Recent Studies on Natural Attenuation at Petroleum UST Sites and Implications on Risk-Based Decision Making

Remediation Technologies Symposium 2019
Banff Springs, Alberta
October 17, 2019

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Acknowledgements

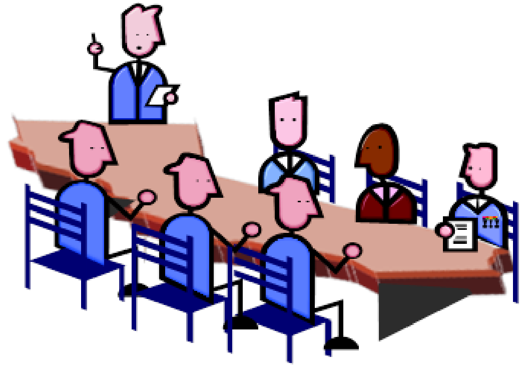
Charles Newell, Poonam Kulkarni, Tom McHugh
GSI Environmental Inc, Houston, Texas

Kirk O’Reilly, Andrew Dienes
Exponent, Bellevue, Washington

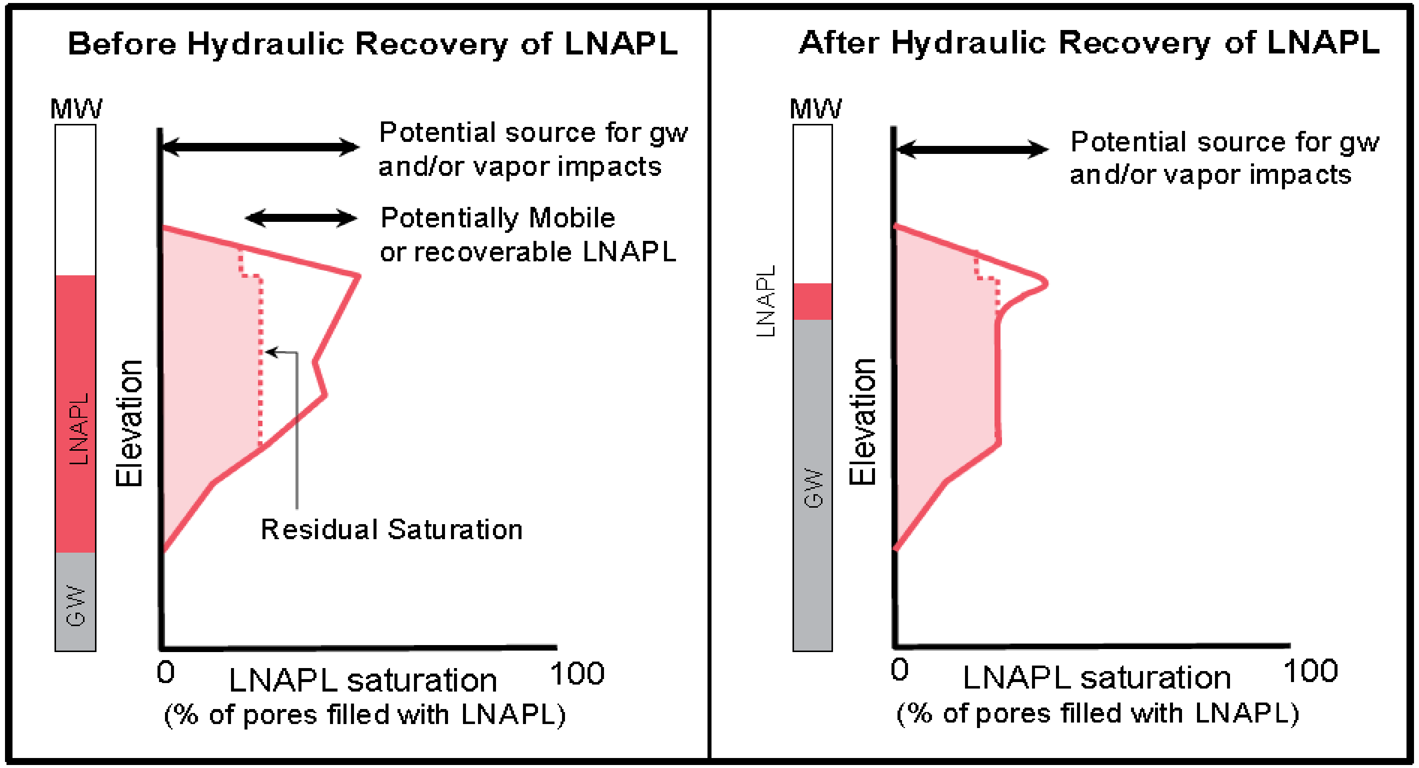
STATE WATER RESOURCES CONTROL BOARD
GEOTRACKER

Issue: Lack of Confidence in Natural Attenuation Affecting Risk-Based Decision Making

- residual LNAPL difficult to remediate
- natural attenuation occurring, but takes time
- low UST case closure rate (sites being monitored for extended time period till MCLs are reached)
- limited consideration of probable future groundwater use



Understanding the Science: Effects of LNAPL Recovery on Source Mass



From Garg, 2010

KEY POINT

- **significant source mass often remains in place after active remediation (source for groundwater and vapor impacts)**
- **further risk-based corrective action requires understanding of:**
  - **natural attenuation (baseline condition)**
  - **what works, what doesn't with respect to active remediation**

GW Attenuation Studies (COPCs): "BIG DATA"

CALIFORNIA GEOTRACKER GW DATABASE

- 12,000+ sites w/ electronic data
- 2 million GW samples; 157,000 MWs
- electronic data from 2001 and after

From McHugh et al., 2013

GOALS

- attenuation rates for key COPCs
  - how do they compare?
  - which COPCs drive risk?
  - have they changed over time?
- key factors that affect attenuation rates
  - LNAPL recovery
  - types of remediation technologies

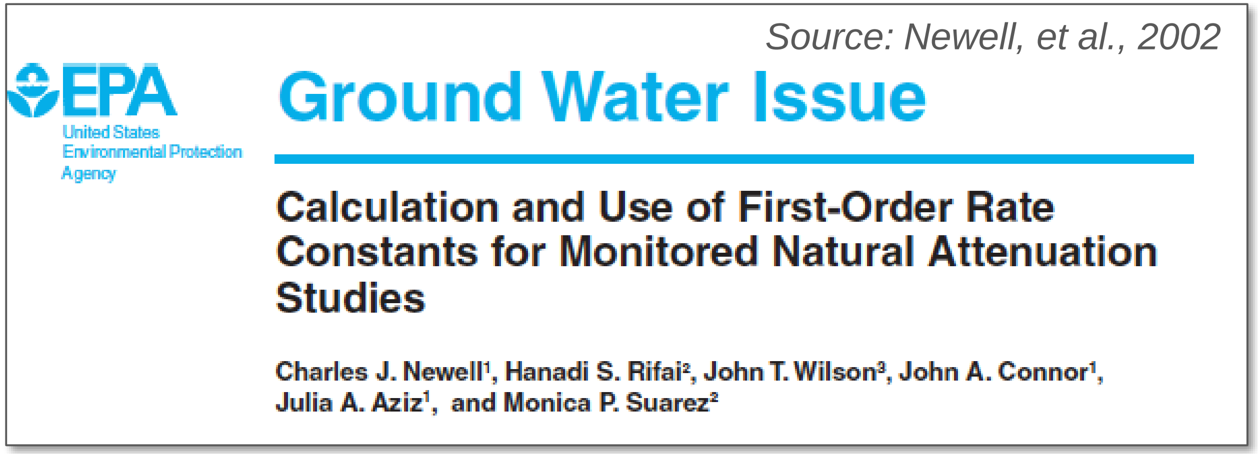
KEY POINT

- **database provides unique opportunity to understand COPC concentration trends and factors that affect**

Approach: Source Zone Attenuation Rates

Process the Data

- sites w/at least 5 yrs of concentration data
- extract maximum site-wide concentrations over six-month periods
  - 1000s of sites w/ GW data
  - 2,253 sites w/ residual LNAPL
  - 972 sites w/ mobile (or migrating) LNAPL
- calculate the source attenuation rate $\mathbf{k}_{\mathbf{source}}$
- assess effects on $\mathbf{k}_{\mathbf{source}}$

