Remediation Technologies Symposium 2017 (RemTech™ 2017)
October 11-13, 2017 - Fairmont Banff Springs

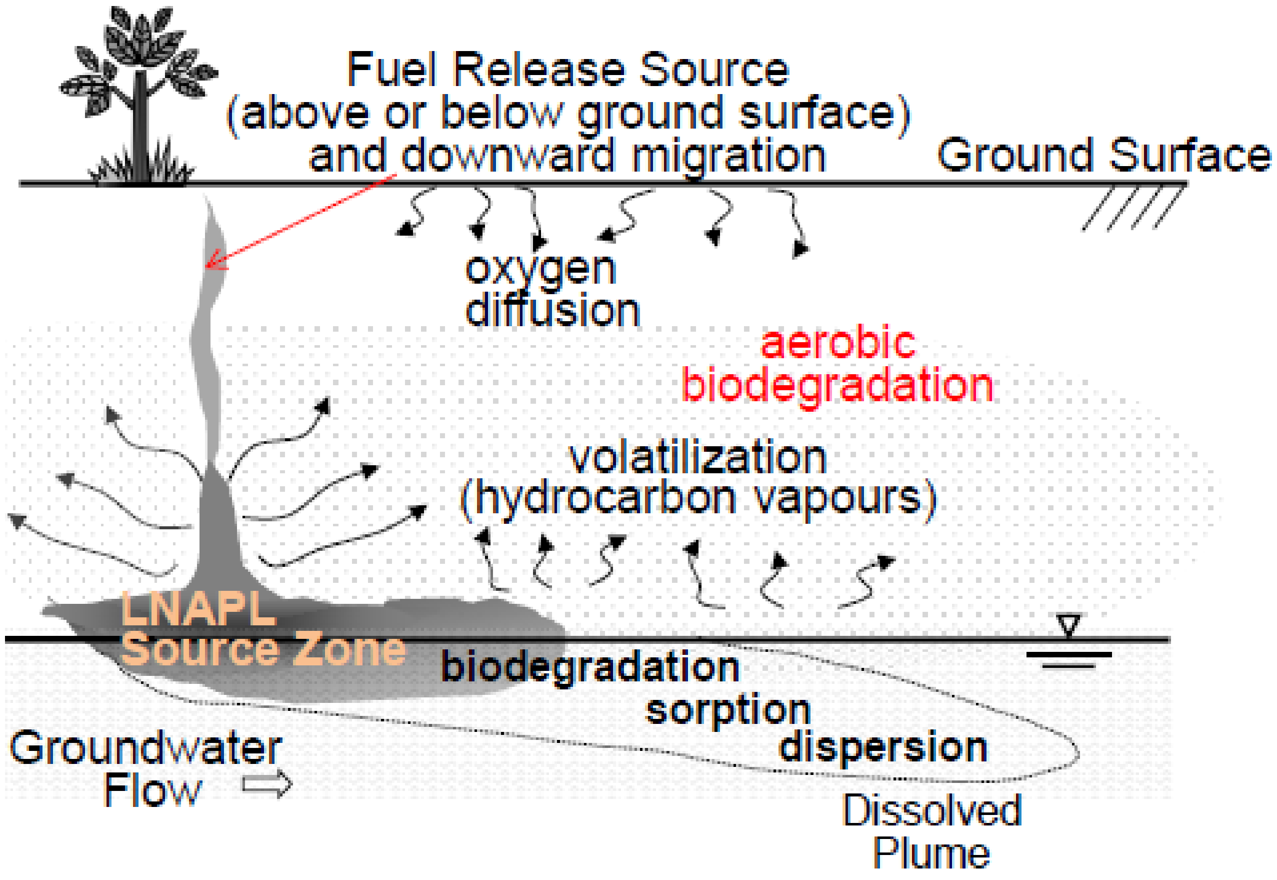
Acknowledgments:
BC Contaminated Sites Approved Professionals (CSAP) Society
Dr. Matthew Lahvis (Shell Global Solutions)
Mr. Harley Hopkins (ExxonMobil Environmental Services)

Parisa Jourabchi and Ian Hers

Evaluating Natural Source Zone Depletion at Petroleum Hydrocarbon Sites – New Toolkit of Technologies

Golder Associates

Natural Source Zone Depletion



Definition:

"NSZD is a combination of processes that reduce the mass of LNAPL in the subsurface" ITRC (2009)

Can occur through volatilization, biodegradation and dissolution

Questions:

- How long take for sources to naturally deplete (e.g., to groundwater standards)?
- How far will dissolved plume migrate?
- How can we enhance attenuation?

MNA and NSZD Toolkits

#1 CSM & Case Study Toolkit

Conceptual Site Model → Multi-Site Database Studies → BC Case Studies

#2 Monitoring and Prediction Toolkit

Methods for evaluation of natural attenuation and source depletion

Toolkits 1 & 2 (Golder, 2016)*

#3 Remediation Technology Toolkit

Screening criteria for technical feasibility & implementability and comparison to NSZD

#4 Sustainability Toolkit

Methods & roadmap for implementing green & sustainable remediation (GSR)

*Golder Associates Ltd. 2016. Toolkits for Evaluation of Monitored Natural Attenuation and Natural Source Zone Depletion. Prepared for the Society of Contaminated Sites Approved Professionals of British Columbia (CSAP) and Shell Global Solutions, July 8th, 2016. Available on CSAP Web Site.

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Plume Lengths and Stability: US Multi-Site Study of Retail Sites with Gasoline Impacts*

Summary of Plume Lengths

Parameter	Total Number of sites	Delineation criteria (µg/L)	Weighted mean on 90th and 50th percentile of plume lengths (m)
Benzene	165	5	130 / 55

Summary of Stability Condition: Concentrations

Parameter	Total Number of sites	Decreasing concentrations (%)	"Non-increasing" concentrations (%)
Benzene	905	63	92

Summary of Stability Condition: Plume lengths

Parameter	Total Number of sites	Decreasing plume lengths (%)	"Non-increasing" plume lengths (%)
Benzene	566	32	94

* From review of 13 multi-site or multi-plume studies (Connor et al., 2015)

California Multi-Site Study of Retail Gasoline Sites - Source Zone Attenuation (McHugh et al. 2014)

- Data from 4,000 sites with monitoring from 2001-2011 with >= 4 years of data
- The estimated median attenuation rate for benzene = 0.18 per year (all sites, most active remediation)
- When data analyzed separately for different technologies only slightly faster attenuation rate, effect of remediation limited

