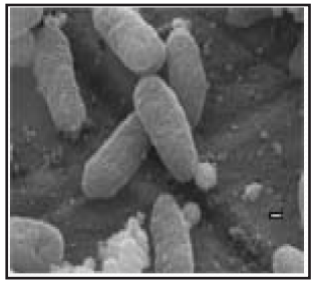
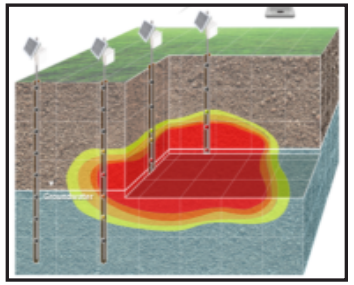
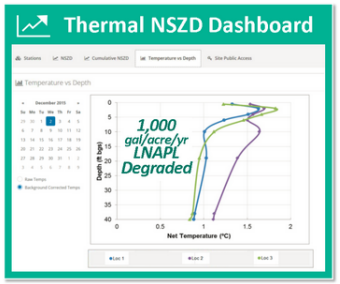
More Data, Less LNAPL: Insights from Over 15 Years of Research on Natural Source Zone Depletion (NSZD)

GSI ENVIRONMENTAL

Battelle Bioremediation Conference







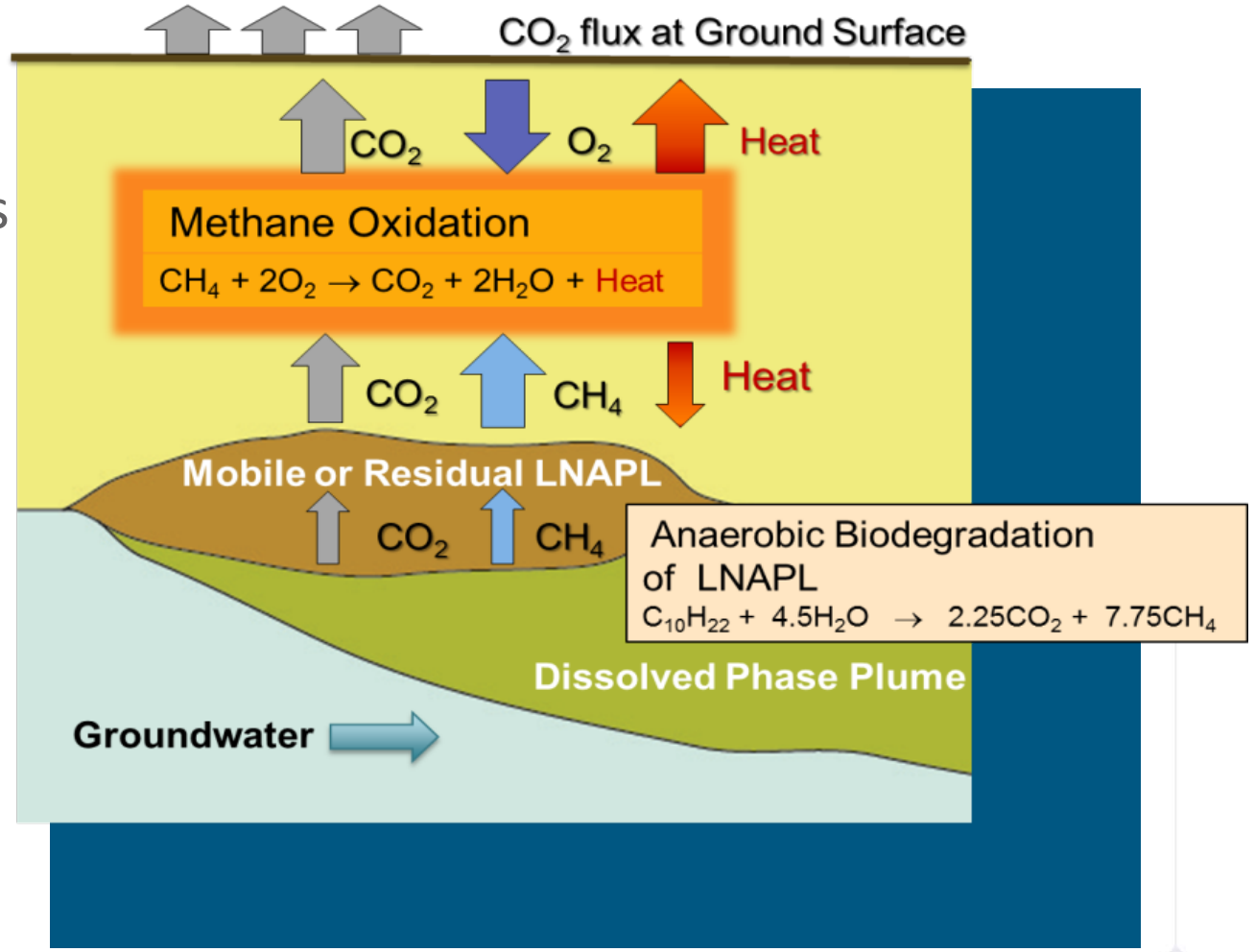
9 May 2023

Kenneth L. Walker, Jr., PE, PG
Poonam Kulkarni, PE
Charles Newell, PhD, PE
Kayvan Karimi Askarani, PhD
Beatrice Yue Li, PhD, PE
Tom McHugh, PhD, DABT

What is NSZD?

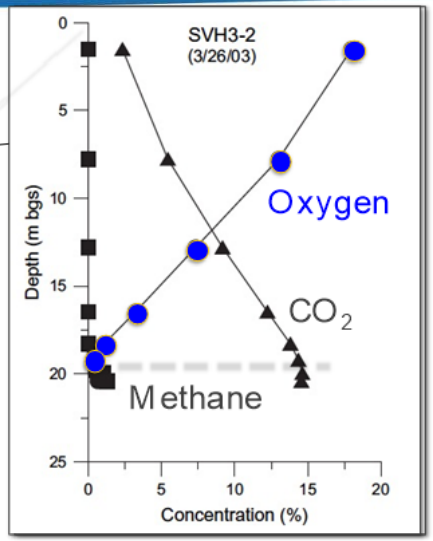
Natural Source Zone Depletion

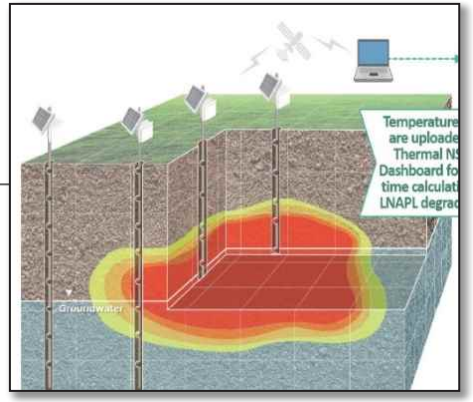
- **Natural Source Zone Depletion (NSZD)** is a combination of processes that reduce mass of LNAPL in the subsurface via dissolution, volatilization, and biodegradation (ITRC, 2009)
- **How are these Rates Used?**
  - Confirm that LNAPL is biodegrading and quantify the rate
  - More accurate estimation of remediation timeframe by NSZD
  - Evaluate effectiveness of active remediation systems



