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Screening Level Calculations of Dissolved Benzene Plume Development

Williams ST012 SEE Evaluation and Other Technical Support

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The purpose of this memorandum is to provide screening level estimates for the potential length of the dissolved benzene plume emanating from the NAPL source zones at Site ST012 following the implementation of steam enhanced extraction (SEE). The models employed for the calculations include simplifying assumptions that yield conservative estimates (i.e., the models are expected to slightly over-predict the length of the dissolved plume). In addition, groundwater extraction associated with the implementation of the enhanced bioremediation pilot study is neglected.

The models, inputs, and results are intended to provide order-of-magnitude estimates for dissolved benzene plumes at the site. Actual site conditions are complex and include multiple NAPL sources with unspecified locations whereas the models assume a single source. Further, the benzene content in remaining NAPL is expected to be highly variable across the site; therefore, it is very difficult to differentiate between a decaying dissolved concentration and a downgradient NAPL source partially depleted of benzene.

Conservative Model for Contaminant Plume Length

The transient transport of a dissolved contaminant emanating from an immobile NAPL source zone under natural groundwater flow conditions and experiencing first order degradation is described by,

$$R_i \frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x_j}\left(D_{jk}\frac{\partial C_i}{\partial x_k}\right) - \frac{\partial}{\partial x_j}\left(u_j C_i\right) - \lambda_i C_i \qquad (1)$$

$$R_i = 1 + \frac{\rho_b k_{d,i}}{\phi}$$

The parameters are,

C_i	=	dissolved contaminant concentration in groundwater
D_{jk}	=	dispersion coefficient tensor
R_i	=	retardation coefficient
λ_i	=	first-order decay constant in ground water
u_j	=	Darcy velocity of ground water in the j-direction

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Consider the following conservative model assumptions:

- Tangential dispersion is neglected
- Vertical dispersion is neglected
- Groundwater extraction is neglected
- The discharge concentration from the NAPL source zone is constant (i.e., does not decay)

Simplify the problem with the following additional assumptions:

- Groundwater flow is one-dimensional in the x-direction
- Dispersion coefficient is linearly related to velocity and dispersivity ($D_{xx} = \alpha_x u_x$)

Steady-State Solution for Contaminant Plume Length

Under the assumptions described above and assuming steady-state conditions have been achieved with no decline in the source concentration, the transport equation (1) reduces to the following one-dimensional form,

$$\alpha_x \frac{\partial^2 C_i}{\partial x^2} - \frac{\partial C_i}{\partial x} - \frac{\lambda_i}{u_x} C_i = 0 \tag{2}$$

The boundary condition at x = 0 is a constant concentration related to dissolution from a residual NAPL and in the far field the concentration goes to zero,

$$C_i(0) = C_{i,N}$$

$$C_i(\infty) = 0$$

The solution to the steady state equation (2) including dispersion and first order degradation is [van Genuchten & Alves, 1982],

$$C_i(x) = C_{i,N} exp\left[\left(\frac{1 - \sqrt{1 + 4\frac{\alpha_x \lambda_i}{u_x}}}{2\alpha_x}\right) x\right] \tag{3}$$

Rearranging equation (3), the length of the plume required for the dissolved concentration to decay to a given value, such as the MCL, is,

$$L_{MCL} = \frac{2\alpha_x}{1 - \sqrt{1 + 4\frac{\alpha_x \lambda_i}{u_x}}} ln\left[\frac{C_i(MCL)}{C_{i,N}}\right] \tag{4}$$

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As indicated in equation (4), the estimate for the length of the dissolved plume is governed by the source zone concentration, the groundwater velocity, the first order decay rate, and the longitudinal dispersivity.

Transient Solution for Contaminant Plume Length

Relaxing the steady-state assumption, the transient form of the problem becomes,

$$R_i \frac{\partial C_i}{\partial t} = \alpha_x u_x \frac{\partial^2 C_i}{\partial x^2} - u_x \frac{\partial C_i}{\partial x} - \lambda_i C_i \tag{5}$$

Assuming the boundary conditions stated above and a zero initial condition, the solution to the transient equation (5) is [van Genuchten & Alves, 1982],

$$C_i(x,t) = \frac{C_{i,N}}{2}\left\{exp\left[\frac{x(1-A)}{2\alpha_x}\right] erfc\left[\frac{xR_i - tu_xA}{2\sqrt{R_i\alpha_x u_x t}}\right] + exp\left[\frac{x(1+A)}{2\alpha_x}\right] erfc\left[\frac{xR_i + tu_xA}{2\sqrt{R_i\alpha_x u_x t}}\right]\right\} \tag{6}$$

With the definition,

$$A = \sqrt{1 + \frac{4\lambda_i \alpha_x}{u_x}}$$

The only additional parameter introduced in the transient solution is the retardation coefficient.

Parameter Values for Estimating the Benzene Plume Length at Site ST012

Site-specific values for each of the input parameters to the plume equations are available from previous work at the site or published literature. Relatively consistent estimates are available for the source benzene concentrations from recent groundwater sampling events (post-SEE) as reported by Wood in recent monthly BCT meetings. Ambient groundwater velocities in each of the three vertical stratigraphic zones have been estimated in multiple studies. The values for these two parameters are listed in Table 1 under the column labeled "Base Value" and the source of the values is listed in the column labeled "References/Notes."