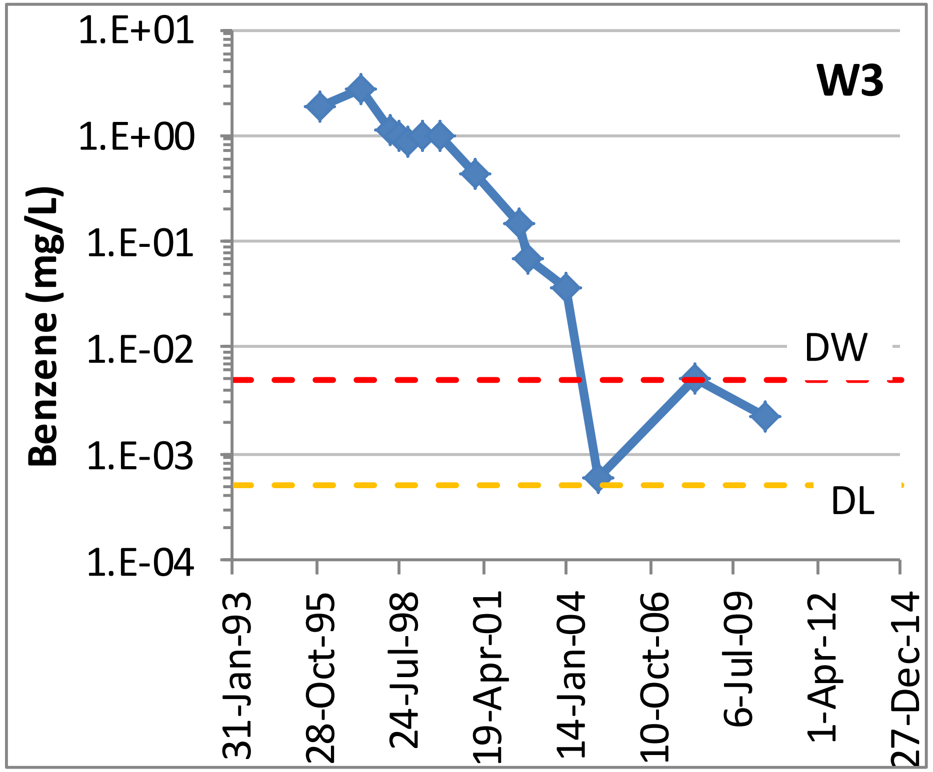
Technology	Constituent	Increase in Source Attenuation Rate (%)
SVE	benzene	28
	MTBE	11
Air Sparging	benzene	53
	MTBE	22
Chemical Oxidation	benzene	20
Pump & Treat	MTBE	17

MNA-only technology:
72 Sites
median benzene attenuation rate of 0.13/year
Timeline to attenuation to 5 µg/L from 10 mg/L: 58 years

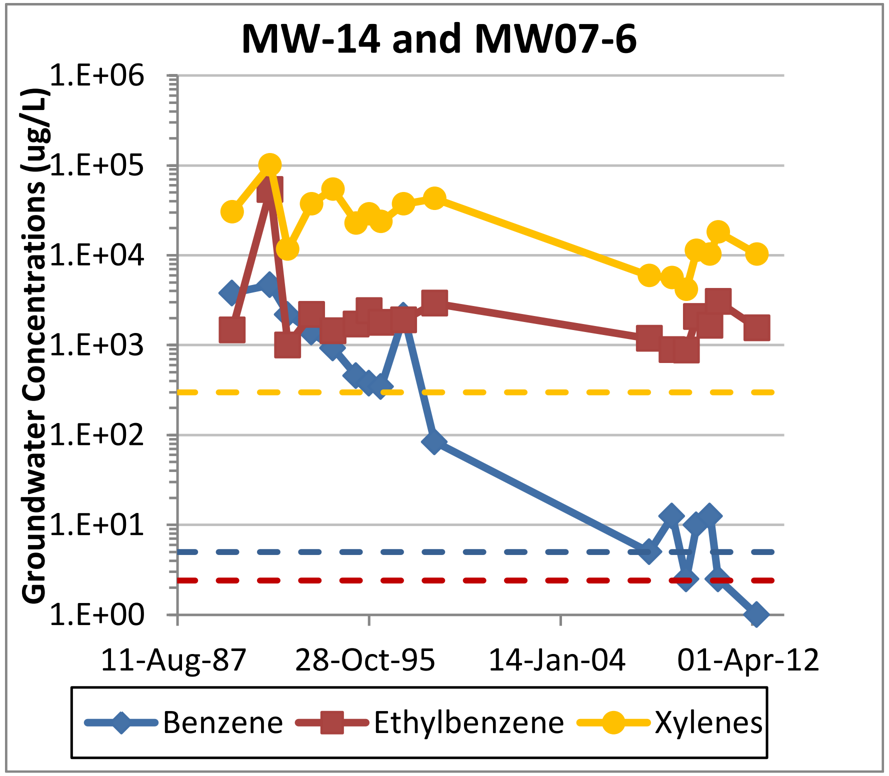
California Geotracker Database

BC Case Study Sites: Gasoline Releases (6 sites)

Site 1 – remedial excavations



Site 2 – extensive SVE



KEY POINT: **Long-term data indicates benzene decreased to < DW std. (5 µg/L) at 5 of 6 sites in 20 years, ethylbenzene did not reach std (2.4 µg/L) at any of the sites!**

Toolkit 2: Monitoring & Prediction

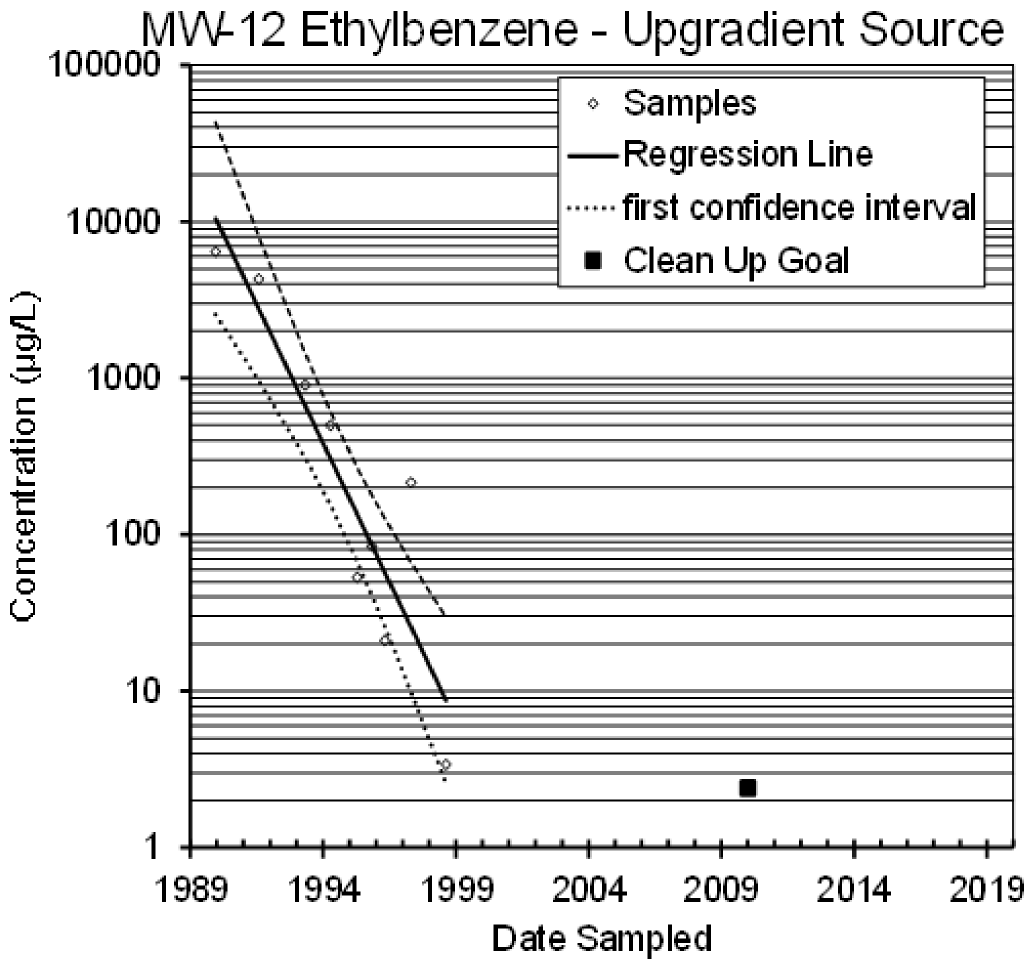
Step 1: Evaluation of Progress of MNA of Dissolved Plumes

