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Colorado State University
Civil and Environmental Engineering
CCH
Center for Contaminant Hydrology

Insights from Continuous Monitoring of LNAPL NSZD Rates

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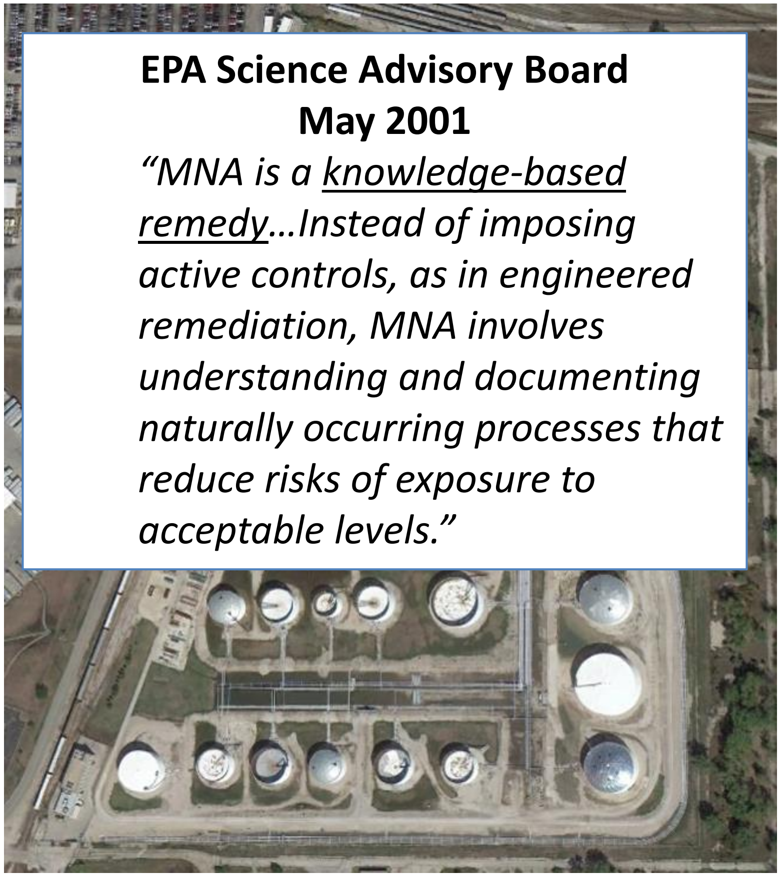
NSZD Rate Measurement Activities