Measuring NSZD: Four Methods

- Gradient Method
- Dynamic Closed Chamber (DCC)
- Carbon Traps
- Thermal Monitoring

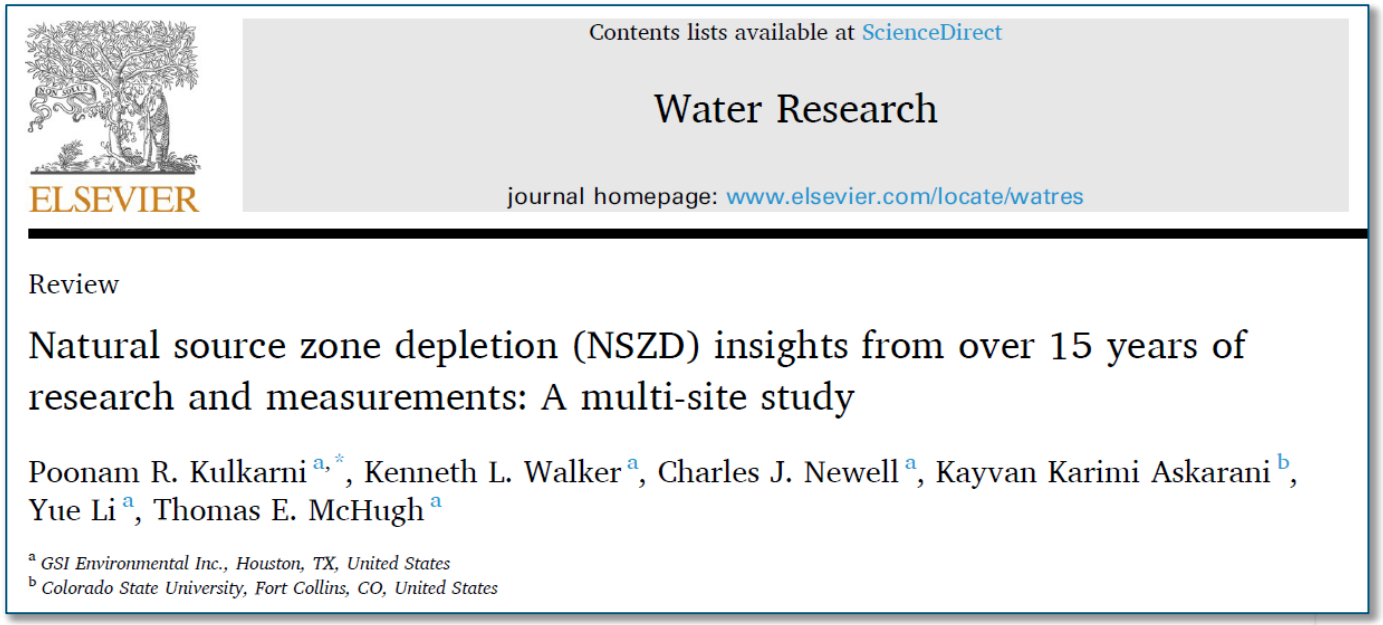




Goals, Methods, and Dataset

Key Study Questions

- Across the range of sites, what are the range of measured site-average NSZD rates?
- Do site-average NSZD rates change with fuel type?
- How comparable are NSZD rate measurement methods when employed at the same site, and is there method bias across sites?
- How do site-average NSZD rates vary over time (seasonal and annual)?



Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Review

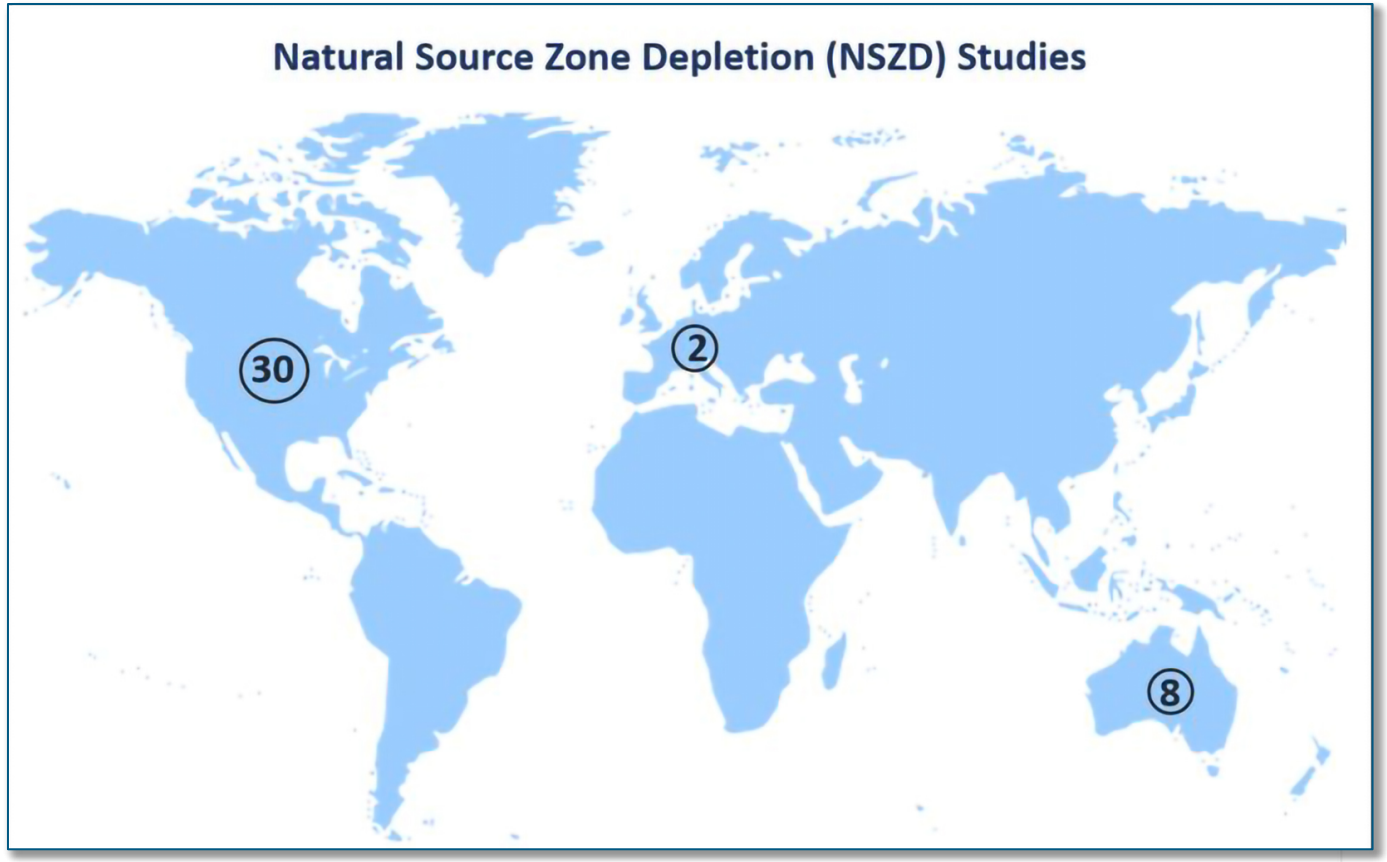
Natural source zone depletion (NSZD) insights from over 15 years of research and measurements: A multi-site study

