E·FLUX

Easy set-up. Expert results.

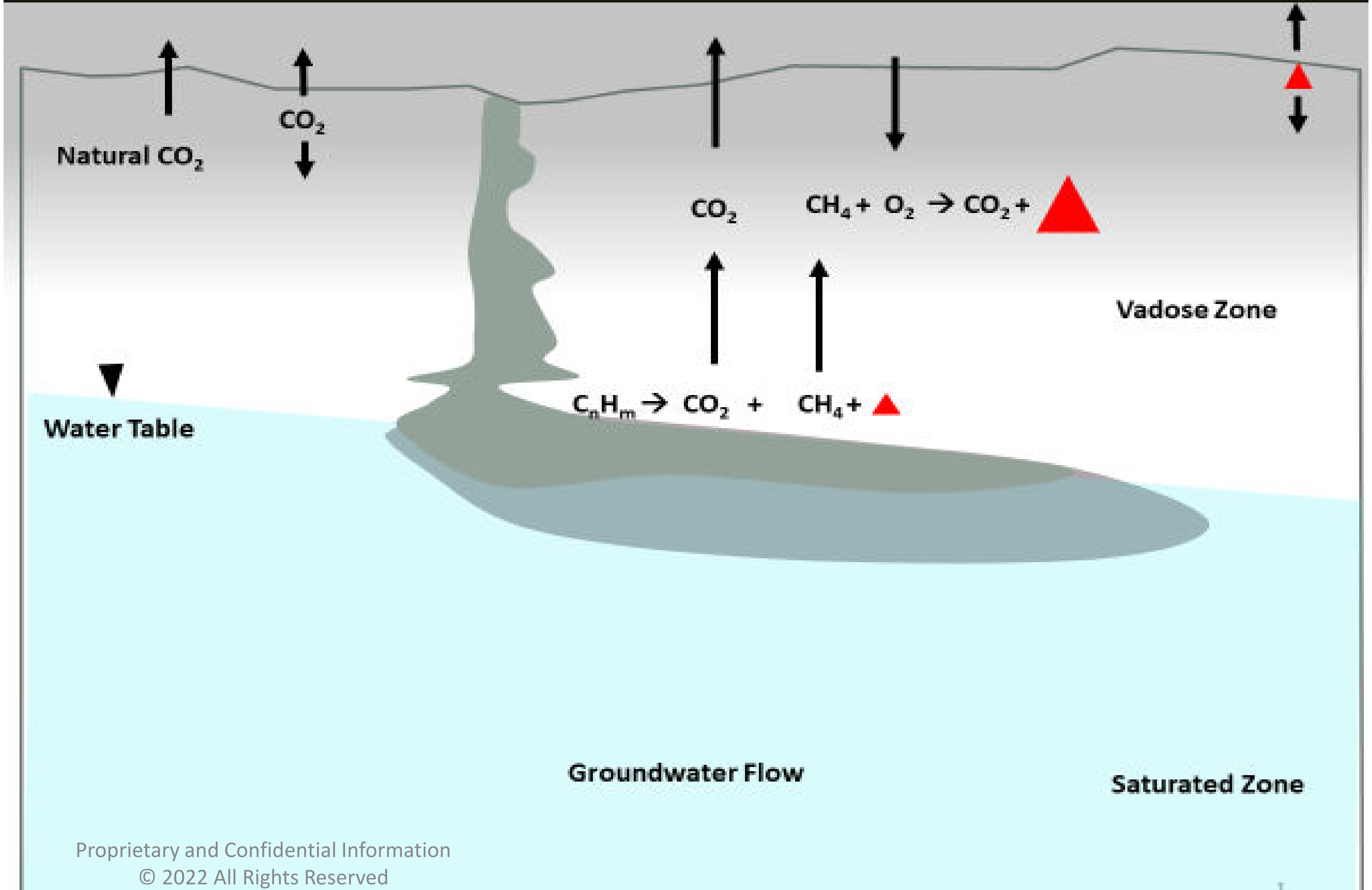
DISTINGUISHING NOISE FROM SIGNAL IN THE MEASUREMENT OF NATURAL SOURCE ZONE DEPLETION (NSZD) RATES AT PETROLEUM CONTAMINATED SITES

JULIO ZIMBRON, PH.D.

2022 REMTECH CONFERENCE
BANFF, CANADA

OCTOBER 14, 2022

Background



Natural CO_2
CO_2
CO_2
$CH_4 + O_2 \rightarrow CO_2 +$
Vadose Zone
Water Table
$C_nH_m \rightarrow CO_2 + CH_4 +$
Groundwater Flow
Saturated Zone

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, stoichiometry
- * Fitting transport parameter
- * Other

Motivation

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

2018 NSZD Guidance Document

INTERSTATE TECHNOLOGY REGULATORY COUNCIL ITRC

FRTR NSZD Resources

Federal Remediation Technologies Roundtable

LNAPL Site Management Document

NAVFAC

"Currently, it [the CO_2 Trap] is the most common method to obtain NSZD rates"

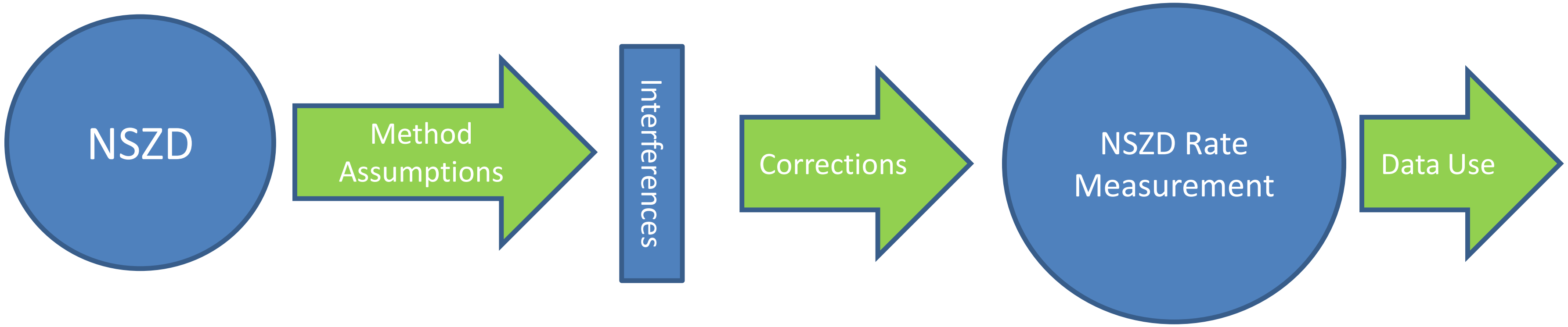
ASTM INTERNATIONAL

Standards Worldwide

- Guidance documents are strong on describing methodologies, and "intrinsic" limitations of the multiple methods
- Yet, direct comparisons of different methods are scarce

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

NSZD Measurements
what is measured vs. what happens



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

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)
- Summary and Conclusions

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 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

