



Use of Natural Source Zone Depletion (“Natural Attenuation”) in Remedial Decision Making

Workshop - Letting Nature Take Its Course: Using Natural Source Zone Depletion of LNAPL to Manage Petroleum Contaminated Sites

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Matthew A. Lahvis

R&D Lead – Soil & Groundwater
Shell Global Solutions (US) Inc.

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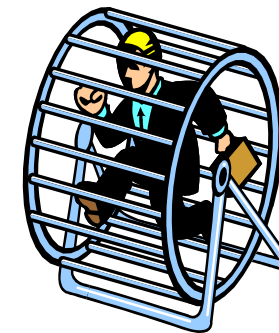
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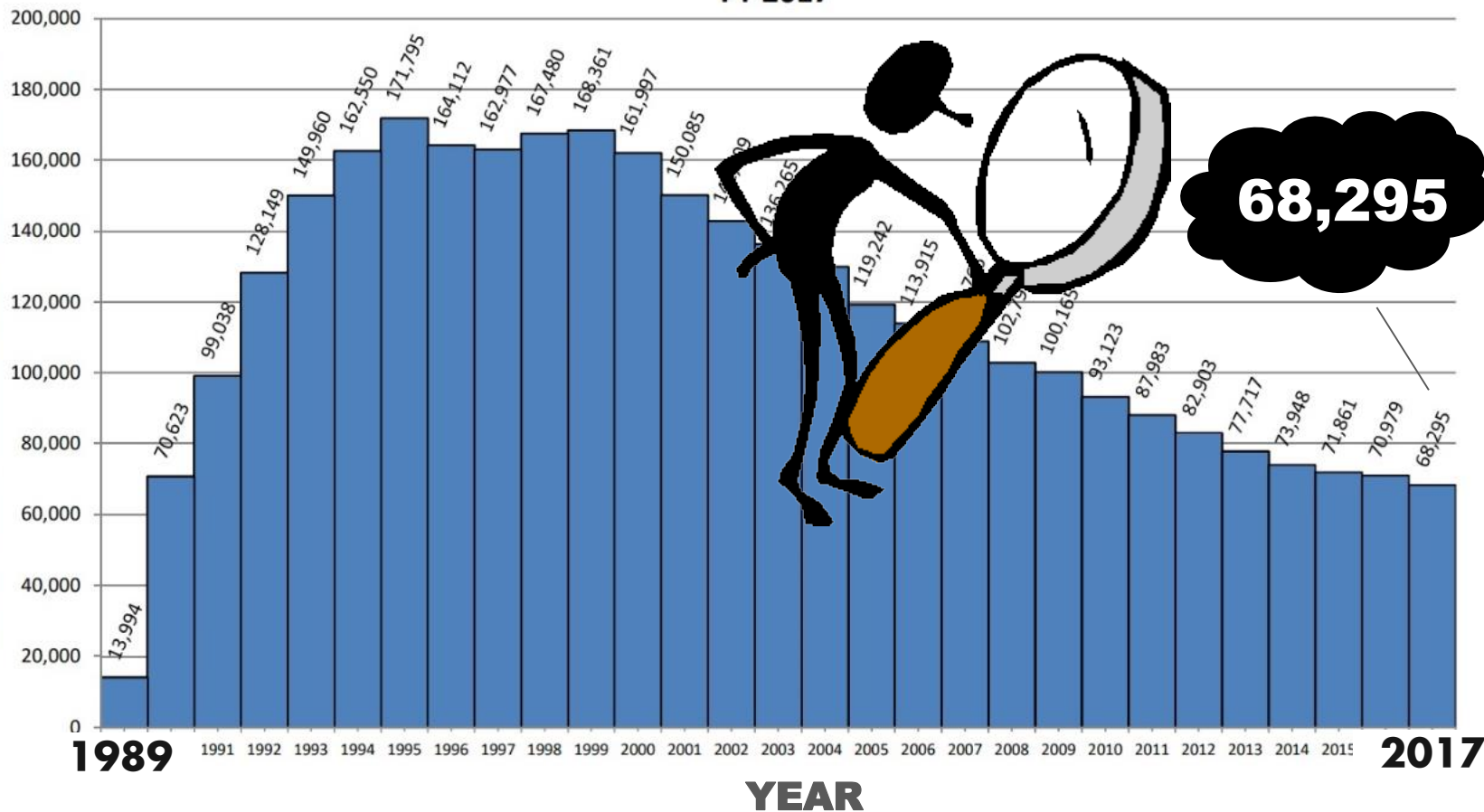
The Challenge

Lots of Open UST Cases Remain



**NATIONAL BACKLOG (CONFIRMED
RELEASES – CLEANUPS COMPLETED)**

UST National Backlog:
FY 1989 Through End-Of-Year
FY 2017

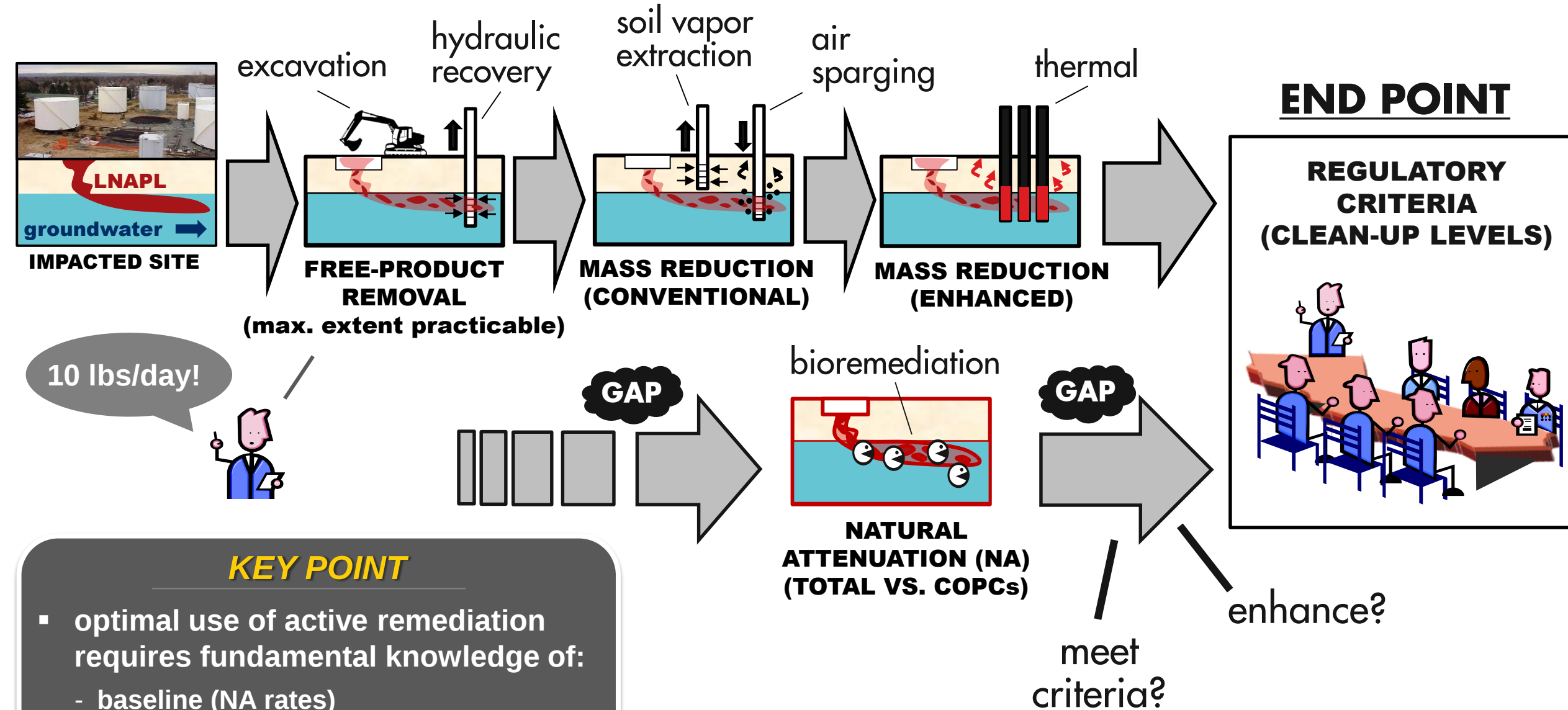


KEY POINT

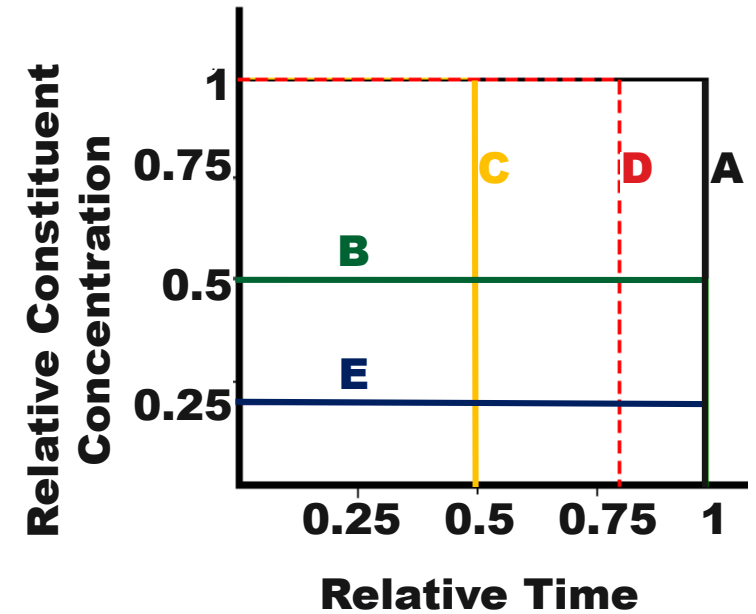
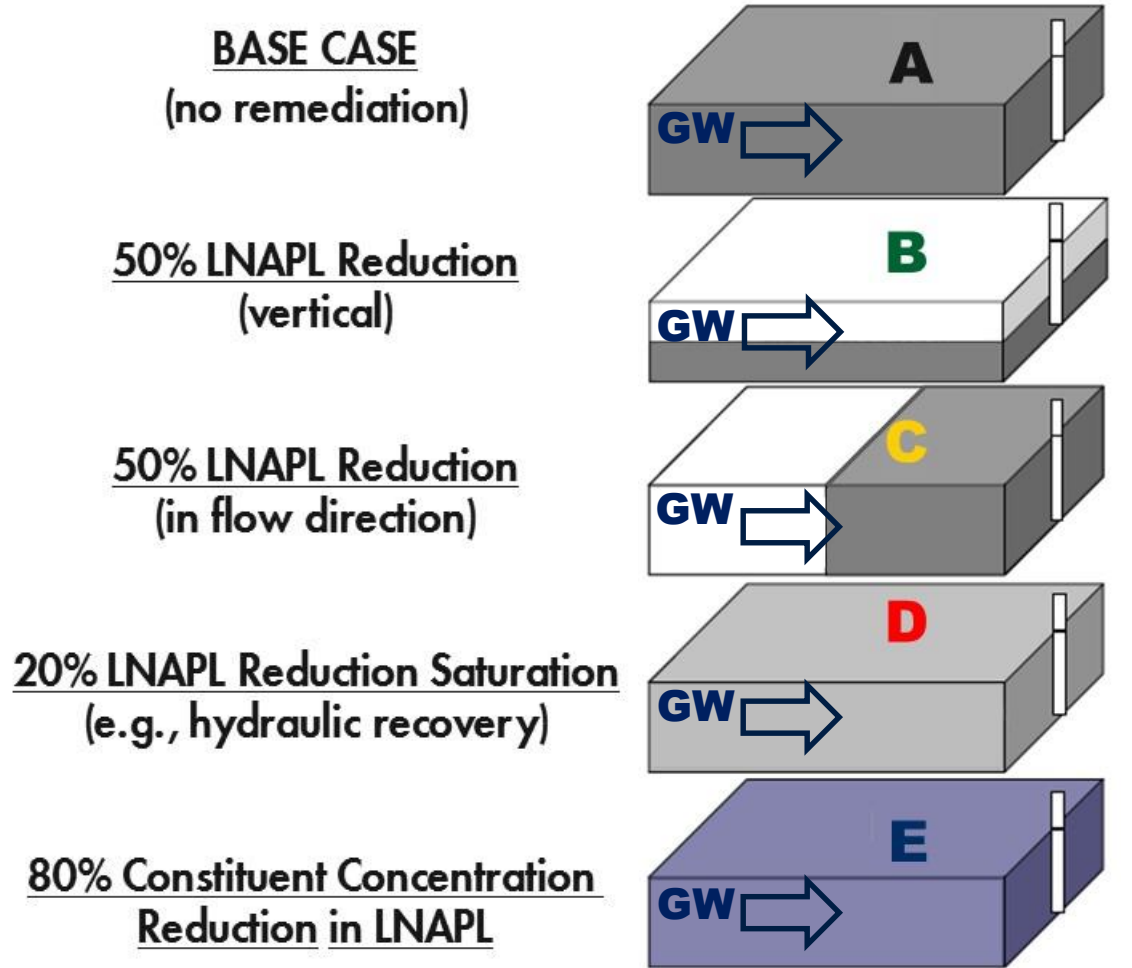
Still over 65,000
Underground
Storage Tank
(UST) sites need
closure; must
understand:

**“WHAT WORKS...
WHAT DOESN'T”**

Active Remediation Systems Rarely Optimized



Technology Selection vs. Remedial Objectives



from ITRC, 2009

KEY POINT

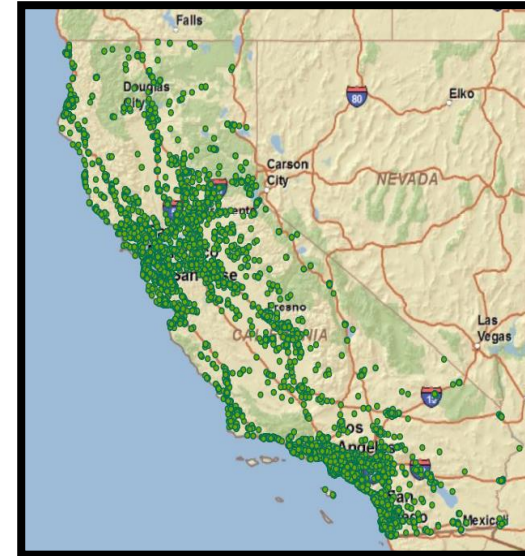
- different methods of remediation will affect concentrations and plume longevity differently

ASSUMPTIONS:

- groundwater flows from left to right
- plug flow through the source
- equilibrium dissolution
- no biodegradation

Big Data – Geotracker (California)

From McHugh et al., 2013



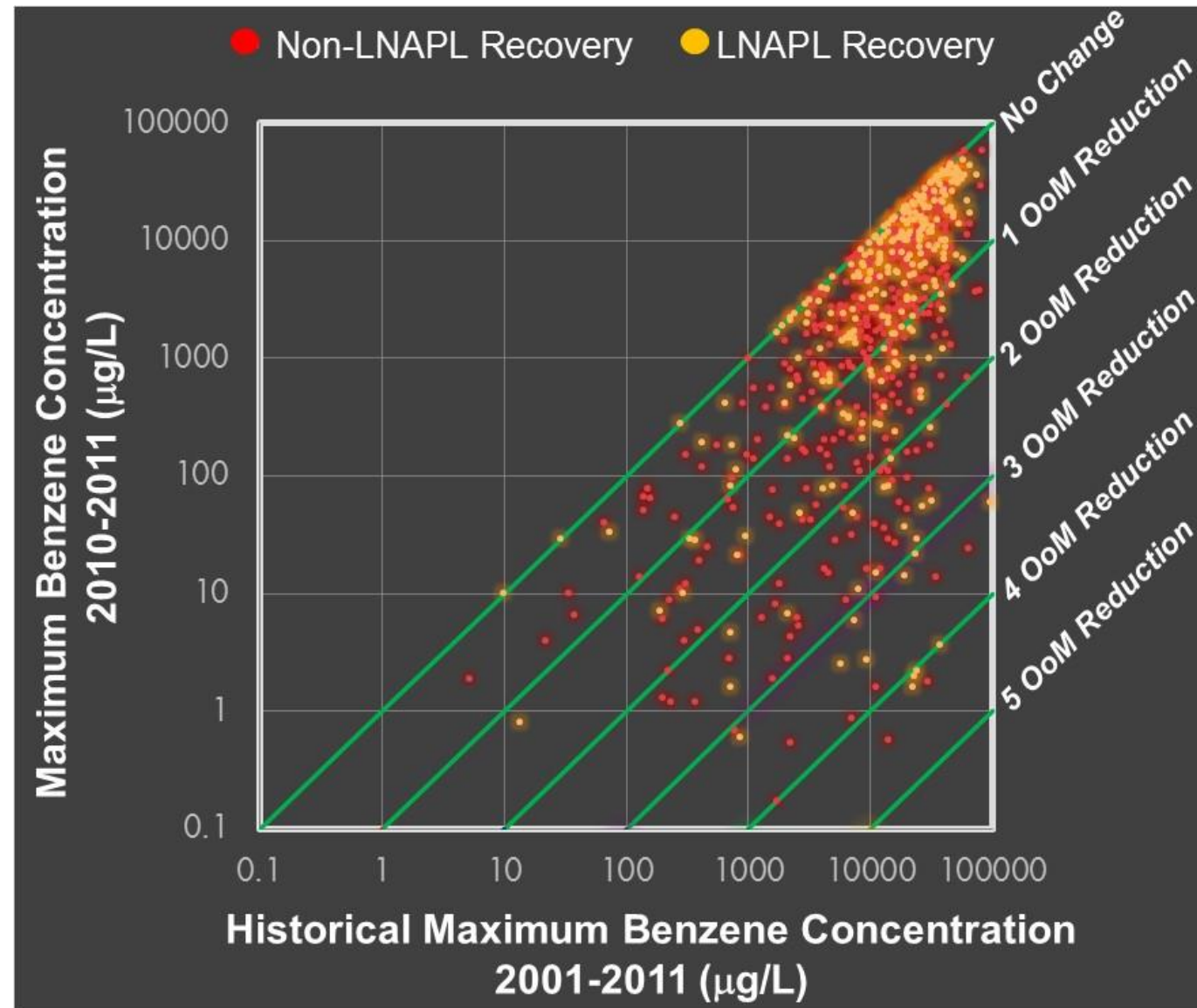
KEY POINT

- attenuation rates (active vs. natural) are site-specific – must evaluate lots of data to understand “what works, what doesn’t”

