RemTech 2022

October 14th, 2022

Session: Natural Attenuation of Petroleum NAPLs (NSZD)

Standard Guide for Estimating Natural Attenuation Rates for NAPL in the Subsurface

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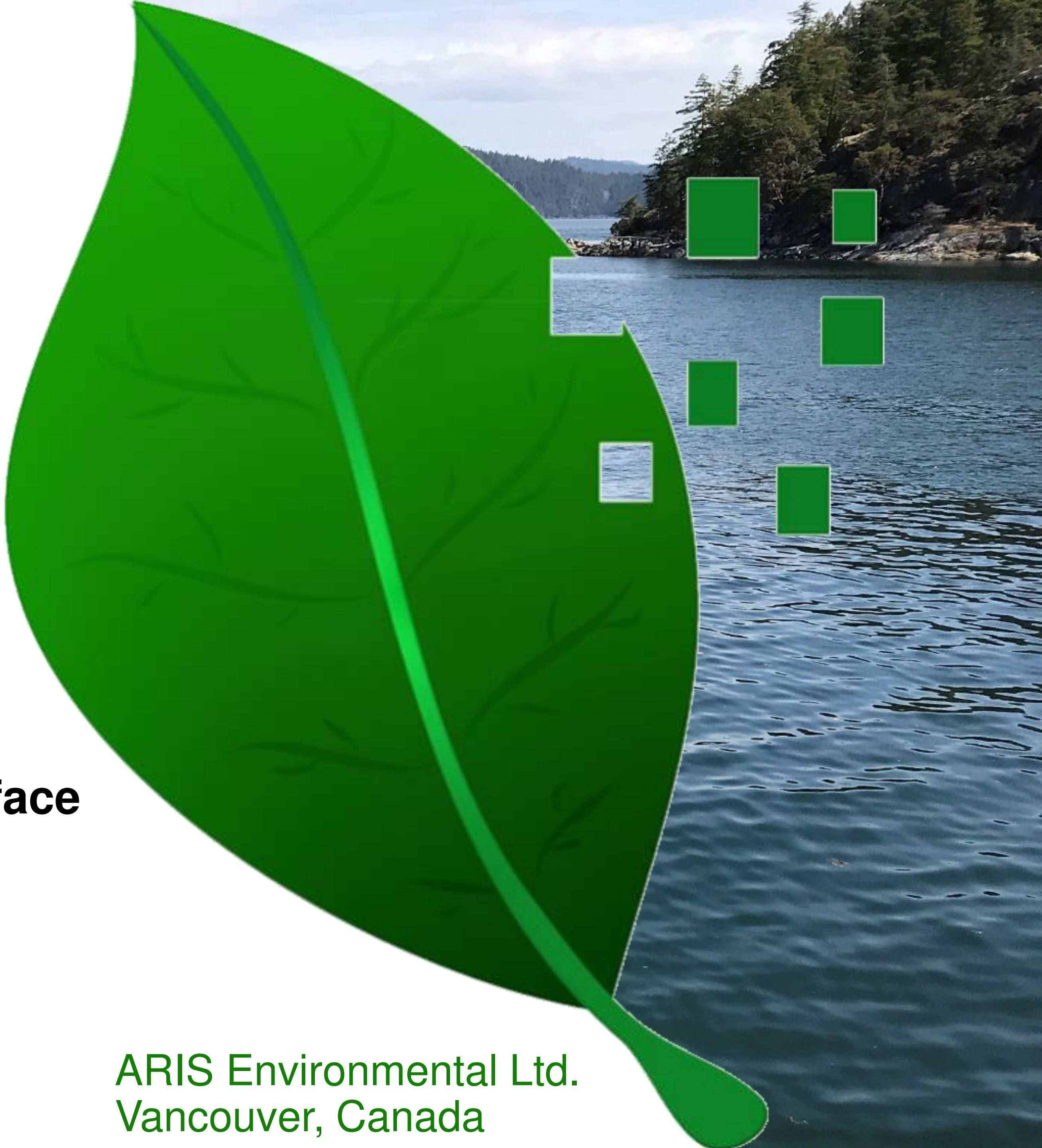
Environmental Engineer



ARIS Environmental Ltd.

Vancouver, Canada

Presentation Roadmap

Example Problems – Case Studies, Applications & Limitations

04

Advances in Technology & Data Analysis
– New Guide Content

Summary of Methods & Comparisons

03

02

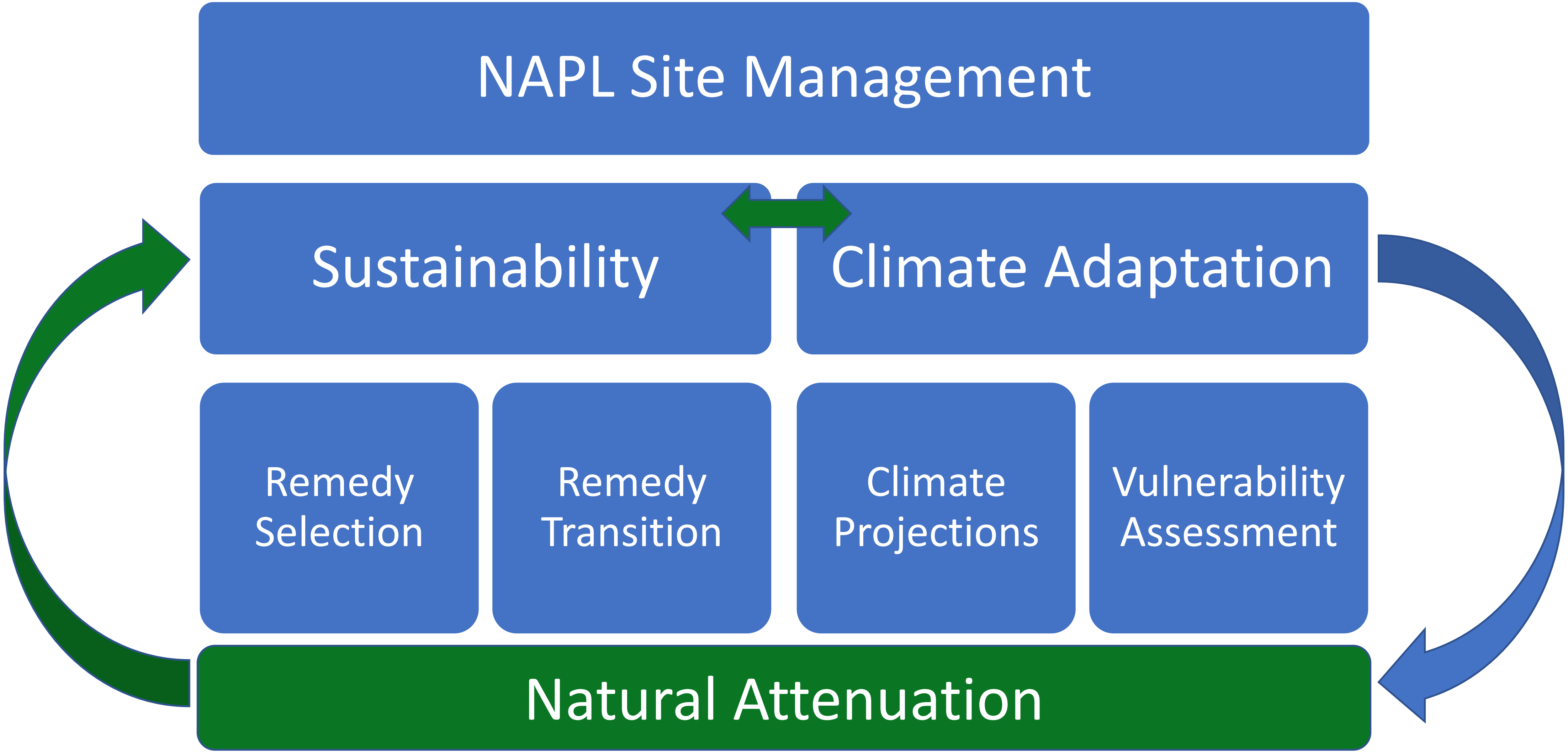
Proposed Standard Guide
ASTM WK76688
E50.04 - Structure

Common Language for Remedy Transition – Standard Terminology

01

Natural Attenuation &
Natural Source Zone Depletion -
Reasons for the New ASTM Standard Guide

