other dissolved organic chemicals (e.g. BTEX) have higher affinity for the activated carbon than MTBE. Therefore, they will displace MTBE from the adsorption sites [8]. Another limitation is that growth of microorganisms and mineral deposit cause fouling of the carbon beds, which results in expensive maintenance costs [12].

Hollow Fiber Membrane
Hollow fiber membrane (HFM) removes pollutants by pumping contaminated water through the lumen side of bundled hollow fibers while a vacuum is drawn counter-currently on the outside of the fibers [8]. While the water is pumped through the hollow fibers, volatile compounds evaporate and diffuse through the pores of the hollow fiber as a result to the large concentration gradient. Volatile compounds in the air phase can then be pulled through by a vacuum, and be treated by additional technologies. Several gas-phase treatment systems are available. The most cost-effective combination, is HFM followed by gas-phase GAC to treat the air stream [8]. The cost estimates presented in Table 1 include the following specific items:
- ➢ membrane module;
- ➢ influent water pump;
- ➢ vacuum pump;
- ➢ instrumentation to monitor pressure and flow rate; and
- ➢ O&M costs.

The advantages of HFM are 1) the construction of the treatment unit is simple and easily assembled and 2) it has high removal efficiency. The disadvantages are 1)HFM is still a novel technology with limited field experience; and 2)precipitates will form on the fiber if the groundwater contains high iron, calcium and manganese [8].

Biological treatments

Trickling biofilters
Trickling biofilters utilize GAC as the filter media inoculated with a microbial culture known to degrade MTBE. Treatment of the MTBE-contaminated water begins when the filter bed of microorganisms fully develops on the GAC. In order to remove 99.5 % of MTBE from a 1000 ppb contaminated water, a trickling filter bed depth of 160 cm is required [5]. A low cost estimate and high cost estimate were performed by Converse and Schroeder (1998) [5] because fixed film biological MTBE degradation had not been practiced in the industry. The low cost estimates were evaluated by constructing and operating a trickling filter with rotary distribution system similar to those used for secondary wastewater treatment. The high cost estimates were evaluated using the construction and operation costs of a carbon adsorption system similar to those used to treat drinking water. The groundwater at Port Hueneme is not used for human consumption, therefore the low cost estimates are presented in Table 1. The costs for trickling biofilters include the following specific items:

➢ biofilter installation with a rotary distribution system;
➢ microbe inoculation and nutrients;
➢ water pumps; and
➢ O&M costs.

The advantages of using biofilters are 1) there are no post-treatment costs since the microbes will degrade MTBE into nontoxic metabolites; and 2) little operation energy is required, thus it will be cheaper than physical treatment technologies. One disadvantage is that the microbes thrive under a narrow range of growth conditions (e.g. neutral pH, ample oxygen, sufficient nutrient, etc.), thus slight variations in the conditions decreases removal efficiency of MTBE. In addition, using biofilters to treat MTBE-contaminated water is not a proven technology since limited field tests have been performed.

RECOMMENDATION

Several assumptions are made in order to obtain a total cost for the mitigation of the MTBE plume at Port Hueneme.

➢ In order to capture all of the MTBE, the groundwater volume to be treated will be 30% more than the characterized plume.
➢ The groundwater will be retreated 4 times to ensure complete removal of MTBE.
➢ The total volume of contaminated groundwater to be treated is 1.5 billion gallons (300 million gallons x 1.30 x 4).
➢ No mechanical failures occur.
➢ The source of the plume is contained.

Table 2 presents the cost to remediate the MTBE plume for each treatment options. The values were calculated by multiplying the costs per 1000 gallon (Table 1) by the total volume of the contaminated groundwater, divided by 1000. The costs for the flow rate at 100 gpm is lower than the costs for the flow rate at 10 gpm for both concentrations. It is assumed that the MTBE plume at Port Hueneme has a concentration of 5000 ppb to take in account of the worst case scenario. Therefore, the costs for the four remediation options treating influent concentration of 5000 ppb at 100 gpm are compared. Air stripping and trickling biofilter have lower total cost estimates ($1.5 million and $1.3 million, respectively) than the other two technologies (Table 2). Trickling biofilter costs $0.2 million less than air stripping, however, the former technology still requires further research and field experience. Air stripping has been proven to be a reliable technology and it is widely used in the industry. Trickling biofilter and HFM are emerging remediation technologies being developed currently. These innovative technologies may be more cost-effective and efficient than air stripping in the future. However, within the next few years, air stripping will be the optimal treatment technology for remediating MTBE-contaminated groundwater. Therefore, the MTBE plume at Port Hueneme will be treated with air stripping down to a concentration of 5 ppb.

