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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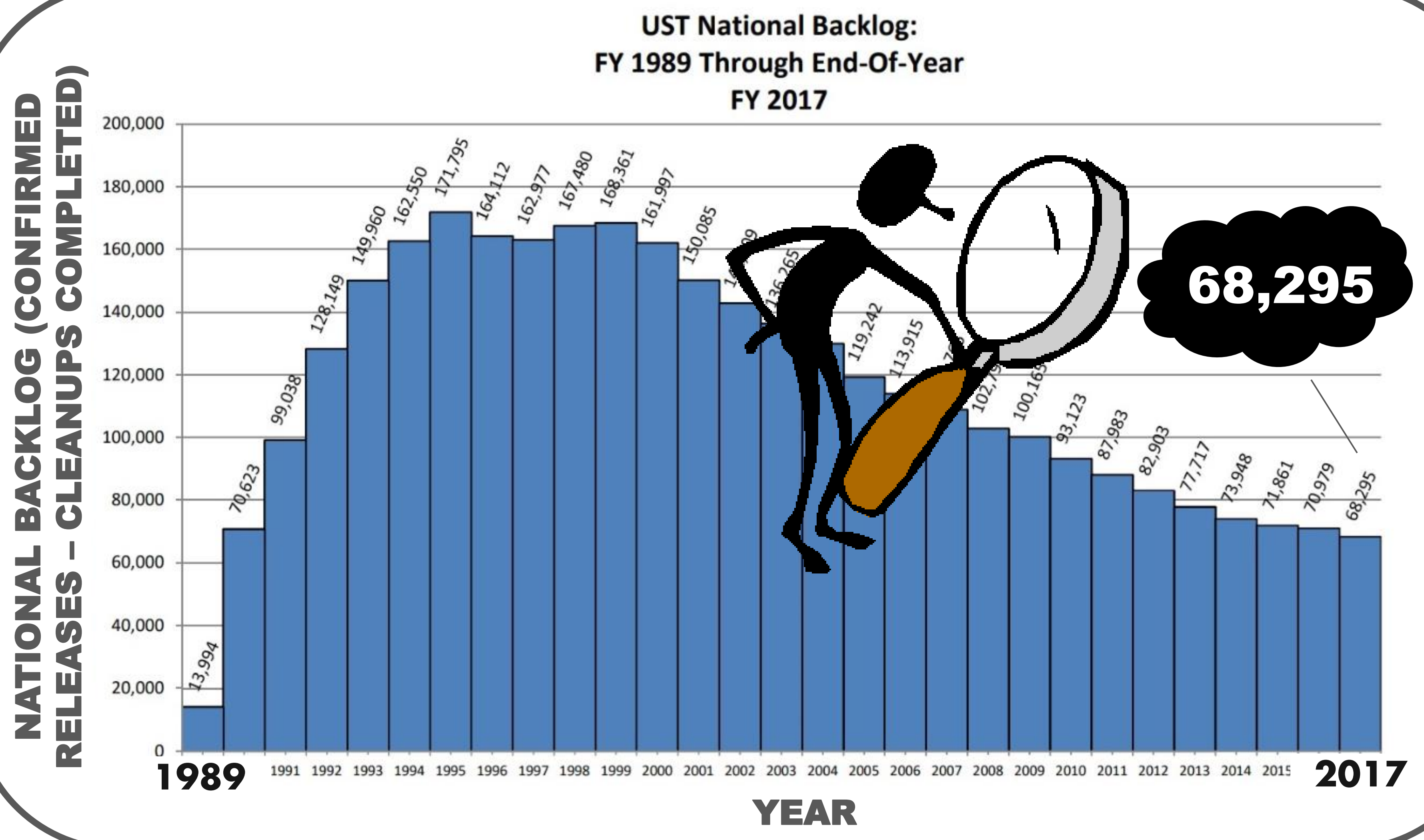
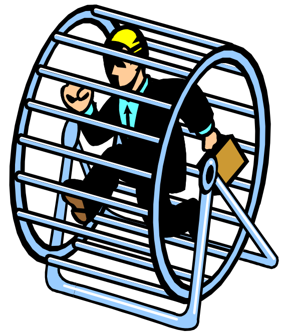
The Challenge

Lots of Open UST Cases Remain



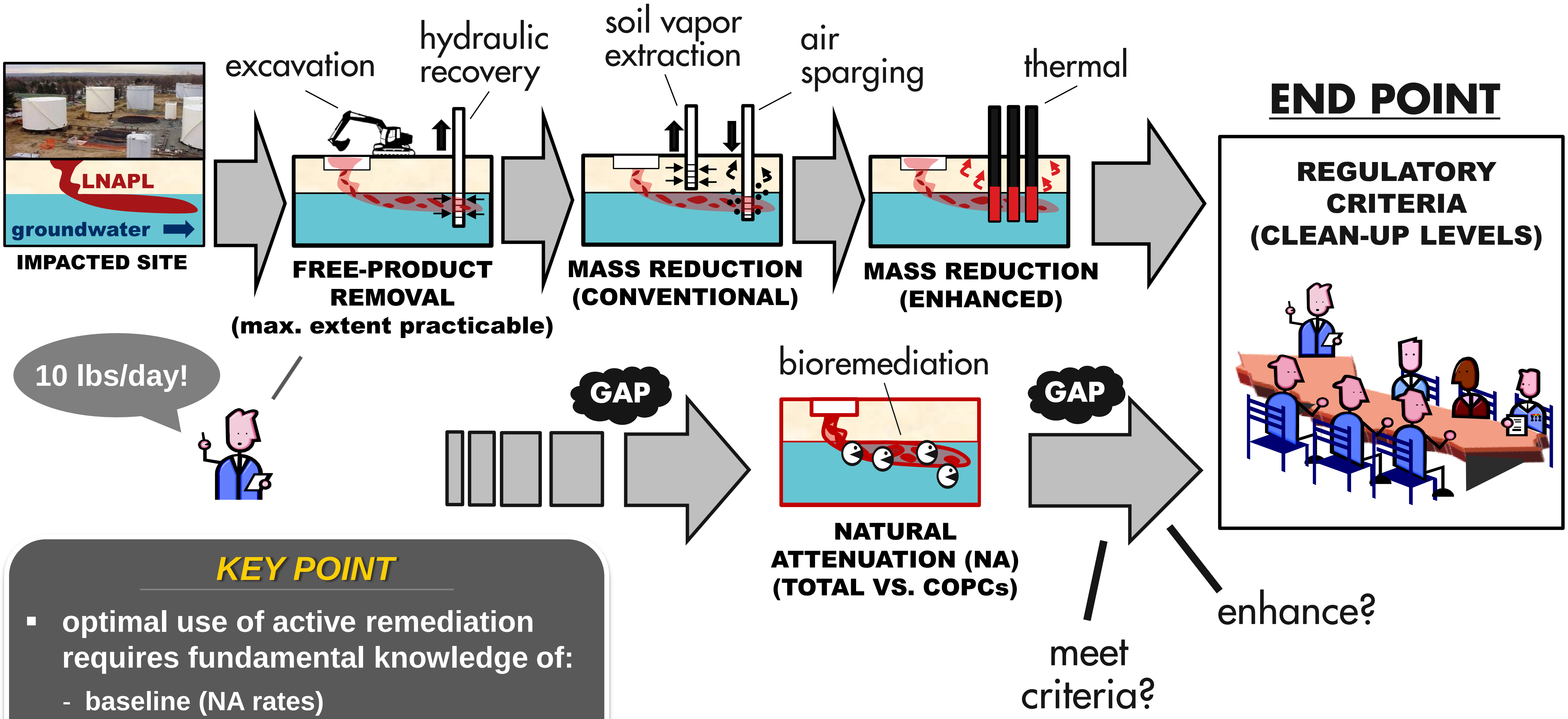


KEY POINT

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

<u>"WHAT WORKS… WHAT DOESN'T"</u>

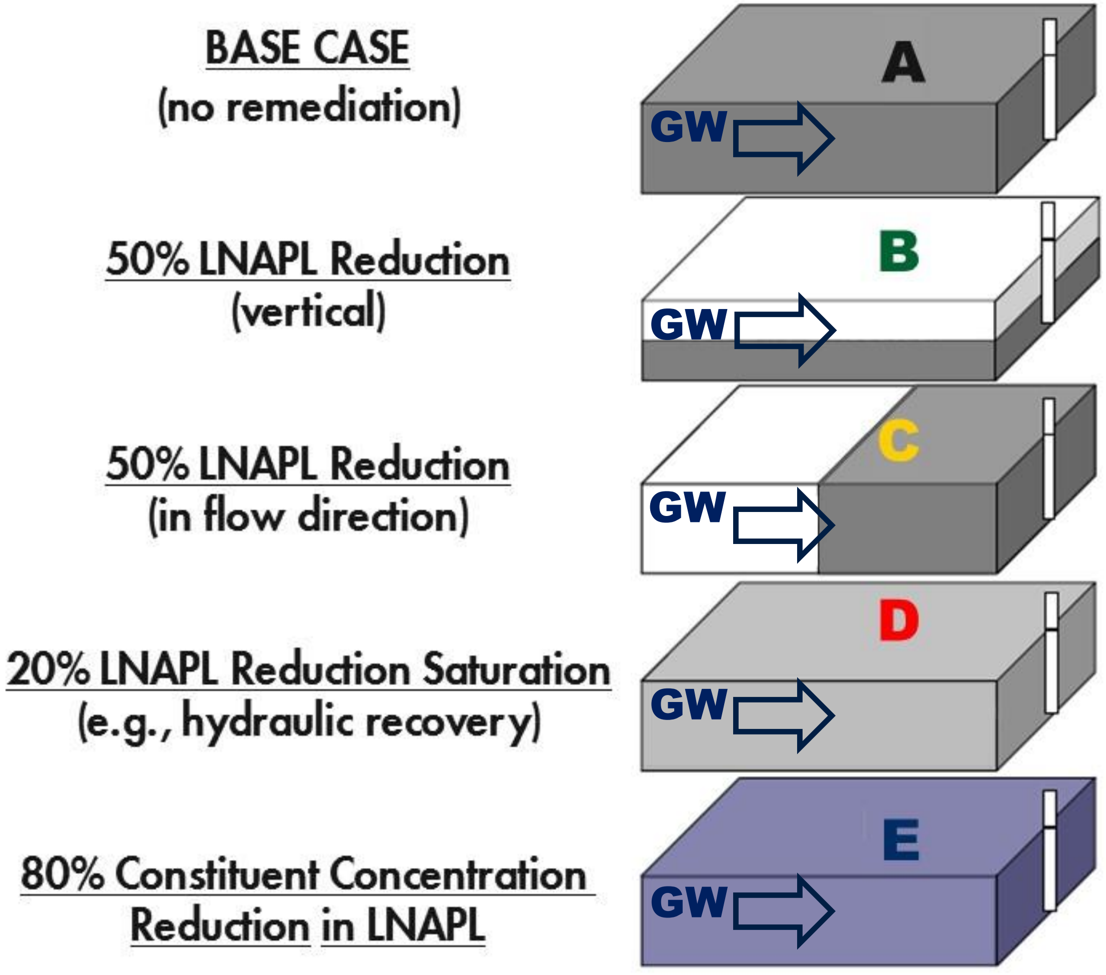
Active Remediation Systems Rarely Optimized



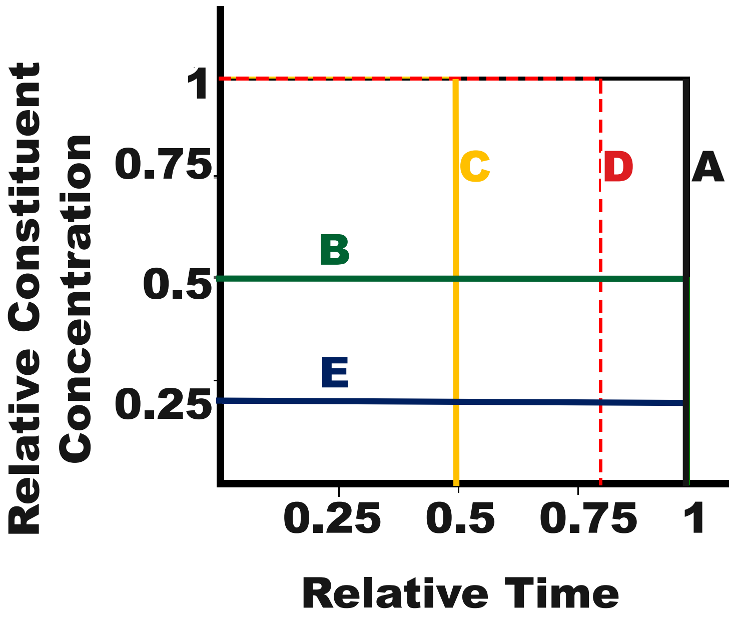
KEY POINT

- optimal use of active remediation requires fundamental knowledge of:
  - baseline (NA rates)
  - remedial objectives (bulk vs. COPCs)

Technology Selection vs. Remedial Objectives



from ITRC, 2009

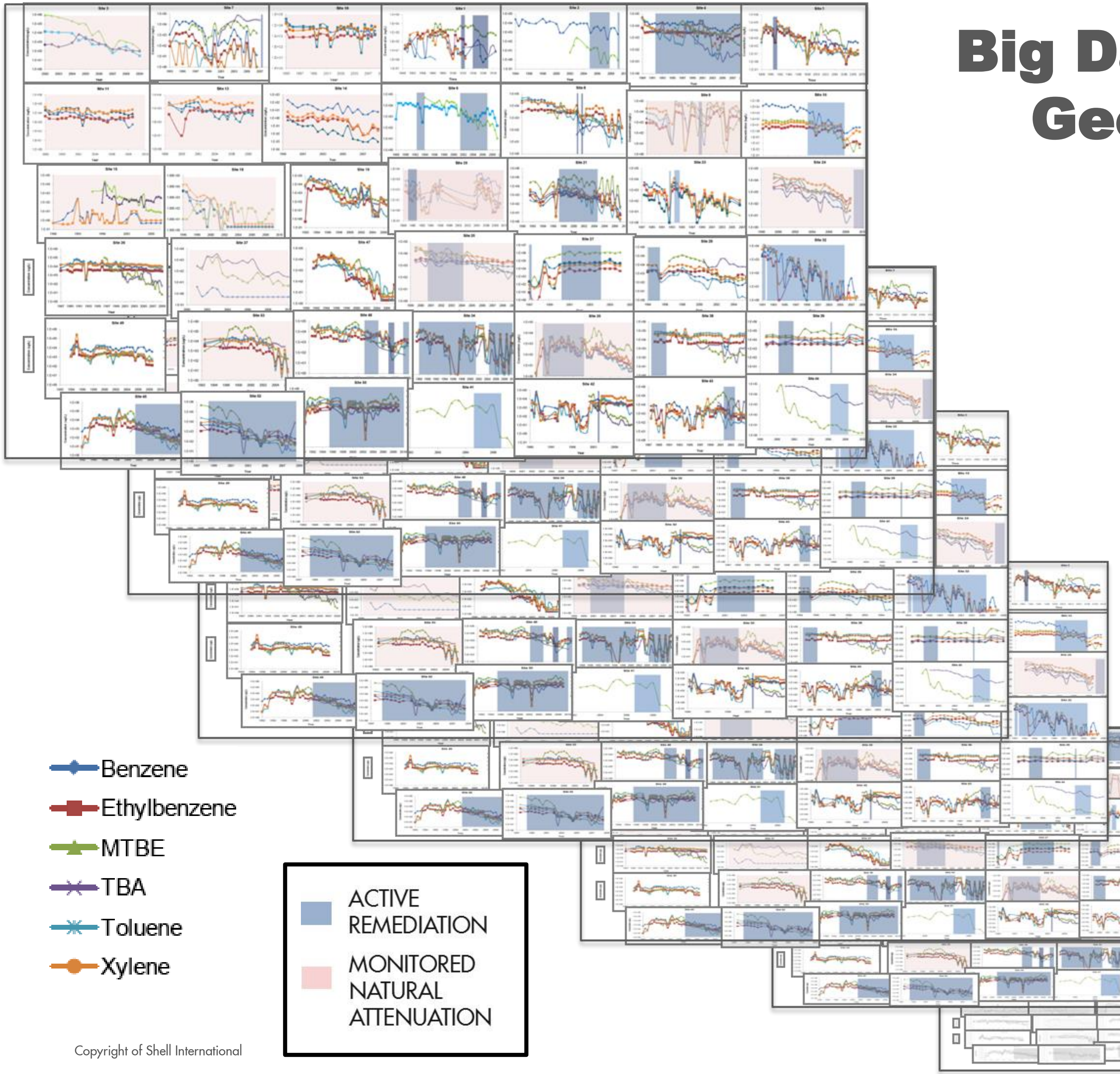


KEY POINT

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

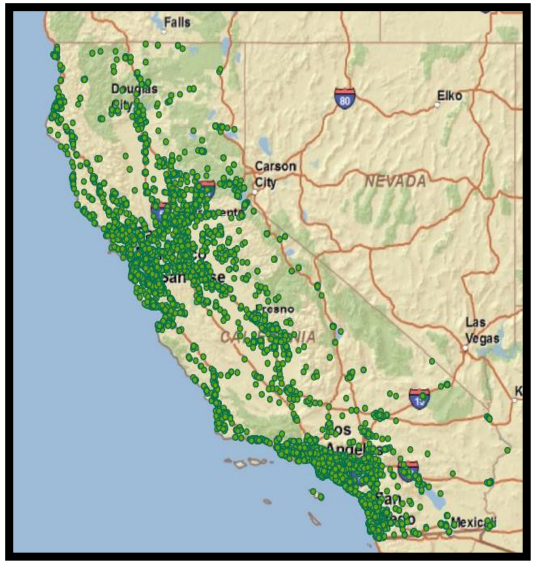
ASSUMPTIONS:

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



Big Data – Geotracker (California)

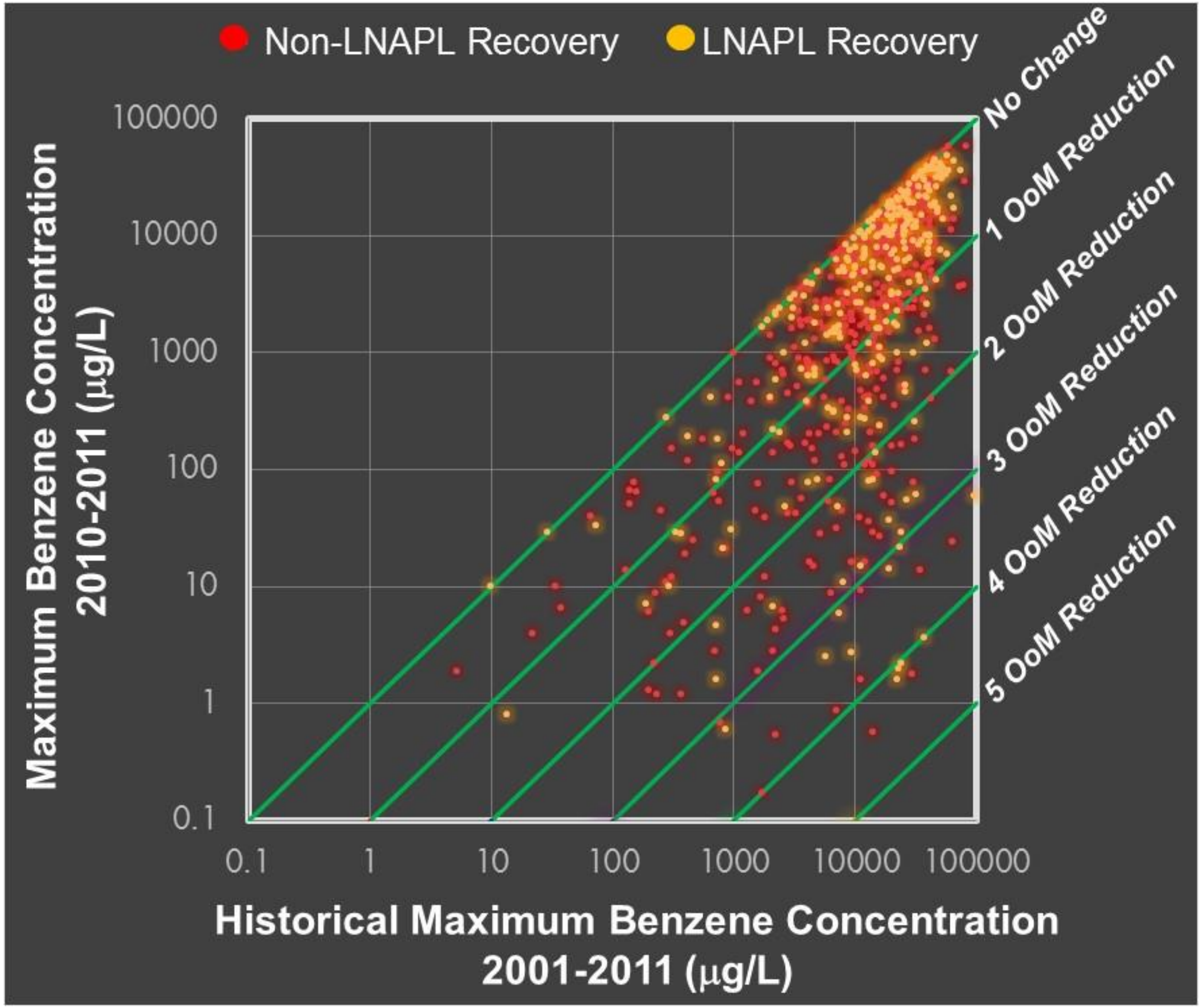
From McHugh et al., 2013



KEY POINT

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

Effect of LNAPL Recovery on Groundwater Concentration

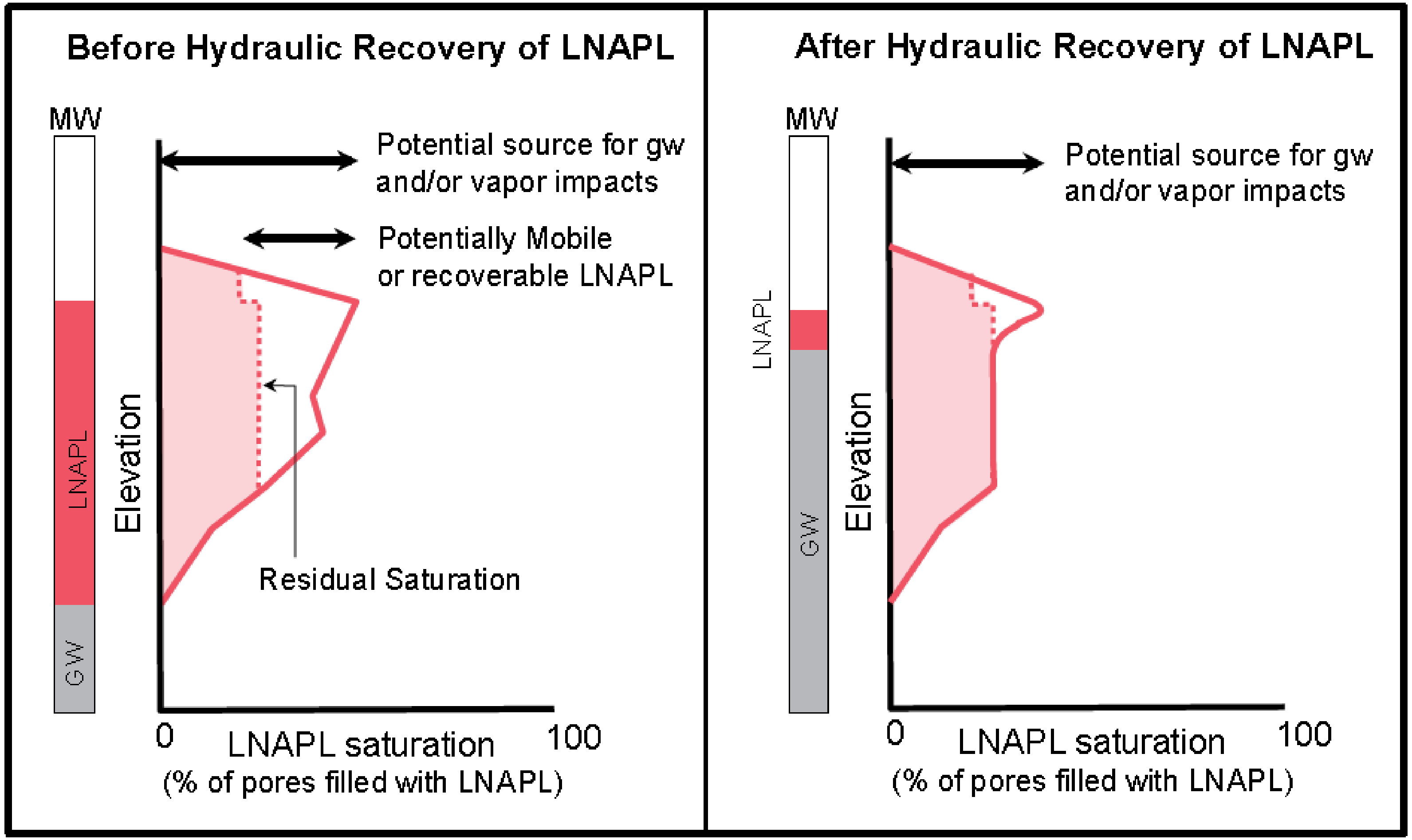


Source: Kulkarni et al., 2015

KEY POINT

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

Effects of Hydraulic Recovery on LNAPL Source Mass

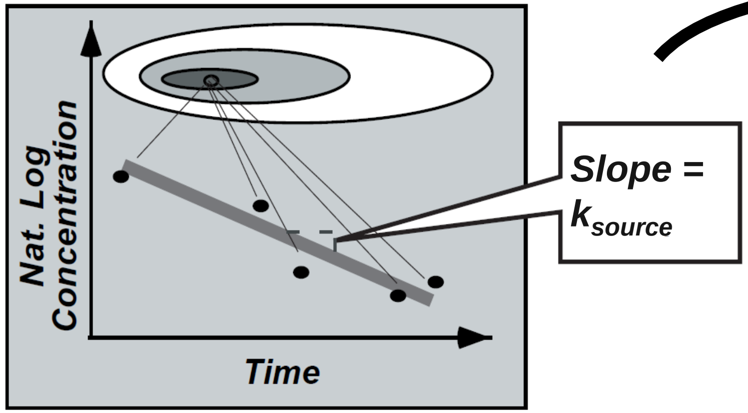


From Garg, 2010

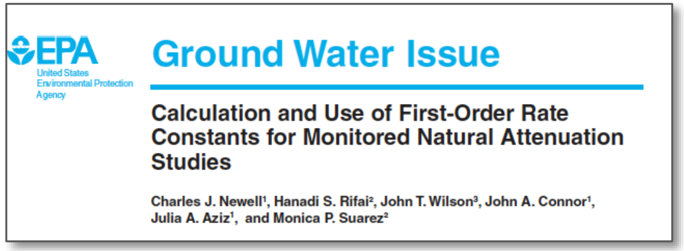
KEY POINT

- **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



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


EPA United States Environmental Protection Agency

Ground Water Issue

Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies

Charles J. Newell[1], Hanadi S. Rifai[2], John T. Wilson[3], John A. Connor[1], Julia A. Aziz[1], and Monica P. Suarez[2]

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

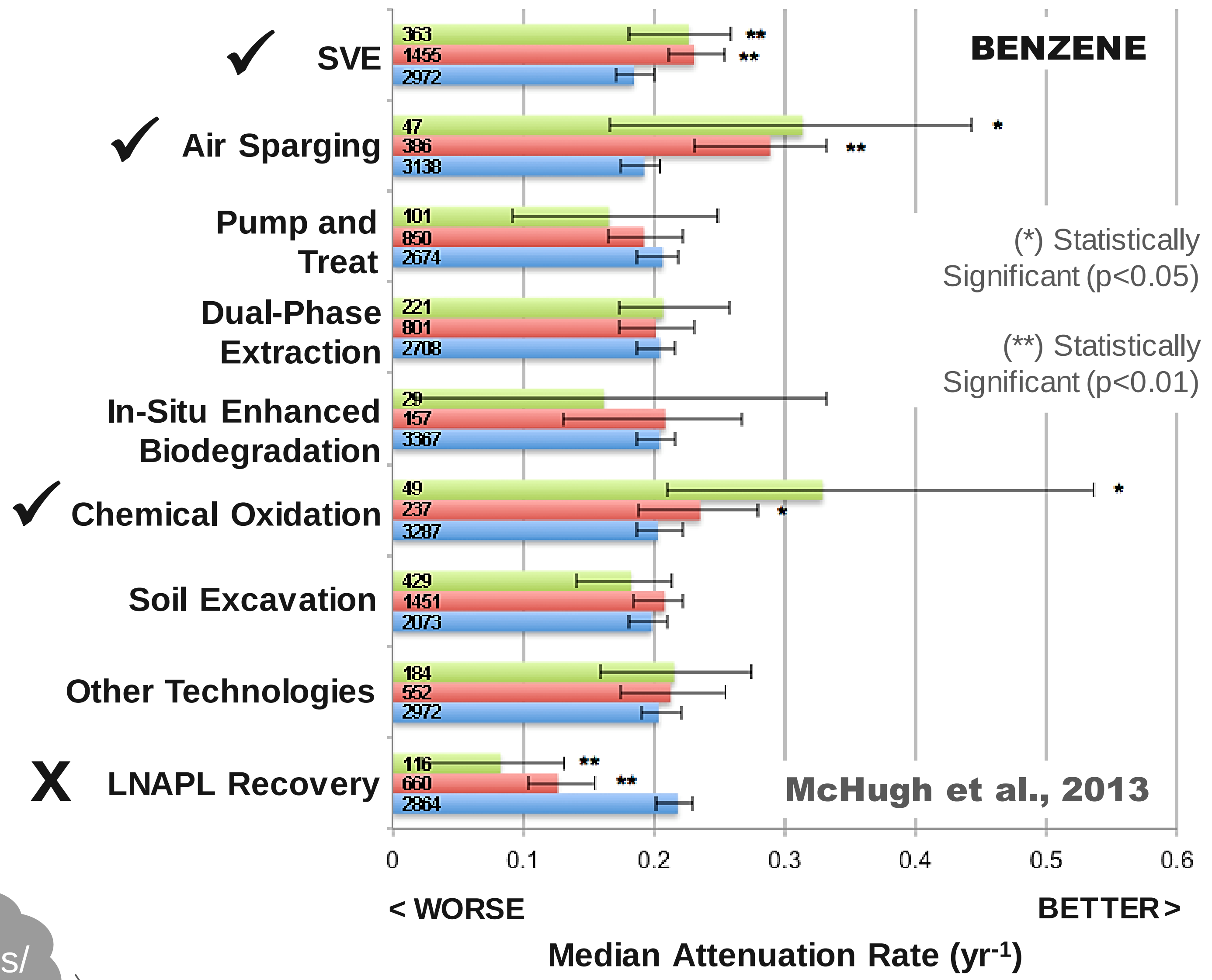
KEY POINT

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

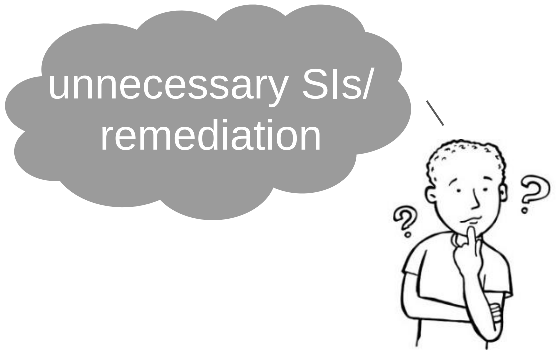
Effect of Remediation Technology on Source Attenuation Rate (Benzene)