Site Management in a Changing Climate



Rationale for a New Guide

- **Unique site conditions**

Tools for customized solutions using accepted methods

- **Rapid technology development**

- **Support remedial decision-making**

- **Improved Conceptual Site Model (CSM)**

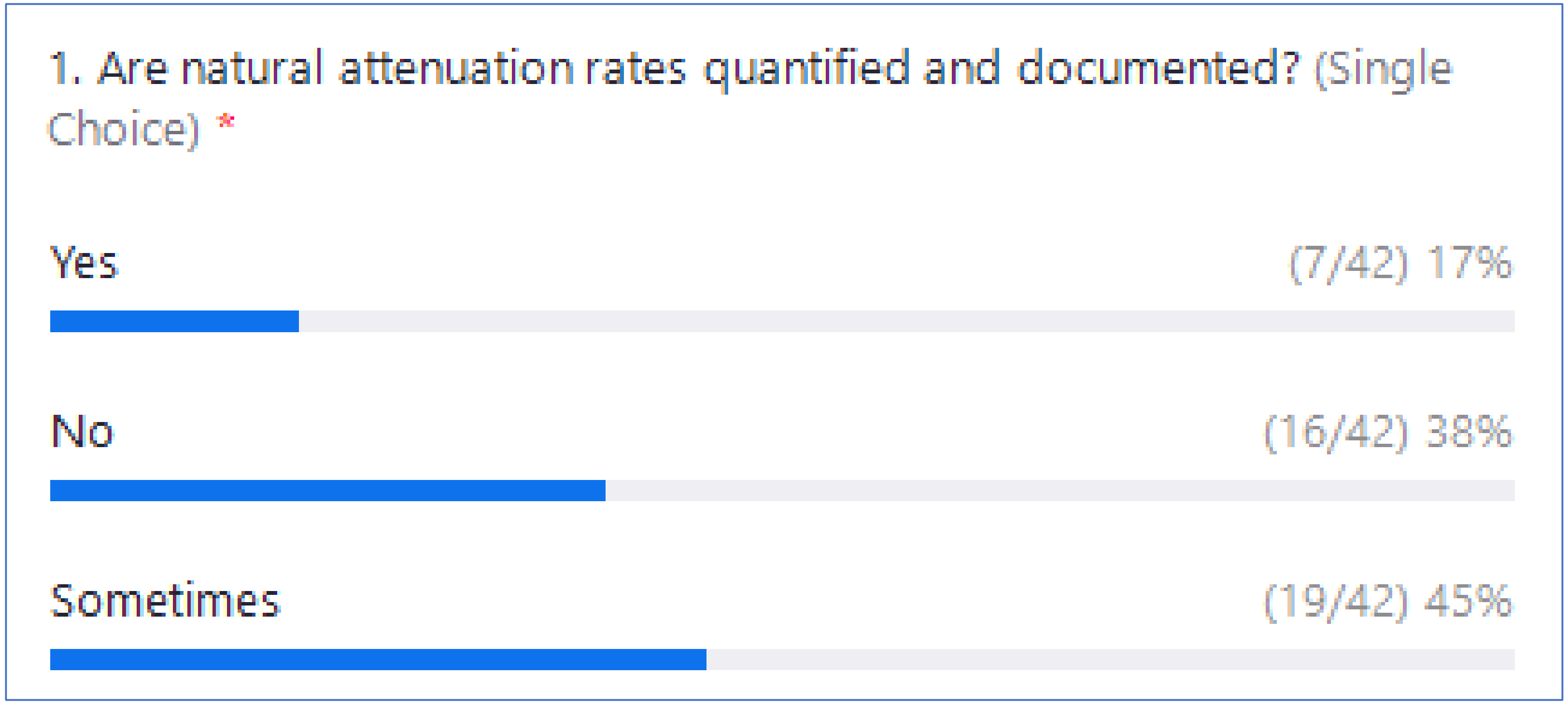
Using available site data collected for investigation/remediation

Additional data by cost-effective and non-invasive methods

- **Addressing challenges & gaps**

Survey results

Survey Results – Rates Quantified & Documented?



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Survey Results – What are the challenges in estimating the rates?

1. What do you see as challenges in estimating natural attenuation rates? (select all that apply) (Multiple Choice) *

a. Unfamiliarity with the methods / lack of consistent standards (25/38) 66%

b. Uncertainty associated with the measurements (22/38) 58%

c. Lack of regulatory guidance on application of the measured rates (23/38) 61%

d. Current remedies deemed effective (8/38) 21%

e. Budgetary constraints (19/38) 50%

Team

- Task Group of 50 members representing:
  - Academia
  - Industry
  - Regulators
  - Consultants

- Tripp Fischer, PhD, PG Brownfield Science and Technology Inc (BSTI)
  chief science officer of BSTI and chair of the ASTM Corrective Action Subcommittee E50.04, and currently serving on the ASTM International board of directors.

- Siggy Johnston, Project Manager (ARIS)

- Parisa Jourabchi, PhD, PEng, Task Group lead and the principal author (ARIS)

Remedy Transition

Engineered Remedy

- More engineered intervention
- Shorter timeframe
- Higher cost
- Higher GHG emissions
- Higher energy use

⟷ Remediation Spectrum ⟷

Natural Remedy

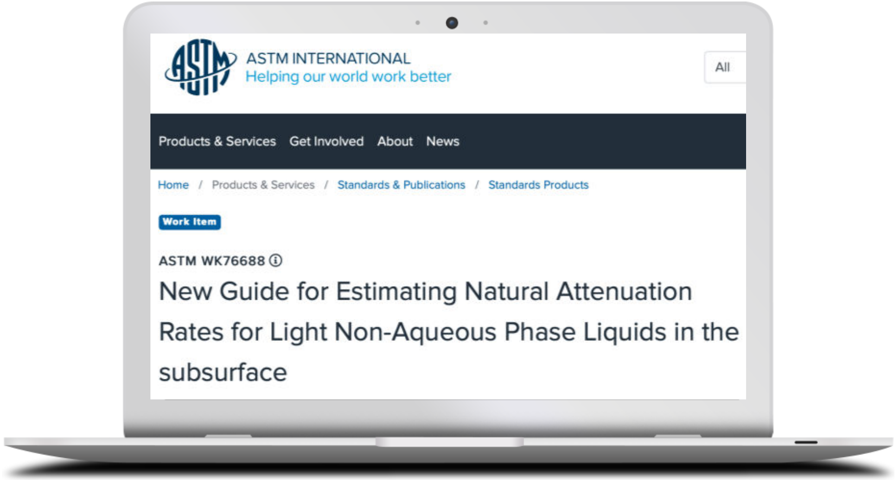
- Less engineered intervention
- Longer timeframe
- Lower cost
- Lower GHG emissions
- Lower energy use

Terminology: Natural & Engineered Remedy

Engineered Remedy: Also referred to in other guidance documents as active remediation, is generally considered to be more resource intensive in terms of cost, energy use and GHG emissions (ASTM E2876).

Natural Remedy: Also referred to in other guidance documents as passive or knowledge-driven remediation, is generally a less resource intensive remediation system mainly relying on natural or in-situ and enhanced bioremediation measures.