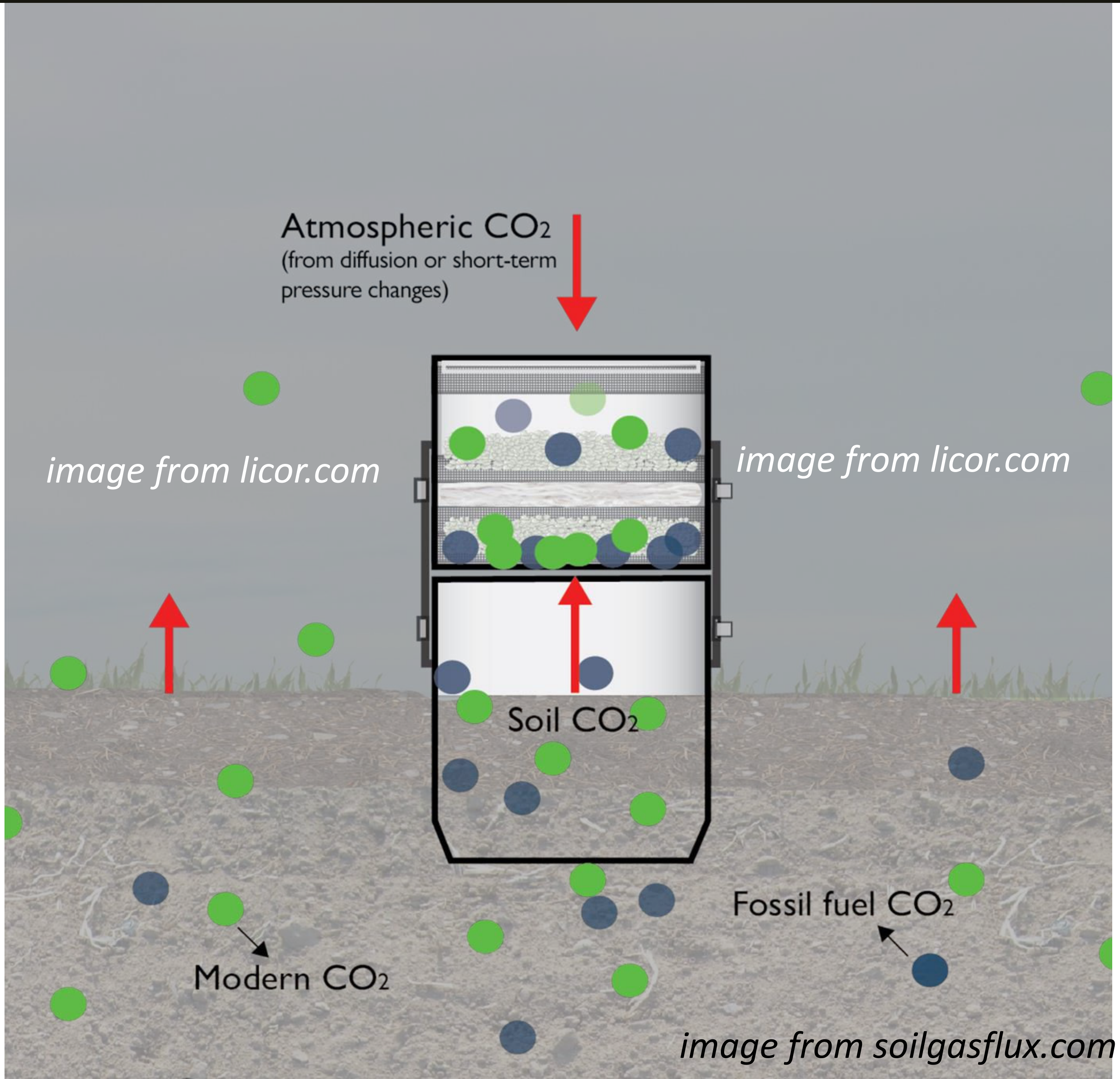
Soil CO_2 Efflux-Based Field NSZD rates

$$Flux_{Tot} = Flux_{Nat} + Flux_{NSZD}$$

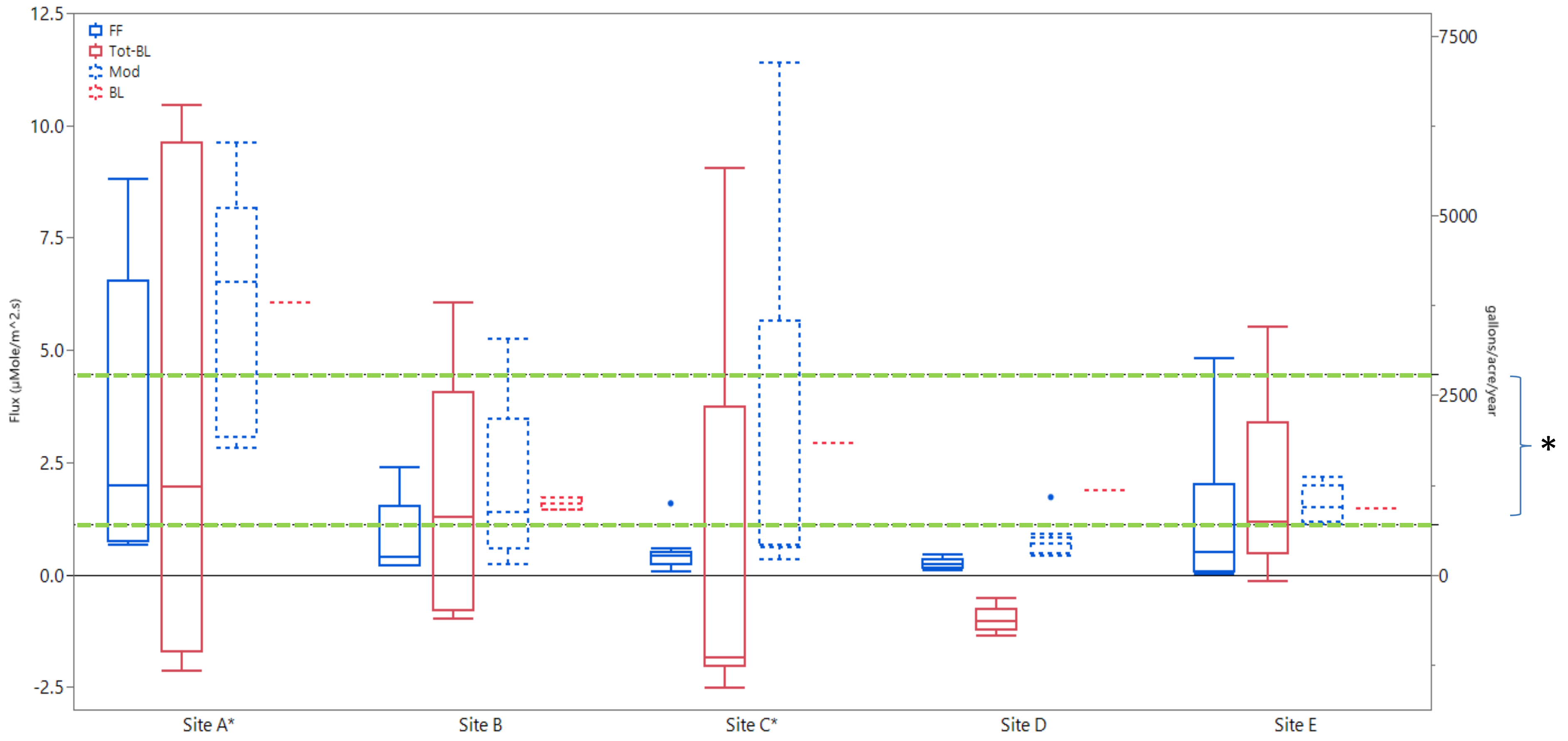
Correction done on the basis of:

a. Background correction (based on single location)
b. Location specific radiocarbon correction

