Standardized Methods for Estimating NAPL Natural Attenuation Rates: Practical Applications of NSZD



28th National Tanks Conference

Session on NSZD- Methods for Estimating/Calculating Depletion Rates

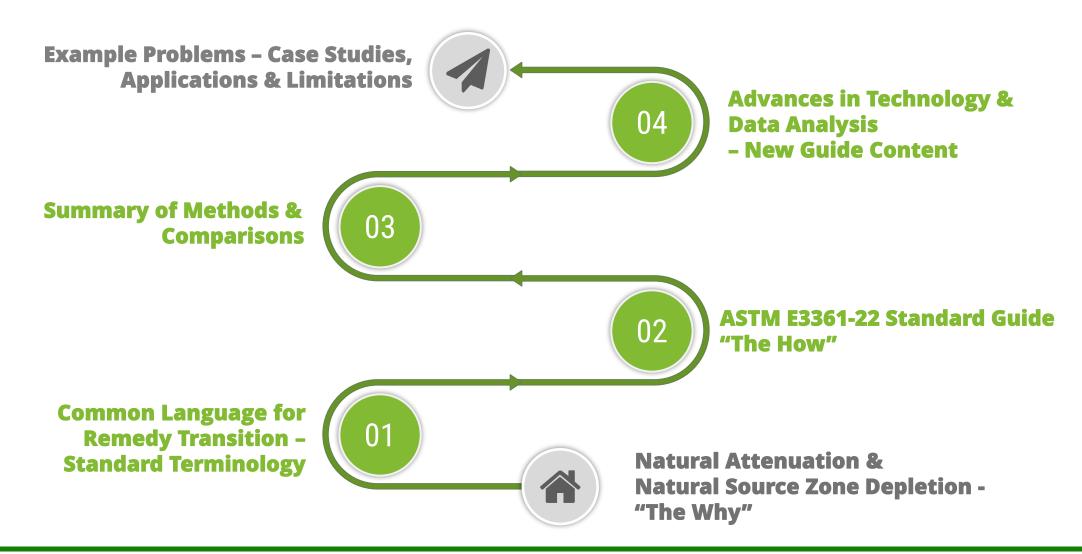
Spokane, WA 24 September 2025

Parisa Jourabchi, Ph.D., P.Eng. Founder & Chief Science Officer, ARIS Environmental Ltd.





Presentation Roadmap



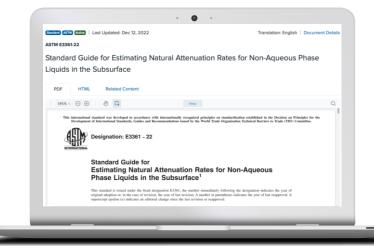


Terminology: Natural & Engineered Remedy

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.

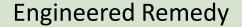
Monitored Natural Attenuation (MNA): A natural remedy documented through site characterization and monitoring.



ASTM E3361







More engineered intervention

Shorter timeframe

Higher cost

Higher GHG emissions

Higher energy use

Natural Remedy

Less engineered intervention

Longer timeframe

Lower cost

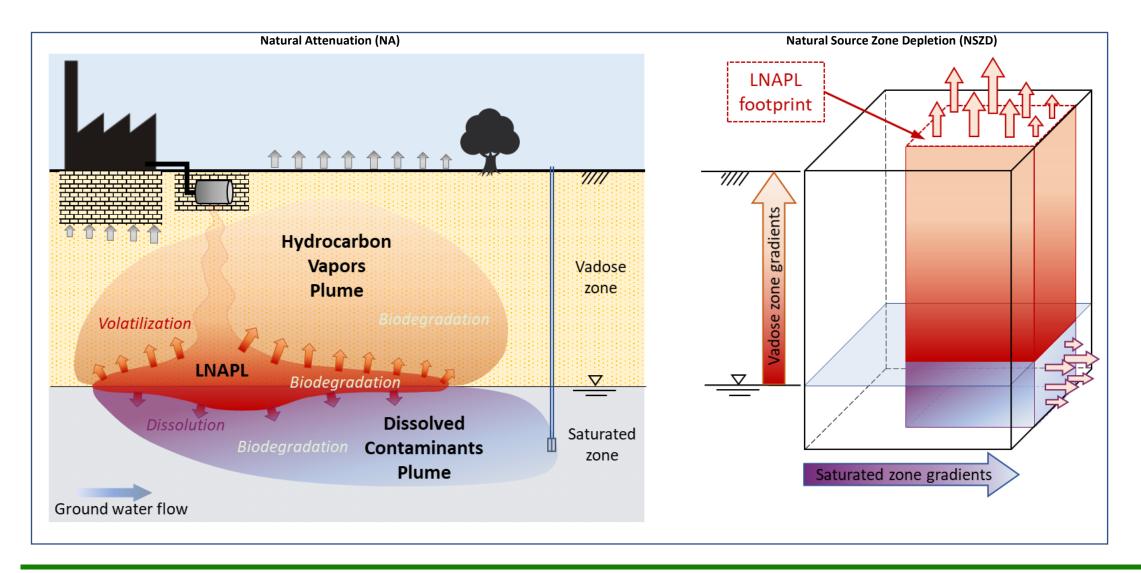
Remediation Spectrum

Lower GHG emissions

Lower energy use



Natural Attenuation & Natural Source Zone Depletion (NSZD)

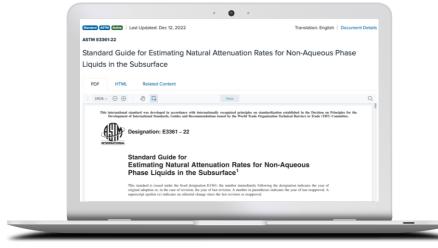






Natural Attenuation Estimation Methods

- 1. CO₂ Efflux Method
- 2. Temperature Gradient Method
- 3. Soil Gas Gradient Method
- 4. Groundwater Monitoring Method
- 5. NAPL Composition Method



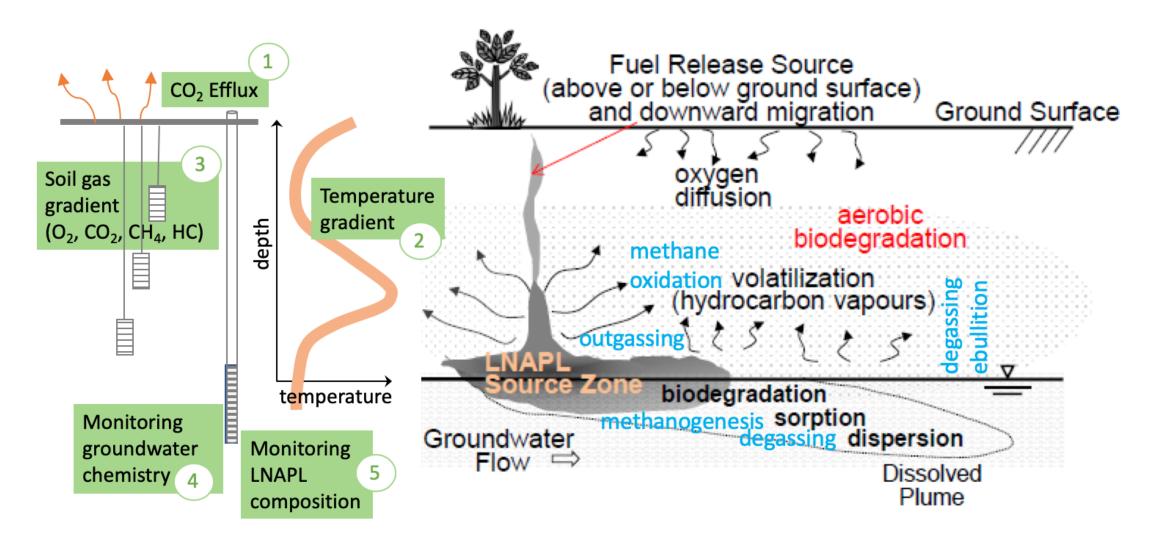
ASTM E3361

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





Natural Attenuation Processes & Pathways





CO₂ Efflux Method - Assumptions & Site-Specific Considerations

Underlying Assumptions	Site Conditions
 Attenuation of NAPL constituents through biodegradation Complete mineralization of NAPL 	 Ground surface cover Vegetation High natural organics (e.g., peat)
 constituents to CO₂ CO₂ transport in soil gas from the source to the ground surface (point of measurement) Background source: CO₂ produced from 	 High permeability soils and barometric pumping Low gas permeability soils Preferential pathways (e.g., utilities)
 natural soil respiration Estimate the portion of CO₂ efflux attributable to contaminant biodegradation 	



CO₂ Efflux Method – Example Implementation

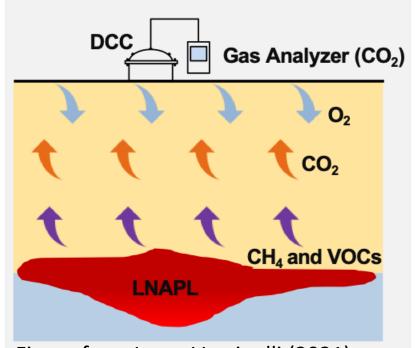


Figure from Iason Verginelli (2021)

Step 1. Install DCC

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

Step 3. Correct for background sources

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

$$J_{CSR} = \text{attributed to NAPL soil respiration } (\mu \text{mol CO}_2/\text{m}^2/\text{s})$$

$$J_{CO_2} = \text{total measured } (\mu \text{mol CO}_2/\text{m}^2/\text{s})$$

$$J_{NSR} = \text{attributed to natural soil respiration } (\mu \text{mol CO}_2/\text{m}^2/\text{s})$$

Step 4. Estimate the NSZD Flux

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

$$J_{NSZD} = J_{CSR} \frac{M_w S_{HC:CO2} U}{\rho_o} = J_{CSR} \frac{M_w S_{HC:CO2} = Stoichiometric ratio of a mole of hydrocarbon degraded per mole of CO2 produced
$$\rho_o = J_{CSR} \frac{M_w S_{HC:CO2} U}{\rho_o} = J_{CSR} \frac{M_w S_{H$$$$



Example: CO₂ Efflux Method

Tools

Dynamic closed chamber

Active air flow connected to infrared detector

Measurement time scale: snapshot (minutes)
Continuous monitoring

Static trap
Sorbent material to passively capture CO₂

Measurement time scale: weeks (~1 to 4 weeks)

Forced diffusion dynamic chamber Flow regulated by gas permeable membrane

Measurement time scale: snapshot (minutes) continuous monitoring

Products / Instruments

LI-COR Biosciences Automated Soil Gas Flux System



E-Flux Fossil-Fuel Trap



Eosense eosFD soil CO₂ flux sensor



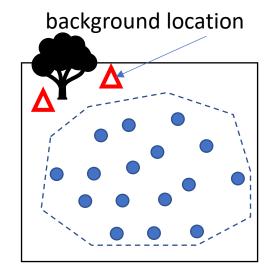


Background Sources of CO₂

CO₂ produced from natural soil respiration

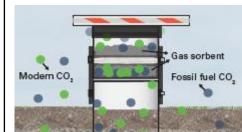
CO₂ Efflux = Contaminant Soil Respiration + Natural Soil Respiration

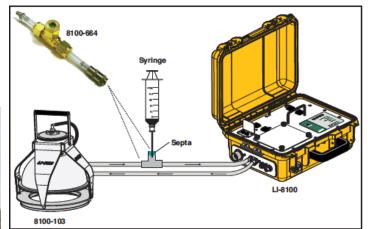
- Two general approaches:
 - Sampling background locations
 - Sampling & analysis of radiocarbon (¹⁴C)
- Design of program for background correction is site specific:
 - Heterogeneity in surface cover & vegetation
 - Heterogeneity in hydrogeologic conditions



Sampling for ¹⁴C Analysis

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



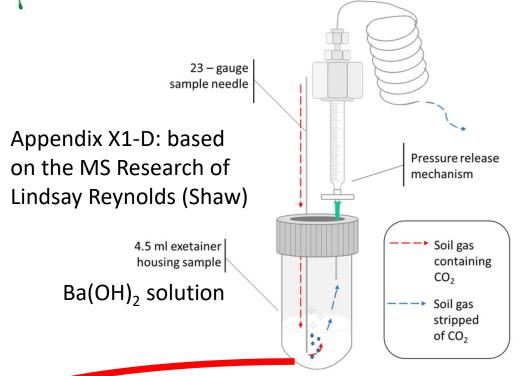


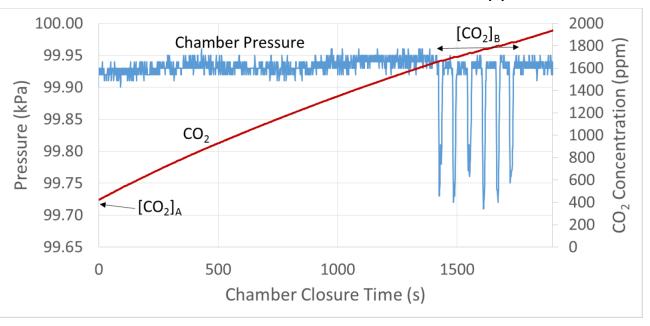




CO₂ Efflux Method – New Guidance Content

Appendix X1-B





BaCO₃ precipitate shipped to the AMS lab for analysis and reporting of fraction of modern carbon

$$F_{CSR} = 1 - \frac{{}^{14}F_B[CO_2]_B - {}^{14}F_A[CO_2]_A}{[CO_2]_B - [CO_2]_A}$$
Laboratory reported fraction of modern carbon

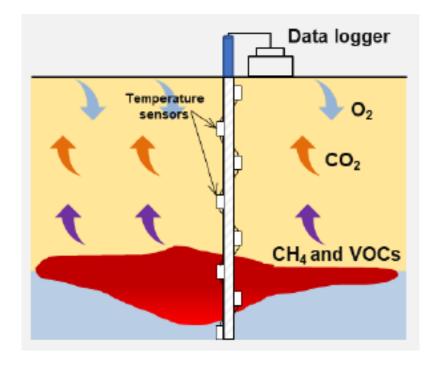


Temperature Gradient Method – Assumptions & Site-Specific Considerations

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



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 O₂, CO₂, or hydrocarbon concentrations in soil gas Diffusive gas transport in the vadose zone 	 Low gas permeability surface cover that could limit O₂ ingress* Low gas permeability soils Soil gas advection from barometric pumping effects or high methane concentrations



Soil Gas Gradient Method – Example Implementation

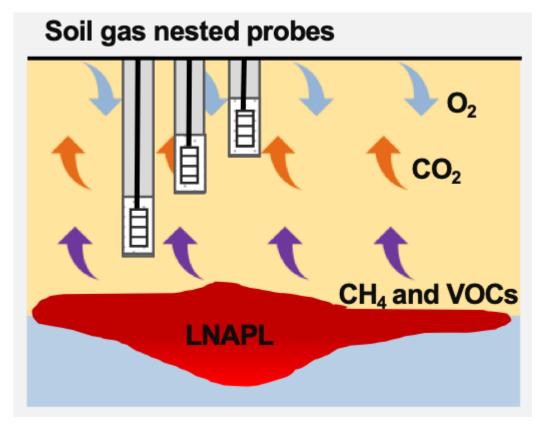


Figure from Dr. Iason Verginelli (2021)

- **Step 1.** Identify the O₂ 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 O₂ 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



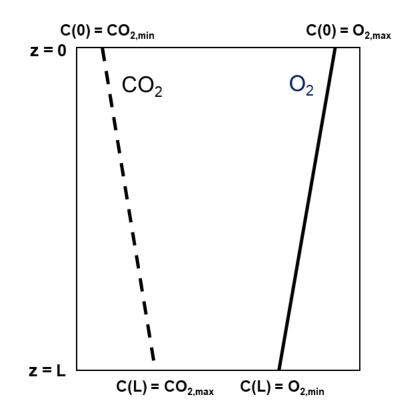
Soil Gas Gradient Method – New Guidance Content

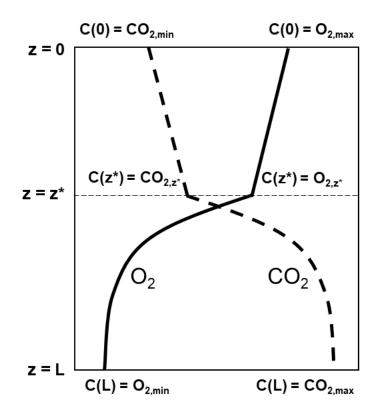
Types of Soil Gas Profiles & Analytical Solutions

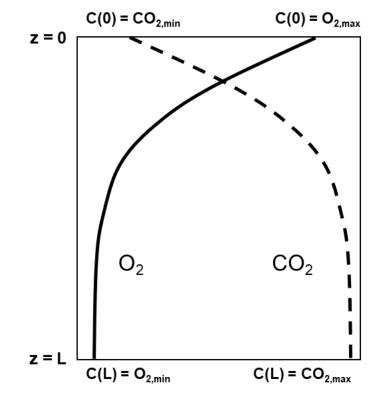
(a) Linear profiles

(b) Semi-curvilinear profiles

(c) Curvilinear profiles







Adapted from Verginelli and Baciocchi (2021)





Soil Gas Gradient Method – New Guidance Content

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

Analytical Models

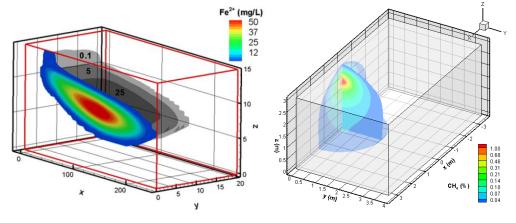
Examples:

- 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

Groundwater monitoring wells INAPL INAPL

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 ($R_{sat-bio}$).