Step 2: Use of Screening Models and Measurements for Estimation of NSZD

Step 3: Use of Multi-Process Models for Evaluation of MNA and Plume Attenuation

Step 1: Evaluation of Progress of MNA of Dissolved Plumes

- MNA basics – lines of evidence
- Statistical methods to evaluate plume behaviour
  - Parametric regression analysis (**Regression Tool Developed**)
  - Non-parametric method (Mann-Kendall)
- GWSDAT Software
- Ricker method
- New ideas for monitoring frequency



Step 2: Use of Screening Models and Measurements for Estimation of NSZD

Processes

- Biodegradation/ Volatilization in unsaturated soil
- Biodegradation in saturated zone
- Dissolution in saturated zone

Tools

- ITRC Control Volume Model (all 3 processes)
- Gradient Method (VZBL Model)
- CO_2 Efflux Method
- Temperature Method
- GSI Mass Flux Toolkit

With estimate of source mass, depletion time can be estimated

Step 2: Methods for Estimation of Unsaturated Source Zone Biodegradation

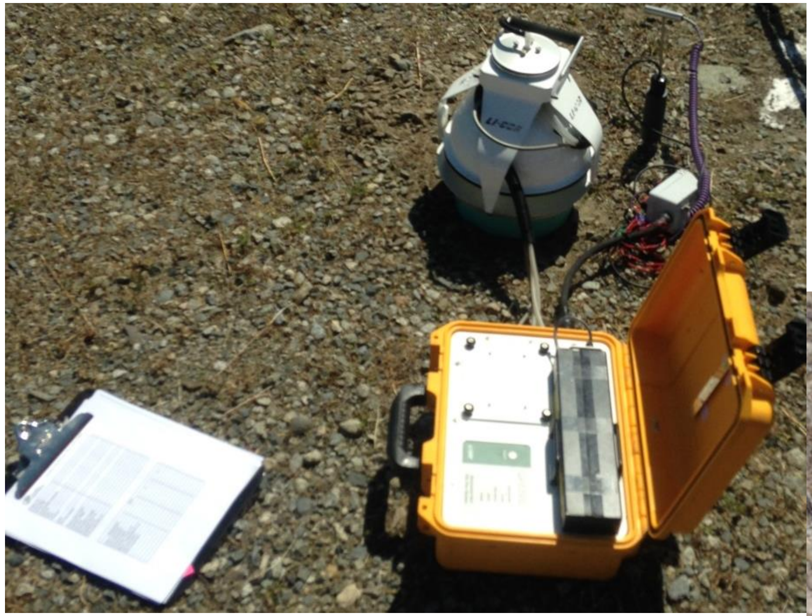
- O_2 Gradient method
  - Initial screening method for approximate estimates
  - Vadose Zone Biodegradation Loss Model[1]
- Carbon dioxide (CO_2) efflux methods
  - Dynamic closed chamber
  - Static trap
- Temperature method
  - Heat generation from aerobic biodegradation
  - Measurement of the thermal gradient

[1] Developed by Dr. Parisa Jourabchi and Dr. Ian Hers, Golder and Dr. John Wilson, Scissortail

Step 2: Comparison of Methods for Estimation of Unsaturated Zone Biodegradation

Method	Key Data Required	Advantages	Disadvantages
Gradient	$[O_2]$ diffusion gradient, porosity, moisture, water table, native organic carbon	Simple method, uses readily available data	Sensitive to moisture and water table
CO_2 Efflux	Surface CO_2 efflux, ^{14}C of CO_2, $\delta^{13}C$ of CO_2 (optional)	Direct measurement, avoids estimation of diffusive flux	Sensitive to natural soil respiration
Temperature	Temperature profile, soil thermal conductivity	Direct measurement	Thermal conductivity difficult to estimate

