

THE
FATE
AND
TRANSPORT
OF
ETHANOL-BLENDED
GASOLINE
IN THE
ENVIRONMENT

A LITERATURE REVIEW
AND TRANSPORT MODELING

Submitted by



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1.0 Executive Summary

The common detection and persistence of methyl-tertiary butyl ether (MTBE) in subsurface waters, and the potential phase-out of this gasoline oxygenate, prompts the need for evaluating the fate and transport of other gasoline oxygenates including ethanol. Because oxygenated gasoline can contain high concentrations of ethanol, which is infinitely soluble in water, high concentrations of ethanol are likely to be found in groundwater contacting non-aqueous phase ethanol-amended gasoline. The ethanol in oxygenated gasoline spills will rapidly partition into groundwater and quickly become the dominant dissolved contaminant immediately downgradient of a spill. The abiotic mechanisms for the attenuation of subsurface contaminants including sorption, volatilization, and abiotic degradation will not contribute substantially to the decreased mobility or loss of ethanol in subsurface aquifers. Therefore, the fate and transport of ethanol and other gasoline oxygenates in groundwater aquifers will primarily be controlled by biodegradation.

Because biodegradability decreases with increased chemical branching, highly branched oxygenated organic compounds including MTBE will have a higher residence time in the environment. In contrast, the structural characteristics of ethanol favor rapid biodegradation. Ethanol is a naturally-occurring intermediate produced during the fermentation of organic matter in anoxic environments and is expected to rapidly biodegrade in essentially all environments with conditions (i.e., temperature, pH, and pressure) that support microbial activity. Microorganisms capable of metabolizing ethanol are ubiquitously distributed in the environment and relatively rapid rates of ethanol biodegradation have been measured under aerobic and anaerobic conditions. Thus, ethanol is a short-lived compound in surface waters and subsurface aquifers.

Due to limited laboratory testing and the absence of field evidence, generalizing conclusions can not yet be made regarding the effect of ethanol on benzene, toluene, ethylbenzene, and xylene (BTEX) biodegradation and migration in subsurface environments contaminated with ethanol-blended fuels. Limited laboratory information suggests that in some instances BTEX biodegradation is inhibited in the presence of

ethanol which can serve as a preferred substrate. However, transport models that incorporated both biological and abiotic factors that impact the transport of contaminants indicated that ethanol will not migrate substantial distances beyond the source of ethanol-amended gasoline. Based on the length of ethanol plumes predicted in the models, and the assumption that benzene will not biodegrade in the presence of ethanol, the presence of ethanol in a gasoline spill is predicted to increase the migration of benzene by no more than 25 percent. This value does not consider the fact that ethanol-blended fuels contain less BTEX in proportion to the volume fraction of gasoline. For example, gasoline amended with 10 percent ethanol contains 10 percent less BTEX available to contaminate the environment relative to the base fuel. Further, due to the short time required for ethanol to completely leach from non-aqueous gasoline relative to hydrocarbons, and due to the rapid rates of ethanol biodegradation, it is not likely that ethanol will persist in gasoline contaminated groundwaters for a significant time relative to BTEX.

While ethanol may not pose a substantial direct impact on hydrocarbon transport, the metabolic intermediate, acetic acid, may accumulate in aquifers contaminated with ethanol-blended fuel due to its low rate of biodegradation relative to ethanol. Whether acetate has an impact on the migration of BTEX plumes is not known and warrants additional scientific evaluation. Acetic acid could potentially enhance or decrease the biodegradation of gasoline hydrocarbons.

Since the migration of ethanol plumes is limited relative to BTEX, ethanol in the subsurface will likely only exist in the presence of other hydrocarbons including benzene, which pose a considerably higher risk to human health and aquatic life. The intermediates and products of ethanol biodegradation likely pose little to no health threat. Acetic acid is the intermediate that is most likely to accumulate to a significant extent, but it is commonly used as a food supplement. The inhalation of ethanol during refueling with ethanol-blended gasoline apparently does not represent a substantial health threat.

While the literature survey and modeling exercises suggest that ethanol may be an ‘environmentally-friendly’ gasoline oxygenate, it should be recognized that field

information documenting the fate and transport of ethanol-amended gasoline in contaminated groundwaters does not exist. Field data would help develop a stronger argument for the fate of ethanol amended gasoline in subsurface and surface water resources.

2.0 Introduction

The frequent detection of the gasoline oxygenate methyl tertiary-butyl ether (MTBE) in surface and groundwaters illustrates that persistent gasoline additives can impact environmental quality. The growing disdain for MTBE (Parkinson, 1998; J. Oil and Gas, 1998) prompted recent legislative efforts to phase out MTBE as a gasoline oxygenate in California (Rhodes, 1999) and potentially in Maine (Environ. Sci. Tech. News, 1999). This has resulted in the current need to identify oxygenates that pose less risk to surface waters and groundwater. A thorough report assessing the health and environmental consequences associated with the use of MTBE suggested that the use of either non-oxygenated reformulated gasoline or ethanol would result in a much lower risk to water supplies (Keller et al., 1998). However, a thorough understanding of the environmental fate of potential gasoline additives and the influence that these compounds may have on the fate of other gasoline constituents should be obtained before replacements for MTBE are selected. To this end, this report (1) outlines information on the use of MTBE and ethanol as gasoline additives; (2) briefly describes the factors affecting the negative impact of MTBE on the environment; (3) offers an extensive review of various considerations for the use of ethanol as a gasoline additive; and (4) presents contaminant transport models that were used to predict any environmental consequences associated with the presence of ethanol in gasoline spills that enter the subsurface. Although the literature survey and modeling exercises both suggest that ethanol will not persist or migrate substantially once released into the environment, there may be indirect effects associated with ethanol that could increase the length of hydrocarbon plumes in the subsurface. Overall, the literature survey and subsurface transport modeling indicate that ethanol may be an ‘environmentally-friendly’ gasoline oxygenate, but it should be recognized that field information documenting the fate and transport of ethanol-amended gasoline in contaminated groundwaters does not appear to exist.

3.0 Background

3.1 History of Requirements for Reformulated Gasoline and Gasoline Oxygenates

Legislative efforts to reduce automotive exhaust emissions have prompted changes in gasoline formulation. The use of automobiles contributes to atmospheric contamination by gasoline components through volatilization and exhaust emissions (Keller et. al, 1998; Calvert, et. al, 1993). The release of hydrocarbons, their partial oxidation products, and associated nitrogen oxides (NO_x) contribute to the formation of ozone through photochemical oxidation reactions. High concentrations of ozone can cause human health problems and crop damage. Furthermore, the incomplete combustion of hydrocarbons in automotive engines results in the formation of carbon monoxide which is also associated with adverse human health effects. In an effort to reduce this pollution, emissions standards were mandated by the U.S. government beginning in 1968. The ensuing use of catalytic converters substantially reduced emissions of hydrocarbon, nitrogen oxides (NO_x), and carbon monoxide (Calvert, 1993), yet additional strategies were needed due to a rapidly growing fleet of automobiles.

Legislative efforts to address the impact of gasoline combustion on air quality continued into 1990 when the U.S. Congress amended the Clean Air Act of 1970. In an effort to increase the efficiency of gasoline combustion, the new law mandated the use of oxygenated fuels containing at least 2.7% oxygen by weight during the winter months in areas of the United States having increased carbon monoxide levels (Saunders, 1997). The law does not specify which oxygenate or combinations thereof should be utilized. However, the minimum oxygen requirement could potentially be met through the addition of a variety of gasoline oxygenates including 15% (by volume) methyl tertiary-butyl ether (MTBE), 5.4% methanol, 7.8% ethanol, 17.3% ethyl tertiary butyl ether (ETBE), or 17.3% tertiary amyl ether (TAME) (Feldman, 1993). The reformulated gasoline program requires that gasoline contain 2% oxygen (by weight) throughout the year in most metropolitan areas with severe air pollution problems (MTBE fact sheet #3). This requirement can be met by incorporating ethanol at 5.4% by volume concentration or MTBE at a concentration of 11% by volume. The air quality benefits associated with

the use of reformulated gasoline and gasoline oxygenates were recently evaluated (Keller, 1998).

The amendments to the Clean Air Act also specified that reformulated gasoline be used in nine areas with increased ozone levels. In addition to oxygen content, it was mandated that the reformulated gasoline contain less than 1% benzene by volume and less than 25% total aromatics in an effort to minimize the release of these toxic compounds (Calvert, 1993). Reformulated gasoline also has a reduced vapor pressure to decrease evaporative emissions and a reduced sulfur content to prevent the poisoning of catalytic converters (Keller, 1998).

3.2 Extent of Ethanol and MTBE Use

MTBE and ethanol were introduced as gasoline additives in 1979 and are currently the most frequently used gasoline oxygenates (MTBE fact Sheet #3). The original use of MTBE was to replace lead as an octane-enhancing additive, while ethanol was initially added to reduce reliance on oil imports. As of 1998, approximately 30 percent of all gasoline in the United States contained MTBE. This ether oxygenate was present in 80% of oxygenated fuels. Ethanol was used in approximately 15% of the oxygenated fuels. As a result of the widespread use of oxygenated fuels, one can not be assured of the oxygenate status of gasoline that is sold, distributed, or leaking in any particular region of the country (MTBE fact sheet #3). However, ethanol is generally used in the winter months since it increases the vapor pressure of gasoline thereby increasing gasoline volatility. Conversely, MTBE is used throughout the year because it reduces gasoline volatility and is consequently useful for reducing the release of hydrocarbons through gasoline volatilization during summer months (MTBE fact sheet #3). Ethanol is also used as a gasoline oxygenate in other countries. In Brazil, ~ 85% of the automobiles use gasoline containing 22 to 24% ethanol. The remaining automobiles use hydrated ethanol for fuel.

3.3 The Production and Distribution of MTBE and Ethanol

The major method of ethanol production is the microbial fermentation of corn (Pimental, 1998) with smaller quantities produced via a variety of chemical syntheses (The Merck index). MTBE is produced from isobutylene at refineries and at chemical companies from either butane or isobutane as raw material (Morse, 1999). The total production of ethanol (Pimental, 1998) and MTBE (Morse, 1999) in 1998 was approximately 1 billion and 3.1 billion gallons, respectively.

Because ethanol has a tendency to separate from gasoline and solubilize water into ethanol blended gasoline, ethanol is typically introduced into gasoline soon before use at or near the distribution terminals (MTBE fact sheet #3). Therefore, ethanol is often produced near the distribution terminals or shipped by rail or truck. MTBE is generally blended with gasoline at refineries and distributed by pipeline.

3.4 Exposure Potential to Ethanol, MTBE, and Other Gasoline Components

The prevalence of petroleum hydrocarbon releases from oil production sites, underground storage tank sites (USTs), and refineries is one of the most important environmental issues that our nation faces. Chemicals of concern at these sites include benzene, toluene, ethyl benzene, xylenes (BTEX), total petroleum hydrocarbons (TPH), lead, and MTBE. Of these constituents, benzene has been demonstrated to be a human carcinogen and the others all pose health risks. Due to the toxic nature of the chemicals released and the fact that many of these sites are located adjacent to residential properties and/or drinking water sources, potential impact to human health is high.

The potential routes of human exposure to ethanol as an oxygenate include inhalation and the ingestion of contaminated groundwater. The sources of ethanol in the air that contribute to exposure via inhalation include: refueling activities, exhaust emissions, and evaporative emissions. Aside from considering the health effects of inhaled ethanol, an evaluation of the health risks associated with evaporative loss of ethanol-blended fuels must also consider the impact of ethanol on the evaporation of gasoline hydrocarbons. Due to the increase in the Reid vapor pressure (a good measure of fuel volatility) of

ethanol-blended gasoline, it could be anticipated that these fuels may emit increased levels of gasoline hydrocarbons, thereby posing an increased inhalation hazard. However, research evaluating the evaporation of ethanol and non-ethanol blended gasoline indicated that while the evaporation rate for the blended gasoline was increased, less hydrocarbon volatilized relative to the base fuel (Aulich, et al., 1994). The increased evaporation of the ethanol-blended fuel was due to ethanol evaporation. It is possible that a decreased potential for toxicological effects is associated with evaporative emissions from ethanol-containing gasoline which contains less hydrocarbon. Research on levels of ethanol in the blood of mice following exposure to several doses of inhaled ethanol suggested that the levels of ethanol likely to be inhaled during typical refueling would not result in toxic effects to humans (Pastino et al., 1997).

The toxic effects associated with changes in exhaust emissions due to the presence of ethanol in gasoline is uncertain. Ethanol decreases carbon monoxide (CO), volatile organic compounds (VOC), and benzene emissions but increases nitrous oxide, acetaldehyde, and peroxyacetyl nitrate (PAN) emissions from automotive exhaust (Auto and Gas 1991). Acetaldehyde and PAN have potential health effects and acetaldehyde has been listed as a toxic air contaminant in California (Keller et al., 1998). Our review of the air quality issues associated with ethanol-blended fuels was cursory. Additional information on these issues including the current debate on whether PAN emissions are actually increased with ethanol-blended fuels combustion should be considered.

The risk of exposure to gasoline oxygenates through the ingestion of contaminated groundwater increases with increasing length and size of the oxygenate plume. In addition, gasoline additives including MTBE that can migrate beyond the benzene, toluene, ethylbenzene, and xylenes (BTEX) plume, are more apt to escape detection because monitoring for gasoline oxygenates is less routine than BTEX monitoring. Consequently, MTBE represents an increased risk to exposure relative to gasoline oxygenates that do not migrate to this extent. Further, gasoline oxygenates that accumulate in surface water resources (i.e. MTBE) pose an increased risk of exposure via ingestion. Consequently, the disdain for MTBE as a gasoline oxygenate in California

continues to grow (Parkinson, 1998; Oil & Gas, 1998; Schwartz, 1999; ES&T News, 1999; Rhodes, 1999). The toxicology of MTBE has been the subject of intensive debate and has recently been reviewed (Keller et al., 1998). Studies with laboratory rodents indicate that MTBE has carcinogenic and neurotoxic effects.

Gasoline oxygenates, including ethanol and methanol, which are more rapidly attenuated in groundwater aquifers and in surface waters are clearly less likely to persist or migrate in aqueous environments. This decreases the chance of accidental exposure via ingestion. Furthermore, since the migration of ethanol plumes is limited relative to BTEX, as discussed below, ethanol will likely only exist in the presence of other hydrocarbons including benzene, which pose a considerably higher health risk (Hartley, 1992; Dean, 1995). Nevertheless, chronic ethanol ingestion in the form of alcoholic beverages can damage the liver and many other organs including the heart (Combs and Acosta, 1990), can be carcinogenic, and has been associated with occurrence of fetal alcohol syndrome (Spagnolo, 1993).

As discussed later in the report, the intermediates and products of ethanol biodegradation likely pose little to no health threat. The toxicology of ethanol to aquatic life is not discussed herein because ethanol will rapidly biodegrade in surface waters thereby substantially limiting the risk to aquatic macroorganisms.

3.5 Release of Gasoline Oxygenates into the Environment

The production, distribution, storage, and use of fuel oxygenates has resulted in their release into the atmosphere, surface waters and groundwaters. Oxygenate release into the atmosphere is quantitatively the largest reported release mechanism (Zorgorski, 1997), but groundwater contamination, especially by MTBE, is currently the major concern. Sources of subsurface contamination include pipelines, refueling facilities, surface spills, precipitation, and especially underground storage tanks (USTs). There are millions of oil production sites, USTs, and refineries located throughout the United States alone. However, the decrease in the number of USTs and the improvement of their structure as mandated by the United States Environmental Protection Agency (USEPA) and state requirements

should reduce the number of leaking USTs. Nevertheless, in 1995 it was estimated that over 200,000 UST sites would require funding for investigation or cleanup (Gurr and Homann, 1996). MTBE has been detected in approximately one half of the groundwaters associated with leaking USTs in California (Keller, 1998). The increased use of ethanol in Brazil has raised concerns and initiated scientific research on the impact of ethanol on the fate and transport of hydrocarbons in subsurface gasoline spills (Corseuil, 1998; Corseuil, 1999; Alvarez, 1997).

4.0 The MTBE Problem

The frequent detection of MTBE in groundwaters prompted scientific research to evaluate the environmental behavior and potential health impacts associated with the use of MTBE as a gasoline oxygenate. A better understanding of the occurrence and persistence of MTBE in the environment (especially in groundwater aquifers) will provide important information necessary for predicting the fate of other gasoline oxygenates for which limited scientific information regarding their environmental behavior as gasoline oxygenates is available. For this reason, the current state of knowledge related to the fate and transport of MTBE in the environment is considered herein.

4.1 Extent of MTBE Contamination

It became clear that MTBE contamination of groundwaters was a substantial problem during a 16-State survey of 60 volatile organic chemicals in shallow groundwaters (Squillance, 1996). MTBE was the second most frequently detected compound, occurring in 27% of the samples. The majority (79%) of samples obtained from Denver, Colorado contained MTBE, but only a small fraction (1.3%) of shallow waters obtained in rural areas were contaminated. MTBE has also been detected in drinking water wells. Between 0.3 and 1.2% of the public drinking water wells tested in California contained MTBE (Keller, 1998). The occurrence of MTBE in drinking water supplies sparked an intensive controversy concerning the health effects of MTBE and other oxygenates.

Surface waters including reservoirs and lakes, especially those used for recreational use, are also vulnerable to MTBE contamination. The monitoring of California's surface waters (mainly lakes and reservoirs) revealed that 47% of the 105 tested water bodies contained detectable levels of MTBE (5 to 14 ug/L) on at least one occasion over an approximate one-year time frame (Keller, 1998). The source of MTBE in the lakes was not identified. However, a separate study found that the use of motor boats and personal water craft were the likely source of MTBE in a multiple-use lake (Reuter, 1998).

4.2 Characteristics That Make MTBE an Important Groundwater Contaminant

The potential health effects and low taste and odor thresholds for MTBE, coupled with its mobility and persistence, make this compound a contaminant of concern. The mobility of MTBE in the subsurface is attributed to its high water solubility, negligible sorption of the compound to sediment, and the fact that MTBE is not easily biodegraded. MTBE is more mobile than BTEX and has been reported to move at the rate of groundwater flow during a field study (Hubbard, 1994). Extensive analysis of contaminated aquifers in Florida revealed that MTBE plumes were longer and wider than benzene plumes (Reid, J.B., 1999). The average MTBE plume length (at the 10 ug/L concentration contour) in the Florida aquifers was 43 m (140 ft.) compared to an average benzene plume length of 35 m (115 ft.). Analyses of contaminant concentrations over time in these aquifers indicated that the length of the MTBE and benzene plumes were slowly decreasing at similar rates. Given the similarity between the dimensions of benzene and MTBE plumes, and the similar biodegradation rate estimates obtained for benzene and MTBE it is reasonable to conclude that MTBE is as resistant to microbial attack as benzene, a compound that is notoriously resistant to anaerobic biodegradation (Krumholz et al, 1996). Recent field and laboratory testing have identified that MTBE can be very slowly biodegraded (Landmeyer et al., 1998; Borden et al., 1997) but the significance of this loss mechanism is currently unknown.

4.3 Biodegradation of MTBE and Other Ether Oxygenates

The resistance of MTBE to complete mineralization (oxidation to carbon dioxide and water) by microorganisms has been reported under both aerobic (Barker et al., 1990) and

anaerobic conditions (Suflita and Mormile, 1993; Mormile, 1994; and Yeh and Novak, 1994). The results of Suflita and Mormile's work shown in Table 1, indicate that the majority of ether oxygenates containing tertiary or quaternary branching, including MTBE were not biodegraded in anaerobic sediment slurries. Similarly, tert-butyl alcohol (an intermediate produced when MTBE it is biodegraded), is also resistant to microbial attack (Novak, et al. 1985; Suflita and Mormile, 1993; Mormile and Suflita, 1994) and has been detected in groundwaters impacted by MTBE (Landmeyer et al., 1998). In contrast, ethanol is a straight-chain alcohol and was rapidly biodegraded in the anaerobic sediment slurries (Table 1). Straight-chain alcohols, ketones, esters, and the straight-chain analog of MTBE, methyl butyl ether, have been found to be biodegradable under a variety of anaerobic conditions (Mormile et al., 1994). Because biodegradability typically decreases with increased chemical branching, highly branched oxygenated organic compounds including MTBE will have a higher residence time in the environment.

Table 1: Rates of Anaerobic Biodegradation of Several Gasoline Oxygenates in Aquifer Slurries

Oxygenate	Rate (ppm C-day ⁻¹)	Oxygenate	Rate (ppm C-day ⁻¹)
Alcohols		Ethers	
Methanol	7.4	Methyl tert-butyl ether	0
Ethanol	17.9	Methyl tert-amyl ether	0
2-proponol	7.6	Ethyl tert-butyl ether	0
tert-butanol	0	Isopropyl ether	0
		Diethyl ether	0
Esters		Propyl ether	0
ethyl acetate	16.6	Butyl ether	0
Ethyl acetate	13.7	Butyl methyl ether	0.5
Methyl propionate	7.3	Butyl ethyl ether	0
Methyl isobutyrate	4.1	Ketones	
		Methyl ethyl ketone	9.4
		Acetone	7.3
		Methyl isobutyl ketone	21-28

*Table redrawn with permission from Suflita et al., 1993

5.0 Fate and Transport of Ethanol in the Environment

The detection of MTBE in ground- and surface waters illustrates that adverse consequences can be anticipated if chemicals that resist biodegradation are added to gasoline. Clearly, the susceptibility of gasoline additives, including ethanol, to biodegradation is an important characteristic in evaluating the fate of gasoline oxygenates in fuels. In addition, an understanding of the fate and transport of oxygenated fuels requires information on the behavior of contaminant mixtures (Brusseau, 1993). That is, the effect of ethanol on the partitioning and biodegradation of gasoline hydrocarbons should be considered and is discussed below. Conversely, the fate of ethanol may be impacted by gasoline hydrocarbons in the subsurface, but information regarding this potential effect has not specifically been evaluated. Further, field measurements of ethanol in gasoline-impacted aquifers are apparently not available, nor are field observations on the impact of ethanol on the transport of hydrocarbons in-situ. Thus, given the current state of information, the evaluation of the fate of ethanol-blended fuels in the subsurface is limited to predictions based on laboratory research and contaminant transport models.