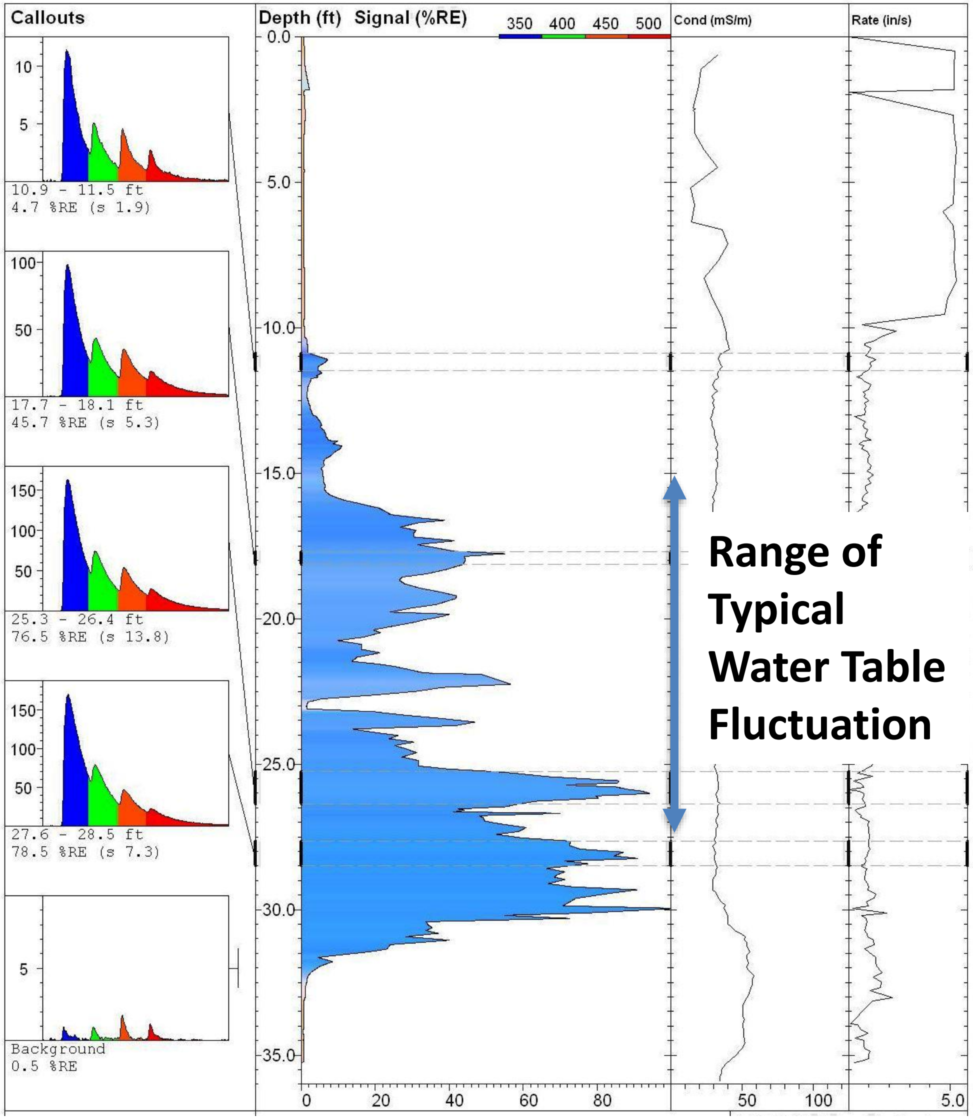


EPA Science Advisory Board
May 2001

"MNA is a knowledge-based remedy…Instead of imposing active controls, as in engineered remediation, MNA involves understanding and documenting naturally occurring processes that reduce risks of exposure to acceptable levels."

- LNAPL Zone
  - Pipeline terminal in the Midwest
  - Historic LNAPL accumulations > 1' over a 10-acre area
  - Weathered fuel mixture, dominated by gasoline and diesel
- Passive CO2 Flux Measurements
  - September 2012 through January 2015
  - 7 multi-location events
- Biogenic Heat Monitoring
  - Phase 1 System became operational April 2014
  - System modified and expanded in November 2016
  - This presentation covers the 2.6 years before system modification

