WASTE KHORO 2019: Asbestos and Land Remediation Summit
18-20 September 2019

"Good Green Deeds towards a Recycling Economy and Sustainable Land Remediation"

Recent Science to Support Light Non-Aqueous Phase Liquid (LNAPL) Remediation Decision Making at Petroleum UST Sites

Waste Khoro 2019: Asbestos and Land Remediation Summit

Kimberley, Northern Cape – South Africa

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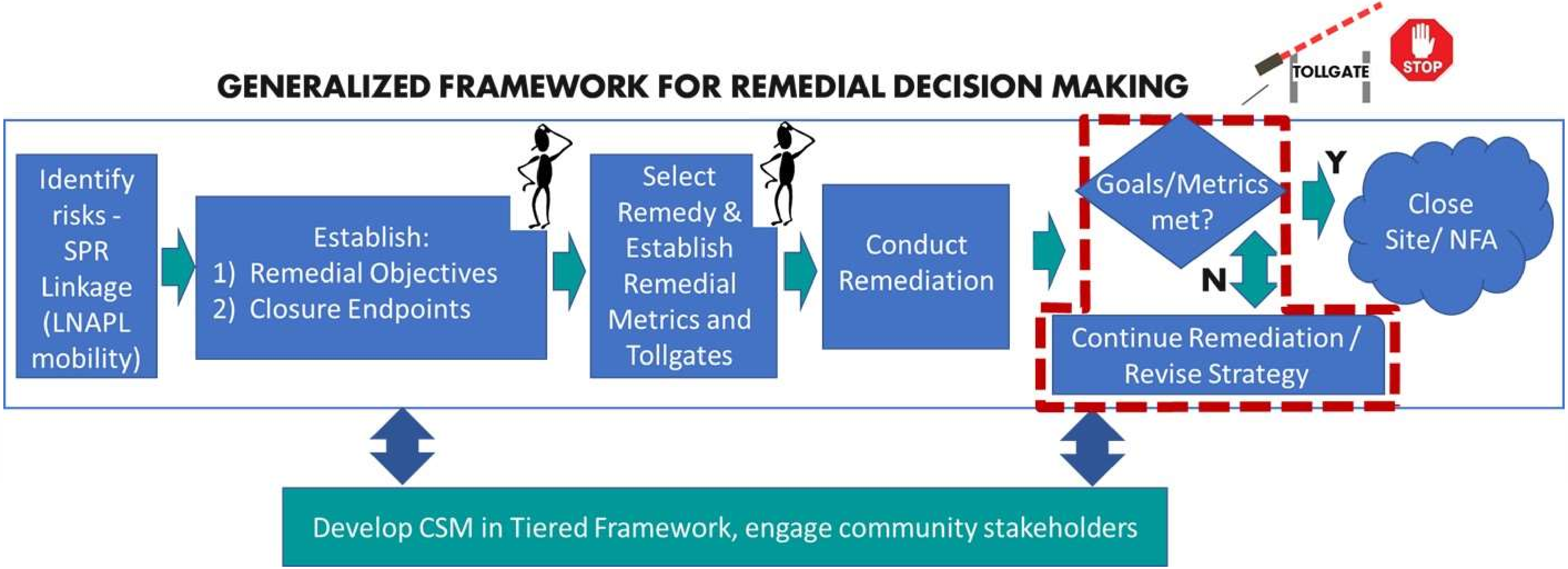
CA.GOV

STATE WATER RESOURCES CONTROL BOARD
GEOTRACKER

Issue: Getting to Closure Often Challenging



KEY POINT

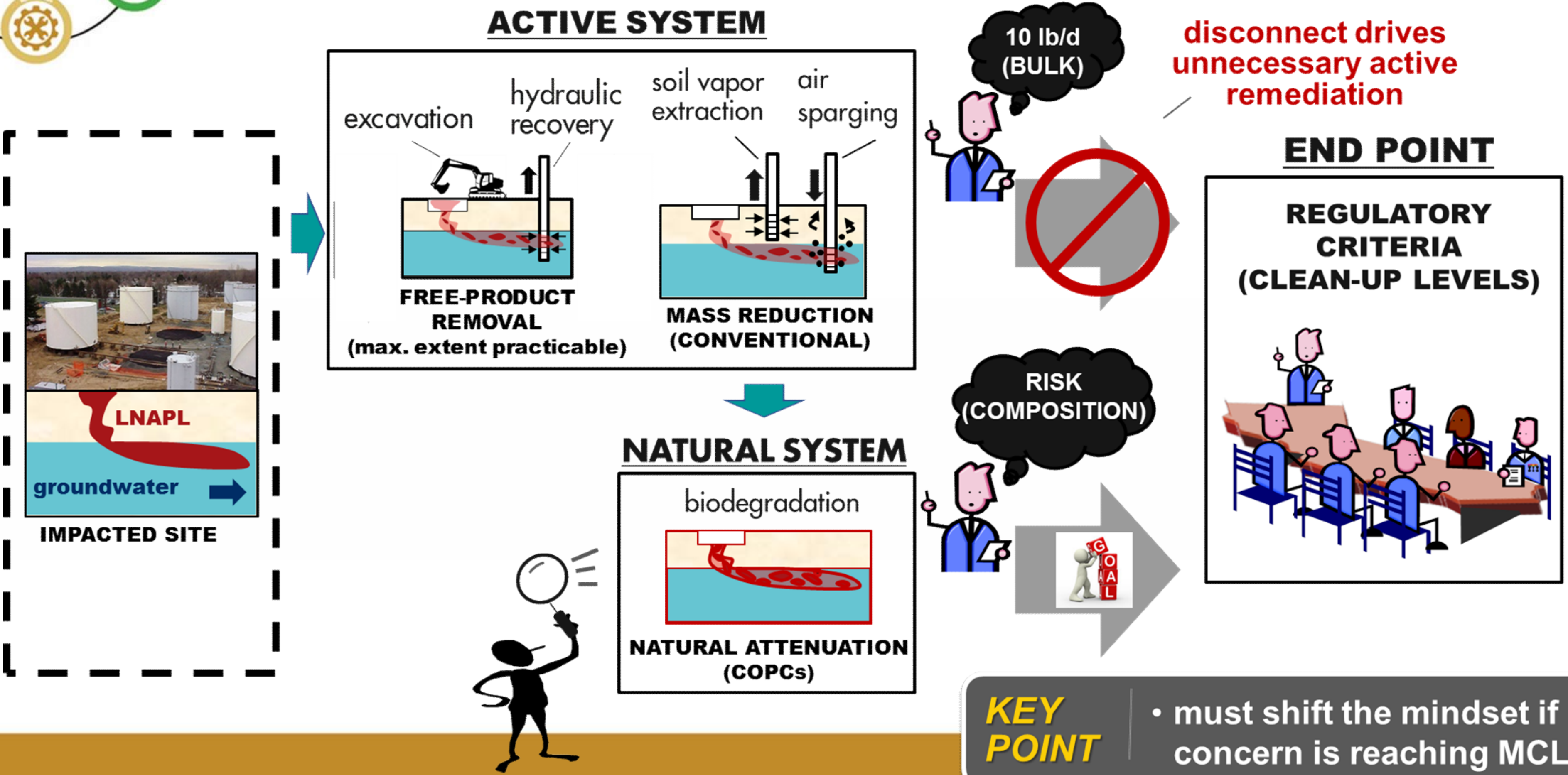
- challenge to terminate active recovery systems and transition to natural attenuation remediation