The Challenge

- Identifying a single model that incorporates all of the relevant processes in saturated and unsaturated zones.
- 2. Interconnected processes through
 - Infiltration (downward towards water table)
 - Soil gas transport (upwards towards ground surface)
- 3. LNAPL source zones typically straddle the water table

More collaborative effort needed towards estimating methane production.

NA in vadose & saturated zones (15)

9 1
0
Multiphase Flow (9)
0 Degassing & Ebullition (2)

Based on review of 35 RTMs by Lari et al. (2019)



Groundwater Monitoring Method - New Guidance Content

Modified Control Volume Method

Estimate methene generation based on:

- Sampling & analysis of dissolved N₂, Ar,
 CO₂ and CH₄ data
- Degassing batch model of Amos et al. (2005)
- 3. Model calibration
- 4. Include degassing into the assimilative capacity, A_C $\propto A_C$

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

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

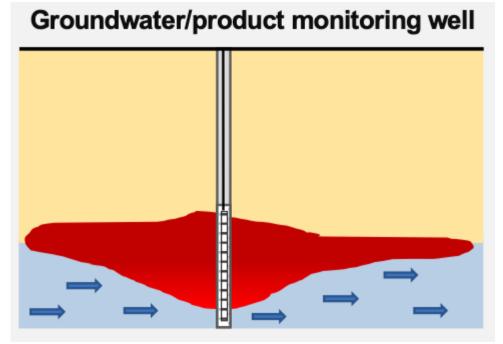


NAPL Composition Method – Assumptions & Site-Specific Considerations

Underlying Assumptions Site Conditions Changes in the composition of NAPL constituents Finite NAPL mass with no additional releases over time during the assessment period NAPL sampled consecutively from a single Availability of NAPL compositional data over time location is representative of the same NAPL body (minimum of approximately four years and 9 to over time (monitoring period) 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

Monitoring&Remediation

DeVaull et al. (2020)

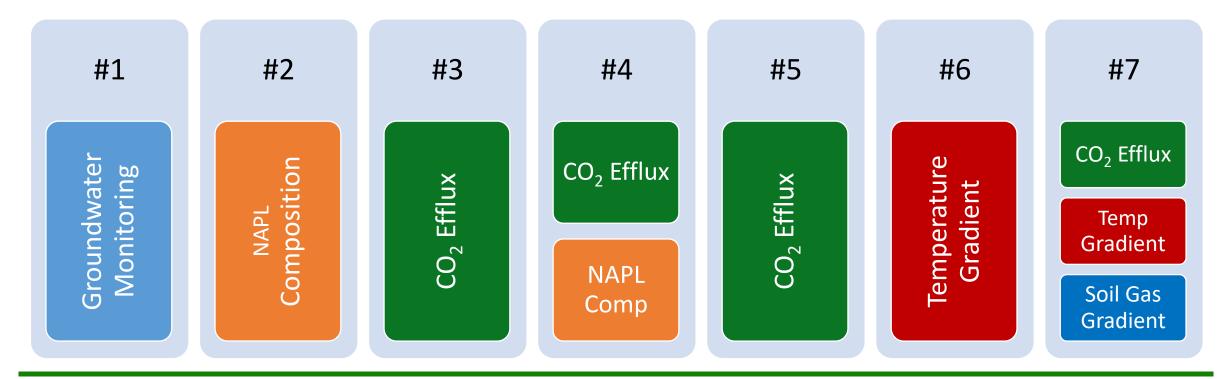
Petroleum NAPL Depletion Estimates and Selection of Marker Constituents from Compositional Analysis

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

- Marker choice is the most persistent and based on measured data (<u>not an a priori marker</u> <u>choice</u>)
- > Applies even if traditional biomarkers are absent (such as for gasoline or diesel)



- Example implementations
- Seven Case Studies





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

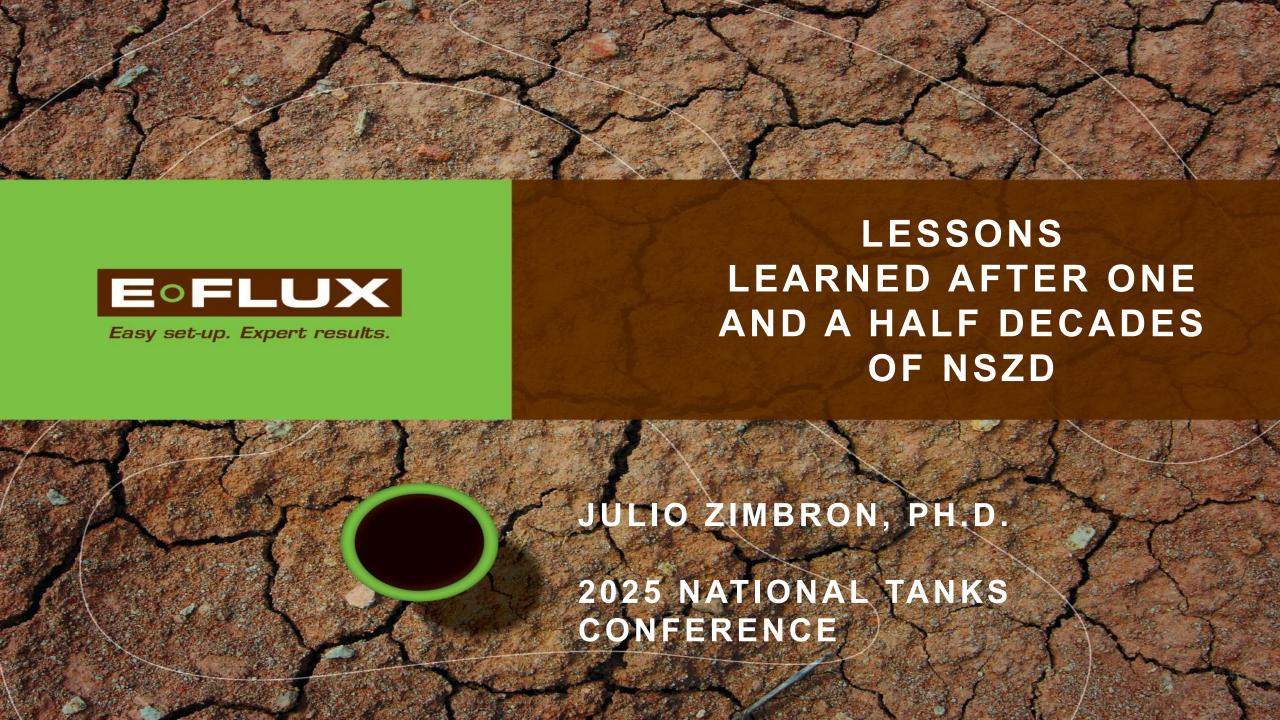
Estimated Rates

Approach to Rate Calculations

Background Sources & Correction Methods

Spatial Coverage

Assessment of Seasonal Variability



Motivation

- NSZD is an important new tool in managing LNAPL contaminated sites
- Many guidance documents describe multiple methods

API Guidance Document (2017)







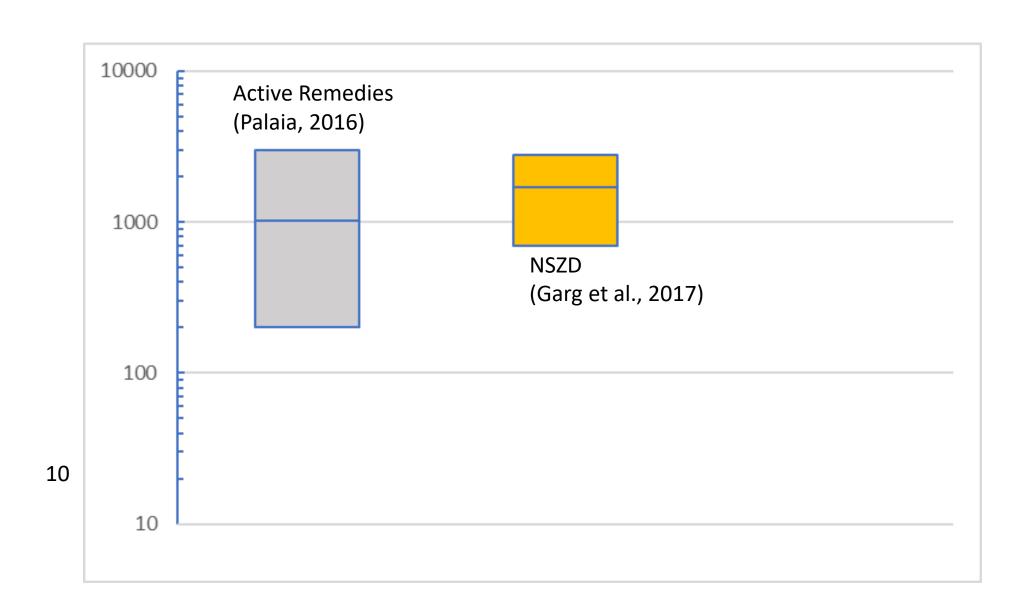




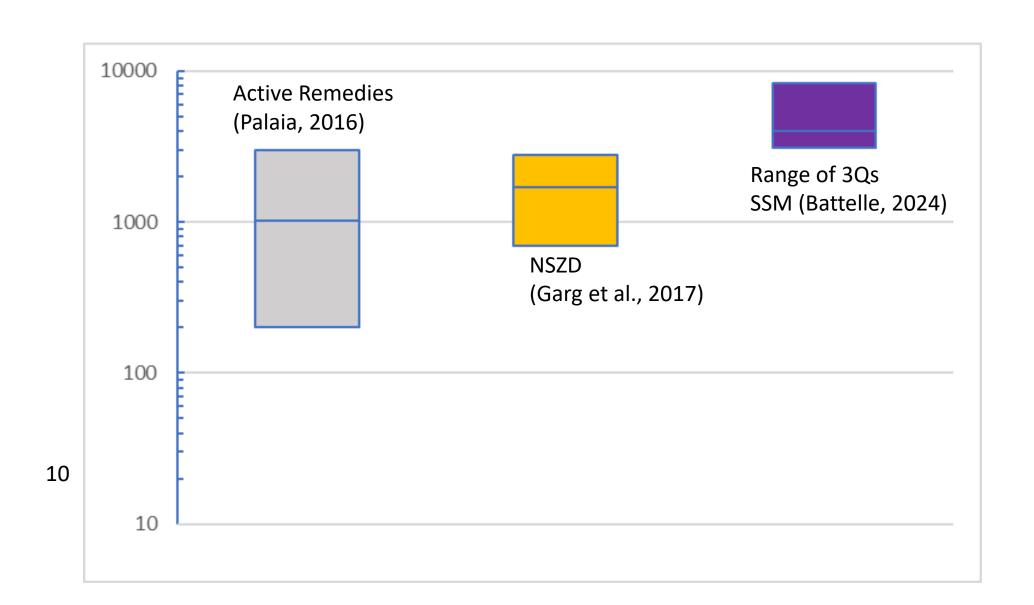


- Guidance documents are strong on describing methodologies, and "intrinsic" limitations of the multiple methods
- Direct comparisons of different methods are scarce
- Guidance documents create a sense of method equivalence
- Users need more direct guidance and pitfall awareness

NSZD Rates and Active Remediation



NSZD Rates and Active Remediation



A Data Review on CO2 Trap Data

- 1) Most of the (more recent) data presented is from CO₂ Traps (unless otherwise noted)
- 2) Materials included in peer reviewed publication
- 3) Materials expected to be thought-provoking



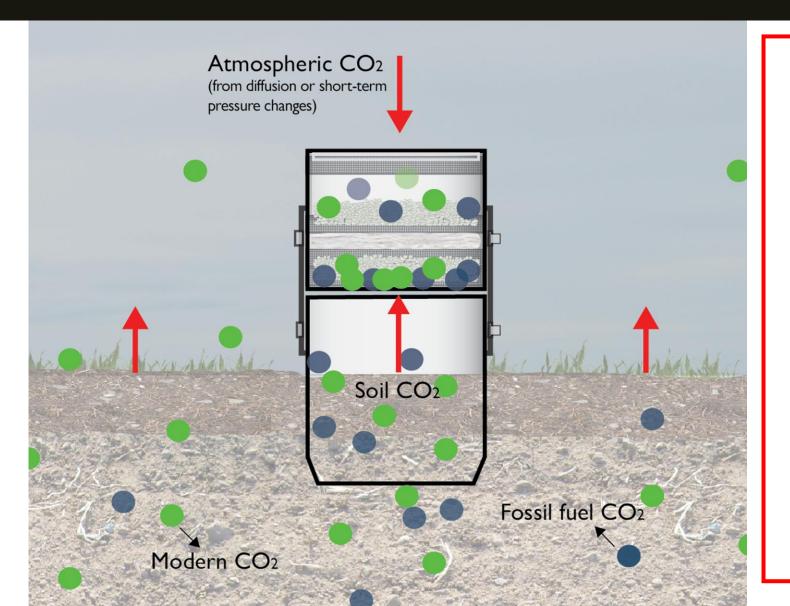
NEIWPCC 650 Suffolk Street, Suite 410 Lowell, MA 01854 Bulletin 95 July 2025



Outline

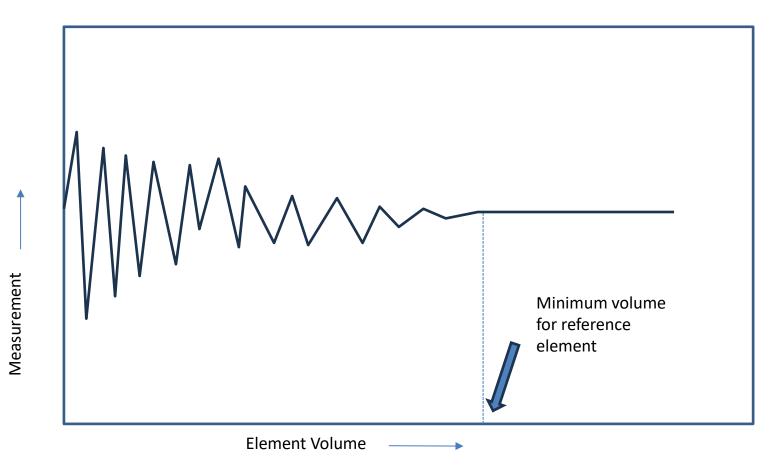
- 1) Review of published data
- 2) Explaining the data
- 3) Why these findings should matter
- 4) Recommendations

CO₂ traps



- Total CO₂ fluxes measured over multiple days
- Radiocarbon (¹⁴C) correction applied to obtain an "old carbon" (fossil fuel) CO₂ production rate- alternative to "background correction"
- Old carbon flux converted to NAPL mass losses using basic stoichiometric assumptions
- This method often used as a reference