5.1 Abiotic Considerations Influencing Ethanol Migration in Subsurface Aquifers

5.1.1 Partitioning of Ethanol Between Groundwater and Gasoline

Because oxygenated gasoline can contain high concentrations of ethanol, which is infinitely soluble in water, high concentrations of ethanol are likely to be found in groundwater contacting non-aqueous phase ethanol-amended gasoline. Due to the low solubility of other gasoline components including the BTEX hydrocarbons relative to ethanol (Table 2), ethanol would likely be the dominant dissolved component near the source areas.

If the concentration of a compound leaching from excess gasoline is allowed to equilibrate with water, the final aqueous concentration of the compound can be estimated by multiplying the aqueous solubility of the compound by its mole fraction in gasoline (Poulsen et al., 1992; Cline et al. 1991). This simplified equation does not apply for

infinitely soluble (miscible) compounds including ethanol. In static systems whereby gasoline is allowed to equilibrate with water, the concentration of miscible compounds is dependent on the water-to-fuel volume ratio. For instance, Barker et al. (1991) noted that at water to fuel ratio of 10:1 (V/V), the aqueous methanol equilibrium concentration derived from gasoline containing 85% methanol was 8% (80,000 mg/L). However, the theoretical solubility limit (infinite for ethanol) will not be reached in aquifers due to dilution with groundwater that continuously flows past a fixed volume of gasoline at the water table. For example, the theoretical aqueous solubility of MTBE for gasoline containing 10% MTBE is 4,800 mg/L at room temperature, yet the MTBE levels in gasoline-contaminated aquifers rarely exceed 4% (200 mg/L) of the theoretical solubility limit (Squillace, 1997; Reid, 1999). Furthermore, the rate of diffusion of gasoline oxygenates from gasoline may limit dissolution of the oxygenates into groundwater.

Since ethanol is completely soluble in water, the primary factor governing its concentration at the non-aqueous phase liquid (NAPL) interface is dilution. Assuming that the upper limit of “subsurface dilution factors” observed for MTBE (~ 4%) is similar to ethanol, an upper estimate of the concentration of ethanol occurring near the NAPL interface of gasoline spills is 4%. High concentrations of ethanol in this range may be more likely in low permeability aquifers in which dilution would be decreased.

Highly soluble gasoline oxygenates including ethanol will likely leach rapidly from free-phase gasoline sources. Poulsen et al; (1992) predicted that at a gasoline-to-water ratio of 1:1, only three pore volumes of water passing by non-aqueous gasoline would be required for the methanol to completely leach from methanol-blended gasoline (85% methanol / 15% gasoline) resulting in a discrete, short, methanol pulse, which would advance at the rate of the groundwater flow.

Table 2: Chemical and Physical Properties of Gasoline, MTBE, Ethanol, Benzene, and Toluene

Property	Gasoline	MTBE	Ethanol	Benzene	Toluene
Molecular weight (g/mole)	~100 100-105gh	88.15	46	78.11	92.13
Specific gravity	0.72-0.74 0.74g	0.74 0.7404-0.7578	0.79 ^a	0.88 0.8765	0.87
Boiling temperature °C	22.5-27	53.6-55.2	78.5 ^a	80.1	110.6
Water solubility (mg/L)	100-200	43,000-54,300	infinite ^a	1,780	534.8
Vapor pressure at 25°C. (mm Hg)		245-251	49-56.5 ^b	95.19	28.4
Log K _{ow}		0.94-1.30		1.56-2.15	2.11-2.8
Henry's Law constant, (H) (atn-m ³)/(g/mole)		5.87 x 10 ⁻⁴ 1.4 x 10 ⁻³ 3 x 10 ⁻³	6.17 x 10 ^{-6b} 5.13 x 10 ^{-6b} 6.29 x 10 ^{-6b}	5.43 x 10 ⁻³	5.91 x 10 ⁻³
Dimensionless Henry's Law constant (HRT)		2.399 x 10 ⁻² 5.722 x 10 ⁻² 2.16 x 10 ⁻²	2.52 x 10 ^{-4b} 2.10 x 10 ^{-4b} 2.57 x 10 ^{-4b}	2.219 x 10 ⁻¹	2.428 x 10 ⁻¹

The constants for gasoline and benzene were obtained from Squillace et al., 1997

^aMerck Index, 1989

^bZogorski et al., 1996

5.1.2 Cosolvency

Cosolvency refers to the increase in aqueous solubility of hydrocarbons due to the presence of other compounds in water that serve as a cosolvent (Cline et al., 1991; Pinal, 1990; Poulsen et al., 1992; Groves, 1988; El-Zoobi et al., 1990). Cosolvency increases with decreasing polarity of the cosolvent and with increasing concentration of the cosolvent (Pinal, 1990). Since high concentrations of ethanol may occur near the NAPL interface and because BTEX hydrocarbons are more soluble in ethanol than in water, the cosolvation of BTEX due to the presence of ethanol in gasoline is conceivable. However, a cosolubility effect on BTEX was not observed for gasoline containing 10% ethanol, 10% tertiary-amyl ether or 10% isopropyl ether, at a water to fuel ratio of 10:1 (Barker et al., 1991). At this water-to-fuel ratio, the ethanol concentration is predicted to have been 1%. Similarly, 15% MTBE did not cosolvate BTEX at a water to gasoline ratio of 10:1 (Poulsen, et al., 1992). Further, when gasoline containing 85% methanol (V/V) was placed in contact with 10 volumes of water, the aqueous BTEX concentration did not

increase relative to the BTEX concentrations observed for gasoline at the same dilution (Barker et al., 1991). Thus, multiple lines of evidence indicate that cosolvation of BTEX hydrocarbons is unlikely at fuel oxygenate concentrations in the low percent range. It is unlikely that a significant BTEX cosolvation effect would occur due to the presence of 10% ethanol in gasoline, because ethanol at this concentration will be diluted with groundwater below concentrations necessary to elicit cosolvation. At higher ethanol concentrations, significant BTEX cosolvation may occur. Noted increases include a 45% and 33% increase in aqueous BTEX concentrations in the presence of 17% methanol (v/v) (Barker et al, 1991) and 10% ethanol (Corseuil, 1999), respectively. Very large increases in aqueous solubility of BTEX have been observed in response to aqueous methanol concentrations above 25%, and BTEX may reside entirely in the aqueous phase in cases of very high methanol content (Barker et al., 1990).

Because the cosolvation effect is concentration dependent, actual field measurements of ethanol and BTEX in ethanol-amended gasoline plumes are necessary to make a definitive assessment of potential cosolvation effects. Nevertheless, ethanol concentrations necessary to increase the solubility of hydrocarbons are likely only at the NAPL / groundwater interface where equilibrium between the aqueous phase and gasoline may occur.

5.1.3 Partitioning of Ethanol Between Ground Water and Sediments

Insignificant sorption of ethanol to sediments is anticipated due to the high water solubility and low adsorption of polar compounds. Ethanol will therefore likely move at the rate of groundwater flow, as has been shown for methanol (Barker et al., 1990), a compound that is also highly polar and completely miscible in water.

Increasing the fraction of an organic cosolvent such as methanol results in an exponential decrease in the sorption of hydrocarbons to sediments (Rao, et al., 1990; Brusseau et al. 1991), thereby increasing the mobility of hydrocarbons (Wood, et al., 1990; Nkedi-Kizza et al, 1987). Thus, high concentrations of ethanol (>50%) can substantially increase the mobility of hydrocarbons. Consequently, flushing cosolvents including ethanol through

subsurface sediments has been used for remediating NAPL's in the subsurface (Sillan, et al., 1998). However, as discussed above, considering that the concentration of ethanol currently used in gasoline (up to 7.3% by volume) would quickly become diluted with groundwater, a significant impact of ethanol on the sorption and cosolvation of hydrocarbons is unlikely.

5.1.4 Volatilization and Abiotic Degradation of Ethanol

The abiotic oxidation of organic contaminants in the subsurface generally does not occur to an appreciable extent and is not expected to contribute to the loss of ethanol from groundwaters. Similarly, the volatilization of ethanol from subsurface spills into the unsaturated zone would be limited because ethanol is expected to leach relatively fast from NAPL's into groundwater (Poulsen et. al, 1992). Once dissolved in groundwater, substantial loss of ethanol through volatilization is unlikely due to its high aqueous solubility and low partitioning from the liquid to gaseous phase. In contrast to subsurface spills, the volatilization of ethanol from gasoline in direct contact with air is expected based on the finding that ethanol is an important component of the evaporative emissions released from gasoline containing 10% ethanol (Aulich et al., 1994).

5.1.5 Section Conclusions

Based on the chemical behavior of ethanol it is expected that ethanol in subsurface oxygenated gasoline spills will rapidly partition into groundwater and become the dominant dissolved contaminant immediately downgradient of the spill. The abiotic mechanisms for the attenuation of subsurface contaminants including sorption, volatilization, and abiotic degradation will not contribute substantially to the decreased mobility or loss of ethanol in subsurface aquifers. Therefore, the fate and transport of ethanol in groundwater aquifers will primarily be controlled by biodegradation.

6.0 Biodegradation of Ethanol

The evaluation of ethanol biodegradation is necessary for predicting the fate and transport of ethanol in the environment. This includes an understanding of the occurrence of ethanol-utilizing bacteria, the metabolic pathways and intermediates involved, the rates of

ethanol biodegradation under diverse environmental conditions, and the factors that may govern ethanol biodegradation and the intermediates of ethanol degradation. An important factor that governs the biodegradation of organic contaminants is the electron-accepting status of the environment. While ethanol is relatively easily degraded under aerobic and anaerobic conditions, the rates and metabolic pathways of ethanol oxidation are clearly impacted by the electron accepting conditions.

6.1 Microbial Metabolism of Ethanol Under Aerobic Conditions

Organic substrates that can easily be converted to compounds that enter central metabolic pathways of bacteria are generally rapidly biodegraded. In this regard, after a limited number of metabolic reactions, ethanol is converted to acetyl coenzyme A which enters the tricarboxylic acid cycle (TCA), the primary energy-generating pathway in aerobic metabolism (Figure 1). The initial oxidation of ethanol and a variety of other alcohols is catalyzed by the enzyme alcohol dehydrogenase, forming the short-lived intermediate acetaldehyde (Gottschalk, 1985). Acetaldehyde is subsequently oxidized by the enzyme acetaldehyde dehydrogenase to acetic acid which is in turn activated to acetyl CoA. Acetyl CoA is also a short-lived intracellular intermediate that enters the TCA cycle where it is completely oxidized (to CO₂), generating energy and precursor metabolites necessary for cellular biosynthesis and growth. Thus, due to the relative ease with which ethanol enters the TCA cycle, ethanol is rapidly metabolized by aerobic microorganisms (McKinney and Jeris, 1954). Further, the enzymes necessary for incorporating ethanol into the TCA cycle (i.e. ethanol and acetaldehyde dehydrogenase) are widely distributed among microorganisms.

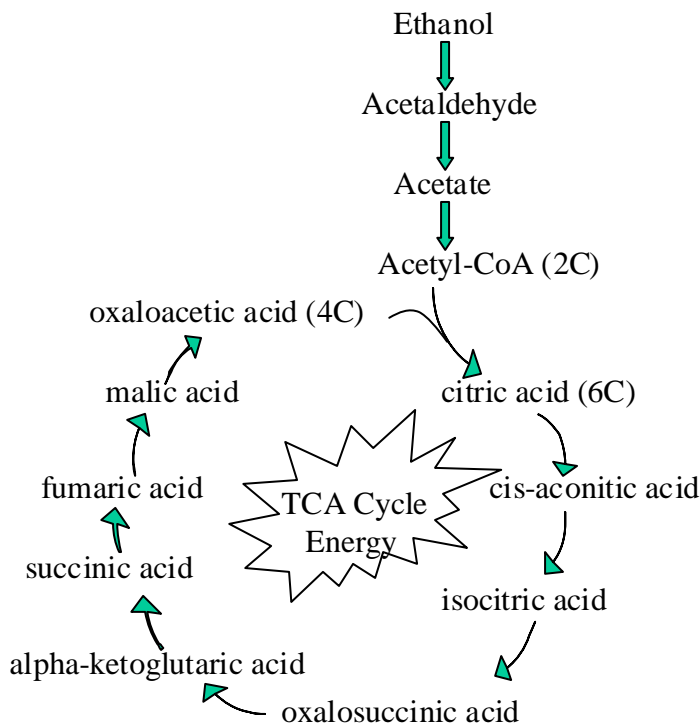


Figure 1: General Pathway of Ethanol Metabolism by Aerobic Microorganisms

The prevalence of aerobic microorganisms capable of degrading ethanol was demonstrated in laboratory screening exercises that identified 363 strains of bacteria capable of growing on 1.5% ethanol (Okumura, 1975). Several of these strains are known soil inhabitants suggesting that these findings have environmental relevance. Ethanol has been shown to rapidly degrade in aerobic sewage sludge (McKinney and Jeris, 1954) and in aerobic subsurface sediments (Corseuil, 1998).

6.2 Ethanol as a Naturally Occurring Intermediate of the Anaerobic Food Chain

While microorganisms are tremendously adept at degrading a wide variety of compounds, anthropogenic materials, including MTBE, are frequently more difficult to biodegrade and in some cases completely recalcitrant. This is not the case for naturally-occurring materials and the products of their decay which microorganisms easily transform. In this regard, ethanol is a naturally-occurring intermediate produced during

the fermentation of organic matter in anoxic environments and is consequently expected to rapidly degrade in essentially all environments with conditions (i.e. temperature, pH, and pressure) that support microbial activity. The exception to this generalization is anaerobic environments that are overloaded with ethanol and thereby produce large amounts of acetic acid and hydrogen which can inhibit ethanol biodegradation. This effect is most likely to occur under methanogenic conditions and is discussed further in this report.

The decay of organic matter in anaerobic environments occurs by microbial consortia that can be viewed as several physiological groups of microorganisms operating at different points in the anaerobic food chain (Figure 2). The first group is composed of fermentative bacteria that degrade polysaccharides, proteins, and lipids with the production of organic acids, alcohols, H₂, and CO₂. Hydrogen gas, a variety of alcohols, and organic acids are in turn utilized in anaerobic respiration with a variety of alternate electron acceptors including manganese oxides, ferric oxides, nitrate, and sulfate. In the absence of alternate electron acceptors, the biodegradation of ethanol and many of the organic acids is catalyzed by syntrophic bacteria to acetic acid and H₂ (McInerney 1981). Methanogenic bacteria catalyze the transformation of H₂ and acetic acid to methane and carbon dioxide. Methanogenic bacteria and microorganisms utilizing alternate electron acceptors (including sulfate-reducing bacteria, nitrate-reducing bacteria, and iron-reducing bacteria) are considered terminal members of the anaerobic food chain because they typically oxidize substrates completely to gaseous endproducts.

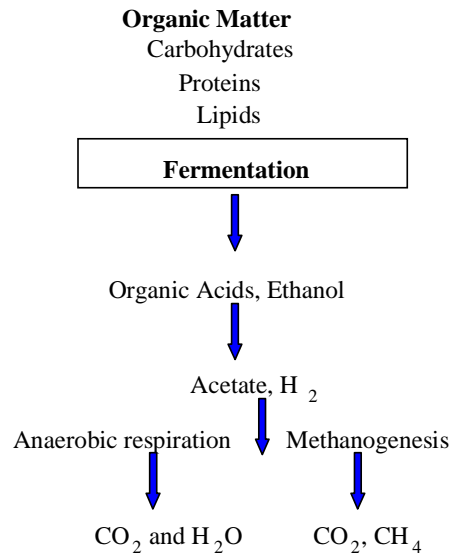


Figure 2: Diagram Showing the Occurrence of Ethanol During the Biodegradation Of Naturally-occurring Organic Matter in the Anaerobic Food Chain

The common occurrence of ethanol in anoxic environments is attributed to the fact that ethanol is produced during the fermentation of a variety of compounds distributed among both aquatic and terrestrial plants. Ethanol is a major product of the fermentation of hemicellulose (Weimer, 1985; Patel et al., 1986), cellulose (Khan and Murray, 1982), pectin (Schink and Zeikus, 1981), and monosacharides (i.e. glucose) (Winter et al., 1987; Schink et al., 1982). Ethanol-producing bacteria have been isolated from soil, sewage sludge, estuarine sediments, decaying grass, and decaying trees.

Ethanol has been detected in lake sediments (Schink et al., 1985), the tissue of living and decaying plants (Jayasekera et al., 1989; Schnik et al., 1981), in sewage sludge (Schink et al., 1985), and is likely present at low concentrations in many other anoxic environments. Interestingly, plants are also known to metabolize ethanol and incorporate the carbon from ethanol into plant tissues (Yasekera et al, 1989).

Despite the importance of ethanol as a fermentation intermediate, it is detected at very low concentrations (uM) in the environment indicating that rapid anaerobic ethanol metabolism occurs, thereby preventing its accumulation in-situ. Indeed, relatively rapid

turnover of ethanol (5.5 to 85 h) has been measured in lake sediments and sewage sludge (Schink et al., 1985).

6.3 Biodegradation of Ethanol Under Iron-and Nitrate-Reducing Conditions

Iron-reducing bacteria have been shown to utilize ethanol as an electron donor (Lovley and Phillips, 1988) and ethanol can biodegrade in aquifer sediments under iron-reducing conditions as shown in Table 3. The biodegradation of ethanol with nitrate serving as an electron acceptor has been shown to occur very rapidly in aquifer sediments (Corseuil et al., 1998). The capacity for very high rates of alcohol biodegradation under nitrate-reducing conditions is utilized in treatment systems for removing ethanol from contaminated water (Hallin and Pell, 1996).

Table 3: Approximate Rates of Anaerobic Ethanol Biodegradation Under Different Electron Accepting Conditions

Electron Accepting Condition	Rate Of Ethanol Degradation (mg/l • d ⁻¹) ^a
Denitrifying	> 100
Iron-reducing	11
Sulfate-reducing	8
Methanogenic	10

^a Estimated from the data of Corseuil et al., 1998. Rates were obtained using 40% sediment slurry incubations. The source of sediment for the denitrifying and iron-reducing experiments was sandy uncontaminated soil. Anaerobic pond sediments were used for the sulfate-reducing and methanogenic incubations.

6.4 Biodegradation of Ethanol Under Sulfate -Reducing Conditions

Ethanol is used as an energy source and growth substrate by several representative genera of sulfate-reducing bacteria (SRB) (Widdel, 1988). The metabolic end product of ethanol metabolism is acetate for some SRB that are not equipped with the biochemical pathway for acetate oxidation. Other species of SRB have the capacity to completely oxidize ethanol. Nevertheless, ethanol oxidation even by cells with the capacity to degrade acetate typically results in the excretion of acetate which may or may not be oxidized at a slow rate (Brysch et al., 1987) by the pure cultures. Acetate is biodegradable by several

species of the “complete oxidizing SRB” (Postgate, 1993) and consequently will not persist indefinitely in anaerobic environments in which sulfate reduction is the primary microbial process. Acetate oxidation by SRB proceeds through the TCA cycle or via a pathway specific to certain species of SRB (Postgate, 1993).

6.5 Biodegradation of Ethanol Under Methanogenic Conditions

The availability of electron acceptors is typically decreased near source zones of hydrocarbon contamination in the subsurface and methanogenic conditions often develop. Because ethanol will likely be rapidly biodegraded and consume large quantities of electron acceptor it is probable that ethanol will reside within the methanogenic zone of contaminated aquifers. Therefore, an understanding of ethanol biodegradation under methanogenic conditions is necessary for predicting the fate of ethanol in contaminated aquifers.

Under methanogenic conditions, the degradation of ethanol and a variety of fatty acids is dependent on the cooperative activity of multiple physiological groups of bacteria (Bryant, 1979). The initial step of ethanol biodegradation under methanogenic conditions is the conversion of ethanol to acetic acid and hydrogen: $\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+ + 2 \text{H}_2$. This reaction is thermodynamically unfavorable under high concentrations of H_2 and consequently is dependent on the consumption of hydrogen by a second group of anaerobic microorganisms (Seitz, 1990) including methanogens in environments depleted of electron acceptors. The dependence for hydrogen removal by methanogens during ethanol metabolism has been demonstrated in pure culture studies (Bryant et al., 1977; Seitz 1988). Similarly, the accumulation of hydrogen can prevent the metabolism of acetic acid (McInerney and Bryant, 1981). Since ethanol oxidation is more energetically favorable than acetate oxidation and will consequently degrade under higher hydrogen concentrations than will acetate, ethanol biodegradation can result in the accumulation of acetic acid (Lee, 1988). Ethanol is generally biodegraded at a faster rate than acetate in the subsurface, thereby increasing the potential for acetic acid accumulation.

The potential for acetic acid build-up is increased when the supply of fermentable electron donors, including ethanol, is increased. For instance, landfill refuse is prone to acetic acid accumulation due to the seemingly large supply of fermentable materials (Mormile et al., 1996). A drop in pH and/or direct effects of acetic acid can inhibit methanogenesis (Beeman and Suflita, 1990) and other microbial activities. Although field information documenting ethanol metabolism was not located for this report, there is evidence indicating that increasing the supply of ethanol to continuous cultures and to flow-through reactors can result in acetic acid accumulation and inhibition of ethanol biodegradation (Tatton et al., 1989).

Since large quantities of ethanol may enter subsurface aquifers contaminated with ethanol-blended fuels, the accumulation of acetic acid could be a concern. Acetic acid at relatively high concentrations (~ 2000 mg/L) can inhibit the biodegradation of environmentally important compounds including p-toluic acid (Macarie and Guyot, 1992) and benzoic acid (Dolfing and Tiedje, 1988; Warikoo et al., 1996), common metabolic intermediates produced during the anaerobic metabolism of aromatic compounds. Whether acetic acid may serve as a preferential substrate and preclude the biodegradation of BTEX hydrocarbons is not clear. Interestingly, Thomas et. al. (1990) showed that the presence of 64 mg/L acetate (ionized acetic acid) slightly increased the rate of aerobic toluene biodegradation. The potential for acetic acid accumulation and the possibility that acetic acid may impact the biodegradation of ethanol and/or hydrocarbons in aquifers contaminated with ethanol-blended fuels is a concern that merits additional scientific evaluation.

