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Simulation of the effect of remediation on EDB and 1,2-DCA plumes at sites contaminated by leaded gasoline

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ABSTRACT

An analytical model is used to simulate the effects of partial source removal and plume remediation on ethylene dibromide (EDB) and 1,2-dichloroethane (1,2-DCA) plumes at contaminated underground storage tank (UST) sites. The risk posed by EDB, 1,2-DCA, and commingled gasoline hydrocarbons varies throughout the plume over time. Dissolution from the light nonaqueous phase liquid (LNAPL) determines the concentration of each contaminant near the source, but biological decay in the plume has a greater influence as distance downgradient from the source increases. For this reason, compounds that exceed regulatory standards near the source may not in downgradient plume zones. At UST sites, partial removal of a residual LNAPL source mass may serve as a stand alone remedial technique if dissolved concentrations in the source zone are within several orders of magnitude of the applicable government or remedial standards. This may be the case with 1,2-DCA; however, EDB is likely to be found at concentrations that are orders of magnitude higher than its low Maximum Contaminant Level (MCL) of 0.05 µg/L (micrograms per liter). For sites with significant EDB contamination, even when plume remediation is combined with source depletion, significant timeframes may be required to mitigate the impact of this compound. Benzene and MTBE are commonly the focus of remedial efforts at UST sites, but simulations presented here suggest that EDB, and to a lesser extent 1,2-DCA, could be the critical contaminants to consider in the remediation design process at many sites.

1. Introduction

Organic contaminants benzene, toluene, ethylbenzene, xylene (known collectively as BTEX), and methyl tert-butyl ether (MTBE), are commonly encountered in soil and groundwater at sites where gasoline spilled or leaked from underground storage tank (UST) systems. In the United States alone, an estimated 400,000 UST releases have been documented (Johnson et al., 2000). Though gasoline is a complex mixture of hundreds of hydrocarbons, historically the United States Environmental Protection Agency (USEPA) and state regulatory programs have required that only BTEX and a small number of other organic contaminants be analyzed during environmental investigations. Two components of leaded gasoline that have not received significant regulatory scrutiny to date are 1,2-dibromoethane (ethylene dibromide, or EDB), and 1,2-dichloroethane (1,2-DCA), which were added to leaded gasoline to prevent engine lead fouling (Falta, 2004). EDB is highly toxic, with the lowest federal MCL (0.05 µg/L) for any compound except dioxin (Falta, 2004). 1,2-DCA is also toxic and a suspected carcinogen, and has the same MCL as benzene (5.0 µg/L). Emerging evidence indicates that EDB and 1,2-DCA persist in groundwater, but to date, no significant research identifying the extent of EDB and 1,2-DCA contamination in groundwater at leaded gasoline release sites has been undertaken, nor is their behavior in the subsurface well understood (Falta, 2004). An in depth review of what is known about natural attenuation of EDB and 1,2-DCA is presented in Wilson et al. (2008).

Benzene has traditionally been considered the key risk driver at UST sites. Given that EDB and 1,2-DCA may also be

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present, commonly applied remedial techniques may not adequately address risk at these sites. To our knowledge, a systematic evaluation of remedial effects on EDB, 1,2-DCA, and hydrocarbon contaminants has not been conducted. The objective of this study is to evaluate the effects of partial LNAPL source removal and plume remediation on EDB, 1,2-DCA, benzene and MTBE at leaded gasoline UST sites. It is anticipated that the results of these simulations will be useful to remedial decision makers, who currently have little or no information about how these leaded gasoline additives might respond to remediation. Experience with natural attenuation as a remedy for plume management has shown that mathematical models can play an important role in selection of a remedy (Wiedemeier et al., 1999; NRC, 2000; Alvarez and Illman, 2006). In many cases, screening level simulations performed with analytical models such as BIOCHLOR (Aziz et al., 2000) or BIOSCREEN (Newell et al., 1996) are effective for demonstrating the applicability of natural attenuation as a remedy. This study uses an analytical model called REMChlor (Remediation Evaluation Model for Chlorinated Solvents) (Falta, 2006; Falta, 2008), which accounts for variable source and plume remediation. REMChlor simulations will be used to evaluate the effects of partial source removal and plume bioremediation on EDB, 1,2-DCA and hydrocarbon plumes at UST sites.

2. Background

Premature ignition, otherwise known as "knocking," was a significant obstacle to the development of the internal combustion engine in the early part of the 20th century (Boyd, 1950). In 1921, researchers discovered that the addition of tetraethyl lead prevented knocking, but found that it also formed solid lead deposits on valves and spark plugs, a condition known as engine fouling (Jacobs, 1980). EDB and 1,2-DCA were added to gasoline because they form volatile lead halides which can easily be removed in exhaust. These compounds were present in virtually all leaded gasoline sold, and are commonly referred to as "lead scavengers" (Jacobs, 1980). In countries where leaded gasoline is still marketed, lead scavengers remain part of the fuel mix formulation (Falta et al., 2005b). Once released to groundwater, the physical properties of EDB and 1,2-DCA suggest they will be mobile. EDB is a moderately soluble compound, with an aqueous solubility of 4300 mg/L (milligrams per liter) (Montgomery, 1997); the solubility of 1,2-DCA is 8500 mg/L (Bedient et al., 1999). Based upon these solubilities and their gasoline–water partition constants, dissolved phase EDB and 1,2-DCA concentrations up to 1900 and 3700 μg/L can be expected in groundwater near the source area of a leaded gasoline release (Falta, 2004). Both EDB and 1,2-DCA have low air–water, soil–water and octanol–water partition constants, so they will not partition out of groundwater into air and soil to any great degree. These factors indicate lead scavengers could form dissolved phase plumes downgradient of the release source zone.

Sites where leaded gasoline LNAPL contamination exists pose significant technical challenges and potential long-term risk to human health and the environment. Though little information exists on the prevalence of LNAPL source zones at sites where USTs leaked, it is commonly assumed that residual LNAPL source zones can be expected at sites where persistent and high-concentration plumes are present (Wilson, 2007). Such sites would be characterized by two primary zones, 1) the source, defined as the area of aquifer or vadose zone where LNAPL is in contact with aquifer materials, and 2) the plume, where contamination is present in adsorbed and dissolved form. Recent attention has focused on the suitability of remediation of LNAPL source zones at these sites, where short and long-term remedial goals may necessitate source removal as well as plume remediation (Falta et al., 2005a). As a consequence, the debate regarding source remediation versus plume remediation has particular relevance to UST sites in general and lead scavengers in particular. Source removal is usually accomplished in order to minimize downgradient impacts of the contaminant plume (Falta et al., 2005a), but currently metrics for establishing the efficacy of such actions are poorly defined, and no tools are in use to promote such an assessment.

3. Modeling approach

Following Parker and Park (2004), Zhu and Sykes (2004), and Falta et al. (2005a), a mass balance on a contaminant species of interest in an LNAPL source zone can be written as

$$\frac{dM}{dt} = -QC_s(t) \tag{1}$$

where Q is the water flow rate through the source zone due to infiltration or groundwater flow, $C_s(t)$ is the average dissolved concentration of contaminant species leaving the source zone, and M is the mass of the contaminant species in the source zone. The source mass is linked to the source discharge through a power function (Rao et al., 2001; Rao and Jawitz, 2003; Parker and Park, 2004; Zhu and Sykes, 2004; Jawitz et al., 2005):

$$\frac{C_s(t)}{C_0} = \left(\frac{M(t)}{M_0}\right)^{\Gamma} \tag{2}$$

where C_0 and M_0 are the initial source dissolved concentration and mass of the contaminant species, respectively. The solution of Eq.(1) with the power function (2) can be used to estimate the time-dependent depletion of the source zone mass by dissolution. The time-dependent mass is then used in Eq. (2) to calculate the time-dependent source discharge. This model can simulate a wide range of source responses to mass loss, depending on the value of Γ. The effect of this parameter is discussed in Parker and Park (2004), Zhu and Sykes (2004) and Falta et al. (2005a), but an important special case occurs when $\Gamma = 1$, and the source contaminant mass and discharge are linearly related. As will be shown, $\Gamma = 1$ may be a good approximation for modeling source behavior at sites contaminated with gasoline. If Eqs. (1) and (2) are solved with $\Gamma = 1$, the source discharge and mass decline exponentially with time (Newell et al., 1996; Parker and Park, 2004; Zhu and Sykes, 2004).

Gasoline is a multicomponent LNAPL. It can be shown that to a reasonable approximation, components of a multicomponent NAPL will weather out of the NAPL according to a first-order process. Assuming linear equilibrium phase partitioning, the following partition coefficients are defined:

$$K_{pnw} = \frac{C_n}{C_w}; \quad H = \frac{C_g}{C_w}; \quad K_D = \frac{X_s}{C_w} \tag{3}$$

where K_{pnw} is the NAPL–water partition constant, C_n is the mass concentration of the component in the NAPL, C_w is the aqueous mass concentration of the component, H is the dimensionless Henry's constant, C_g is the mass concentration in the gas phase, K_D is the soil–water distribution coefficient, and X_s is the mass fraction adsorbed to soil. The NAPL–water partition coefficient, K_{pnw} can be calculated assuming Raoult's law, using the component and mixture molecular weights, the NAPL density, and the component pure solubility (Cline et al., 1991):

$$K_{pnw} = \frac{M_{wt}\rho_n}{M_{wt}^{ave}\overline{C_w}} \tag{4}$$

where M_{wt} is the compound's molecular weight, ρ_n is NAPL density, M_{wt}^{ave} is the average molecular weight of the NAPL, and $\overline{C}_w$ is the component's pure solubility in water. The total concentration (C_T) of the gasoline component is defined as follows:

$$C_T = \phi S_w C_w + \phi S_g C_g + \phi S_n C_n + \rho_b K_D C_w \tag{5}$$

where ϕ is porosity, S_w is water phase saturation, S_g is gas phase saturation, S_n is NAPL phase saturation, and ρ_b is bulk soil density. For a multicomponent NAPL with linear phase partitioning, C_T is a linear function of any phase concentration. The mass balance on a control volume containing soil, gas, water, and NAPL, with gas and water flushing, and first-order aqueous phase decay of the species leads to a differential equation:

$$V\frac{dC_T}{dt} = -Q_w C_w - Q_g C_g - V\phi S_w C_w \lambda \tag{6}$$

where V is the volume of the system, Q_w and Q_g are the water and gas flushing rates (volume per time), and λ is the pseudo first-order decay rate, which combines biotic and abiotic destruction as well as non-destructive mechanisms such as dispersion, adsorption and volatilization processes. C_T can be defined in terms of the aqueous concentration using the phase partitioning relationships in Eq. (3):

$$C_T = \left(\phi S_w + \phi S_g H + \phi S_n K_{pnw} + \rho_b K_D\right) C_w = K_w^* C_w \tag{7}$$