Poonam R. Kulkarni [a,*], Kenneth L. Walker [a], Charles J. Newell [a], Kayvan Karimi Askarani [b], Yue Li [a], Thomas E. McHugh [a]

[a] GSI Environmental Inc., Houston, TX, United States
[b] Colorado State University, Fort Collins, CO, United States

Dataset Overview

- Compilation of published literature (individual site NSZD assessments)
- LNAPL-impacted sites across: US, Australia, Canada, Europe
- Data Collected:
  - Site location
  - LNAPL fuel type
  - NSZD rates and measurement method
  - # of measurement locations, and sampling frequency
- Calculated: Site-average NSZD rate



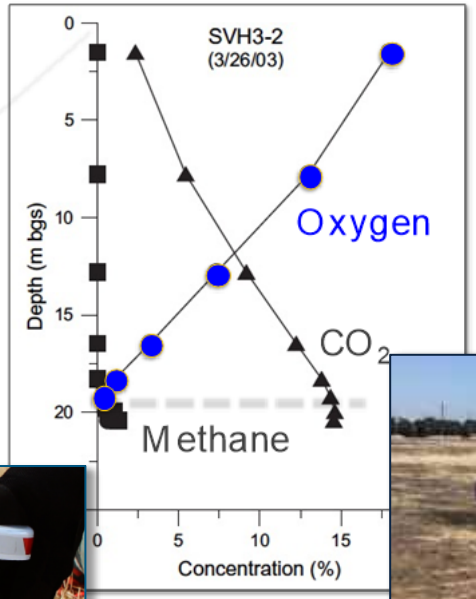
Final Dataset: 40 Sites

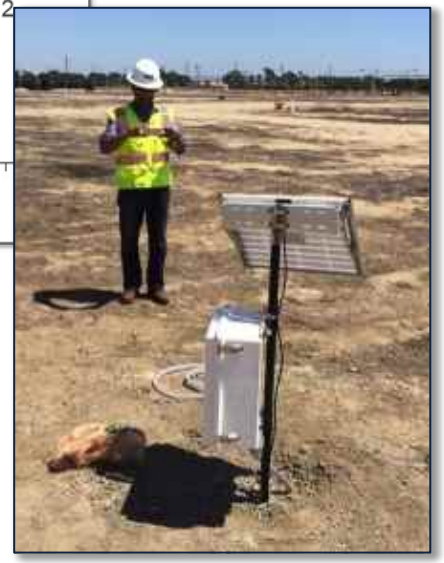
Dataset
Method and Measurement Frequency

# of Locations per Site:
Gradient Method: 1-6
DCC: 2-150
Carbon Traps: 2-17
Thermal Monitoring: 1-21

Total Measurements:
Gradient Method: 2-32
DCC: 4-332
Carbon Traps: 2-26
Thermal Monitoring: 2-4,160

# of Sites:
Gradient Method: 11
DCC: 16
Carbon Traps: 22
Thermal Monitoring: 18





Varying Method Sampling Frequency and Number of Locations per Site

Results

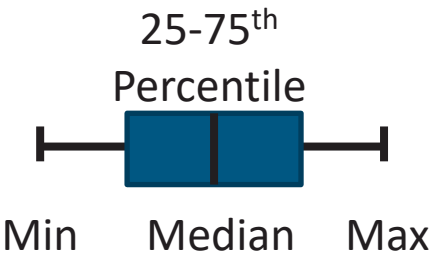
Across the Range of Sites, What are the Range of Measured Site-Average NSZD Rates?

	Site-Average NSZD Rate, All Methods (gal/acre/yr)
Minimum	70
10th Percentile	170
25th Percentile	300
Median	1,020
75th Percentile	2,720
90th Percentile	5,490
Maximum	16,250

