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Development of Methods, Tools and Models for Assessment of Natural Source Zone Depletion at Petroleum Hydrocarbon Impacted Sites

Dr. Ian Hers, Golder Associates Ltd., Vancouver, BC, Canada

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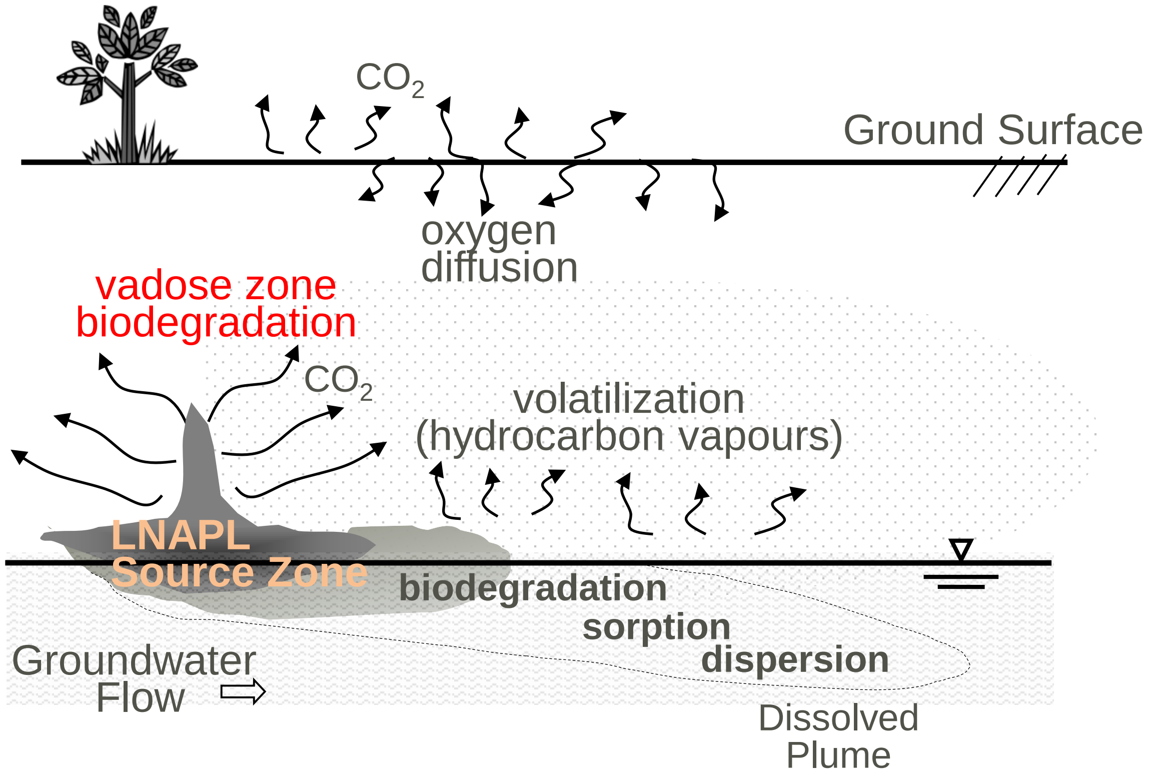
Outline

1. Natural Source Zone Depletion (NSZD) conceptual model
2. Value of NSZD estimates
3. Estimation of NSZD using CO_2 efflux methods
4. Incorporation of NSZD in remedy transition framework
5. Conclusions

Natural Source Zone Depletion Conceptual Model

KEY QUESTIONS



- What are the key processes
- What is the NSZD rate?
- What are the effects of NSZD on groundwater and vapour plumes?

Mass Depletion Processes

KEY PROCESSES

- BIODEGRADATION
- DISSOLUTION
- VOLATILIZATION

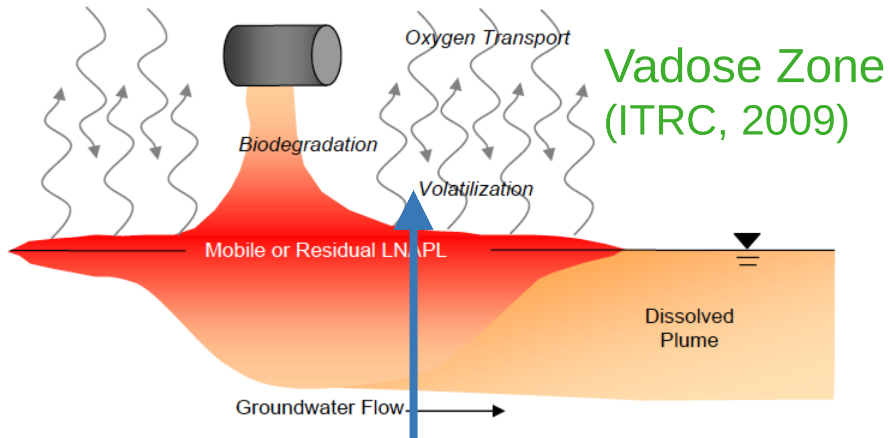


Figure 2-2. Vapor transport–related NSZD processes.

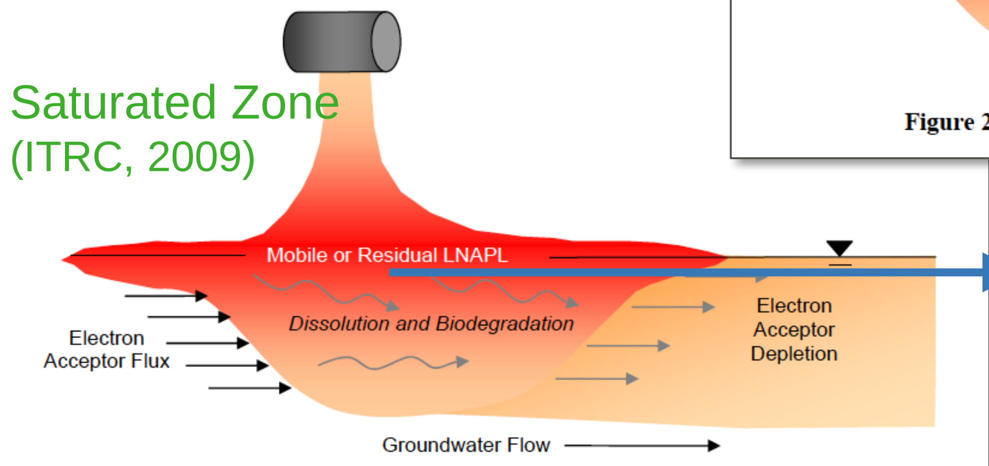


Figure 2-1. Groundwater transport–related NSZD processes.