The $1.5 million used for the air stripping treatment includes capital, and O&M costs. However, it does not include pre-treatment, monitoring and permitting costs. The additional capital and O&M costs are presented in Table 3. Pre-treatment for the MTBE plume at Port Hueneme will be using sand filters to remove suspended solids in the groundwater. The total dissolved solids in the groundwater is high (1,212 mg/L)[9]. Therefore, filtering the solids from the groundwater before treatment would protect the air stripper from fouling and improve treatment efficiency. The costs of plume monitoring were not included in the cost estimates for air stripping. Currently, there are 60 monitoring wells set up to characterize the plume [9]. Twelve more monitoring wells are needed at the air stripper site in order to monitor the remediation progress closely. Table 4 presents the monitoring scheme and costs through out the 20-year duration of the project. Close monitoring of the plume in the first year should be performed to ensure that the air stripper is working properly. Therefore, samples from a total of seventy-two wells will be analyzed. After the first year, assurance that the treatment is controlling the plume will be confirmed, and monitoring efforts can be reduced. Permits are required for construction of the air stripper before treatment can begin. The cost for permits and project management (e.g. labor for obtaining permits) is listed in Table 3.

The total cost for remediating the MTBE plume at Port Hueneme is estimated to be $4,178,547 (Table 3). The cost estimate for air stripping is –30% to 50% accurate [7], therefore, the actual cost of the mitigation ranges from $2.8 million

to $6.1 million. Caveats for the total cost estimate are that the $4 million does not include inflation rate and technology advancement within the next 20 years. If real discount rate is used, the total cost would be greater than $4 million. If advancement in technology increases the efficiency of air stripping, the total cost would be lower than $4 million.

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Table 1.Cost estimate for each treatment technology in dollars per 1000 gallons(in 1998 dollar).				
Concentration(ppb)	**1000**	**1000**	**5000**	**5000**
Flow Rate (gpm)	**10**	**100**	**10**	**100**
Treatment Technology				
Physical Treatment[1]				
Air Stripping	$2.84	$0.88	$3.22	$0.97
GAC	$2.62	$2.08	$4.71	$3.77
Hollow Fiber Membrane	$2.96	$2.25	$3.96	$3.05
Biological Treatment[2]				
Trickling Biofilter	$3.40	$0.53	$3.96	$0.84

Table 2. Costs for mitigation of the MTBE plume at Port Hueneme for each treatment technology (in 1998 dollar).				
Concentration(ppb)	**1000**	**1000**	**5000**	**5000**
Flow Rate (gpm)	**10**	**100**	**10**	**100**
Physical Treatment				
Air Stripping	$4,428,254	$1,372,135	$5,020,766	$1,512,467
GAC	$4,085,220	$3,243,228	$7,344,040	$5,878,351
Hollow Fiber Membrane	$4,615,363	$3,508,299	$6,174,607	$4,755,695
Biological Treatment				
Trickling Biofilter	$5,301,430	$826,399	$6,174,607	$1,309,765

Footnotes
1   Nyer, E. 1998

Table 3. Total cost for using air stripping to treat the MTBE plume (1998 dollar).				
Air Stripping Capital, and O&M Costs			$1,512,466.88	
	Units	**dollar/Unit**	**Total**	
Other Capital Costs[10]				
Monitoring wells installation	12	$2,000	$24,000	
Project management and engineering permits			$734,000	
Sand filter			$140,000	
Monitoring -labor, equipment & analysis (see Table 4)			$1,108,080	
	20	$33,000	$660,000	
Total Cost			**$4,178,547**	

Table 4. Total cost for monitoring the MTBE plume over 20 years (in 1998 dollar).				
Time	**number of monitoring wells**	**frequency of sampling/year**	**cost/sample**	**Total**
Year 1	72	12	$855	$738,720
Year 2	30	6	$855	$153,900
Year 3	12	4	$855	$41,040
Years 4-20	12	1	$855	$174,420
Total Cost				**$1,108,080**

Critique of Ecological Risk Assessment

This discussion of the Ecological Risk Assessment process represents a broader examination of the ERA methodologies and their value, including the current role of an ERA, it's strengths, weaknesses, and ways in which it can be improved.

