E·FLUX

Easy set-up. Expert results.

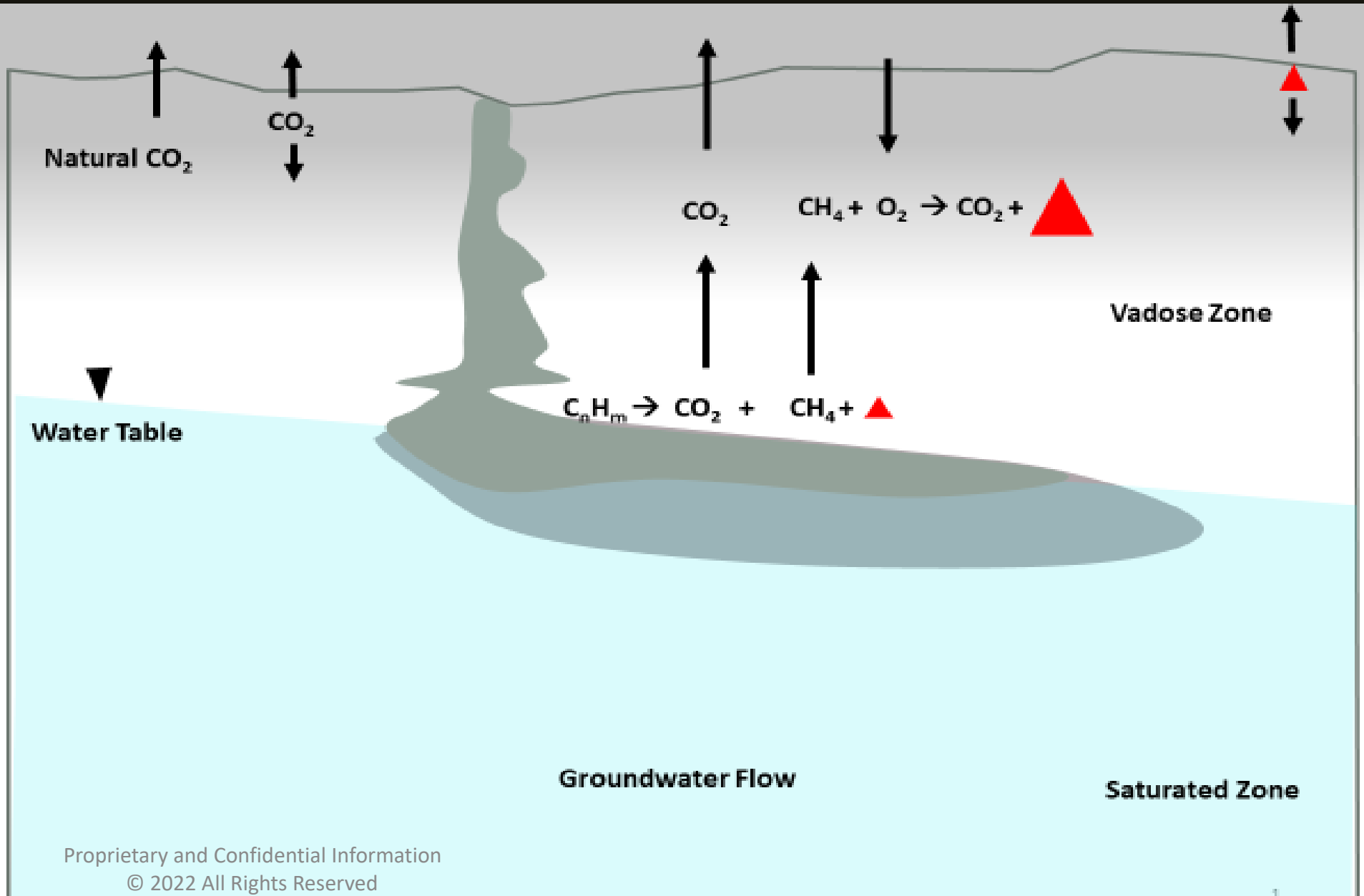
DISTINGUISHING NOISE FROM SIGNAL IN THE MEASUREMENT OF NATURAL SOURCE ZONE DEPLETION (NSZD) RATES AT PETROLEUM CONTAMINATED SITES

JULIO ZIMBRON, PH.D.

2023 BATTELLE CONFERENCE

MAY 8-10, 2023

Background



Motivation

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

- Guidance documents are strong on describing methodologies, and “intrinsic” limitations of the multiple methods
- Yet, direct comparisons of different methods or examples with shortcomings are scarce

Intent of this talk is to discuss common pitfalls and promote discussions about best practices

Alternatives to Measure NSZD Rate

Method	Variants (* assumptions)	Basis
Concentration Gradient	**	Concentration profile fitted to diffusion-based vertical transport (Fick's law)
Surficial CO_2 Efflux	Dynamic Closed Chamber **	Short term measurement (typically background corrected)
	Passive CO_2 Traps *	Long term measurement + ^{14}C Correction
Temperature Gradient (heat balance)	Background Corrected ***	Short term measurement of temperature gradients
	"Single Stick Method" **	Long term measurement of temperature gradients
Compositional Change	*	Uses non-biodegradable markers to track individual compound concentration changes in time

Assumptions
* 1-D transport, stoich
* Fitting transp. parameter
* Other

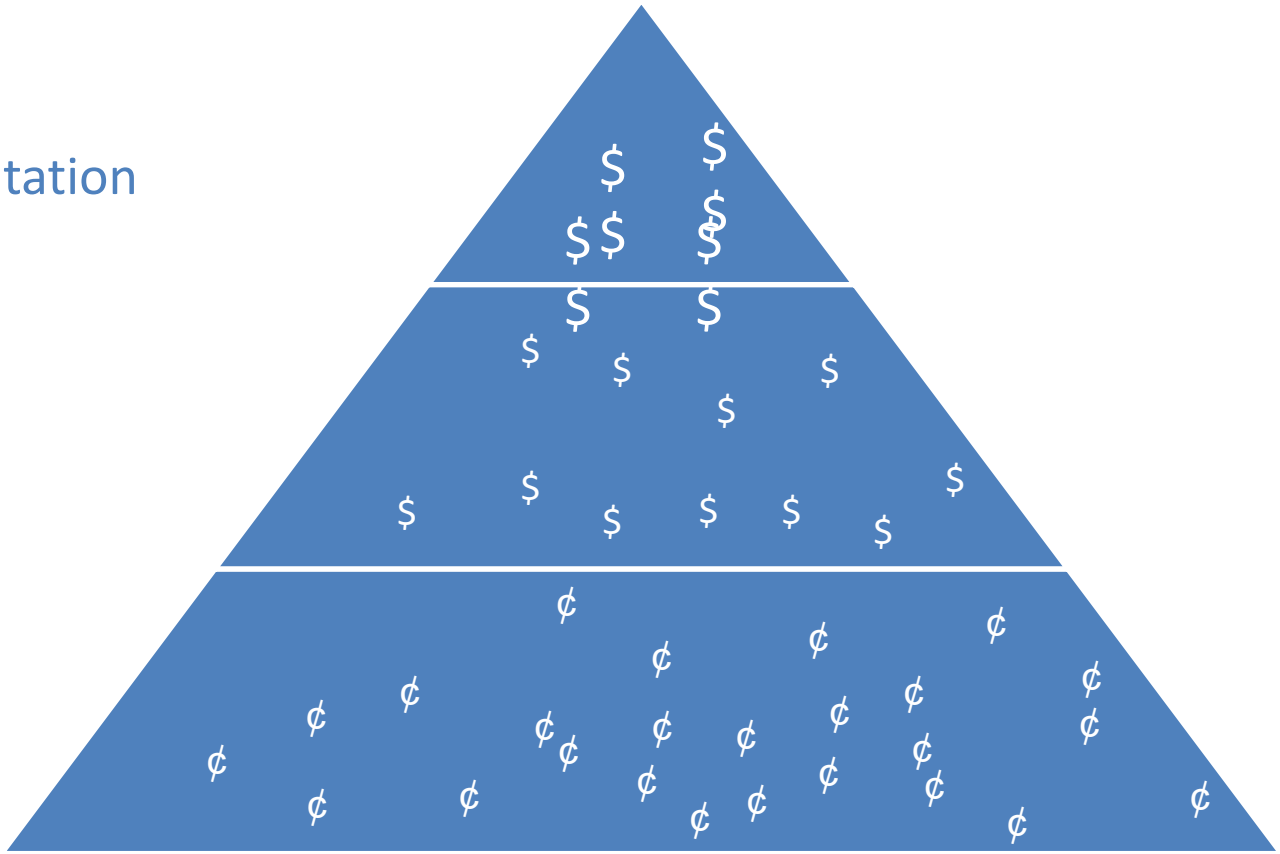
NSZD data quality

NSZD rate quantitation

qualitative

quantitative

Line of evidence



Line of Evidence? Direct Quantitation? Both?

- OSWER Directive 9200.4, 1999 on MNA
  - GW or soil chemistry data that shows clear trends (over time)
  - Hydrogeologic or geochemical data to demonstrate **indirectly** the types of NA processes active at the site
  - Field of microcosm studies to demonstrate **direct** occurrence of a NA process

- From EPA-sponsored Workshop (Wilson, 2006):

  "The strongest line of evidence is a reduction in concentration over time (at source area)."
  "Compound specific stable isotope analyses can provide an unambiguous conservative boundary on the extent of biodegradation along the flow path for some contaminants including chlorinated solvents, benzene, and MTBE."
  "DNA in ground water samples … does not provide a quantitative estimate of the rate of biological reductive dechlorination in the aquifer system."