A dispersivity in the LSZ was estimated from data collected during the push-pull tests of the Enhanced Bioremediation Field Test as reported in Appendix C of Addendum #2 Remedial Design and Remedial Action Work Plan (Amec, 2018). The dispersivity does not have a strong influence on the plume length, as compared to the decay constant, therefore the LSZ value of 20 feet from the push-pull tests was assumed as the base value in all three stratigraphic zones.

Table 1. Site-Specific Input Parameter Estimates for Benzene

	Unit	Base Value	High (x3.33)	Low (/3.33)	References/Notes
Cobble Zone (CZ)					
Source Concentration	µg/L	1,200	4,000	360	ST012-CZ15 (Apr 18)
Groundwater Velocity	ft/day	0.343	1.14	0.114	Amec, 2018, Appendix E
Dispersivity	ft	20	67	6.7	Amec, 2018, Appendix C
First Order Decay Constant	1/day	0.0036	0.012	0.0012	Aronson, 1997, 1999
Upper Water Zone (UWBZ)					
Source Concentration	µg/L	6,000	20,000	1,800	ST012-UWBZ30 (May 18)
Groundwater Velocity	ft/day	0.0635	0.21	0.021	Amec, 2018, Appendix E
Dispersivity	ft	20	67	6.7	Amec, 2018, Appendix C
First Order Decay Constant	1/day	0.0036	0.012	0.0012	Aronson, 1997, 1999
Lower Saturated Zone (LSZ)					
Source Concentration	µg/L	4,700	15,667	1,410	ST012-W36 (Nov-17)
Groundwater Velocity	ft/day	0.2	0.67	0.067	Amec, 2018, Appendix E
Dispersivity	ft	20	67	6.7	Amec, 2018, Appendix C
First Order Decay Constant	1/day	0.0036	0.012	0.0012	Aronson, 1997, 1999

Previous estimates for a first order decay constant for dissolved benzene under natural conditions at Site ST012 are uncertain as subsurface conditions vary across the site and over time. However, the length of the benzene plume to MCL values has not exceeded several hundred feet in the past as illustrated in Slide 19 of the October 2018 BCT Meeting Presentation. Similar distances were calculated with the SEAM3D numerical model that included multiple terminal electron acceptors and Monod kinetics (BEM, 2011, Appendix M). Biodegradation of the contaminant plume is most likely a combination of aerobic biodegradation at the periphery and anaerobic biodegradation within the plume (Wiedemeier et al. 1995). Benzene is readily degraded aerobically and background dissolved oxygen concentrations at ST012 are reported to be relatively high at about 7 mg/L in all three zones (Amec, 2018, "ST012 Field Parameter Summary Table").

Current conditions for biodegradation within much of the remaining NAPL source zones have been altered by the implementation of steam enhanced extraction; however, conditions well beyond the thermal zones are likely unaffected. Aerobic degradation utilizing background dissolved oxygen is a probable process for limiting the length of the dissolved benzene plume. Estimates for the benzene degradation rate constant are available from literature. For aerobic degradation, Aronson et al. (1999) report a median for the aerobic benzene biodegradation rate constant of 0.096 day^{-1} for 118 studies. Aronson et al. (1997) found a mean benzene anaerobic biodegradation rate constant of 0.0036 day^{-1} for 41 field studies. In the calculations to follow, the mean anaerobic rate constant was employed as the base case to provide a conservative estimate for the benzene MCL plume length downgradient from the NAPL source zone.

Reported measures of the organic carbon fraction in the soil solids is low at ST012; therefore, the retardation coefficient of 1.14 used in previous groundwater modeling (BEM, 2011, Appendix M) is assumed for the transient modeling to follow.

Estimates for the Steady-State Benzene Plume Lengths at Site ST012

Equation (1) was utilized to estimate the benzene concentration profiles extending downgradient from the remaining NAPL sources in all three vertical stratigraphic zones. The base values provided in Table 1 were input to the equation and the results are plotted in Figure 1. The cobble zone yielded a plume of about 600 feet assuming the source benzene concentration persists at 1,200 µg/L. The length of the plume is primarily the result of the relatively high groundwater velocity. Similarly, the UWBZ plume length is relatively short at 200 feet because of the low groundwater velocity despite the high source benzene concentration of 6,000 µg/L. The base case estimate for the length of the benzene plume in the LSZ is about 500 feet and is consistent on an order-of-magnitude basis with historical measures at the site.

