27th National Tanks Conference (NTC) 2022

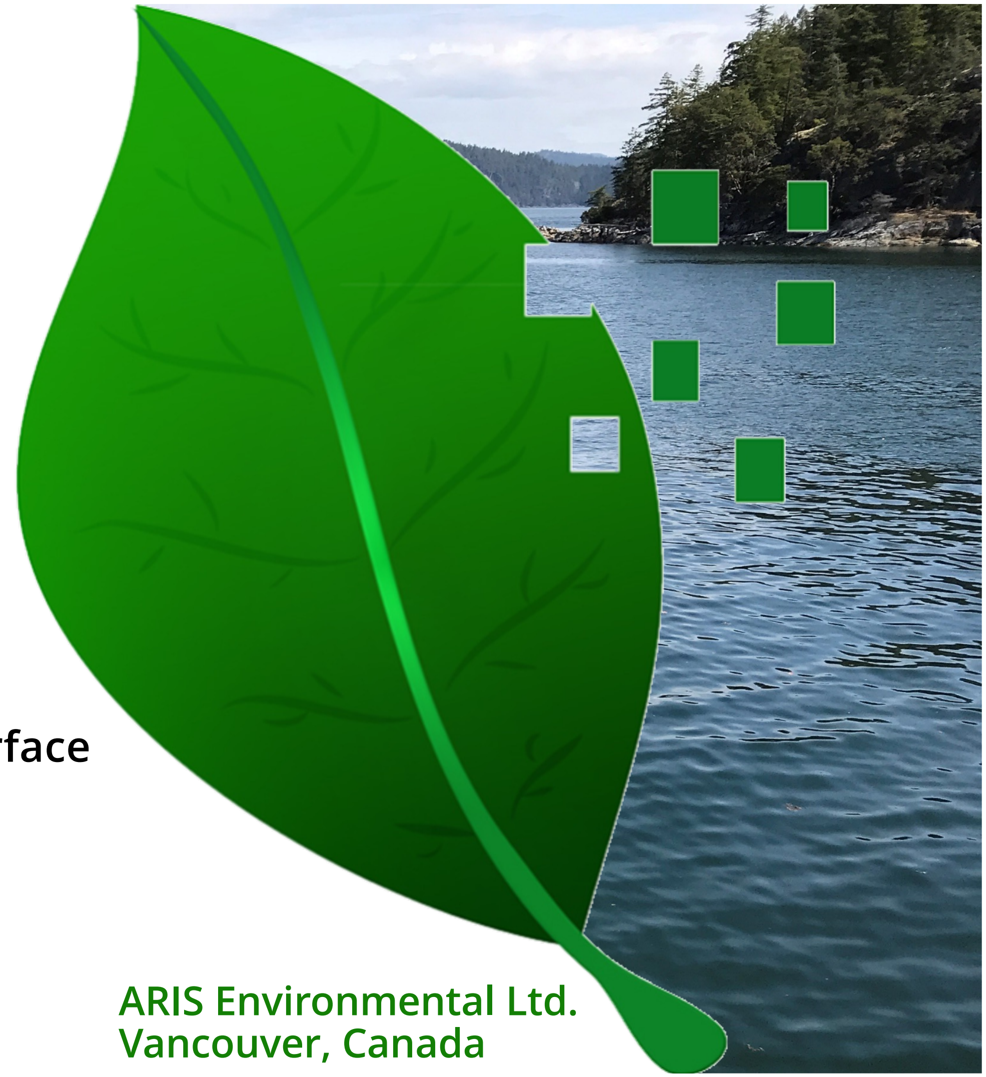
ARIS

Natural Source Zone Depletion Session - September 14th, 2022

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

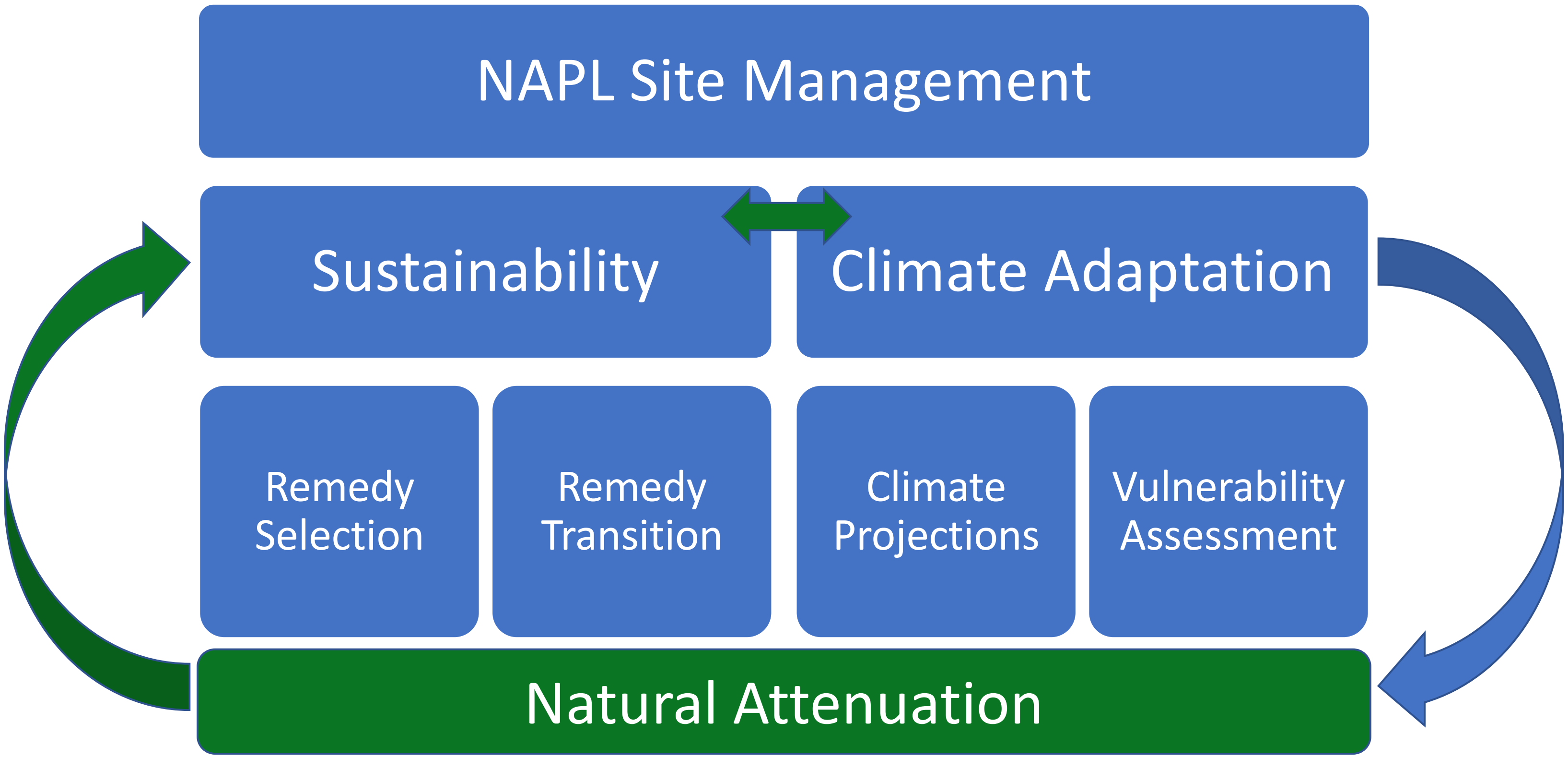
Parisa Jourabchi, Ph.D., P.Eng.

