Integrated Site Closure Based on Natural Attenuation

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Goal:

Allow redevelopment of brownfield sites

Site at "no further action" or low intensity management stage

The Challenge:

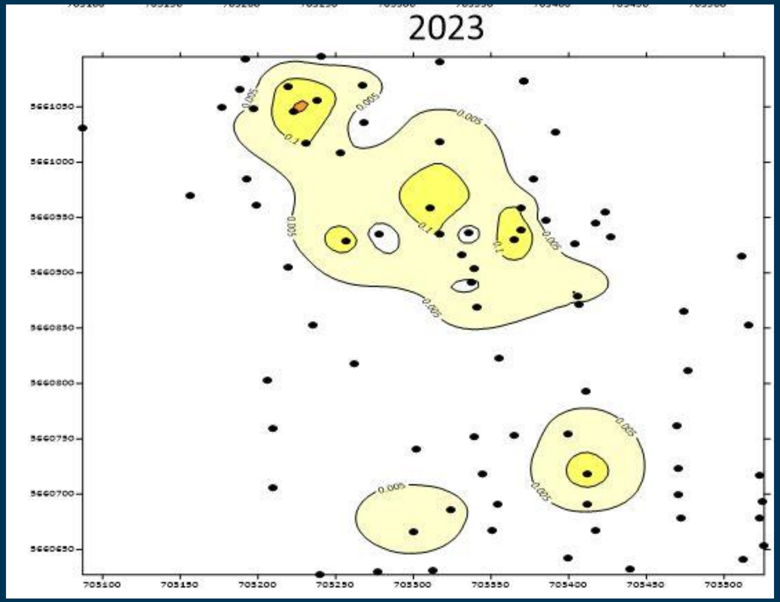
Many sites exceed guidelines but no current or anticipated risk, remediation not practical? Examples:

- Sites with drinking water guideline exceedances, water use controlled but not eligible for elimination
- Sites with unrecoverable/non-migrating LNAPL or management limit exceedance at depth
- Sites where next land use is known and low risk (e.g. solar redevelopment)

How do we progress these sites to redevelopment?

Key requirement:

Demonstration of no current and no future risk



No risk to current receptors

Future land use known or controlled

Plume stability

Understanding of attenuation

Regulatory Acceptance:

<u>Consistent</u> and <u>protective</u> approach

Clear demonstration of CSM

- Plume visualization (e.g. IntelleKt^{EIG})

Defensible demonstration of plume stability

- Multi-year data sets, analysis

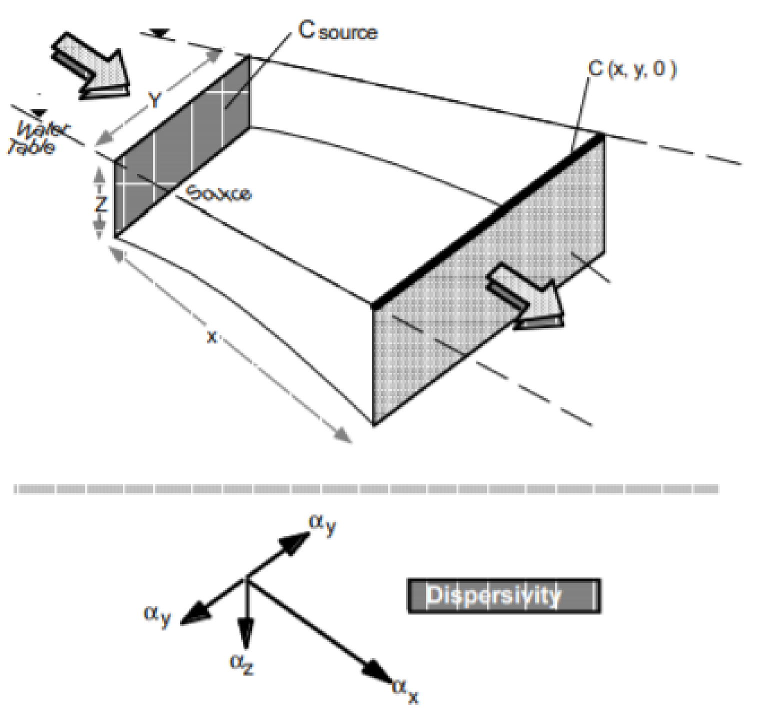
Accepted approaches for predicting attenuation

- Focus of next few slides

US EPA Bioscreen Model

Domenico Transport Model with First Order Plume Decay and Source Attenuation Option (Exponential Decay in Mass Discharge)

Domenico Model with First Order Decay Algorithm



$$C(x,y,o,t) = C_o \exp\left[-k_s(t - x/v)\right] \frac{1}{8} \exp\left[\frac{x}{\alpha_x 2}\left(1-\left(1+4\lambda\alpha_x/v\right)^{1/2}\right)\right] \operatorname{erfc}\left[\frac{\left(x - vt\left(1+4\lambda\alpha_x/v\right)^{1/2}\right)}{2(\alpha_x vt)^{1/2}}\right] \left\{\operatorname{erf}\left[\frac{(y+Y/2)}{2(\alpha_y x)^{1/2}}\right] - \operatorname{erf}\left[\frac{(y-Y/2)}{2(\alpha_y x)^{1/2}}\right]\right\} \left\{\operatorname{erf}\left[\frac{(Z)}{2(\alpha_z x)^{1/2}}\right] - \operatorname{erf}\left[\frac{(-Z)}{2(\alpha_z x)^{1/2}}\right]\right\}$$

where: $v = \frac{K \cdot i}{\theta_e R}$

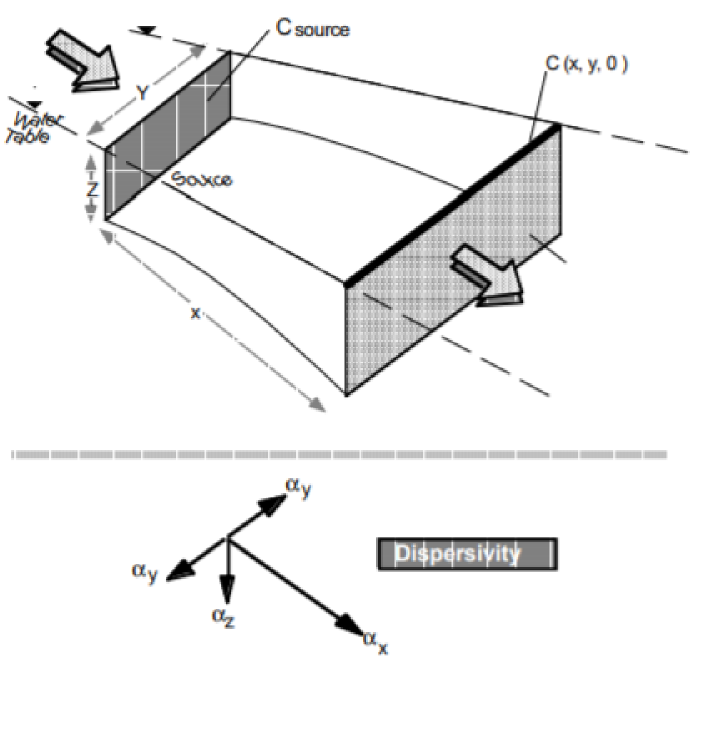
Exponential Source Attenuation / Depletion

Graphic from Bioscreen Manual

US EPA Bioscreen Model

Domenico Transport Model with First Order Plume Decay and Source Attenuation Option (Exponential Decay in Mass Discharge)

Domenico Model with First Order Decay Algorithm



$$C(x,y,o,t) = C_o \exp[-k_s(t - x/v)] \; \frac{1}{8}\exp\left[\frac{x}{\alpha_x 2}\left(1-(1+4\lambda\alpha_x/v)^{1/2}\right)\right] \; erfc\left[\frac{\left(x - vt(1+4\lambda\alpha_x/v)^{1/2}\right)}{2(\alpha_x vt)^{1/2}}\right] \left\{erf\left[\frac{(y+Y/2)}{2(\alpha_y x)^{1/2}}\right] - erf\left[\frac{(y-Y/2)}{2(\alpha_y x)^{1/2}}\right]\right\} \left\{erf\left[\frac{(Z)}{2(\alpha_z x)^{1/2}}\right]-erf\left[\frac{(-Z)}{2(\alpha_z x)^{1/2}}\right]\right\}$$

where: $v = \dfrac{K \cdot i}{\theta_e R}$

Exponential Source Attenuation / Depletion (does not include source biodegradation)