Characteristic Scale and Measurement Error

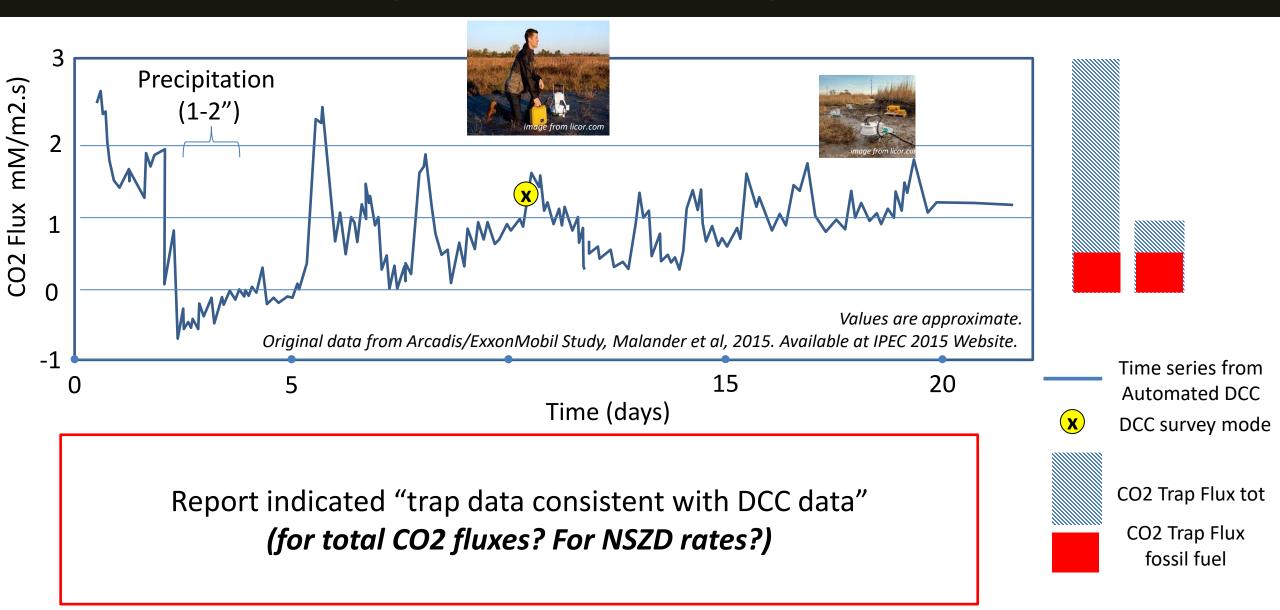




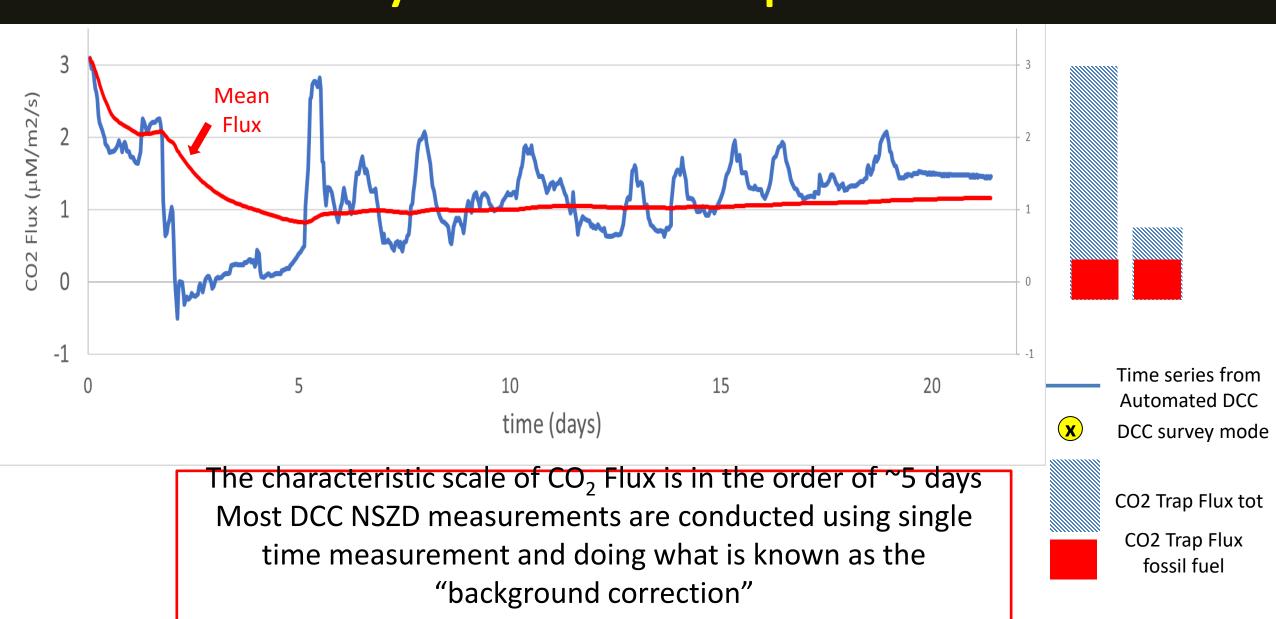
After: A. Corey, 1994

Mechanics of Immiscible Fluids
in Porous Media
(pic from engr.colostate.edu)

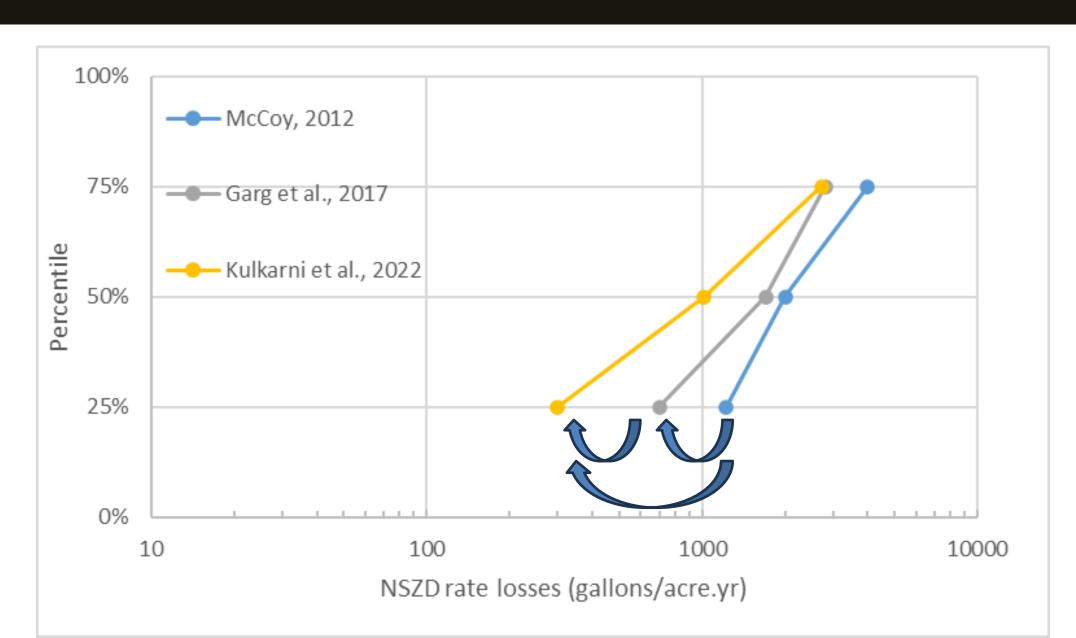
Dynamics of Soil Respiration

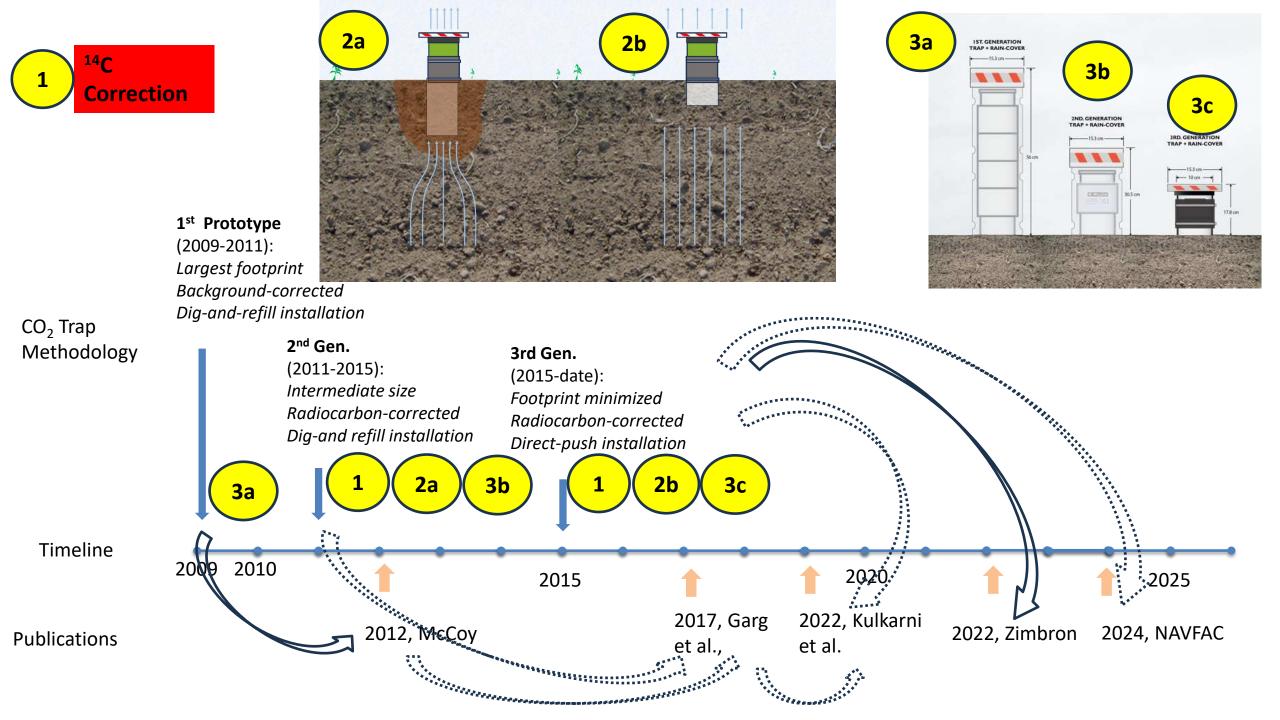


Dynamics of Soil Respiration

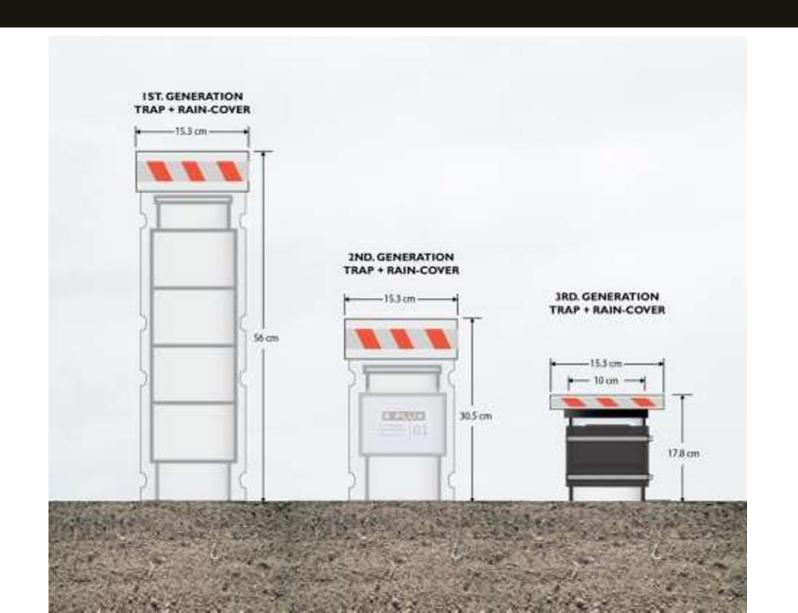


The Magnitude of the Measured Rates (an evolving target)





CO2 traps: earlier prototypes



Radiocarbon Correction Effects CO₂ Efflux, background correction vs ¹⁴C

Monitoring&Remediation

Practical Applications

Comparison of Radiocarbon- and Background Location-Corrections on Soil-Gas CO₂ Flux-Based NSZD Rate Measurements at Petroleum Impacted Sites

by Julio A. Zimbron

Abstract

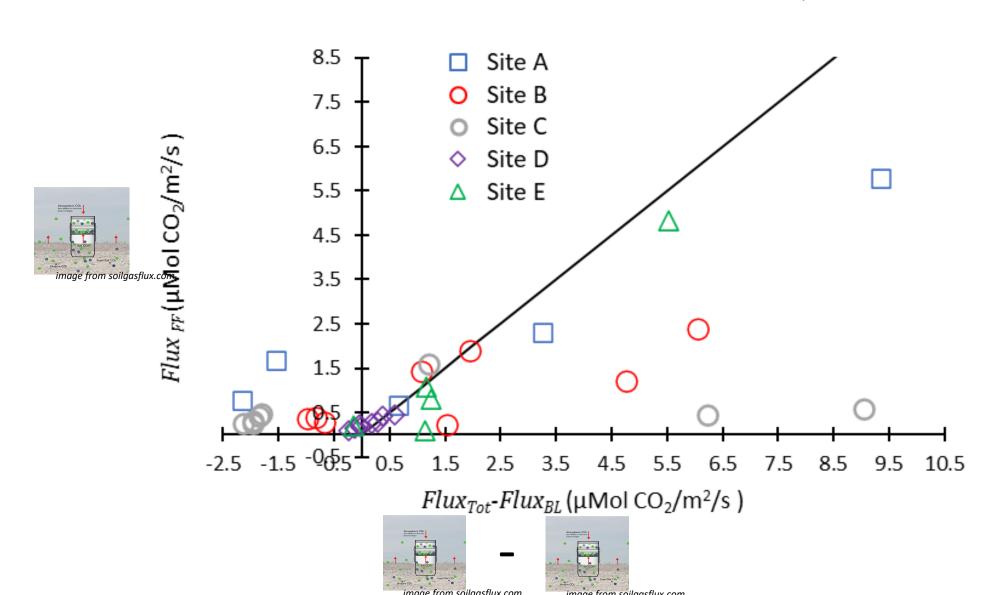
The measurement of contaminant natural source zone depletion (NSZD) rates has become an important tool to manage petroleum contaminated sites. Most NSZD rate measurement methods rely on a balance on the biodegradation by-products (either carbon or heat). Carbon balance-based methods stoichiometrically convert measured soil-gas CO_2 flux related to contaminant degradation to equivalent contaminant mass loses. CO_2 flux-based methods require separating the fraction of the total CO_2 flux produced by NSZD from the fraction of CO_2 flux

Study focused on two practices to estimate noise (background correction and ¹⁴C correction) on the same measurement

Effect of measurement error (special variability, different deployment periods, method biases) is minimized, allowing focus on given practice

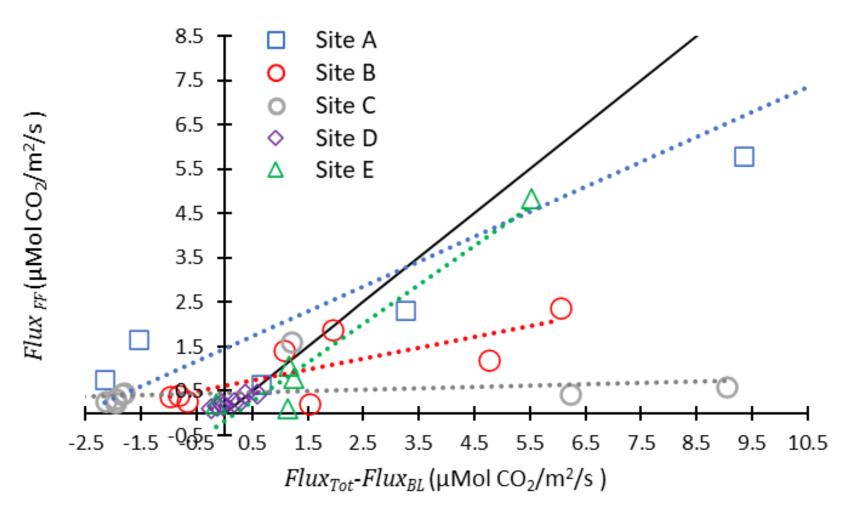
Comparing Both Corrections

Zimbron, 2022. GWMR



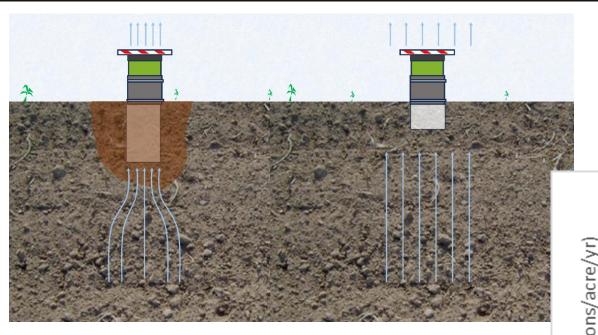
Comparing Both Corrections

Zimbron, 2022. GWMR

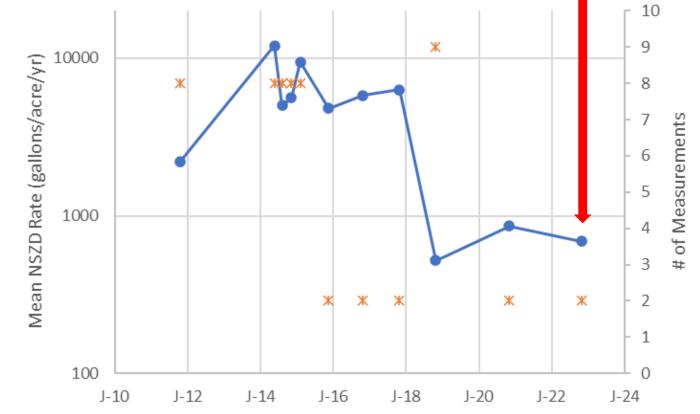


- Five sites data suggests high biass of background correction
- However, Kurkarni, et al, 2022 (40 sites) found no consistent bias of any method tested

Soil Installation Method



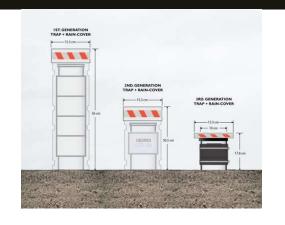
"The biennial NSZD monitoring event was conducted in November 2022 using direct-push, one-time use, shallow-install, low-profile CO₂ trap receivers."