◆ Benzene
■ Ethylbenzene
◆ MTBE
◆ TBA
◆ Toluene
◆ Xylene

■ ACTIVE
REMEDATION
■ MONITORED
NATURAL
ATTENUATION

Effect of LNAPL Recovery on Groundwater Concentration

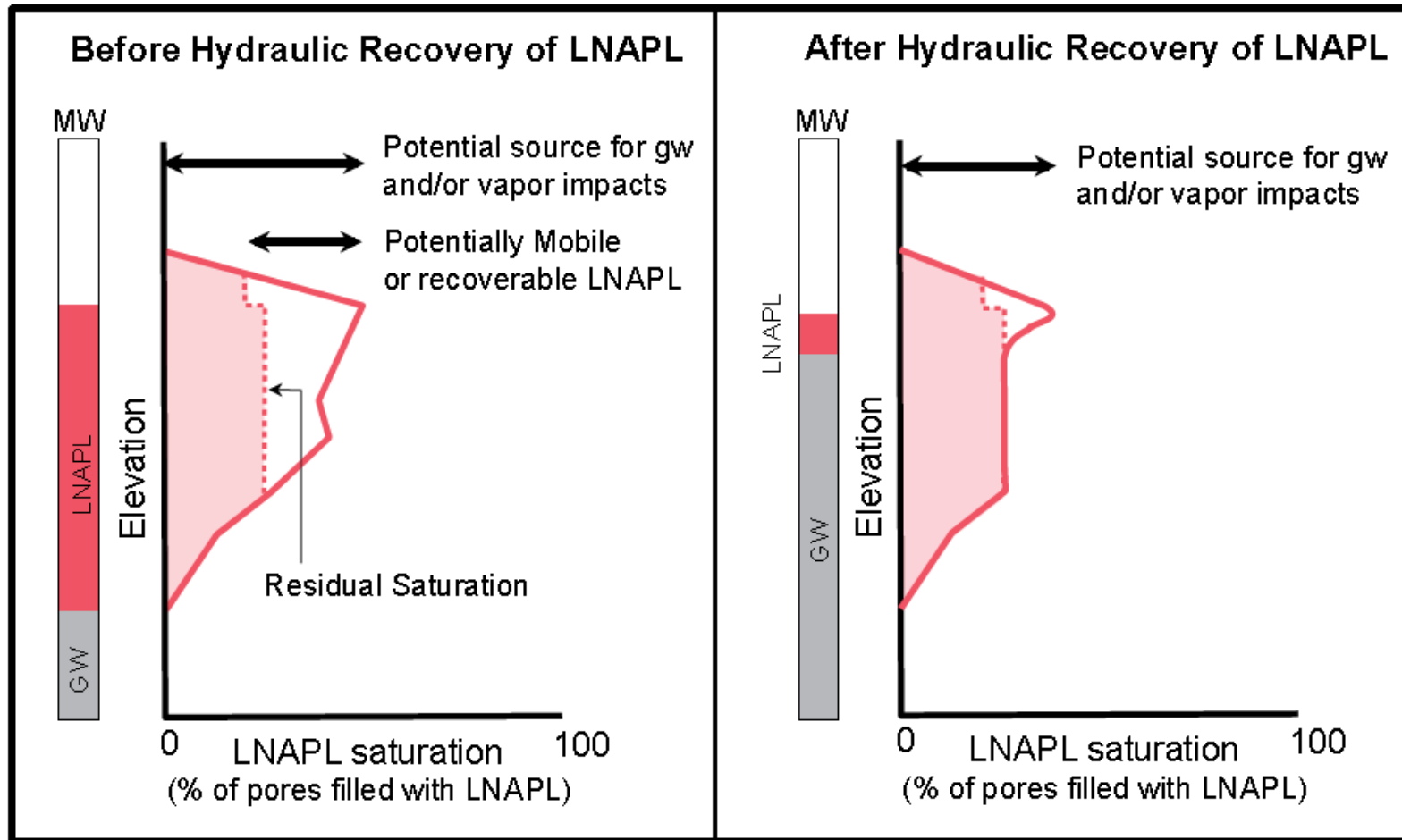


KEY POINT

- LNAPL recovery did not have a significant effect on reducing benzene concentrations in groundwater

Source: Kulkarni et al., 2015

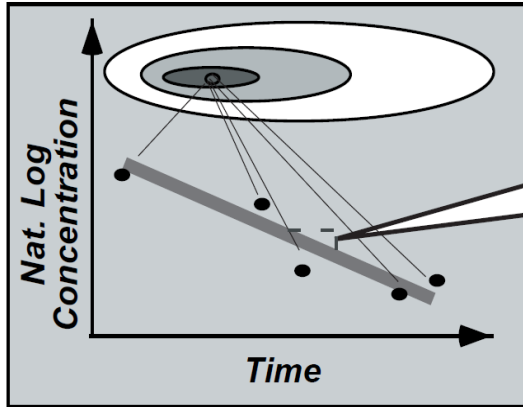
Effects of Hydraulic Recovery on LNAPL Source Mass



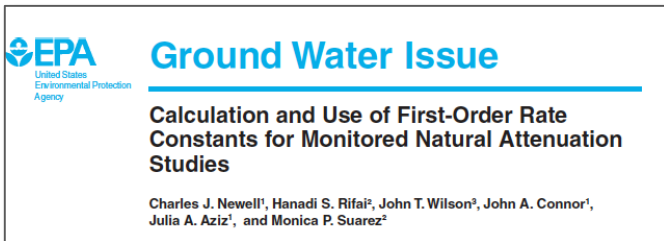
KEY POINT

- significant source mass will remain in place after hydraulic recovery (source for groundwater and vapor impacts)

Effect of LNAPL Recovery at Sites with Mobile LNAPL Over 10 Years



$$C = C_0 e^{-(k_{source} t)}$$



Newell et al. (2002)

Remedy Type	Median Source Attenuation Rates (yr ⁻¹)	Median Concentration Reduction (%)	Median Reduction in LNAPL Thickness (%)
	Benzene	Benzene	
LNAPL Recovery (n=327)	Slower 0.09	Lower 75%	87%
Non - NAPL Recovery (n=444)	0.19 Faster	86% Higher	91%

Kulkarni et al., 2015

KEY POINT

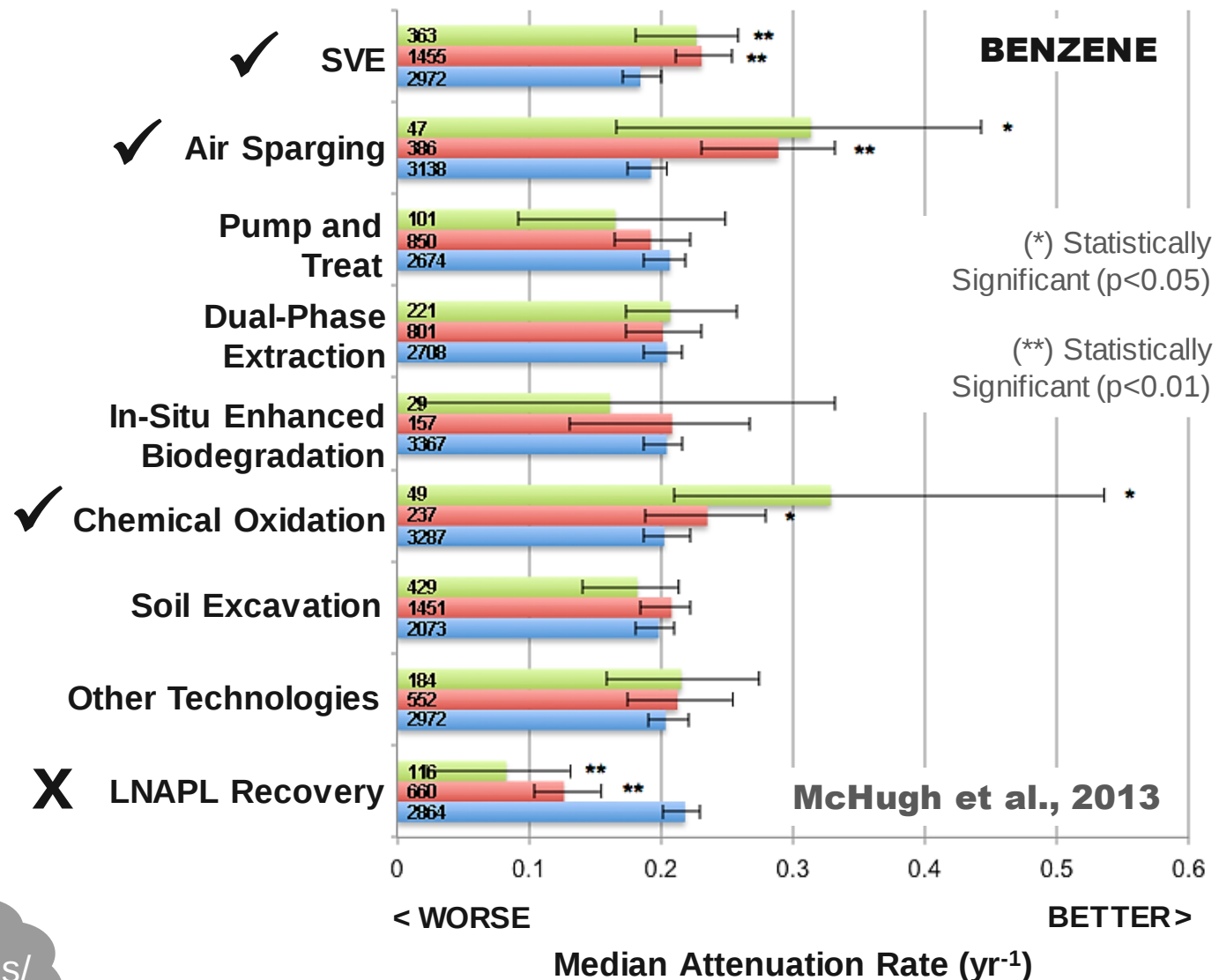
- LNAPL recovery may have little impact on reducing concentrations or thickness, or increasing source attenuation rates

Effect of Remediation Technology on Source Attenuation Rate (Benzene)

KEY POINT

- air-based technologies more effective than others for helping expedite “getting to closure” for benzene; LNAPL recovery not effective

unnecessary SIs/
remediation



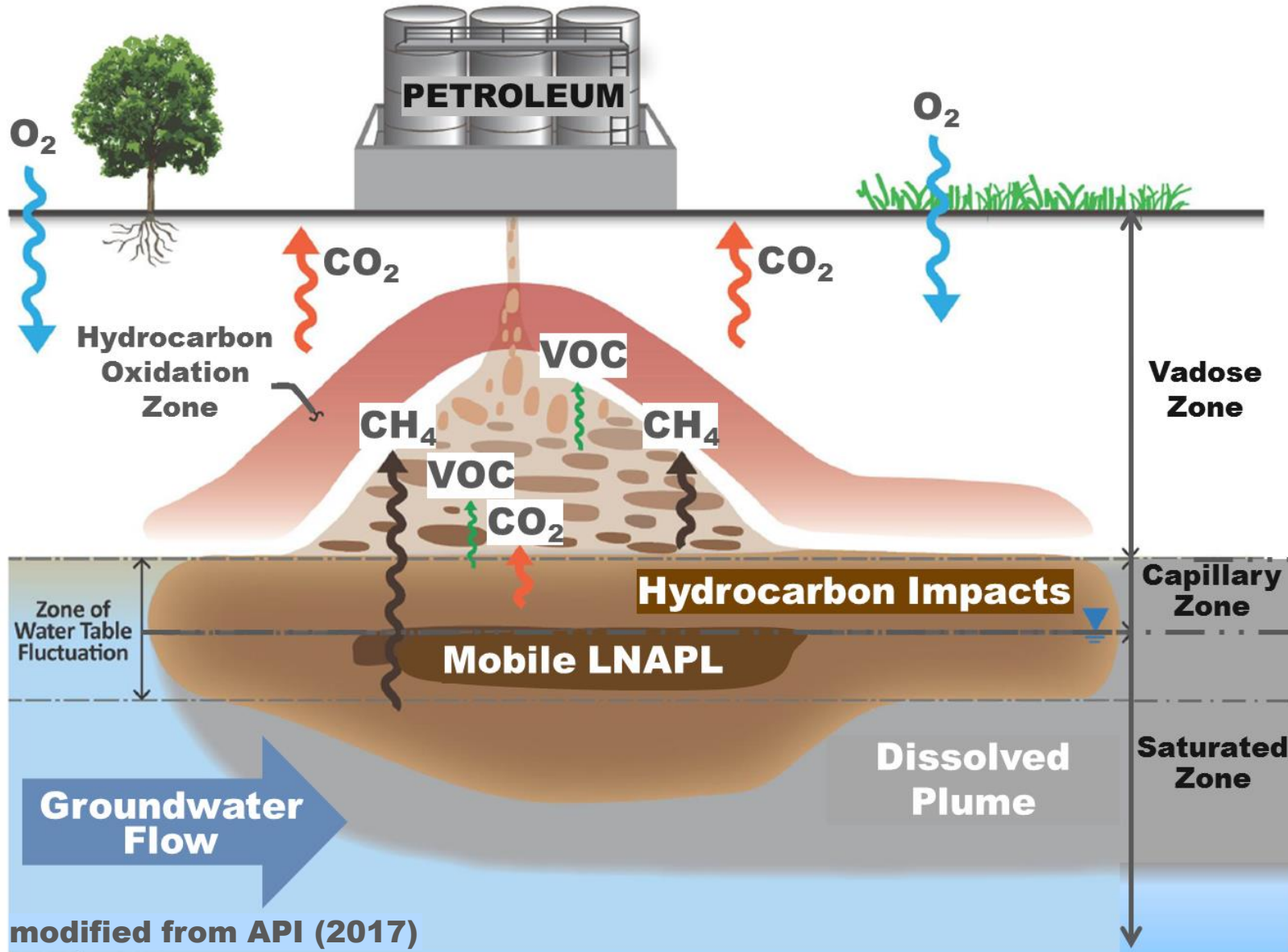
LEGEND

n	Sites with Only Technology
n	Sites with Technology and Some Other Technology
n	Sites without Technology

Efforts to Address the Challenge

NSZD

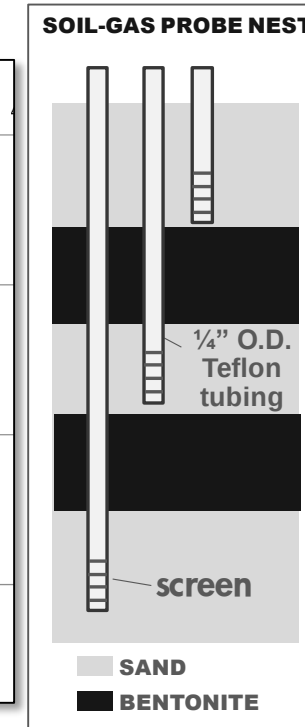
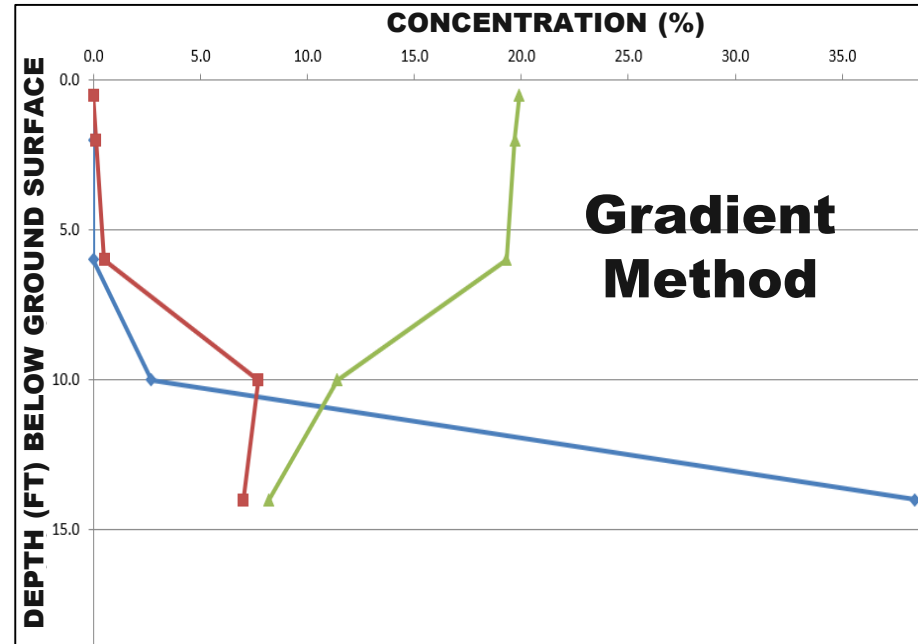
NSZD – Conceptual Model