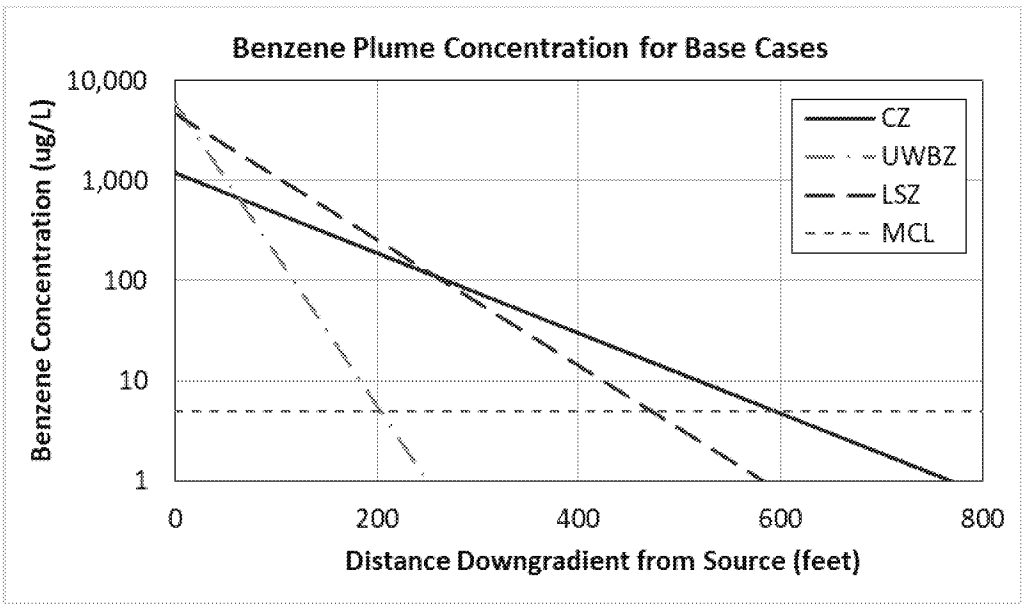


Figure 1. Base Case Estimates for the Dissolved Benzene Plume Profiles

The impact of variations in the source concentration on the benzene MCL-plume length were estimated with equation (2) assuming base values for the groundwater velocity, dispersivity, and first order decay constant . As illustrated in Figure 2, source benzene concentrations above roughly 2,000 µg/L yielded very modest increases on the plume length. For example, doubling the source concentration does not double the estimate for the groundwater plume length because the relationship is not linear.

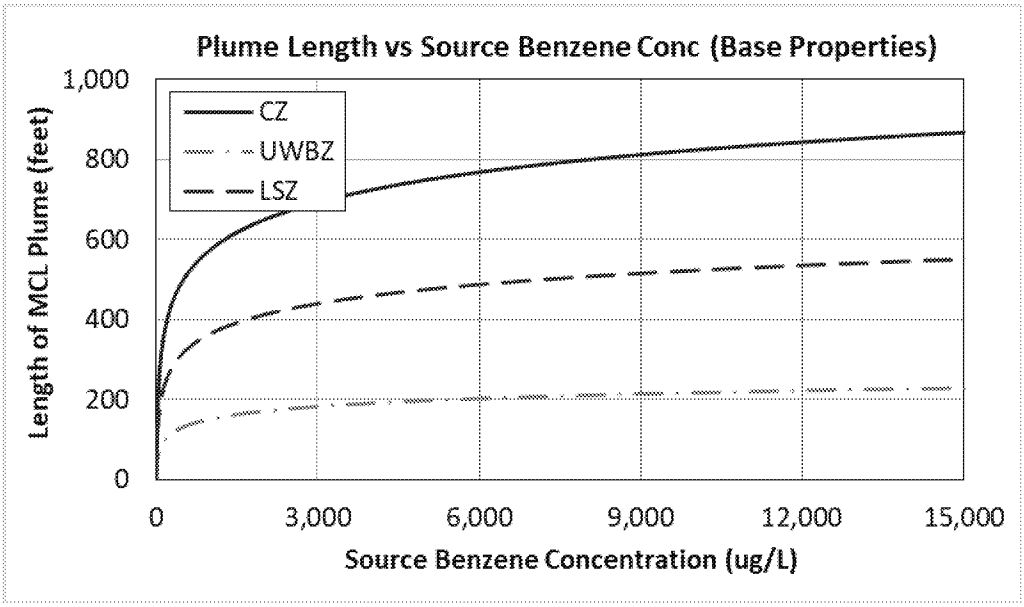
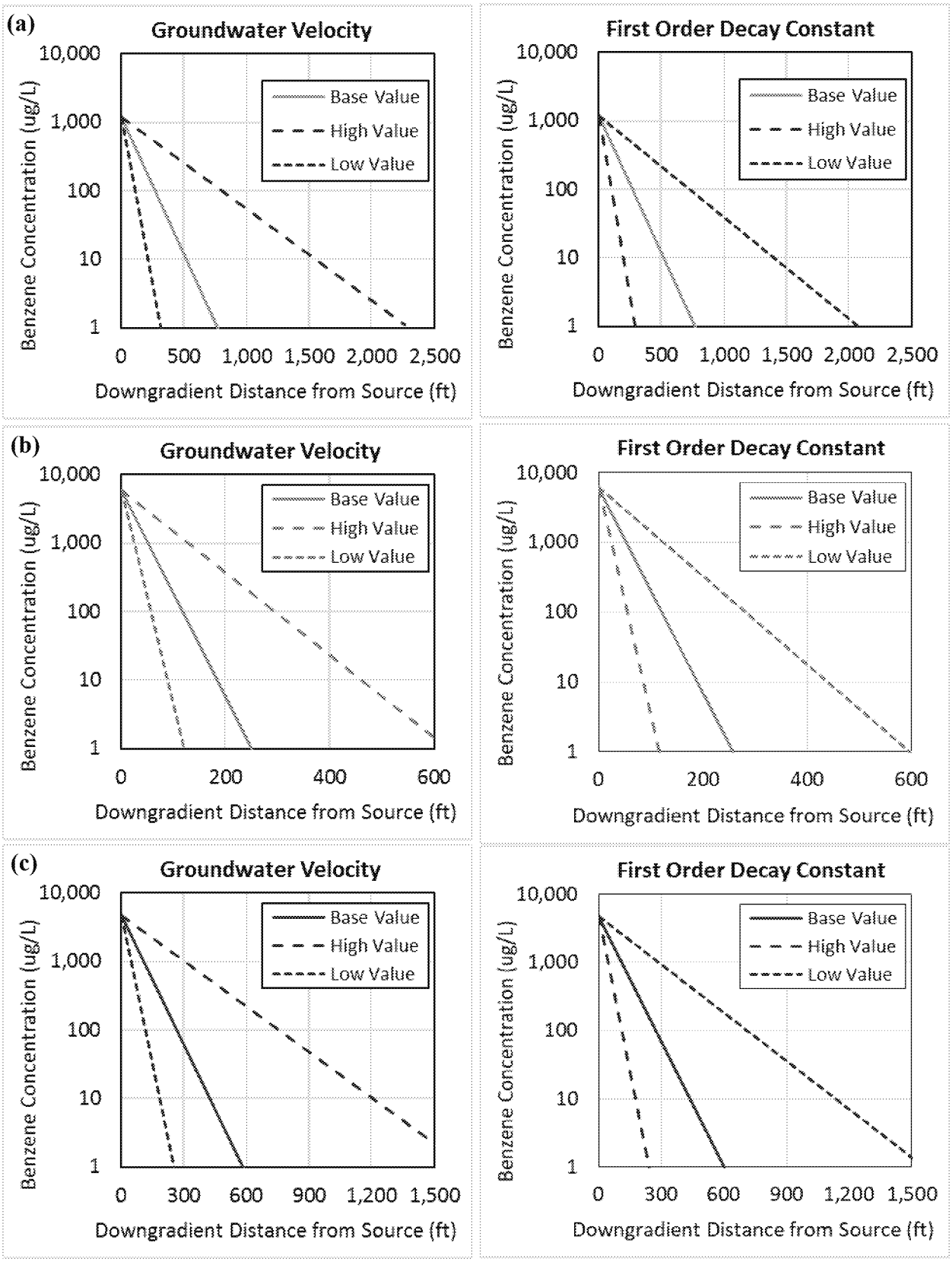