Environmental Engineer



ARIS Environmental Ltd.
Vancouver, Canada

Site Management in a Changing Climate



ARIS

Presentation Roadmap

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

01 ASTM WK76688 - Terminology

02 Overview of the Five Methods

03 Method Assumptions & Site-Specific Considerations

04 Example Implementation

Each of the Five Methods (03–04)

Advances in Technology & Data Analysis – New Guide Content

ARIS

Rationale for a New Guide

- Unique site conditions

Tools for customized solutions using accepted methods

- Rapid technology development

- Support remedial decision-making

- Improved CSM

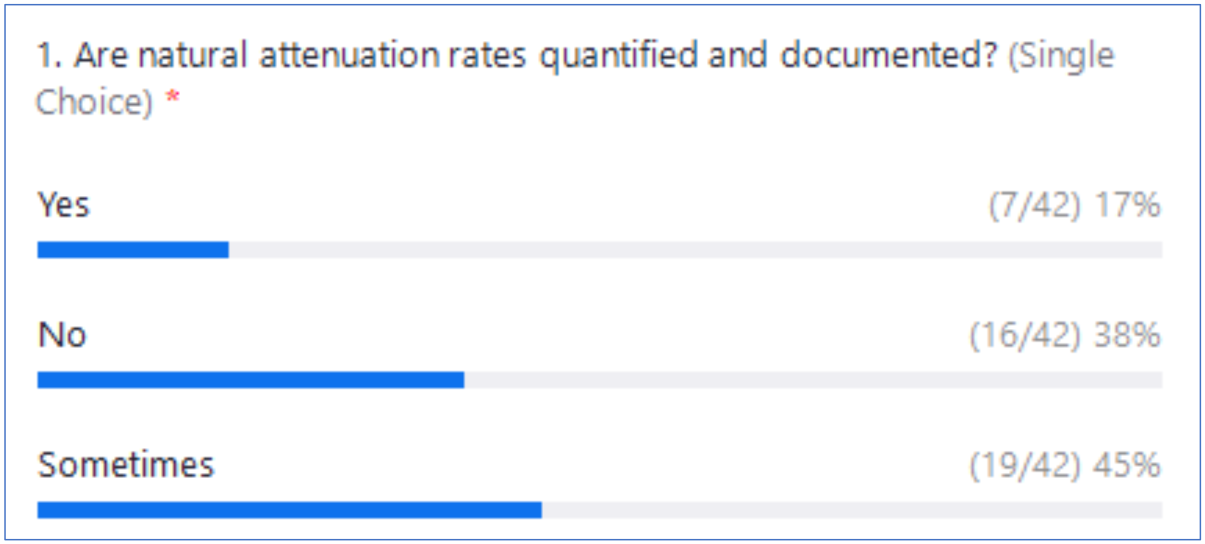
Using available site data collected for investigation/remediation

Additional data by cost-effective and non-invasive methods

- Addressing challenges & gaps

Survey results

Survey Results – Rates Quantified & Documented?



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%

Remedy Transition

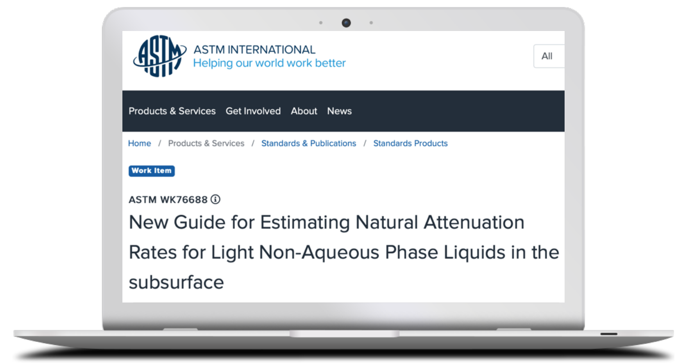
Engineered Remedy	Remediation Spectrum	Natural Remedy
More engineered intervention	⟷	Less engineered intervention
Shorter timeframe		Longer timeframe
Higher cost		Lower cost
Higher GHG emissions		Lower GHG emissions
Higher energy use		Lower energy use

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).