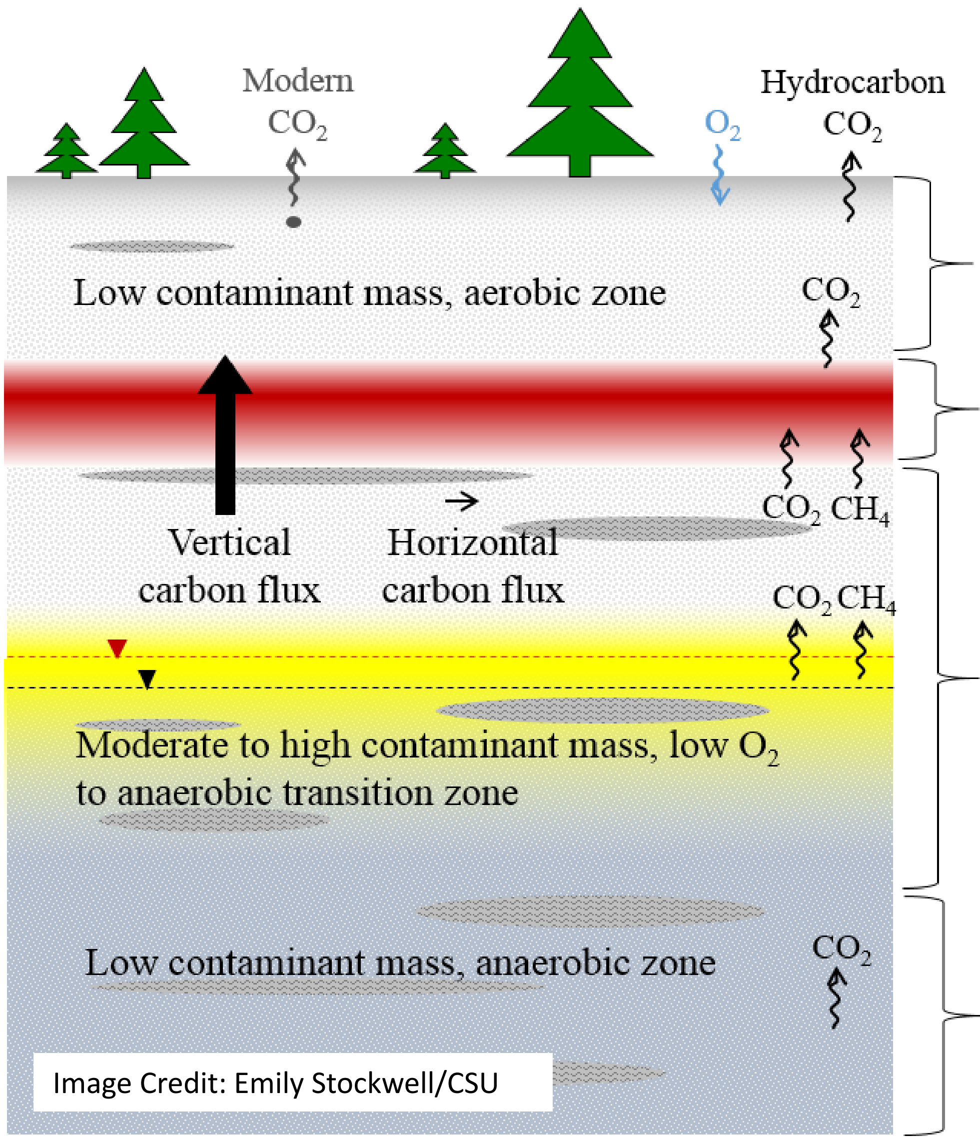
Hydrogeologic Setting



Fine-grained overbank deposits

Alluvial sands

NSZD Conceptual Model



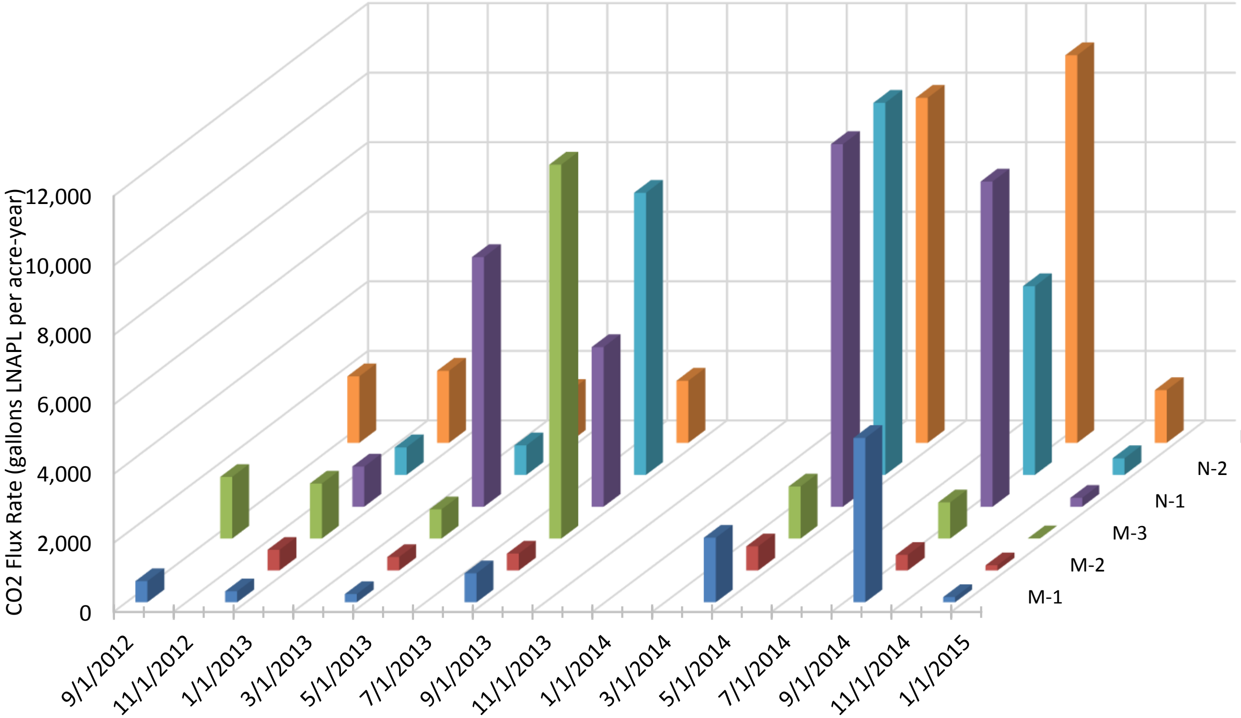
