



## Role of back diffusion and biodegradation reactions in sustaining an MTBE/TBA plume in alluvial media

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### ABSTRACT

A methyl tert-butyl ether (MTBE) / tert-butyl alcohol (TBA) plume originating from a gasoline spill in late 1994 at Vandenberg Air Force Base (VAFB) persisted for over 15 years within 200 feet of the original spill source. The plume persisted until 2010 despite excavation of the tanks and piping within months after the spill and excavations of additional contaminated sediments from the source area in 2007 and 2008. The probable history of MTBE concentrations along the plume centerline at its source was estimated using a wide variety of available information, including published details about the original spill, excavations and monitoring by VAFB consultants, and our own research data. Two-dimensional reactive transport simulations of MTBE along the plume centerline were conducted for a 20-year period following the spill. These analyses suggest that MTBE diffused from the thin anaerobic aquifer into the adjacent anaerobic silts and transformed to TBA in both aquifer and silt layers. The model reproduces the observation that after 2004 TBA was the dominant solute, diffusing back out of the silts into the aquifer and sustaining plume concentrations much longer than would have been the case in the absence of such diffusive exchange. Simulations also suggest that aerobic degradation of MTBE or TBA at the water table in the overlying silt layer significantly affected concentrations of MTBE and TBA by limiting the chemical mass available for back diffusion to the aquifer.

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### 1. Introduction

Multispecies reactive transport models are increasingly used to characterize field and environmental conditions at sites with contaminated groundwater, and in particular to assess natural attenuation processes. From such modeling efforts and detailed field data, it has become clear that back diffusion of contaminants from low permeability layers

within or contacting contaminated aquifers can lead to persistence of a plume in an aquifer despite source depletion, isolation or removal (Chapman and Parker, 2005; Harrison et al., 1992; Harvey and Gorelick, 2000; LaBolle and Fogg, 2001; NRC, 1994; Parker et al., 2008; Sale et al., 2008). Most modeling of back diffusion to date has addressed the fate of trichloroethylene (TCE), generally without consideration of biotransformation reactions. Sale et al. (2008) provide an analytical solution for a simple scenario of an aquifer overlying a low permeability layer that includes first-order degradation, showing that degradation in low permeability zones can significantly reduce back diffusion. Recently, Chambon et al. (2010) showed transport of TCE and its daughter products in a fracture-clay matrix system under anaerobic conditions was

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more impacted by diffusion and other physical processes in the matrix than by dechlorination reactions.

The effects of diffusive mass transfer and biodegradation on the fate of MTBE and TBA plumes have received less attention. Yet releases of MTBE-blended gasoline from leaking underground storage tanks have led to many cases of groundwater contamination; over 400,000 sites with MTBE detections have been identified by the US Environmental Protection Agency since 1988 (Small et al., 2001). LaBolle et al. (2008) studied the isotopic fractionation of MTBE and TBA that may occur due to diffusion from aquifers into low permeability layers, but they did not address subsequent back diffusion. To our knowledge this is the first study involving detailed collection of field data with associated modeling incorporating both diffusion and reactions for MTBE and TBA.

The objective of this study was to develop and apply a reactive transport model to elucidate processes that likely controlled the persistence of an MTBE/TBA plume at Site 60, Vandenberg Air Force Base (VAFB), CA. Simulations are compared with long term monitoring data to evaluate the importance of diffusive mass transfer and the likely timing, location and importance of biodegradation reactions.

## 2. Biodegradation of MTBE and TBA

In recent years, a significant amount of insight has emerged on the potential for biodegradation of MTBE and TBA under anaerobic and aerobic conditions. An overview is provided immediately below.

Under anaerobic conditions, MTBE biodegradation has been observed in laboratory experiments under nitrate-, iron-, manganese- and sulfate-reducing conditions, as well as under methanogenic conditions (reviewed in Haggblom et al., 2007). If anaerobic biodegradation occurs, MTBE is usually transformed to TBA, which often persists (Somsamak et al., 2006). Acetogenic bacteria, members of methanogenic food webs, are hypothesized to be responsible for ether cleavage of the MTBE molecule and use the released methyl group as a carbon source; however, the pathway and particular organisms responsible are yet to be defined (Youngster et al., 2010a, 2010b). Field experiments at VAFB have shown that MTBE transforms to TBA under strongly anaerobic conditions induced by experimental ethanol addition (Mackay et al., 2007; McKelvie et al., 2007), with an estimated pseudo-first-order reaction rate constant of  $0.046 \text{ day}^{-1}$  (after a lag period of about two months). Other lab and field evidence of in situ transformation of MTBE under anaerobic conditions is summarized by Wilson et al. (2005).

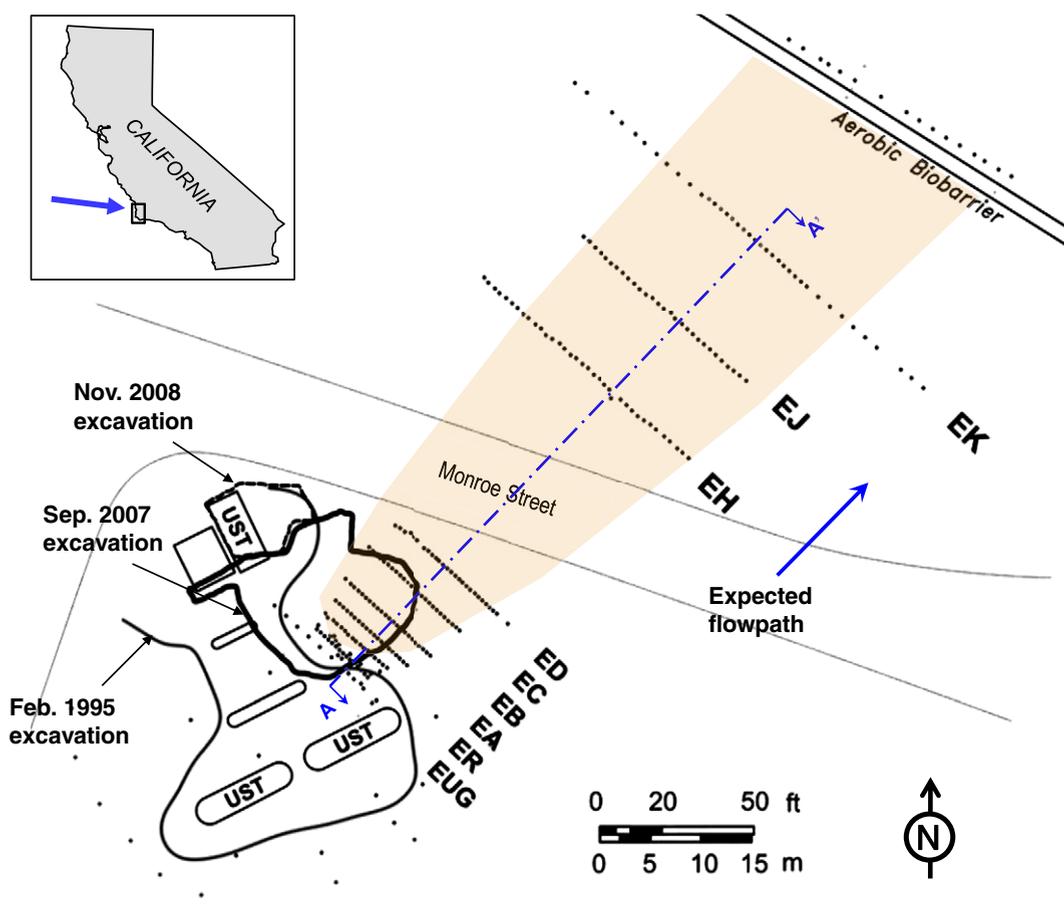
Aerobic biodegradation of MTBE is well demonstrated in lab and controlled field experiments (Kayne, 2008; Landmeyer et al., 2001; Mackay et al., 2002; North, 2011; Salanitro, 2000; Wilson et al., 2002). MTBE can be mineralized or cometabolized by a variety of organisms under aerobic conditions (Schmidt et al., 2004). Among them, the bacterium, *Methylibium petroleiphilum* strain PM1, can use MTBE and TBA as sole carbon and energy source (Schmidt et al., 2008), and PM1-like organisms have been detected in a number of MTBE-contaminated aquifers including VAFB (Hristova et al., 2003). Many bacteria that degrade alkanes and isoalkanes can simultaneously cometabolize MTBE (Hyman et al., 2001; Morales et al., 2009) and these organisms are common in contaminated groundwater; a major concern surrounding MTBE cometabolism, however, is

accumulation of TBA as a metabolite (Nava et al., 2007). For aerobic biodegradation in general, potential intermediate compounds include TBA, formaldehyde, tert-butyl formate (TBF), 2-methyl-2-hydroxy-1-propanol (MHP), 2-hydroxyisobutyric acid (HIBA), 2-propanol, and acetone (Lopes Ferreira et al., 2006; Martienssen et al., 2006; Wilson, 2003).