KEY POINT

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



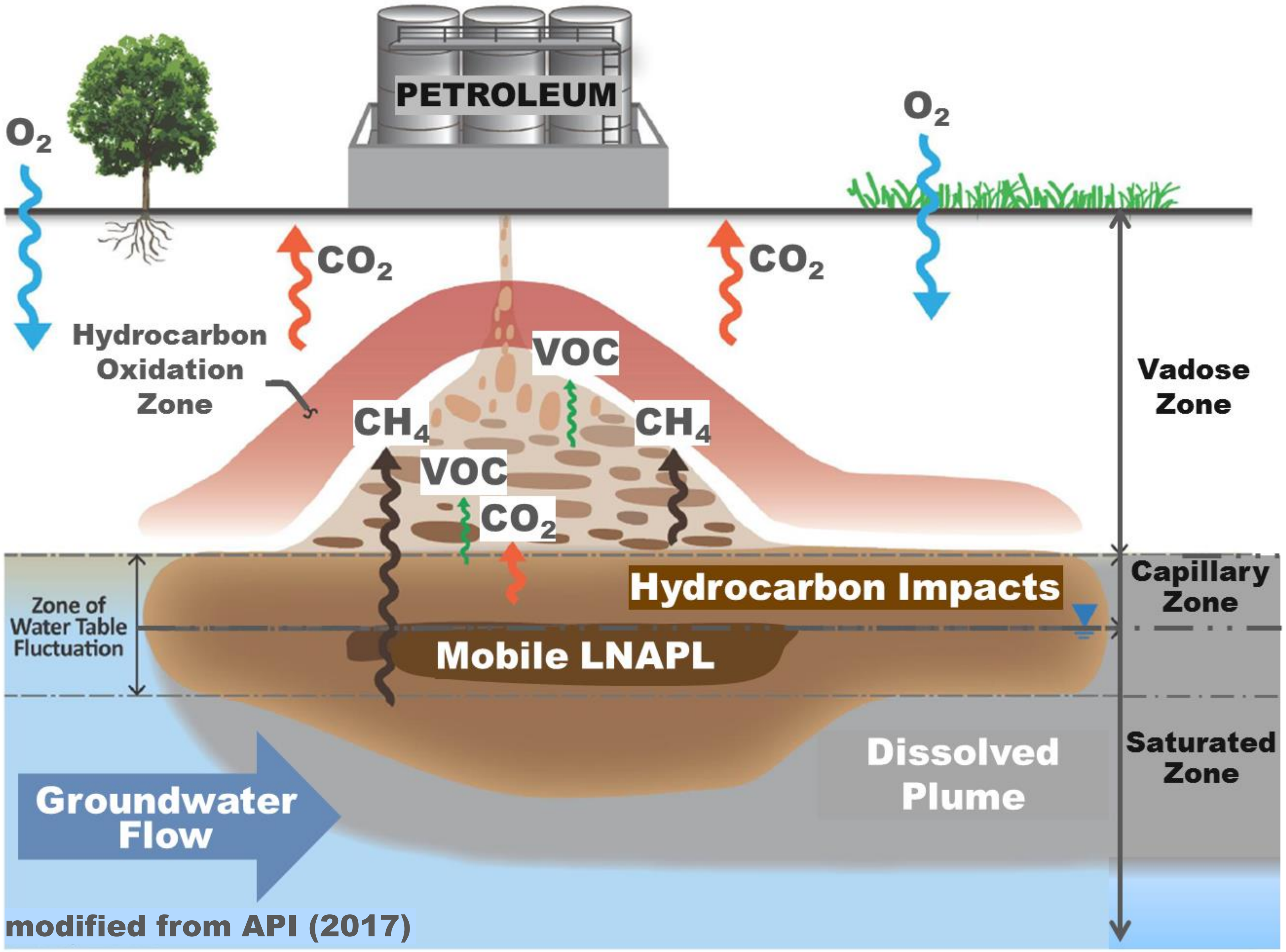
LEGEND



Efforts to Address the Challenge

NSZD

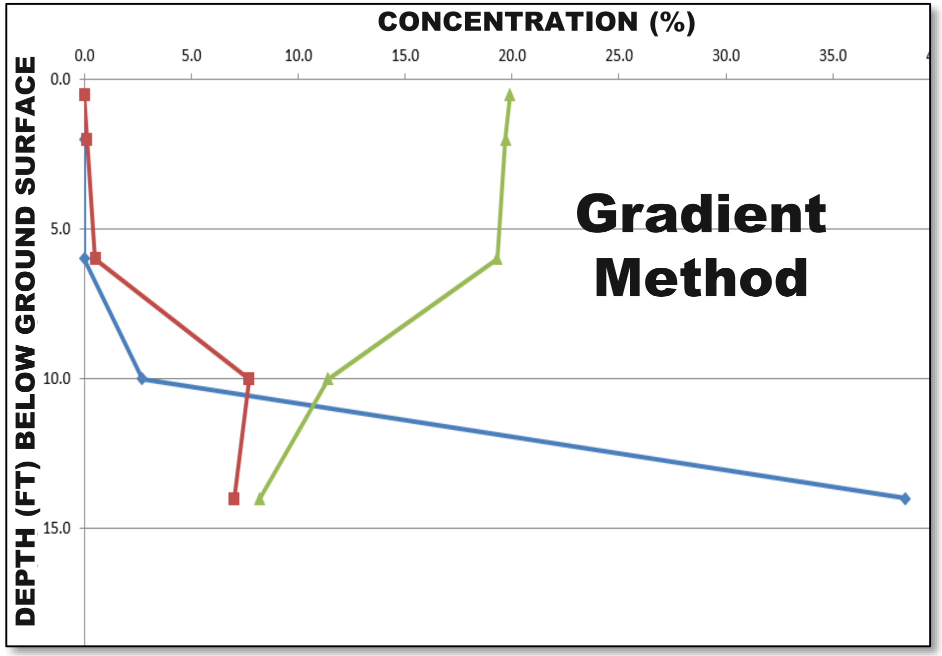
NSZD – Conceptual Model

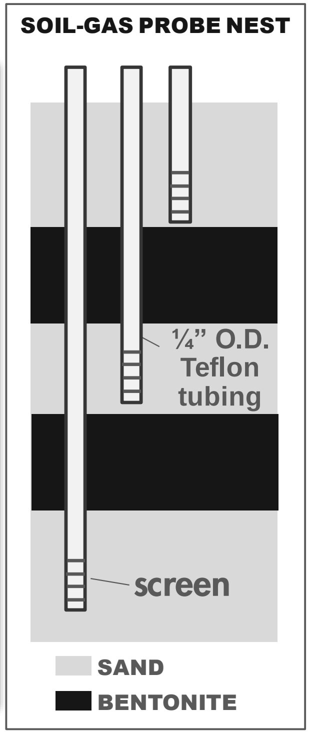


- NSZD is critical hydrocarbon mass-loss pathway:
  - 70% of hydrocarbon can directly outgas to vadose zone (Ng et. al., 2015)
  - rates consistent w/ some engineered remediation (700 – 4,000 gal/acre-yr: Garg et al., 2017)
- NSZD method/tools well established (ITRC, 2009)
- primary applications (to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

Various NSZD Measurement Techniques

Thermal NSZD





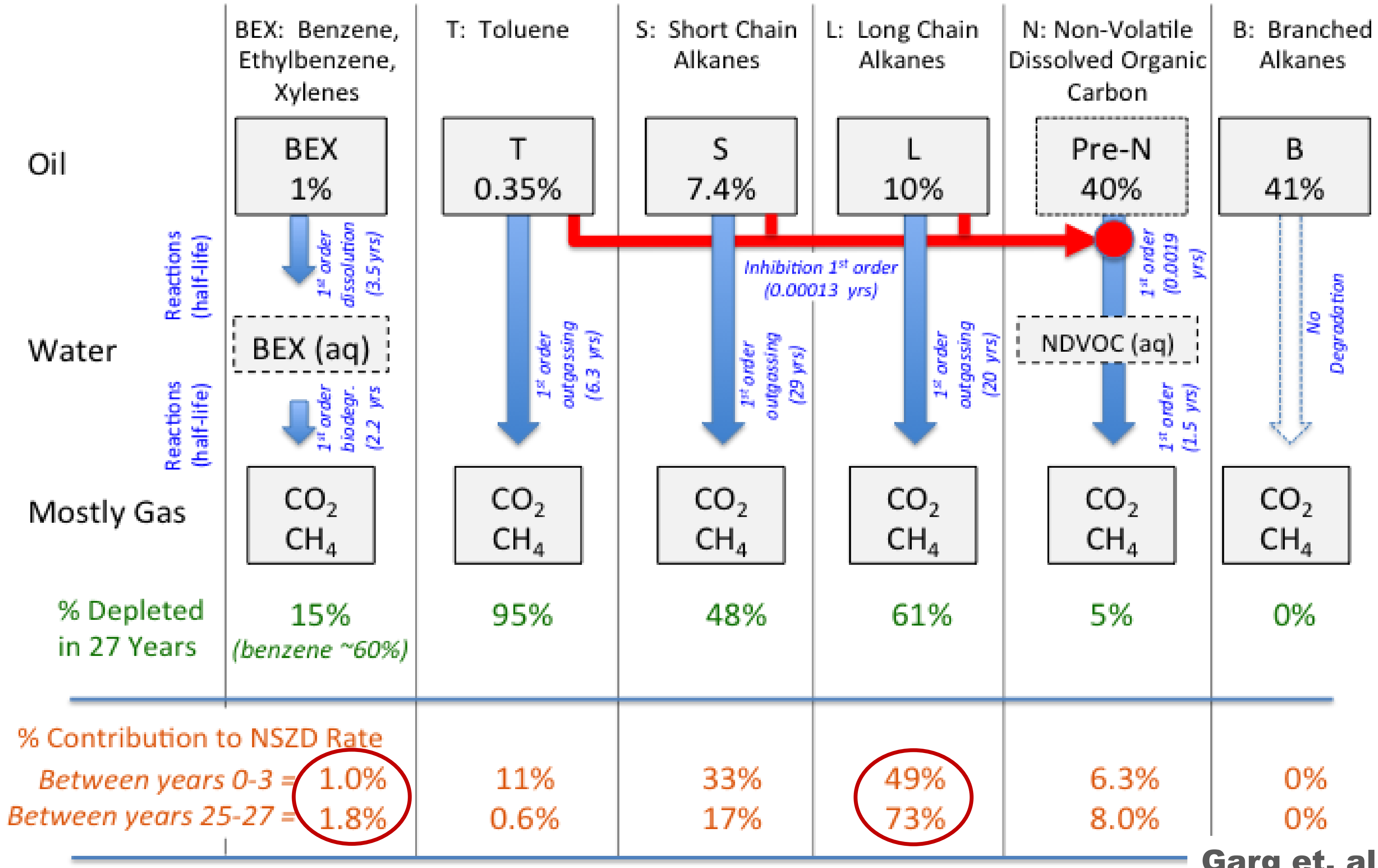
CO_2 Trap

Dynamic Closed Chamber

KEY POINT

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

NSZD Rate vs. Composition



Garg et. al 2018

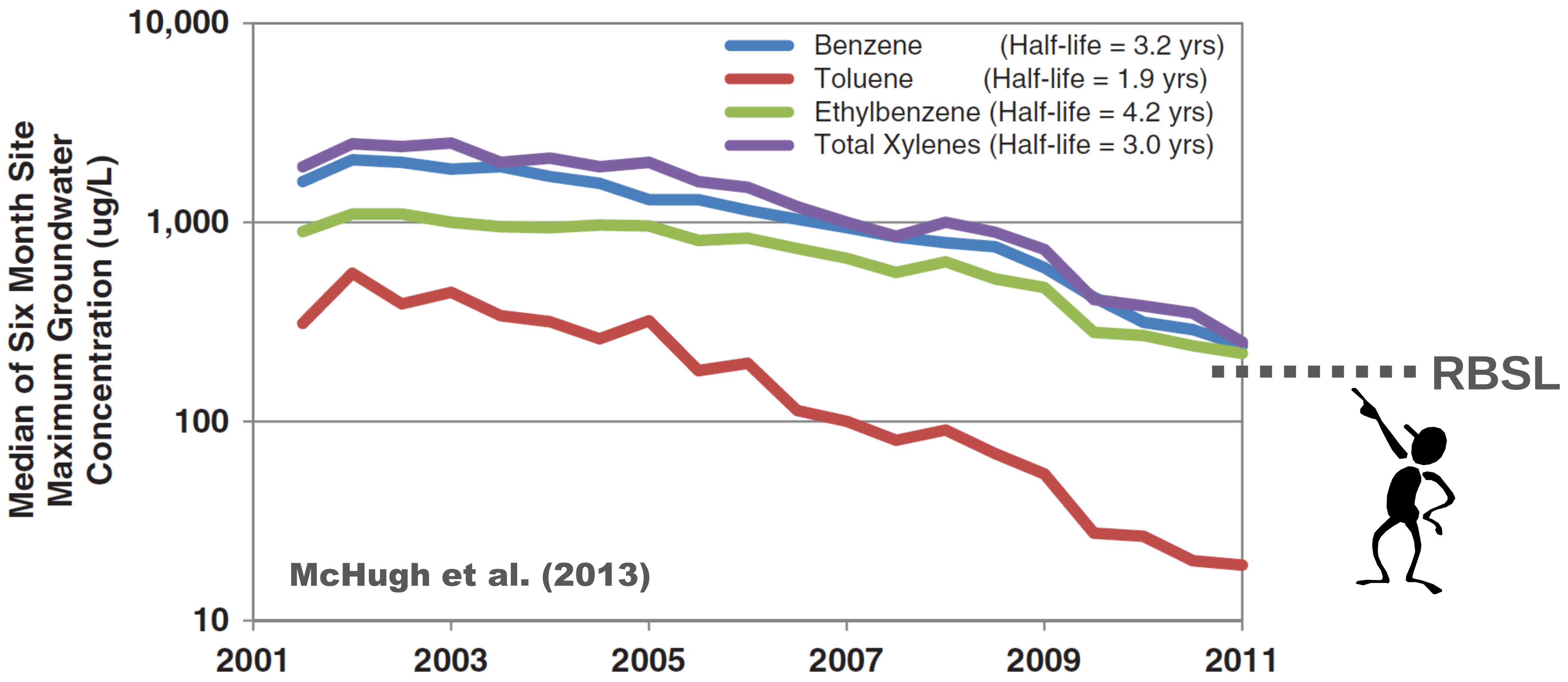
KEY POINT

- 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

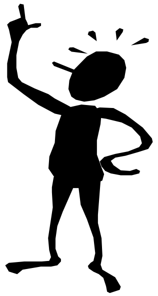
- soil-gas method & application dates back to mid-late 80s (USGS)
  - ✓ bulk hydrocarbon (TPH, CO_2, O_2)
  - ✓ specific hydrocarbons (BTEX, cyclohexane)
  - ✓ carbon ranges ($C_6 – C_9$ aliphatics, $C_6 – C_9$ aromatics)

KEY POINT

- soil-gas method well documented

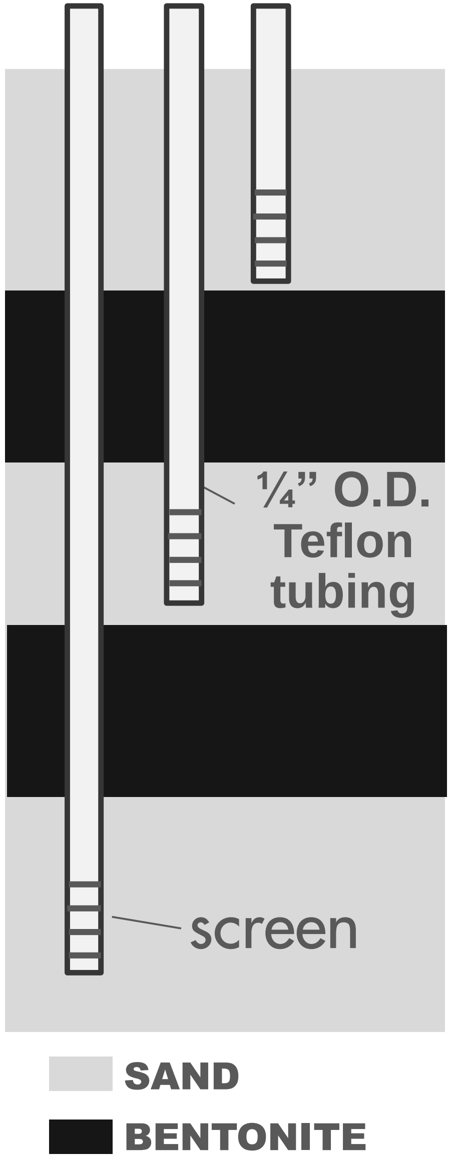
Objectives

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



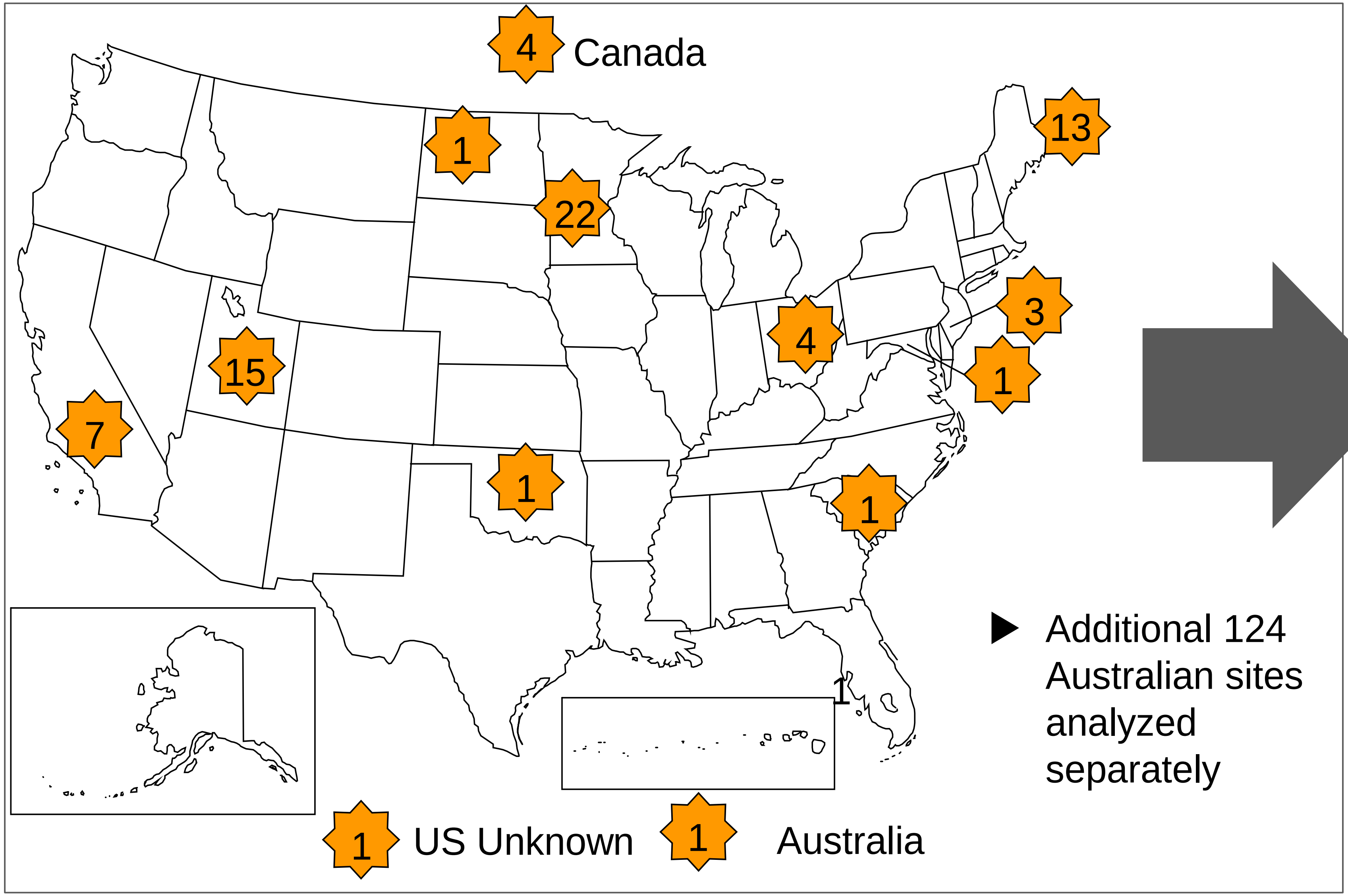
SOIL-GAS SAMPLING
(summa canister)

