# Compendium of Tools and Methods to Support the Optimization and Sustainable Transition and Termination of Active Remediation Systems

Dr. Ian Hers, Hers Environmental Consulting, Inc., Dr. Parisa Jourabchi, ARIS Environmental Ltd., Dr. Matthew Lahvis, Shell Global Solutions

**SABCS/GeoEnviroPro Workshop**
**7 October 2020**

HERS Environmental Consulting, Inc.

Shell

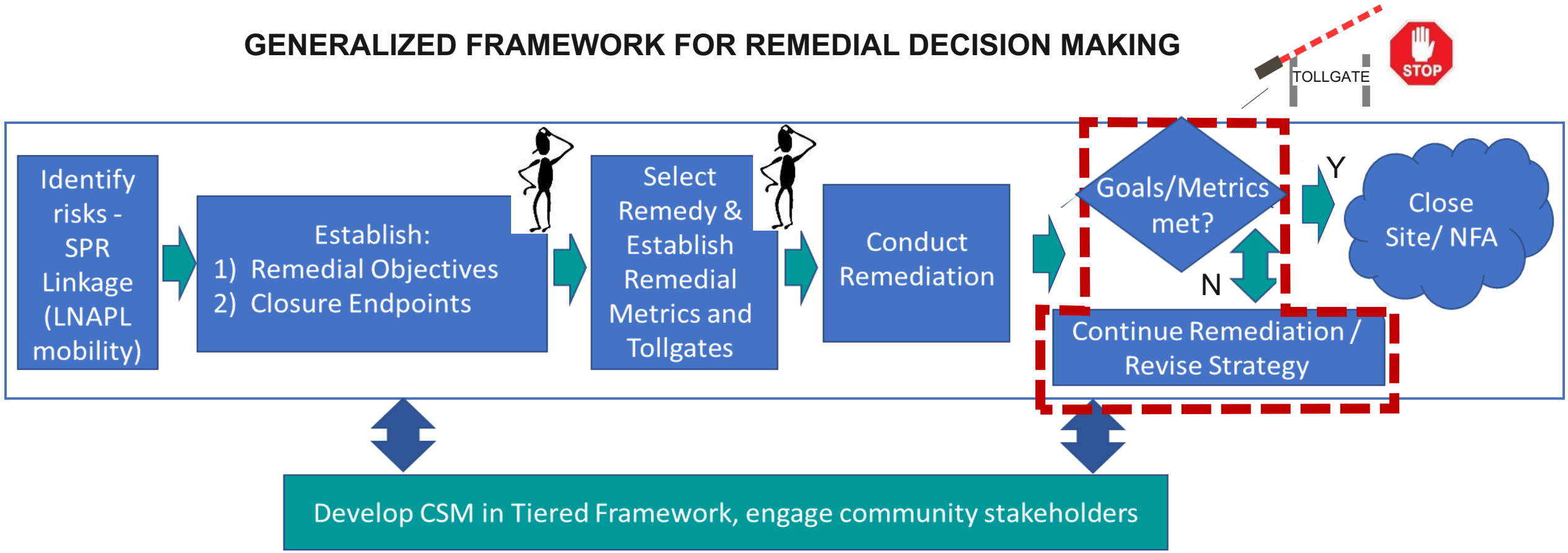
ARIS
Applied Research for Innovative Solutions

# Outline

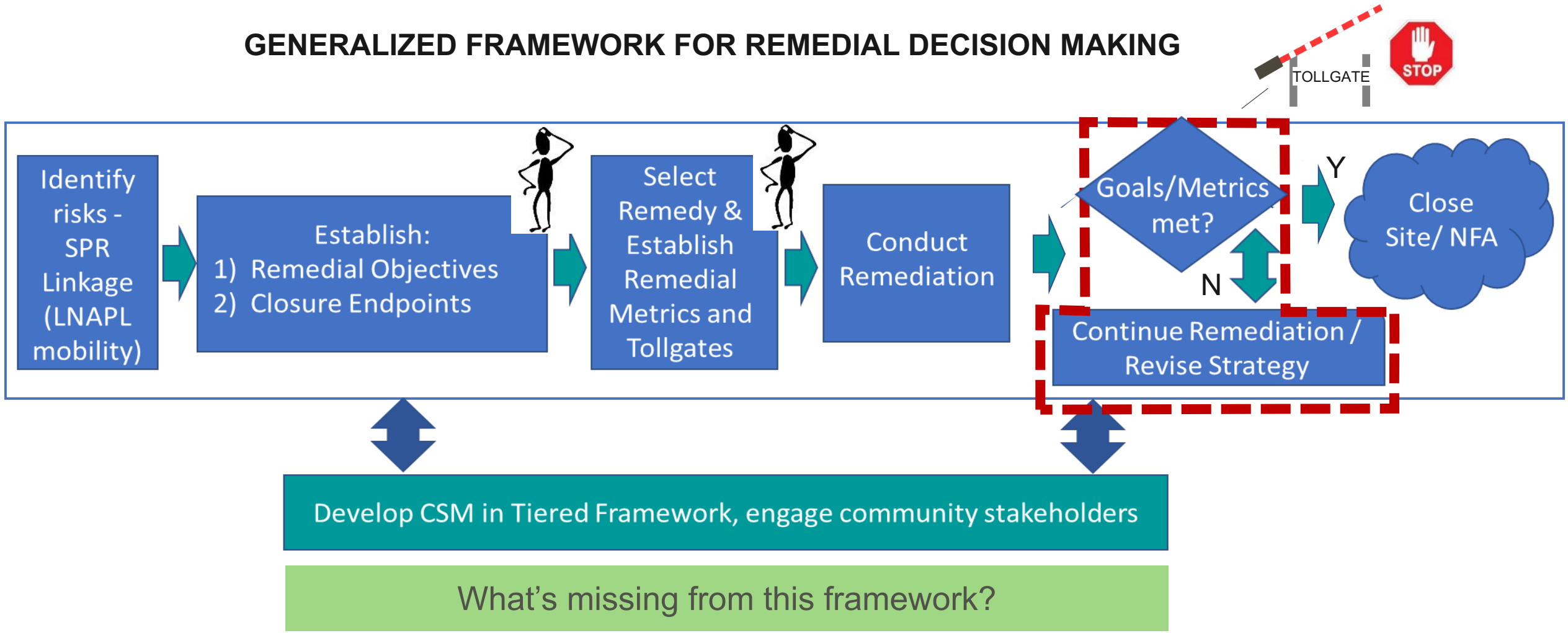
1. Background on Natural Attenuation
2. Motivation for Compendium
3. Compendium Roadmap
4. Compendium SVE Factsheet
5. Summary

Compendium context are petroleum hydrocarbon impacted sites, but principles apply to any contaminant that undergoes natural attenuation

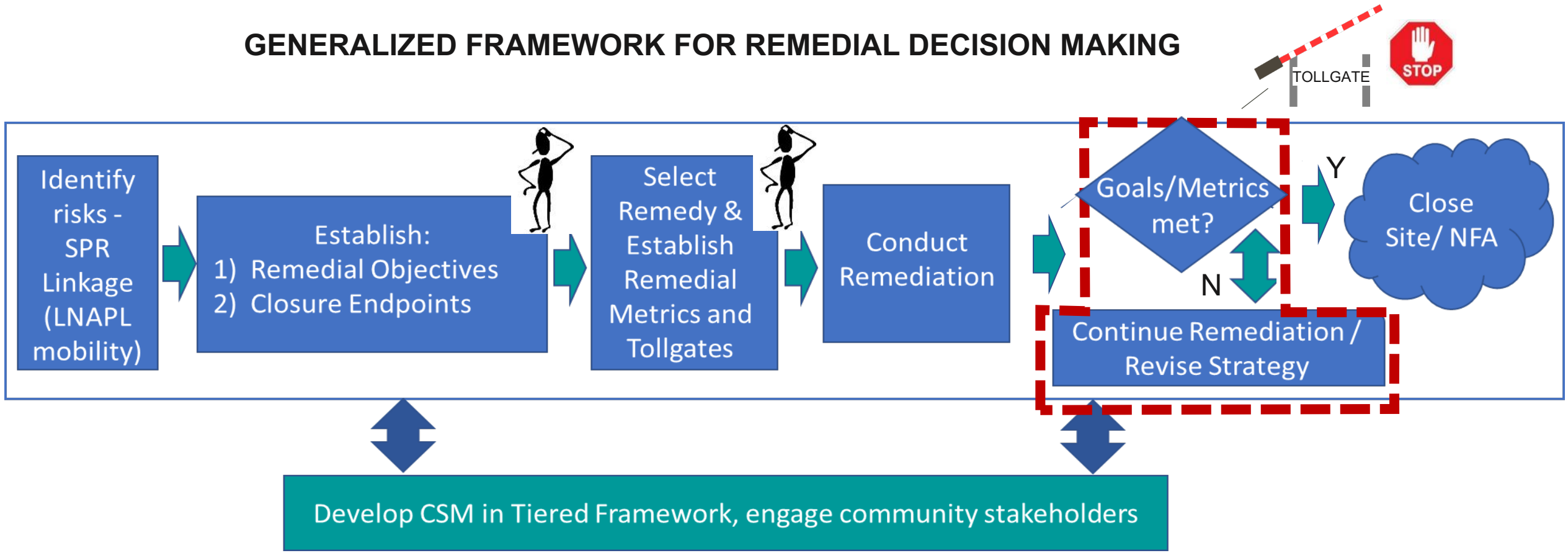
# Issue: Getting to Closure Often Challenging



# Issue: Getting to Closure Often Challenging



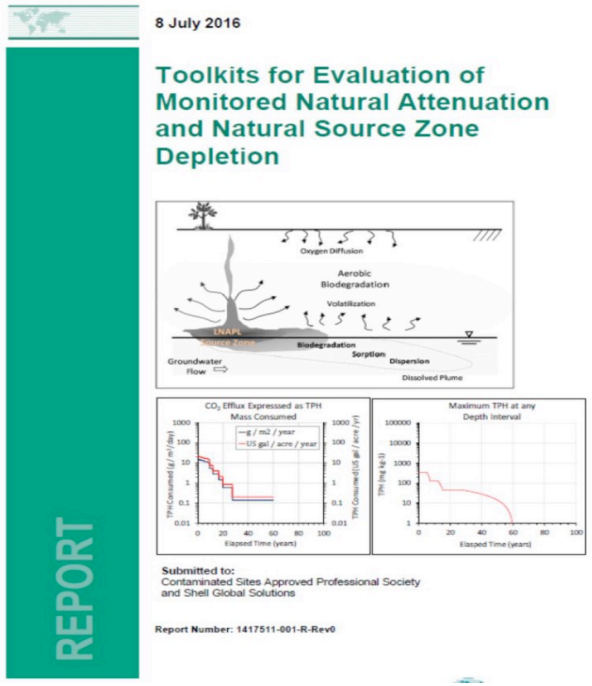
# Issue: Getting to Closure Often Challenging



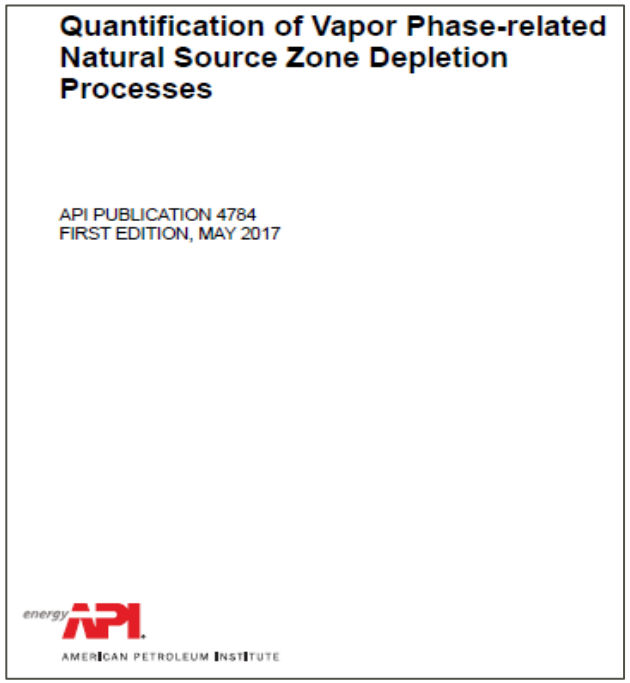

Understanding of and incorporation of natural attenuation and sustainability in framework can help in getting to closure (or selecting right remedy in the first place)

# Numerous Guidance & Research on Natural Attenuation Exist

CSAP-Shell-Golder Remediation "Toolkits" 2016 (1&2)




API 2017




CRC Care 44 2018

CRC Care 47 2020

Groundwater Monitoring&Remediation

Garg et al 2017

ITRC 2018

REFERENCES ARE PROVIDED AT END OF PRESENTATION

# Natural Attenuation and Source Depletion Processes

**ARIS ENVIRONMENTAL**

**BIODEGRADATION**

**DISSOLUTION**

**VOLATILIZATION**

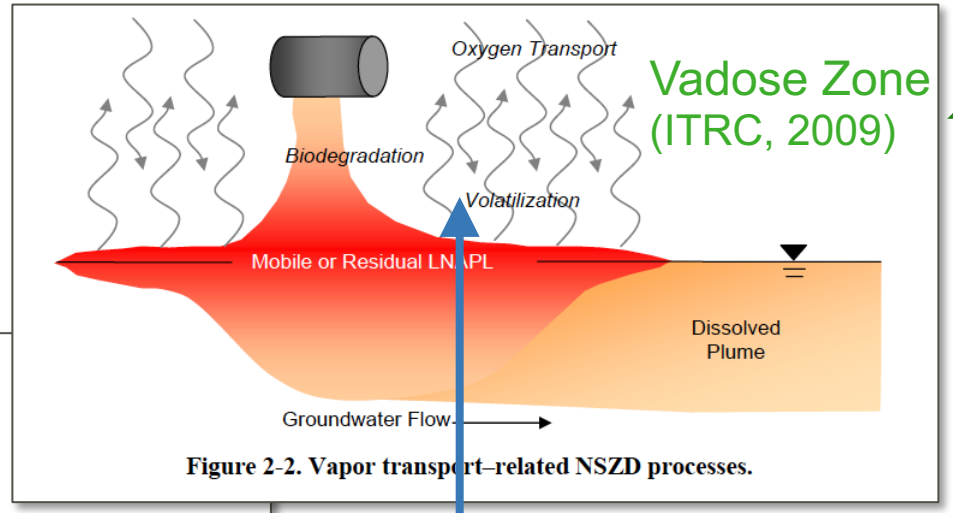



Figure 2-2. Vapor transport–related NSZD processes.

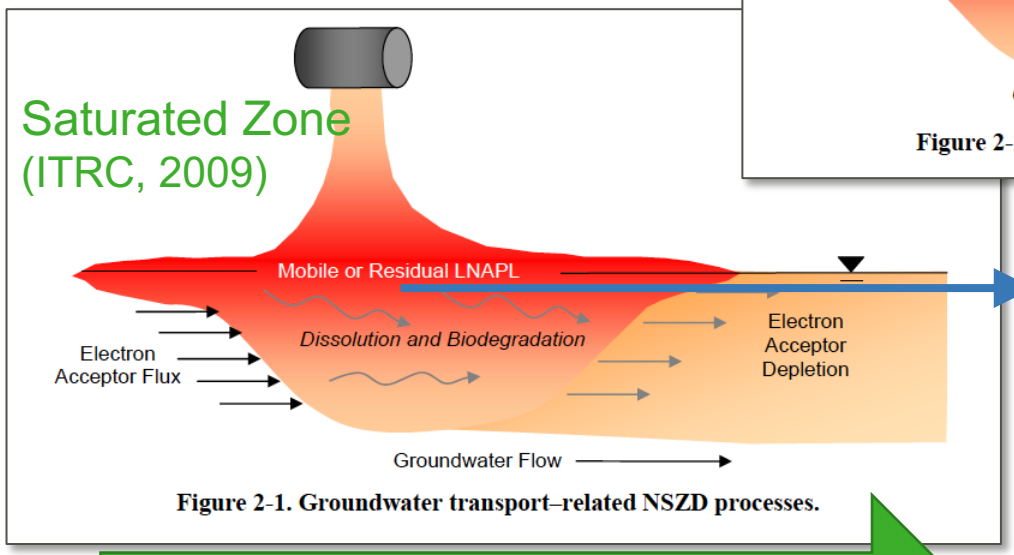



Figure 2-1. Groundwater transport–related NSZD processes.