Salanitro (2000) reported evidence of MTBE biodegradation with or without bioaugmentation at an MTBE contaminated aquifer in California sparged with oxygen. Mackay et al. (2002) and Wilson et al. (2002) showed aerobic degradation of MTBE in two types of field experiments involving oxygen release into an MTBE contaminated aquifer at VAFB. Martienssen et al. (2006) reported biodegradation of MTBE in an aquifer in Germany under what they termed “microaerobic” conditions (dissolved oxygen under 0.4 mg/L) that occurred naturally. Thornton et al. (2011) discussed lab experiments with sediments from an MTBE-contaminated chalk aquifer in the UK which showed evidence of “ubiquitous potential for aerobic MTBE degradation in the aquifer”, concluding that significant aerobic MTBE biodegradation could occur under the low oxygen concentrations in the reactive fringes of such plumes.

## 3. Description of the research site and relevant prior experimental results

VAFB Site 60 (Fig. 1), was described in detail by Mackay et al. (2006) and references therein. In brief, consultants to VAFB estimated that 2165 liters (572 gallons) of unleaded gasoline containing MTBE was released to the subsurface on 20 December 1994 (SPGC, 1995). By February 1995 the underground storage tanks, associated piping, and approximately 570 cubic meters of soil were removed and the excavated area was backfilled with clean coarse aggregates; no special efforts were made to remove spilled gasoline at that time, nor were any source remediation efforts other than excavation undertaken then or later. Based on extensive characterization efforts (e.g. Mackay et al., 2006) it is known that upgradient and downgradient of the original backfill, several thin, horizontal, sandy layers exist within 8 meters of ground surface (Fig. 2). The depth of the original backfill extended to approximately the bottom of the S3 sand (Mackay et al., 2006). Thus, water and contaminants from the original backfill around the tanks migrated into the S3 aquifer, which was always fully saturated; the approximate extent of the contaminant plume in 2004 is illustrated in Fig. 1 and discussed in more detail later. After the 1995 excavation, a portion of the original gasoline spill and associated dissolved contamination was still present in the subsurface, some likely diffused into low permeability layers adjacent to the S3 aquifer. Within the research study area (i.e., extending 60 m downgradient of the source area) the S3 aquifer (~1 m thick and adjacent to overlying and underlying silty layers) is the primary pathway for downgradient advection of water and contaminants from the backfill. To reduce or eliminate residual source mass, consultants to VAFB conducted additional excavations in the source area in September 2007 and November 2008 (Figs. 1 and 2). The 2007 excavation illustrated in Fig. 2b extended to a depth approximately equal to the top of the S3 aquifer. This excavation is of most relevance to this modeling study since it significantly reduced or eliminated the residual source mass along the flowline through the area originally impacted directly by the fuel spill.



**Fig. 1.** Map of study area at Site 60, Vandenberg Air Force Base (VAFB), California, illustrating the location of former underground storage tanks (USTs), areas of three excavations in 1995, 2007, and 2008, the approximate location of the MTBE/TBA plume in 2004, and monitoring well transects perpendicular to the direction of groundwater flow. The vertical cross section AA' is the focus of this 2D modeling study and is presented in Fig. 2. Monitoring wells south of Monroe Street were removed after the 2007 excavation.

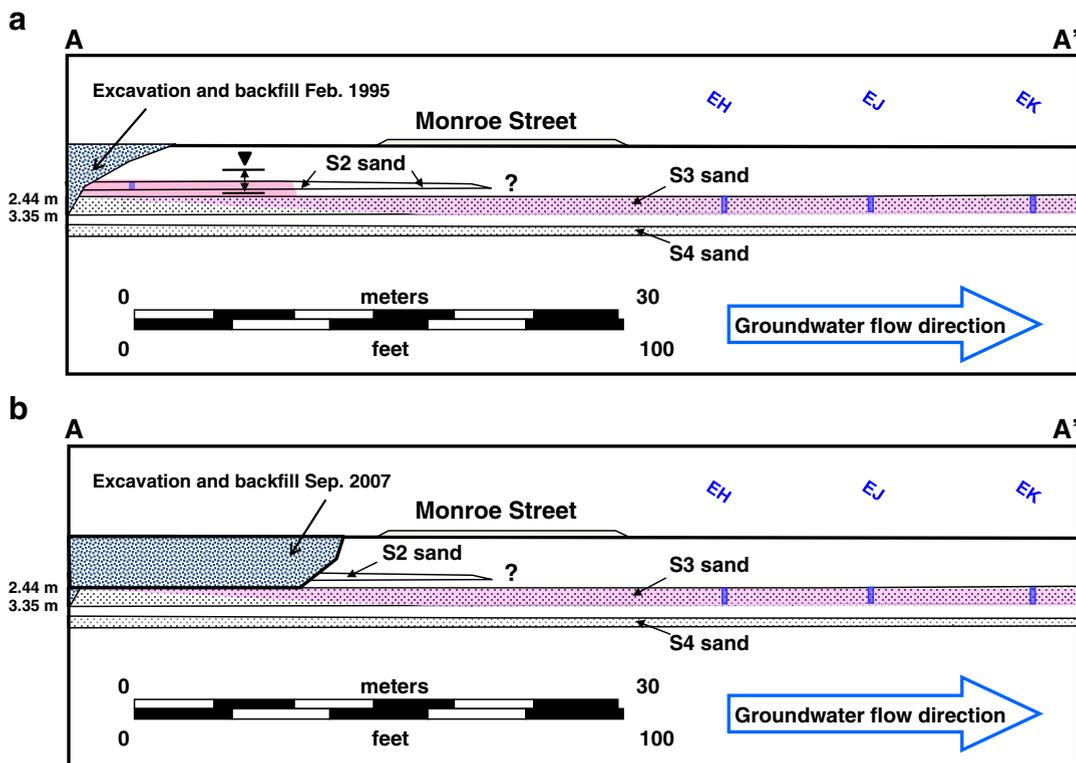
The predominant dissolved electron acceptor within the S3 aquifer was sulfate, for which the mean concentration was 96 mg/L during 2004–05 (Mackay et al., 2006). Dissolved oxygen has never been detected within the S3 aquifer, except as a result of engineered addition. Oxygen is likely to be transported by diffusion through the thin unsaturated zone to the capillary fringe, located approximately 2 m below ground surface. A portion of the land surface at the site (south of Monroe St, Fig. 1) is covered by pavement, which may have affected diffusion rates of atmospheric oxygen through the vadose zone, as discussed more later.

Based on extensive sampling of the monitoring well network, comprised of several transects of short interval monitoring wells screened in the S3 aquifer (Fig. 1), and monitoring of the plume much further along the flow path by VAFB consultants (data not shown), the predominant contaminant along the centerline of the plume emanating from the former source area from 1995 through 2004 was MTBE. However a narrow, short, and very low concentration (<0.2 mg/L) plume of TBA was detected in the S3 aquifer in 2003, perhaps due to in situ transformation of MTBE under highly reduced conditions caused by reduction of other petroleum hydrocarbons producing areas of methanogenic conditions (Mackay et al., 2007). It is

also possible that some of the TBA detected in 2003 was in the original gasoline spill, and slowly leaching from the source area.