When one thinks of risk, it is usually in association to humans. Risk is typically described in terms of impairment of health or the likelihood that it could affect a person's lifestyle or their ability to produce children. However, for ecological systems, the concern is more with the persistence of populations, which depends not just on survival chances, but also on the functionality of populations within the overall ecosystem as well as the ability for the ecosystem to support and recruit new individuals to sustain this functionality (Calow 1998). Therefore, an Ecological Risk Assessment involves computing a probability for effect by considering the extent of overlap between likely exposure and likely effect concentrations (Calow 1998).

In the conducting the Ecological Risk Assessment (ERA) for the groundwater plume of MTBE at the Port Hueneme site, several aspects of the process appeared less then efficient in terms of the quality of decision-making and comprehensiveness of coverage. The ERA process, as described by the EPA, was designed to evaluate adverse ecological effects that are the result of exposure to one or more stressors. It is intended for the organization and analysis of data and information, while taking into account both assumptions and uncertainties. The process is also meant to provide a critical element for environmental decision-making by giving risk managers and assessors the "best" available scientific information along with other factors (social, legal, political, or economic) in selecting a course of action (EPA 1998). ERAs can be viewed as an exercise in environmental problem solving. They provide a systematic means of assessing the state of ecological resources and determining remediative priorities for the myriad of potential ecological problems human action has caused (Power and Adams 1997).

The EPA guidelines for Ecological Risk Assessment separate the ERA process into three stages: (1) Problem Formulation, (2) Analysis, (3) Risk Characterization. Each stage is evaluated below for perceived inefficiencies and disadvantages to risk assessors.

➢ The Three Stages of Ecological Risk Assessment

In the initial stage, "Problem Formulation", risk assessors need to define goals, identify possible ambiguities inherent in endpoint selection criteria, provide definitions within a standard metric for the particular project, and comment on significant risks within the context of the study area and their associated uncertainties (EPA 1998). When an assessment is undertaken due to concerns about perceived stressors on the ecological system, risk assessors tend to focus their efforts solely on the effect of the stressor(s) on the endpoints rather than on the system as a whole. It should be noted that endpoints, as defined in an ERA, are typically individual organisms. However, organisms react differently at different stages of development and, therefore, selection of endpoints should be considered subjective, at best (Montague 1995). Typically, assessors only select endpoints that are deemed to be the most important, due to cost and time constraints; the selection of which endpoints to consider should be viewed as a value-based decision made by each assessor. These assessors then determine which data to collect, how to simplify available facts into simple models, which statistical tests be used, the sample size to be selected, and which exposure-response model to employ (Power and Adams 1997).

One of the goals for risk assessment procedure has been to develop an environmental equivalent to the litmus test. A limited number of indicator or test species, suited and bred for the laboratory (ex. Daphnia, Water fleas, Rats, etc.), are compared with spatially or temporally limited field work. This information is then used to predict deleterious effects of exposure for all species inhabiting an ecosystem (Power and McCarty 1997). This intense focus for a surrogate test-species discounts the contribution of the remaining endpoints as either an indication of health or stress on/to the system. In a similar manner, the choice of any one endpoint is subjective as it is based on the perceived risk to the assessor and his/her experiences and background in risk assessment. As a result of this subjectivity, important endpoints may be missed or discounted because certain individuals or species, like microorganisms, are not typically valued highly by humans.

In the second stage, "Analysis", risk hypotheses are evaluated to determine how they will be assessed using available and new data. The actual analysis plan may be extensive or brief, depending on the assessment being conducted (EPA 1998). Exposure of the stressor to the environment, and hence the endpoints, will be the determining factor for stress measurement. In order to determine the effect on biological endpoints, a baseline indication is established. This is typically referred to as a dose-response, where endpoints (biological organisms) are exposed to greater doses for acute

measurements or longer terms for chronic measurements with greater doses or longer exposure usually causing greater effects.