SOIL-GAS PROBE NEST



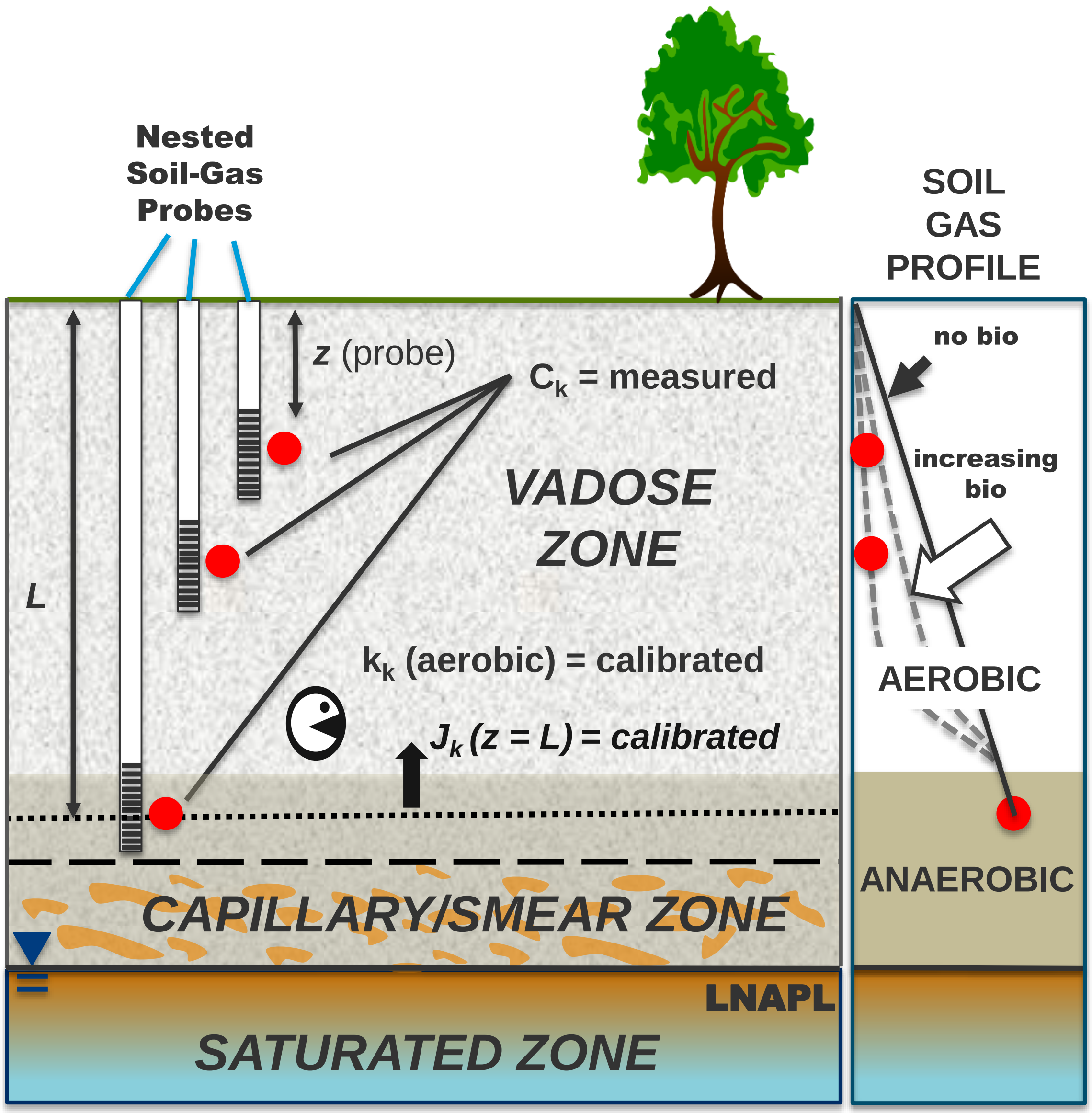
Empirical Soil-Gas Database

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



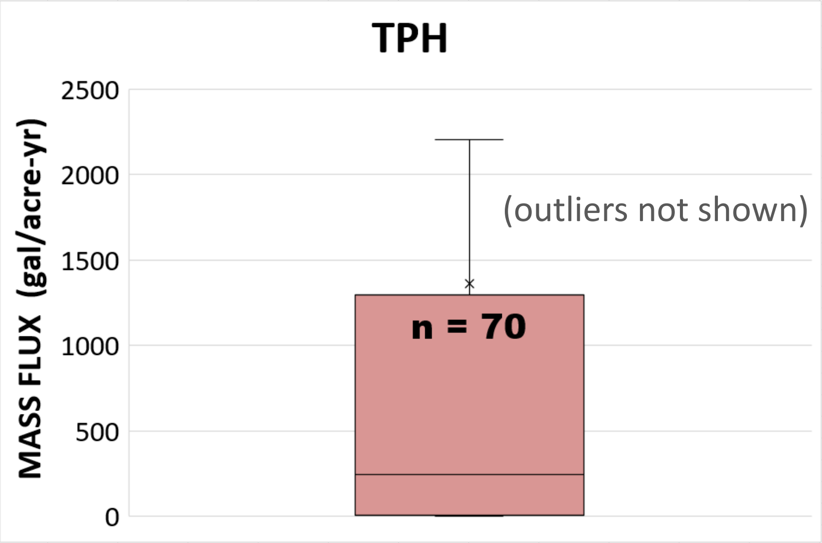
- TPH and benzene soil-gas data
- 82 samples; 35 sites; 55 probe locations
- SOILS
  - 28% sands
  - 51% loams/silts
  - 21% clays
- SURFACE COVER
  - 56% pavement
  - 29% open ground
  - 15% buildings

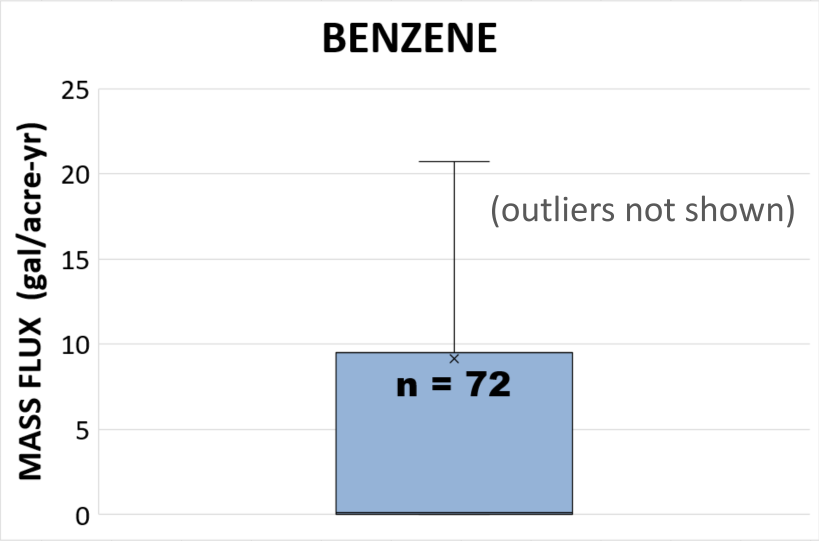
Soil-Gas Method

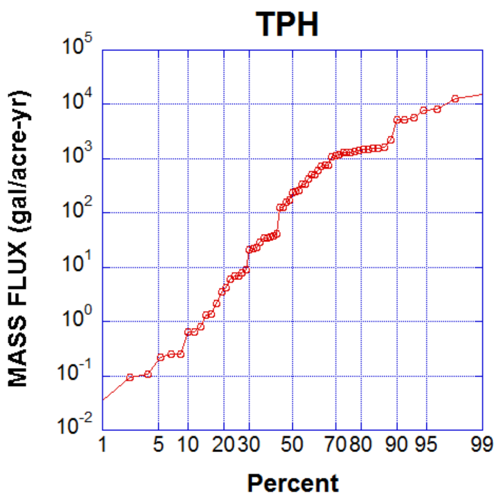


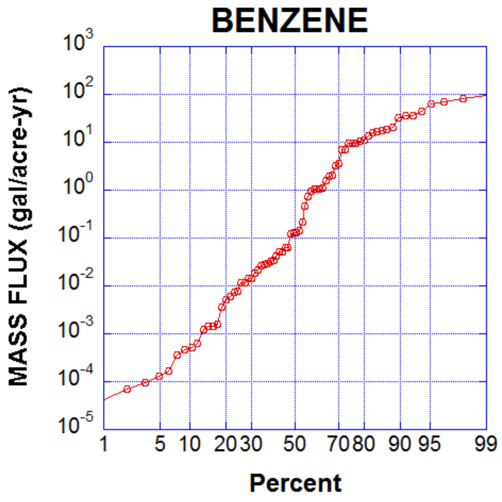
- mass transport (1-D vertical): BioVapor - ***http://www.api.org/***
  - simple (promote method uptake)
  - gas-phase diffusion dominated (Fick's Law)
  - 1st-order biodegradation kinetics (O_2 - limited)
  - TPH and benzene simulated
  - ND soil-gas concentrations = DL
  - best fit of predicted and 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*









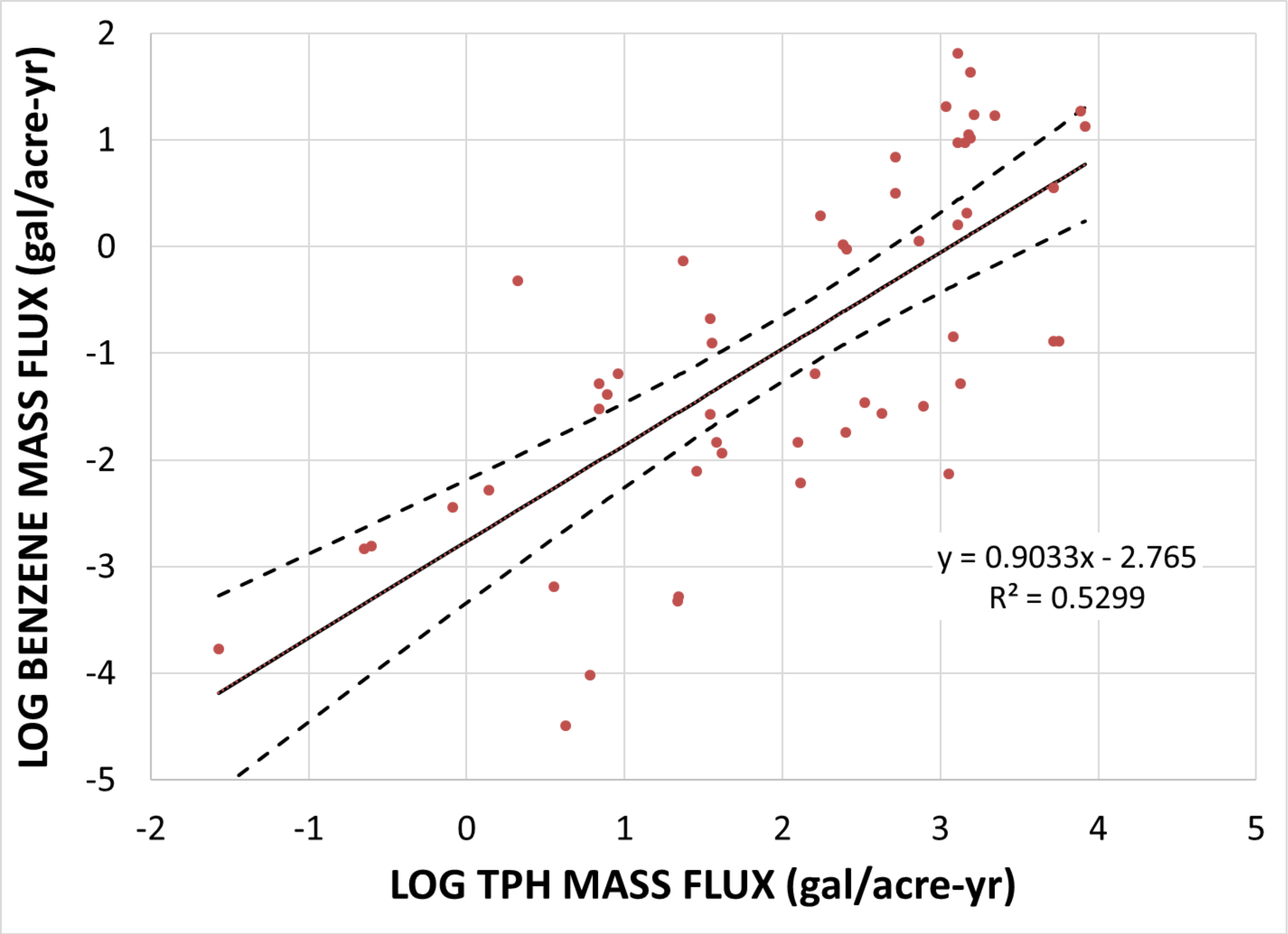
median rate: 240 gal/acre-yr
average rate: 1400 gal/acre-yr

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**

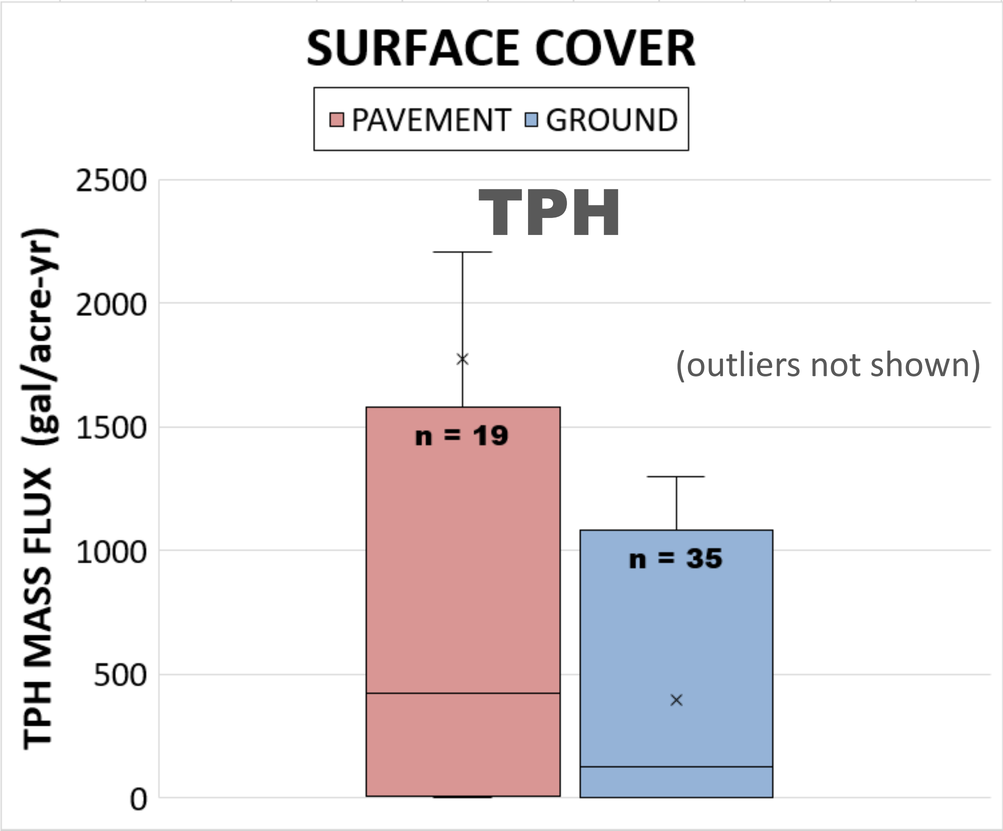
Natural Attenuation (NA) Rates: *Benzene vs. TPH*