- 

  Multiple Lines of Evidence for Estimating NSZD Rates Overlying a Shallow LNAPL Source Zone

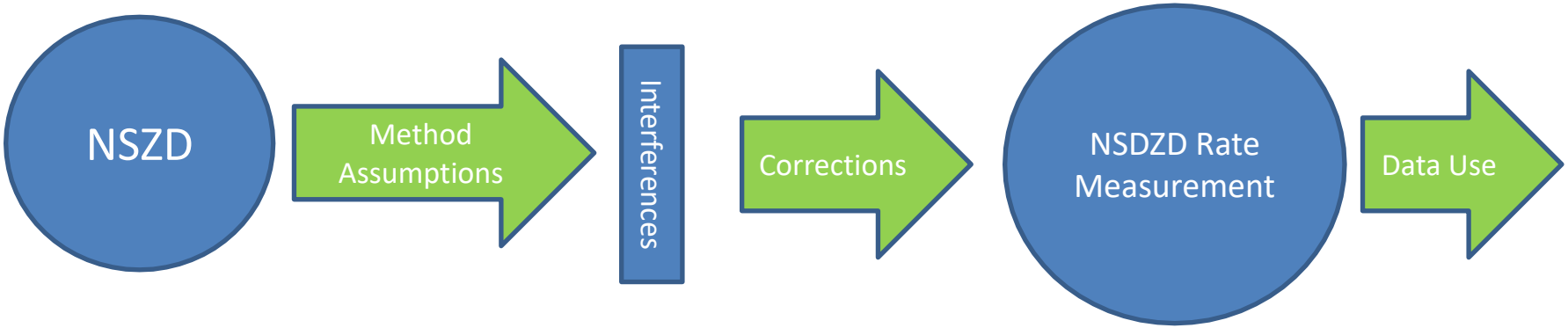
  by Anne Wozney, Ian Hers, Krista Stevenson, Calista Campbell, Nick Nickerson and Colleen Gosse

Hypothesis: Existing Guidance Documents Lack Sufficient Detail to Properly Select a Quantitation Methodology

Examples of Error Sources

- Background and Motivation
- CO_2 Efflux: Background correction vs ^{14}C correction
- CO_2 Efflux: Temporal variability
- Thermal Gradient: Background correction vs long term measurement (single stick method)
- Others (brief)
  - Gradient methods and soil transport properties
  - Impervious surfaces
  - Biomarker choice for compositional method

NSZD Expressions and Ways to Measure Them



$$\text{total signal} - noise = signal$$

Case Study 1
CO_2 Efflux, background correction vs ^{14}C

Groundwater Monitoring&Remediation

Practical Applications

Comparison of Radiocarbon- and Background Location-Corrections on Soil-Gas CO_2 Flux-Based NSZD Rate Measurements at Petroleum Impacted Sites

by Julio A. Zimbron

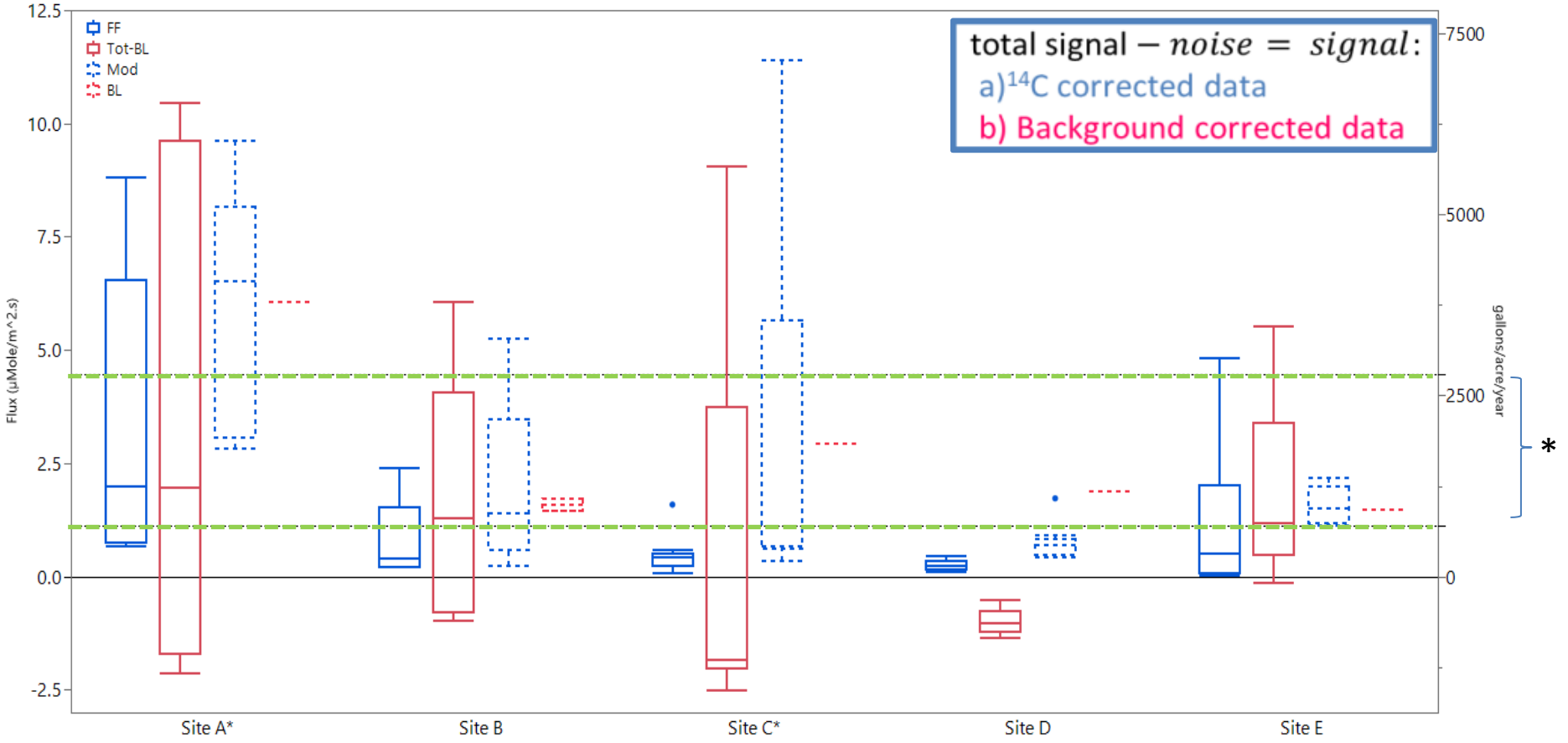
Abstract

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

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

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

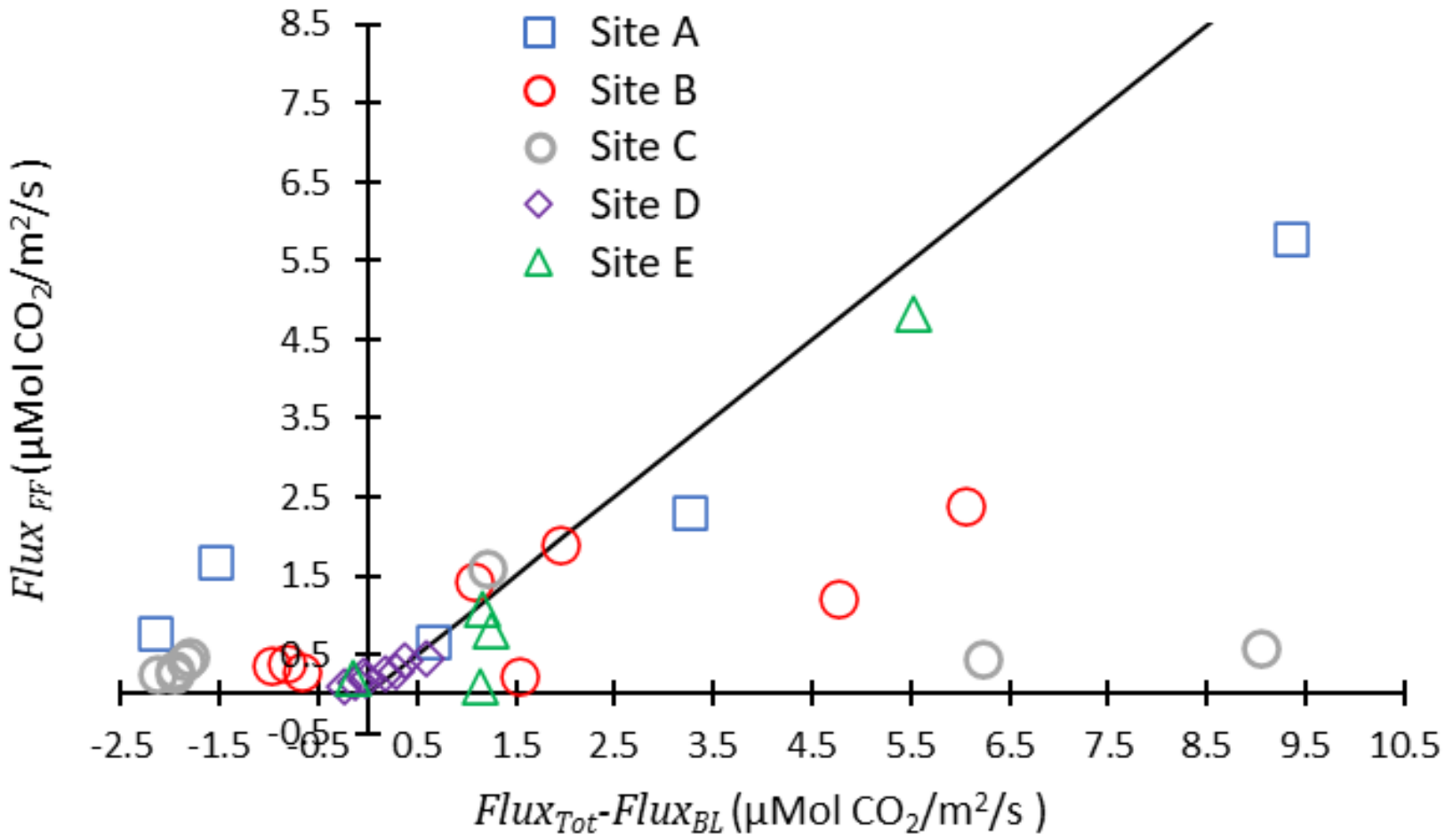
Five Sites Study



- Reported 25-75 percentile from Garg et al, 2017 (25 sites)
- XXX measurements out of YYY showed lower FF Fluxes than those of Garg et al, 2017
- larger mid 50% than all 5 sites, except Site A (Midwest Refinery)
- Garg et al, study relied in different measurement techniques