Monitored Natural Attenuation (MNA): A natural remedy documented through site characterization and monitoring.



https://www.astm.org/workitem-wk76688

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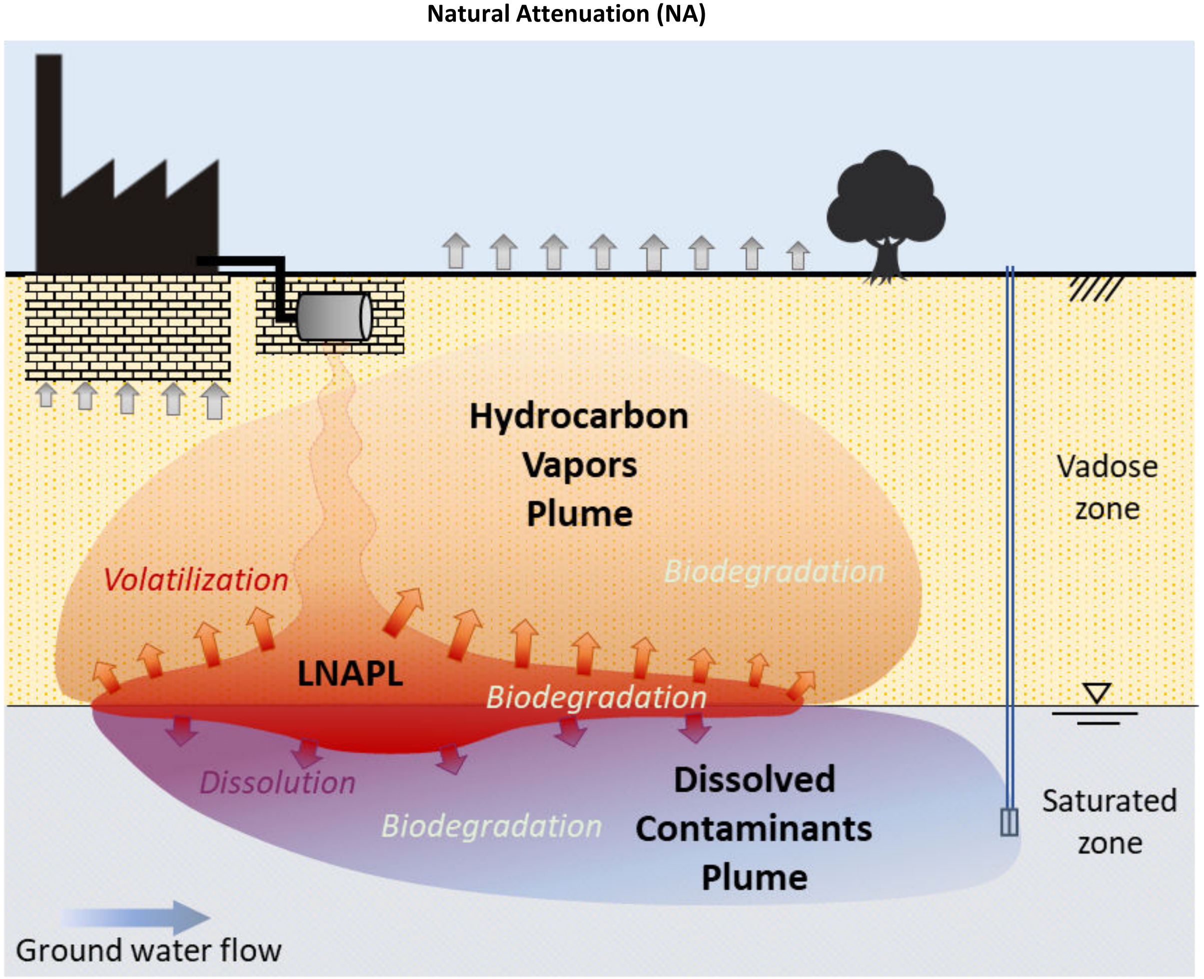
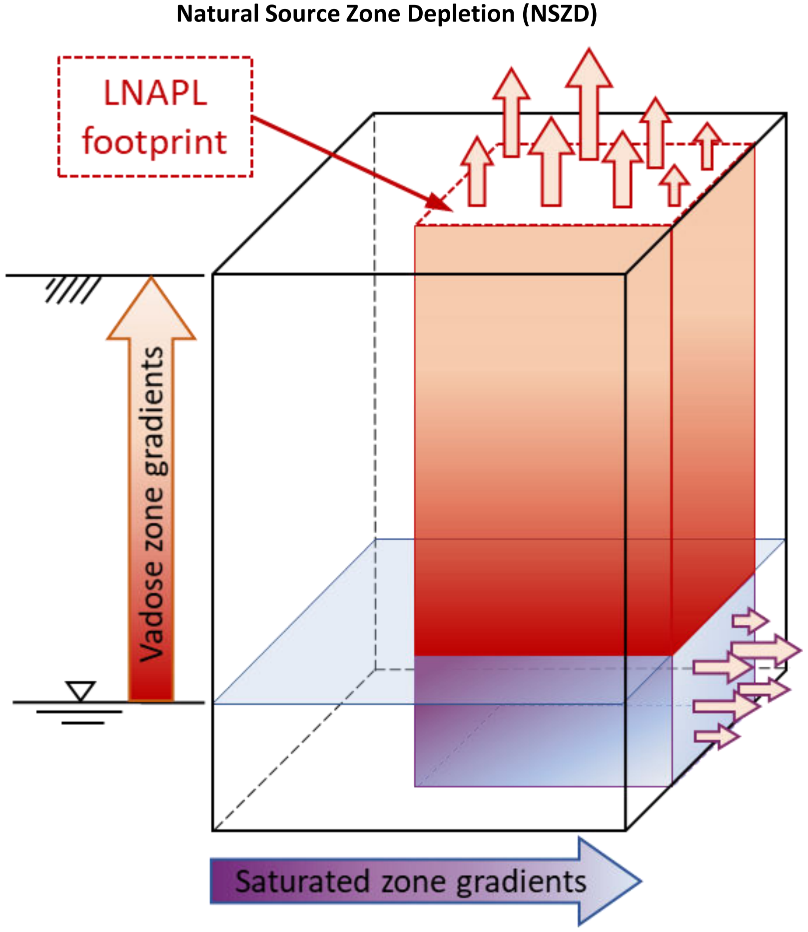
Natural Attenuation & Natural Source Zone Depletion (NSZD)





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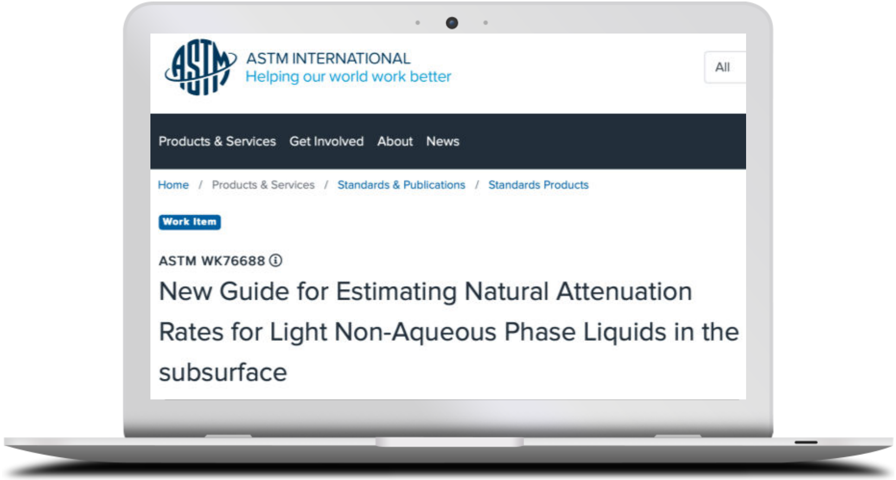
Terminology: Natural Attenuation & NSZD

Natural Attenuation: The naturally occurring mass loss of hydrocarbons in various phases and media (NAPL, vapor, soil, and groundwater) within a volume of soil or groundwater contamination.



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Natural Source Zone Depletion (NSZD): The naturally occurring mass loss of hydrocarbons in NAPL source zones as a result of dissolution, volatilization, and biodegradation.