Figure 2. Dissolved Benzene MCL-Plume Length as a Function of Source Concentration (Base Case Properties)

The impacts of changes in the groundwater velocity and first order decay constant were assessed by varying these parameter inputs. Table 1 presents "High" parameter values obtained by multiplying the base value by 3.333 and "Low" values by multiplying the base value by 0.333. The high and low values represent a range of one order-of-magnitude around the base value. Calculations of benzene profiles using equation (1) with the high-low range of values, while holding other parameters at base values, are provided in Figure 3. The title of each graph represents the varied parameter. The individual variations with high groundwater velocity and low first order decay constant yield similar plume lengths for pessimistic scenarios. As indicated in Figure 3, pessimistic plume lengths for MCL are on the order of 2,000 feet for the cobble zone, 600 feet for the upper water bearing zone, and 1,500 feet for the lower saturated zone. Conversely, optimistic scenarios yield plume lengths on the order of 300 feet for the cobble zone, 150 feet for the upper water bearing zone, and 300 feet for the lower saturated zone.

Figure 3. Parametric Evaluation of Plume Length (a) CZ, (b) UWBZ, (c) LSZ



Estimates for the Transient Benzene Plume Lengths at Site ST012

Equation (6) was utilized to estimate the changes in benzene concentration profiles over time after the groundwater pumping associated with the steam enhanced extraction (SEE) process was terminated (Time 0 = April 30, 2016). The base values provided in Table 1 and a retardation coefficient of 1.14 were input to the equation. The calculated profiles after 1, 2, and 3 years are plotted in Figure 4 for each of the three stratigraphic zones. The steady-state profile was attained after roughly 6 to 7 years. These calculations do not consider the ongoing changes in the former thermal treatment zones where temperatures are decaying slowly or changes in conditions for NAPL dissolution and degradation of contaminants.

The cobble zone parameters yielded an MCL-plume length of about 400 feet after two years with the assumptions that the areas downgradient from NAPL were initially free of contaminant and no additional pumping occurred. In UWBZ, the calculated MCL-plume extends to about 150 feet after two years. The calculated MCL-plume in the LSZ reaches about 300 feet after two years.

A qualitative assessment of these model results can be performed by comparing the calculated profiles with measures of benzene concentrations in select monitoring wells located in areas expected to be downgradient from remaining NAPL sources. The wells considered are listed in Table 2 along with the date of sampling, the benzene concentration, and a very rough estimate of the downgradient distance from NAPL. The samples were collected around two years after the cessation of the groundwater extraction associated with SEE.

Table 2. Groundwater Sampling Results for Benzene Approximately Two Years After SEE

Monitoring Well (Date of Sampling)	~Distance (ft)	Concentration (µg/L)
Cobble Zone (CZ)		
Source Zone, CZ15 (Apr 18)	0	1,200
CZ14 (Apr 18)	150	560
CZ12 (Apr 18)	200	590
CZ21 (Apr 18)	210	680
CZ09 (Apr 18)	250	210
C02 (Nov 17)	450	<1
Upper Water Zone (UWBZ)		
Source Zone, UWBZ30 (May 18)	0	6,000
Source Zone, UWBZ18 (Apr 18)	0	5,000
UWBZ09 (Apr 18)	45	810
UWBZ21 (Aug 17)	60	3,400
UWBZ38 (Apr 18)	230	<1
U02 (Nov 17)	300	0.41
Lower Saturated Zone (LSZ)		
Source Concentration, W36 (Nov 17)	0	4,700
LSZ44 (Dec 17)	140	2,100
LSZ54 (Aug 18)	170	<0.4
W34 (Jul 18)	250	<0.4
LSZ55 (Aug 18)	260	0.21
W38 (Jul 18)	300	<0.4