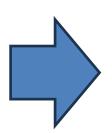
Data and report available at: colorado.gov/cdphe

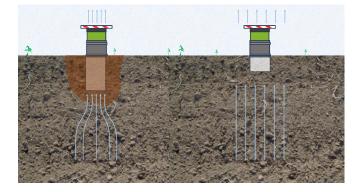
Evolution of CO₂ Trap Best Practices

a) Trap Design



b) Soil Installation







Monitoring&Remediation

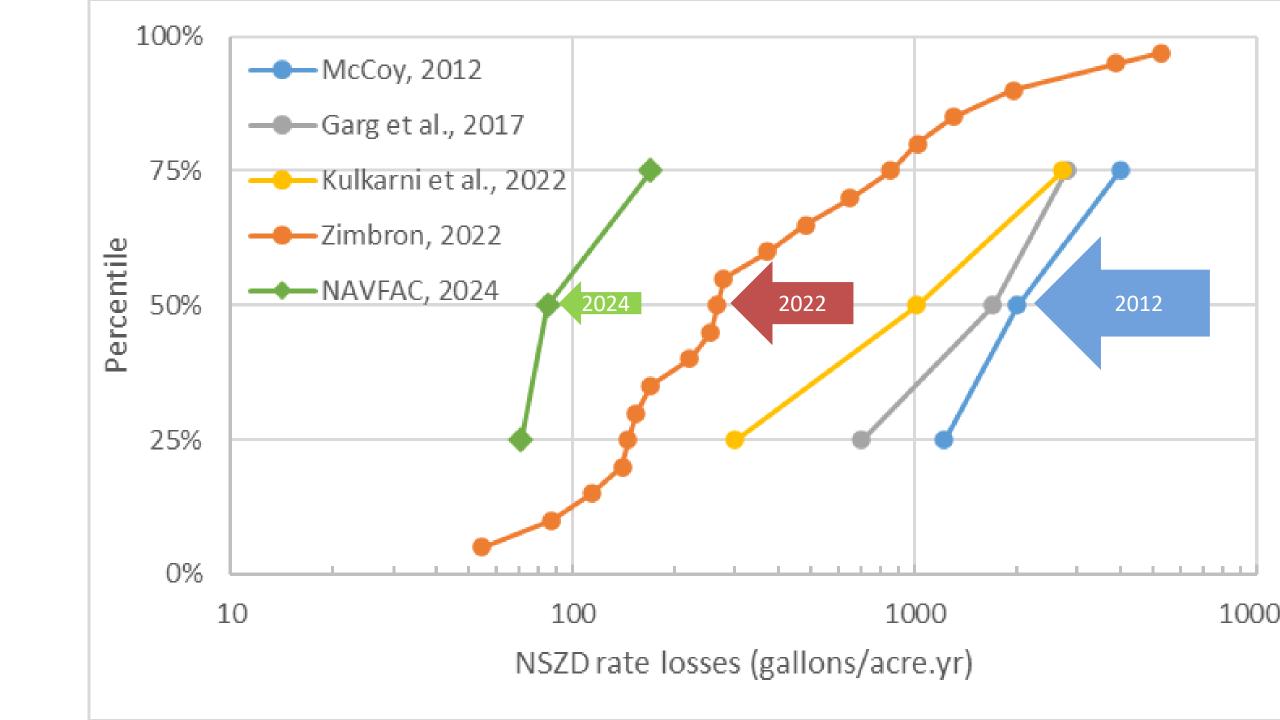
Practical Applications

c) Radiocarbon Correction Comparison of Radiocarbon- and Background Location-Corrections on Soil-Gas CO₂ Flux-Based NSZD Rate Measurements at Petroleum Impacted Sites Data using up to date practices:

Zimbron, Julio A. "Comparison of Radiocarbon-and Background Location-Corrections on Soil-Gas CO2 Flux-Based NSZD Rate Measurements at Petroleum Impacted Sites." Groundwater Monitoring & Remediation 42.3 (2022): 116-122.

(5 sites, n=36 observations)

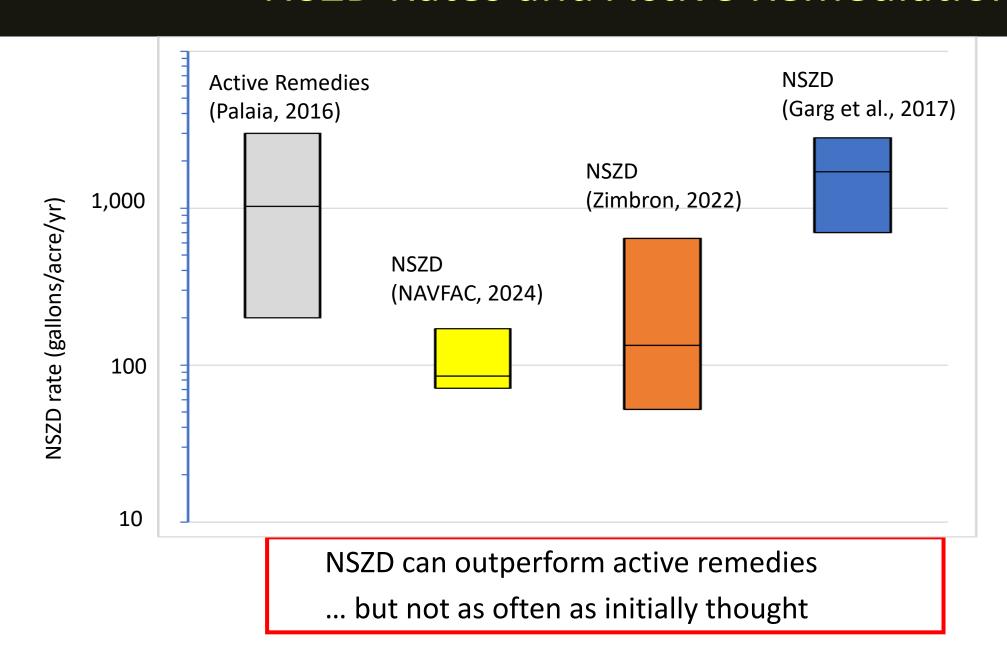
NAFVAC, 2024. Fact Sheet: Natural Source Zone Depletion. Available at exwc.nafvac.navy.mil (5 sites, averages reported)



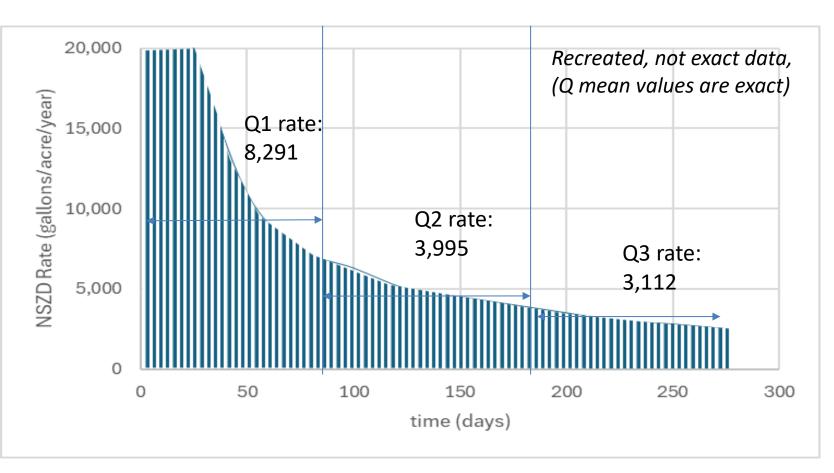
Why the OM of NSZD rates matter?

- 1) Remedy transition (population example)
- 2) Remedy transition into NSZD as a remedy (2024 Battelle Example)
- 3) Site longevity: ASTM Example

NSZD Rates and Active Remediation



An (Not Uncommon) Example



- 1) Single Stick Method
- 2) 09/2022-06/2023 (Q1-Q3)
- 3) Multiple locations
- 4) Soil Transport Properties from Reported Values
- 5) Seasonal results not consistent with Conceptual Site Model
- 6) Site-wide value: ~8,000 gallons/acre/yr led to site closure

Recreated data
(Q mean values are exact)

Hypothetical Example: Site Longevity

From ASTM Guidance Document:

"Site with LNAPL mass of 32,000 gallons/acre

NSZD rate: 700 gallons/acre/year

-> 30 years to nearly complete depletion"

Same example, but NSZD rate of 150 gallons/acre/year

- →~130 years to nearly complete depletion
 - Expected site longevity can change from decades to centuries, based on NSZD rates
 - Perhaps the final outcome (NSZD is an acceptable remedy) would not change, but seems these comparisons should be based on more realistic rates, rather than those based on early data

Top Qa/QC flags

- 1) Measurement at a scale below the characteristic scale of the problem
- 2) Background correction (i.e., applied to short term CO2 fluxes or the thermal gradient method)
- 3) Outlier values (i.e., site wide average > 1,000 gallons/acre)
- 4) Calculated values using soil transport property from literature
- 5) Modeled NSZD values

A QA/QC (non-exhaustive) Checklist

- Are values outliers (> 1,000 gallons/acre per year)?
- Is a background correction being used?
- Are soil transport properties measured?
- If measured, were they measured outside relevant location and time?
- Are measurements too sparse (i.e., < characteristic scale)? - Geospatial bias: NSZD measurements at prescreened high NSZD locations (rather Y
- than distributed across NAPL source)
- Are results inconsistent with conceptual site model?

- Were part of the data edited because "did not make sense"?

- Examples:
 - Shark-fin temperature profile with maximum outside Aerobic Anaerobic Interface

Marinaum NC7D rates during caldon coocons (winter coning)

N

N

N

N N

N

N

N

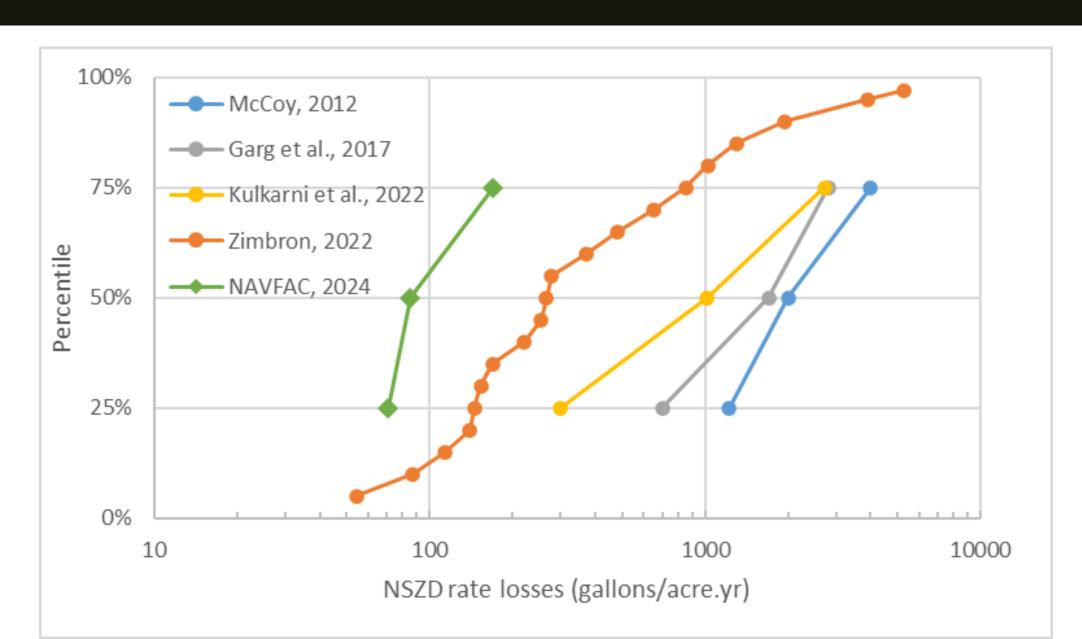
Y

Closing Thoughts

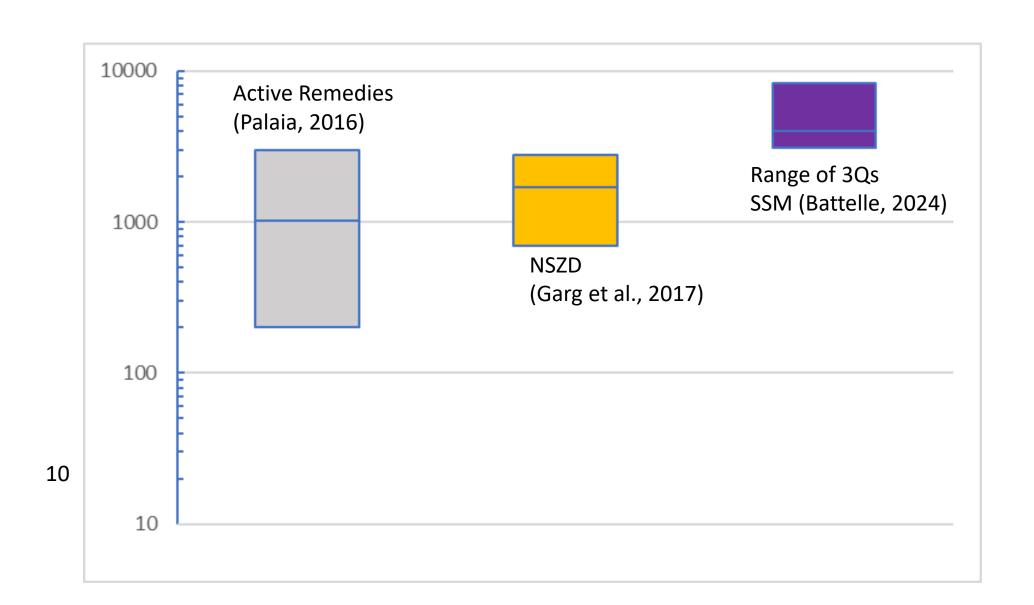
- 1) An NSZD target of 1,000 gallons/acre/yr is overly optimistic
- 2) Industry should continue to improve best practices (expect NSZD rates to drop)
- 3) Incorrect characteristic scale can be a significant source of error- available guidance documents have been silent on this
- 4) The apparent agreement between different methods that use different characteristic scale should be further investigated



Measured Rates: an evolving target?



NSZD Rates and Active Remediation

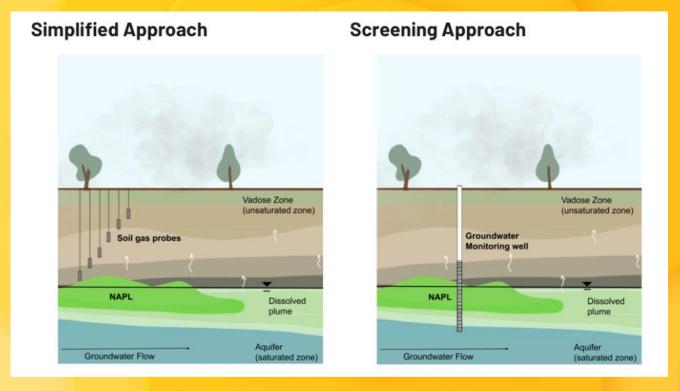




Soil Gas Gradient Method for Estimating Natural Source Zone Depletion (NSZD)

National Tanks Conference Spokane, Washington September 24, 2025

Presenter: Matthew Lahvis Shell Oil Products US



Adapted from P. Jourabchi – ARIS Environmental

58

Cautionary Note

The companies in which Shell plc directly and indirectly owns investments are separate legal entities. In this content "Shell", "Shell Group" are sometimes used for convenience to reference Shell plc and its subsidiaries in general. Likewise, the words "we", "us" and "our" are also used to refer to Shell plc and its subsidiaries in general or to those who work for them. These terms are also used where no useful purpose is served by identifying the particular entity or entities. "Subsidiaries" and "Shell companies" as used in this content refer to entities over which Shell plc either directly or indirectly has control. The terms "joint venture", "joint operations", and "associates" may also be used to refer to a commercial arrangement in which Shell has a direct or indirect ownership interest with one or more parties. The term "Shell interest" is used for convenience to indicate the direct and/or indirect ownership interest held by Shell in an entity or unincorporated joint arrangement, after exclusion of all third-party interest.