If the phase saturations and partition coefficients are constant, then K_w^* is constant. Substituting, we get:

$$\frac{dC_w}{dt} = -\left(\frac{Q_w + HQ_g}{K_w^* V} + \frac{\phi S_w \lambda}{K_w^*}\right) C_w = -k_s C_w \tag{8}$$

So, for constant phase saturations and partition coefficients, NAPL weathering is a first-order decay process with an exponential decay solution:

$$\frac{C_w}{C_{w,0}} = e^{-k_s t} \tag{9}$$

with a source decay rate of k_s. The source decay rate is a measure of processes such as dissolution, volatilization, and aqueous phase biodegradation that over time remove the LNAPL component from the source zone. Since all of the concentrations are linearly related, they will all decline exponentially, with the same source decay rate coefficient:

$$\frac{C_w}{C_{w,0}} = \frac{C_n}{C_{n,0}} = \frac{C_T}{C_{T,0}} = e^{-k_s t} \tag{10}$$

Therefore, this equation can be used to model NAPL composition, soil mass fractions, and dissolved concentrations in the source zone. Because the decay of the source zone is exponential, it can thus be assumed that Γ is equal to 1 in Eq. (2). If the only depletion process taking place in the source zone is aqueous dissolution of the LNAPL component, then using Eqs. (1) and (2) (or Eq. (10) with no gas flushing or biodegradation) lead to an exponential decay solution, where C_s is the dissolved concentration discharging from the source zone:

$$C_s(t) = C_o e^{-\frac{QC_o}{M_o}t} \tag{11}$$

and

$$M(t) = M_o e^{-\frac{QC_o}{M_o}t} \tag{12}$$

The REMChlor code simulates source depletion by dissolution, first-order decay (by biological or chemical processes), and aggressive source remediation. Aggressive source remediation involves removing a large fraction of the source mass in a short period of time. REMChlor simulates this by rescaling the source zone mass, M, to reflect the fraction of the source that was removed. Then the source concentration, C_s is recalculated using the power function defined by Eq. (2), and the mass balance Eq. (1) is solved using these new values as the initial condition. Full details of this source model are given in Falta et al. (2005a), and Falta (2006, 2008).

REMChlor also includes an analytical model capable of simulating plume remediation of compounds that is variable in space and time (Falta, 2006, 2008). This plume model can consider independent variations in parent and daughter compound decay rates and yield coefficients in the plume. The plume model is based on a distance–time plot for the plume behavior (Fig. 1). Here, distance is the distance downgradient of the LNAPL source, and time is the time since the LNAPL release. The distance–time domain is divided into 9 "reaction zones," where the contaminant first-order decay rates are independently specified. Thus the code can simulate temporal and spatial changes in the contaminant decay rate that arise from natural and enhanced plume biodegradation. These space–time reaction zones are described in more detail below.

4. Simulation development

The conceptual plume model employed here incorporates three spatial zones. The first, termed zone 1, is found directly downgradient from the contamination source (a leaking UST or former tank excavation), and is characterized by high dissolved phase concentrations of EDB, 1,2-DCA, and BTEX (Fig. 2). At sites where historic releases of leaded gasoline are commingled with later releases of unleaded fuel, oxygenates

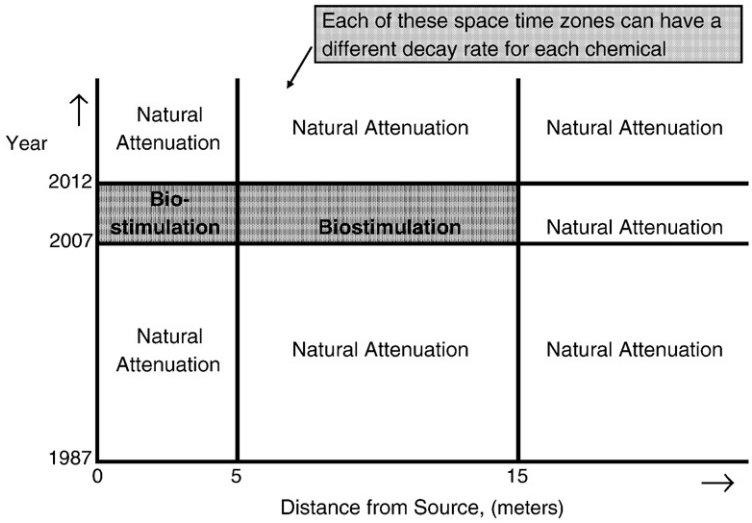

Fig. 1. Distance–time plot for advective transport with multiple sets of plume reaction rates.

such as MTBE may also be present. In zone 2, dissolved phase concentrations decline by orders of magnitude at varying distances downgradient from the source depending on site conditions. Both zones 1 and 2 are assumed to be anaerobic, given that available oxygen is depleted quickly by an abundance of fuel hydrocarbons, some of which can serve as electron donors in anaerobic dehalogenation processes (Suarez and Rifai, 1999). Finally, low concentrations (but above the MCL) of EDB and 1,2-DCA may exist in the downgradient portion of the plume, though BTEX compounds may not be present, given that these compounds are more biodegradable in the aerobic setting (Suarez and Rifai, 1999) (Fig. 2). The downgradient zone is usually (but not always) aerobic, and is termed here zone 3.

We consider two extremes in UST plume behavior. At sites where natural attenuation processes are robust, EDB and 1,2-DCA plumes are likely to be short, but at other sites, long plumes of either or both contaminants may exist (Fig. 2). The short plume simulations are based on a site in Clemson, SC where EDB and 1,2-DCA plume extent is limited. In June 2005, three soil borings were advanced at the Former Clemson Tiger Mart in zones 1, 2 and 3, and soil and groundwater collected for the purpose of establishing laboratory microcosms (Henderson et al., 2008). This site sold leaded gasoline and various formulations of unleaded gasoline until the tanks were removed in 2000 (BLE, 2005). Subsequent groundwater investigations revealed high levels of EDB, 1,2-DCA, BTEX, and MTBE downgradient of the source zone. Concentrations of EDB and 1,2-DCA

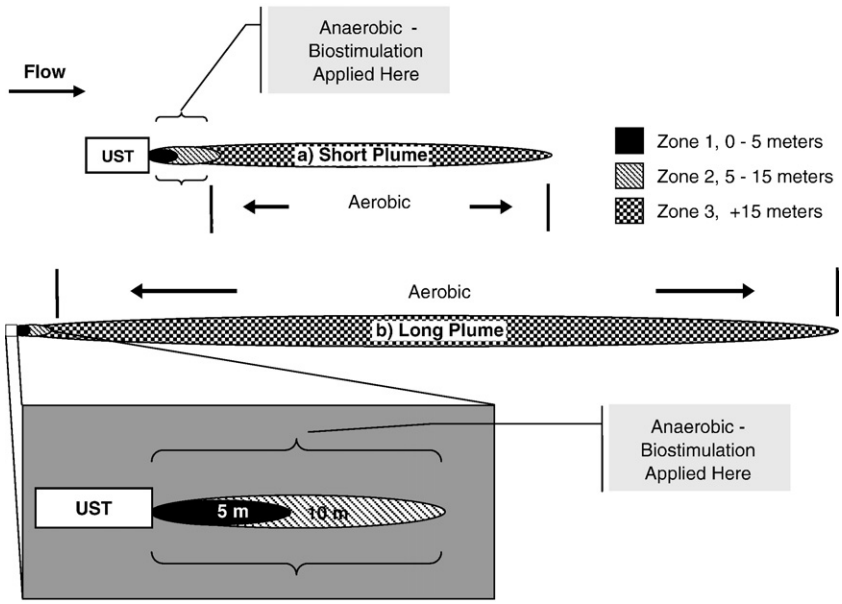

Fig. 2. Site conceptual model for short and long plume cases (not drawn to scale), including biostimulation schemes.

Table 1
Comparison of first-order biodegradation rates (yr^{-1}) [a].

	Zone 1		Zone 2		Zone 3
	Natural attenuation	Biostimulation	Natural attenuation	Biostimulation	Natural attenuation
Short plume					
EDB	1.49	5.47	5.37	9.4	3.93
1,2-DCA	1.34	0.77	0.34	0.43	1.46
Benzene	1.47	2.26	3.5	3.09	122 [b]
MTBE	2.2 [c]	5.0 [d]	2.2 [c]	5.0 [d]	8.0 [e]
Long plume					
EDB	1.49	5.47	5.37	9.4	0.5 [f]
1,2-DCA	1.34	0.77	0.34	0.43	0.5 [f]
Benzene	1.47	2.26	3.5	3.09	9.13 [g]
MTBE	2.2 [c]	5.0 [d]	2.2 [c]	5.0 [d]	0.365 [h]

[a] Unless otherwise noted, rates are calculated as triplicate mean ± one standard deviation from Clemson University microcosm study.
[b] Value represents the mean of surveyed field and laboratory aerobic first-order rates in Suarez and Rifai (1999).
[c] Rate represents low value in range of anaerobic rates under methanogenic conditions reported by Wilson et al. (2000), as cited in Schmidt et al. (2003).
[d] Rate represents high value in range of anaerobic rates under methanogenic conditions reported by Wilson et al. (2000), as cited in Schmidt et al. (2003).
[e] Rate represents approximate mean of aerobic rates from Borden et al. (1997), Landmeyer et al. (2001), Kane et al. (2001), Hunkeler et al. (2001), Schirmer et al. (2003), and Zoeckler et al. (2003), as summarized in Schmidt et al. (2003).
[f] Arbitrarily selected low rate, based in part on Massachusetts Military Reservation EDB case described in Falta (2004).
[g] Value represents the geometric mean of surveyed field and laboratory aerobic first-order rates in Suarez and Rifai (1999).
[h] Rate represents upper value in range of aerobic rates reported by Borden et al. (1997), as cited in Schmidt et al. (2003).

are approximately 300 µg/L and 800 µg/L respectively in this area. High part-per-million concentrations of BTEX and MTBE are present in groundwater in zone 1. The presence of MTBE is attributable to a later release of unleaded fuel, since this compound would not have been present in the original release of leaded fuel. Over the next 10 m downgradient, concentrations are attenuated by one to two orders of magnitude (zone 2). Site lithology at the Former Clemson Tiger Mart consists of poorly sorted sand, clay and silt (BLE, 2005) and groundwater Darcy velocity is approximately 10 m/yr.