Dissolved Phase Gradients

Vapour Phase Gradients

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

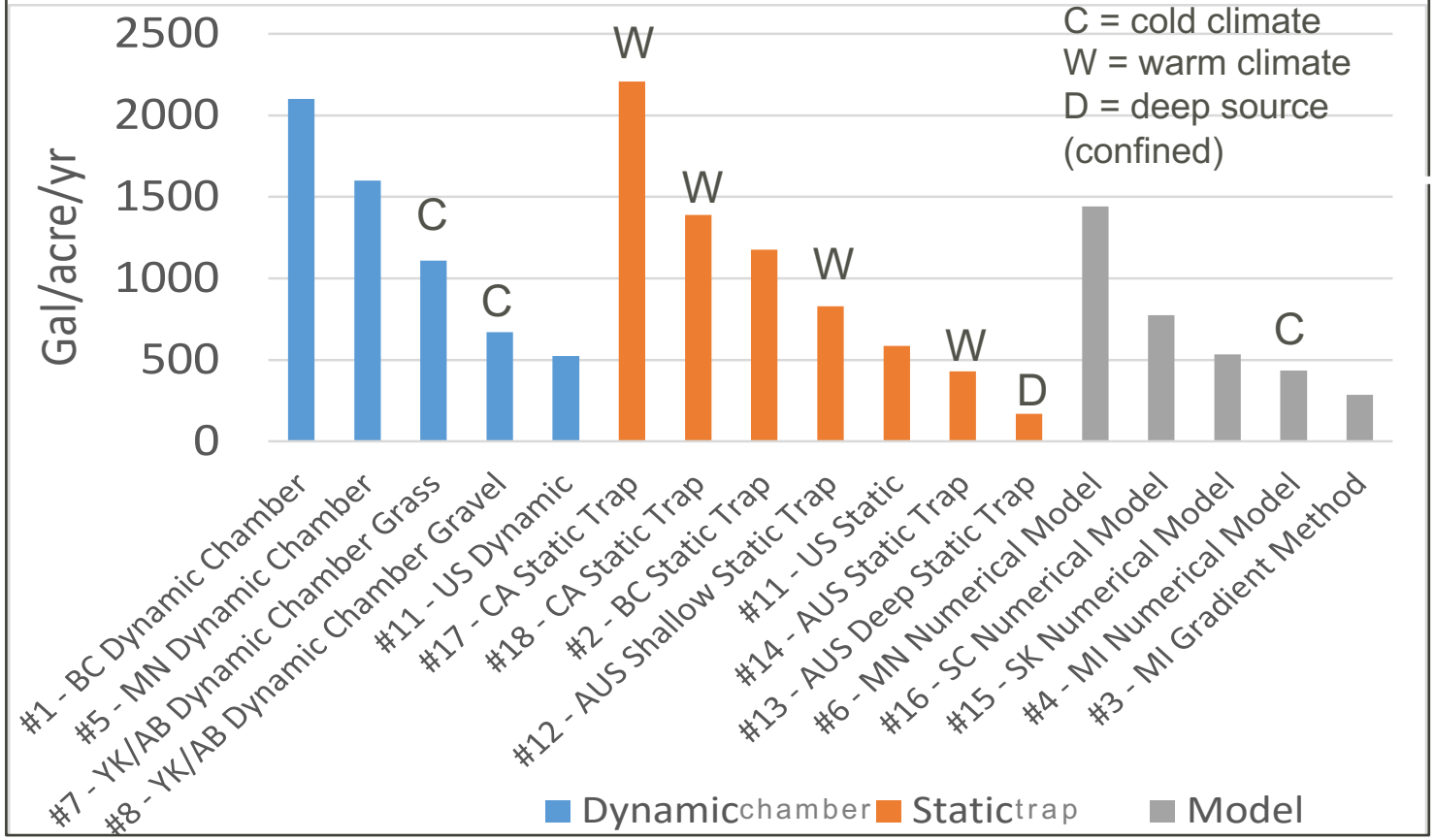


Photograph from ITRC LNAPL Guidance (2018)

# Natural Source Zone Depletion (NSZD) Rates

## PRIMARILY UNSATURATED ZONE

**CSAP-Shell-Golder Remediation Toolkits (2016)[1]: N = 17 Typical range site means: 500-1500 US gal/acre/yr**




**Garg et al. 2017**
N = 25 sites
Primarily $CO_2$ efflux method
$25^{th}$,$50^{th}$,$75^{th}$ percentiles = **700, 1100, 2800** US gal/acre/yr

**CRC Care 47 2020**
N = 6 sites
$CO_2$ efflux, soil gas gradient & temperature methods
Highly variable site conditions
Range site average = **240-9,500** US gal/acre/yr

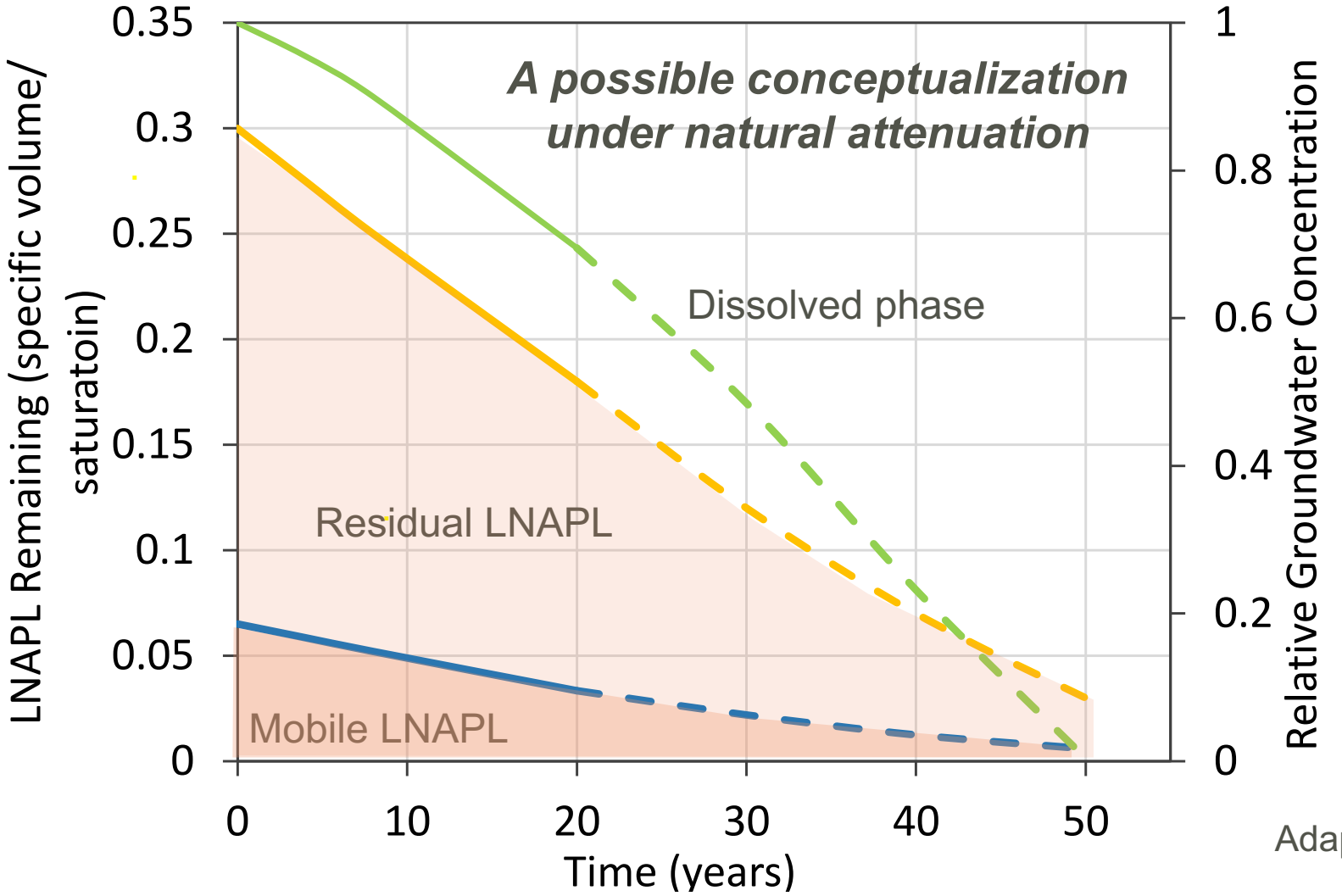
1 USgal/acre/yr = 9.35 L/hectare/yr

HERS Environmental Consulting, Inc.

[1] https://csapsociety.bc.ca/wp-content/uploads/Monitored-Natural-Attenuation-Toolkit-for-Evaluation-1-and-2_combined-FINAL-.pdf CSAP = Contaminated Sites Approved Professional Society of BC

# Natural and Enhanced Attenuation Path (NEAP) Model

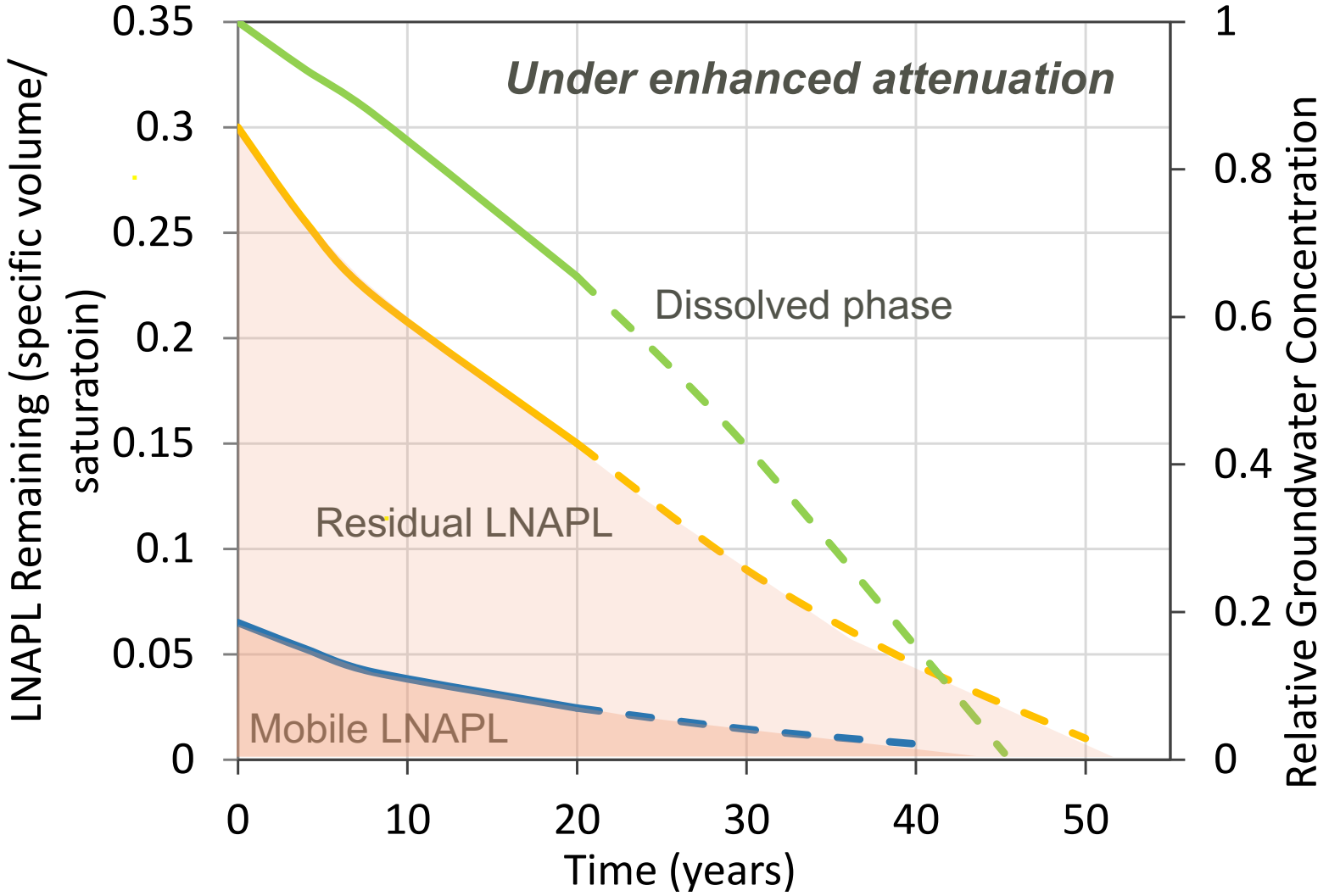
## WHAT IS APPROX. REMEDIAL TIME FRAME UNDER NATURAL ATTENUATION?




Adapted from API (2018)

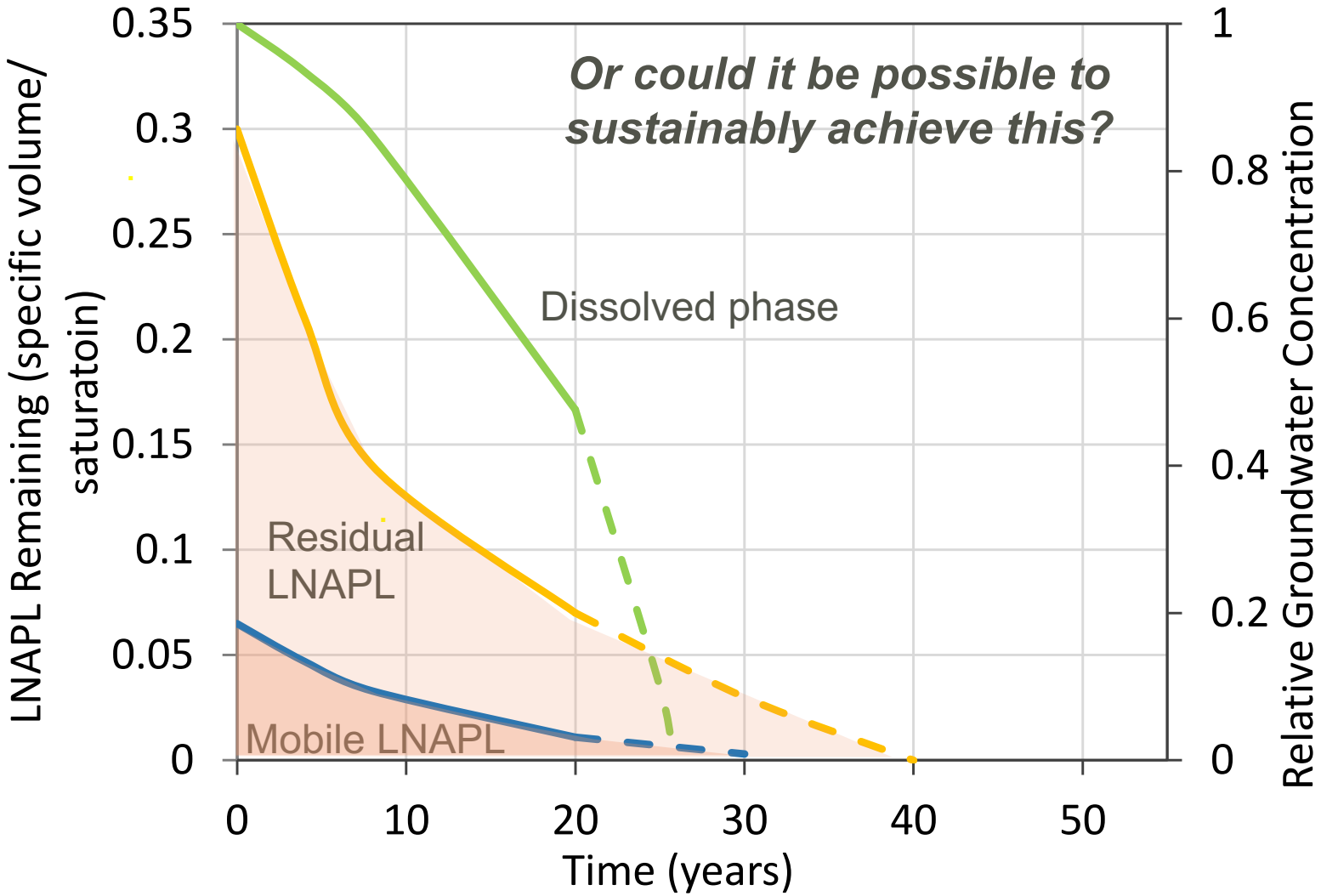
# Natural and Enhanced Attenuation Path (NEAP) Model