6.6 Conclusions Regarding Ethanol Biodegradation

Due to the ubiquity of microorganisms capable of metabolizing ethanol and the relatively rapid rates of ethanol biodegradation measured under all of the major electron-accepting conditions, ethanol is a short-lived compound in the environment whether occurring as a natural intermediate of anaerobic fermentation or as a potential contaminant.

6.7 Intermediates/products of Ethanol Biodegradation

Due to the diverse metabolic routes by which ethanol can be metabolized, including various fermentations (Wu and Hickey, 1996; Laanbroek et al., 1982; Schink, 1984), there are several intermediates and products of ethanol metabolism (Table 4). Most of these compounds are themselves rapidly biodegraded and do not accumulate to a significant extent and consequently pose little or no toxicological threat. Of these intermediates, acetate is the most likely to accumulate, as discussed above. Acetate, though, is commonly used as a food additive and is a primary ingredient of vinegar and is unlikely to pose a threat to human health.

Table 4: List of Metabolic Intermediates Produced During Ethanol Biodegradation

Metabolic intermediate or product	Mechanism of production	Produced aerobically or anaerobically
Acetic acid	Ethanol fermentation product	Aerobic or Anaerobic
H ₂	Ethanol fermentation product	Anaerobic
CH ₄	Ethanol degradation product	Anaerobic
Proponal	Ethanol fermentation product	Anaerobic
Propionic acid	Ethanol fermentation product	Anaerobic
Butyric acid	Ethanol fermentation	Anaerobic
Acetaldehyde	Ethanol fermentation intermediate	Anaerobic or Aerobic
Isobutyric acid	Ethanol fermentation product	Anaerobic
Glutamic acid	Excretion of central intermediate during growth on ethanol	Aerobic

6.8 Limitations of Ethanol Biodegradation

Since microorganisms capable of degrading ethanol are ubiquitously distributed in the environment, ethanol biodegradation will not be limited by the availability of the requisite microorganisms. Factors that have been shown to limit ethanol metabolism include the availability of certain key inorganic nutrients and toxicity effects elicited by high ethanol concentrations.

A large base of information on the toxicity of alcohols to microorganisms is available through research identifying the mechanism of action of alcohols used as disinfectants

and ways to increase the production of ethanol in the fermentation industry. Detailed information on the mechanisms of ethanol toxicity to prokaryotic and eukaryotic microorganisms is available in two thorough reviews (Ingram and Buttke, 1984 and Ingram, 1990). Generally, the toxicity of alcohols increases with increasing hydrophobicity of the alcohol. Therefore, short-chain alcohols (including ethanol) are less toxic than the more hydrophobic longer-chain alcohols. However, ethanol is freely permeable across the cell membrane and partitions within the cytoplasm and the inner hydrophobic core of the membrane. This distribution of ethanol increases the ability of the membrane core to accommodate charged or polar molecules, thereby increasing membrane leakage to small charged molecules such as magnesium. Ethanol-induced leakage of ions is the primary mechanism of ethanol toxicity to microorganisms (Ingram, 1990).

In general, only high concentrations of ethanol are toxic to prokaryotic microorganisms but bacteria vary considerably in their resistance. Enteric bacteria are sensitive to ethanol concentrations above 6% but others are much more resistant. For instance, various species of *Lactobacilli* are very tolerant, capable of growing in the presence of 18% ethanol (Ingram, 1990). This degree of tolerance is unusual as most bacterial growth is inhibited in a dose-dependent manner in the presence of ethanol at concentrations between 1% and 10% (Ingram and Buttke, 1984). Relatively high ethanol concentrations (up to 1%) did not inhibit aerobic ethanol biodegradation in sewage sludge (Gerike and Gode, 1990). The aerobic biodegradation of 1% to 10% ethanol has been reported to occur in sandy aquifer sediments, but ethanol biodegradation in these samples was completely inhibited in the presence of 40% ethanol (Hunt and Alvarez, 1997). The anaerobic biodegradation of 0.5 % ethanol has also been reported (Hunt and Alvarez, 1998). Thus, given the capacity of both aerobic and anaerobic microorganisms to metabolize ethanol at high concentrations and the fact that ethanol will be diluted rapidly only a short distance from a gasoline spill, it is not likely that ethanol toxicity will limit ethanol biodegradation in gasoline impacted aquifers. However, it is possible that the effects of ethanol-hydrocarbon mixtures on microbial toxicity may be unique relative to the impact of ethanol or hydrocarbons alone. This possibility is plausible because ethanol

is known to affect the transport of compounds across the cell membrane and therefore could impact the availability of other contaminant molecules to the inside of bacterial cells.

During studies with the bacterium *Acinetobacter calcoaceticus* growing on ethanol, it was noted that the depletion of magnesium and sulfate ions from the medium resulted in the accumulation of acetaldehyde and acetate. Acetaldehyde at concentrations greater than 0.001% inhibited ethanol metabolism. Magnesium and sulfate are constituents of acetyl coenzyme A, an enzyme necessary for incorporating acetate into biosynthetic pathways. Consequently, the depletion of these ions may prevent acetate and acetaldehyde metabolism. Increasing the magnesium and sulfate concentrations in culture media has been shown to increase microbial growth on ethanol (Okmura, 1975). While the environmental relevancy of these findings is not known, these results indicate that nutrient limitations could potentially impact ethanol biodegradation. However, inorganic nutrients that are needed only in trace amounts such as magnesium generally are not limiting in subsurface environments where groundwater flow replenishes dissolved nutrients.

7.0 Transport and Fate of Ethanol-Blended Gasoline in Groundwater

7.1 Role of Biodegradation in the Natural Attenuation of Hydrocarbons in Contaminated Aquifers

It is well documented that the biodegradation of hydrocarbons by indigenous subsurface bacteria is the primary mechanism for the natural attenuation of fuel spills in aquifers (Salanitro et al., 1997; Davis, et al, 1993; refer to Figure 3). Aerobic microorganisms have the physiological capacity to oxidize the majority of hydrocarbons including BTEX, which are of increased concern due to their high aqueous solubility and toxicity. Aerobic degradation does play an important role in the removal of BTEX from groundwater naturally (Salanitro, 1993), but the available oxygen reserves are usually rapidly depleted once a site is contaminated with gasoline hydrocarbons. Biodegradation in the resulting anaerobic environments is dependent on the availability of alternate electron acceptors including solid-phase manganese and ferric oxides along with soluble electron acceptors

including nitrate and sulfate. In subsurface aquifers contaminated with petroleum products or landfill leachate, the availability of electron acceptors decreases with distances towards the source of contamination. This results in the zonation of terminal electron accepting processes (Baedecker, et al., 1993; Lyngkilde et al., 1992). Oxygen is generally more available near the leading fringe (farthest from source) of a hydrocarbon plume where the more soluble hydrocarbons (ie. BTEX) are the dominant contaminants. Oxygen quickly becomes depleted moving towards the source area where anaerobic respiratory processes supported by nitrate, ferric iron, and sulfate, are dominant. Methanogenesis is most important adjacent to the source area where electron acceptors are exhausted due to the increased contaminant load and the increased time in which the source areas have been contaminated.

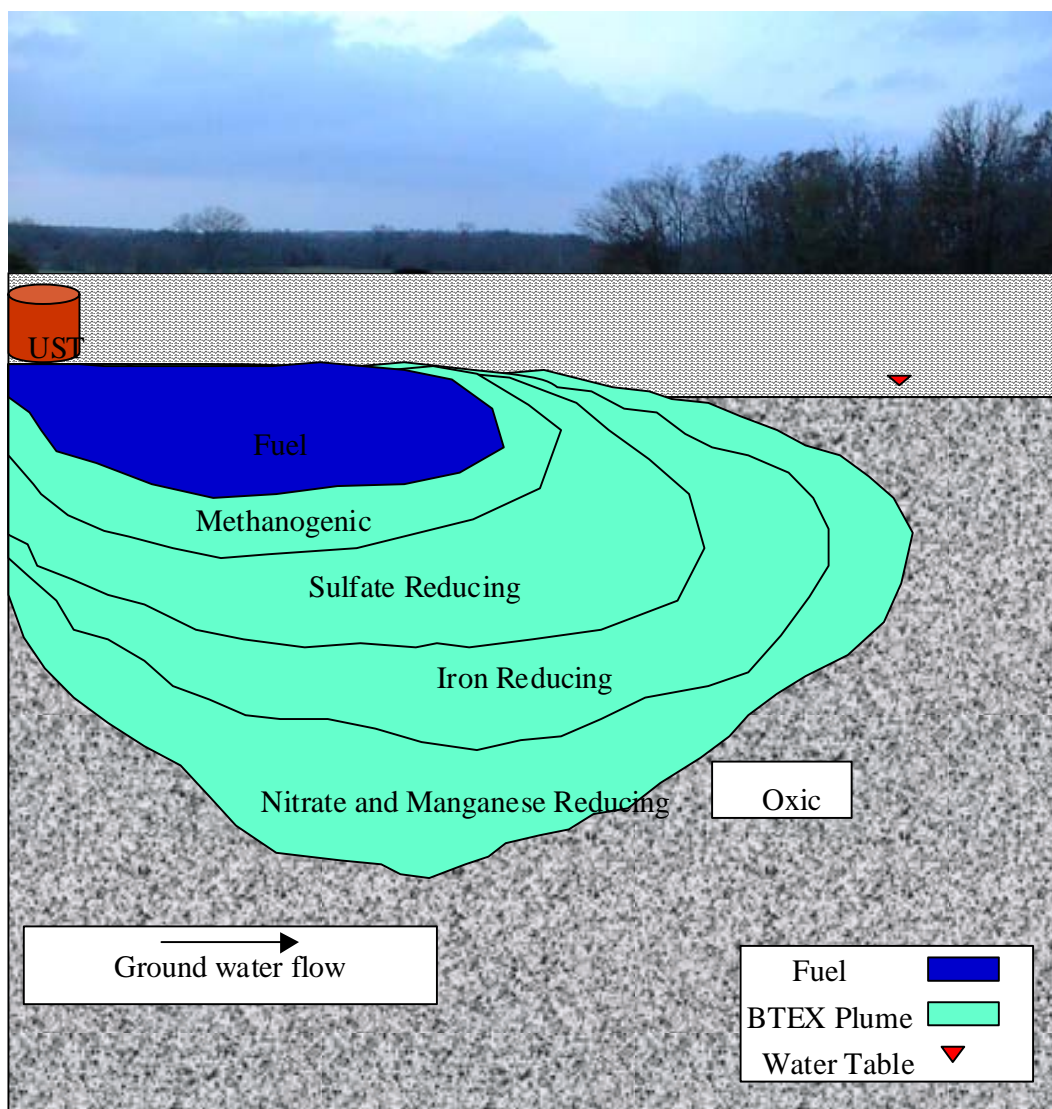


Figure 3: Diagram of the Orientation of the Electron-accepting Reactions in Groundwater Contaminated with Gasoline Hydrocarbons from a Leaking Underground Storage Tank (UST)

Despite traditional views, anaerobic microorganisms have the capacity to oxidize a wide range of petroleum hydrocarbons including BTEX (Krumholz et al., 1996 and references therein), alkanes (Reuter et al., 1994; Caldwell et al., 1998), and polycyclic aromatic hydrocarbons (Coates et al., 1996). The contribution of anaerobic processes towards the degradation of hydrocarbons in contaminated aquifers is well documented (Barbaro, J.R. et al., 1992; Chapelle et al., 1995; Schmitt et al., 1996; Lovley, 1997; Gieg et al., 1999).

Thus, it is primarily through the activity of both aerobic and anaerobic microorganisms that hydrocarbon plumes eventually stabilize and eventually shrink in size. It is therefore important to consider the influence that ethanol may have on the biodegradation of hydrocarbons.

7.2 Influence of Ethanol on Aerobic and Anaerobic BTEX Biodegradation

Because ethanol does not affect the abiotic factors that govern the transport of monoaromatic hydrocarbons, the mechanism by which ethanol is most likely to impact the length and persistence of BTEX plumes is its potential impact on biodegradation. Limited information regarding the effects of ethanol on the biodegradation of hydrocarbons is available. The majority of such research has been conducted in Brazil where 85 % of the cars run on gasoline containing 22% ethanol. Experiments conducted using slurries of sediment with no previous exposure to gasoline hydrocarbons revealed both inhibitory and stimulatory effects on BTEX biodegradation, depending on the electron accepting conditions tested. Under aerobic conditions, BTEX was not degraded until ethanol was biodegraded to low levels, apparently due to the preferential utilization of ethanol (Corseuil et al, 1997) (Hunt et al., 1997). However, additional studies demonstrated that *Pseudomonas putida*, a well studied aerobic hydrocarbon-degrading microorganism, degraded benzene, toluene, and ethanol simultaneously under aerobic conditions (Hunt et al., 1997). This finding demonstrates that additional research is needed before the effects of ethanol on aerobic BTEX biodegradation can be fully understood. Nevertheless, because large quantities of ethanol are released from spills of ethanol-blended gasoline, ethanol may deplete the available oxygen thereby limiting the aerobic biodegradation of BTEX. Since anoxic conditions will likely prevail in aquifers impacted with ethanol, the impact of ethanol on anaerobic BTEX biodegradation deserves consideration.

The effect of ethanol on the anaerobic biodegradation of toluene, which was the only BTEX hydrocarbon found to degrade anaerobically in the experiments of Corseuil et al (1997), depended on the electron-accepting conditions. Ethanol did not affect the rate or extent of toluene biodegradation under nitrate-reducing conditions provided that ethanol

biodegradation did not deplete the available nitrate. The presence of ethanol decreased toluene biodegradation in iron-reducing and methanogenic incubations but stimulated toluene biodegradation under sulfate-reducing conditions. Again, the inhibitory effect was attributed to the preferential utilization of ethanol.

Due to limited laboratory testing and the absence of field evidence, general conclusions can not yet be made regarding the effect of ethanol on BTEX biodegradation in subsurface environments contaminated with ethanol-blended fuels. The laboratory-based information obtained thus far suggests that ethanol may in some instances prevent BTEX biodegradation. However, the consequences of such an effect, should it be realized in-situ, is dependent on the length and duration of the ethanol plume emanating from a gasoline source (hence the purpose of the transport modeling presented later in this report). Although field studies documenting ethanol biodegradation were not found, the fate of methanol and MTBE in the subsurface has been evaluated (Barker et al., 1990) due to the environmental concerns associated with the release of MTBE and methanol-blended gasoline into subsurface aquifers. In these studies, the effect of MTBE and methanol on the migration of BTEX hydrocarbons through a shallow aerobic aquifer was determined. Three aqueous solutions, one containing only BTEX hydrocarbons, the second BTEX plus methanol at a concentration of 7000 mg/L, and the third BTEX plus 289 mg/L MTBE, were injected into the aquifer and allowed to migrate with the natural groundwater flow. Both MTBE and methanol migrated at the same rate as the conservative tracer indicating that these compounds migrated at the rate of groundwater flow. Neither compound had a discernible effect on the rate of migration of the BTEX, but methanol decreased the disappearance of benzene and m-xylene (by ~30%) relative to the benzene and m-xylene plumes that did not contain a gasoline oxygenate or contain MTBE. This effect was not observed for MTBE, which was found to be recalcitrant during the field tests. The increased persistence of BTEX in the methanol plume was not specifically evaluated but was speculated to be attributed to the removal of oxygen during methanol biodegradation. Because of the low solubility of oxygen in water (~12 mg/L), Barker (1990) calculated that only a small amount of the injected methanol at a concentration of 7000 mg/L would consume all the available dissolved oxygen in and

along the flow path of the aquifer thereby inhibiting aerobic biodegradation of BTEX. Because methanol and ethanol have similar chemical structures, aqueous solubility, partitioning characteristics, and susceptibility to biodegradation, the impact of methanol on the migration and biodegradation of BTEX in aquifers is likely to be similar to that of ethanol.

The greatest impact would occur if BTEX biodegradation were completely inhibited in the presence of ethanol either due to preferential biodegradation or the exhaustion of available electron acceptors during ethanol metabolism. In either case, the extent to which ethanol would extend the size of a BTEX plume is dependent on how far and for what period of time the ethanol and BTEX plumes are in contact.

Based on the relatively short time required for ethanol to completely leach from pools of nonaqueous gasoline (Poulsen et al., 1992) relative to hydrocarbons and on the rapid rates of ethanol biodegradation, it is not likely that ethanol will persist in gasoline-contaminated groundwaters for a significant time relative to BTEX which are biodegraded at much lower rates. During the field injection experiments discussed above, methanol was completely removed from the groundwater within 470 days. Similar rates of methanol biodegradation have been observed in subsurface sediments at concentrations up to 1000 mg/L at rates sufficient to remove this concentration in less than one year (Novak et al., 1985). Since the biodegradability and transport behavior of ethanol are similar to methanol (suggesting similar residence times in subsurface aquifers), it is anticipated that the effects of ethanol due to direct contact with BTEX will be short-lived.

7.3 Modeling the Migration of Ethanol and Benzene in Subsurface Aquifers Contaminated with Ethanol-Blended Gasoline

Since ethanol is rapidly metabolized, it is unlikely that ethanol will travel a substantial distance once spilled into the subsurface or persist in subsurface and surface waters. Therefore, ethanol likely poses little threat to contaminating drinking water wells or

surface water receptors. However, the potential for ethanol to decrease the biodegradation of BTEX hydrocarbons either by serving as a preferred substrate, by depleting available electron acceptors, or through the release of acetic acid during ethanol metabolism, merits additional consideration. Thus, we have performed a series of fate and transport modeling exercises to predict the consequences of ethanol on the biodegradation and transport of benzene through aquifers contaminated with ethanol-blended gasoline. Benzene was selected as the model compound because it poses an increased risk due to its relatively high toxicity (Hartley, 1992), resistance to biodegradation, and relatively high water solubility.

7.4 Preliminary Modeling

Preliminary modeling exercises were used to identify the trends and differences in the transport behavior of benzene and methanol through two aquifers each with distinctly different sediment characteristics and hydrology. Methanol was used in the preliminary modeling due to the availability of methanol's chemical parameters in the model's database. However, as described above, methanol and ethanol are expected to transport through the subsurface to a similar extent. The Borden aquifer was selected as an example of a highly permeable sandy aquifer in which the migration of water soluble contaminants is increased due to increased flow and decreased sorption of the contaminant onto sands relative to clay and organic matter-rich sediments. In contrast, the Xerox aquifer is a local study site that was selected on the basis of its low permeability and high content of organic matter which decrease the rate of contaminant transport.

We modeled the transport of both a continuous supply of these compounds, which is indicative of a leaking underground storage tank (LUST) and an instantaneous (pulse) release into groundwater. The amount of benzene and methanol released in the model was 25 kg per year each for the continuous release and 500 kg each for the pulse release. The organic carbon content of the Borden and Xerox sediments is 0.015 and 0.9% respectively. The biodegradation rate constants used were 0.003 (1/d) for benzene and 0.3 (1/d) for methanol. As described later in the report, these values are within the range

of rates reported in the literature. The migration of benzene and methanol was evaluated with and without a biodegradation rate constant in an effort to discern the effects of abiotic and biological attenuation mechanisms. The printouts of the results of the preliminary modeling are presented in an appendix.

7.5 Results of the Preliminary Modeling

The modeling of the Xerox site indicated that the methanol plume traveled 20 m and the benzene plume traveled 79 m, with biodegradation rate constant included in the model input. When biodegradation was not included in the model, chromatographic separation of the benzene and methanol plumes occurred at approximately 35 m at which point the methanol plume advanced ahead of the benzene plume. This separation occurred due to the sorption of benzene to the sediments thereby decreasing benzene migration relative to methanol. This suggests that benzene and methanol plumes originating from an instantaneous release will migrate separately provided that significant quantities of organic matter exist in the aquifer and if methanol is not biodegraded. Therefore, even in the unlikely event that ethanol biodegradation does not occur, ethanol would only travel with the benzene plume for 35 m in an instantaneous release potentially limiting the impact of methanol (i.e. ethanol) on benzene biodegradation. With the biodegradation term included in the model, methanol would increase the benzene plume length by approximately 25 %, assuming that benzene does not biodegrade in the presence of methanol.

The methanol plume in the Borden aquifer traveled roughly the same distance as it did within the Xerox aquifer. The rate of methanol transport in the model when biodegradation was included, compares very well with the experimental results of Barker et al., (1990) showing the actual rate of methanol movement through the Borden aquifer. The benzene plume traveled substantially farther relative to the benzene plume in the Xerox aquifer. Thus, the impact of methanol or ethanol on the biodegradation of benzene would be decreased in the Borden aquifer assuming that the mechanism of ethanol's influence on benzene biodegradation was preferential biodegradation.

7.6 Tentative Modeling Conclusion

The presence of methanol or ethanol in a gasoline spill will increase the migration of benzene by no more than 25%. Previous modeling exercises predicted a similar increase in the length of benzene plumes due to the presence of ethanol (Malcom Pirnie, 1998)

7.7 Three-Dimensional Modeling

While the preliminary modeling provided important information regarding the transport of benzene and ethanol, a more powerful model was necessary to simulate the migration of contaminant plumes in the subsurface. Modflow/MT3D was therefore used to model the transport and fate of ethanol-blended gasoline from a LUST.

7.8 Model Input

The modeling provided in this section is intended to help determine the effect ethanol has on the migration of a gasoline plume. Based on laboratory studies, it appears that BTEX biodegradation may be inhibited in the presence of ethanol. It is therefore important to estimate the size of an ethanol plume originating from a subsurface source of gasoline amended with ethanol. Once the ethanol plume has been characterized, the impact it has on a gasoline plume can be quantified by modeling a gasoline spill with no ethanol present and comparing it to a gasoline spill amended with ethanol. For modeling purposes, it is assumed that no degradation of BTEX compounds will occur in the presence of ethanol. MODFLOW/MT3D will allow only one contaminant to be modeled at a time, so benzene was selected to represent gasoline since it is considered to be the most hazardous of the BTEX compounds. It will also be necessary to make several modeling runs to simulate a multi-component plume.