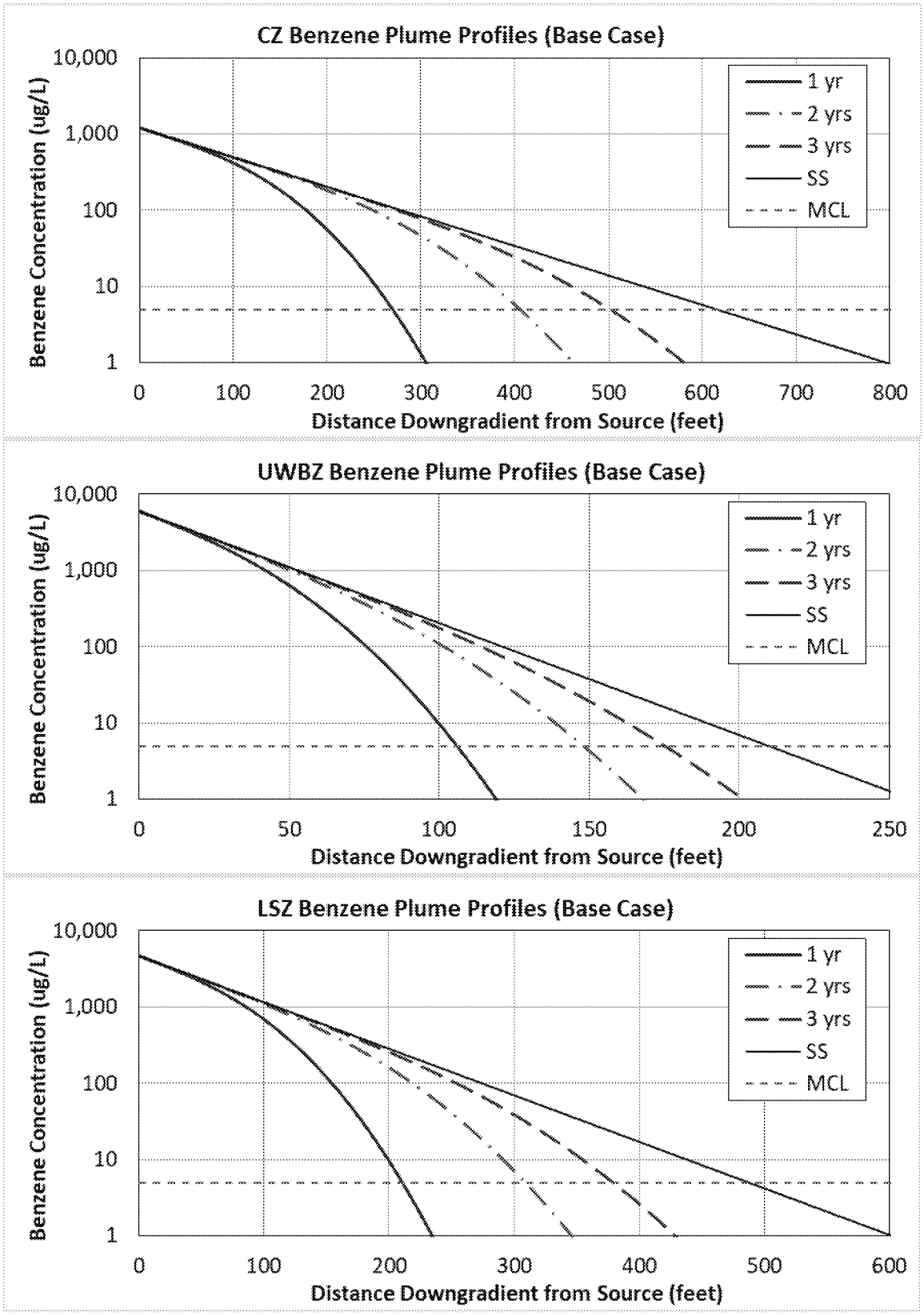
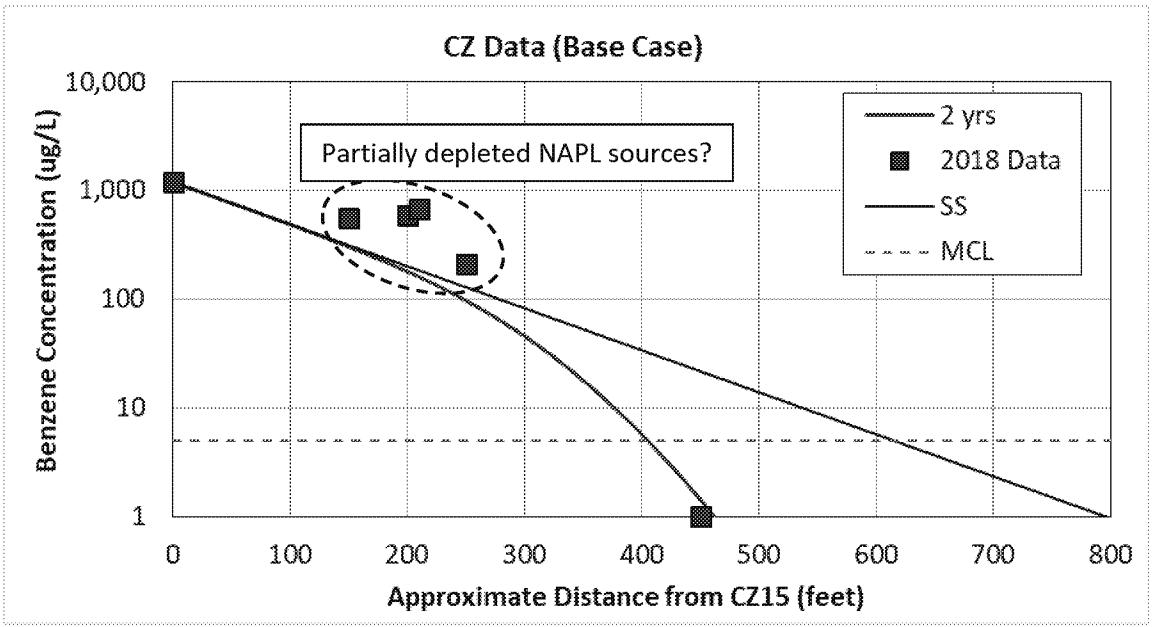