## WHAT IS APPROX. REMEDIAL TIME FRAME UNDER ENHANCED ATTENUATION?



# Natural and Enhanced Attenuation Path (NEAP) Model

## WHAT IS APPROX. REMEDIAL TIME FRAME UNDER ENHANCED ATTENUATION?



# Insight from Big Data - Multi-Site Study of Retail Gasoline Sites

**MCHUGH ET AL. 2014**

- Data from 4,000 sites in California with monitoring from 2001-2011 with ≥ 4 years of data
- Estimated median benzene attenuation rates:
  - All sites (most with active remediation) = 0.18 $yr^{-1}$
  - NSZD/MNA only (72 sites) = 0.13 $yr^{-1}$
- Only slightly faster attenuation rate for active remediation – effect of remediation limited

***California GeoTracker Database "Big-data"***

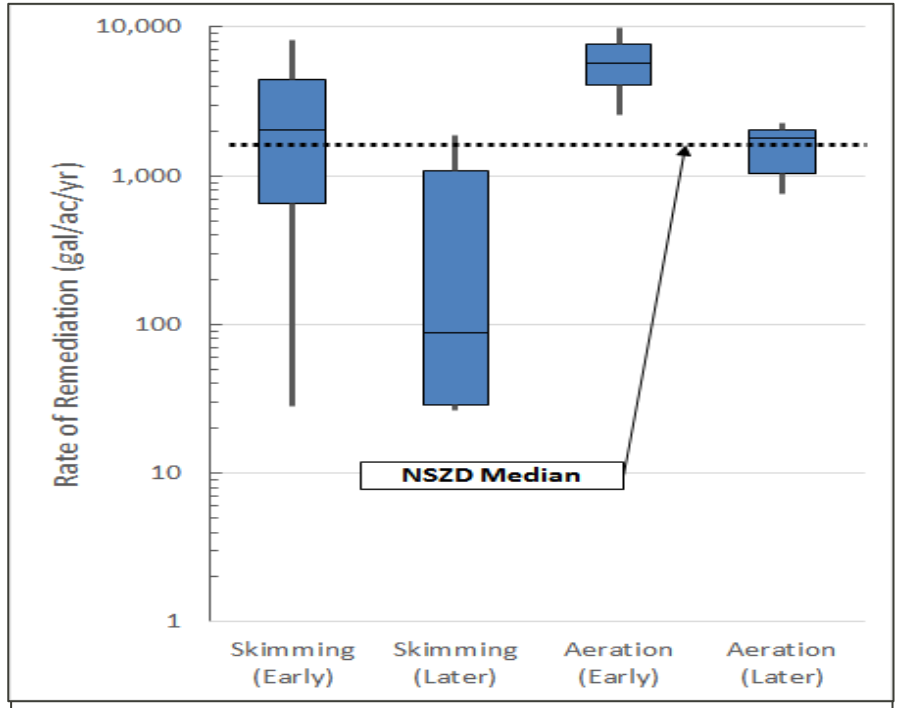
| Technology | Constituent | Increase in attenuation rate at wells in/adjacent source zone (%) |
|---|---|---|
| **SVE** | benzene | 28 |
| | MTBE | 11 |
| **Air Sparging** | benzene | 53 |
| | MTBE | 22 |
| **Chemical Oxidation** | benzene | 20 |
| **Pump & Treat** | MTBE | 17 |

Assuming median benzene attenuation rate = 0.13 $yr^{-1}$ the timeline for attenuation from 10 mg/L to 5 µg/L = 58 years

# Insight from Comparisons of Active to Natural Depletion Rates

- Case studies indicate NSZD rates are typically 500-1,500 US gal/acre/yr (Remediation Toolkits 2016)
- Longer-term rates appear to be quasi zero-order (Garg et al. 2017)
- NSZD rates are often similar to or greater than later-stage active LNAPL removal rates for technologies such as LNAPL pumping, SVE, and MPE

**Key points:** Baseline & subsequently measured NSZD rates can support decisions for technology selection and transition over project life-cycle as a more sustainable approach




(Median NSZD rate from Garg et al., 2017. Remedial system depletion rate data modified from Palaia, T. 2016. NSZD rate assessment. Applied NAPL Science Review 6.)

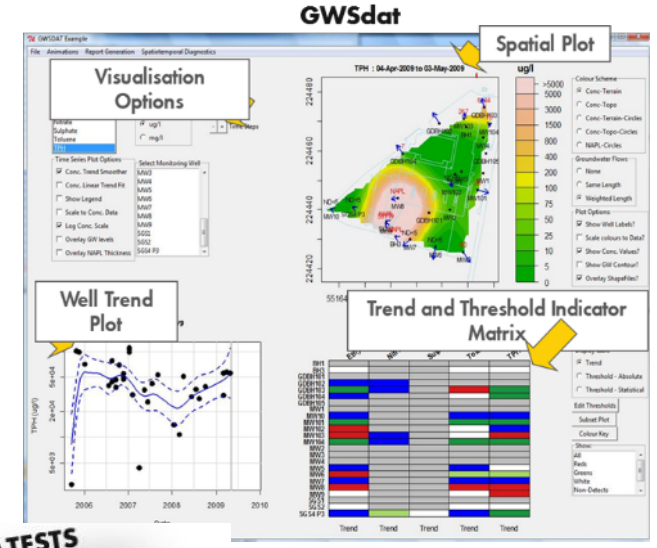
**CRC Care 47 2020**: NSZD rates > active LNAPL recovery rates at 5 of 6 sites

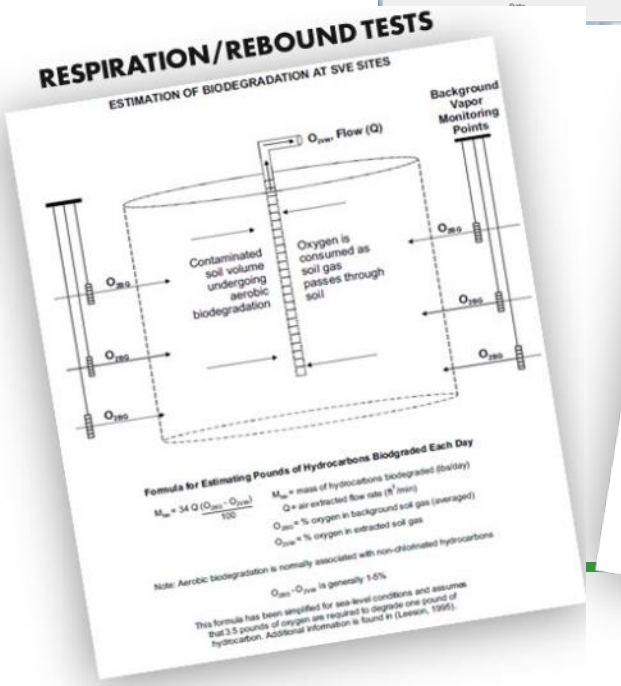
# Compendium Project - "Exit Strategy" Toolkit

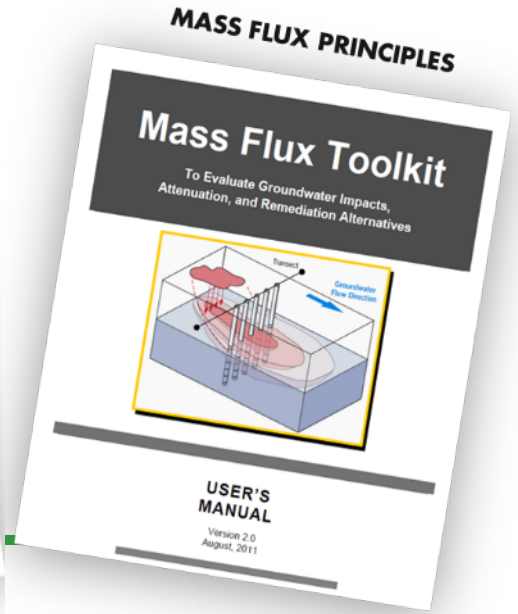
## A MLE Approach to Terminating Active Recovery (and Selecting Right Remedy in First Place)

- **ISSUE:** challenge w/ terminating active recovery
  - poorly defined remedial objectives and performance metrics
  - insufficient documentation of natural attenuation
  - lots of available tools to assess performance, yet applied ad hoc
  - limited (if any) consideration of transition thresholds or points (which in some cases may be endpoints)
  - mechanistic guidance is lacking

- **GOAL:**
  - improved remedial decision making
    - ✓ systematic MLE approach to initiating/ terminating active recovery
    - ✓ optimized active recovery systems
    - ✓ more successful stakeholder communication




HERS Environmental Consulting, Inc.

# Compendium Project Overview

## COLLABORATION OF SHELL/ARIS ENVIRONMENTAL/HERS ENVIRONMENTAL

**Roadmap:**

- Stage 1: Risk Evaluation & Identification
- Stage 2: Baseline Assessment
- Stage 3: Remedy Selection & Implementation
- Stage 4: Performance Evaluation, Optimization & Transition Assessment

**Factsheets:**

1. **SVE**
2. **Natural Source Zone Depletion (NSZD)**
3. LNAPL Hydraulic Recovery
4. Bioventing

Tentative publication date: early 2021

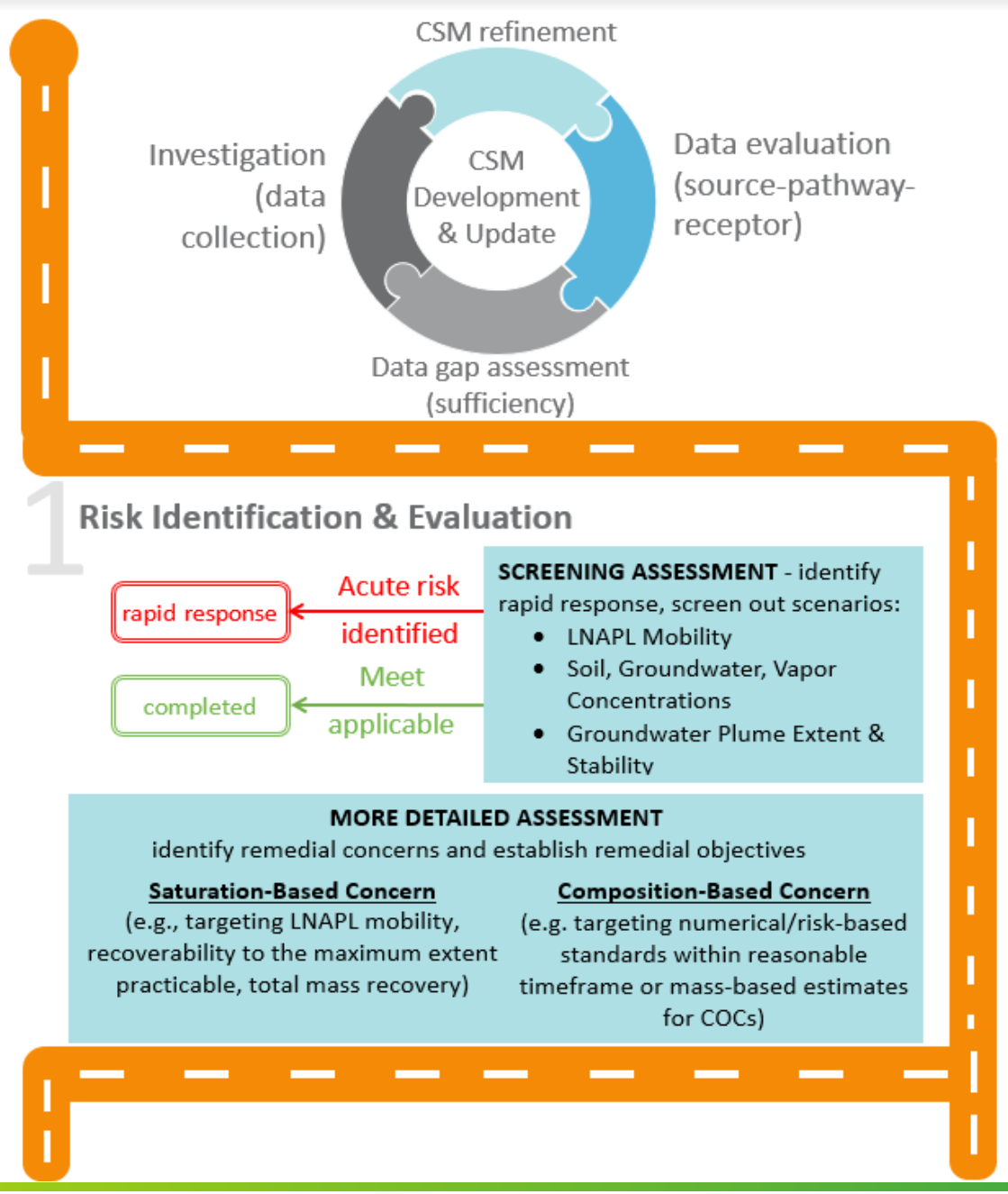
**Key Aspects to Approach:**

- Define performance metrics and transition thresholds
- Conduct baseline natural attenuation assessment (confirm need for active remediation) and validation (rebound) assessment
- Incorporate sustainability concepts
- Focus on optimization and transition

Ultimate goal is to transition confidently from active remediation to natural attenuation or “no further action”.

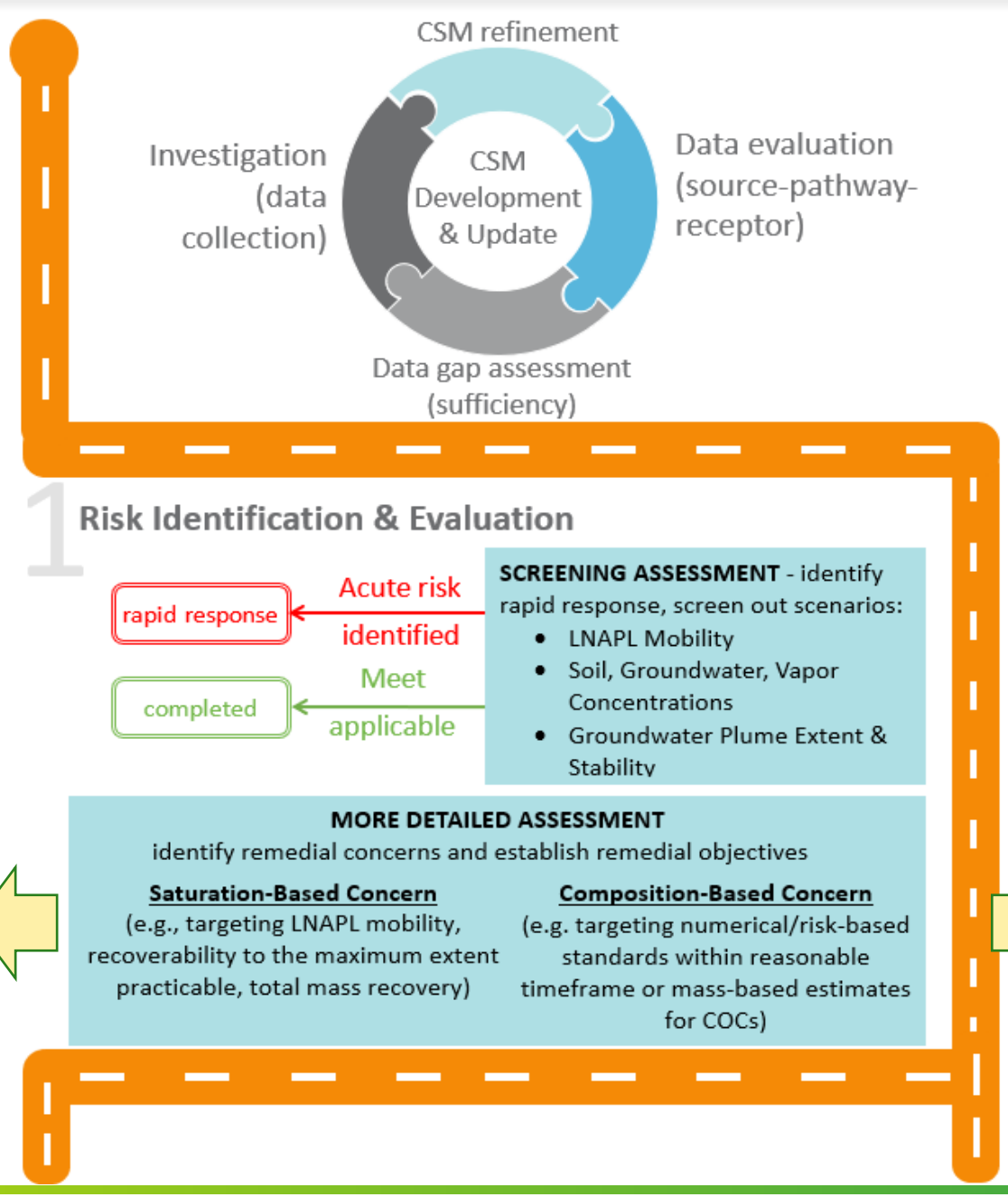
# Compendium Roadmap (1/2)