Graphic from Bioscreen Manual

Natural Attenuation & Source Zone Depletion Processes

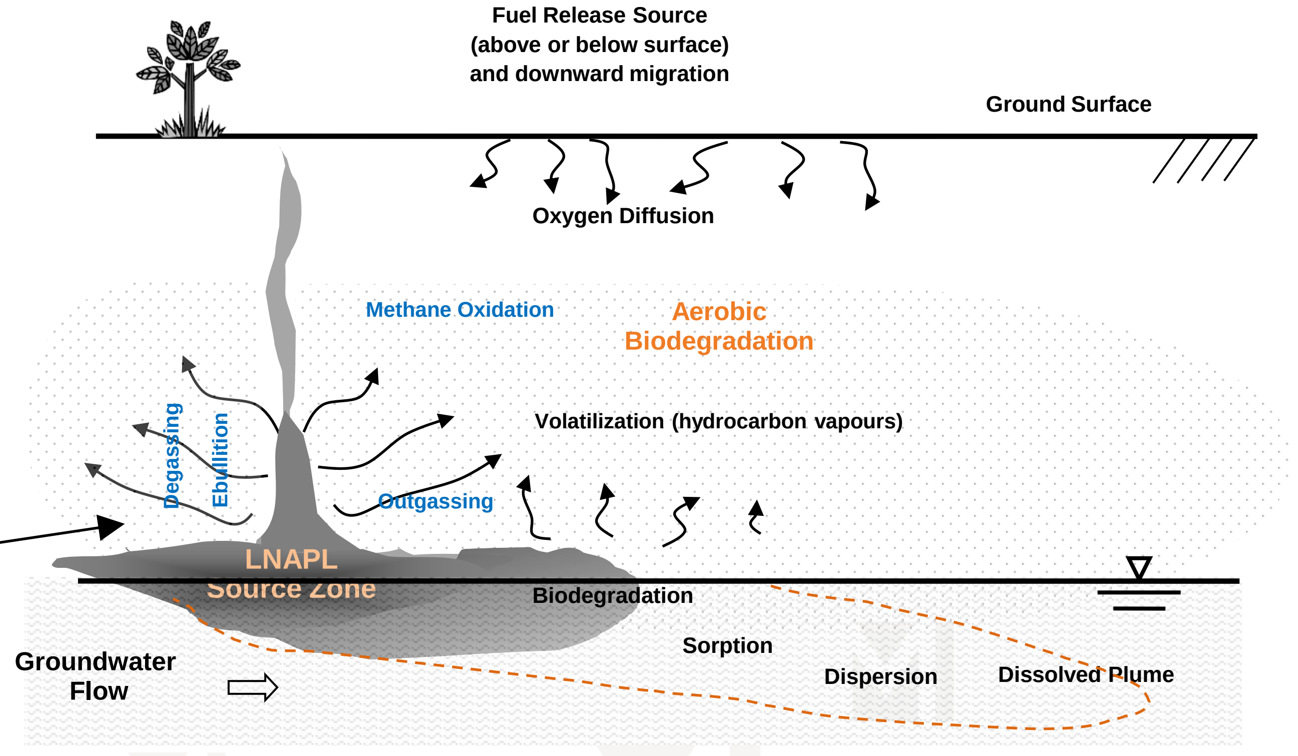
- From CSAP/SHELL Remediation Toolkit #1

Vadose zone rates typically one to two orders of magnitude greater than saturated zone processes

Direct degassing & ebullition (Amos et al, 2005)

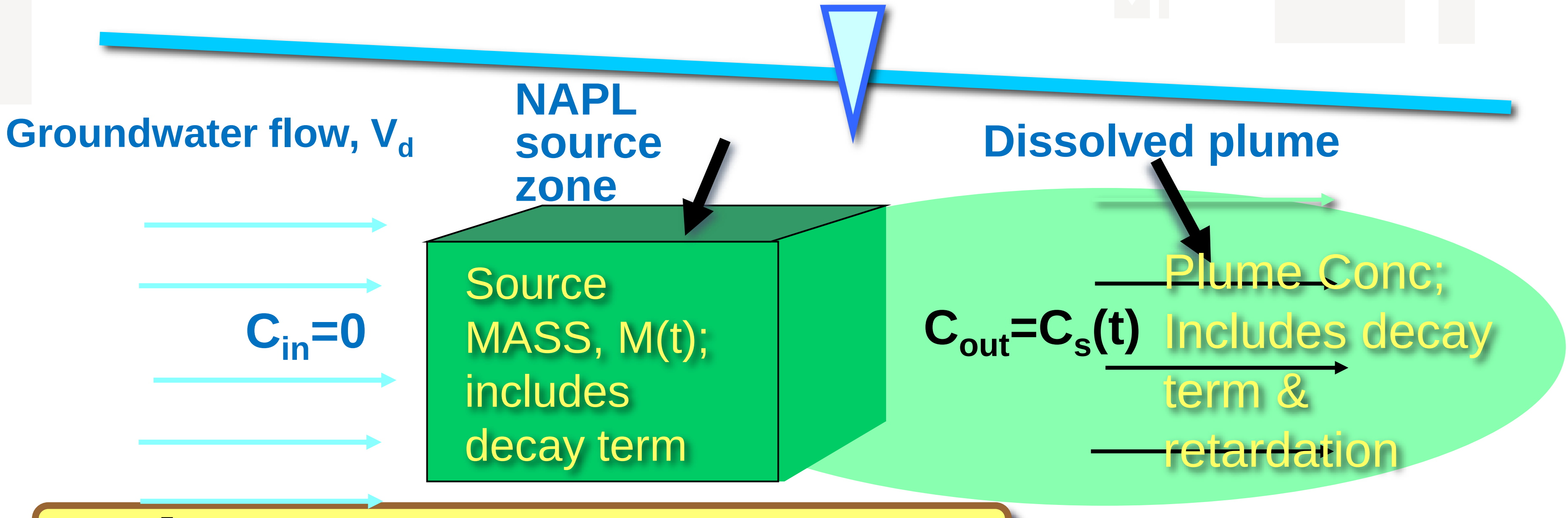
Photograph ITRC LNAPL Guidance

CH_4 generation can be important source depletion mechanism



Conceptual Site Model

US EPA RemFUEL Model



$$\frac{dM}{dt} = -Q(t)C_s(t) - \lambda_s M$$

$$R\frac{\partial C_i}{\partial t} = -v\frac{\partial C_i}{\partial x} + \alpha_x v\frac{\partial^2 C_i}{\partial x^2} + \alpha_y v\frac{\partial^2 C_i}{\partial y^2} + \alpha_z v\frac{\partial^2 C_i}{\partial z^2} + rxn_i$$

Graphic from RemFUEL Training

Mass discharge: Dissolved concentration (Cs) depends on mass remaining in source zone (M)

Plume migration: estimated using Streamtube method + Domenico approximation

Expanded source attenuation model that includes added first-order decay (biodegradation) and generalized mass versus concentration discharge relationship

RemFUEL Source Zone Decay Algorithms - General Form of Equations

$$C_s = \frac{C_0}{M_0^{\Gamma}}\left\{\frac{(\Gamma-1)(Q+\phi\forall\lambda_s)C_0}{M_0^{\Gamma}}t^{*} + M_0^{1-\Gamma}\right\}^{\frac{\Gamma}{1-\Gamma}}$$

$$M = \left\{\frac{(\Gamma-1)(Q+\phi\forall\lambda_s)C_0}{M_0^{\Gamma}}t^{*} + M_0^{1-\Gamma}\right\}^{\frac{\Gamma}{1-\Gamma}}$$

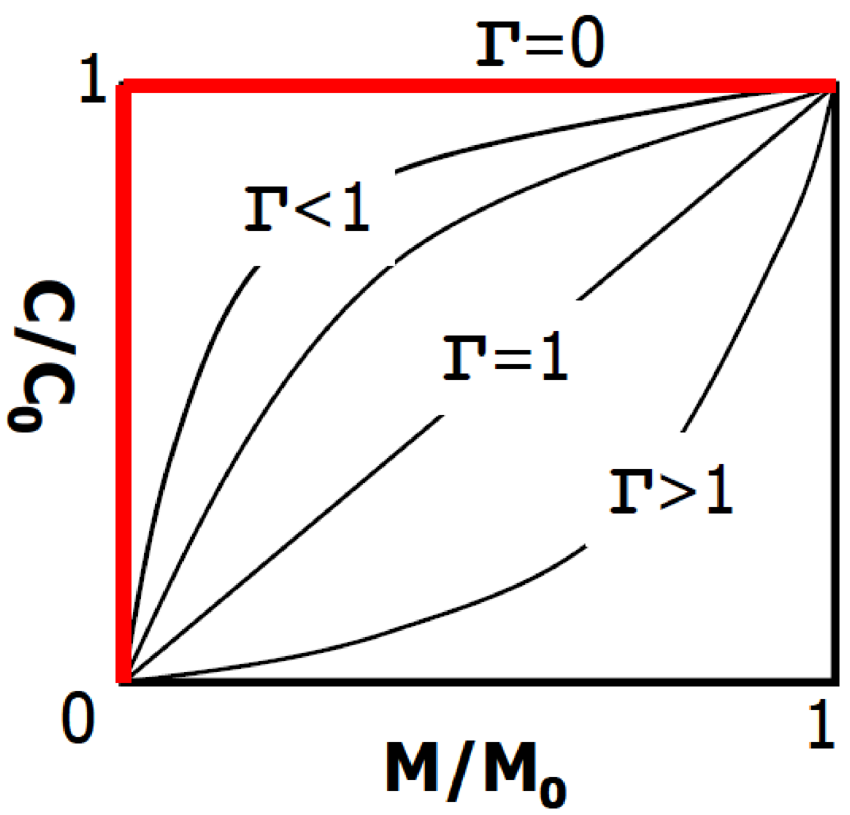
$$t^{*} = t - x/v$$

	Description	Unit
Cs	GW Concentration	mg/L
Co	Initial GW Conc.	mg/L
M	Soluble mass	mg
Mo	Initial soluble mass	mg
Γ	Gamma	-
λs	Source decay term	1/day
ϕ	Porosity	-
Q	Flow rate	L/day
	Volume source zone	L
$\forall$	Distance along flow path	m
v	GW velocity	m/day