Region 1 – Soil respiration modern carbon
Organic Carbon + O_2 ➔ CO_2

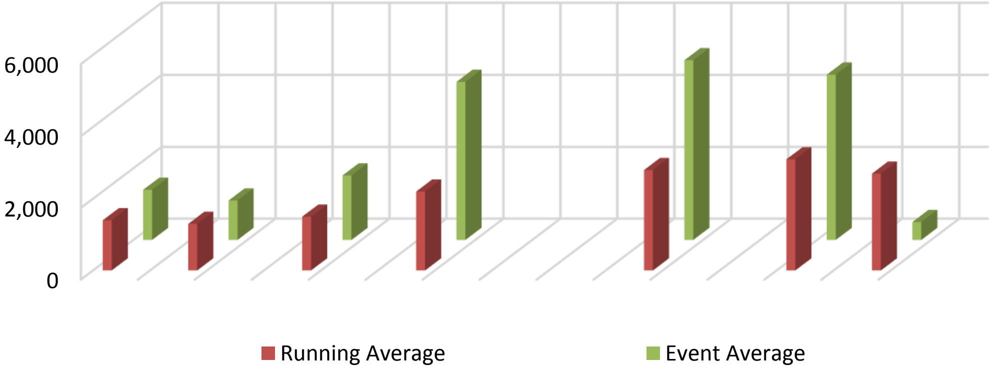
Region 2 – Methanotrophs
$CH_4 + 2O_2$ ➔ $CO_2 + 2H_2O$