ARIS ENVIRONMENTAL



# Compendium Roadmap (1/2)

ARIS ENVIRONMENTAL




## Saturation Concern

Migrating LNAPL body
Mobile LNAPL > threshold

## Composition Concern

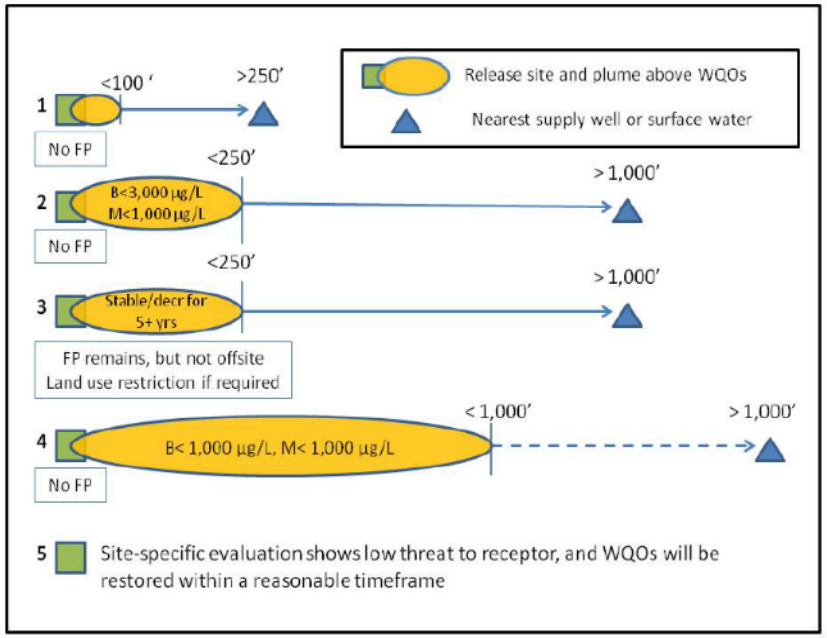
Concentration or mass discharge > criteria

# 1. Natural Attenuation (NA) Screening Approaches

## AIR FORCE CENTRE ENVIRONMENTAL EXCELLENCE(AFCEE)

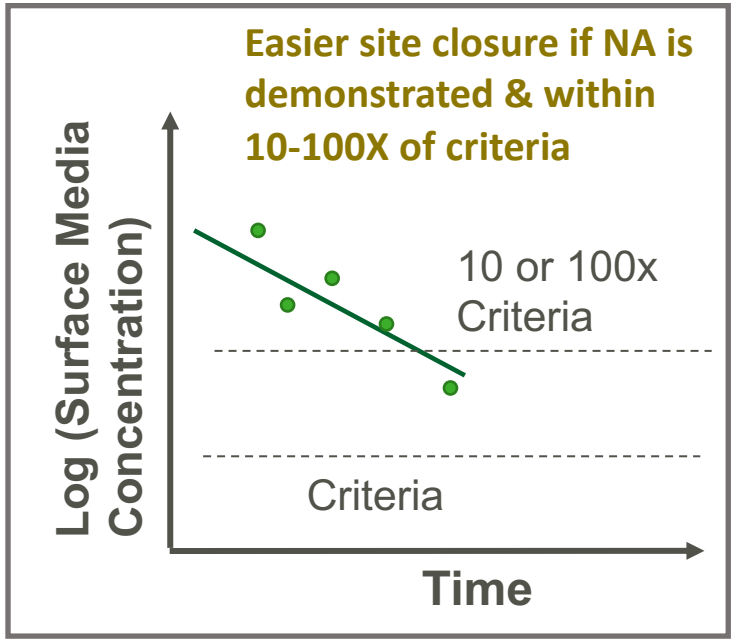
GSI website

## CALIFORNIA LOW THREAT UST CLOSURE




https://www.waterboards.ca.gov/ust/lt_cls_plcy.html

## FLORIDA NA DEFAULT CONCENTRATIONS

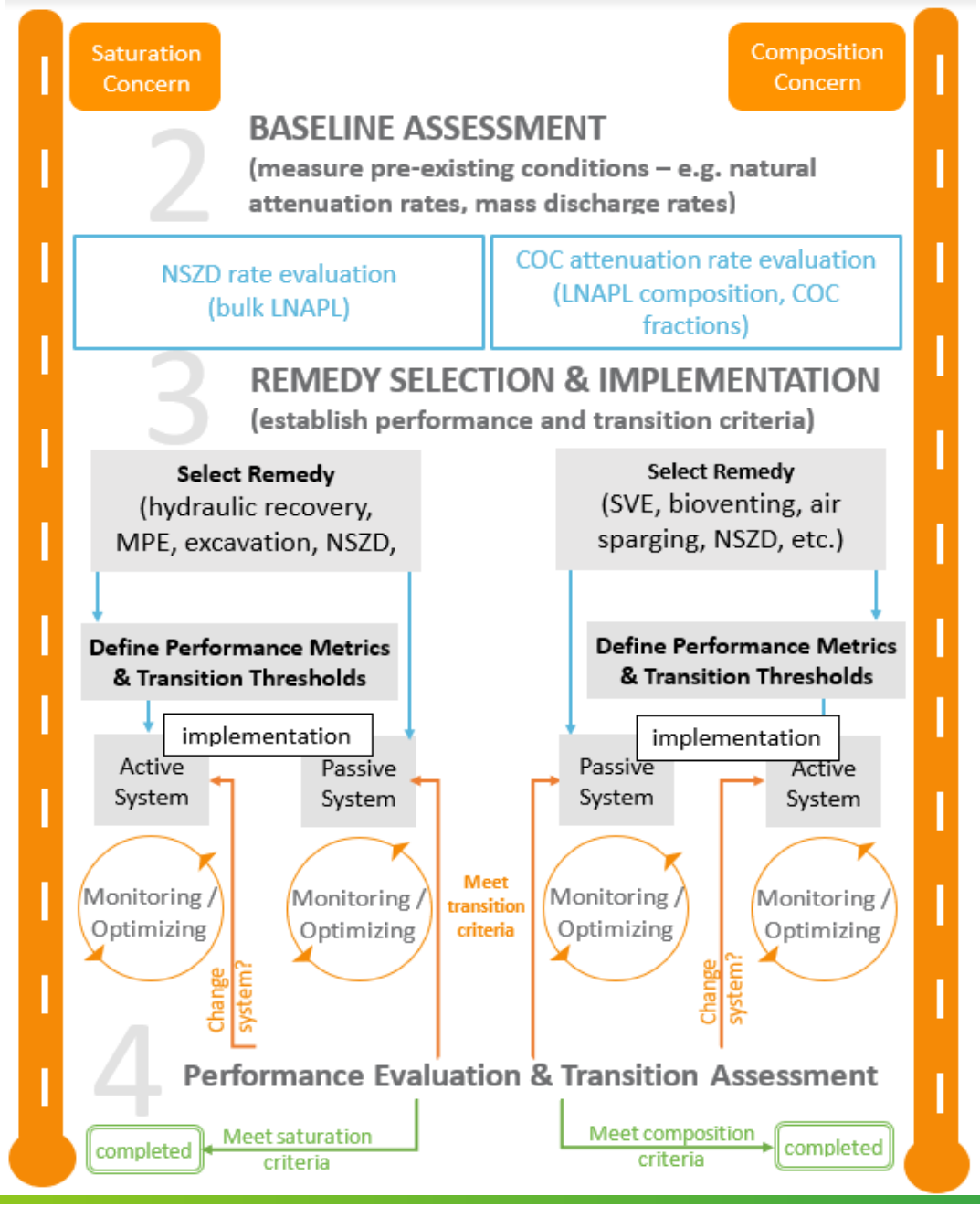



https://floridadep.gov/sites/default/files/Evaluating_NAM_31Jan18v2.pdf

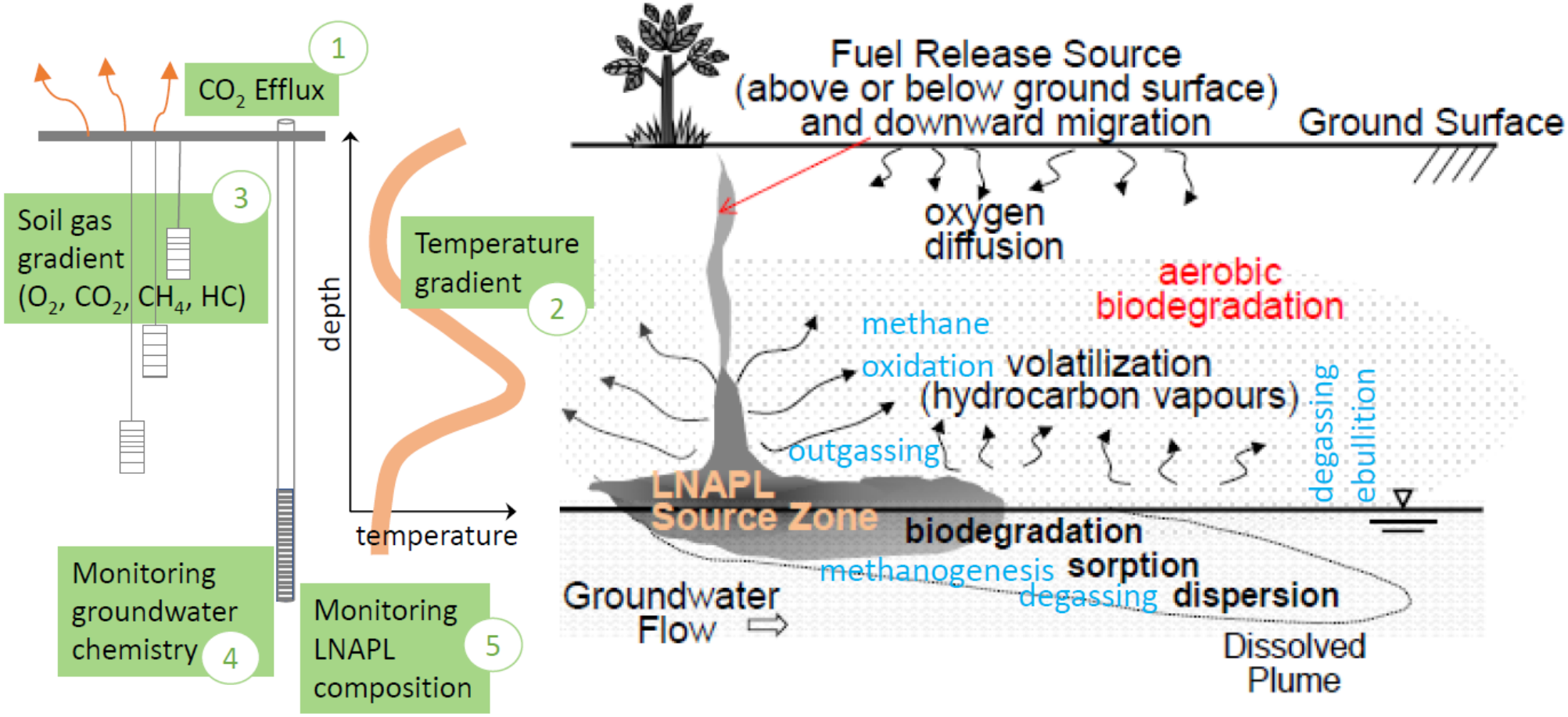
Approaches vary but factors include LNAPL body stability, evidence of source zone attenuation, dissolved plume stability, concentrations or concentration attenuation trends, proximity to receptors. BC ENV SLRA (Protocol 13) another example, although application limited by vapour prohibition

# Compendium Roadmap (2/2)

ARIS ENVIRONMENTAL

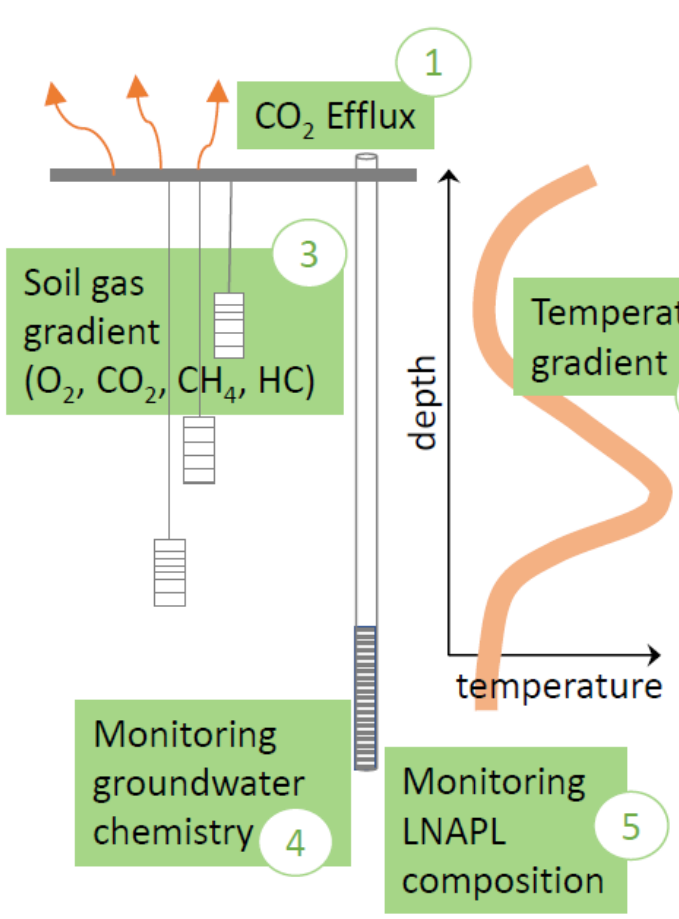


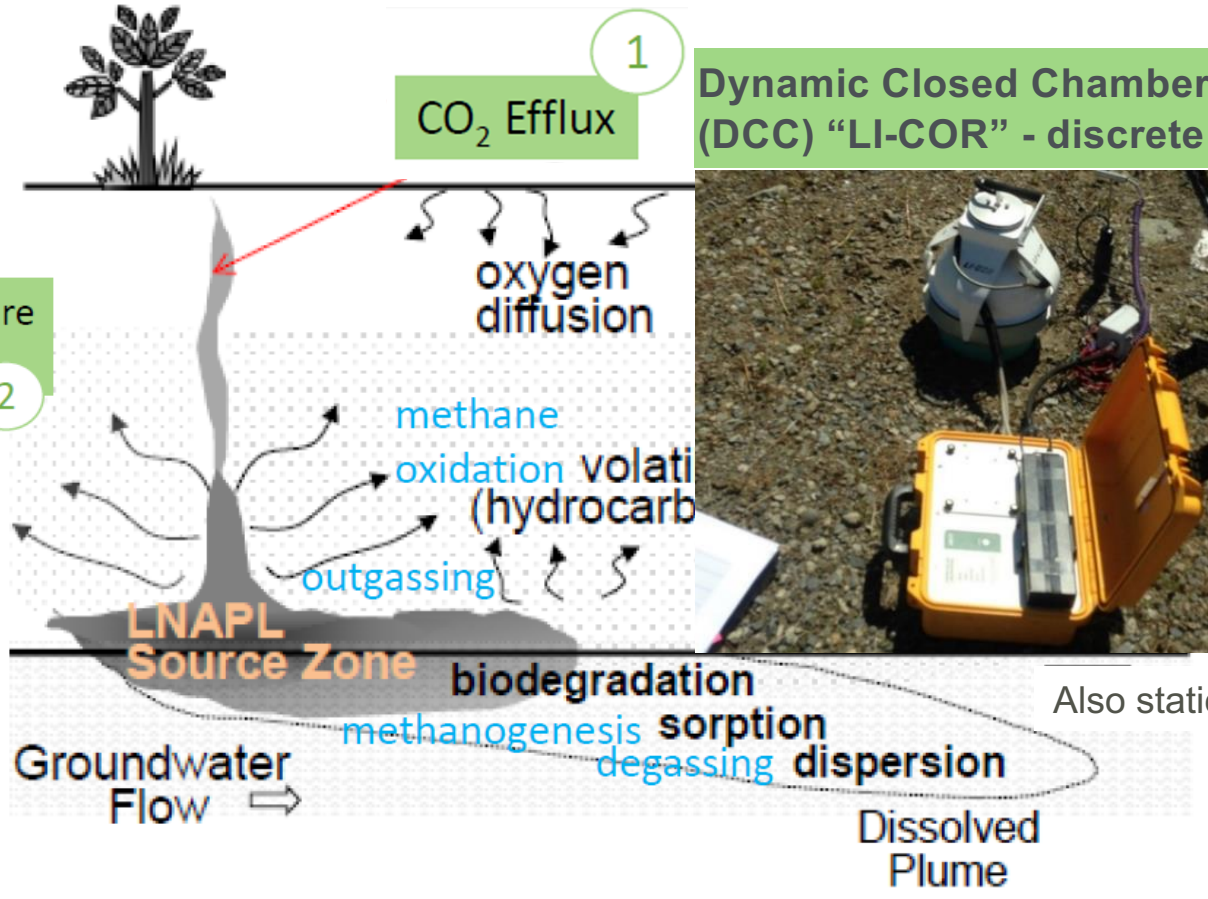
# 2. Baseline Assessment – LNAPL Depletion Processes & "Bulk" NSZD Measurement Methods JOURABCHI ET AL. 2019