Above equations incorporate first-order biodegradation; equations can also be derived for zero-order decay or based on assimilative or biodegradation capacity

Adapted from RemFUEL

RemFUEL Mass vs Concentration Discharge Relationship in Source Zone

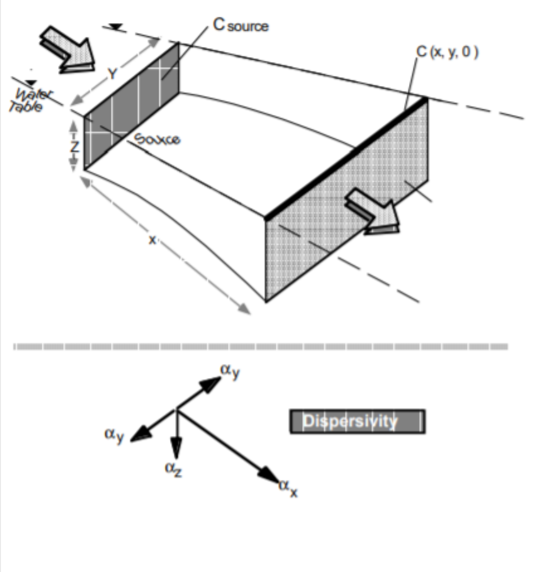


- RemFUEL training states that Γ is thought to vary from 0.5 to 2.0
- Γ = 0.5 recommended for sites with relatively extensive LNAPL, including in higher permeability zones
- Γ = 1.0 recommended for multi-component LNAPL that is more weathered with lower saturations (incorporated in Bioscreen)
- Γ = 2.0 recommended when there is extensive mass diffusion

Modified Source Attenuation and Plume Transport Model in this Study

Domenico Transport Model in Bioscreen + RemFUEL Source Depletion Model

Domenico Model with First Order Decay Algorithm



$$C(x,y,o,t) = C_o \exp\left[-k_s(t - x/v)\right]$$

$$\frac{1}{8}\exp\left[\frac{x}{\alpha_x 2}\left(1-\left(1+4\lambda\alpha_x/v\right)^{1/2}\right)\right]$$

$$erfc\left[\frac{\left(x - vt\left(1+4\lambda\alpha_x/v\right)^{1/2}\right)}{2(\alpha_x vt)^{1/2}}\right]$$

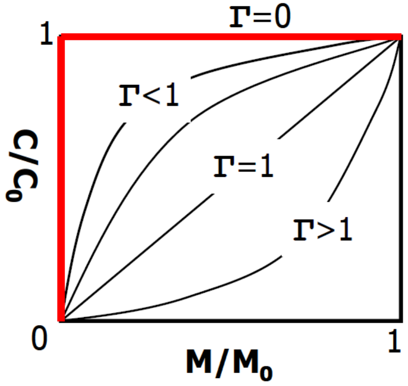
$$\left\{erf\left[\frac{(y+Y/2)}{2(\alpha_y x)^{1/2}}\right] - erf\left[\frac{(y-Y/2)}{2(\alpha_y x)^{1/2}}\right]\right\}$$

$$\left\{erf\left[\frac{(Z)}{2(\alpha_z x)^{1/2}}\right] - erf\left[\frac{(-Z)}{2(\alpha_z x)^{1/2}}\right]\right\}$$

where: $v = \frac{K \cdot i}{\theta_e R}$

Adapted from BioScreen

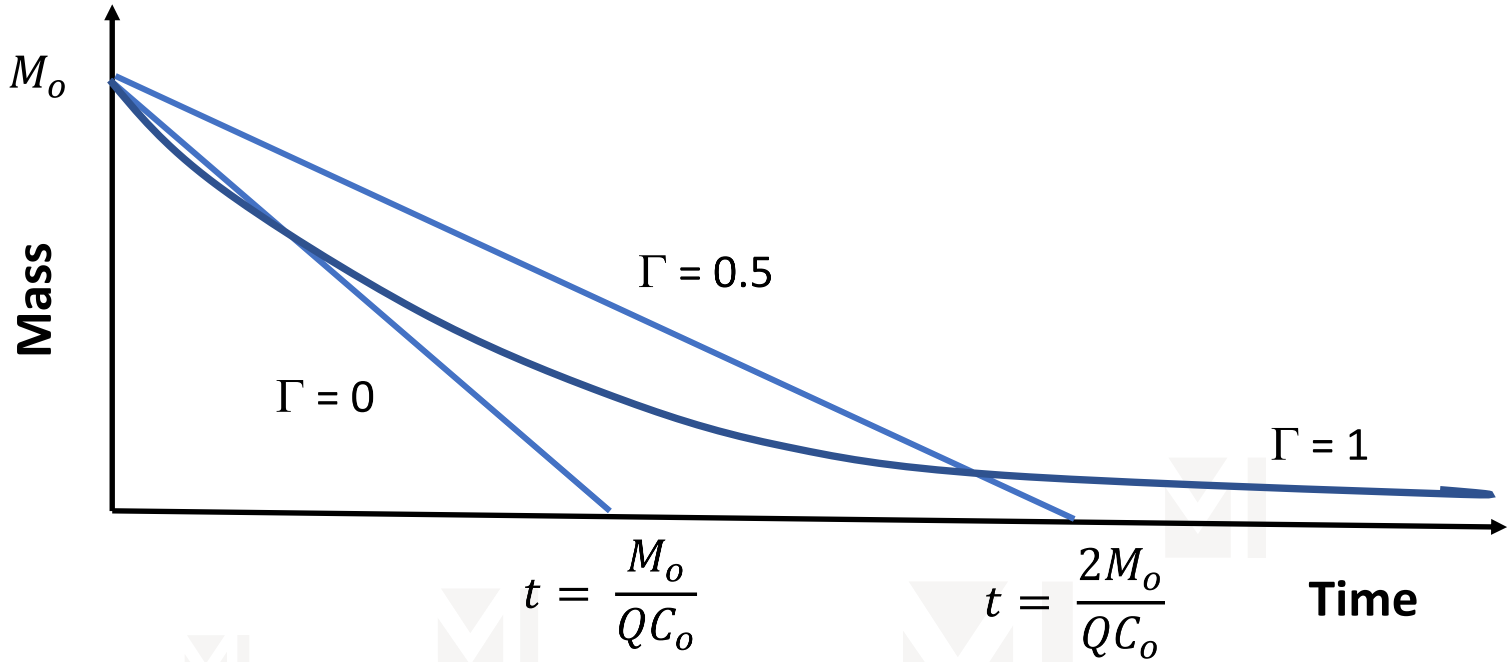
$$\frac{dM}{dt} = -Q(t)C_s(t) - \lambda_s M \qquad \frac{C_s(t)}{C_0} = \left(\frac{M(t)}{M_0}\right)^{\Gamma}$$



Currently Γ = 1 - Exponential attenuation, as per Bioscreen) + optional biodegradation based on first-order decay or biodegradation capacity