In an assessment analysis, risk assessors determine which pathways to focus on. This exclusion of other pathways, or a significant portion of them, acts to ignore the contribution of minor pathways and their cumulative effect on the system as a whole. This also ignores the fact that the chosen endpoints may be immune or resistant to the chosen pathway which, in turn, may skew the conclusions and recommendations of the assessment. Furthermore, high-dose animal responses are often extrapolated to low-dose human effects, but it is questionable whether the assumptions necessary for such an extrapolation are viable (Montague 1995). Due to the complex nature of biological endpoints and the genetic uniqueness within individuals and species, there exists a significant amount of uncertainty in this animal-human extrapolation.

In the final stage, "Risk Characterization", the risk assessor needs to account for the diverse relationships between stressors, their effects on the environment, and, ultimately, their effects on the ecological endpoints. Risk is often expressed as the probability of a particular harm to specified endpoints during a stated period (Montague 1995). Therefore, the risk assessor compiles information from the literature to (1) assess the hazard (or risk) exposure and (2) to develop dose-response estimation. Typically, the assessor will attempt to characterize the potentially affected population of the endpoints by examining a variety of ecological metrics such as population size, diversity, and health. This imposes a certain degree of subjectivity into the decision-making process, since the biological endpoint chosen and the exposure pathway of that endpoint may not be characteristic of the hazard or risk associated with the affected ecological system.

➢ **Risk Assessment: It's Uses (and Abuses)**

Although risk assessment is widely used, the consensus on an acceptable, comprehensive decision-making framework that can be effectively used by environmental managers has not yet emerged (Power and McCarty 1997). Some critics contend that risk assessment is deeply flawed and subject to abuse (Montague 1995). Another area of criticism is the contention that Ecological Risk Assessment, as currently practiced, is nothing more than "the paradigm of human health risk assessment, laying on an underlying, unsophisticated ecological veneer" (Lackey 1997b). Whatever the criticisms, anthropogenic stresses have forced society to use science to comprehend these impacts on ecological systems and science has, currently, decided that the Ecological Risk Assessment process is the best method to do so.

Risk assessment has been used effectively in many fields as an aid in decision-making (Lackey 1997b). It can help decision-makers allocate scarce (typically, governmental) resources and estimate the likelihood of an adverse event occurring. When the ERA process attempts to clearly identify an adverse risk, more problems may arise. This is due, in part, to the complexity of ecological systems and an inability to understand issues on more than one level. To be tractable and credible, the problem must be defined in narrow terms (Lackey 1997b). If this can be done, the risk assessment becomes fairly simple in terms of analysis: an examination of one of a few chemicals/stressors causing an adverse reaction on a chosen endpoint. This narrowing illustrates the one-dimensionality of the ERA process. However, it is important to remember that risk assessment, when done properly, is merely a tool. When used properly, it is a tool that can assist in presenting the likely consequences of various decisions, usually after an adverse event.

➢ **Concerns**

Some government agencies are strongly supportive of the ERA process, to the point of implementing polices that encourage and validate their results, as is the case with the Environmental Protection Agency (EPA). Yet, there are concerns regarding the ERA process. Some critics allege that, with enough creativity, any policy position can be supported by risk assessment. The most common criticism is that the policy questions are formulated in a way that will produce virtually any result and that the results have the aura of scientific credibility (Montague 1995). Likewise, existing regulations are set up with the idea that risk can be evaluated using a standard approach and that assessment is completely objective, neutral, and value free (Power and Adams 1997).

A risk assessment never reaches the conclusion that a risk is avoidable because risk assessment never asks whether a particular risk can be avoided (Montague 1995). Avoidance of risk is never considered because risk assessments are inherently reactive and not proactive.