In anaerobic laboratory microcosms, EDB was observed to degrade to its low MCL of 0.05 µg/L in the presence of 1,2-DCA and fuel hydrocarbons (Henderson et al., 2008). However, 1,2-DCA was not significantly biodegraded. Biodegradation of BTEX was also observed in the anaerobic microcosms. The addition of lactate greatly stimulated biodegradation of EDB, but had no apparent effect on 1,2-DCA in the microcosm experiments. The addition of lactate yielded mixed effects in the case of the BTEX compounds. Table 1 summarizes pseudo first-order decay rates derived from incubating the microcosms from 284 to 380 days for EDB, 1,2-DCA, and benzene. These laboratory-derived biodegradation rates are used in the present study and are assumed to be representative of in-situ rates at similar UST sites. Aerobic degradation rates for benzene, and aerobic and anaerobic degradation rates for MTBE were taken from Schmidt et al. (2003) (Table 1).

The second set of simulations is based on a site where long EDB plumes have been extensively delineated. The Massachusetts Military Reservation (MMR) is situated on Cape Cod, and has been in operation since 1911, providing mechanized and aircraft training for the Army and Air Force. A total of four EDB plumes exist at MMR, ranging in length from 1400 to 2400 m (Falta, 2004). Concentrations of EDB detected in the subsurface at MMR range from 0.071 to over 600 µg/L (Falta, 2004). Geology at MMR is comprised of glacial deposits characterized by fine to coarse sands and groundwater seepage velocity ranges from 100 to 200 m/yr (Falta, 2004). Concentrations of EDB in several of these plumes have declined little, which would indicate that natural attenuation processes are not effective at limiting the transport of EDB (CH2MHILL, 2004). Based upon available groundwater concentrations of EDB in one of the plumes at MMR, the computed EDB in-situ degradation rate at MMR was estimated at 0.04 yr^{-1}, or a half-life of approximately 18 years (Falta, 2004).

Table 2 compares parameters used to model the short plume and long plume scenarios. A release of 18,927 L (5000 gal) of leaded gasoline is assumed to have occurred in 1987, which is roughly when leaded gasoline was phased out of existence in the US. This release would have contained EDB,

Table 2
Simulation parameters, short and long plume scenarios.

Simulation parameters	Value
Volume of release 1 (1987) [a]	18,927 L (5000 gal)
Volume of release 2 (1997) [b]	3785 L (1000 gal)
Release 1 source depth	3 m
Release 1 source width	10 m
Release 2 source depth	2 m
Release 2 source width	3 m
Gamma (Γ)	1
Short plume Darcy velocity	10 m/yr
Long plume Darcy velocity	20 m/yr
Porosity [c]	0.35
Coefficient of variation, velocity field	0.1
Transverse dispersivity	0.05
Vertical dispersivity	0.005
Soil bulk density [c]	1.4 g/mL
Fraction of organic carbon [c]	0.001
Spatial zone 1 (near source, anaerobic)	0–5 m
Spatial zone 2 (midgradient, anaerobic)	5–15 m
Spatial zone 3 (downgradient, aerobic)	>15 m
Time period 1 (pre-remediation)	1987–2007
Time period 2 (active remediation)	2007–2012
Time period 3 (post-remediation)	>2012

[a] Release of leaded gasoline containing EDB, 1,2-DCA, and BTEX.
[b] Release of conventional unleaded gasoline containing MTBE and BTEX.
[c] Taken as reasonable median value from (Watt, 1998).

1,2-DCA and BTEX, but not MTBE. A second, smaller release of 3785 L (1000 gal) is modeled 10 years afterwards (in 1997). Such a release could have resulted from an overfill or localized piping leak, and it would have contained MTBE and benzene, but not EDB and 1,2-DCA, since only unleaded gasoline was marketed at this point. Benzene is thus the only contaminant that is common to both releases. Both releases would have contained other hydrocarbons that are not simulated here (although they could contribute to the formation of the anaerobic zone geometry).

Basic simulation parameters for the short and long plume cases are similar for most parameters, save for groundwater Darcy velocity, which is assumed in the long plume case to be double (20 m/yr) the value of the short plume case (10 m/yr) (Table 2). It is to be expected that faster groundwater velocity would form longer plumes, though it should be noted that more widely divergent velocities may be expected at field sites, which would accentuate plume length variability among different compounds. Small transverse and vertical dispersivities of 0.05 and 0.005 m, respectively, are selected to emphasize contaminant destruction and removal effects on the plumes, rather than dilution effects, and also to minimize errors related to the Domenico approximation for transverse dispersion. In REMChlor, longitudinal dispersivity is scale dependent, and is calculated as

$$\alpha_x = \frac{1}{2}\left(\frac{\sigma_v^2}{\bar{v}^2}\right)\bar{x} \tag{13}$$

where α_x is longitudinal dispersivity, $\sigma_v/\bar{v}$ is the ratio of pore velocity standard deviation to the mean pore velocity, and $\bar{x}$ is the average of the front location at a given time (Falta, 2006). A σ_v of 0.1 produces a longitudinal dispersivity of 1/200 the travel distance, and this value is used here.

EDB and 1,2-DCA concentrations in gasoline ranged from about 0.3 g/L before the 1970s to around 0.07 g/L at the time leaded gasoline was banned (Falta et al., 2005b). The lower value is selected here because it was assumed that the first release occurred in 1987, when leaded gasoline was phased out of existence and concentrations of the lead additives were at their lowest. This would produce a total mass of 1.3 kg of EDB and 1,2-DCA in the subsurface if 18,927 L (or the entire contents of a 5000-gallon UST) were released. Historical releases of leaded gasoline that occurred prior to the late 1980s would have contained higher concentrations of EDB and 1,2-DCA, which would result in proportionately greater EDB and 1,2-DCA mass in the subsurface, so in this respect the selection of lower concentrations used in these simulations is conservative. Benzene concentrations in leaded and unleaded gasoline have also varied over time (Weaver, unpublished data). In release 1, a 2% benzene content by mass in leaded gasoline is assumed, producing a benzene concentration of 13 g/L (Falta, 2004), or a total mass of benzene of 246 kg released into the subsurface. For the second, smaller release in 1997, benzene concentrations would have been different, and probably lower. Based on the data from Weaver (unpublished data), a benzene concentration of 3.8 g/L will be used for the smaller 1997 release, producing 14 kg of benzene mass added to the source. The addition of benzene from the second release is modeled additively; the source mass of benzene at the point of the second release equals residual mass from the first release at that time plus the mass attributable to the second release. This results in an increase in benzene concentration discharging from the source zone at the time of the second release. Modeling the benzene release in this fashion mimics the effects of multiple releases at UST sites. MTBE concentration in the gasoline at the time of the second release is taken from the data characterizing conventional fuel marketed in 1997 in Charleston, SC (Weaver, unpublished data). Using a concentration of 13.8 g/L (1.8% by mass), a 1000 gal release would result in 52 kg of MTBE in the source zone. We note that reformulated gasoline that was used in many parts of the country could contain as much as eight times this amount of MTBE.

For release 1, cross-sectional (perpendicular to flow) source zone dimensions of 10 m wide by 3 m deep are specified in REMChlor. Dissolution of source mass occurs when groundwater flux discharges from this 30 m^2 area, but the total volume of gasoline resulting from the releases would be dispersed throughout the subsurface, as calculated by the equation

$$V_{tot} = \frac{V_n}{\phi S_n} \tag{14}$$

where V_{tot} is contaminated volume of soil in the subsurface, V_n is the volume of NAPL (18,927 L, or 18.9 m^3), ϕ is porosity

Table 3
Calculation of compound-specific simulation parameters.

Compound	Concentration in gasoline (g/L)	Gasoline water partition coefficient	Modeled aqueous concentration (μg/L) [e]	Initial source mass (kg)	Organic carbon partition constant (mL/g)	Retardation coefficient [i]
EDB	0.07 [a]	152 [b]	230	1.3 [f]	44.0 [h]	1.18
1,2-DCA	0.07 [a]	84 [b]	417	1.3 [f]	17.4 [h]	1.07
Benzene	13 [b]/3.8 [c]	350 [b]	18,500 [f]/5440 [g]	246 [f]–14 [g]	58.9 [h]	1.24
MTBE	13.8 [c]	15.5 [d]	446,000	52 [g]	6.0 [h]	1.02

[a] Approximate concentration in 1984, leaded gasoline (Falta et al., 2005b).
[b] As reported by Falta (2004).
[c] Calculated from the average of available data on fuel marketed in Charleston, SC in winter of 1997 (Weaver, unpublished data).
[d] Reported by Zwank et al. (2002), as cited in Schmidt et al. (2003).
[e] Equal to one-half the equilibrium aqueous concentration.
[f] From release of 5000 gal of leaded fuel, 1987.
[g] From release of 1000 gal of conventional unleaded gasoline, 1997.
[h] USEPA, 2007.
[i] Calculated using values for porosity, fraction organic carbon content, and soil bulk density listed in Table 2.

