

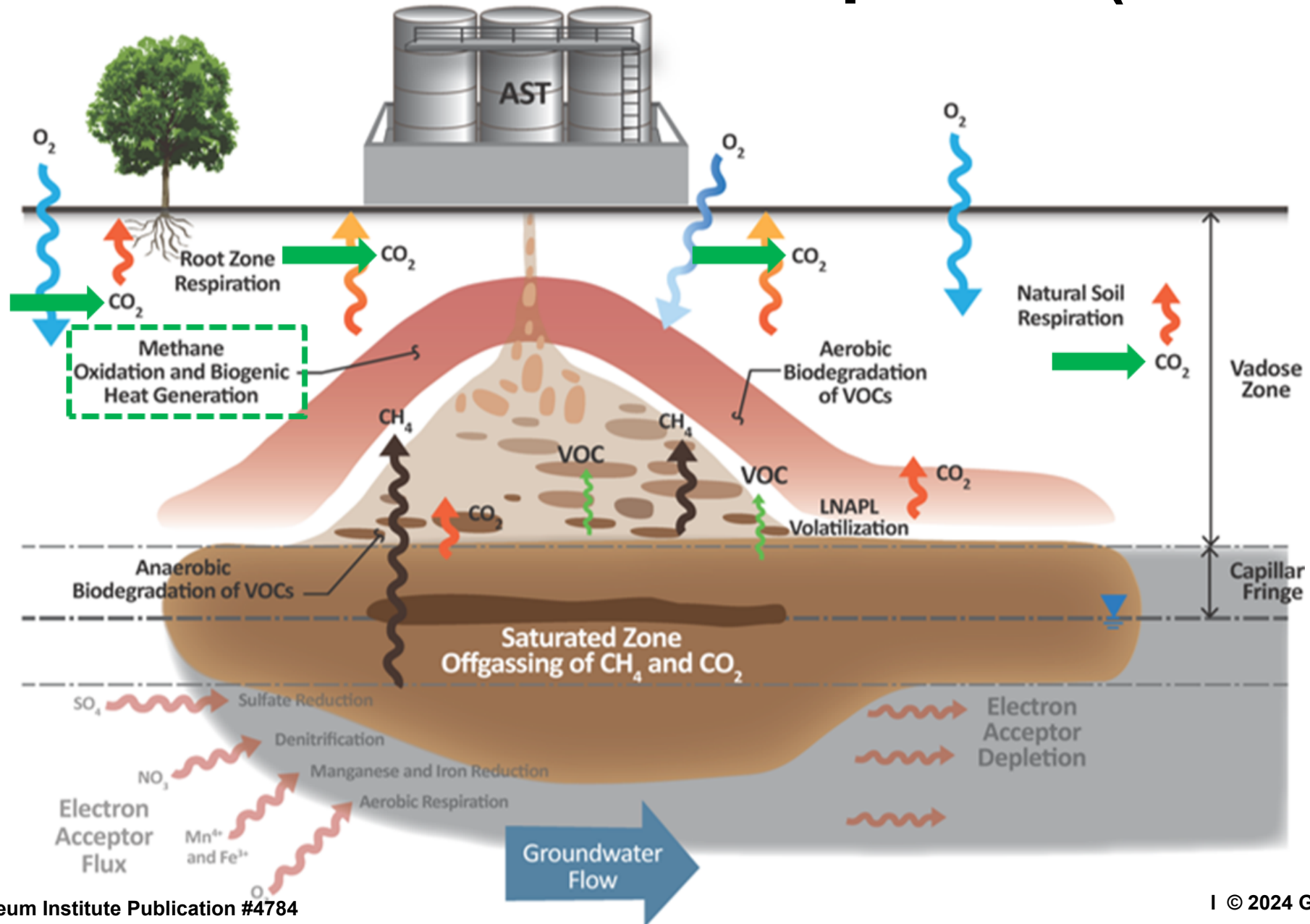


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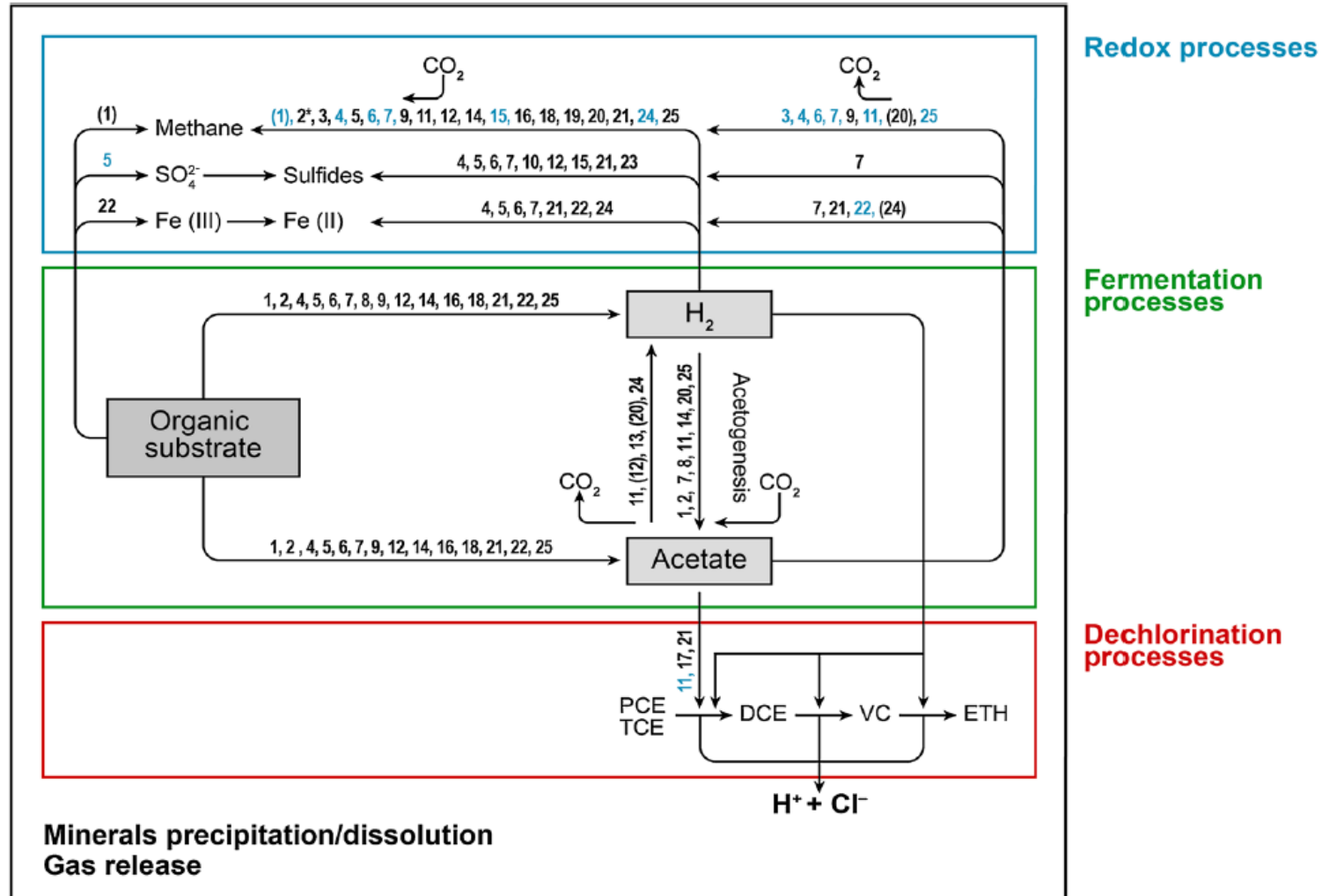
**In Search of Correlations
Between Natural Source Zone Depletion
Rates, Site Conditions, and Underlying
Processes in NAPL-Impacted Systems**

Welcome

What is natural source zone depletion (NSZD)?