Reasons (Examples)

- poorly defined remedial objectives (e.g., bulk vs. composition)
- knowledge of the conceptual model and the science
- lack of confidence in natural attenuation
- insufficient data – not knowing what data to collect/when

- "non-technical"
  - future land use
  - responsible party's obligation, regardless

Understanding Remedial Objectives



KEY POINT

- must shift the mindset if concern is reaching MCLs

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

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

From McHugh et al., 2013

KEY POINT

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

Approach: Source Zone Attenuation Rates


Source: Newell, et al., 2002

EPA United States Environmental Protection Agency

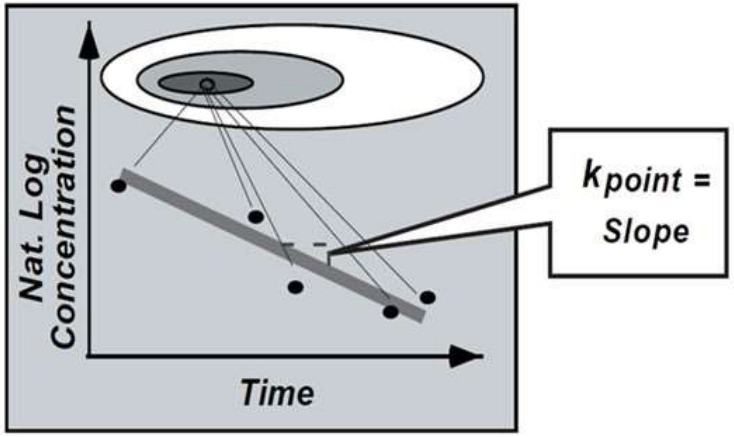
Ground Water Issue

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]

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/ groundwater data
  - 2,253 sites w/ residual LNAPL
  - 972 sites w/ mobile (or migrating) LNAPL
- calculate the source attenuation rate - $\mathbf{k_{source}}$
- assess effects on $\mathbf{k_{source}}$



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

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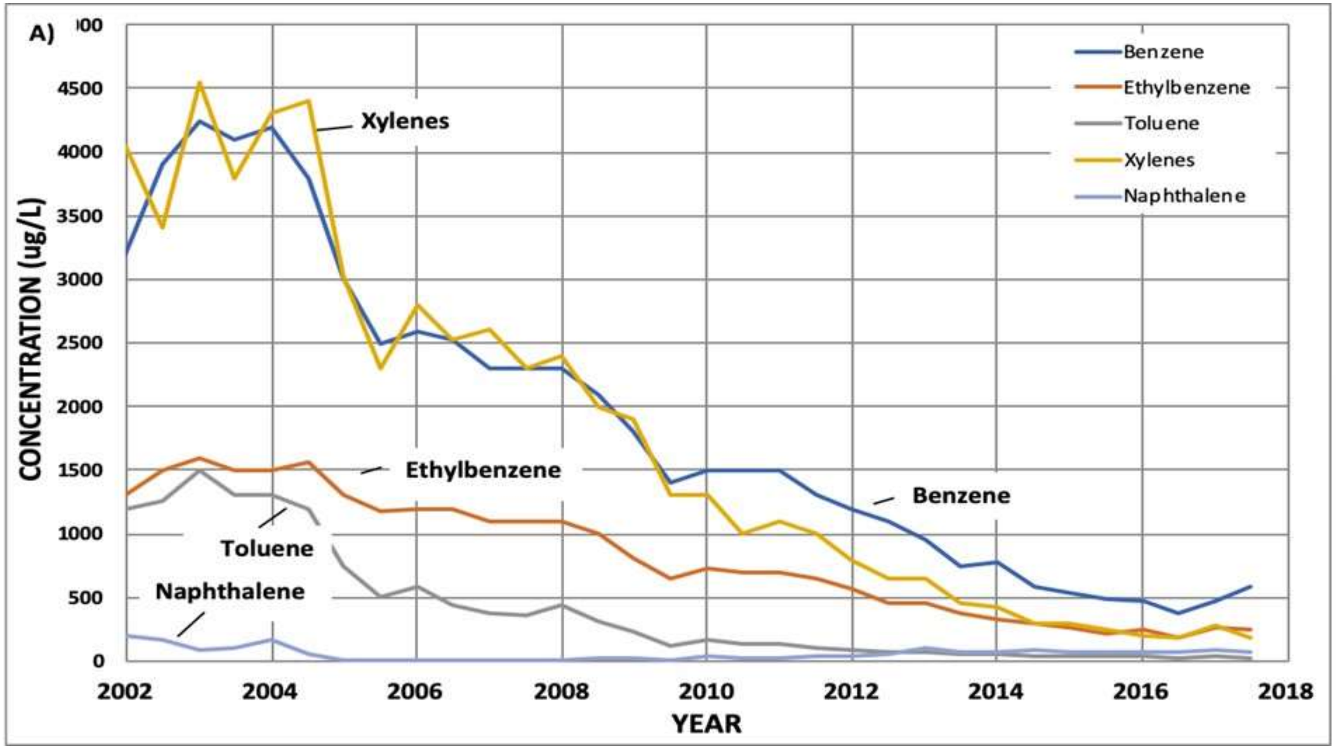
Median GW Source Area Concentrations over Time