Forward-Looking statements

This content contains forward-looking statements (within the meaning of the U.S. Private Securities Litigation Reform Act of 1995) concerning the financial condition, results of operations and businesses of Shell. All statements of future expectations that are based on management's current expectations and assumptions and involve known and unknown risks and uncertainties that could cause actual results, performance or events to differ materially from those expressed or implied in these statements. Forward-looking statements sorphard-looking statements sorphard-looking statements sorphard-looking statements. Porward-looking statements are identified by their use of terms and phrases such as "aim"; "ambition"; "anticipate"; "aspire", "aspiration", "believe"; "commit"; "commit "commit "commit "commit "commit "commit "commit "co

Shell's net carbon intensity

Also, in this content we may refer to Shell's "net carbon intensity" (NCI), which includes Shell's carbon emissions from the products, our suppliers' carbon emissions in supplying energy for that production and our customers' carbon emissions associated with their use of the energy products we sell. Shell's NCI also includes the emissions associated with the production and use of energy products produced by others which Shell purchases for resale. Shell only controls its own emissions. The use of the terms Shell's "net carbon intensity" or NCI is for convenience only and not intended to suggest these emissions are those of Shell plc or its subsidiaries.

Shell's net-zero emissions target

Shell's operating plan and outlook are forecasted for a three-year period and ten-year period, respectively, and are updated every year. They reflect the current economic environment and what we can reasonably expect to see over the next three and ten years. Accordingly, the outlook reflects our Scope 1, Scope 2 and NCI targets over the next ten years. However, Shell's operating plan and outlook cannot reflect our 2050 net-zero emissions target, as this target is outside our planning period. Such future operating plans and outlooks could include changes to our portfolio, efficiency improvements and the use of carbon capture and storage and carbon credits. In the future, as society moves towards net-zero emissions, we expect Shell's operating plans and outlooks to reflect this movement. However, if society is not net zero in 2050, as of today, there would be significant risk that Shell may not meet this target.

Forward-Looking non-GAAP measures

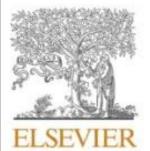
This content may contain certain forward-looking non-GAAP measures such as adjusted earnings and divestments. We are unable to provide a reconciliation of these forward-looking non-GAAP measures to the most comparable GAAP financial measures because certain information needed to reconcile those non-GAAP measures to the most comparable GAAP financial measures is dependent on future events some of which are outside the control of Shell, such as oil and gas prices, interest rates and exchange rates. Moreover, estimating such GAAP measures with the required precision necessary to provide a meaningful reconciliation is extremely difficult and could not be accomplished without unreasonable effort. Non-GAAP measures in respect of future periods which cannot be reconciled to the most comparable GAAP financial measure are calculated in a manner which is consistent with the accounting policies applied in Shell plc's consolidated financial statements.

The contents of websites referred to in this content do not form part of this content.

We may have used certain terms, such as resources, in this content that the United States Securities and Exchange Commission (SEC) strictly prohibits us from including in our filings with the SEC. Investors are urged to consider closely the disclosure in our Form 20-F and any amendment thereto, File No 1-32575, available on the SEC website www.sec.gov

Verginelli et al. (2024)

Water Research 267 (2024) 122559



Contents lists available at ScienceDirect

Water Research







Soil gas gradient method for estimating natural source zone depletion rates of LNAPL and specific chemicals of concern

Iason Verginelli a, , Matthew A. Lahvis b, Parisa Jourabchi G, George E. DeVaull b

^a Laboratory of Environmental Engineering, Department of Civil Engineering and Computer Science Engineering, University of Rome Tor Vergata, Via del Politecnico 1, 00133 Rome, Italy

b Equilon Enterprises LLC doing business as Shell Oil Products US, Houston, TX, USA

c ARIS Environmental Ltd., Vancouver, BC, Canada

Motivation for Study

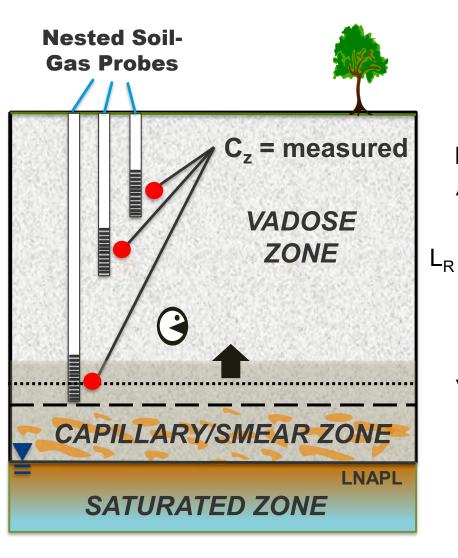
- NSZD rate measurements are recommended as routine best practice to support remedial decision making (baseline)
- NS7D methods:
 - often require additional instrumentation (chambers, canisters, thermistors) or a high level of effort, sophistication (numerical or analytical models)
 - non-compositional (bulk LNAPL only)
- NSZD rates can vary significantly over time and space
- NSZD is often used as <u>one</u> of multiple lines of evidence for terminating active remediation



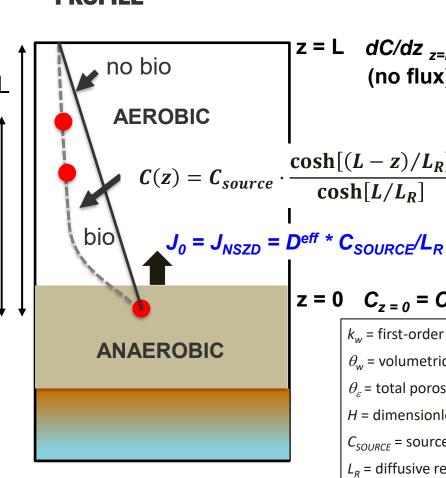
Goal: Develop **simple** compositional NSZD method to facilitate broader uptake of NSZD measurements in support of improved remedial decision making at petroleum release sites



Soil-Gas Method Based on Vapor Transport Modeling (Verginelli and Baciocchi, 2021)







1-D Steady State Vapor **Diffusive-Reactive Transport**

$$D^{eff}\frac{d^2C}{dz^2} - \frac{k_w \cdot \theta_w}{H} \cdot C = 0$$

Effective Diffusion Coefficient

$$D^{eff} = D_{air} \cdot \frac{\theta a^{10/3}}{\theta e^2}$$

Reactive Pathlength

$$L_R = \sqrt{\frac{D^{eff} \cdot H}{\theta_w \cdot k_w}}$$

$$z = 0 \quad C_{z=0} = C_{SOURCE}$$

 $dC/dz_{z=1} = 0$

(no flux)

 k_{w} = first-order biodegradation rate constant

 $\theta_{\rm w}$ = volumetric moisture content of soil

 θ_c = total porosity of soil

H = dimensionless Henry's Constant

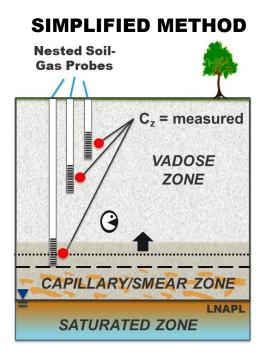
 C_{SOURCE} = source vapor concentration

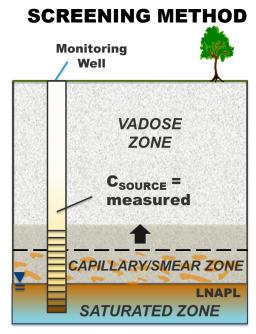
 L_R = diffusive reactive length (reaction rate/diffusion rate = 1)

Deff = effective diffusion coefficient

Approach

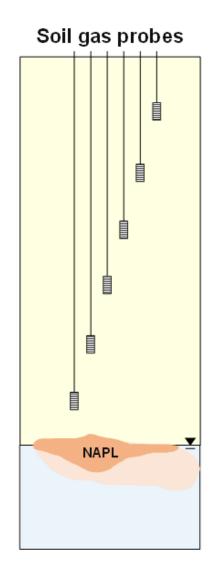
- 2 Methods
 - Simplified Approach: based on depth-discrete soil-gas concentration data)
 - Screening Approach: based on maximum concentrations measured in MWs
- methods can be applied to assess both bulk and chemical specific NSZD rates
- both methods involve 3 general steps:
 - Step 1: Estimate the diffusive "reactive" pathlength (L_R)
 - distance above vapor source where reaction rate / diffusion rate or
 Damköhler Number = 1
 - location roughly coincides where maximum source vapor concentrations (C_{SOURCE}) decrease by 0.37x (ITRC, 2014)
 - Step 2 Estimate the effective diffusion coefficient (Deff)
 - Step 3 Estimate the NSZD rate (J_{NSZD} = D^{eff} * C_{SOURCE}/L_R)



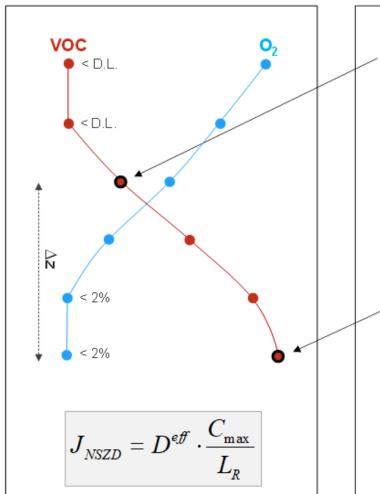


Simplified Method: Step 1

Estimate the L_R (from Soil-Gas Data)







Selection of control points

Minimum soil gas concentration in the aerobic zone above the detection limit (D.L.)

Diffusive reaction length (L_R)

$$L_{R} = \frac{\Delta z}{\ln\left(C_{lower}/C_{upper}\right)}$$

Clower

Maximum soil gas concentration at the greatest depth

Nomenclature

J_{NSZD}: NSZD flux

Deff: Diffusion coefficient

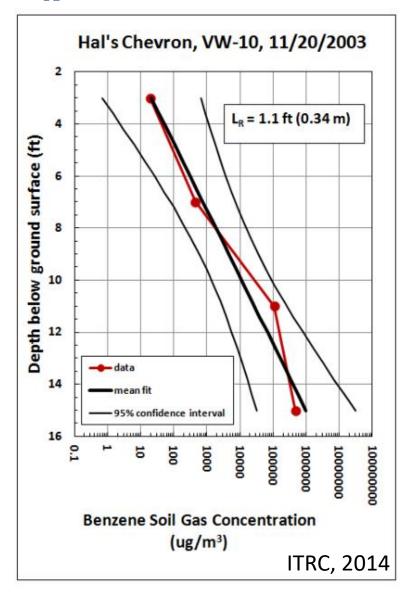
L_R: Diffusive reaction length

C_{max}: maximum soil gas concentration

- C_{upper} should be selected as minimum soil gas concentration > DL*
 - * will underestimate NSZD rate if use $C_{upper} < DL$
- selected preferably in the aerobic zone (O₂ > 1 2%)
- method requires a
 minimum 2 depth
 discrete vapor
 concentrations > DLs

Simplified Method: Step 1

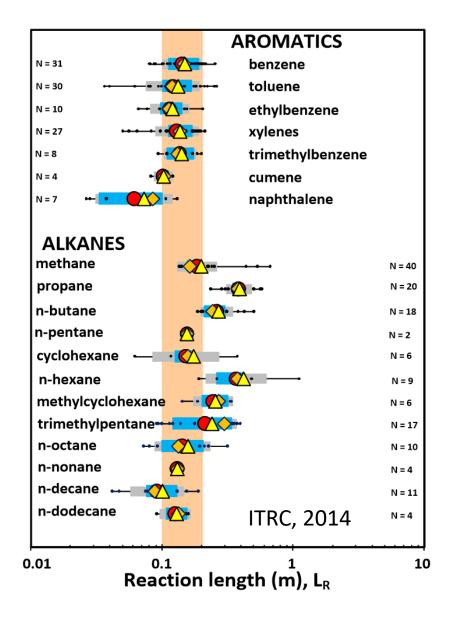
Estimate the L_R (from Soil-Gas Data)



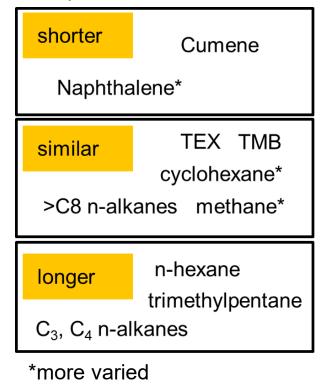
$$L_{R} = \frac{\Delta z}{\ln\left(C_{lower}/C_{upper}\right)}$$

- fit a regression line through depth vs. log soil gas concentration (L_R = slope)
- requires a minimum 2 depth discrete vapor concentrations > DLs

L_R from Aerobic Biodegradation Rates Reported in the Literature (*Important for Screening Method)

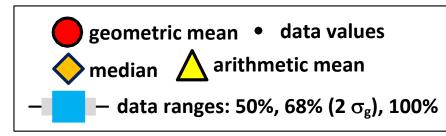


Compared to benzene:



$$L_R = \sqrt{\frac{D^{eff} \cdot H}{\theta_w \cdot k_w}}$$

- water-phase degradation rates (k_w)
 from field studies
- effective diffusivity (D^{eff}) from assumed:
 - soil moisture, $\theta_{\rm w}$ = 0.13 cm³/cm³
 - total soil porosity, $\theta_e = 0.425 \text{ cm}^3/\text{cm}^3$
- chemical-specific parameters (H, D^{eff}) at reference temp (20°C to 25°C)



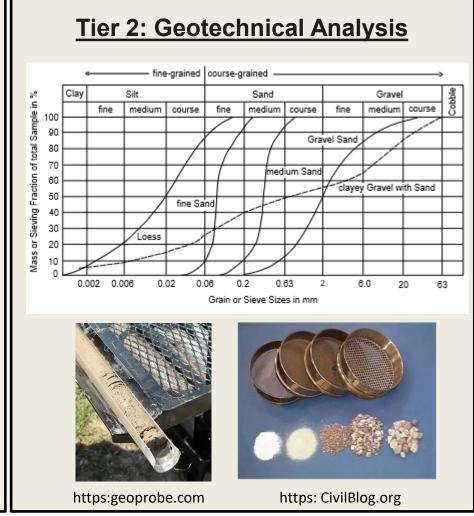
Estimate the Effective Diffusion Coefficient (Deff)

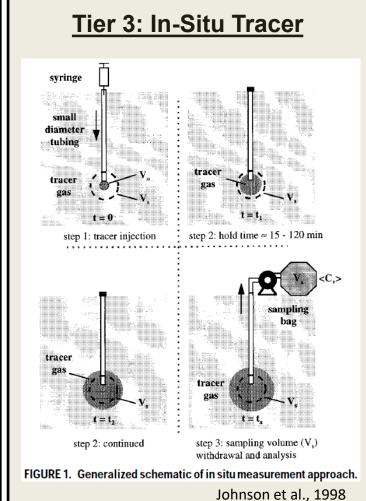
$$D^{eff} = \frac{L}{\sum_{i}^{n} \left(\frac{d_{i}}{D_{i}^{eff}}\right)}$$

Tier 1: Default Values

TABLE 3. CLASS AVERAGE VALUES OF THE VAN GENUCHTEN SOIL WATER RETENTION PARAMETERS FOR THE 12 SCS SOIL TEXTURAL CLASSIFICATIONS

Soil texture	Saturated water	Residual water	van Genuchten parameters		
(USDA)	content, θ_s	Content, θ_r	α ₁ (1/em)	N	M
Clay	0.459	0.098	0.01496	1.253	0.2019
Clay loam	0.442	0.079	0.01581	1.416	0.2938
Loam	0.399	0.061	0.01112	1.472	0.3207
Loamy sand	0.390	0.049	0.03475	1.746	0.4273
Silt	0.489	0.050	0.00658	1.679	0.4044
Silty loam	0.439	0.065	0.00506	1.663	0.3987
Silty clay	0.481	0.111	0.01622	1.321	0.2430
Silty clay loam	0.482	0.090	0.00839	1.521	0.3425
Sand	0.375	0.053	0.03524	3.177	0.6852
Sandy clay	0.385	0.117	0.03342	1.208	0.1722
Sandy clay loam	0.384	0.063	0.02109	1.330	0.2481
Sandy loam	0.387	0.039	0.02667	1.449	0.3099