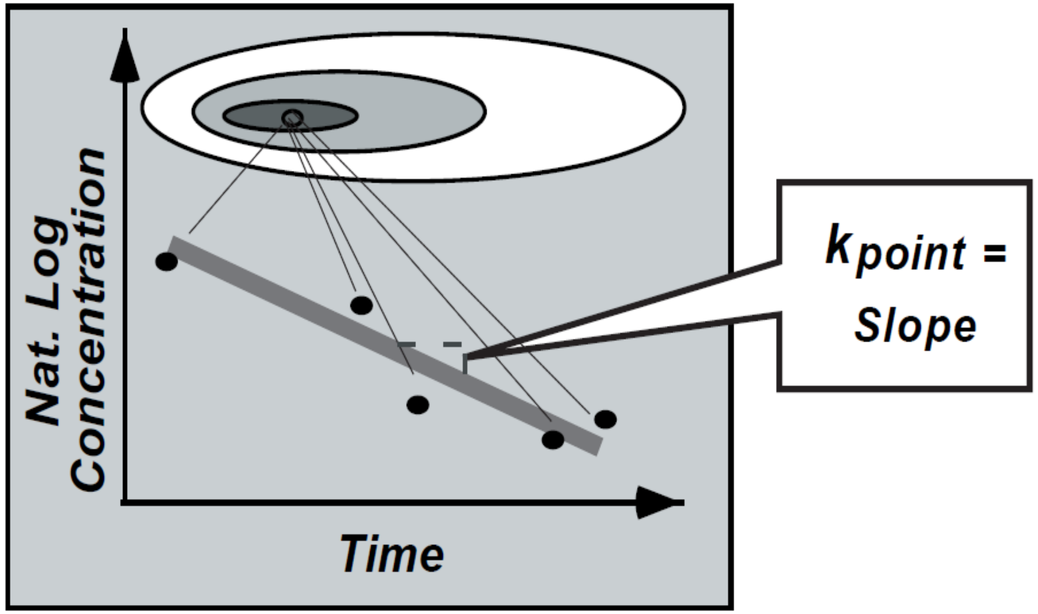

Source: Newell, et al., 2002

EPA United States Environmental Protection Agency

Ground Water Issue

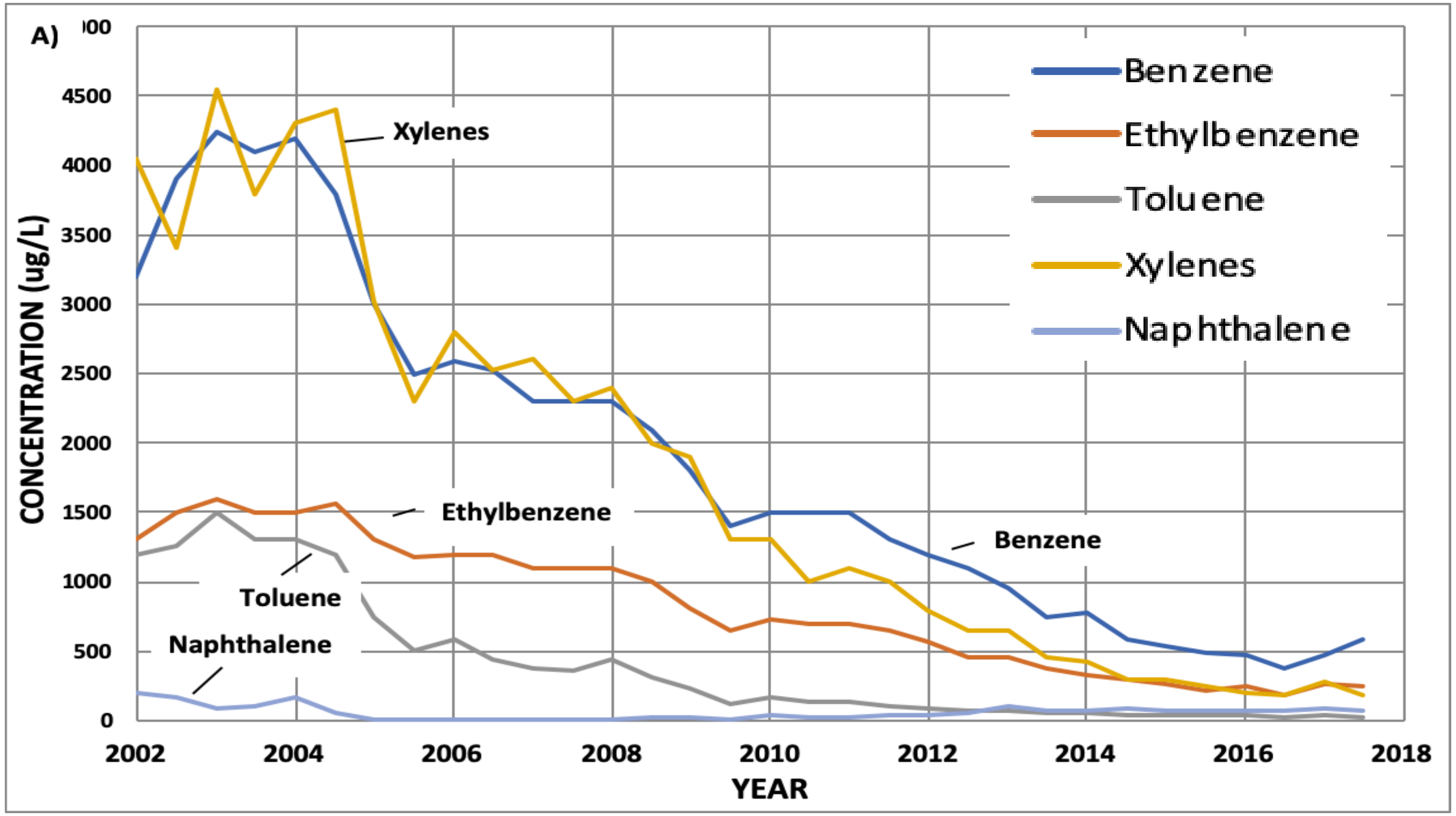
Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies

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]



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

Median GW Source Area Concentrations over Time

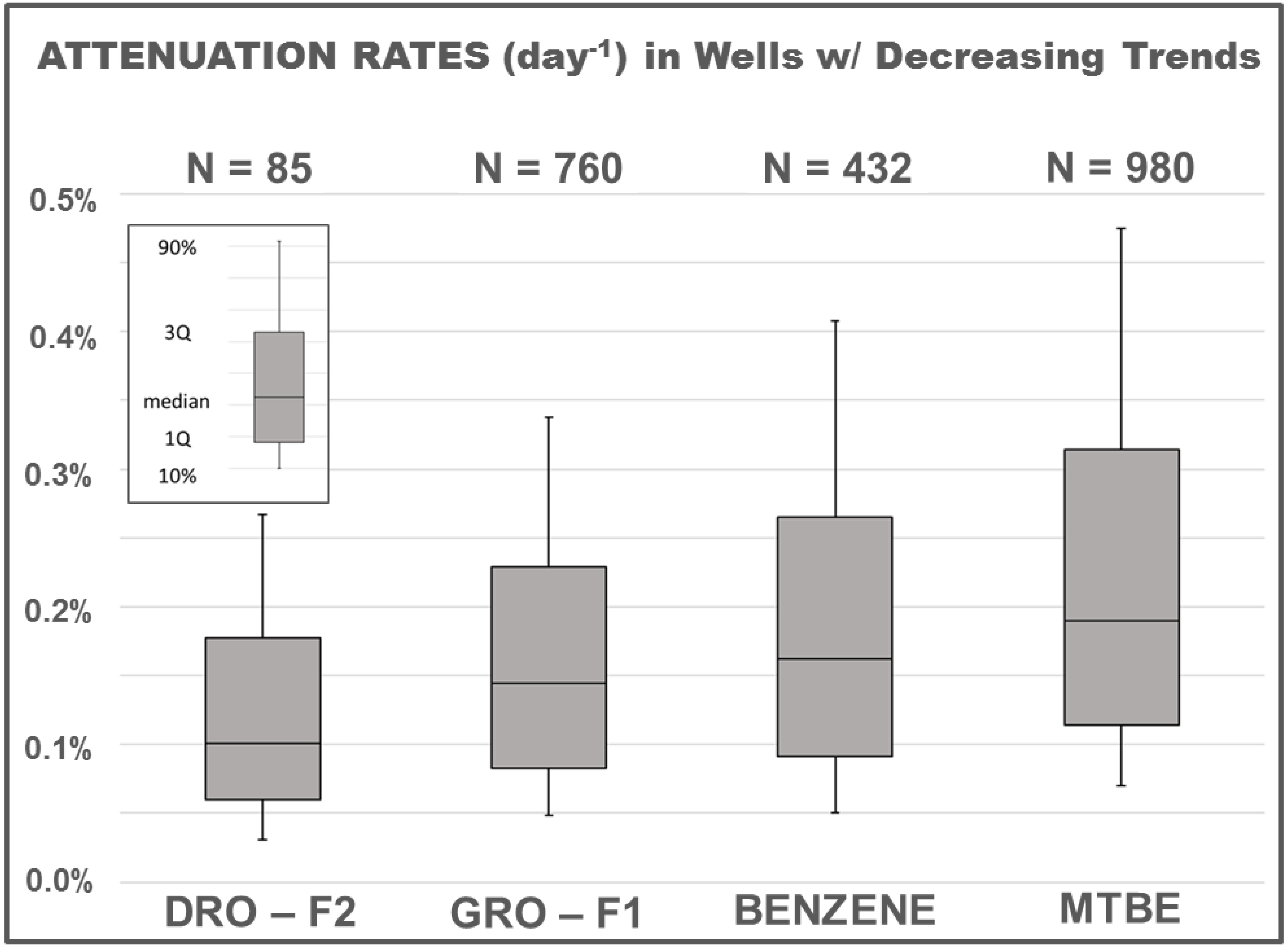


From McHugh et al. (written communication – 2019)