Other hydrocarbon compounds previously present (such as benzene, toluene, ethylbenzene, and xylenes, BTEX) were at very low concentrations; gasoline-range total petroleum hydrocarbons (TPHg) were less than 0.04 mg/L within 50 meters of the backfill in 2004 (Mackay et al., 2006). After 2004, the predominant contaminant within the aquifer was TBA. Fig. 3 illustrates this shift by presenting plume maps covering 8 sampling times from September 2004 through June 2006.

The most likely cause of the shift in plume composition was in situ transformation of MTBE to TBA stimulated by injection of ethanol into the aquifer starting in 2004 (Mackay et al., 2007). During that experiment groundwater was extracted, spiked with ethanol to an average concentration of about 500 mg/L and reinjected (200 mL/min) for about 9 months (13 May 2004 to 20 February 2005) in the ER transect shown in Fig. 1 to evaluate the effect of ethanol release on the fate of pre-existing MTBE contamination. Even after cessation of ethanol addition, TBA continued to be the dominant volatile organic carbon (VOC) in what had formerly been an MTBE-dominated plume, suggesting the transformation of



**Fig. 2.** Cross-section of subsurface in the experimental zone along the historic centerline of the MTBE/TBA plume (Section AA' in Fig. 1), showing the S2, S3 and S4 sands (stippled) interbedded with less permeable silt layers (no fill) illustrating the excavation and backfill location in (a) 1995 and (b) 2007. Bold vertical lines indicate the approximate positions of well screens in the noted transects. Pink shading above the S3 aquifer denotes original source contamination, whereas pink shading within the S3 denotes dissolved contamination migrating from the source area. The S3 (within 2.44–3.35 meters below ground surface) sand layer has been identified as the main pathway for downgradient transport of contamination.

MTBE to TBA was initiated somehow by ethanol addition but persisted even after ethanol addition ceased (Fig. 3). A later experiment included injection of TBA spiked groundwater into wells between the EA and ER wells in Fig. 1 at an average concentration of 2.8 mg/L from 22 September 2005 to 15 March 2006 (unpublished results).

Based on a mean aquifer groundwater flow rate of 0.46 m/day and neglecting diffusion and dispersion, the MTBE and TBA from the original spill or the experiments should have been completely flushed to beyond the EH transect by about 76 days after the September 2007 excavation. However, monitoring in 2010 showed that the MTBE/TBA plume still persisted suggesting that a study evaluating the roles of diffusion from adjacent silt layers and biodegradation reactions would be illuminating.

## 4. Model description

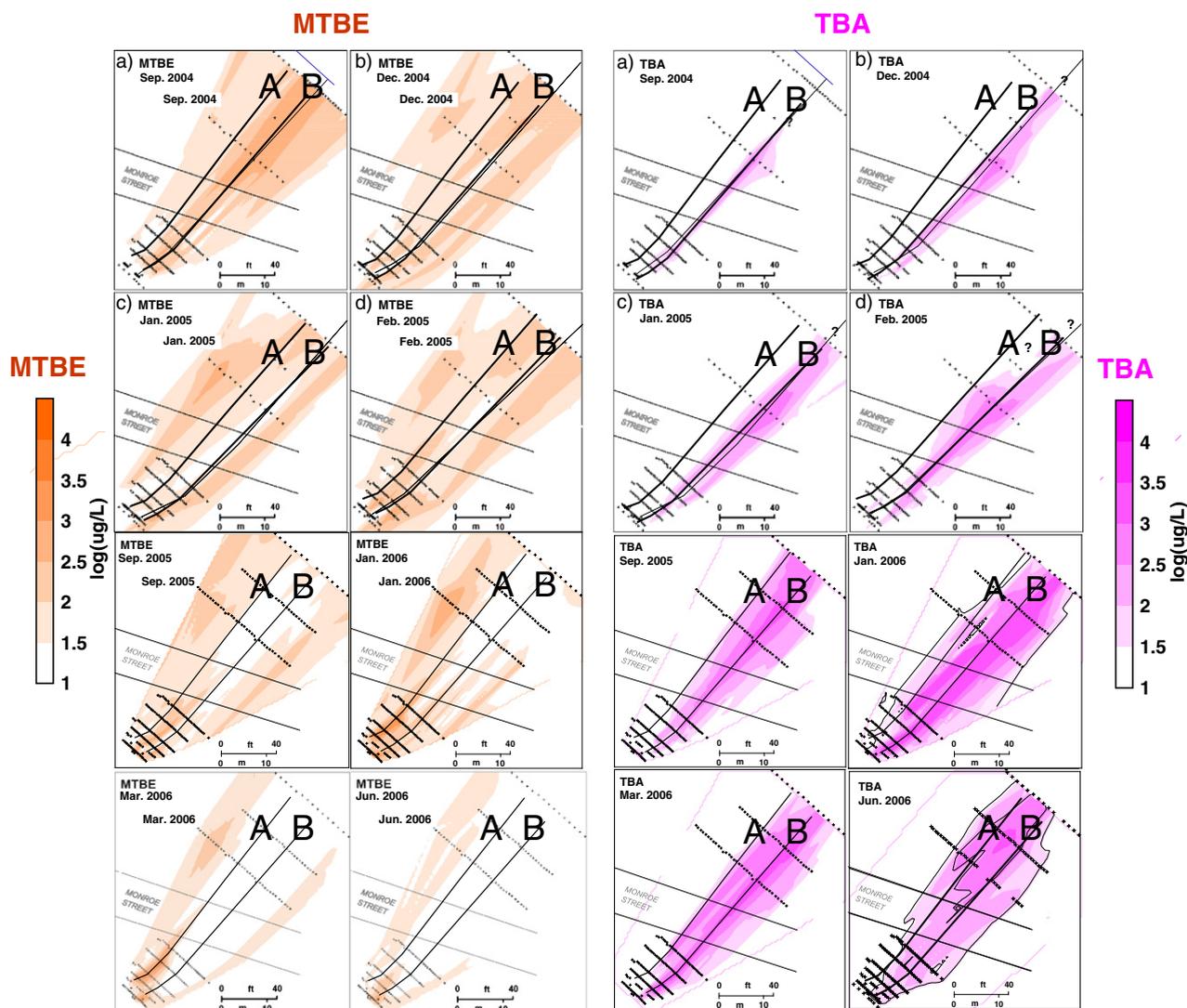
### 4.1. Conceptual model

The model domain is two-dimensional (2D) in vertical cross section and simulations focus on evolution of contamination along the centerline of the plume, which is considered reasonable given the large plume width compared to the S3 aquifer thickness. Comparison of simulations in two and three dimensions showed that the results for the centerline, the focus in this paper, were not different when a 10-meter wide

source is used, consistent with site monitoring data (e.g. plume width in Fig. 3 just upgradient of Monroe Street). Therefore in this paper only 2D results are presented, focusing attention on processes affecting vertical distribution of contaminants.

The model domain is limited to saturated media only (Fig. 4) and consists of four horizontal layers; from top to bottom these are an upper silty aquitard, the S3 aquifer, a lower silty aquitard, and the S4 aquifer. The model domain is 150 m along the direction of groundwater flow ( $x$ ) and 2.9 m in the vertical direction ( $z$ ), with grid discretizations of 0.5 m and 0.05 m in  $x$  and  $z$  directions, respectively. The tight grid discretization in the vertical dimension was applied to represent transverse vertical dispersion in the S3 aquifer and diffusion processes in the adjacent silt layers. The simulation time was 20 years, with average transport time steps of 0.1 days. Groundwater flow was assumed to be steady state with no sources or sinks and a constant hydraulic gradient of 0.015 [–] based on field measurements of hydraulic head in the area shown in Fig. 1. Since this modeling study focuses on long term plume behavior, effects of seasonal water table fluctuations and groundwater recharge were ignored.