Simplified Method Validation

NSZD Rates Consistent with Those Determined Using Numerical Model – Site in Beaufort, SC (Lahvis et al., 1999)

Constituent	Cmax (g/m ³) a	Reaction length, L_R (m) $^{ m b}$	<i>Deff</i> (m²/day) ^c	NSZD flux (g/m²/day)	
				Simplified approach ^d	Lahvis et al. (1999) ^e
Benzene	0.145	0.15	1.35E-02	0.013	0.02 (0.00736-0.0433)
Toluene	5.41	0.19	1.33E-02	0.379	0.47 (0.198-0.839)
Ethylbenzene	0.592	0.11	1.14E-02	0.059	0.06 (0.0233-0.117)
Xylenes	3.12	0.10	1.33E-02	0.34	0.36 (0.117-0.691)

^a Gaseous phase concentrations detected at 12 cm distance from the water table (ref. Table 1 of Lahvis et al. 1999)

$$L_{R} = \frac{\Delta z}{\ln\left(C_{lower}/C_{upper}\right)}$$

Deff based on average total and air-filled porosities (reported in Lahvis et al., 1999)

$$D^{eff} = D_{air} \cdot \frac{\theta a^{10/3}}{\theta e^2}$$

^b Calculated with eq. (11) using the gaseous phase concentrations detected at 12 cm and 73 cm distance from the water table (ref. Table 1 of Lahvis et al. 1999)

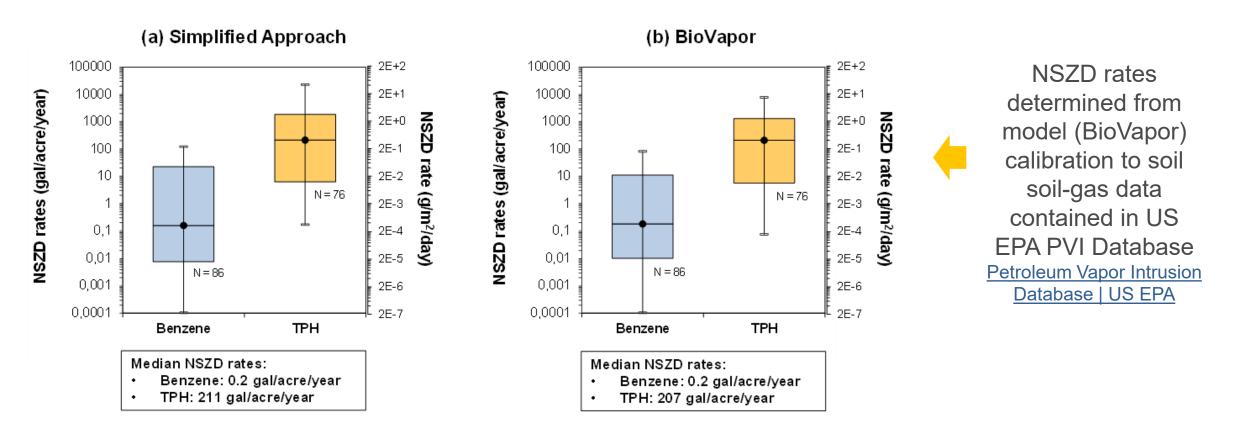
^cCalculated with the Millington and Quirk (1961) equation assuming an average porosity of 0.36 and air-filled porosity of 0.17 (geometric mean of the values between 12 and 104 cm above the water table. Ref. Table 2 of Lahvis et al. 1999). The diffusion coefficients in air for the different BTEX were taken from the database of BioVapor (API, 2012)

d Calculated with eq. (13)

^e Average mass fluxes from groundwater to the unsaturated zone (Ref. Table 9 of Lahvis et al. 1999). The range values in parentheses represent the minimum and maximum values obtained from three different assumptions in extrapolating mass flux from the base of the model domain (z = 43 cm) to the water table (z = 0): 1) no reactions in this zone; 2) reaction rates remain constant; and 3) reaction rates are proportional to mass flux of O_2 at z = 43 cm.

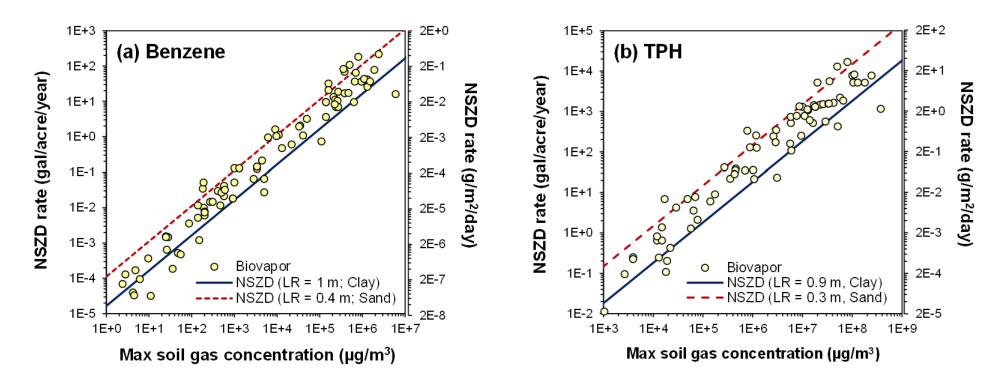
Simplified Method Validation:

NSZD Rates Consistent w/ Those Derived Using BioVapor Applied to USEPA (2013) PVI Database



 PVI database filtered to eliminate data from a) locations where < 2 soil-gas samples were collected from single borehole and b) dissolved-phase sources (only analyzed data associated with LNAPL (weathered gasoline sources) (variety of soil types, surface covers)

NSZD Rates Strongly Correlated w/ Maximum Source Vapor Concentrations (C_{SOURCE})



- results imply that maximum source vapor concentrations (C_{SOURCE}) collected from groundwater monitoring wells screened across the water table could be used for NSZD screening
- NSZD rates were bounded by 25th and 75th percentile L_R, which allows for broader application to other COCs

Screening Method: COC-Specific NSZD Rates Based on Maximum Vapor Concentrations (C_{SOURCE}) in Monitoring Wells

Compound	Diffusion coefficient in air	Dimensionless Henry's constant	First-order water phase biodegradation rate constants (k_w)		
	$oldsymbol{D_{air}}$	H	25 th percentile	75 th percentile	
	(m^2/h)	(-)	(h ⁻¹)	(h ⁻¹)	
Benzene	0.0317	0.227	0.087	0.78	
Toluene	0.0313	0.276	0.19	1.4	
Ethylbenzene	0.0270	0.328	0.31	1.4	
Xylenes	0.0257	0.218	0.089	0.64	
Naphthalene	0.0212	0.020	0.054	5	
Hexane	0.072	75.2	6.3	50	
ТРН	0.0317	-	_	-	

Doguiros

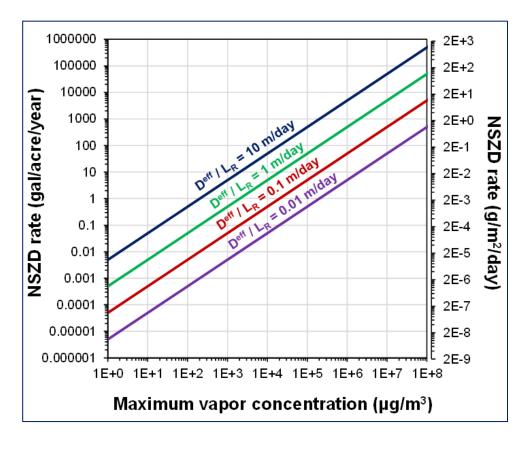
o 1st-order reaction rates (k_w) from DeVaull (1997) reported in ITRC (2014)

site-specific D^{eff}

maximum vapor concentrations (C_{SOURCE}) measured in monitoring wells

$$D^{eff} = D_{air} \cdot \frac{\theta a^{10/3}}{\theta e^2}$$

$$L_R = \sqrt{\frac{D^{eff} \cdot H}{\theta_w \cdot k_w}}$$



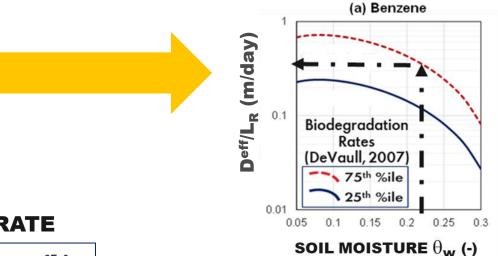
$$J_{NSZD} = D^{eff} \cdot C_{SOURCE} / L_R$$

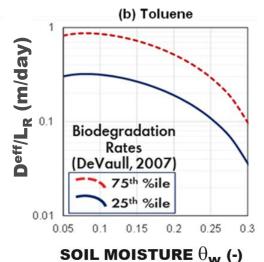
Screening Method: NSZD Rates from C_{SOURCE} Measurements

1: SELECT BIODEGRADATION RATE

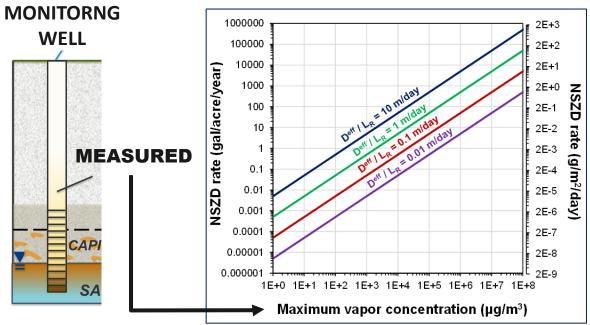
First-order water phase biodegradation rate constants (k_w) Compound 25th percentile 75th percentile (h⁻¹) (h⁻¹) 0.087 0.78 Benzene Toluene 0.19 1.4 Ethylbenzene 0.31 1.4 0.089 **Xylenes** 0.64 Naphthalene 0.054 Hexane 6.3 50 **TPH**

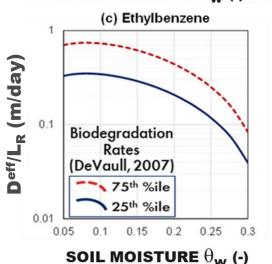
2: DETERMINE Deff//L_R

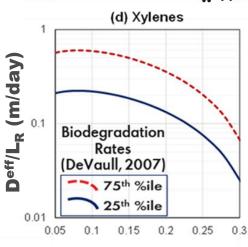










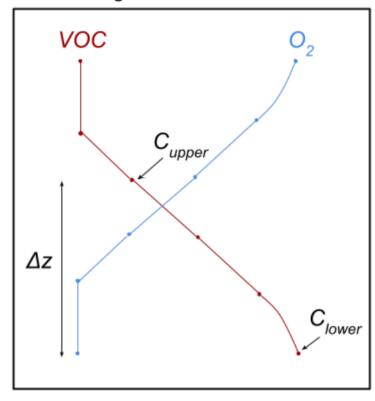


SOIL MOISTURE θ_{w} (-)

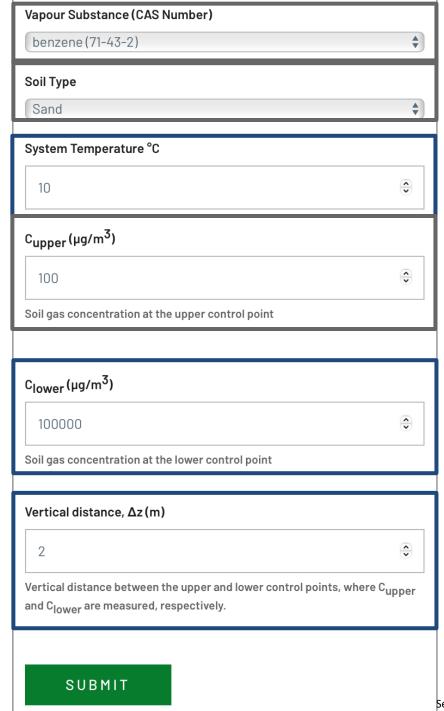
ARIS ETools

https://arisenv.ca

Soil gas concentrations



Full details and references in the User Guide and FAQs



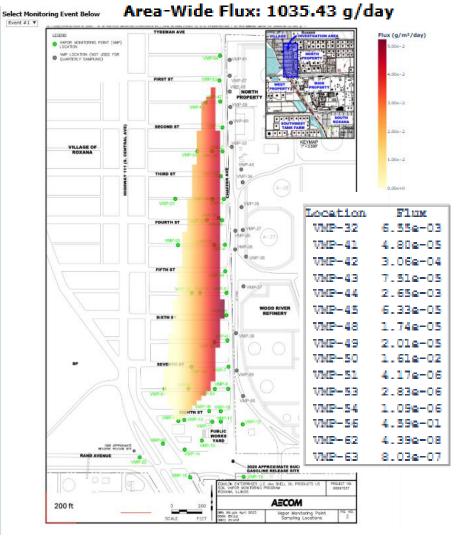
ARIS ETools

https://arisenv.ca

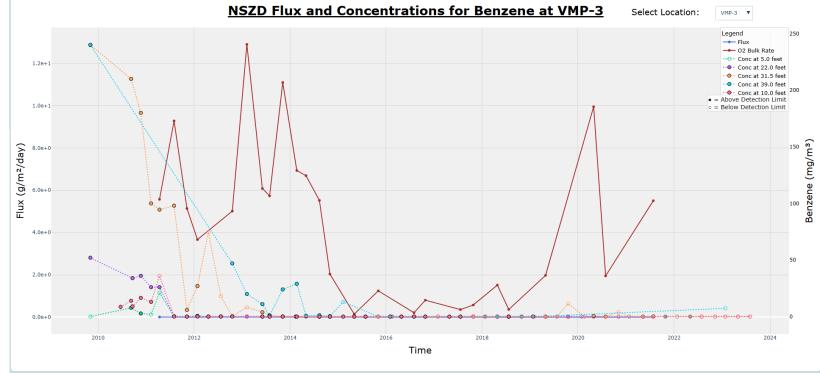
	SGM Output		
System Temperature Kelvin	T_S	2.83E+02	Kelvin
Diffusivity in air	Dair	7.73E-01	m ² /day
Diffusivity in water	D _{h2o}	8.90E-05	m ² /day
Henry's law constant at the system temperature	H_{S}	1.24E-01	2
Effective diffusion coefficient	D _{eff}	1.44E-06	m ² /s
Reactive diffusive length	L_R	2.90E-01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

Application – US Refinery Site

Benzene NSZD Flux Heat Map for Monitoring Event #1

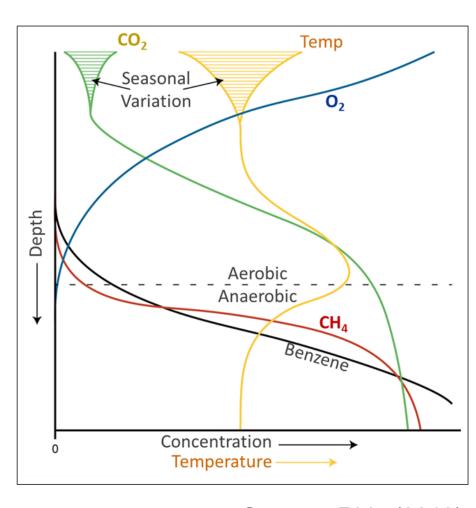


63 multi-level vapor wells (benzene and bulk NSZD rates)



Method Limitations Related to Gas-Phase Advection

- vapor transport must be diffusion dominated:
 - gas-phase advection is generally considered negligible (McHugh and McAlary, 2009; USEPA, 2015; Jourabchi and Lin, 2021; Lari et al., 2024)
 - gas-phase advection associated with barometric pumping generally < 1 m bgs (McHugh and McAlary, 2009; Eklund, 2016)
 - exception - near LNAPL source zones where rate of gas production from methanogenesis is high (Thorstenson and Pollock, 1989; Molins et al., 2010; Yao et al., 2015)
- neglecting gas—phase advection results in conservative NSZD rates (underestimates)



Source: Ririe (2013)

Practical Considerations

o suitable sites:

- those that benefit from baseline NSZD estimates to support remedial decision making, as advocated in
 - Exit Strategy Toolkit (L.U.S.T.Line Bulletin 94, September 2024) (https://neiwpcc.org/our-programs/underground-storage-tanks/l-u-s-t-line/
 - ASTM E3488-25 Moving Sites to Closure https://store.astm.org/e3488-25.html)
- those with relatively deep vadose zones (i.e., > 1 m thick)

less suitable sites:

- those where accuracy is needed as the method tends to underestimate NSZD rate because method only quantifies mass loss from volatilization and if C_{lower} located in anaerobic region of vadose zone
- those with significant variability in D^{eff}

References

- API (2012). API. BioVapor, A 1-D Vapor Intrusion Model with Oxygen-Limited Aerobic Biodegradation. American Petroleum Institute 2012. Available at: http://www.api.org
- ASTM (draft). WK78667 ASTM Guide for Advancing Stalled Corrective Action Sites Toward Site Closure. ASTM International, West Conshohocken, PA. https://www.astm.org/workitem-wk78667.
- ANSR EST (2024). Tools and methods to support the optimization and termination of active remediation systems. Exit Strategy Toolkit. Applied NAPL Science Research, Available at: https://naplansr.com/tools/exit-strategy-toolkit/.
- DeVaull, G.E., Ettinger, R.A., Salanitro, J.P., Gustafson, J.B. (1997). Benzene, toluene, ethylbenzene, and xylenes (BTEX) degradation in vadose zone soils during vapor transport: first-order rate constants (No. CONF-971116-). Ground Water Publishing Co., Westerville, OH (United States).
- DeVaull, G.E. (2007). Indoor vapor intrusion with oxygen-limited biodegradation for a subsurface gasoline source. Environ. Sci. Technol. 41(9), 3241-3248.
- Eklund, B. (2016). Effect of environmental variables on vapor transport. In Proceedings of the 26th Annual International Conference on Soil, Water, Energy, and Air, San Diego, CA
- ITRC (2014). Petroleum Vapor Intrusion: Fundamentals of Screening, Investigation, and Management. Interstate Technology and Regulatory Council, Vapor Intrusion Team, Washington, D.C. (October 2014).
- ITRC (2009). Evaluating Natural Source Zone Depletion at Sites with LNAPL. Interstate Technology and Regulatory Council, LNAPLS Team, Washington, D.C., (April 2009)
- Johnson, P.C., Bruce, C., Johnson, R.L., M.W. Kemblowski (1998). In situ measurement of effective vapor-phase porous media diffusion coefficients. Environ. Sci. Technol., 32(21), 3405-3409.
- Jourabchi, P., Lin., G.K. (2021). Modeling vapor migration for estimating the time to reach steady state conditions. Ground Water Monit. Rem. 41, 25 32.
- Lahvis, M., Hers, I. (2024). Exit strategy toolkit for optimization and termination of active remediation systems. L.U.S.T.Line Bulletin 94, NEIWPCC, September 2024.