- NSZD is critical hydrocarbon mass-loss pathway:
 - 70% of hydrocarbon can directly outgas to vadose zone (Ng et. al., 2015)
 - rates consistent w/ some engineered remediation (700 – 4,000 gal/acre-yr: Garg et al., 2017)
- NSZD method/tools well established (ITRC, 2009)
- primary applications (to date)
 - shut-down of active LNAPL recovery systems

Various NSZD Measurement Techniques

Thermal NSZD



CO₂ Trap



Dynamic Closed Chamber



KEY POINT

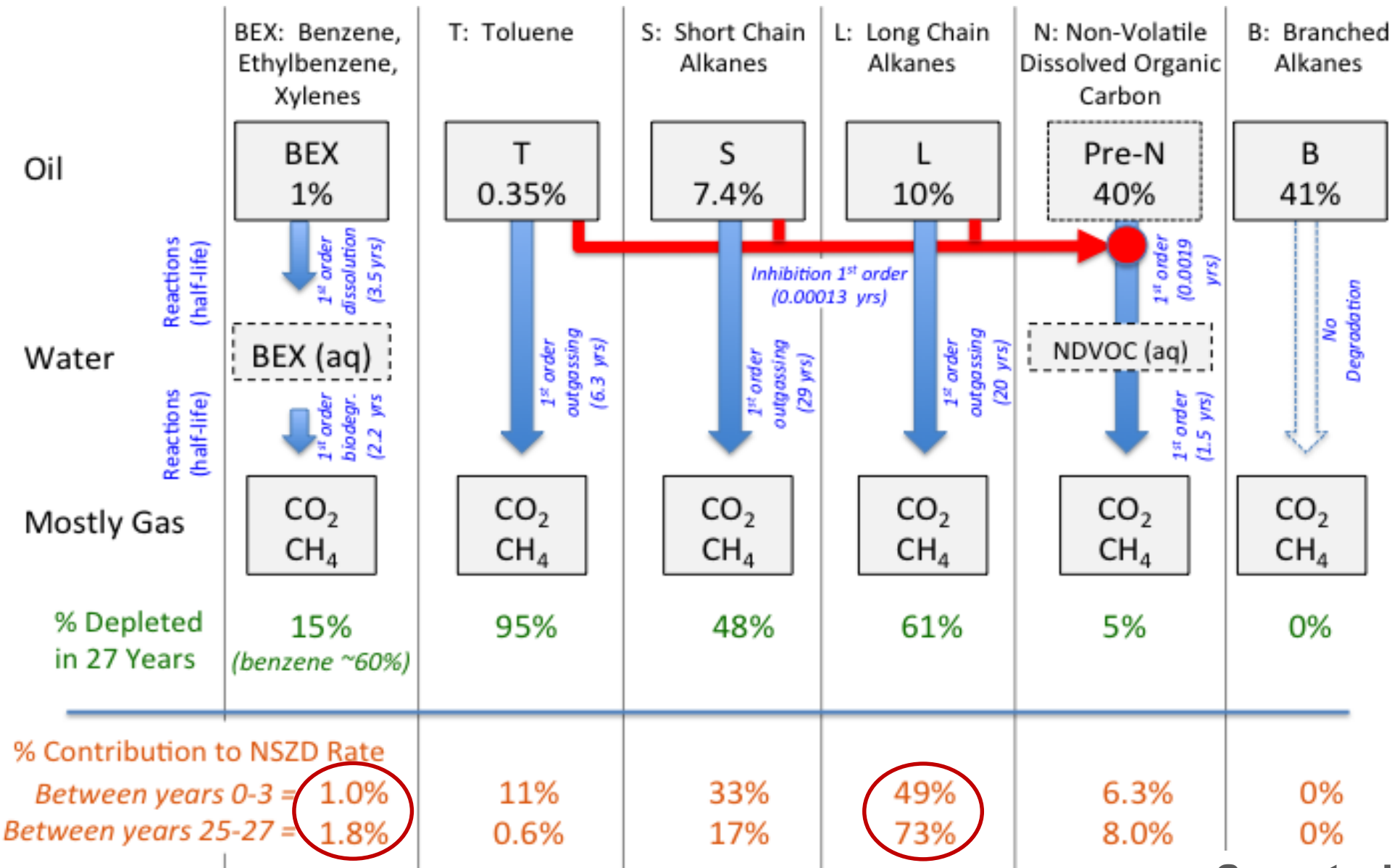
- several methods, each with advantages and limitations
- NSZD methods focus on bulk (total) TPH attenuation

NSZD Rate vs. Composition

KEY POINT

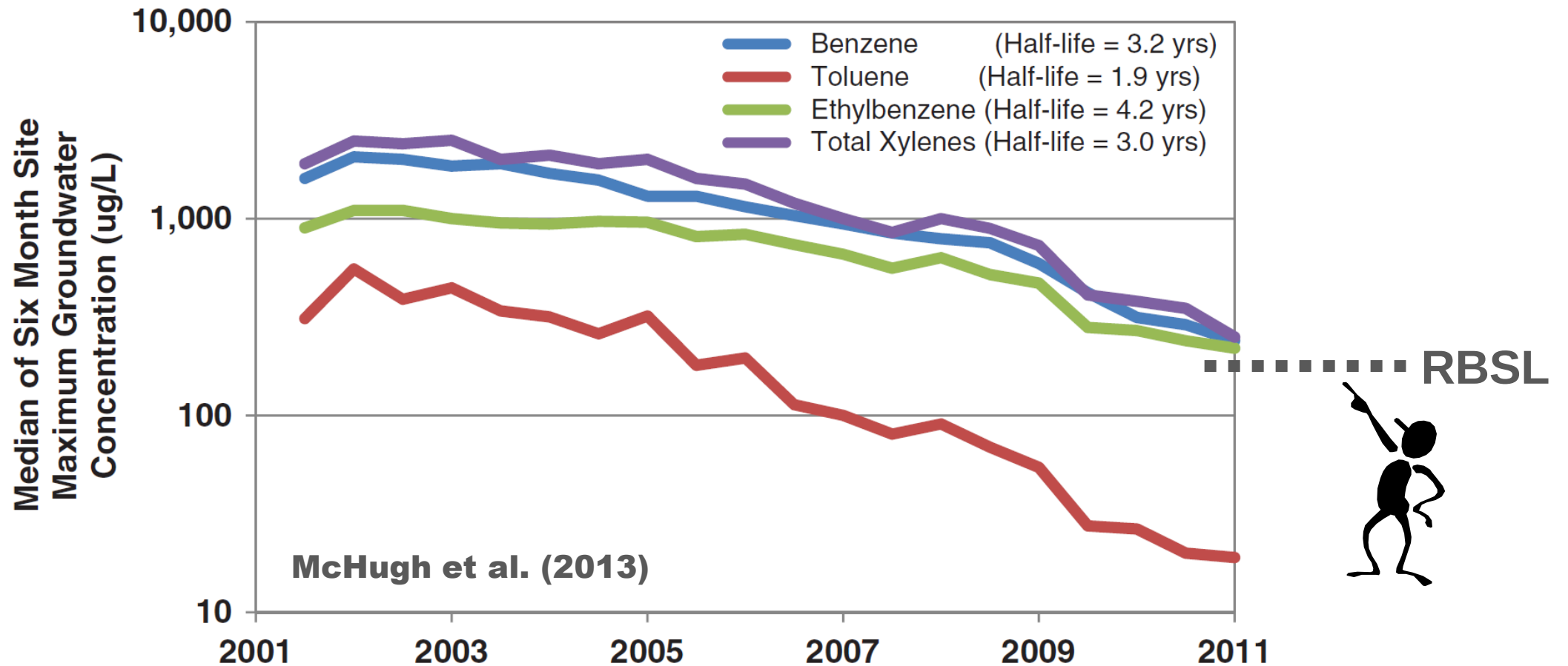
- NSZD (TPH) rate integrates volatilization and biodegradation rates for range of hydrocarbons, which vary independently over time and space
- bulk rates don't necessarily reflect attenuation of key risk drivers (e.g., BTEX)

total mass recovery or COPCs?



Plume Longevity is Often of Interest in Risk-Based Decision Making

data from 1130 California gasoline UST sites from 2001 to 2011



Efforts to Address the Challenge

SOIL GAS COMPOSITION

Attenuation Rates for COPCs Based on Soil-Gas Concentration Gradients

- soil-gas method & application dates back to mid-late 80s (USGS)

- ✓ bulk hydrocarbon (TPH, CO₂, O₂)
- ✓ specific hydrocarbons (BTEX, cyclohexane)
- ✓ carbon ranges (C₆ – C₉ aliphatics, C₆ – C₉ aromatics)

KEY POINT

- soil-gas method well documented

Long-Term Evolution of Biodegradation and Volatilization Rates in a Crude Oil-Contaminated Aquifer

B.P. Chaplin,¹ G.N. Delin,¹ R.J. Baker,² and M.A. Lahvis³

¹U.S. Geological Survey, Water Resources Department, Mounds View, MN 55112, ²U.S. Geological Survey, Water Resources Department, West Trenton, NJ, ³Equilon Enterprises, LLC, Houston, TX

WATER RESOURCES RESEARCH, VOL. 35, NO. 3, PAGES 753–765, MARCH 1999

Quantification of aerobic biodegradation and volatilization rates of gasoline hydrocarbons near the water table under natural attenuation conditions

Matthew A. Lahvis, Arthur L. Baehr, and Ronald J. Baker
Water Resources Division, U.S. Geological Survey, West Trenton, New Jersey

Abstract. Aerobic biodegradation and volatilization near the water table are coupled pathways that contribute significantly to the natural attenuation of gasoline at gasoline spill sites. Rates of hydrocarbon biodegradation and volatilization were quantified by analyzing vapor transport in the unsaturated zone near the water table, ranging from 0.20 to 1.5 g m⁻³ d⁻¹ for toluene, 0.09 to 0.24 g m⁻³ d⁻¹ for xylene, 0.02 to 0.08 g m⁻³ d⁻¹ for ethylbenzene, and from 0.02 to 0.08 g m⁻³ d⁻¹ for benzene. In the capillary zone, where 68% of the total hydrocarbon mass that was estimated to have been biodegraded. Hydrocarbons were degraded within 1 m above the water table. This large loss under natural attenuation in limiting the transport of hydrocarbon vapor and implies that vapor-plume migration to basements and may only be significant if a source of free product is present. Full-scale transport of the hydrocarbon in the unsaturated zone can be limited by the inclusion of oxygen- and carbon-dioxide-gas concentration data. Aerobic degradation kinetics in the unsaturated zone were approximately order rate constants near the water table were highest for cyclohexane (0.09–0.30 d⁻¹), and benzene (0.07–0.31 d⁻¹). Hydrocarbon mass loss determined by extrapolating gas transport rates through the capillary zone from groundwater were highest for toluene (0.20–0.84 g m⁻² d⁻¹),

WATER RESOURCES RESEARCH, VOL. 32, NO. 7, PAGES 2231–2249, JULY 1996

Estimation of rates of aerobic hydrocarbon biodegradation by simulation of gas transport in the unsaturated zone

Matthew A. Lahvis and Arthur L. Baehr
U.S. Geological Survey, West Trenton, New Jersey

Abstract. The distribution of oxygen and carbon dioxide gases in the unsaturated zone provides a geochemical signature of aerobic hydrocarbon degradation at petroleum product spill sites. The fluxes of these gases are proportional to the rate of aerobic biodegradation and are quantified by calibrating a mathematical transport model to the oxygen and carbon dioxide gas concentration data. Reaction stoichiometry is assumed to convert the gas fluxes to a corresponding rate of hydrocarbon degradation. The method is applied at a gasoline spill site in Galloway Township, New Jersey, to determine the rate of aerobic degradation of hydrocarbons associated with passive and bioventing remediation field experiments. At the site, microbial degradation of hydrocarbons near the water table limits the migration of hydrocarbon solutes in groundwater and prevents hydrocarbon volatilization into the unsaturated zone. In the passive remediation experiment a site-wide degradation rate estimate of 34,400 g yr⁻¹ (11.7 gal. yr⁻¹) of hydrocarbon was obtained by model calibration to carbon dioxide gas concentration data collected in December 1989. In the bioventing experiment, degradation rate estimates of 46.0 and 47.9 g m⁻² yr⁻¹ (1.45 × 10⁻³ and 1.51 × 10⁻³ gal. ft.⁻² yr⁻¹) of hydrocarbon were obtained by model calibration to oxygen and carbon dioxide gas concentration data, respectively. Method application was successful in quantifying the significance of a naturally occurring process that can effectively contribute to plume stabilization.

Introduction

Petroleum product spills from underground storage tanks and pipelines are a common cause of groundwater contamination throughout the industrialized world. Typically, significant volumes of the contaminant remain immobilized by capillary forces after the primary response of physical product removal

to have been achieved. This phenomenon also is evident at a gasoline spill site in Galloway Township, New Jersey, where microbial degradation limits the lateral spreading of dissolved hydrocarbons and prevents vertical diffusion of hydrocarbons into the overlying unsaturated zone [Baehr and Fischer, 1996]. The environmental regulatory community has recently acknowledged the limitations of engineered remediation solu-

Objectives

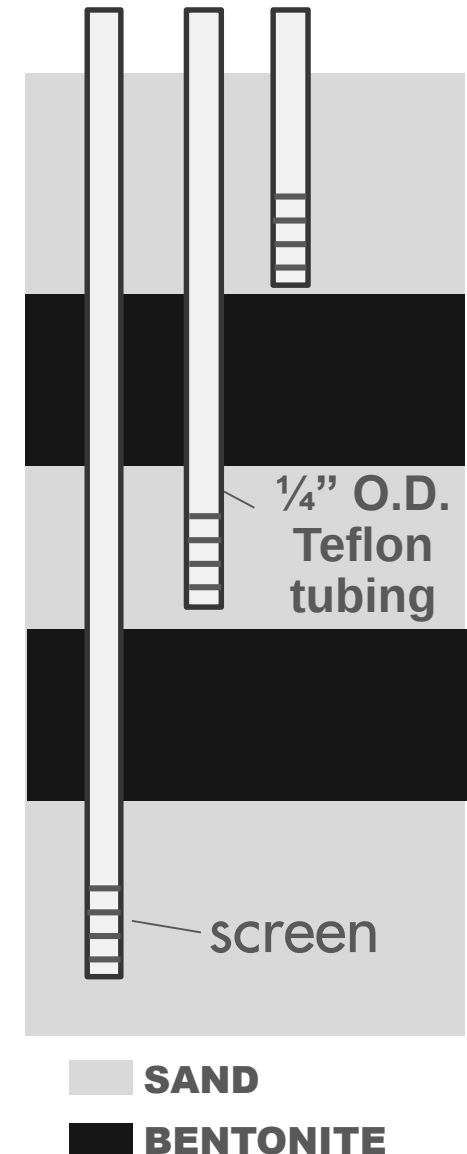
- demonstrate soil-gas method to assess natural attenuation (NSZD) rates for TPH & benzene
- evaluate factors that affect natural attenuation rates