Step 2: CO_2 Efflux Measurement Methods

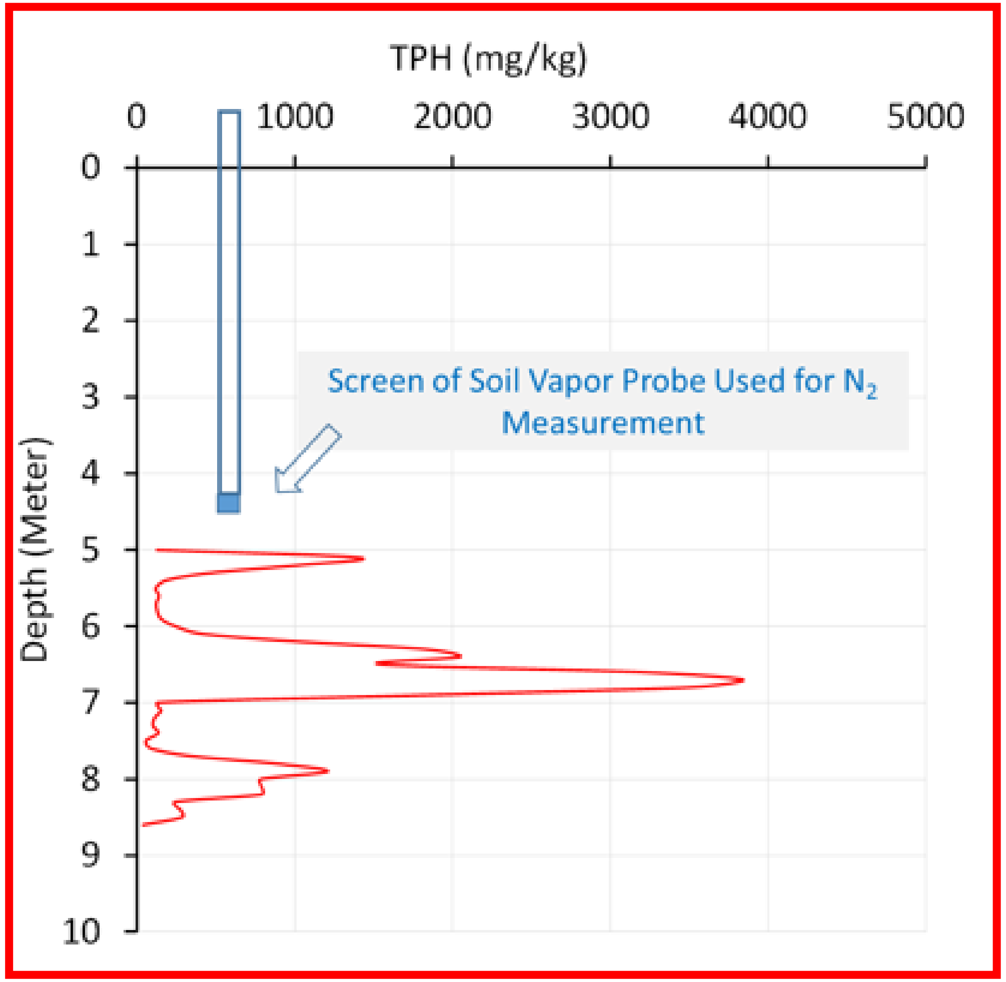


- Dynamic Closed Chamber (DCC)
- LI-COR Instrument: LI-8100A Automated Soil Gas Flux System
- Infrared Detector
- Survey System with 20 cm diameter chamber

- E-Flux Low Profile Static Trap Units
- Sorbent material made from calcium and sodium hydroxides

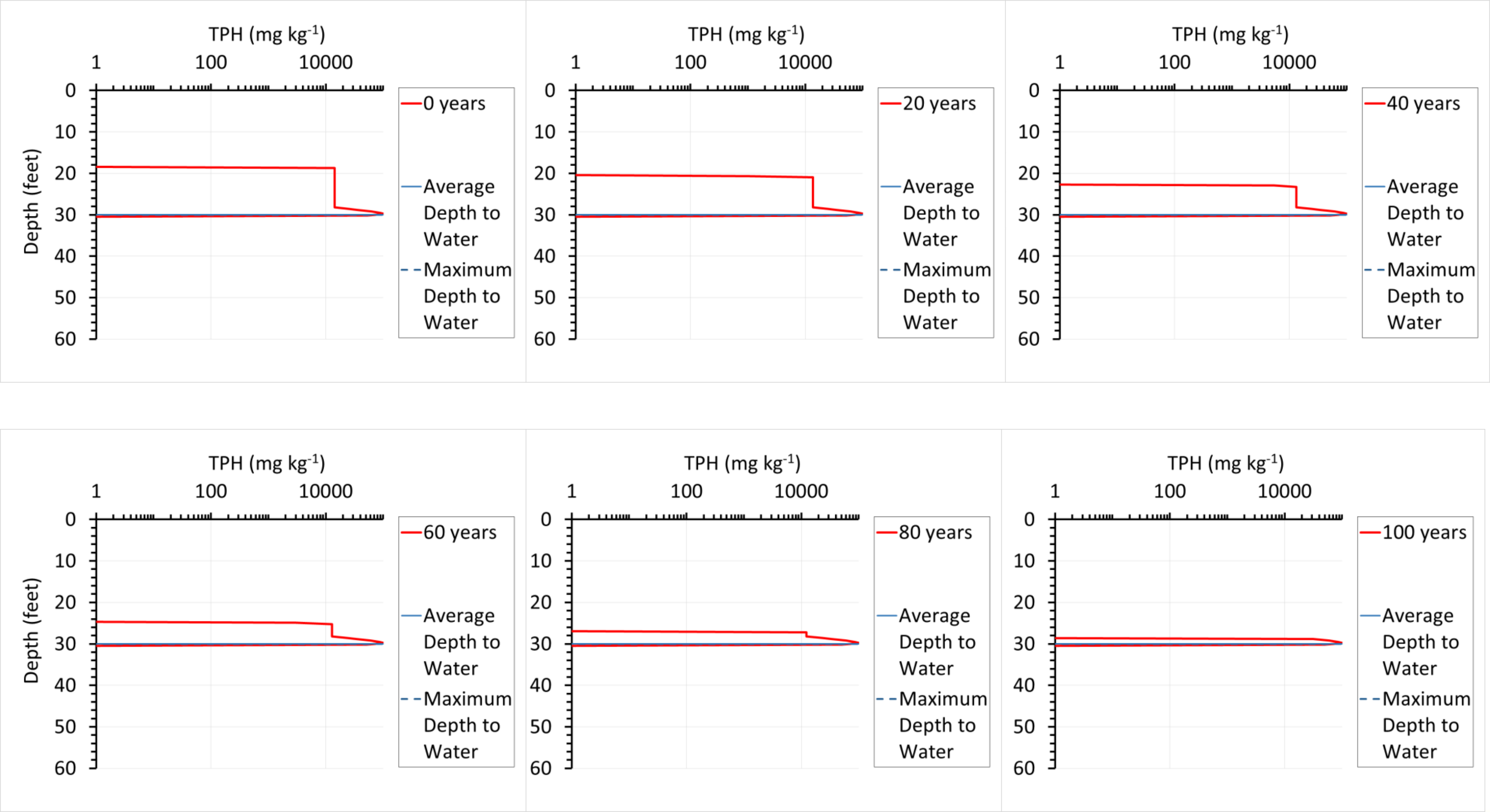
Step 2: Vadose Zone Biodegradation Loss (VZBL) Model*

- Method calculates the biodegradation rate based on:
  - O_2 flux estimated from O_2 gradient and effective O_2 diffusion coefficient
  - Methane flux from TPH degradation under methanogenic conditions based on decrease in soil gas N_2 concentration
- Simple to use model with several features to improve estimation process
  - Variable water table
  - Multi-layered soil
  - Optional baseline O_2 respiration
  - Mass balance for depletion



* Developed by Dr. Parisa Jourabchi and Dr. Ian Hers, Golder and Dr. John Wilson, Scissortail

VZBL Predicted TPH Profiles in Soil - example



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Case Study - Former Refinery and Distribution Terminal

- Field trial conducted in area of former refinery and distribution terminal
- Petroleum hydrocarbon plume: weathered middle distillate with lesser amounts of lube oil
- Silty sand and silt (1.8 to 4.0 m thick) over coarse sand
- Depth to corrected water table:

  2.7 - 4.7 m
- Apparent in-well LNAPL thickness 0.01 to 0.6 m
- Relatively high organic carbon content near ground surface