KEY POINT

- **GW quality has greatly improved over time for key petroleum COPCs at UST sites as a result of a) mitigation/remediation, b) improved leak prevention and detection, and c) natural attenuation**

Attenuation Rate Summary For Key COPCs



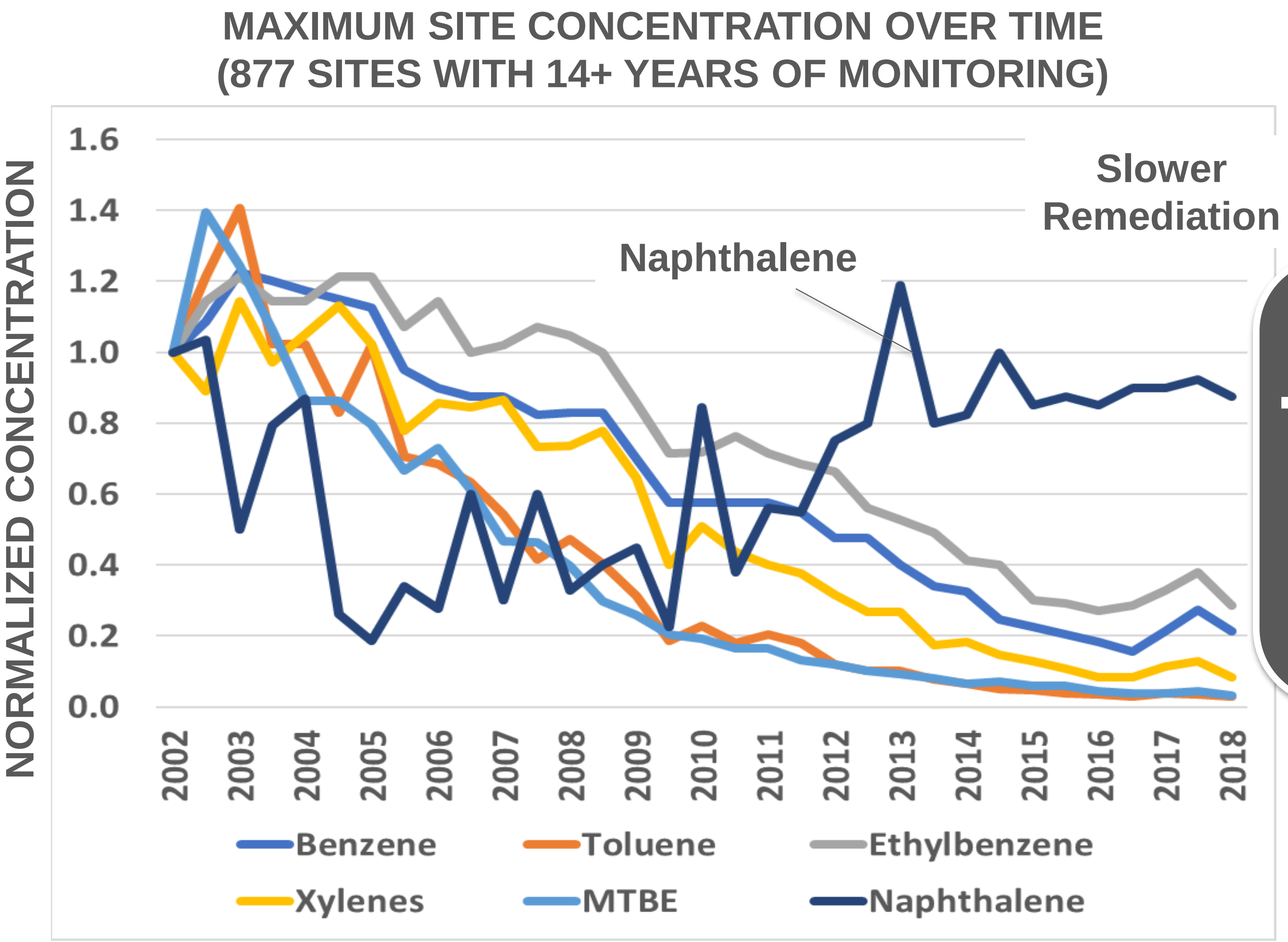
From O'Reilly et al. (written communication – 2019)

Constituent	Number of Sites	Median Attenuation Rate (d^{-1})	Median Half-Life (yr^{-1})
Benzene	432	0.0016	1.2
MTBE	980	0.0019	1.0
TPH GRO – F_1	760	0.0015	1.3
TPH DRO – F_2	85	0.0010	1.9

KEY POINT

- median half-lives range from 1-2 yrs, implying median source area concentrations decreasing by 50% every 1-2 yrs
- median attenuation rates for DRO (F2) slightly less than gasoline constituents (benzene and MTBE) and GRO (F1), again, consistent with lesser volatility and solubility (bioavailability)

Relative Concentration Trends For Key COPCs

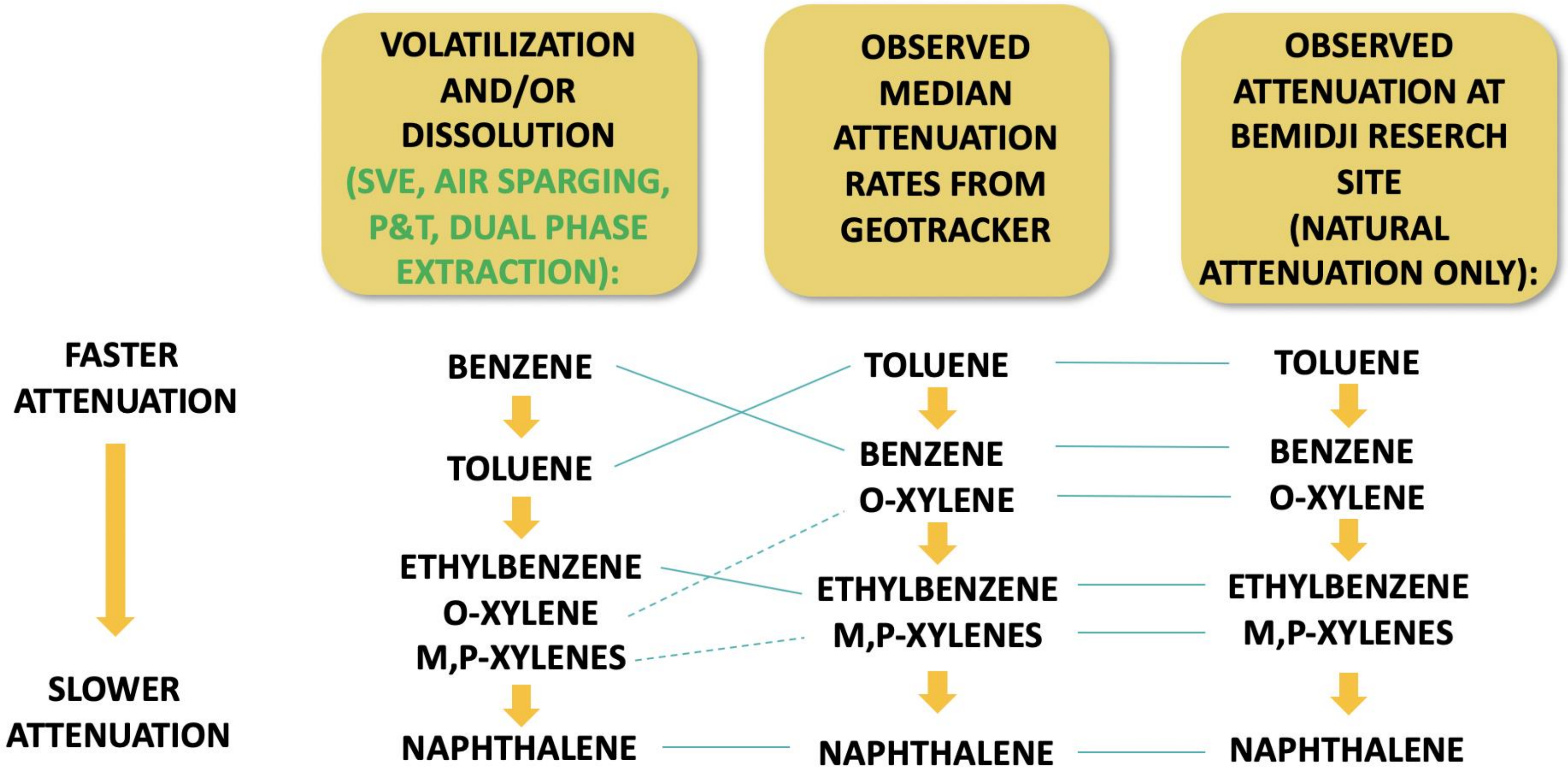


KEY POINT

- relative attenuation of BTEX is generally greater than N because of lower relative volatility and solubility (i.e., bioavailability)

From McHugh et al. (written communication – 2019)