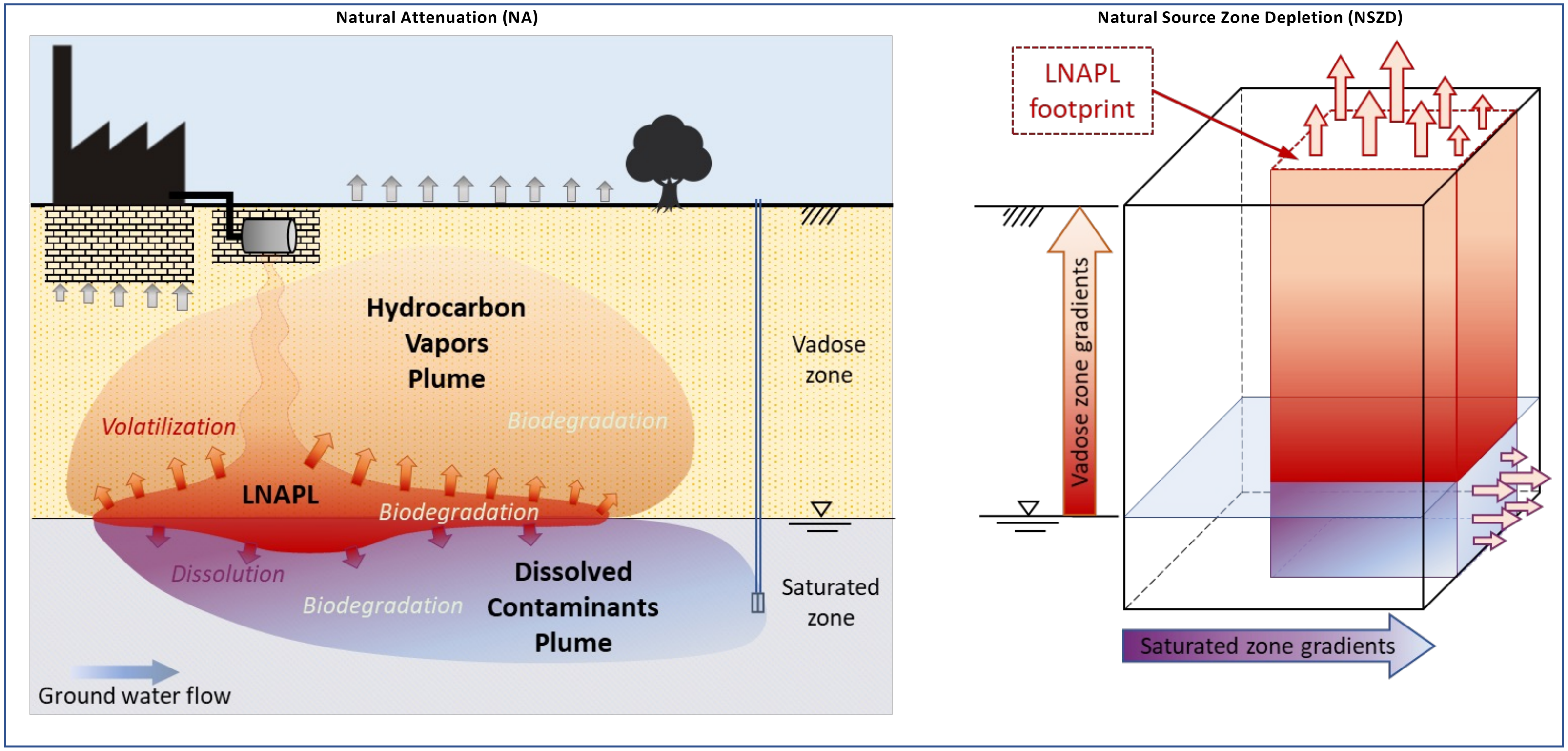
Natural Remedy: Also referred to in other guidance documents as passive or knowledge-driven remediation, is generally a less resource intensive remediation system mainly relying on natural or in-situ and enhanced bioremediation measures.

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



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

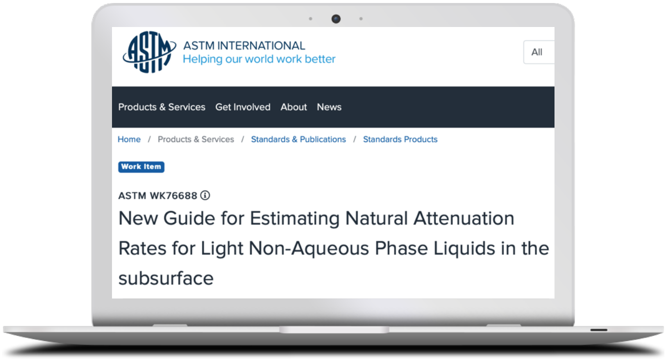
Natural Attenuation & Natural Source Zone Depletion (NSZD)