It should be pointed out that this model is intended to provide preliminary fate and transport trends. It assumes horizontal layering and does not account for horizontal anisotropy concerning conductivity or variations in thickness. The model also assumes that the biodegradation rate is constant throughout the year and is not affected by variations in temperature or other environmental parameters. The Borden site was selected because extensive natural gradient tracer tests have been performed in the

aquifer allowing us to compare modeling results with actual measurements of contaminant transport in-situ.

7.8.1 Model Grid

The MODFLOW model is set up using a 2000 ft x 2000 ft area divided into 100 ft² grids. Since the model uses the grid size as a step size when calculating solutions, the 100 ft² grids are refined to 10 ft² in the area around the simulated LUST. The 10 ft² grids are further refined to 3 ft² where concentrations will be in the most transient state. The model grid is shown below in Figure 4. Past experience with grid size analysis has shown that minimal benefit in sensitivity is gained by further grid resolution. An injection well with 5 ft of screen is used as a point source to represent the LUST. The location of this well is indicated on Figure 4 and a magnified view of the well and immediate areas are shown in Figure 5. Horizontal and vertical scales are given in [ft].

7.8.2 Constant Heads

To simulate the general groundwater flow at the Borden site, constant head boundaries have been assigned to the model ground water aquifer. According to previous site investigations, ground water flow was determined to be in a northeasterly direction with a gradient of 0.0043 ft/ft. To match the natural gradient, the water table was initially set at -7 feet below ground surface (bgs) and constant head boundaries were assigned to the southwestern corner (-1 ft) and the northeastern corner (-13 ft) of the model boundary. This gives the model an overall gradient of 0.0043 ft/ft from the southwest to the northeast. Prior to each plume simulation the model was run for 2000 days so the constant head boundaries would have sufficient time to reach equilibrium with the initially assigned water table. This allows the model to simulate natural groundwater gradient conditions before plumes are introduced. The water table at equilibrium (2000 days) is shown in Figure 6.

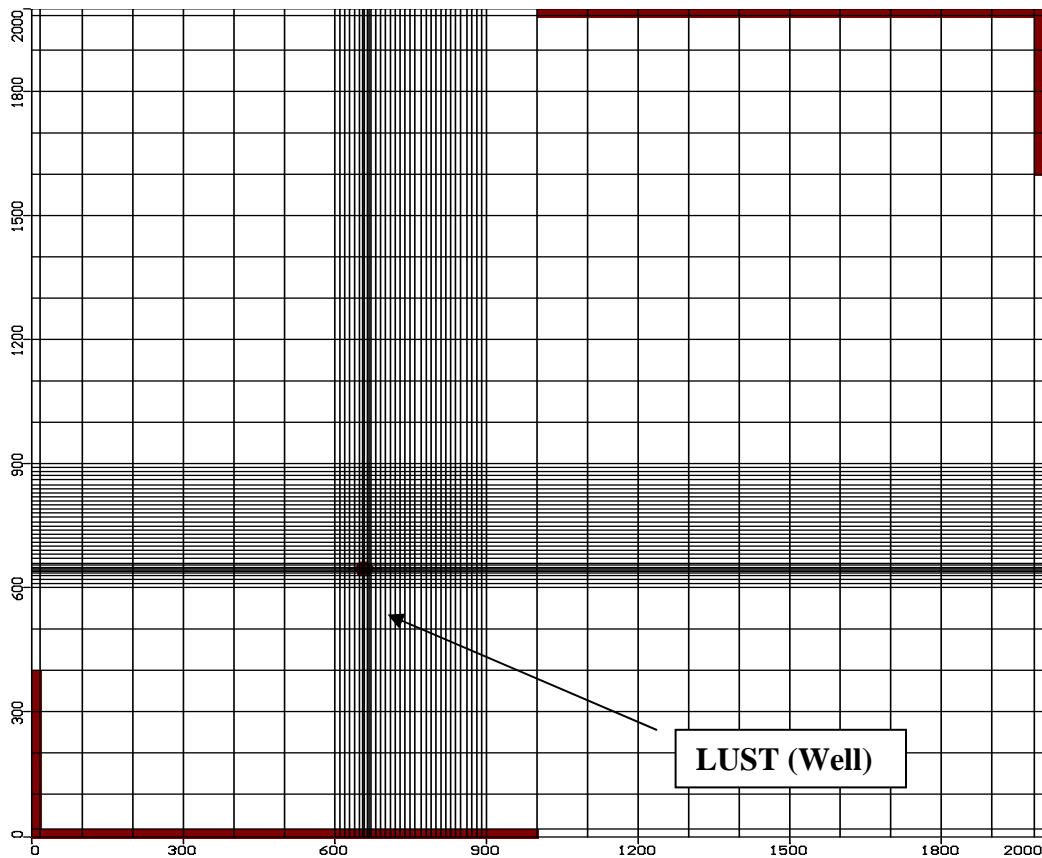


Figure 4: Plan View of Model Grid (Units given in feet)

7.8.3 Hydraulic Conductivity

Hydraulic conductivity is one of the most crucial parameters in groundwater flow and assigning an accurate hydraulic conductivity is very important in setting up the model. Hydraulic conductivity is proportionality constant that is used in Darcy’s law (used for determining velocity of a fluid through a media) and has units of length/time. Hydraulic conductivity is higher for sandy soils than for clays. For the Borden site, reliable data is readily available due to the extensive amount of research performed at the site. A conductivity of 20 ft/day was assigned (McKay et. al.,1994). The geology at the site is relatively simple; it consists of a sandy layer that extends from the ground surface to –36 feet below ground surface (bgs) with a consolidating clay layer below –36 bgs. Figure 7 shows the final cross section used in the model along with the conductivities assigned.

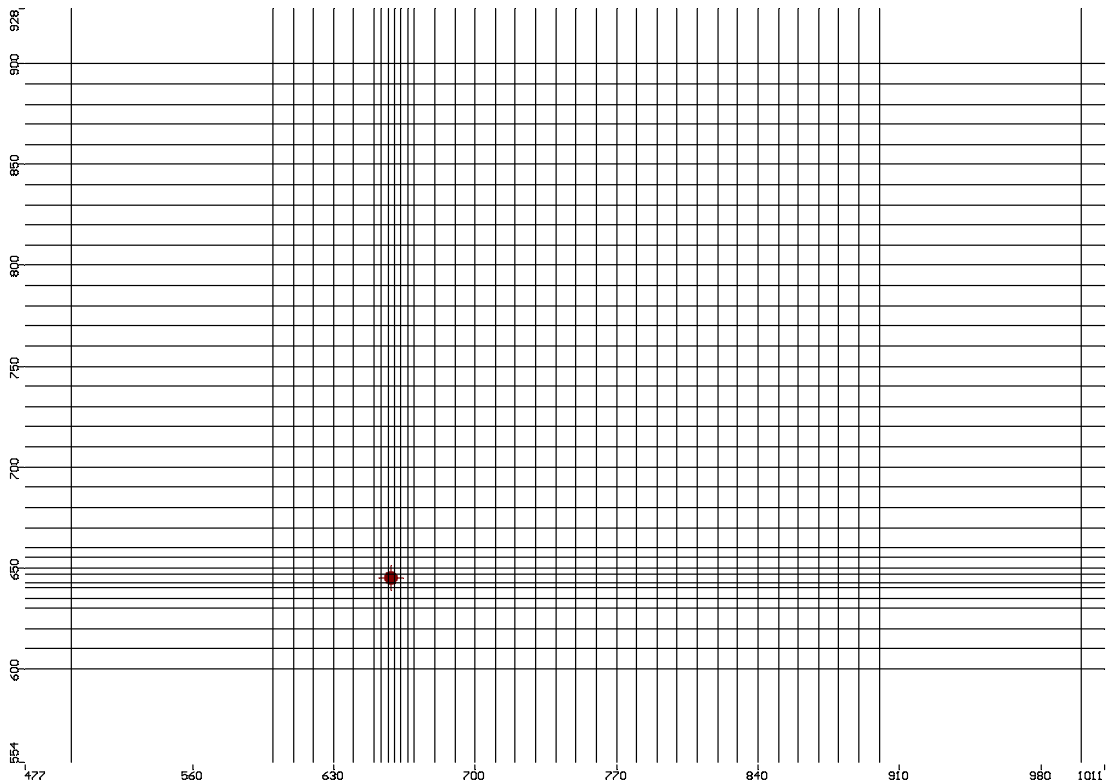


Figure 5: Magnified View of the Model Grid (Units given in feet)

7.8.4 Porosity

Porosity of a groundwater aquifer is defined as the volume of void space divided by the total volume of media. It is the space in an aquifer in which fluid can flow. Porosity is typically presented as a percent or decimal and may be as high as 70% for clay or as low as 25% for sand or gravel. Previous model sensitivity analysis has shown that small changes to porosity (i.e. 5-10%) have minimal impact on solute fate and transport results. Laboratory porosity measurements have been made for the sandy layer at the Borden site and reported as 33% (McKay et. al., 1994). This value is used in the model. No porosity measurements have been made for the confining clay layer, so a common value for this type of soil is used. The confining layer is assigned a porosity value of 50% (Freeze and Cherry, 1979).

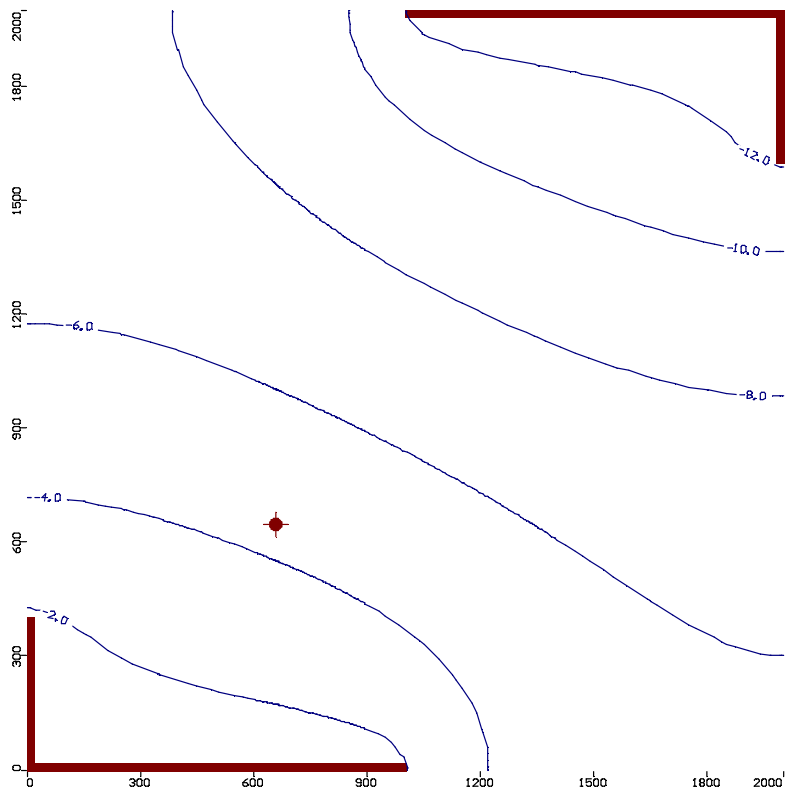


Figure 6: Water Table Contours at Equilibrium (2000 days)

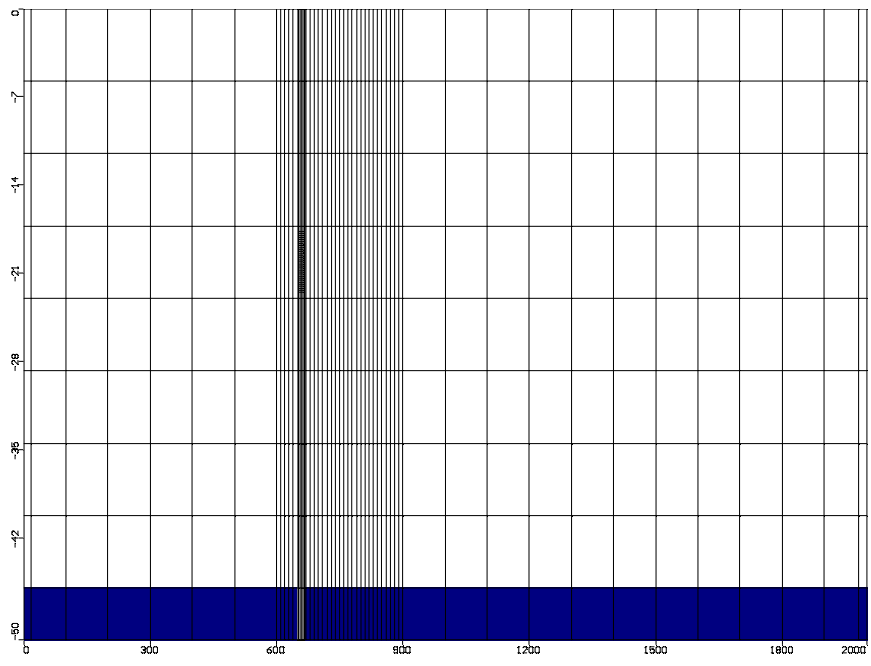


Figure 7: Model Cross Section

7.8.5 Specific Yield

Specific yield relates to an unconfined aquifer and is the volume of water that is released from a unit area of aquifer for every unit drop in the water table. No specific yield data was available for the site, so a common value for a related sediment of 0.25 was used.

7.8.6 Dispersion

Dispersion is the process of mixing and spreading of a solute as it flows through a groundwater aquifer. Dispersion acts to lengthen, widen, and dilute a contaminant plume as it travels with the groundwater. It is primarily due to the tortuous paths created by the porous medium and the mixing that occurs as groundwater flows through it. A longitudinal dispersion coefficient of 0.3 ft is used in the model. This value is based on the assumption of a Peclet (Pe) number of 85 and a travel distance of 25 ft ($L/Pe = D$). Higher Peclet numbers represent soil types in which advection is dominant and diffusion limited; numbers usually range from below 10 (high dispersion or tighter soils) to over 100 (low diffusion or coarser soils).

7.8.7 Sorption

Since the primary goal of this analysis is to simulate fate through the subsurface, the transport model has to account for sorption of the contaminants on this porous media. Sorption of the chemicals on the soil has been determined for this site through laboratory analysis or theoretical results. For modeling purposes a linear isotherm has been utilized. Sorption parameters for the various contaminants modeled are listed in Table 1. Due to the low organic carbon content of the soils in the Borden aquifer, sorption plays a minimal role in attenuating the benzene plume. Ethanol does not adsorb.

Table 5: Chemical Parameters and Biodegradation Rate Constants Used in the Model

Parameter Input for Groundwater Model (Borden Aquifer Modeling)	Value	Methodology	Reference
Soluble benzene conc. near source	10 mg L ⁻¹	Field measurement	Salinitro, 1993;1997
Soluble ethanol conc. near source	10,000 mg L ⁻¹	Theoretical	
Anaerobic benzene biodegradation rate constant	0.002 (d ⁻¹)	Field and Laboratory	Chapelle, 1995
Ethanol biodegradation rate constant	0.045 (d ⁻¹)	Laboratory	Momille, 1994
Acetic acid accumulation rate constant	0.045 (d ⁻¹)	Laboratory	
Acetic acid degradation rate constant	0.0014 (d ⁻¹)	Laboratory	Beeman, 1987
Hydrodynamic dispersion			
Groundwater flow velocity	0.09 m d ⁻¹	Field measurement	Barker, 1990
Groundwater flow direction	N 40 E to N 53E	Field measurement	Barker, 1990
Average hydraulic conductivity	7.2 x 10 ⁻⁵ m s ⁻¹	Laboratory	McKay et. al., 1994
Hydraulic gradient	0.0043	Field measurement	McKay et. al., 1994
Depth to water table	1 m (below surface)	Field measurement	McKay et. al., 1994
Depth to consolidating clay layer	11 m (below surface)	Field measurement	McKay et. al., 1994
Organic carbon content	0.015%	Laboratory	Ball, 1991
Benzene sorption constant	1.0	Theoretical	Davis, 1993
Acetic acid sorption	0	Theoretical	Sutton, 1985
Ethanol sorption	0	Theoretical	
bulk density	1.81 g cm ⁻¹	Laboratory	Mackay, 1994
porosity	0.33	Laboratory	Mackay, 1994

Sediment description: sandy with negligible clay. Clean, well-sorted, fine to medium grained sand (Mackay, 1994). Grain size distribution: 0.42-0.075 mm with the average being ~ 0.18.

7.8.8 Biodegradation

Because oxygen is typically depleted in a large portion of gasoline contaminated aquifers, anaerobic rather than aerobic biodegradation rate constants for ethanol, acetic acid, and benzene were used in the model. However, oxygen is potentially available to stimulate biodegradation rates (especially benzene) near the leading fringe of the contaminate plume and during the influx of oxygenated rainwater. It has been shown that even low amounts of oxygen can support relatively high rates of benzene biodegradation (Salinitro, 1993). Therefore the biodegradation rate constants used in the model are considered to

be conservative. The benzene decay constant was obtained from Chapelle et al. (1996) because both laboratory and field measurements were utilized to estimate the in-situ rate of benzene biodegradation in an anaerobic aquifer. The benzene decay constant used was 0.002 d^{-1} , a value that lies within the range of benzene biodegradation rates summarized in Krumholz et al.(1996). The ethanol and acetic biodegradation rate constants were derived from the data of Beeman et al. (1989) and Mormile et al. (1994), respectively. Both of these estimates were obtained from laboratory biodegradation experiments performed with sediment slurries using aquifer material from an anaerobic leachate-impacted aquifer. Because the rates were obtained with material from the same aquifer, it was assumed that the decreased rate of acetate biodegradation relative to ethanol reflected differences in the biodegradability of these two compounds. Seasonal and regional differences in temperature and other environmental parameters which are known to impact biodegradation rates were not taken into account. It was also assumed that the rate constants used in the model are representative of the rates of biodegradation in other aquifers.

7.8.9 Model Runs

Each model run began by allowing the constant head boundaries to reach equilibrium with the water table for 2000 days (Figure 6). The different chemicals that were modeled were continuously injected into the well at 0.5 g d^{-1} through a 5 ft screen. It is assumed that this leakage rate is representative of a LUST. The concentrations of ethanol and benzene in the injected fluid were set at 10,000 mg/L and 10 mg/L respectively. These concentrations are slightly higher than the concentrations expected in a spill as describe above and therefore represent a “worst case scenario”. The model was run for 10 years after the initial 2000 days. We found that this was sufficient time for the plume to reach equilibrium and for the migration of the plume to cease. Since MODFLOW/MT3D will allow only one chemical to be run at a time, several runs are required.

7.8.9.1 Borden Site – Benzene with no Ethanol

The first model run is benzene with no ethanol added to act as a baseline of comparison for the rest of the runs. The result from this run after 10 years is shown in Figure 8. The

benzene degradation constant used in the model is 0.002 1/day. This constant was determined using field and laboratory methods at an anaerobic aquifer contaminated with BTEX (Chapelle, 1995). The benzene plume migrated about 200 ft (60 m) from the point of injection to the edge of the plume. This value does not consider the fact that ethanol-blended fuels contain less BTEX in proportion to the volume fraction of gasoline.

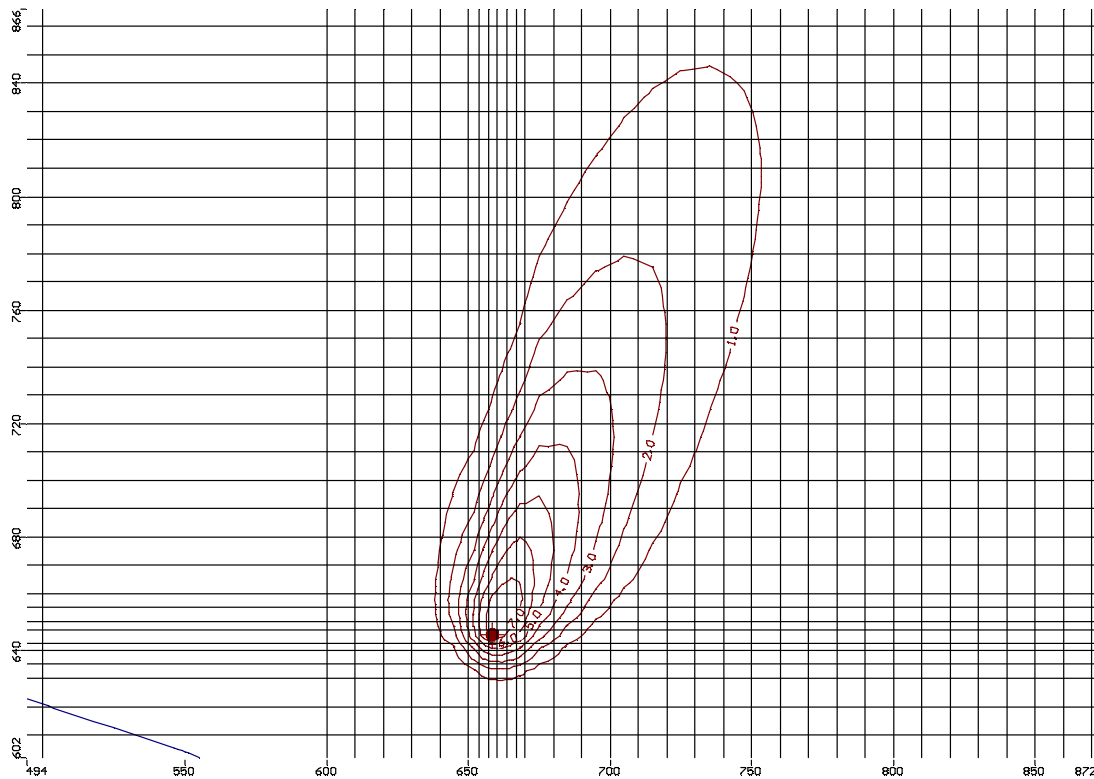


Figure 8: Benzene Plume After 10 Years With No Ethanol Present, the Plume Migrated Approximately 200 ft

7.8.9.2 Borden Site - Ethanol

The next run is ethanol by itself to determine the plume size. The degradation constant used for the ethanol is 0.045 1/day (Momile, 1994) injected at the same 0.5 g d⁻¹ and a concentration of 10,000 mg/l (Salinitro, 1993; 1997). Ethanol is much more soluble than benzene and the ethanol degradation rate is more than an order of magnitude greater. The result from the run is shown in Figure 9. The plume migrated about 30 ft (9 m) from the source and was quickly degraded.

