Quantifying Natural NAPL Attenuation: Practical Tools to Support Remedy Transition

Remediation Technologies Symposium

RemTech 2025 – LNAPL Session

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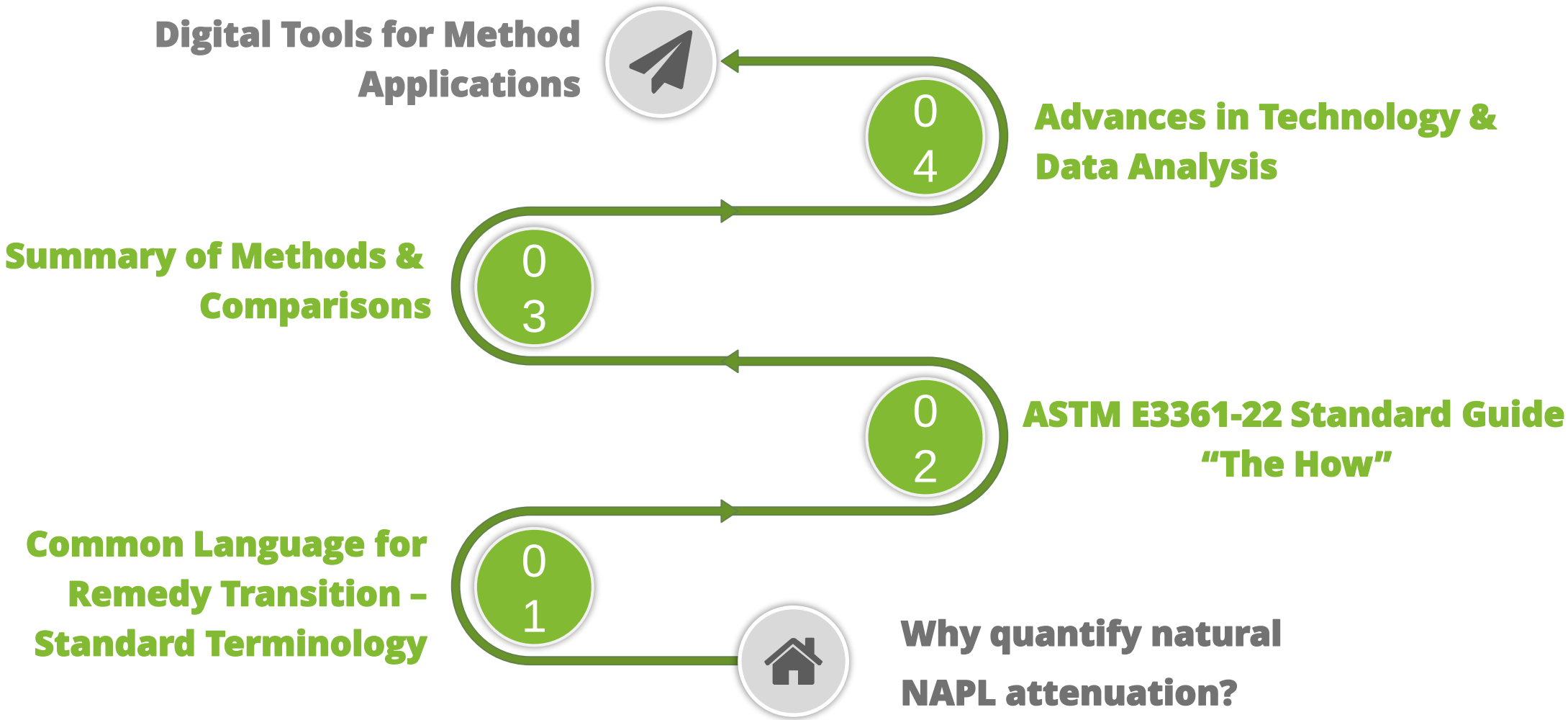
Roadmap


Digital Tools for Method Applications
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Advances in Technology & Data Analysis
Summary of Methods & Comparisons
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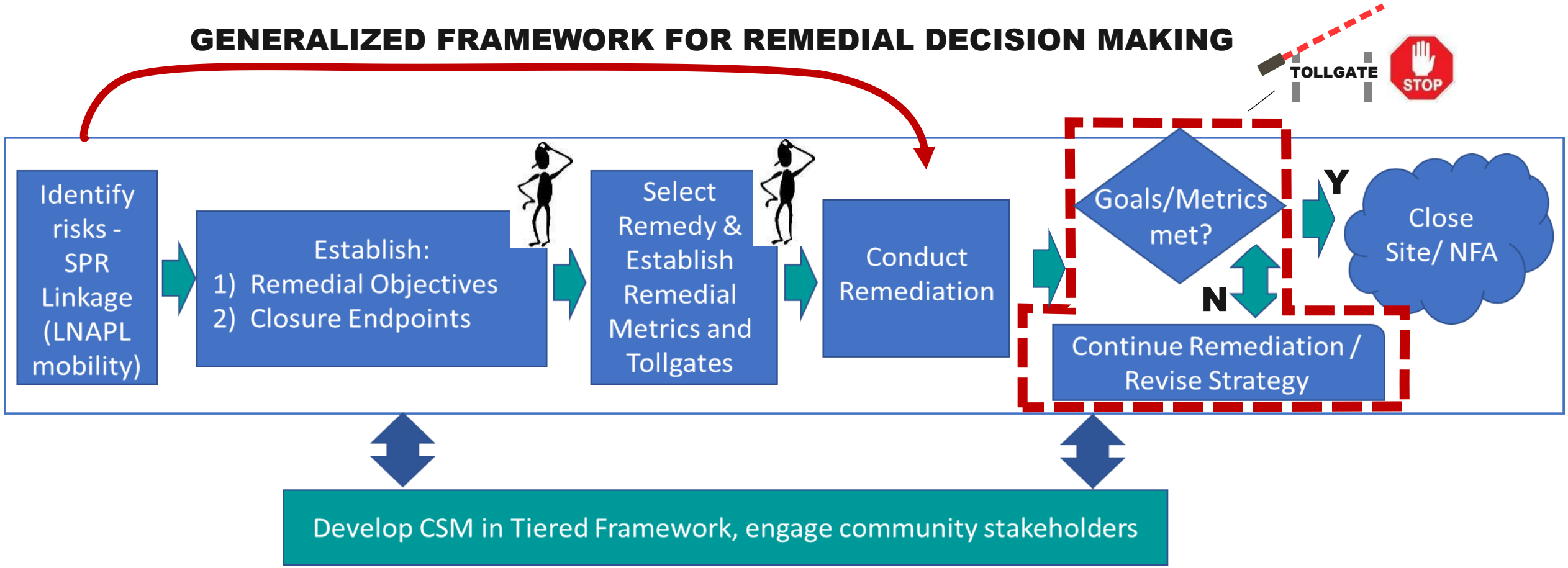
ASTM E3361-22 Standard Guide "The How"
Common Language for Remedy Transition – Standard Terminology
01
Why quantify natural NAPL attenuation?