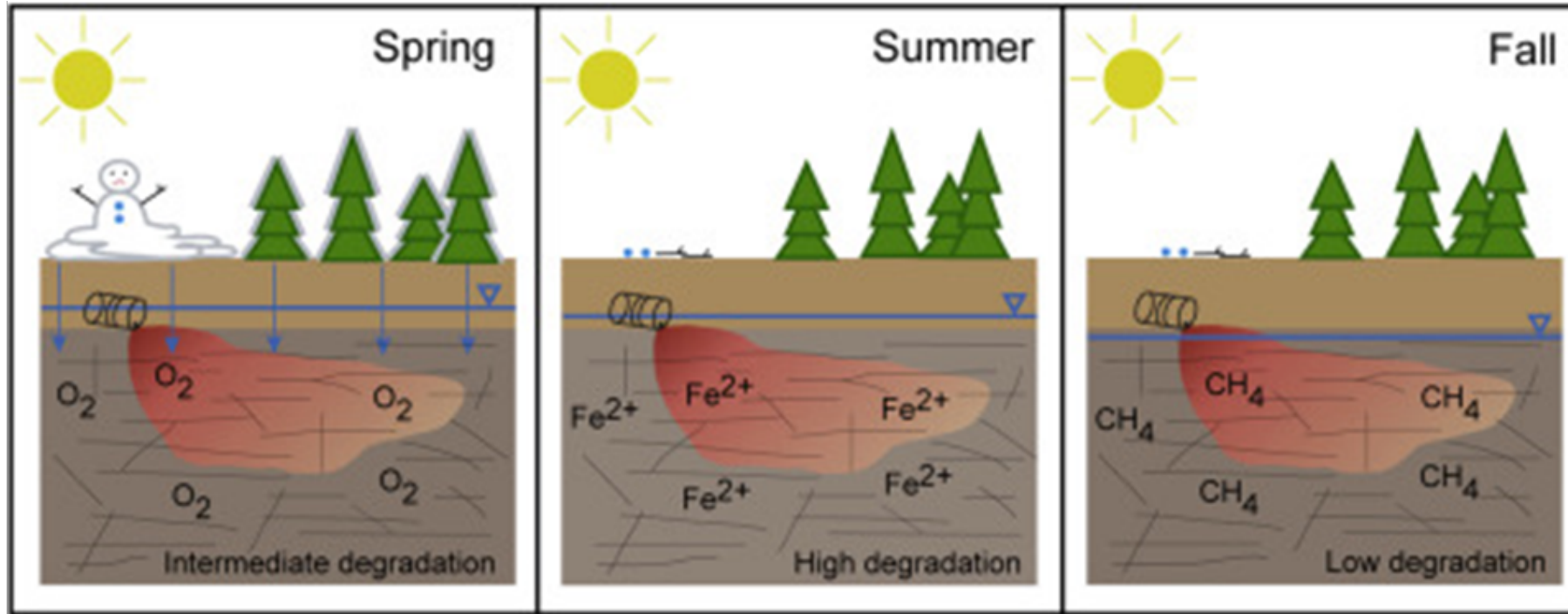
Complementary Reactions in Contaminated Environments



Chambon et al. (2012)

Fluctuating Redox Conditions

Seasonal variability in biodegradation processes



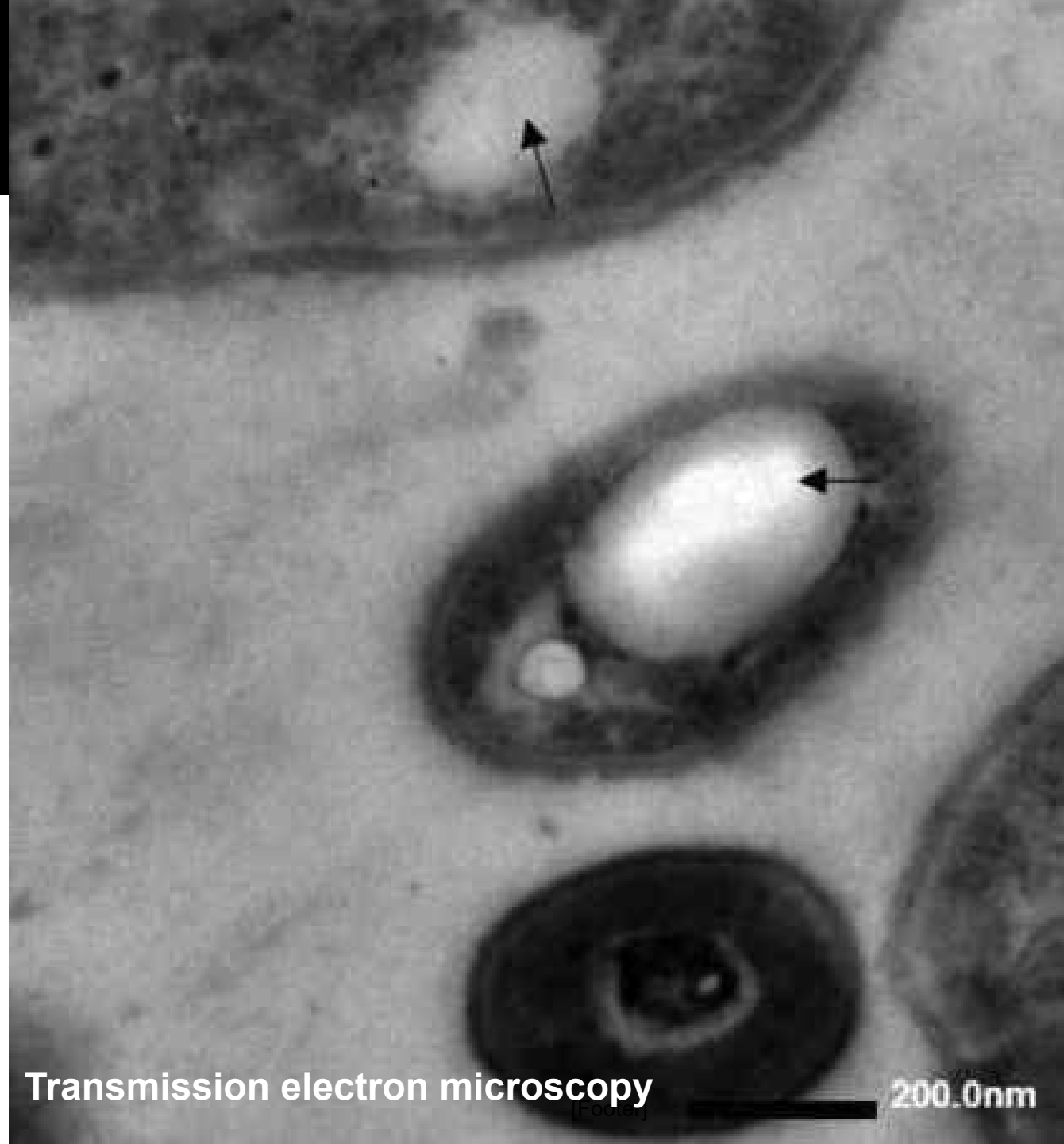
Wanner et al. (2019)