^{14}C correction



Five Sites Study

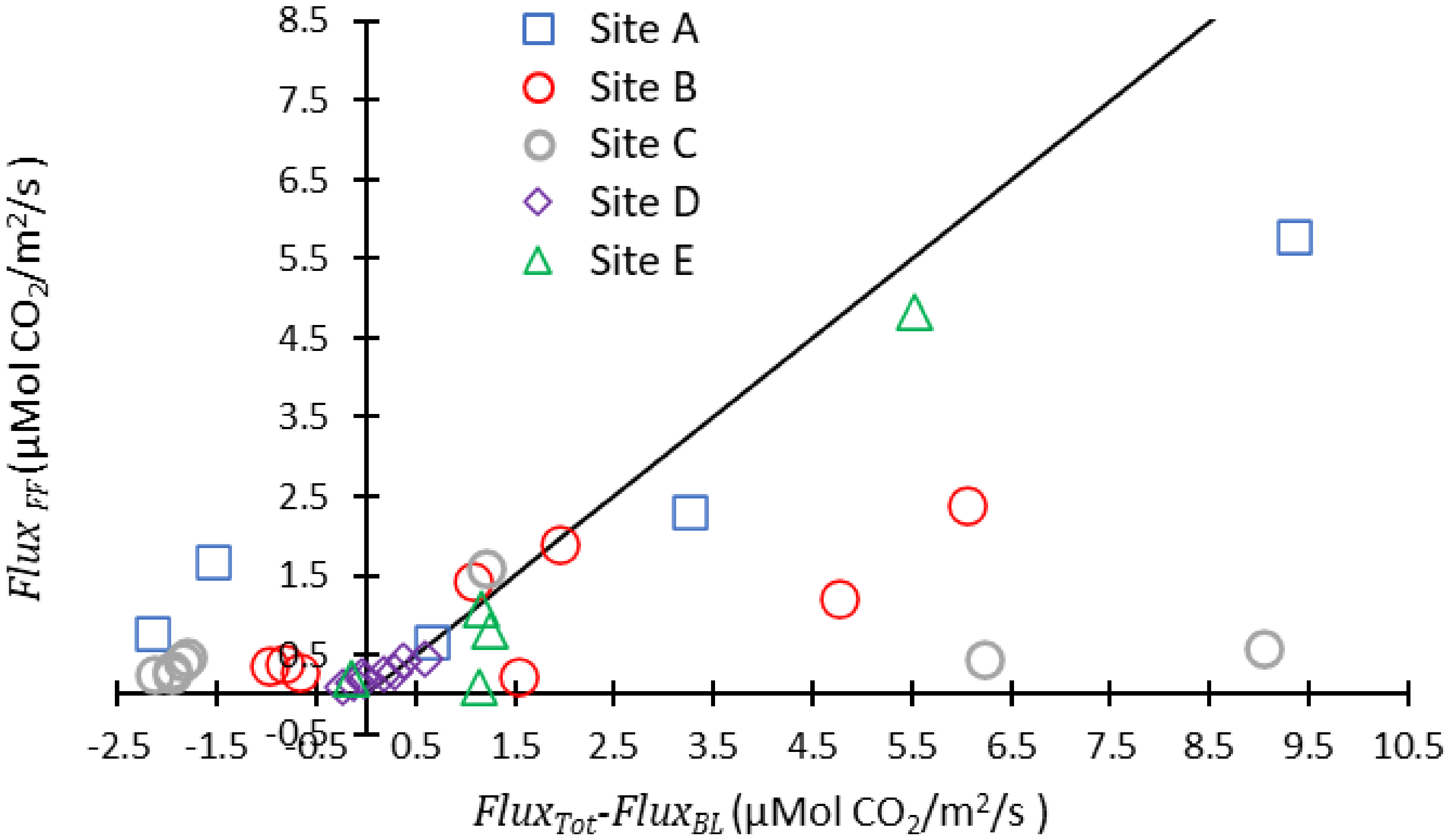


*

- Reported 25-75 percentile from Garg et al, 2017 (25 sites) larger mid 50% than all 5 sites, except Site A (Midwest Refinery)
- Garg et al, study relied in different measurement techniques