Case for Change:
Systems Operating Beyond Useful Lifespan

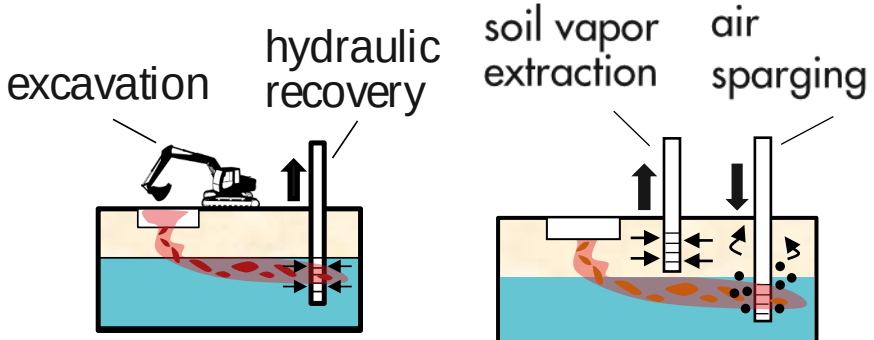


Matthew Lahvis (Shell)

Case for Change: Poorly Defined Remedial Concerns

IMPACTED SITE

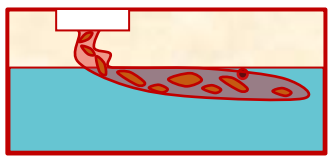
ACTIVE SYSTEM



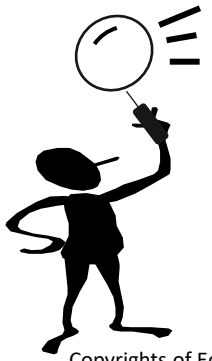
FREE-PRODUCT REMOVAL (max. extent practicable)

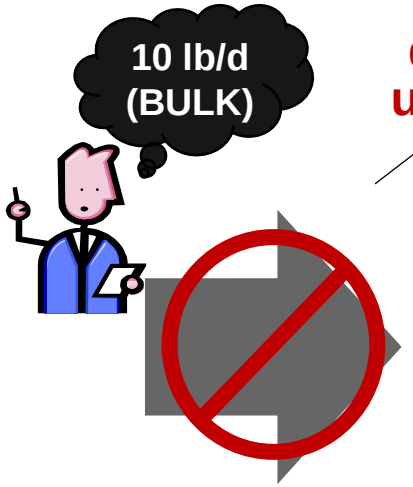
MASS REDUCTION (CONVENTIONAL)

NATURAL SYSTEM



NATURAL ATTENUATION (COPCs)

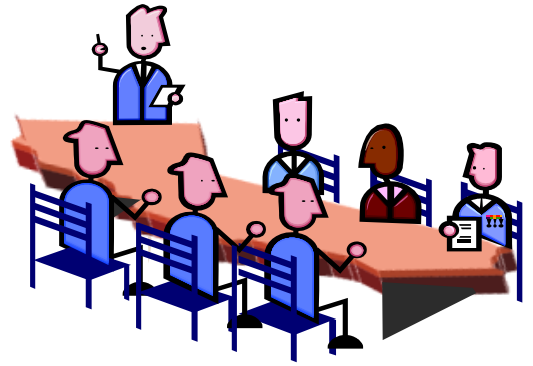




disconnect drives unnecessary active remediation

END POINT

REGULATORY CRITERIA (CLEAN-UP LEVELS)



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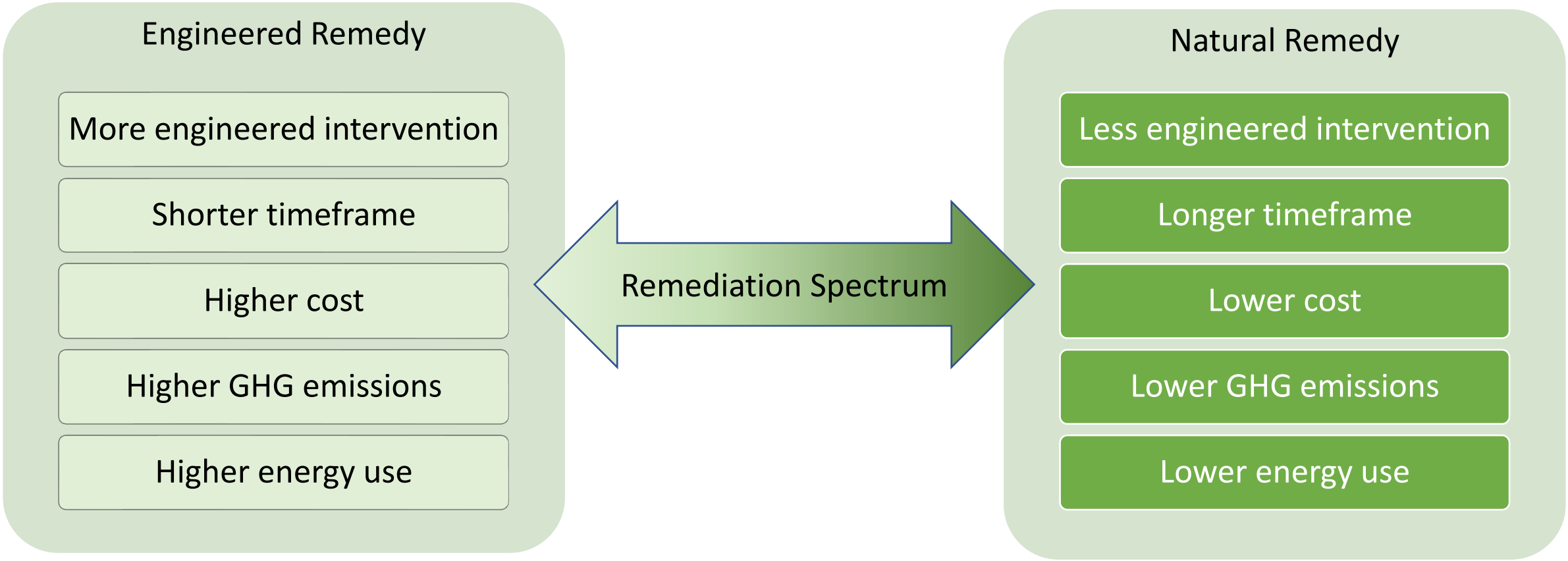
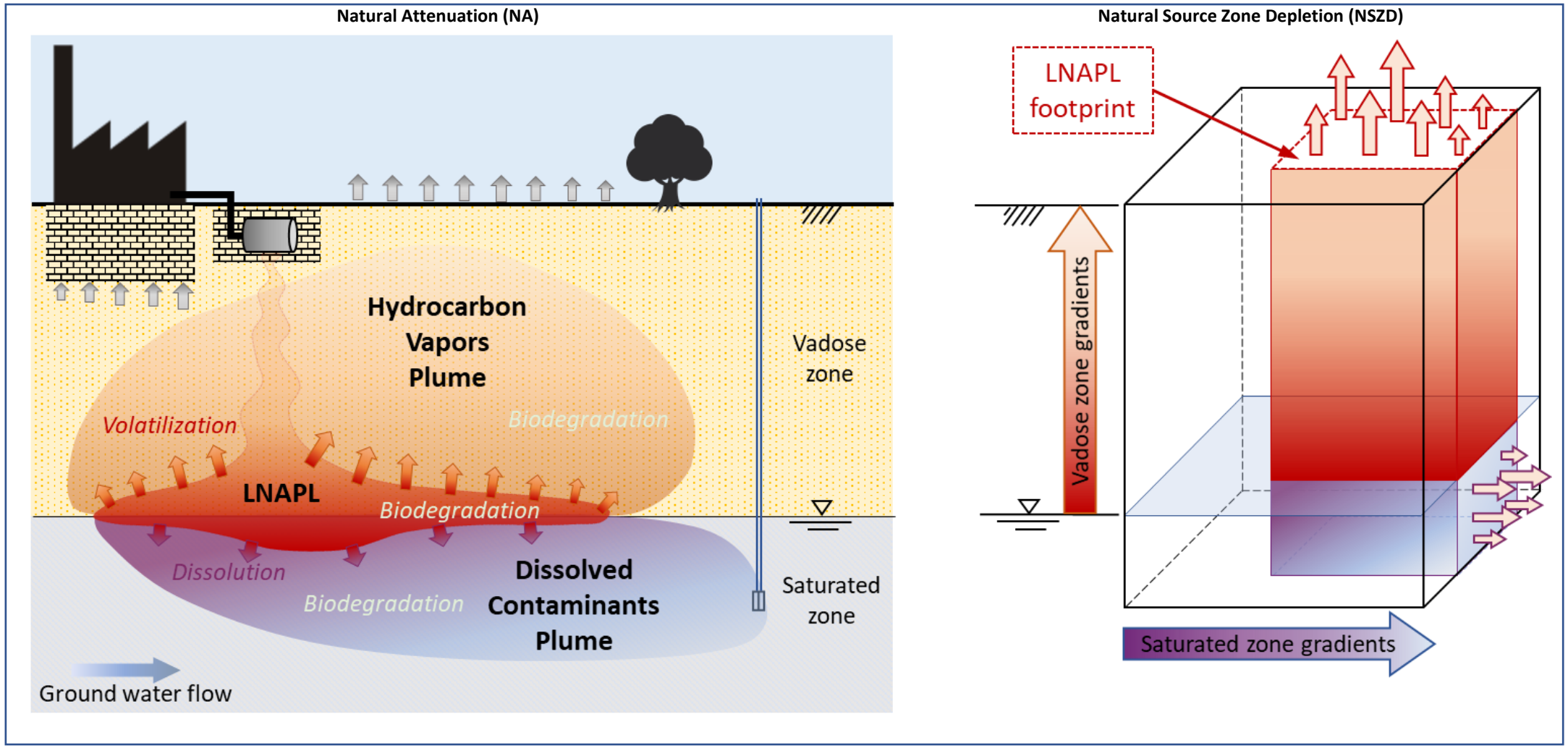
Remedy Transition