**SOIL-GAS SAMPLING
(summa canister)**

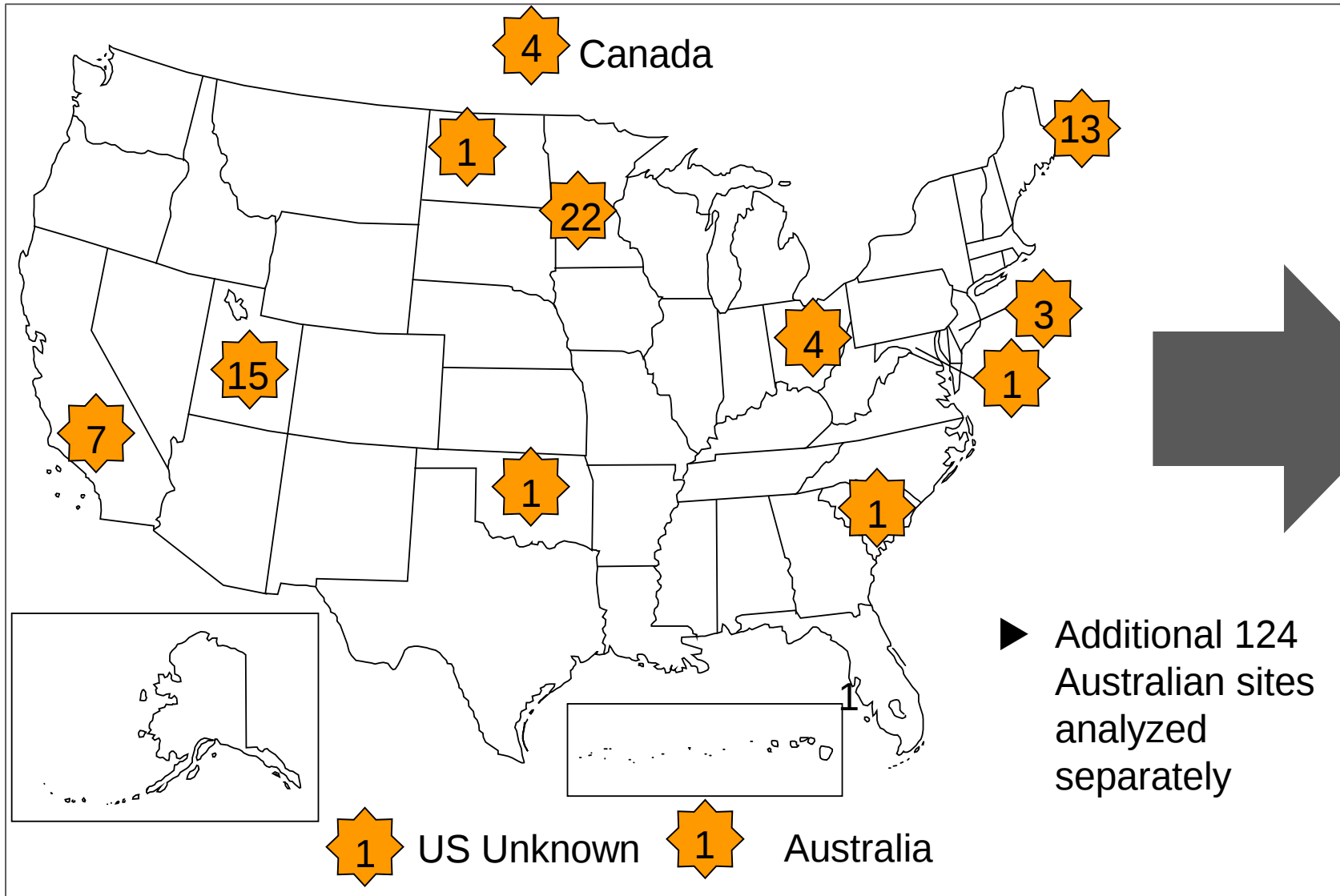


SOIL-GAS PROBE NEST



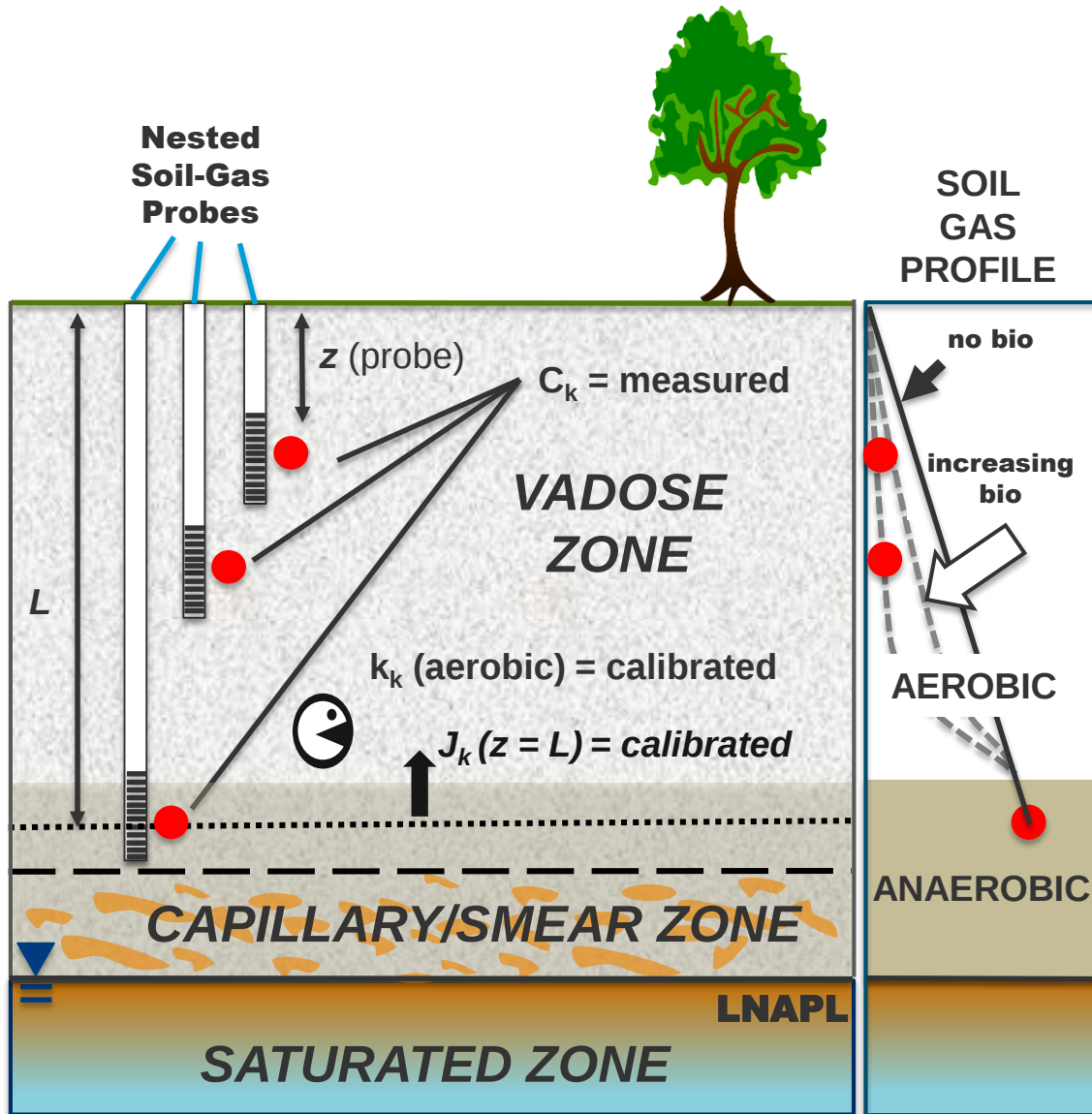
Empirical Soil-Gas Database

(<https://www.epa.gov/ust/petroleum-vapor-intrusion-database>)



- TPH and benzene soil-gas data
- 82 samples; 35 sites; 55 probe locations
- SOILS
 - 28% sands
 - 51% loams/silts
 - 21% clays
- SURFACE COVER
 - 56% pavement
 - 29% open ground
 - 15% buildings

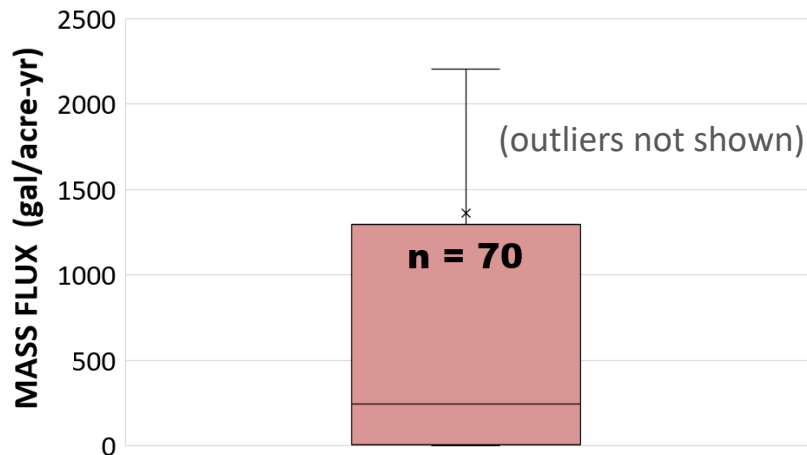
Soil-Gas Method



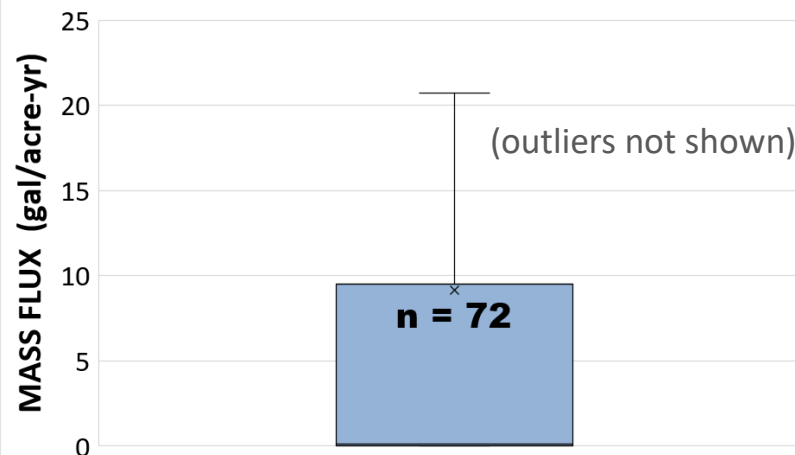
- mass transport (1-D vertical): BioVapor - <http://www.api.org/>
 - simple (promote method uptake)
 - gas-phase diffusion dominated (Fick's Law)
 - 1st-order biodegradation kinetics (O_2 - limited)
 - TPH and benzene simulated
 - ND soil-gas concentrations = DL
 - best fit of predicted and measured soil-gas data – (see ITRC PVI (2014) - Appendix I) <http://www.itrcweb.org/PetroleumVI-Guidance/>
- effective diffusion coefficient (**estimated**)
 - site specific soil types (known)
 - vadose zone - homogeneous/isotropic
 - default soil properties (USEPA, 2004)
- 1st-order aerobic degradation rate constant (k_k) and source-vapor flux (J_k) (**calibrated**)
 - no biodegradation anaerobic zone
 - soil respiration ($f_{oc} = 0.002$: USEPA, 1996)

Natural Attenuation (NA) Rates: *TPH* vs. *Benzene*

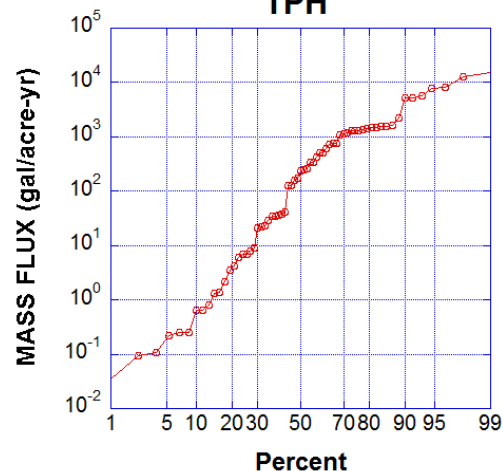
TPH



BENZENE

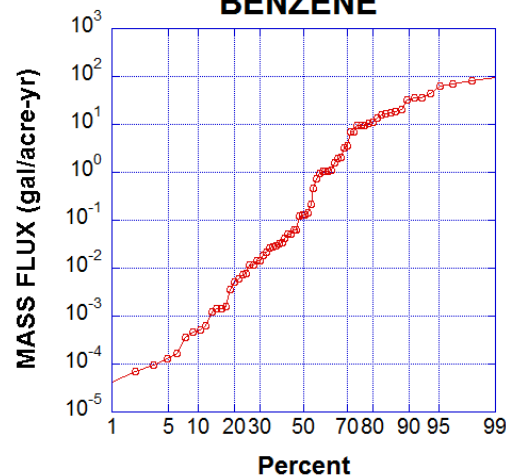


TPH



median rate: 240 gal/acre-yr
average rate: 1400 gal/acre-yr

BENZENE

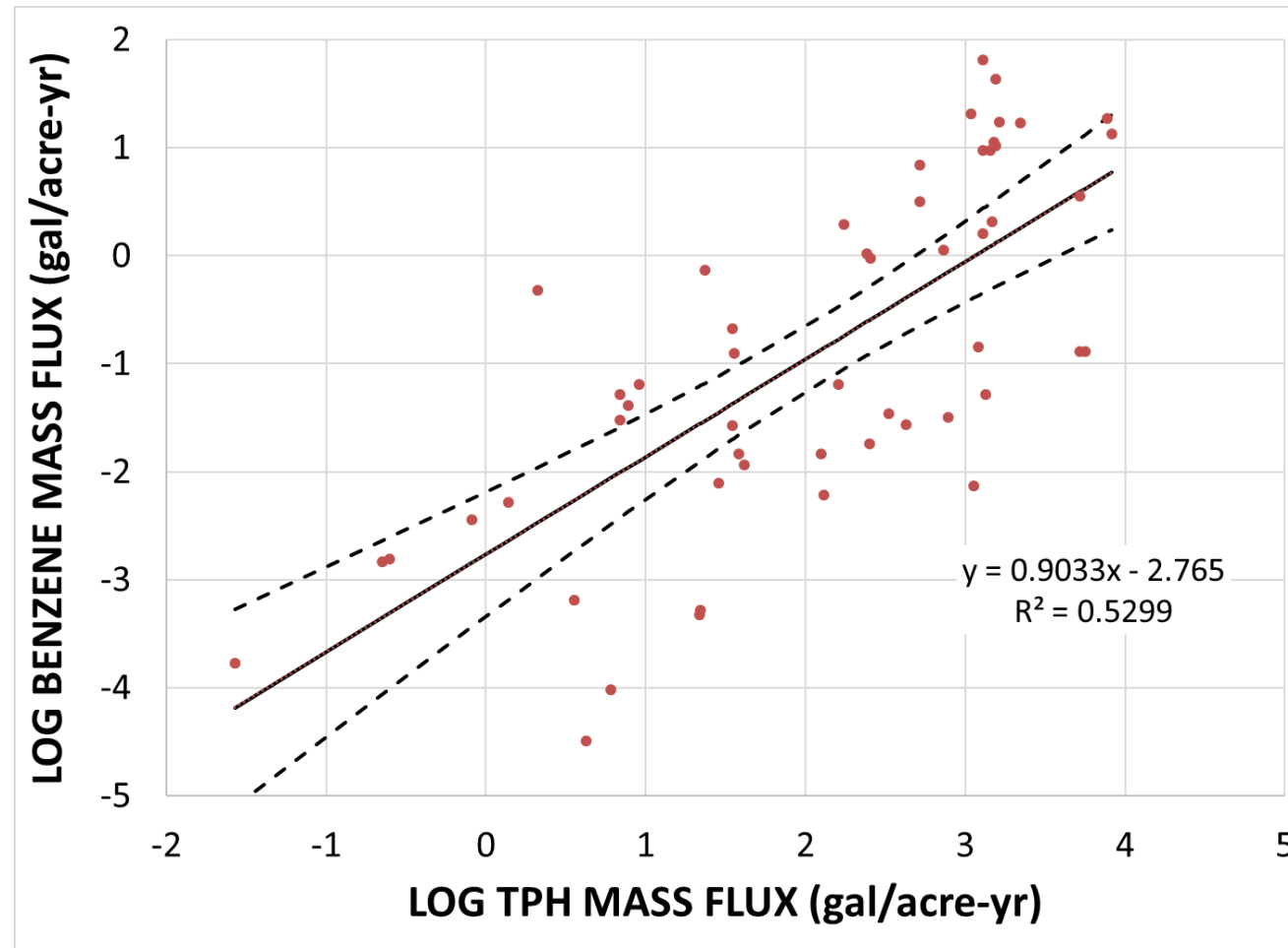


median rate: 0.13 gal/acre-yr
average rate: 9.2 gal/acre-yr

KEY POINT

- results generally make sense:
 - TPH NA rates roughly consistent w/ NSZD rates from literature
 - benzene NA rates < 100x TPH rates; consistent w/ mass fraction in gasoline