**"Bulk" NSZD methods applicable for saturation concern.** Select Method Comparisons Studies: Sweeney et al. 2018; Hers et al. 2019; Kulkarni et al. 2020; CRC Care 47 2020

# 2. Baseline Assessment – LNAPL Depletion Processes & "Bulk" NSZD Measurement Methods JOURABCHI ET AL. 2019




**Dynamic Closed Chamber (DCC) "LI-COR" - discrete**



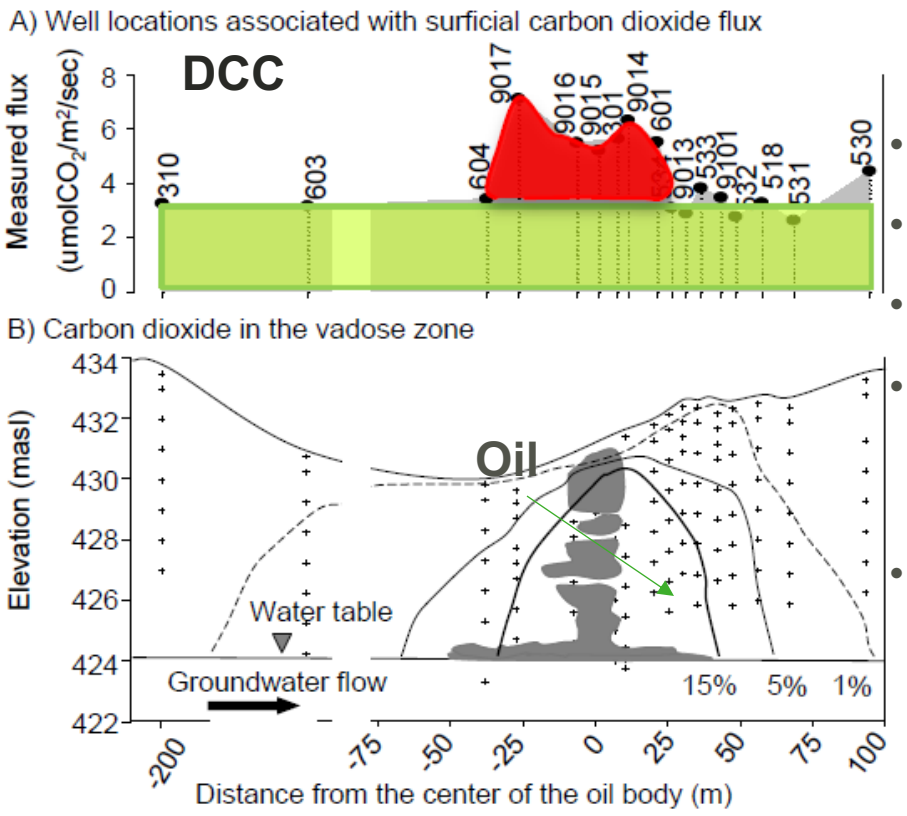
**Forced Diffusion "Eosense" - continuous**

Also static trap method available (E-flux)

**"Bulk" NSZD methods applicable for saturation concern.** Select Method Comparisons Studies: Sweeney et al. 2018; Hers et al. 2019; Kulkarni et al. 2020; CRC Care 47 2020

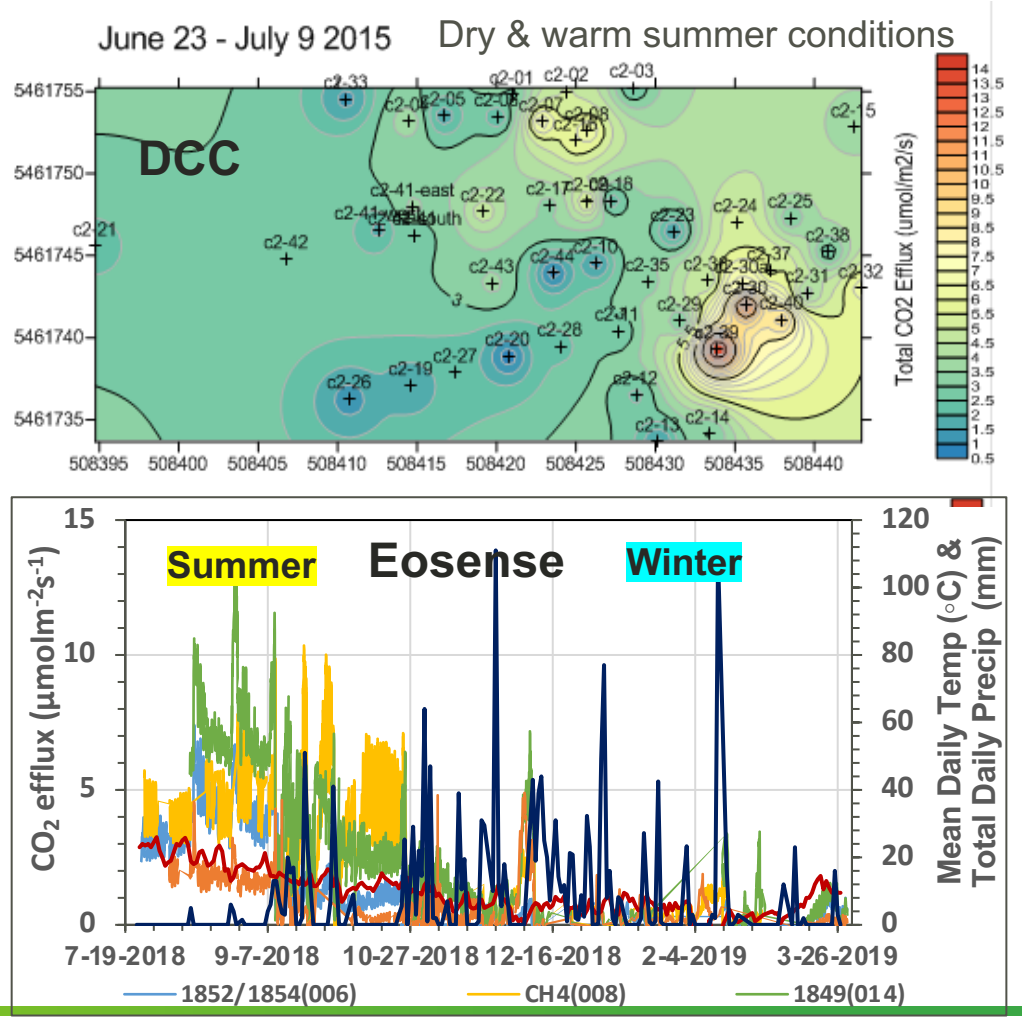
# 2. $CO_2$ Efflux – Spatial & Temporal Variability

## Bemidji Site (Sihota et al. 2011)




- NSZD Rates
- Annual
- ~ 1300 g/a/yr
- Consistent with modeling studies
- Seasonal ~ 3X variability

## Former Refinery Site (Hers et al. 2019)




- NSZD Rates
- Summer: ~1200 g/a/yr
- Winter ~ 100 g/a/yr
- Seasonal > 1 order magnitude variability
- 2 m annual precip!

Red – temperature, blue – precipitation, rest of colours - efflux

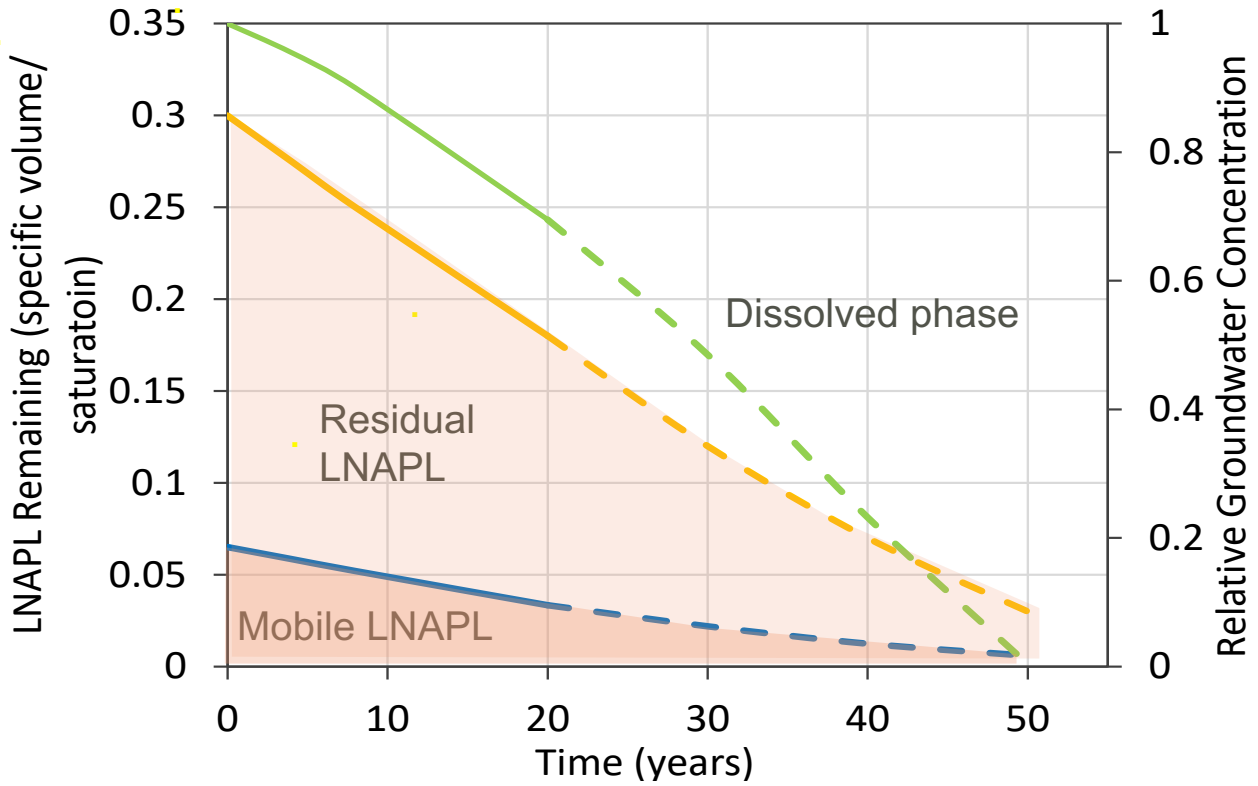
# 2. Baseline Assessment – COC Attenuation Methods

1. GW concentration trend plots (e.g., Mann-Kendall, regression)
2. Plume stability & mass reduction (area, avg conc, attenuation rates) using GWSdat (e.g., Ricker)
3. Weathering assessments to compare current constituent ratios to those of fresh gasoline from full-scan GC/FID (or using (B+T)/(E+Xs) ratios) – also used for source depletion (next slides)
4. Attenuation rate/plume longevity estimates from either GWSdat, regression plots, or model (e.g., Bioscreen, BioPlume) simulations (how long is it going to take to reach DW standards?)
5. Mass discharge estimates, either using transects, well pumping tests, passive meters or using model (e.g., prediction of COC concentrations in supply wells as a function of discharge rate)

COC attenuation methods applicable for compositional concern, ideally measure key data (e.g., concentration trends and attenuation rate) before, during and after remediation)

# 2. Natural and Enhanced Attenuation Path (NEAP) Model

## WHAT IS APPROX. REMEDIAL TIME FRAME?



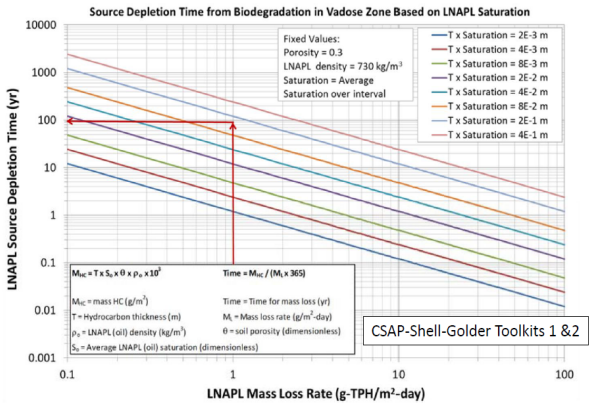

HERS Environmental Consulting, Inc.