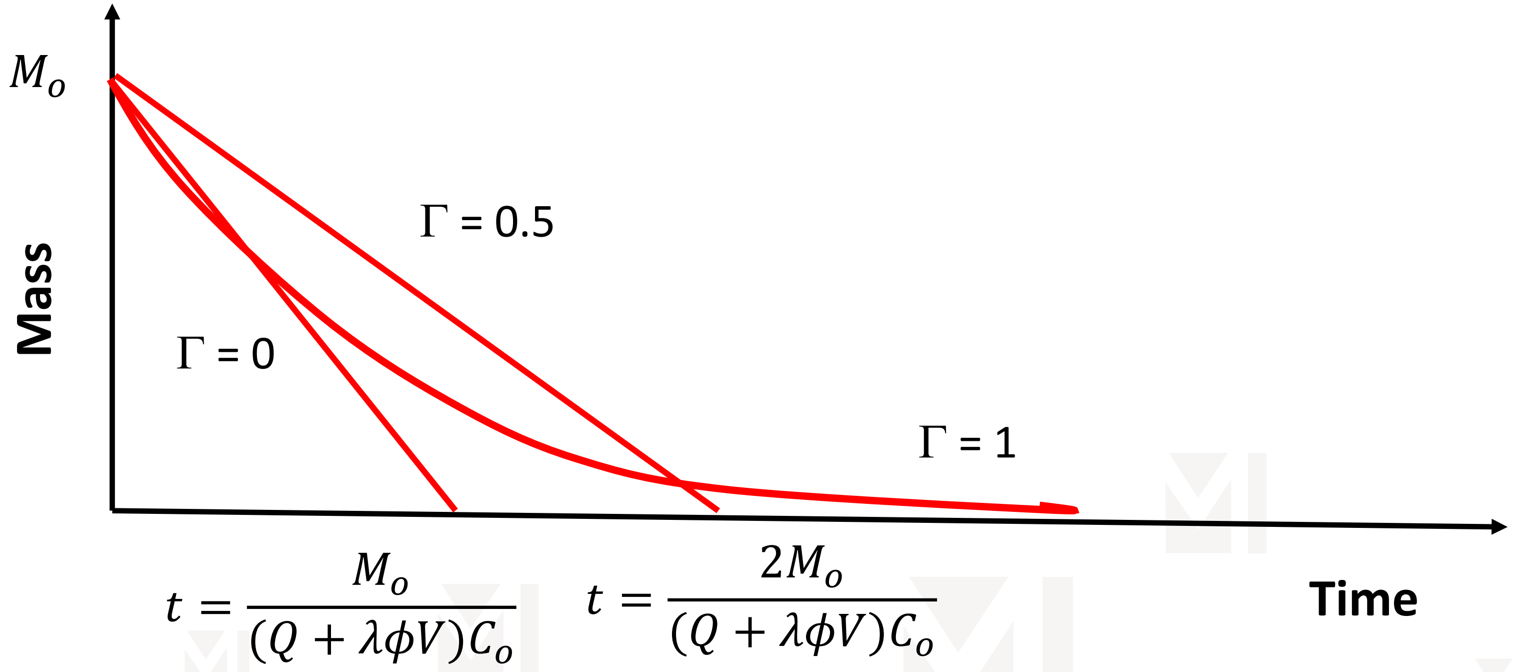
Source Zone Mass Depletion

Sub-Model 1: Dissolution only



Source Zone Mass Depletion

Sub-Model 2: Dissolution + 1st-order bio ($\lambda > 0$)



Source Zone Depletion Models

No depletion: Baseline

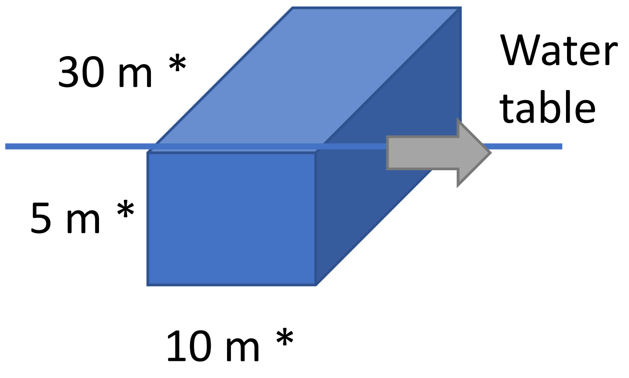
Sub-Model 1: Dissolution or mass discharge only – based on physical processes only

Sub-Model 2: Dissolution + Saturated Zone Biodegradation based on 1st-order decay, which is constrained by estimated NSZD rate

Sub-Model 3: Dissolution + Saturated Zone Biodegradation based on biodegradation capacity (BC) calculation from terminal electron acceptors

Source Zone Depletion and Plume Transport – Small Release Example

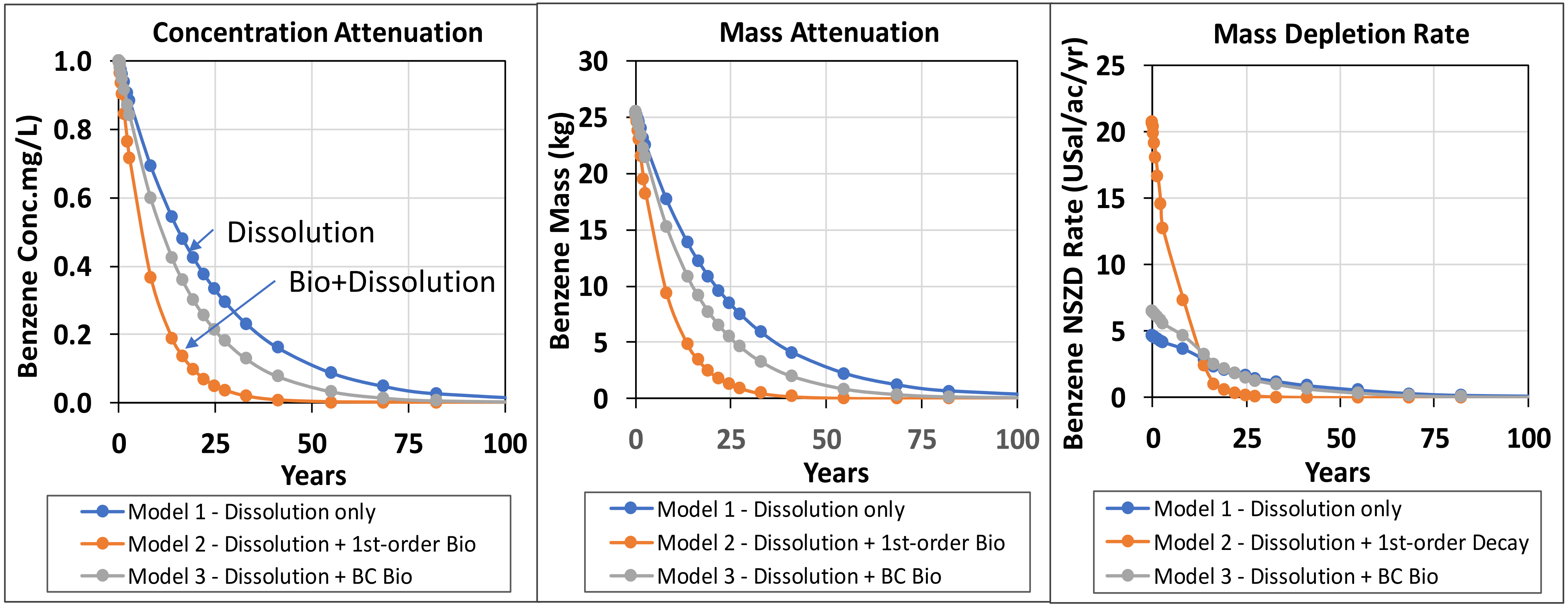
Benzene



BC GPM Defaults used where possible

	Description	Unit	Value	Source
K	Hydraulic conductivity	m/s	3E-5	GPM
I	Hydraulic gradient	-	0.008	GPM
U	Darcy velocity	m/yr	7.57	GPM
L	Source length	m	10	GPM
W	Source width	m	30	GPM
t	Source thickness	m	5	GPM
Ac	Area perpendicular to flow	m^2	150	GPM
ρ_b	Density of soil	kg/L	1.7	GPM
Φ	Total porosity	-	0.36	GPM
f_{oc}	Fraction organic carbon	-	0.005	GPM
K_d	Soil partitioning coefficient	L/kg	146	GPM
C_{soil}	Soil concentration	mg/kg	10	Site
C_o	Initial groundwater conc	mg/L	10	Site
M_o	Initial soluble mass	kg	25.6	Site
BC	Biodegradation capacity	mg/L		Site
BF	Biodegradation factor (mole fraction)	-	0.01	Site
Γ	Gamma	-	0.5-1.0	RemFUEL

Benzene Source Zone Depletion Example



Key Input Parameters

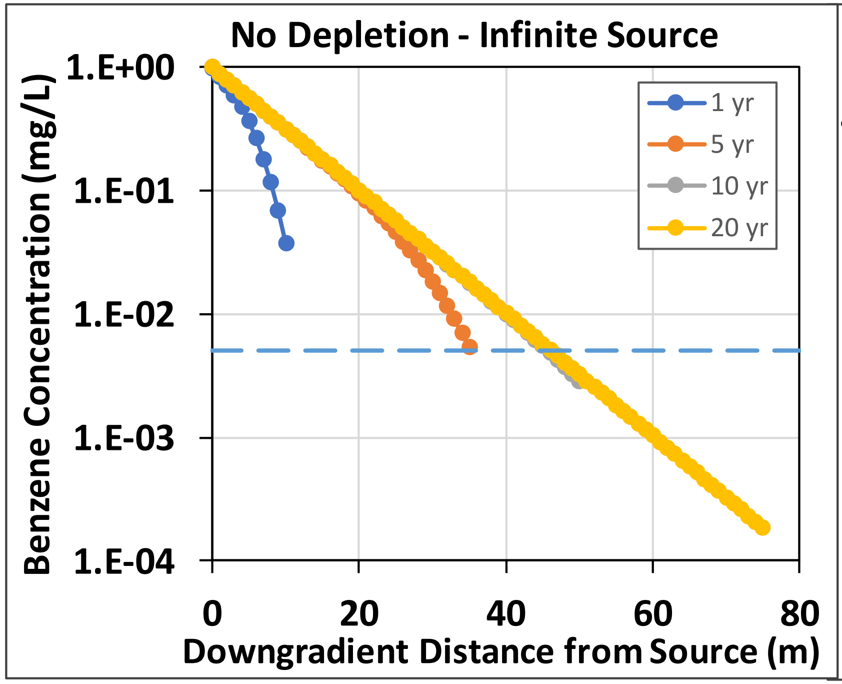
Co = 1 mg/L
Cs = 10 mg/kg
Γ = 1
λ = 0.01 day^{-1} (Model 2)
BC = 40 mg/L (Model 3)
BF = 0.01 (Model 3) (mole fraction)

Key Result: Faster source depletion for Models 2 and 3 that include biodegradation compared to Model 1 that is just based on physical dissolution. Concentration and mass stay the same for no dissolution or biodegradation.