References

- Lahvis, M.A., Baehr, A.L., Baker, R.J. (1999). Quantification of aerobic biodegradation and volatilization rates of gasoline hydrocarbons near the water table under natural attenuation conditions. Water Resour. Res. 35(3), 753-765.
- Lari, K.S., Davis, G.B., Rayner, J.L., Bastow, T.P. (2024). Advective and diffusive gas phase transport in vadose zones: Importance for defining vapour risks and natural source zone depletion of petroleum hydrocarbons. Water Res. 255, 121455.
- McHugh, T.E., McAlary, T. (2009). Important physical processes for vapor intrusion: a literature review. In Proceedings of AWMA Vapor Intrusion Conference, San Diego, CA.
- Millington, R.J., Quirk, J.P. (1961). Permeability of porous solids. Trans. Faraday Soc. 57, 1200-1207.
- Molins, S., Mayer, K.U., Amos, R.T., Bekins, B.A. (2010). Vadose zone attenuation of organic compounds at a crude oil spill site—Interactions between biogeochemical reactions and multicomponent gas transport. J. Contam. Hydrol. 112(1-4), 15-29.
- Thorstenson, D. C., Pollock, D. W. (1989). Gas transport in unsaturated zones: Multicomponent systems and the adequacy of Fick's laws. Water Resour. Res. (3), 477-507.
- USEPA (2015). Technical guide for addressing petroleum vapor intrusion at leaking underground storage tank sites. EPA 510-R-15-001, Office of Underground Storage Tanks, Washington, D.C. Available at http://www.epa.gov/oust/cat/pvi/pvi-guide-final-6-10-15.pdf.
- Verginelli, I., Lahvis, M.A., Jourabchi, P., and G.E. DeVaull. (2024). Soil gas gradient method for estimating natural source zone depletion rates of LNAPL and specific chemicals of concern. Water Research (267) 122559. https://www.sciencedirect.com/science/article/pii/S0043135424014581?via%3Dihub.
- Verginelli, I., Baciocchi, R. (2021). Refinement of the gradient method for the estimation of natural source zone depletion at petroleum contaminated sites. J. Contam. Hydrol. 241, 103807.
- Yao, Y., Wu, Y., Wang, Y., Verginelli, I., Zeng, T., Suuberg, E.M., Jiang, L., Wen, Y., Ma, J. (2015). A petroleum vapor intrusion model involving upward advective soil gas flow due to methane generation. Environ. Sci. Technol. 49 (19), 11577–11585





Natural Source Zone Depletion (NSZD)

Estimated from NAPL Composition Change over Time

28th National Tanks Conference (NTC) Spokane, Washington, September 23-25

5B. NSZD Wed., Sept. 24, 2025, 10:00 a.m. – 11:30 a.m.

George DeVaull Shell george.devaull@shell.com

Cautionary note

The companies in which Shell plc directly and indirectly owns investments are separate legal entities. In this content "Shell", "Shell Group" are sometimes used for convenience to reference Shell plc and its subsidiaries in general. Likewise, the words "we", "us" and "our" are also used to refer to Shell plc and its subsidiaries in general or to those who work for them. These terms are also used where no useful purpose is served by identifying the particular entity or entities. "Subsidiaries", "Shell subsidiaries" as used in this content refer to entities over which Shell plc either directly or indirectly has control. The terms "joint venture", "joint operations", and "associates" may also be used to refer to a commercial arrangement in which Shell has a direct or indirect ownership interest with one or more parties. The term "Shell interest" is used for convenience to indicate the direct and/or indirect ownership interest held by Shell in an entity or unincorporated joint arrangement, after exclusion of all third-party interest.

Forward-Looking statements

This content contains forward-looking statements (within the meaning of the U.S. Private Securities Litigation Reform Act of 1995) concerning the financial condition, results of operations and businesses of Shell. All statements of future expectations that are based on management's current expectations and involve known and uncertainties that could cause actual results, performance or events to differ materially from those expressed or implied in these statements. Forward-looking statements include, among other things, statements concerning the potential exposure of Shell to market risks and statements expressing management's expectations, beliefs, estimates, forecasts, projections and assumptions. These forward-looking statements are identified by their use of terms and phrases such as "aim"; "ambition"; "anticipate"; "aspiration", "believe"; "commit"; "commit"; "commit"; "commit"; "commit"; "commit"; "commit"; "intendition"; "intendition of suitable potential acquisition properties and targets, and successful negotiation and completion of such transactions; (i) brain the intendition of suitable potential acquisition properties

Shell's net carbon intensity

Also, in this content we may refer to Shell's "net carbon intensity" (NCI), which includes Shell's carbon emissions from the production of our energy products, our suppliers' carbon emissions in supplying energy for that production and our customers' carbon emissions associated with their use of the energy products we sell. Shell's NCI also includes the emissions associated with the production and use of energy products produced by others which Shell purchases for resale. Shell only controls its own emissions. The use of the terms Shell's "net carbon intensity" or NCI is for convenience only and not intended to suggest these emissions are those of Shell plc or its subsidiaries.

Shell's net-zero emissions target

Shell's operating plan and outlook are forecasted for a three-year period and ten-year period of the current economic environment and what we can reasonably expect to see over the next three and ten years. Accordingly, the outlook reflects our Scope 1, Scope 2 and NCI targets over the next ten years. However, Shell's operating plan and outlooks could include changes to our portfolio, efficiency improvements and the use of carbon capture and storage and carbon credits. In the future, as society moves towards net-zero emissions, we expect Shell's operating plans and outlooks to reflect this movement. However, if society is not net zero in 2050, as of today, there would be significant risk that Shell may not meet this target.

Forward-Looking non-GAAP measures

This content may contain certain forward-looking non-GAAP measures such as adjusted earnings and divestments. We are unable to provide a reconciliation of these forward-looking non-GAAP measures to the most comparable GAAP financial measures is dependent on future events some of which are outside the control of Shell, such as oil and gas prices, interest rates and exchange rates. Moreover, estimating such GAAP measures with the required precision necessary to provide a meaningful reconciliation is extremely difficult and could not be accomplished without unreasonable effort. Non-GAAP measures in respect of future periods which cannot be reconciled to the most comparable GAAP financial measure are calculated in a manner which is consistent with the accounting policies applied in Shell plc's consolidated financial statements.

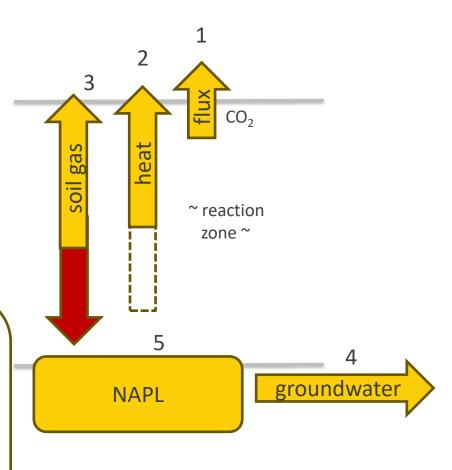
The contents of websites referred to in this content do not form part of this content.

We may have used certain terms, such as resources, in this content that the United States Securities and Exchange Commission (SEC) strictly prohibits us from including in our filings with the SEC. Investors are urged to consider closely the disclosure in our Form 20-F and any amendment thereto, File No 1-32575, available on the SEC website www.sec.gov

Natural Source Zone Depletion (NSZD)

Consolidation of Several Methods (ASTM E3361-22):

- 1. CO₂ Surface Efflux
- 2. Temperature Gradient
- 3. Soil Gas Gradient (O₂, CO₂, CH₄, HC)
- 4. Monitoring Groundwater Chemistry (gases, hydrocarbons, electron acceptors)
- 5. Monitoring NAPL Composition (over time)
- #1 through #4
 - monitor parameters for rates out of (or into) NAPL body
 - snapshot of loss in time rate [kg-loss/day]
 - #s 4 & 3 HC can be 'constituent-specific'
- #5
 - monitor NAPL composition change over time
 - relative mass loss of NAPL itself rate [kg-loss/(kg-NAPL)-day]
 - Bulk Rates & Constituent-specific
 - #4 HC (groundwater monitoring over time) depletion rates for soluble chemicals



NAPL Composition Method

How does this work?

A conserved marker (chemical) in the NAPL

- Example
 - Initial concentration = 1%
 - Later concentration = 2%

 $\frac{\text{initial}}{\text{final}} = \frac{1\%}{2\%} = 50\% \text{ of initial total is remaining}$

- This works for any ratio
 - If the marker depletes the bulk NAPL depletion estimate is a (conservative) underestimate

In practice: multiple NAPL sampling events & composition analyses

- We fit a trend to the conserved 'marker' concentration (mass fraction) over time
- To yield an estimate of trend in bulk NAPL depletion rate

$$\frac{c_T(t)}{c_T(t_0)} = \frac{\chi_{marker}(t_0)}{\chi_{marker}(t)}$$

$$c_T(t)$$
 = NAPL total concentration in soils (g-NAPL) / (g-soil) $\chi_{marker}(t)$ = 'Marker' concentration in NAPL (g-marker) / (g-NAPL)

NAPL composition method

How to choose markers:

Analyze and quantify constituents in the NAPL (g-compound/g-oil)]

- As many constituents as possible / practicable
- Fit a trend to each mass fraction constituent in the NAPL

DeVaull, et al., 2020

- o 'Best' marker (case-by-case) is the constituent that increases at the greatest rate
 - With checks and validation of the confidence intervals on the trend
 - Multiple markers can be summed to improve the confidence intervals
 - And because we're fitting mass fraction trends to all constituents combine with bulk trend to get constituent depletion

Other (older) methods make an a priori choice of 'biomarkers'

o biomarkers: hopanes, steranes, isoprenoids (from chemistry) in crude oil

Douglas et al, 1996

- 'Markers' may turn out to be either be traditional biomarkers or other constituents
- Now can use this method to be used when no traditional 'biomarkers' are present (such as gasoline, diesel)
- If the marker depletes the bulk NAPL depletion estimate is a (conservative) underestimate

Application Steps

Sampling and Analysis

- NAPL collection quarterly samples for about minimum two to four years (or more) approximately
 - Analysis methods → ASTM D3328-06, USEPA methods 8015 (GC-FID) & 8260 (GC-MS); others (modified)

Data Quality, Assurance

- Application Options:
 - 1. All data together (such as for a single petroleum release)
 - 2. Well-by-well analysis (multiple spills, treatment areas, complex sites)

Data Analysis: calculations

- Fit trends / Rank order / Identify 'markers'
- Set of equations [DeVaull et al, 2020]; or an on-line calculator [ARIS]: https://arisenv.ca/e-tools/

Results

- Total rate of bulk NAPL depletion (% per year, half-life)
- Constituent-specific depletion rates (any constituent measured in the NAPL)
 - Qualified (confidence limits on trends for constituents and bulk NAPL)

Consolidated Results – Compositional NSZD

Use Half-life or time to 50% depletion (useful when monitored time intervals vary)

Index	Site / Description	Est. Half Life (or Time to 50% Depletion)
1 [BE]	Crude Oil Spill. one-time. (Bemidji, MN. USGS Study Site)	13.6 ± 2.9 years
2 [FY]	Terminal. USA. Mixed gasoline/diesel. one monitoring well	7.3 ± 1.8 years
3 [CA]	Former Refinery. USA. Mixed gasoline/diesel. each of 11 wells (well-by-well)	12 (4.9 to 39) years (median, range)
4 [HT]	Terminal. USA. Mixed gasoline/diesel. (well-by-well)	4.6, 12.3, 18.3, 20.3 years
5 [PC]	Former Refinery. EU. Mixed gasoline/diesel. Multiple extraction wells pumped to 6 technical chambers, each evaluated.	12 (11 to 15) years Average (quartiles)
6 [BK]	Former Refinery. USA. Mixed gasoline/diesel. Each of 7 wells. 6 in water-table NAPL, one (outlier) submerged.	Average 3 (-0.3 to 6); outlier 20 (13 to 27)
7 [LA]	Former Refinery. USA. Mixed gasoline/diesel. 38 wells, each evaluated (3 to 6 samples, 2 to 8 years of monitoring)	Average (quartiles) 10 (4 to 17) years

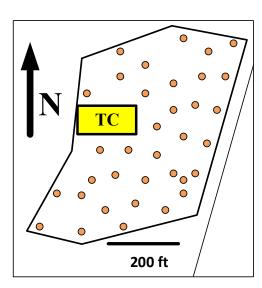
Many instances: 50% total depletion in 7 to 15 years

Method quantifies
NAPL depletion due
to composition
change

- EU
- Former refinery and product distribution terminal
- Varied gasoline and diesel —range LNAPL
- delineated LNAPL at/near the water table
- Pumped LNAPL recovery from multiple wells into technical chambers [TC]
- ~18 NAPL Analyses over 5 years
- Similar composition across technical chambers

Case Example

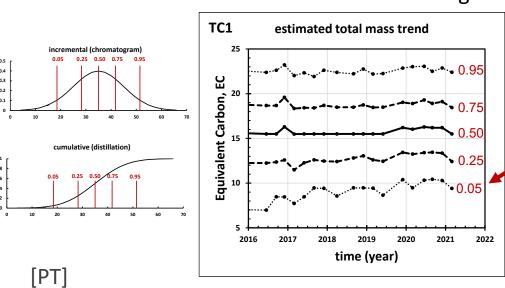
[PT]