Figure 4. Transient Benzene Concentration Profiles (SS = Steady-State)

A qualitative comparison of the measured benzene concentrations in the Cobble Zone (Table 2) with the calculated downgradient benzene concentration profile after two years is illustrated in Figure 5. This comparison is qualitative at best as the location and benzene content of remaining NAPL in the CZ are not known accurately. However, using the location of well CZ15 as the NAPL boundary yields a reasonable match. As noted in the graph, it is reasonable to presume that additional NAPL exists downgradient of CZ15 that is partially depleted of benzene. Additional characterization wells located 300 to 400 feet downgradient of CZ15 (shown as green dots in the site map) would be beneficial for understanding the plume migration.



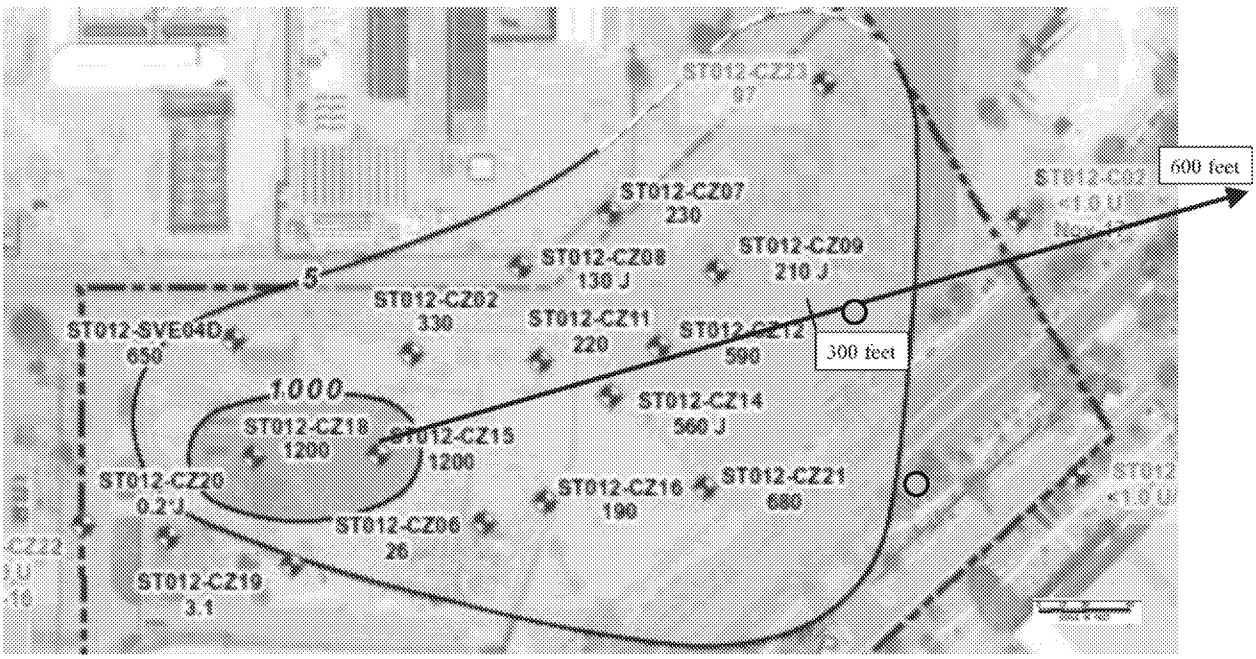
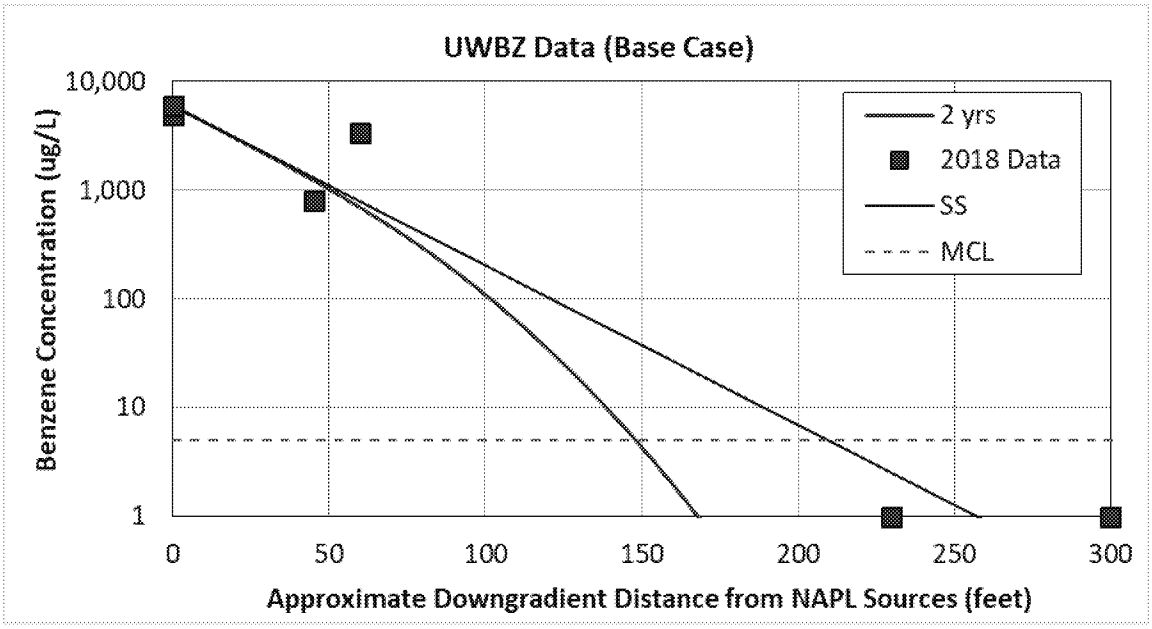