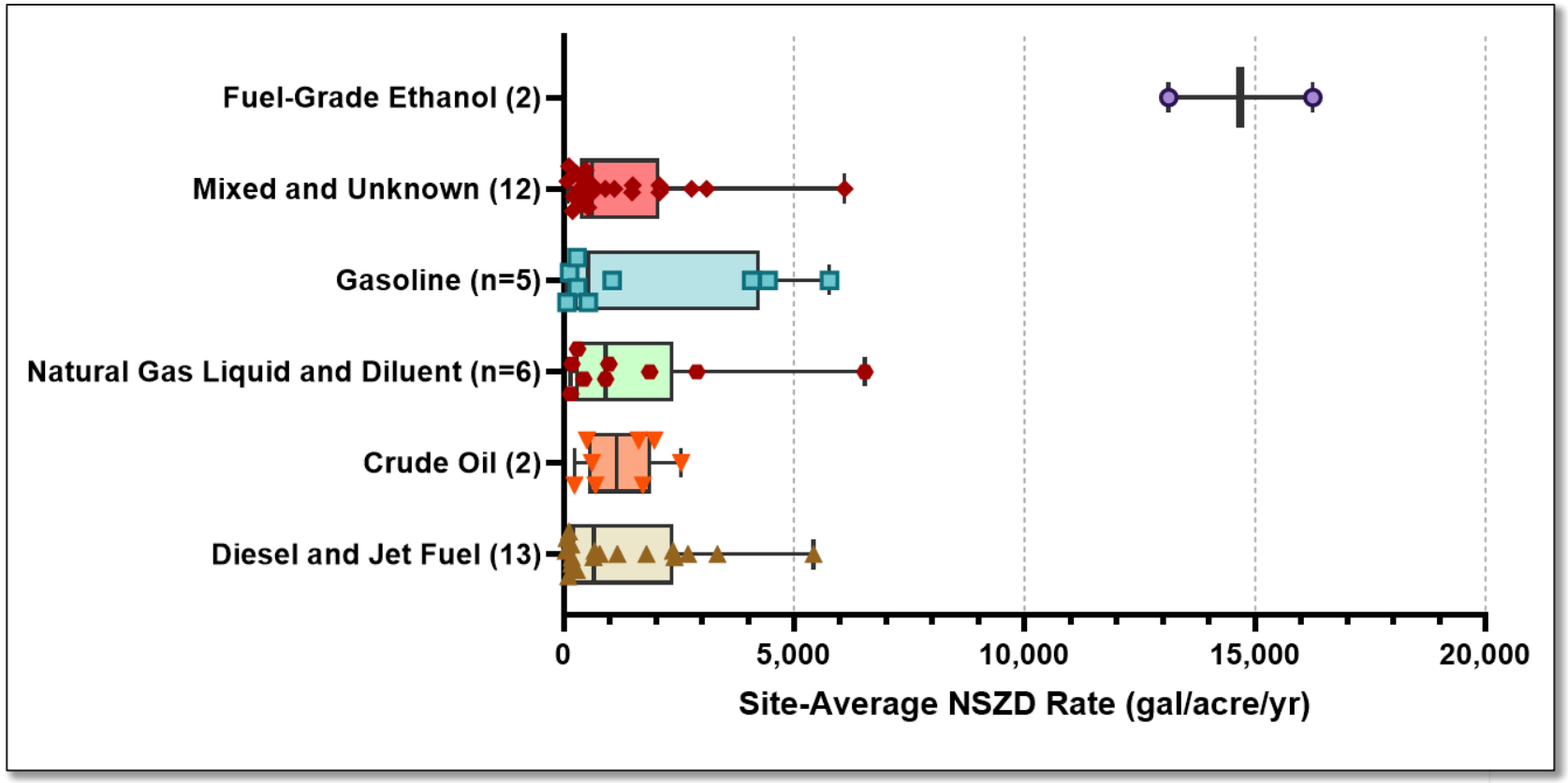
Key Points:

- *All sites studied had measurable NSZD rates, with **90% of sites >170 gal/ac/yr***
- *Median Site-Average NSZD Rate of **1,020 gal/ac/yr***

Do Site-Average NSZD Rates Vary with Fuel Type?



Fuel Type and Number of Sites	Median Site-Wide NSZD Rate (gal/acre/year)
Natural Gas Liquid (n=5)	540
Mixed (n=7)	430
Crude Oil (n=2)	1,160
Gasoline (n=5)	580
Diesel (n=7)	810
Jet Fuel (n=6)	170
Unknown (n=2)	630
Fuel-Grade Ethanol (n=2)	14,730

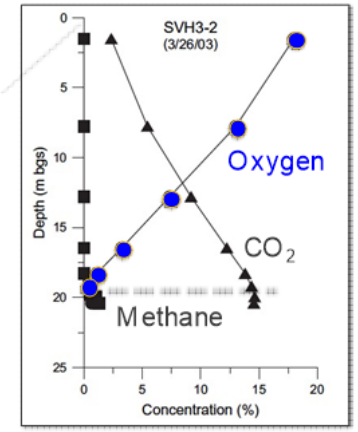


GSI ENVIRONMENTAL

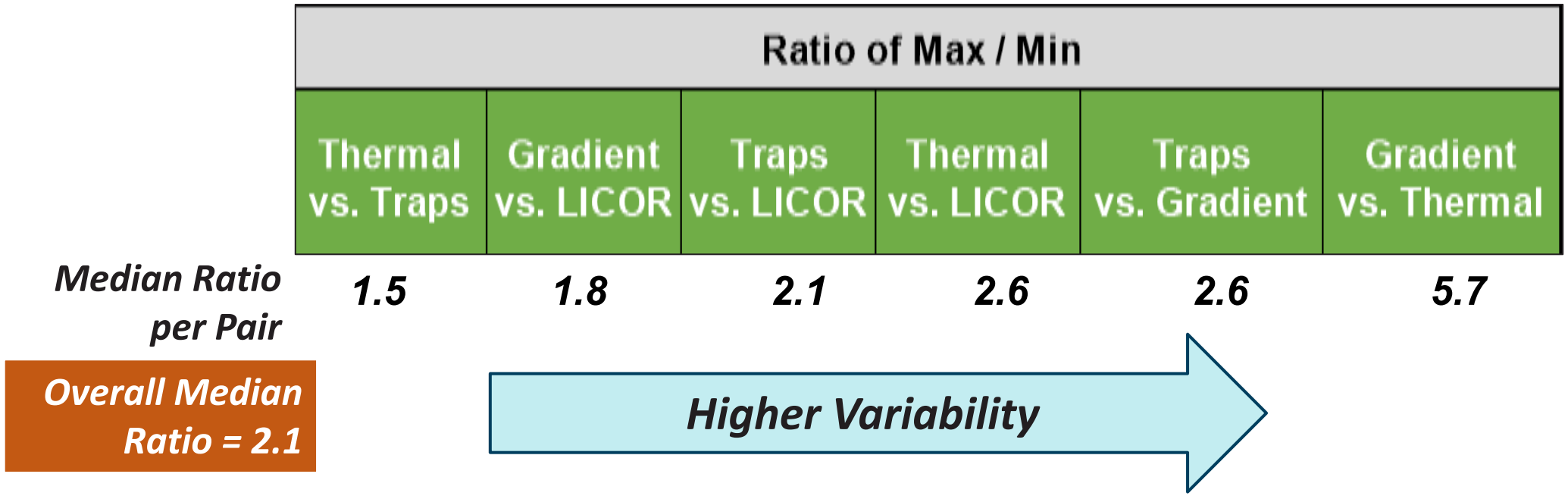
Key Point: Fuel type is not a primary driver of NSZD rates, indicating other site-specific factors have more of an impact

How comparable are NSZD rate measurement methods when employed at the same site?