Dissolved Phase Gradients

Vapour Phase Gradients

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

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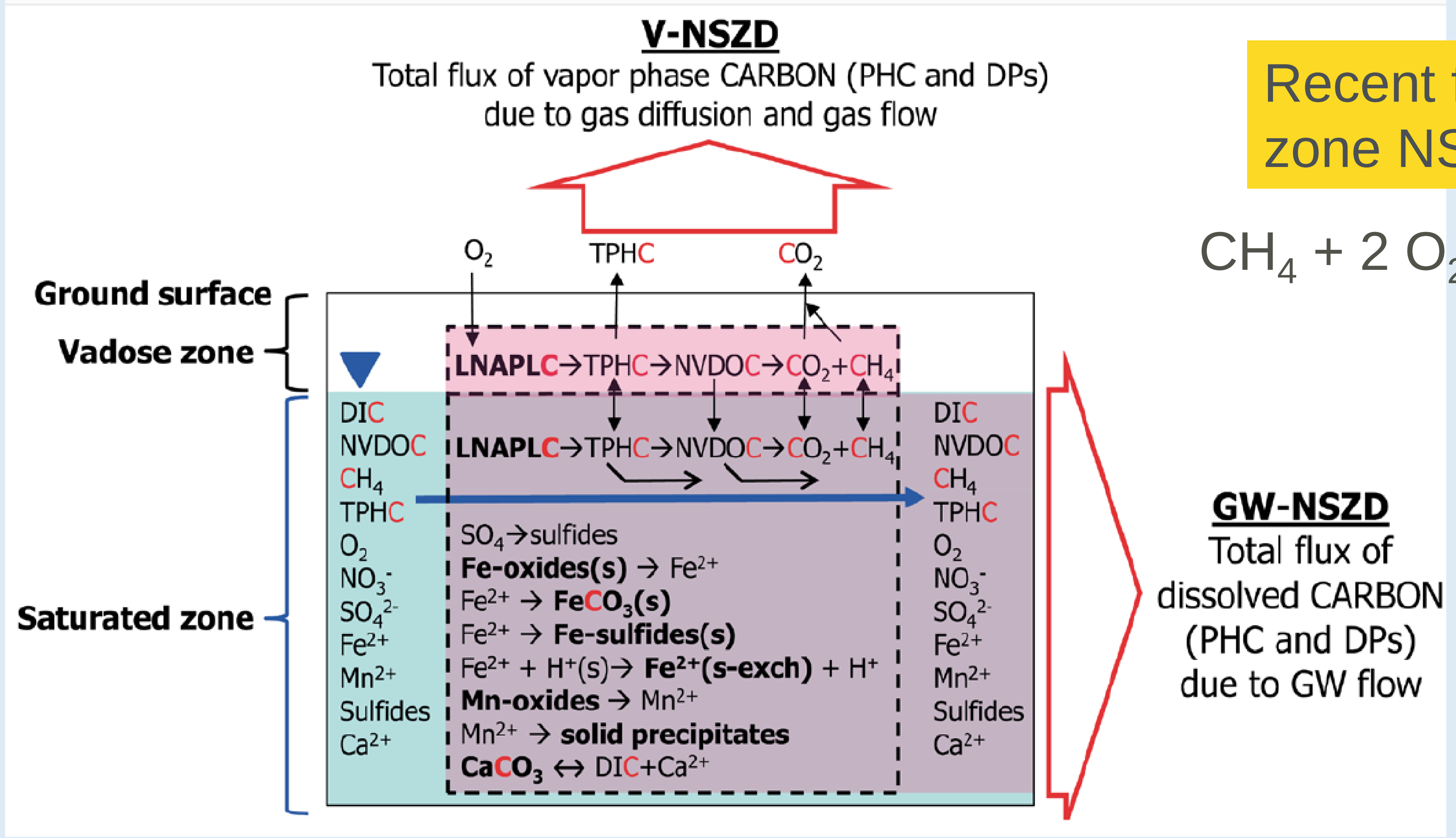
Photograph from ITRC LNAPL Guidance (2018)

Quantification of NSZD Processes

MACKAY ET AL. 2018

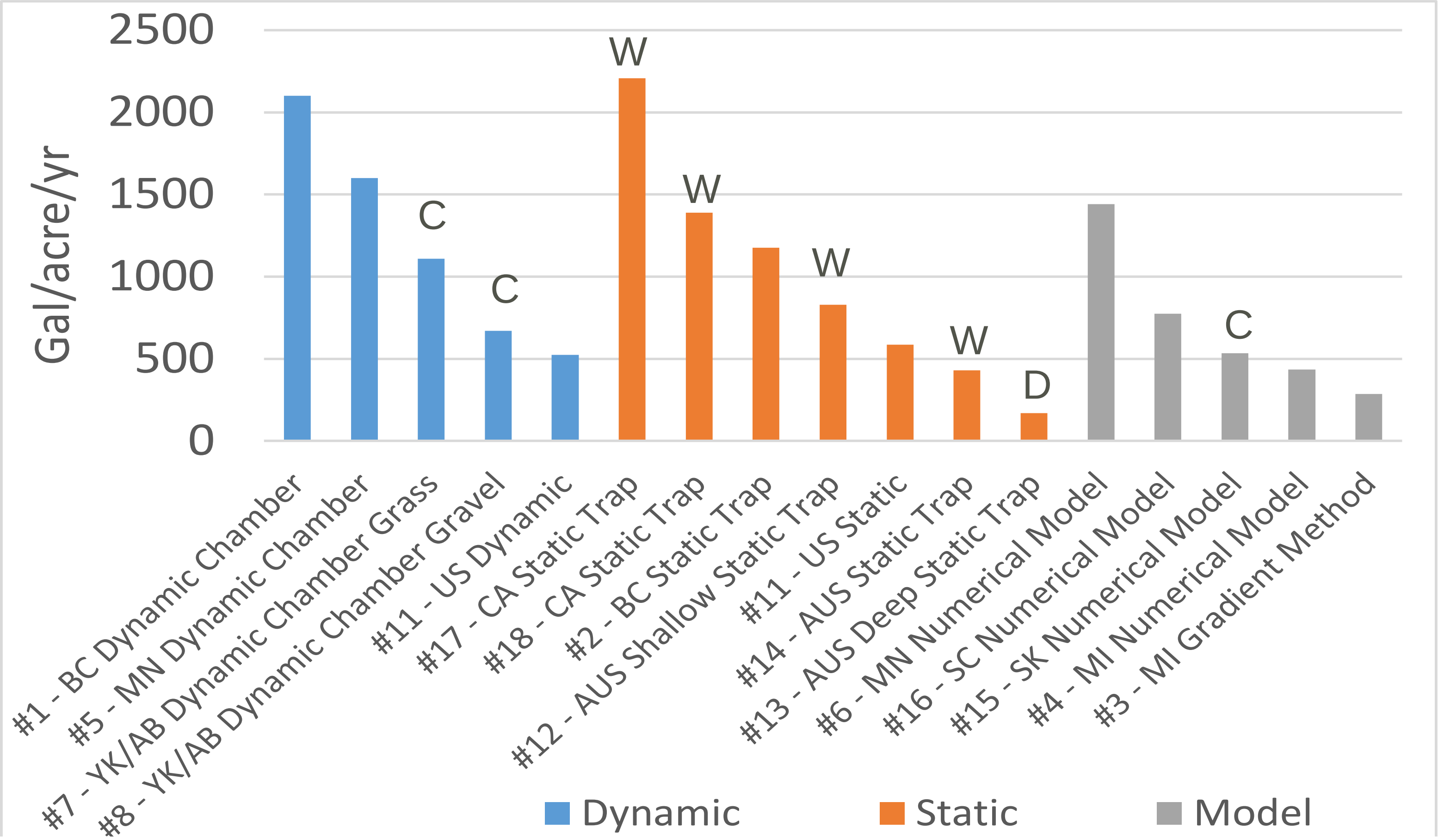


Recent focus is unsaturated zone NSZD rates

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_20 + heat$$

Unsaturated Zone Biodegradation Rates

LITERATURE REVIEW – SHELL/CSAP/GOLDER TOOLKIT 2 (GOLDER, 2016)