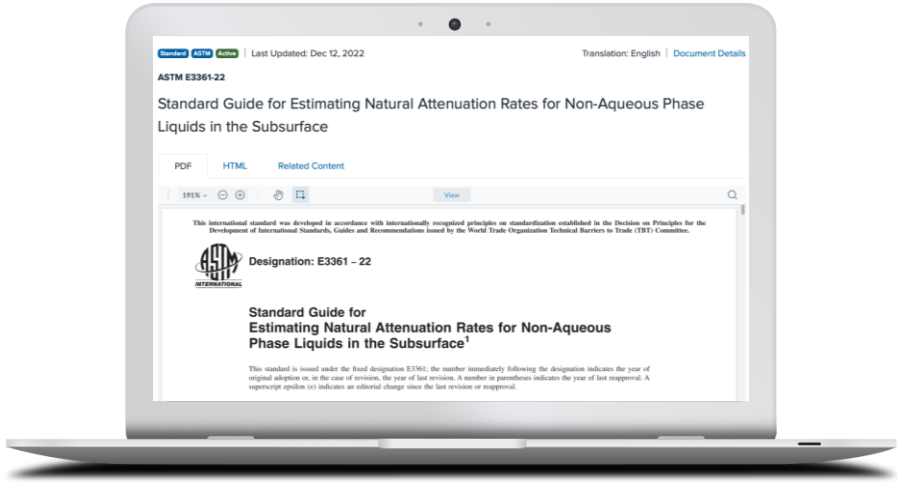


Natural Attenuation & Natural Source Zone Depletion (NSZD)



Natural Attenuation Estimation Methods

1. CO_2 Efflux Method
2. Temperature Gradient Method
3. Soil Gas Gradient Method
4. Groundwater Monitoring Method
5. NAPL Composition Method



ASTM E3361

Multiple technologies & approaches for data collection & interpretation for each method…

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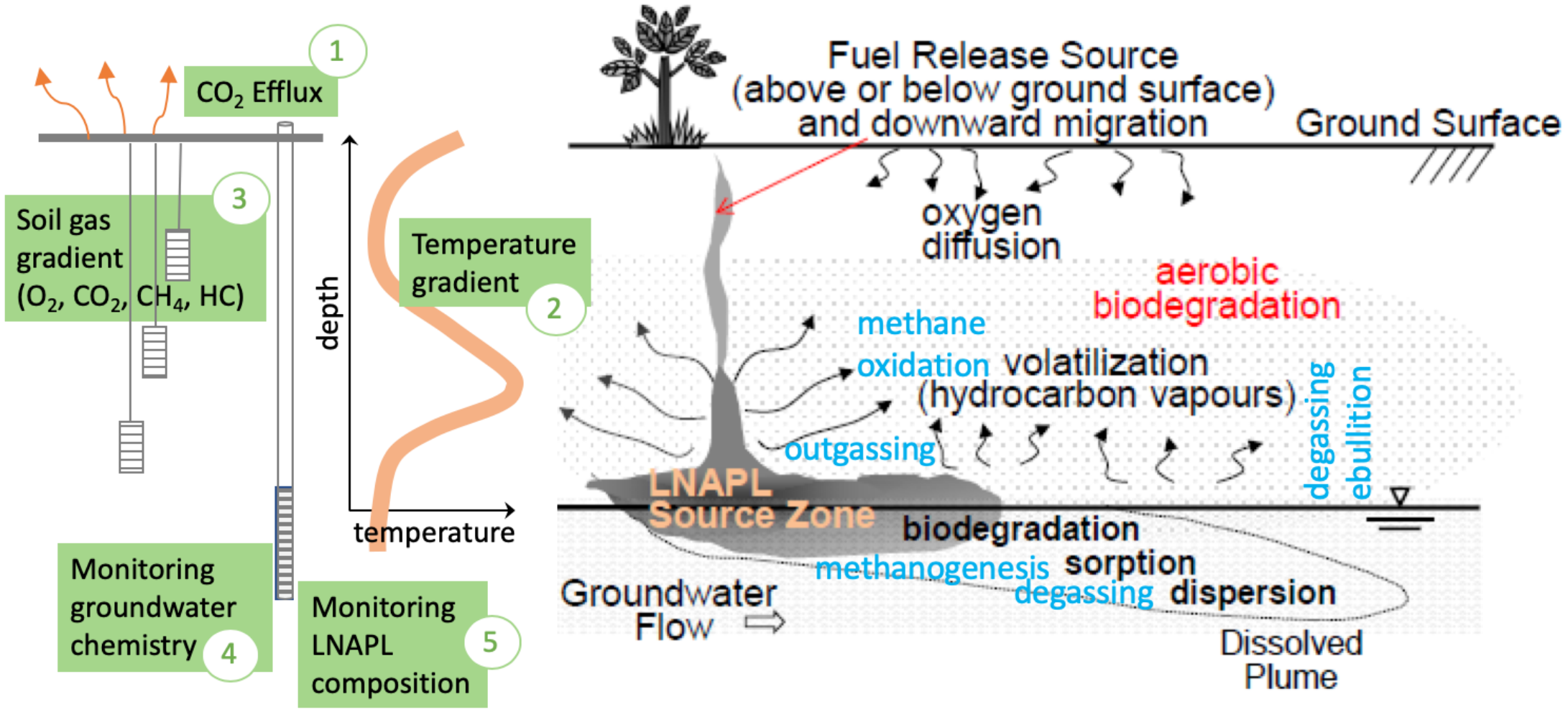
Natural Attenuation Processes & Pathways



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CO_2 Efflux Method – Example Implementation

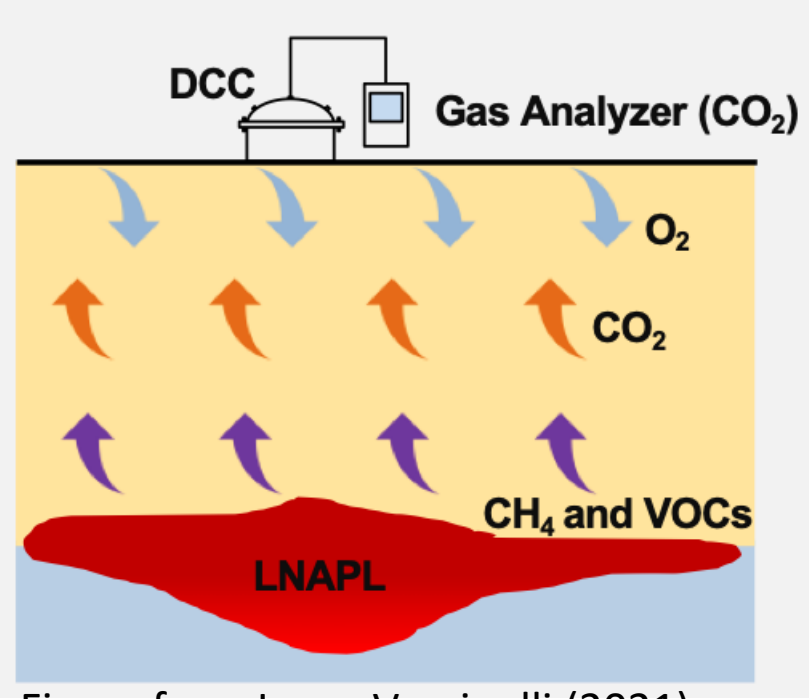

Figure from Iason Verginelli (2021)