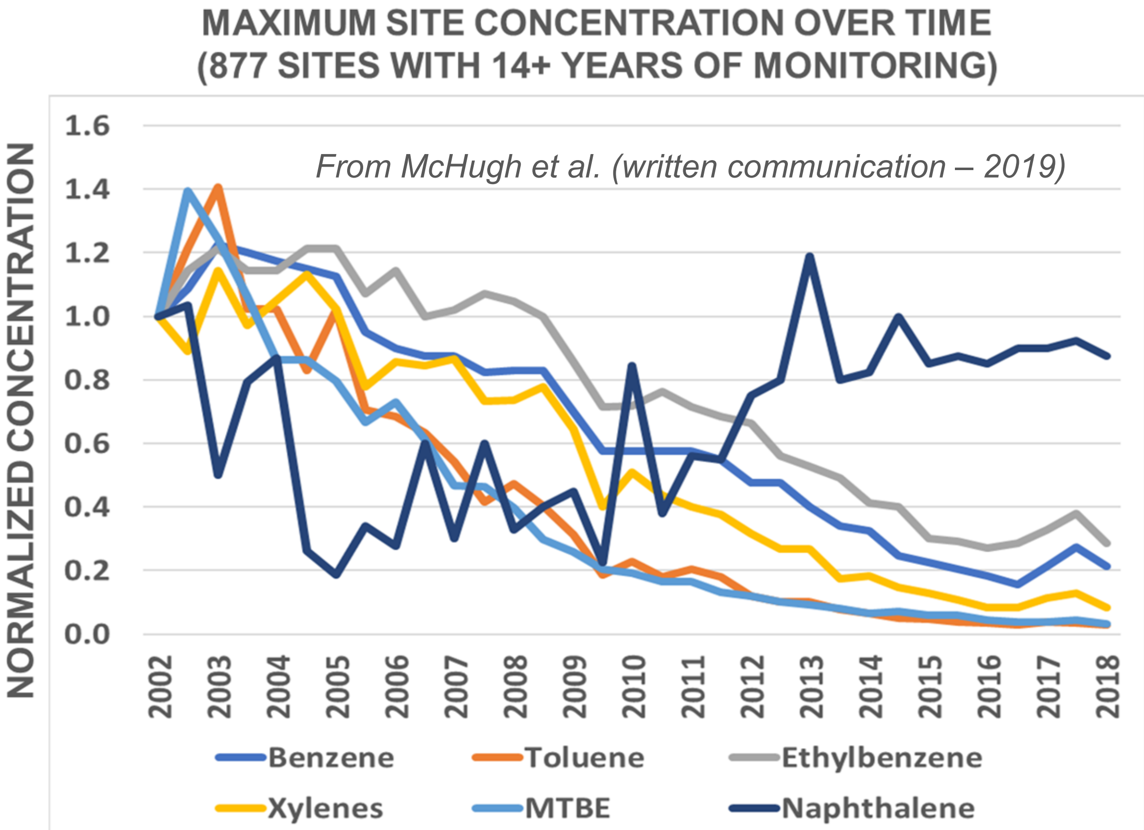


From McHugh et al. (written communication – 2019)

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**

Median GW Source Area Concentrations over Time

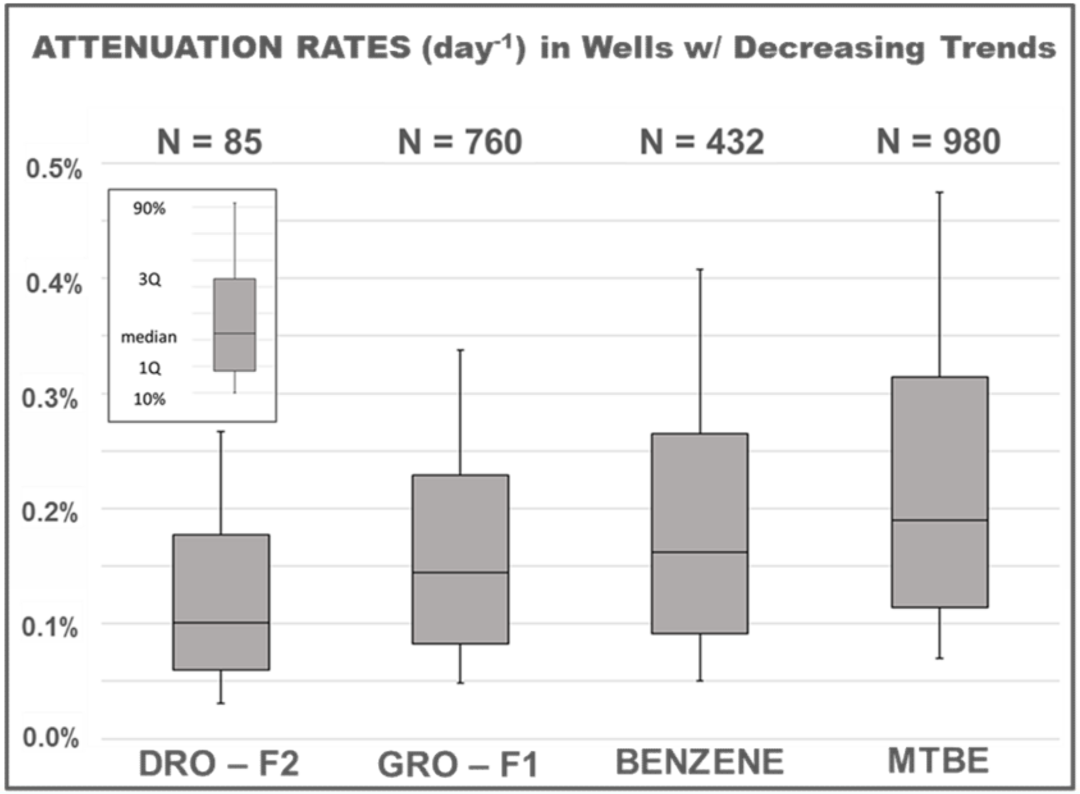


KEY POINT

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

Attenuation Rate Summary For Key COPCs

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

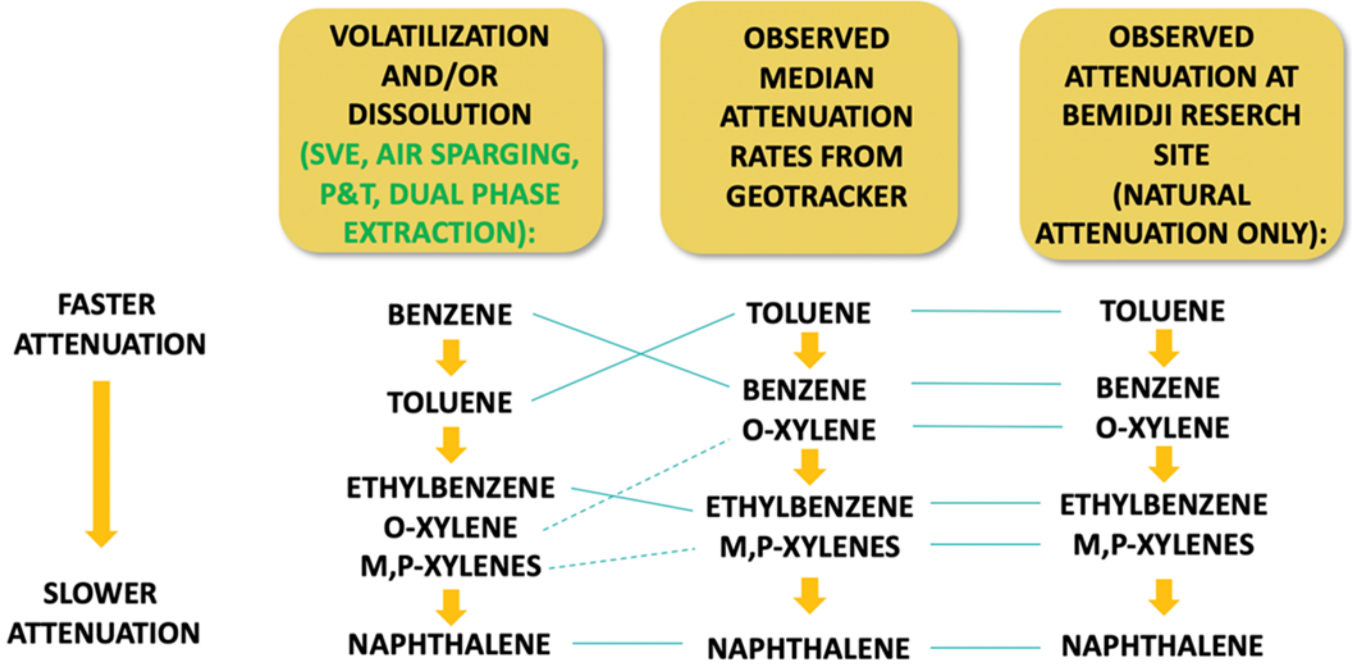


Constituent	Number of Sites	Median Attenuation Rate (d^{-1})	Median Half-Life (yr^{-1})
Benzene	432	0.0016	1.2
MTBE	980	0.0019	1.0
TPH GRO – F_1	760	0.0015	1.3
TPH DRO – F_2	85	0.0010	1.9