(assumed to be 0.35), and S_n is NAPL saturation (assumed to be 0.3). This calculation yields a total contaminated volume of 180 m^3. The 1997 release is assumed to be one-fifth the volume of the first release, so benzene and MTBE mass from this release would likely spread over a smaller volume. If the flux plane is 30 m^2 for the first release, then the second release might discharge through a proportionately smaller flux plane of 6 m^2.

Aqueous concentrations are highest immediately downgradient of the source, and can be estimated using gasoline–water partition constants (Table 3). It is unlikely that field scale groundwater concentrations downgradient of the NAPL source would be this high due to mixing and dilution with clean groundwater, and therefore, initial groundwater concentrations in the NAPL source zone are assumed to be half of the highest concentrations that might be expected due to equilibrium with the NAPL source. On this basis, it is calculated that the initial source concentration of EDB and 1,2-DCA would be 230 µg/L and 417 µg/L, respectively. Similarly, modeled initial source benzene concentrations of 18,500 µg/L and 5440 µg/L are calculated for releases 1 and 2 respectively. The initial MTBE source concentration is 446,000 µg/L. As noted earlier, these source concentrations (C_s) would tend to decline exponentially as groundwater flows through the source zone. Retardation coefficients for the 4 contaminants were calculated assuming an organic carbon fraction of 0.001 (Watt, 1998). Of the four compounds modeled here, benzene is the most retarded in groundwater (1.24), while MTBE is the least (1.02) (Table 3), and, as a whole, retardation plays a relatively small role in the transport of these compounds.

Following the conceptual model, natural attenuation biodegradation rates from the laboratory microcosms are applied to zones 1, 2 and 3 for the short plume scenario (Table 1). Rates utilized in the short and long plume case are identical through zones 1 and 2, but an arbitrarily selected low rate of 0.5 yr^{-1} is assigned to both EDB and 1,2-DCA in the aerobic zone (zone 3) for the long plume case in order to produce more extensive plumes. While not all sites will have extensive aerobic plume zones, it should be noted that for EDB, the assumed aerobic decay rate for the long plume scenario is much higher than the rate of 0.038 yr^{-1} (or a half-life of approximately 18 years) estimated at the MMR site (Falta, 2004). Similarly low aerobic rates have been inferred for 1,2-DCA based on UST field data (Falta et al., 2005b). In this respect, use of these rates will result in faster simulated aerobic decay than that evident at some sites. Aerobic rates for benzene and MTBE, and anaerobic rates for MTBE, are taken from Schmidt et al. (2003) as summarized in Table 1. The MTBE aerobic rate (8.0 yr^{-1}) selected for the short plume case is a rough median of values reported in Schmidt et al. (2003). The long plume aerobic rate (0.365 yr^{-1}) is the lowest aerobic rate cited in Schmidt et al. (2003). Biostimulation rates were taken from the Clemson microcosm study, and given the variable response to lactate addition, these rates may be higher or lower than natural attenuation rates, and may also vary between zones 1 and 2. This fact demonstrates the complexity of response that may result from performing biostimulation for multiple compounds at UST sites, as detailed in Henderson et al. (2008). MTBE anaerobic rates for natural attenuation and biostimulation are the low and high ends of the range observed by Wilson et al. (2000) in a field study, as reported in the Schmidt et al. (2003) survey.

A total of four remediation scenarios are presented for both the short and long plume case:

(1) *Natural attenuation of both the LNAPL source and the plume*. Natural attenuation is modeled by incorporating biodegradation rates from Clemson University microcosms over nine spatial–temporal plume zones (Fig. 1, Table 1). The purpose of these simulations is to illustrate the behavior of each of the modeled compounds at UST sites in the absence of remediation, thereby permitting a point of comparison for remedial simulations.

(2) *Aggressive LNAPL source remediation with natural attenuation of the plume*. The effects of LNAPL source remediation are modeled to determine how such a remedial action might decrease the extent of the EDB, 1,2-DCA, benzene and MTBE plumes. An assumed 90% removal of residual LNAPL source mass is modeled 20 years after the first release (i.e. in 2007) as a one-time event. It should be noted that REMChlor can simulate removal of any fraction of the source over any timeframe (Falta, 2006). Prior to and after the source remediation effort, the system undergoes only natural attenuation, as in scenario (1), above.

(3) *Natural attenuation of the LNAPL source with enhanced biodegradation in the plume*. Given EDB's positive response to lactate addition in laboratory microcosms (Henderson et al., 2008), the second set of remedial simulations explores plume remediation through biostimulation. This would involve providing electron donor to microorganisms through direct injection or some other in-situ delivery method. Degradation rates achieved in microcosms through addition of lactate are used (Table 1) and are thus assumed to be uniformly achievable at the field scale. Lactate would be applied in 2007 for 5 years (i.e., from 20 to 25 years after the initial release) in the anaerobic areas of the plume (zones 1 and 2), where abundant fuel hydrocarbons rapidly deplete available oxygen (Suarez and Rifai, 1999). Accelerated biostimulation would occur in near-downgradient areas of the source but not in downgradient aerobic portions of the plume. Fig. 2 provides a graphical comparison of the location of biostimulated zones within short and long plumes, showing clearly that as a percentage of total plume area, biostimulation occurs over a very small portion of the long plume case, relative to the short plume case.

(4) *Aggressive LNAPL source remediation combined with enhanced plume biodegradation*. The combined effects of source removal and biostimulation are simulated, following the methods described above. The purpose of these simulations is to determine the benefit of applying both partial source removal and plume remediation at UST sites, relative to relying on one or the other technique. It is anticipated that this will permit a determination of the maximum benefits that might be expected through the best possible use of remedial technology at UST sites.

5. Results

The simulations demonstrate how the impact of source and/or plume remediation of each contaminant varies over time throughout the plume. To facilitate comparison of the modeled compounds, concentrations are normalized by dividing the applicable standard and evaluating how this ratio (termed here "relative importance") changes over time along the plume center line. Relative importance can be considered a surrogate indicator of the risk posed by each compound. Federal MCLs exist for EDB (0.05 μg/L), 1,2-DCA and benzene (5.0 μg/L), but not for MTBE, for which the US EPA Region 9 tap water Preliminary Remediation Goal (PRG) (11.0 μg/L) is used as an applicable regulatory standard (USEPA, 2007).

5.1. Relative importance

Fig. 3 presents the relative importance of EDB, 1,2-DCA, benzene, and MTBE over 100 years in the short plume natural attenuation case at three points within the plume: a) 0 m (discharging source concentrations), b) 15 m downgradient of the source zone, and c) 25 m downgradient of the source zone. Over time, concentrations discharging from the source zone (Fig. 3a) change according to Eq. (11), and since Γ is assumed to be 1, the relationship between source discharge and source mass is linear. At the time of release 1 (1987), the ratio of source discharge concentrations of EDB and benzene to their MCLs is similar (4590 and 3714 times, respectively). Though discharging concentrations of EDB are lower, so too is its MCL when compared to benzene's. By contrast, 1,2-DCA

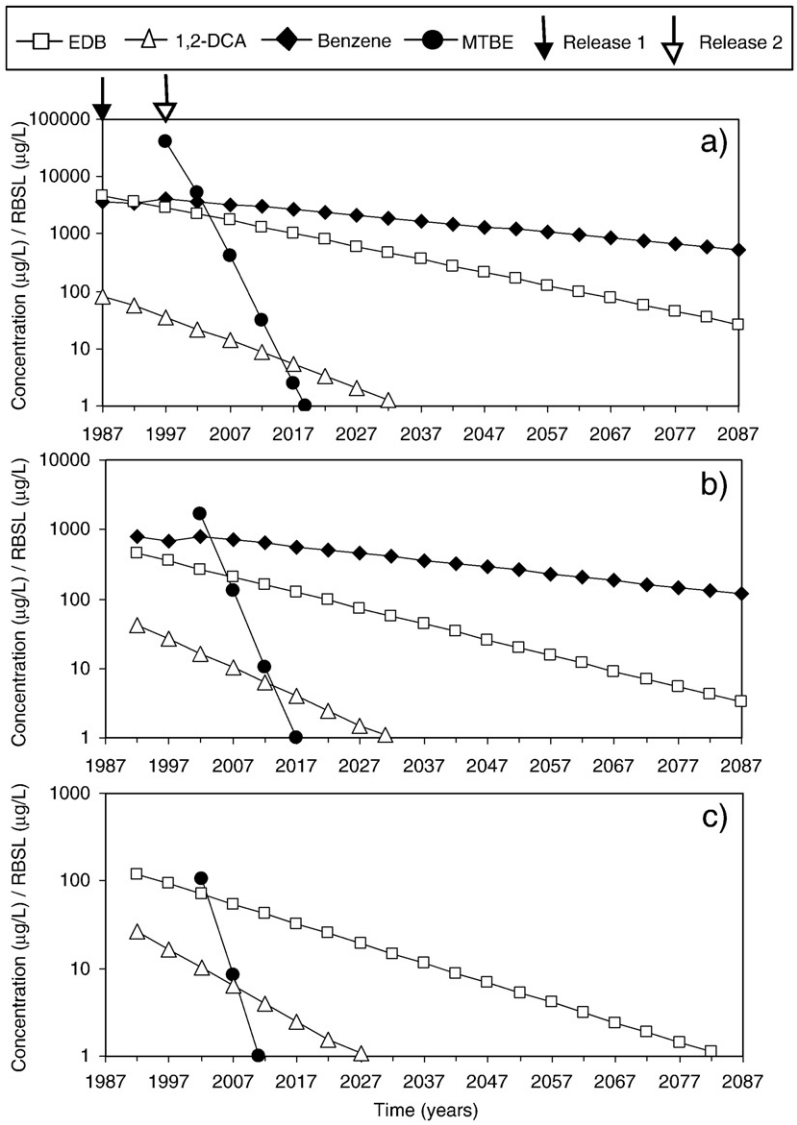

Fig. 3. Short plume natural attenuation relative importance (concentration divided by risk-based screening level (RBSL)) of EDB, 1,2-DCA, benzene and MTBE at a) 0 m, b) 15 m, and c) 25 m. Compounds not graphed are degraded below the RBSL.

discharges from the source at an initial concentration that is 83 times its MCL (5.0 µg/L). The second release (in 1997) adds benzene mass to the source, increasing its concentration and relative importance (Fig. 3a). MTBE is a constituent of the second release but not the first. Given its higher solubility, it exceeds the applicable standard (11.0 µg/L) 40,581 times, more than both EDB and benzene at the time of its release. Fig. 3a demonstrates how the source strength varies as a function of time under natural dissolution conditions; this process depends on the dissolution characteristics of each contaminant. Compounds that have high aqueous solubility can be expected to wash out of the source zone quickly. This characteristic of source strength (Falta et al., 2005a) has its mathematical expression in the exponent of Eq. (11). If initial concentration (C_o) is large relative to initial mass, the magnitude of the negative exponent is larger, producing accelerated source dissolution. Near UST source zones where more recent releases of conventional unleaded fuel occurred, MTBE may be a regulatory driver, but this condition will tend to be short-lived based upon its dissolution characteristics. EDB and benzene attenuate from the source more slowly, exceeding applicable standards in 2087 by 27 and 540 times respectively, 100 years after the initial release of leaded gasoline. In contrast, 1,2-DCA and MTBE do not exceed their respective screening values after 2034 and 2019, respectively.