Golder 2016 (this study):
500 -1500 US Gal/acre/yr
320-970 L/Ha/yr

Garg et al. 2017: 700 - 2,800 US Gal/acre/yr (25-75th percentile)
452 – 1,800 L/Ha/yr

Gap is long term NSZD rates; suggested to be quasi first-order rate see Garg et al. 2017)

C = cold climate W = warm climate D = deep source (confined)

Value of NSZD

TO EVALUATE LNAPL STABILITY

- NSZD rate can be used in evaluation of LNAPL body stability
- Compare mass flux from the LNAPL seepage rate to the NSZD rate
- LNAPL seepage rate can be obtained from LNAPL transmissivity and thickness

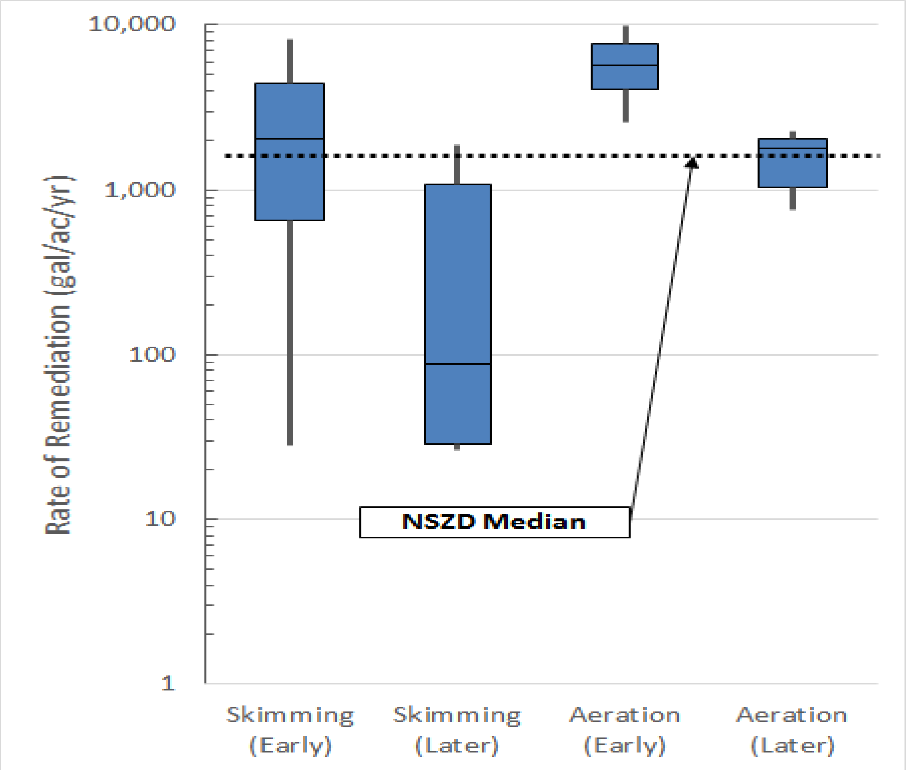
Wedgemount Glacier near Whistler, BC

Analogy between glacier, which moves slowly but looses mass because of melting and evaporation, and LNAPL body (adapted from ITRC IBT 2018)

Value of NSZD

AS TECHNOLOGY & METRIC FOR DECISION-MAKING

- NSZD rates are often similar to or greater than later-stage active LNAPL removal rates for technologies such as LNAPL pumping, SVE, and MPE
- Consequently, NSZD rate comparisons can inform evaluation of practicality of remediation and decisions for technology transition as more sustainable approach
- NSZD rate can be benchmark to enhanced depletion technologies:
  - Soil vapour extraction/bioventing
  - Enhanced bioremediation
  - Thermal technologies

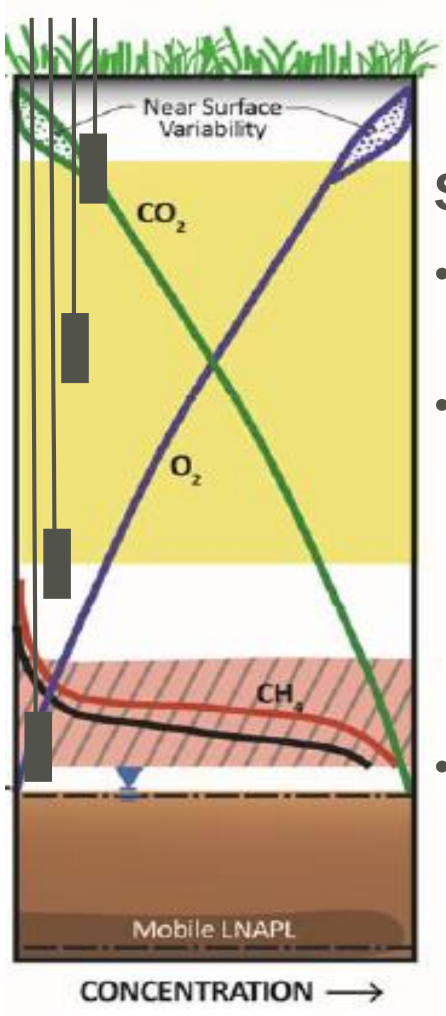


(Median NSZD rate from Garg et al., 2017. System data modified from Palaia, T. 2016. Natural source zone depletion rate assessment. Applied NAPL Science Review 6.)