A R I S

Terminology: Natural Attenuation & NSZD

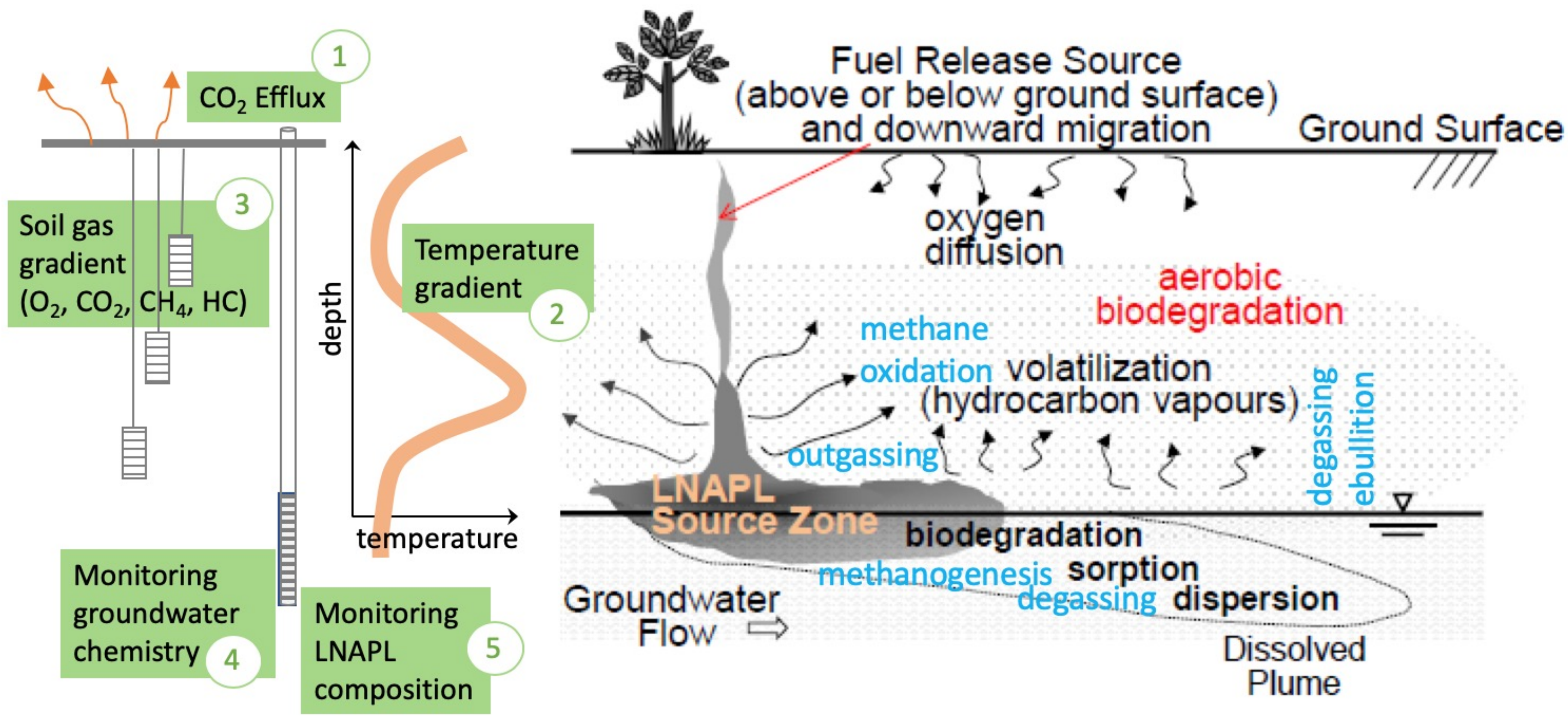
Natural Attenuation: The naturally occurring mass loss of hydrocarbons in various phases and media (NAPL, vapor, soil, and groundwater) within a volume of soil or groundwater contamination.



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

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

Natural Attenuation Processes & Pathways



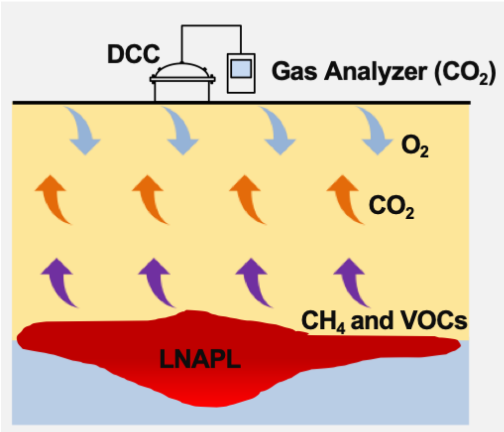
Summary of Methods

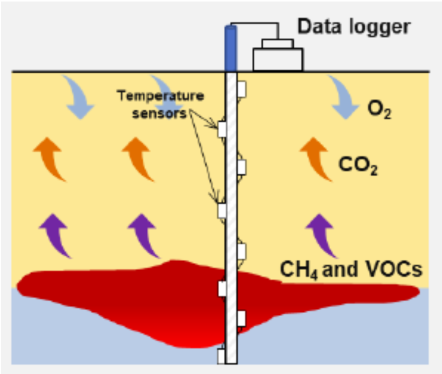
Method	Type of Attenuation Measured[1]	Location of Processes & Pathway	Measurement Location
1. CO_2 Efflux	Bulk NAPL	Vadose zone[2]	Ground surface
2. Temperature Gradient	Bulk NAPL	Vadose zone[2]	Vertical profile mostly in the vadose zone & straddling the capillary fringe above the source zone
3. Soil Gas Gradient	Bulk NAPL & COCs	Vadose zone[2]	Vertical profile in the vadose zone above the source zone
4. Groundwater Monitoring	Bulk NAPL & COCs	Saturated zone	Profile along the groundwater flow path up- and down-gradient from the source zone; includes monitoring of dissolved gases
5. NAPL Composition	COCs	NAPL Source zone	Source zone

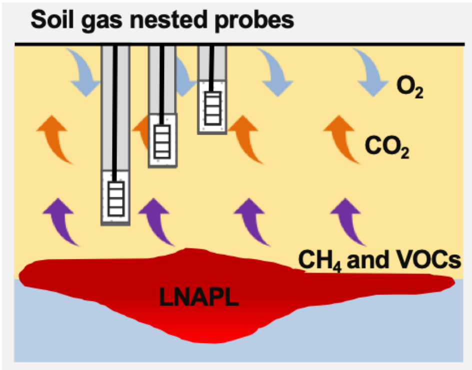
[1]The depletion rate of bulk NAPL directly addresses saturation-based concern. While estimates of COC attenuation rates have a more direct impact on composition-based concern, both bulk depletion of NAPL and COC attenuation impact the extent and longevity of the COCs in soil vapor and groundwater.

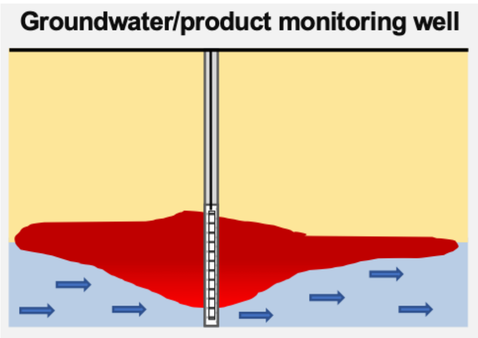
[2]Includes the transport of methane and other hydrocarbons produced from the biodegradation of NAPL in the saturated zone; and methane oxidation at the aerobic/anaerobic interface.