Fig. 3b portrays relative importance 15 m from the source, at the end of the anaerobic portion of the plume. Because EDB was assigned a higher decay rate in the anaerobic zone, its relative importance decreases somewhat compared to benzene at this location. The MTBE concentration drops quickly because of its short residence time in the source zone. EDB and 1,2-DCA are much less biodegradable in the aerobic zone than benzene and they appear to have first-order decay rates roughly similar to MTBE. Fig. 3c shows relative importance

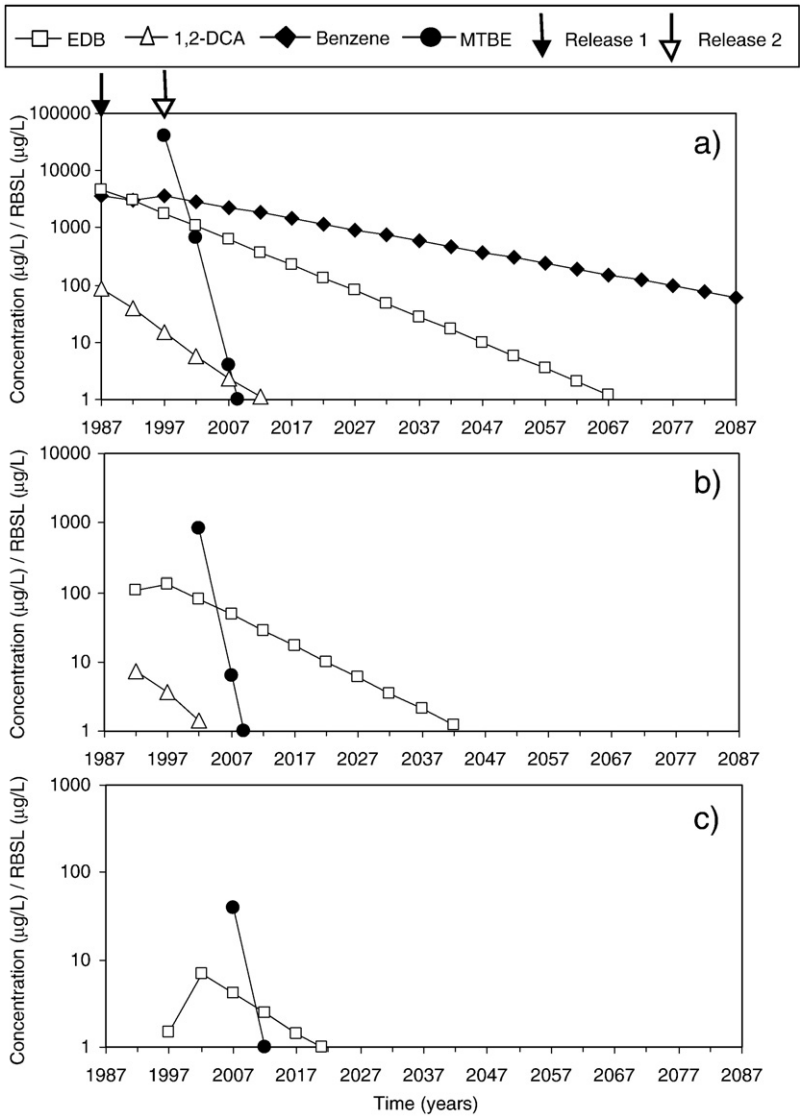

Fig. 4. Long plume natural attenuation relative importance (concentration divided by risk-based screening level (RBSL)) of EDB, 1,2-DCA, benzene and MTBE at a) 0 m, b) 200 m and c) 500 m. Compounds not graphed are degraded below the RBSL.

Table 4a
Maximum extent above MCL/PRG in the years 2012 and 2017, short plume.

Simulated scenario			Plume length (m) [a]			
	Year	Plume length	EDB	1,2-DCA	Benzene	MTBE
Natural attenuation	2012	Short	54	52	17	21
	2017	Short	52	41	15	6
90% Source removal	2012	Short	37	0	15	15
	2017	Short	35	0	15	0
Biostimulation	2012	Short	41	53	17	15
	2017	Short	52	41	15	6
90% Source removal + BST [b]	2012	Short	21	0	15	6
	2017	Short	35	0	15	0

[a] Plume length is defined as maximum extent above the MCL (EDB MCL = 0.05 μg/L; 1,2-DCA = 5.0 μg/L; benzene MCL = 5.0 μg/L; no MCL available for MTBE, USEPA Region 9 tap water Preliminary Remediation Goal = 11.0 μg/L (USEPA, 2007).
[b] BST = biostimulation.

Table 4b
Maximum extent above MCL/PRG in the years 2012 and 2017, long plume.

Simulated scenario			Plume length (m) [a]			
	Year	Plume length	EDB	1,2-DCA	Benzene	MTBE
Natural attenuation	2012	Long	605	0	57	911 [b]
	2017	Long	535	0	56	0 [c]
90% Source removal	2012	Long	605	0	42	911 [b]
	2017	Long	265	0	41	0 [c]
Biostimulation	2012	Long	605	0	57	911 [b]
	2017	Long	408	0	57	0 [c]
90% Source removal + BST [d]	2012	Long	605	0	43	911 [b]
	2017	Long	239	0	41	0 [c]

[a] Plume length is defined as maximum extent above the MCL (EDB MCL = 0.05 μg/L; 1,2-DCA = 5.0 μg/L; benzene MCL = 5.0 μg/L; no MCL available for MTBE, USEPA Region 9 tap water Preliminary Remediation Goal = 11.0 μg/L (USEPA, 2007).
[b] Rapid source dissolution and low aerobic decay of MTBE in the long plume case produces detached plumes downgradient of the source.
[c] Detached plume still exists, but at concentrations just below 11 μg/L.
[d] BST = biostimulation.

25 m downgradient of the source, or 10 m into the aerobic zone. At this location, the benzene plume has completely attenuated below its MCL concentration, and the plume risk is dominated by EDB concentrations except for a brief period where MTBE concentrations are high. EDB requires 96 years to decline below its MCL 25 m downgradient of the source zone; 39 years would be required for 1,2-DCA to degrade to its MCL at the same location. This suggests that EDB (and to a lesser degree, 1,2-DCA) are likely to be regulatory drivers where aerobic conditions predominate. While EDB requires nearly 100 years to decline below its MCL 25 m downgradient of the source, MTBE drops below its regulatory standard in 13 years at this location. Longer-lasting MTBE plumes result if lower aerobic rates are used. For example, if a rate of 4.0 yr^{-1} is used instead of 8.0 yr^{-1}, 16 years are required to attenuate MTBE at 25 m downgradient to below its PRG.

Relative importance is presented for the long plume case at 0, 200 and 500 m (Fig. 4a, b, and c, respectively). At the time of release (1987) the ratio of source discharge concentrations of EDB (4600) and benzene (3714) is identical to the short plume case. Darcy velocity used in long plume simulations is twice that of the short plume case, and since higher groundwater flow through the source area accelerates dissolution of the source, source discharging concentrations are sustained for a shorter period of time. However, at the time of release, this difference has not yet impacted the dissolution profile, and so the relative importance of the modeled compounds is the same for both the short and long plumes. Over time, the relative importance of the compounds declines more quickly than in the short plume case. EDB concentrations in groundwater discharging from the source drop below the MCL in 2069 (82 years after release 1). By comparison, the short plume requires 161 years to do so at the same point in space. Likewise, benzene, MTBE, and 1,2-DCA require shorter timeframes to discharge at concentrations below their respective screening levels in the long plume. Benzene is attenuated in 2177 (190 years after release 1) to below its MCL, but in the short plume case, 340 years are required. 1,2-DCA and MTBE decline below their respective screening values in 25 and 12 years, respectively, compared to 48 and 22 years respectively, in the short plume case (Fig. 3a and 4a).

Higher groundwater flow and low aerobic plume degradation rates increase relative importance farther away from the source in the long plume, and this relationship is portrayed at 200 and 500 m in Fig. 4b and c, respectively. Benzene does not appear because it is degraded below its MCL by plume aerobic biodegradation prior to 200 m. EDB presents the most sustained risk at 200 m, persisting above its MCL until 2045. 1,2-DCA and MTBE exceed their applicable standards until 2004 and 2009, respectively. Only EDB and MTBE are detected 500 m downgradient of the source (Fig. 4c). Though 1,2-DCA is present 200 m downgradient, the plume degradation rate of 1.46 yr^{-1} is sufficient to attenuate its concentration to

Table 5
Summary of plume characteristics/remedial benefit.