Relative Attenuation Rates For Key COPCs



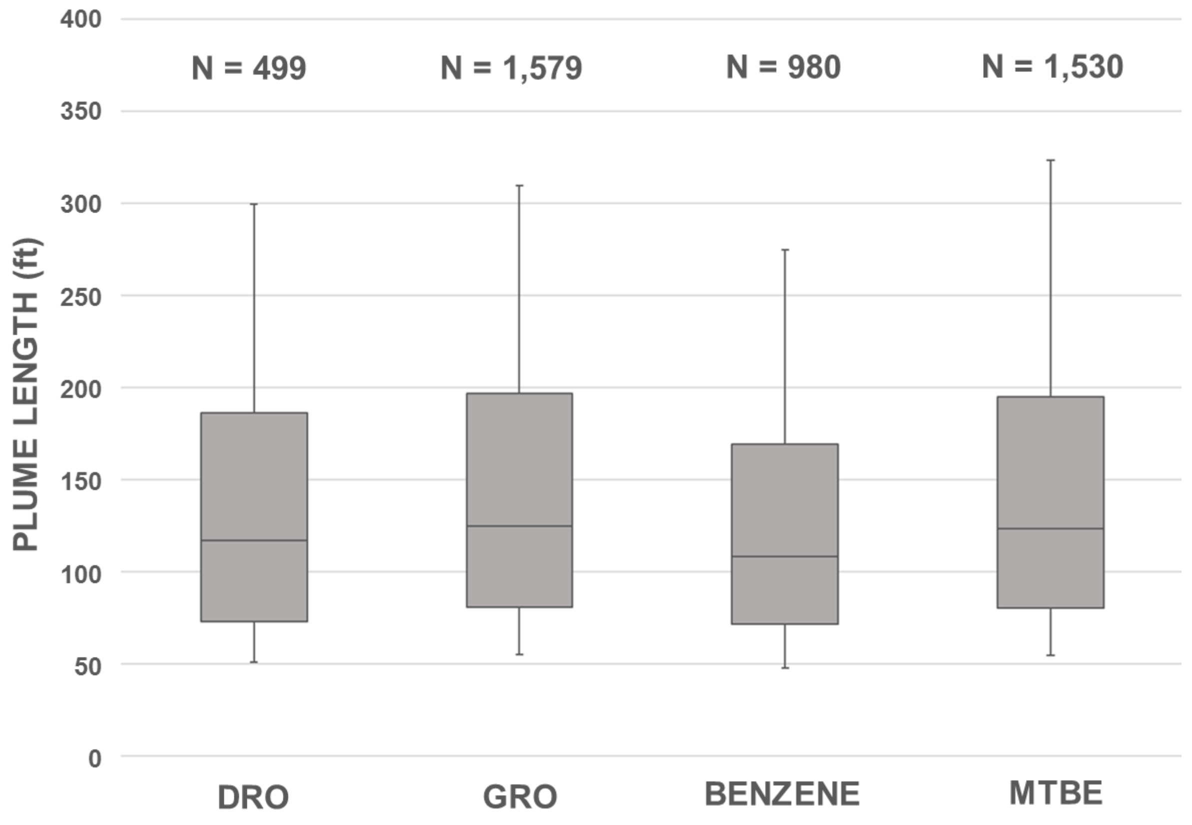
From: McHugh et al. (written communication – 2019)

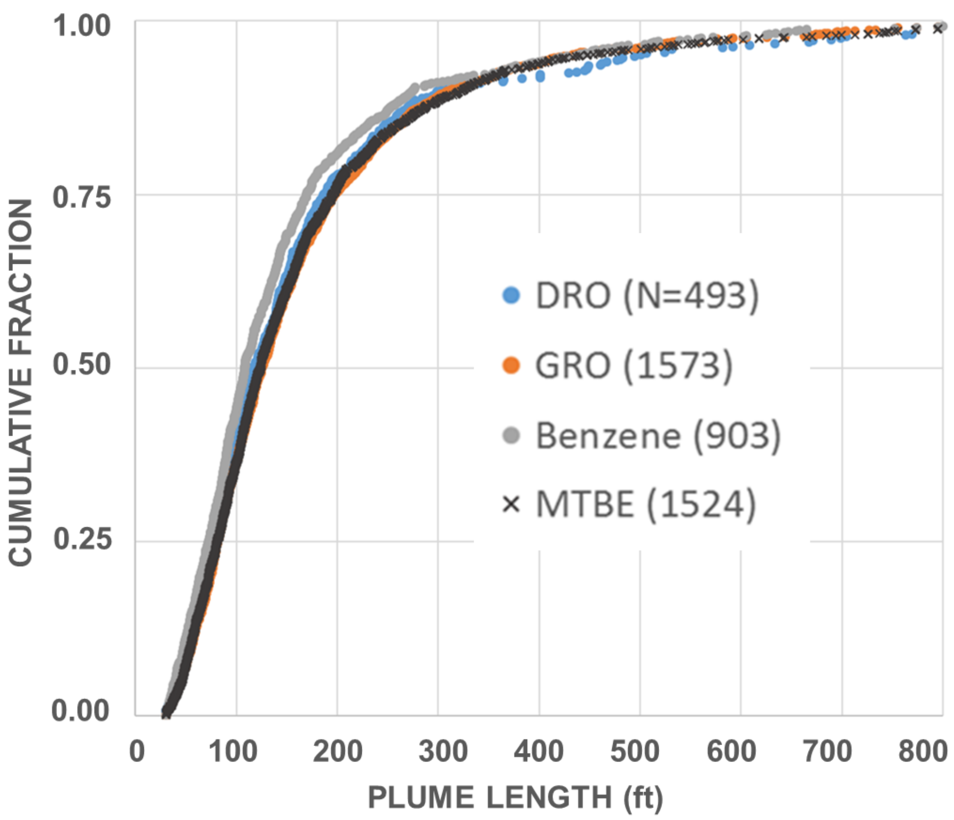
KEY POINT

- relative attenuation rates of BTEX and N are consistent with those observed at a well-studied (USGS) crude oil release site undergoing long-term natural attenuation
- relative rates of natural attenuation of BTEX, N are relatively independent of fuel type, release volume

Plume Lengths*

*** greatest distance between well w/highest COPC concentration and well w/ COPC concentration > ND**





From O'Reilly (written communication, 2019)

KEY POINT

- **plume lengths are similar for the 4 COPCs**
- **data suggest no need to manage petroleum UST sites differently based on TPH**

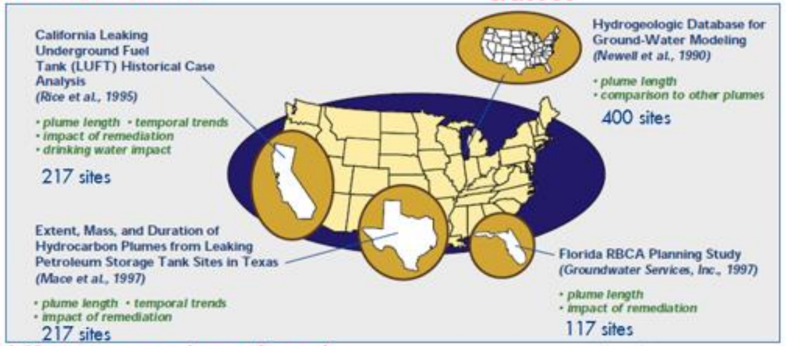
Plume Lengths: Published Studies @ Multiple Sites

From Connor et al. (2015)

(A)	Results for MTBE, Benzene, and TBA Plumes at UST Sites	
10 µg/L		
MEDIAN PLUME LENGTHS	391 sites	MTBE 165 feet
	826 sites	Benzene 140 feet
	108 sites	TBA 190 feet
90th-PERCENTILE PLUME LENGTHS	336 sites	MTBE 400 feet
	772 sites	Benzene 345 feet
	108 sites	TBA 420 feet

"…significant reductions in benzene concentrations can occur with time, even without active Remediation"

"BTEX plumes are significantly smaller than the other chemical classes"



Newell And Connor, 1998

"We found no difference in plume length between different remediation techniques and sites with no remedial action"