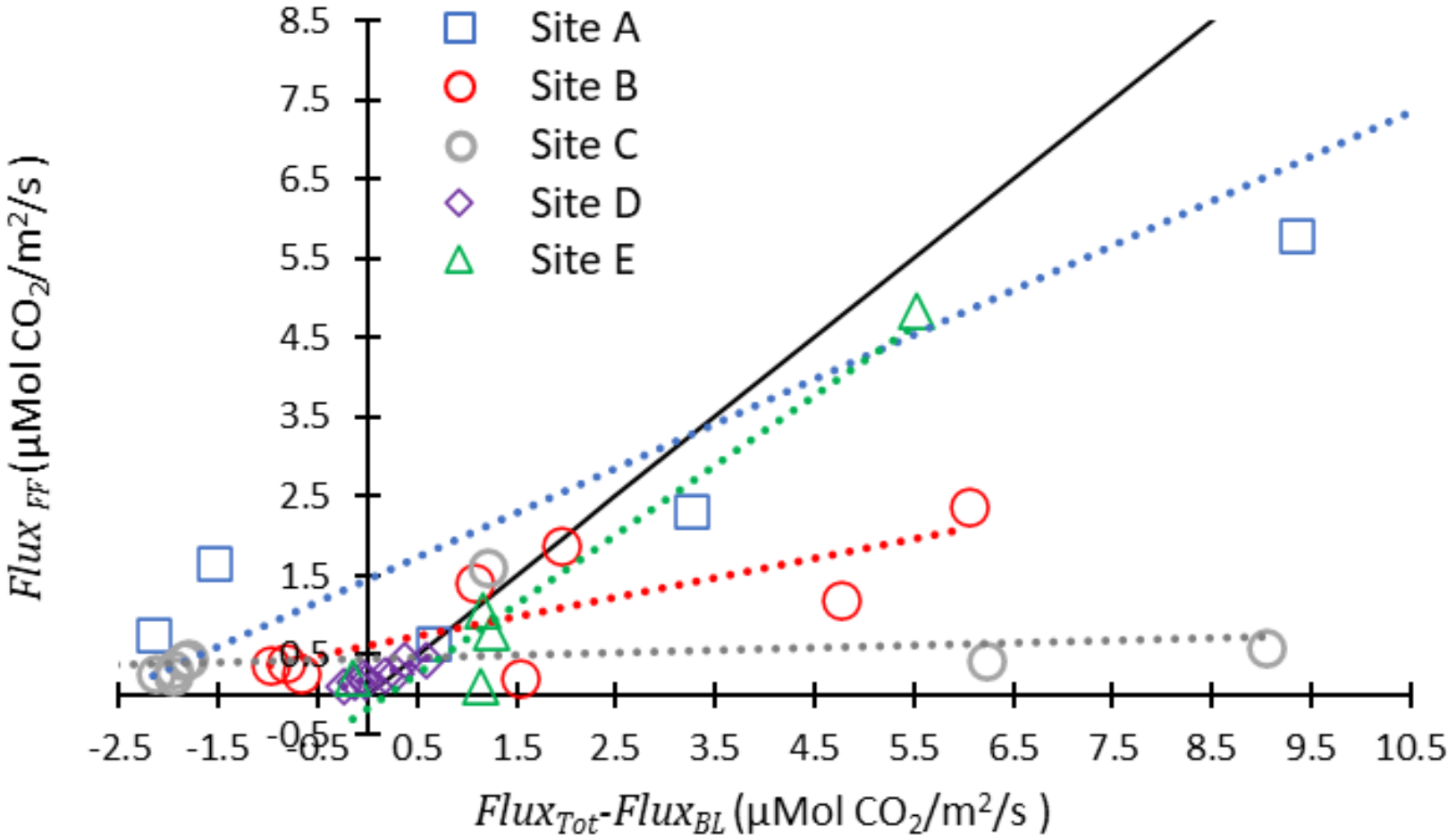
Comparing Both Corrections

Zimbron, 2022. GWMR



Comparing Both Corrections

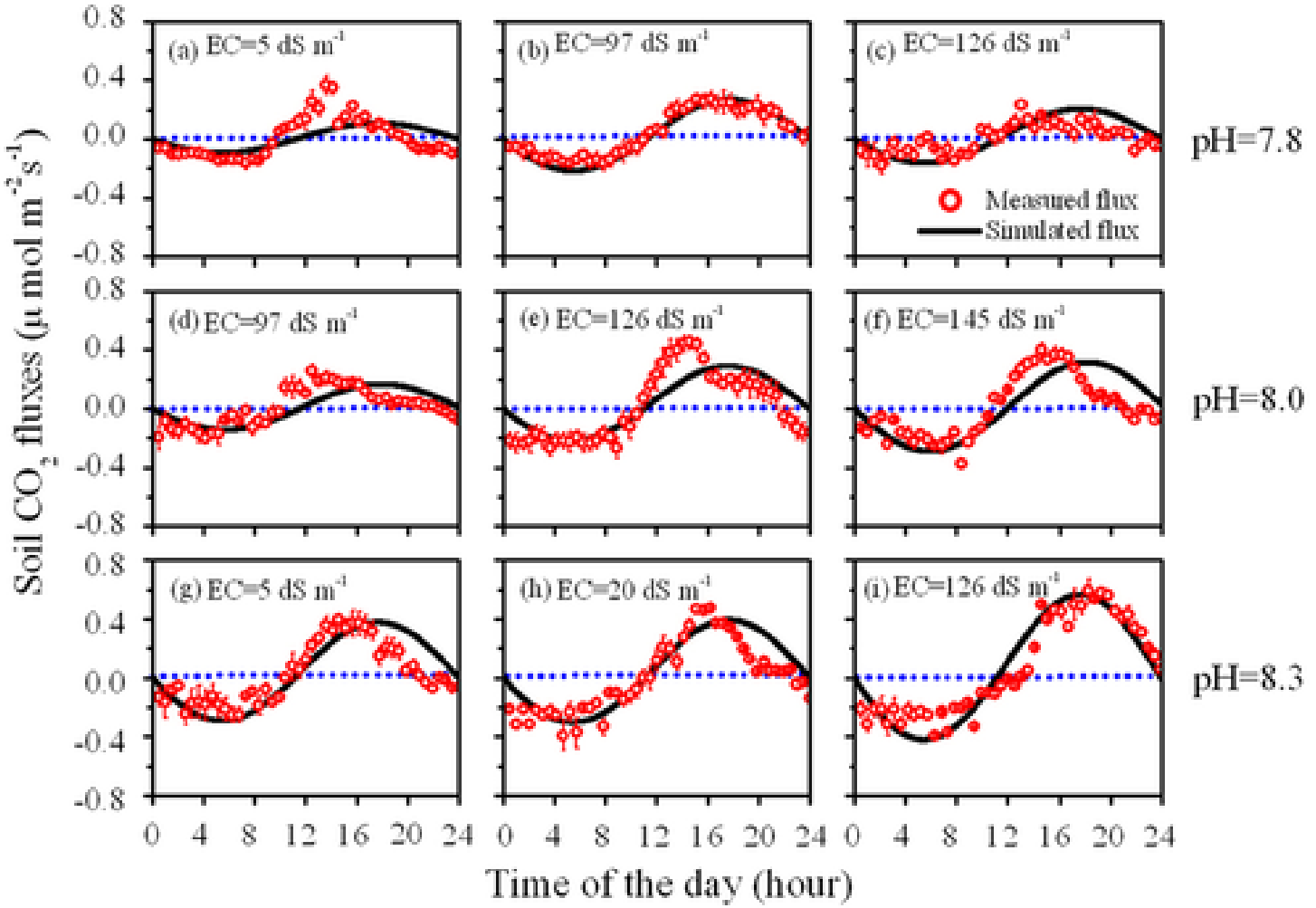
Zimbron, 2022. GWMR



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

Case Study 2
Temporal variability on CO_2 Efflux

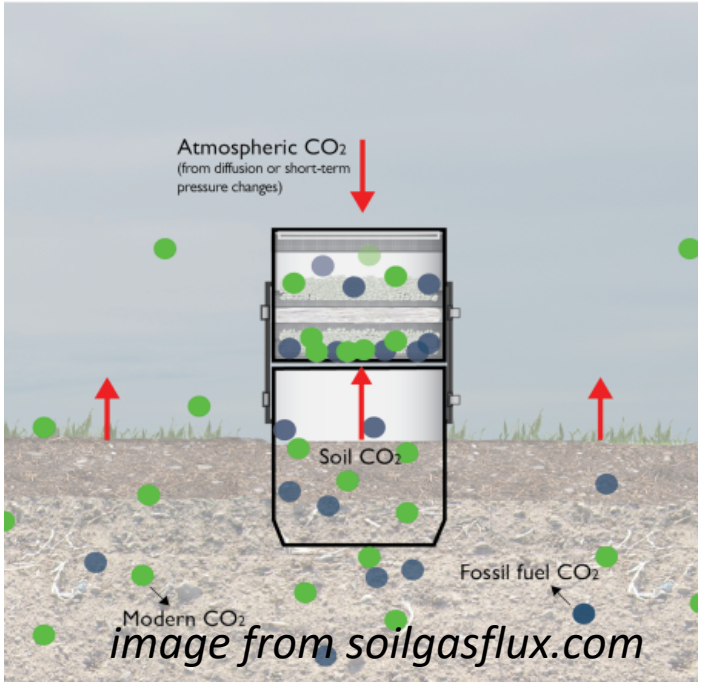
Dynamics of Soil Respiration



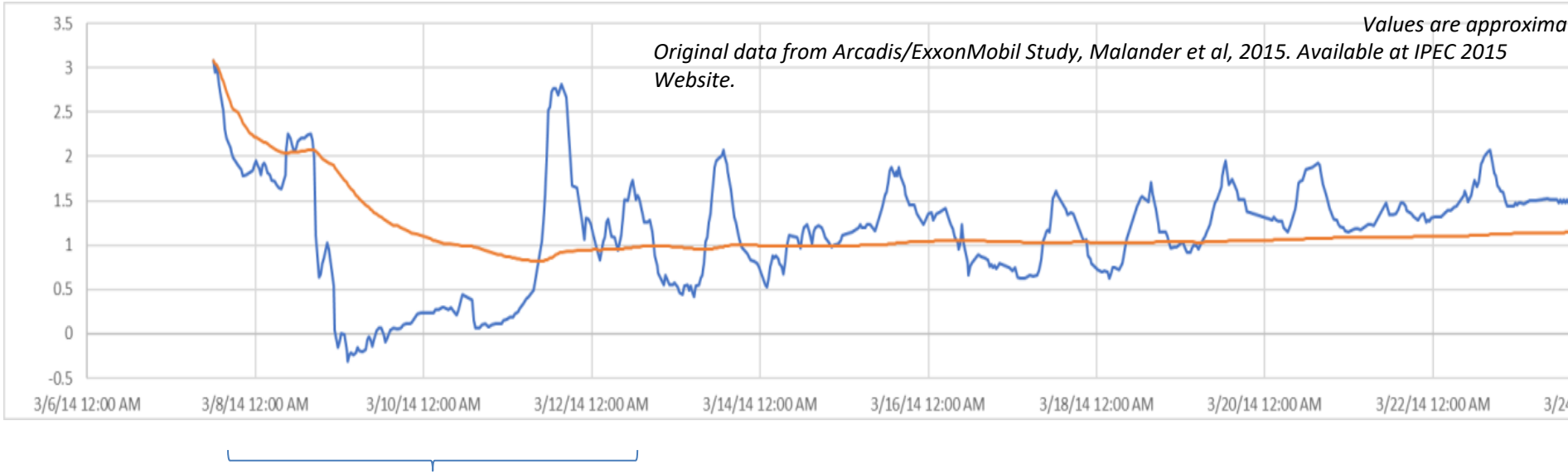
Ma, J., Z.-Y. Wang, B. A. Stevenson, X.-J. Zheng, and Y. Li (2013), An inorganic CO2diffusion and dissolution process explains negative CO2 fluxes in saline/alkaline soils, Sci. Rep., 3, 1–7, doi:10.1038/srep02025.

Dynamics of Soil Respiration

Short Term Vs. Long Term



Temporal Variability of CO_2 Effluxes

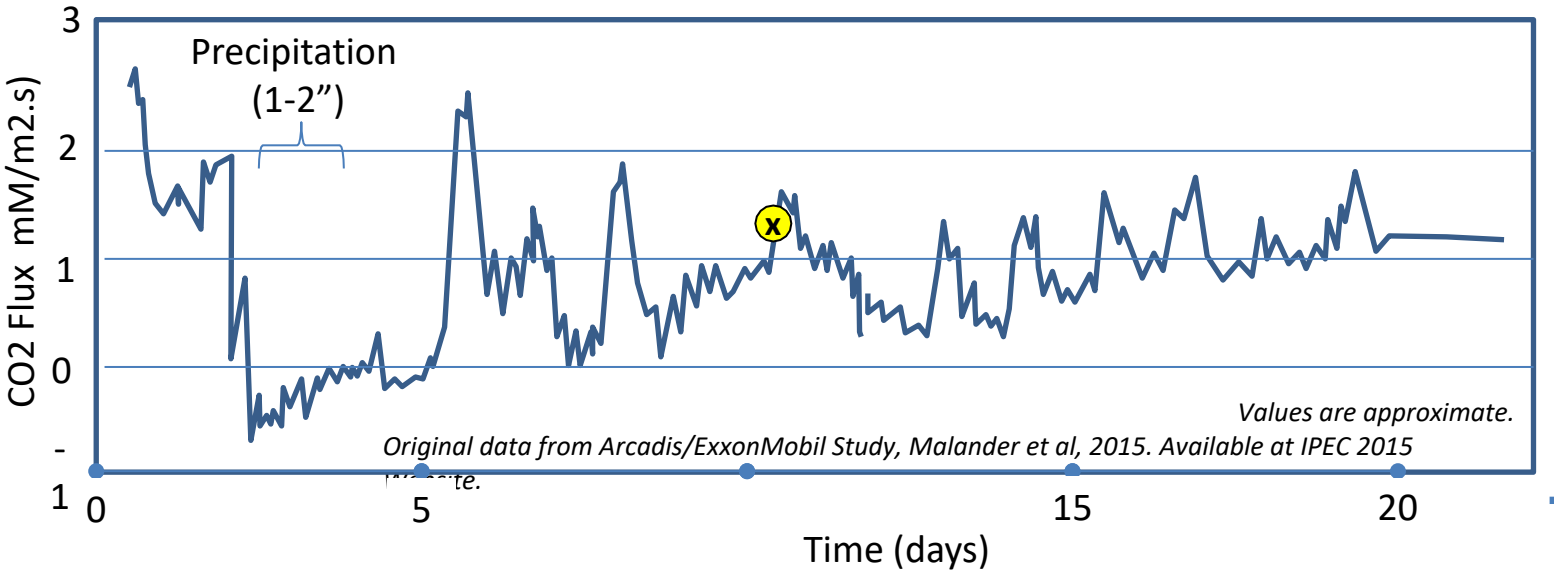


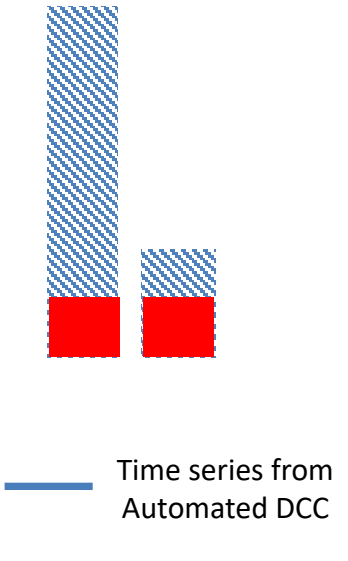