Simulated scenario		Plume characteristics [a]/remedial benefit [b]
Natural attenuation	Short	EDB and benzene plumes stable, 1,2-DCA and MTBE plumes shrinking, all plumes limited relative to the long plume case
	Long	EDB extent significant and slowly shrinking, no 1,2-DCA plume exists, benzene extent limited and shrinking, MTBE plume detached far from the source
90% Source removal	Short	Effective for 1,2-DCA, somewhat effective for EDB and MTBE, no effect on benzene extent
	Long	Somewhat effective for EDB and benzene, unnecessary for 1,2-DCA, no effect on MTBE
Biostimulation	Short	Temporarily effective for EDB and MTBE, no effect on 1,2-DCA or benzene
	Long	Delayed and temporary effectiveness for EDB, unnecessary for 1,2-DCA, no effect on benzene and MTBE
90% Source removal + BST [c]	Short	Relative to 90% source removal alone, temporary added benefit for EDB and MTBE, no additional benefit for 1,2-DCA and MTBE
	Long	Relative to 90% source removal alone, negligible added benefit for EDB, no additional benefit for 1,2-DCA, benzene or MTBE

[a] Plume characteristics are presented for the Natural Attenuation case from 2012 to 2017.
[b] Remedial benefit is relative to Natural Attenuation plume characteristics from 2012 to 2017.
[c] BST = biostimulation.

below the MCL before 500 m. At 500 m, EDB persists until 2022, MTBE until 2012.

Given the range of behaviors detailed above, contaminant response to remediation varies significantly. The results of remedial scenarios are presented along with simulations of natural attenuation to provide a point of comparison. Tables 4a and 4b summarize the maximum plume center line extent above applicable regulatory standards in 2012 (25 years after release 1) and 2017 (30 years after release 1) for the short and long plume cases, respectively. It should be noted that these times (2012 and 2017) do not necessarily correspond to maximum plume lengths for the various compounds, but were selected in order to be able to compare the future effect of actions taken in the 2007 timeframe. The maximum plume lengths for EDB and 1,2-DCA occurred well before this date. Table 5 summarizes general plume behavior for all four compounds under each short and long plume simulation scenario.

5.2. Natural attenuation

The effect of natural attenuation processes on plume length is portrayed in plume centerline plots for EDB, 1,2-DCA, benzene and MTBE in the short and long plume cases in 2012, 25 years after release 1 (Figs. 5 and 6, respectively). The MCLs of the compounds are shown as horizontal dashed lines, and markers suspended above the plots represent the start of zones 1, 2, and 3. Under natural attenuation short plume conditions, EDB and 1,2-DCA have roughly the same extent in 2012 (54 and 52 m, respectively), while benzene and MTBE have shorter plume lengths due to their higher aerobic decay rate in this case (Fig. 5). As discussed above, benzene is completely biodegraded at the start of the aerobic zone, extending no further than 17 m, indicating that even where multiple historic releases have occurred, benzene plumes are likely to be short at sites where aerobic conditions predominate in downgradient areas of the plume. MTBE is less biodegradable aerobically than benzene, but

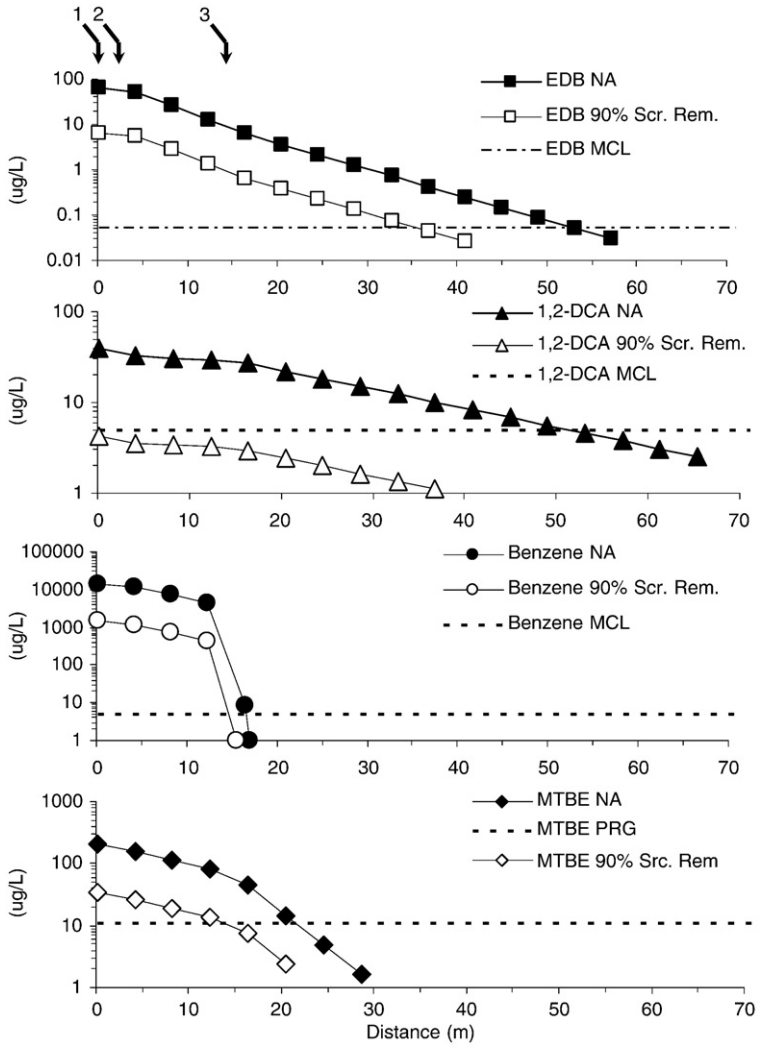

Fig. 5. REMChlor simulation results of natural attenuation and 90% source removal, short plume scenario, 2012. Zone 1, 2, and 3 markers are suspended above graphs at 0, 5 and 15 m downgradient, respectively. NA = natural attenuation; Scr. Rem. = source removal; MCL = maximum contaminant level; PRG = USEPA Region 9 Preliminary Remediation Goal.

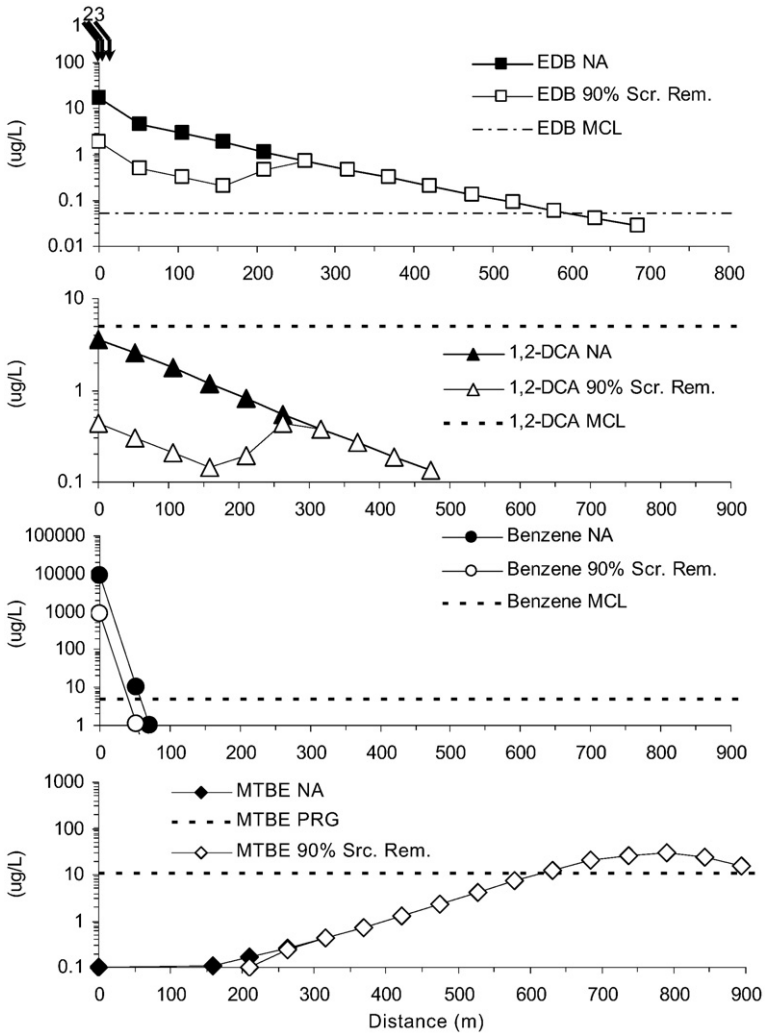

Fig. 6. REMChlor simulation results of natural attenuation and 90% source removal, long plume scenario, 2012. Zone 1, 2, and 3 markers are suspended above graphs at 0, 5 and 15 m downgradient, respectively. NA = natural attenuation; Scr. Rem. = source removal; MCL = maximum contaminant level; PRG = USEPA Region 9 Preliminary Remediation Goal.

the rate (8.0 yr^{-1}) is still high in this case, so it extends only a short distance into the aerobic zone, attaining a maximum plume length of 76 m within 4 years of its release. Comparing the plume lengths in 2012 to the plume lengths in 2017 (Table 4a), one could conclude that the EDB and benzene plumes are stable, while the 1,2-DCA and MTBE plumes are shrinking (Table 5).

As discussed above, short and long plume simulations are differentiated by aerobic rate (Table 1) and groundwater flow (Table 2), with the expectation that these differences will produce markedly different plume lengths. This effect is most striking in the case of EDB, which in the long plume simulations extends downgradient 605 and 535 m in 2012 and 2017, respectively (Fig. 6, Table 4b). In contrast to EDB, 1,2-DCA centerline extent above its MCL in 2012 is zero. Higher groundwater velocity produces more flushing of the source zone, and since both 1,2-DCA's solubility and MCL are higher than EDB's, this compound dissolves away more quickly. However, this also means that longer plume lengths of these compounds result at earlier timeframes, which is not reflected in Table 4b. The lower aerobic rate also produces a longer benzene plume (Fig. 6), but like 1,2-DCA, MTBE washes out of the source zone before 2012, producing a detached plume above 11 µg/L between 620 and 915 m downgradient of the source (Fig. 6).