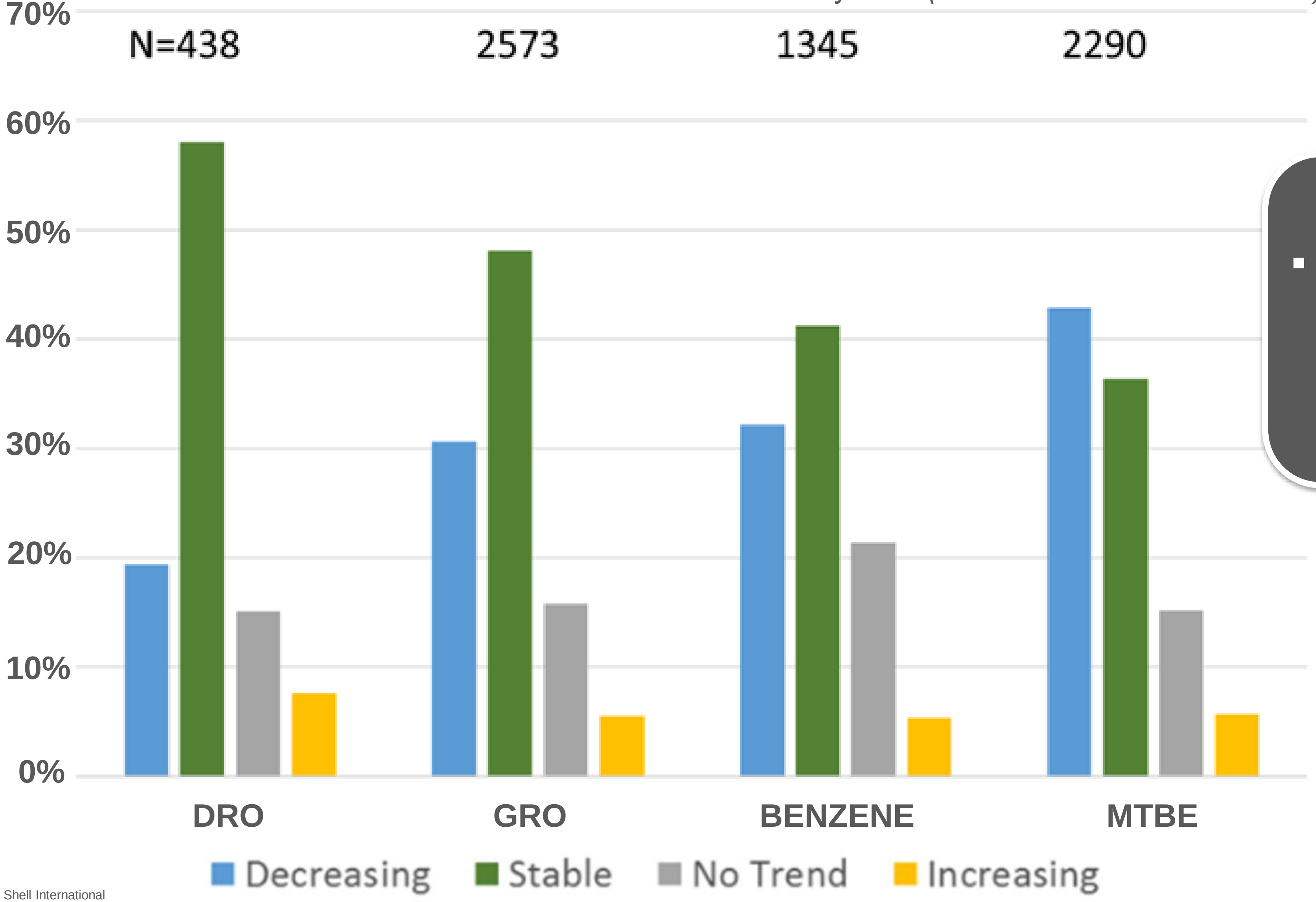
"..soil removal would not significantly affect groundwater remediation requirements"

KEY POINT

- median plume lengths for MTBE and BTEX are generally similar - multiple different sites
- median and 90th percentile plume lengths generally similar for various COPCSs (benzene, MTBE, and TBA)

Plume Stability

From O'Reilly et al. (written communication – 2019)

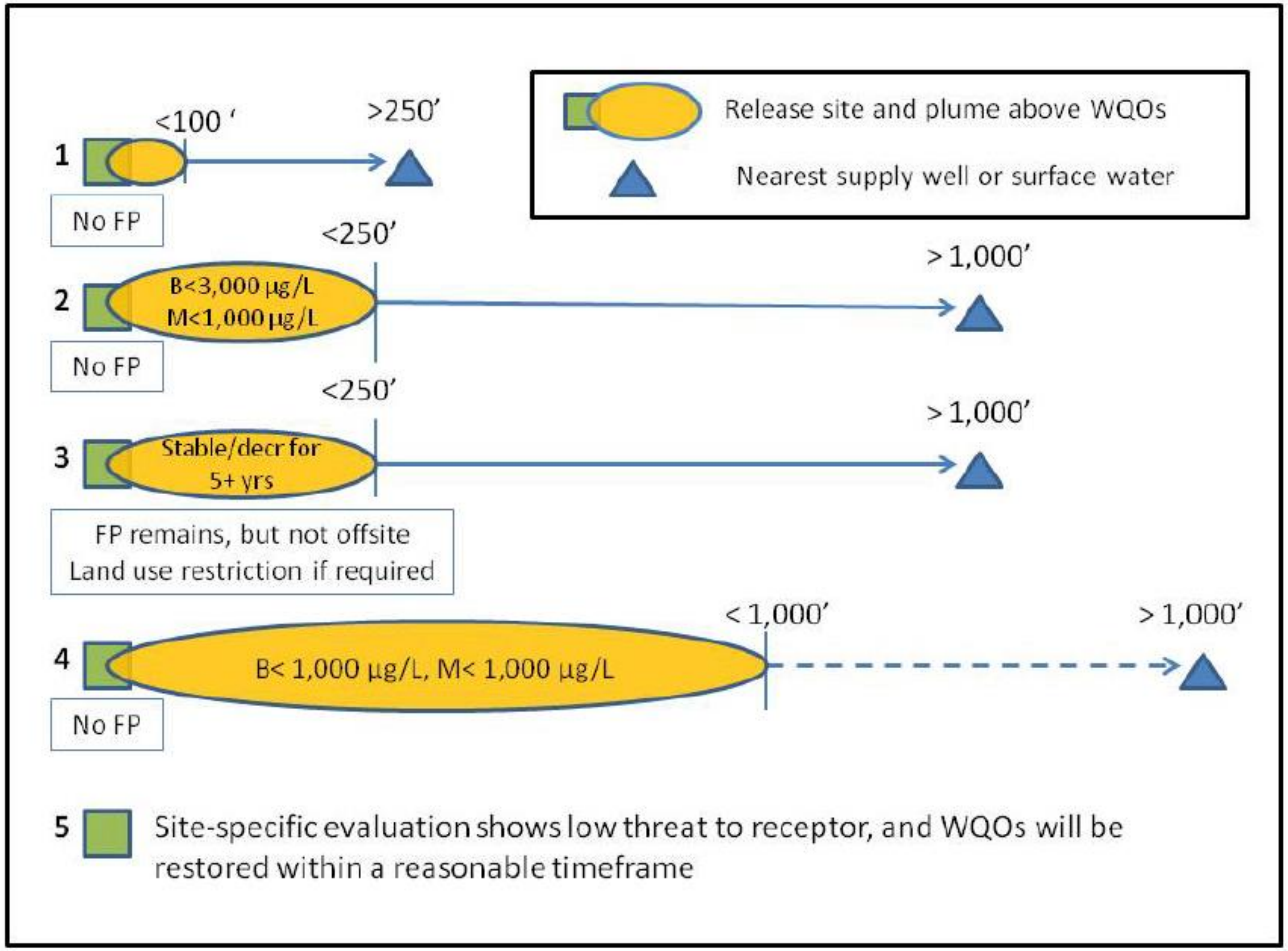


KEY POINT

- COPC plumes are generally stable or decreasing after monitoring is initiated

GW Criteria in California Low-Threat Tank Closure Policy (2012) Underpinned by McHugh et al. (2012)

Figure 17-1: Groundwater Plume Classes for Low-Threat UST Case Closure Policy



Notes:

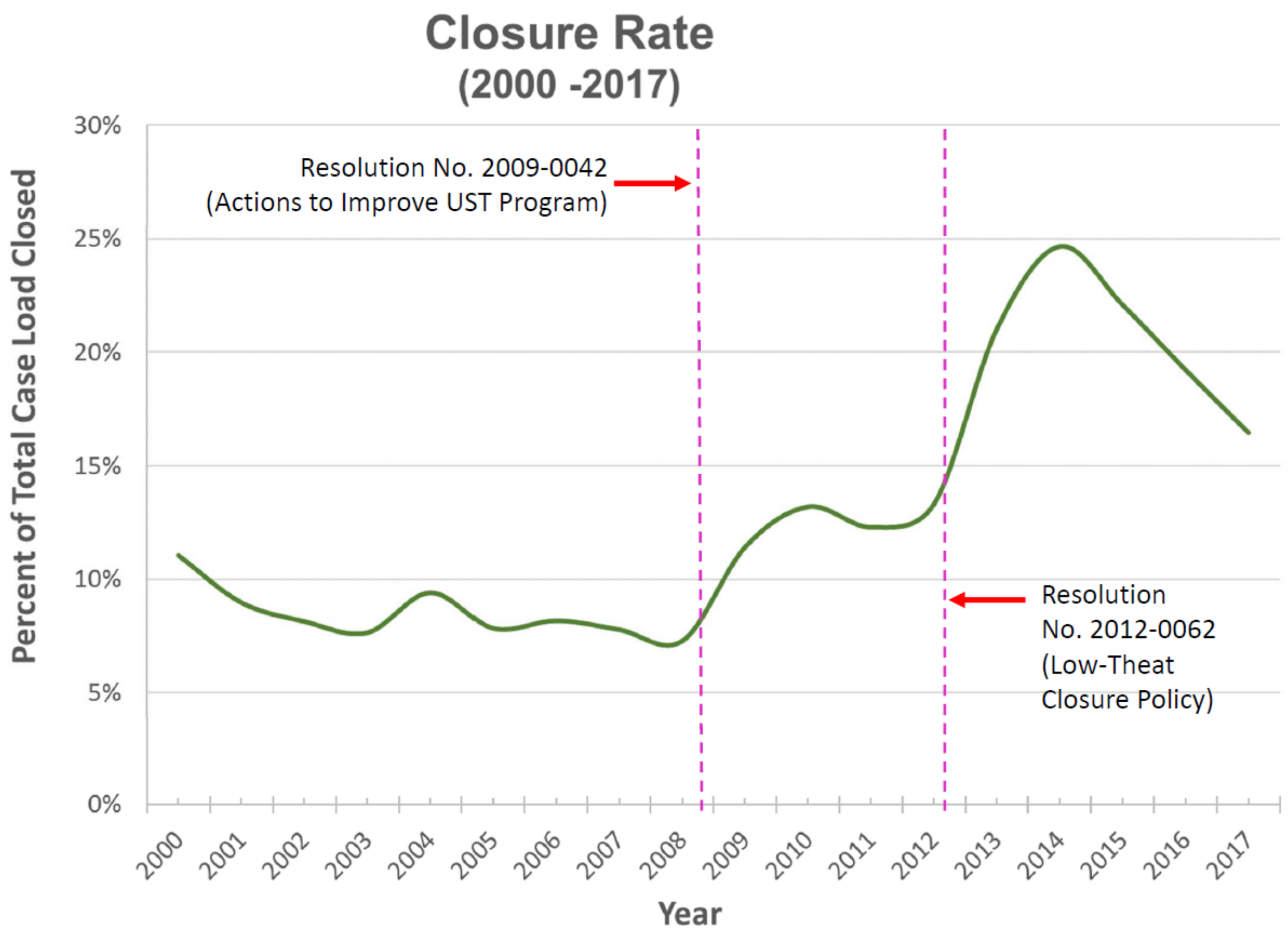
B	Benzene
FP	Free Product
M	Methyl tert butyl ether
Stable/decr	Stable or decreasing in areal extent
WQO	Water Quality Objective