Comparing Both Corrections

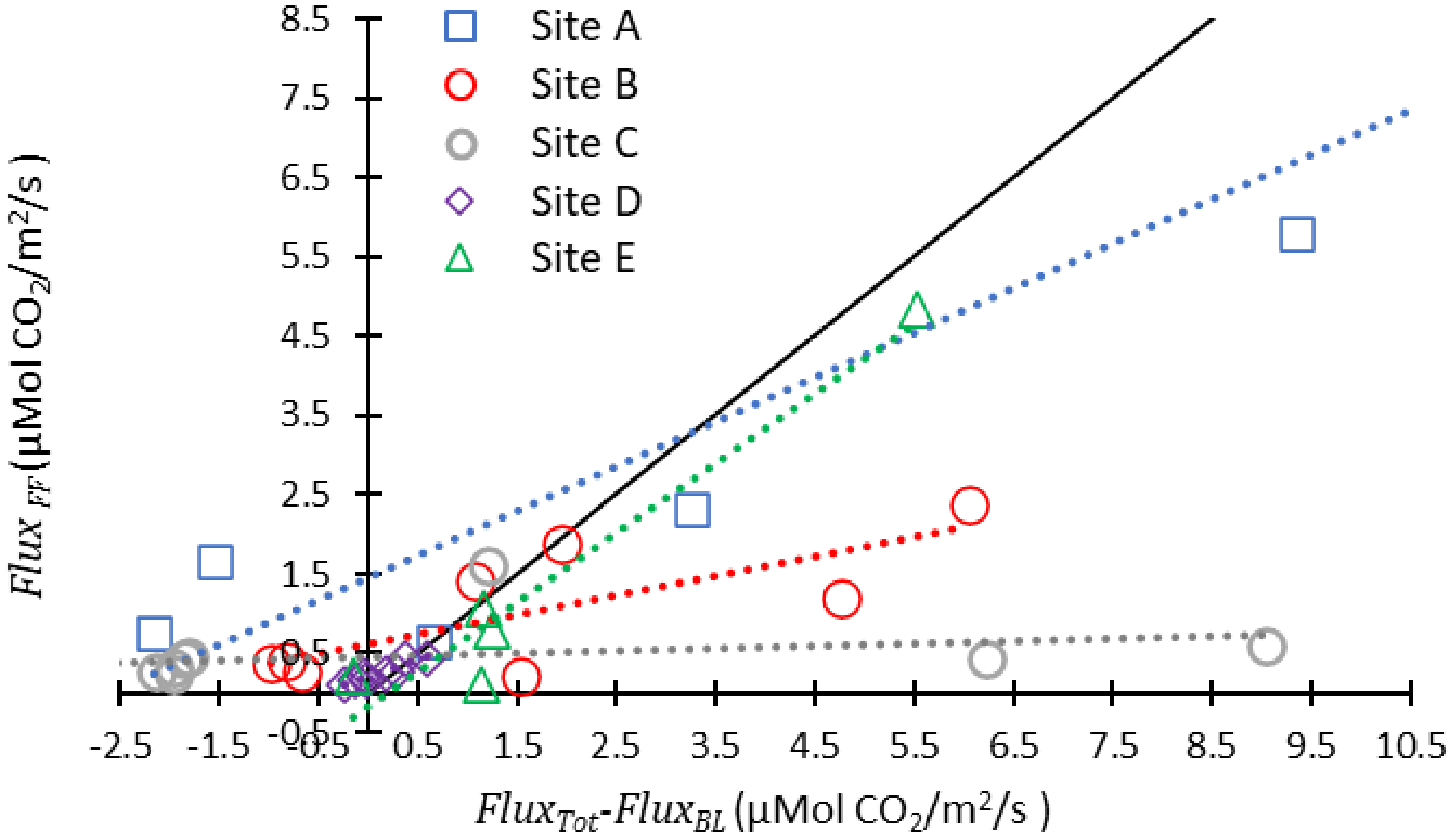
Zimbron, 2022. GWMR



Up to 4,300% differences
1,000% differences not uncommon

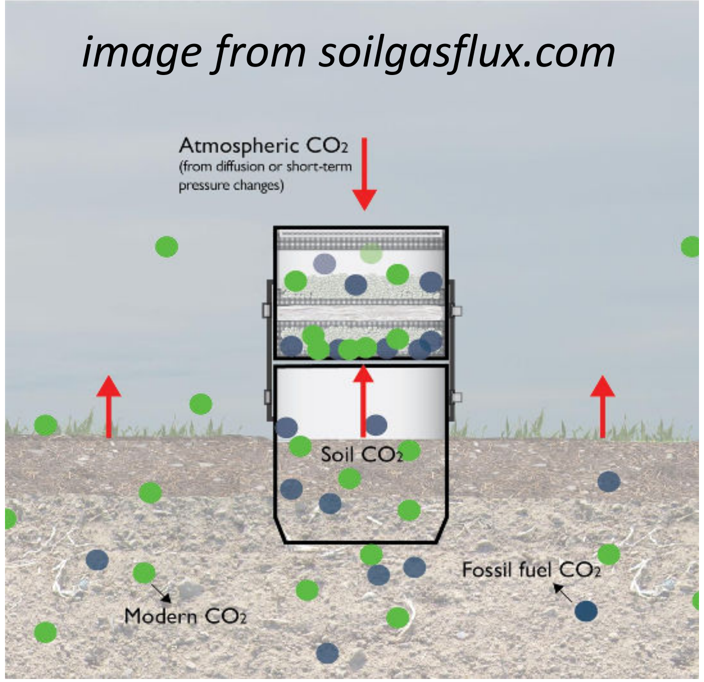
Comparing Both Corrections

Zimbron, 2022. GWMR

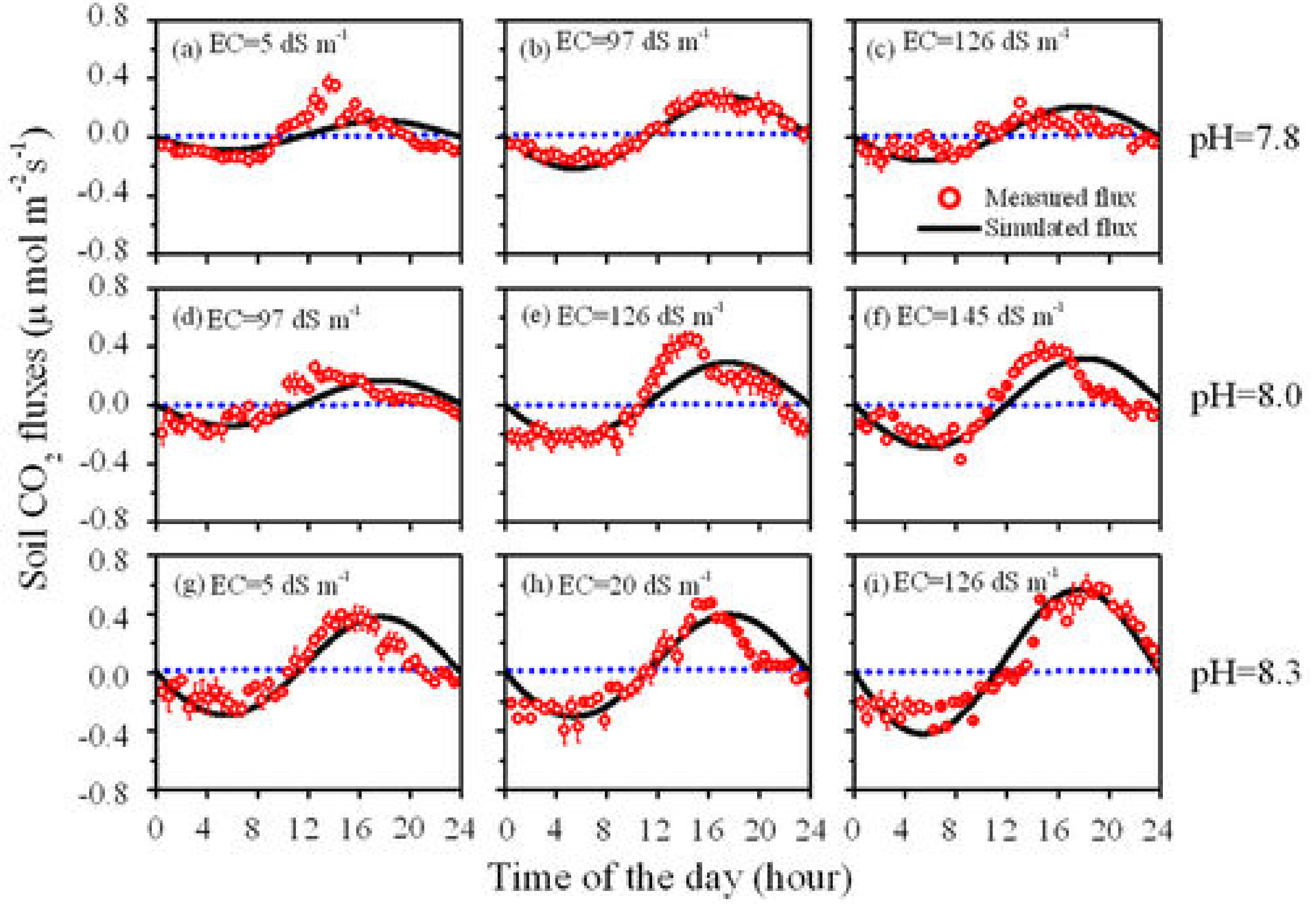


Case Study 2
Temporal variability on CO_2 Efflux

Dynamics of Soil Respiration
Short Term Vs. Long Term

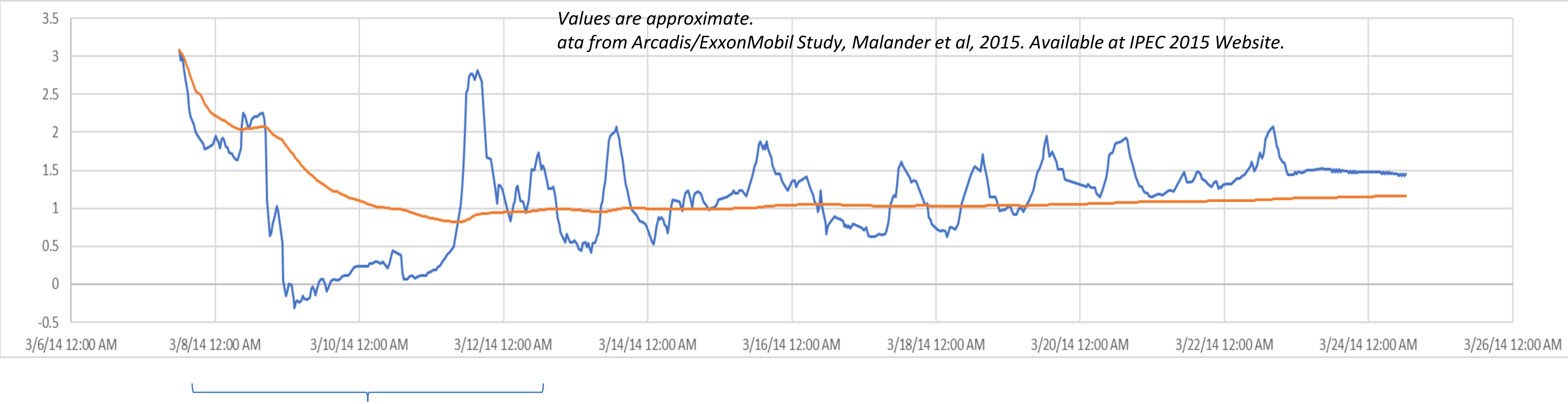


Dynamics of Soil Respiration



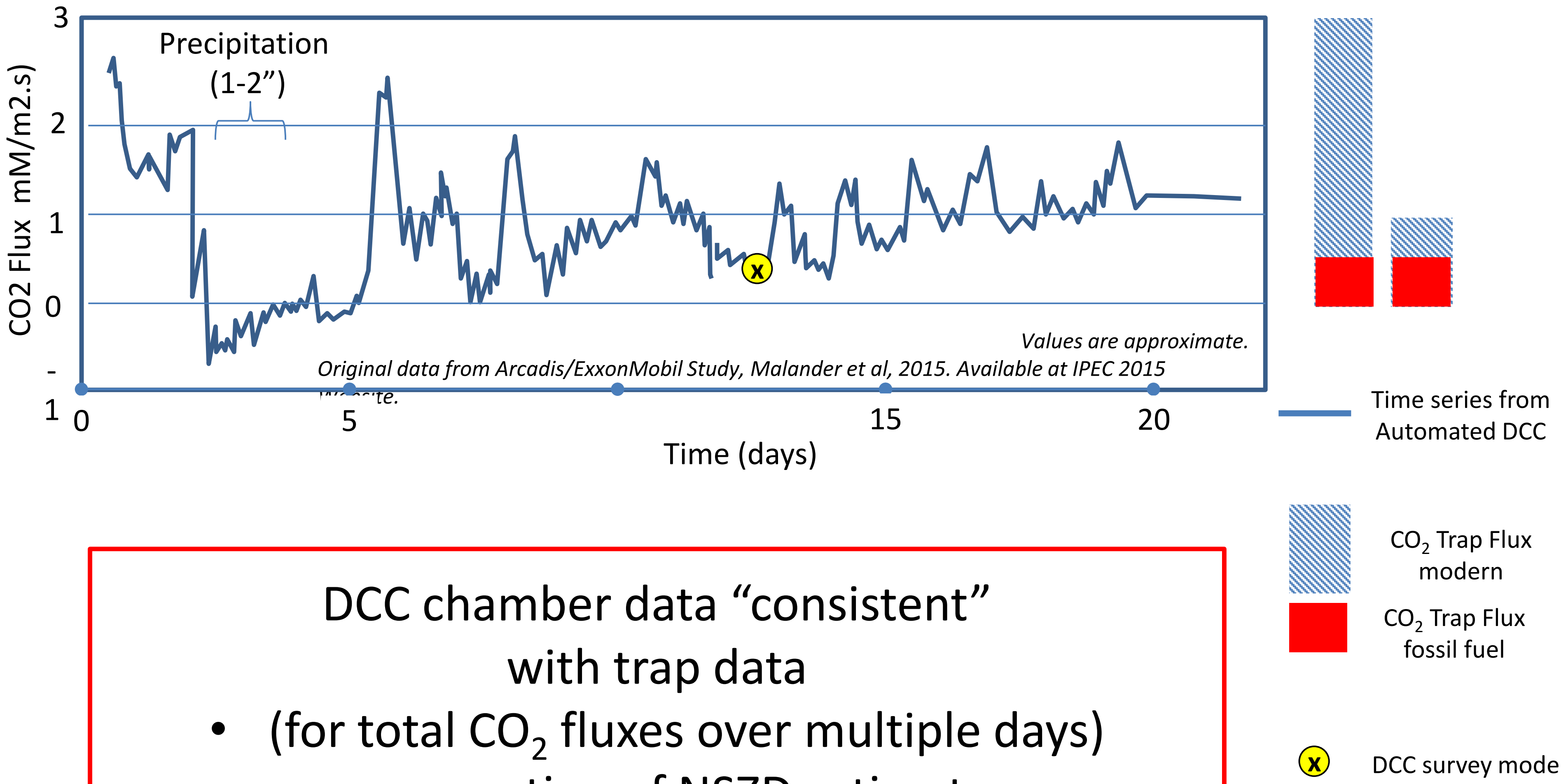
Ma, J., Z.-Y. Wang, B. A. Stevenson, X.-J. Zheng, and Y. Li (2013), An inorganic CO2diffusion and dissolution process explains negative CO2 fluxes in saline/alkaline soils, Sci. Rep., 3, 1–7, doi:10.1038/srep02025.

Temporal Variability of CO_2 Effluxes



Data set from Malander et al, 2015 suggests need ~5 days of continuous data monitoring to approach long term average