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)

Attenuation Rate Summary For Key COPCs



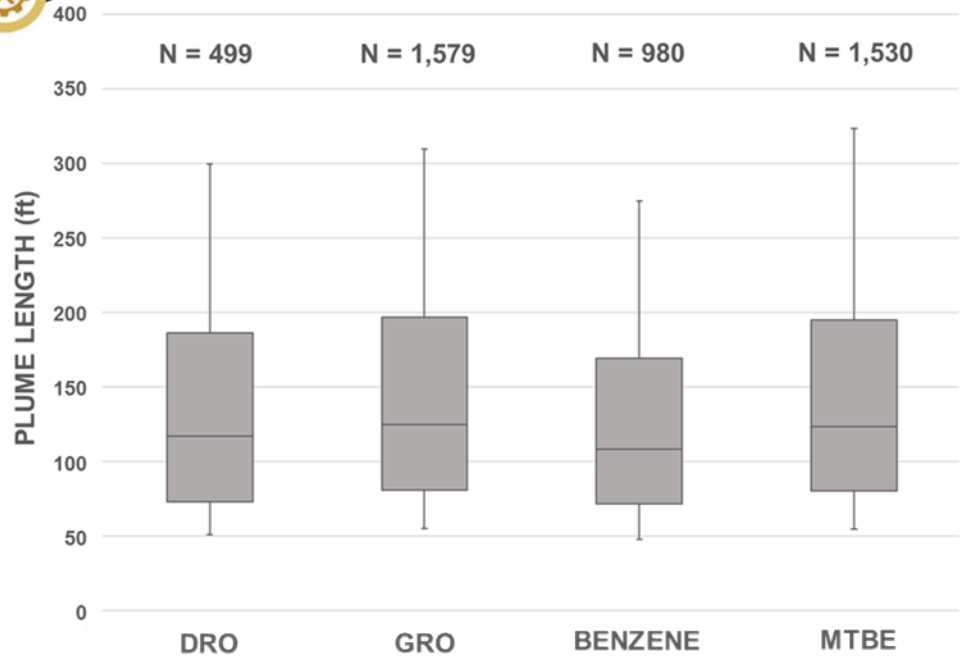
From: McHugh et al. (written communication – 2019)

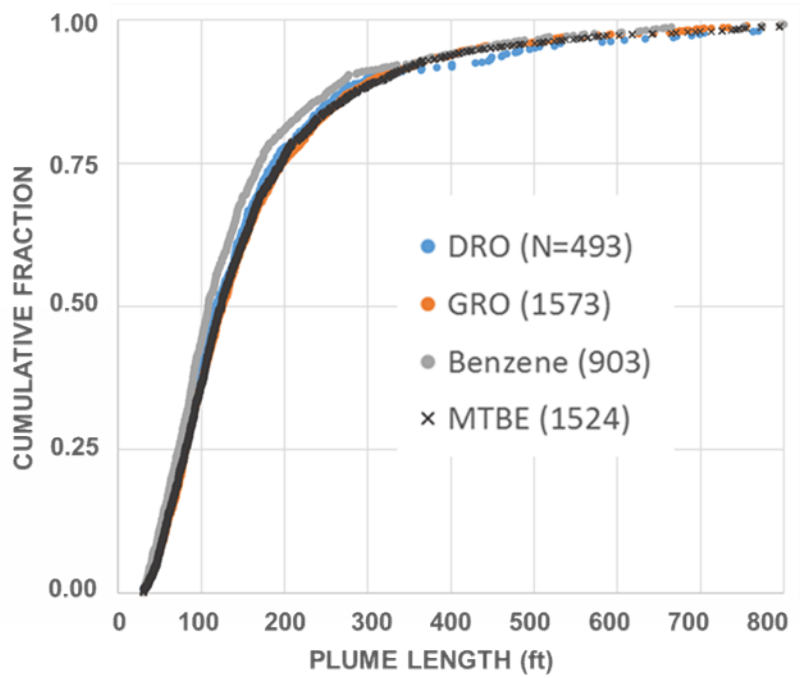
KEY POINT

- 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



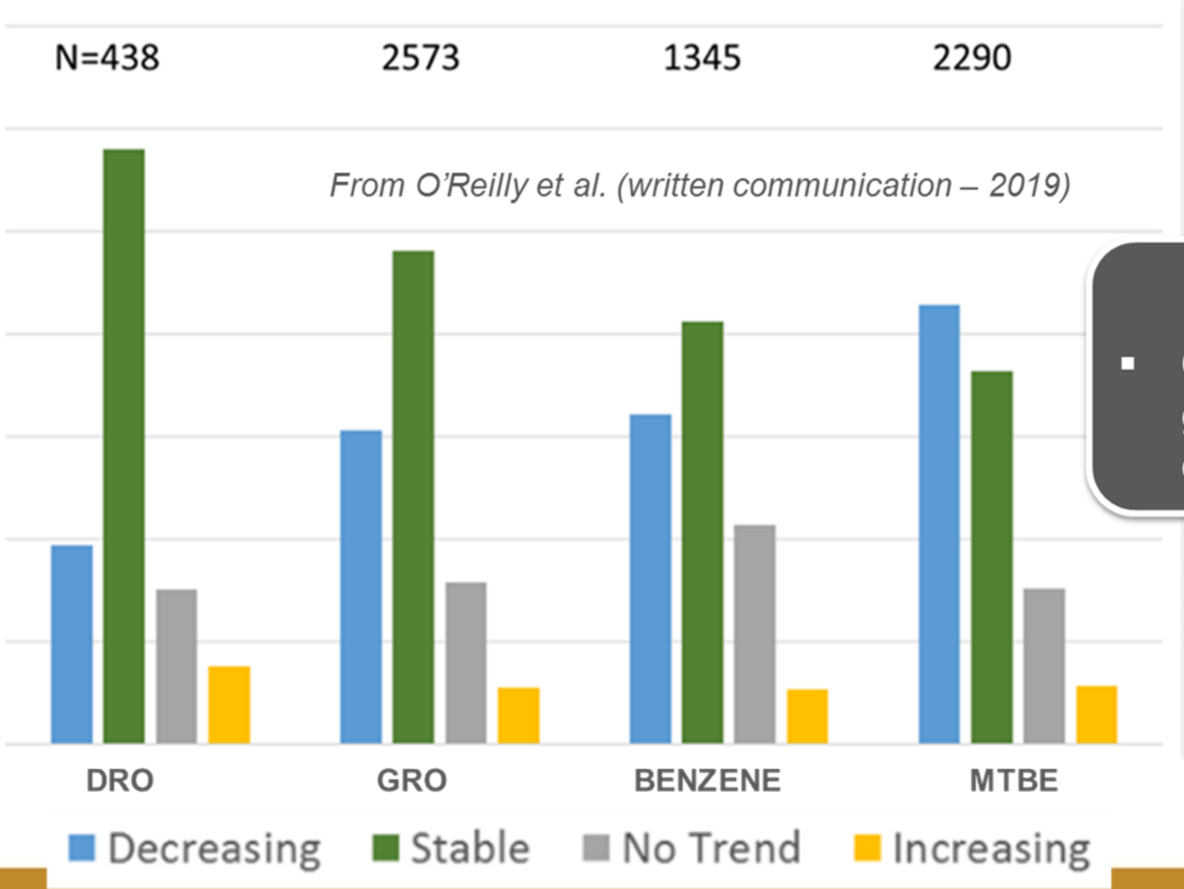


From O'Reilly (written communication, 2019)