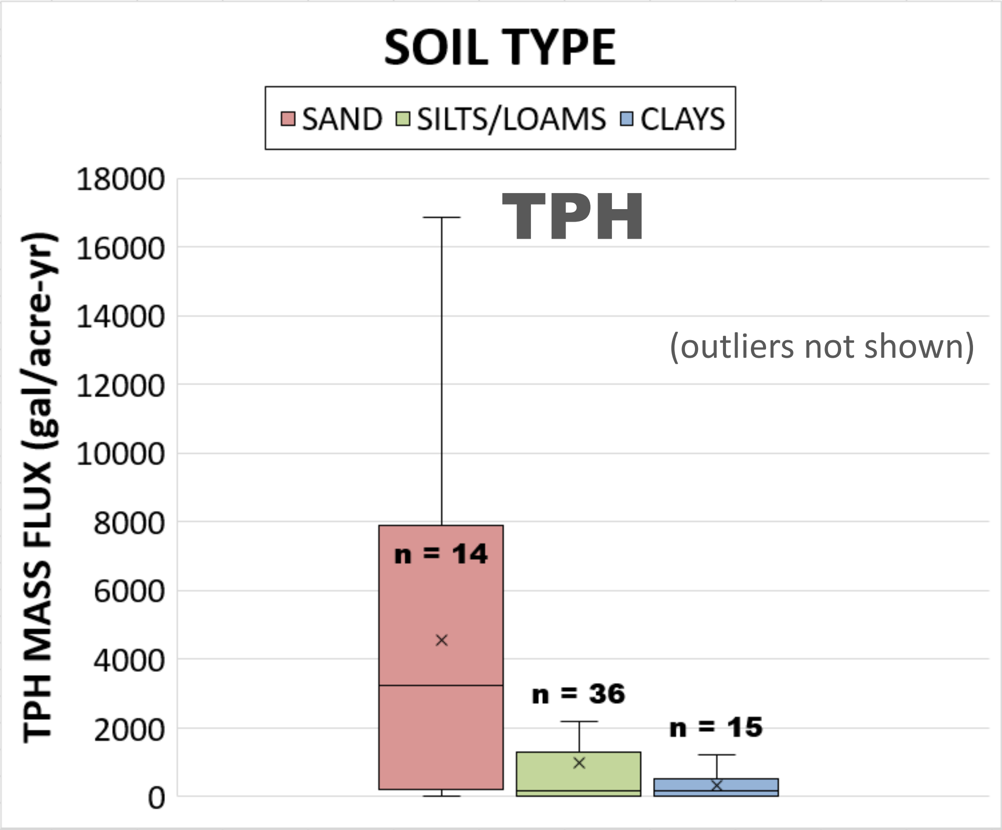


KEY POINT

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

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

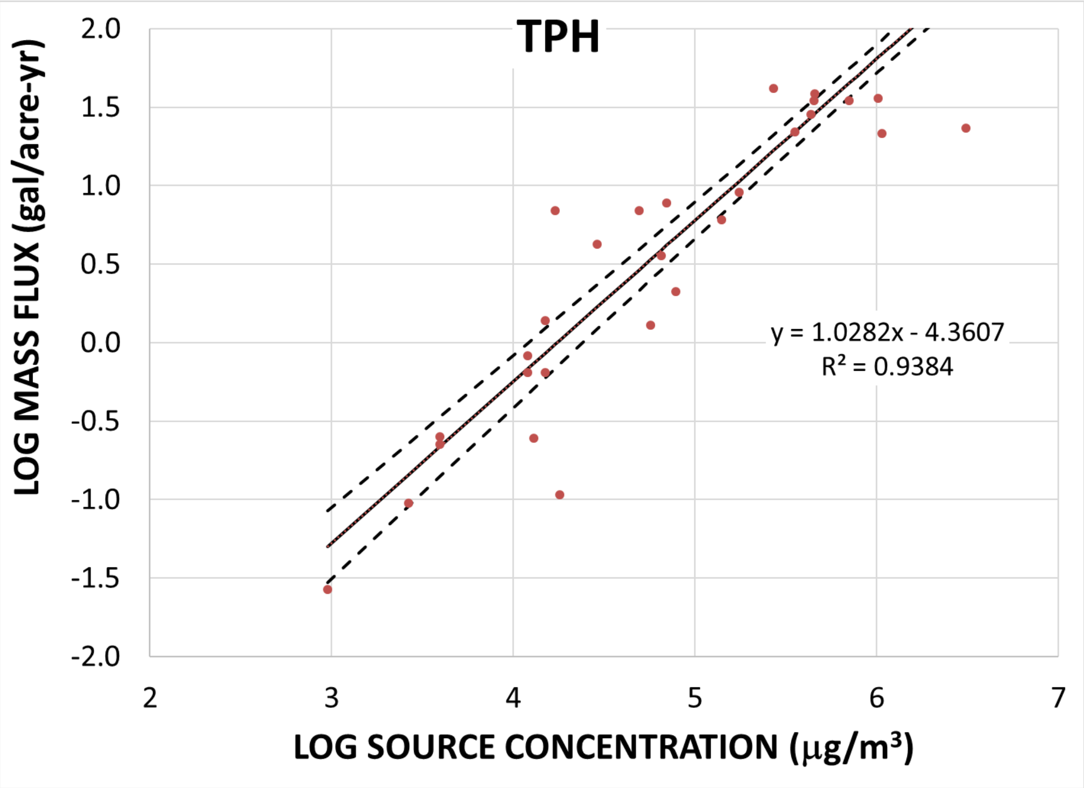


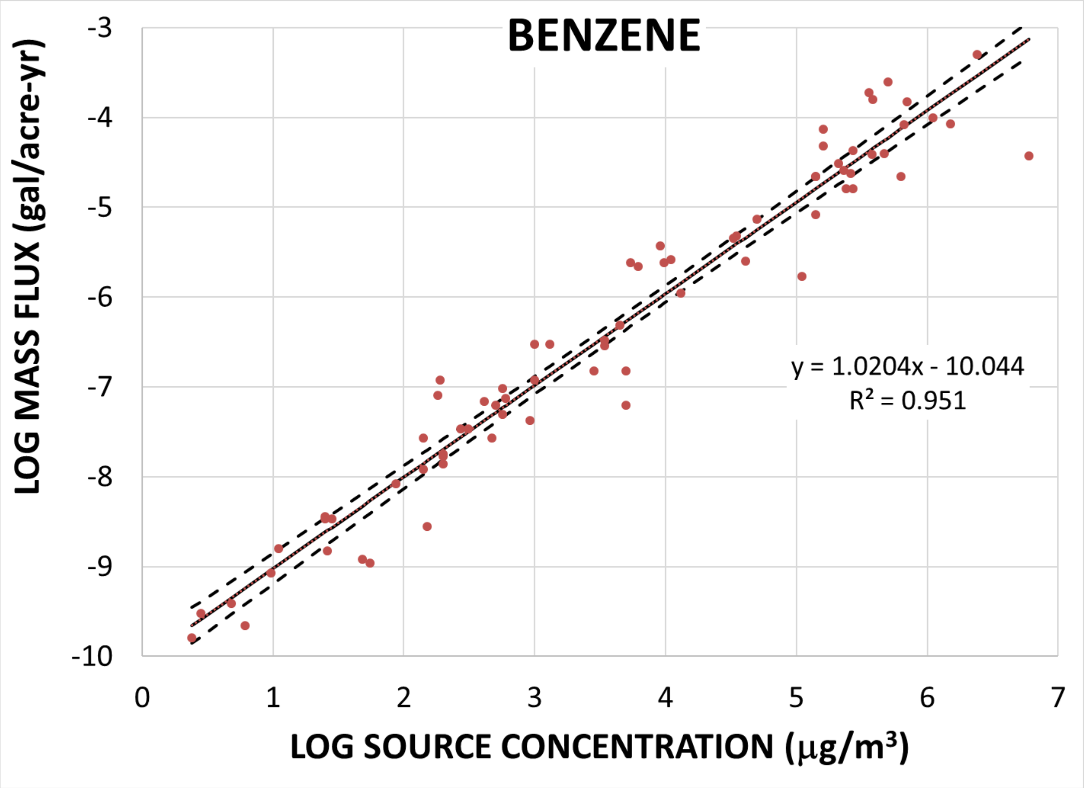


KEY POINT

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

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

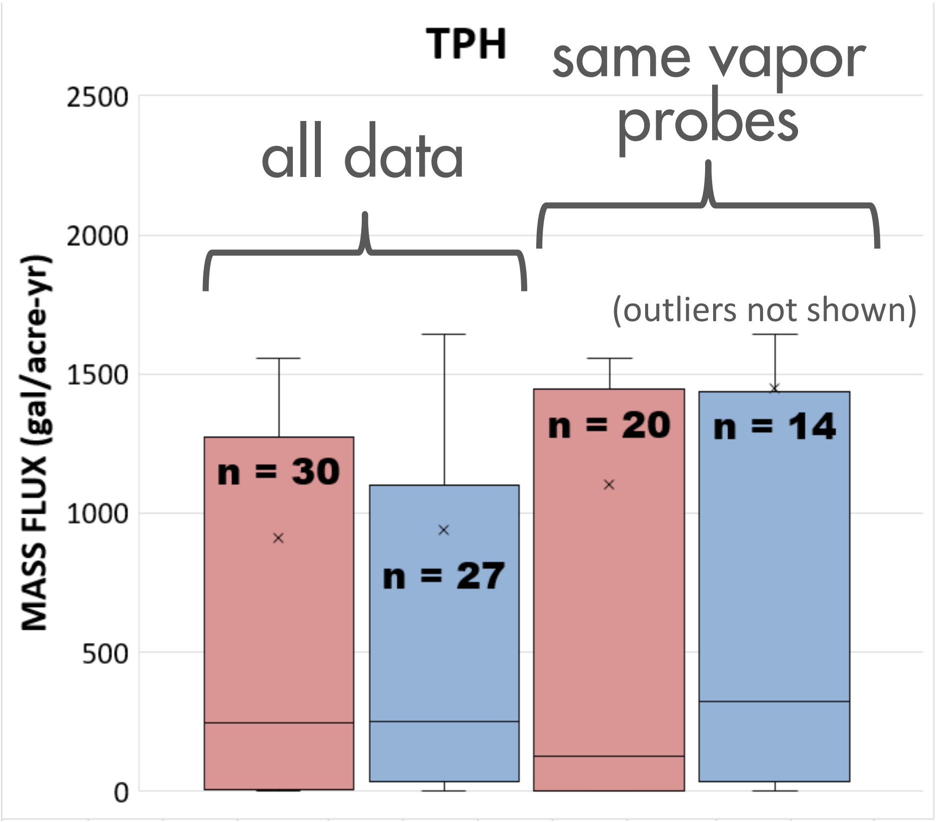


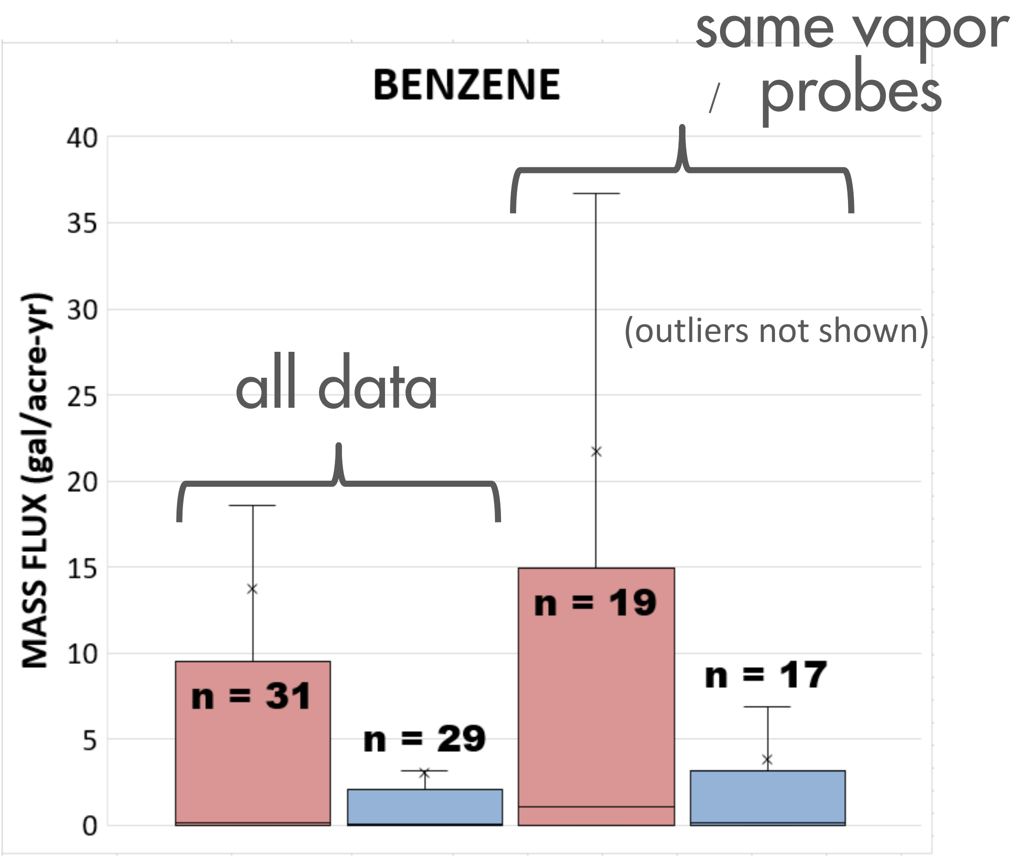


KEY POINT

- 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*



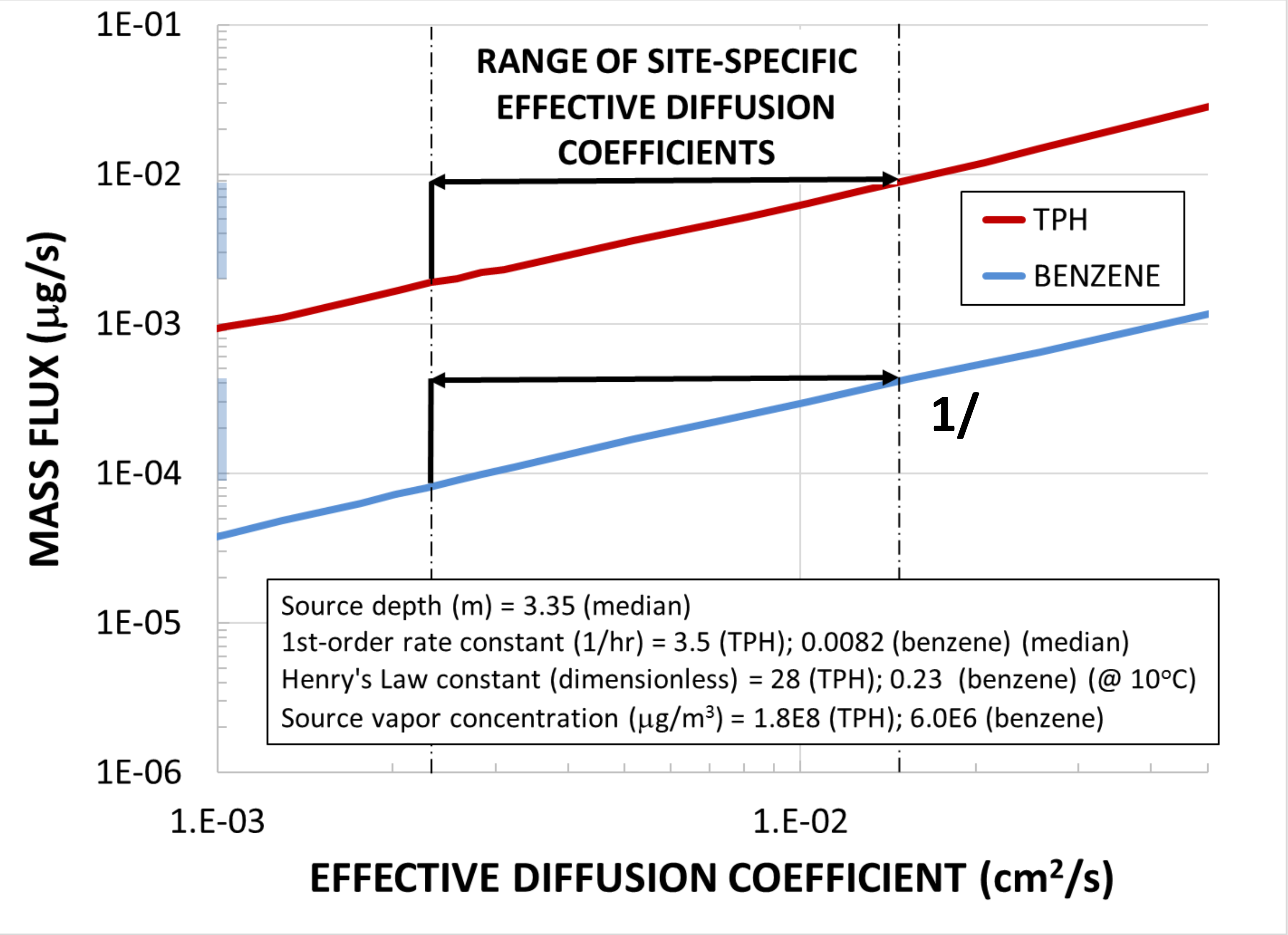


Summer (Apr – Sep) Winter (Oct – Mar)