When the decision is made to conduct an ERA (normally *ex post facto*), there is the belief that the problem at a site can, and will, be defined. This use of ERAs illustrates how they are reactive not proactive. Since ecosystems are intrinsically complex, with many unique individual "sub-systems", and overall understanding of them is incomplete, this presupposition fails to take into consideration that the ERA process forms the question in such a manner so that it can be answered (Power and Adams 1997). Without clear knowledge of what should be measured, how can endpoints be properly

selected or defined? Another problem caused by this oversimplification occurs in endpoint replication. The fact that available data indicates a low frequency of observed effects does not prove a low probability of occurrence if each observation cannot be viewed as the product of an identical, repeatable experiment (Power and Adams 1997). Without repetition, the basic statistical foundation of any risk assessment becomes weak and questionable.

There is also an illusion that deleterious effects can be effectively measured on chosen endpoints. The theory contends that, if the most sensitive species are identified and adjusts for media quality are performed, then all other ecosystem's inhabitants will be sufficiently protected (Power and McCarty 1997). If this theory were correct, it would simplify monitoring and enforcement costs and most likely would have already evolved—thus the illusion.

As mentioned before, another assumption in selecting a sensitive species is that it relies on selecting one from a limited array of test organisms, specifically bred for laboratory conditions to reduce individual variability and improve the consistency of experimental results. These candidate species are routinely selected based on their economic importance, protected status, or other human-based bias, even before their sensitivity to stressors has been determined (Power and McCarty 1997). It should also be noted that the response by these chosen endpoints is only descriptive and is not necessarily predictive in how stressors will react within an ecosystem. Furthermore, the use of extrapolation assumes that an individual's response to a stressor can be precisely measured by controlled tests and used to predict a population's response to that stressor in its natural environment (Power and McCarty 1997). This myth is the most universal misnomer professed by those who support the ERA process.

The focus of ecotoxicologists lies in the dose-response relationship for a limited number of chosen test organisms in artificial test containers. In doing so, they attempt to simulate field conditions and, ultimately, to extrapolate those results to natural environments (Power and McCarty 1997). This method fails to take into consideration the actions of biotic and abiotic factors present within the ecosystem (including *in situ* synergies between organisms) because heterogeneity within ecosystems will always be problematic for laboratory to field extrapolations.

There is no ideal way to carry out Ecological Risk Assessments (Calow 1998). It is important to be aware of the portion of the ecological system that will be protected by the recommendations of the ERA, and it is equally important to

be aware of the anthropocentric values inherent in the decision-making process. Other, more rigorous, treatments for risk which are less biased by anthropocentric valuation should be considered. Lackey (1997b) reports on an alternative to Ecological Risk Assessment that eliminates the risk aspect of the assessment and simply assesses ecological consequences without defining good or bad, adverse ecological health or risk.

➢ **Some Suggestions**

By eliminating risk from the equation, the amount of value-laden choices made by scientists and assessors is reduced. This allows for a more open and democratic forum that would include all interested stakeholders while creating an accountable decision-make process. The product of such a process would resemble an ecological consequence assessment rather than an Ecological Risk Assessment (Lackey 1997b). This type of assessment would alter the process of problem formulation—by including a variety of stakeholders each defining the effects of the problem uniquely—and lessen the traditional constraints on the number and type of policy options under consideration (Lackey 1997b). Empowering those who are most directly affected by the problem may increase the value of assessment.

➢ **Conclusions**

Although a useful tool, an Ecological Risk Assessment is an incomplete decision-making technique because it focuses solely on endpoints and not the system as a whole and endpoint selection is selective at best. It excludes many pathways and focuses on only a few easily quantifiable ones, relies on high-dose animal response extrapolation to low-dose human exposure, fails to recognize genetic uniqueness within individuals, is not proactive, does not consider alternatives adequately, and examines single exposures in a multi-exposure reality. The very nature of the ERA process requires that assessors make many value-based decisions, excluding other pertinent stakeholders, suggesting that the process should not be considered to be thorough or democratic (Lackey 1997b).

Conclusions

Several conclusions can be generated about both the level of risk associated with the MTBE plume at Port Hueneme and the ERA process in general.

In the process of exploring the ecological risk associated with the MTBE and BTEX release at Port Hueneme, several conclusions were drawn regarding toxicity and MTBE pathways. First, it was found that MTBE and BTEX concentrations could not be correlated with toxicity. It could not be determined whether BTEX, MTBE, daughter products, or the synergistic relationship between them was the cause of the observed toxicity. In addition, it could not be determined if the presence of MTBE affected the attenuation of BTEX or the health microbial communities in general; however, the identification of toxicity in the groundwater within Zone 1 should be considered deleterious to microorganism health.