From ITRC IBT (2018)

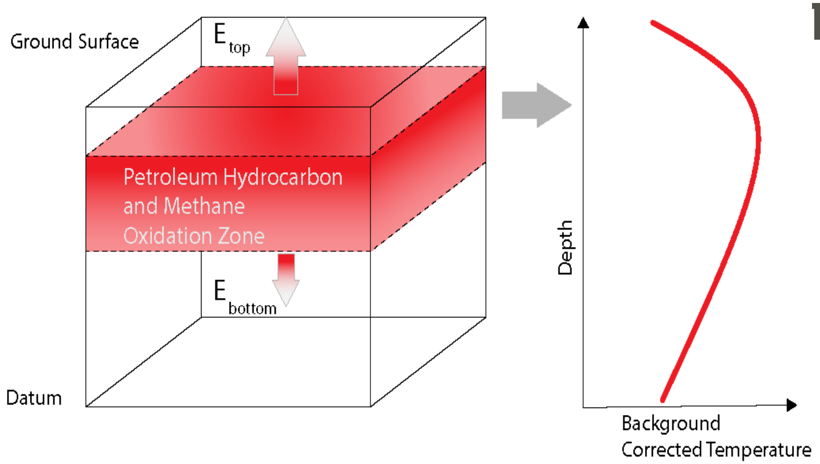
NSZD Estimation Methods

UNSATURATED ZONE METHODS



Soil Gas Gradient

- Based on vertical soil gas profiles
- Can be obtained from oxygen or VOC gradient and consideration of biodegradation stoichiometry
- Requires accurate estimate of the effective diffusion coefficient



Carbon dioxide (CO_2) efflux

- Requires estimate of the soil effective diffusion coefficient
- Requires correction for natural soil respiration
- Recommend radiocarbon (C14) method to distinguish natural & fossil fuel respiration

Temperature method

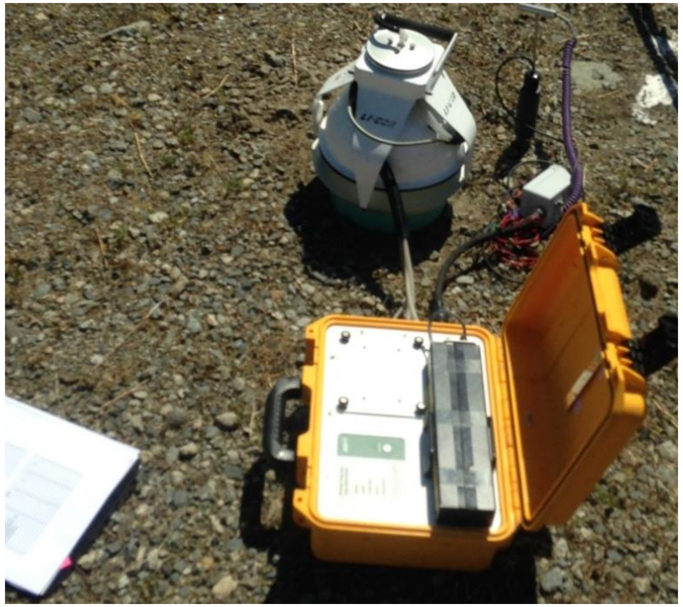
- Heat generation from aerobic biodegradation
- Measure the thermal gradient
- Requires measurement of thermal conductivity

Soil gas gradient and temperature method graphics from API NSZD Guidance (2017)

CO_2 Efflux Measurement Methods

NON-INTRUSIVE METHODS

Dynamic Closed Chamber (DCC)



LI-COR Instrument: LI-8100A
Automated Infrared Detector
20 cm dia chamber
Short-term measurement (few minutes)

Field Cost ~ $50-$100/location *

EoSense Forced Diffusion Sensors

EoSense Forced Diffusion Sensor
Infrared Detector, 10 cm dia. chamber
continuous measurements, low power (solar)

Field Cost = variable depending on study duration

E-Flux Low Profile Static Trap Units

E-Flux Sorbent trap
Sorbent material made from calcium and sodium hydroxides
Composite (1-2 week) measurement

Field Cost ~ $1,000 CDN/location

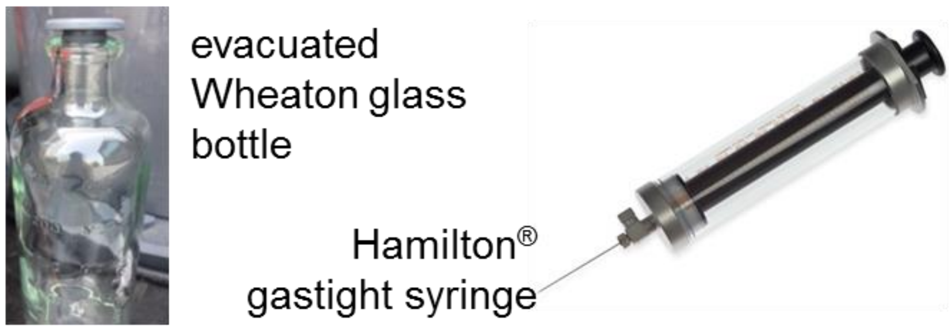
* Does not include radiocarbon analyses

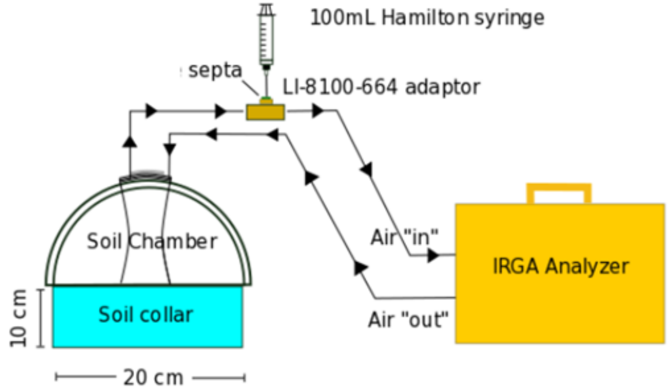
CO_2 Efflux Correction for Natural Organic Matter

RADIOCARBON CORRECTION METHOD

- Analysis of radiocarbon (^{14}C), a carbon isotope generated by cosmic rays in the atmosphere with half-life of ~ 5,700 yrs, is used to differentiate between CO_2 from fossil fuel (contaminant soil respiration, CSR) and natural sources (natural soil respiration, NSR)
- Fraction of ^{14}C content of carbon ($F^{14}C$) is measured by accelerator mass spectrometry (AMS)
- Assumes $F^{14}C$ associated with fossil fuels (CSR) is zero
- Fraction CSR (F_{CSR}) estimated from 2-component mass balance; Sample A: Ambient air; Sample B: Mixture air and soil gas

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





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

Sihota and Mayer (2012); Jourabchi et al. (2017); Wozney (2017)

CO_2 Efflux Research – Temporal Variability Examples

Site	Time	NSZD rate (as CO_2 efflux $\mu mol m^{-2} s^{-1}$)
1. Former Refinery	Fall	1.24 ± 0.07
Eichert et al. 2017	Spring	0.47 ± 0.03
	Winter	0.14 ± 0.01
	Summer	1.2 ± 0.02
	Seasonal Avg	0.68 ± 0.01
2. Former Refinery	Summer	2.0+-0.04
Jourabchi et al. 2017	Fall (moist)	0.44
Hers et al. 2019	Fall (very wet*)	0.01
	Winter	0.13
3. Bemidj Site (Pipeline)	Spring	0.5
Sihota et al. 2018	Summer	1.4
	Fall	1.7
	Winter	0.8