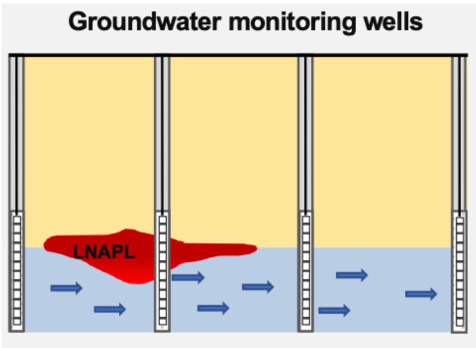
Example Implementations of Each Method











ARIS

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

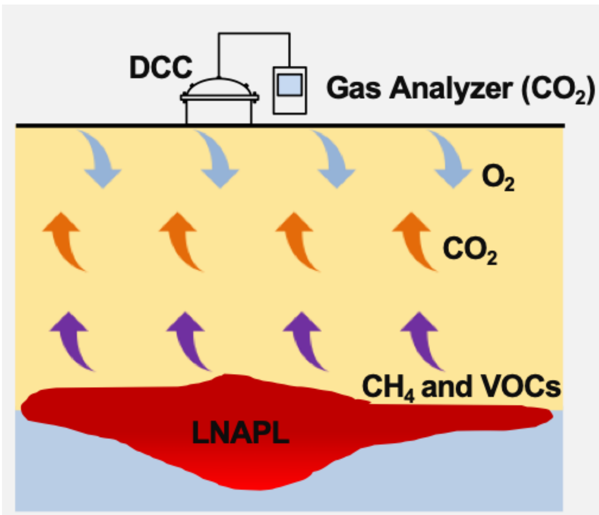


Figure from Iason Verginelli (2021)

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/m²/s)
J_{CO2} = total measured (μmol CO_2/m²/s)
J_{NSR} = attributed to natural soil respiration (μmol CO_2/m²/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 = $33.7 \frac{s}{year} \times \frac{kg}{\mu g} \times \frac{m^2}{acre} \times \frac{gallon}{L}$

ARIS

Example: CO_2 Efflux Method

Tools	Products / Instruments	
Dynamic closed chamber Active air flow connected to infrared detector Measurement time scale: snapshot (minutes) ^{14}C correction	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) ^{14}C correction	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	

ARIS

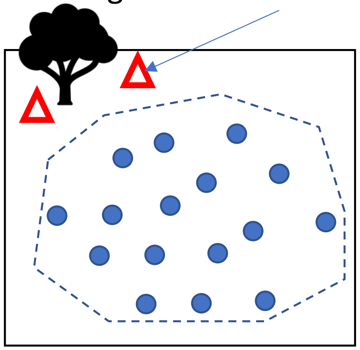
Background Sources of CO_2

- CO_2 produced from natural soil respiration

CO_2 Efflux = Contaminant Soil Respiration + Natural Soil Respiration

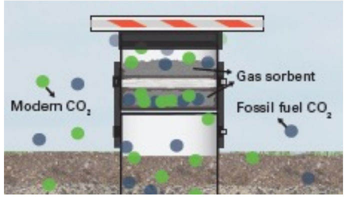
- Two general approaches:
  - Sampling background locations
  - Sampling & analysis of radiocarbon (^{14}C)
- Design of program for background correction is site specific:
  - Heterogeneity in surface cover & vegetation
  - Heterogeneity in hydrogeologic conditions over the LNAPL footprint

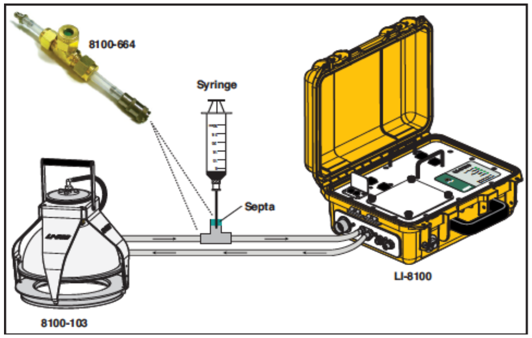
background location



Sampling for ^{14}C Analysis

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

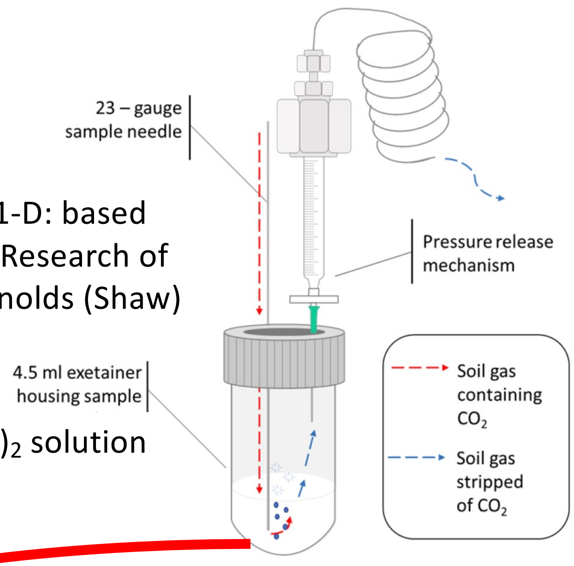




ARIS

CO_2 Efflux Method – New Guidance Content

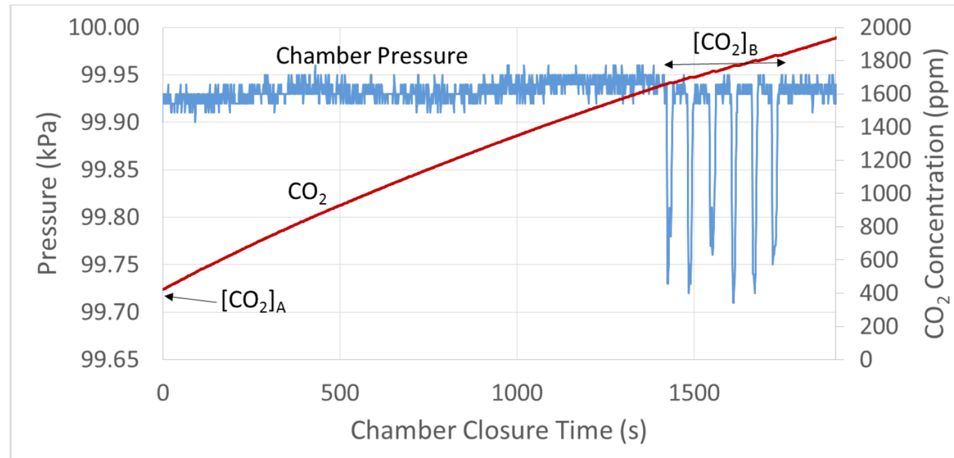
Appendix X1-D: based on the MSs Research of Lindsay Reynolds (Shaw)