Region 3 – Methanogenesis
Hydrocarbon + H_20 ➔ $CO_2 + CH_4$

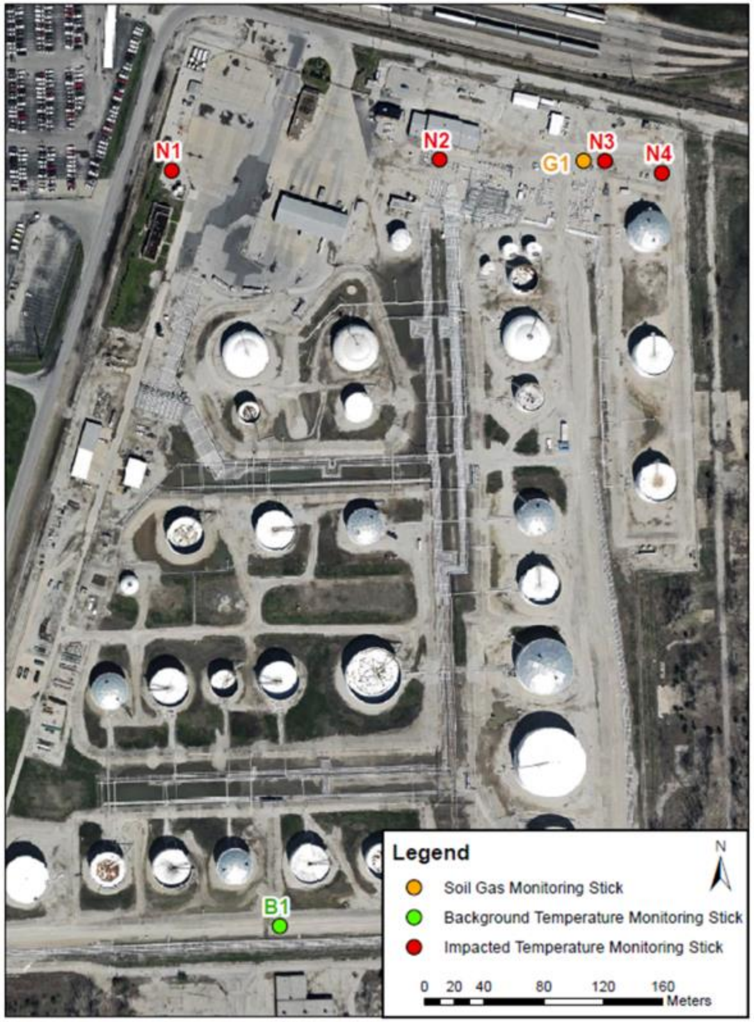
Region 4 –
Hydrocarbon + e^- acceptor* ➔ CO_2
* NO_3^-, Fe^{3+} or SO_4^{2-}

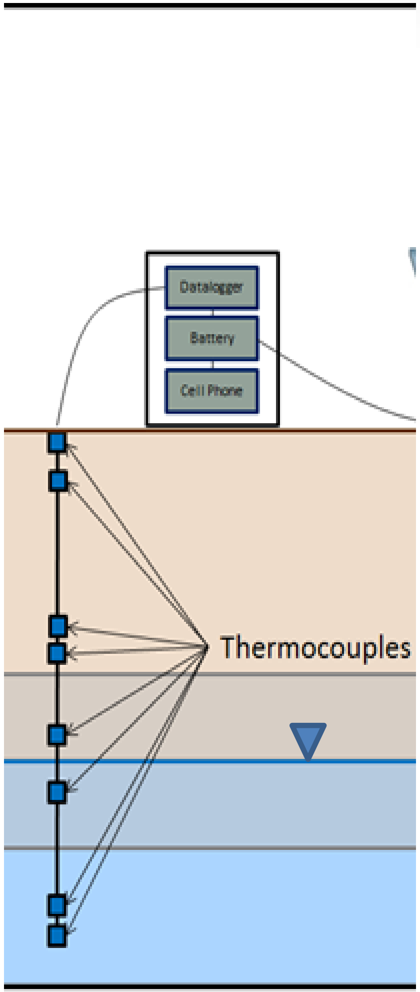
NSZD Rate Measurements – Passive CO_2 Flux Method