The MTBE source was idealized as a vertical line immediately downgradient of the 2007 excavation (Fig. 4). In the model MTBE biotransforms to TBA under anaerobic conditions, and both MTBE and TBA degrade under aerobic conditions that are believed to exist in the shallow part of the system. These assumptions bear on the kinetic expressions for the biodegradation



**Fig. 3.** Concentration contours of MTBE and TBA at the site based on eight monitoring snapshots from September 2004 through June 2006. Note that over time the plume shifts from predominantly MTBE to predominantly TBA. Along the centerline of the plume (line denoted B, and the focus of this modeling study) the shift from MTBE to TBA occurred starting in September 2004. (Ethanol injection duration: 13 May 2004 to 20 February 2005).

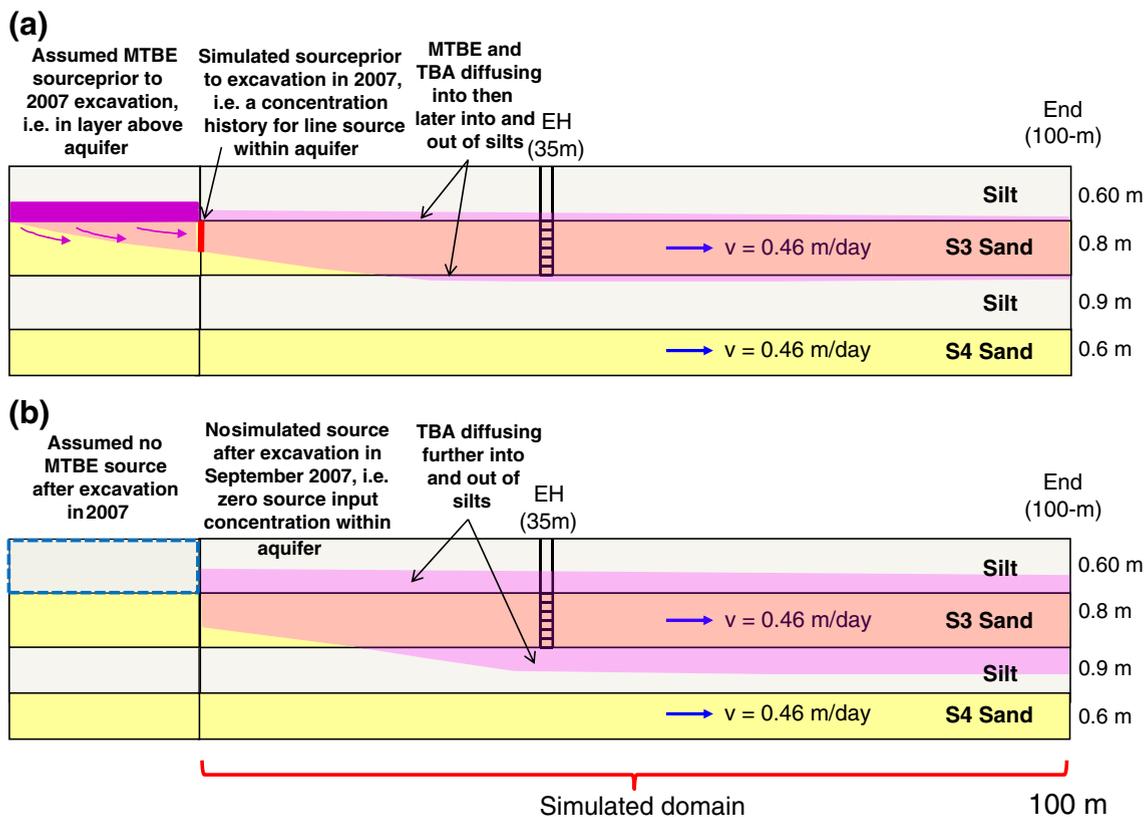
reactions that are described below. Sorption of MTBE and TBA was assumed to be negligible, consistent with analysis of the organic carbon content of the aquifer media (Mackay et al., 2006, Supporting Information) and the silty layers (unpublished data). This assumption is consistent with prior conclusions by others (Moyer and Kosteci, 2003; Zeeb and Wiedemeier, 2007). Volatilization and loss of MTBE and TBA by diffusion through the vadose zone were also assumed to be insignificant, consistent with the conclusions of Lahvis et al. (2004), who showed that appreciable volatilization of MTBE from the fully saturated zone downgradient from source areas is not likely. This results in part from the relatively low dimensionless Henry's Law constants of 0.018 and  $4.8 \times 10^{-4}$  for MTBE and TBA, respectively (ITRC, 2005; NSTC, 1997). Other model parameters are summarized in Table 1.

The model used two forms of MTBE-TBA anaerobic transformation kinetics: 1) first order reaction kinetics with rate inferred from the ethanol injection experiment at the VAFB

site (Mackay et al., 2007), and 2) Michaelis-Menten kinetics derived by manual calibration of the model to the observations in this work, as discussed later. In both efforts, the kinetics were assumed to apply to any anaerobic zone within the modeled area after September 2004. Prior to that time, the anaerobic reaction rate was set to zero.

Field and laboratory microcosm studies summarized earlier confirm that native organisms at the VAFB site are capable of degrading MTBE and TBA if aerobic conditions are established and maintained in situ. In the model discussed herein, the aerobic reaction zone in the model was arbitrarily assumed to be 2-cm thick and the aerobic reaction rates of MTBE and TBA are assumed to be the same and equal to the apparent first-order degradation rate constant in a series of field experiments involving release of oxygen to the S3 aquifer (Wilson et al., 2002).

Reformulated gasoline contains many different hydrocarbons, the interactions, transport and reactions of which affect



**Fig. 4.** Conceptual model considered in this study: (a) from 1994 spill to 2007 excavation, (b) after 2007 excavation. The location of the hypothesized line source (vertical red line) is at the downgradient extent of the 2007 excavation (Fig. 2). The model domain is two-dimensional and consists of saturated zone only. The figure is not to scale to allow clearer presentation of concepts. Pink shading denotes contamination as in Fig. 2. MTBE from the source diffuses into adjacent silt layers from the S3 aquifer, as illustrated here, but gradually reaches the top of the upper silt and the S4 sand aquifer beneath the bottom silt based on the simulation results. EH is the monitoring well transect 35 meters downgradient of the source (also shown in Fig. 1).

exposures to contamination from leaking underground storage tanks (Weaver et al., 2010). However, early monitoring by consultants to VAFB did not detect BTEX more than a few 10s of meters from the source. Also, the concentration of organic hydrocarbons other than MTBE/TBA was very low by 2004 (TPHg < 0.04 mg/L; Mackay et al., 2006), consistent with the rapid biodegradation of experimentally injected BTEX species in 2004–05 (Mackay et al., 2006). Thus, this study only considers MTBE and TBA and ignores the effect of other organic compounds present in the released gasoline on the fate and transport of the MTBE/TBA plume.

#### 4.2. Contaminant source

It is expected that the MTBE source was either floating gasoline, or dissolved constituents arising from it, in the original backfill around the tanks or the backfill later added after the 1995 excavation of tanks and piping. To enter the S3 aquifer from the zone of water table fluctuation in the backfill, dissolved contamination had to migrate downward, suggesting that the dissolved plume would have been restricted to the upper portion of the S3 aquifer. Thus 50% was arbitrarily selected as the penetration of the line source into the S3 aquifer (Fig. 4a). Further it was assumed that the 2007 excavation

removed all remaining contaminant mass, and thus that the source dropped to zero at that time (Fig. 4b).

The probable history of MTBE concentrations along the plume centerline at its source was estimated using available information including published details about the original spill, details of excavations and monitoring by VAFB consultants, and our own characterization and monitoring data. Although there are no monitoring data defining the initial MTBE concentrations dissolved in groundwater immediately after the spill, Wilson et al. (2005) summarized maximum MTBE concentrations detected in studies of 13 MTBE plumes in California (Los Angeles and Orange Counties), Texas and Kansas indicating maximum values detected on the order of 500 mg/L. In 2004, 10 years after the spill, monitoring of the S2 sand, a localized, thin sand layer within the depth of water table fluctuation, in the source area south of Monroe Street (Figs. 1 and 2) indicated a maximum MTBE concentration of 72 mg/L, suggesting that the maximum concentration of MTBE dissolved in water immediately after the spill would have been considerably higher. For modeling here, an initial MTBE concentration of 400 mg/L was assumed, within the range of estimates by Wilson et al. (2005). This value is about an order of magnitude lower than the theoretical effective solubility of MTBE (approximately 4300 mg/L) immediately

**Table 1**

Model parameters. See text for discussion, assumed locations and time periods for reactions, etc.