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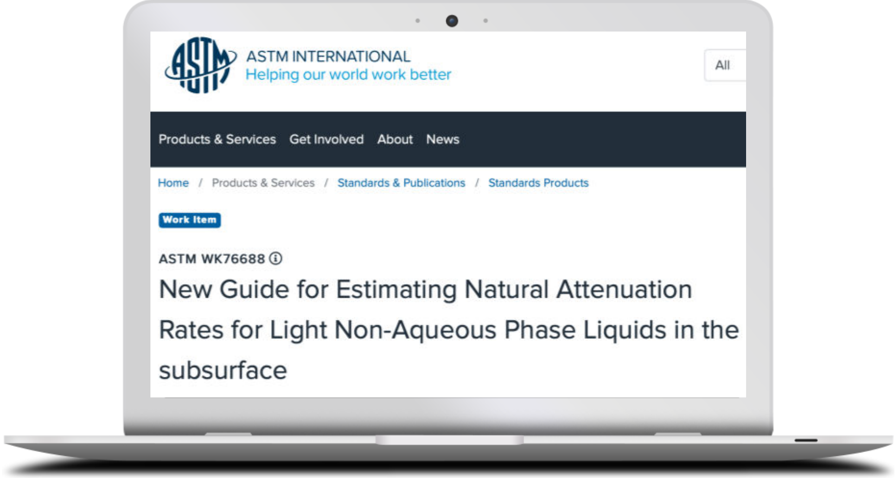
Standard Guide for Estimating Natural Attenuation Rates for Non-Aqueous Phase Liquids in the Subsurface

1. Scope
2. Referenced Documents
3. Terminology
4. Significance and Use
5. Conceptual Model of Natural Attenuation Processes & Pathways
6. Natural Attenuation Estimation Methods
7. Decision Process for Appropriate Selection of Method and Application
8. Example Problems
9. Keywords

Section 6. 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**



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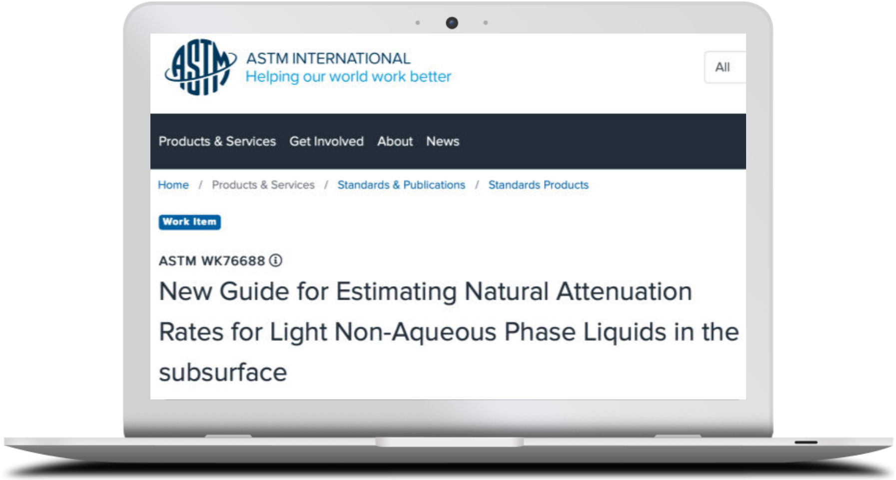
Multiple technologies & approaches for data collection & interpretation for each method…

Section 6. Natural Attenuation Estimation Methods

- Description of method & available technologies
- Screening or feasibility assessment of the method based on site conditions
- Background sources and correction methods
- Data interpretation and key considerations and challenges
- Applicability of the method for evaluating the performance of enhanced attenuation (bioremediation) systems
- Other method applications



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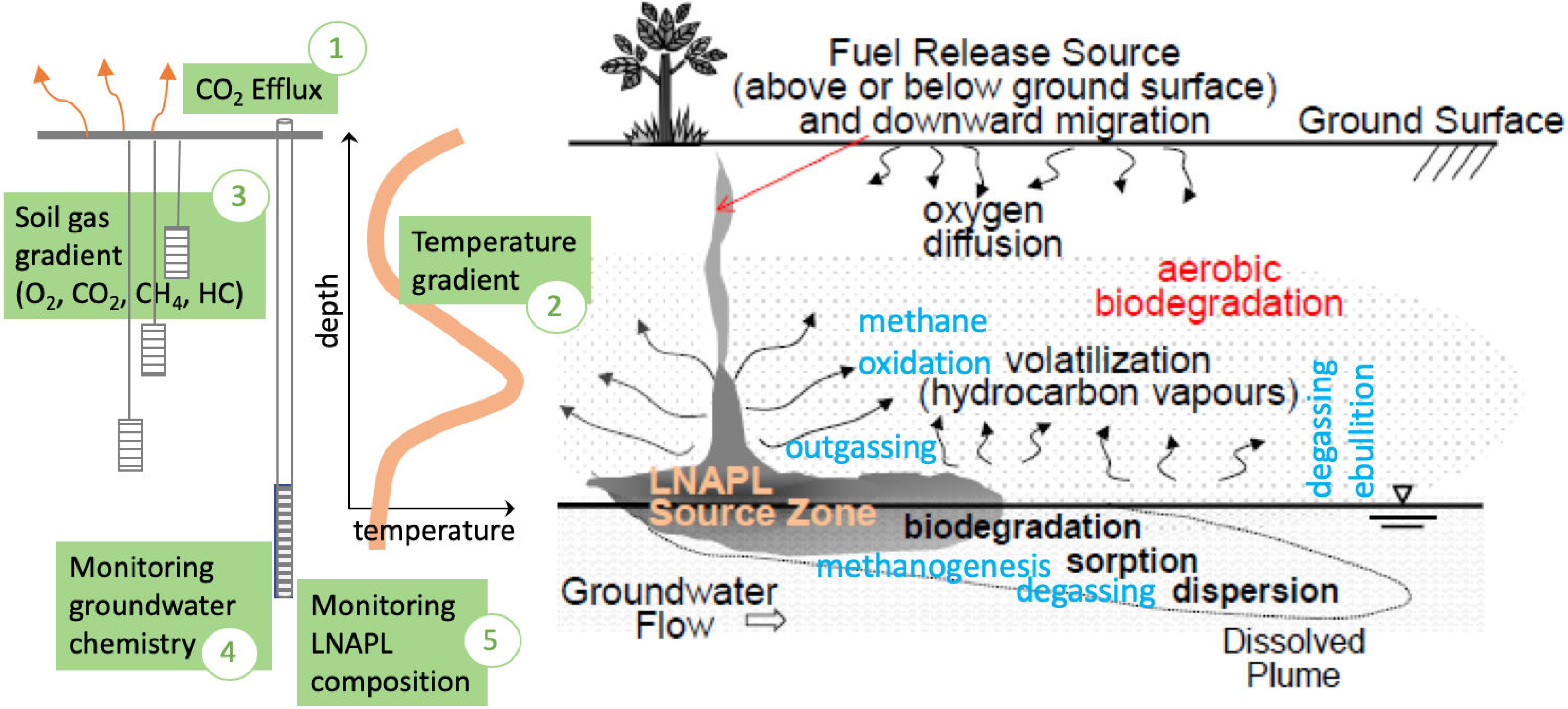
Topics covered for each of the five methods – details in Appendices X1 to X5

Natural Attenuation Processes & Pathways



CO_2 Efflux Method - Assumptions & Site-Specific Considerations

Underlying Assumptions	Site Conditions
• Attenuation of NAPL constituents through biodegradation • Complete mineralization of NAPL constituents to CO_2 • CO_2 transport in soil gas from the source to the ground surface (point of measurement) • Background source: CO_2 produced from natural soil respiration • Estimate the portion of CO_2 efflux attributable to contaminant biodegradation	• Ground surface cover • Vegetation • High natural organics (e.g., peat) • High permeability soils and barometric pumping • Low gas permeability soils • Preferential pathways (e.g., utilities)

CO_2 Efflux Method – Example Implementation

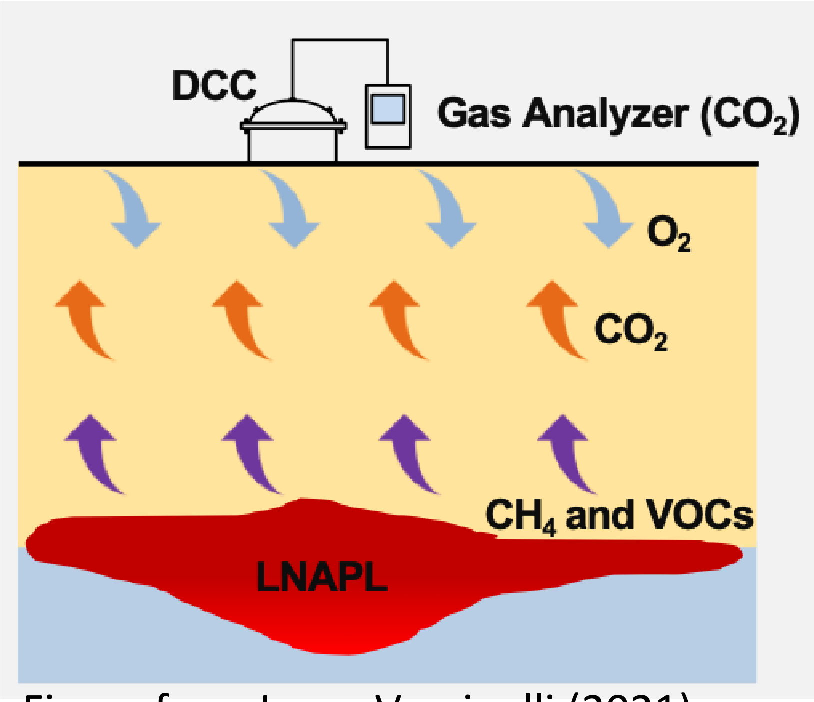


Figure from Iason Verginelli (2021)