5.3. Source remediation case

The effect of removing 90% of the LNAPL source is portrayed in plume centerline plots for EDB, 1,2-DCA, benzene and MTBE in the short and long plumes (Figs. 5 and 6, respectively). Given that Γ in Eq. (2) equals 1.0, 90% source removal produces the same decrease in concentrations discharging from the source zone. Five years after the removal, the extent of EDB has dropped from 54 to 37 m in the short plume case, though EDB concentrations continue to discharge from the source zone several orders of magnitude above the MCL. By contrast, source removal lowers concentrations of 1,2-DCA to below its MCL throughout the plume. Partial source depletion has negligible impact on benzene extent, which is more effectively limited by its high aerobic biodegradation

rate, but does shorten MTBE maximum extent from 21 to 15 m. In 2017, MTBE does not occur above the regulatory standard with source removal in short plume simulations (Table 4a). Source removal is therefore most effective as a stand alone remedial measure for 1,2-DCA, somewhat effective for EDB and MTBE, and has no effect on benzene extent in the short plume case (Table 5).

The effects of 90% source removal in the long plume case are portrayed in Fig. 6. The maximum extent of EDB is the same as in the natural attenuation case (605 m), given that insufficient time has elapsed for reduced concentrations to propagate downgradient. Over longer timeframes the reduced concentrations caused by source removal continue to propagate downgradient, shortening the length of the long plume from 535 to 265 m 10 years after the removal (Table 4b). Though this represents roughly a 50% reduction in plume extent, longer plumes will require significant timeframes to realize the benefits of source depletion in downgradient plume zones. No removal would be necessary for 1,2-DCA and MTBE because both are attenuated by dissolution of the source in the long plume case. In other words, source removal that occurs 20 years after a release will not lessen the impact of compounds like 1,2-DCA, whose maximum extent occurs earlier, or MTBE, which forms a detached plume that is logically not affected by a source removal action. Benzene extent is shortened from 57 to 42 m in 2012 and 56 to 41 m in 2017 (Fig. 6, Table 4b). In the long plume case, source removal alone is somewhat effective for EDB and benzene, is unnecessary for 1,2-DCA, and has no effect on MTBE (Table 5).

5.4. Biostimulation case

In the short plume case, biostimulation yields similar results to partial source removal for EDB (Fig. 7). Biostimulation produces accelerated decline in plume concentration relative to the natural attenuation case, as evidenced by the steeper slope of the biostimulated trend line. This contrasts with the partial

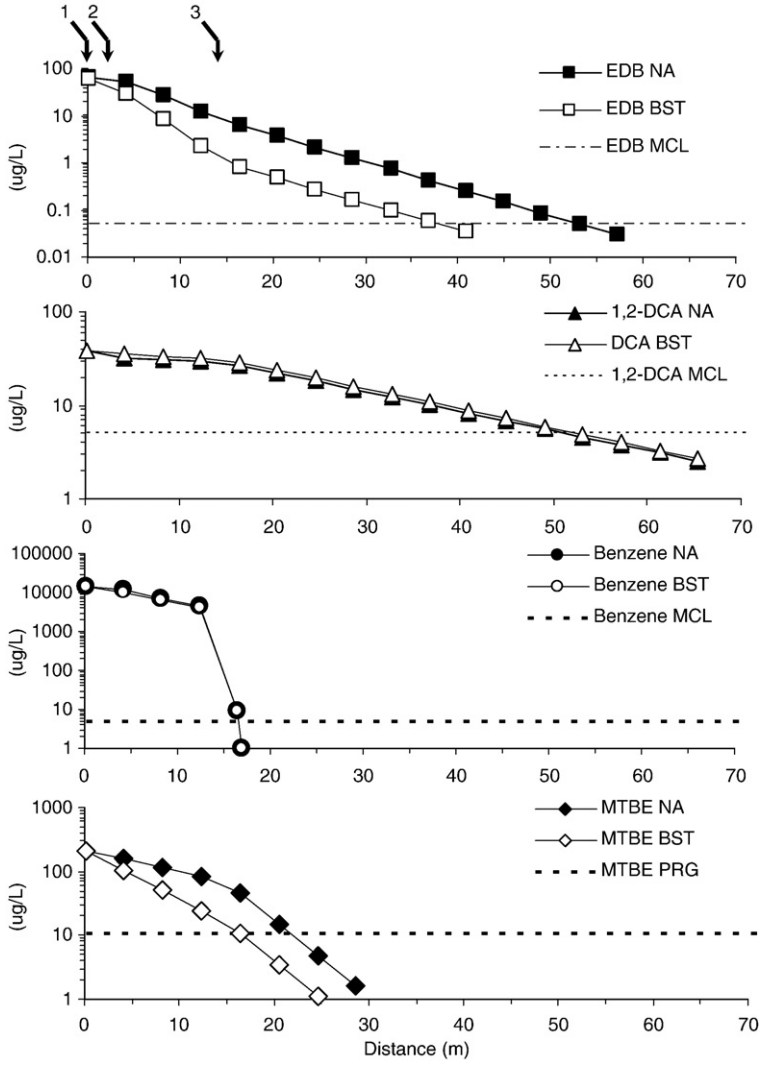

Fig. 7. REMChlor simulation results of biostimulation, short plume scenario, 2012. Zone 1, 2, and 3 markers are suspended above graphs at 0, 5 and 15 m downgradient, respectively. NA = natural attenuation; BST = biostimulation; MCL = maximum contaminant level; PRG = USEPA Region 9 Preliminary Remediation Goal.

source removal case, in which EDB concentrations discharging from the source zone are 90% lower initially, while plume concentrations decline at the same rate (i.e., the slopes of the natural attenuation and source removal trend lines are parallel). The maximum extent of EDB above its MCL in 2012 in the biostimulated short plume is 41 m, compared to 37 m in the 90% source removal case (Table 4a). Unlike partial source removal, lasting change in plume concentrations is not achieved through biostimulation because source mass is unaffected. Upon cessation of biostimulation in 2012, plume concentrations begin to return to natural attenuation conditions, and by 2017, the EDB extent matches the natural attenuation case (52 m) (Table 4a). Therefore, in this case, biostimulation is capable of shortening plume length, but only so long as it is actively applied. In laboratory microcosms, addition of lactate had little effect on 1,2-DCA, and as a consequence, little change in maximum 1,2-DCA extent is evident in biostimulation simulations, relative to the natural attenuation case (Fig. 7). Likewise, biostimulation does not alter the maximum extent of the benzene plume, though MTBE plume extent is shortened from 21 to 15 m in 2012. Like EDB, MTBE plume extent returns to natural attenuation conditions in 2017, upon cessation of biostimulation (Fig. 7, Table 4a). On the whole, biostimulation shows some temporary effectiveness for EDB and MTBE, but none for 1,2-DCA and benzene (Table 5).

In the long plume case, biostimulation achieves temporary reductions in EDB concentrations by 2012, but they are limited in extent (by the advective velocity of the plume), and concentrations remain an order of magnitude above the MCL. In 2017, concentrations of EDB return to pre-biostimulation concentrations in the near-downgradient portions of the plume, but by this time reduced concentrations brought on by biostimulation have moved into the far downgradient portions of the plume, decreasing maximum plume extent from 535 to 408 m (Table 4b). This represents a 24% reduction in plume extent, compared to the roughly 50% reduction that was achieved in the source removal case. However, for reasons stated above, the EDB plume would begin to lengthen

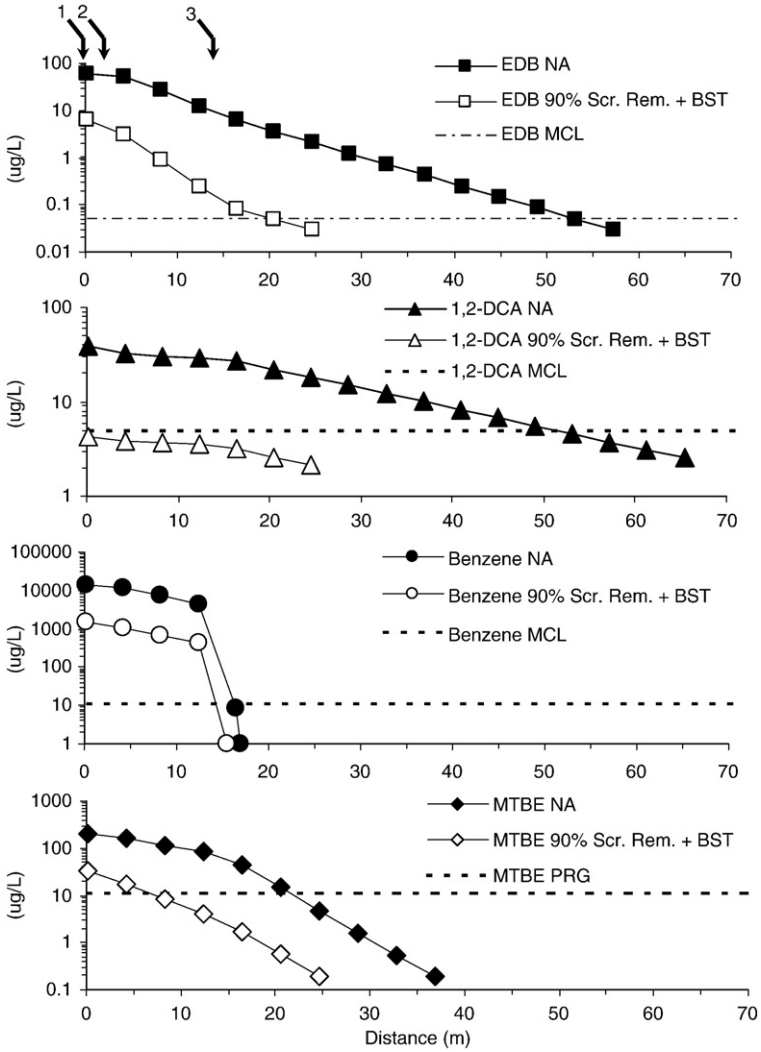

Fig. 8. REMChlor simulation results of 90% source removal combined with biostimulation, short plume scenario, 2012. Zone 1, 2, and 3 markers are suspended above graphs at 0, 5 and 15 m downgradient, respectively. NA = natural attenuation; Scr. Rem. = source removal; BST = biostimulation; MCL = maximum contaminant level; PRG = USEPA Region 9 Preliminary Remediation Goal.

and eventually stabilize at natural attenuation length once biostimulation ceases. Given the similarity of benzene natural attenuation and biostimulation rates, there is negligible difference in their plume extent (Table 4b). No remediation would be necessary for 1,2-DCA since it attenuates below the MCL by 2012. As discussed above, MTBE forms a detached plume of uniformly declining concentrations between 600 and 900 m downgradient in the long plume case, but this would logically not be affected by plume biostimulation that only extends 15 m from the source. Relative to the short plume case, biostimulation of the long plume is less effective for EDB, unnecessary for 1,2-DCA, and has no effect on benzene and MTBE (Table 5).