* Testing after 211 cm rain in two weeks

Seasonal efflux variability

- Site 1: ~ 1 OM
- Site 2: > 2 OM (<3-1,100 gal/acre/yr!)
- Site 3: ~ 3X

- However, at Site 2 if avoid extreme rainfall events may be closer to 1 OM

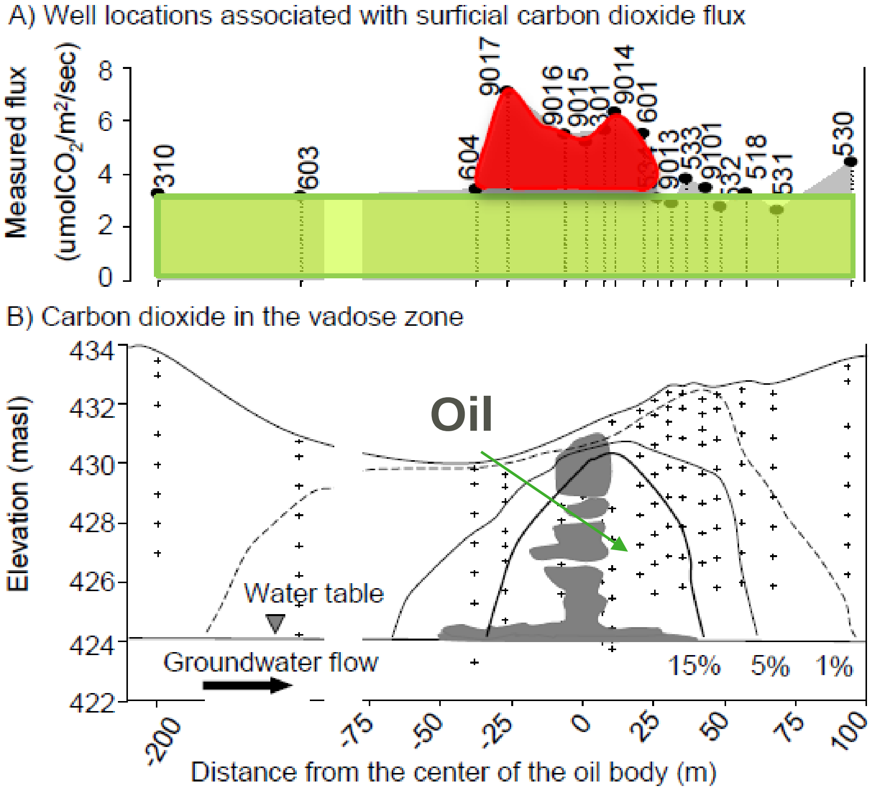
Diurnal efflux variability

- Site 2: Up to 2X

CO_2 Efflux – Spatial Variability Examples

Bemidji Site

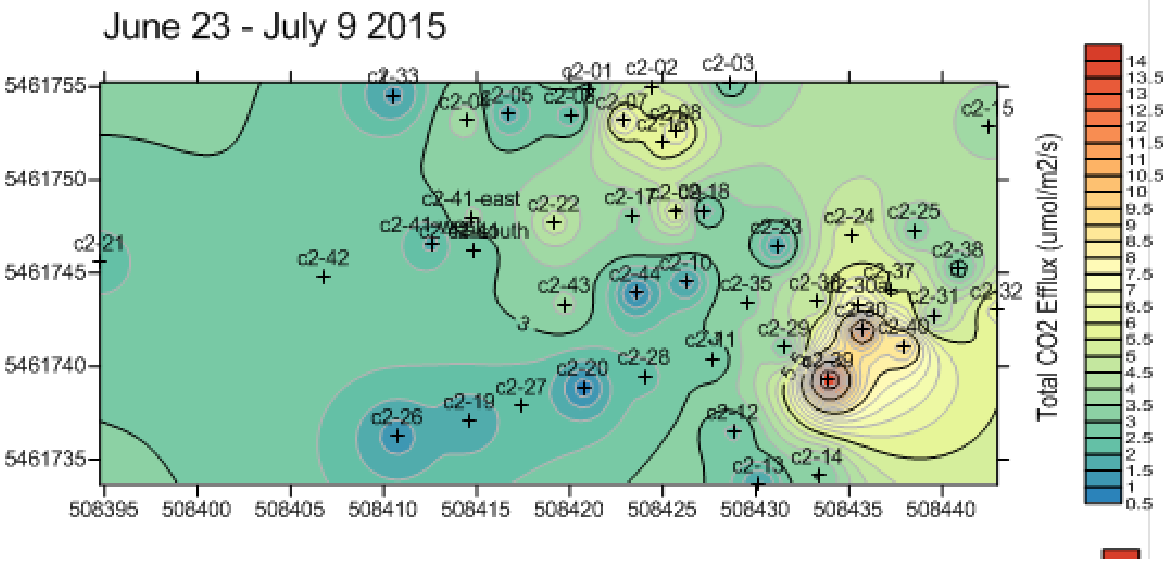
Sihota et al (2011)



- flux attributable to NSZD is 2.6 µmol m^{-2}s^{-1} ~1,400 gal-diesel acre^{-1} yr^{-1}
- agreement with previous estimates:
  Revesz et al. (1995), Chaplin et al. (2002), Molins et al. (2010)

Former Refinery Site

Jourabchi et al (2017)



Dry & warm summer conditions

Case Study

FORMER REFINERY

- Conducting R&D program in one area of site (~ 50 m by 25 m LNAPL body)
  - Petroleum hydrocarbon: weathered middle distillate with lesser amounts of lube oil
  - Silty sand and silt (1.8 - 4.0 m thick) underlain by coarse sand
  - Depth to corrected water table: 2.7 - 4.7 m
  - Soil contamination from 0.5 to 4.7 m depth
- Research program
  - Estimation of NSZD by three methods
    - **CO_2 efflux measurements (DCC, Forced Diffusion,** Static Trap)
    - Temperature monitoring
    - Soil gas oxygen gradient method
  - Enhanced bioremediation trials in-progress (solarization to be followed by bioventing)

Case Study - CO_2 Efflux by DCC Method – Seasonal & Spatial Data

HIGH SEASONAL AND SPATIAL VARIABILITY

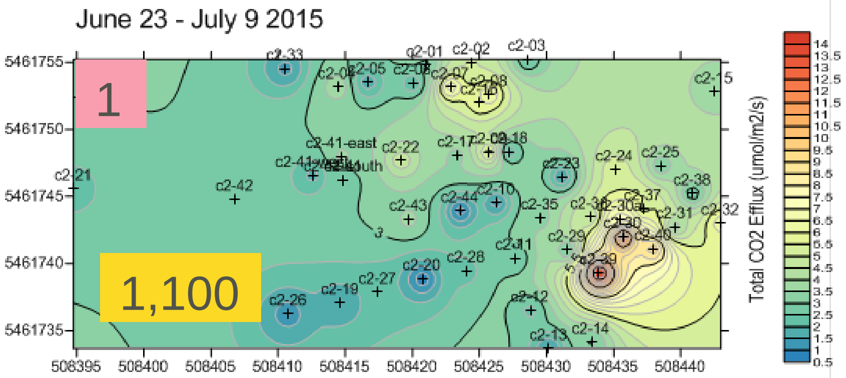
20-30 measurements over 50 m by 22 m area (Rounds 1 & 2)