Values are approxima

Original data from Arcadis/ExxonMobil Study, Malander et al, 2015. Available at IPEC 2015 Website.

Data set from Malander et al, 2015 suggests nee
continuous data monitoring to approach long ter

Dynamics of Soil Respiration





DCC chamber data "consistent" with trap data (for total CO_2 fluxes over multiple days)

Consider temporal flux changes (and weather) when using soil respirometry to measure NSZD rates

Case Study 2b
"measurements indicated a good correlation"

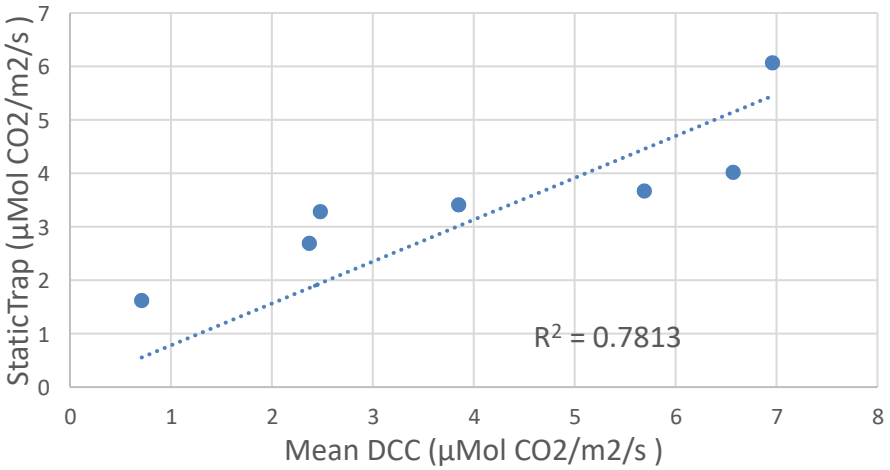
Groundwater Monitoring&Remediation

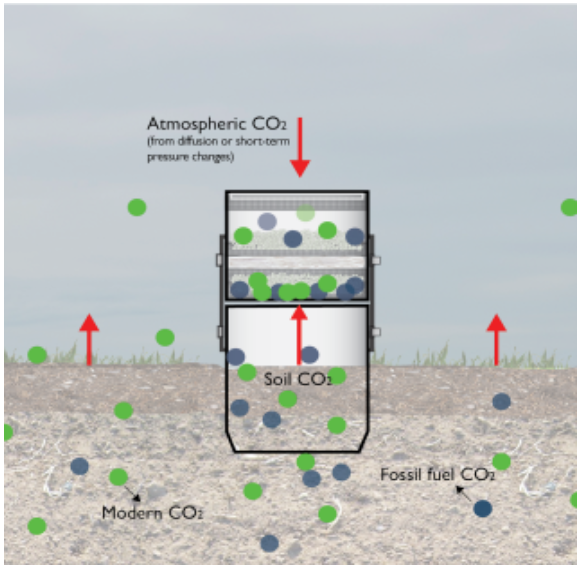
Multiple Lines of Evidence for Estimating NSZD Rates Overlying a Shallow LNAPL Source Zone

by Anne Wozney, Ian Hers, Krista Stevenson, Calista Campbell, Nick Nickerson and Colleen Gosse