Dynamics of Soil Respiration



DCC chamber data "consistent"
with trap data

- (for total CO_2 fluxes over multiple days)
- no mention of NSZD estimates

Dynamics of Soil Respiration

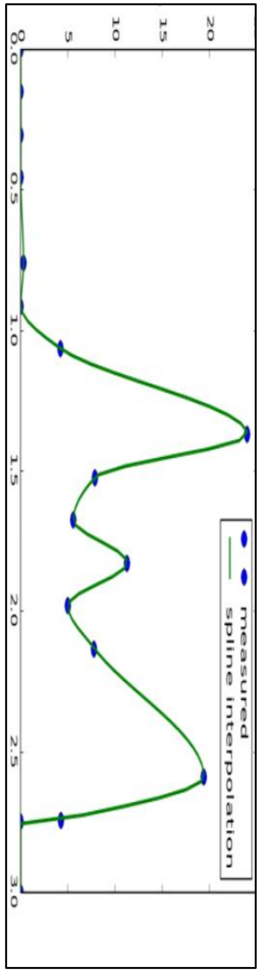
- Soil gas effluxes are cyclical
  - Daily: following daily ambient pressure and temperature cycles
  - (tidal)- 2 cycles per day at tidal cycles
  - Seasonal – soil generation process for both modern and fossil fuel CO_2 depend on soil temperature (and moisture)
  - Soil gas fluxes are susceptible to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

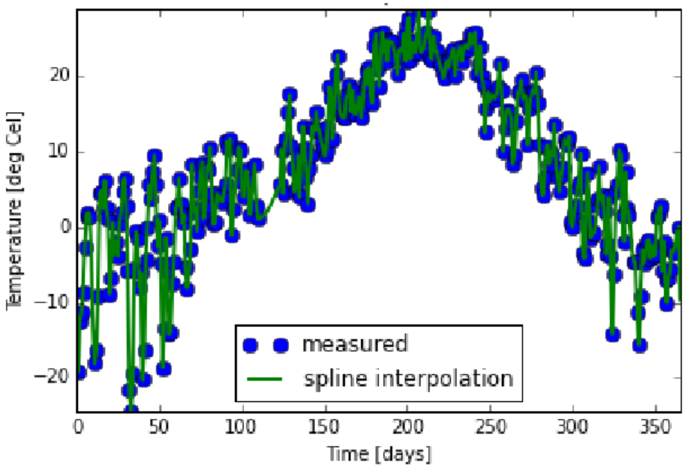
Consider temporal flux changes (and weather) when using soil respirometry to measure NSZD rates

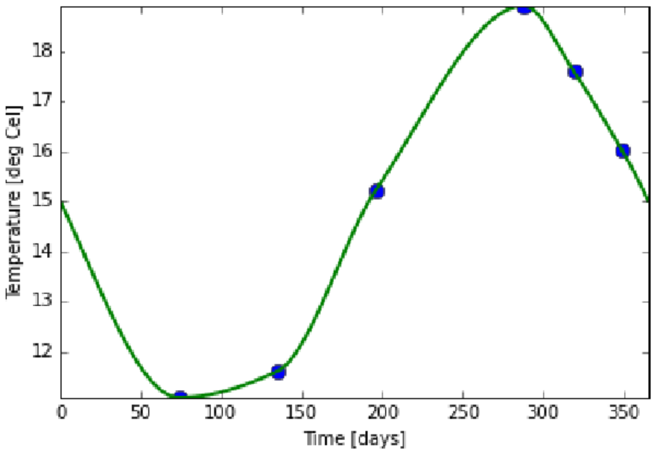
Case Study 3
Thermal Gradient: Background Correction vs. Time-Integrated Measurement