Benzene Groundwater Plume Example

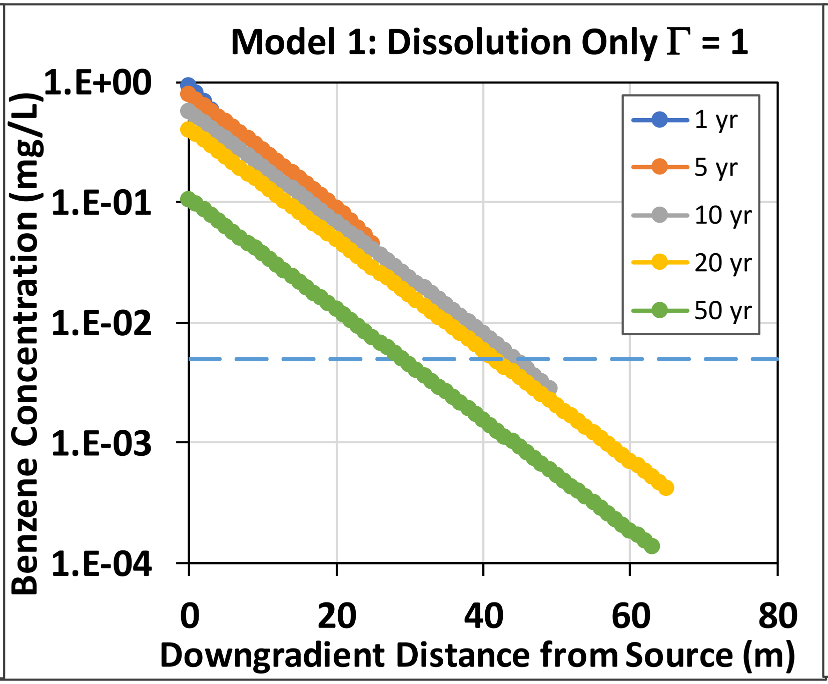
(all model runs include plume 1st order degradation)