Abstract

Quantitative methods of monitoring natural source zone depletion (NSZD) via biodegradation of petroleum hydrocarbons (PHC) are required to investigate source zone longevity and guide long-term management of PHC impacted sites. Vadose zone NSZD processes can be monitored using analysis of surficial CO_2 effluxes, soil-gas gradients, and thermal gradients. This study describes an applied research and development program conducted at a former refinery site over a 4-year period (2015 to 2019) on quantitative technologies for evaluation of NSZD of PHC light nonaqueous phase liquid (LNAPL) present within a shallow soil zone. A multiyear study using discrete CO_2 efflux measurements from dynamic closed chambers was compared with estimates obtained using static traps and continuous monitoring using forced diffusion (FD) technology. Thermistor strings along a transect were used to monitor hourly thermal gradients and assess NSZD rates using the temperature gradient method. Discrete soil-gas data were used to quantify the vertical oxygen gradient to estimate NSZD rates using the concentration





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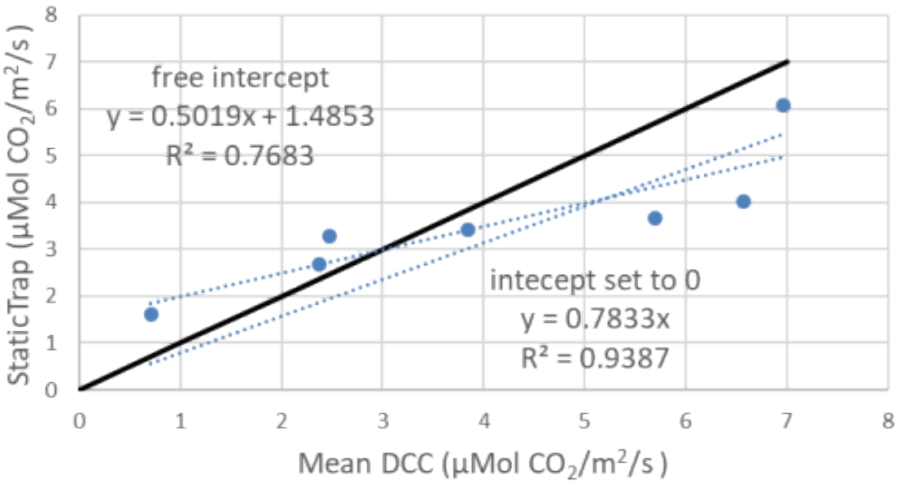
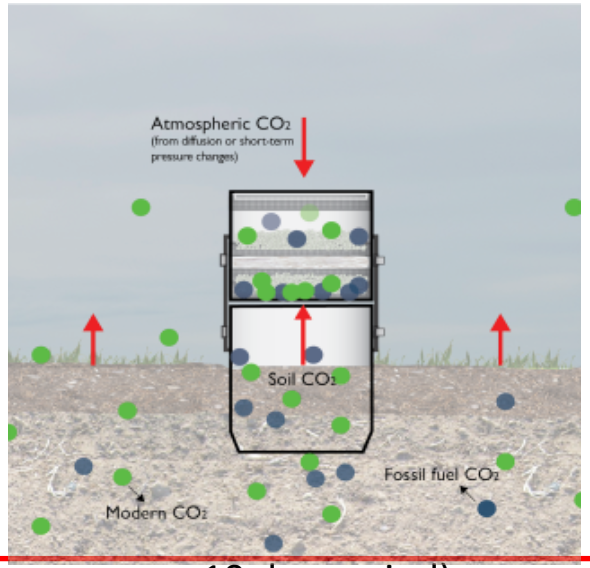




Even under similar basis (average CO_2 flux in this case over ~10 day period), agreement among methods is not ideal

Perhaps more important question is not about agreement of total CO2 flux, but about agreement of NSZD estimates

Dynamics of Soil Respiration

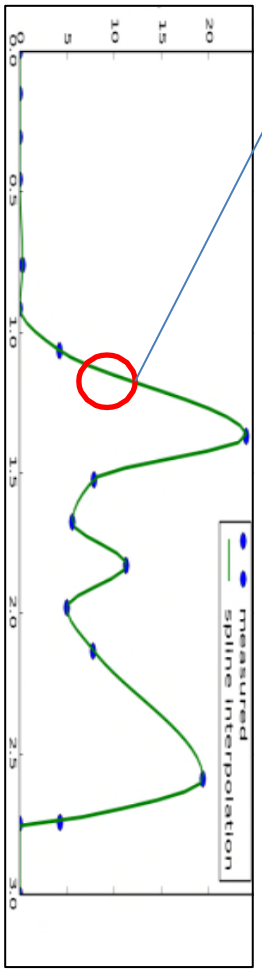
- Soil gas effluxes are cyclical
  - Daily: following daily ambient pressure and temperature cycles
  - Tidal sites: 2 cycles per day
  - Seasonal – soil generation process for both modern and fossil fuel CO_2 depend on soil temperature (and moisture)
  - Soil gas fluxes are susceptible to short term soil water saturation

Consider temporal flux changes (and weather) when using soil respirometry to measure NSZD rates

Case Study 3
Thermal Gradient: Background Correction vs. Time-Integrated Measurement

Model Approach

Inputs



Approach

At each elevation account for

a) Local LNAPL concentration

b) Correct for local temperature

c) Estimate “local biodegradation rate”

d) Cumulative biodegradation rate results in a bulk methane oxidation rate at A/A interface