Second, it was discovered that large amounts of MTBE could be (and likely were) removed from the system via an under-emphasized pathway. MTBE concentrations were 14 fold smaller in the Summer of 1999 than they were in December of 1996, suggesting that most of the MTBE had been removed from the system over the course of three years. A pathway analysis using fate and transport models suggested that the processes of advection, dispersion, adsorption, hydrolysis, and biological degradation could not account for the observed decrease in MTBE concentrations. Another analytical model illustrated that volatilization could account for several times the observed reduction over that time frame. Therefore, it is possible (if not likely) that volatilization is the primary pathway by which MTBE is removed from the groundwater at Port Hueneme.

The second set of conclusions arising from this project pertain to the Ecological Risk Assessment process itself. These conclusions include both positive and negative observations:

Ideally, Ecological Risk Assessments provide risk managers with information about the potential adverse effects of different management decisions and action is taken to generate a base of useful information on the impact of human activities on the environment (EPA 1998). There are several aspects of the Ecological Risk Assessment process that makes it a useful tool to risk managers.

First, since the process can be iterative, new information is easily added into risk assessments. Second, risk assessments allow comparisons, rankings, and prioritizing of risks. Third, during this process uncertainties in the data are assessed. Fourth, risk assessments describe how changes in stressor exposures can lead to changes in ecological effects. Fifth, during the risk assessment process not only are scientific data and conceptual models relied upon, but management goals and objectives are also considered.

However, there are several aspects of the ERA process that could be improved. First, the process is not proactive. A better ecological tool would help risk managers prevent adverse events *a priori* by being more predictive than just descriptive. Second, the process relies on decisions that are value-laden and often subjective in nature. This leads the risk manager to focus on pathways and endpoints, which may not adequately represent the system and associated risk from contaminants.

Team MTBE2000 has created recommendations on how to improve the quality of results of the ERA process and their usefulness, in particular, for the Port Hueneme site. The recommendations presented in this section include suggestions that are (1) specific to the investigation conducted in this report and (2) more generally related to when and how risk assessment is performed.

To better characterize the risks created by the plume, it is recommended that several aspects be researched on the base. First, due to the location of the sampling wells, it is unclear which direction the plume is currently heading. Further sampling needs to be performed in order to determine if the plume will intercept a nearby drainage channel and, if so, to identify organisms that may potentially be affected.

Second, further research needs to be performed in order to determine if MTBE and BTEX daughter products (TBA, TCE, etc.) are responsible for the toxicity observed within Zone 1 of the plume, or if it is caused interactions among these metabolites. Furthermore, the interactions between BTEX and MTBE may be directly (or indirectly) causing the toxicity within Zone 1; this is another area that needs further research.

Finally, a more thorough geological survey should be performed. To date, the potential for fissures or sinks between the two groundwater aquifers has not been adequately determined. The potential for subsurface channeling through utility trenches or paleochannels must also be investigated.

Recommendations for improving the Ecological Risk Assessment process require a restructuring of the guiding framework, rather than an increase in research or

data acquisition. Complete understanding of complex ecological systems is limited; there is a strong tendency to define risk assessment problems in ways that can be observed through science alone.

The EPA guidelines for conducting Ecological Risk Assessments are written in very general terms with cumbersome language; a streamlining of the process would greatly improve the efficiency and effectiveness of the assessment. This should include centralized data sets, better human-animal dose-response extrapolation models, and a stronger reliance on a more holistic approach rather than simply focusing on a few surrogate species.

Due to the fact that risk assessments are inherently reactive and not proactive, there is a need for a mechanism to determine consequences without applying risk based definitions of "good" or "bad". A set of questions or flow charts can be created so that they can be applied to the decision-making process in terms of ecological consequences and provide the primary investigator with an innovative, forward-looking means of determining the possible fate of ecological systems from planned anthropogenic activities. With these value-based decision tools, ecological damage considerations would be taken into consideration prior to the initiation of events that would, today, require a *post facto* Ecological Risk Assessment to address the consequences.

Acknowledgements

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