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 $CO_2/m^2/s$)

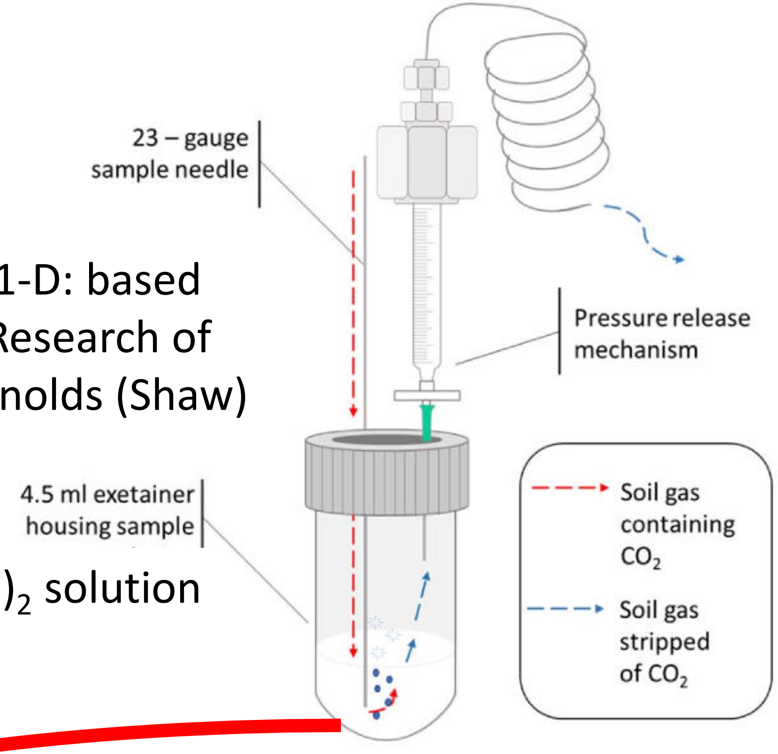
Step 4. Estimate the NSZD Flux

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

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 $= 33.7\frac{s}{year}\times\frac{kg}{\mu g}\times\frac{m^2}{acre}\times\frac{gallon}{L}$

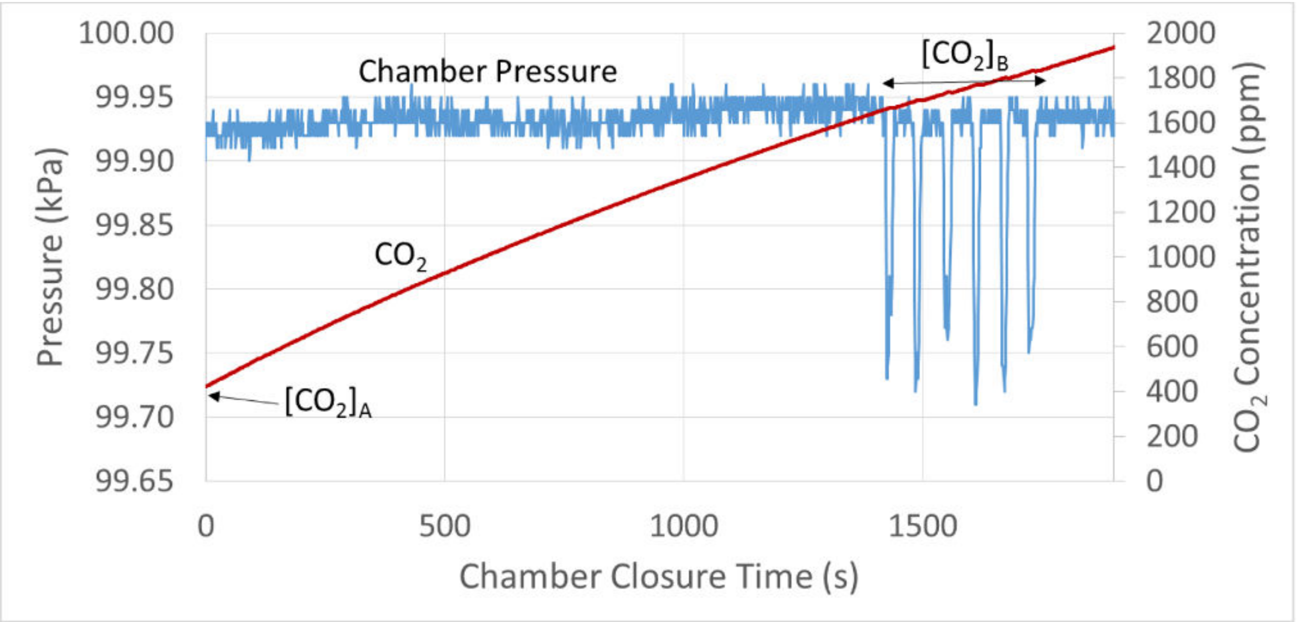
CO_2 Efflux Method – New Guidance Content

Appendix X1-D: based on the MS Research of Lindsay Reynolds (Shaw)



$BaCO_3$ precipitate shipped to the AMS lab for analysis and reporting of fraction of modern carbon

Appendix X1-B



$$F_{CSR} = 1 - {}^{14}F_s = 1 - \frac{{}^{14}F_B[CO_2]_B - {}^{14}F_A[CO_2]_A}{[CO_2]_B - [CO_2]_A}$$

Laboratory reported fraction of modern carbon

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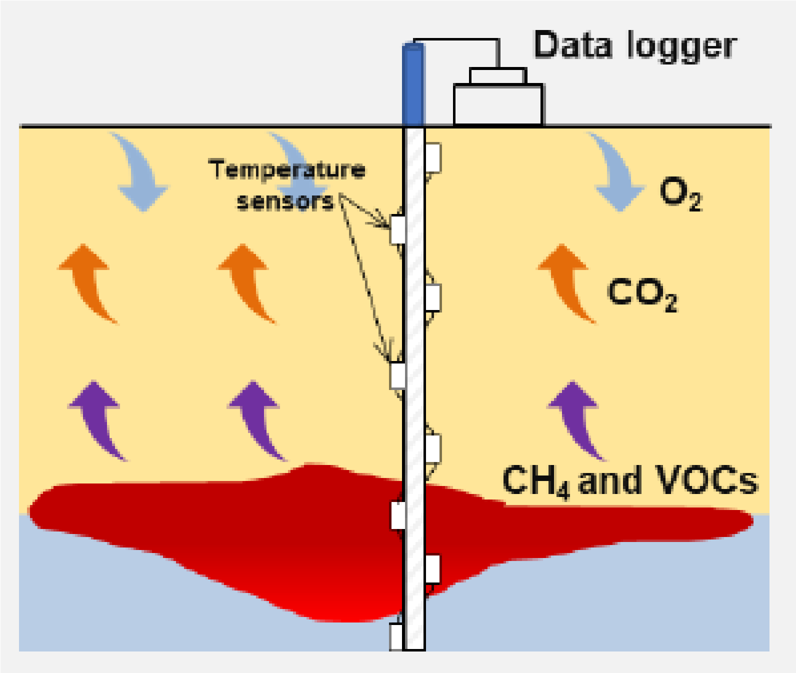
Temperature Gradient Method – Assumptions & Site-Specific Considerations

Underlying Assumptions	Site Conditions
• Attenuation of NAPL constituents through aerobic biodegradation and oxygen availability • Production of biogenic heat from aerobic oxidation of hydrocarbons (notably methane) • Background correction for heat exchange with the atmosphere and other sources of heat in the subsurface	• Low gas permeability surface cover that could limit soil gas transport* • High natural organics (e.g., peat) • Confined NAPL conditions (ASTM E2856) • Geologic or anthropogenic sources of heat not related to the NAPL