Figure 5. Comparison of Calculated Benzene Profile at 2 years with Data from the CZ

A qualitative comparison of the measured benzene concentrations in the Upper Water Bearing Zone (Table 2) with the calculated downgradient profile after two years is illustrated in Figure 6. As described above, this comparison is qualitative at best. Using the locations of wells UWBZ18 and UWBZ30 as the NAPL boundary yields a reasonable match. Additional characterization wells located 100 to 150 feet downgradient of NAPL boundaries (shown as green dots in the site map) would be beneficial for understanding the plume migration.



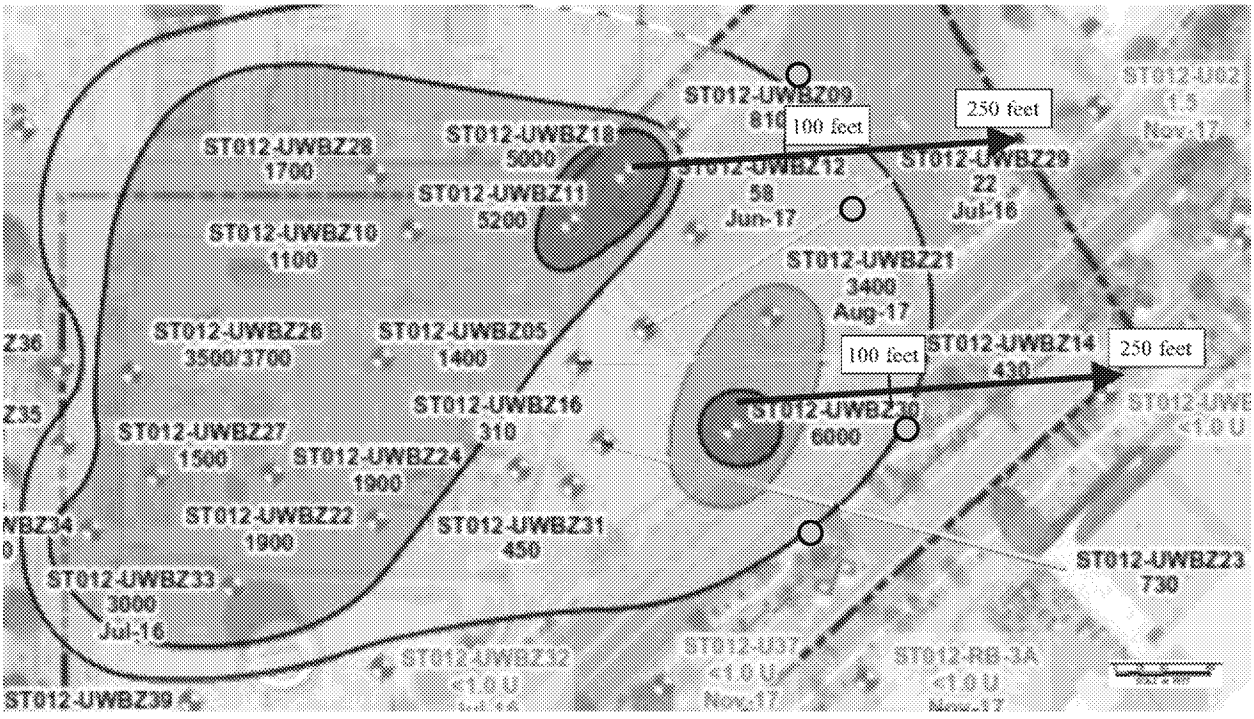
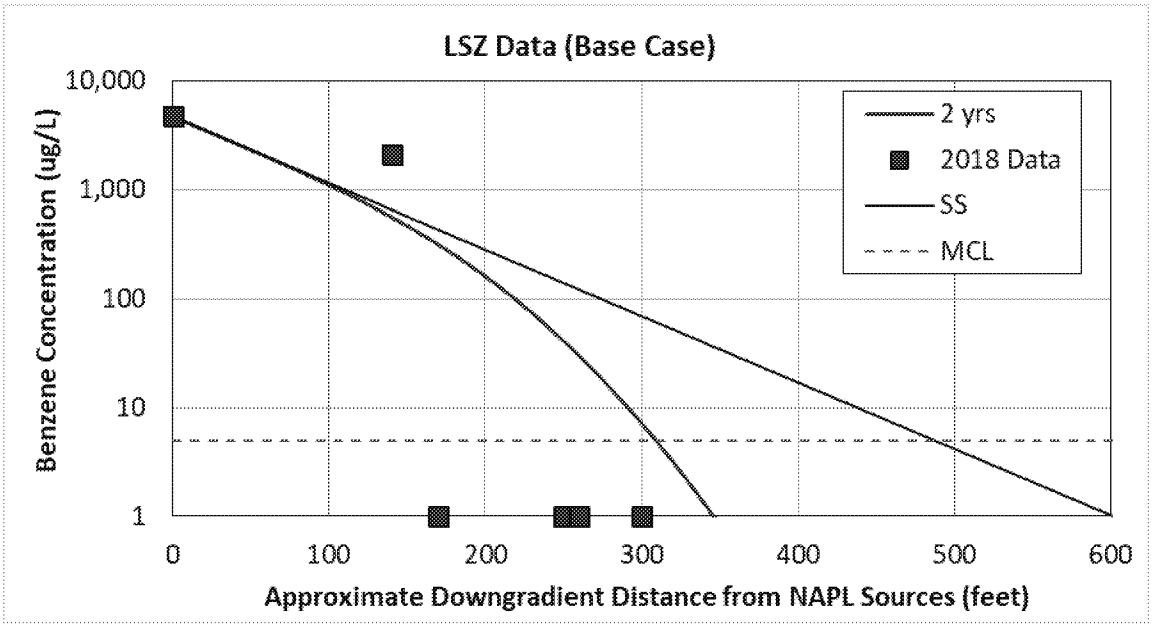