Step 1. Install DCC

Step 2. Estimate the CO_2 Efflux, J_{CO2}

Step 3. Correct for background sources

$$J_{CSR} = J_{CO_2} - J_{NSR}$$

J_{CSR} = attributed to NAPL soil respiration (μmol CO_2/m^2/s)
J_{CO2} = total measured (μmol CO_2/m^2/s)
J_{NSR} = attributed to natural soil respiration (μmol CO_2/m^2/s)

Step 4. Estimate the NSZD Flux

$$J_{NSZD} = J_{CSR}\frac{M_w S_{HC:CO2} U}{\rho_o}$$

J_{NSZD} in gallons/acre/year.
M_w = Molar weight of hydrocarbon (g/mol)
$S_{HC:CO2}$ = Stoichiometric ratio of a mole of hydrocarbon degraded per mole of CO_2 produced
ρ_o = Density of hydrocarbon (kg/L)
U = Unit conversion factor = $33.7\frac{s}{year}\times\frac{kg}{\mu g}\times\frac{m^2}{acre}\times\frac{gallon}{L}$

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Example: CO_2 Efflux Method

Tools	Products / Instruments
Dynamic closed chamber Active air flow connected to infrared detector Measurement time scale: snapshot (minutes) Continuous monitoring	LI-COR Biosciences Automated Soil Gas Flux System
Static trap Sorbent material to passively capture CO_2 Measurement time scale: weeks (~1 to 4 weeks)	E-Flux Fossil-Fuel Trap
Forced diffusion dynamic chamber Flow regulated by gas permeable membrane Measurement time scale: snapshot (minutes) continuous monitoring	Eosense eosFD soil CO_2 flux sensor

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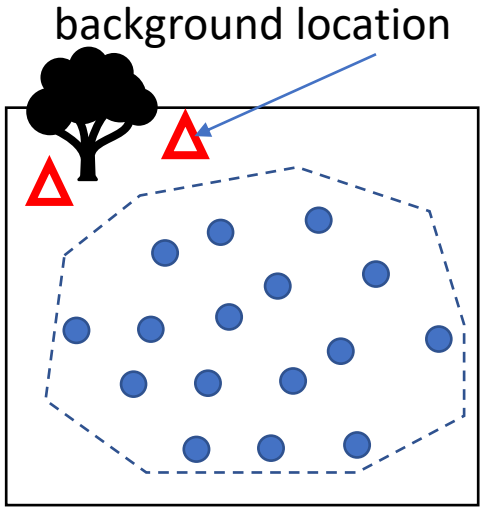
Background Sources of CO_2

- CO_2 produced from natural soil respiration

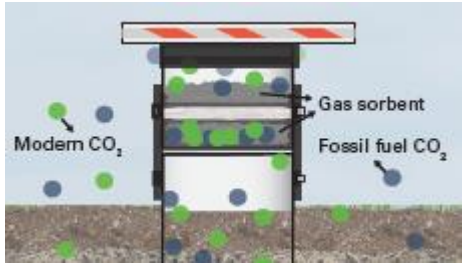
CO_2 Efflux = Contaminant Soil Respiration + Natural Soil Respiration

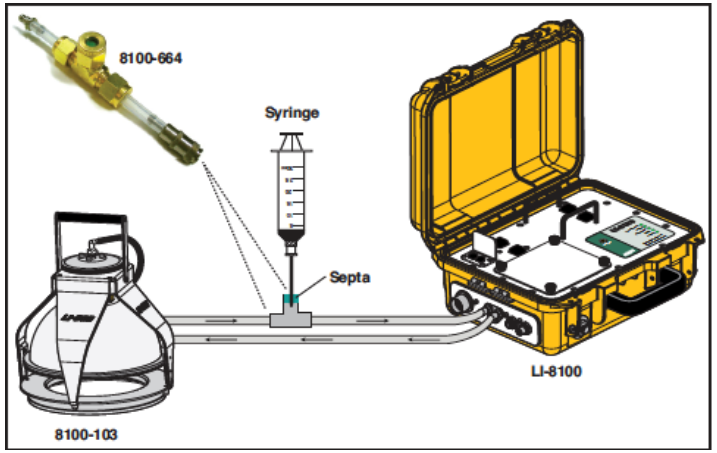
- Two general approaches:
  - Sampling background locations
  - Sampling & analysis of radiocarbon (^{14}C)
- Design of program for background correction is site specific:
  - Heterogeneity in surface cover & vegetation
  - Heterogeneity in hydrogeologic conditions



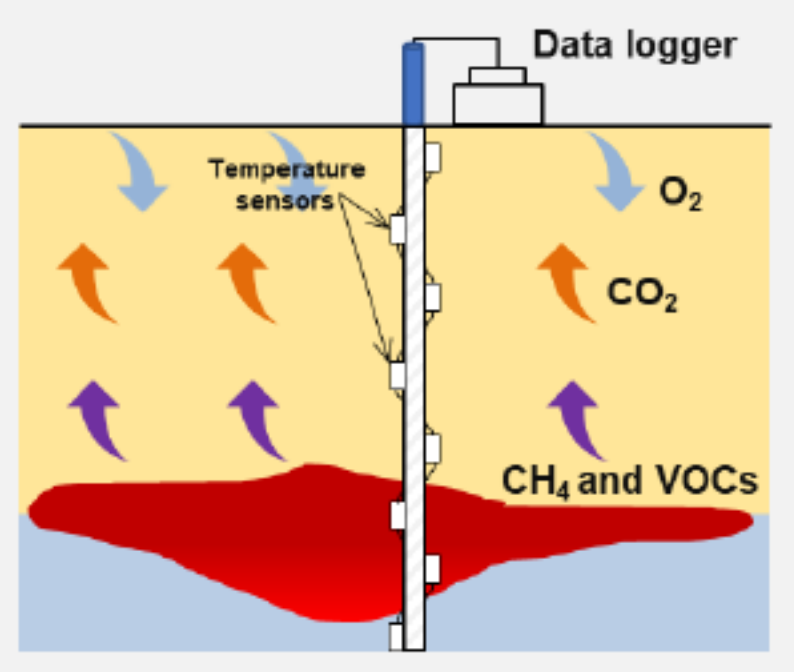
Sampling for ^{14}C Analysis

Contemporary (modern) organic carbon is ^{14}C-rich, while fossil fuel carbon is ^{14}C-depleted





Temperature Gradient Method – Example Implementation



Step 1. Identify the temperature profile

Step 2. Correct for background sources (select from three approaches)

Thermal correction approach	Measurement at background location
Background correction	yes
Thermal correction from surface heating and cooling – "single-stick" method	no
Thermal correction from surface heating and cooling - modeling	no

Step 3. Estimate the NSZD Flux, J_{NSZD}

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Temperature Gradient Method – New Guidance Content

Advances in the in-situ estimation of soil thermal conductivity

1. Active heat source is supplied and changes in temperature are monitored (Karimi Askarani et al. 2021)
2. Long-term temperature monitoring to estimate thermal diffusivity (Sweeney, unpublished and Kulkarni et al. 2021)

– requires estimate of volumetric heat capacity based on soil type and moisture content.