No Depletion



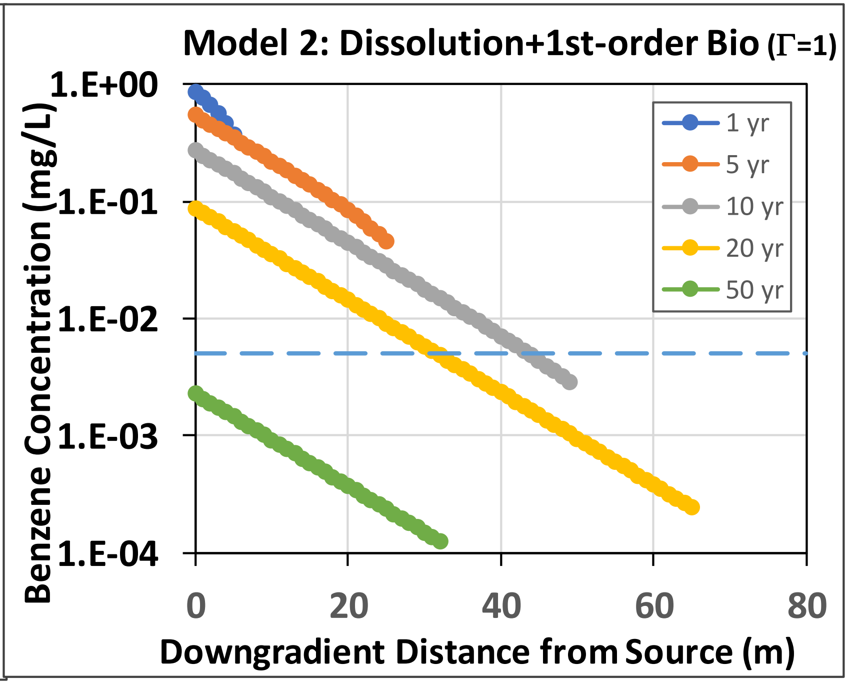
Plume never attenuates

Model 1



Plume eventually attenuates

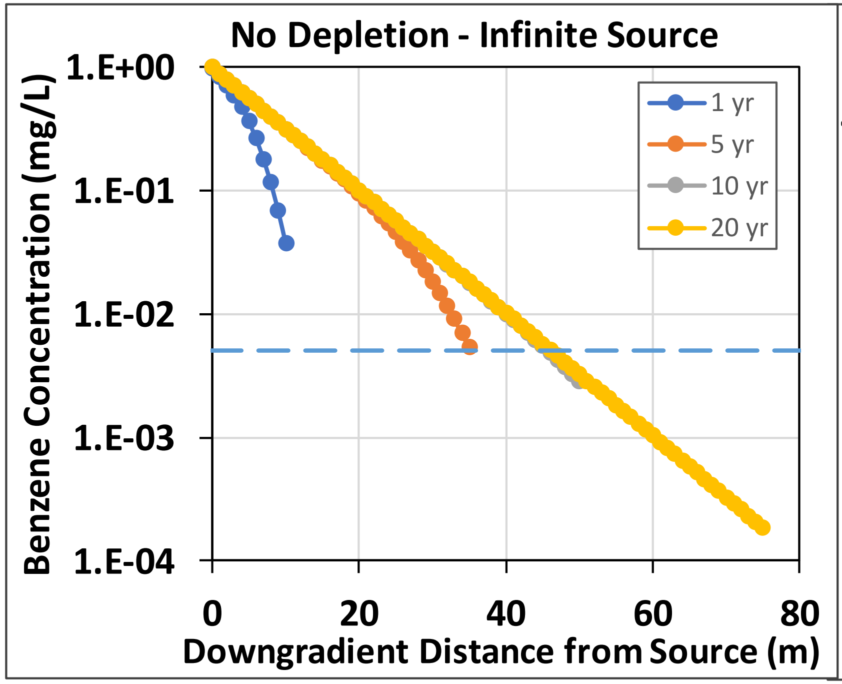
Model 2



Plume attenuates < 50 yr

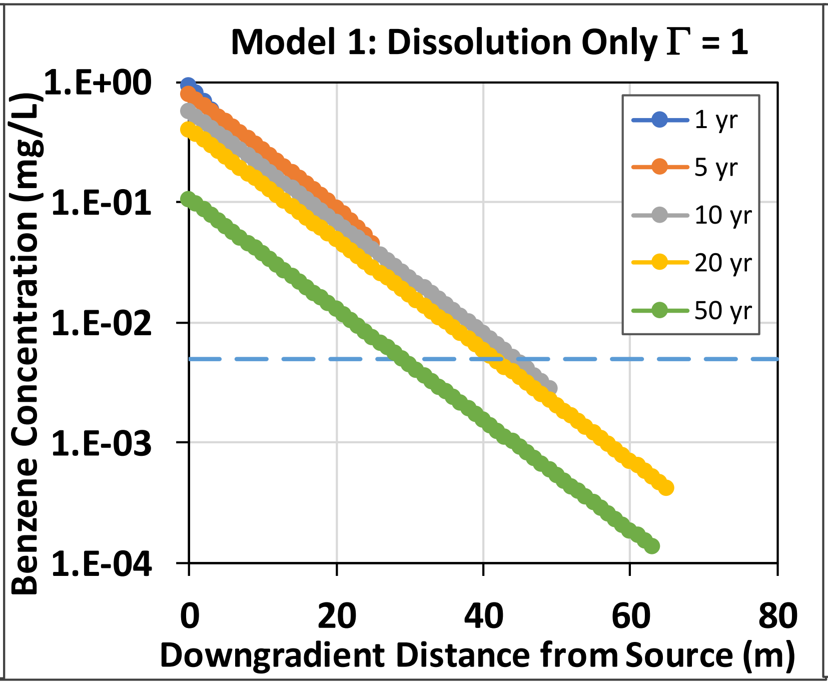
Benzene Groundwater Plume Example

No Depletion



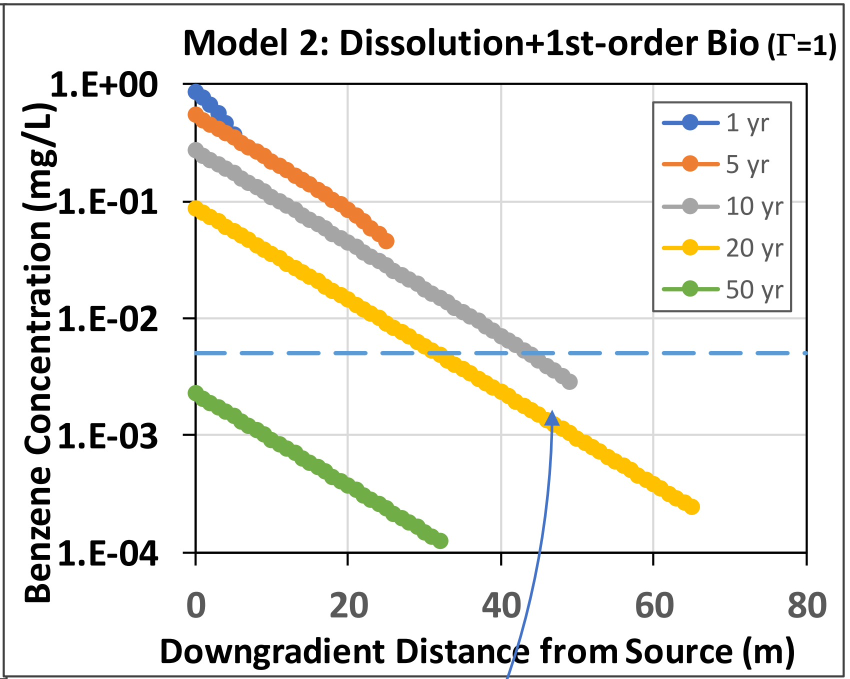
Plume never attenuates

Model 1



Plume eventually attenuates

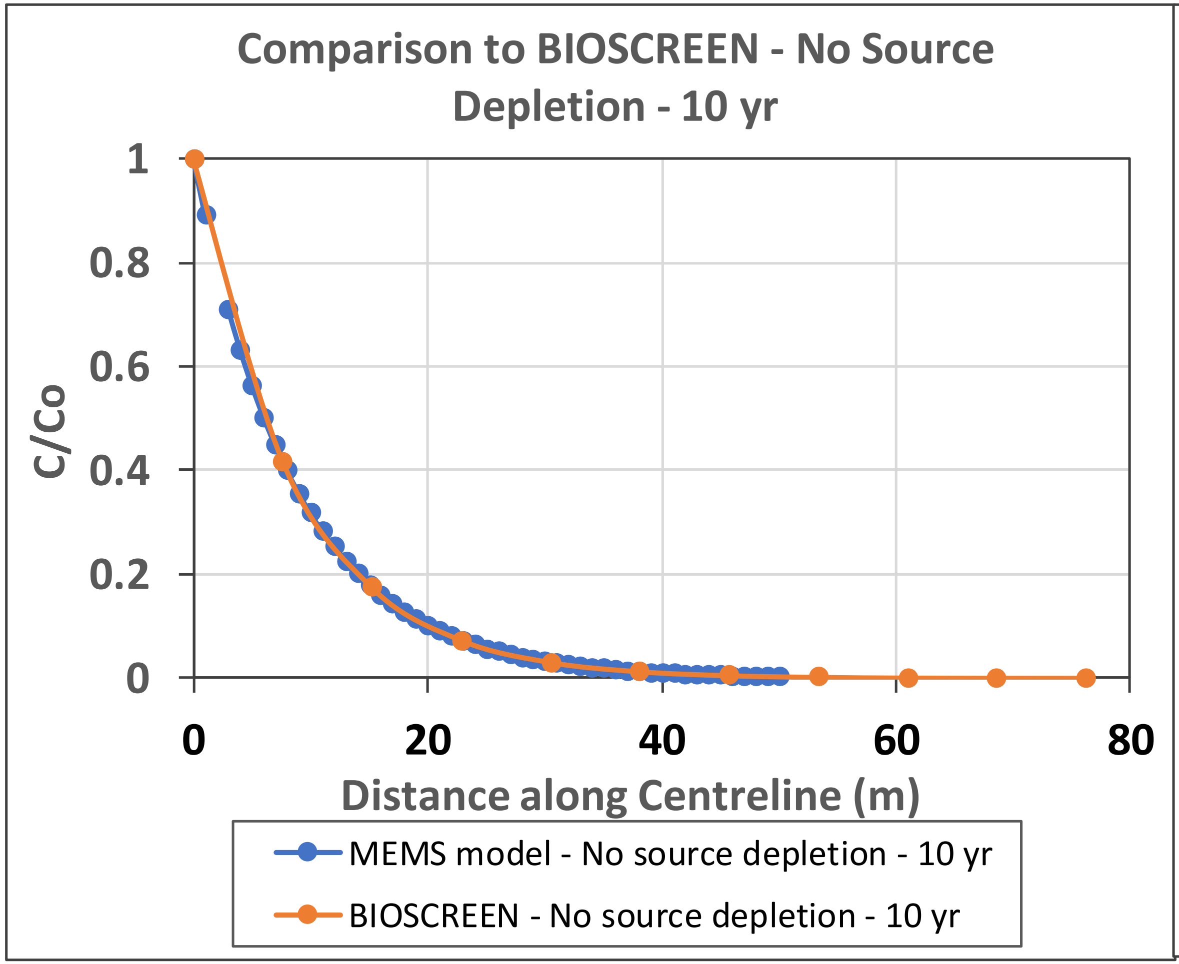
Model 2

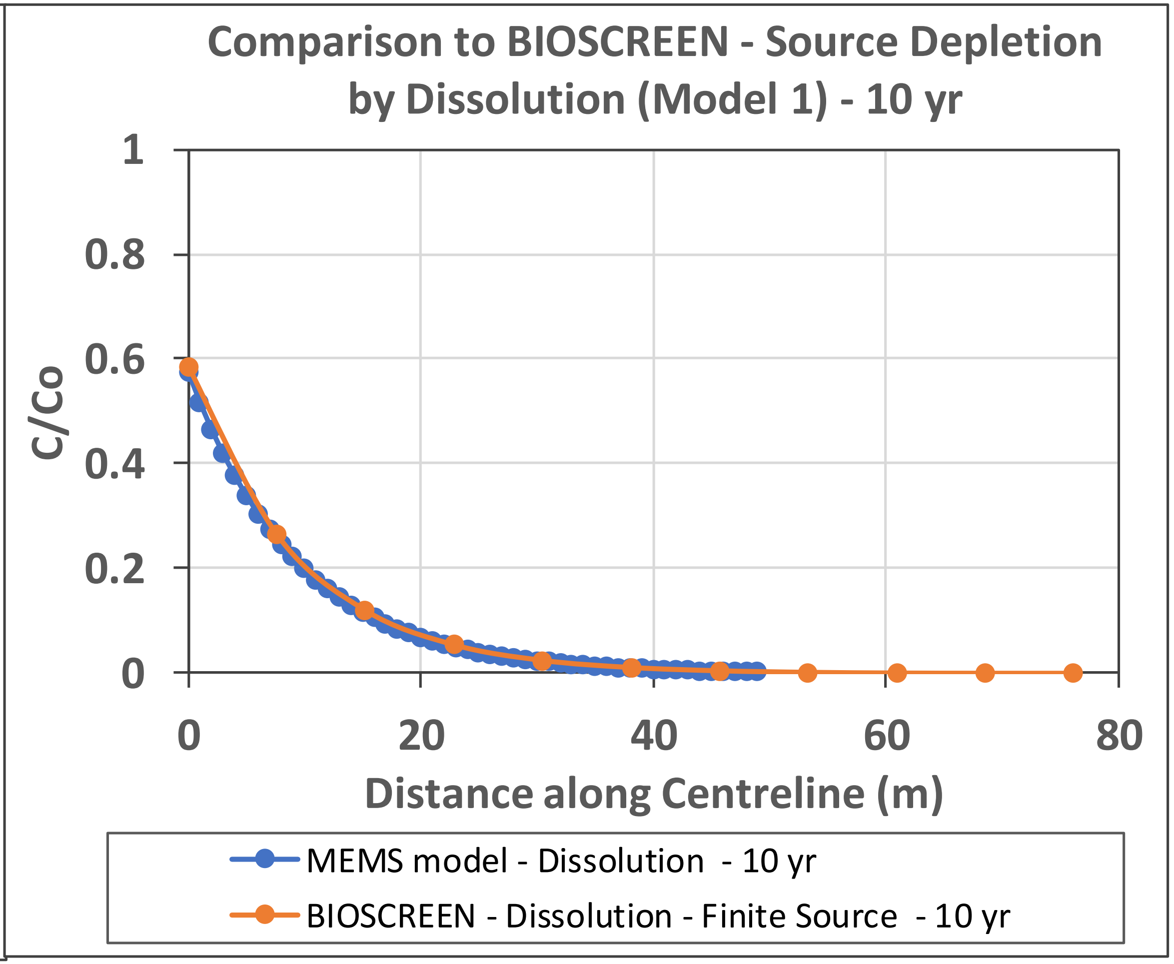


Plume attenuates < 50 yr

Plume > 0.005 mg/L (DW std) migrates just over 40 m from source then shrinks

Model Validation – Comparison to Bioscreen





Model Validation – Source Depletion

Compare to Literature NSZD Rates

CSAP-Shell Remediation Toolkits (2016) (N = 17)	Garg et al. 2017 (N=25)	CRC Care 47 2020 (N = 6)
CSAP-Shell Remediation Toolkits (2016) (N = 17) Typical Site average rates = **500-1500** US gal/ac/yr	**Garg et al. 2017** (N=25) 25th,50th,75th percentiles = **700, 1100, 2800** USgal/ac/yr	**CRC Care 47 2020** (N = 6) Site average rates = **240-9,500** US gal/ac/yrg