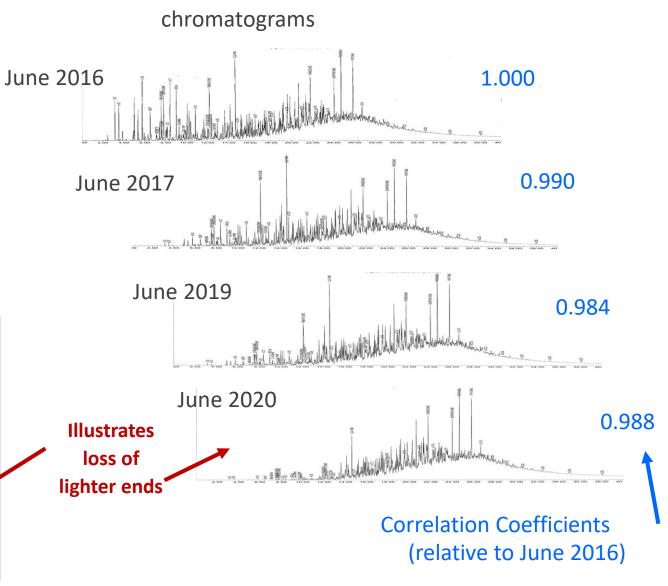


LNAPL Analysis and Preliminary Evaluation

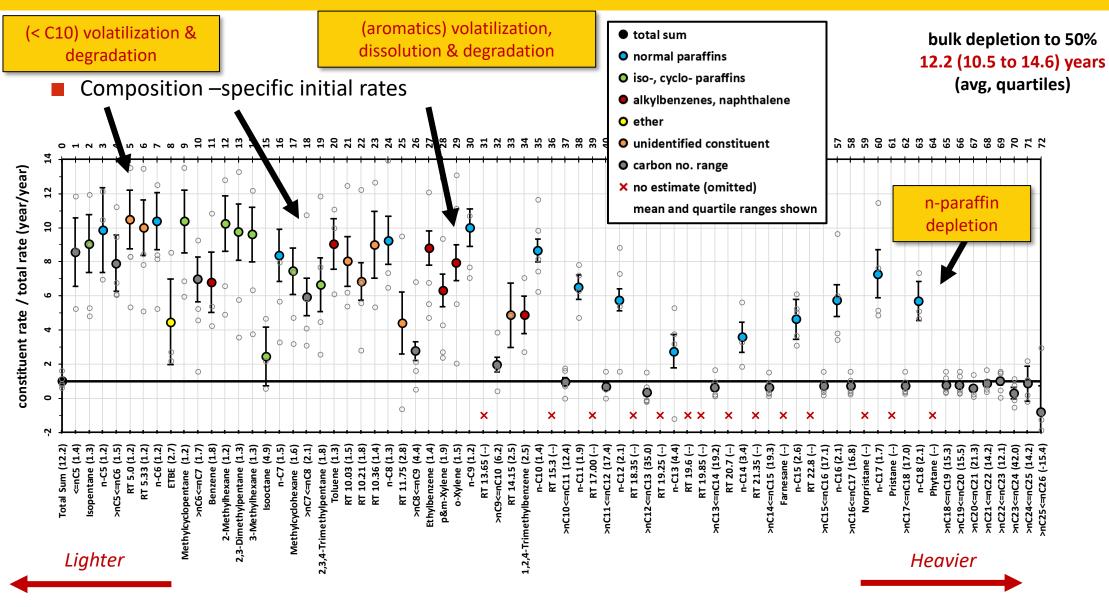
GC/FID & GC/MS analysis

- Qualitative chromatogram comparisons
- Similar composition, not identical
- Expert check: peak baseline and integration
- Chromatogram (non-polar separation)
 - Integrate: simulate a batch distillation
 - "% distillation" cuts illustrate bulk change





Constituent Depletion: Example



Case Example

[CA]

- USA
- Former refinery and product distribution terminal
- Varied gasoline and diesel —range LNAPL
- Assessed, remediated, delineated remaining petroleum LNAPL
- Well-by-well trend analysis (2 to 4 samples each)
- 14 wells, 4 to 13 years of data
- Varied attenuation across site (spatial)

LNAPL Depletion Estimates Based on LNAPL Compositional Analysis

All Locations. Median for 50% Depletion: 12 Years

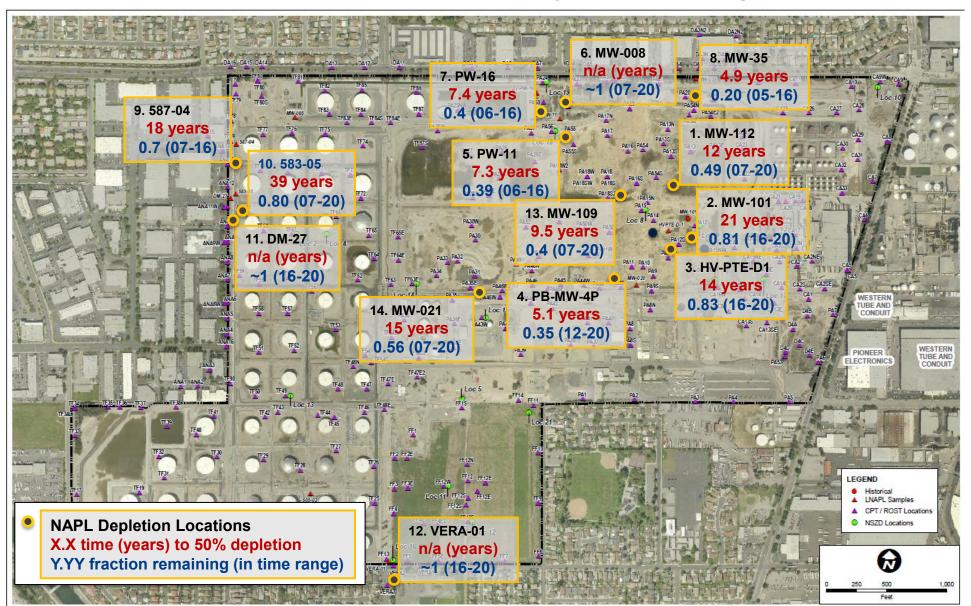
		Total Estimated NAPL		Elapsed Time	Estimated Time for 50%
	Well Identifier	Mass Fraction Remaining	Overall Date Range	(years)	Total Depletion (years)
1	MW-112	0.49	2007 to 2020	12.6	12
2	MW-101	0.81	2016 to 2020	3.49	21
3	HV-PTE-D1	0.83	2016 to 2020	3.49	14
4	PB-MW-4P	0.35	2012 to 2020	7.80	5.1
5	PW-11	0.39	2006 to 2016	9.95	7.3
6	MW-008	~ 1	2007 to 2020	12.6	
7	PW-16	0.4	2006 to 2016	9.95	7.4
8	MW-35	0.20 (0.29 to 0.02)	2005 to 2016	11.5	4.9 (6.4 to 1.9)
9	587-04	0.7	2007 to 2016	9.12	18
10	583-05	0.80 (0.80 to 0.79)	2007 to 2020	12.6	39 (41 to 38)
11	DM-27	~ 1	2016 to 2020	3.47	
12	VERA-01	~ 1	2016 to 2020	3.49	
13	MW-109	0.4	2007 to 2020	12.6	9.5
14	MW-021	0.56	2007 to 2020	12.6	15

Copyright of Shell International B.V.

Copyright of Equilon Enterprises LLC, 2025

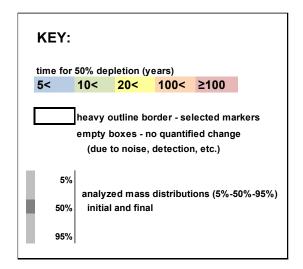
September 23-25, 2025

NSZD Rates: Estimates from NAPL Composition Change



Composition – Specific Results

- **Comparison across all evaluated wells**
- Time to 50% depletion (years)

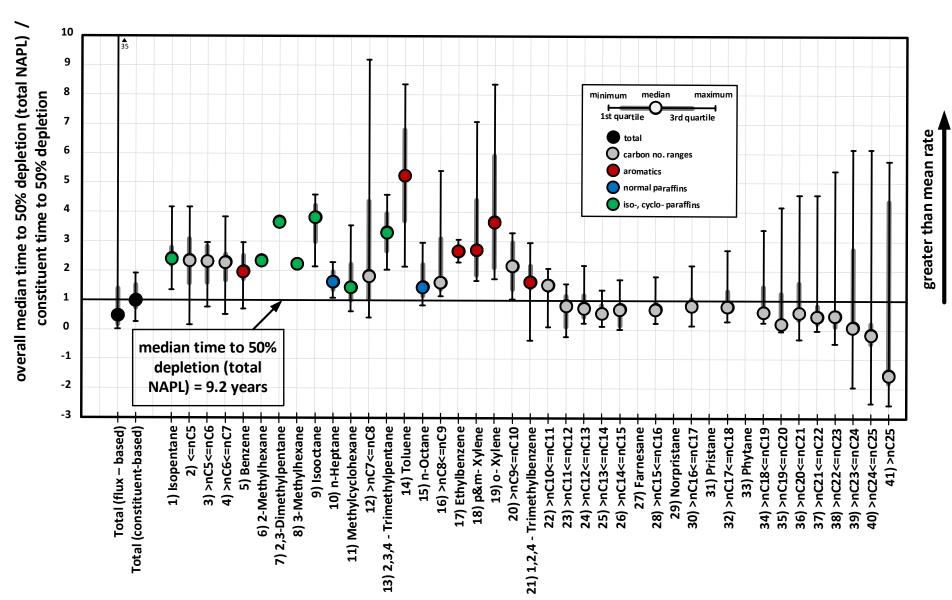


*[blank spaces] insufficient confidence in estimate

Γ	$C\Delta$	1
L	C/ \	J

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	MW-	MW-	HV-PTE-	PB-MW-		MW-						VERA-	MW-	MW
name	112	101	D1	4P	PW-11	008	PW-16	MW-35	587-04	583-05	DM-27	01	109	021
1 Isopentane				3.8	4.2		3.3	2.2		6.8				
2 <=nC5			55.2	3.9	4.6		3.5	2.2		8.2				2.
3 >nC5<=nC6							4.9	3.1	3.3	12				
4 >nC6<=nC7					4		5.5	3.6	0.0	18				2.
5 Benzene	5.2		4.2		13		5.4	3.1		3.5				
6 2-Methylhexane								3.9						
7 2,3-Dimethylpentane								2.5						
8 3-Methylhexane								4.1						
9 Isooctane							4.3	2						2.
n-Heptane							5.6	4		8.5	ll			
11 Methylcyclohexane	8.1						5.2			15				2.0
12 >nC7<=nC8		1						23	5				2.1	8.
13 2,3,4-Trimethylpentane								2						4.
14 Toluene					4.3		1.1							
15 n-Octane									3.1	11				6.
16 >nC8<=nC9		1.7		6.2	5.1			5.7	7.3				2.1	8
17 Ethylbenzene							4	3						
18 p&m-Xylene		1.3			5.5		4.8	2.6						
19 o-Xylene		1.8			5.3		4.1	1.1						
20 >nC9<=nC10		3.2	1	1	6.2				8.8				2.8	
1,2,4-Trimethylbenzene			-25	î l	5.6		5.6	3.6	5.1	7.7			3.1	
22 >nC10<=nC11		7.1			5.8		6.2	5.6	1	90			4.4	1
23 >nC11<=nC12		11	95					8	1	-39			5.9	
24 >nC12<=nC13		19		4.2				9	43				7.5	21
25 >nC13<=nC14		11		7.2	11		17	16	86	inf.			6.8	32
26 >nC14<=nC15	7.9	 ''	5.4		13		11	17	127	409	1		11	58
27 Farnesane	7.5		3.4		13			11	121	403				30
27 Famesane 28 >nC15<=nC16	8		5.1		13		13	18					13	41
1	•		3.1		13		13	10					13	4
1 .	8.4		4.2		11		11	19	1	9			13	70
	0.4		4.2		11		11	19	4	9			13	
Pristane	14	3.4	3.7		40		12	23		11			12	33
32 >nC17<=nC18		3.4	3.7		10		12	23		11			12	33
Phytane		0.7	2.5		45		40	20		0.5			45	20
34 >nC18<=nC19		2.7	3.5	7.4	15 136		-222	26	20.4	8.5			15	38
35 >nC19<=nC20		2.2	3.3	7.4	136		-222	43	394	40			15	68
36 >nC20<=nC21	23	2	3.1	8.1				-28		16			15	48
37 >nC21<=nC22	61	2	3.2	21.3	11		12		-353	19			20	60
38 >nC22<=nC23	68	1.7	2.6	-19.8	16		18	ļ.		-462			19	64
39 >nC23<=nC24	-49	1.7	2.6	-4.7	131		72	!	1.5	-80			29	24
40 >nC24<=nC25	-6.7	1.5	2.7	-3.7	-61		45			-20			213	-2
41 >nC25		1.6	2.1							-3.6			-6	-5.
Total	12	5.3	11	5	7.1	n/a	7.2	4.8	18	35	n/a	n/a	9.2	1:

Relative Depletion – Total & Constituents



[CA]

- USA
- Former refinery
- Varied gasoline and diesel —range LNAPL
- delineated LNAPL
- Adjacent SVE
- 7 wells, 3 to 13 samples, over 2 to 14 years
- Varied composition in different wells

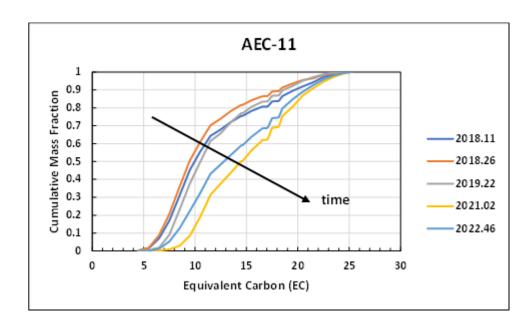
Case Example

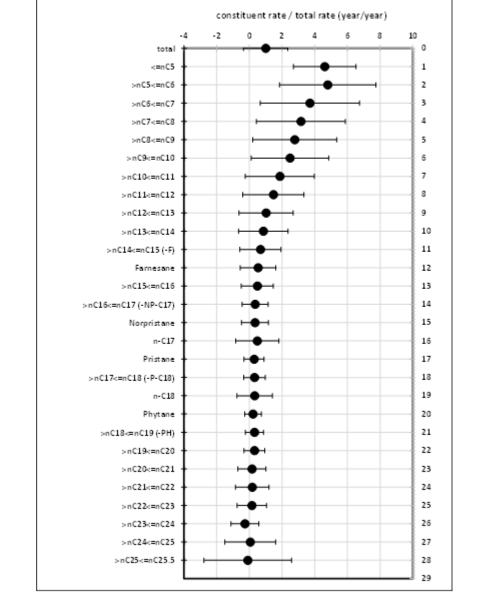
[BK]

Results

Average: 2.4 year half-life

Outlier: 20 year half-life (submerged NAPL)





Realative Constituent Depletion Rates

Summary:

Potential Candidate Sites

- Anywhere NAPL can be sampled over time (monitoring or extraction wells).
- Single spill or complex sites
- Also applicable for petroleum in soils, and/or oil spills to surface water
- Analytical data needs QA / QC need: guidance

Results

- Total bulk NAPL depletion (% per year, half-life)
- Constituent-specific depletion (any constituent measured in the NAPL)
 - Anything that can be analyzed and quantified (not just volatile or soluble chemicals)
- With Confidence Limits; Method is biased conservative if markers deplete calculator

Possible Applicability

- Comparisons to and evaluation of active remediation effectiveness (and why)
- Trajectory to depletion (risk); correlate composition change to viscosity, surface tension, mobility
- General trends across portfolios of similar sites

References

- ASTM E3361 22: Standard Guide for Estimating Natural Attenuation Rates for Non-Aqueous Phase Liquids in the Subsurface, ASTM Intl, West Conshohocken, PA, USA.
- Baedecker, M.J., R.P. Eganhouse, H. Qi, I.M. Cozzarelli, J.J. Trost, and B.A. Bekins. 2018. Weathering of oil in a surficial aquifer. *Groundwater* 56, no. 5: 797–809. https://doi.org/10.1111/gwat.12619
- DeVaull, G. E., et al., Petroleum NAPL Depletion Estimates and Selection of Marker Constituents from Compositional Analysis, *Groundwater Monitoring* and Remediation, 40, 4, 2020, 44-53. https://doi.org/10.1111/gwmr.12410
- Douglas et al.. Environmental Stability of Selected Petroleum Hydrocarbon Source and Weathering Ratios, Environmental Science & Technology 1996, 30, 7, 2332-2339. DOI: 10.1021/es950751e
- Lundy, D.A., 2014. An investigation of the relationship between lateral spreading and mass depletion of an LNAPL body in contact with groundwater at the Bemidji, MN Crude Oil Release Site. PhD thesis, Department of Geology, University of Georgia, Athens, Georgia
- Oudot, J., Rates of microbial degradation of petroleum components as determined by computerized capillary gas chromatography and computerized mass spectrometry, *Marine Environmental Research*, 13, 4, 1984, 277-302.
- Smith, JWN, Davis, GB, DeVaull, GE, Garg, S, Newell, CJ, Rivett, MO. Natural Source Zone Depletion (NSZD): From process understanding to effective implementation at LNAPL-impacted sites. *Quarterly Journal of Engineering Geology and Hydrogeology.* 55, 4, November 2022. https://doi.org/10.1144/gjegh2021-166
- Statham, T.M., Sumner, R., Hill, A.F.M., Smith, J.W.N.. Transition from active remediation to natural source zone depletion (NSZD) at a LNAPL-impacted site, supported by sustainable remediation appraisal. *Quarterly Journal of Engineering Geology and Hydrogeology*. 56, 3, August 2023.