Very large seasonal variability in CO_2 efflux measurements

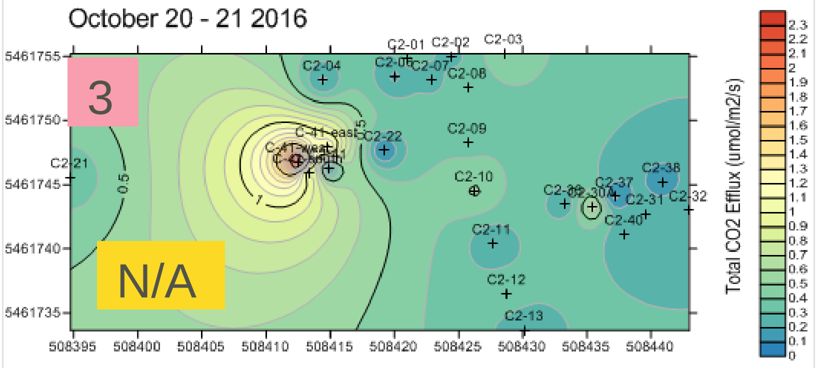
The lowest values represent an extreme short term, wet condition

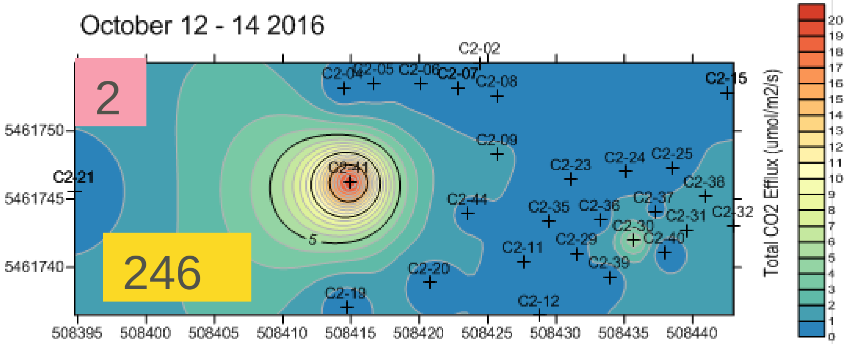
Soil moisture critical parameter

Dry & warm summer conditions

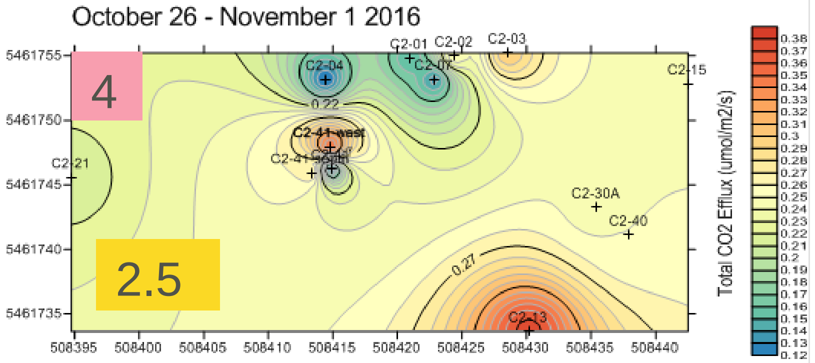


Very wet & cool fall conditions





Moist & cool fall conditions



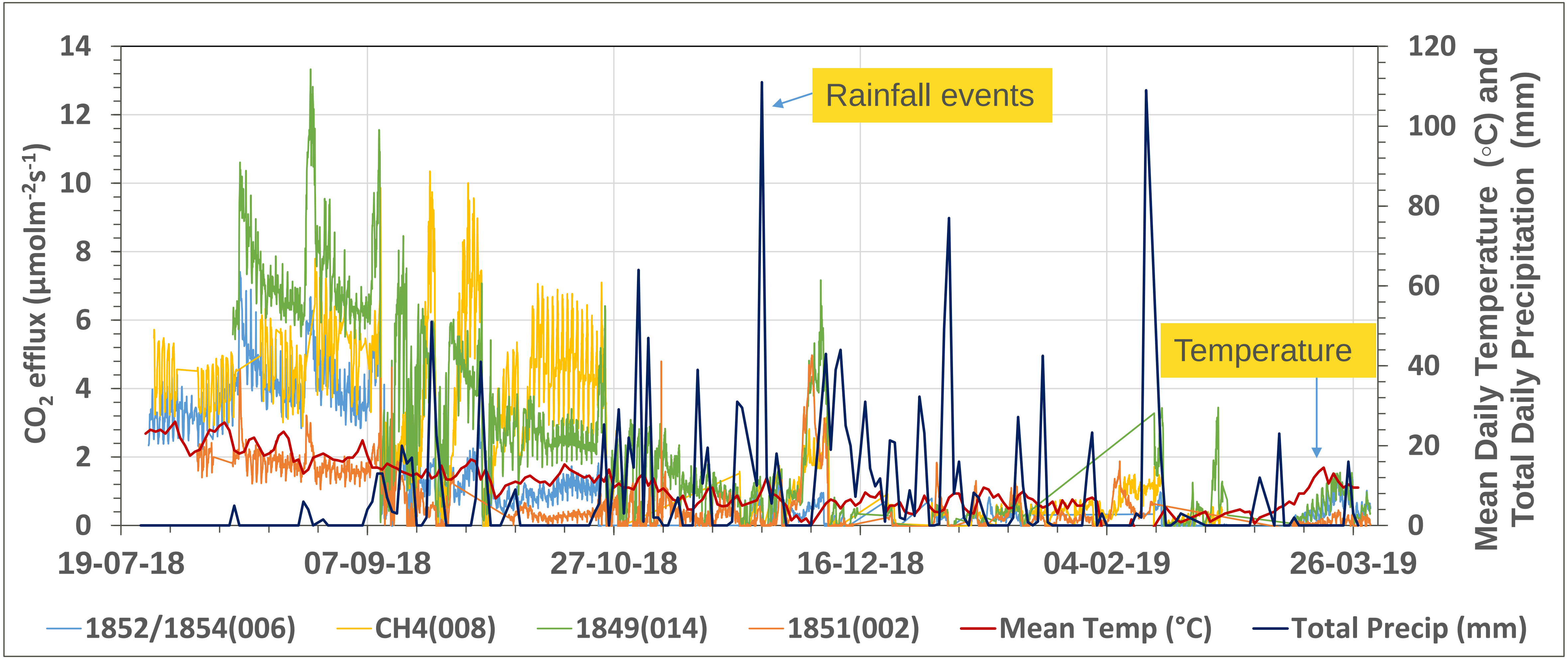
Very wet & cool fall conditions

1,100 Average NSZD rate (gal/acre/yr)

Note different scales are used for each plot.