As a sensitivity test, ethanol was also modeled with degradation rates of 0.0045 1/day and 0 1/day. The results of these runs are shown in Figures 10 and 11, respectively. The ethanol plume with the degradation constant of 0.0045 1/day migrated about 115 ft (35 m). The plume with no degradation migrated about 650 ft. With no degradation the plume is subject to dispersion, sorption and diffusion so the plume dilutes but none of the injected mass is removed.

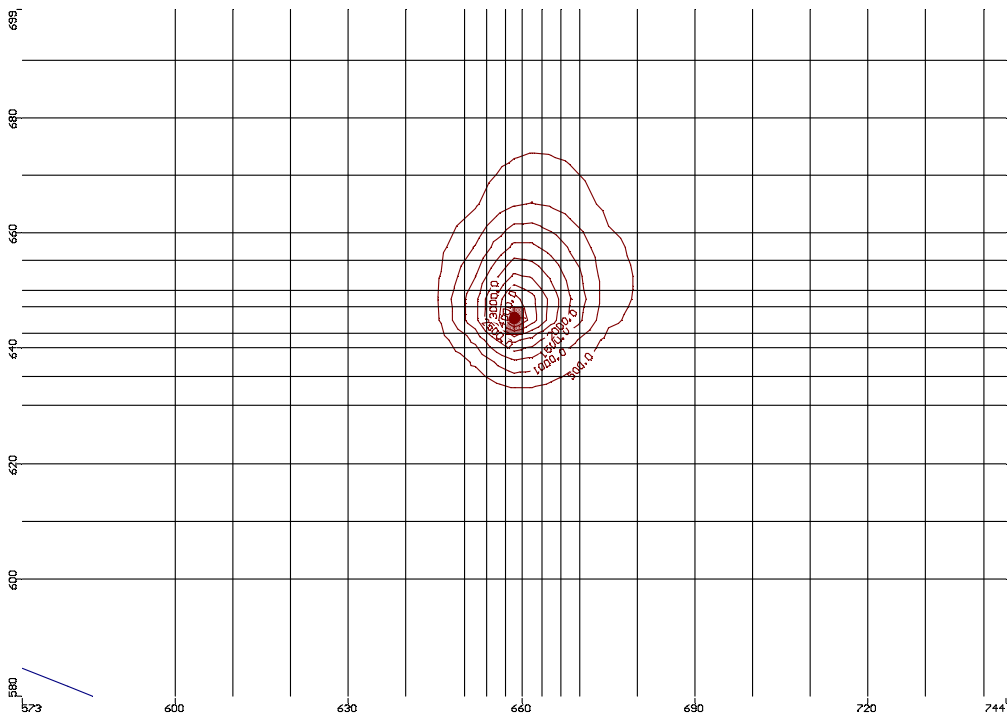


Figure 9: Ethanol Plume After 10 Years (0.045 1/day)

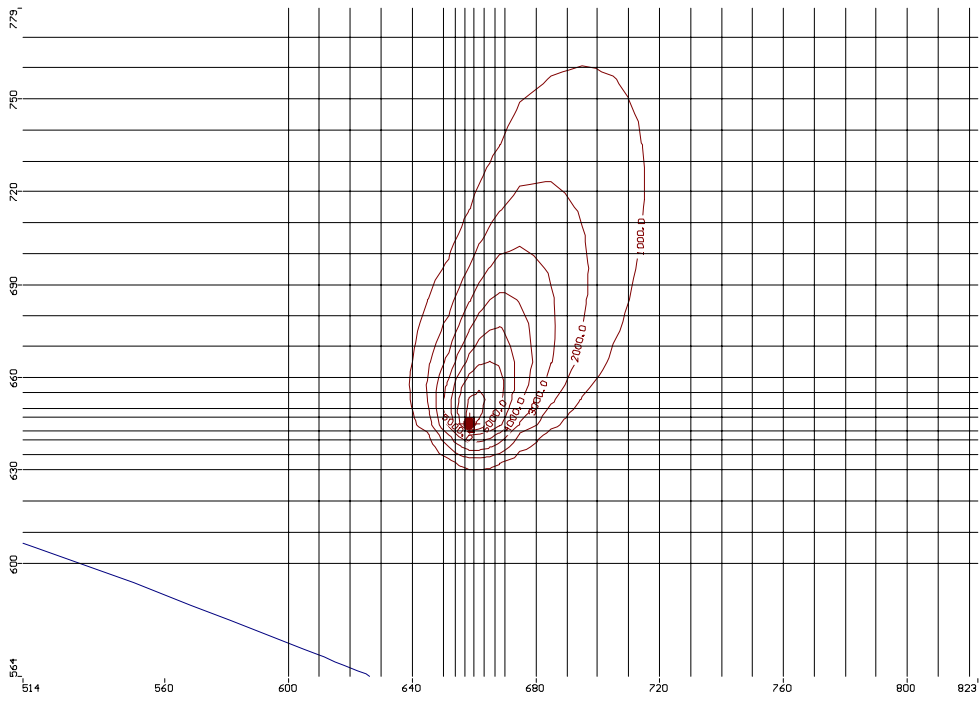


Figure 10: Ethanol Plume After 10 Years (0.0045 1/day)

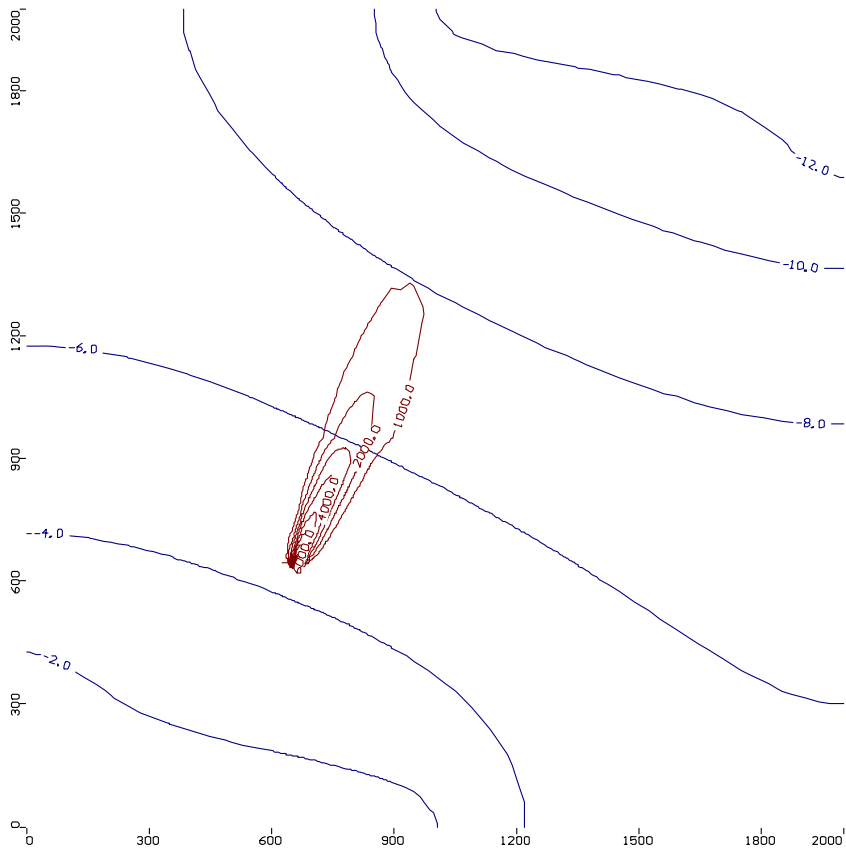


Figure 11: Ethanol Plume After 10 Years (no degradation)

7.8.9.3 Borden Site – Ethanol and Benzene

Since the ethanol is a preferred source for the microbial populations it will be assumed that no benzene will be degraded where ethanol is available. Once the ethanol plume is defined (0.045 1/day, Figure 9) the model grid cells that the ethanol plume occupied were assigned 0 degradation and the benzene modeled again. This is assuming that all the ethanol will be used by the microbes before any of the benzene will be used. This should be a conservative approach. The model grids that were assigned 0 degradation are shown in Figure 12 and are the dark blue cells. The light blue cells are assigned a degradation constant of 0.045 1/day, the degradation constant for benzene. Since the ethanol will be degraded first, this should simulate the benzene and ethanol mixture being released together.(refer to Figure 13). The edge of the plume migrated about 220 ft from the point of the release. This is 10% longer than the benzene alone.

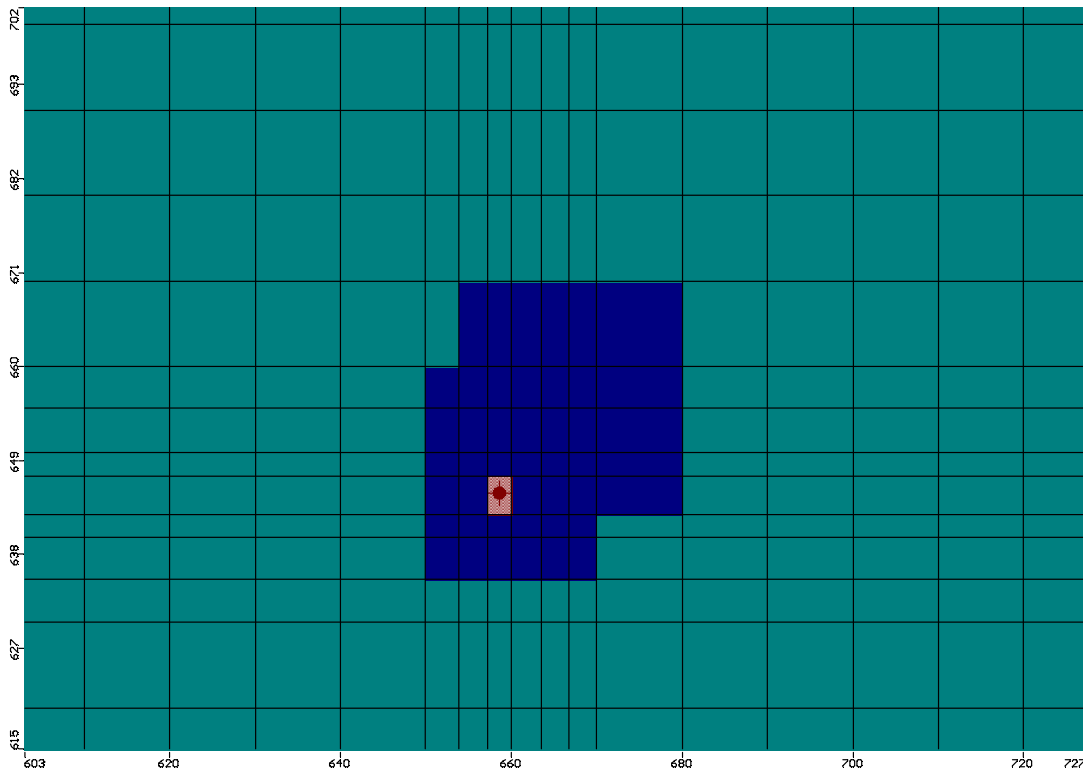


Figure 12: Cells Assigned 0 Degradation for Benzene Run (0.045 1/day ethanol run)

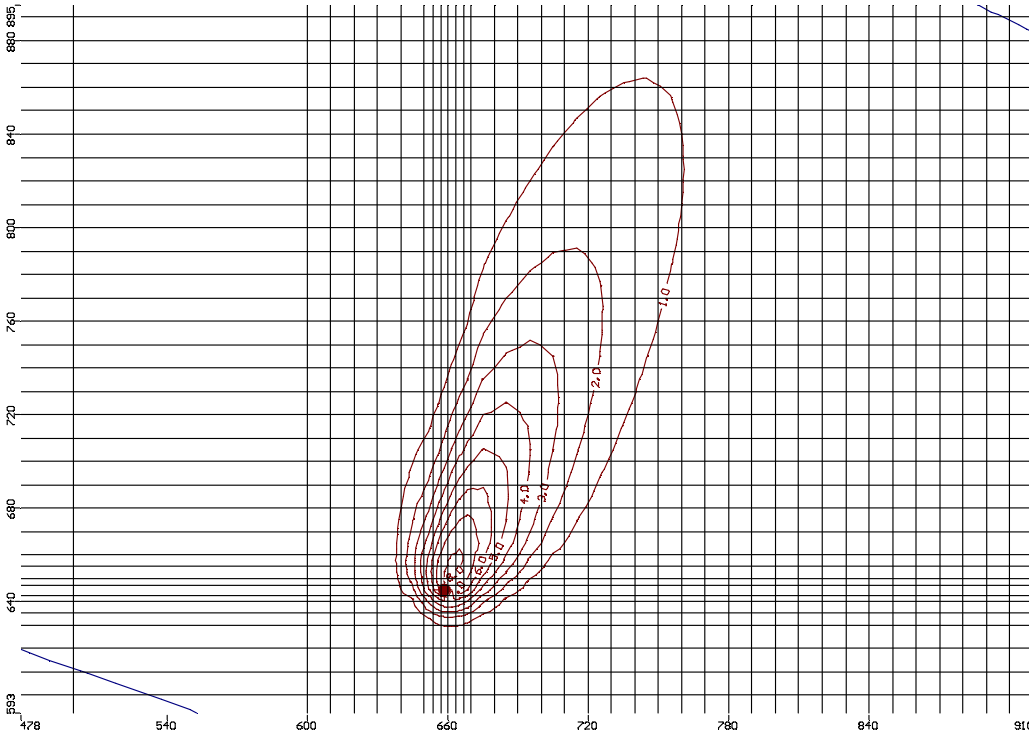


Figure 13: Benzene Plume with Ethanol

7.8.9.4 Borden Site – Benzene, Ethanol and Acetic Acid

Now that the benzene plume is defined with the ethanol taken into consideration, another concern is that the ethanol will be converted to acetic acid. Acetic acid has a much slower degradation rate (0.0014 1/day, Beeman, 1987) than ethanol but is still preferred over benzene. To evaluate the benzene plume with ethanol and acetic acid, the ethanol plume is defined for an acetic acid run which in turn is defined for a benzene run. The acetic acid was modeled with the cells in Figure 14 assigned 0 degradation and rest 0.0014 1/day. The acetic acid was injected at the same 0.5 gpm, but at half the concentration (5000mg/l) of the ethanol since all the ethanol may not be converted to acetate. This plume was in turn assigned 0 degradation for a benzene run. The result of this run is shown in Figure 14. This plume migrated about 365 ft from the point of injection. Compared to the benzene plume with no ethanol added (200 ft), this is about 1.8 times longer.

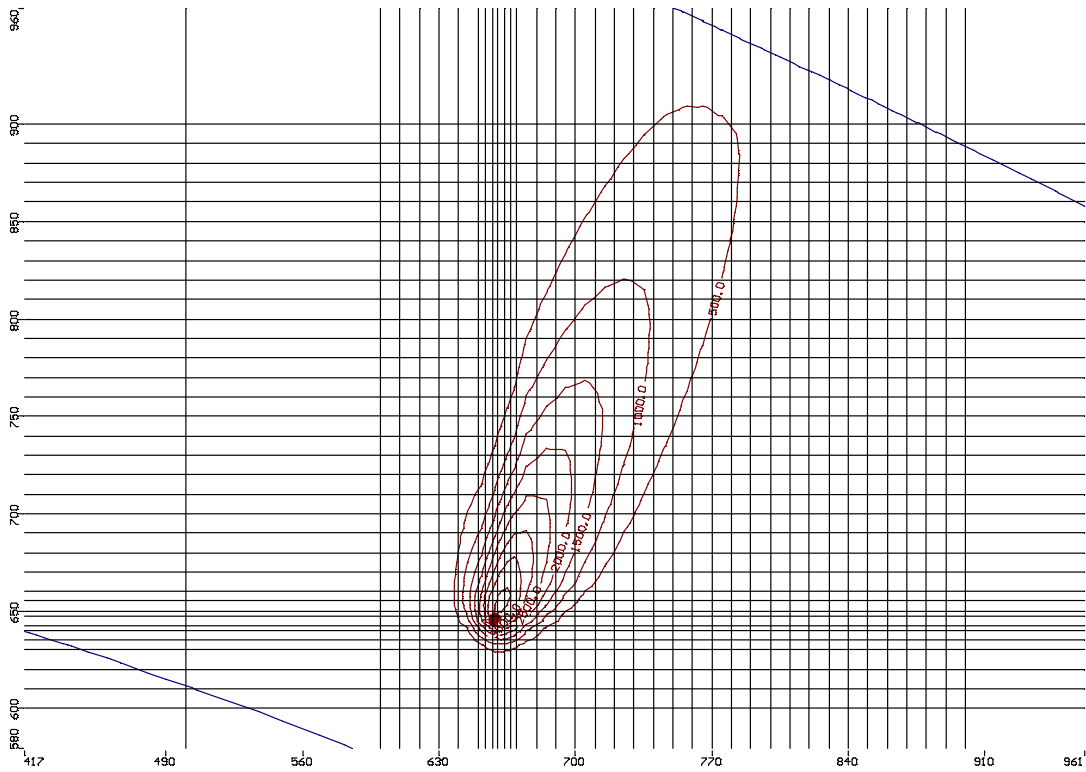


Figure 14: Acetic Acid Plume at 10 Years

8.0 Predictions of the Impact of Ethanol on BTEX Plumes Based on Model Results and the Literature Survey

Due to the rapid rate of ethanol biodegradation noted throughout the scientific literature under all of the electron-accepting conditions in a wide array of environments and on the modeling results which incorporated both biological and abiotic factors that impact the transport of contaminants, it is unlikely that ethanol will migrate substantial distances beyond the source of ethanol-amended gasoline. Thus, the preferential utilization of ethanol relative to BTEX which has been reported under certain conditions is not expected to substantially increase the length of BTEX plumes. However, the modeling exercises suggest that there is the potential for acetic acid accumulation leading to substantial acetic acid plumes in aquifers contaminated with ethanol-blended gasoline. Whether acetate has an impact on the migration of BTEX plumes is not known. However, a survey on the stability and length of gasoline plumes conducted by the Lawrence Livermore National Laboratory indicated that the vast majority of gasoline

plumes are not increasing in length and naturally attenuated. An argument can be made that if the presence of ethanol does substantially increase the length of gasoline plumes then such plumes should have been recognized. Expansive BTEX plumes emanating from point sources of gasoline spills are essentially non-existent.

9.0 Treatment of Groundwater Contaminated with Ethanol-Blended Fuels

Although it is unlikely that ethanol will migrate or persist in gasoline impacted aquifers to the extent of BTEX hydrocarbons, there may be impetus to treat source areas where ethanol is most likely to occur, especially if the spill threatens groundwater drinking wells or environmentally sensitive surface waters. In such instances, the focus will likely be the removal of gasoline hydrocarbons using traditional groundwater treatment technologies including air stripping and activated carbon. While air stripping is relatively effective at removing volatile hydrocarbons, this process is inefficient at removing ethanol from water due to its low partitioning from the aqueous to the gaseous phase. Treatment with activated carbon will also be ineffective due to the high water solubility and low sorption coefficient of ethanol. Thus, traditional technologies for the treatment of gasoline contaminated water will not be useful for ethanol.

Fortunately, biological treatment systems including bioreactors and biologically activated filters are likely to be effective for the treatment of ethanol contaminated groundwater. Ethanol has been shown to be effectively removed from synthetic brewery waste water (Wu and Hickey, 1996) and other ethanol-containing waters (Lettinga et al. 1981) using methanogenic up-flow anaerobic sludge blanket reactors. Denitrifying and aerobic microbial treatment systems are also likely to be efficient in treating ethanol-contaminated water due to the rapid rates of ethanol biodegradation under these electron accepting conditions (Hallin and Pell, 1996; McKinney and Jeris, 1954).

10.0 Conclusions

Because ethanol is rapidly biodegraded in subsurface and surface systems, it is not expected to persist or migrate substantially in the aqueous environment. As a result,

ethanol should pose little health risk relative to the hydrocarbons that will accompany ethanol plumes.

The results of this study indicate that the direct effects of ethanol on the fate and transport of BTEX in the subsurface may be limited. The absence of ‘field evidence’ documenting the transport of ethanol-blended fuel in the subsurface does not allow us to back any hypothesis with field data. It is Surbec’s opinion that field data would help develop a stronger argument for the fate of ethanol amended gasoline in the subsurface.

The modeling exercises indicated that large acetic acid plumes may form in aquifers contaminated with ethanol due to its low rate of biodegradation rate relative to ethanol. The potential impacts include: (1) a drop in pH due to acetic acid build up resulting in decreased microbial activity including BTEX biodegradation; (2) preferential use of acetic acid relative to BTEX hydrocarbons; (3) the depletion of electron acceptors available for BTEX biodegradation; and (4) stimulation of BTEX biodegradation due to the availability of acetate as a preferred substrate. The potential impact of acetic acid on the migration of gasoline plumes warrants additional scientific evaluation.