Parameter	Value	Source
<i>Hydraulic parameters</i>		
Aquifer horizontal hydraulic conductivity	10.4 m/d	(Mackay et al., 2006)
Silt layers horizontal hydraulic conductivity	$5 \times 10^{-2}$ m/d	site characterization*
Horizontal to vertical hydraulic conductivity ratio	10	assumed
Hydraulic gradient ( <i>i</i> )	0.015	(Mackay et al., 2006)
Aquifer effective porosity	0.34	(Mackay et al., 2006)
Silt layers effective porosity	0.4	assumed
<i>Transport parameters</i>		
Retardation factor ( <i>R</i> )	1	(Mackay et al., 2006)
Longitudinal dispersivity ( $\alpha_L$ )	0.1 m	Rasa, unpublished results**
Transverse vertical dispersivity ( $\alpha_V$ )	$5 \times 10^{-4}$ m	Rasa, unpublished results**
TBA aqueous diffusion coefficient ( $D_{aq}$ )	$6.70 \times 10^{-5}$ m <sup>2</sup> /d	(EPA, 2011)
Tortuosity ( $\tau$ )	0.40	(Parker et al., 2004)
<i>Degradation parameters</i>		
MTBE to TBA Yield coefficient ( $\beta$ )	1.19	Eq. (5)
<i>Aerobic degradation of MTBE and TBA</i>		
1st order rate constant ( $k_{aer}$ )	$5.3 \text{ d}^{-1}$	(Wilson et al., 2002)
<i>Anaerobic MTBE to TBA transformation</i>		
Scenario 1: First-order		
1st order rate constant ( $k_{anaer}$ )	$0.046 \text{ d}^{-1}$	(Mackay et al., 2007)
Scenario 2: Michaelis-Menten		
Maximum substrate utilization rate ( $V_{max}$ )	$1.015 \times 10^{-2}$ mg/L/d	calibrated***
Half saturation concentration of MTBE ( $K_S$ )	$10^{-3}$ mg/L	calibrated***

\* estimated based on site characterization tests and also literature (Fetter, 2001; Freeze and Cherry, 1979).

\*\* longitudinal and vertical dispersivity estimated by inverse modeling of long term tracer study at the site.

\*\*\*method of calibration discussed in the text.

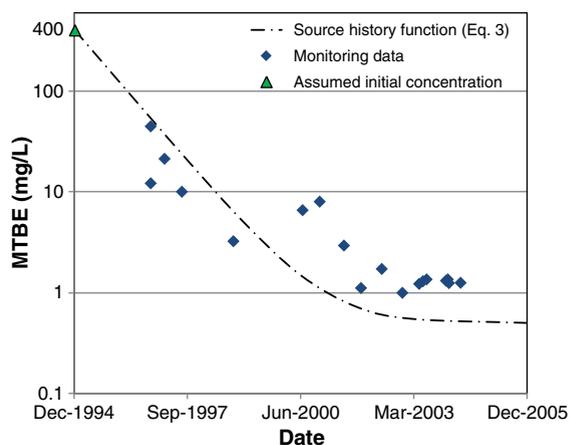
adjacent to a gasoline phase containing 10% MTBE (pure phase solubility 43,000 mg/L; Zeeb and Wiedemeier, 2007); dilution by a factor of ten by uncontaminated water would not be surprising in typically screened monitoring wells (5–10 ft) such as sampled at the sites reviewed by Wilson et al. (2005) or for a well screened across the S3 aquifer at this site. Wilson et al. (2005) also noted that decreases in source area MTBE groundwater concentrations generally followed an exponential decay curve at the sites they studied, with apparent half lives on the order of 1–3 years for six sites studied in detail. Thus, a decaying first-order source function was assumed for this study, adjusted to match VAFB monitoring data (Fig. 5). Starting from an initial MTBE concentration of 400 mg/L, the source centerline concentrations were assumed to decrease exponentially with a decay rate of  $1.1 \text{ year}^{-1}$ , but reaching an asymptotic value of 0.5 mg/L; this combination of assumptions fit the monitoring data well (Fig. 5). Note that it was also assumed that the September 2007 excavation was completely successful in removing 100% of the residual MTBE mass within its reach. Since the model idealized the MTBE source as a line just downgradient of the 2007 excavation, after September 2007 the MTBE source concentration was assumed to be zero.

TBA was assumed to be absent in groundwater migrating from the source area, i.e. upgradient of the hypothetical line source except during a controlled experiment from September 2005 to March 2006 when groundwater spiked with TBA was injected into the S3 aquifer (unpublished results). During this time interval, TBA concentration at the location of the hypothesized line source was specified to be the experimental injection concentration of 2.8 mg/L across the full S3 aquifer thickness. The resulting

mathematical source functions used for MTBE and TBA were:

$$C_1(x, z, t) = \begin{cases} 2(400 \exp(-0.003t) + 0.5) & 20 \text{ Dec } 1994 \leq t \leq 15 \text{ Dec } 2007 \\ 0 & \text{otherwise} \end{cases} \quad (1a)$$

$$C_2(x, z, t) = \begin{cases} 2.8 & 22 \text{ Sep } 2005 \leq t \leq 15 \text{ Mar } 2006 \\ 0 & \text{otherwise} \end{cases} \quad (1b)$$



**Fig. 5.** MTBE monitoring data (diamonds) by VAFB and UC Davis from fully screened monitoring wells at or near the source location. For model simulations an initial concentration of 400 mg/L was assumed and site monitoring data were used to estimate a mathematical form (dashed line) for source centerline concentrations averaged over the full aquifer thickness.

where  $t$  is time [days],  $C_1$  are  $C_2$  MTBE and TBA concentrations [mg/L] respectively. In both cases the source function was at  $x = 15$  m (Fig. 4). The source vertical interval was  $z = 1.9$ – $2.3$  and  $z = 1.5$ – $2.3$  m for MTBE and TBA, respectively. To conserve mass, the source (Eq. 1a) is specified at twice the fitted function (Fig. 5) because the model source spans only half of the S3 aquifer while the fitted data are from wells that span the full aquifer. More complicated dissolution functions were not employed in this work because the distribution of non-aqueous phase liquid (NAPL) was unknown whereas actual site groundwater monitoring data were available. The simple approach described above was chosen to focus on examining the roles of diffusion and degradation reactions on the fates of MTBE and TBA.

#### 4.3. Governing equations

In this study the groundwater flow system is assumed at steady-state with no sources/sinks. The two-dimensional advection-dispersion equation of reactive species in a unidirectional flow field is described in Eq. (2):

$$\frac{\partial C_i}{\partial t} = D_x \frac{\partial^2 C_i}{\partial x^2} + D_z \frac{\partial^2 C_i}{\partial z^2} - v \frac{\partial C_i}{\partial x} + \sum R_i \quad i = 1, 2 \quad (2)$$

where,  $v$  is groundwater velocity [ $LT^{-1}$ ],  $C_i$  is dissolved concentration of the  $i_{th}$  species (i.e., MTBE and TBA) [ $ML^{-3}$ ],  $R_i$  is the net reaction rate for the  $i_{th}$  species [ $ML^{-3}T^{-1}$ ].  $D_x$  and  $D_z$  are longitudinal and vertical hydrodynamic dispersion coefficients [ $L^2T^{-1}$ ], respectively, where  $D_x = \alpha_L v + \tau D_m$  and  $D_z = \alpha_V v + \tau D_m$  and  $\alpha_L$  is the longitudinal dispersivity [L],  $D_m$  is the aqueous molecular diffusion coefficient [ $L^2T^{-1}$ ],  $\alpha_V$  is the vertical transverse dispersivity [L], and  $\tau$  is tortuosity [–] (Scheidtger, 1961). This paper studies reactive transport of two solutes (MTBE and TBA). All reactions that occur in the aqueous or solid phase are included in the equation by the  $R_i$  term in Eq. (2). For this two-dimensional simulation dispersivities,  $\alpha_L$  and  $\alpha_V$ , are assumed uniform in space. Different values for porosity and hydraulic conductivity were used in the sand and the silts based on site specific analyses or literature (Table 1).