# 2. Natural and Enhanced Attenuation Path Model - Tools

## WHAT IS APPROX. REMEDIAL TIME FRAME?

**Initial LNAPL**
TPH/Sn measurements
Modeling (API 4760)

**LNAPL Longevity**
Nomographs, VZBL (gradient method – see Toolkits), Composition



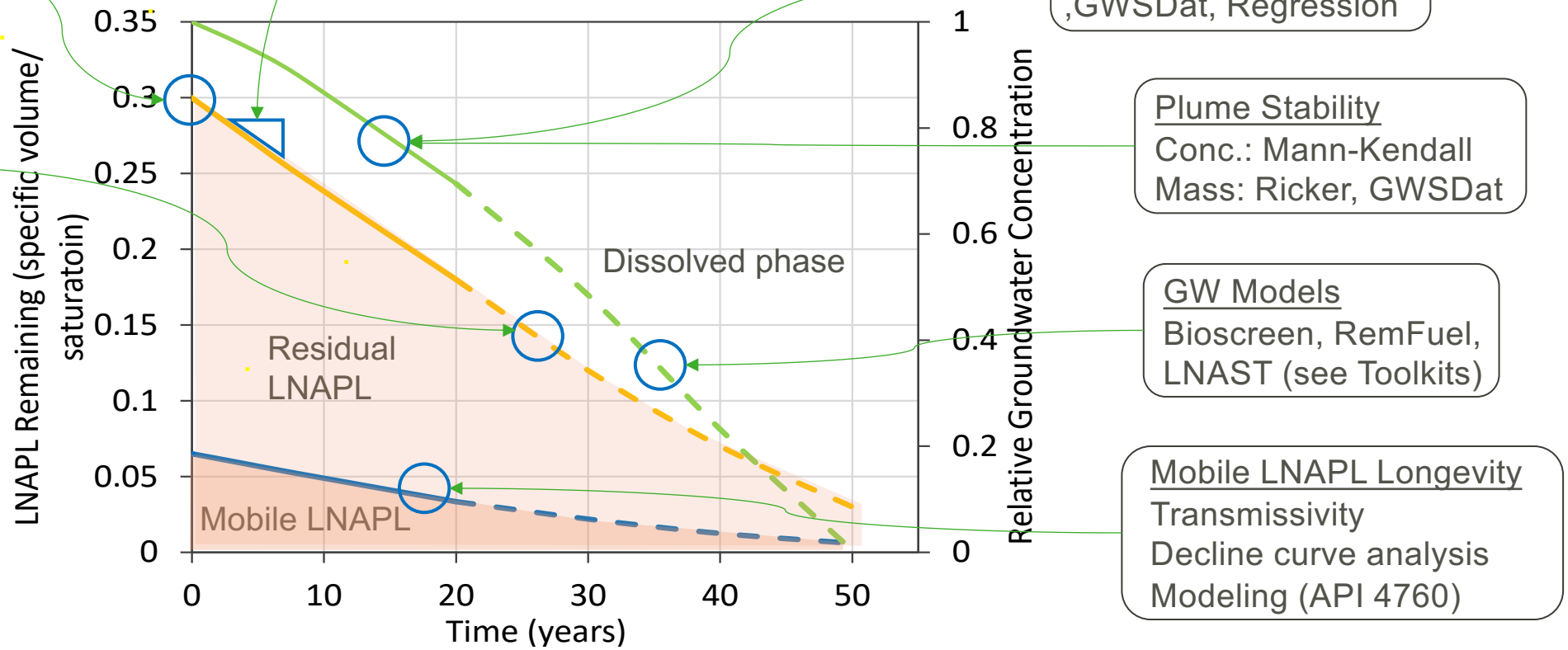

**NDZD Measurements**
$CO_2$ efflux, $O_2$ gradient, temperature, composition

**GW Trends**
Mann-Kendall, MAROS ,GWSDat, Regression

**Plume Stability**
Conc.: Mann-Kendall
Mass: Ricker, GWSDat

**GW Models**
Bioscreen, RemFuel, LNAST (see Toolkits)

**Mobile LNAPL Longevity**
Transmissivity
Decline curve analysis
Modeling (API 4760)



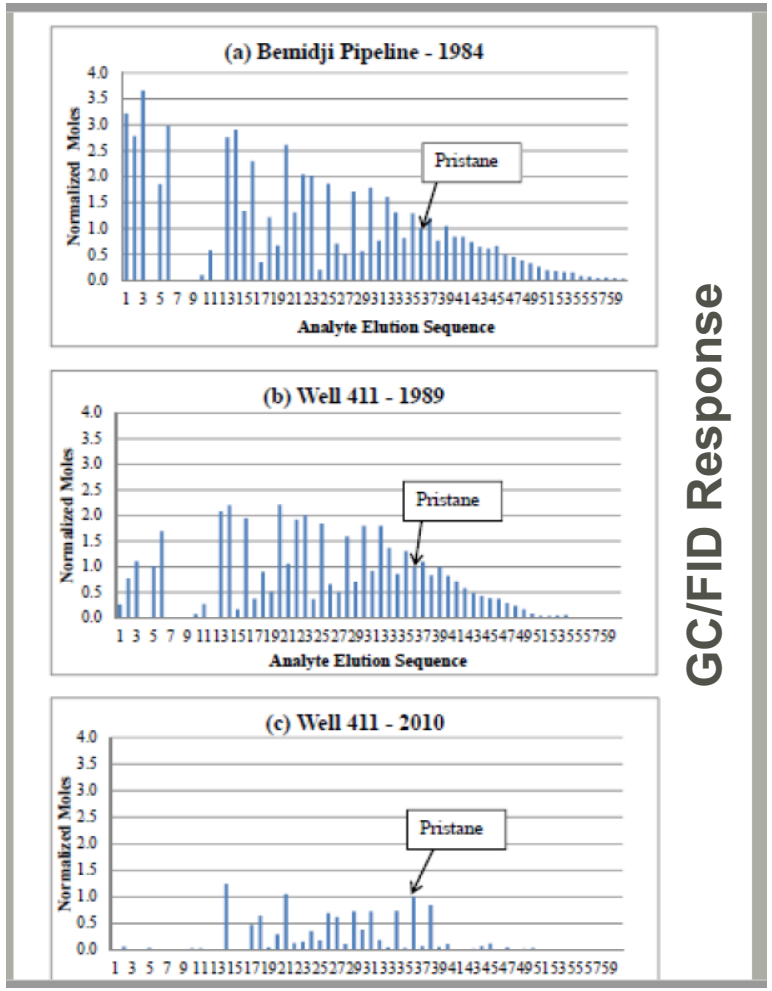

Numerical Models: PHT3D (Ng et al. 2015); MIN3P-DUSTY (Jourabchi & Hers 2013); TMVOC (Lari et al. 2019)

HERS Environmental Consulting, Inc.

# 2. Source Depletion Times – LNAPL Composition Analysis

- Time series analysis of LNAPL composition change based on chemical analysis (GG/FID) of oil
- Analysis is performed relative to conservative (recalcitrant) marker chemical (e.g., phytane, pristane) or group of chemicals (Douglas et al. 1996; CRC Care 44 2018)
- Kulkarni et al. 2020 light-end hydrocarbons: 30% depletion in 9 yrs (relative to somewhat depleted starting point)
- Baedecker et al. 2018 Bemidji crude oil: 18–31% depletion in 30 yrs
- Lundy 2018 Bemidji crude oil: 30-70% depletion in 32 yrs (may be because of different wells/area assessed)

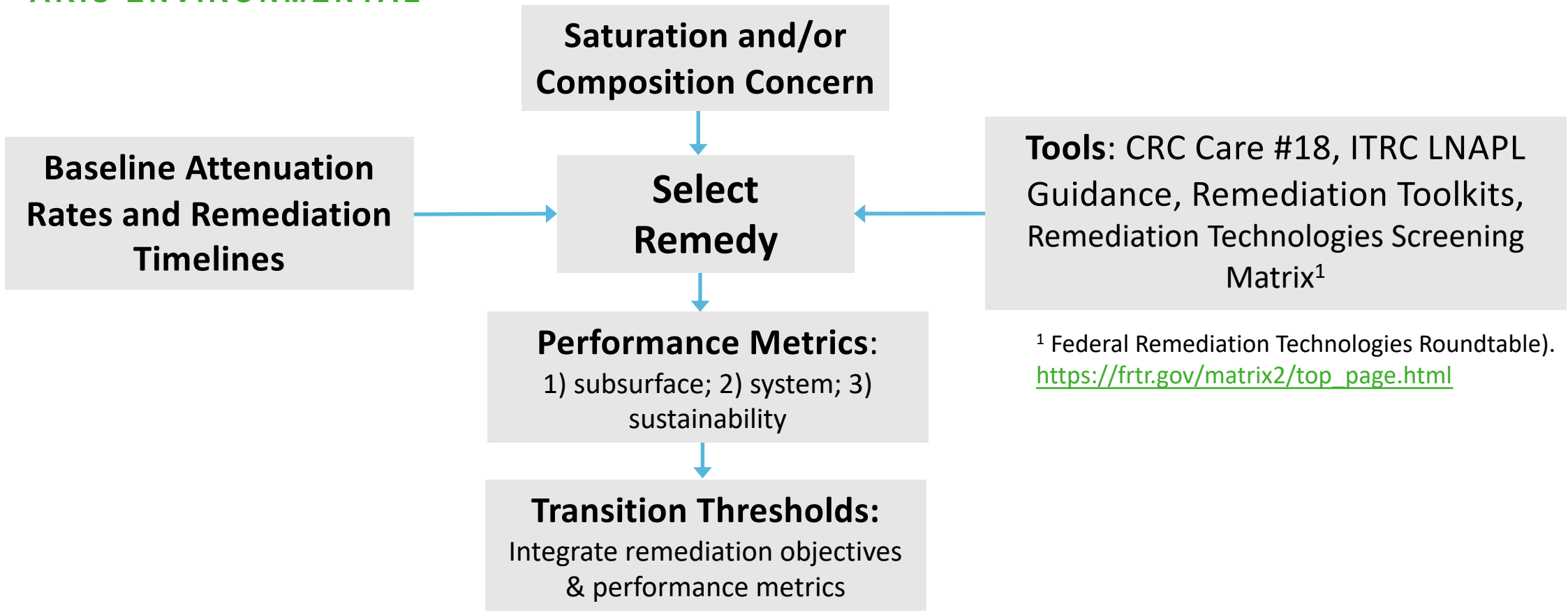
Promising method as can estimate individual compound and total LNAPL depletion rate and % depleted. Potentially extrapolate using curve-fitting to estimate source depletion time




**Bemidji Site (Lundy 2018)**

# 3. Remedy Selection and Implementation

ARIS ENVIRONMENTAL




[1] Federal Remediation Technologies Roundtable). https://frtr.gov/matrix2/top_page.html

**Key point**: Essential to define & agree to performance metrics & transition thresholds upfront with all stakeholders prior to the implementation of active remediation

# 3. Performance Metrics & Transition Threshold Examples

ARIS ENVIRONMENTAL

**Performance Metric - Subsurface**

- LNAPL presence/absence in wells (S)
- LNAPL transmissivity (S)
- LNAPL saturation (mobile fraction remaining)
- NSZD (bulk TPH or COC) rate (S&C)
- Concentration and mass discharge – absolute value or attenuation rate (C)
- Push-pull respiration test (bio) (C)

**Performance Metric - System**

- LNAPL recovery vs. time (S)
- LNAPL/vapour ratio or LNAPL/water ratio (S)
- TPH/COC mass recovery vs. time (C)
- COC ratios in water or vapour (C)
- $CO_2$ in system exhaust (bio) (S&C)

S = Saturation: C = Composition

**Performance Metric - Sustainability/Cost (both subsurface & system)**

- LNAPL recovery vs cost or GHG emissions or other metric (e.g., water use) (S)
- TPH/COC mass recovery vs. cost or GHG emissions of other metric (C)

**Transition Threshold**

- Recovery of 90-95% of mobile LNAPL based on decline curve analysis (S);
- LNAPL transmissivity below ITRC (2018) threshold of 0.1 to 0.8 $ft^2$/day (S)
- Concentrations or mass discharge at or approaching criteria within accepted statistical certainty (C)
- Active mass recovery rates similar to or less than NSZD (bulk) rates (S).
- Active attenuation rates similar to natural attenuation rates (C)

# 4. Performance Evaluation and Transition Assessment

**Performance & Optimization** → **Transition** → **Validation**

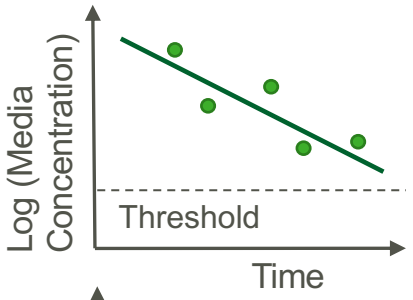
LNAPL body/plumes stable or shrinking?
Progress to remedy criteria acceptable?
Progress to transition acceptable?

Yes

No

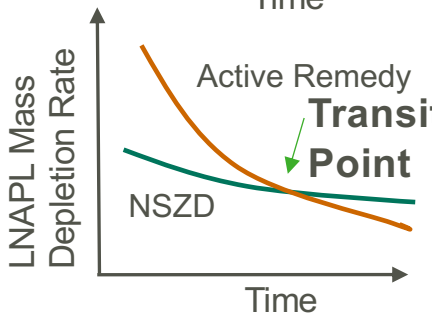
**Monitoring / Optimizing**

I. Evaluate technology performance and limits



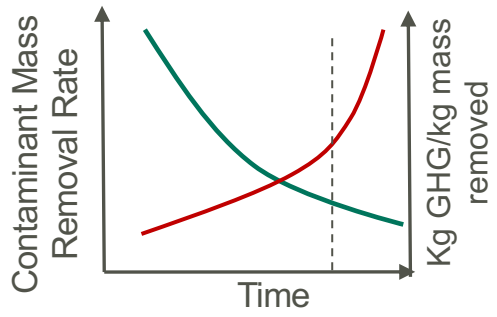

Concentration attenuation progressing to threshold or reaching asymptotic level

II. Compare mass depletion rate for active & passive remediation




Active removal rate (excluding NSZD)) similar or less than NSZD rate

III. Evaluate sustainability and cost for project lifecycle




Point of diminishing returns as normalized GHG emissions are increasing rapidly

Results of validation assessment acceptable (e.g., rebound, monitoring, modeling)

Yes

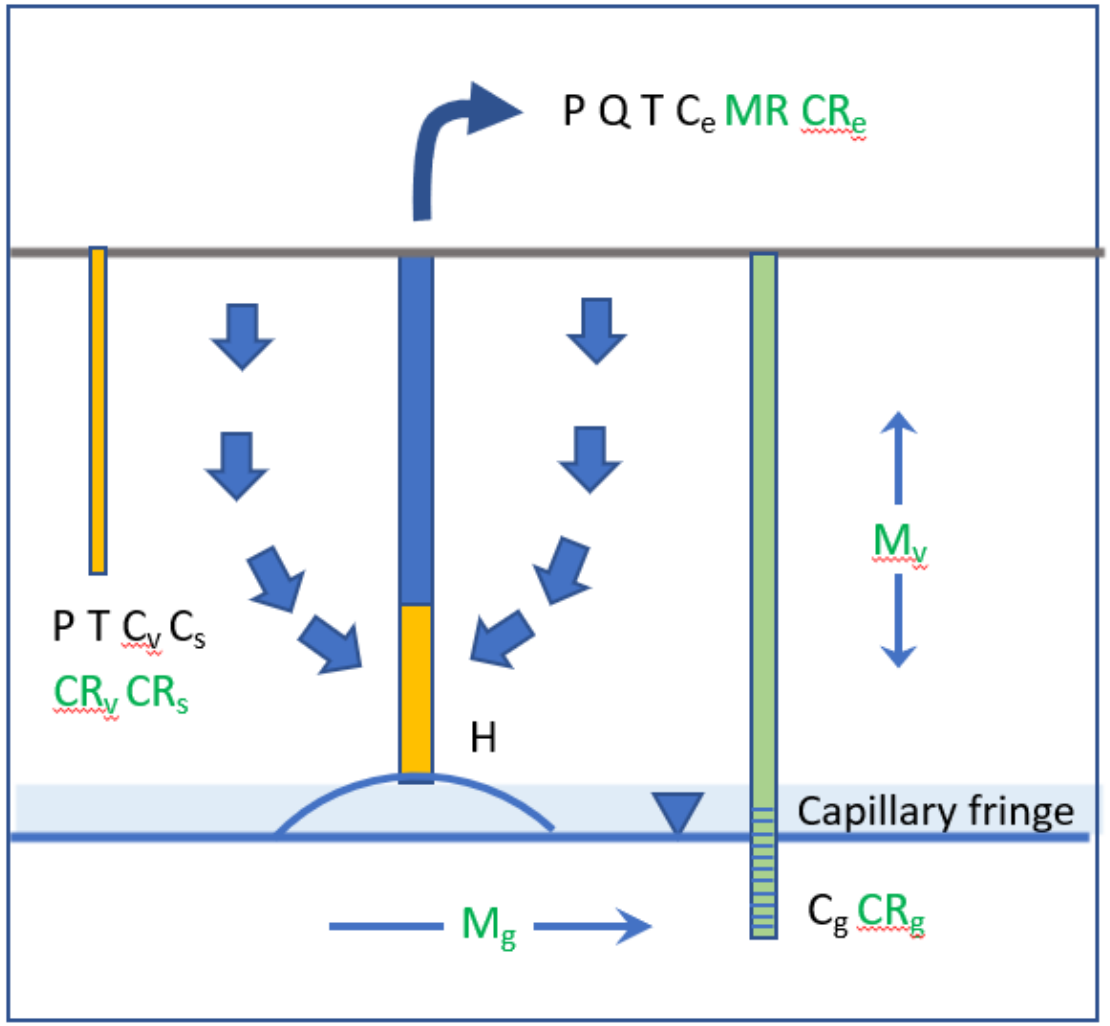
Progress to closure

No

HERS Environmental Consulting, Inc.