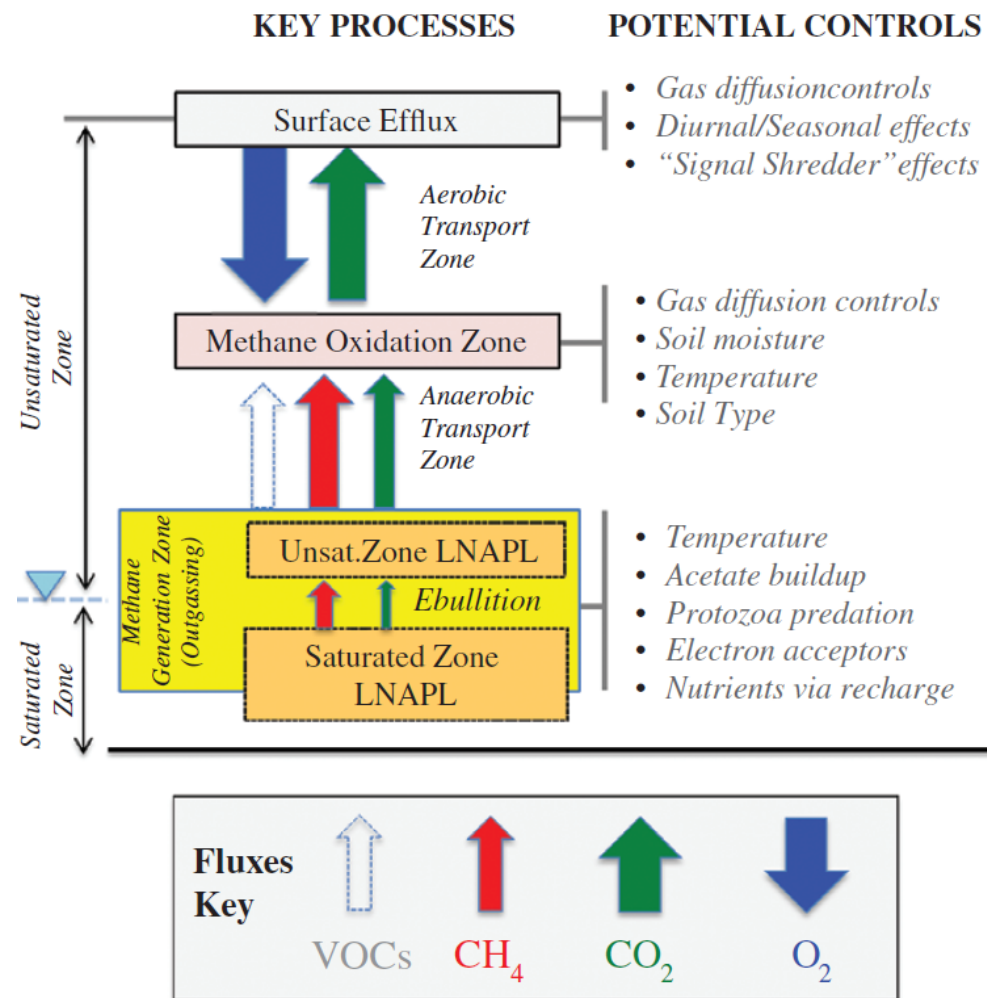
Overview of NSZD

NSZD occurs through:

- **Direct LNAPL biodegradation**
- Biodegradation at oil/water interface
- LNAPL volatilization and biodegradation
- Dissolution and biodegradation

Source: *Hua & Wang, 2014,*
doi:10.1080/13102818.2014.906136





Processes

Representative Degradation Rates from Different Methanogenic Systems

Methanogenic System	Equivalent LNAPL Degradation Rate (Gal/Acre/Year)	Original Measurement	Reference
Anaerobic digesters	500,000	Methane generation ¹	Gerardi 2003
Ethanol release sites	20,000	Carbon dioxide, methane efflux ¹	Sihota et al. 2013
Landfills	10,000	Methane generation ^{1,2}	Spokas et al. 2006
NSZD at LNAPL sites	2000 ³	Carbon dioxide efflux	Table 3 ³
Wetlands	200	Methane flux to atmosphere ¹	Le Mer and Roger 2001
Peat	4	Methane ebullition ¹	Stamp et al. 2013

1,000 US gallons LNAPL depleted/acre/year
 ≈ 1 litre LNAPL depleted/m²/year
 ≈ 1 mm depletion in LNAPL thickness/year

Typical magnitudes

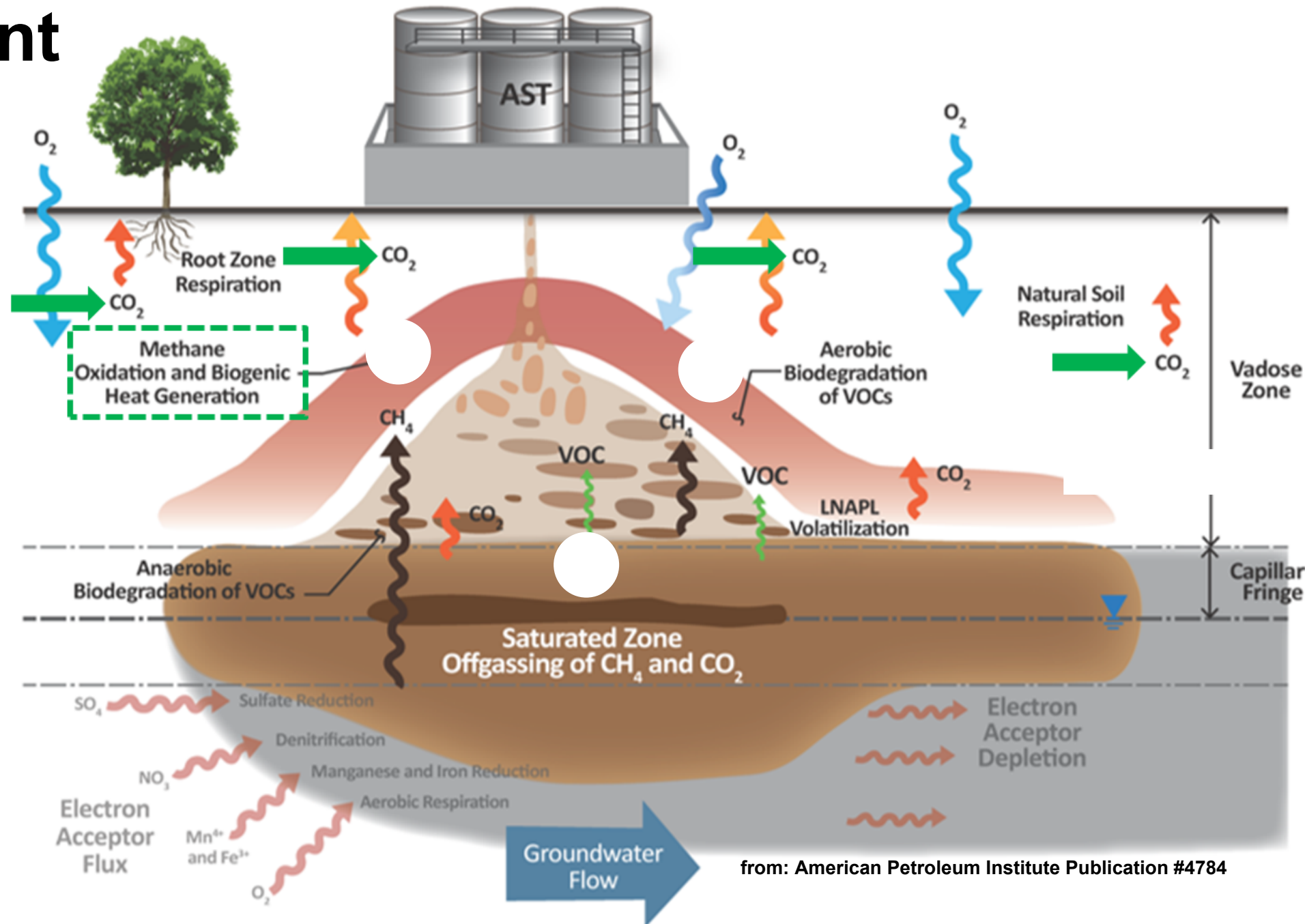
Measurement Methods

Surficial CO₂ Efflux (dynamic closed chamber, CO₂ Trap)

Biogenic heat

Vertical soil gas gradients (CO₂, O₂, CH₄)