- Subset of 13 sites where more than one method was used
  - Site-Average NSZD rates known to vary with measurement method
- Ratio of Max/Min rates per combination (e.g., Ratio of Thermal vs. Traps; Gradient vs. LI-COR)
- Total Combinations: 31



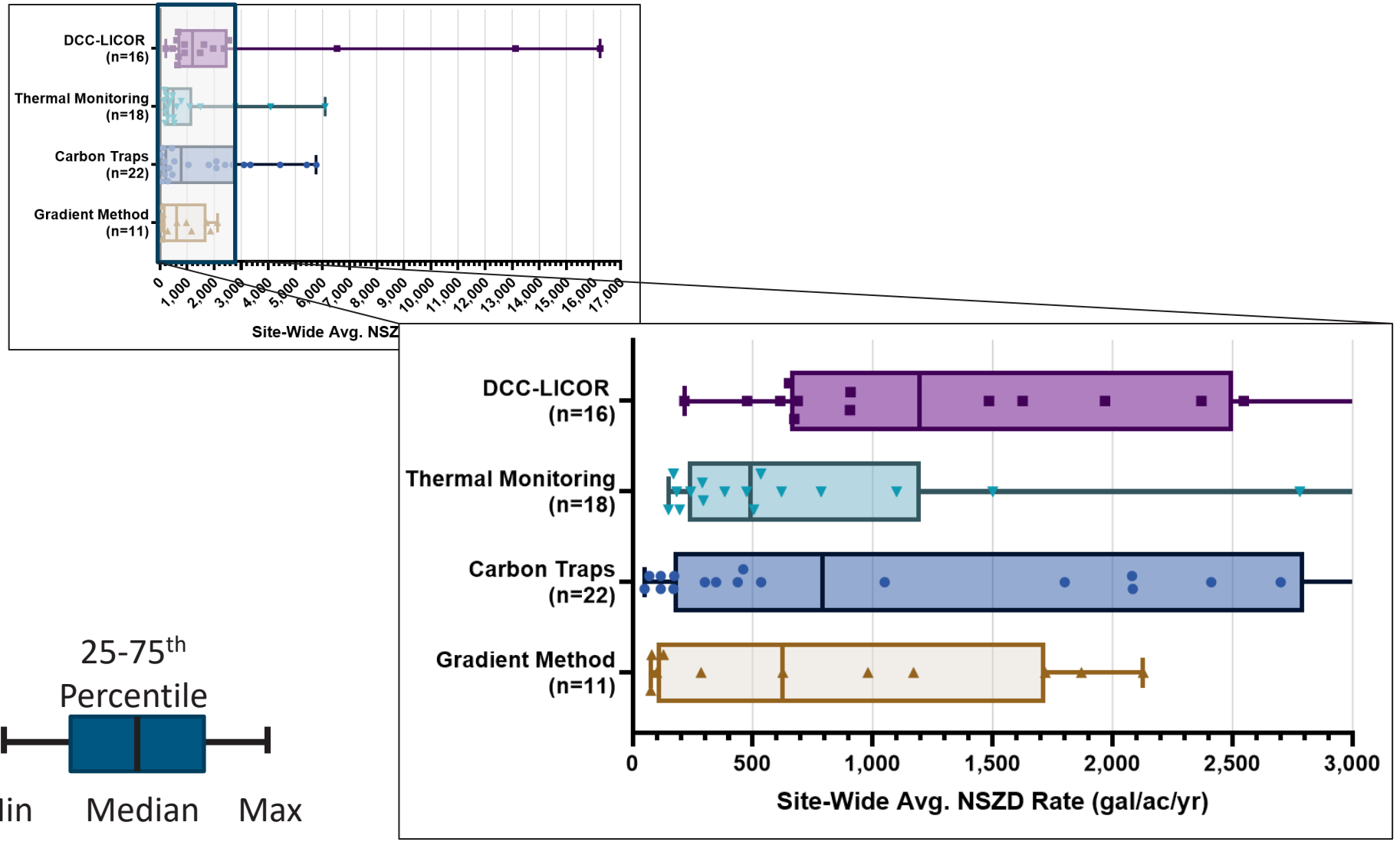
How comparable are NSZD rate measurement methods when employed at the same site?



Key Points:

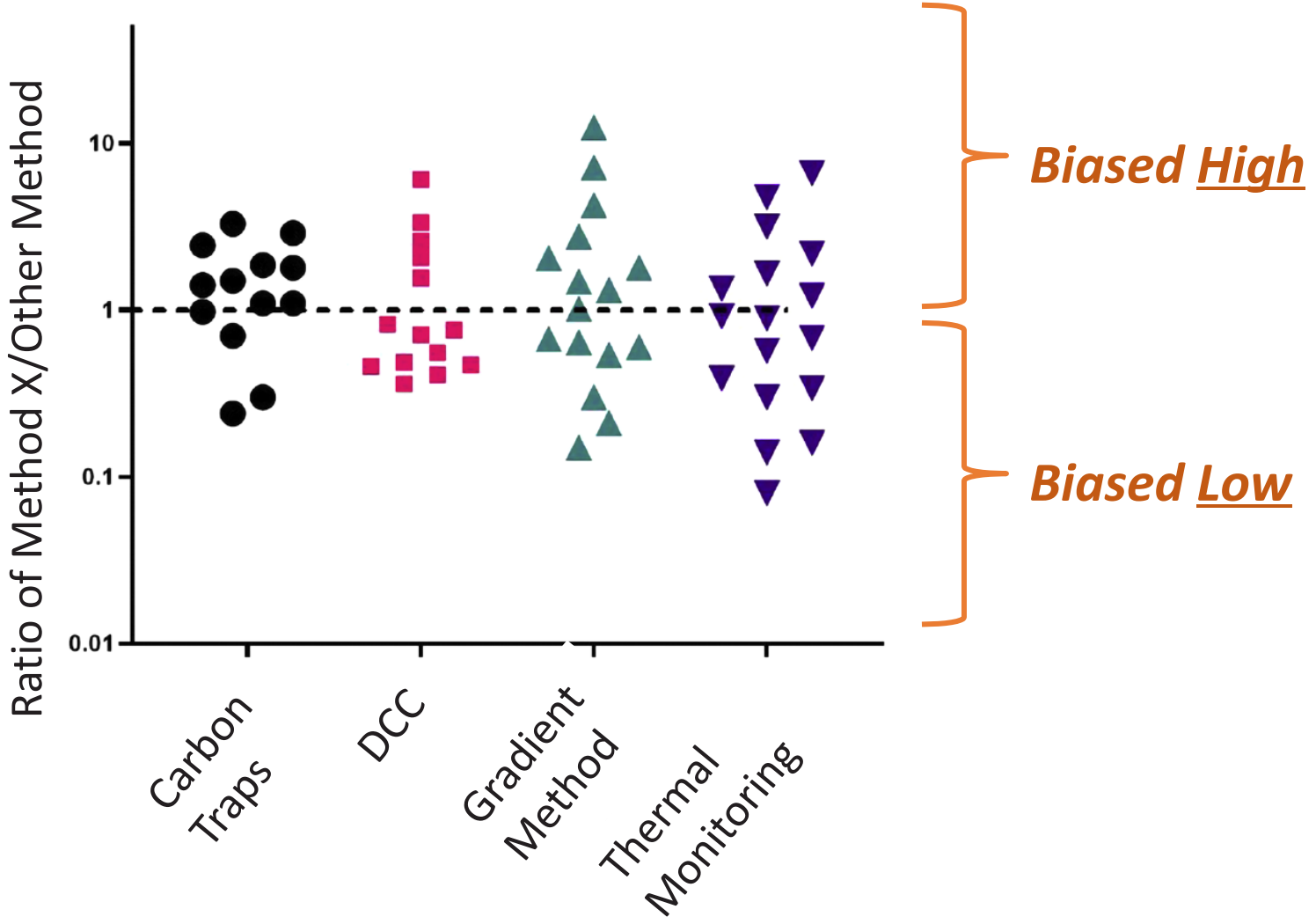
- *Median ratios vary with paired methods*
- *Overall Median Ratio = **2.1** (e.g., at a typical site, NSZD rates vary by a factor of 2 with different measurement methods)*

Is there Measurement Method Bias?
Distribution Across All Sites



Using Kruskal Wallis Test, no statistically significant difference in rates for any method ($p>0.05$)

Is there Measurement Method Bias?
Paired Methods



Key Point:

- *No single method had statistically significant high or low bias ($p>0.05$)*

How do site-average NSZD rates vary over time (seasonal)?

- Warmer temperatures enhance biodegradation
  - Application in wastewater treatment (anaerobic digesters)
  - Microcosm studies (Zeman et al., 2014)
  - Big data evaluation (>2,000 sites) of source attenuation rates in groundwater (Kulkarni et al., 2017)
- Natural seasonal subsurface temperate fluctuations
- Arrhenius Equation: $Q_{10} = (R_2/R_1)^{[10/(T2-T1)]}$

Groundwater Monitoring&Remediation

Impact of Temperature on Groundwater Source Attenuation Rates at Hydrocarbon Sites

by Poonam R. Kulkarni, David C. King, Thomas E. McHugh, David T. Adamson, and Charles J. Newell