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APPENDIX OF PRELIMINARY MODELING RESULTS

Borden Site

Continuous Release

Borden, 25 meter, Benzene, Biodegradation

Borden, 25 meter, Methanol, Biodegradation

Pulse Release

Borden, 20 meter, Methanol, Biodegradation

Borden, 20 meter, Benzene, Biodegradation

Borden, 25 meter, Methanol, Biodegradation

Borden, 25 meter, Benzene, Biodegradation

Borden, 50 meter, Methanol No, Biodegradation

Borden, 50 meter, Benzene No, Biodegradation

Borden, 100 meter, Benzene, Biodegradation

Borden, 250 meter, Methanol No, Biodegradation

Borden, 250 meter, Methanol, Biodegradation

Borden, 250 meter, Benzene, Biodegradation

Borden, 500 meter, Methanol No, Biodegradation

Borden, 500 meter, Benzene No, Biodegradation

Xerox Site

Continuous Release

Xerox, 1 meter, Methanol, Biodegradation
Xerox, 15 meter, Methanol, Biodegradation
Xerox, 22 meter, Methanol, Biodegradation
Xerox, 25 meter, Methanol, Biodegradation
Xerox, 25 meter, Benzene, Biodegradation
Xerox, 50 meter, Benzene, Biodegradation
Xerox, 76 meter, Benzene, Biodegradation
Xerox, 77 meter, Benzene, Biodegradation
Xerox, 79 meter, Benzene, Biodegradation

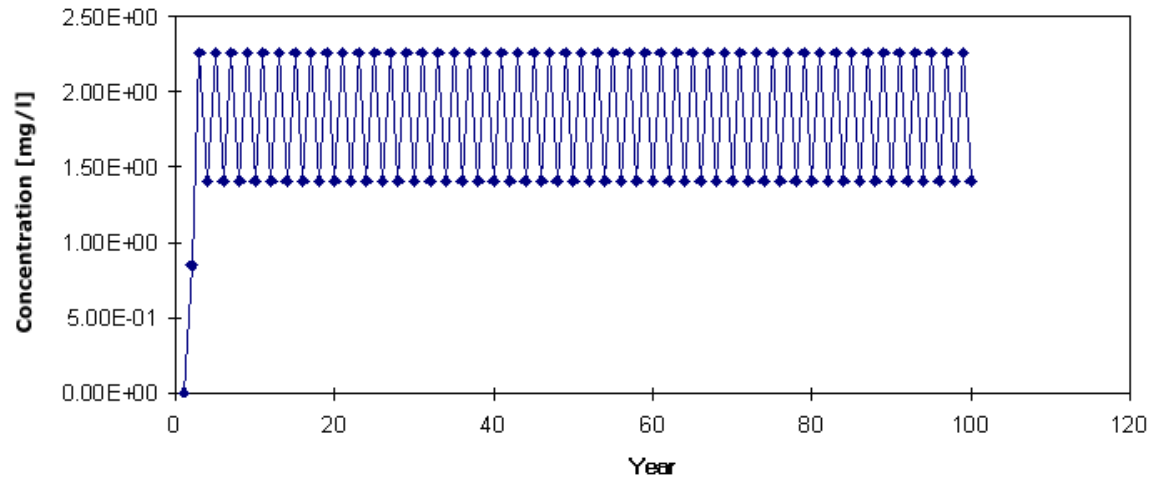
Pulse Release

Xerox, 20 meter, Methanol, Biodegradation
Xerox, 21 meter, Methanol, Biodegradation
Xerox, 35 meter, Methanol, Biodegradation
Xerox, 35 meter, Methanol No, Biodegradation
Xerox, 35 meter, Benzene, Biodegradation
Xerox, 35 meter, Benzene No, Biodegradation
Xerox, 50 meter, Methanol, Biodegradation
Xerox, 50 meter, Methanol No, Biodegradation
Xerox, 50 meter, Benzene, Biodegradation
Xerox, 50 meter, Benzene No, Biodegradation
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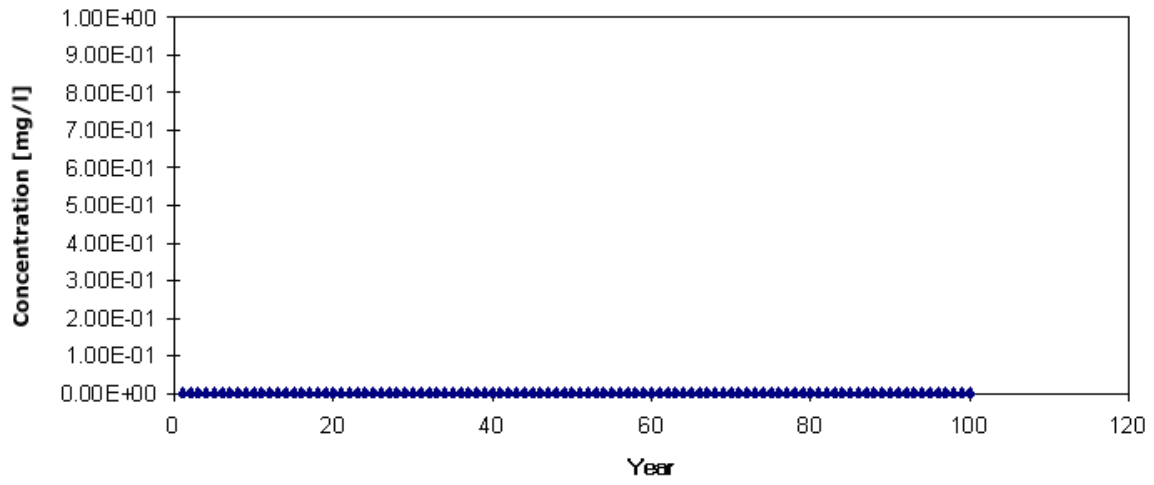
Borden Site

Continuous Release

Borden Site 25 meter, Benzene Biodegradation Continuous Release

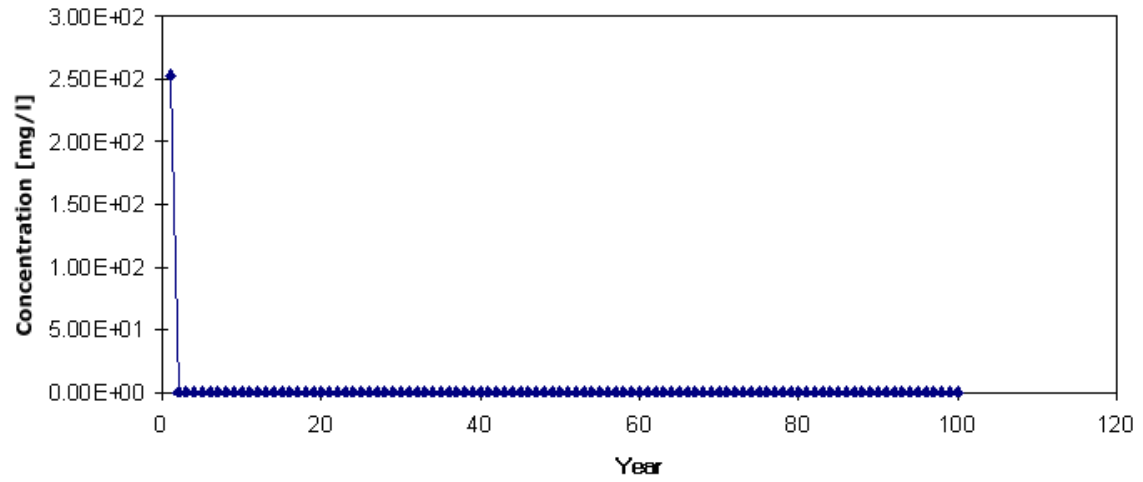


Borden site, 25 meter, Benzene Biodegradation Continuous Release

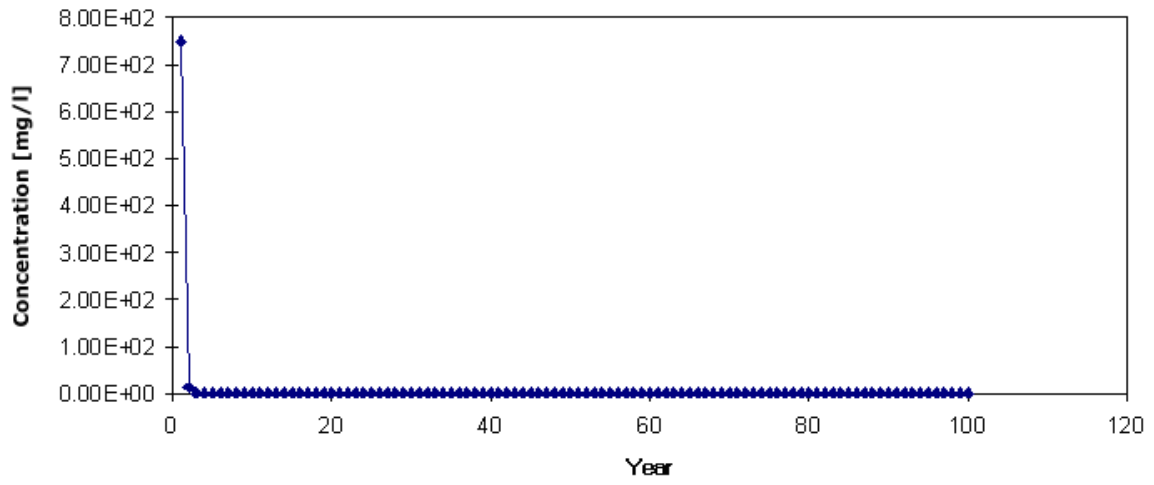


Pulse Release

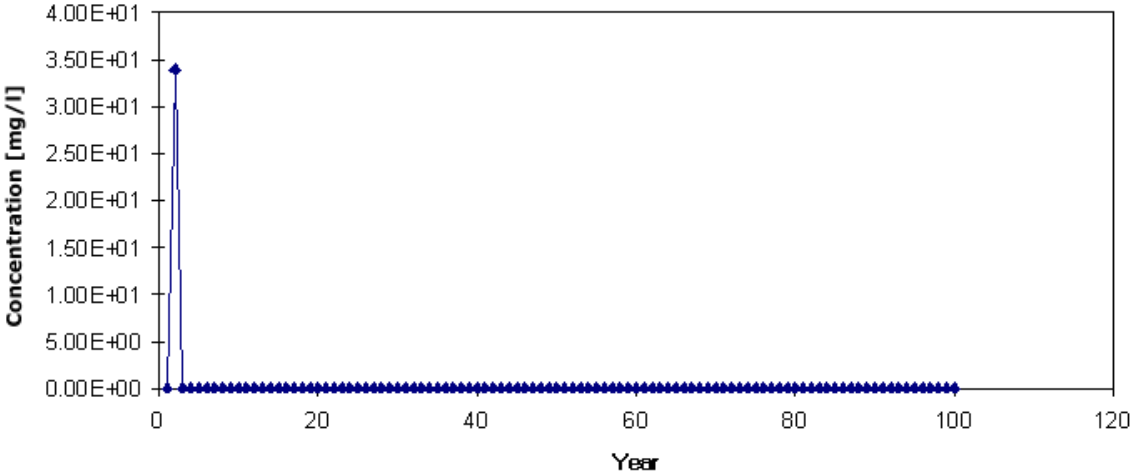
Borden Site 20 meter, Methanol Biodegradation Pulse Release



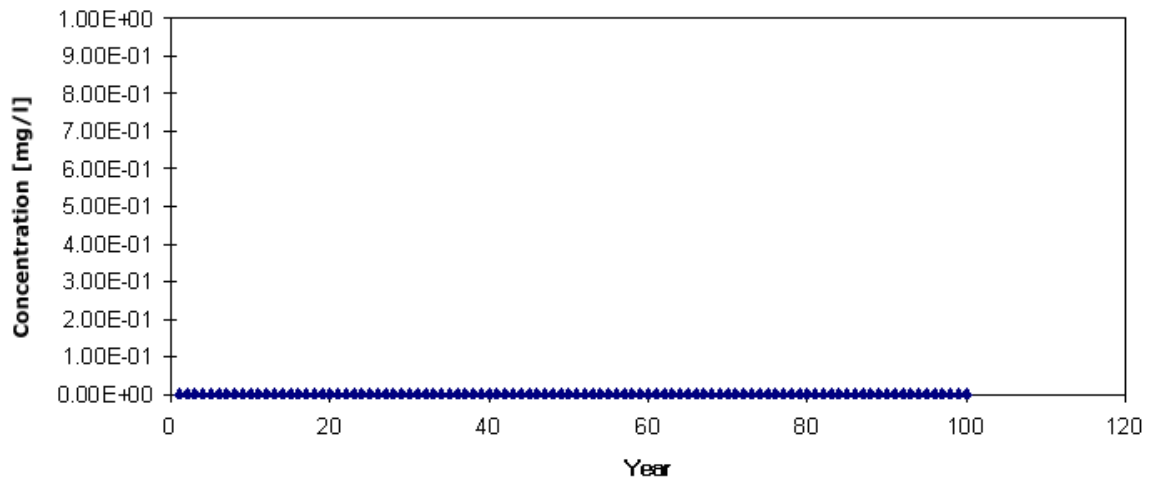
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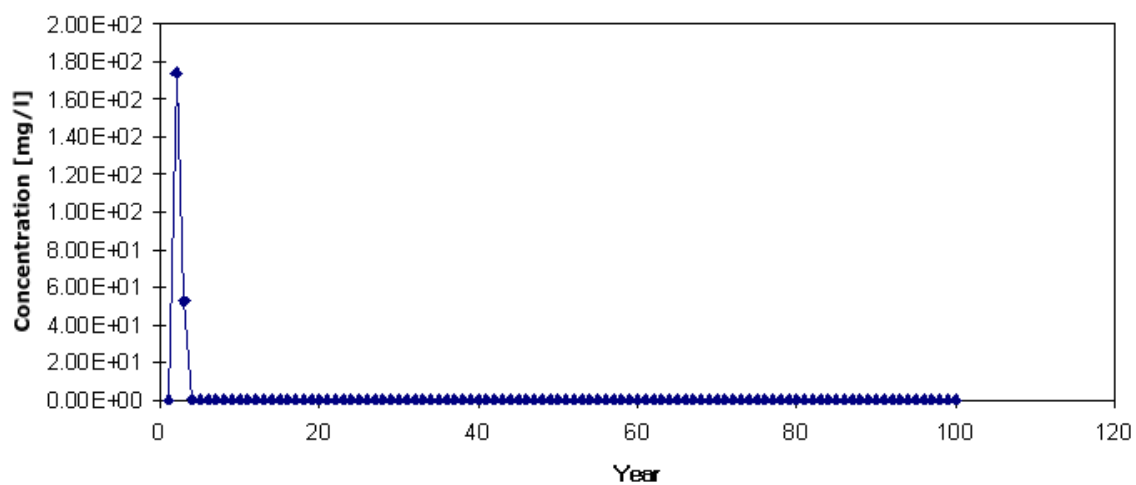
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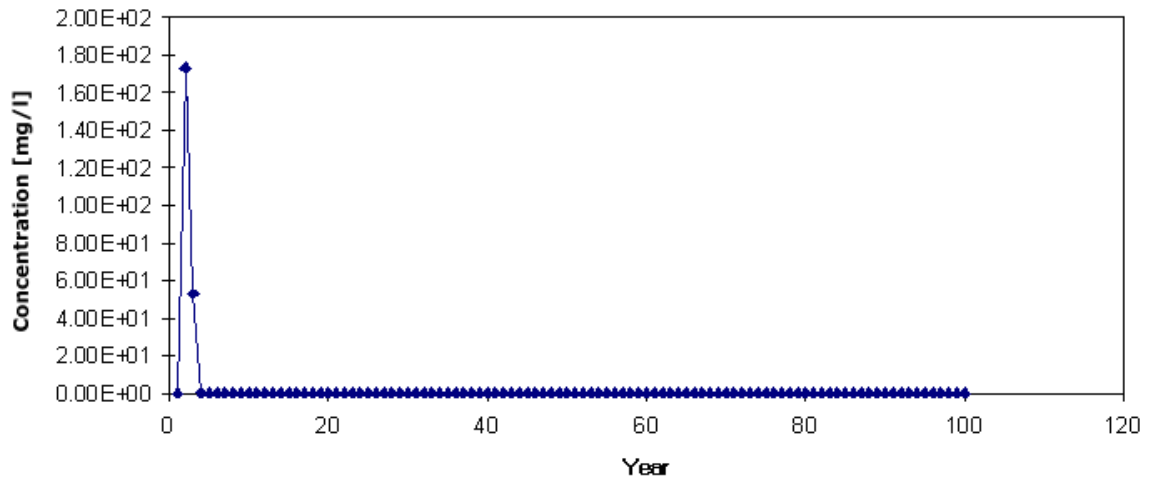
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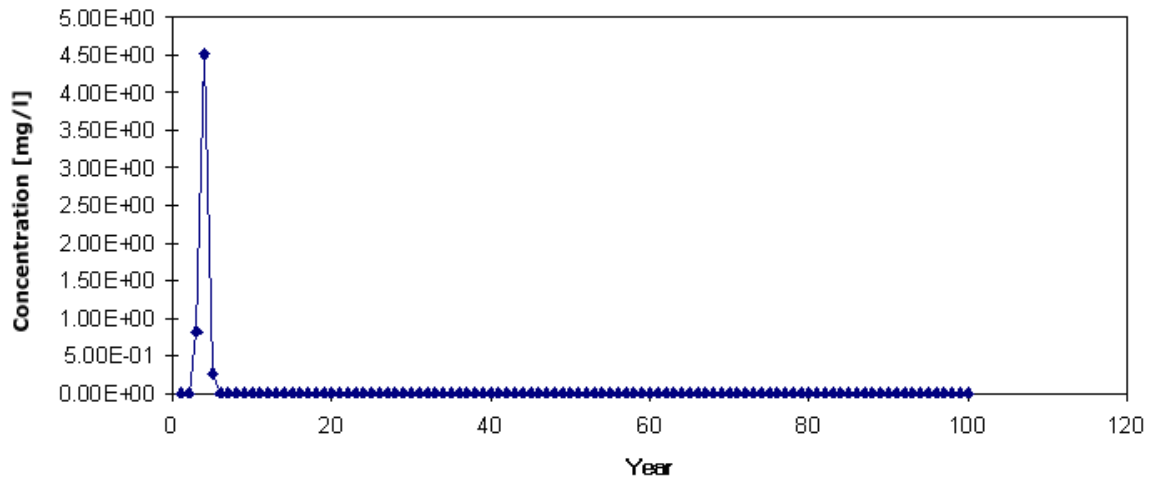
Borden Site 50 meter, Methanol No Biodegradation



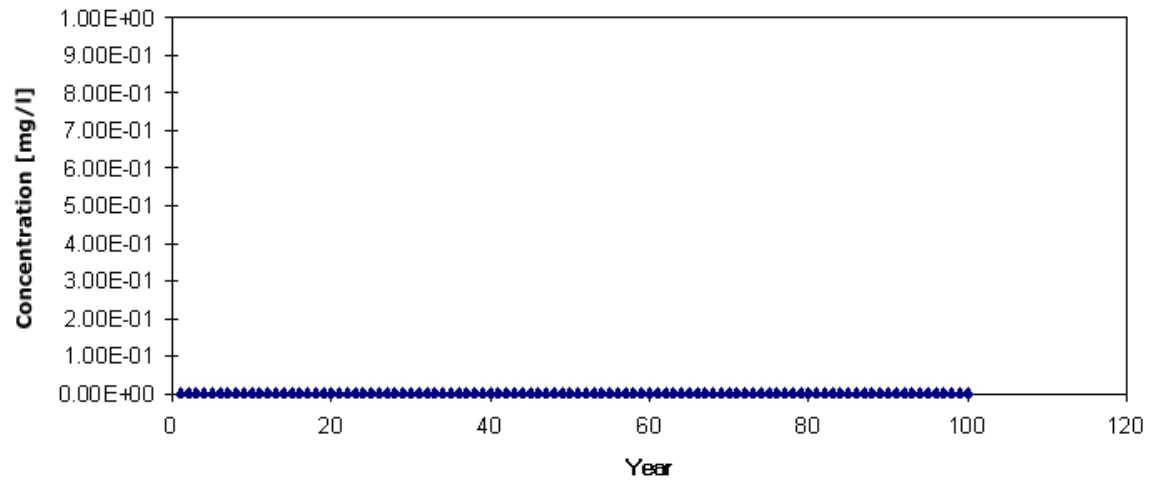
Borden Site 50 meter, Benzene No Biodegradation



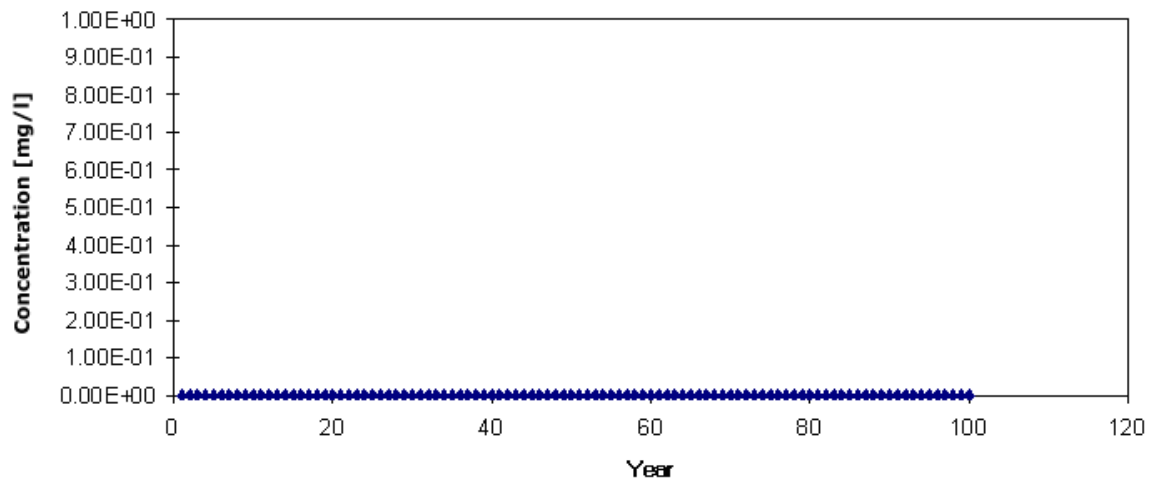
Borden Site 100 meter, Benzene Biodegradation Pulse Release