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}

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

Soil Gas Gradient Method – Assumptions & Site-Specific Considerations

Underlying Assumptions	Site Conditions
• Spatial Changes in soil gas composition – vertical profile in the vadose zone resulting from biodegradation of NAPL constituents • Vertical gradients in O_2, CO_2, or hydrocarbon concentrations in soil gas • Diffusive gas transport in the vadose zone	• Low gas permeability surface cover that could limit O_2 ingress* • Low gas permeability soils • Soil gas advection from barometric pumping effects or high methane concentrations

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Soil Gas Gradient Method – Example Implementation

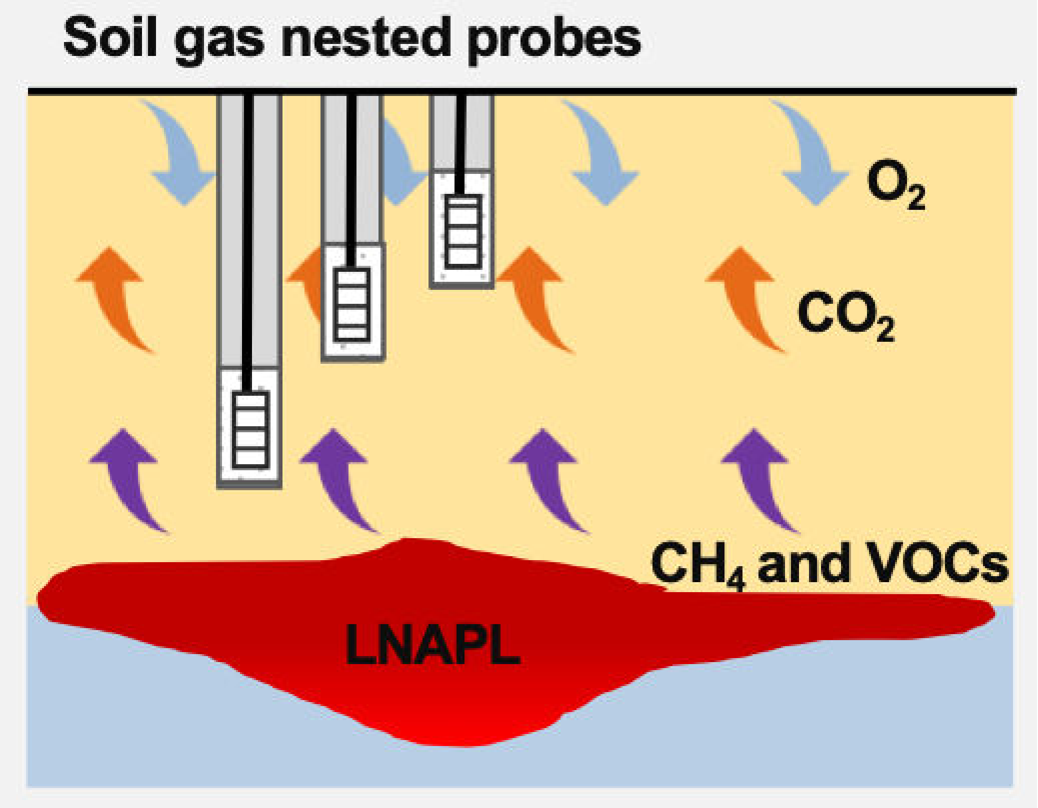

Figure from Dr. Iason Verginelli (2021)

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}

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

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

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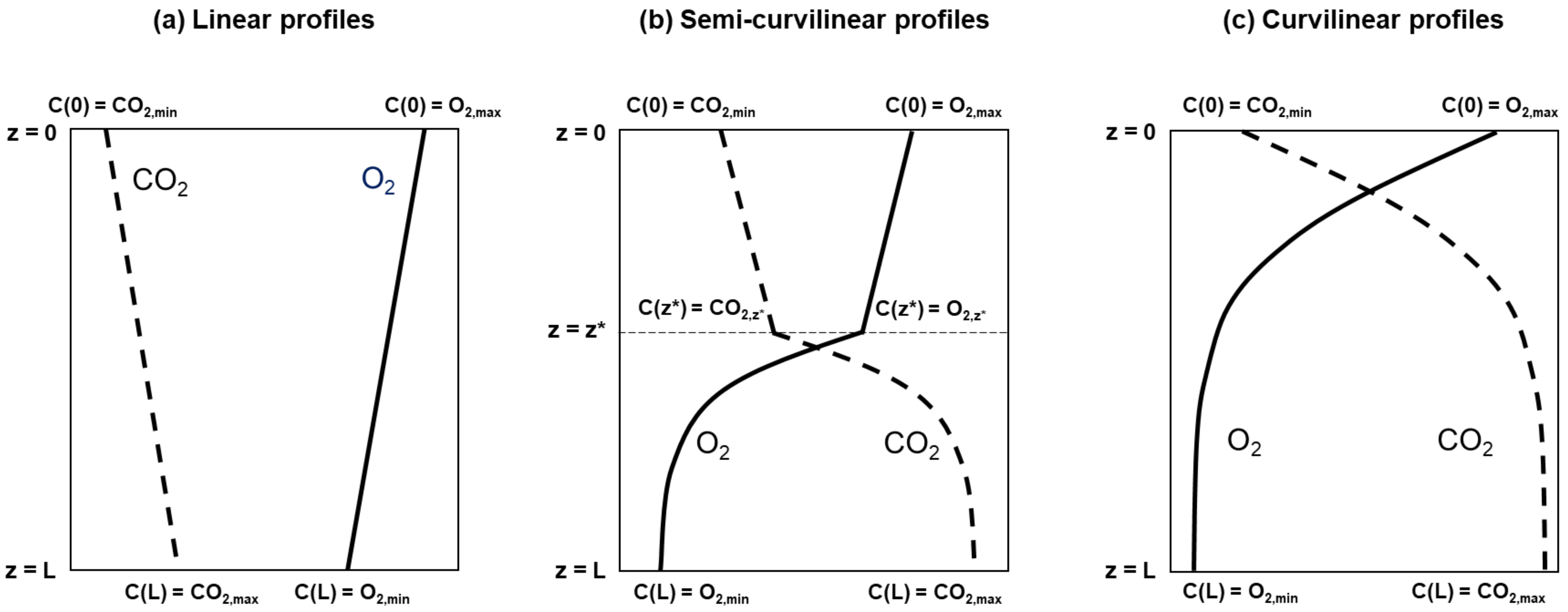
Soil Gas Gradient Method – New Guidance Content

Types of Soil Gas Profiles & Analytical Solutions



Adapted from Verginelli and Baciocchi (2021)

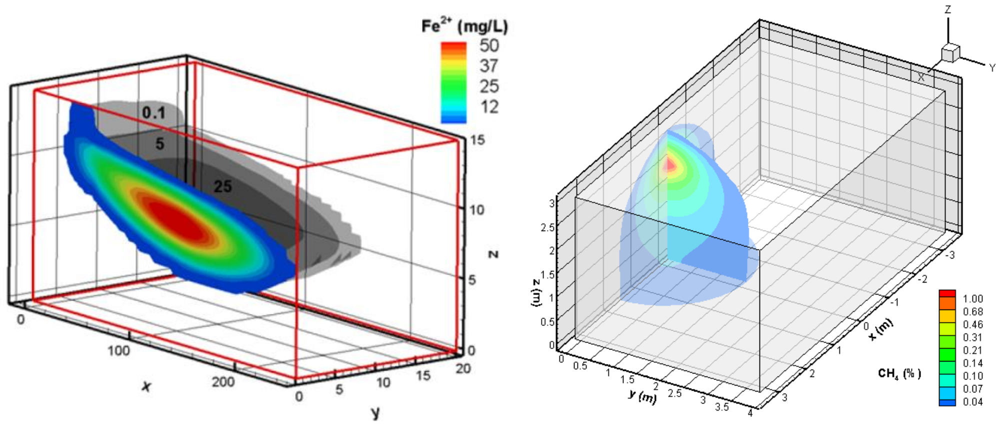
Review of Chemical of Concern (COC) - Specific Attenuation Rates

- Analytical Models

  Examples:
  - BioVapor (DeVaull, 2007; API 2010)
  - PVI Screen (US EPA, 2016)
  - PVI2D (Yai et al., 2016)