$Ba(OH)_2$ solution

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

Appendix X1-B



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

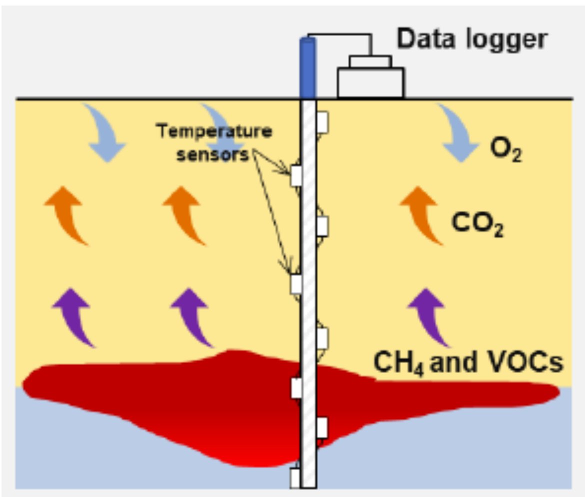
Laboratory reported fraction of modern carbon

ARIS

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}

ARIS

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

ARIS

Soil Gas Gradient Method – Example Implementation

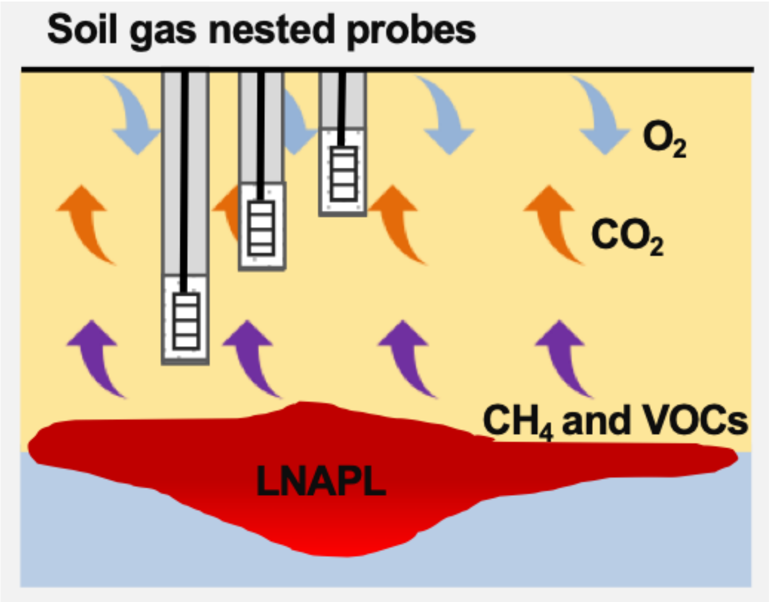


Figure from Dr. Iason Verginelli (2021)

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 sources (two approaches)
Step 7. Estimate the NSZD Flux, J_{NSZD}

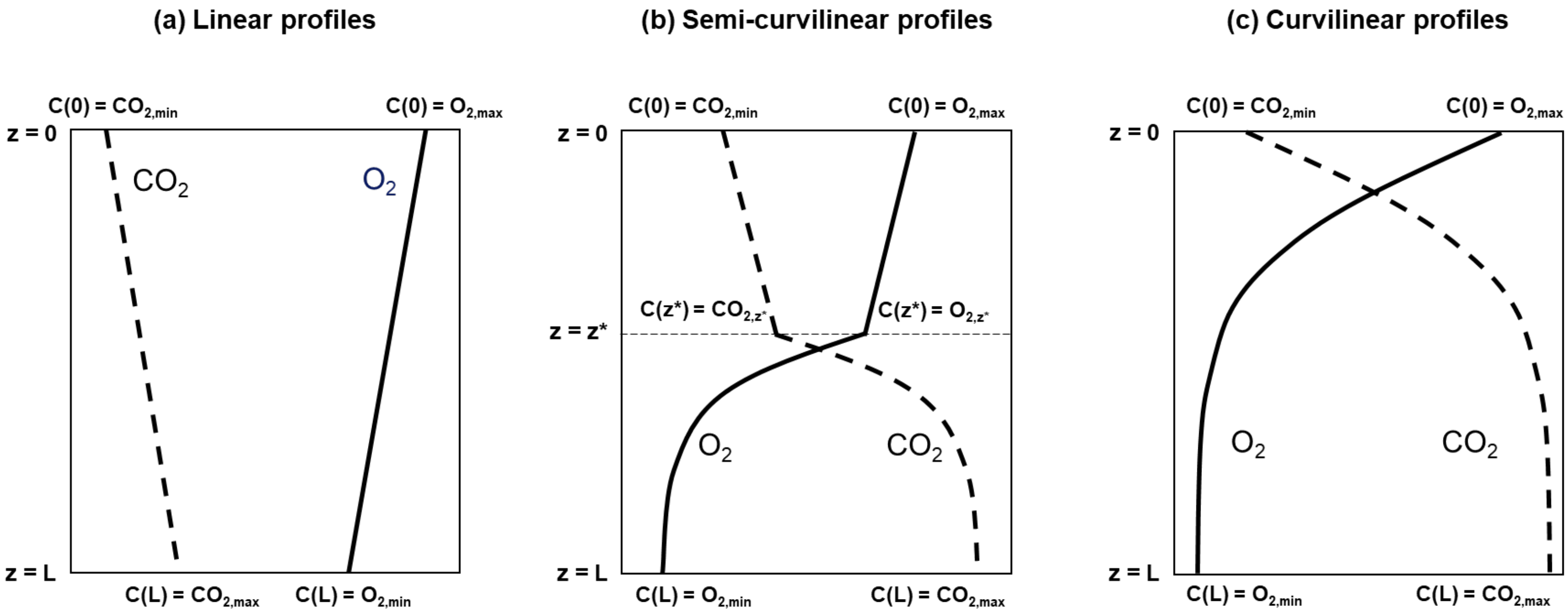
$$J_{NSZD} = J_{CSR} S_{HC:O2}$$

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

ARIS

Soil Gas Gradient Method – New Guidance Content

Types of Soil Gas Profiles & Analytical Solutions



Adapted from Verginelli and Baciocchi (2021)