Case Study - Continuous CO_2 Efflux (Eosense Technology)

PRELIMINARY DATA JULY 24 2018 TO MARCH 29 2019 Hers et al. 2019

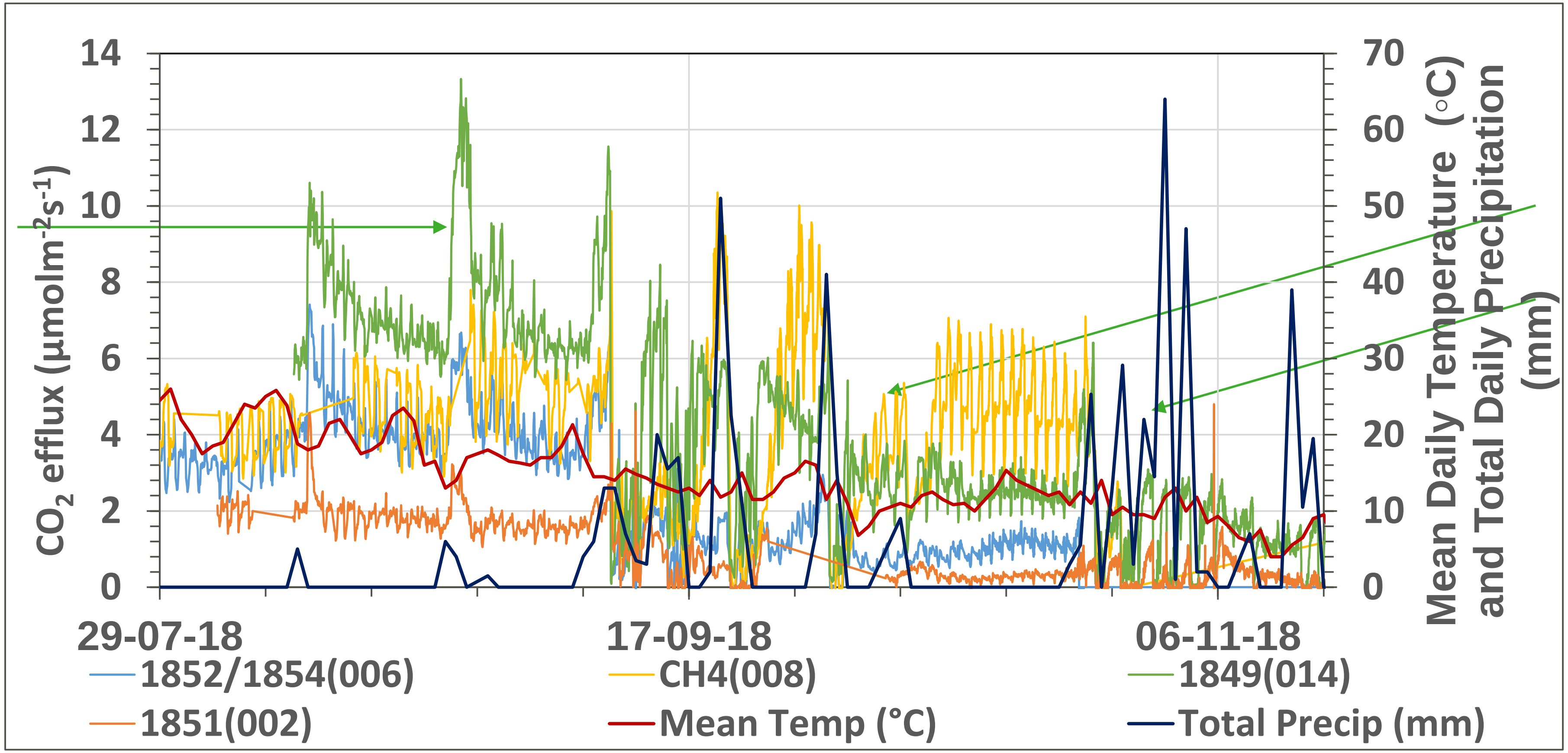


Continuous monitoring effectively characterizes seasonal variability in CO_2 efflux

Preliminary Results of Continuous CO_2 Monitoring

PRELIMINARY DATA JULY 24 2018 TO NOVEMBER 18 2018 Hers et al. 2019

In summer efflux increases due to rain – could microbial activity be limited by low moisture during extended dry periods?



In fall after heavy rains efflux decreases

* Climate data obtained from Environment Canada Glenarye Station

Continuous monitoring effectively captures diurnal and rainfall-related fluctuations for developing CSM

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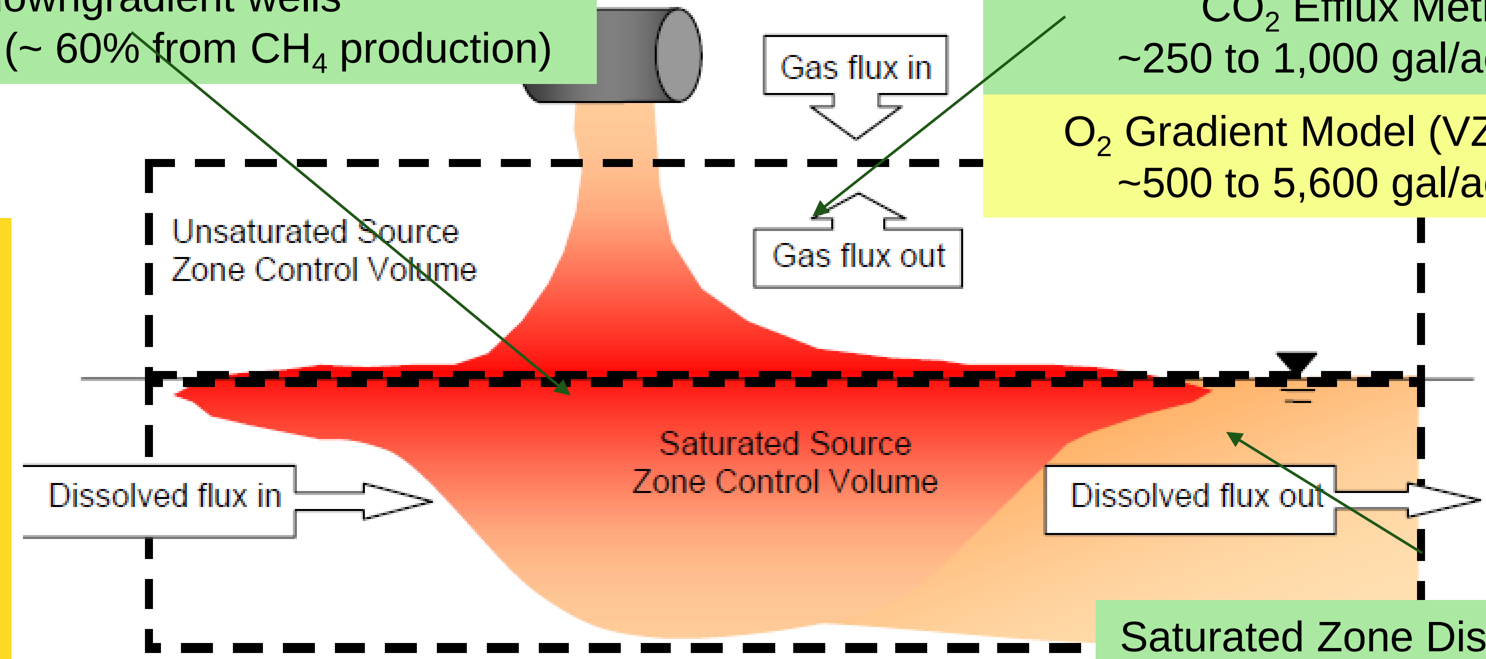
NSZD Rate Estimate Based on Control Volume Concept (ITRC, 2009)