Case Study – Former Refinery and Distribution Terminal

Objectives	**Approach**
Compare CO_2 efflux methods	CO_2 efflux - DCC and Static Trap
Better understand spatial and temporal variability	DCC repeat measurements short term and seasonal monitoring
Develop new method of correction for natural soil respiration	Use of radiocarbon (^{14}C) analyses & air sample collection
Compare CO_2 efflux to Gradient method for estimation of NSZD rates	Average DCC estimates to gradient method estimates (VZBL model)
Estimate NSZD rates for study area	Combination of vadose zone estimates (CO_2 efflux) plus saturated zone processes

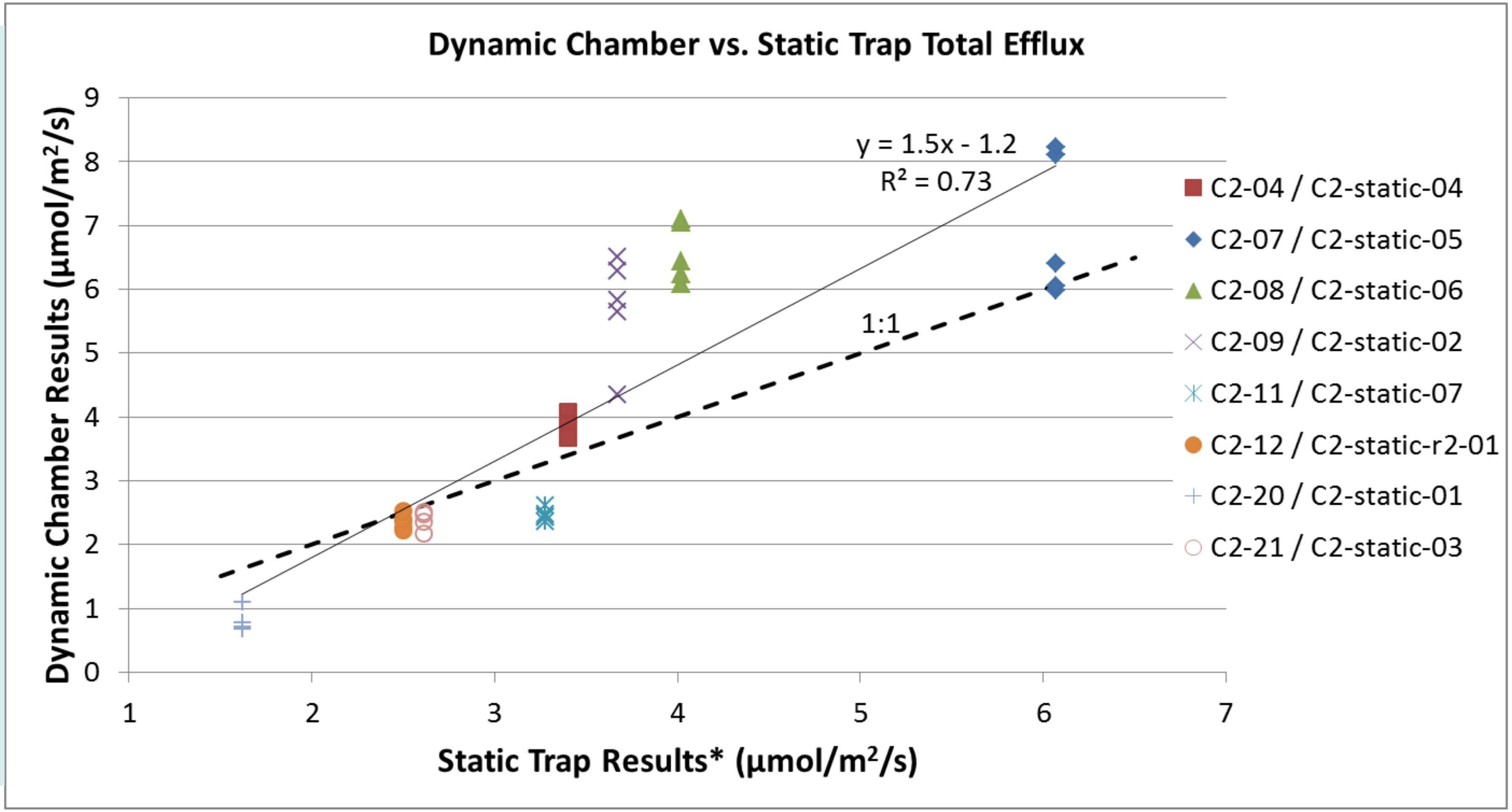
Method Comparison of DCC and Static Trap Methods

Method Comparison – Total CO_2 Efflux by DCC and Static Trap

Key Points:

- Relatively high spatial variability in DCC effluxes
- Low temporal variability in DCC effluxes (measured over several days and during one day): RPD ranged between 11 and 51 %
- Relatively good correlation between static trap and DCC total effluxes (R^2 = 0.73)

RPD = relative percent difference



*blank corrected results

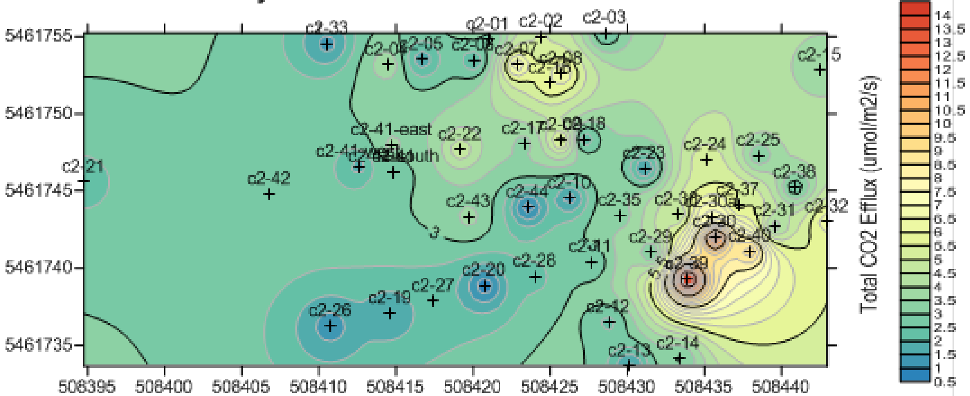
Total CO_2 Efflux by DCC Method

Key Points:

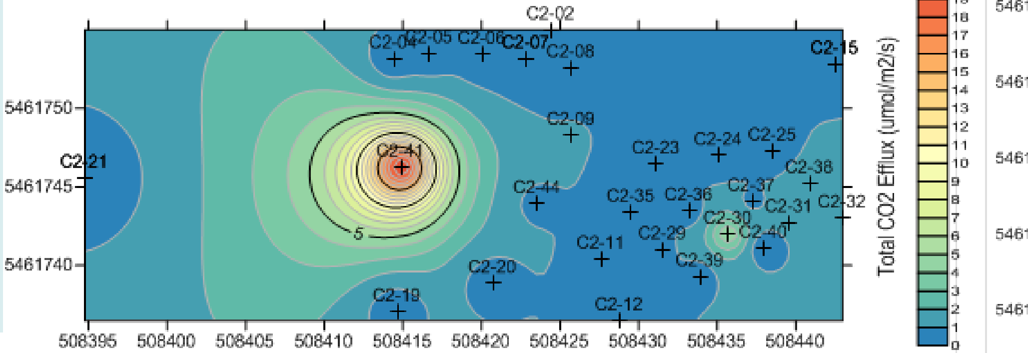
- Very large seasonal variability in CO_2 efflux measurements
- NSZD rates based on this data are considered to span the likely seasonal range, however, the lowest value represents an extreme short term condition.