Solve coupled

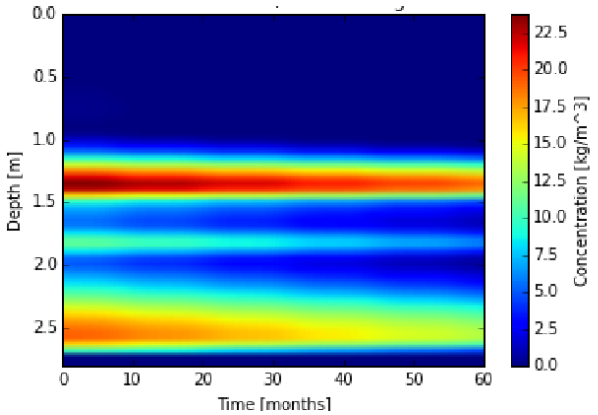
Local temperatures determined by

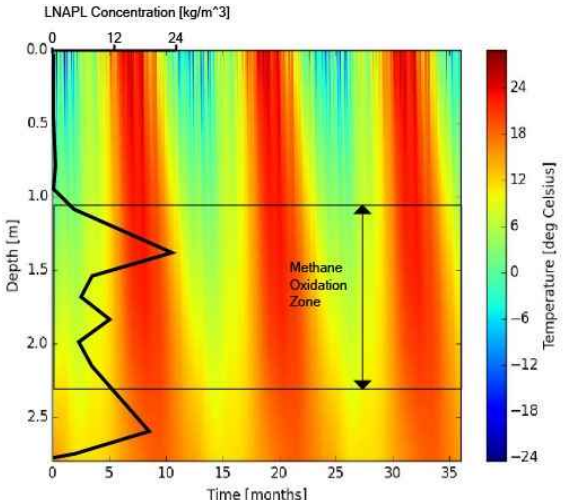
a) Boundary conditions

b) Heat produced by reactions

c) Soil heat transfer

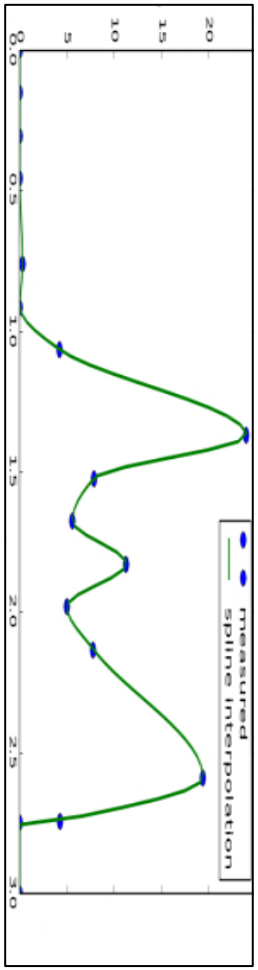
Outputs

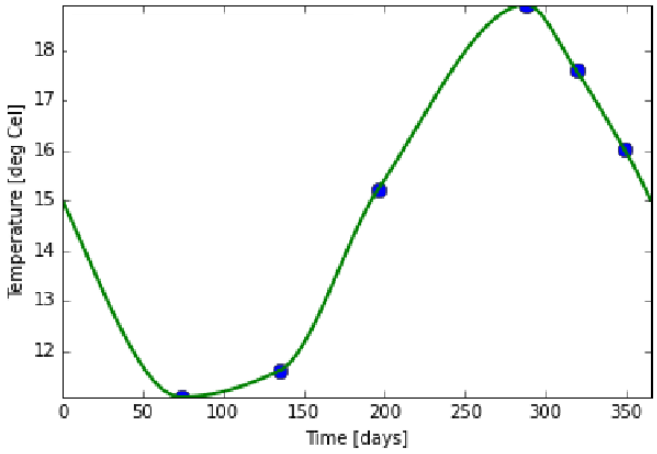


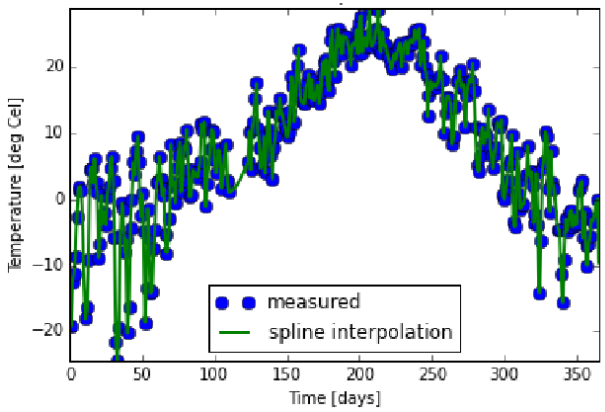


Model Inputs/Outputs

Inputs

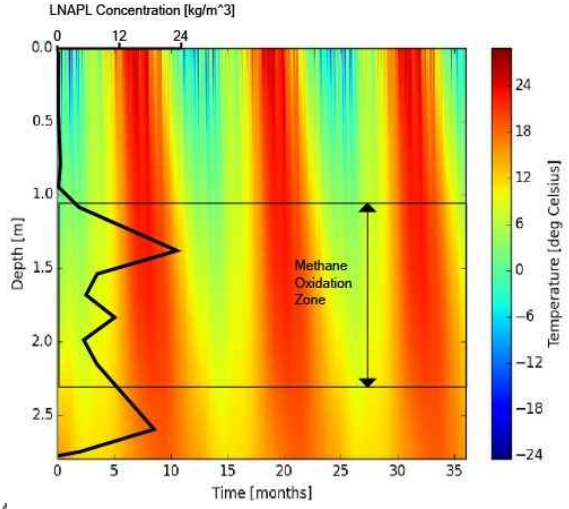


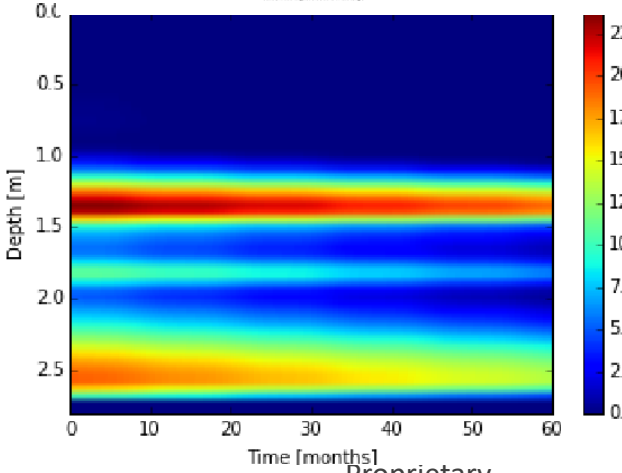




Model

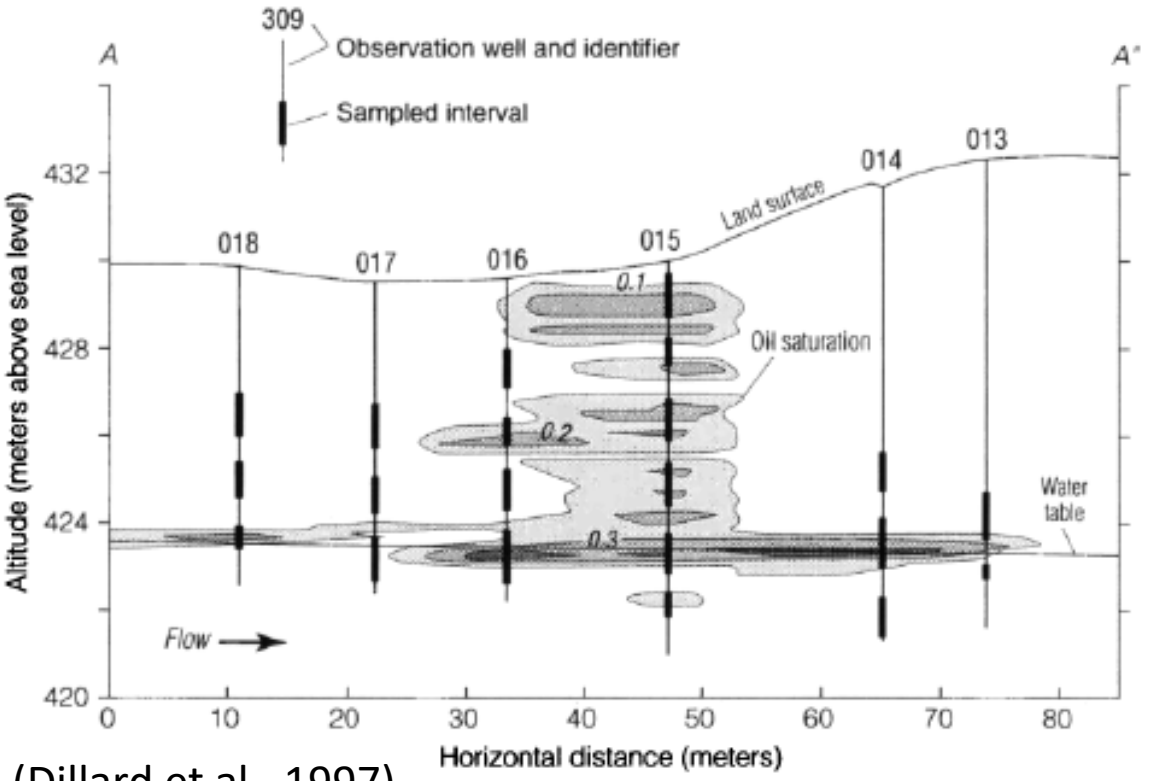
Outputs



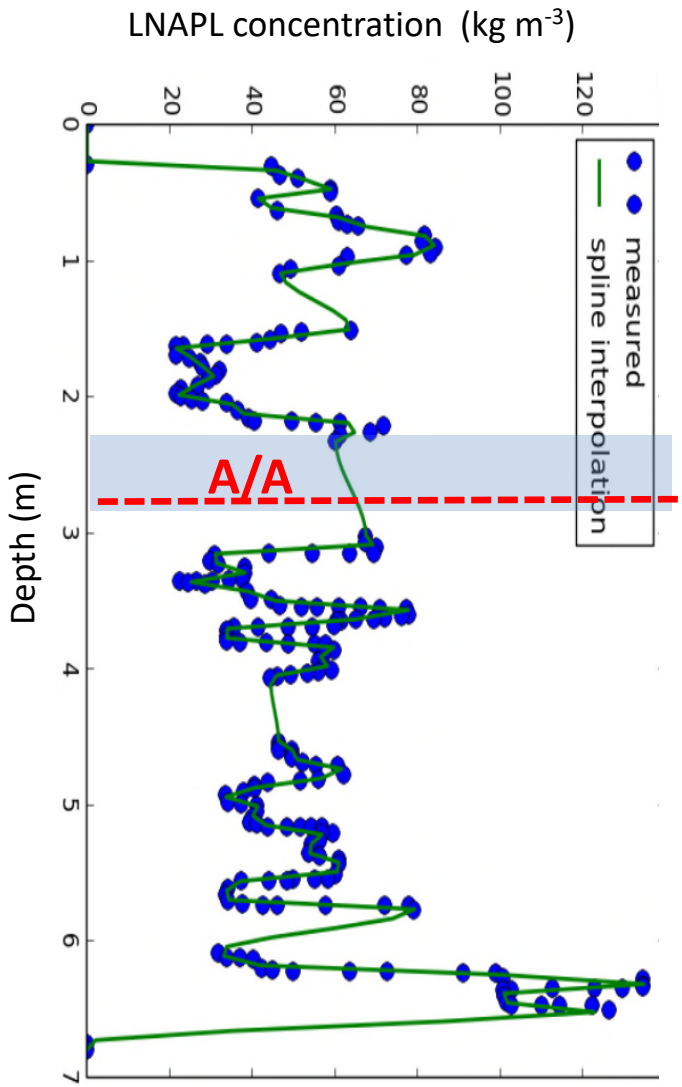


Base Case: Bemidji

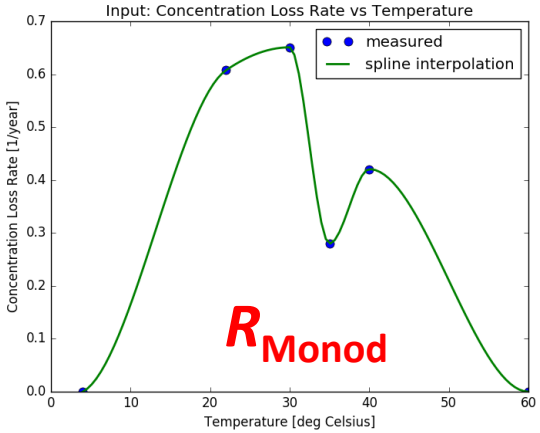
- Crude oil spill site
- Depth to Groundwater: 7 m
- Average Groundwater Temperature: 9 °C