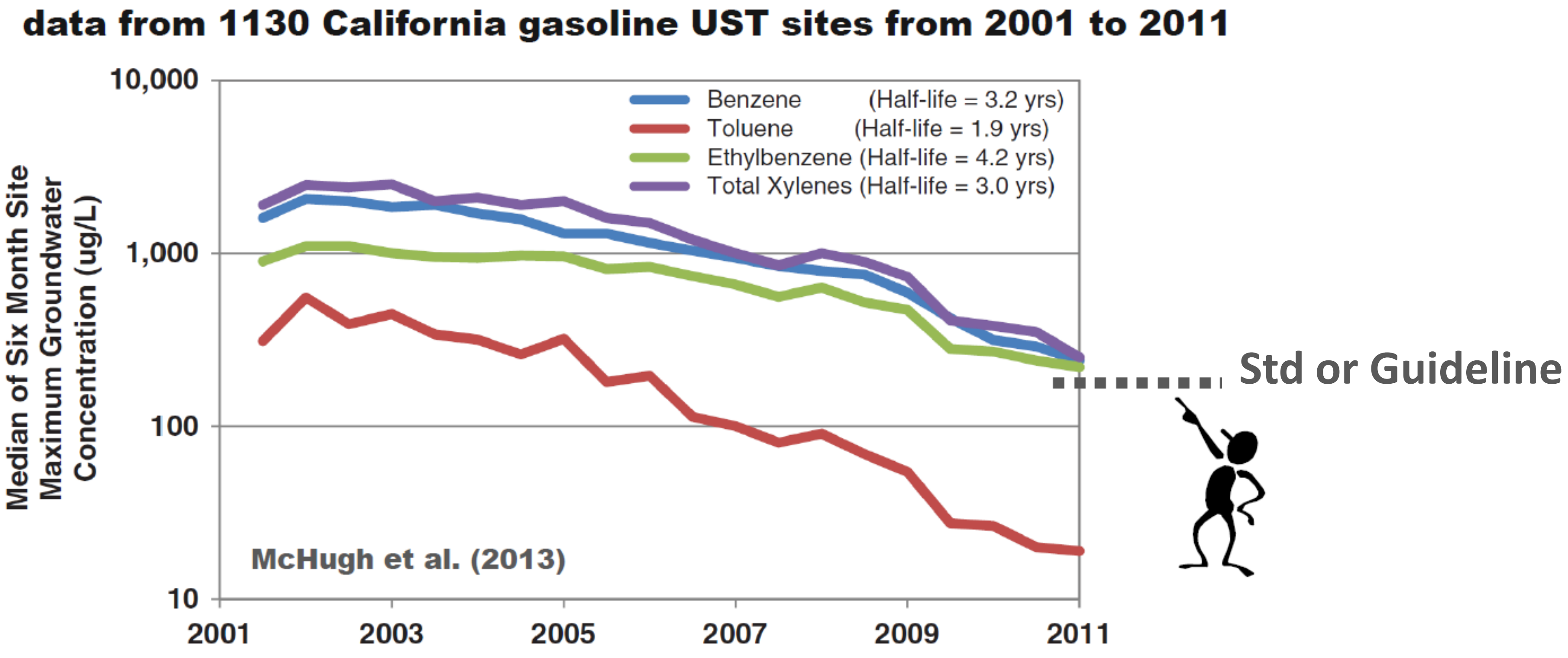
Compare source biodegradation predictions to literature NSZD rates. For example provided, benzene NSZD rate < 20 Usgal/ac/yr. If benzene is 1% in gasoline, ~ < 2000 Usgal/ac/yr. for mixture. More work needed to validate this approach.

Compare to Measured NSZD Rates

1. CO_2 efflux method
2. Soil gas gradient method
3. Thermal gradient method

Wozney, Hers et al. 2022
ASTM 3361-22 Standard Guide for Estimating Natural Attenuation Rates for Non-Aqueous Phase Liquids in the Subsurface
Numerous other papers

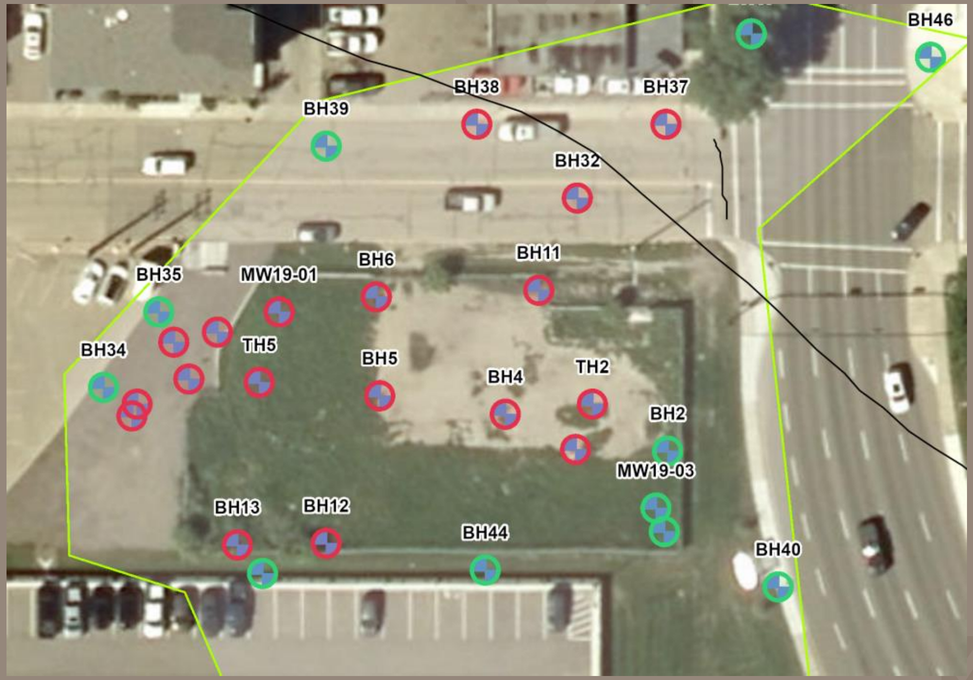
Model Validation – Big Data Analysis Shows Source Attenuation

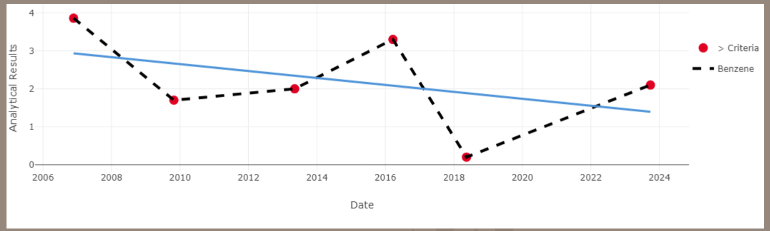


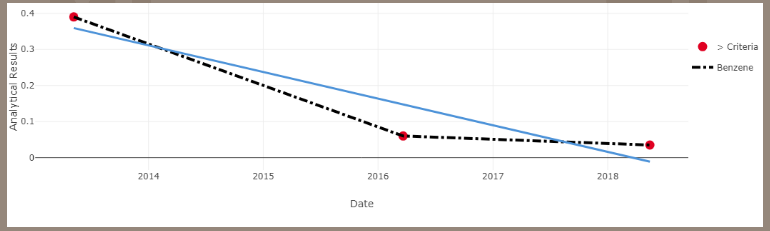
- Empirical plume length studies also show relatively short BTEX plume lengths, e.g., benzene median plume length = 55 m (O'Conner 2015)
- May be useful to summarize available Canadian data

Example: Former Service Station

- Multi-year data set available (2006 – 2024)
- Primary COPC: benzene (max concentration ~4 mg/kg in 2016)
- Trend analyses show decreasing concentrations
- Goal: hot spot remediation and redevelop







Figures from IntelleKt^{EIG}

Example: Former Service Station

Assess natural attenuation over 18 year period

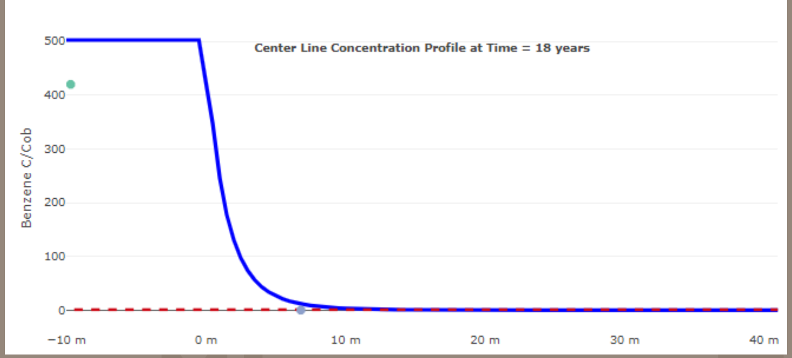
(IntelleKtEIG natural attenuation module – Domenico model)

No source depletion: minimal further transport but no decrease in source concentrations

Dissolution only: ~50% reduction in source concentration.