Dry & warm summer conditions

June 23 - July 9 2015

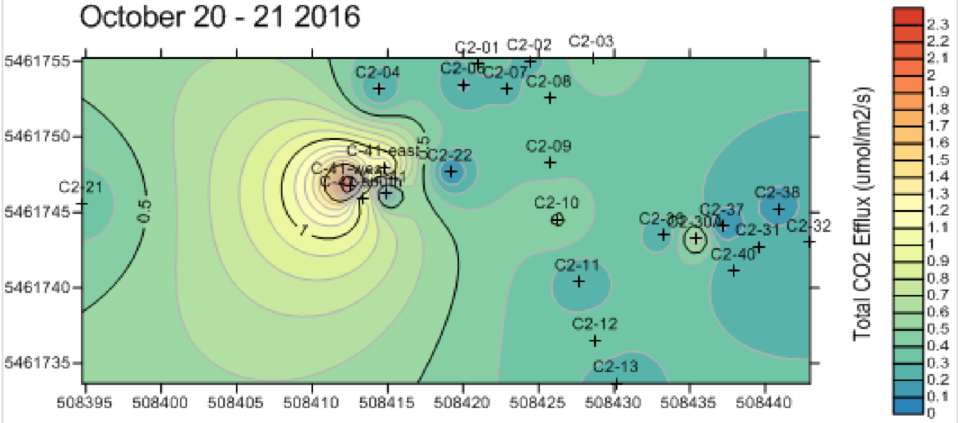


October 12 - 14 2016

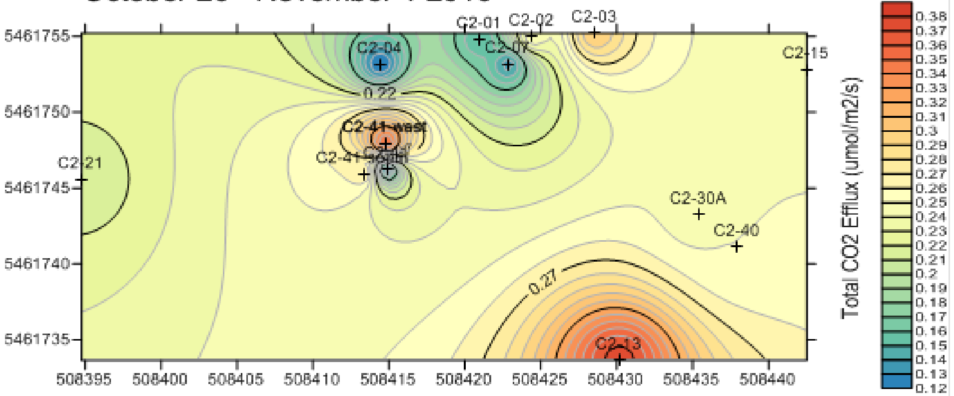


Moist & cool fall conditions

October 20 - 21 2016



October 26 - November 1 2016



Very wet & cool fall conditions

Note different scales are used for each plot.

Radiocarbon Estimation of Contaminant Soil Respiration

Total Efflux = Contaminant Soil Respiration + Natural Soil Respiration

$$J_{CO2} = J_{CSR} + J_{NSR}$$

Objective: to estimate J_{CSR} or the fraction of J_{CSR} to J_{NSR}

$$F_{CSR} \equiv \frac{J_{CSR}}{J_{CO2}}$$

- Radiocarbon or ^{14}C analysis has been used to differentiate between CO_2 derived from fossil fuel and natural sources of atmospheric CO_2.
- Technique relies on ^{14}C analysis, an unstable carbon isotope (with a half-life of approximately 5700 years) generated by cosmic rays in the atmosphere.
- Method builds on research studies conducted by Sihota and Mayer (2012) and Wozney (2017).

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

Sihota and Mayer (2012) Characterizing Vadose Zone Hydrocarbon Biodegradation Using Carbon Dioxide Effluxes, Isotopes and Reactive Transport Modeling. Vadose Zone Journal.

Wozney (2017) Biodegradation rates of petroleum in contaminated aquifers: a comparison of radiocarbon correction methods for determining source zone natural attenuation. Masters Thesis., University of Ottawa

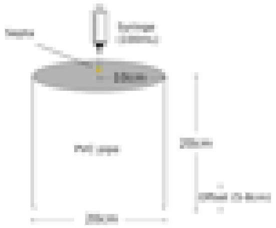
Radiocarbon Estimation of Contaminant Soil Respiration

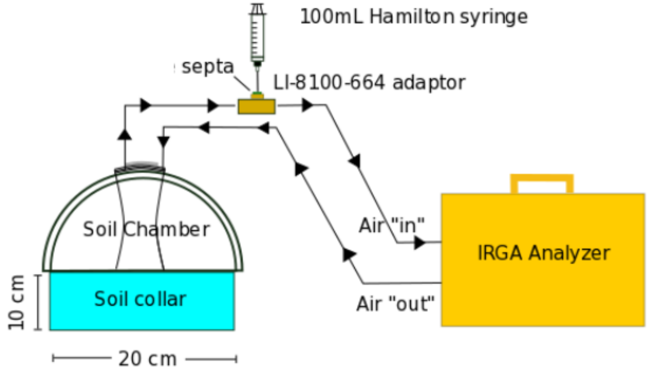
- Novel method based on mass balance at each test location:
  - Sample collected is a mixture of ambient air (A) and soil gas (B)
  - CO_2 concentrations and fraction of modern carbon (^{14}F) measurements of air samples
- Fraction of ^{14}C content of carbon ($F^{14}C$) is measured by accelerator mass spectrometry
- Assumes $F^{14}C$ associated with CSR is zero
- The decrease in fraction of modern carbon measured in soil gas and the ambient air represents fraction of CSR

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

evacuated Wheaton glass bottle

Hamilton® gastight syringe





NSZD Estimates – Total CO_2 Efflux & ^{14}C Data

Table A: CO_2 Efflux Method

Time Period	Average Contaminant CO_2 Efflux, J_{CSR} (µmol/m²/s)	Average NSZD Rate (US gal/acre/year)	Minimum NSZD Rate (US gal/acre/year)	Maximum NSZD Rate (US gal/acre/year)
June 23 to July 10, 2015 (dry and warm)	2.0	1,100	200	4,000
October 12 to 14, 2016 (moist and cool)	0.44	246	3.3	6,200
October 26 to November 1, 2016 (very wet and cool)*	0.010	5.5	2.5	9.4