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**

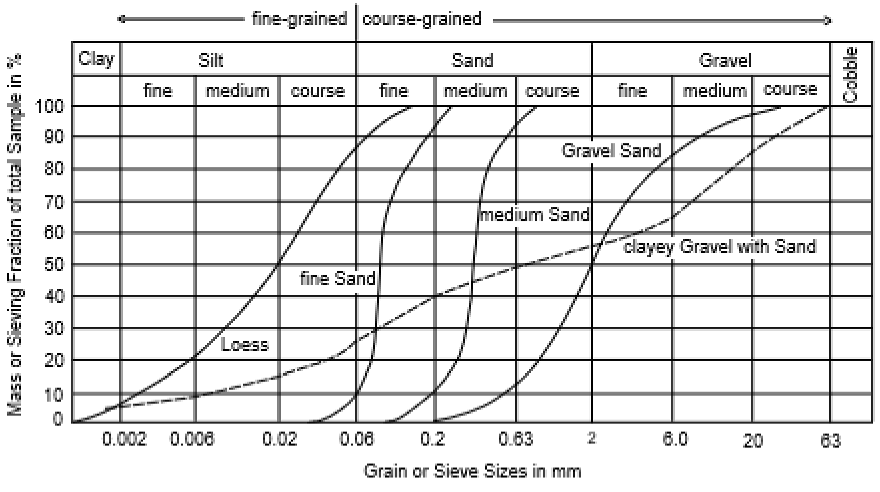
Opportunities to Improve NA Rate Estimates

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

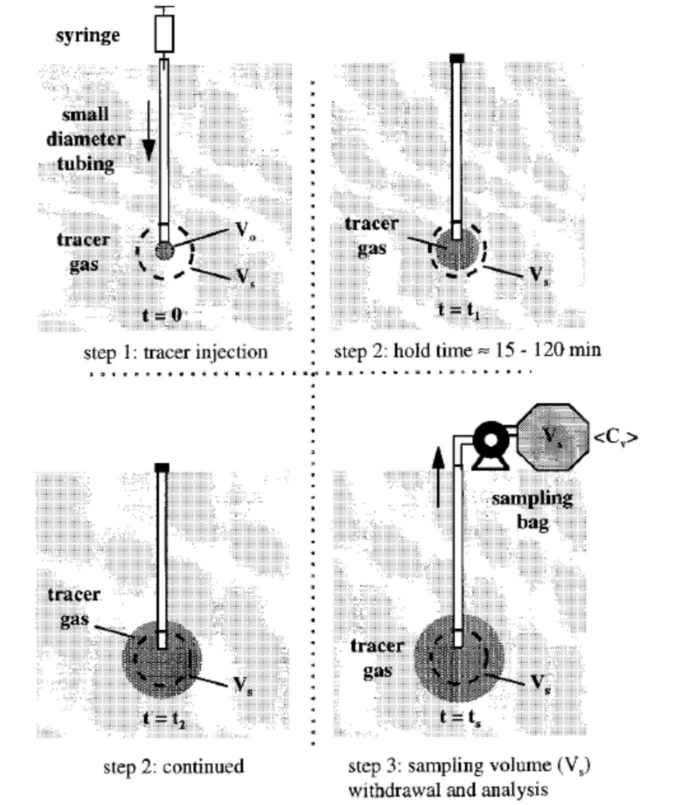
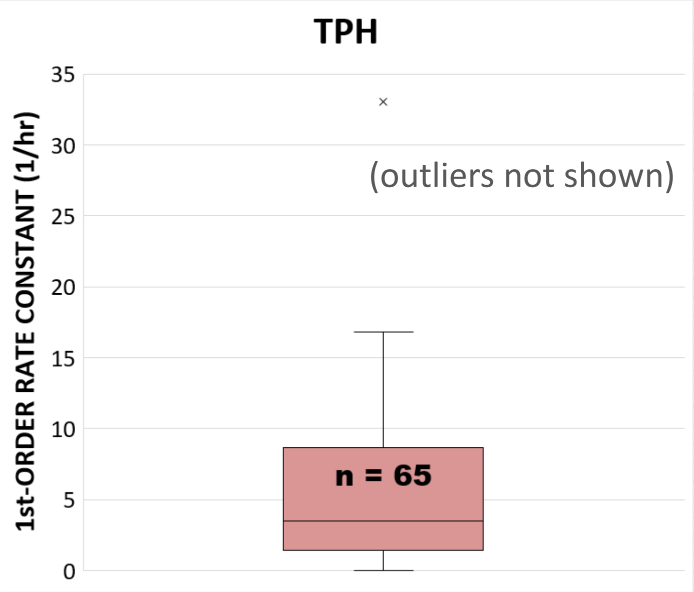


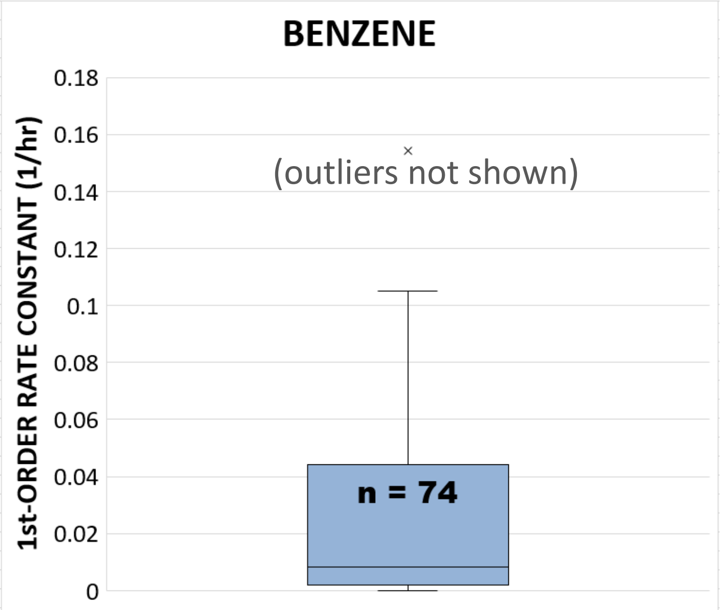
FIGURE 1. Generalized schematic of in situ measurement approach.

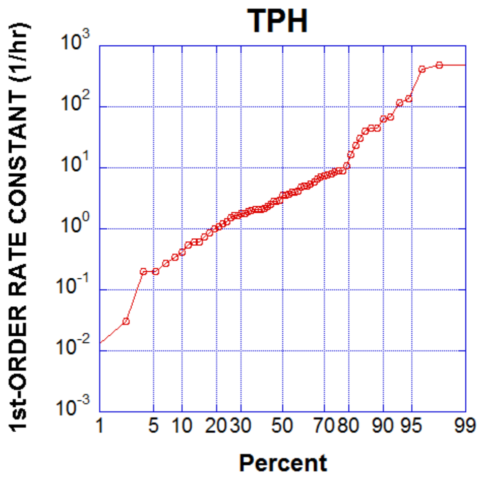
KEY POINT

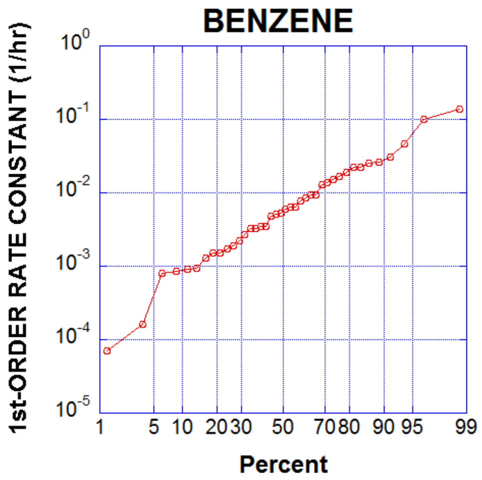
- data quality objectives need to be established upfront and will be site-specific

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









median rate: 3.5 1/hr

mean rate: 33 1/hr

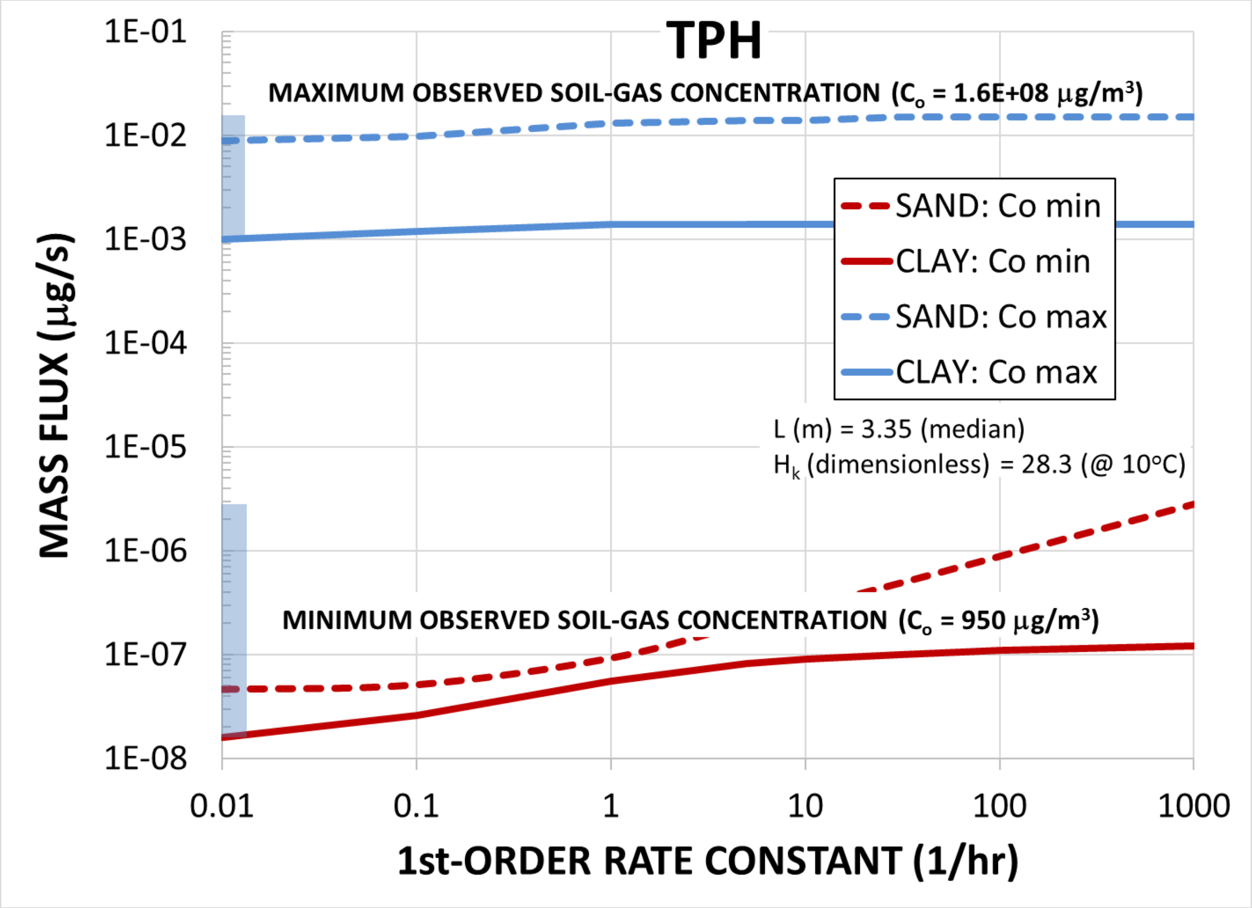
median rate: 0.0082 1/hr

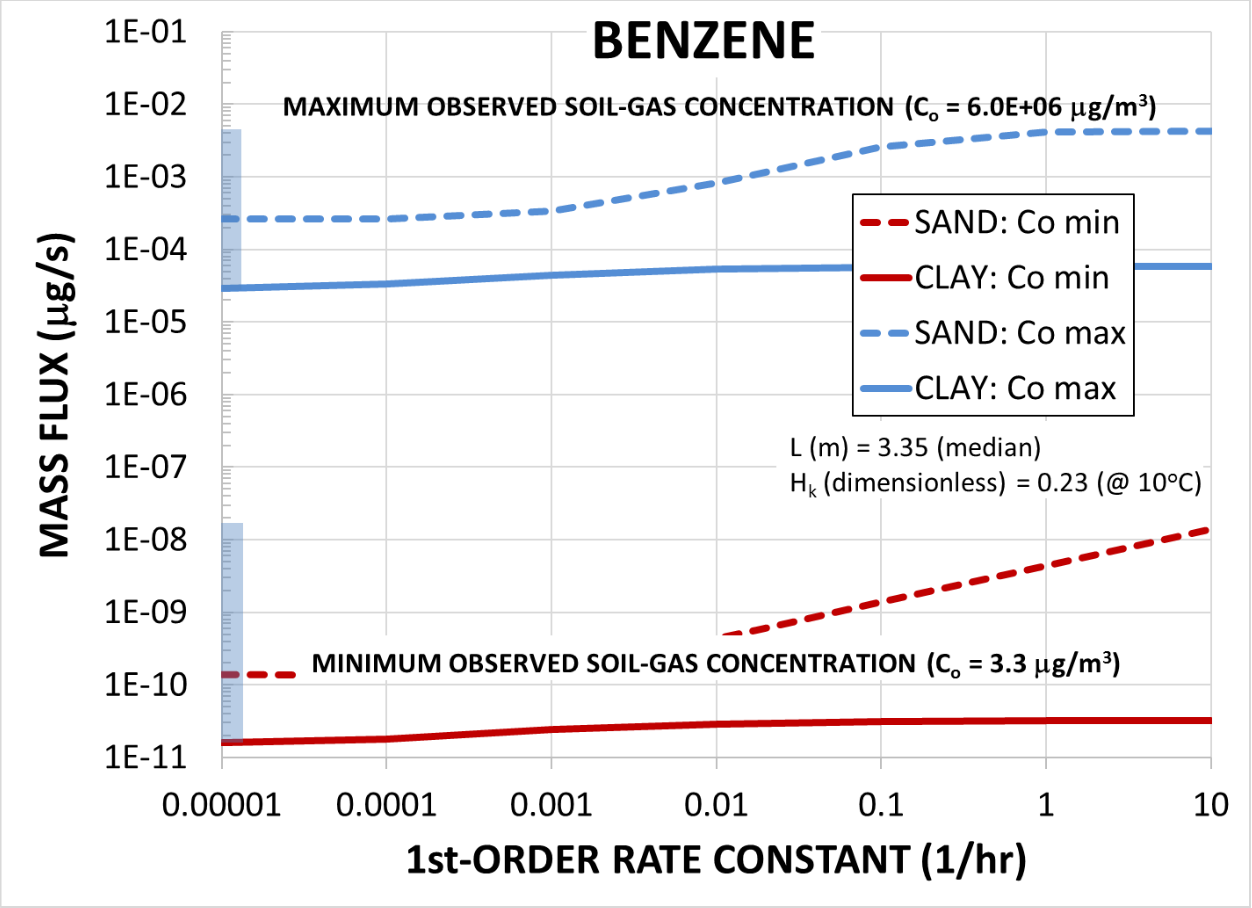
mean rate: 0.15 1/hr

KEY POINT

- **mean aerobic biodegradation rates for TPH and benzene are ~2 - 5x less than mean values reported from literature survey (DeVaull, 2007):**
  - **TPH = 71 1/hr**
  - **benzene = 0.79 1/hr**