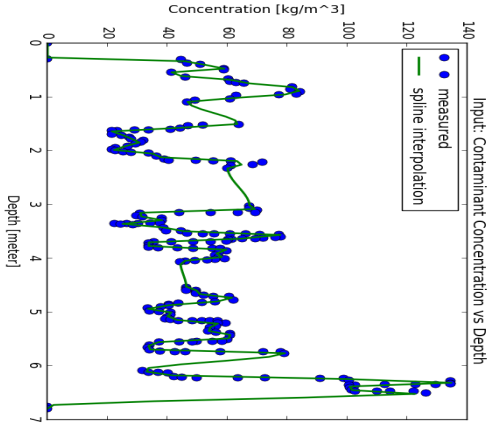


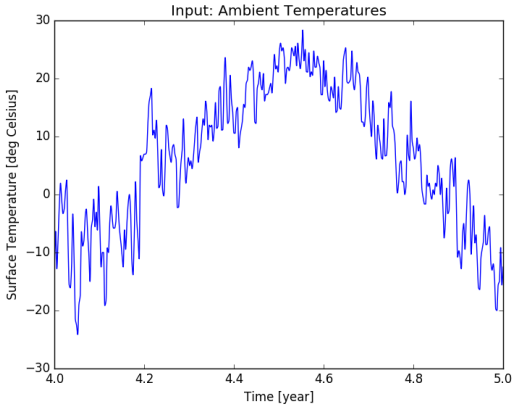
(Dillard et al., 1997)



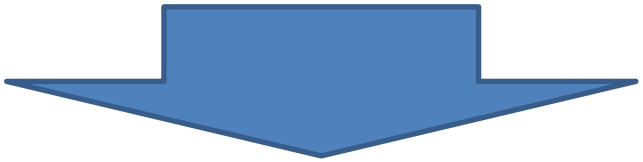
Base Case : Bemidji

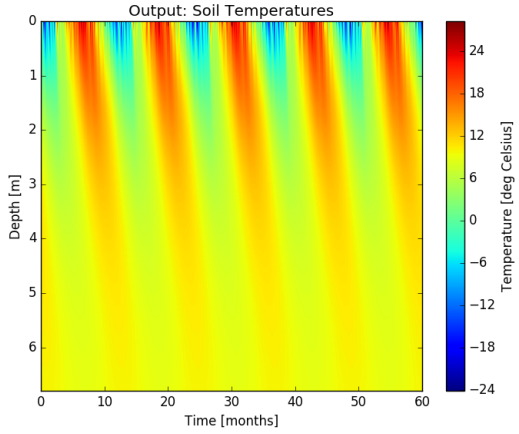


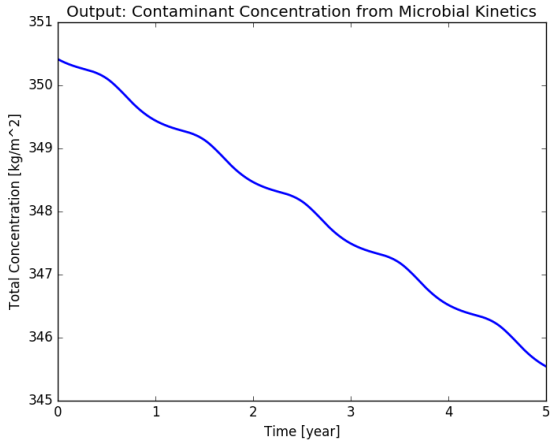


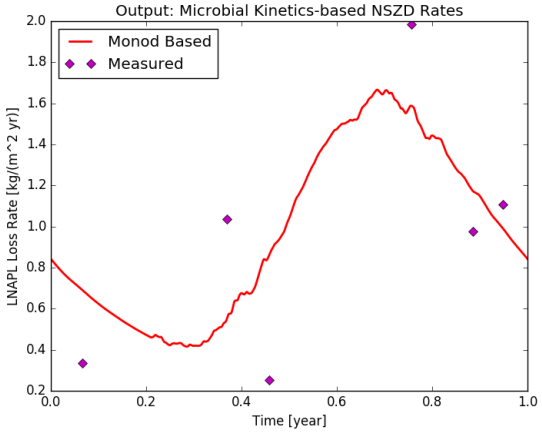


Lab data from Zeman, et al, 20??







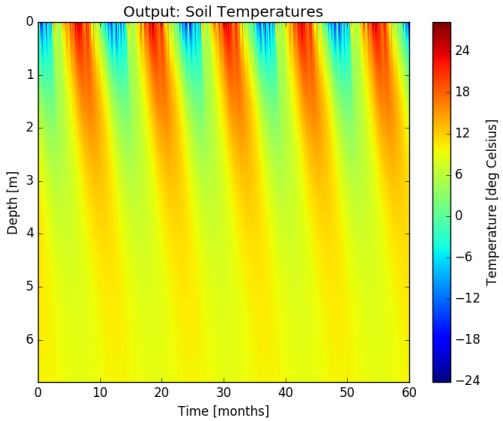


Field rates from Sihota, 2014.

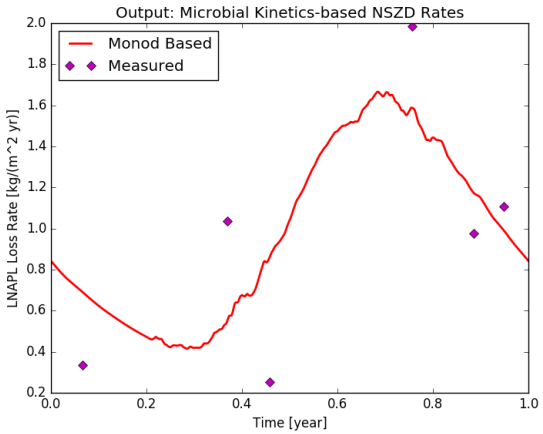
1 No Background Correction

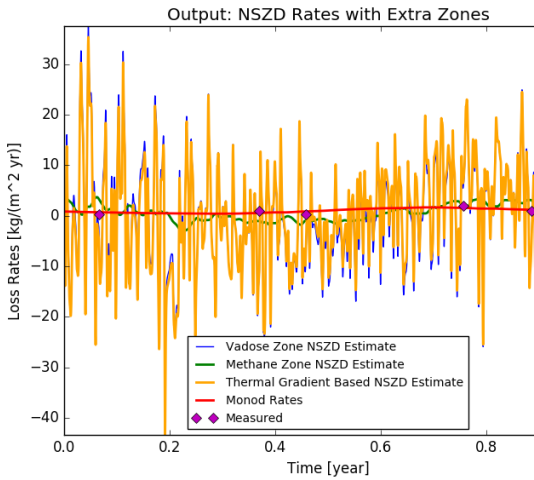
α_{site} = 3.58 x 10 $^{-07}$ m^2/s

Model Output

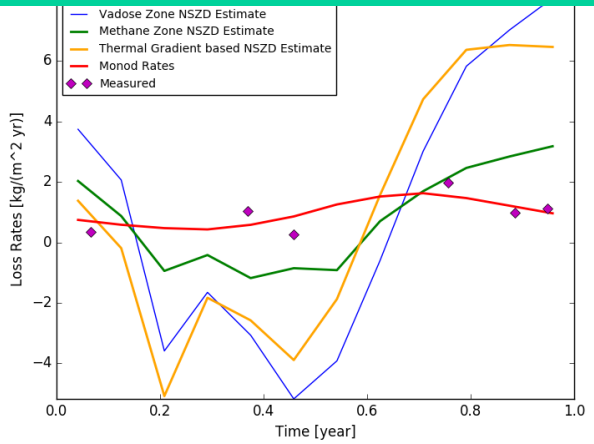


Short term Average Thermal Gradient NSZD rates



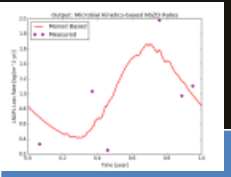


Monthly Average Thermal Gradient NSZD rates

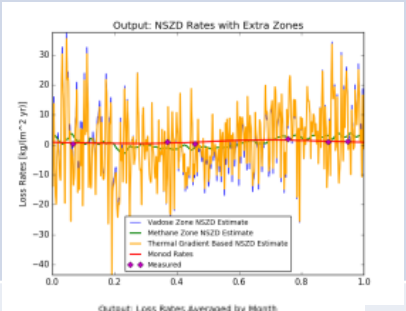
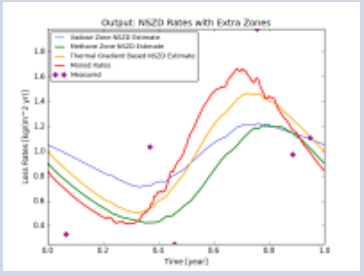
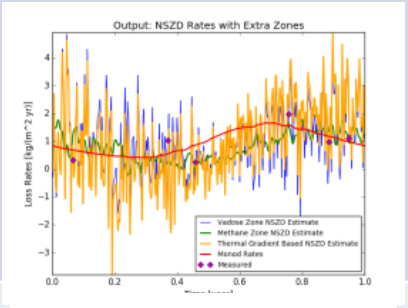
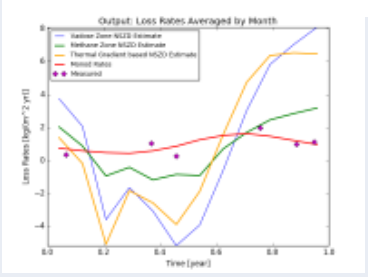
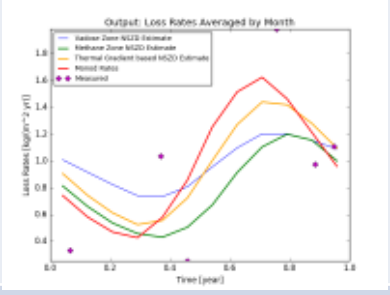
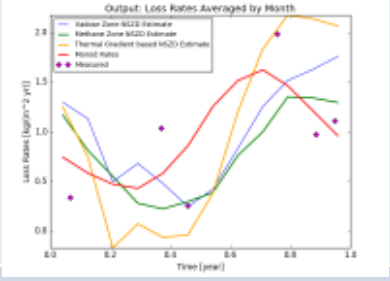