KEY POINT

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

Plume Stability

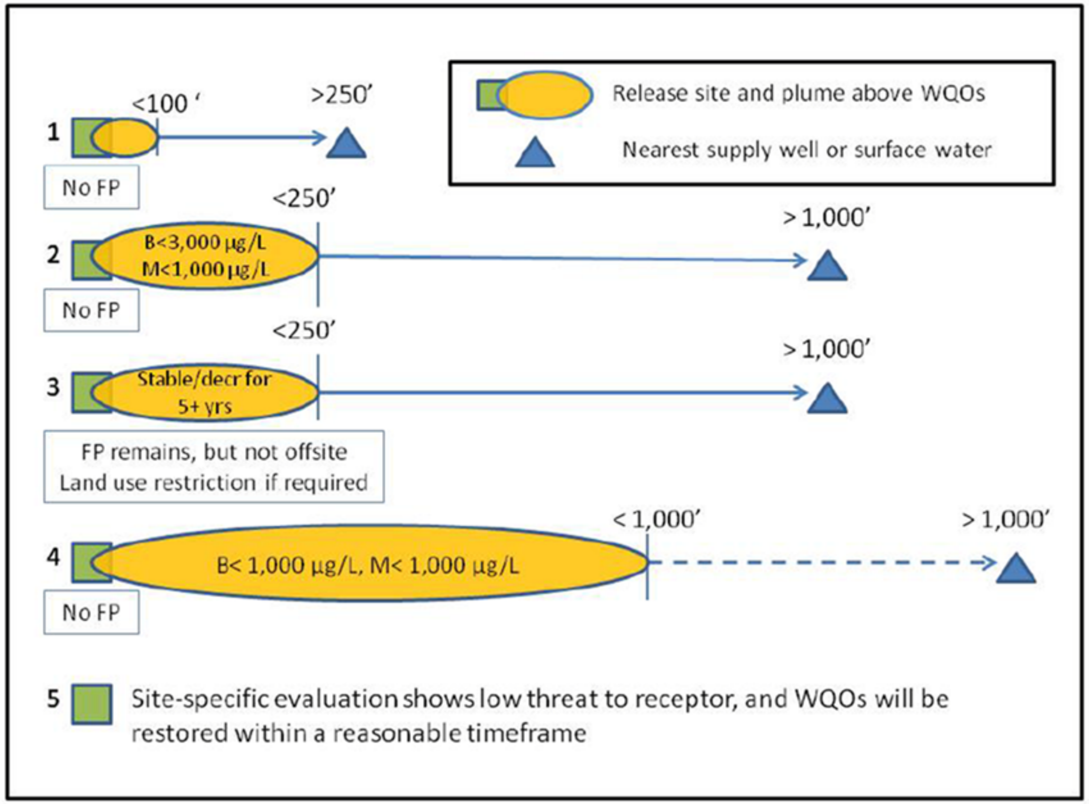


KEY POINT

- COPC plumes are generally stable or decreasing over time

Similar Studies Used to Support US Regulation (California Low-Threat Tank Closure Policy – 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

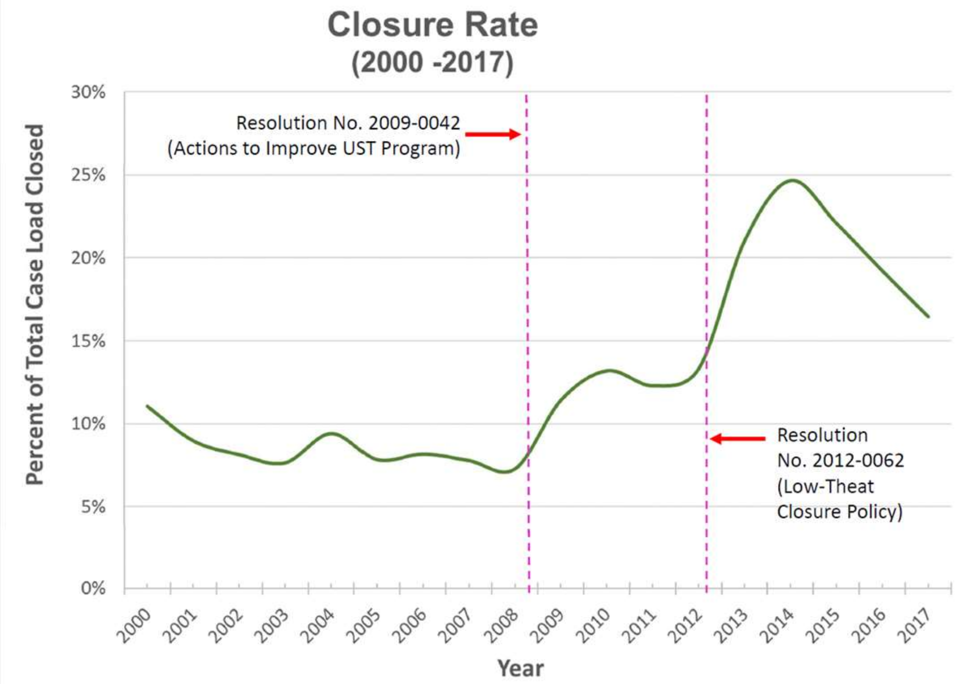
Figure is not to scale

WQO Water Quality Objective

KEY POINT

- science can be used to underpin sustainable, risk-based regulations that address long-term site management (close sites in long-term monitoring)

Similar Studies Used to Support US Regulation (California Low-Threat Tank Closure Policy – 2012)



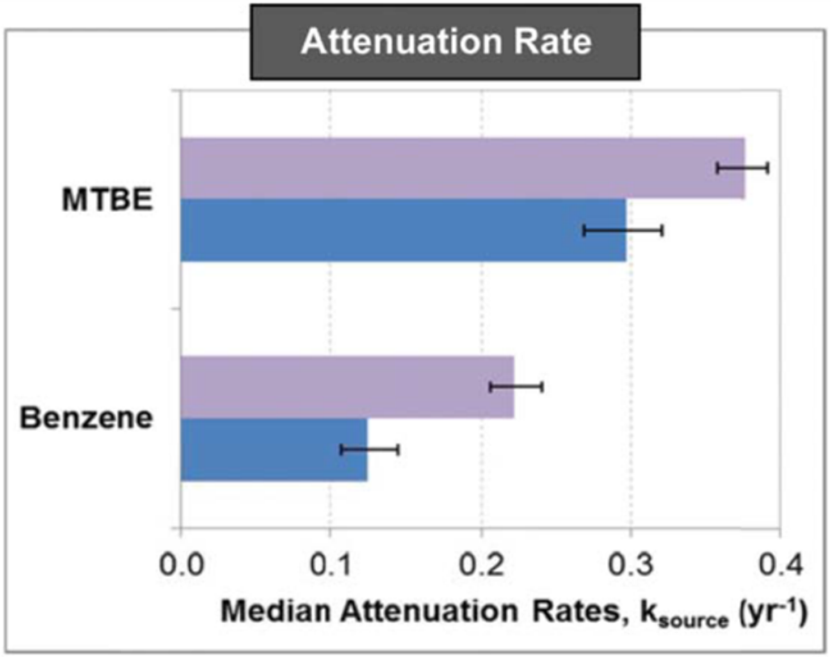
From: California State Water Resources Control Board (2018)