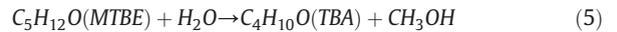
Two different kinetics cases were examined for anaerobic transformation of MTBE to TBA: first-order kinetics, as assumed in past studies (Eq. 3) and Michaelis-Menten kinetics (Eq. 4):

$$\frac{dC_1}{dt} = -k_{anaer} C_1 \quad (3)$$

$$\frac{dC_1}{dt} = -V_{max} \frac{C_1}{C_1 + K_s} \quad (4)$$

where  $C_1$  is MTBE concentration [ $ML^{-3}$ ],  $k_{anaer}$  is the anaerobic degradation first-order rate constant [ $T^{-1}$ ],  $V_{max}$  is the maximum substrate utilization rate [ $ML^{-3}T^{-1}$ ], and  $K_s$  is the half-saturation in concentration of MTBE [ $ML^{-3}$ ]. First-order kinetics were applied with the rate constant estimated by Mackay et al. (2007) for anaerobic transformation of MTBE to TBA. The TBA production rate is  $\frac{dC_2}{dt} = -\frac{1}{\beta} \frac{dC_1}{dt}$ , where  $C_2$  is TBA concentration [ $ML^{-3}$ ] and  $\beta$  is the mass ratio of MTBE

consumed to TBA produced [–] calculated to be 1.19 assuming the following reaction stoichiometry:



The model assumes no anaerobic degradation of TBA, consistent with field results at VAFB (Mackay et al., 2007; McKelvie et al., 2007).

Eq. (6) shows the first-order reactions assumed in the model for aerobic degradation of both MTBE and TBA:

$$\frac{dC_i}{dt} = -k_{aer} C_i \quad (6)$$

where  $k_{aer}$  is the first-order aerobic rate constant [ $T^{-1}$ ] and  $C_i$  refers to concentrations of MTBE and TBA [ $ML^{-3}$ ]. Although field estimates of TBA aerobic degradation rate are not available, early lab work suggests TBA aerobically degrades as fast or perhaps faster than MTBE (Wilson et al., 2002), so  $k_{aer}$  is assumed to be  $5.3 \text{ day}^{-1}$  for both in this work. These aerobic reactions are assumed to occur only in a thin vertical interval below the upper boundary of the model in the silt overlying the S3 aquifer. The total reaction rate for MTBE and TBA ( $\sum R_i$ ) is then the sum of the anaerobic and aerobic degradation rates.

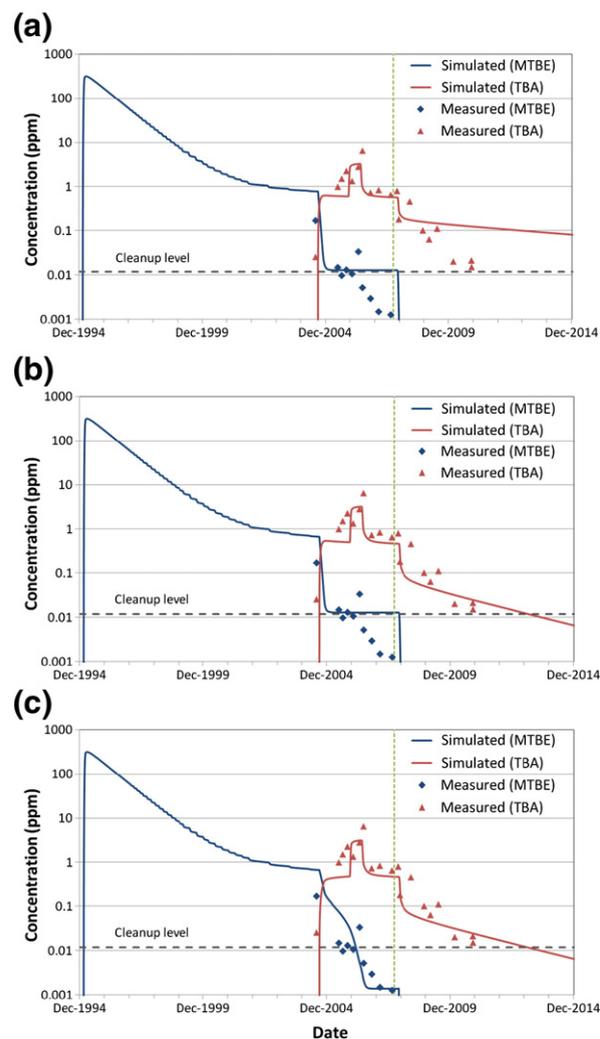
#### 4.4. Numerical solution

Groundwater flow was solved using the U.S. Geological Survey MODFLOW model (Harbaugh et al., 2000) with PCG2 solver (Hill, 1990). A head change value of 0.1 mm was used as the convergence criterion in MODFLOW when solving for groundwater flow. MTBE and TBA reactive transport was numerically solved using the RT3D v2.5 model (Clement et al., 1998) with a user-defined reaction module (Eqs. 3, 4, and 6). A third-order total-variation-diminishing (TVD) scheme (Harten, 1983; Harten, 1997), which tends to minimize numerical dispersion and artificial oscillation, was used to solve the advection term. The standard explicit method was used to solve the dispersion term, and the automatic switching Gear-stiff/non-stiff solver was used to solve the reaction term of the transport equation. Absolute and relative tolerance parameter values of  $10^{-10}$  and  $10^{-9}$  were used, respectively, to control the convergence of the reactive transport model. The absolute and relative tolerance parameters are usually needed for the reaction solver to determine how accurate the solution for each of the species concentrations must be and there are recommendations in RT3D manual (Clement et al., 1998) on how to set these two values. The RT3D v2.5 reactive transport model used in this study is built based on v3.50 of the MT3DMS code (Zheng and Wang, 1999) in which only one uniform diffusion coefficient can be specified for the entire model layer, and thus all solute components (MTBE and TBA) are assumed to have the same diffusion coefficient. This simplification may have slightly affected the simulation results since the diffusion coefficient of MTBE is about 15% lower than TBA (EPA, 2011).

## 5. Results

### 5.1. Anaerobic transformation of MTBE to TBA

Fig. 6a shows the simulation results for a scenario in which the only assumed reaction was first-order anaerobic transformation. The solid lines in the figure depict simulated concentrations of MTBE and TBA over time averaged vertically over the S3 aquifer layer at the EH transect (35 m downgradient of the source as shown in Fig. 4). The symbols are monitoring data from the EH well in the plume centerline, which was



**Fig. 6.** Comparison of field-measured MTBE and TBA concentrations at the EH transect: (a) the entire model domain is assumed anaerobic and thus simulations include only anaerobic transformation of MTBE to TBA using first-order kinetics, (b) aerobic reactions are assumed in the top 2 cm of the model domain; both aerobic and anaerobic reactions are assumed to be first-order, and (c) aerobic reactions are assumed in the top 2 cm of the model domain (first-order) while Michaelis-Menten kinetics is assumed for the anaerobic transformations of MTBE to TBA. The vertical dashed line marks the time of source excavation in 2007. The horizontal dashed line is California MTBE and TBA cleanup levels for leaking underground storage tank sites as of 2005 at 13 and 12 ppb, respectively. Ethanol injection duration was 13 May 2004 to 20 February 2005, whereas TBA injection duration was 22 September 2005 to 15 March 2006.

screened across the S3 aquifer. As evident in the figure, this simulation does not match the MTBE data in general or the TBA results after 2007. Sensitivity analysis indicated that a different first-order rate constant would change the initial plateau value in simulated MTBE concentration that occurs in 2005 (Fig. 6a) but would not provide a better fit to the fast decline observed in MTBE concentration thereafter.