Advances in correcting for background sources

- Solution to heat conduction in 1-D at steady state
- Solving for three unknown variables:
  1. boundary condition of heat source/sink at the ground surface
  2. NSZD related heat source
  3. depth of the heat source
- Iterative algorithm & optimized fit between the observed and predicted temperature profiles

"Single-Stick" Method

Thermal estimation of natural source zone depletion rates without background correction

Water Research 169 (2020) 115245

Kayvan Karimi Askarani, Thomas Clay Sale*

Civil and Environmental Engineering Department, Colorado State University, 1320 Campus Delivery, B01, Fort Collins, CO. 80523-1320, USA

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Soil Gas Gradient Method – Example Implementation

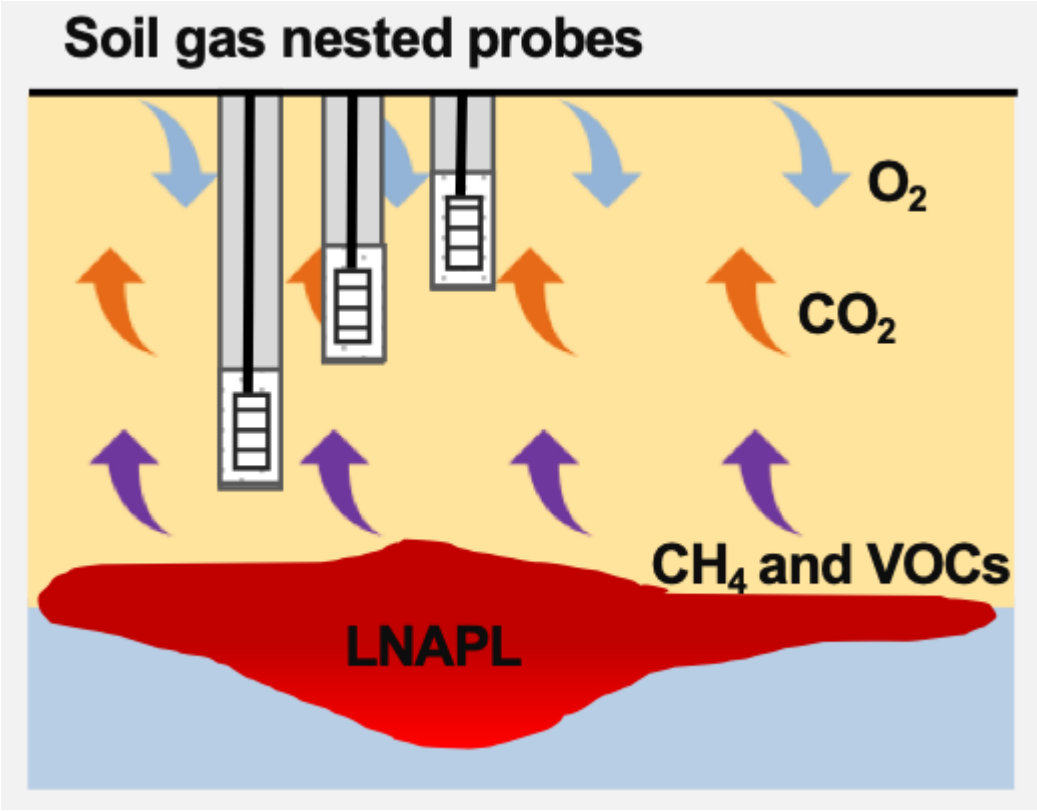


Figure from Dr. Iason Verginelli (2021)

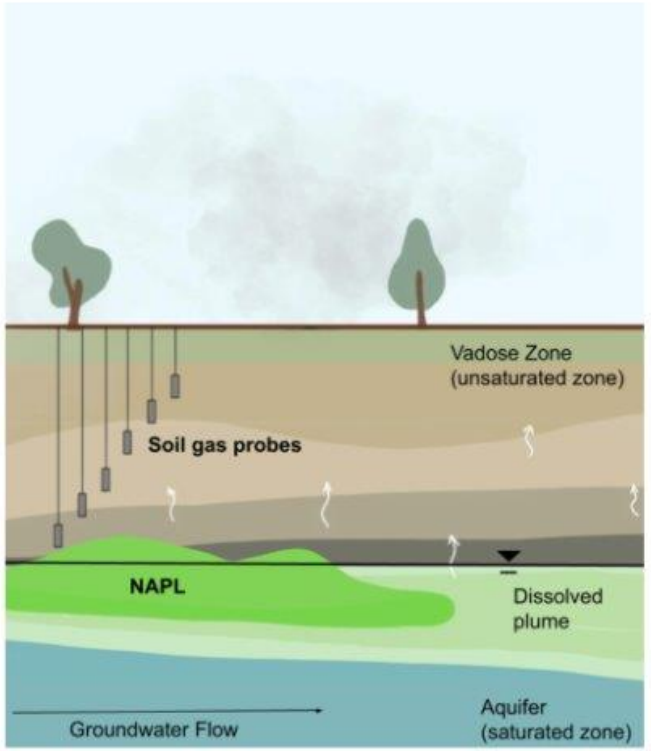
Step 1. Identify the O_2 concentration profile in soil gas
Step 2. Estimate the concentration gradient of O_2 in soil gas
Step 3. Estimate the reaction length
Step 4. Estimate the diffusion coefficient
Step 5. Estimate the mass flux
Step 6. Correct for background O_2 demand (two approaches)
Step 7. Estimate the NSZD Flux, J_{NSZD}

$$J_{NSZD} = J_{CSR} S_{HC:O2}$$

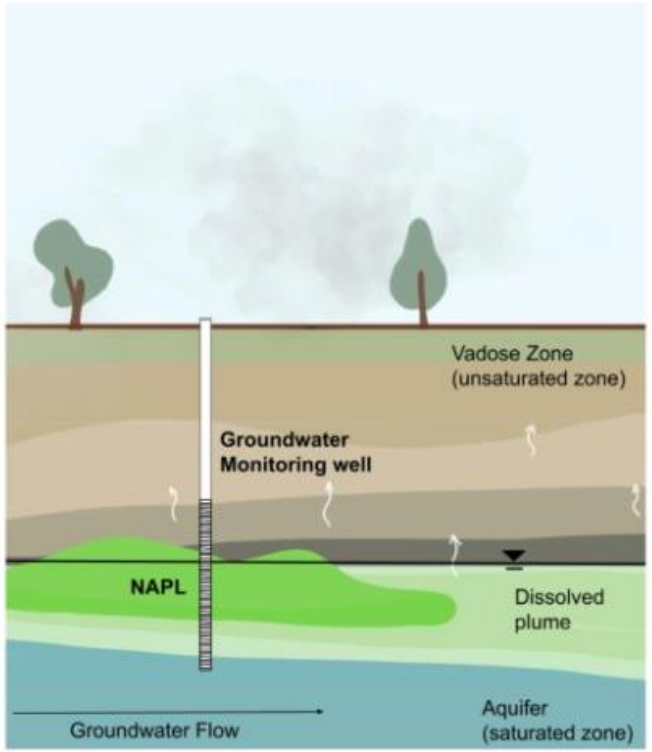
J_{NSZD} in gallons/acre/year
$S_{HC:O2}$ = Stoichiometric mass ratio of g of hydrocarbon degraded per g of O_2 consumed