ARIS

Soil Gas Gradient Method – New Guidance Content

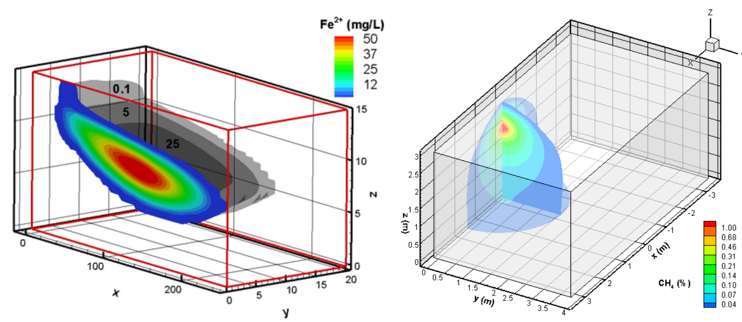
Review of COC-Specific Attenuation Rates

- 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)



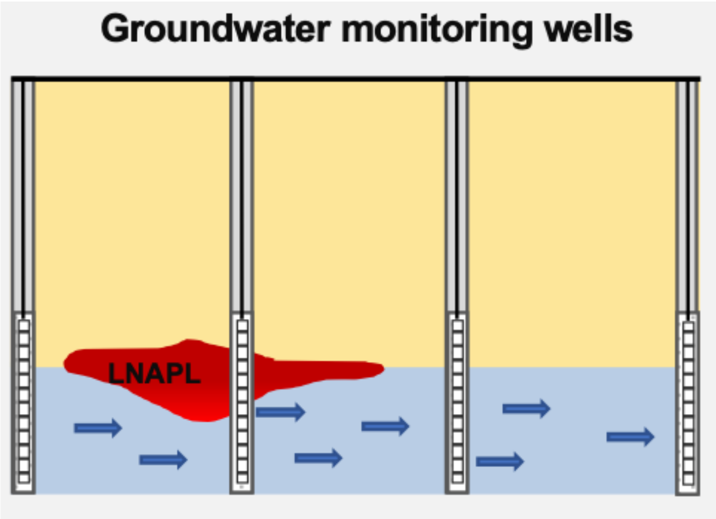
MIN3P-Dusty Simulations: Jourabchi and Hers (2013) and Jourabchi et al. (2016)

ARIS

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)

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

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 ($R_{sat-bio}$).

ARIS

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

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

$R_{sat-bio} \propto A_C$

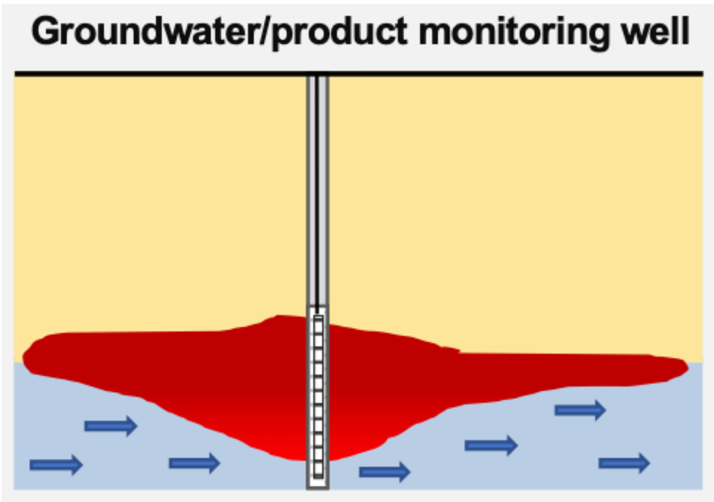
Degassing Method Natural Source Zone Depletion Case Study
Reyenga (2020)
Applied NAPL Science Review (ANSR)