Model Inputs/Outputs

Inputs

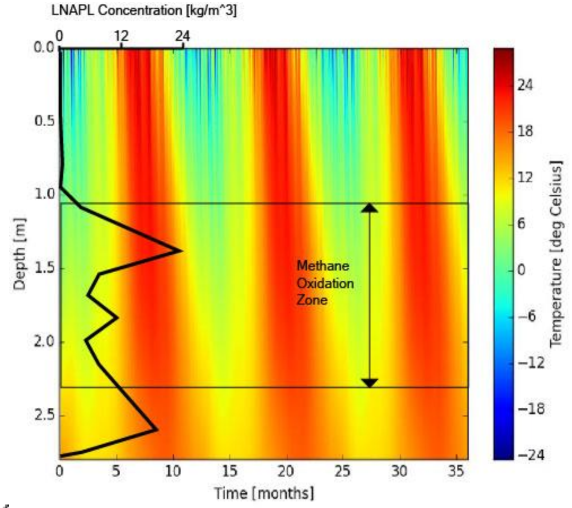


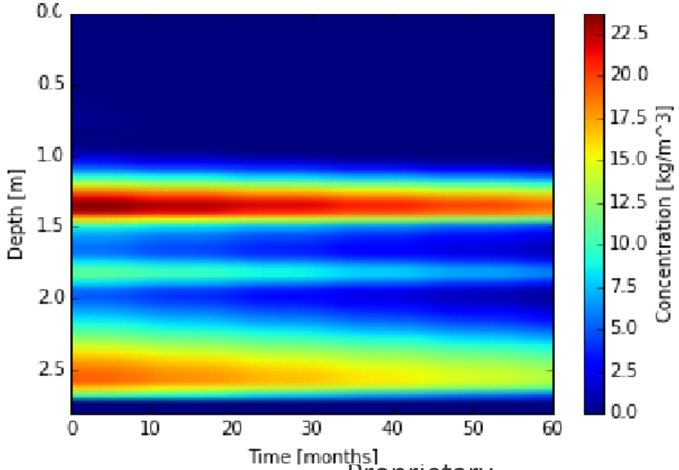




Model

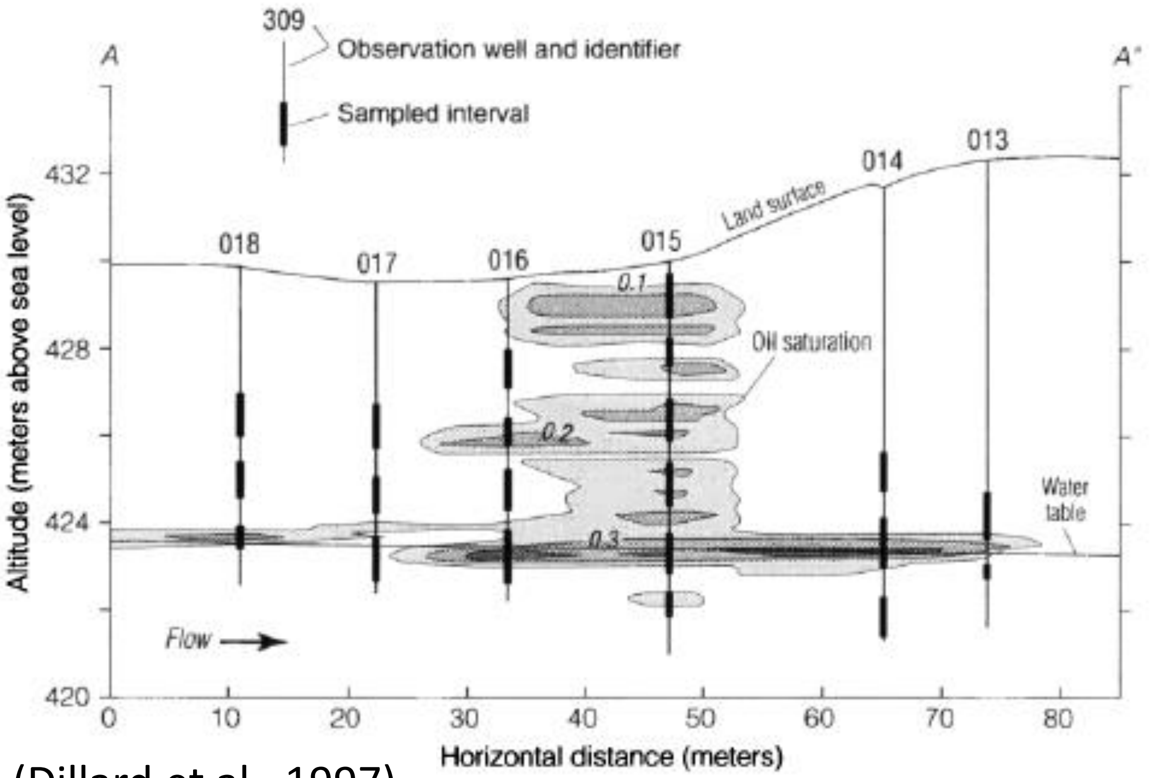
Outputs



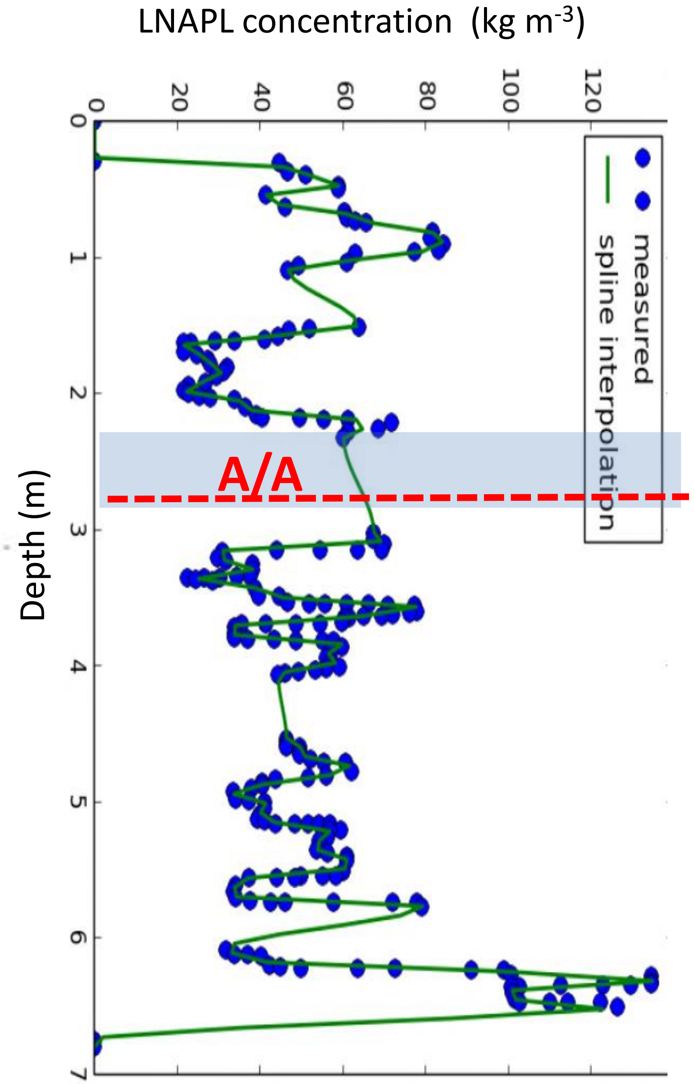


Base Case: Bemidji

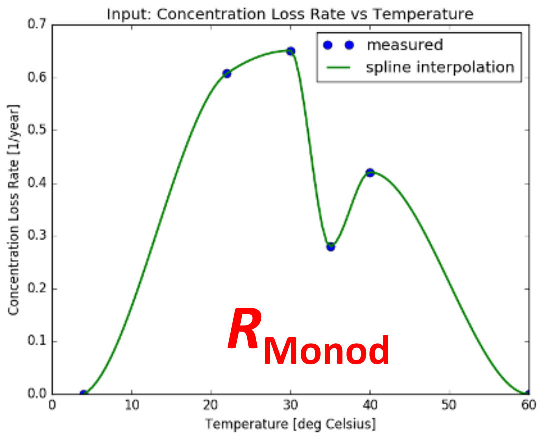
- Crude oil spill site
- Depth to Groundwater: 7 m
- Average Groundwater Temperature: 9 °C

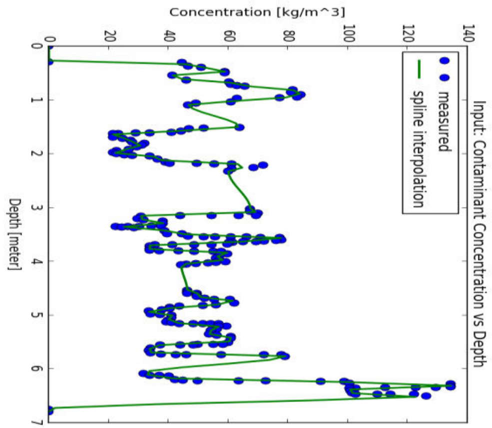


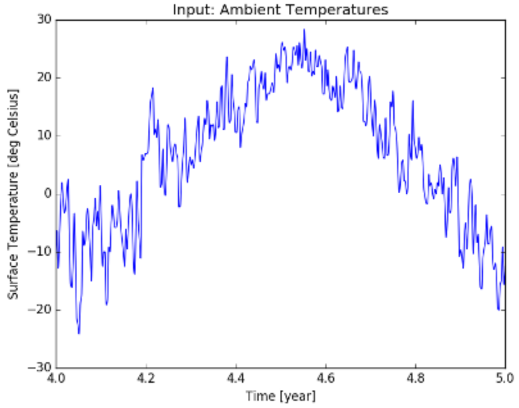
(Dillard et al., 1997)