Figure is not to scale

KEY POINT

- science used to support rational, risk-based policy in California for managing long-term petroleum hydrocarbon impacts at UST sites (closing sites in long-term monitoring)

Closure success…



From: California State Water Resources Control Board (2018)

KEY POINT

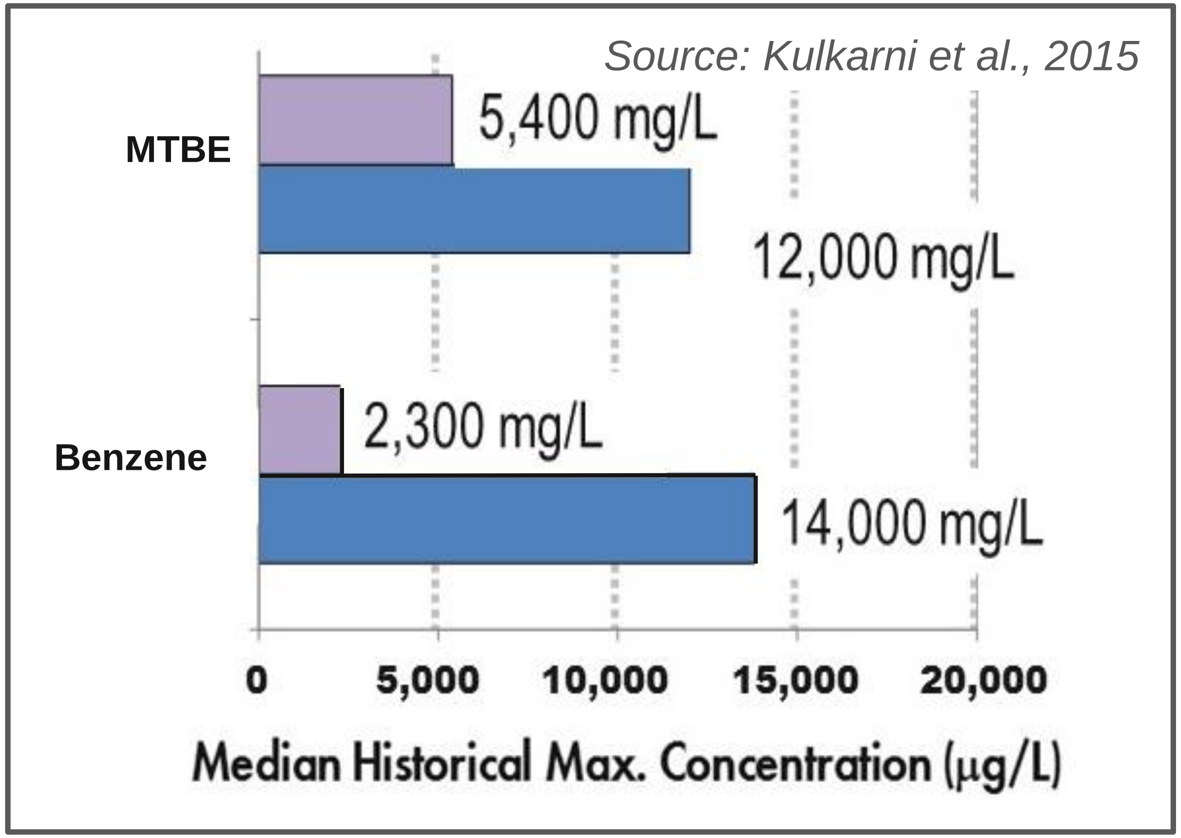
- **# of sites being monitored has decreased by 70% since 2008**
- **higher concentration sites retained (consistent with intent of low threat policy)**
- **great example of developing practical regulations in partnership (regulators, water districts, NGOs, industry, tank owners/operators, environmental consultants)**

For additional information see:
https://www.waterboards.ca.gov/water_issues/programs/ust
https://www.waterboards.ca.gov/water_issues/programs/ust/publications/docs/agency_status_report_jul_2017.pdf

Closure success…

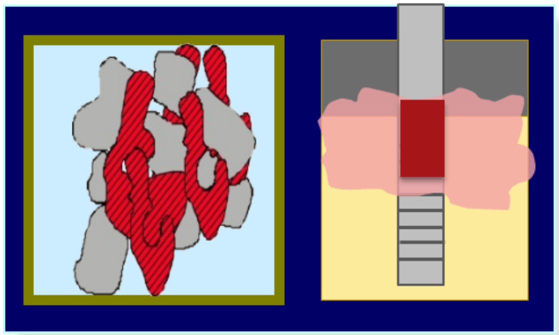
- Brownfields and Land Revitalization initiatives
  - economic growth
  - job creation
  - revitalize communities

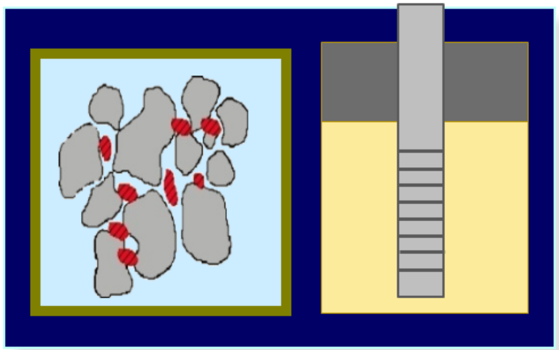
Higher Dissolved-Phase Concentrations At Sites With Mobile LNAPL



Non-LNAPL Sites (n = 2,253) LNAPL Sites (n = 972)

Mobile LNAPL:
"LNAPL Site"