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

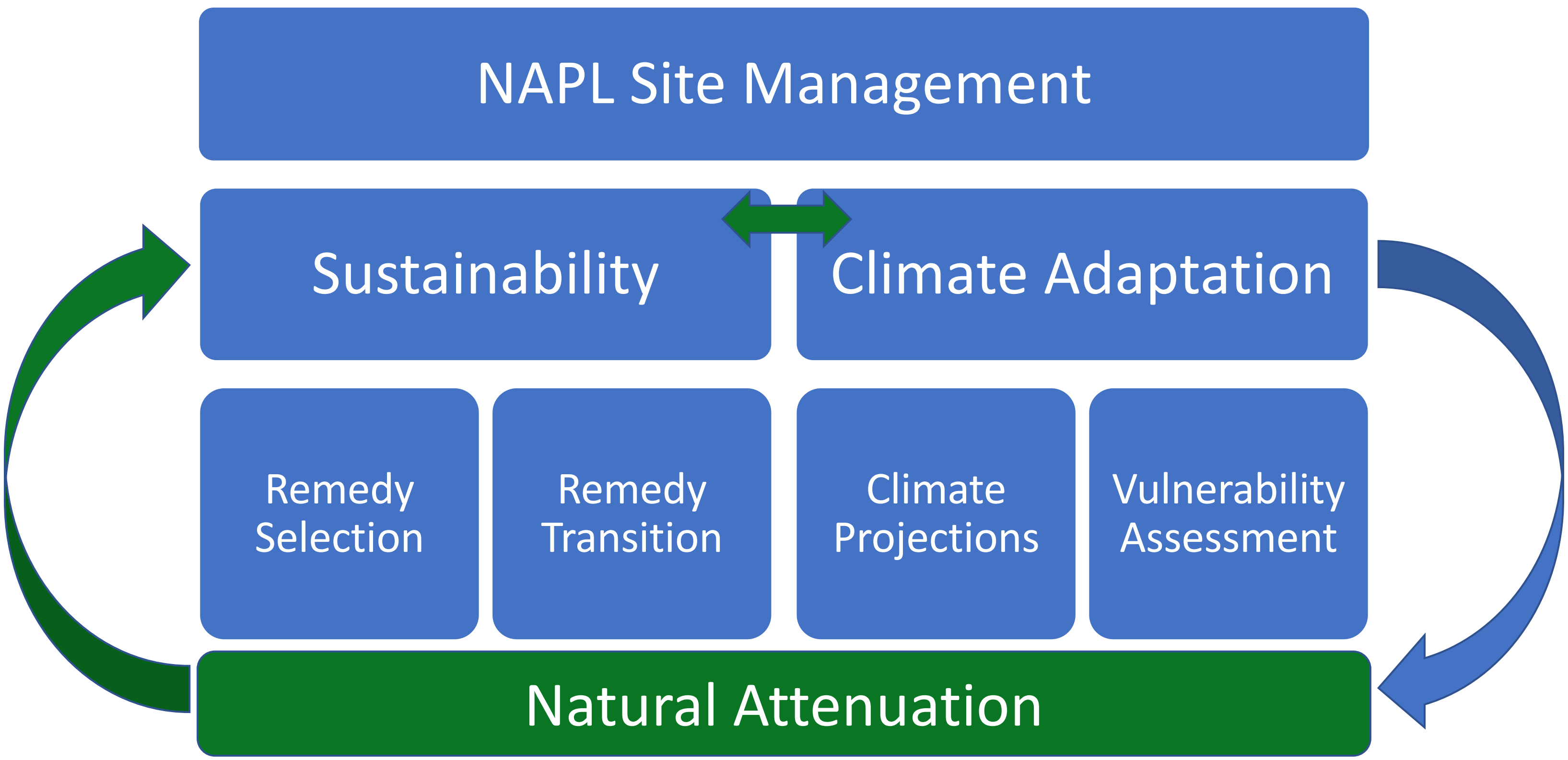
$$Remaining\ fraction\ at\ time, t = \frac{\chi_{A,q}(0) + (1 - \chi_{A,q}(0))e^{-\kappa_{A,q}t}}{\chi_{A,i}(0) + (1 - \chi_{A,i}(0))e^{-\kappa_{A,i}t}}$$

mass fractions

relative rates

ARIS

Site Management in a Changing Climate

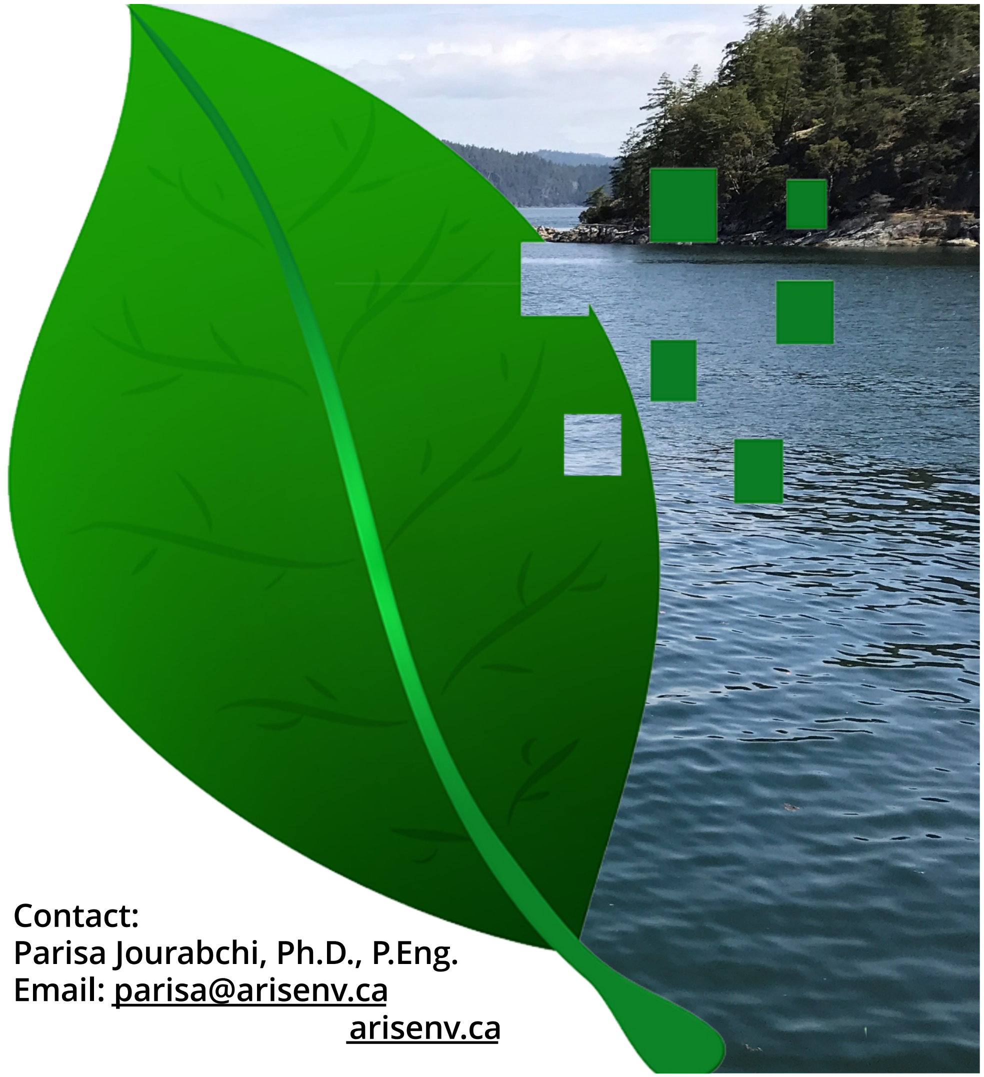


ARIS

ARIS

Thank You

See the New ASTM Standard Guide (currently under review) for full method descriptions, related technologies & data analysis, as well as cases studies of method applications.



Contact:
Parisa Jourabchi, Ph.D., P.Eng.
Email: parisa@arisenv.ca
arisenv.ca