KEY POINT

- # of sites being monitored has decreased by 70% since 2008
- higher concentration sites retained (consistent with intent of low threat policy)

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

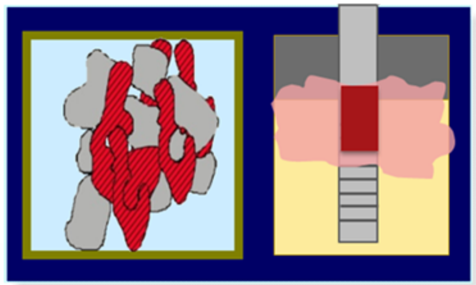
Slower Attenuation Rates At Sites with Mobile LNAPL

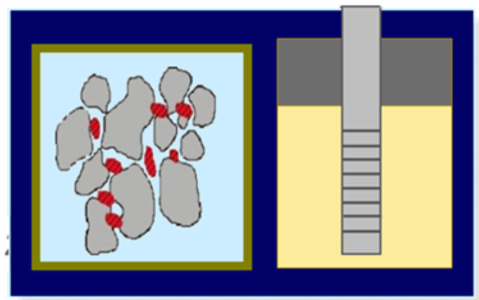


Non-LNAPL Sites (n = 2,253)   LNAPL Sites (n = 972)

Source: Kulkarni et al.,

Mobile LNAPL:
"*LNAPL Site*"





Residual LNAPL:
"*Non-LNAPL Site*"

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

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

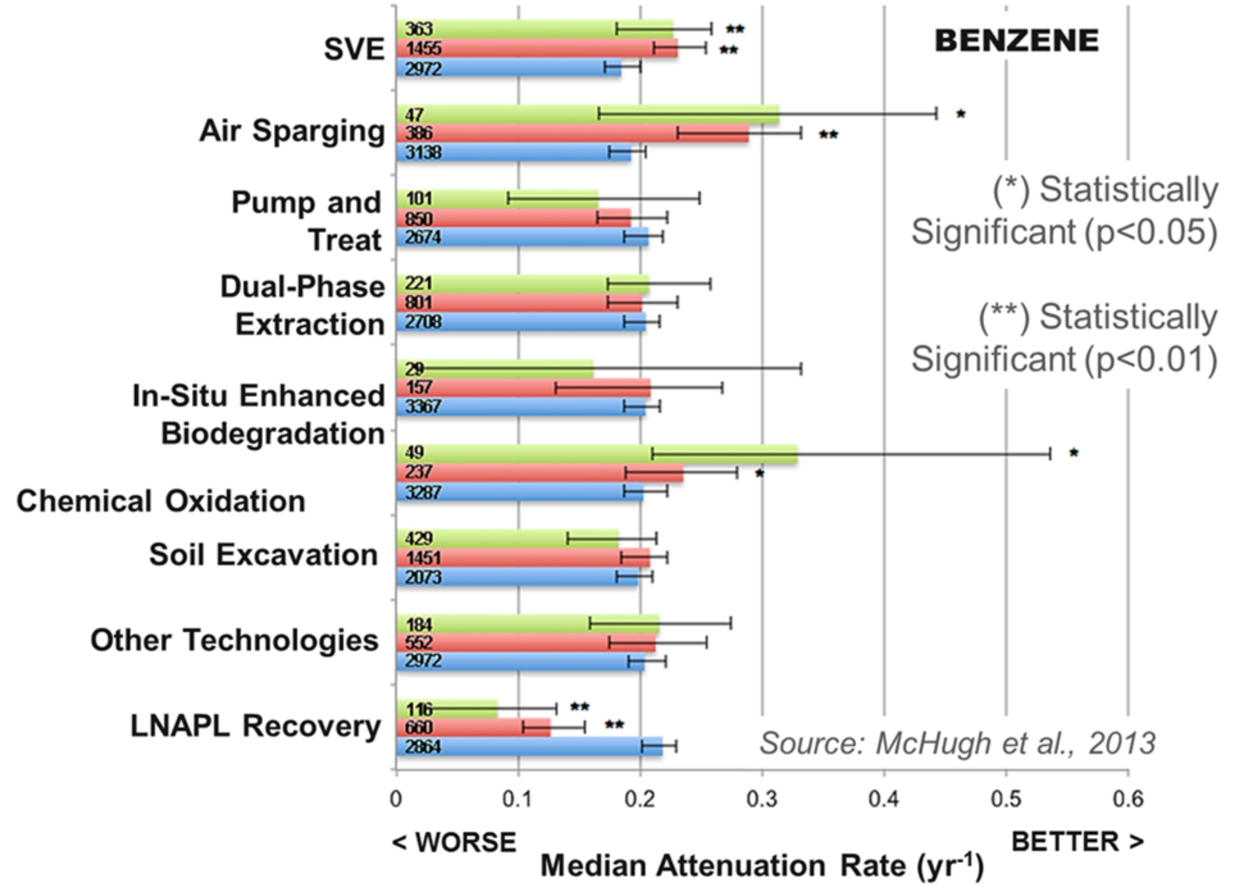
Remedy Type	Median Source Attenuation Rates (yr^{-1}) Benzene	Median Concentration Reduction (%) Benzene	Median Reduction in LNAPL Thickness (%)
LNAPL Recovery (n=327)	*Slower* 0.09	*Lower* 75%	87%
Non - NAPL Recovery (n=444)	0.19 *Faster*	86% *Higher*	91%

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



Legend

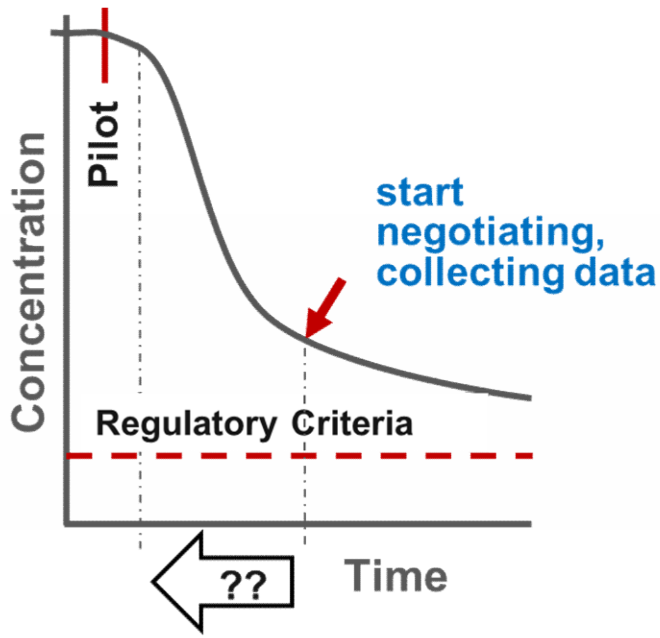
- n Sites with Only Technology
- n Sites with Technology and Some Other Technology
- n Sites without Technology