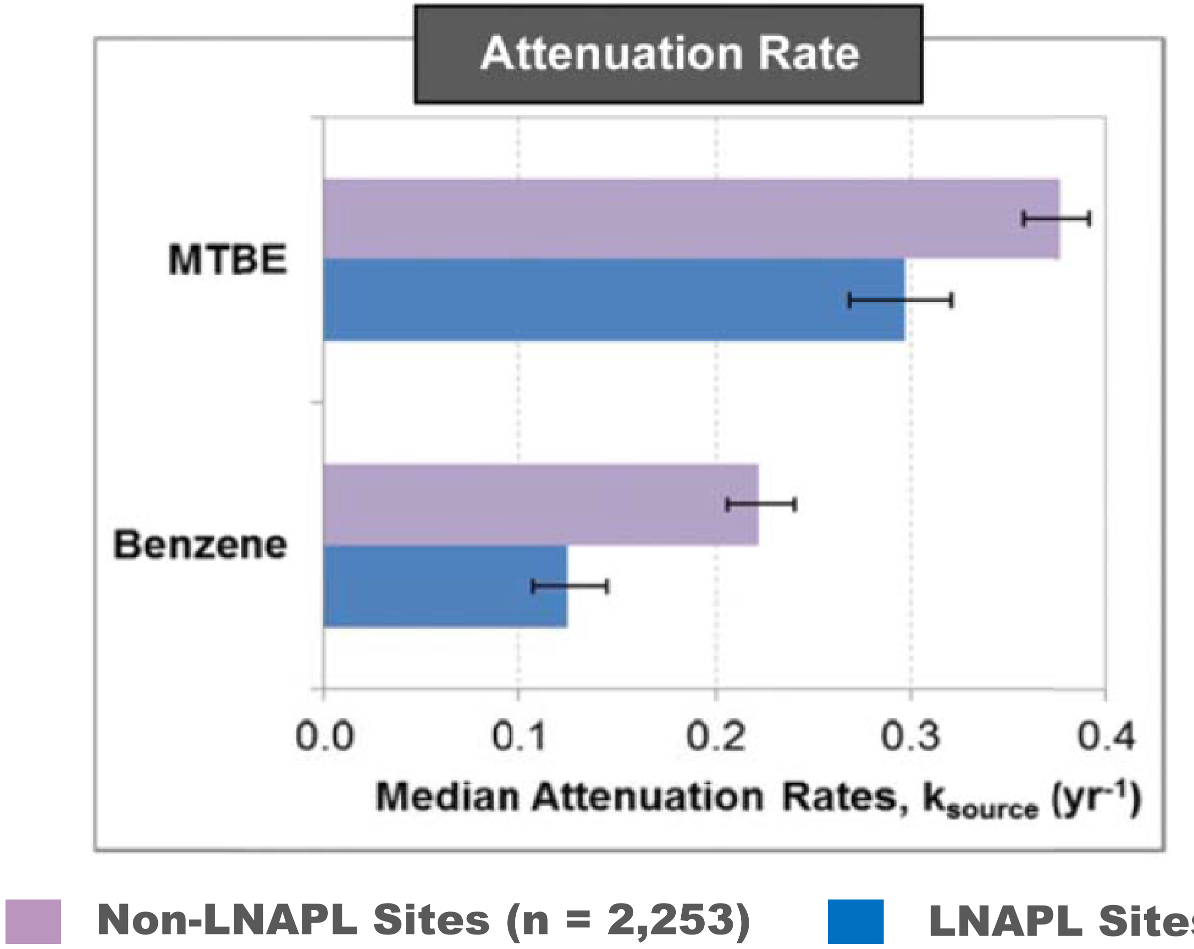


Residual LNAPL:
"Non-LNAPL Site"

KEY POINT

- mobile LNAPL sites have higher maximum dissolved concentrations than sites with residual LNAPL

Slower Attenuation Rates At Sites with Mobile LNAPL

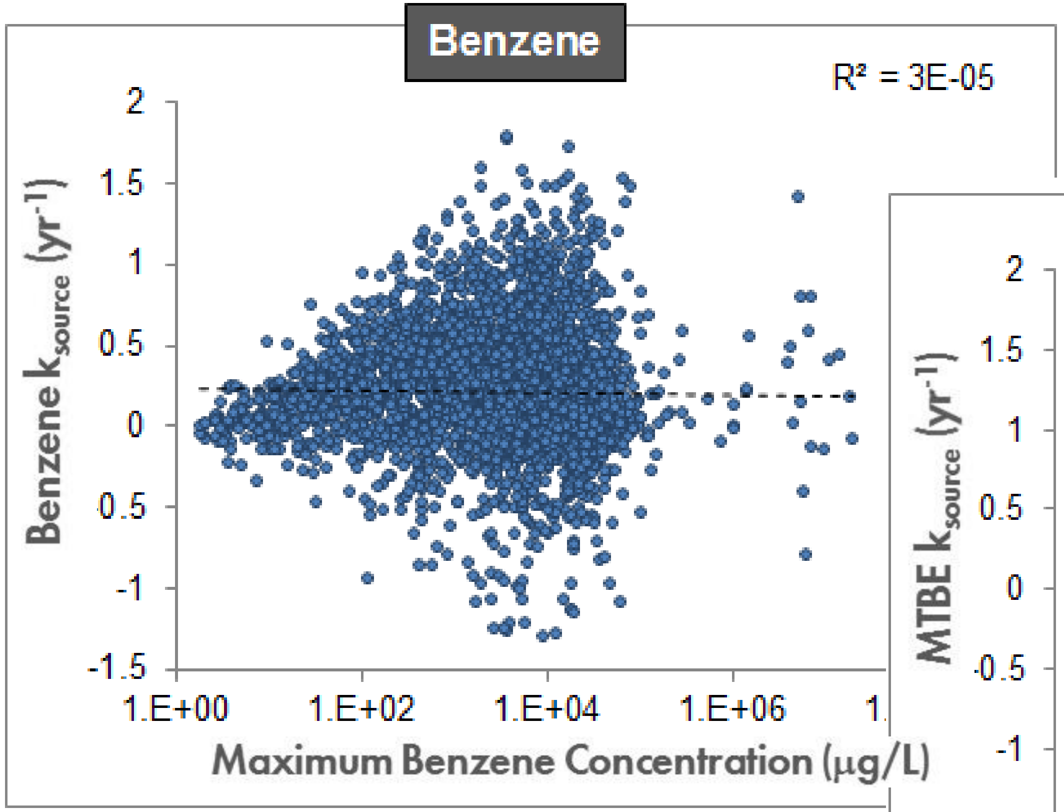


Source: Kulkarni et al., 2015

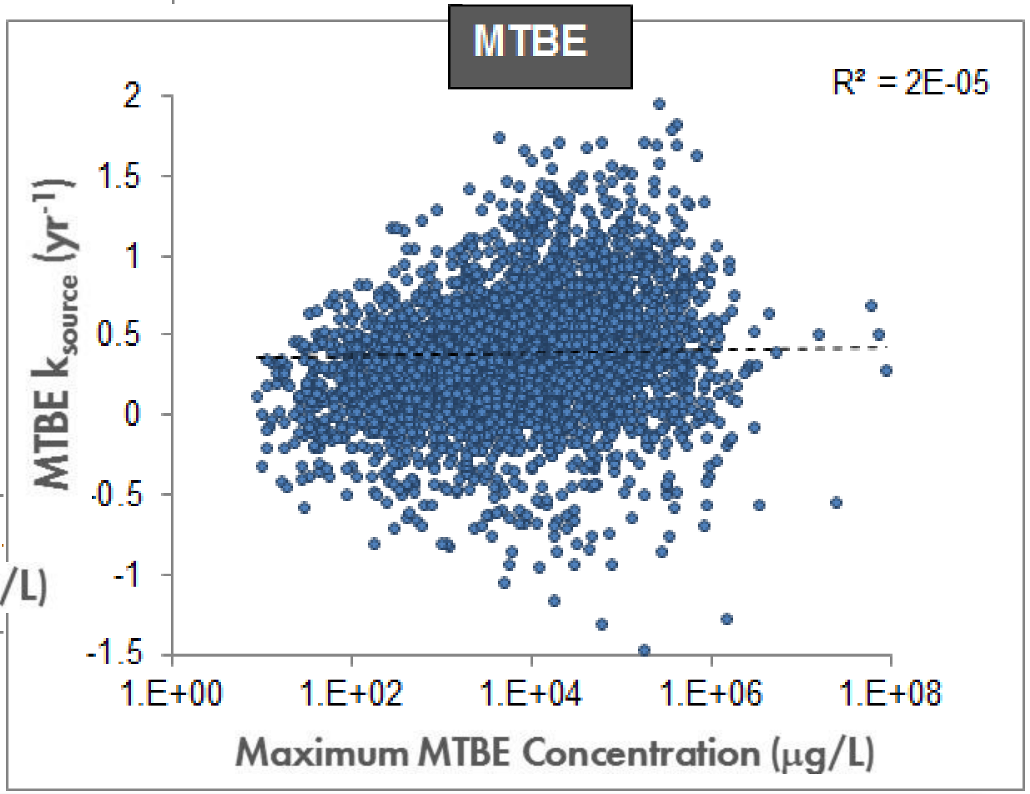
KEY POINT

- mobile LNAPL sites have slower attenuation rates than sites with residual LNAPL