- Numerical Models

  Example reactive transport models
  - Lahvis et al. (1999)
  - MIN3P-Dusty, Molins and Mayer (2007) & other models used in assessing vapor intrusion: Yao and Suuberg (2013) and SERDP (2014)

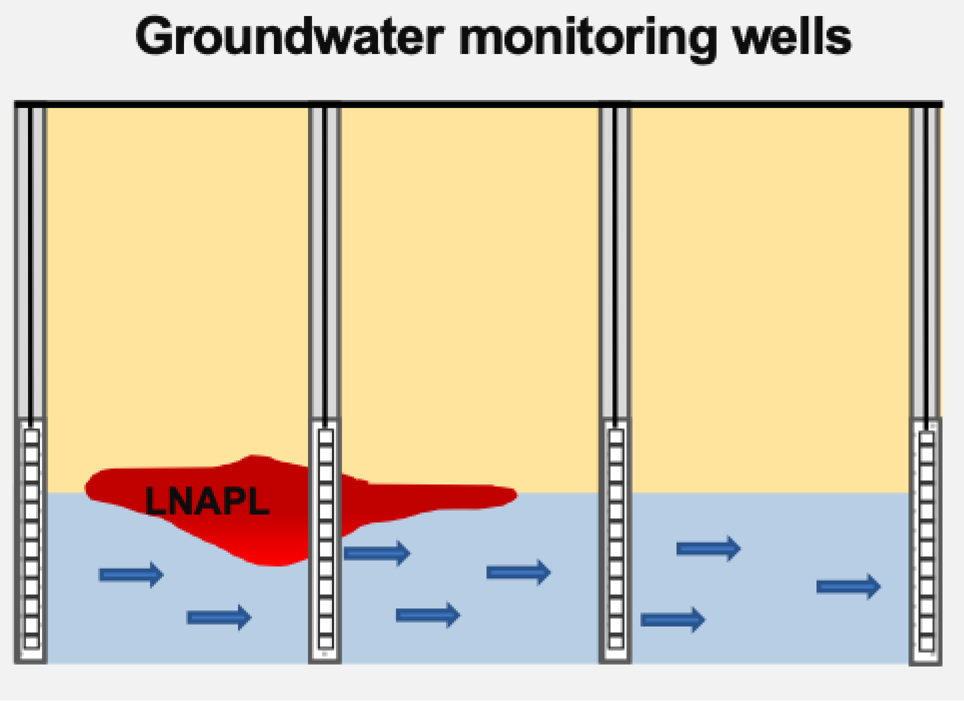


MIN3P-Dusty Simulations: Jourabchi and Hers (2013) and Jourabchi et al. (2016)

Groundwater Monitoring Method – Assumptions & Site-Specific Considerations

Underlying Assumptions	Site Conditions
• Spatial (up-and down-gradient of the source) changes in the groundwater chemistry including dissolved gas concentrations resulting from biodegradation of NAPL constituents in the saturated zone • Dissolution and flow of NAPL constituents in groundwater	• Availability of groundwater monitoring data and hydrogeologic parameters • Assessment of confined NAPL conditions (ASTM E2856) for data interpretation

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)

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

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 ($R_{sat-bio}$).

Groundwater Monitoring Method – New Guidance Content

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

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

$\propto A_C$

Using a Batch Model to Estimate Methane Production

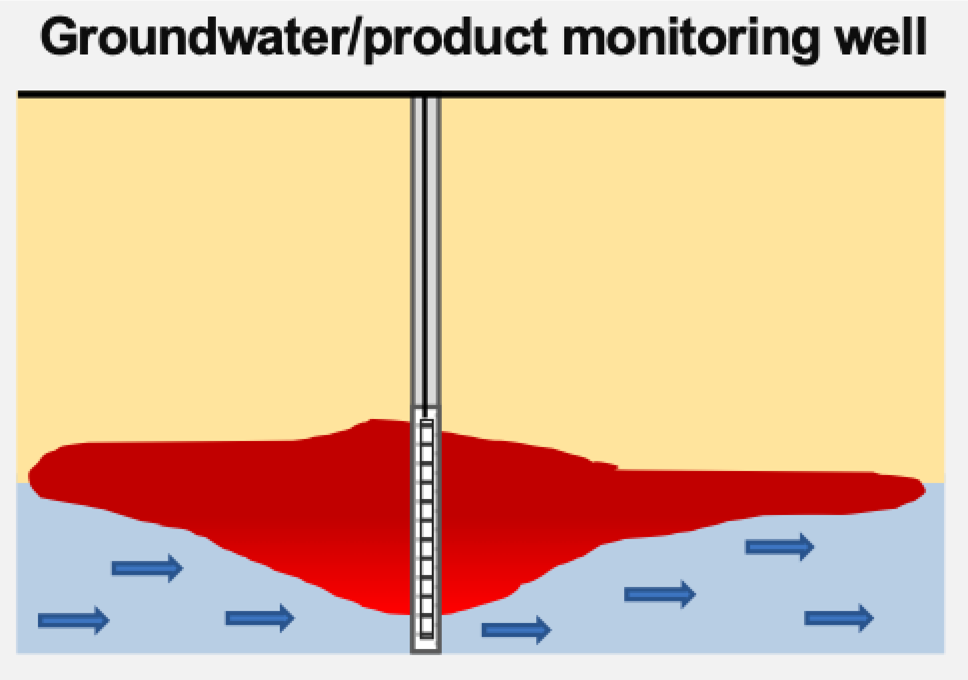
Degassing Method Natural Source Zone Depletion Case Study
Reyenga (2020)
Applied NAPL Science Review (ANSR)

Degassing can be significant for confined NAPL/low permeability conditions

NAPL Composition Method – Assumptions & Site-Specific Considerations

Underlying Assumptions	Site Conditions
• Changes in the composition of NAPL constituents over time • NAPL sampled consecutively from a single location is representative of the same NAPL body over time (monitoring period)	• Finite NAPL mass with no additional releases during the assessment period • Availability of NAPL compositional data over time (minimum of approximately four years and 9 to 10 NAPL samples) • Conversion of fraction/percent rates into volumetric rates will require an estimate of total NAPL volume at the onset of the monitoring period

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 – New Guidance Content

Groundwater Monitoring&Remediation

DeVaull et al. (2020)

Petroleum NAPL Depletion Estimates and Selection of Marker Constituents from Compositional Analysis

by George E. DeVaull, Ileana A. L. Rhodes, Emiliano Hinojosa, and Cristin L. Bruce

at $(t = 0)$ for total NAPL $(k_{eff,T}(t = 0)$; per year)

or individual constituents $(k_{eff,i}(t = 0)$; per year)

Or the half-life, $t_{half} = \frac{-\ln(0.5)}{k_{eff}}$ (years)

Step 1. Identify the relevant constituents
Step 2. Analyze data on mass fractions of NAPL constituents
Step 3. Identify potential markers
Step 4. Refinement on identifying potential markers
Step 5. Estimate the effective rates

$$\textit{Remaining fraction at time}, t = \frac{\chi_{A,q}(0) + (1 - \chi_{A,q}(0))e^{-\kappa_{A,q}t}}{\chi_{A,i}(0) + (1 - \chi_{A,i}(0))e^{-\kappa_{A,i}t}}$$

mass fractions

relative rates

Section 8. Example Problems

- ❖ Example implementations
- ❖ Seven Case Studies

#1	#2	#3	#4	#5	#6	#7
Groundwater Monitoring	NAPL Composition	CO_2 Efflux	CO_2 Efflux NAPL Comp	CO_2 Efflux	Temperature Gradient	CO_2 Efflux Temp Gradient Soil Gas Gradient

Example Problems - Case Studies

- Location & Climate
- NAPL Type
- Lateral & Vertical Extent of Source Zone
- Ground Surface Cover
- Remedial Concern(s)
- Intended Application of the Estimated Rates
- Factors in Method Selection
- Applicability in Support of Decision(s)
- Method-Specific Technologies
- Estimated Rates
- Approach to Rate Calculations
- Background Sources & Correction Methods
- Spatial Coverage
- Assessment of Seasonal Variability