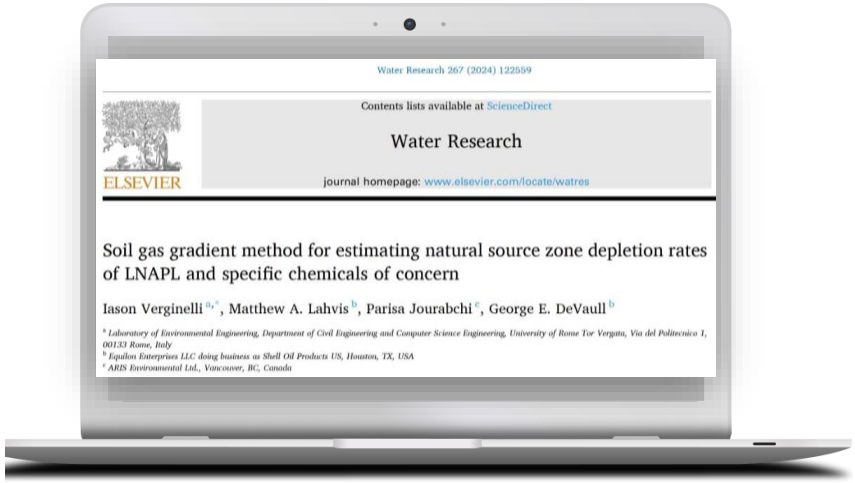
Advances in Soil Gas Method (SGM E-Tool)

Simplified Approach



Screening Approach





Verginelli et al (2024) Water Research

COC-specific rates directly linked to risk reduction

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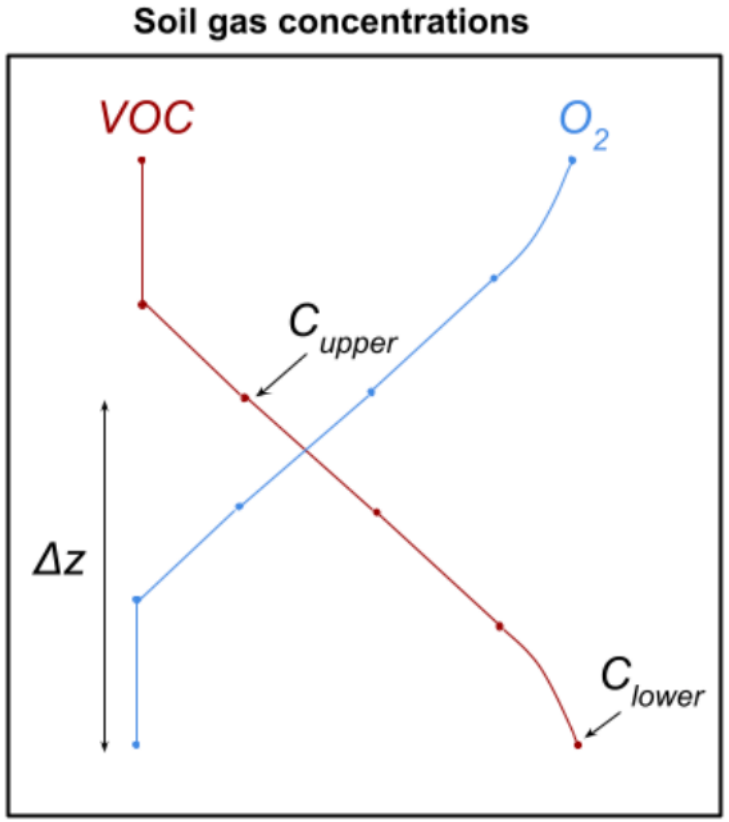
SGM Input



Full details and references
in the User Guide and FAQs of the SGM E-Tool

Vapour Substance (CAS Number)

benzene (71-43-2)

Soil Type

Sand

System Temperature °C

10

C_{upper} (µg/m^3)

100

Soil gas concentration at the upper control point

C_{lower} (µg/m^3)

100000

Soil gas concentration at the lower control point

Vertical distance, Δz (m)

2

Vertical distance between the upper and lower control points, where C_{upper} and C_{lower} are measured, respectively.

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SGM Output

SGM Output			
System Temperature Kelvin	T_s	2.83E+02	Kelvin
Diffusivity in air	D_{air}	7.73E-01	m^2/day
Diffusivity in water	D_{h2o}	8.90E-05	m^2/day
Henry's law constant at the system temperature	H_s	1.24E-01	-
Effective diffusion coefficient	D_{eff}	1.44E-06	m^2/s
Reactive diffusive length	L_R	2.90E-01	m
NSZD flux	J	4.300E-02	g/m^2/day

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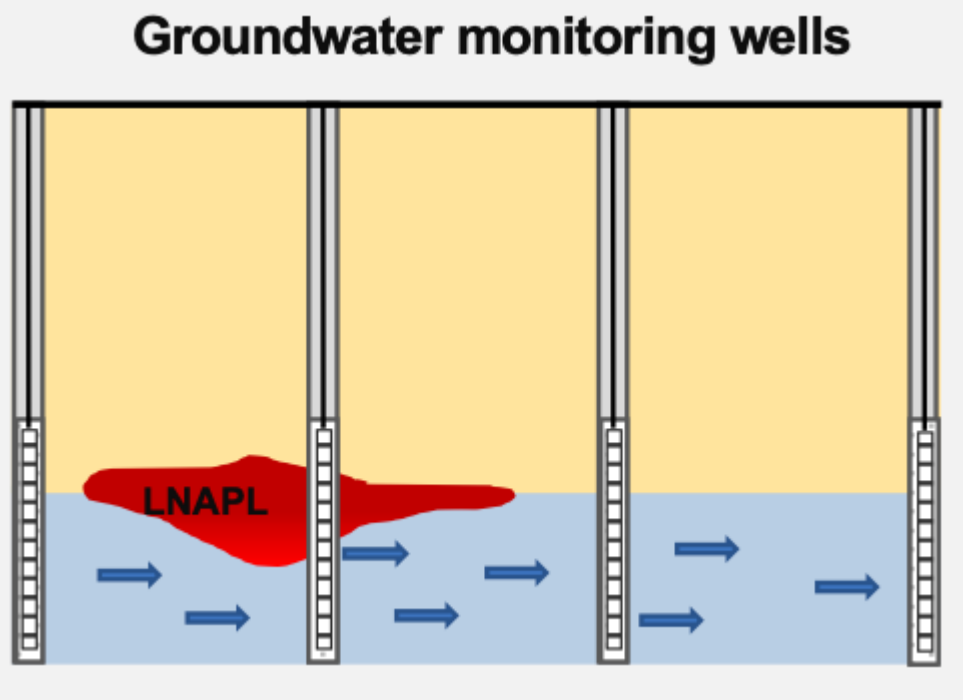
Groundwater Monitoring Method – Example Implementation



Step 1. Estimate source mass depletion due to dissolution & flow

Step 2. Estimate the assimilative capacity, A_c, based on groundwater monitoring data

Step 3. Assess conditions for **degassing & calculate A_c accordingly**

Step 4. Estimate the rate of biodegradation in the saturated zone

Step 5. Estimate the total rate in the saturated zone, R_{sat} (kg/day)

$$R_{sat} = R_{sat-dis} + R_{sat-bio}$$

R_{sat} = total mass loss of hydrocarbons in the saturated source zone combination of dissolution and flow of the hydrocarbons ($R_{sat-dis}$) and the rate of hydrocarbons biodegraded ($R_{sat-bio}$).