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

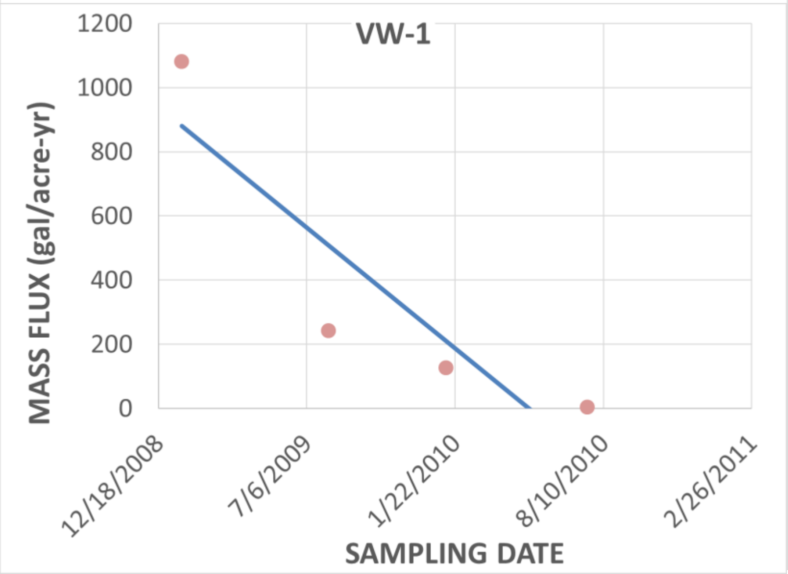


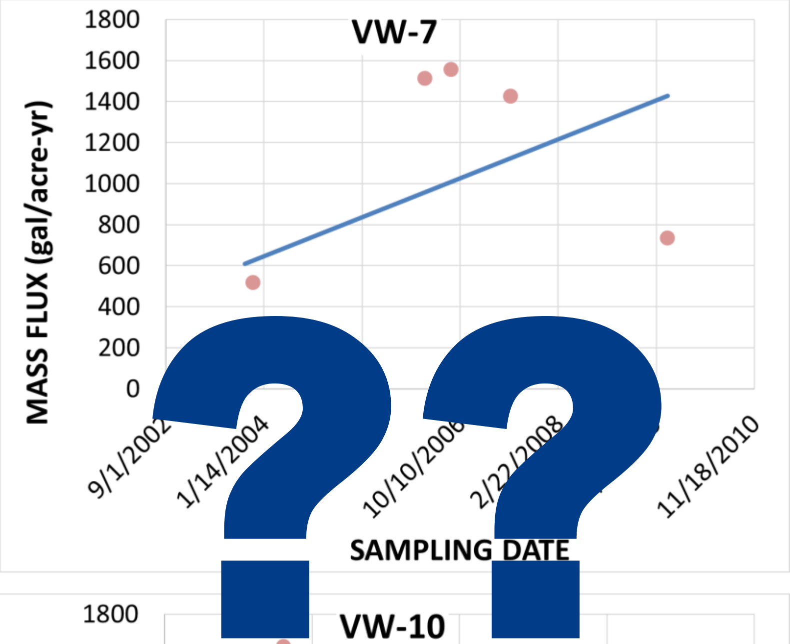


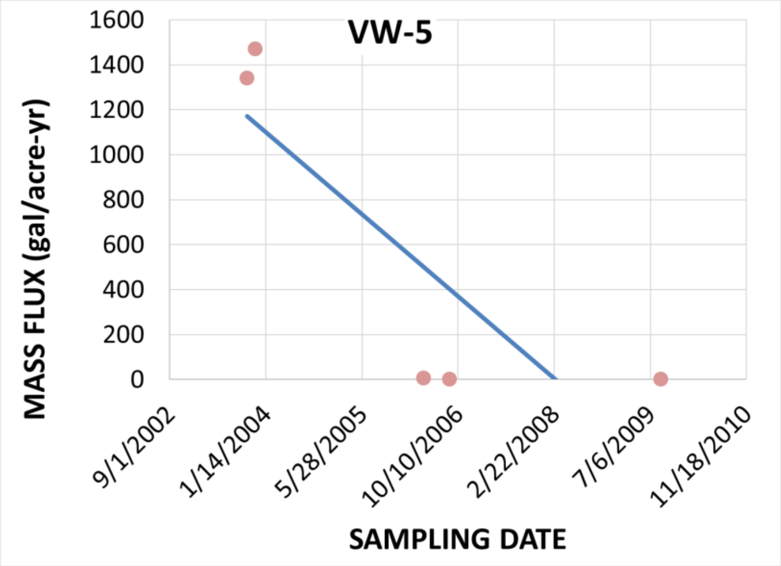
KEY POINT

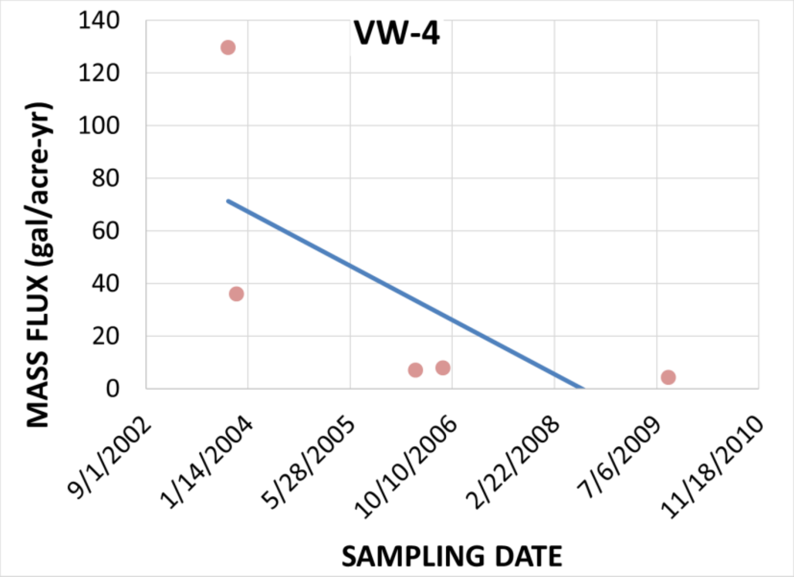
- the sensitivity of the NA rate varies depending on constituent (greater for benzene than TPH); increases for higher permeability soils (sands)
- NA rate are more sensitive to the aerobic biodegradation rate than soil type across range of calibrated values

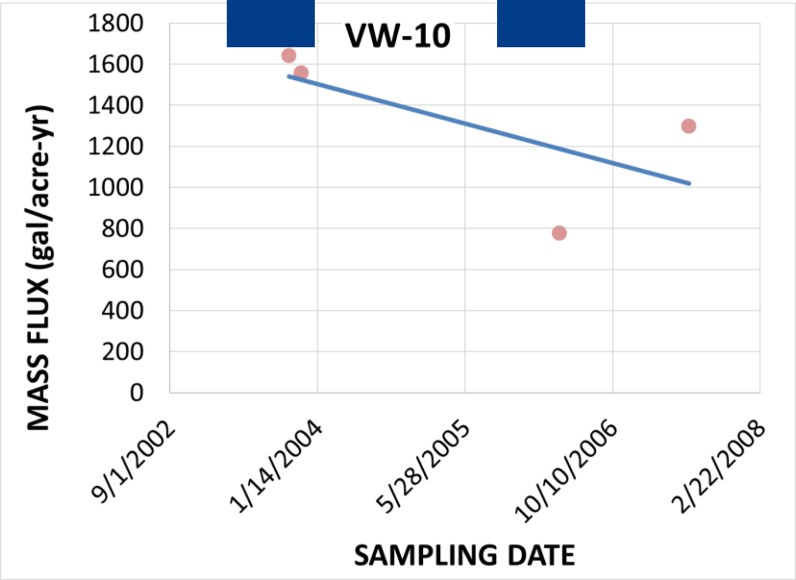
Temporal Trends in Natural Attenuation (NA) Rates









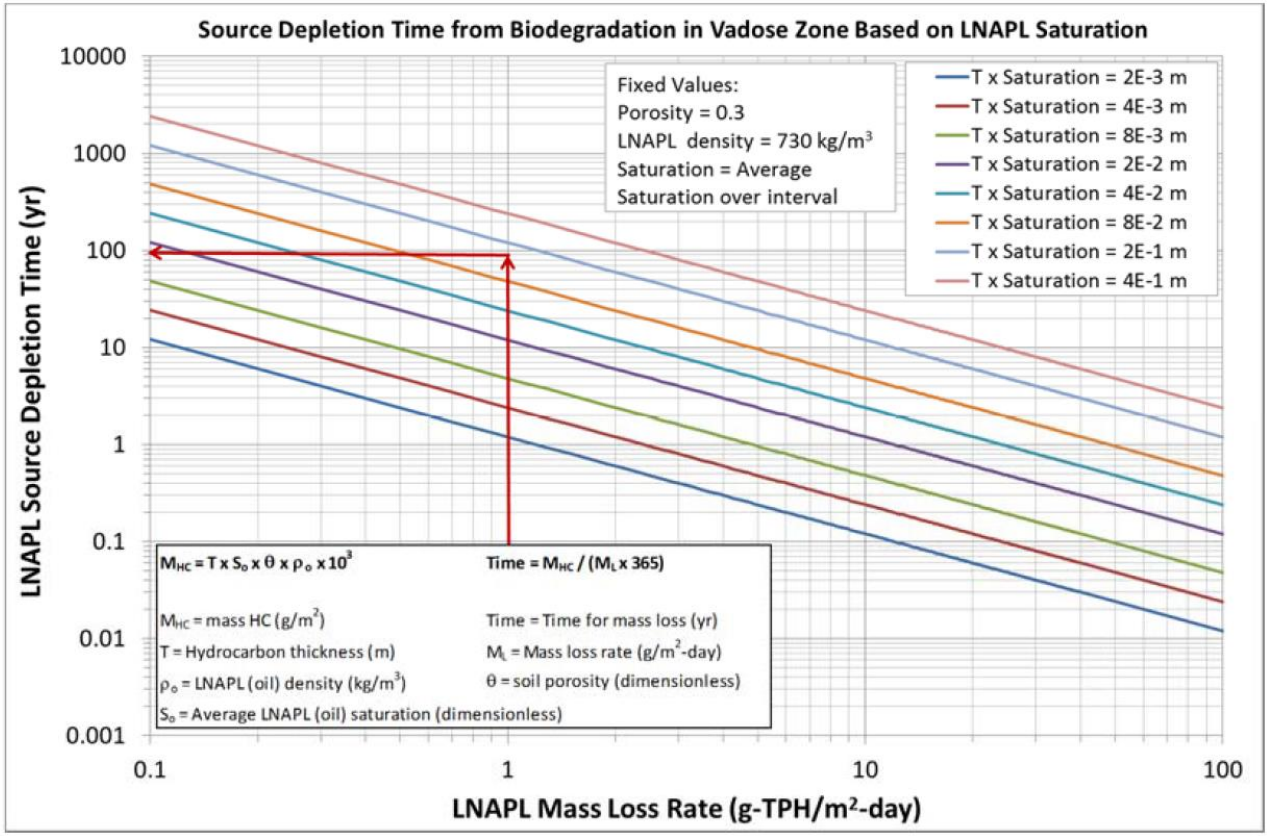


KEY POINT

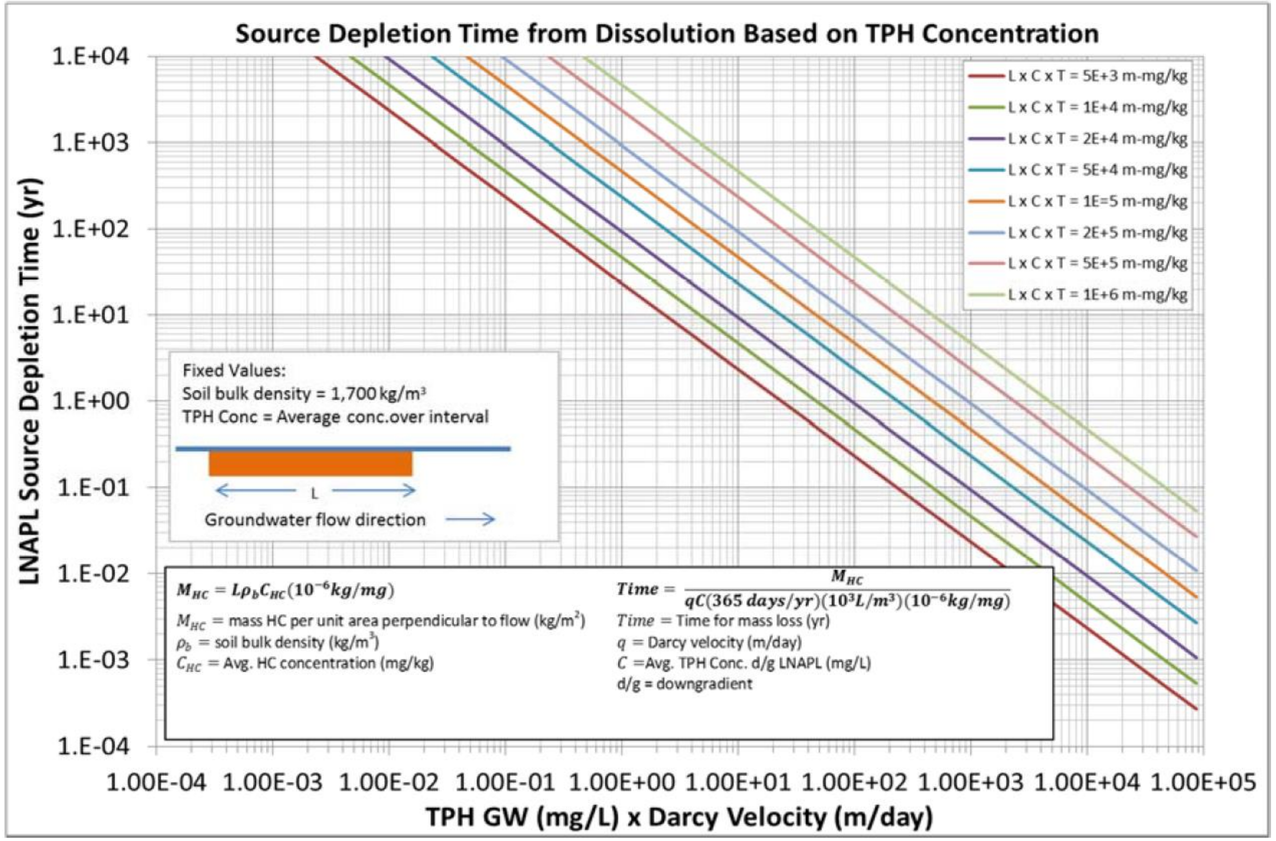
- NA rates in source areas will vary over time
- trends & source mass critical for predicting plume longevity
- more frequent data = improved remediation decision making