Compositional change

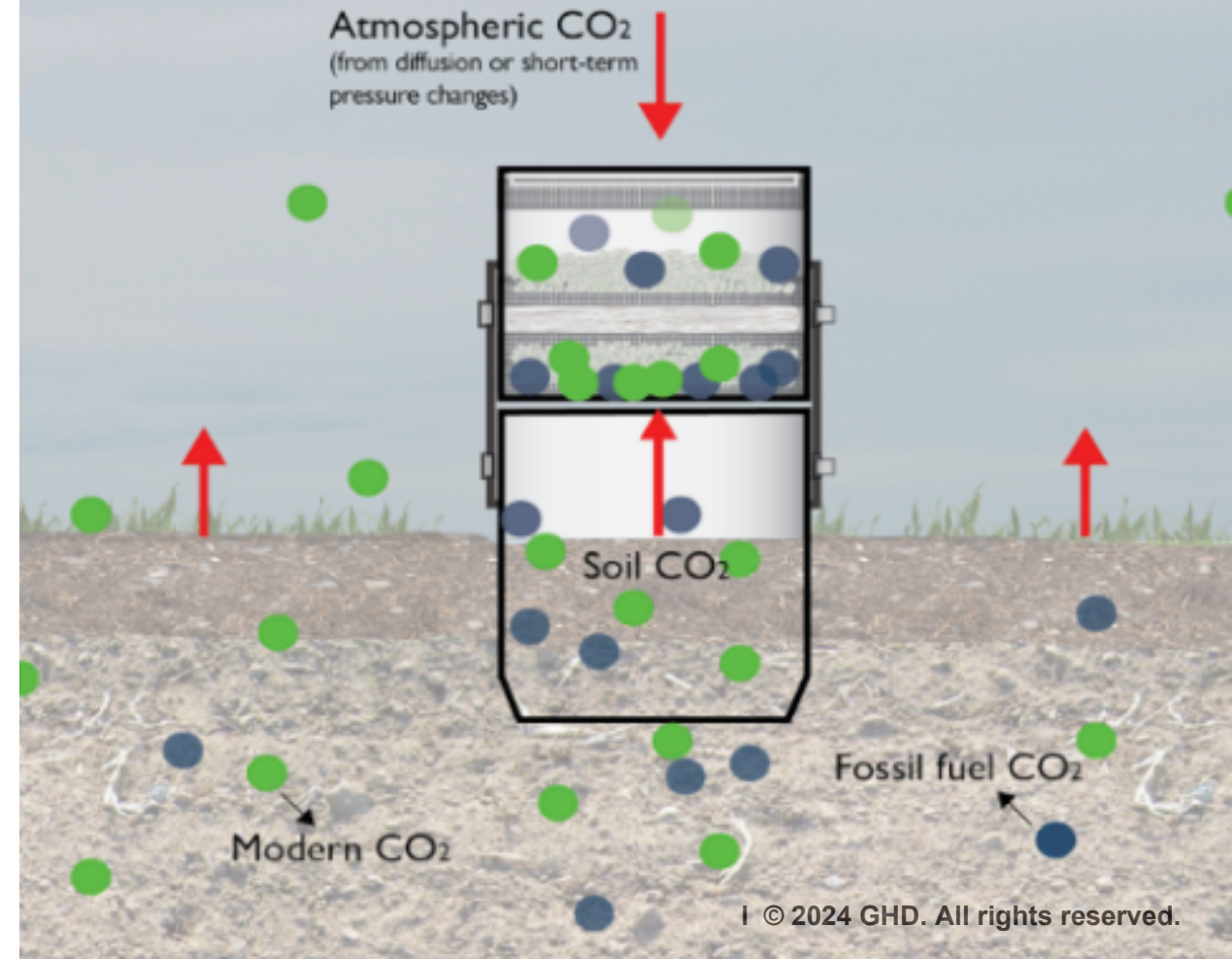


Technique 1A: dynamic closed chamber (DCC)