Attenuation Rate vs. Groundwater Concentration



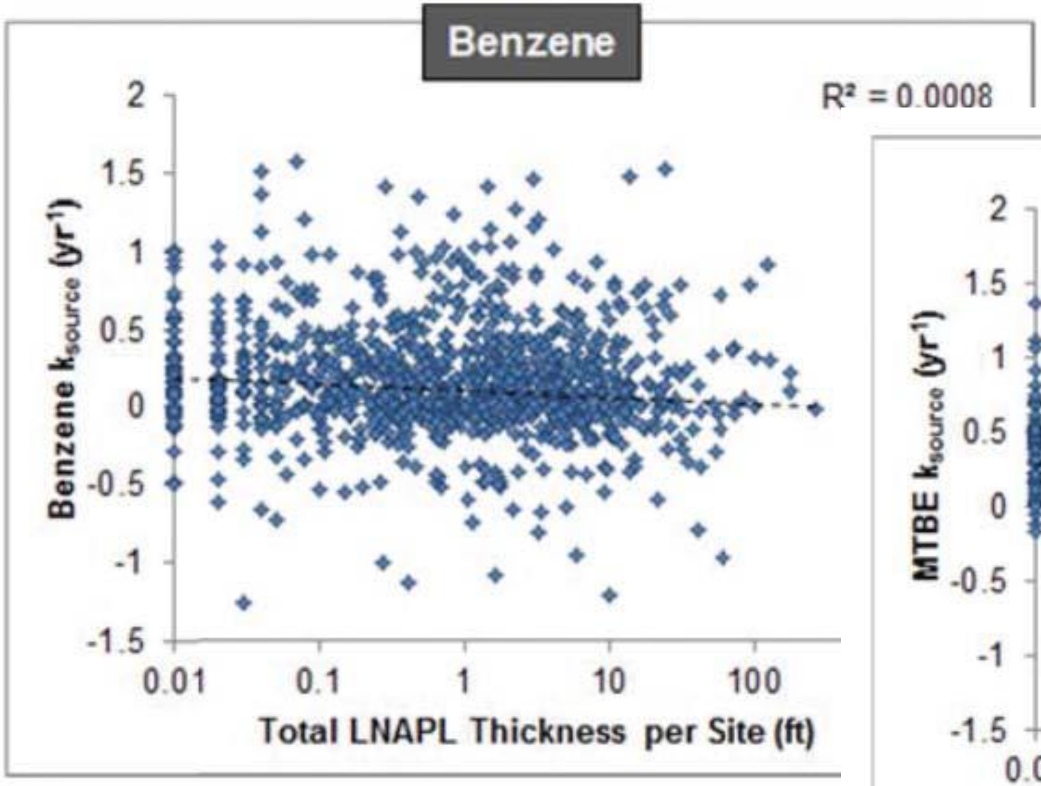
Source: Kulkarni et al., 2015



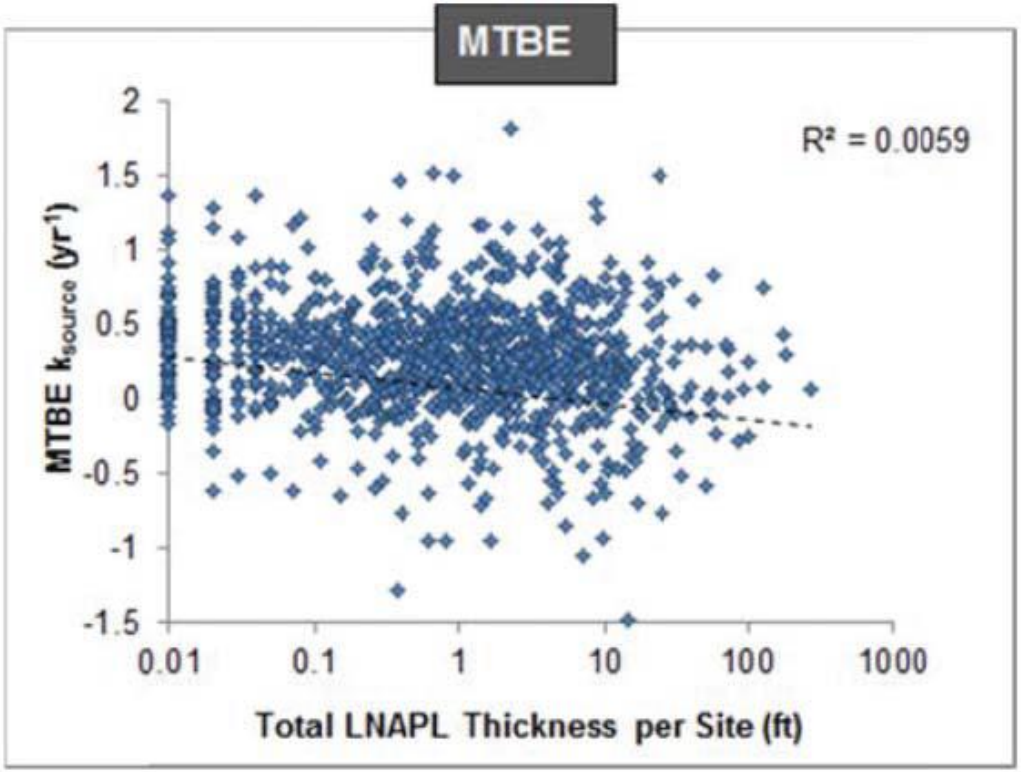
KEY POINT

- **difference in attenuation rates was not related to difference in maximum concentrations at the two types of sites**

Attenuation Rate vs. LNAPL Thickness (Release Volume)



Source: Kulkarni et al., 2015



Total LNAPL Thickness = sum of maximum LNAPL thickness in each well

KEY POINT

- **factors other than release volume and site geology affect attenuation rates**

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

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

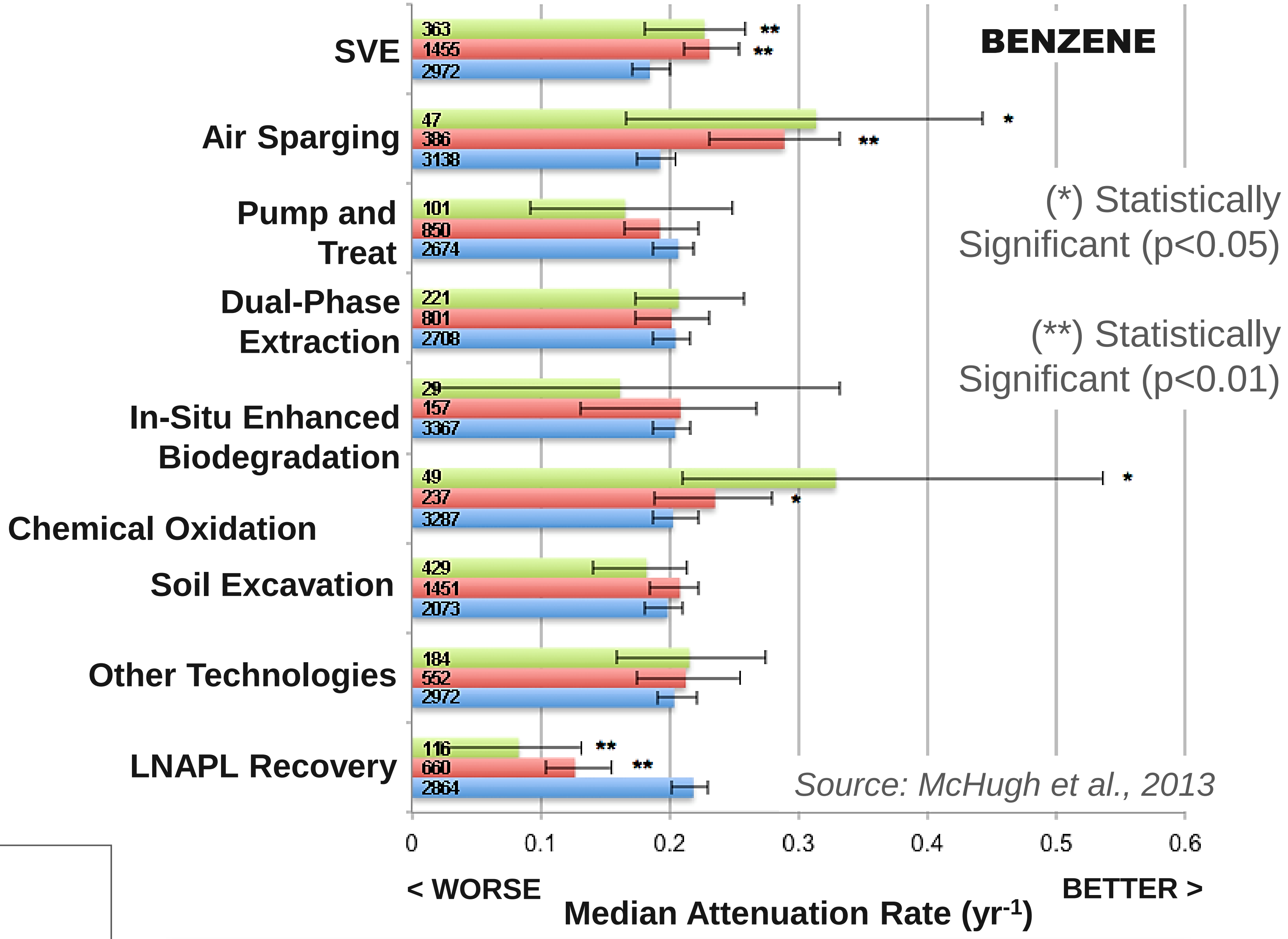
Source: Kulkarni et al., 2015

KEY POINT

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

Effect of Remediation Technology on Source Attenuation Rate

What about NA sites only?



Legend

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

KEY POINT

- air-based remediation technologies (and chemical oxidation) had greatest effect on enhancing attenuation rate for benzene

Key Take Aways

- hydrocarbon generally remains despite best efforts to recover/remediate
- must rely on natural attenuation to reach risk-based clean-up goals (e.g., MCLs) w/in a reasonable timeframe
- attenuation rates of petroleum hydrocarbons are well documented
  - rates relatively consistent for wide-range of key COPCs
  - rates significant (most plumes are stable or decreasing)
  - few petroleum hydrocarbon plumes extend beyond 500 ft
  - rates are not necessarily significantly increased by hydraulic LNAPL recovery
- science can be used to underpin regulations that prevent risks to human health and the environment, focus limited resources on sites that matter most, and give back to the community through redevelopment

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