KEY POINT

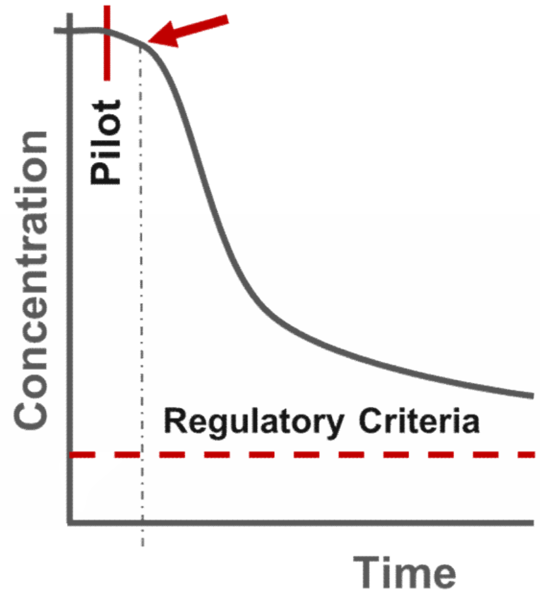
- air-based remediation technologies (and chemical oxidation) had greatest effect on enhancing attenuation rate for benzene

Knowing What Data to Collect… When

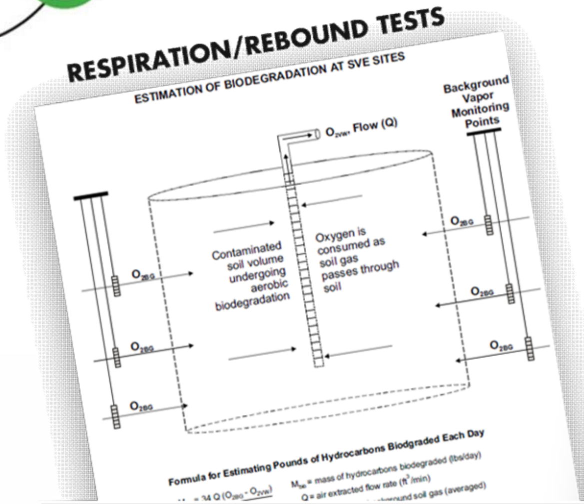
EXISTING SITES

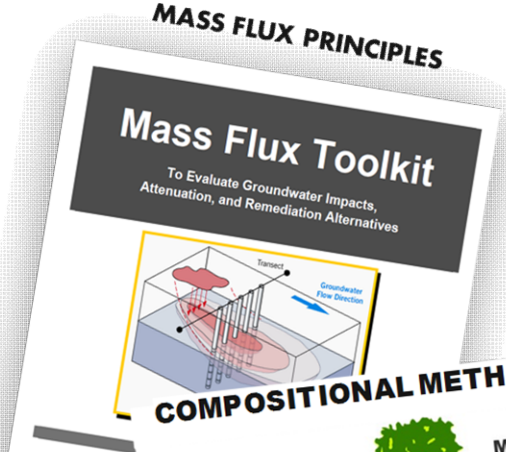


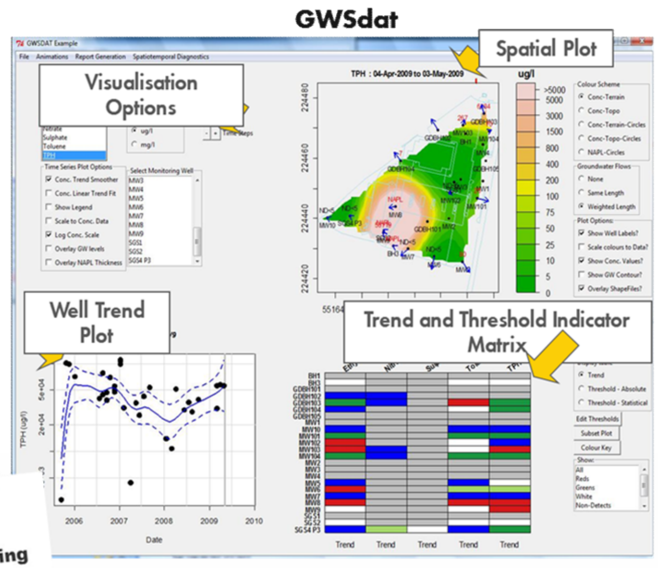
NEW (IDEAL) SITES

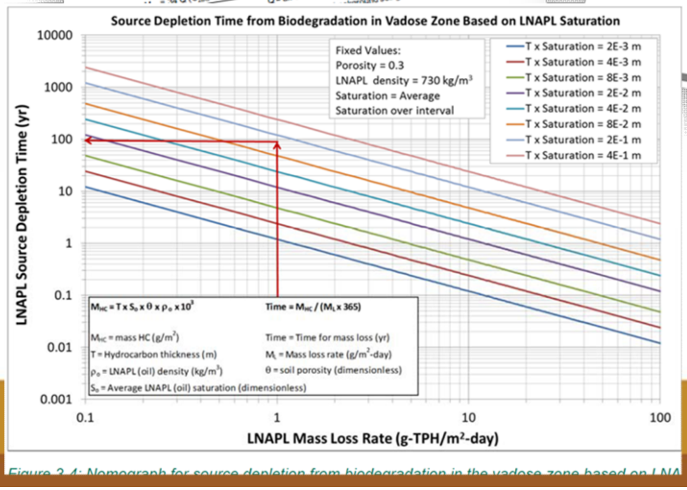


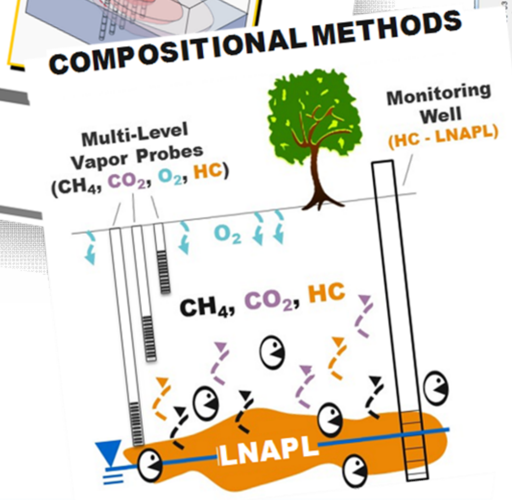
Numerous Tools Exist

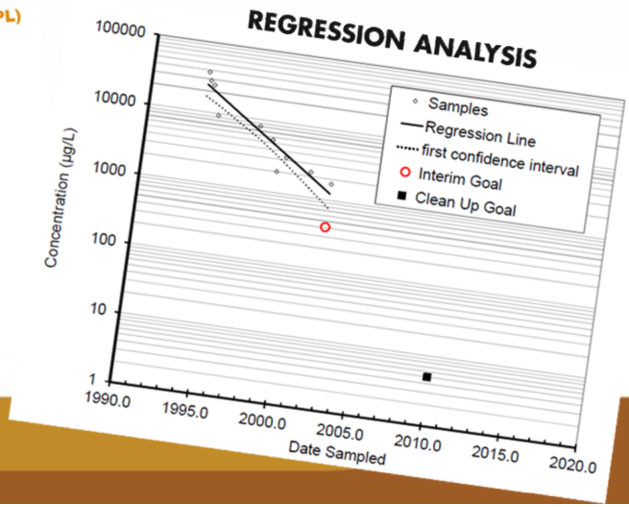






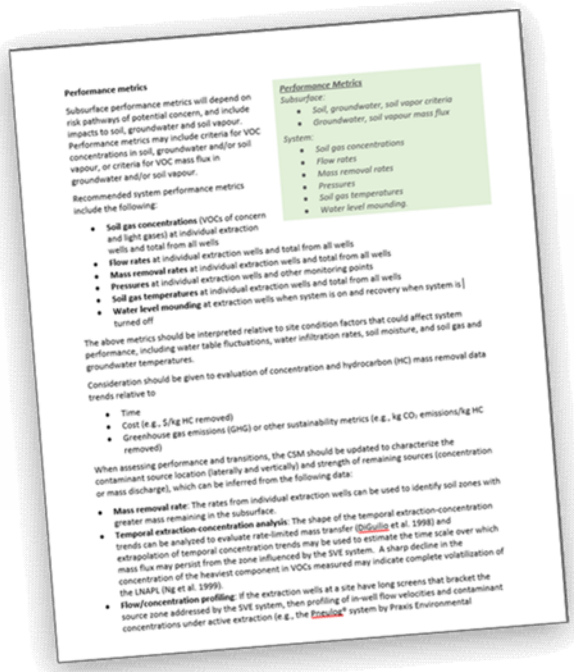






Remedial Technology (e.g., SVE) Fact Sheets

- **GOAL:** more systematic, multiple lines of evidence approach to support transition
- transition (& performance) metrics, e.g.,
  - subsurface concentrations approaching asymptote or regulatory criterion
  - extraction-well concentrations and/or mass-removal rates approaching asymptote
  - rebound tests
  - mass removal rate comparable to or < NSZD rate
  - SVE mass removal rate approaching asymptote while GHG emissions and/or cost per unit mass removal increasing



Performance metrics

Subsurface performance metrics will depend on risk pathways of potential concern, and include impacts to soil, groundwater and soil vapour. Performance metrics may include criteria for VOC concentrations in soil, groundwater and/or soil vapour, or criteria for VOC mass flux in groundwater and/or soil vapour.

Recommended system performance metrics include the following:

- **Soil gas concentrations** (VOCs of concern and light gases) at individual extraction wells and total from all wells
- **Flow rates** at individual extraction wells and total from all wells
- **Mass removal rates** at individual extraction wells and total from all wells
- **Pressures** at individual extraction wells and other monitoring points
- **Soil gas temperatures** at individual extraction wells and total from all wells
- **Water level mounding** at extraction wells when system is on and recovery when system is turned off

Performance Metrics
Subsurface:
- *Soil, groundwater, soil vapor criteria*
- *Groundwater, soil vapour mass flux*

System:
- *Soil gas concentrations*
- *Flow rates*
- *Mass removal rates*
- *Pressures*
- *Soil gas temperatures*
- *Water level mounding.*

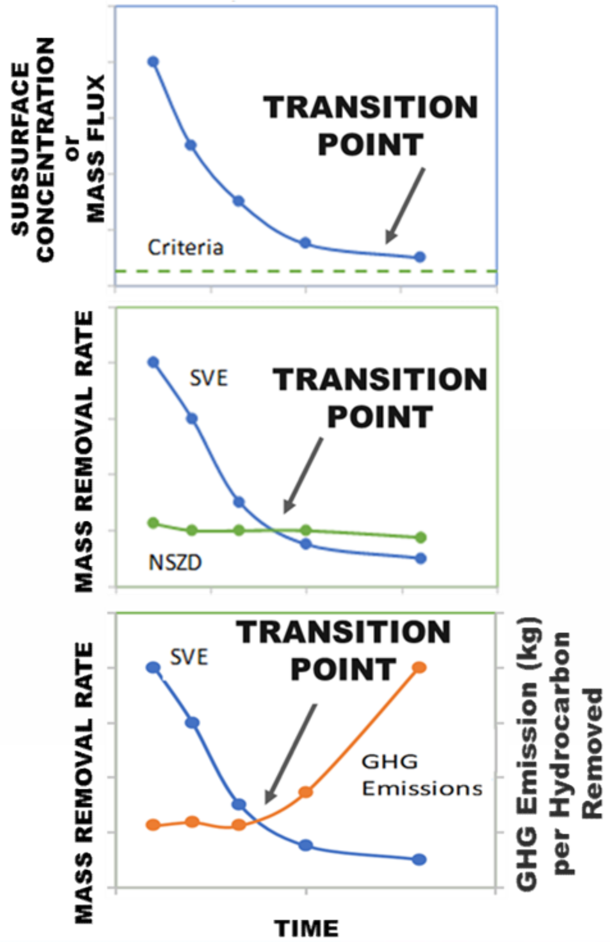