*Short-term unseasonally high precipitation and essentially saturated conditions

NSZD Estimates – VZBL Spreadsheet Tool

Table B: Oxygen gradient-based method

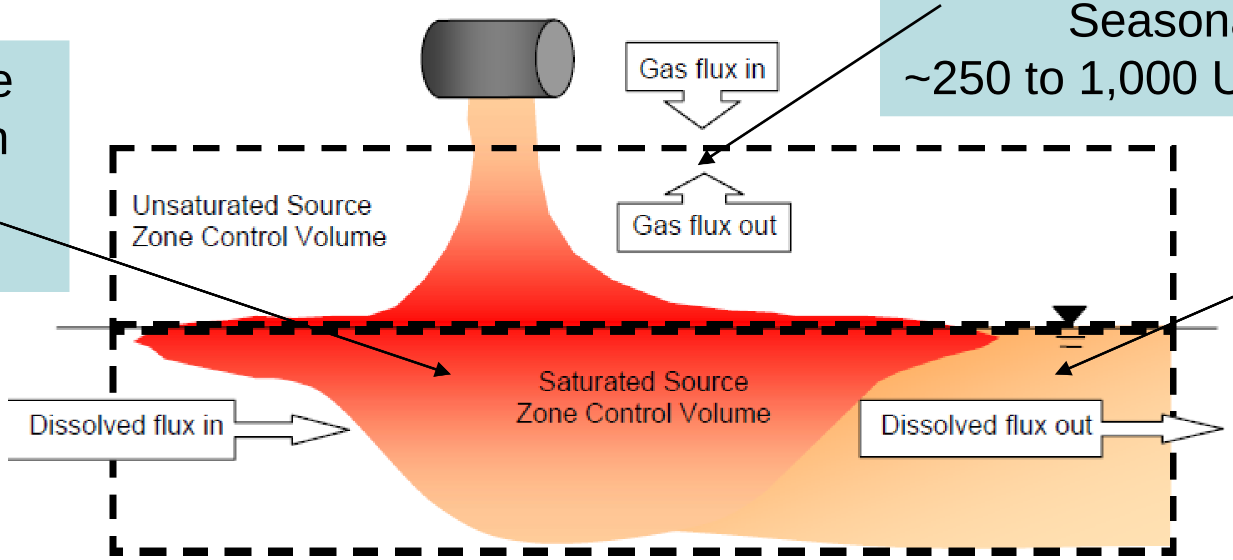
Scenario			Estimated NSZD Rate		Equivalent CO_2 Efflux
Soil Moisture Condition	Baseline Soil Respiration (mg O_2/g-OC/day)	Surficial Soil Type	$g/m^2/day$	US gallons/acre/year	CO_2 ($\mu mol/m^2/s$)
Wet Fall (Oct 17-19)	0.11	NA	1.1	510	0.90
Dry Summer	0.35	Sandy loam	13	5,600	10.6
Dry Summer	0.35	Loam	3.6	1,600	2.9

Key Points: The site-wide estimate of mass loss from the VZBL model higher than estimates from contaminant CO_2 efflux measurements, but within the same order of magnitude.

NSZD Processes & Rate Estimates

Saturated Zone Biodegradation
35 US gal/acre/year

Vadoze Zone Biodegradation
Seasonal range
~250 to 1,000 US gal/acre/year



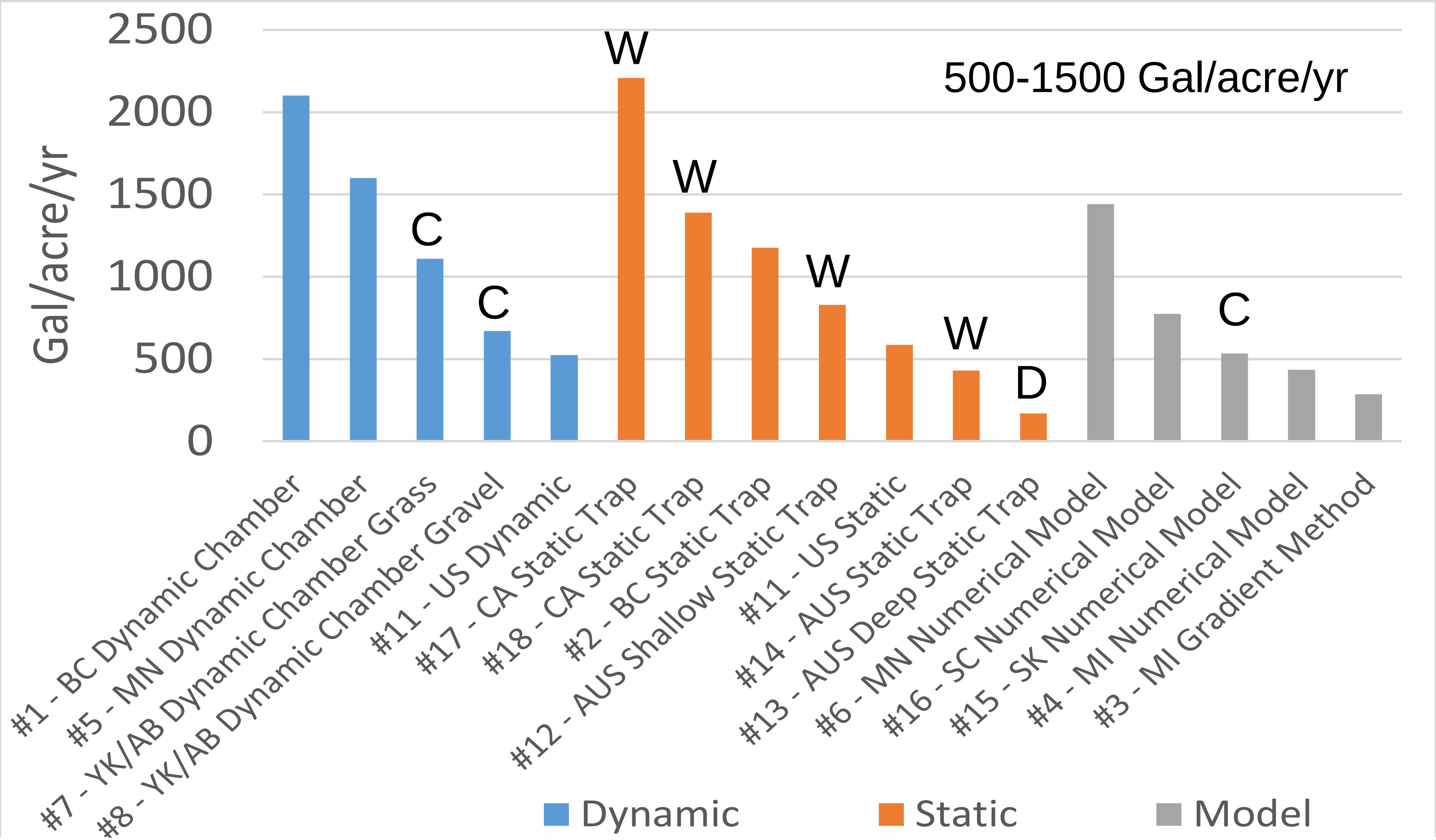
Saturated Zone Dissolution & Flow
72 US gal/acre/year