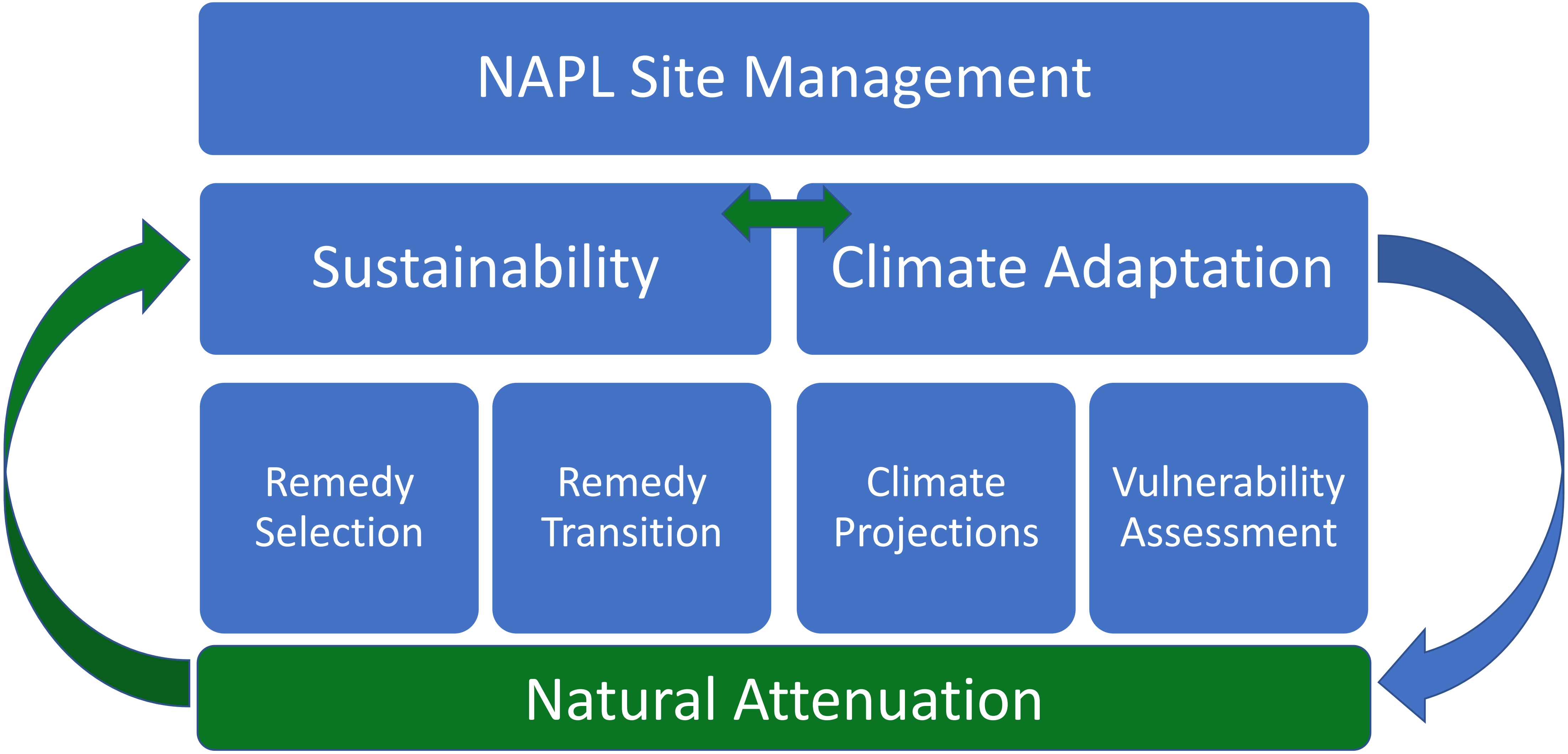
Example Problems – Applications & Limitations

1. In one case study, an estimated rate of 200 gallon/acre/year was used as a baseline metric to assess the performance of the engineered (active) remedy vs. MNA.
2. Rates can vary seasonally, and are expected to decrease over time as the more soluble, volatile and biodegradable constituents of the NAPL diminish.

An assumption of constant NSZD rate over time for estimating the timeframe for remediation under natural attenuation is not recommended.

3. Trend analyses of the attenuation of COC-specific concentrations may be more appropriate than estimates of timeframe for complete NAPL depletion.
4. Bench scale accelerated weathering experiments (Liu 2004) highlight the relatively higher reduction rates in specific chemicals of interest as compared to bulk NAPL.

Site Management in a Changing Climate



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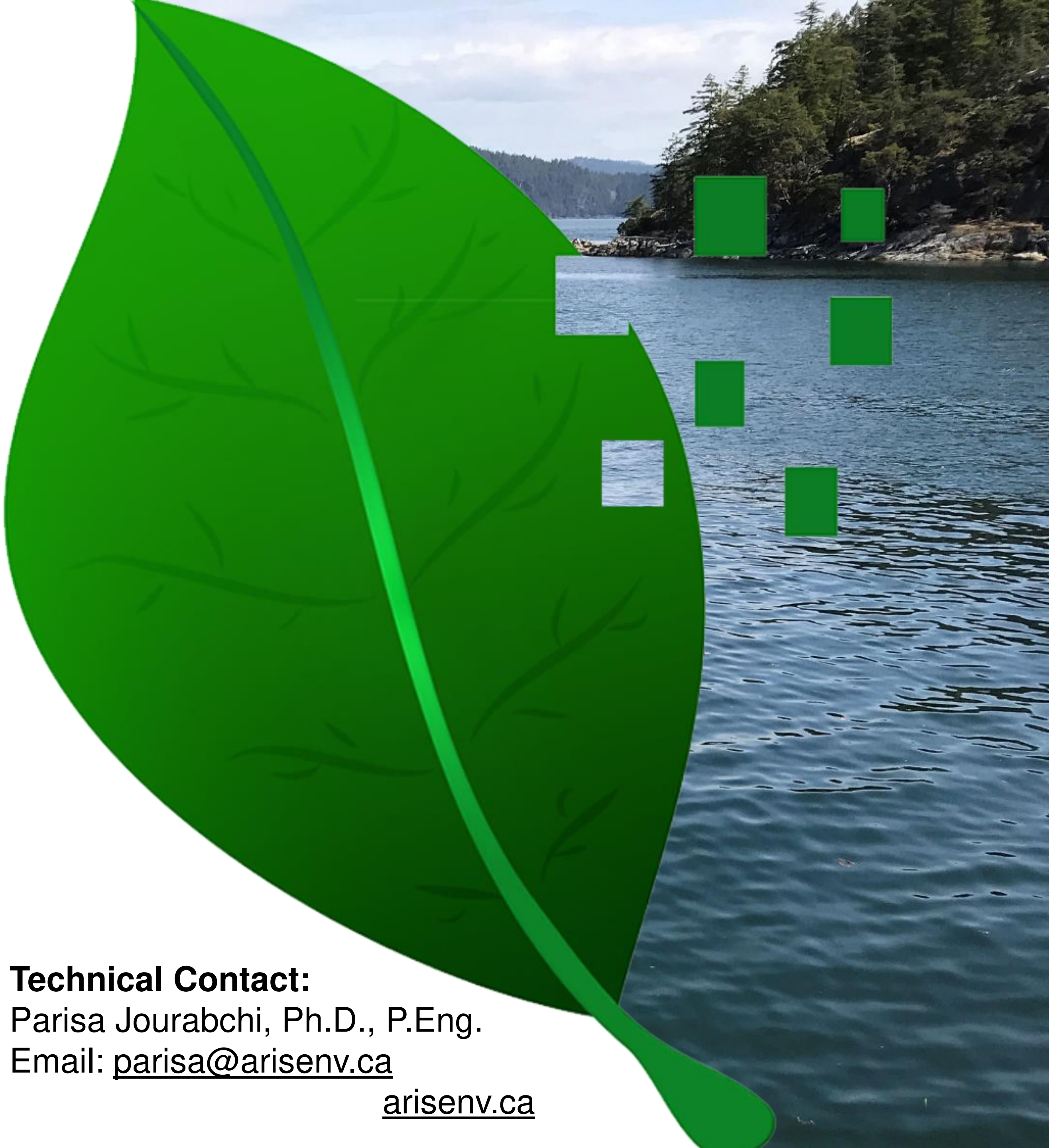
Thank You

See the New ASTM Standard Guide for full method descriptions, related technologies & data analysis, as well as case studies of method applications.

(publication expected towards the end of the year)



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