Figure 6. Comparison of Calculated Benzene Profile at 2 years with Data from the UWBZ

A highly qualitative comparison of the measured benzene concentrations in the Lower Saturated Zone (Table 2) with the calculated benzene concentration profile after two years is illustrated in Figure 7. Using the locations of wells W36, W37 and LSZ33 as the NAPL boundary indicates the decay rate constant in the LSZ is significantly higher than the assumed value of 0.0036 day^{-1}. Additional characterization wells located 100 to 150 feet downgradient of NAPL boundaries (shown as green dots in the site map) would be beneficial for understanding the plume migration.



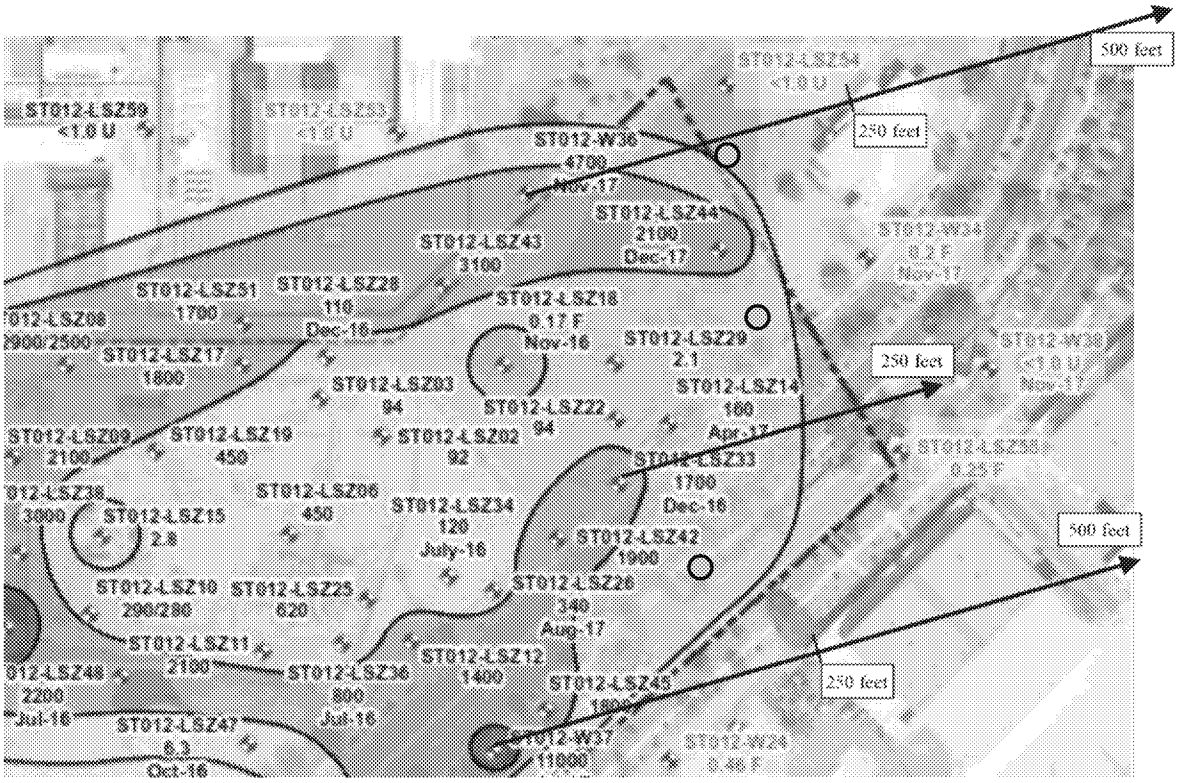


Figure 7. Comparison of Calculated Benzene Profile at 2 years with Data from the LSZ

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