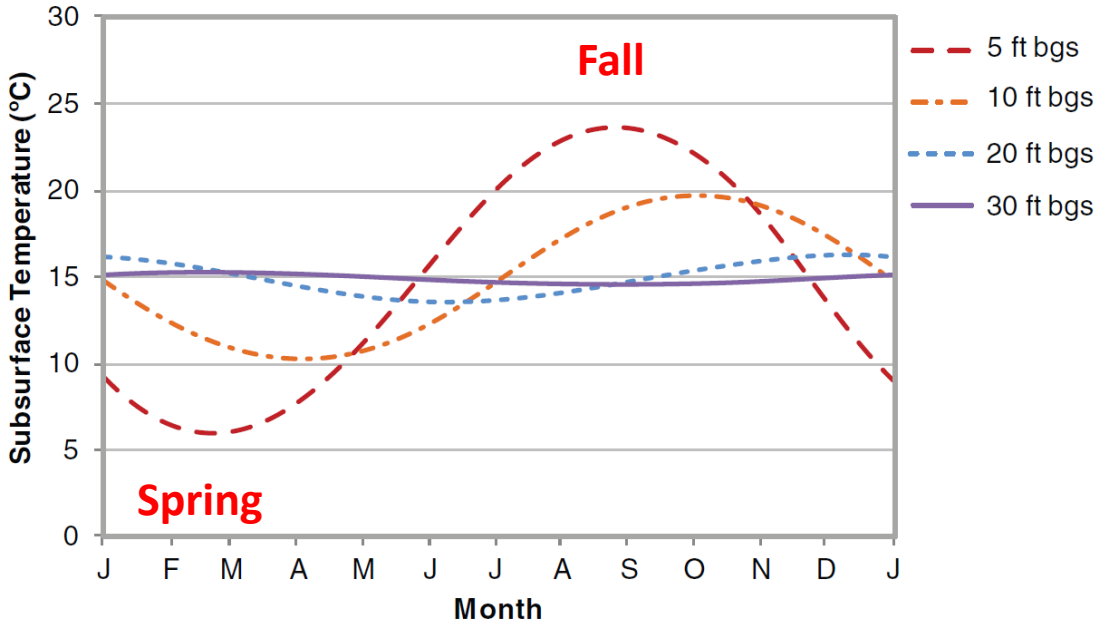
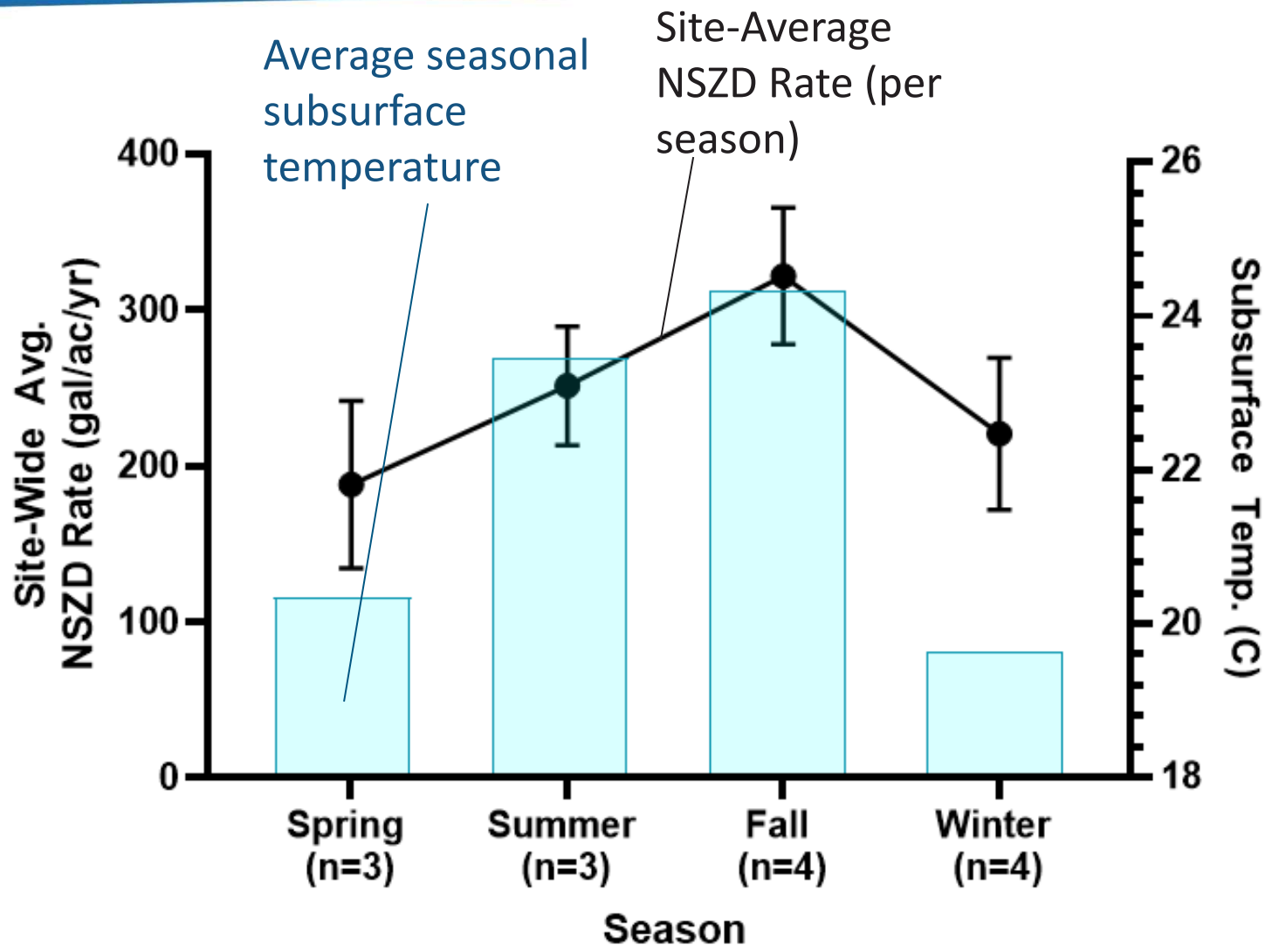


Figure 2. Typical subsurface temperature profiles over time at various depths.

Key Point: *Typical Q_{10} value = 2.0 (doubling of rate with 10 °C increase in temperature)*

How do site-average NSZD rates vary over time (seasonal)?

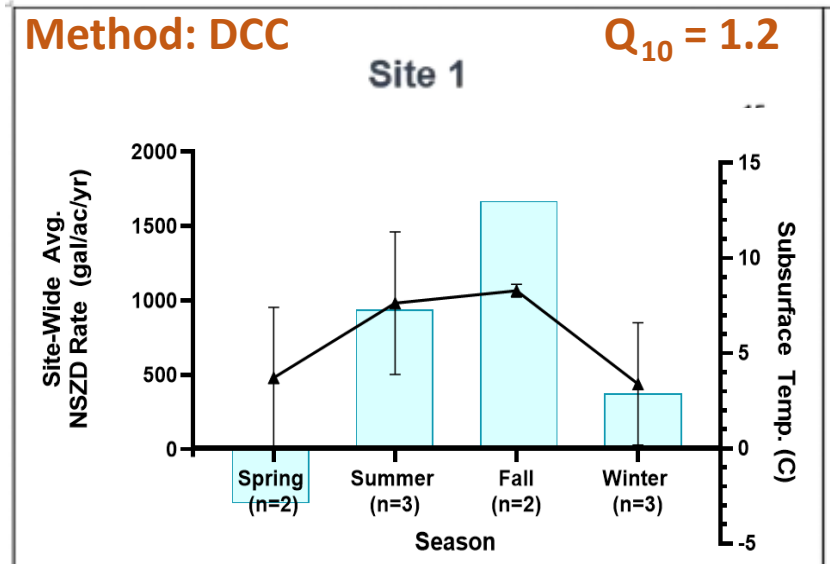
- Highest rates in Fall, when subsurface temperatures are highest (2 sites)
- Little or no seasonal variation due to variability (2 sites)
- Q_{10} values using subsurface temperatures and NSZD rates measured in Fall vs. Spring