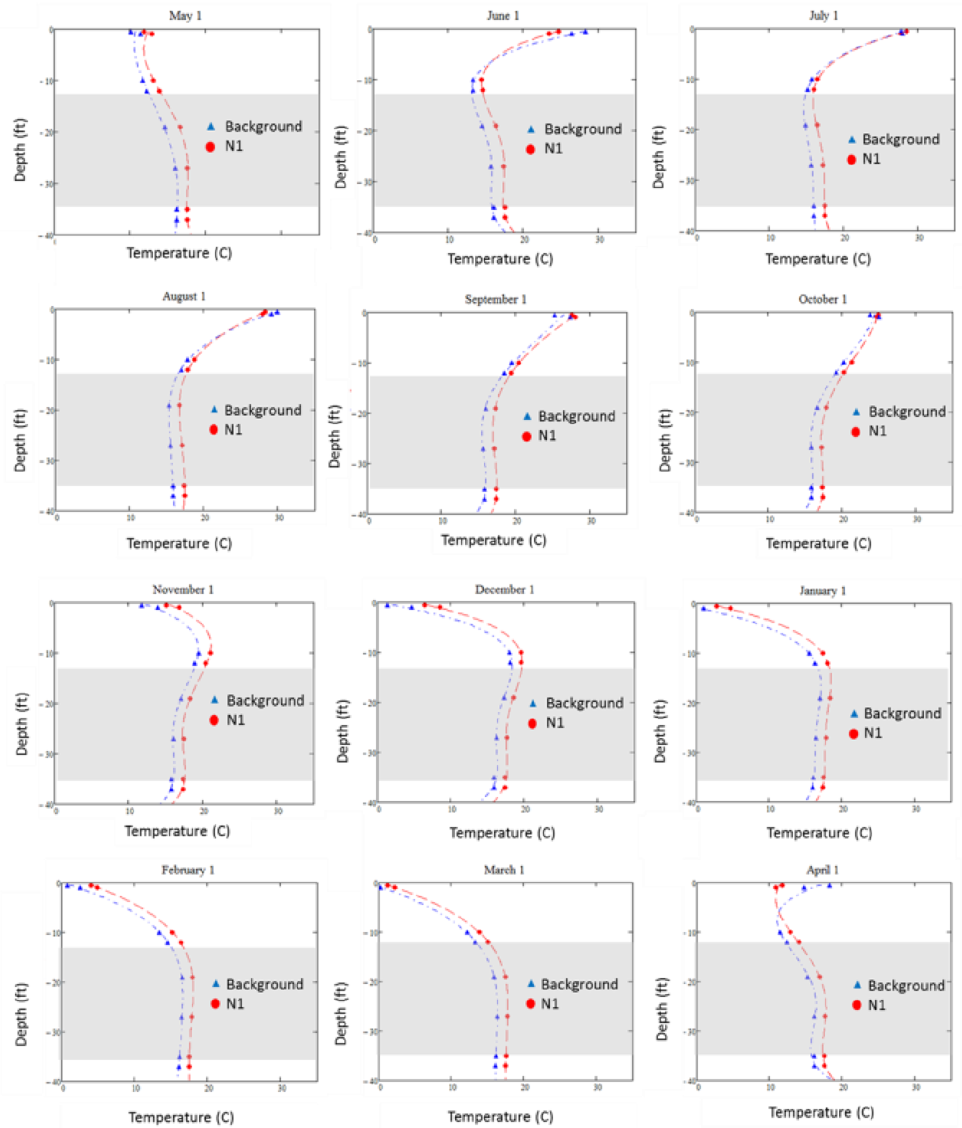
Biogenic Heat Monitoring System





Observed Temperatures

N1

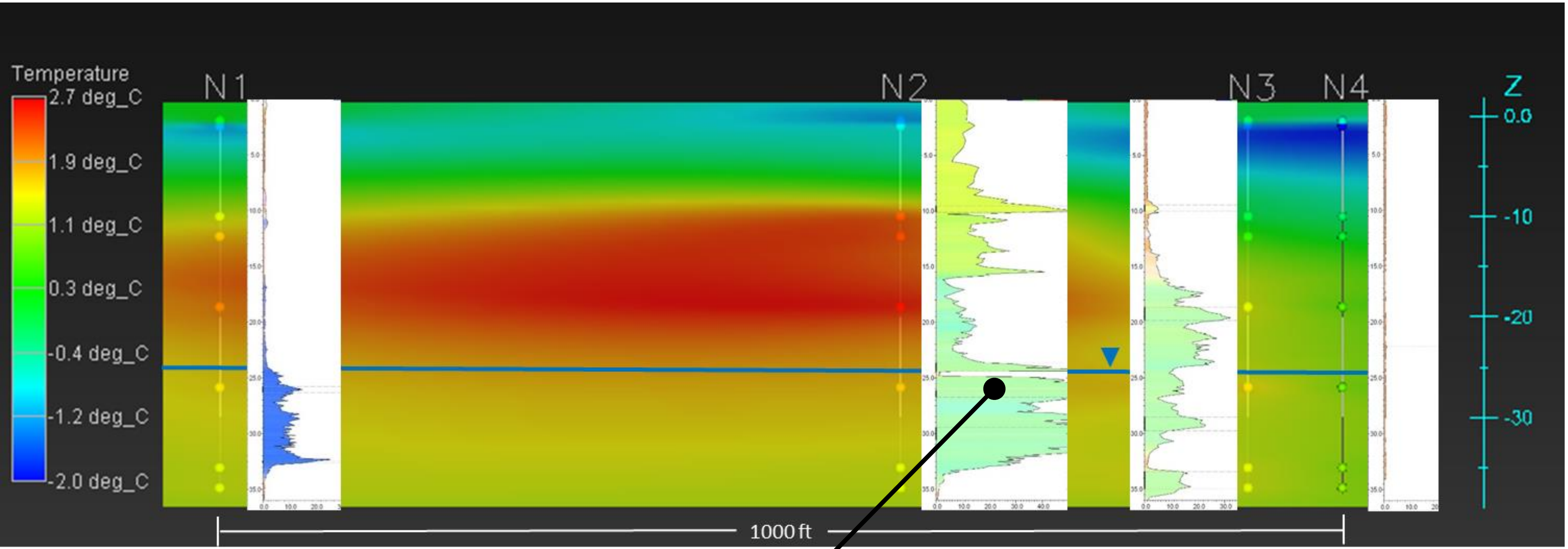


- Elevated T (red v blue) reflects exothermic degradation of hydrocarbons
- T provides a signal to track extent of active NSZD and LNAPL