Fig. 7a and b present simulations of vertical concentration profiles through the modeled domain at the EH transect. At early time (December 1995), diffusion of MTBE into the upper and lower silt in the model is evident with over 0.5 m diffusive penetration. At later times, the simulation suggests that MTBE and TBA penetrate through both silt layers. The model indicates that MTBE and TBA may have diffused through the lower silt and then advected downgradient in the S4 sand. It is not possible to confirm this via field data as there was no monitoring of the S4 sand downgradient of Monroe Street, but it may be of practical interest that the modeled concentrations within the S4 sand are relatively low ( $< 0.1$  mg/L) even immediately adjacent to the silt. The modeled diffusive flux of MTBE plus TBA from the aquitard to S4 sand was about  $8 \times 10^{-4}$  mg/m<sup>2</sup>/day at EH location from 2004 to 2010. Also evident in the lower silt is that at later times both MTBE and TBA diffuse in two directions: back (upward) toward the S3 aquifer and downward toward the S4 aquifer owing to declining concentrations in the S3 aquifer (Fig. 7a and b).

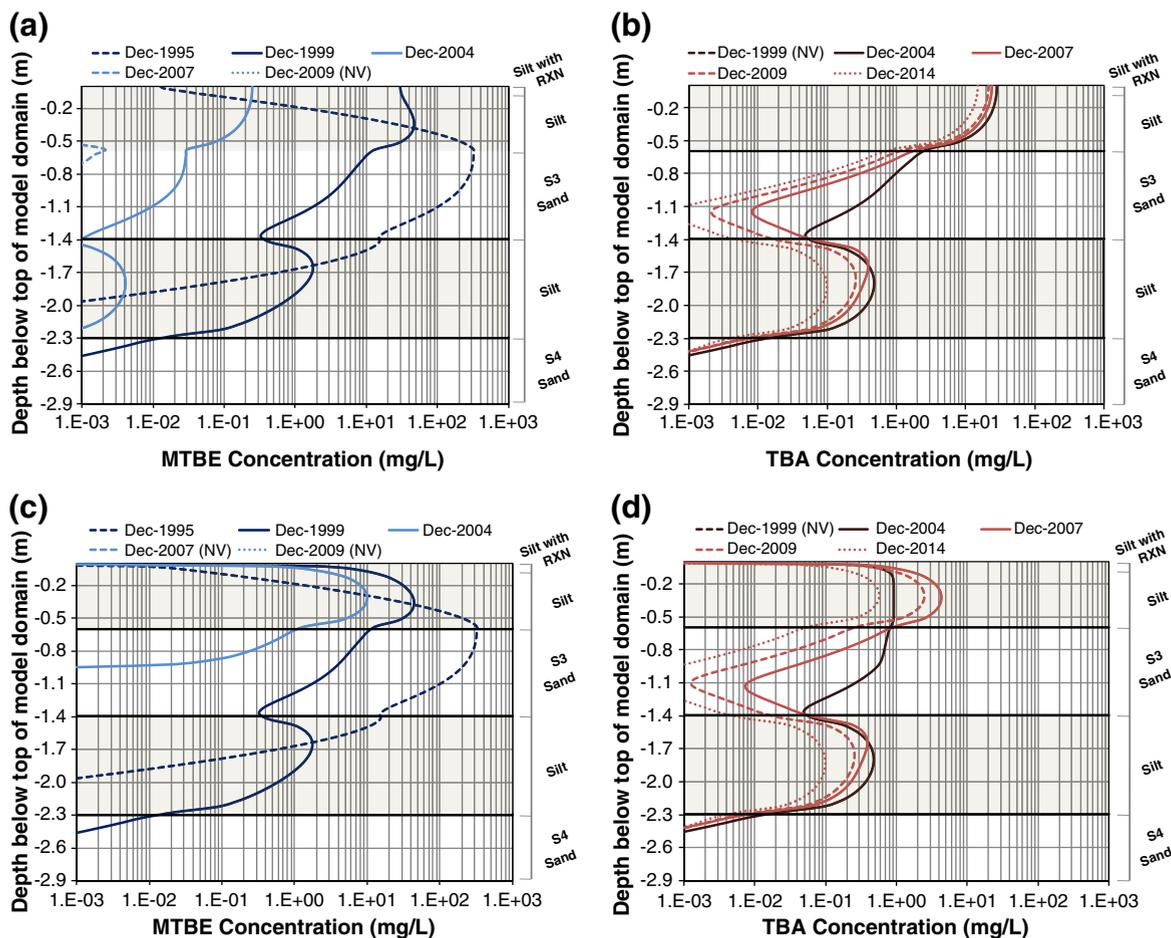
At the upper boundary, the model shows MTBE and TBA reaching the assumed top of the saturated zone within 4 years of the spill, with MTBE concentrations as high as 20 mg/L. However, this is an artifact of the model boundary condition and is not physically reasonable, since the MTBE or TBA that reached that location would migrate beyond it, e.g. by volatilization into and diffusion within soil gas, and/or degrade under the aerobic conditions that may be sustained there, as discussed in the next section.

### 5.2. Anaerobic transformation of MTBE and aerobic degradation of MTBE and TBA

It is hypothesized that oxygen penetration could exceed the oxygen demand at the top of the upper silt layer, creating a thin aerobic zone there. To evaluate this hypothesis, the flux of oxygen from ground surface to the top of the saturated zone was estimated, assuming complete utilization of all oxygen at the top of the saturated zone. The flux of oxygen from ground surface was compared to the flux required for aerobic degradation of MTBE and TBA that was predicted to reach that interface. In the atmosphere, the concentration of oxygen is 273.3 mg per liter of air (oxygen density of 1.308 kg/m<sup>3</sup> at 25 °C and oxygen content of 20.9%). If it is assumed that the oxygen concentration at the water table is zero, due to degradation of MTBE and TBA, the oxygen concentration gradient ( $\frac{dC_{O_2}}{dz}$ ) through the unsaturated zone (2 m) would be  $1.37 \times 10^5$  mg/m<sup>4</sup>. The effective diffusion coefficient of oxygen can be calculated using Eq. (7) (Amos et al., 2005; Chaplin et al., 2002):

$$D_{eff, O_2} = D_m \theta \tau \quad (7)$$

Where  $D_{eff, O_2}$  is the oxygen gas effective diffusion coefficient [L<sup>2</sup>T<sup>-1</sup>],  $D_m$  is the binary gas-phase diffusion coefficient



**Fig. 7.** Simulated vertical profiles (dashed or solid lines) of porewater concentrations in the various layers of the modeled domain at the EH transect: (a) and (b) MTBE and TBA profiles, respectively, with only anaerobic transformation assumed in the model; (c) and (d) MTBE and TBA profiles, respectively, when first-order aerobic degradation of MTBE and TBA in top two centimeters of the modeled domain and anaerobic transformation of MTBE to TBA (using Michaelis-Menten kinetics) were assumed. Relatively impermeable silt layers are shaded. Note also that the model does not allow MTBE to TBA transformation before September 2004, so frame (b) and (d) present no simulation results for 1995 and 1999 since no TBA is present in the simulation at these times. (NV = not visible at the current graph scale). RXN refers to the aerobic reaction assumed to occur in a portion of the silt at the top of the saturated zone.

[ $L^2T^{-1}$ ],  $\theta$  is the air-filled porosity [-], and  $\tau$  is tortuosity [-]. Fuller et al. (1966) suggests a  $D_m$  value of  $0.565 \text{ cm}^2/\text{sec}$  at  $24^\circ\text{C}$  for oxygen in air. Using Eq. (7) provides an effective diffusion coefficient of  $0.781 \text{ m}^2/\text{d}$  and thus a maximum diffusive flux of oxygen of  $1.07 \times 10^5 \text{ mg/m}^2/\text{d}$ .