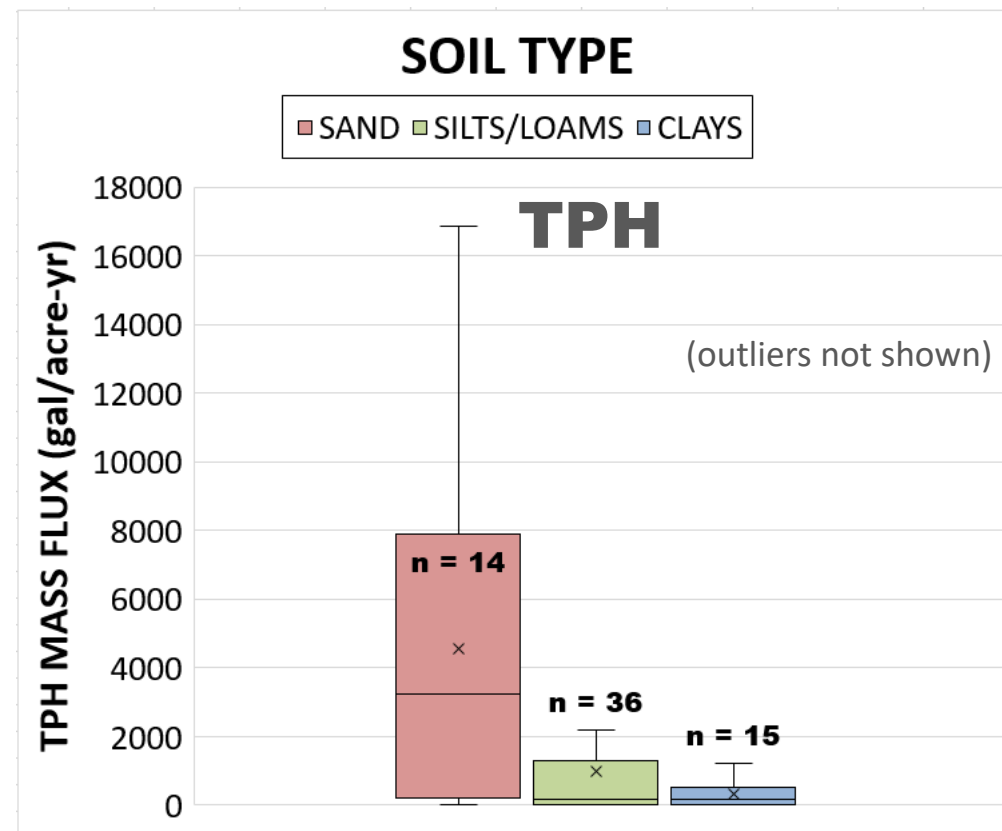
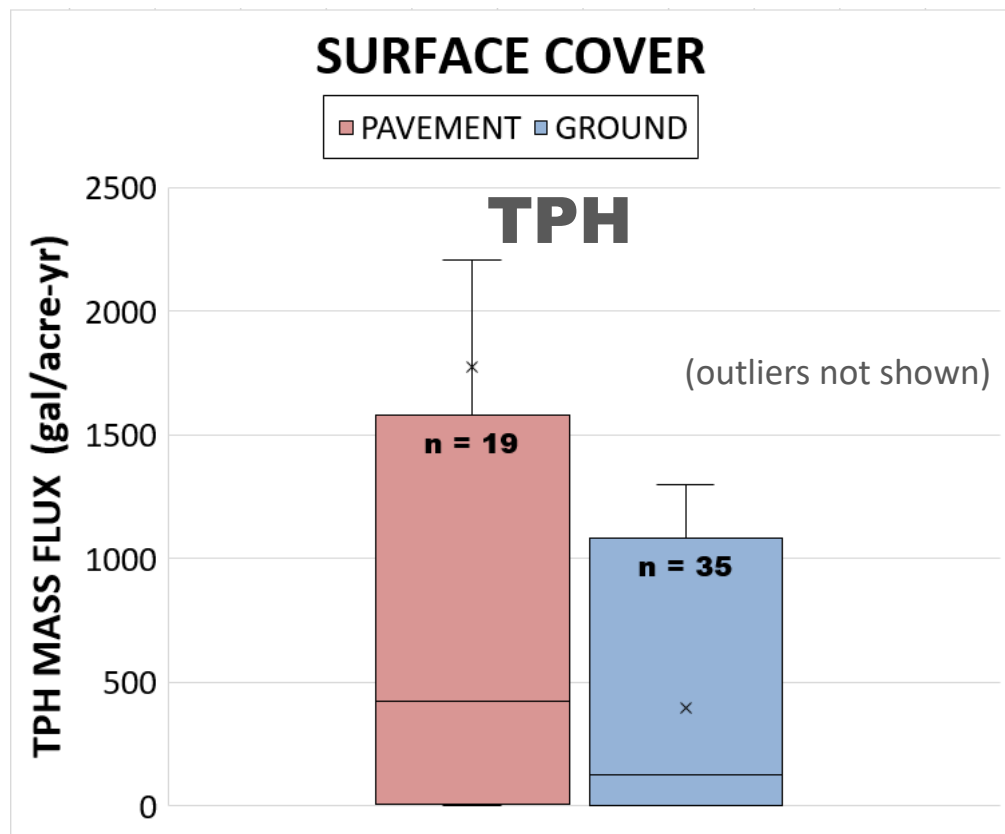
Natural Attenuation (NA) Rates: *Benzene vs. TPH*



KEY POINT

- difficult to predict constituent specific NA rates from bulk TPH NSZD rates

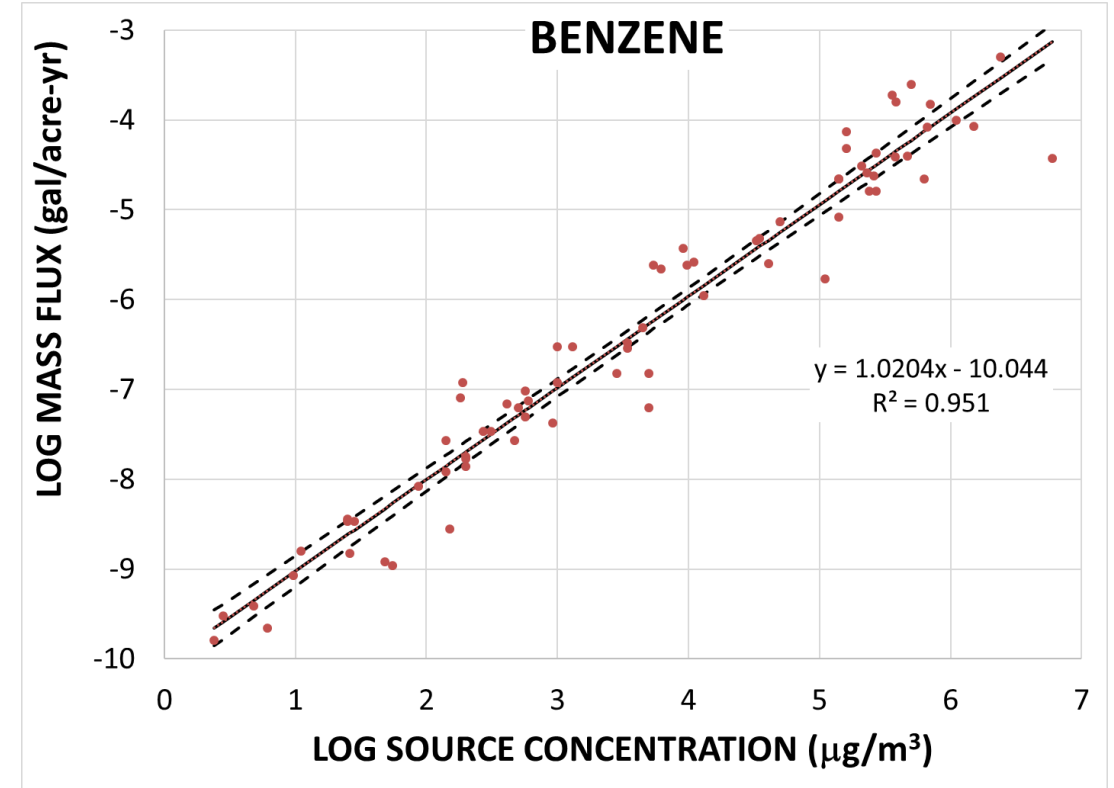
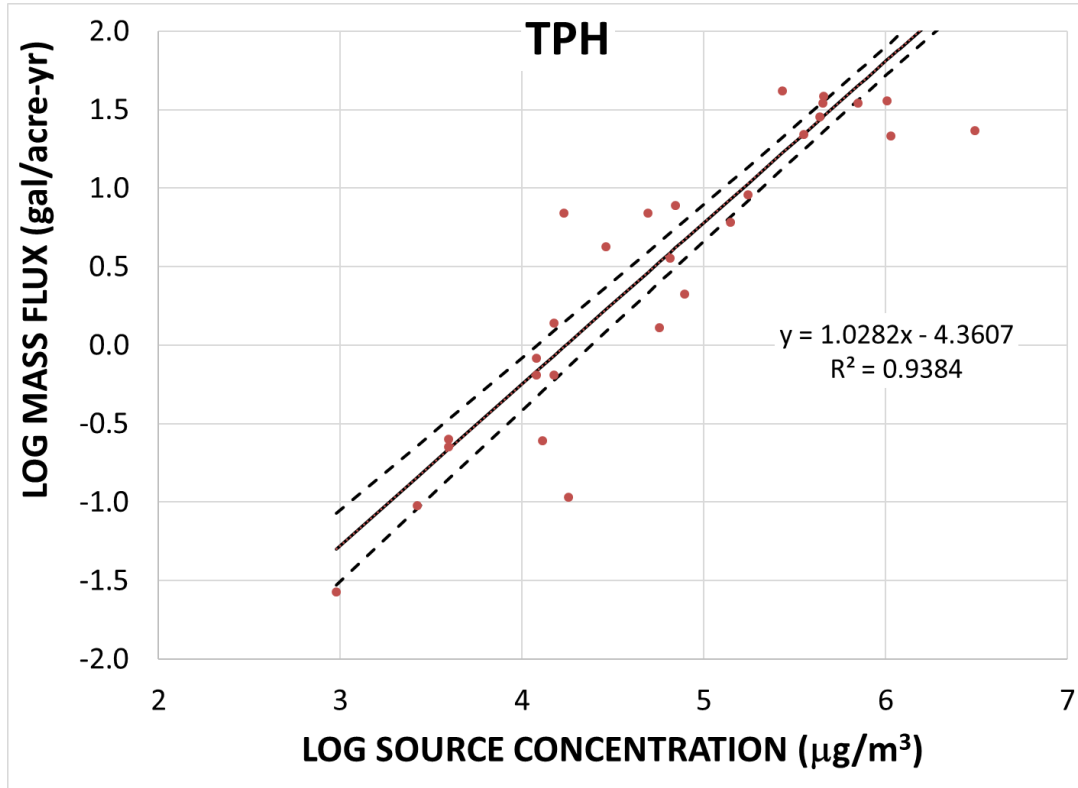
Factors That Affect Natural Attenuation (NA) Rates: *Surface Cover & Soil Type*



KEY POINT

- NA rates more affected by proximity to source and soil type than surface cover

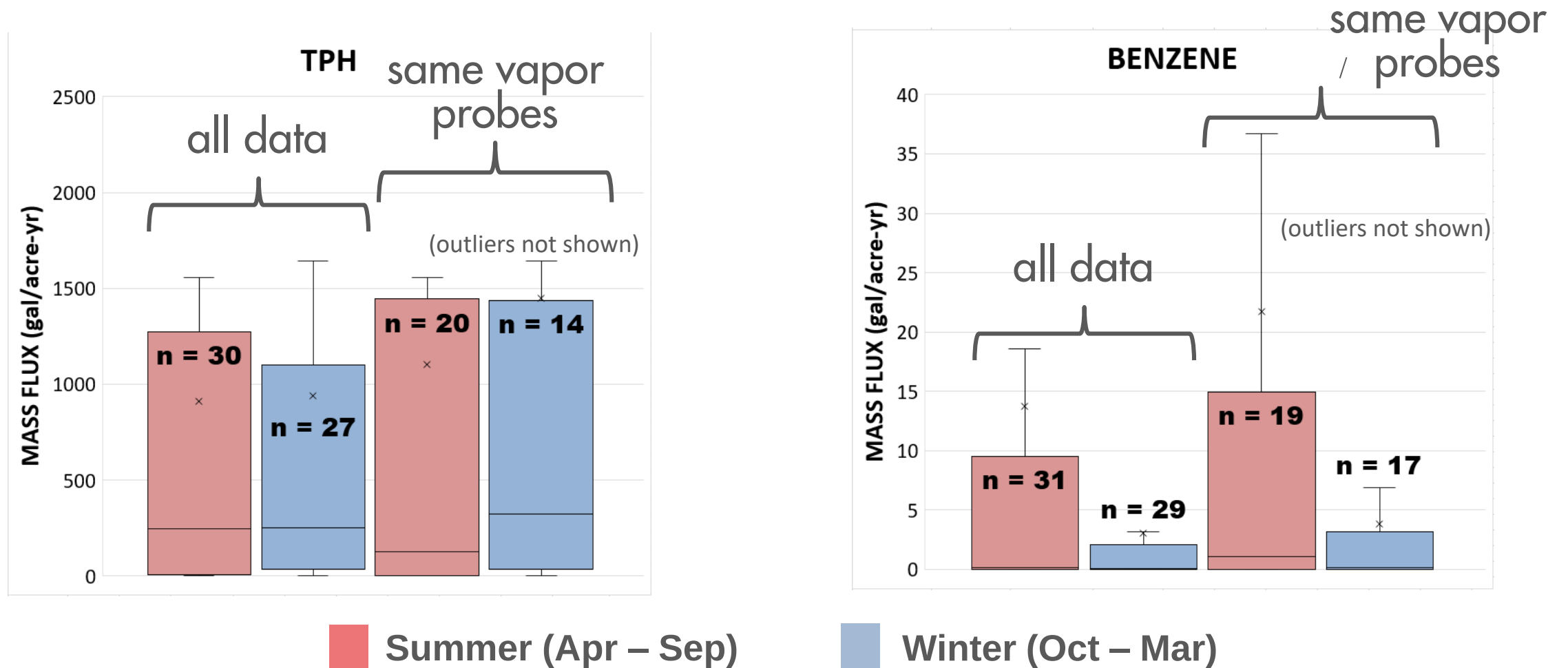
Factors That Affect Natural Attenuation (NA) Rates: *Source Vapor Concentration*



KEY POINT

- NA rate (mass flux) strongly correlated with vapor source concentration
- source vapor concentration measurements may be sufficient for NA rate determinations

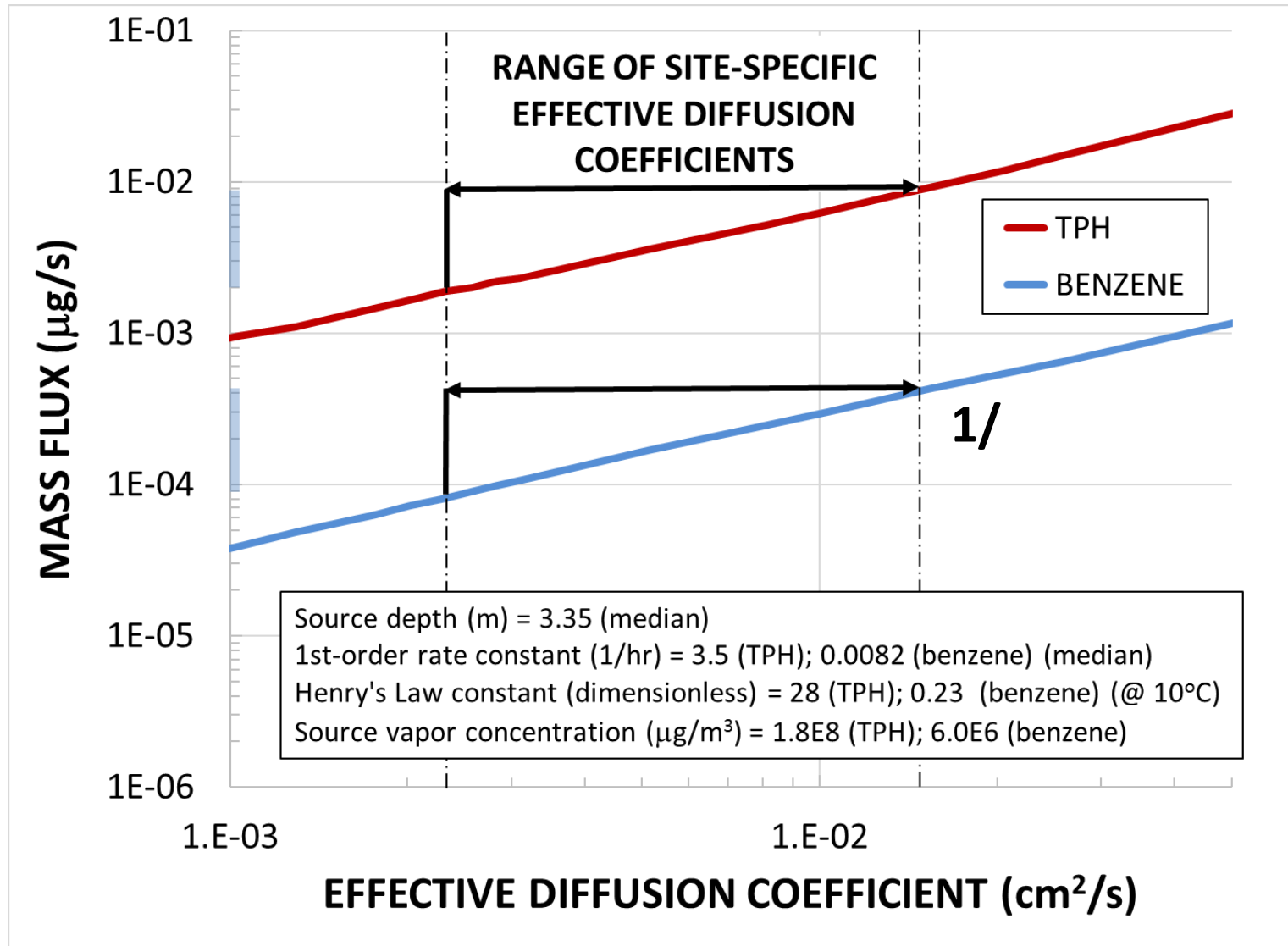
Factors That Affect Natural Attenuation Rates: *Seasonality*



KEY POINT

- median NA rates generally unaffected by seasonality

Sensitivity Analysis – *Effective Diffusion Coefficient*



variability in mass flux
for specified range of
variables

KEY POINT

- TPH and benzene
NA rates vary by < 1
order of magnitude
for range of
documented soil
types (sand – sandy
clay) and default
soil properties