Depletion rate = $f(\text{flux}_{in} - \text{flux}_{out})$

Control volume "box" for quantitative assessment of NSZD (from ITRC, 2009)

- Hydrocarbon dissolution & flow: 72 US gal/acre/year
- Saturated zone biodegradation reactions: 35 US gal/acre/year (Approximately 60% is estimated to be from methane production)

Vadose Zone Biodegradation Loss Rates

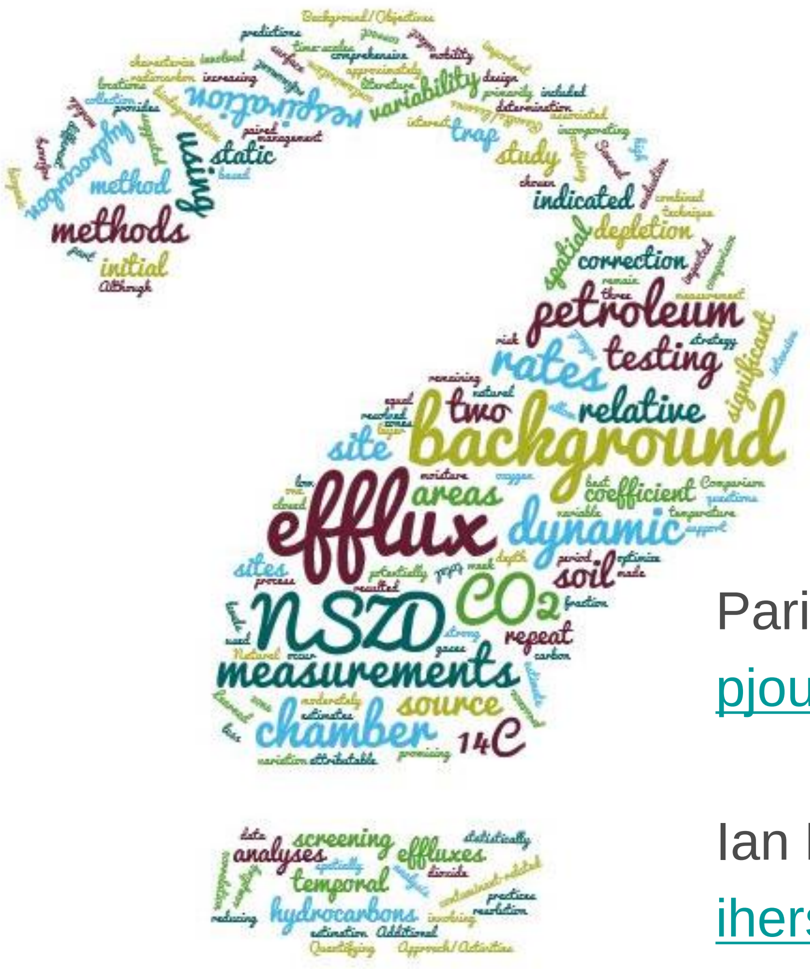


C = cold climate
W = warm climate
D = deep source (confined)
Hers et al. (Battelle 2016)

Toolkits: NSZD & Sustainability

- NSZD rate measurements serve as basis for assessing NSZD as a remedy and can be compared to measured or estimated rates for other technologies
- Typically NSZD should be considered as a secondary remedy after primary active remediation is no longer effective or sustainable
- Recent case studies including the study presented here indicate that NSZD rates, though seasonally variable, can be significant and exceed rates for later stage active remediation
- Sustainability and lifecycle principles can aid in assessment of technologies and evaluation of technology transition – this is key – the sustainability Toolkit that Golder is currently developing addresses this
- Emerging focus is on evaluating compositional changes associated with NSZD and relative depletion rates

Thank You!



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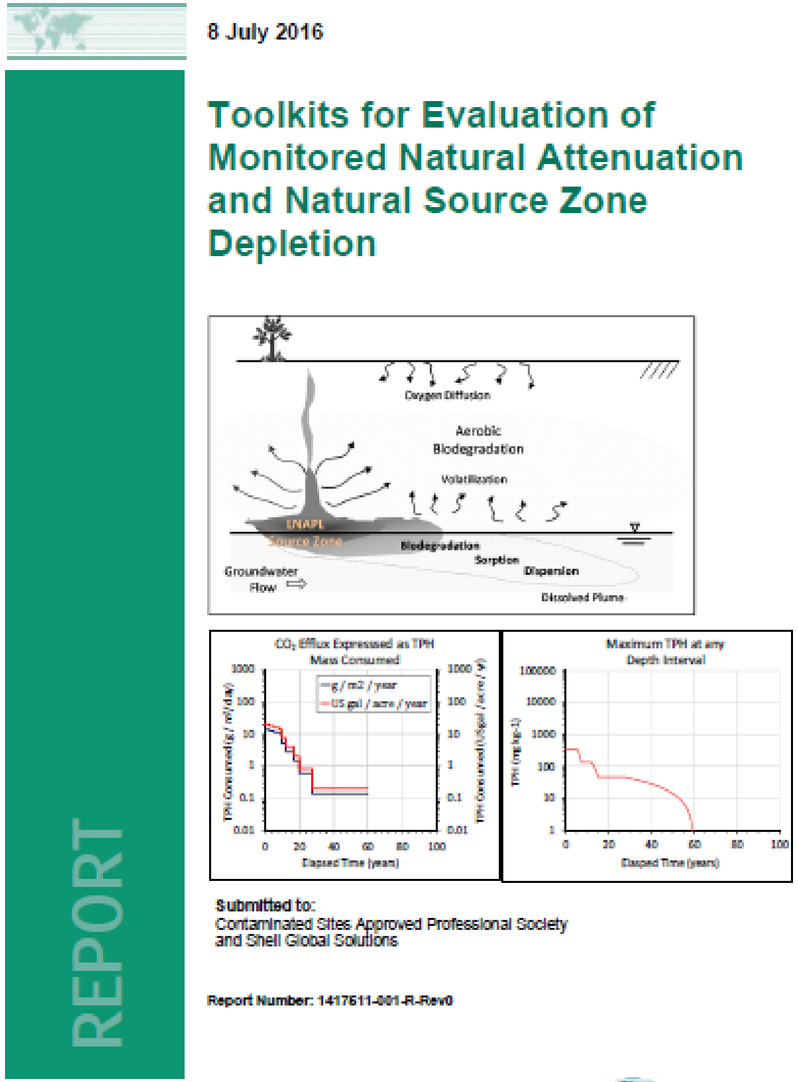

8 July 2016

REPORT

Toolkits for Evaluation of Monitored Natural Attenuation and Natural Source Zone Depletion

Submitted to:
Contaminated Sites Approved Professional Society and Shell Global Solutions

Report Number: 1417611-001-R-Rev0