Select examples of transition metrics shown, see additional metrics in factsheets

# SVE Factsheet – Performance Metrics




Calculated metrics are indicated in green

***Performance Metrics***

*Subsurface:*

- *$C_s$ = Soil concentration*
- *$C_g$ = Groundwater concentration*
- *$C_v$ = Soil vapor concentration*
- *$CR_s$ $CR_v$ $CR_g$ = Concentration ratios*
- *$M_g$ = Groundwater mass flux or discharge*
- *$M_v$ = Soil vapor mass flux or discharge*

*System:*

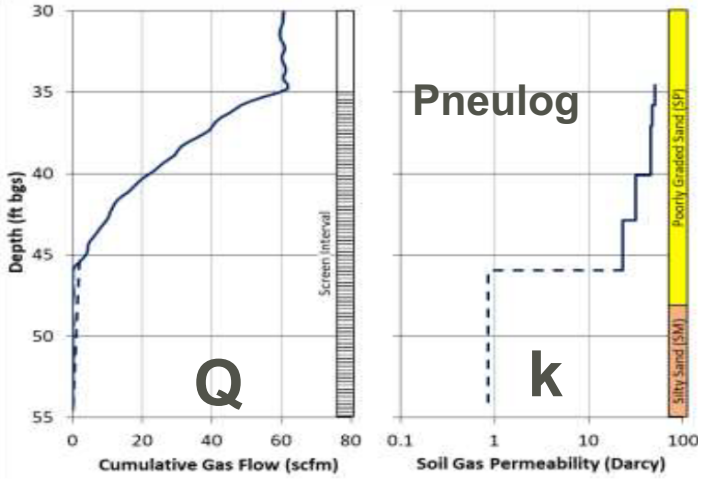
- *$C_e$ = Soil gas concentration in extracted gas*
- *Q = Flow rate*
- *P = Pressure*
- *T = Temperature (optional)*
- *H = Water level mounding*
- *MR = Mass removal rate (Q x $C_e$)*
- *$CR_e$ = Concentration ratios*

# SVE Factsheet - Optimization

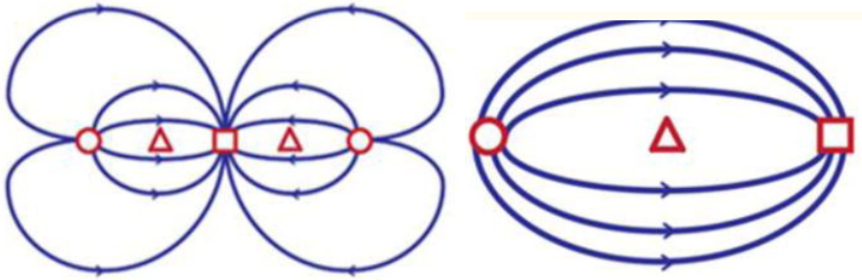
1. Rebalance air flow to increase flow rates in zones with highest mass removal rates (e.g., Pneulog system)
2. Add passive/active air injection wells (e.g., dipole or multi-well system); consider pulsed operation
3. Add wells with screens that target remaining areas of higher mass
4. Reduce air flow rate to balance mass discharge to wells
5. Hydraulic or pneumatic fracturing.
6. Convert SVE system to lower-energy bioventing system or barometric pumping system (1-way valves)

Optimized system likely get to transition point faster

Pneumatic logging & soil vapour concentrations - system optimization (fig provided by Praxis)

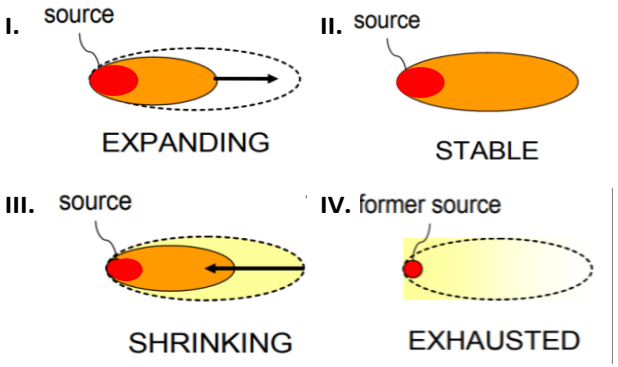



Dipole or multi-well injection/extraction optimization

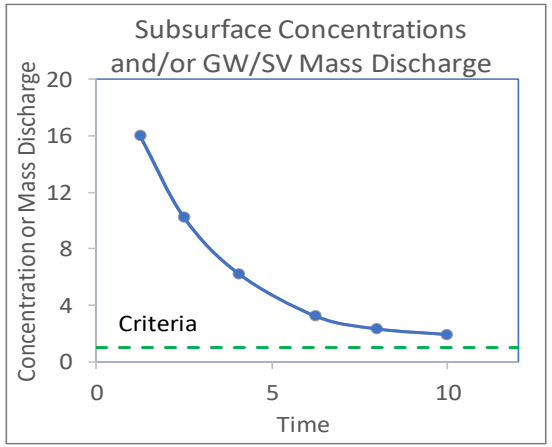


Possibility for chaotic advection? Cho et al. 2019.

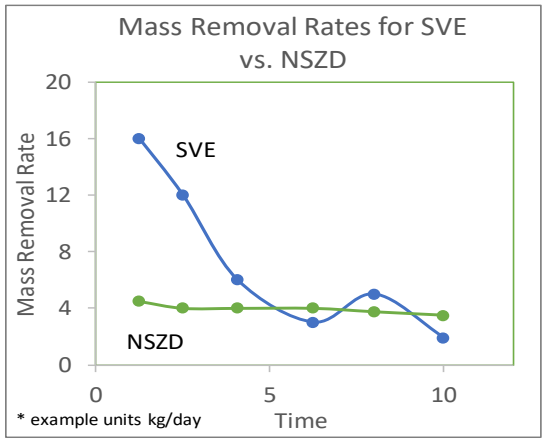
# SVE Factsheet – Transition Threshold Examples



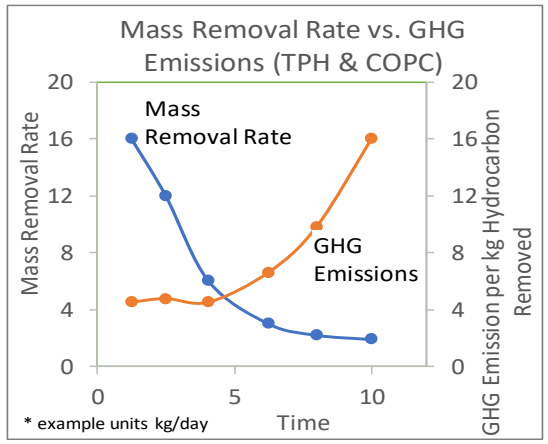

**T1. Groundwater Plume is Stable or Shrinking (see Toolkit 2)**



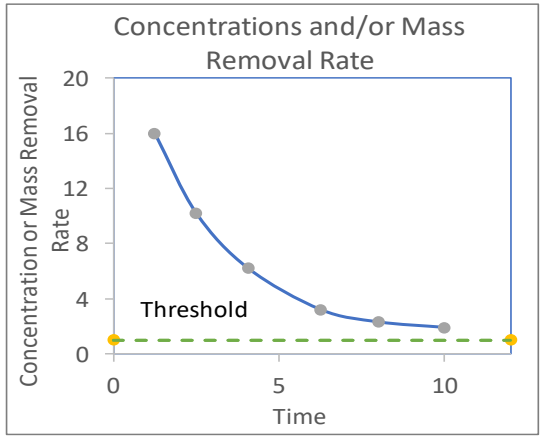

**T2. Concentration/Mass Flux Approaching Asymptote or Criteria (see Toolkit 2)**



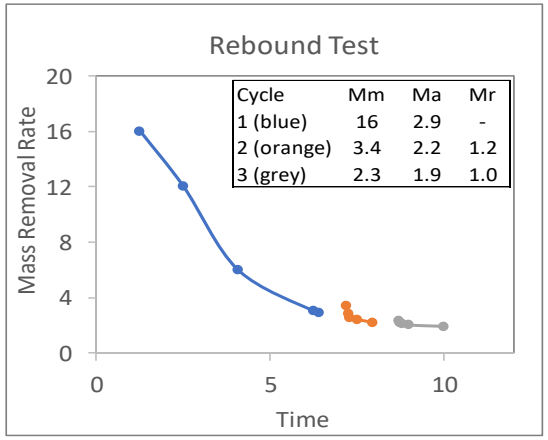

**T5. Active Mass Removal Rate Approaching or is Less than NSZD Rate (see this Compendium)**



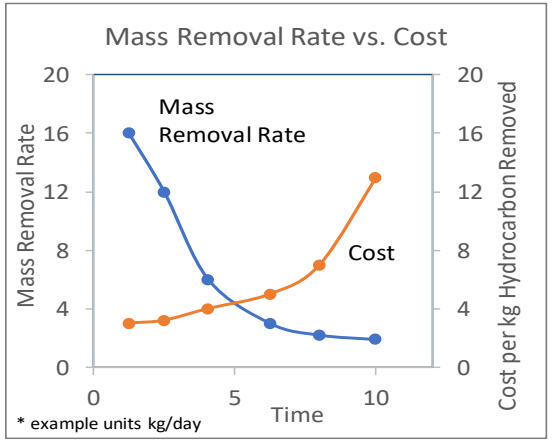

**T6. Normalized GHC Emissions (or other metric) Increasing with Little Benefit from Continued Operation (see Toolkit 4)**



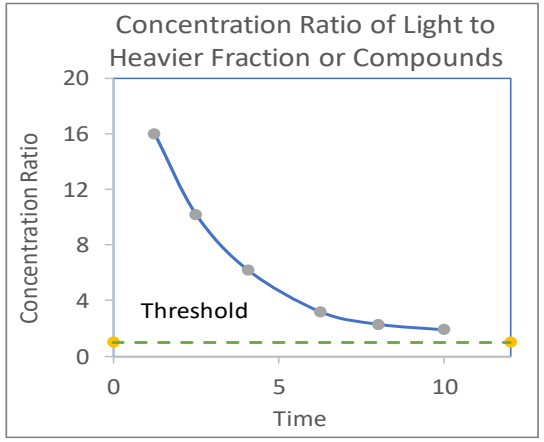

**T3. Extracted Soil Gas Concentration/ Mass Removal Rate Approaching Asymptote or Risk-based Threshold (see Toolkit 2)**




**T4. Acceptable Mass Discharge and Mass Removal Rate (see this Compendium - - Appendix III)**

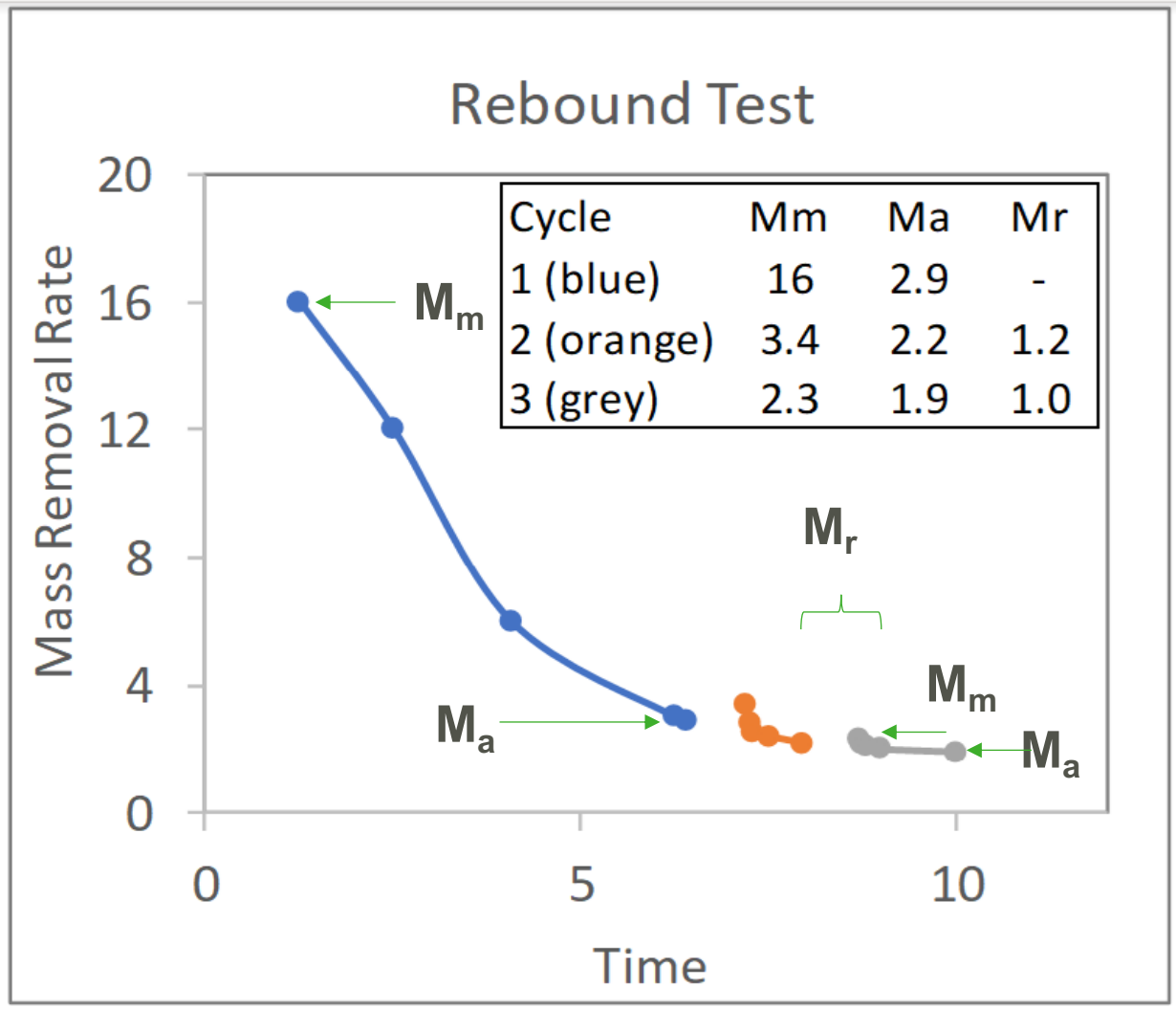



**T7. Normalized Cost Increasing with Little Benefit from Continued Operation (see Toolkit 4)**




**T8. Concentration Ratio Approaching Asymptote or Risk-based Threshold (this Compendium)**

# SVE Factsheet – Validation – Rebound Test




## Simple model (Brusseau et al. 2010; PNNL 2013)

- $M_{pv} = \sum_{i=1}^{n}(C_i - C_a)Q_i\Delta T_i$ **mass**
- $M_r = \frac{M_{pv}}{T}$ **Diffusive mass discharge (mass/time), often from low permeability zones, after termination**
- Convergence of $M_m$ and $M_a$; and $M_a$ and $M_r$ suggests approaching end of operational life

## More complex models (PNNL models)

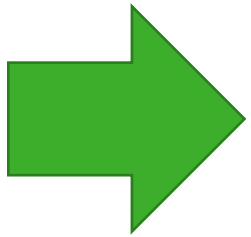
- "SVEET" quantifies mass discharge and impact of remaining vadose zone contaminant sources on groundwater https://bioprocess.pnnl.gov/SVEET_Request.htm
- "VIETUS" quantifies mass discharge on soil vapour intrusion into buildinghttps://bioprocess.pnnl.gov/VIETUS_Request.htm
- Decision-making approach to address SVE optimization, transition, and closure decisions.