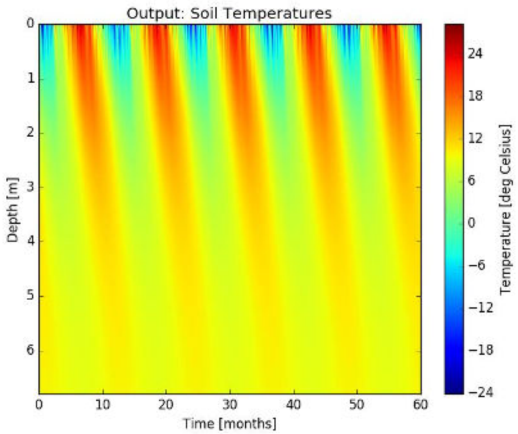
Base Case : Bemidji

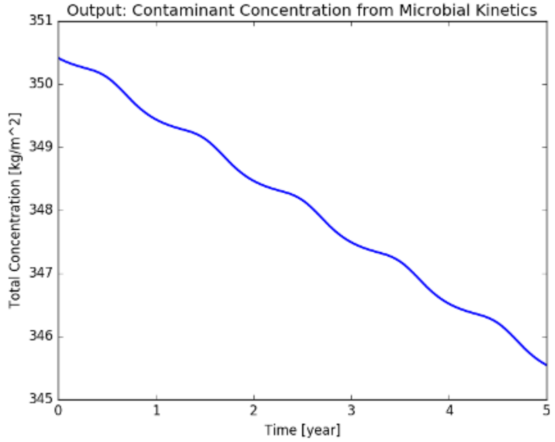


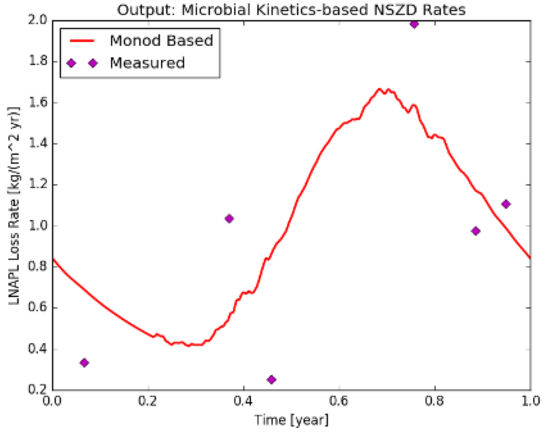




Lab data from Zeman, et al, 20??







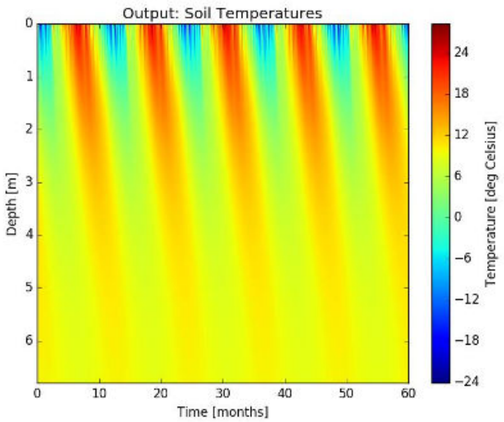
Field rates from Sihota, 2014.

1

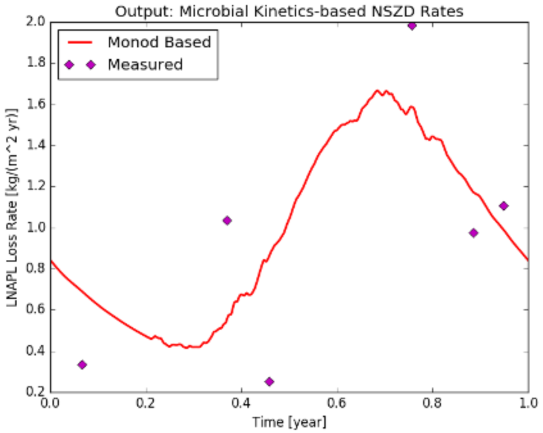
No Background Correction

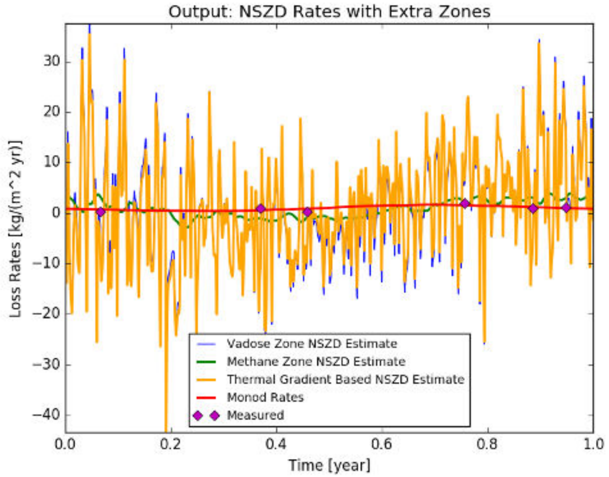
$\alpha_{site} = 3.58 \times 10^{-07}\ m^2/s$

Model Output

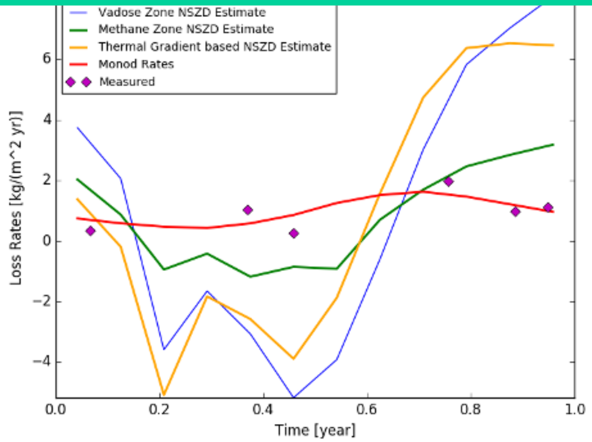


Short term Average Thermal Gradient NSZD rates



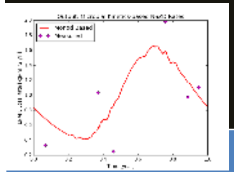


Monthly Average Thermal Gradient NSZD rates

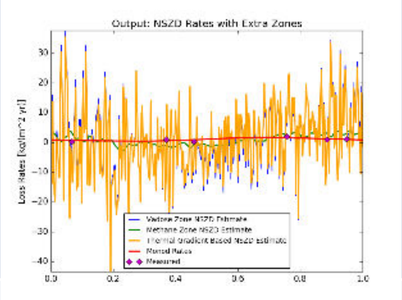
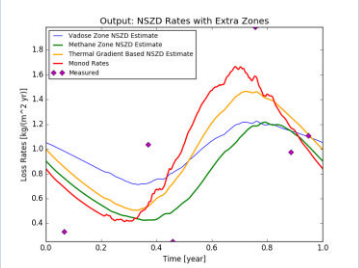
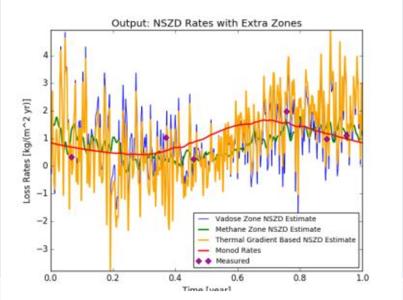
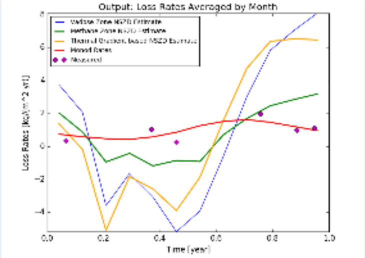
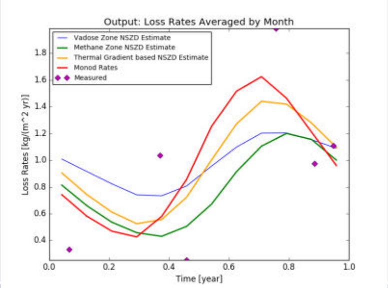
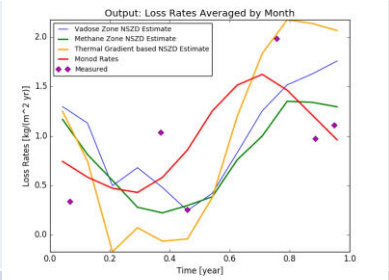