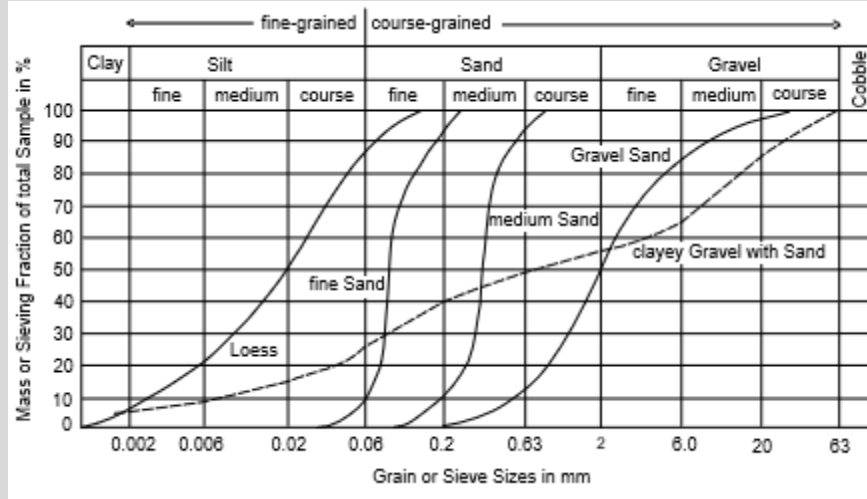
Opportunities to Improve NA Rate Estimates

Tier 1: Default Values

TABLE 3. CLASS AVERAGE VALUES OF THE VAN GENUCHTEN SOIL WATER RETENTION PARAMETERS FOR THE 12 SCS SOIL TEXTURAL CLASSIFICATIONS

Soil texture (USDA)	Saturated water content, θ_s	Residual water Content, θ_r	van Genuchten parameters		
			α_1 (1/cm)	N	M
Clay	0.459	0.098	0.01496	1.253	0.2019
Clay loam	0.442	0.079	0.01581	1.416	0.2938
Loam	0.399	0.061	0.01112	1.472	0.3207
Loamy sand	0.390	0.049	0.03475	1.746	0.4273
Silt	0.489	0.050	0.00658	1.679	0.4044
Silty loam	0.439	0.065	0.00506	1.663	0.3987
Silty clay	0.481	0.111	0.01622	1.321	0.2430
Silty clay loam	0.482	0.090	0.00839	1.521	0.3425
Sand	0.375	0.053	0.03524	3.177	0.6852
Sandy clay	0.385	0.117	0.03342	1.208	0.1722
Sandy clay loam	0.384	0.063	0.02109	1.330	0.2481
Sandy loam	0.387	0.039	0.02667	1.449	0.3099

Tier 2: Geotechnical Analysis



Tier 3: In-Situ Tracer

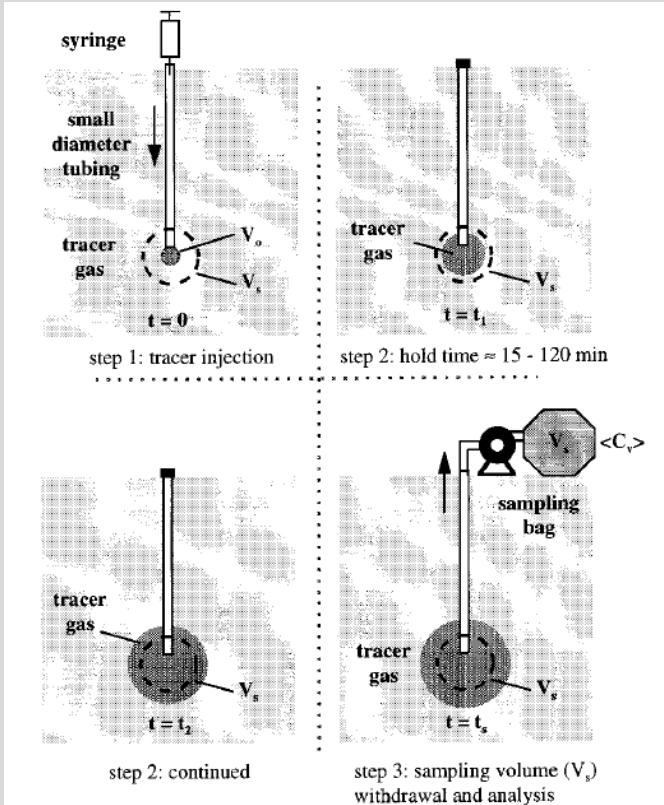


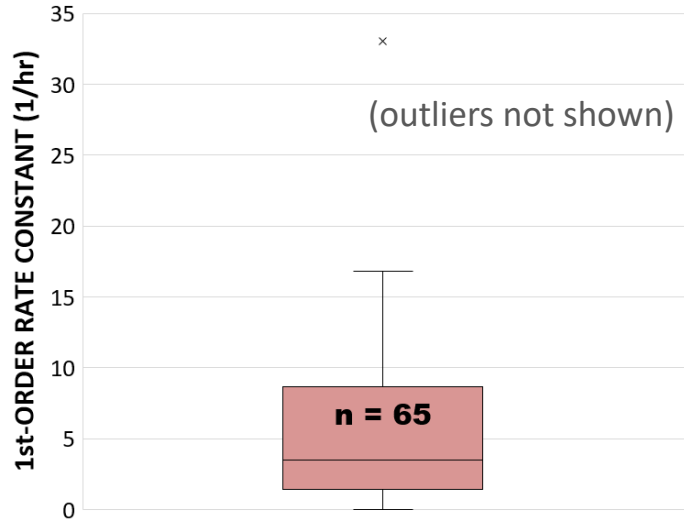
FIGURE 1. Generalized schematic of in situ measurement approach.

**KEY
POINT**

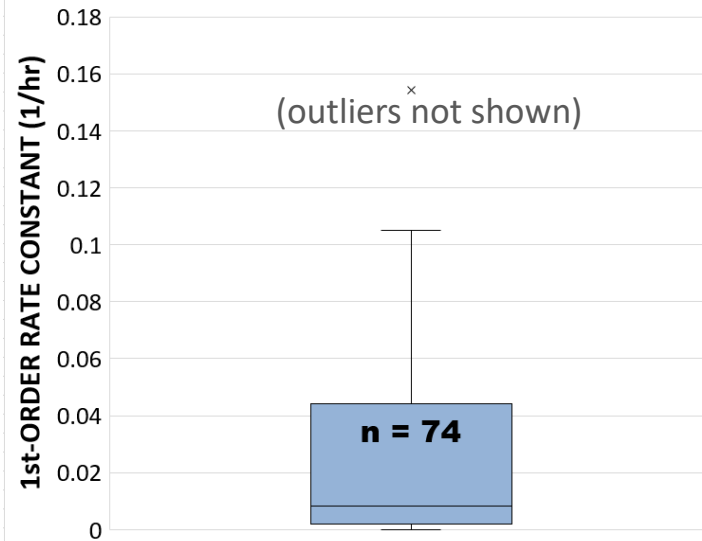
- data quality objectives need to be established upfront and will be site-specific

1st Order Aerobic Degradation Rate Constant - *TPH & benzene*

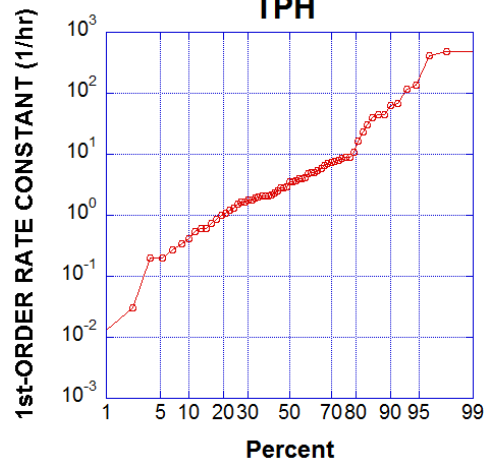
TPH



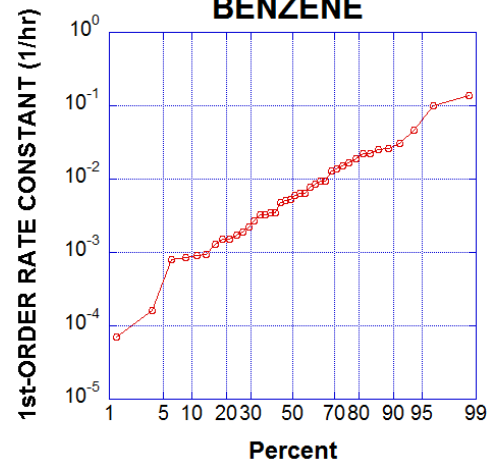
BENZENE



TPH



BENZENE



KEY POINT

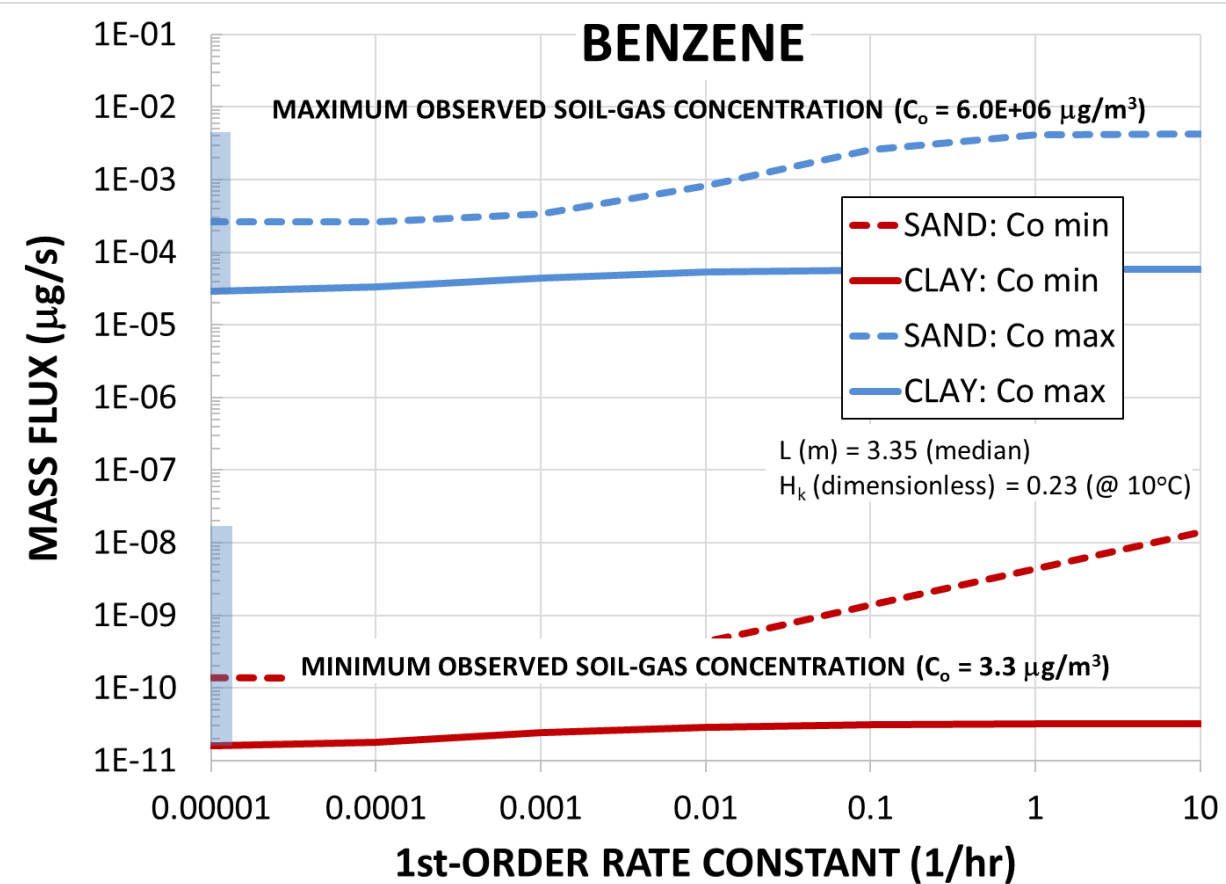
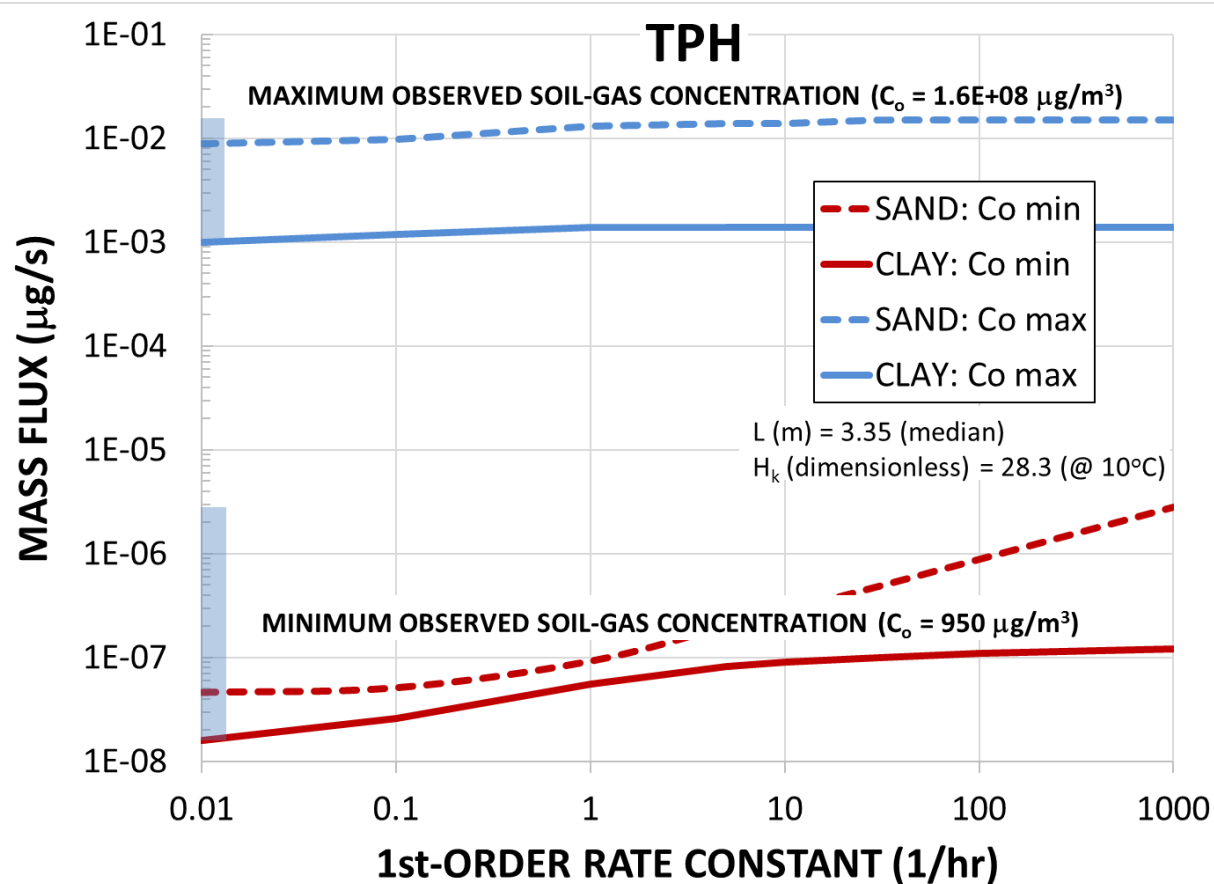
- mean aerobic biodegradation rates for TPH and benzene are ~2 - 5x less than mean values reported from literature survey (DeVaul, 2007):