$M_{pv}$ = mass removed 1st pore volume after start up; $C_i$ = conc. system turned on; $C_a$ = conc. at end of previous cycle; $\Delta T_i$ = time 1 pore volume; T = rebound period

# SVE Factsheet – Summary of Key Transition Concepts

- Select relevant transition MLE, e.g., common MLE are:

- Stable or shrinking plume
- Concentration in extraction wells approaching asymptotic levels
- Rebound test indicates acceptable risk and convergence between rate of natural mass release of COCs with rate of active mass recovery
- Consequently, little difference in concentration attenuation trend for active and NA conditions expected
- Acceptable groundwater/soil vapour concentration trend (i.e., relative to reasonable timelines)



Transition

# Sustainability - Environment Footprint Analysis

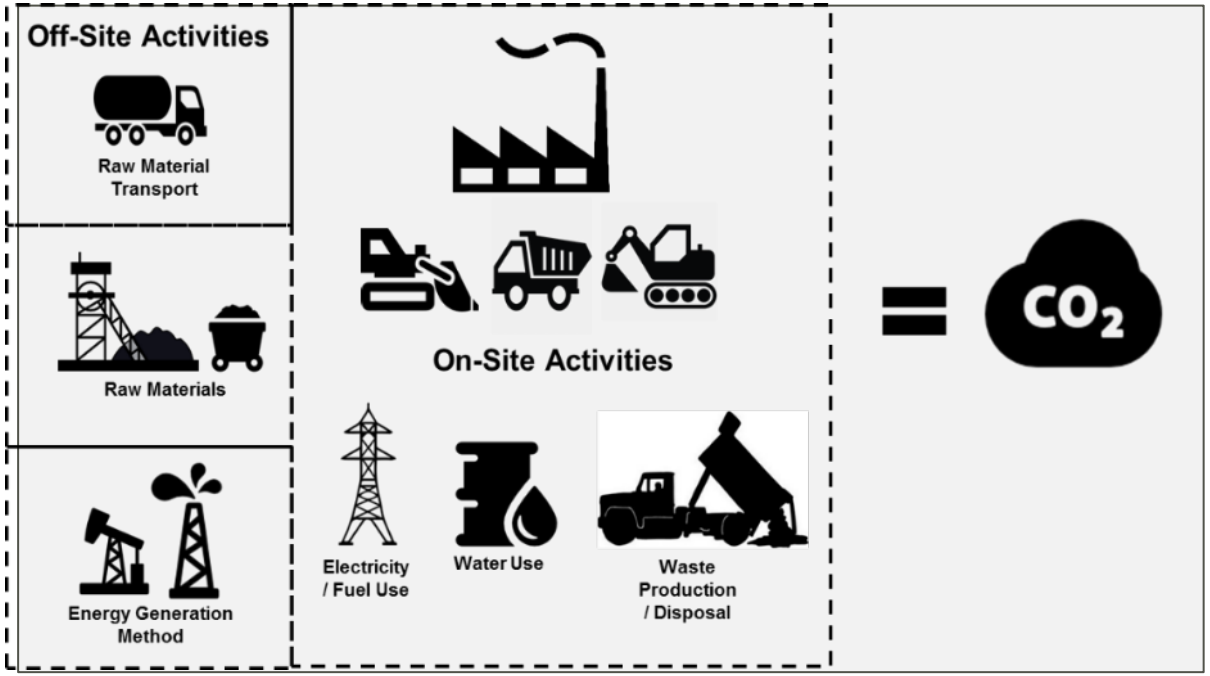
**Key Steps**

Identify Goals
Identify Indicators
Establish System Boundaries
Conduct Environmental Inventory
Footprint Calculation
Documentation

**Key Environmental Indicators**

GHG emissions & air pollutants
Energy use
Waste generation
Materials use
Land use and ecosystem

Examples of on-site and off-site inputs




Select Tools:
SiteWise
SimaPro
US SEFA
GoldSET
SR Dashboard (developed for Remediation Toolkits project)

Simplified life cycle analysis (LCA) can be used to guide the analysis – Critical to establish consistent boundaries (time, space)

Incorporation of sustainability in remediation is complex and goes beyond footprint to broader environmental and societal aspects – we need more guidance and case studies on best practices

# Summary

- Many available tools to assess remedial performance, but consistent framework for application lacking
- Numerous guidance documents and research on natural attenuation and depletion
- But limited consideration of and guidance on transitions and where often remediation is performed without defined performance metrics or transition thresholds or points
- Emerging recognition active remediation “can’t get all the way there” or may not be needed and that often rates of natural attenuation or depletion will be similar to active remedy rates (particularly for later stages of remediation)
- Compendium Project aims to provide a clear roadmap to remedial decision-making with supporting factsheets and tools for common technologies as more sustainable approach
- Gaps and questions include 1) prediction of long-term depletion rates and compositional change, 2) what are reasonable attenuation timelines and 3) additional case studies

# References


Brusseau, M. L., V. Rohay and M.J. Truex (2010). Analysis of soil vapor extraction data to evaluate mass-transfer constraints and estimate source-zone mass flux. Ground Water Monitoring and Remediation, 30(3), 57-64. https://doi.org/10.1111/j.1745-6592.2010.01286.x

CRC Care 44 Technical measurement guidance for LNAPL natural source zone depletion

Garg et al. 2017. Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change. GWMR, Summer, 37(3).

Hers et al. 2019. NSZD Rates under Natural & Solarization Conditions. Battelle Bioremediation Conf., April 15-18, Baltimore.

Jourabchi et al. 2019. Compendium of Tools and Methods for Systematic Approach to Sustainable Site Closure for Petroleum Hydrocarbon Sites. RemTech Conf., Oct., Banff, AB

Jourabchi and Hers 2013. Modeling Study of Manganese and Iron in Groundwater. Report for CSAP https://csapsociety.bc.ca/wp-content/uploads/Golder-CSAP-Modeling-Iron-Manganese-in-Groundwater-2013.pdf

Lari et al 2019. Natural source zone depletion of LNAPL: A critical review supporting modelling approaches. Water Research 157

Lundy, D. 2018 A Method to Estimate Historical LNAPL Volume and Mass Losses from Compositional Changes. AEHS Conference. San Diego, Mar20

Ng et al. 2015. Reactive transport modeling of geochemical controls on secondary water quality impacts at a crude oil spill site near Bemidji, MN. Water Resources Research.

Mackay et al. 2018. Comparing Natural Source Zone Depletion Pathways at a Fuel Release Site. GWMR. Spring.

McHugh et al. (2014). Progress in Remediation of Groundwater at Petroleum Sites in California. Groundwater, 52, November-December 2014, 898–907

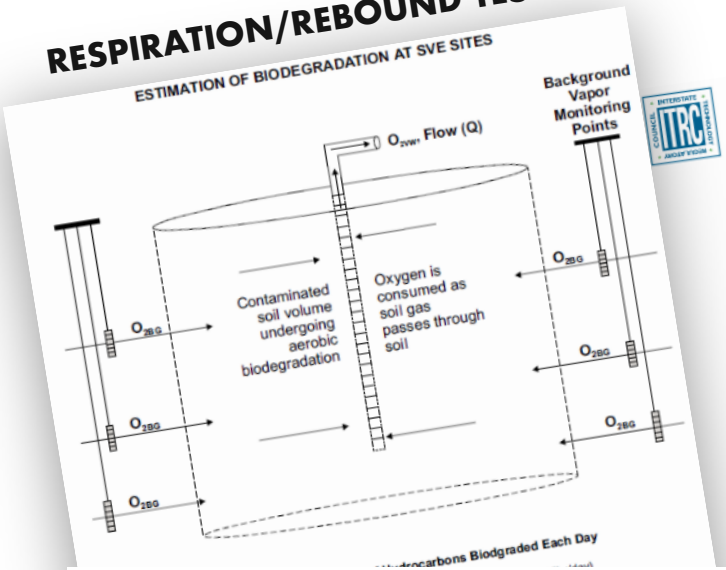
Kulkarni et al. 2020 Application of 4 Measurement Techniques to Understand NSZD Processes at an LNAPL Site. GWMR. Summer.

Pacific Northwest National Laboratory (PNNL) 2013. Soil Vapor Extraction System Optimization, Transition, and Closure Guidance RPT-DVZ-AFRI-006 Prepared for the U.S. Department of Energy.

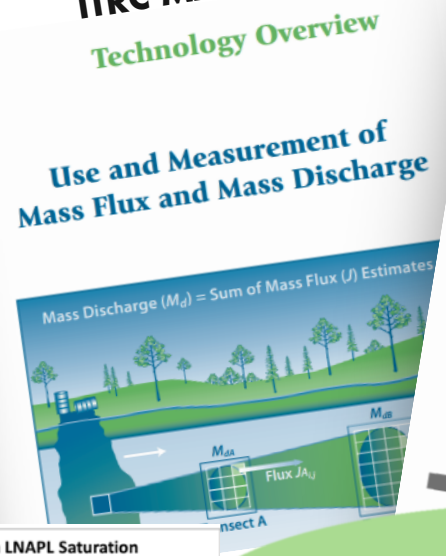
Sweeney et al. 2018; . Natural Source Zone Depletion Investigation of a Paved UST Site in Spain. Battelle Chlorcon Conf

https://csapsociety.bc.ca/wp-content/uploads/Golder-CSAP-Modeling-Iron-Manganese-in-Groundwater-2013.pdf
https://www.esaa.org/wp-content/uploads/2019/10/19-Jourabchi.pdf

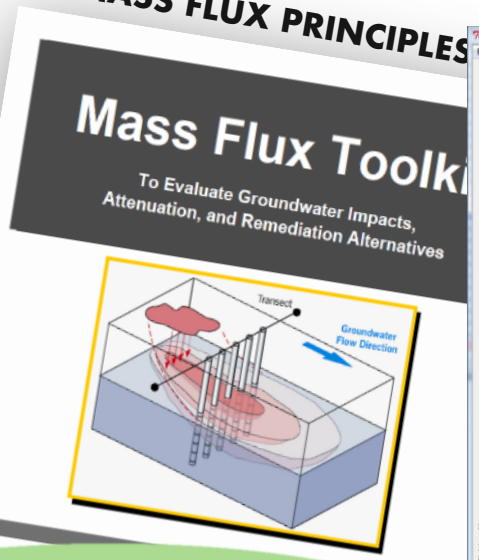
## RESPIRATION/REBOUND TESTS



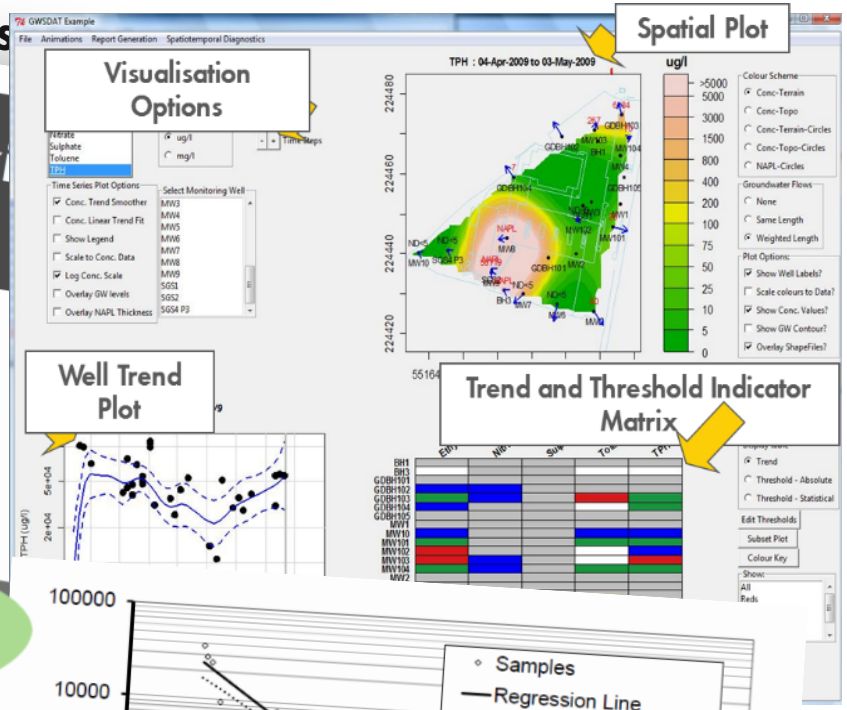

## ITRC MASS FLUX



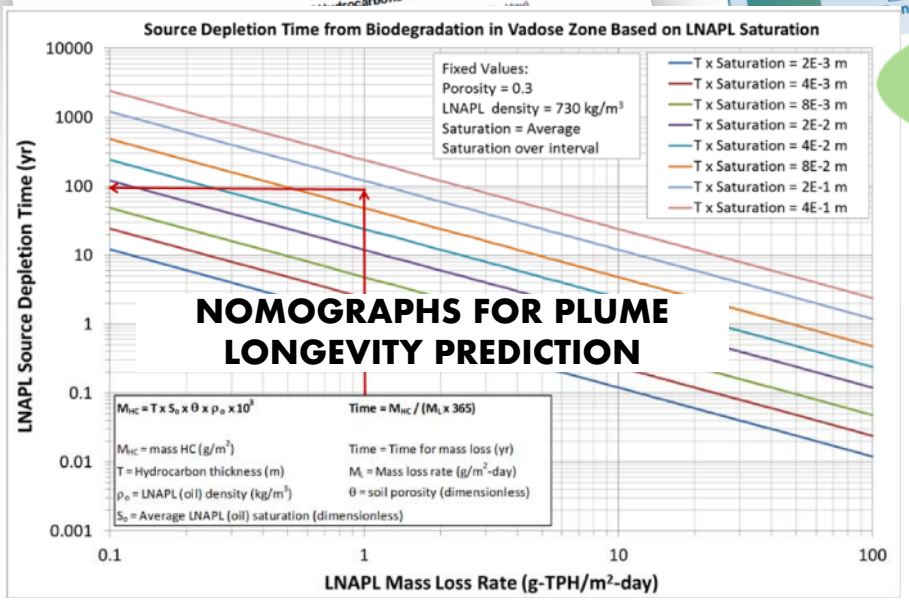

## MASS FLUX PRINCIPLES



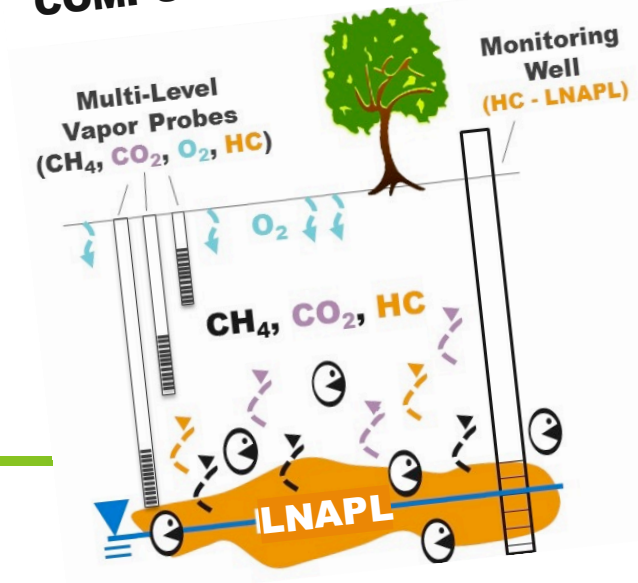

## GWSdat

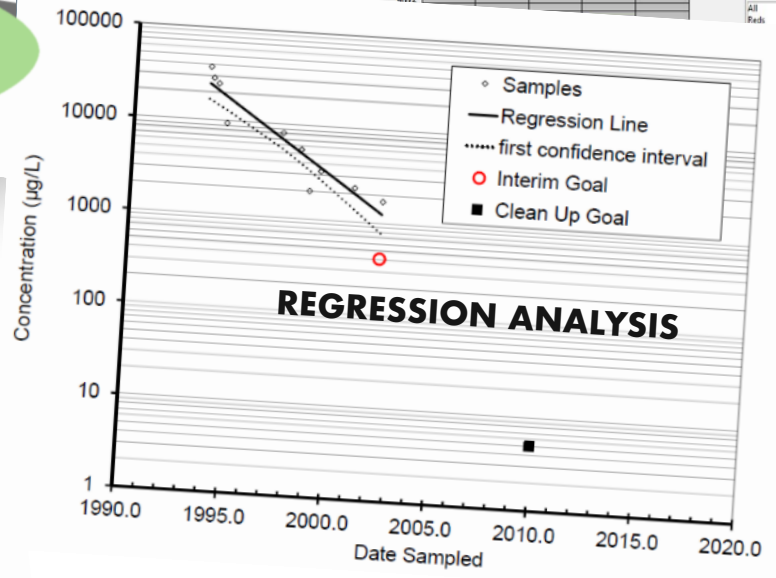



# Thank you!




## COMPOSITIONAL METHODS





ian@hersenviro.com

parisa@arisenv.ca

HERS Environmental Consulting, Inc.