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

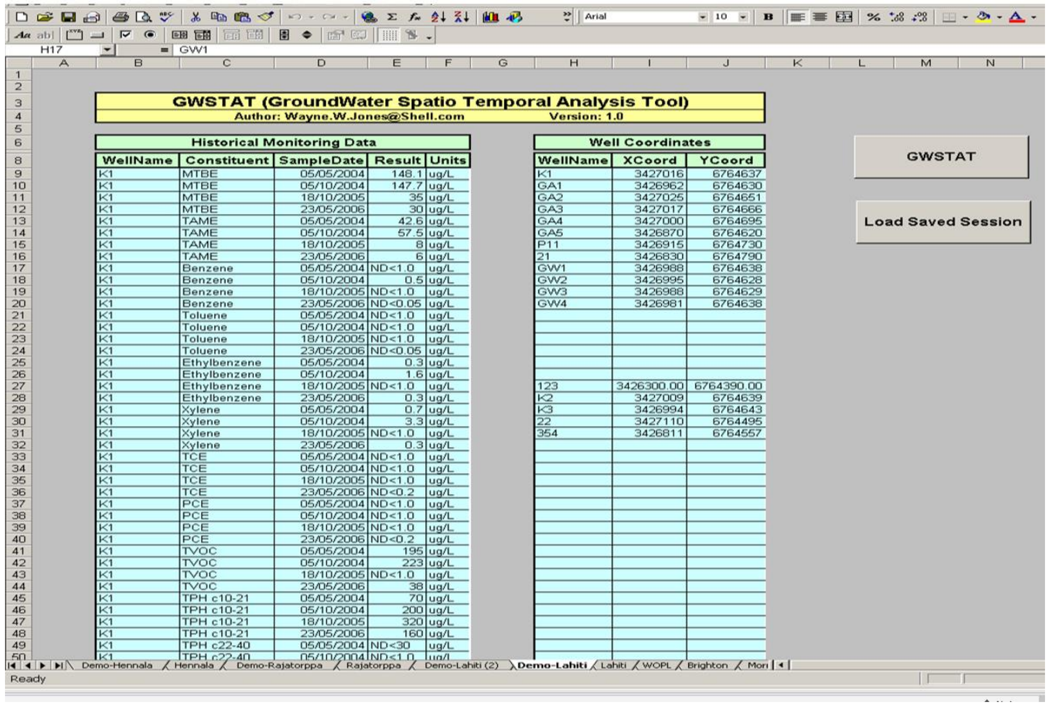
Efforts to Address the Challenge

GROUNDWATER COMPOSITION

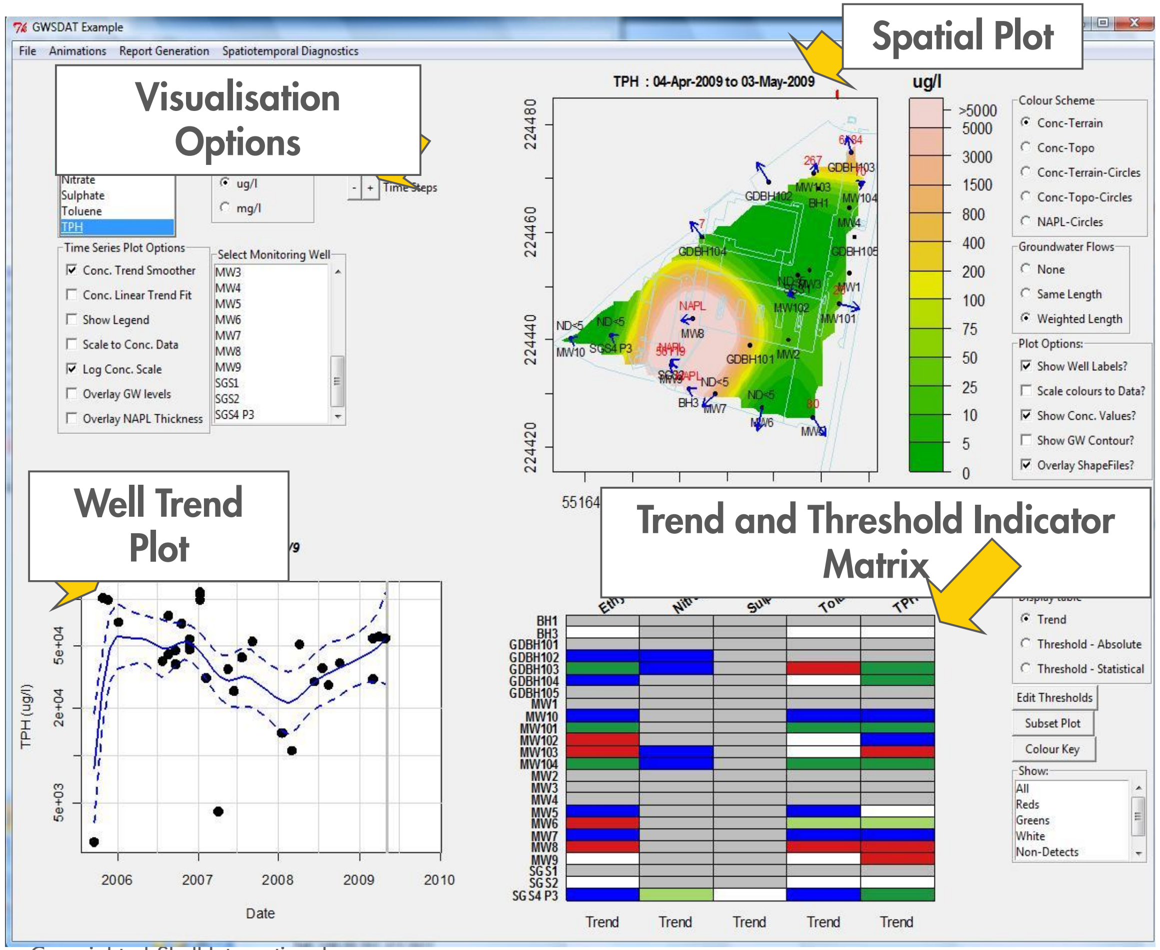
GWSdat: Ground Water Spatial-Temporal Analysis Tool

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

INPUT



OUTPUT



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

Regression Tool (Wilson, 2011)

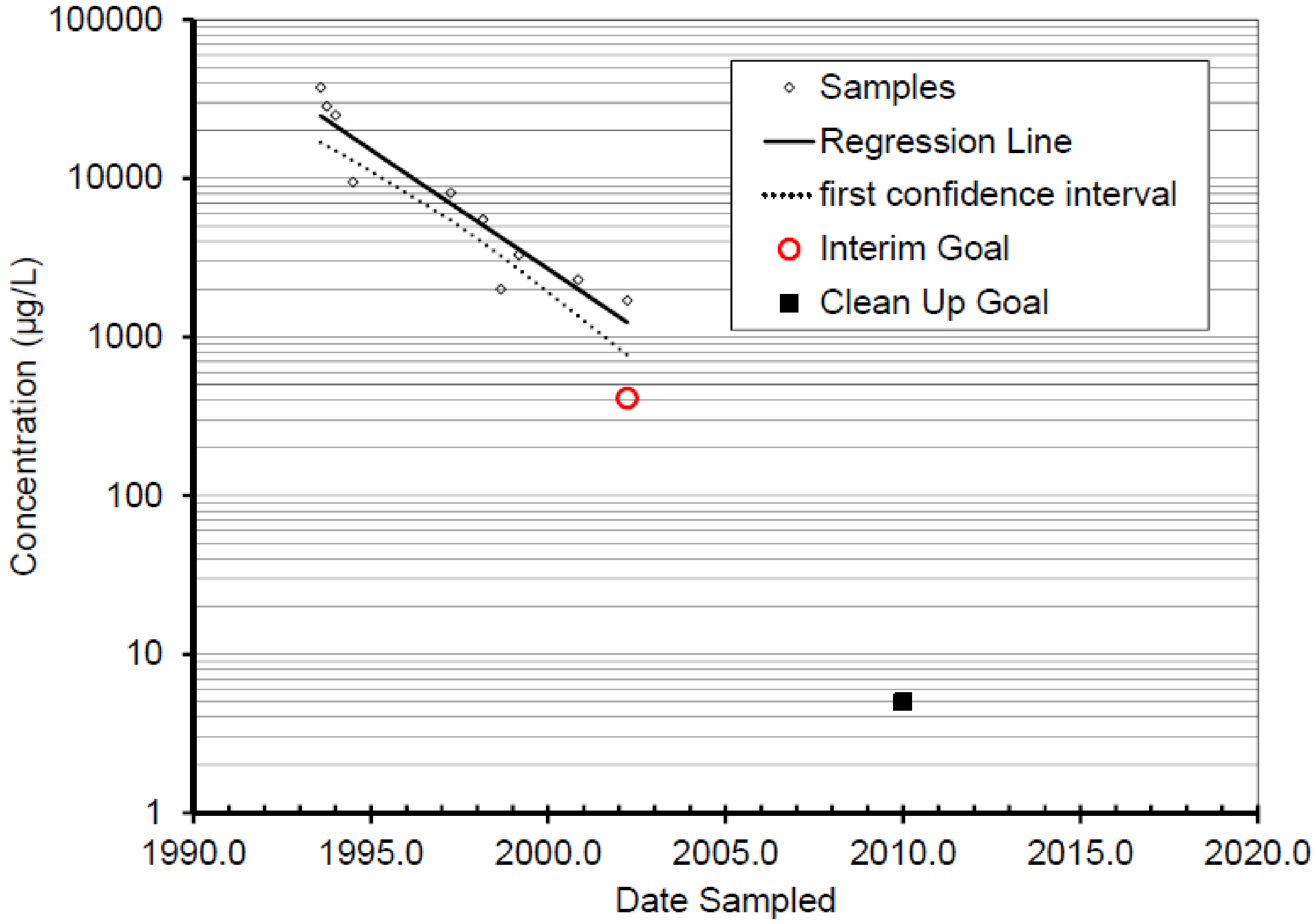
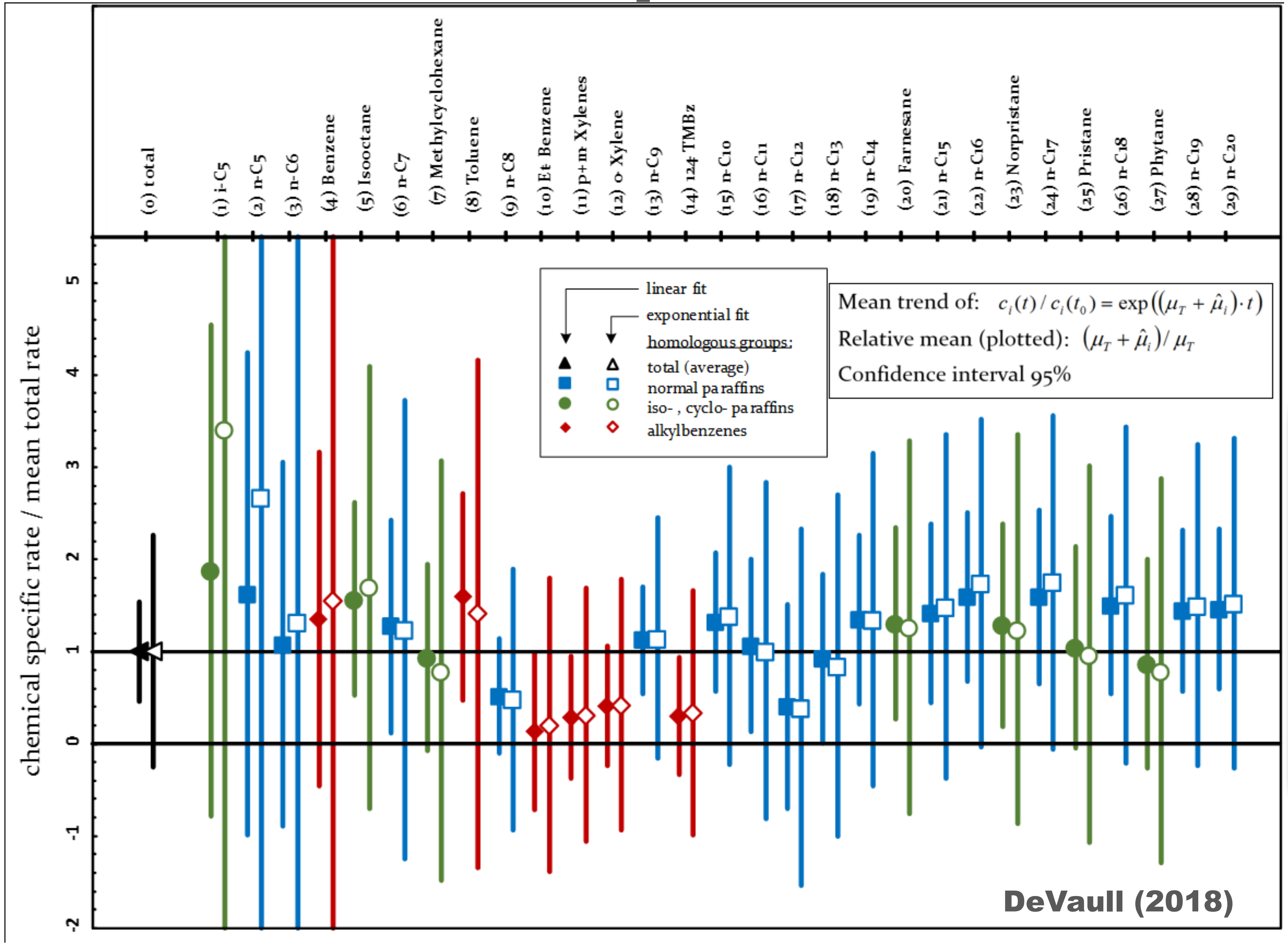


Figure A-3: Evaluating the uncertainty in the extrapolation of the trend in concentrations of MTBE in well CBC-25.

Efforts to Address the Challenge

LNAPL COMPOSITION

Attenuation Rates for COPCs Based on Trends in LNAPL Composition



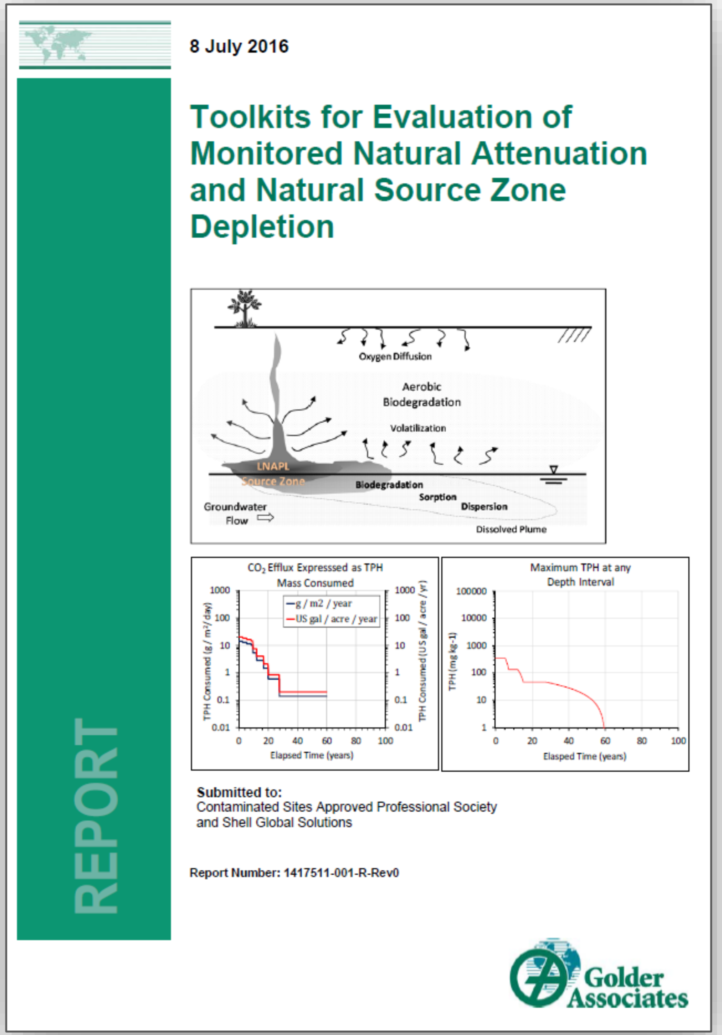
- diesel-like oil product (C_5 – C_{20}) from single monitoring well over 4-yr period

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!**

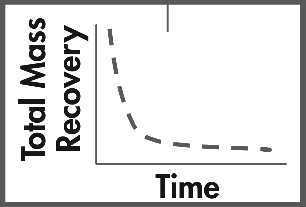
Example – Mass Recovery/Control

REGULATORY MILESTONES

CSM DEVELOPMENT

REMEDIAL OBJECTIVES

ACTIVE RECOVERY (e.g., LNAPL recovery)



REMEDIATION TOLLGATE

END POINT

MAXIMUM EXTENT PRACTICABLE

NSZD ASSESSMENT

DATA COLLECTION & ANALYSIS

SYSTEM PERFORMANCE

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

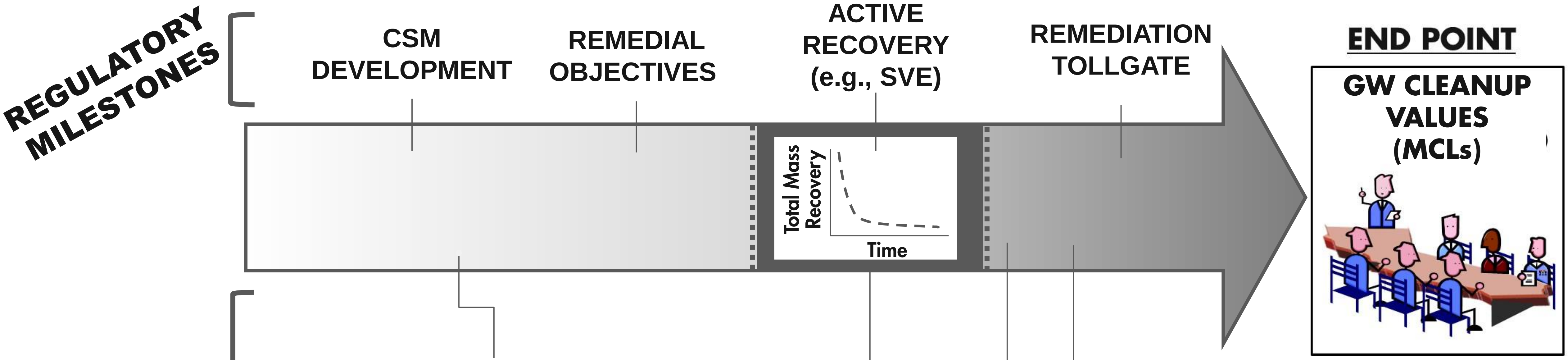
SATURATED ZONE

- 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

Example: Composition



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

SATURATED ZONE

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

VADOSE ZONE

- COPC VOLATILIZATION TEST (SOIL-GAS GRADIENT METHOD)

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