Based on the concentrations simulated by the reactive transport model, estimates were made of the mass flux of MTBE and TBA entering the aerobic reaction zone and the required flux of oxygen to completely degrade this flux (Table 2). The estimated maximum oxygen diffusive flux is at least five orders of magnitude higher than that required for MTBE and TBA biodegradation indicating oxygen is not a limiting factor, and therefore there exists a potential for aerobic degradation of all MTBE and TBA at the top of the saturated zone. Indeed, MTBE and/or TBA degradation has occurred in every field test in which oxygen was introduced to previously anaerobic portions of the subsurface at the site, as discussed earlier.

Two scenarios were examined for simulations incorporating aerobic degradation at the upper boundary, namely

assuming first-order kinetics for aerobic biodegradation of MTBE and TBA and anaerobic transformations of MTBE to TBA (scenario 1) and Michaelis-Menten kinetics for anaerobic transformation and first-order kinetics for aerobic degradations (scenario 2). Simulation parameters are summarized in Table 1. To apply the Michaelis-Menten kinetics, manual calibrations of the parameters defined in Eq. (4) were made to provide the best fits to the measured data shown in Fig. 6c, which resulted in a  $V_{max}$  of  $6.2 \times 10^{-3} \text{ mg/L/d}$  and MTBE  $K_s$  of  $10^{-3} \text{ mg/L}$ .

Fig. 6b and c show the simulated MTBE and TBA concentrations vertically averaged across the S3 aquifer at 35 meters from the source when aerobic degradation was simulated in the top 2 cm of the modeled domain and two different kinetics were used for anaerobic transformation of MTBE to TBA. Comparing Fig. 7a and b with c and d, it is clear that aerobic degradation had a relatively insignificant impact on MTBE prior to December 2004, likely because MTBE had not yet reached the aerobic layer in significant concentrations and thus back diffusion of solutes from the upper silt had not yet

been significantly impacted by the aerobic reaction. After 2004, the aerobic reaction strongly affected the concentrations of MTBE within the aquifer, since during this time higher concentrations of MTBE existed in the silt than in the aquifer (Fig. 7c) and aerobic degradation significantly impacted the concentration gradient controlling back diffusion towards the aquifer. Fig. 6c shows that the resulting simulation using Michaelis-Menten kinetics fitted the observed trend of the MTBE data after December 2004 better than the first-order simulation. Finally the impact of aerobic degradation of TBA is most evident after the source excavation in 2007, because by then only TBA was back diffusing to the aquifer from the overlying silt.

Overall, these modeling results suggest that assuming a thin aerobic layer at the top of the overlying silt layer significantly impacted the modeled concentrations of MTBE and TBA over time in the S3 aquifer. The removal of contaminant mass near the upper boundary limited the build-up of solute mass within the overlying low permeability layer, which in turn limited the available mass for back diffusion to the S3 aquifer.

## 6. Discussion

The analysis in this paper makes a number of assumptions in order to test hypotheses regarding the long term fate and transport of MTBE and TBA at the study site. Using these assumptions, the model results indicate that the long term fate and transport of MTBE and TBA within a thin aquifer at the site were strongly influenced both by diffusion within adjacent silt layers and also by biodegradation processes. Diffusion caused contaminants to persist much longer within the aquifer following depletion / removal of the source than would be expected from rates of groundwater flow in the aquifer. However transformation or degradation reactions also acted to limit this persistence compared to expectations from diffusion processes alone.

The model of course does not provide perfect matches to the observations. Nevertheless, the matches are quite good and it is our opinion that the proposed assumptions are reasonable and consistent with field observations in prior studies at the site.

Our analysis indicates that aerobic degradation of MTBE and TBA at the vadose zone interface may have been an important sink for these contaminants. Although simulations reported here assumed the aerobic zone was 2-cm thick, essentially

**Table 2**

Calculated fluxes of MTBE and TBA reaching the top of the saturated zone and required flux of oxygen to achieve complete degradation, at different simulation times. Based on assumptions in the text, the estimated maximum diffusive flux of oxygen is  $1.07E+05$  mg/m<sup>2</sup>/d, which is at least five orders of magnitude higher than that required for biodegradation.

Time (years)	Diffusive flux of MTBE + TBA (mg/m <sup>2</sup> /day)	Oxygen flux required to biodegrade MTBE + TBA (mg/m <sup>2</sup> /day)
1	6.36E-03	1.74E-02
5	1.14E+00	3.11E+00
10	3.40E-01	9.28E-01
15	8.92E-02	2.43E-01
20	2.08E-02	5.66E-02

the same concentration history for the S3 aquifer is obtained by assuming a thicker reaction zone (20 cm) or specifying a zero-concentration boundary. This indicates that the exact model implementation of mass loss at the water table by aerobic degradation does not affect the conclusions.

Fig. 1 shows that a part of land surface at the site is covered by pavement. As discussed earlier, the estimated oxygen diffusive flux is several orders of magnitude higher than sufficient to support the aerobic degradation of MTBE and TBA. While pavement would certainly limit the local air permeability near ground surface, it is reasonable to assume that oxygen could reach the lower portion of the unsaturated zone beneath the pavement through non-vertical pathways through native media from unpaved surfaces, and therefore the effect of pavement surfacing was ignored in this study.

It is interesting to note that since most MTBE concentrations along the plume centerline at the site are significantly greater than  $K_s$  ( $10^{-3}$  mg/L), the Michaelis-Menten relation proposed in this study practically takes the form of zero-order kinetics (constant rate). Based on a laboratory microcosm study, Wilson et al. (2005) concluded that at concentrations below 2–4 mg/L the anaerobic biodegradation of MTBE would be adequately described as a first-order process. The reason plume monitoring data at VAFB suggest anaerobic kinetics closer to zero-order than first-order, even though the MTBE concentrations were low is uncertain. The ability of this study to constrain the correct kinetic expression is limited due to monitoring wells that span the full aquifer thickness and the associated modeling approach of averaging simulated concentration over the aquifer thickness. Mackay et al. (2007) reported that during the controlled release experiment at the VAFB site in 2004–05, MTBE was rapidly transformed to TBA under the methanogenic/acetogenic conditions induced by ethanol biodegradation. They reported a first-order fit to their monitoring data, but only to allow comparison to first-order rates reported by others. The experimental data were not sufficient to allow evaluation of the best rate model for the reaction in that work. More research is needed to evaluate the appropriate rate model for the anaerobic transformation of MTBE to TBA under a range of redox conditions such as would be expected downgradient of fuel spills over time.

Most modeling of back diffusion to date has addressed the fate of sorbing trichloroethylene (TCE). To our knowledge this is the first study involving detailed collection of field data with associated modeling incorporating both diffusion and reactions for fuel oxygenates such as MTBE and TBA. This study shows that long-term back-diffusion had significant effects in a thin aquifer after only a few years of leaching contaminants from the source. The results might also apply at enhanced remediation sites when reducing conditions are created artificially, possibly producing a long-term effect of persistence of metabolites diffusing from low permeability layers. An additional finding with potentially broad implications is that in a confining layer overlying a contaminated aquifer, the availability of atmospheric oxygen at the water table can have significant effects on long term mass loss rates of organic contaminant plumes such as MTBE and TBA.

## 7. Conclusions

The numerical model simulations suggest that after the original spill of MTBE-containing fuel, a portion of the MTBE

migrating with groundwater through the aquifer diffused into silts above and below the aquifer. As a result, back-diffusion of mass stored in silt layers above and below the aquifer caused elevated concentrations of MTBE and its anaerobic transformation product, TBA, to persist in the aquifer long after the original source was depleted or removed. Anaerobic transformation of MTBE to TBA within the aquifer and silts gradually led to TBA being the dominant contaminant in the aquifer and silts. Due to availability of oxygen at the top of the saturated silt, aerobic degradation of MTBE and TBA may have significantly affected concentrations of MTBE and TBA within the aquifer over time by limiting mass available for back diffusion to the aquifer from the upper silt. Overall, these degradation reactions reduced the long-term persistence of MTBE and TBA in the aquifer compared to expectations if only diffusive processes were active.

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