Alignment on maximum concentration

Over-predicts most of plume significantly



Figures from IntelleKt^{EIG}

Example: Residential Community

Impacted by historical gasoline release

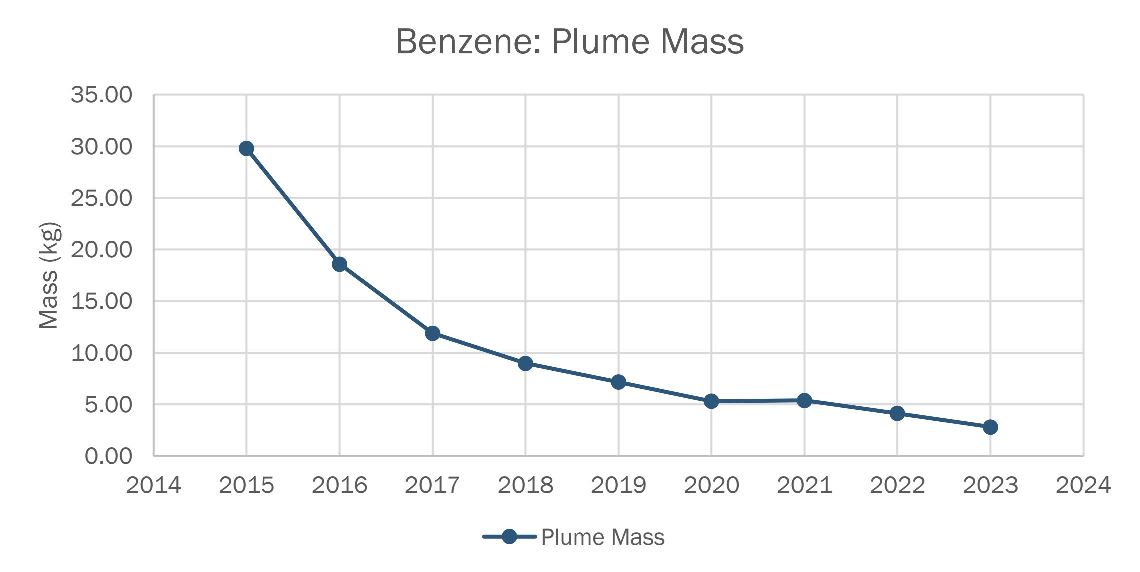
Groundwater exceeds Tier 1

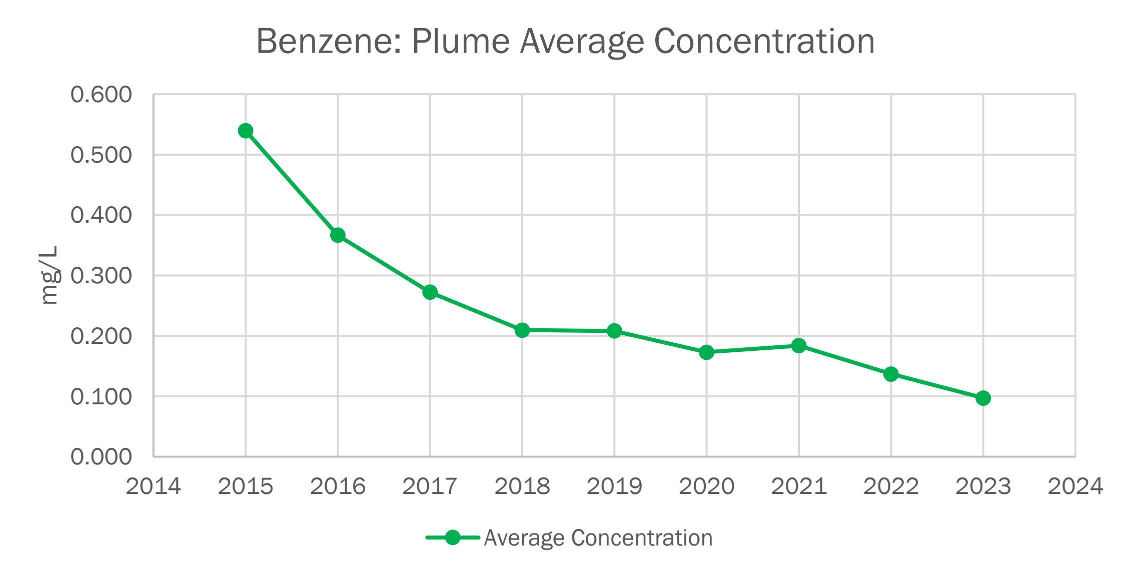
Soil vapour meets guidelines

Groundwater meets guidelines for operative pathways

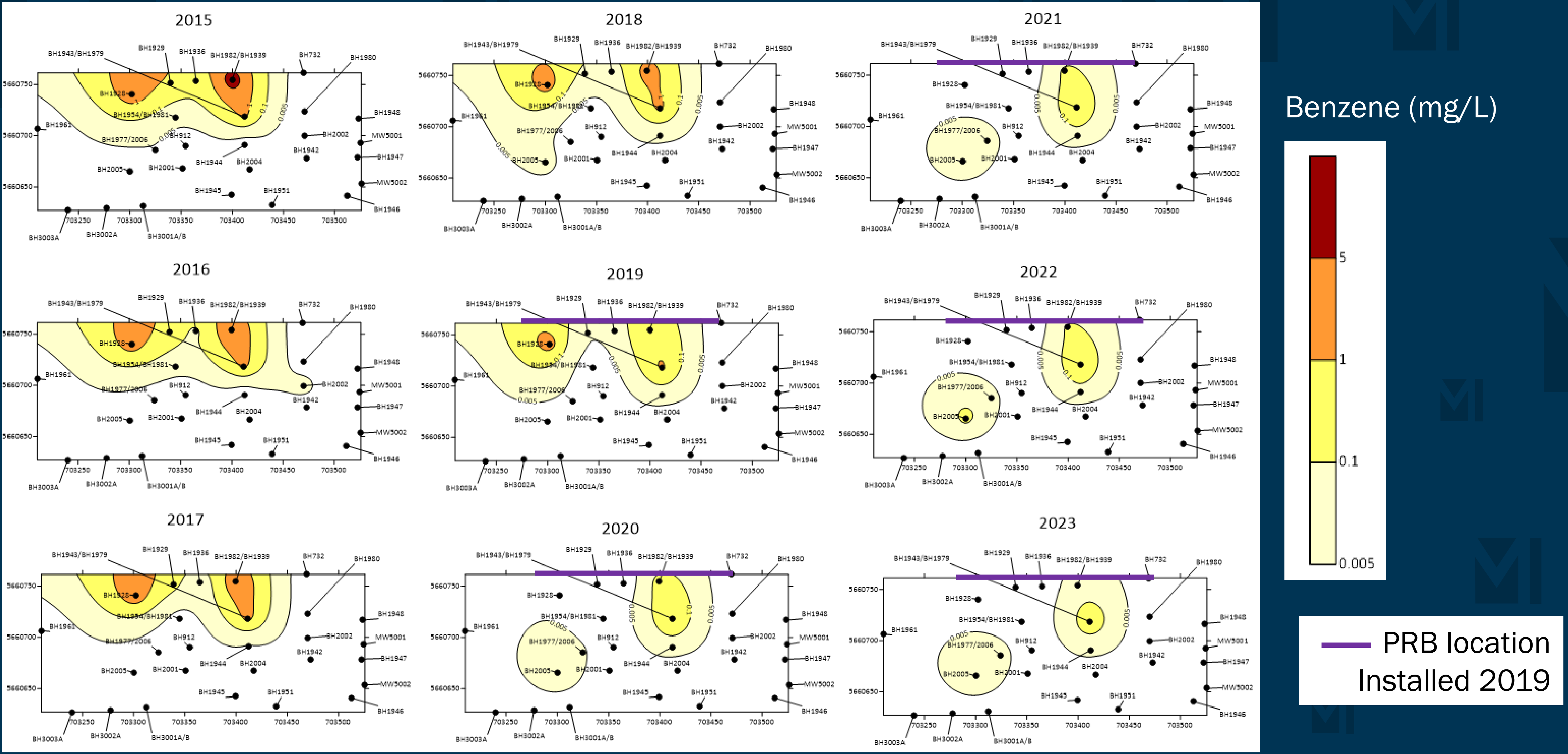
Shrinking plume demonstrated overall

Staged approach: reduce assessed area





Example Site: Benzene past PRB



Questions?