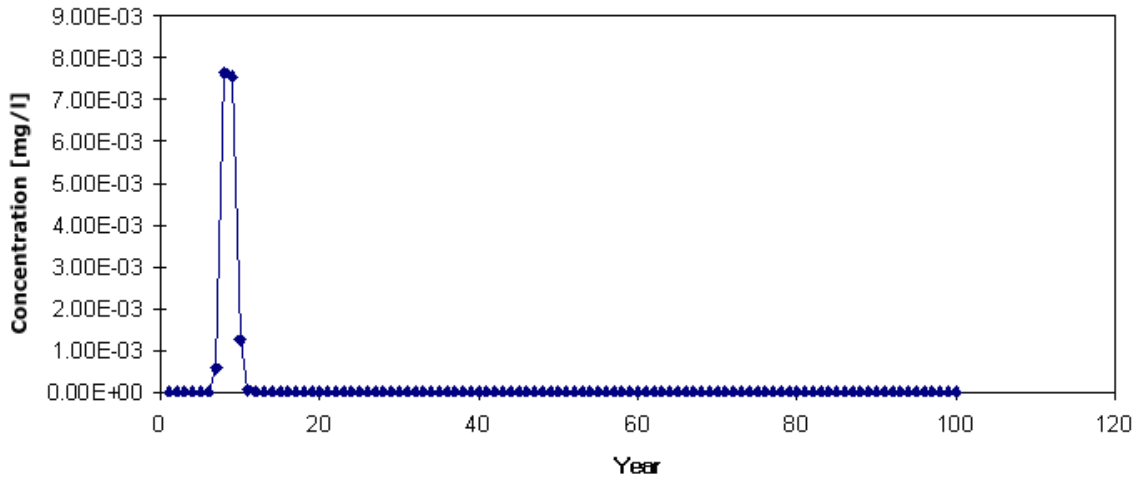
Borden Site 250 meter, Methanol No Biodegradation



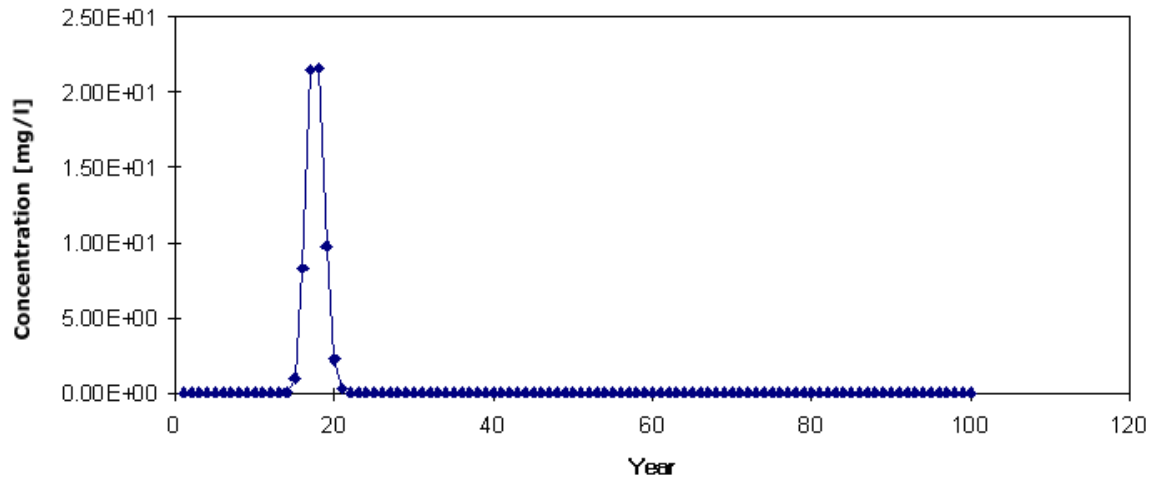
Borden Site 250 meter, Methanol Biodegradation Pulse Release



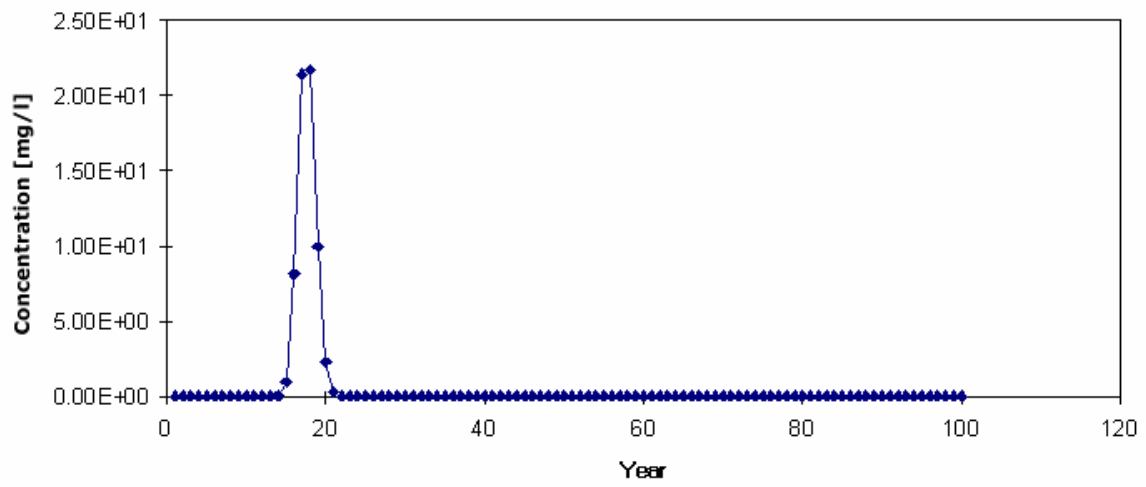
Borden Site 250 meter, Benzene Biodegradation Pulse Release



Borden Site 500 meter, Methanol No Biodegradation

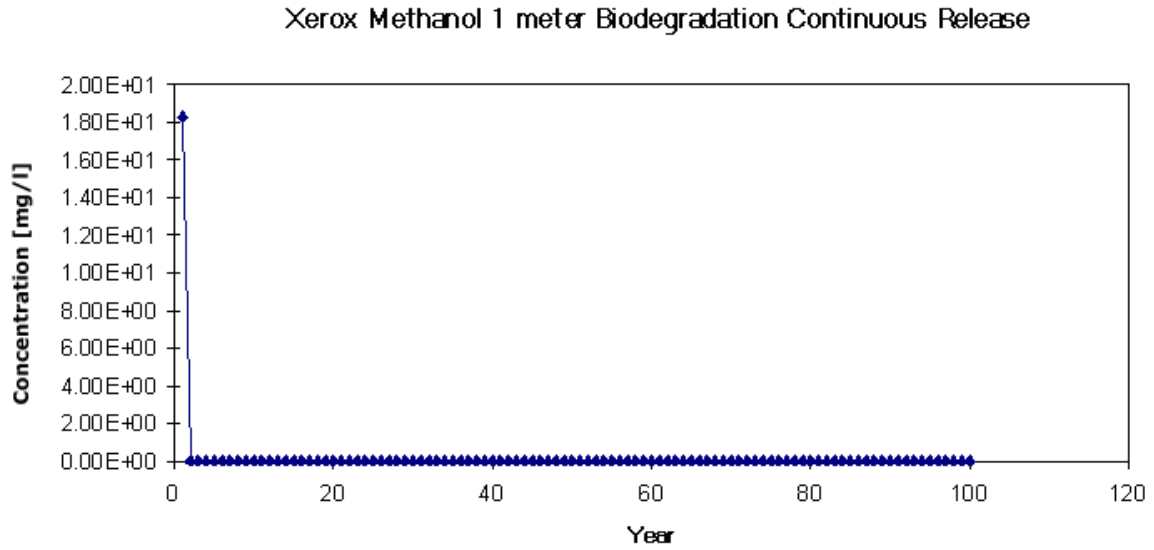


Borden Site 500 meter, Benzene No Biodegradation

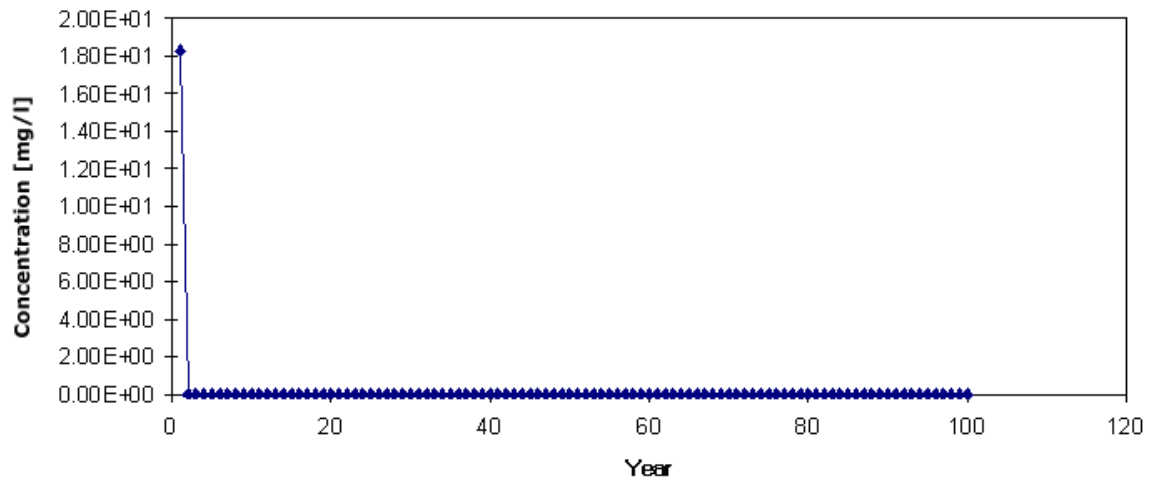


Xerox Site

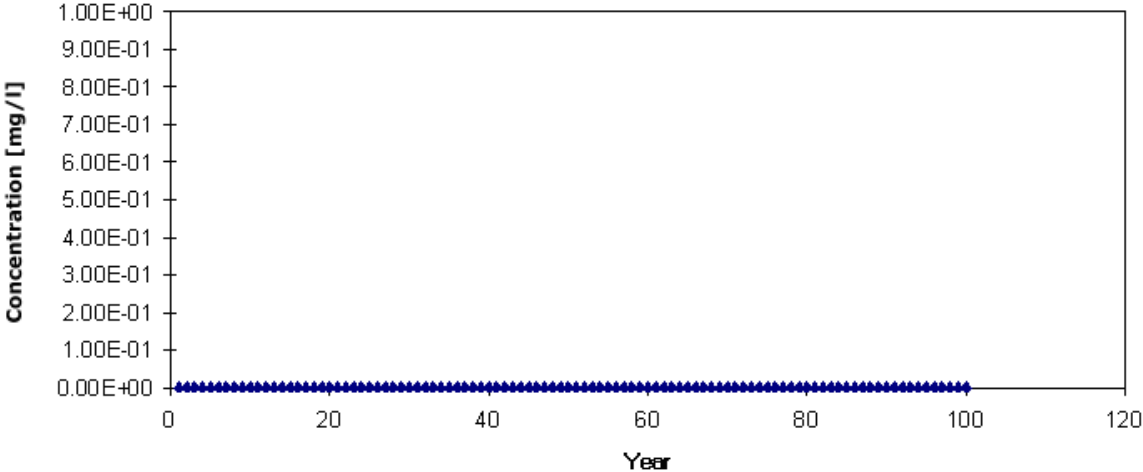
Continuous Release



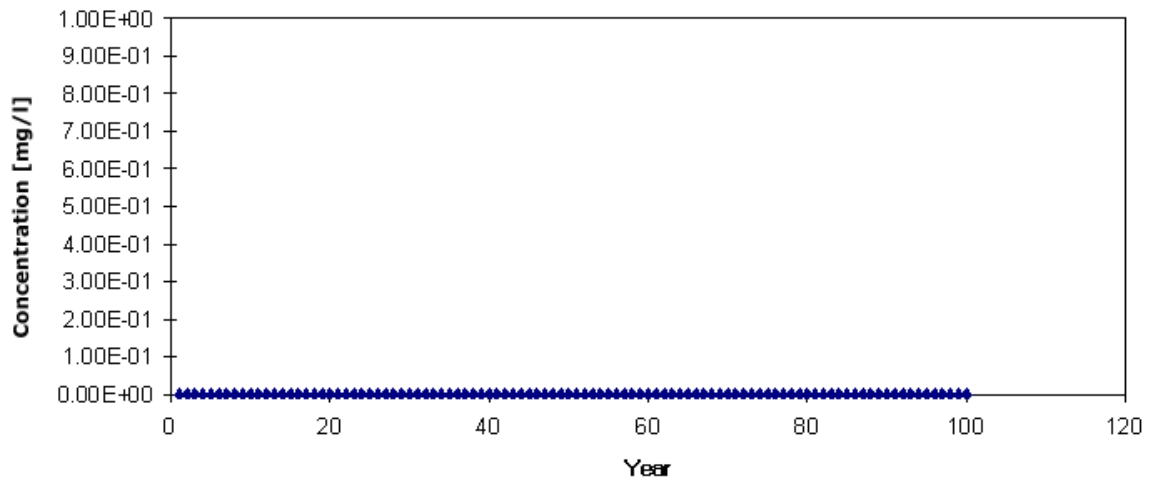
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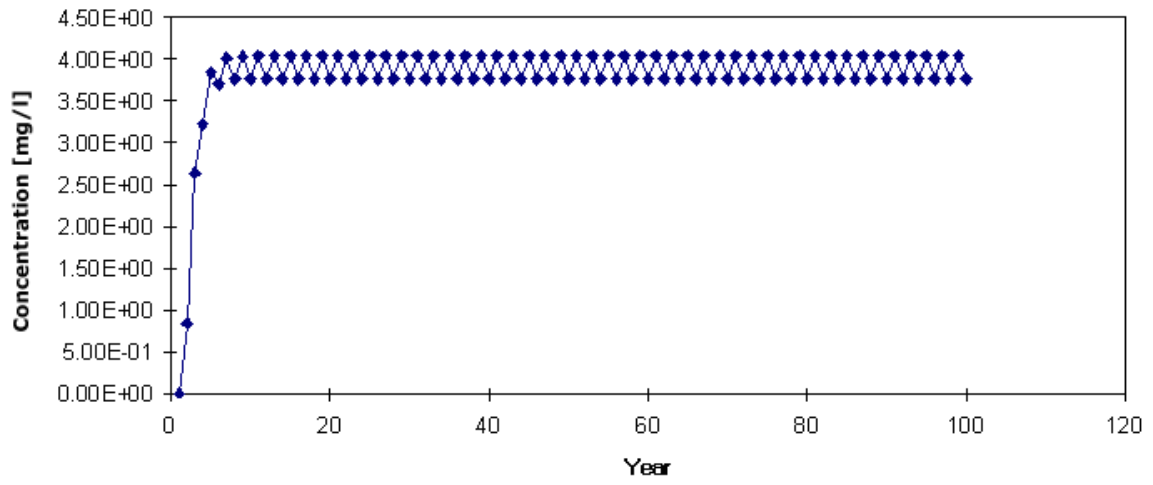
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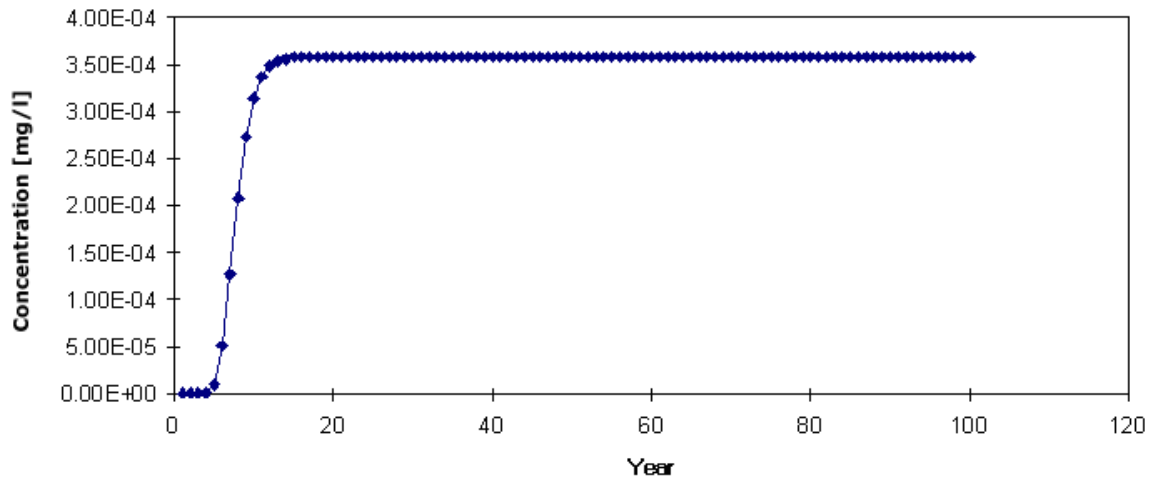
Xerox 25 meter, Methanol Biodegradation Continuous Release



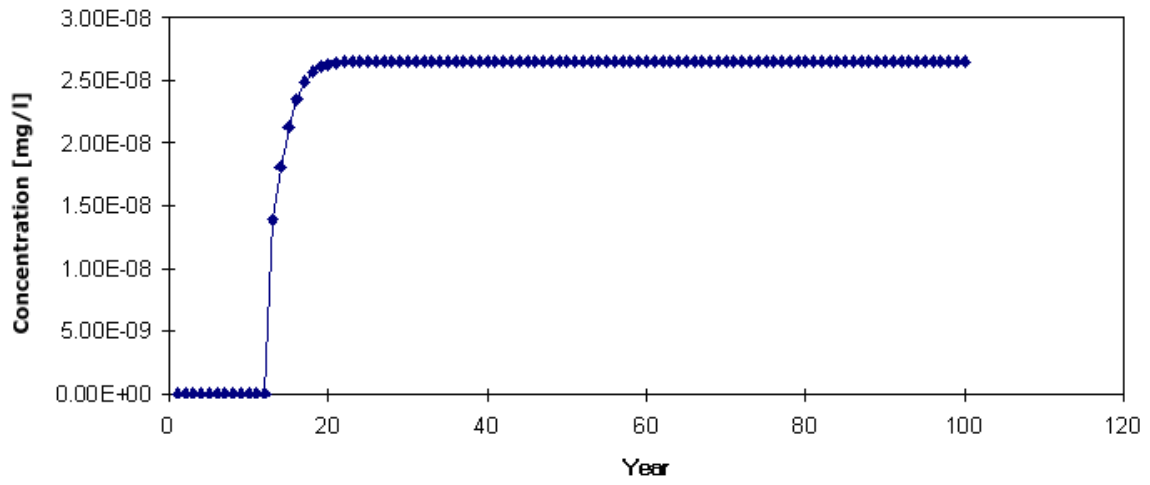
Xerox 25 meter, Benzene Biodegradation Continuous Release



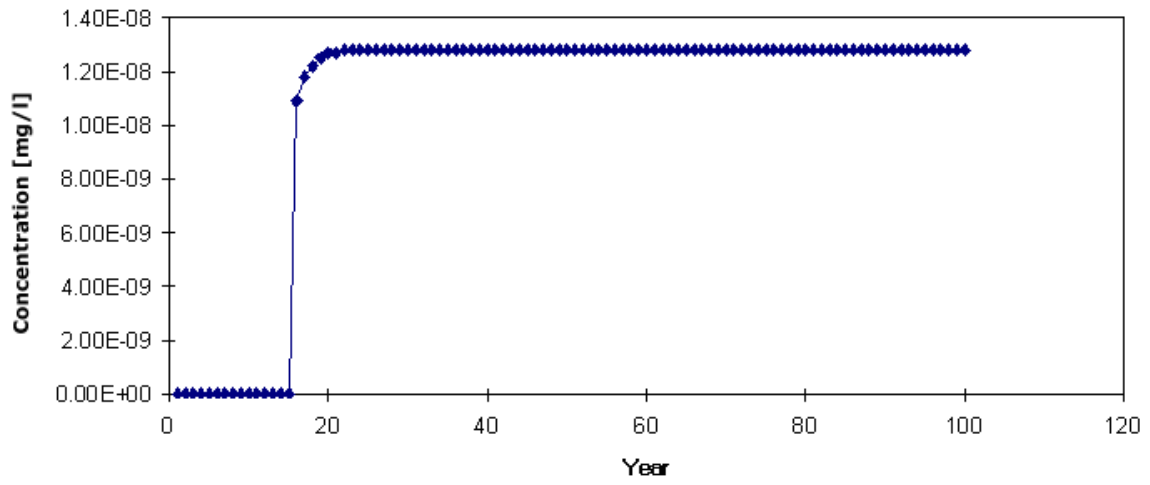
Xerox 50 meter, Benzene Biodegradation Continuous Release



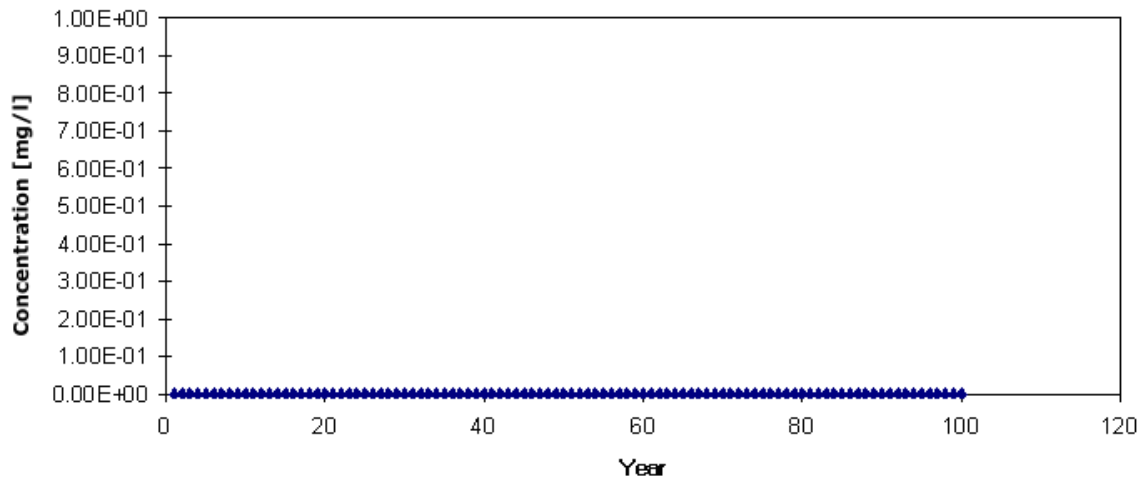
Xerox 76 meter, Benzene Biodegradation Continuous Release