Technique 1B: passive CO₂ traps

From E-Flux LLC

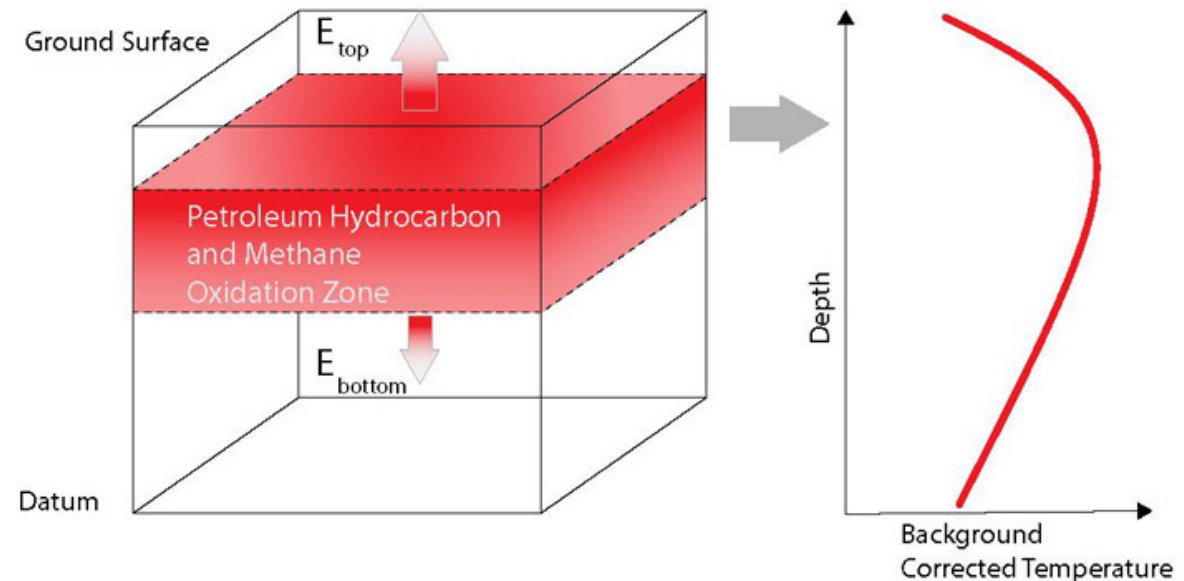


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Technique 2: biogenic heat

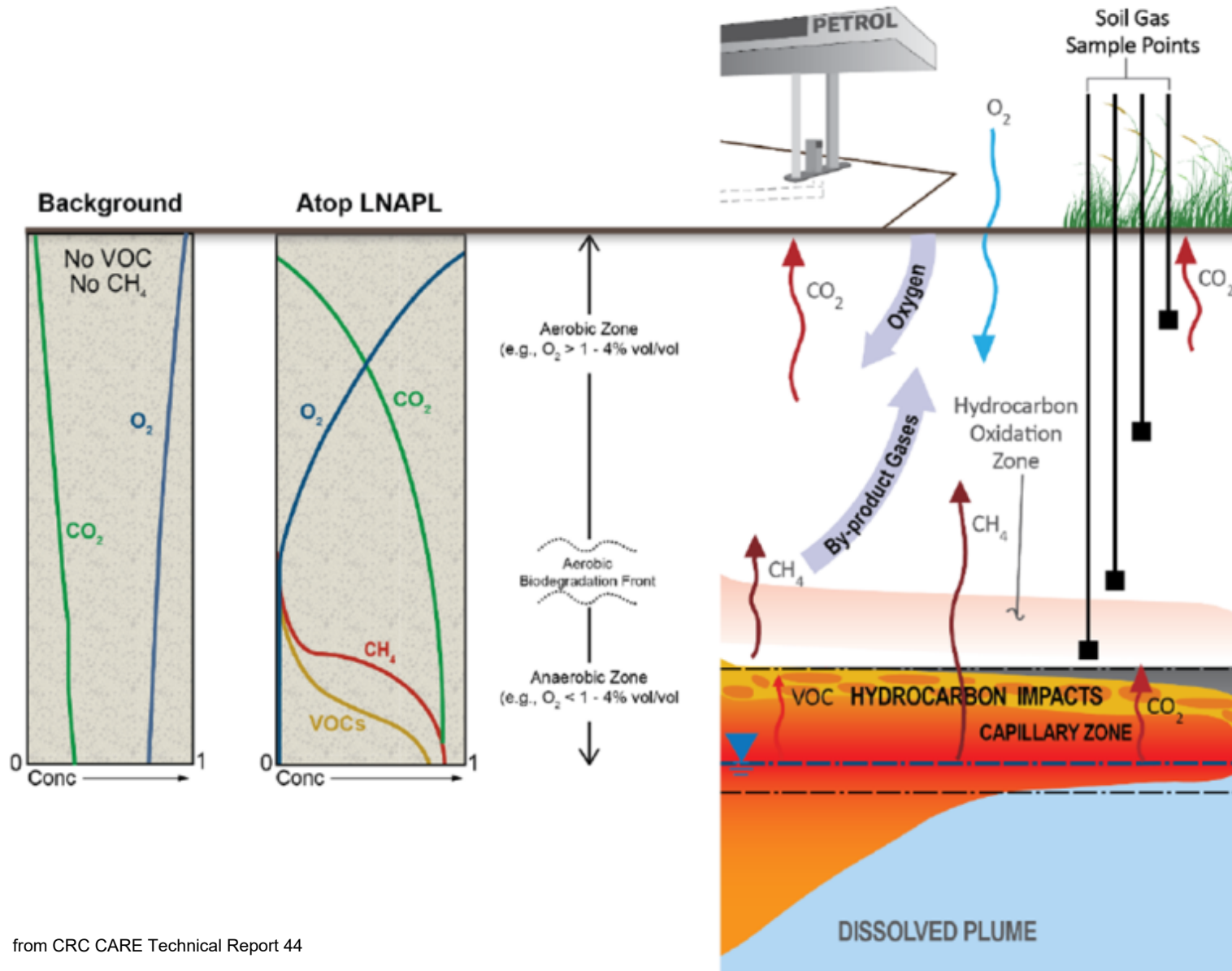


- Existing wells or dedicated installations
- Measure temperature at multiple depths through methane-oxidation zone
 - determine temperature gradients up and down
 - $\text{heat flux} = \text{temperature gradient} \times \text{thermal conductivity of soil/rock}$
 - $\text{NSZD rate} = \text{heat flux} / \text{heat of reaction}$



From ITRC LNAPL-3

Technique 3: soil gas gradient



from CRC CARE Technical Report 44

Investigated Sites

- Thirteen LNAPL contaminated Sites
- Three different countries
- Seven different categories of datasets

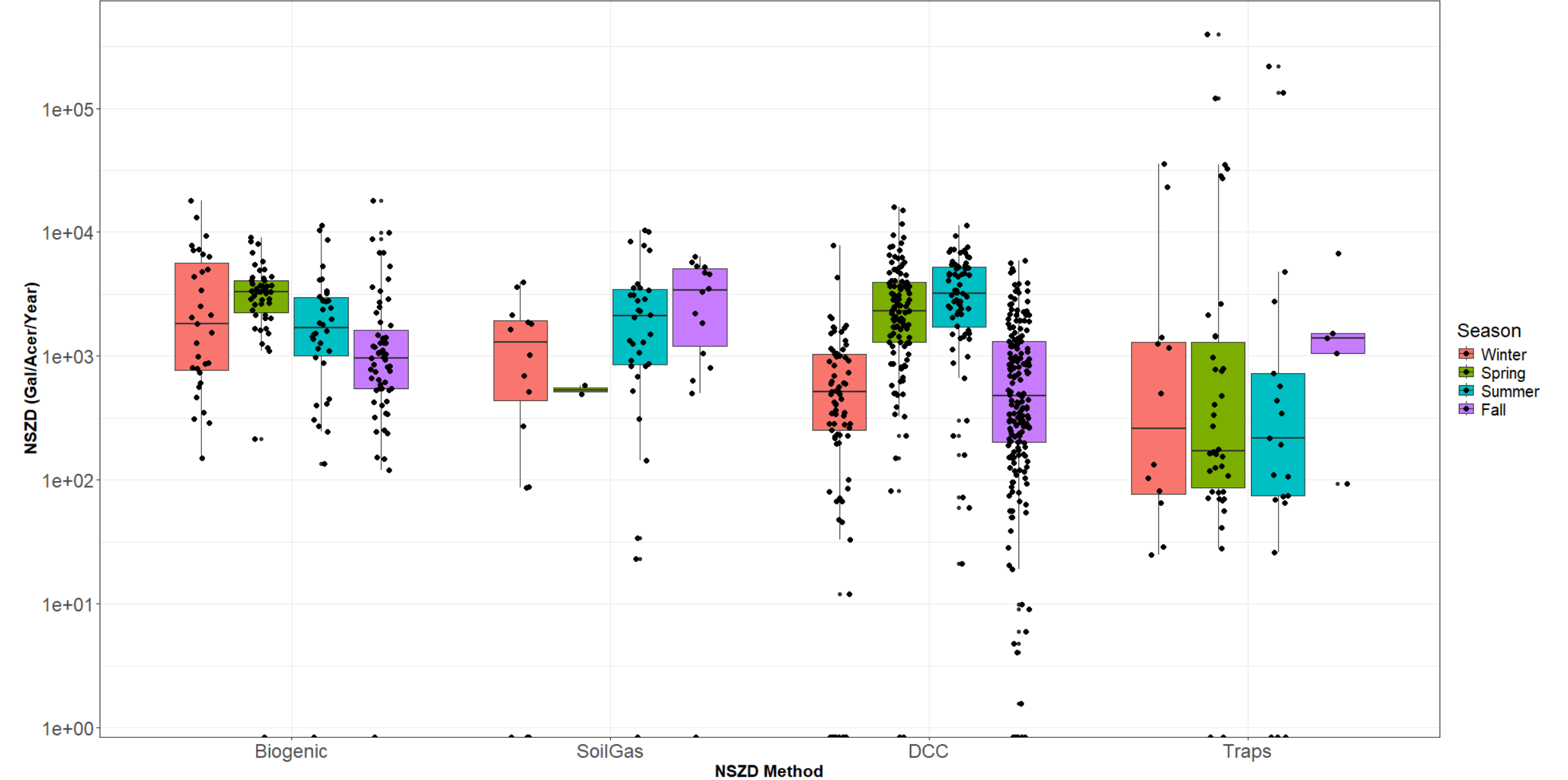
Site	Country	NSZD Rates	NAPL Thickness	Electron Accep.	Field Parameters	Geology	BTEX	Depth to Fluid
1	US	✓	✓	✓	✓	✓	✓	✓
2	Australia	✓	✓	✓	✓	✓	✓	✓
3	Canada	✓	✗	✗	✗	✓	✗	✗
4	Australia	✓	✓	✓	✓	✓	✓	✓
5	US	✓	✗	✓	✓	✗	✗	✓
6	US	✓	✗	✗	✗	✗	✓	✓
7	US	✓	✓	✗	✓	✓	✓	✓
8	Australia	✓	✗	✗	✓	✗	✗	✓
9	US	✓	✓	✓	✓	✗	✓	✓
10	US	✓	✓	✓	✓	✓	✓	✓
11	US	✓	✗	✗	✗	✗	✗	✗
12	US	✓	✓	✗	✗	✓	✗	✓
13	Australia	✓	✓	✓	✓	✓	✓	✓