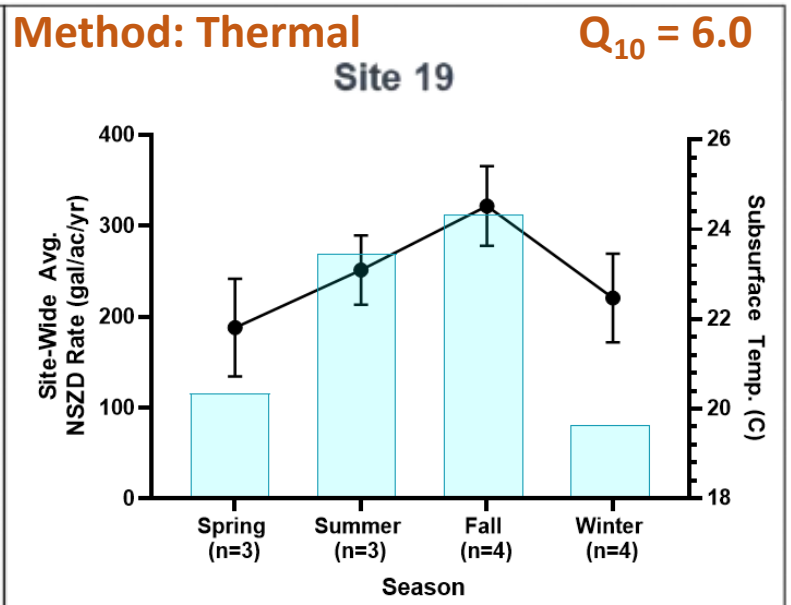


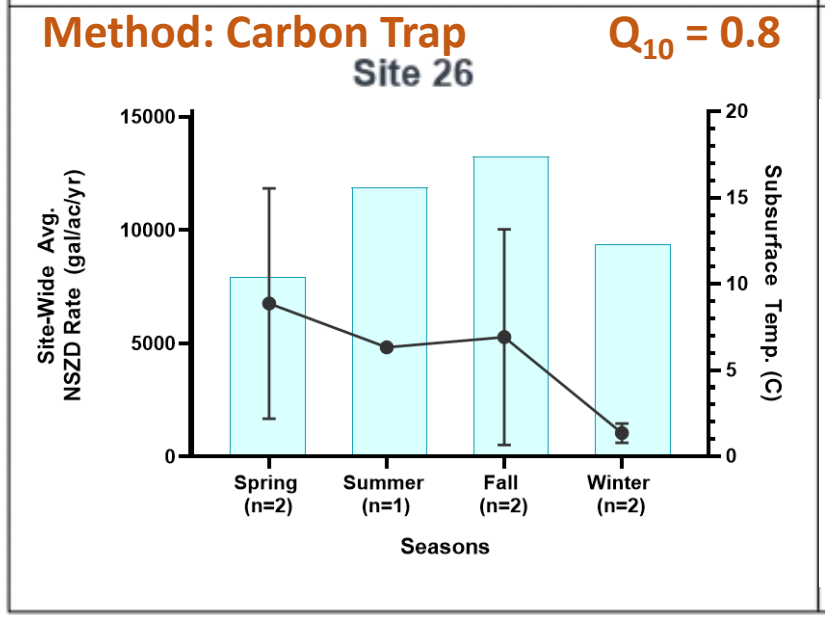
How do site-average NSZD rates vary over time (seasonal)?

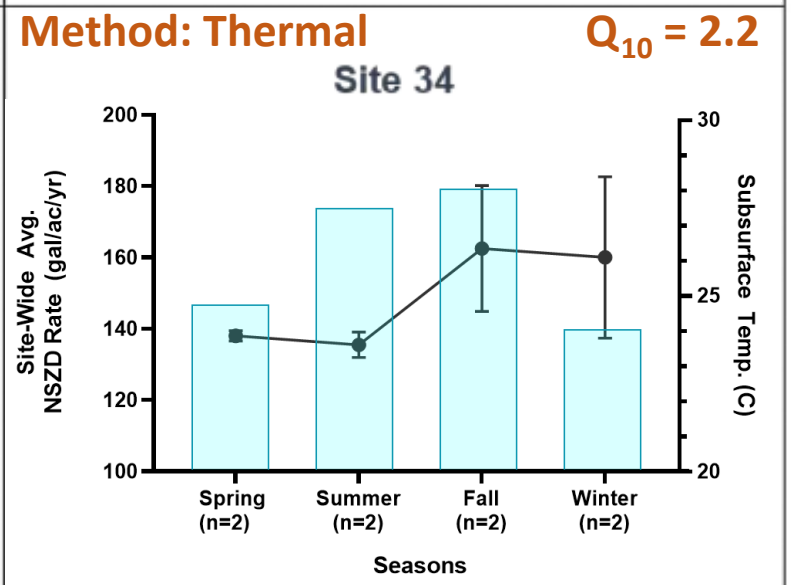
Key Points:

- *Some sites show clear seasonal differences in NSZD rates*
- *Median Q_{10} = 2.2*
- *Potential for doubling biodegradation rates with a 10 °C increase in subsurface temperature*









GSI ENVIRONMENTAL

How do site-average NSZD rates vary over time (Annual)?

- Subset of 5 sites
  - Multiple years
  - At least 2 seasons per year
- Annual site-average NSZD rates vary 1.1 - 4.9X across years
- Temperature-based methods show lower annual variability (1.4 - 1.9X) compared to other methods (4.1 – 4.9X)

Method	Site-average NSZD Rate (gal/acre/year)				
	Year 1	Year 2	Year 3	Year 4	Max/ Min
DCC	1,150	810	240	--	4.9
Thermal	300	240	210	--	1.4
Carbon Trap	1,620	4,000	6,600	--	4.1
Thermal	160	140	--	--	1.2
DCC	2,030	2,740	560	610	4.9

Conclusions

Conclusions

- Site-Average NSZD rates range from **70-16,250 gal/acre/year**, with a median of **1,020 gal/acre/year**
- Fuel type **not a primary factor controlling NSZD rates**
- Different measurement methods typically **within a factor of 2 of each other**, with no clear bias.
  - Using any particular method is “good enough” in most cases.
- Increasing mean annual soil temperatures **could potentially increase the biodegradation rate at some sites**

Conclusions

- At majority of sites, a reasonable estimate of **long-term NSZD rate** (within factor of 2-3) can be achieved by:
  - **Single** measurement **method**
  - Method employed at **3-7 locations per site**
  - Measurements taken at least **two semi-annual** (fall and spring) **or four seasonal measurements per location**

Acknowledgements

- Naval Facilities Engineering and Expeditionary Warfare Center (NAVFAC EXWC)
- Environmental Security Technology Certification Program (ESTCP) ER19-5091
- Michael Singletary - NAVFAC
- Stephen Rosansky - Battelle
- Jovan Popovic - Noblis

Questions

Kenneth (“Neth”) L. Walker, Jr., PE, PG

SENIOR GEOLOGIST AND ENGINEER

klwalker@gsi-net.com

713-522-6300 (office)