The above metrics should be interpreted relative to site condition factors that could affect system performance, including water table fluctuations, water infiltration rates, soil moisture, and soil gas and groundwater temperatures.

Consideration should be given to evaluation of concentration and hydrocarbon (HC) mass removal data trends relative to

- Time
- Cost (e.g., $/kg HC removed)
- Greenhouse gas emissions (GHG) or other sustainability metrics (e.g., kg CO_2 emissions/kg HC removed)

When assessing performance and transitions, the CSM should be updated to characterize the contaminant source location (laterally and vertically) and strength of remaining sources (concentration or mass discharge), which can be inferred from the following data:

- **Mass removal rate**: The rates from individual extraction wells can be used to identify soil zones with greater mass remaining in the subsurface.
- **Temporal extraction-concentration analysis**: The shape of the temporal extraction-concentration trends can be analyzed to evaluate rate-limited mass transfer (DiGulio et al. 1998) and extrapolation of temporal concentration trends may be used to estimate the time scale over which mass flux may persist from the zone influenced by the SVE system. A sharp decline in the concentration of the heaviest component in VOCs measured may indicate complete volatilization of the LNAPL (Ng et al. 1999).
- **Flow/concentration profiling**: If the extraction wells at a site have long screens that bracket the source zone addressed by the SVE system, then profiling of in-well flow velocities and contaminant concentrations under active extraction (e.g., the Pneulog® system by Praxis Environmental



Conclusions

- hydrocarbon generally remains despite best efforts to recover/remediate
- must rely on natural attenuation to reach risk-based clean-up goals (drinking water standards) w/in a reasonable timeframe
- attenuation rates of petroleum hydrocarbons are well documented
  - rates relatively consistent for wide-range of key COPCs
  - rates are significant (most plumes stable or decreasing)
  - few petroleum hydrocarbon plumes extend beyond 150 m
  - rates are not significantly increased by hydraulic LNAPL recovery
- science can be used to underpin regulations that prevent risks to human health and the environment and focus limited resources on sites that matter most