Data Summary

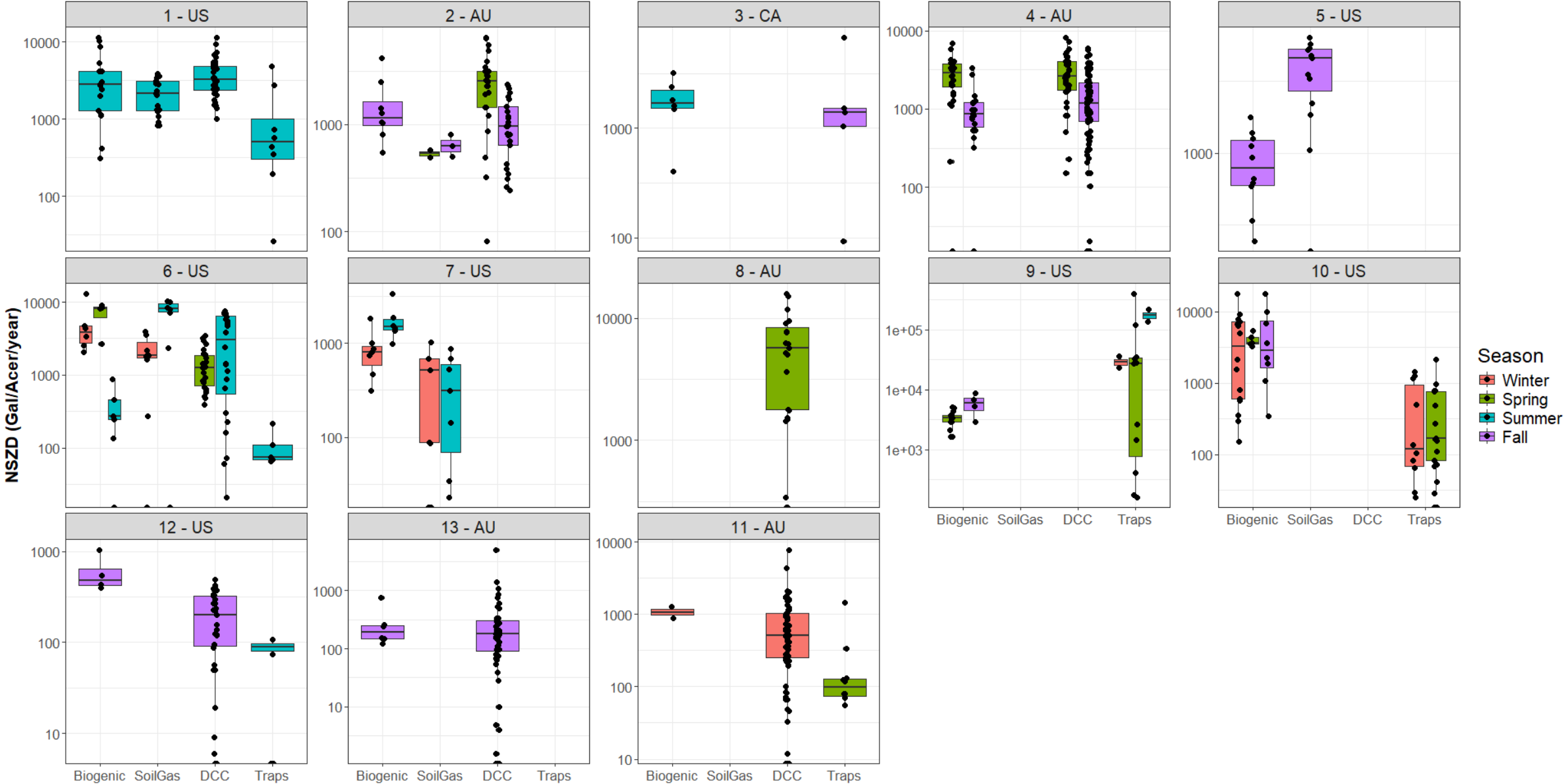
– Available data for each specific NSZD method

NSZD Method	Number of Sites	Number of NSZD Rates	Field Parameters	EA Conc.	BTEX Conc	Depth to Fluid
Bigenic Heat	12	175	77	19 - 28	98	154
Soil Gas Gradient	5	65	25	12	20	54
DCC	8	456	NA	NA	NA	NA
CO ₂ Traps	7	77	NA	NA	NA	NA
Total	13	773	102	80	118 x 4	208

Overall Seasonal Effects



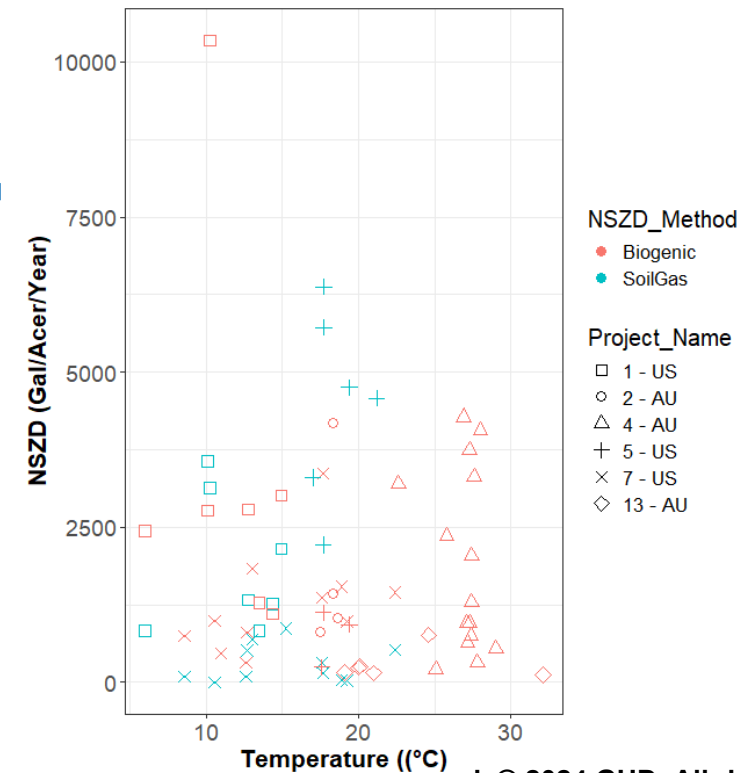
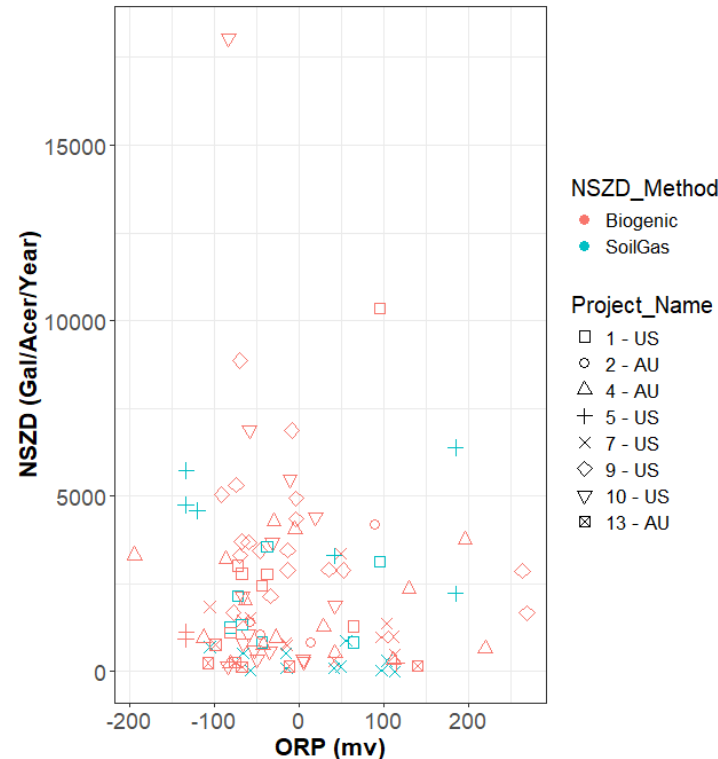
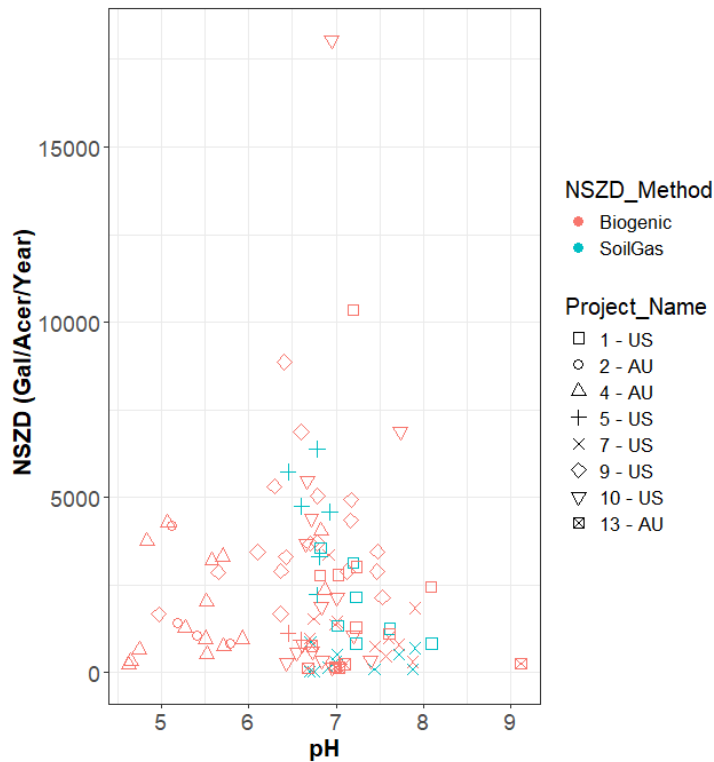
Site-Specific Seasonal Effects