Xerox 77 meter, Benzene Biodegradation Continuous Release

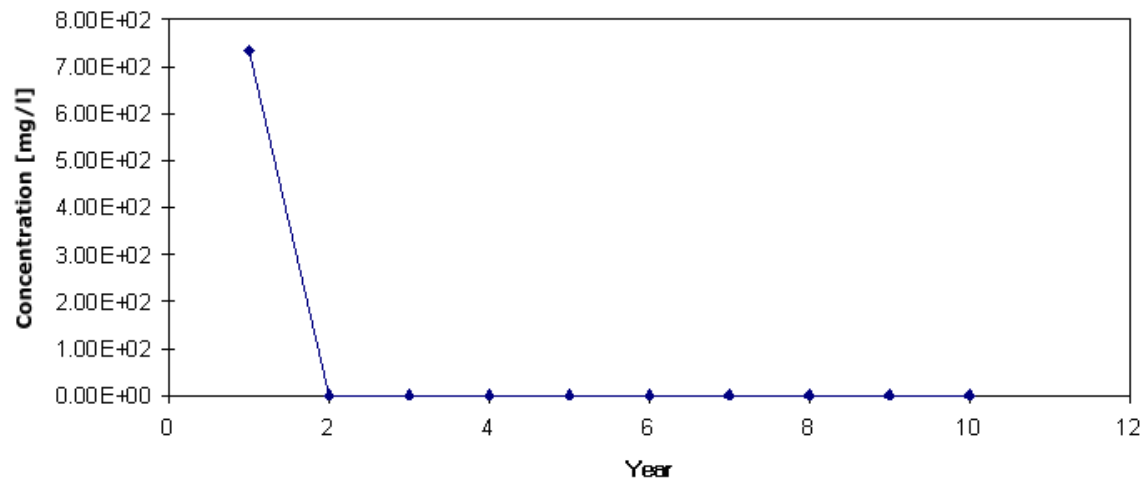


Xerox 79 meter, Benzene Biodegradation Continuous Release

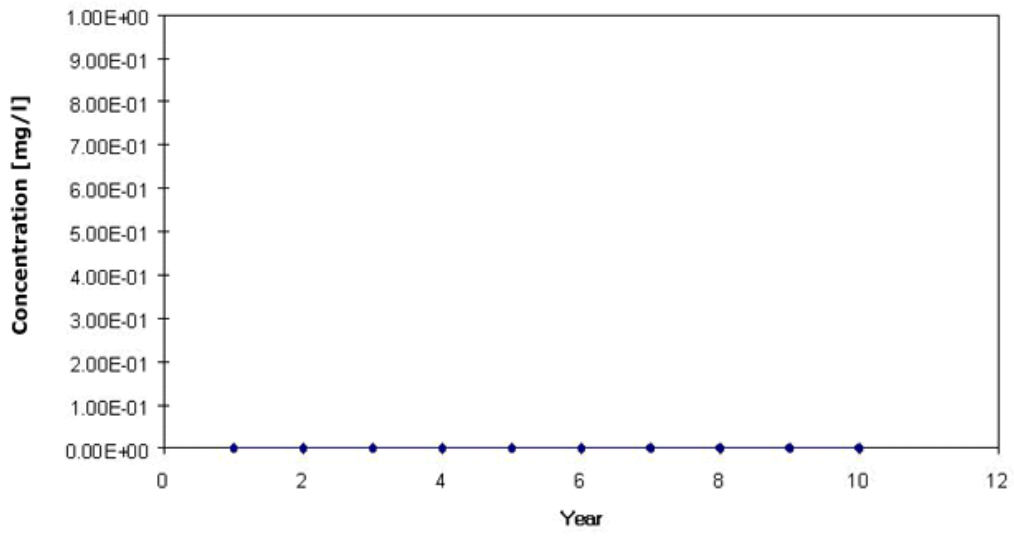


Pulse Release

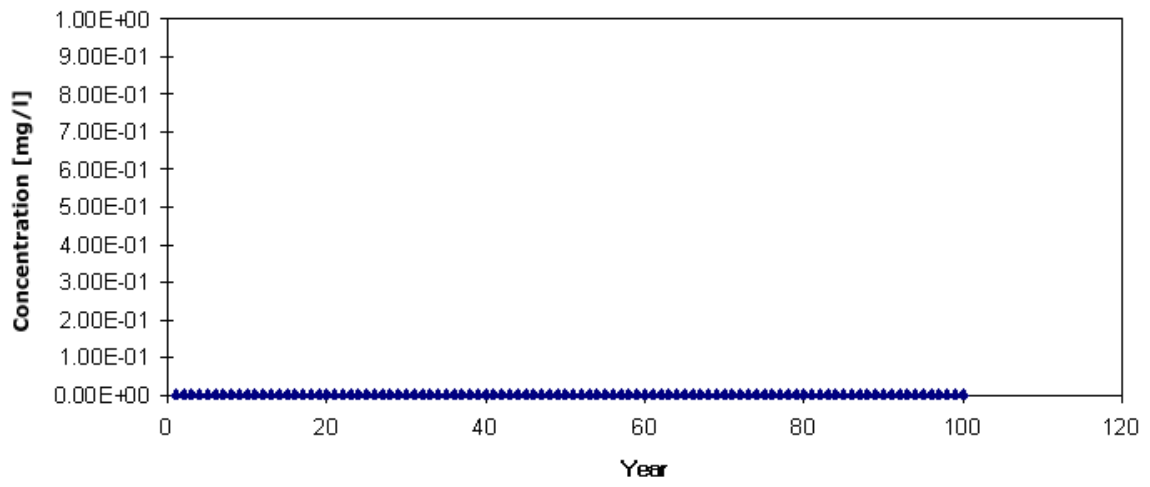
Xerox 20 meter, Methanol Biodegradation Pulse Release



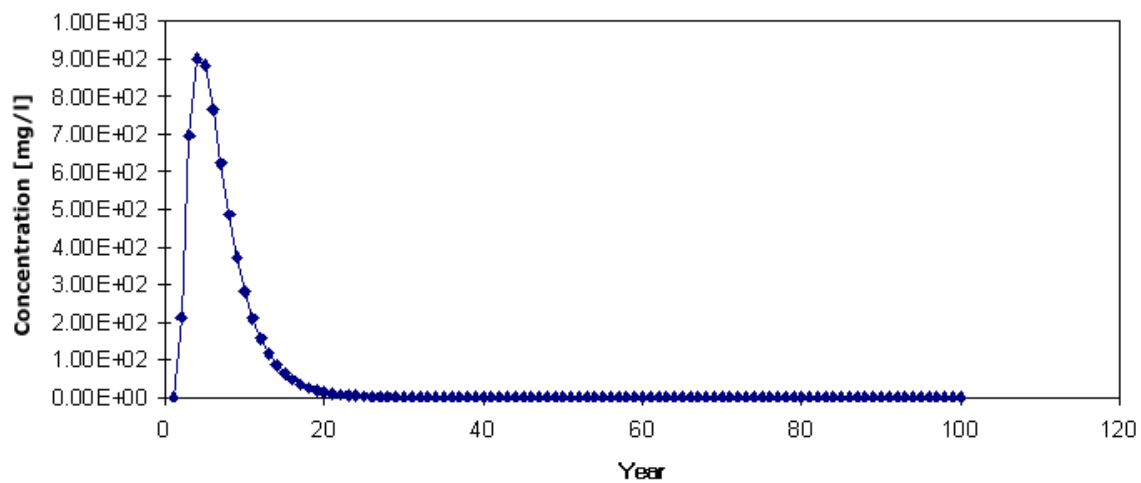
Xerox 21 meter, Methanol Biodegradation Pulse Release



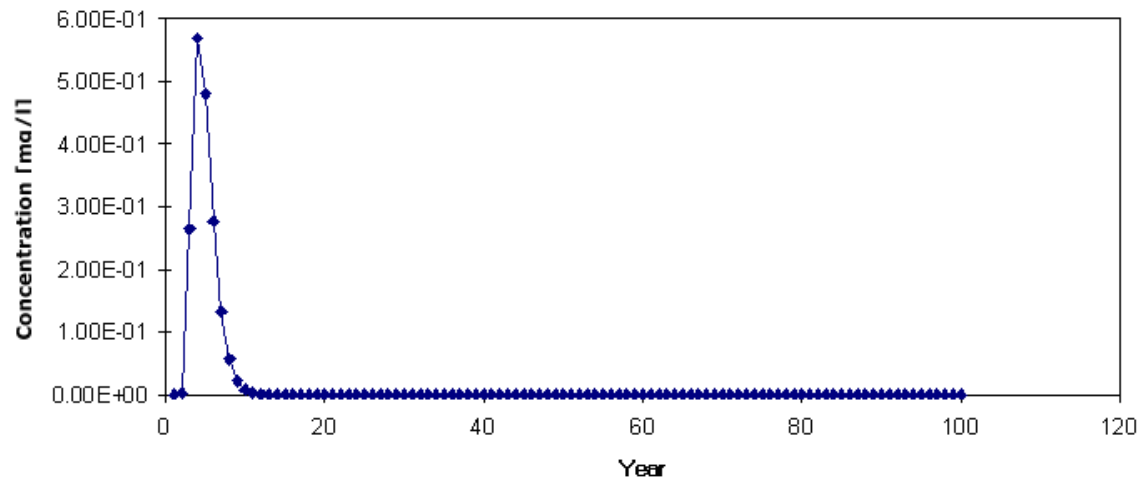
Xerox 35 meter, Methanol Biodegradation Pulse Release



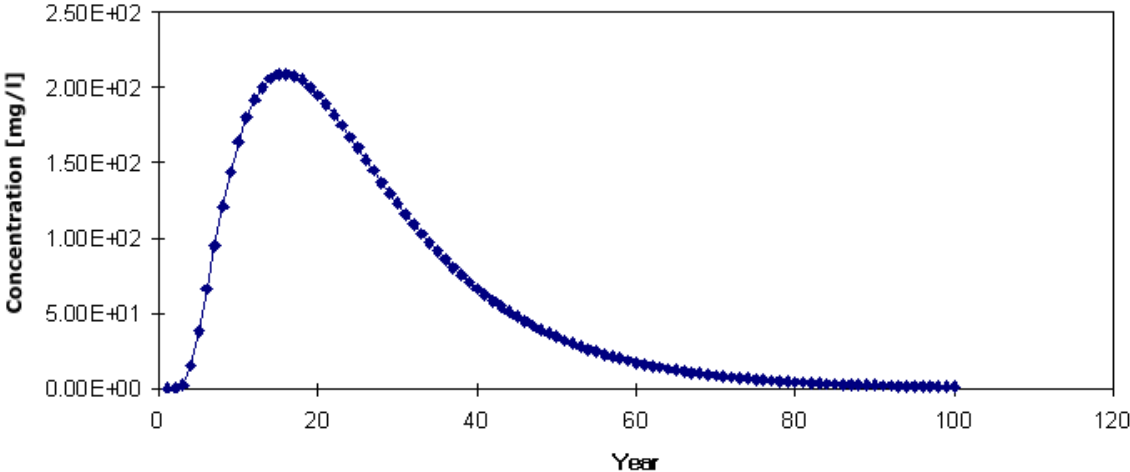
Xerox 35 meter, Methanol No Biodegradation



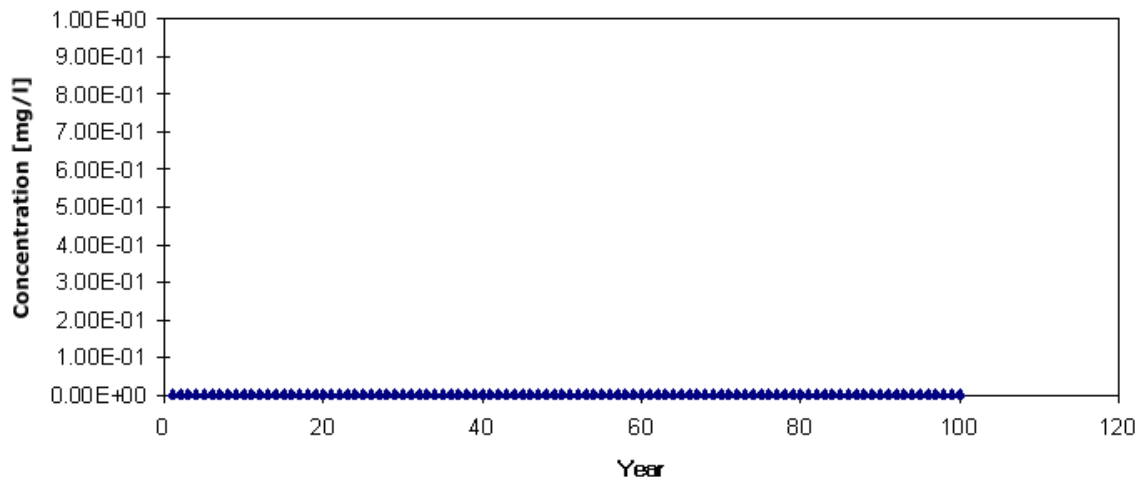
Xerox 35 meter, Benzene Biodegradation Pulse Release



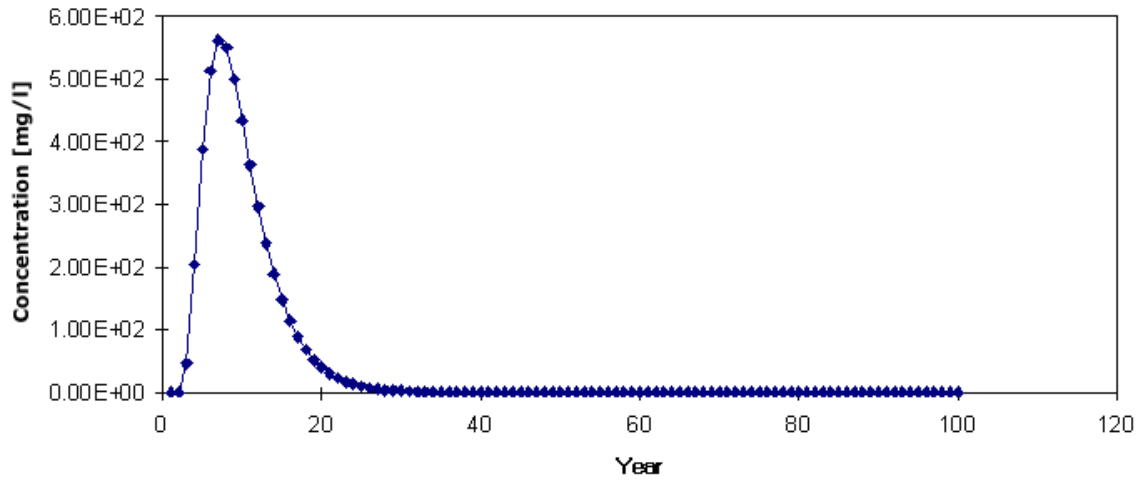
Xerox Benzene 35 meter. No Biodegradation



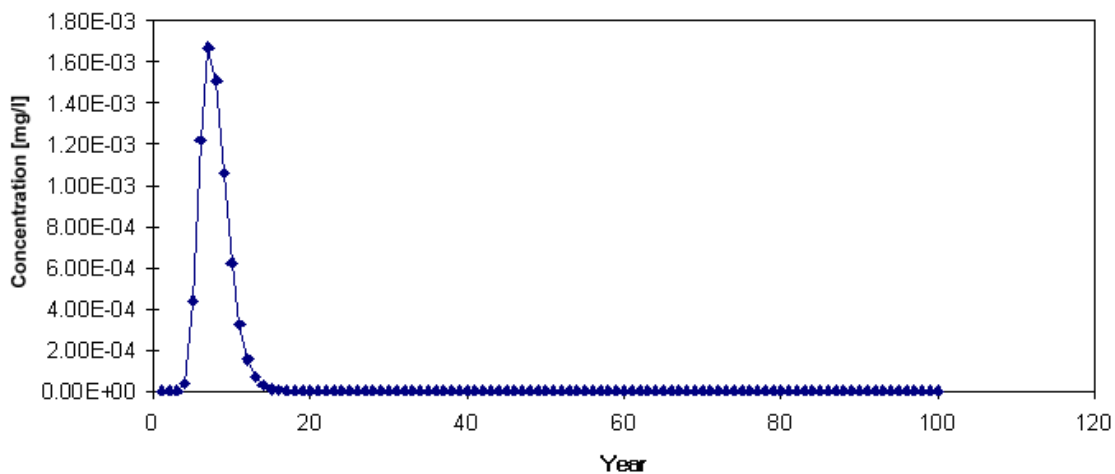
Xerox 50 meter, Methanol Biodegradation Pulse Release



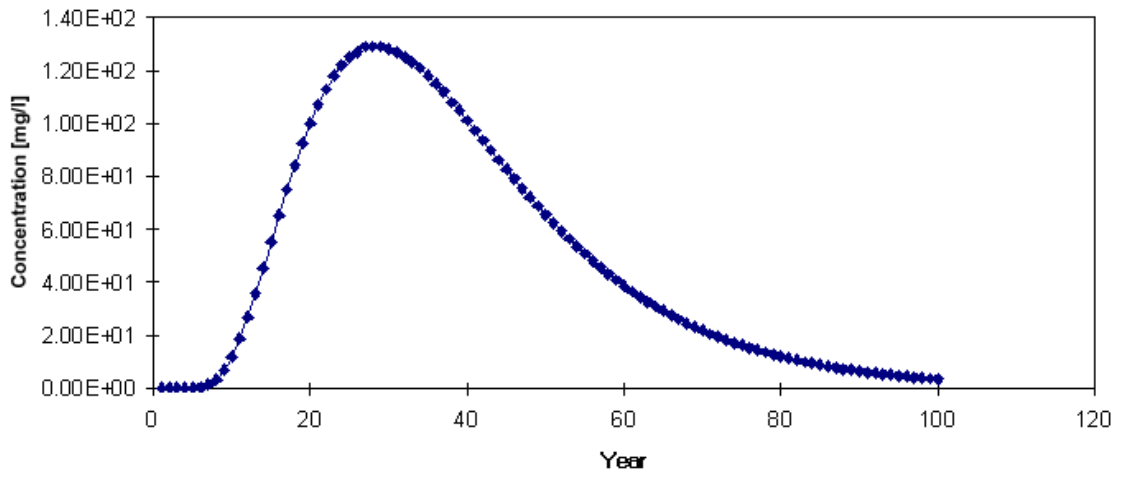
Xerox Methanol 50 meter No Biodegradation



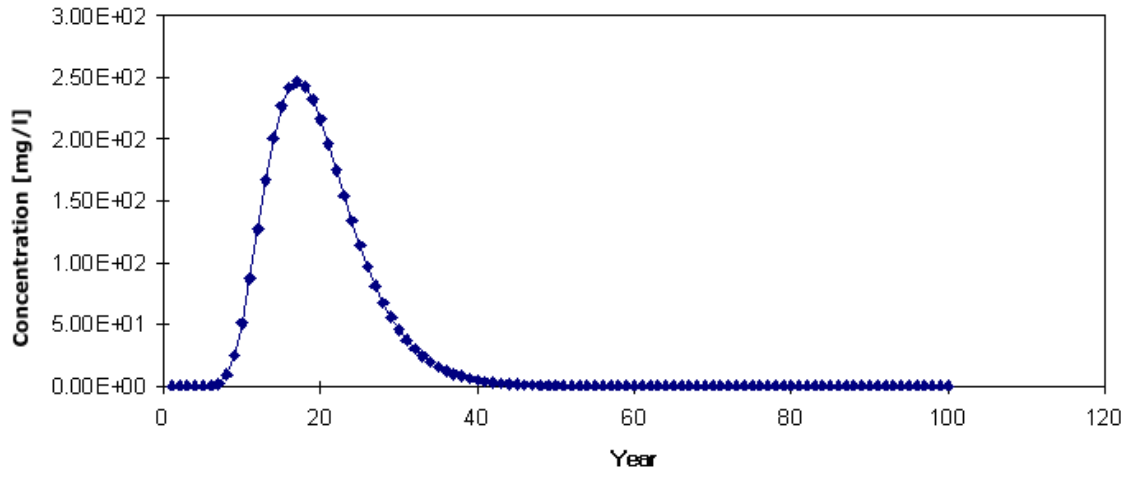
Xerox 50 meter, Benzene Biodegradation Pulse Release



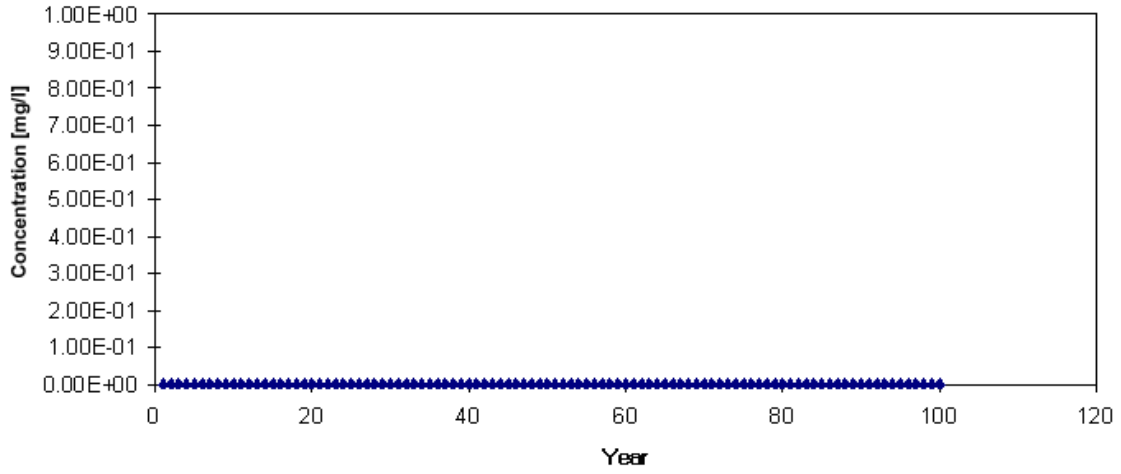
Xerox Benzene 50 meter, No Biodegradation



Xerox 100 meter, Methanol No Biodegradation



Xerox, 100 meter Benzene Biodegradation Pulse Release



Xerox 100 meter, Benzene No Biodegradation