- TPH = 71 1/hr
- benzene = 0.79 1/hr

median rate: 3.5 1/hr
mean rate: 33 1/hr

median rate: 0.0082 1/hr
mean rate: 0.15 1/hr

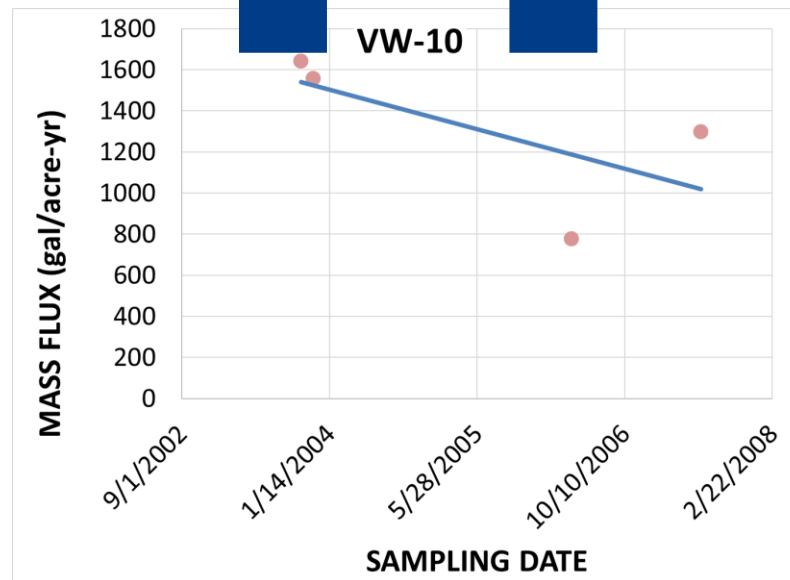
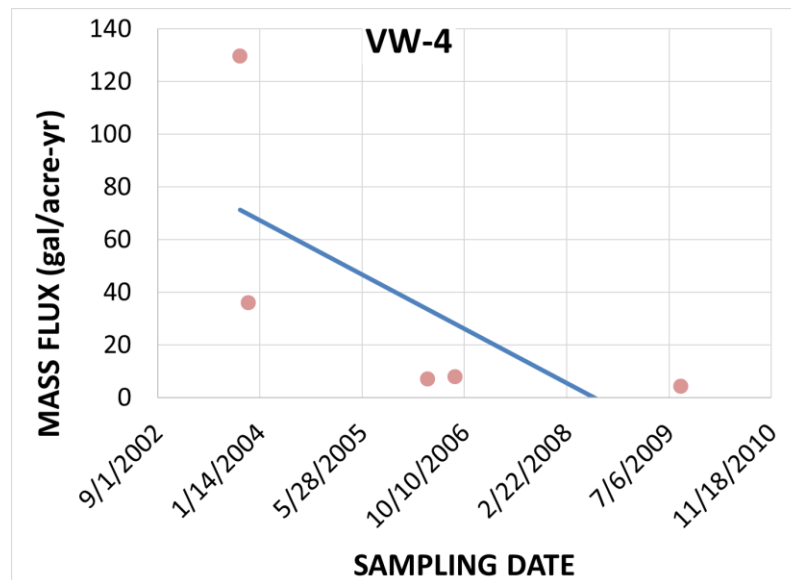
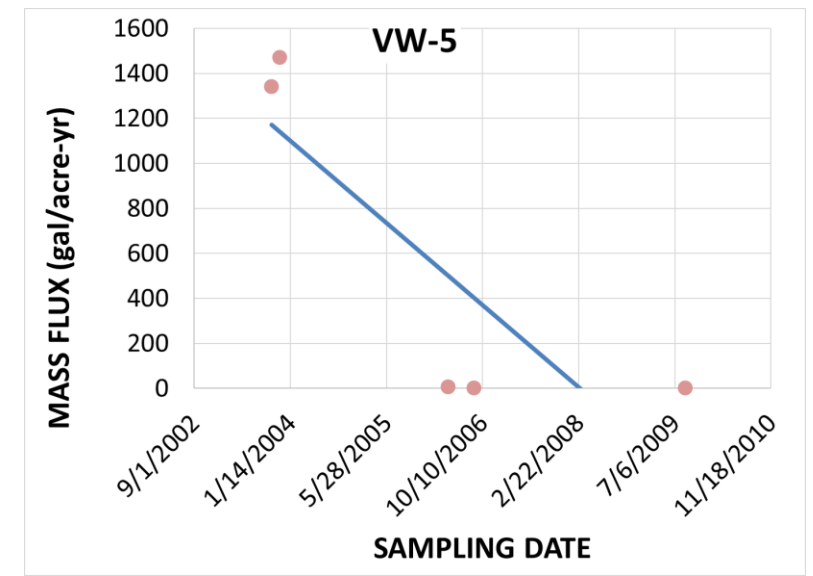
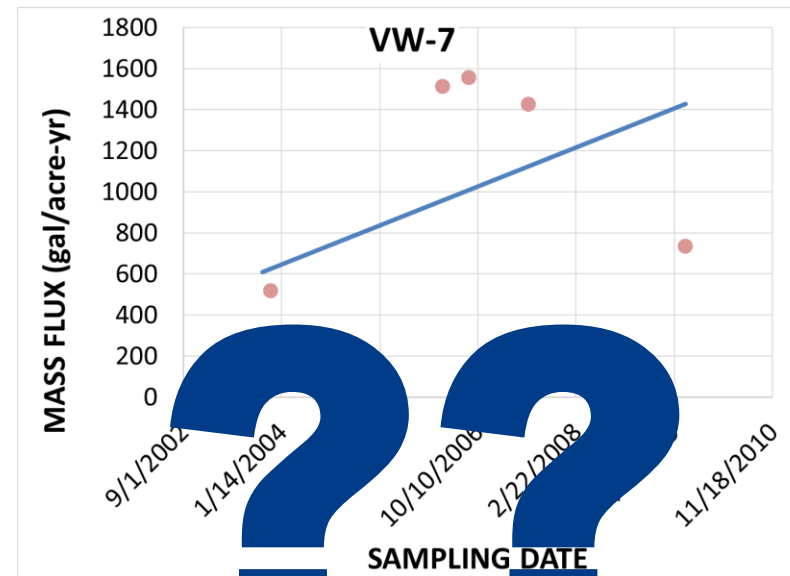
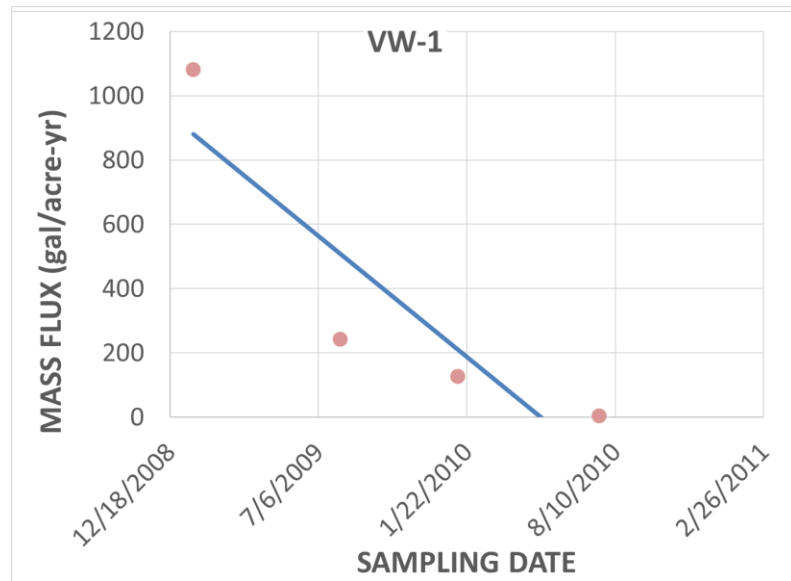
Sensitivity Analysis – 1st-Order Rate Constant (k_w)



KEY POINT

- the sensitivity of the NA rate varies depending on constituent (greater for benzene than TPH); increases for higher permeability soils (sands)
- NA rate are more sensitive to the aerobic biodegradation rate than soil type across range of calibrated values

Temporal Trends in Natural Attenuation (NA) Rates

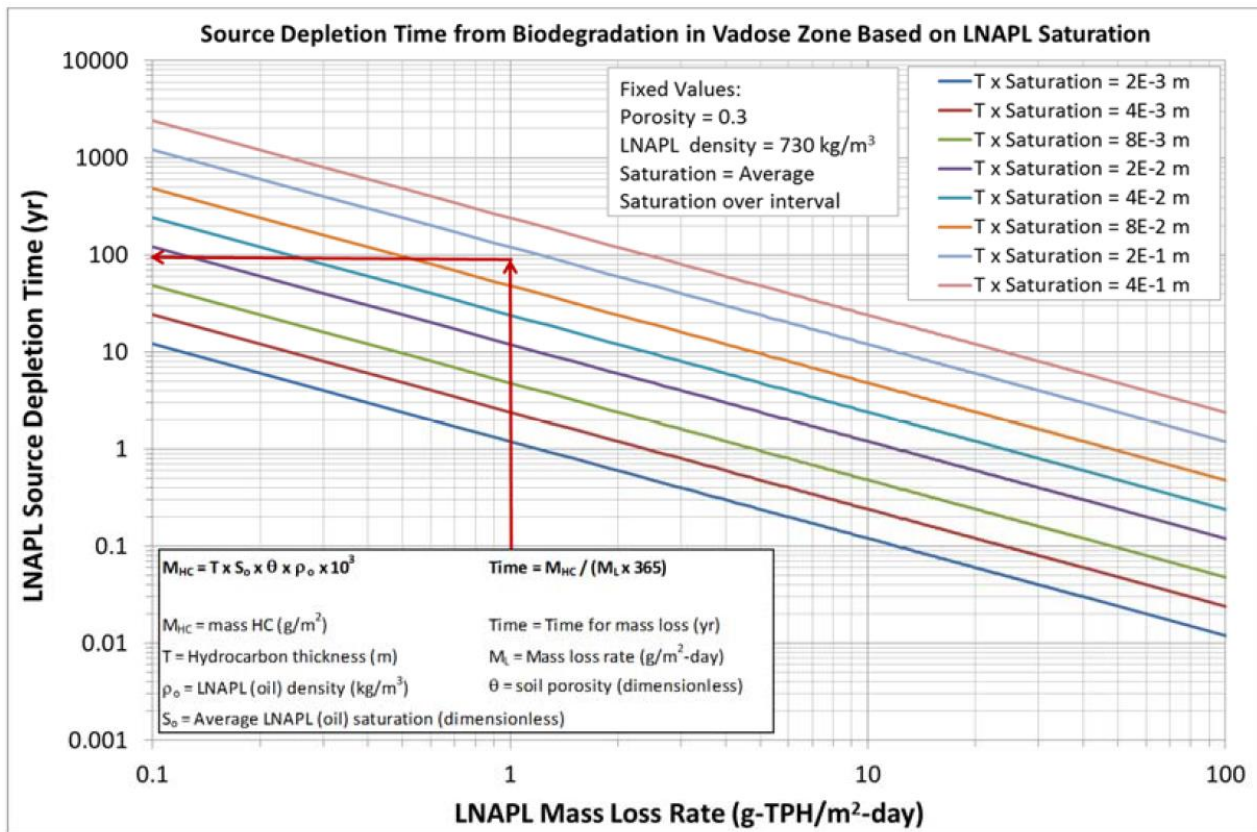


KEY POINT

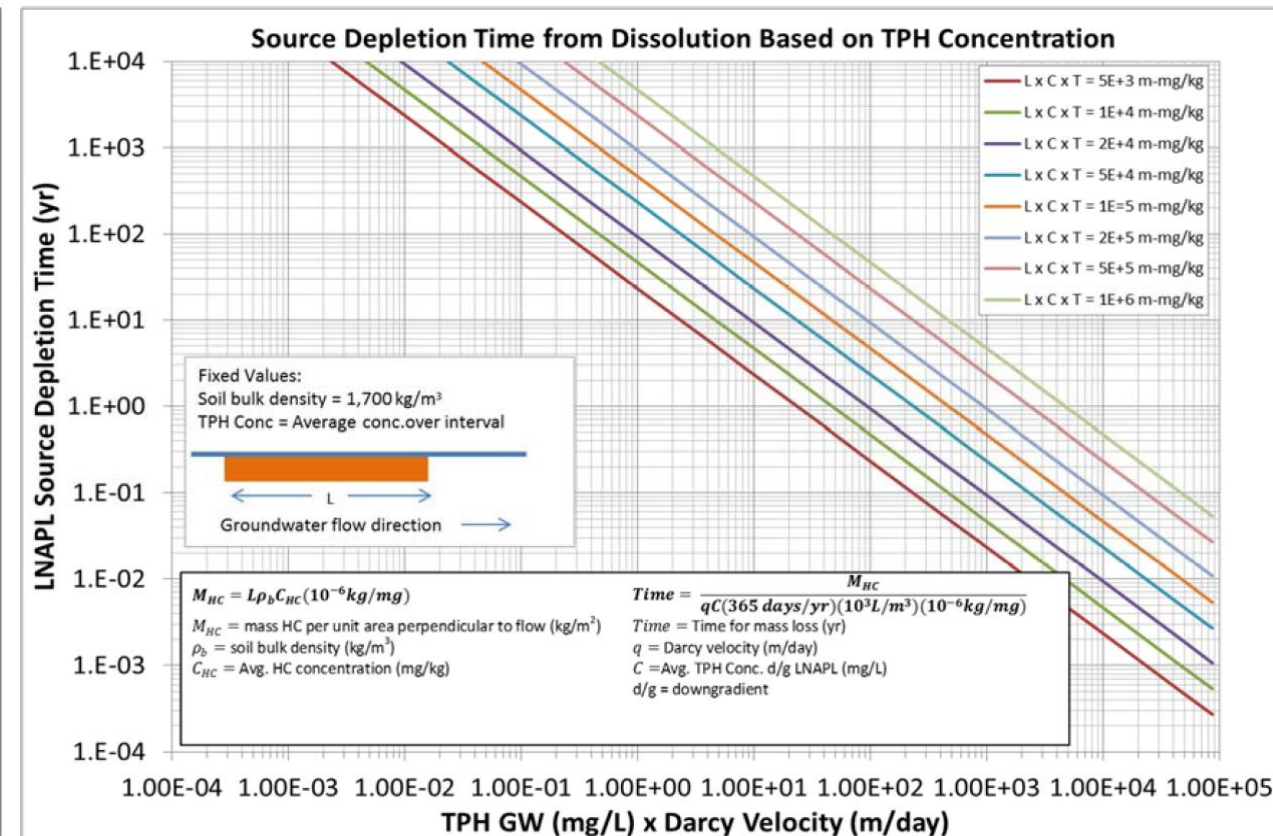
- NA rates in source areas will vary over time
- trends & source mass critical for predicting plume longevity
- more frequent data = improved remediation decision making

Plume Longevity Prediction: *Source Mass – Mass Loss Rates*

Vadose Zone – NA Rate Estimates



Saturated Zone – Mass Flux Estimates



**KEY
POINT**

- the more site-specific data, in general, the better the prediction

Efforts to Address the Challenge

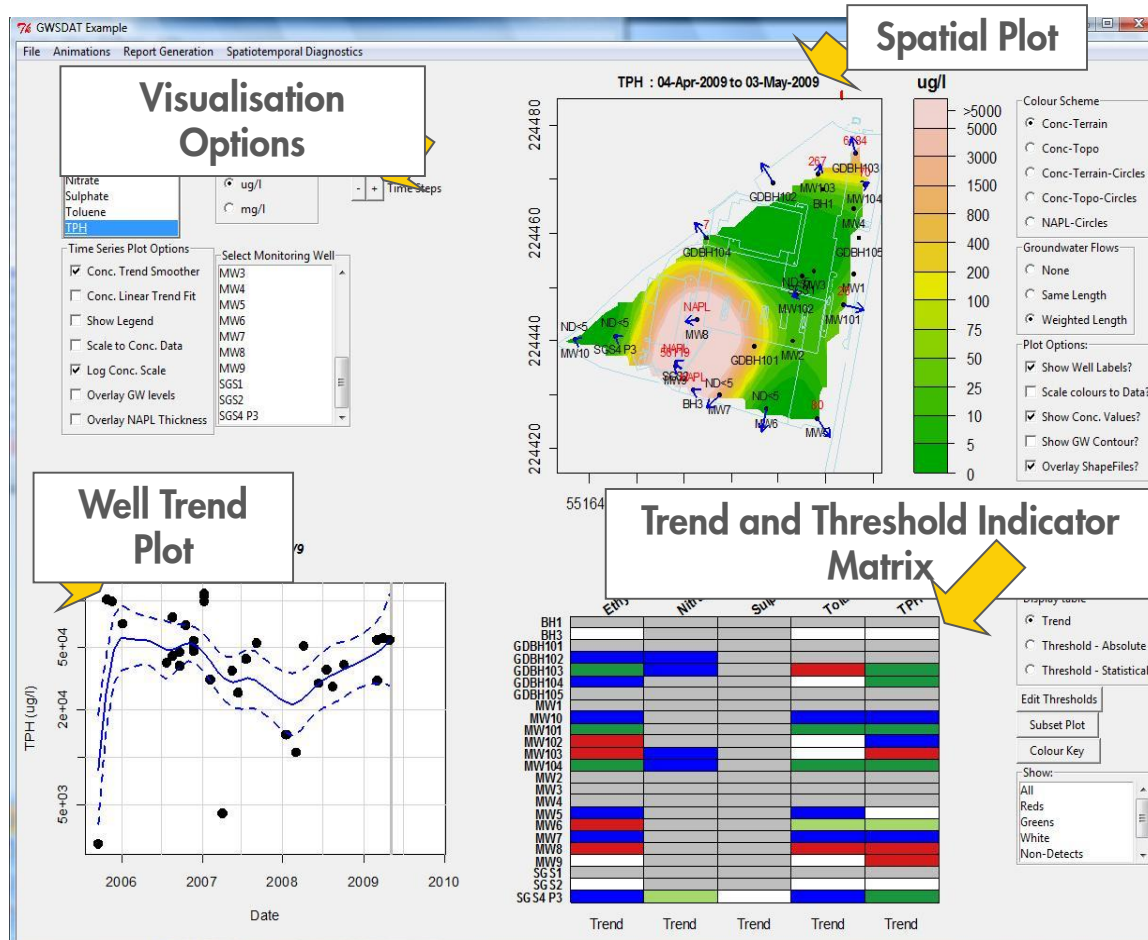
GROUNDWATER COMPOSITION

GWSDat: Ground Water Spatial-Temporal Analysis Tool

(<http://www.api.org/oil-and-natural-gas/environment/clean-water/ground-water/gwsdat>)