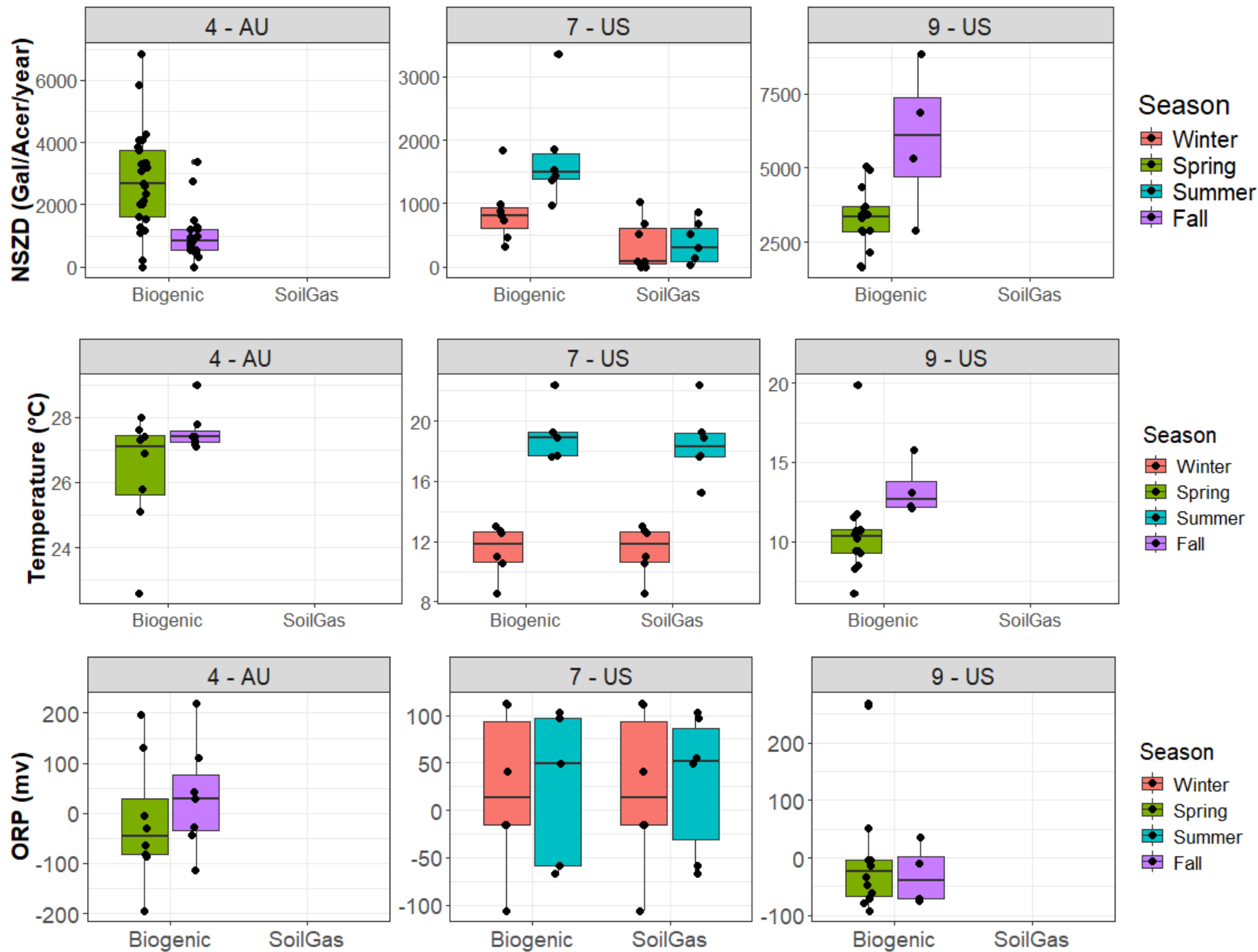
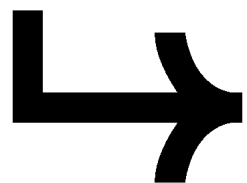
Correlation Between NSZD and pH/ORP/Temperature

Optimum conditions for NSZD:

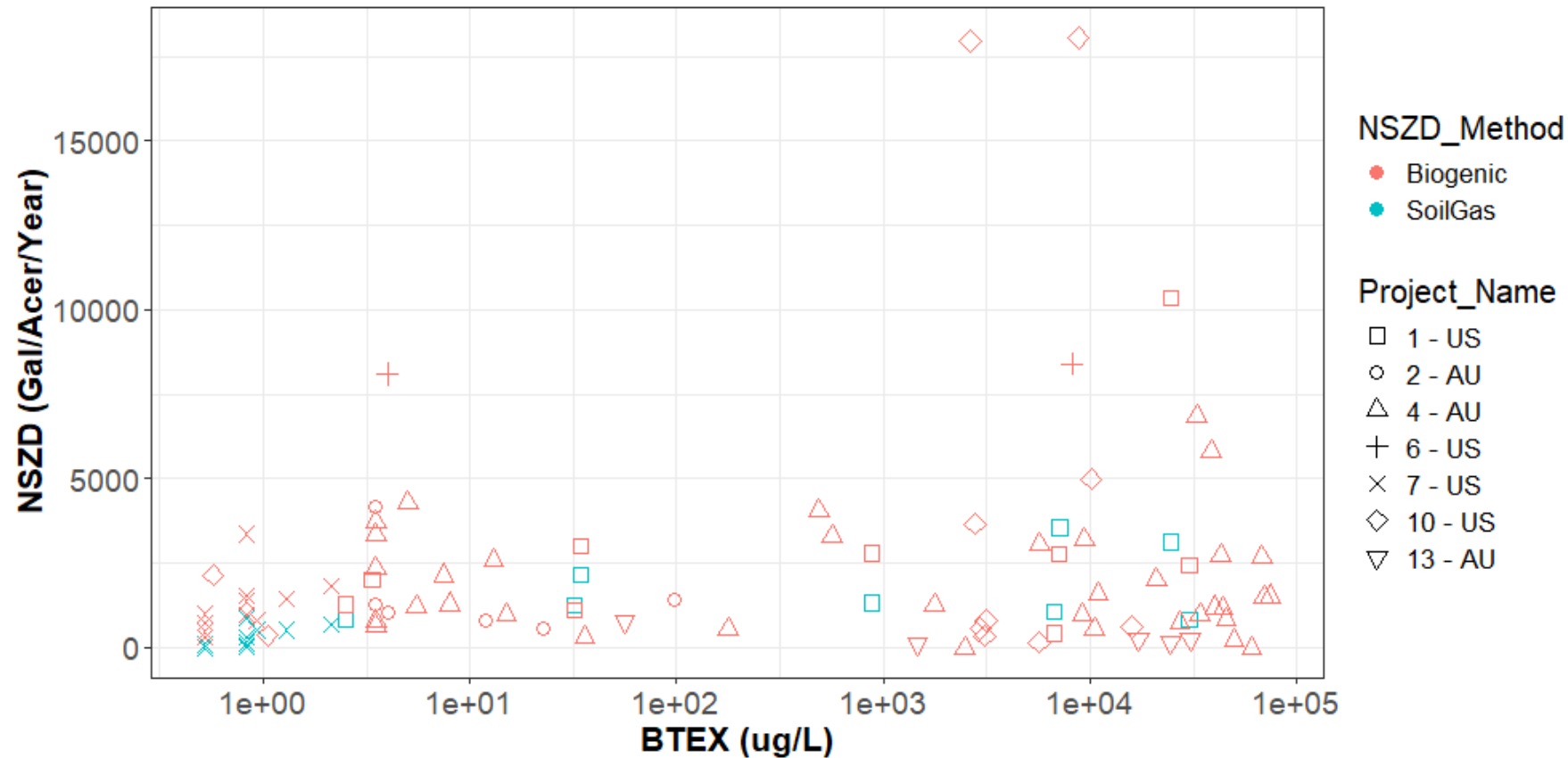
- Natural pH
- More reducing conditions
- Temperature range of 15 to 20°C