ESTIMATE TOTAL NSZD RATES

Saturated Zone Biodegradation – Requires geochemical data from appropriately located up and downgradient wells
35 gal/acre/year (~ 60% from CH_4 production)

Vadose Zone Biodegradation Seasonal Range
CO_2 Efflux Method
~250 to 1,000 gal/acre/year

O_2 Gradient Model (VZBL model)
~500 to 5,600 gal/acre/year



Depletion rate = $f(flux_{in} - flux_{out})$

Saturated Zone Dissolution & Flow
72 gal/acre/year

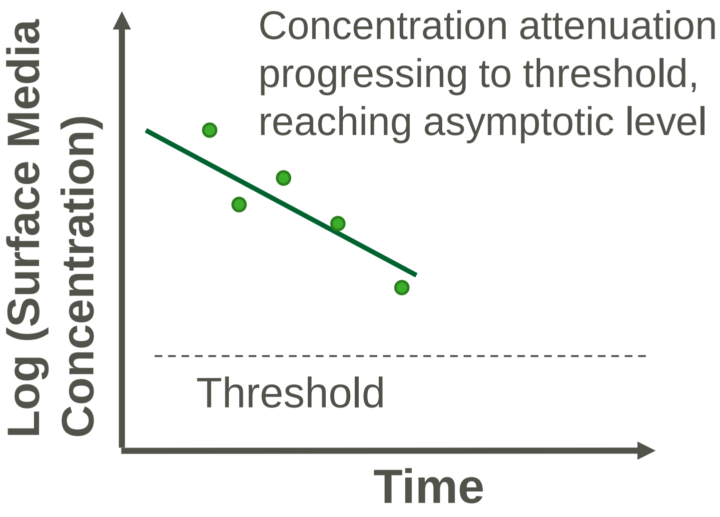
While vadose zone biodegradation rates are largest, it is important to quantify all depletion mechanisms

NSZD rates at this site supported a passive remedy approach

Remedy Transition Framework and NSZD

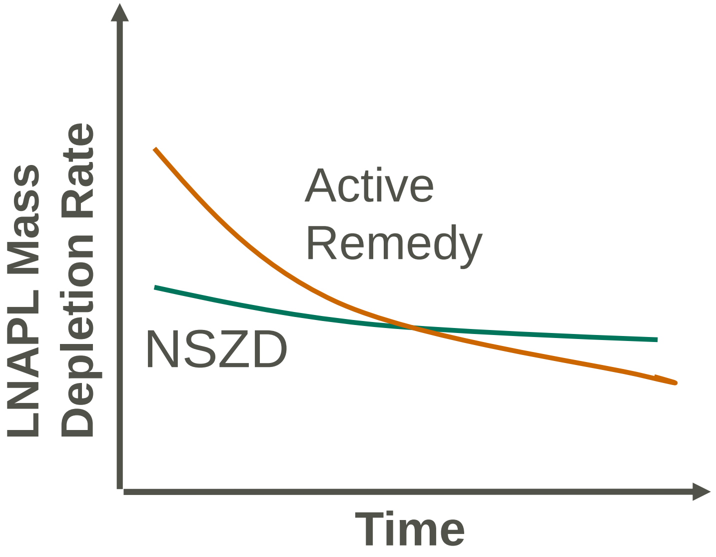
MULTIPLE LINES OF EVIDENCE BASED ON TRANSITION METRICS – SHELL PROJECT

I. Evaluate Technology Limits & Performance



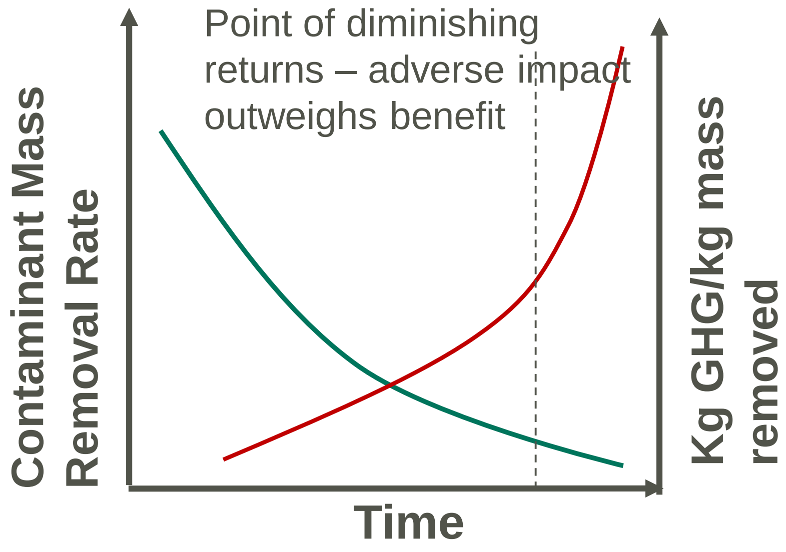
- Metric reaching asymptotic limit
- Important to conduct rebound tests

II. Compare Relative Performance of Technologies



- Active depletion rate < NSZD rate
- Important to conduct rebound tests

III. Evaluate Sustainability for Project Lifecycle



- Normalized GHG emissions or other metric increasing rapidly

Framework being developed to incorporate NSZD or Nature-based Remediation into remediation framework and remedy transition as more sustainable approach. Only select metrics are shown - there are others that should be considered

Conclusions

- Case studies indicate petroleum hydrocarbon NSZD rates can be significant and lead to long-term depletion of source zones
- New measurement technologies have been developed
- For CO_2 efflux method, important to distinguish natural from contaminant (fossil fuel) respiration
- Seasonal variability can be large and consequently seasonal testing may be important
- An emerging area of research is compositional change through NSZD (in the LNAPL and associated plumes)
- Key use of NSZD data: Baseline and subsequently measured NSZD rates can support decisions for technology transition over the project life-cycle as a more sustainable approach

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Thank You!

ihers@golder.com