INPUT

OUTPUT



A B C D E F G H I J K L M N

GWSTAT (GroundWater Spatio Temporal Analysis Tool)							
Author: Wayne.W.Jones@Shell.com				Version: 1.0			
Historical Monitoring Data				Well Coordinates			
WellName	Constituent	SampleDate	Result	Units	WellName	XCoord	YCoord
K1	MTBE	05/05/2004	148.1	ug/L	K1	3427016	6764637
K1	MTBE	05/10/2004	147.7	ug/L	GA1	3426962	6764630
K1	MTBE	18/10/2005	35	ug/L	GA2	3427025	6764651
K1	MTBE	23/05/2006	30	ug/L	GA3	3427017	6764666
K1	TAME	05/05/2004	42.6	ug/L	GA4	3427000	6764656
K1	TAME	05/10/2004	57.5	ug/L	GA5	3426970	6764620
K1	TAME	18/10/2005	8	ug/L	P11	3426915	6764730
K1	TAME	23/05/2006	6	ug/L	21	3426830	6764790
K1	Benzene	05/05/2004	ND<1.0	ug/L	GW1	3426969	6764639
K1	Benzene	05/10/2004	0.5	ug/L	GW2	3426995	6764628
K1	Benzene	18/10/2005	ND<1.0	ug/L	GW3	3426988	6764629
K1	Benzene	23/05/2006	ND<0.05	ug/L	GW4	3426981	6764638
K1	Toluene	05/05/2004	ND<1.0	ug/L			
K1	Toluene	05/10/2004	ND<1.0	ug/L			
K1	Toluene	18/10/2005	ND<1.0	ug/L			
K1	Toluene	23/05/2006	ND<0.05	ug/L			
K1	Ethylbenzene	05/05/2004	0.3	ug/L			
K1	Ethylbenzene	05/10/2004	1.6	ug/L			
K1	Ethylbenzene	18/10/2005	ND<1.0	ug/L	123	3426300.00	6764390.00
K1	Ethylbenzene	23/05/2006	0.3	ug/L	K2	3427009	6764639
K1	Xylene	05/05/2004	0.7	ug/L	K3	3426994	6764643
K1	Xylene	05/10/2004	3.3	ug/L	22	3427110	6764495
K1	Xylene	18/10/2005	ND<1.0	ug/L	354	3426811	6764557
K1	Xylene	23/05/2006	0.3	ug/L			
K1	Xylene	05/05/2004	ND<1.0	ug/L			
K1	TCE	05/10/2004	ND<1.0	ug/L			
K1	TCE	18/10/2005	ND<1.0	ug/L			
K1	TCE	23/05/2006	ND<0.2	ug/L			
K1	PCE	05/05/2004	ND<1.0	ug/L			
K1	PCE	05/10/2004	ND<1.0	ug/L			
K1	PCE	18/10/2005	ND<1.0	ug/L			
K1	PCE	23/05/2006	ND<0.2	ug/L			
K1	TVOC	05/05/2004	195	ug/L			
K1	TVOC	05/10/2004	223	ug/L			
K1	TVOC	18/10/2005	ND<1.0	ug/L			
K1	TVOC	23/05/2006	38	ug/L			
K1	TPH c10-21	05/05/2004	70	ug/L			
K1	TPH c10-21	05/10/2004	200	ug/L			
K1	TPH c10-21	18/10/2005	320	ug/L			
K1	TPH c10-21	23/05/2006	160	ug/L			
K1	TPH c22-40	05/05/2004	ND<30	ug/L			
K1	TPH c22-40	05/10/2004	ND<1.0	ug/L			

GWSTAT

Load Saved Session

Ready
 Demo-Hennals
 Hennals
 Demo-Rajatorppa
 Rajatorppa
 Demo-Lahuti (2)
 Demo-Lahuti
 Lahuti
 WGPL
 Brighton
 Mon

- Ricker (2008) Method
 - average GW concentration
 - average mass
 - average plume area

Regression Tool (Wilson, 2011)

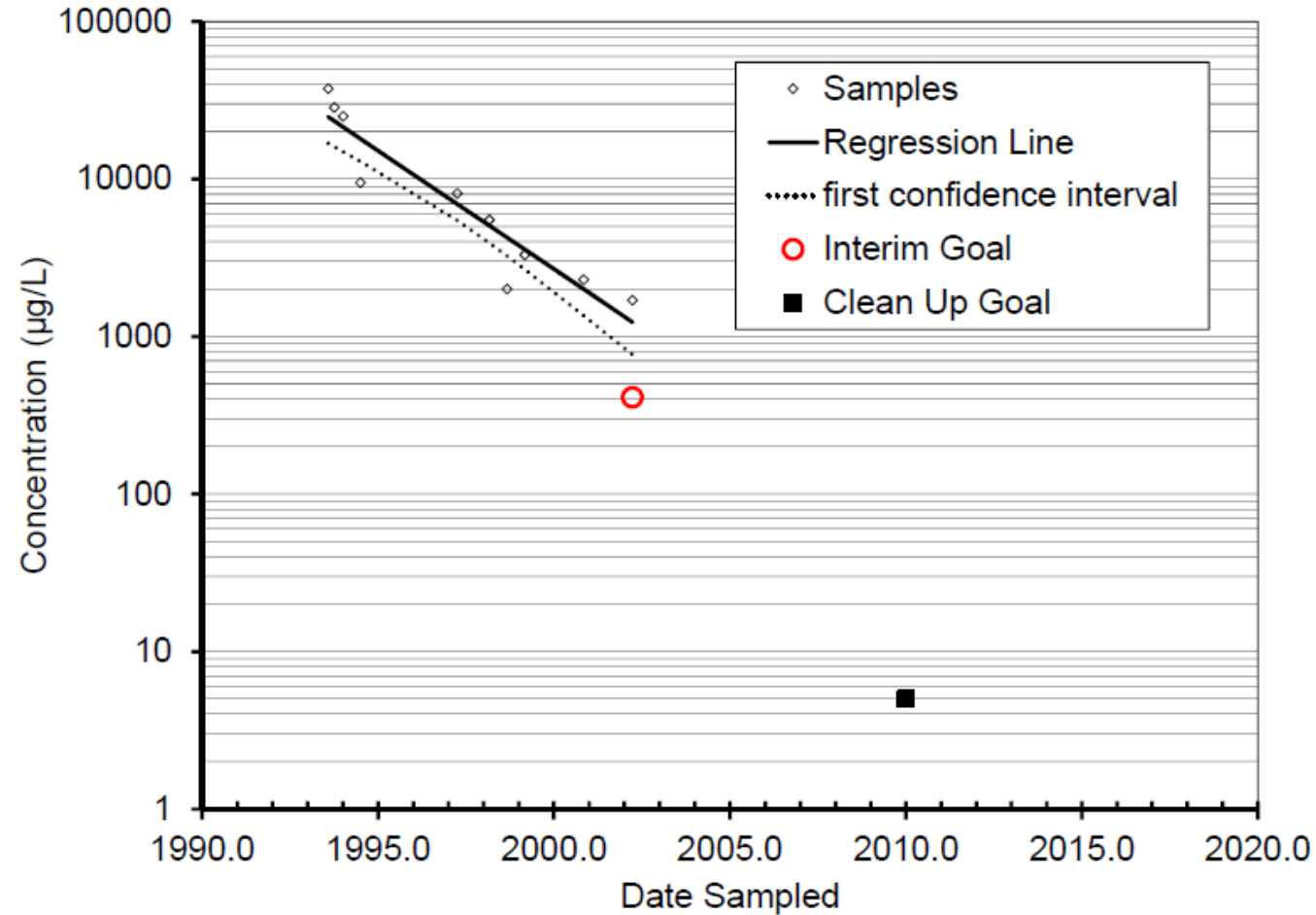
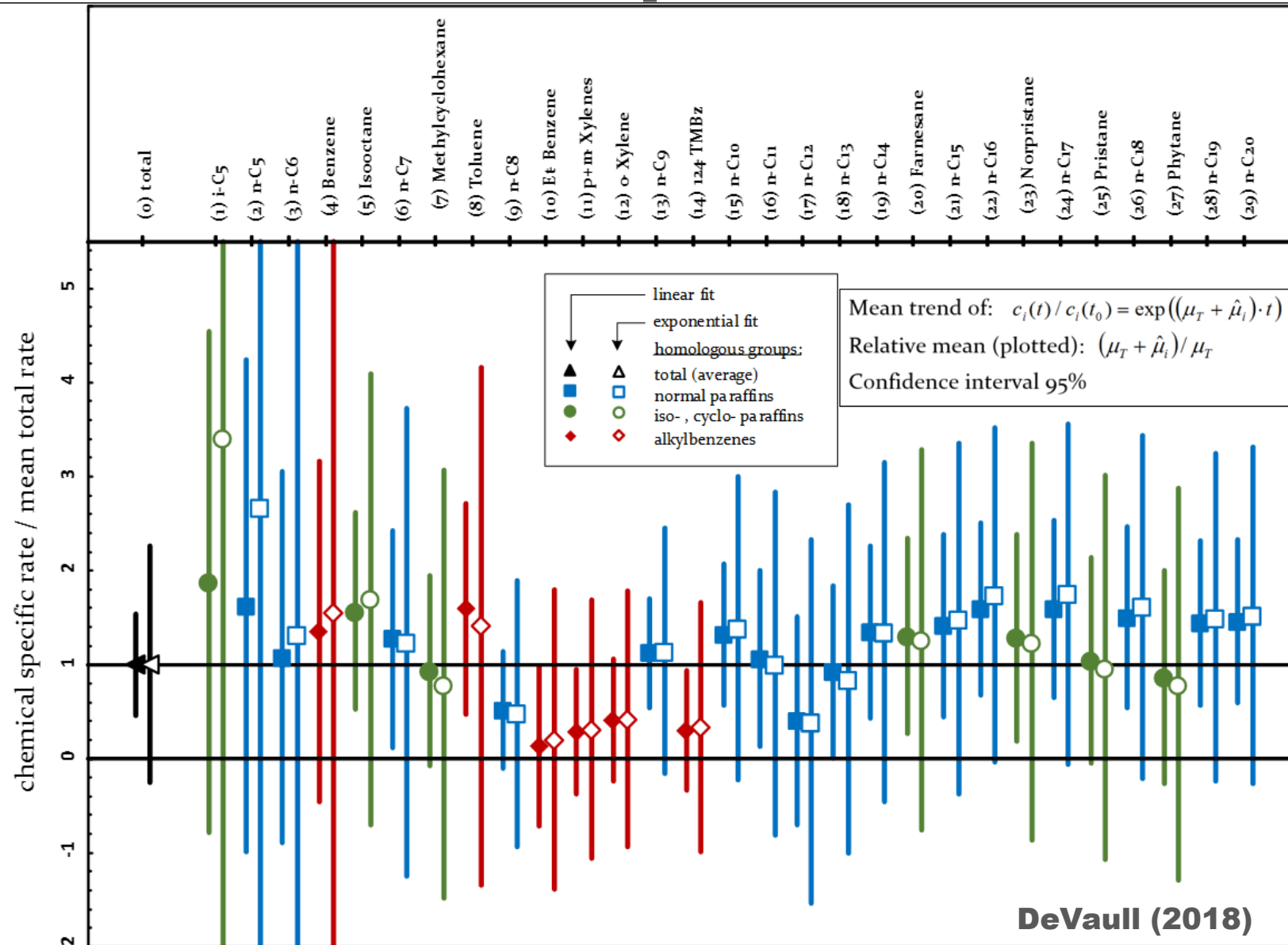


Figure A-3: Evaluating the uncertainty in the extrapolation of the trend in concentrations of MTBE in well CBC-25.

Efforts to Address the Challenge

LNAPL COMPOSITION

Attenuation Rates for COPCs Based on Trends in LNAPL Composition



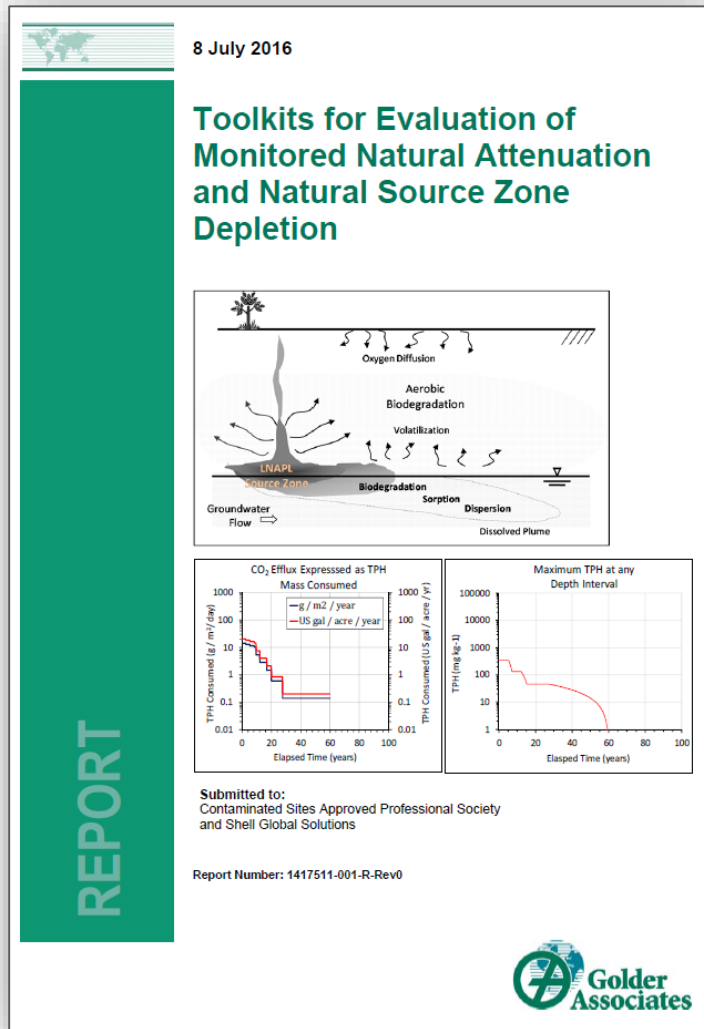
- diesel-like oil product (C₅ – C₂₀) from single monitoring well over 4-yr period

**KEY
POINT**

- LNAPL compositional analysis is an alternative (developing) method for assessing attenuation rates for specific hydrocarbons

CONCLUSIONS

Recommended Measurements to Support Remediation Optimization / “Getting to Closure”



STEPS

1. REMEDIAL OBJECTIVE

Mass
Recovery/Control
(LNAPL, TPH)

Risk-Based
Clean-Up Standard
(COPCs)

2. DATA NEEDS

SYSTEM

System Performance
(e.g., cost, recovery)

ENVIRONMENTAL

Saturated
Zone

Vadose
Zone

3. REMEDIAL TARGET ASSESSMENT

Active vs. Natural Rate Comparison
Tools (Tier I, II, III)

KEY POINT

- tools are available... let's use them!

Example – Mass Recovery/Control

**REGULATORY
MILESTONES**

CSM
DEVELOPMENT

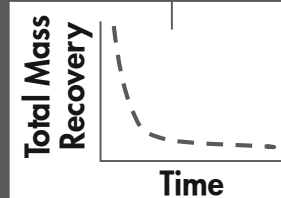
REMEDIAL
OBJECTIVES

ACTIVE RECOVERY
(e.g., LNAPL
recovery)

REMEDATION
TOLLGATE

END POINT

**MAXIMUM
EXTENT
PRACTICABLE**



SYSTEM PERFORMANCE

- TPH MASS RECOVERY VS. TIME OR COST
- LNAPL/WATER VOLUME RECOVERY VS. TIME
- TPH MASS RECOVERY VS. CO₂

**NSZD
ASSESSMENT**

SATURATED ZONE

- LNAPL TRANSMISSIVITY ANALYSIS
- LNAPL VOLUME/FOOTPRINT
- LNAPL VELOCITY
- TPH/COPC MASS FLUX/DISCHARGE
- TPH/COPC CONCENTRATIONS VS. TIME/DISTANCE
- TPH/COPC CONCENTRATIONS (REBOUND)

VADOSE ZONE

- TPH VADOSE ZONE (SOIL-GAS GRADIENT METHOD)
- O₂ FLUX (O₂ GRADIENT METHOD)
- CO₂ FLUX (TRAPS, SURFACE FLUX CHAMBER)
- TEMPERATURE FLUX

**DATA
COLLECTION
& ANALYSIS**

Example: Composition

**REGULATORY
MILESTONES**

CSM
DEVELOPMENT

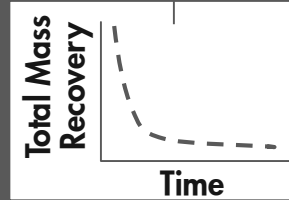
REMEDIAL
OBJECTIVES

ACTIVE
RECOVERY
(e.g., SVE)

REMEDATION
TOLLGATE

END POINT

**GW CLEANUP
VALUES
(MCLs)**



VADOSE ZONE

- COPC VOLATILIZATION TEST (SOIL-GAS GRADIENT METHOD)

SYSTEM PERFORMANCE

- COPC MASS RECOVERY VS. TIME OR COST
- COPC/VAPOR RECOVERY VS. TIME
- COPC MASS RECOVERY VS. CO₂
- REBOUND TEST

VADOSE ZONE

- COPC VOLATILIZATION TEST (SOIL-GAS GRADIENT METHOD)

SATURATED ZONE

- COPC CONCENTRATION VS. TIME & SPACE
- LNAPL COMPOSITION VS. TIME
- COPC DISSOLUTION TEST (*could also be pre-remediation)

**DATA
COLLECTION
& ANALYSIS**

Conclusions

- quantification of natural attenuation rates is critical for improved, more sustainable remediation/risk-based decision making
- compositional analysis is needed for meaningful risk assessment and plume longevity prediction
- natural attenuation rates are more sensitive to space (source concentration, proximity to source, soil type) than time (seasonality)
- we can do better:
 - improved data collection
 - Implementation of existing methods and tools ... let's use them!



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Questions and Answers

Q&A