Annual Average Thermal Gradient NSZD rates

1. Thermal gradient location	Error Rate
Methane oxidation zone	**26.78%**
Aerobic Zone	**0.64%**
Entire Vadose Zone	**-0.57%**

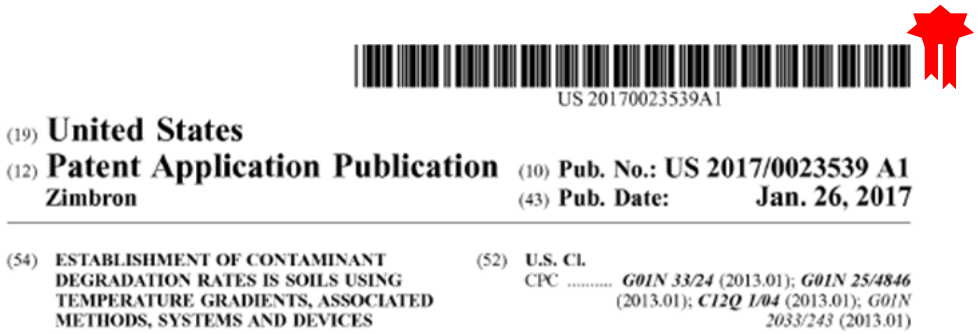


Average Annual Thermal Gradients

	1 Absolute temperatures	2 Perfect Background	3 Imperfect Background
Short term			
Monthly Averages			
Annual Averages	Target:		
	$R_{Monod,annual}$ = 0.97 kg/m2.yr = 1,200 gallons/ac.yr		
Methane Oxidation Zone	0.79 kg/m2.yr (19%)	0.788 (19%)	0.78 (19%)
Entire vadose zone	0.97 (0.4%)	0.97 (0.4%)	0.978 (0.4%)
Aerobic zone	0.96 (1%)	0.97 (1%)	0.96 (1%)

Further Reading on Long-Term Thermal

- Battelle 2018 Conference



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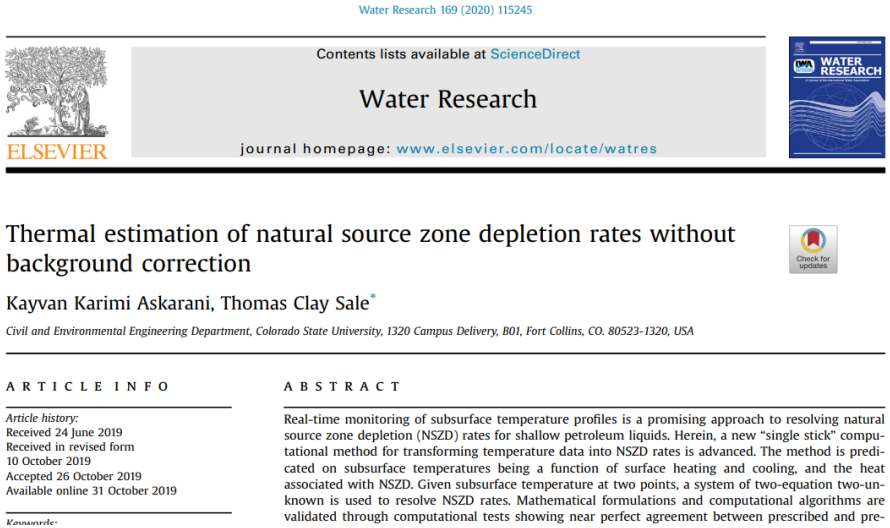
(54) **ESTABLISHMENT OF CONTAMINANT DEGRADATION RATES IS SOILS USING TEMPERATURE GRADIENTS, ASSOCIATED METHODS, SYSTEMS AND DEVICES**

(52) **U.S. Cl.**

CPC ***G01N 33/24*** (2013.01); ***G01N 25/4846*** (2013.01); ***C12Q 1/04*** (2013.01); *G01N 2033/243* (2013.01)

- Askarami and Sale, 2020



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Thermal estimation of natural source zone depletion rates without background correction

Kayvan Karimi Askarani, Thomas Clay Sale*

Civil and Environmental Engineering Department, Colorado State University, 1320 Campus Delivery, B01, Fort Collins, CO. 80523-1320, USA

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ABSTRACT

Real-time monitoring of subsurface temperature profiles is a promising approach to resolving natural source zone depletion (NSZD) rates for shallow petroleum liquids. Herein, a new "single stick" computational method for transforming temperature data into NSZD rates is advanced. The method is predicated on subsurface temperatures being a function of surface heating and cooling, and the heat associated with NSZD. Given subsurface temperature at two points, a system of two-equation two-unknown is used to resolve NSZD rates. Mathematical formulations and computational algorithms are validated through computational tests showing near perfect agreement between prescribed and pre-

Thermal gradient method very sensitive to background location selection (Rayner et al, 2020)
Both long term approaches reduce to similar practice: long term heat balances reduces error

Food for Thought: Measuring Reality

Image from istockphoto.com

Closing Thoughts

Yes!! NSZD is pervasive at LNAPL sites (and now DNAPL)…
but expectations have been set high

how some methods are more prone to “tweaking” to reach preset outcomes

Scale of processes

- Temporal
- Spacial
- … and the innate capabilities/limitations of each method

- Errors not discussed here but that merit discussion
  - Site-specific ^{14}C correction
  - Wind biases for surface methods (proportional to device profile)
  - ….
- Available guidance documents do not address these aspects…
- Need to acknowledge results discrepancies (as in 2020, Rayner et al)

Food for Thought: Measuring Reality

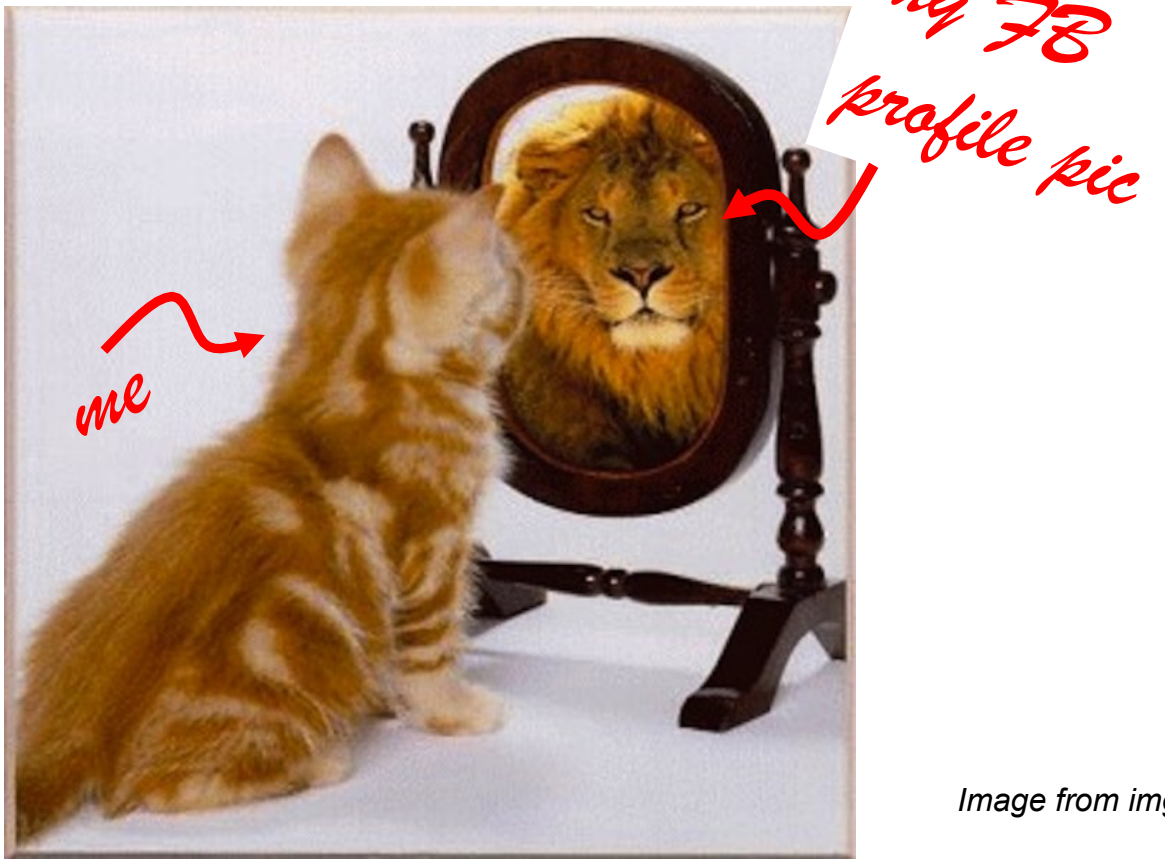

Image from imgflip.com

Julio Zimbron, Ph.D.
www.soilgasflux.com
jzimbron@soilgasflux.com

Conclusions

- More discussions needed on the nature of the processes measured and the method capabilities (i.e., inadequate snap shot measurements for processes with high diurnal variability)
- Current language in guidance documents leaves a lot of room for “tweaking” results and curve fitting to reach a pre desired outcome (i.e., 1,000 gallons/acre.yr)
- Need to acknowledge discrepancies of results