5.5 90% source removal + biostimulation

Simulations were conducted to determine the effects of combined 90% source removal and biostimulation. Fig. 8 presents results for the short plume case in 2012 and Fig. 9 shows long plume extent in 2017. The combined action of partial source removal and biostimulation effectively halves the maximum extent of EDB to 21 m in the short plume case (Fig. 8). An immediate 90% reduction in concentrations discharging from the source zone is achieved through source depletion, but additional plume destruction occurs for 15 m downgradient of the source. Biostimulation ceases in 2012, and as a result EDB extent in 2017 matches that of source removal alone (35 m) (Table 4a). Because 1,2-DCA and benzene did not respond to lactate addition in the laboratory, the results of these simulations were not substantially different from those in which source removal alone was evaluated (Table 4a). Source depletion and biostimulation together reduce MTBE extent to 6 m in 2012 and 0 m in 2017 (Table 4a). The combined effects of source removal and biostimulation provide temporary added benefit in the case of EDB and benzene when compared to the source removal case, but none for 1,2-DCA and MTBE (Table 5).

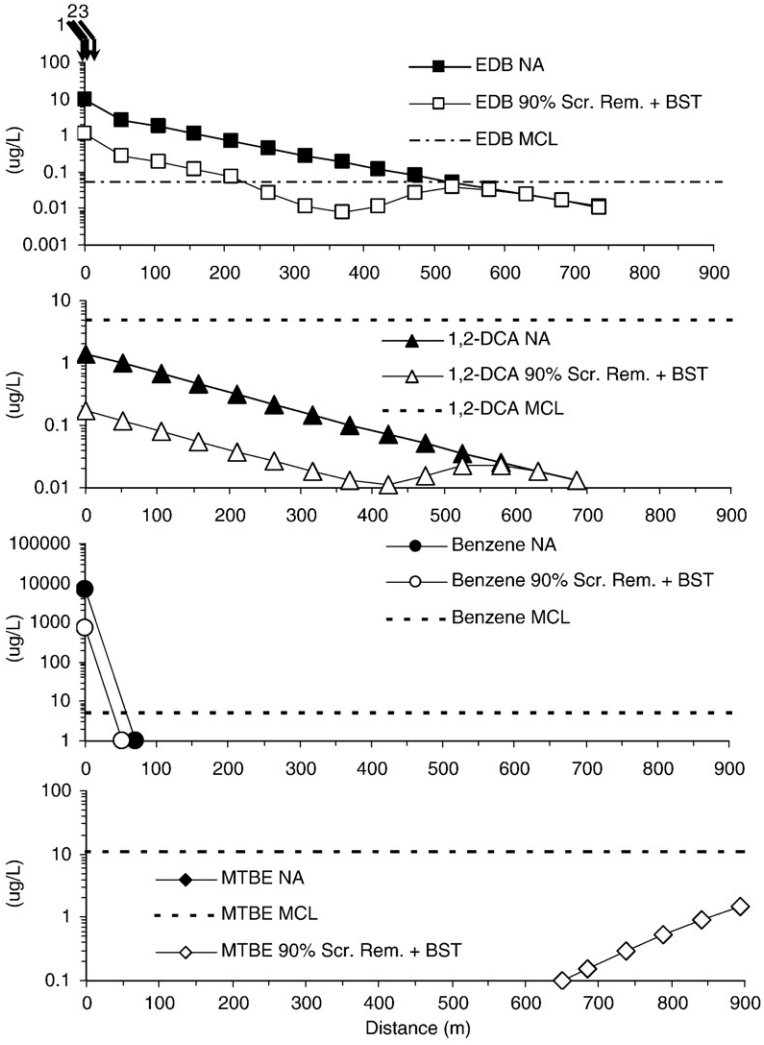

Fig. 9. REMChlor simulation results of 90% source removal combined with biostimulation, long plume scenario, 2017. Zone 1, 2, and 3 markers are suspended above graphs at 0, 5 and 15 m downgradient, respectively. NA = natural attenuation; Scr. Rem. = source removal; BST = biostimulation; MCL = maximum contaminant level; PRG = USEPA Region 9 Preliminary Remediation Goal.

More extensive timeframes are necessary for the benefits of remediation to propagate downgradient in long plumes, so maximum plume extent is presented within 10 years of the onset of remediation (i.e., in 2017) (Fig. Fig. 9). Partial source depletion and plume remediation together are not sufficient to reduce concentrations of EDB to its MCL at any point in the plume within 5 years of the start of remediation. However, 10 years after the onset of remediation, reduced concentrations brought on by remediation have had sufficient time to propagate farther downgradient, shortening the plume to 239 m, or a 55% reduction (Fig. 9). This represents only a 5% improvement relative to applying source removal alone, indicating that biostimulation over relatively short distances and timeframes will yield little additional benefit at sites where long plumes of EDB exist. The same is true for 1,2-DCA and benzene for reasons stated above. Combined source and plume remediation do not attenuate the detached MTBE plume in 2017, as natural attenuation processes alone are sufficient to decrease MTBE plume concentrations to below 11 μg/L (Fig. 9). Relative to 90% source removal alone, negligible additional benefit is provided for EDB, and none is provided for the other compounds (Table 5).

6. Discussion

It is difficult to compare this evaluation to other studies, given that such an analysis has not been conducted for EDB and 1,2-DCA, and the fact that other screening level analytical models do not simulate the effects of variable source depletion and plume remediation. Relative importance, an indirect measure of the risk posed by each compound (the ratio of aqueous concentration to applicable regulatory screening value), varies by contaminant across space and time. Near UST source zones, EDB and benzene can have similar relative importance. If later releases of unleaded gasoline occur, the relative importance of benzene (and other hydrocarbons) will increase. The relative importance of MTBE is greatest among the four compounds modeled here, but it sustains brief (but mobile) plumes, given rapid source dissolution. Plume biodegradation is not likely to significantly attenuate high MTBE concentrations, and significant detached MTBE plumes may result. To our knowledge, no studies have evaluated the co-occurrence of the lead additives and MTBE at UST sites. The relative importance of 1,2-DCA near the source zone is lowest of the four compounds due to its lower ratio of source concentration to MCL. Plume degradation rates become more important as distance downgradient of the source zone increases, and the order of relative importance may change as a result. One case in point is benzene, which has high relative importance in anaerobic near-source zones, but due to its aerobic biodegradability may not occur at all in downgradient areas. Although EDB and 1,2-DCA are aerobically biodegradable, field evidence suggests they degrade in the aerobic setting at much slower rates compared to other components of gasoline and they may persist downgradient of the source even when they are released prior to other hydrocarbons (Falta et al., 2005b).

A single remedial technique may not adequately address commingled plumes of lead scavengers, hydrocarbons, and oxygenates. If equilibrium aqueous concentrations exceed regulatory standards by more than a couple of orders of magnitude, and plumes are already established, source depletion alone is unlikely to be protective. Source depletion and plume remediation together achieve roughly two orders of magnitude reduction in EDB concentration (a 99% decrease in mass) in these simulations, although this may still not be enough to achieve its low MCL of 0.05 μg/L.

Remediation will occur decades after EDB and 1,2-DCA were released to the environment, so extensive timeframes may be required for the positive effects of treatment to be realized where long plumes exist. If robust aerobic degradation occurs, benzene may degrade very quickly, but this same condition favors the persistence of EDB and 1,2-DCA. In the event plume remediation of both EDB and benzene is required, sequenced treatment may be necessary, one near the source zone that focuses on anaerobic degradation of EDB, and another downgradient where aerobic degradation of benzene can be effected without the risk of encouraging the persistence of EDB (and 1,2-DCA). Given the toxicity of EDB, it may be preferable that this compound be treated at the expense of increasing benzene transport so long as the benzene can be expected to degrade readily in downgradient aerobic zones. It should be pointed out that this modeling exercise did not account for the potential effects of benzene on biotransformation of other compounds, such as MTBE. Such spatial considerations and sequenced plume remediation has not typically been required at UST sites. Given rapid source dissolution of MTBE, this compound may no longer be present at all at UST sites where remediation of EDB and 1,2-DCA is undertaken, despite the fact that more recent releases may have occurred.

As experience with commingled plumes of EDB, 1,2-DCA, fuel hydrocarbons, and oxygenates grows, the efficacy of source and plume remediation will improve. Plume bioremediation might be optimized by increasing the area over which it is applied, and bioaugmentation might also be implemented for 1,2-DCA, which did not respond to biostimulation with lactate in laboratory microcosms (Henderson et al., 2008). Bioaugmentation may also be used to increase anaerobic biodegradation rates for EDB, although commercial cultures for this purpose are not yet available. Where both source and plume remediation are necessary, it is unclear if source removal would perturb subsurface conditions and have negative impacts on downgradient plume bioremediation. It is important that aerobic remedial techniques for EDB and 1,2-DCA be explored at UST sites. Aerobic bioremediation may hold promise given that both EDB and 1,2-DCA serve as growth substrates under these conditions. Currently there is no S_{min} value (the minimum substrate concentration that supports growth) (Rittmann and McCarty, 2001) for EDB, so it is impossible to say if aerobic biodegradation can be sustained at the very low levels necessary to attain its MCL.

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