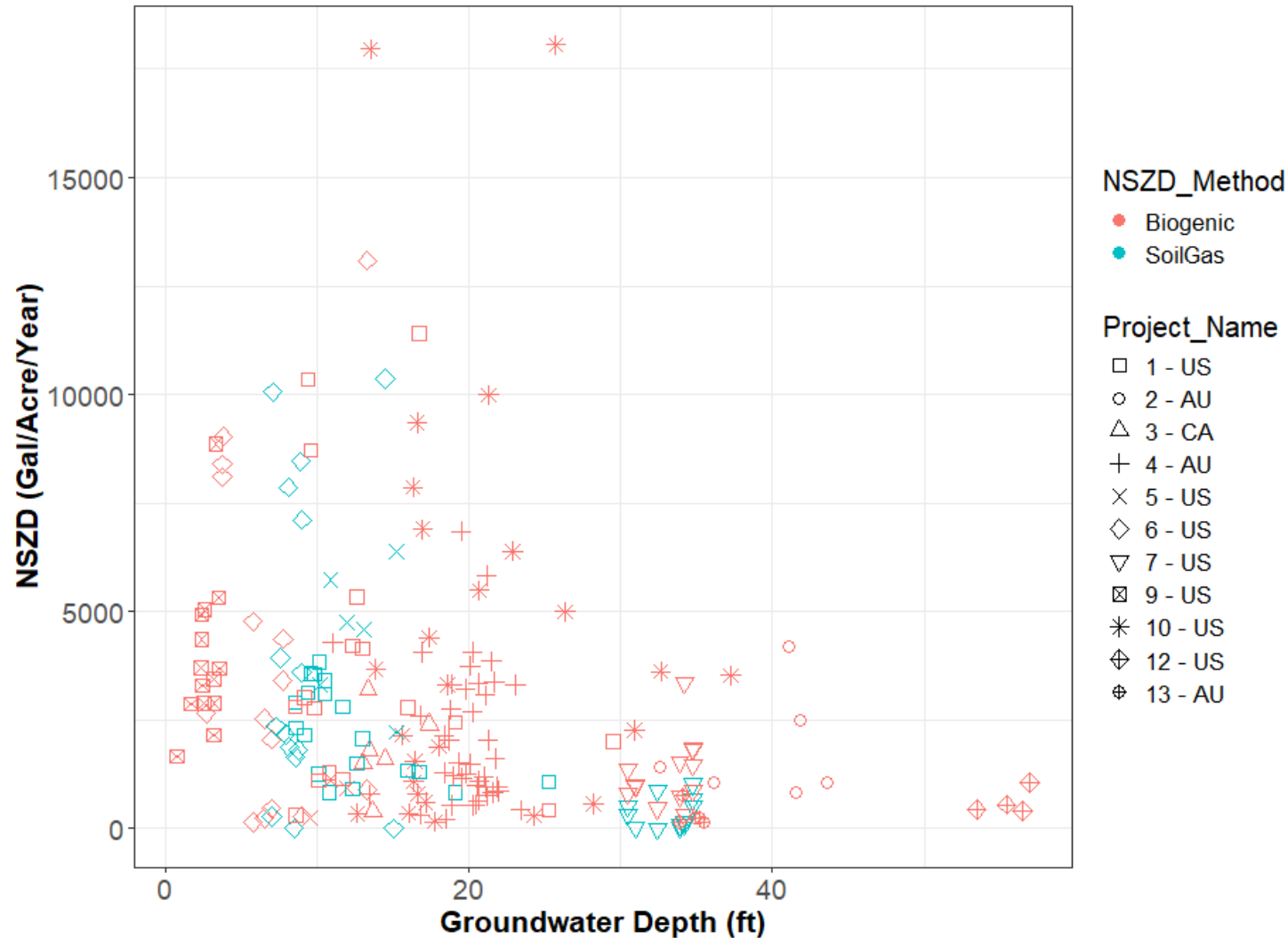
Interactions of seasonal effects, temperature, and microbial metabolism



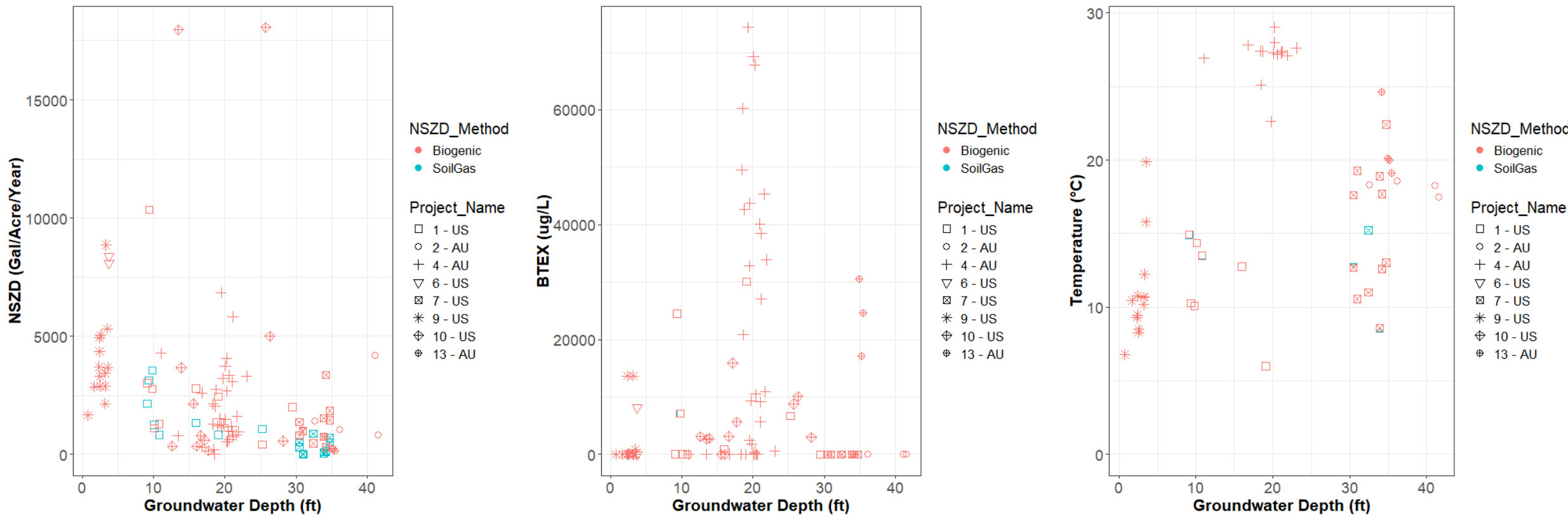
No Correlation Between Dissolved Phase Concentrations and NSZD Rates



Correlation Between NSZD and Groundwater Depth



Correlation Between NSZD and Groundwater Depth





*** Thank You**

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