Annual Average Thermal Gradient NSZD rates

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

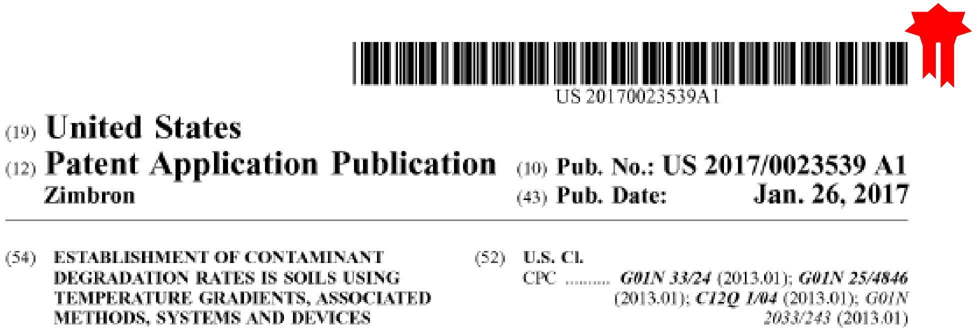


Average Annual Thermal Gradients

	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



US 20170023539A1

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Zimbron
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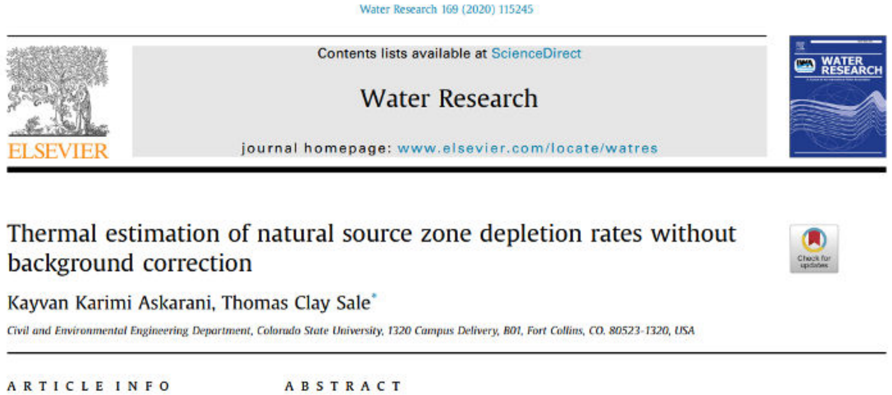
(43) Pub. Date: Jan. 26, 2017

(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

ARTICLE INFO

ABSTRACT

Both long term approaches boil down to similar practice: need long term thermal gradient-based estimates to reduce error
Other sources cite extreme sensitivity of thermal gradient to background location selection (Rayner et al, 2020)

Finishing Thoughts and Best Practices

- Indirect methods + "fitting parameter within literature range value" (gradient methods) can easily be made consistent with direct methods used as reference (i.e., CO_2 flux methods) – questionable predictive value

- Background correction method is a rough approximation
  - CO_2 efflux, thermal gradient method

- Long term, time-integrated measurements over multiple days even out diurnal nature of system measured (and seasonal, for thermal gradient)

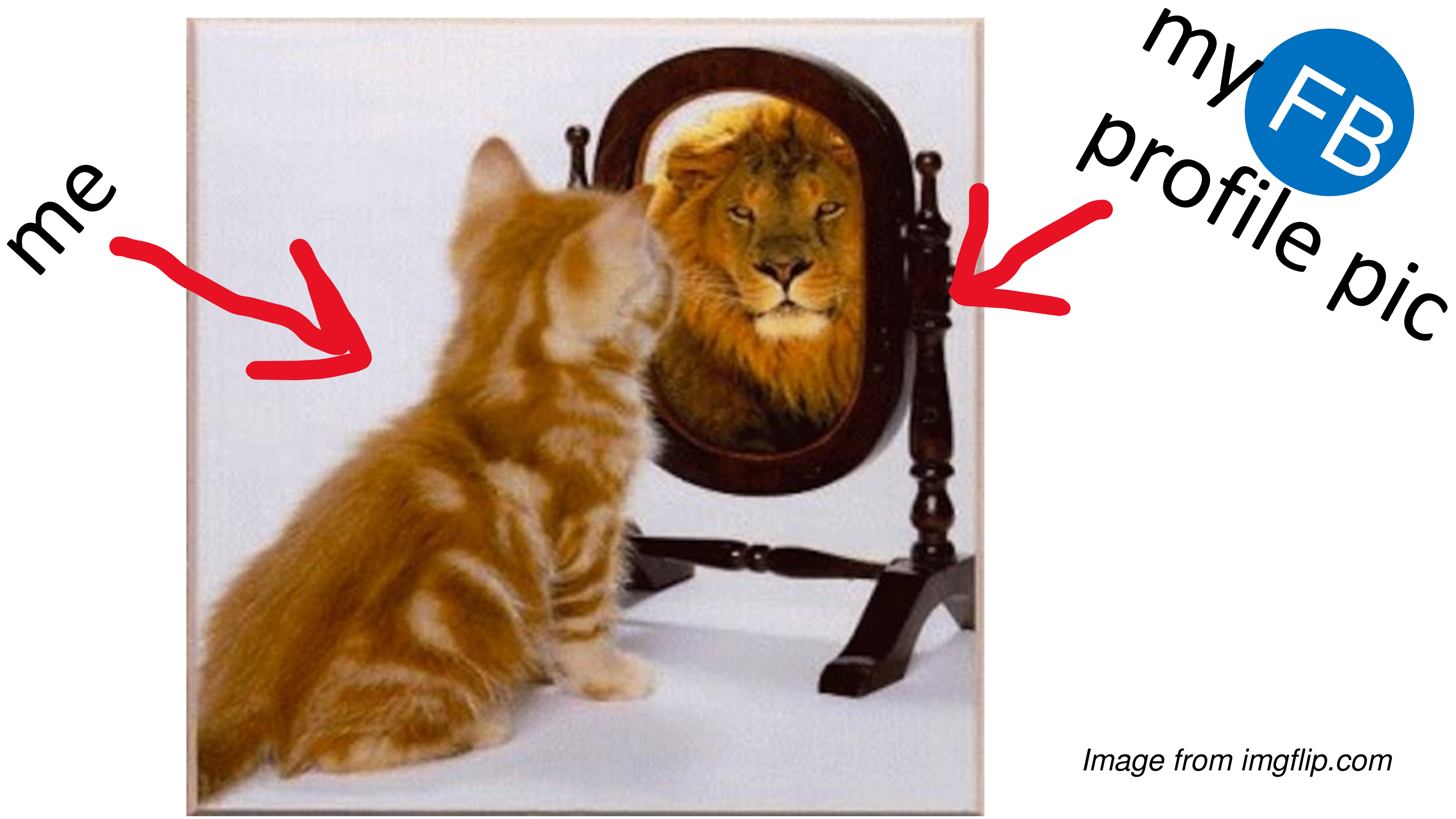
- Mass balance methods: ^{14}C correction provides higher reliability
  - When coupled with long term measurement

- After many consensus guidance documents, the messaging on NSZD and NSZD rate measurement is still confusing
  - Unclear distinction between line of evidence and rate measurement
  - Publication bias in NSZD?

Food for Thought: Measurement Uncertainty

Image from istockphoto.com

Food for Thought: Measurement Uncertainty



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