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Groundwater Monitoring Method – Confined NAPL Conditions

Modified Control Volume Method

Estimate methene generation based on:

1. Sampling & analysis of dissolved N_2, Ar, CO_2 and CH_4 data
2. Degassing batch model of Amos et al. (2005)
3. Model calibration
4. Include degassing into the assimilative capacity, A_C

$$R_{sat} = R_{sat-dis} + R_{sat-bio} \propto A_C$$

Using a Batch Model to Estimate Methane Production

Degassing Method Natural Source Zone Depletion Case Study
Reyenga (2020)
Applied NAPL Science Review (ANSR)

Degassing can be significant for confined NAPL/low permeability conditions

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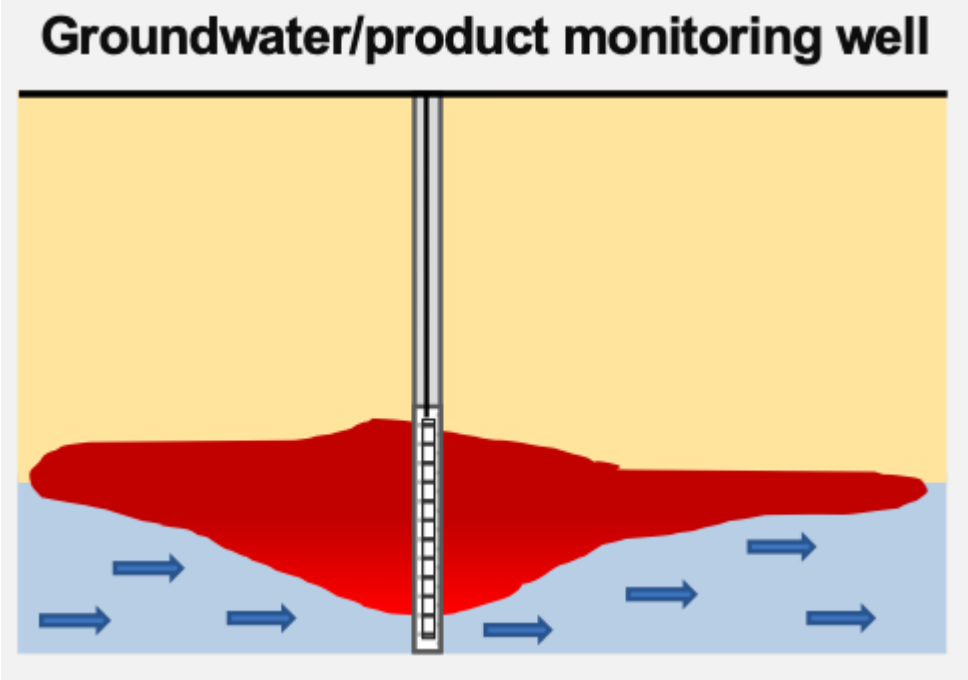
NAPL Composition Method – Example Implementation



- Conservative compound(s) increase in concentration due to weathering NAPL
- Mass loss of other compounds due to biodegradation, volatilization and dissolution
- Absolute mass loss rate estimated relative to the increase in conservative compound(s)
- Mass loss from single conservative compound

  Douglas et al. (1996)

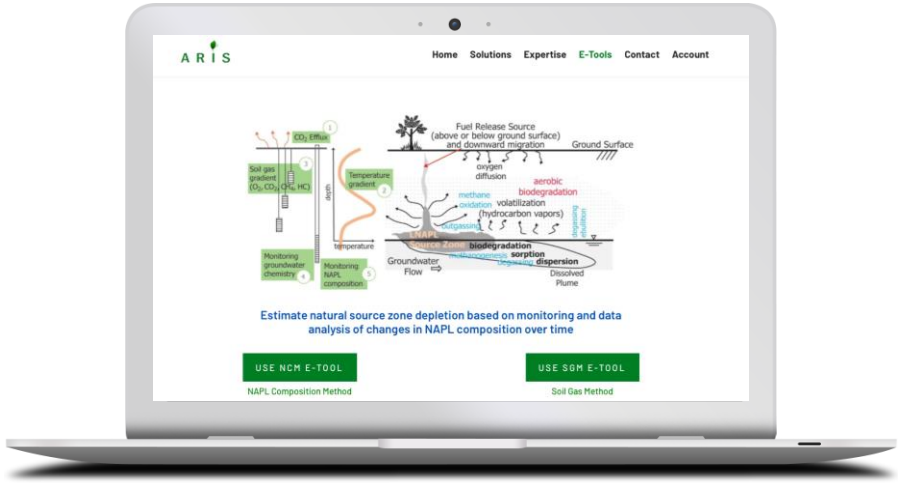
  Environmental Stability of Selected Petroleum Hydrocarbon Source and Weathering Ratios - ES&T

  Baedecker at al. (2018)

  Weathering of Oil in a Surficial Aquifer - Groundwater

NAPL Composition Method (NCM) E-Tool

Streamlining the calculations!



https://arisenv.ca/e-tools/

Input is a file containing mass fractions of each chemical

Example:

Elapsed years	0	0.025	0.5	...
benzene	0.00863	0.0095	0.00847	...
toluene	0.0653	0.0388	0.0366	...
...	...	...	...	...

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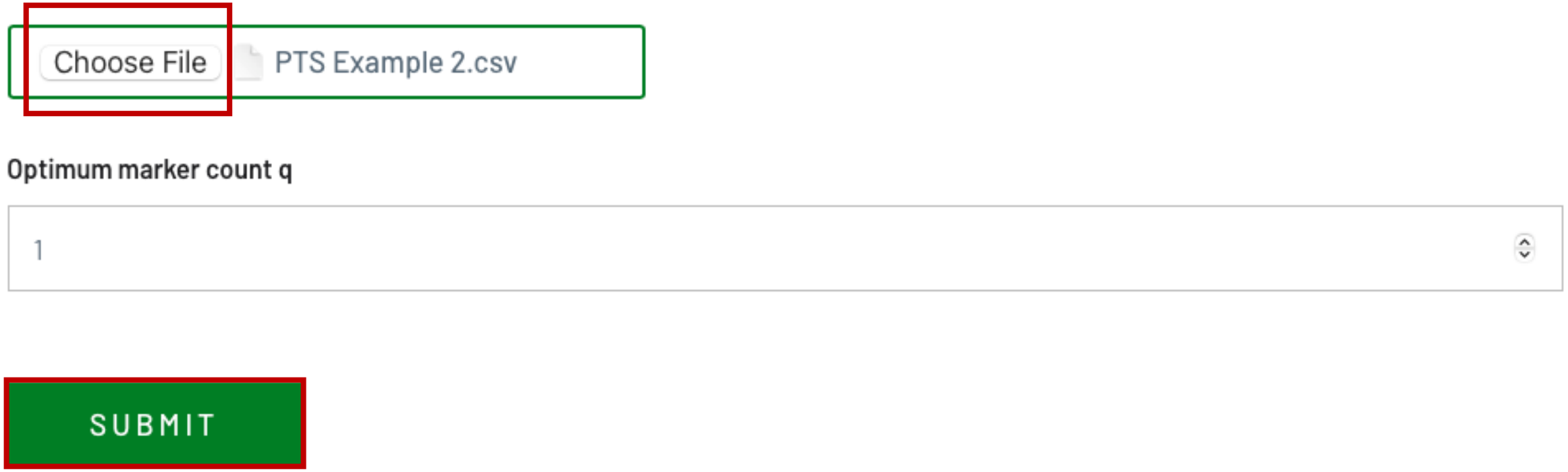
NCM Input


Choose File
PTS Example 2.csv
Optimum marker count q
1
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Rank-Ordered Output

Rank Order	Chemical Names	Relative Rates (per year)	
		Mean	95% Confidence Interval (±)
1	n-C10	1.25E-01	6.18E-02
2	n-C13	9.65E-02	1.22E-01
3	n-C5	9.06E-02	1.19E-01
4	n-C6	5.94E-02	6.99E-02
5	n-C14	5.30E-02	6.21E-02
6	n-C8	4.33E-02	3.66E-02
7	n-C12	2.63E-02	2.68E-02
8	Benzene	1.66E-02	1.27E-01
9	Toluene	1.43E-02	9.84E-02
10	n-C7	1.19E-02	4.39E-02
11	Et-Benzene	-2.16E-03	4.53E-02
12	Farnesane	-2.30E-03	5.48E-02
13	Isooctane	-2.72E-03	3.89E-02
14	n-C15	-6.62E-03	5.51E-02

Determining Site-Specific & NAPL-Specific Marker(s)

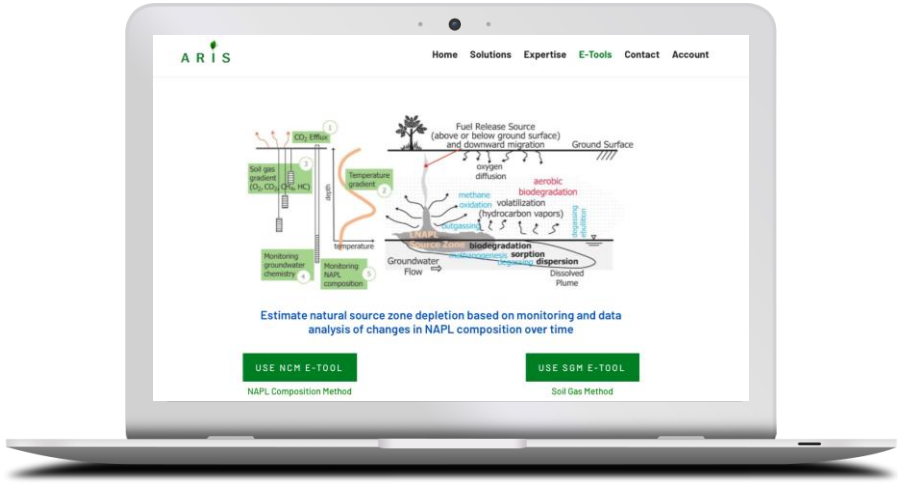
- Identify relevant constituents ☑
- Calculate relative rates ☑

$$\ln\left(\frac{\chi_{A,i}(t)}{1-\chi_{A,i}(t)}\right) = \ln\left(\frac{\chi_{A,i}(0)}{1-\chi_{A,i}(0)}\right) - \kappa_{A,i}t$$

- Highest rates, $\kappa_{A,i}$ represent most conservative constituents
- Refinement step: summed marker constituents

$q = 1 \cdots i$ (ordered ranking of rates; top 1, 2, 3, …)

NCM Output: fraction of total mass versus ordered summed constituents



https://arisenv.ca/e-tools/

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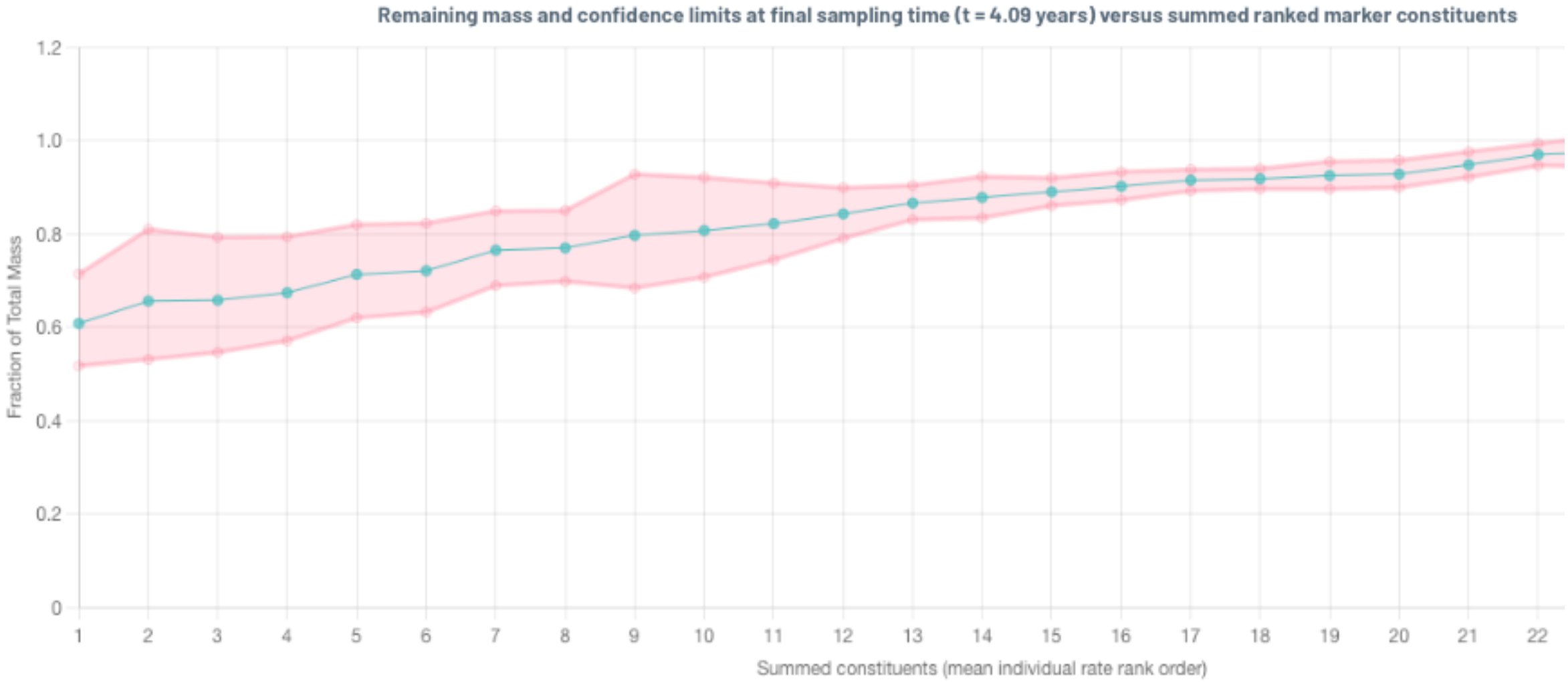
Optimum q Selection: Analysis of Fraction of Total Mass



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NCM Output with Adjusted q = 4

NCM Output for the Selected q = 4

Rank Order	Chemical Names	Relative Rates (per year)		K_{eff} (per year) (t = 0)	Half-life (years)
		Mean	95% Confidence Interval (±)	Mean	Mean
1	n-C10	1.25E-01	6.18E-02	2.36E-02	-
2	n-C13	9.65E-02	1.22E-01	-7.18E-03	96.6
3	n-C5	9.06E-02	1.19E-01	-8.81E-03	78.7
4	n-C6	5.94E-02	6.99E-02	-4.03E-02	17.2
5	n-C14	5.30E-02	6.21E-02	-4.81E-02	14.4
6	n-C8	4.33E-02	3.66E-02	-5.60E-02	12.4
7	n-C12	2.63E-02	2.68E-02	-7.41E-02	9.4
8	Benzene	1.66E-02	1.27E-01	-8.24E-02	8.4
9	Toluene	1.43E-02	9.84E-02	-8.51E-02	8.1
10	n-C7	1.19E-02	4.39E-02	-8.72E-02	7.9
11	Et-Benzene	-2.16E-03	4.53E-02	-1.01E-01	6.9

Effective Rate (per year) at t = 0

$$\kappa_{eff,i}(t=0) = \kappa_{A,q}\left(1-\chi_{0,A,q}\right) + \kappa_{A,i}\left(1-\chi_{0,A,i}\right)$$

Half-life (years)

$$t_{1/2,eff} = -\ln(0.5)/\kappa_{eff,i}$$

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Method Strengths & Limitations

Considerations & Limitations

- Long-term monitoring data representative of site-conditions
- Method assumes no additional releases during monitoring period
- Consistent analytical method and normalization over the monitoring period
- Variations in marker selections
- Constituents with non-detects
- If best available markers are not conserved -> rates are underestimated

Key Advantages

- Application of the method is not limited by location of the NAPL source zone, soil type or ground surface conditions
- Marker selection method expands applicability of method to NAPL types, such as petroleum products, that don't typically contain "presumed" markers (less soluble, volatile, higher molecular weight chemicals)
- Though computationally more complex, online tools are available for efficient data analysis

Constituent-specific depletion rates for any constituent that can be measured in the NAPL

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Key Points

- ASTM E3361 is the quantitative foundation for natural NAPL attenuation assessment.
- Framework documents (ASTM E3488, ANSR 2024) define the “why” and “when”.
- New digital tools make the methods faster, transparent, and scalable — moving quantification from research to practice.