Credit: Emily Stockwell/CSU

NSZD Thermal Signature

$$T_{Corrected} = T_{LNAPL} - T_{Background}$$

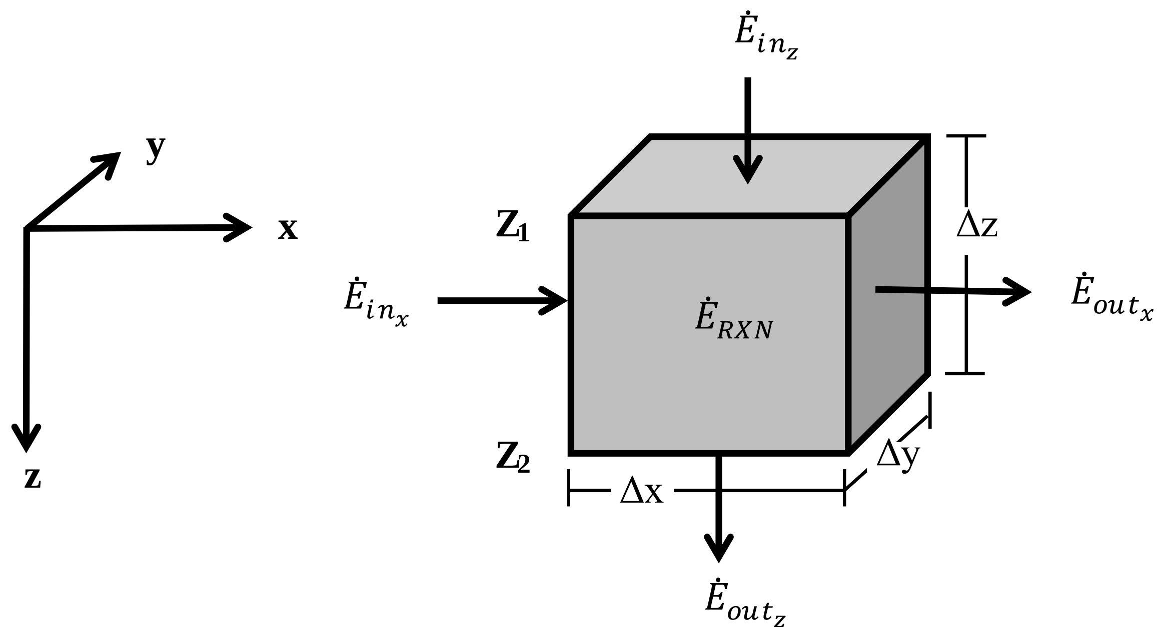


Subsurface Temperatures minus Background Temperatures

LIF Data

Thermal Image Credit: Emily Stockwell/CSU

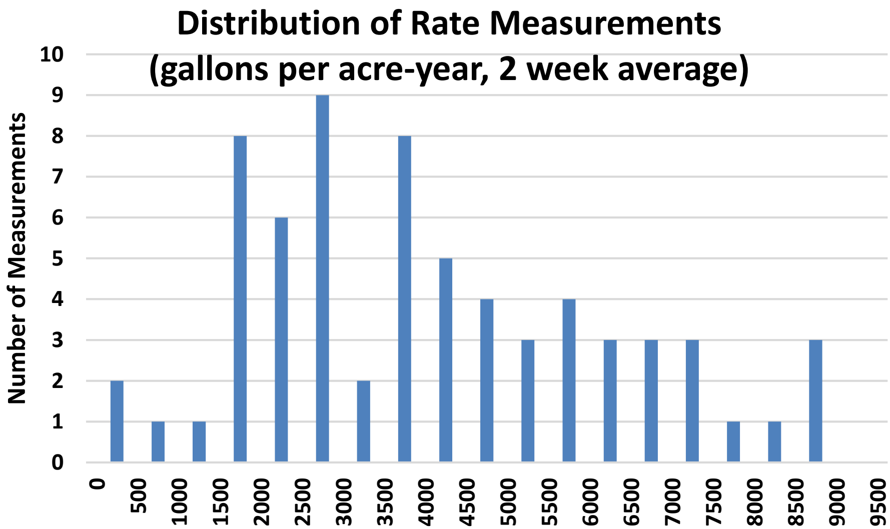
Estimating NSZD Rates

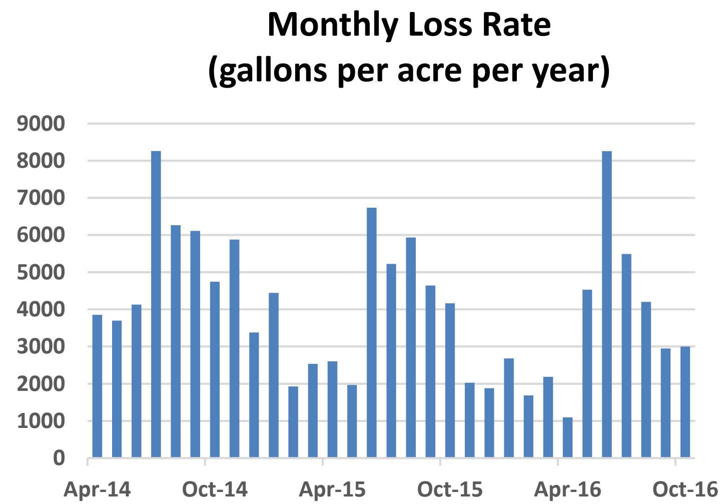


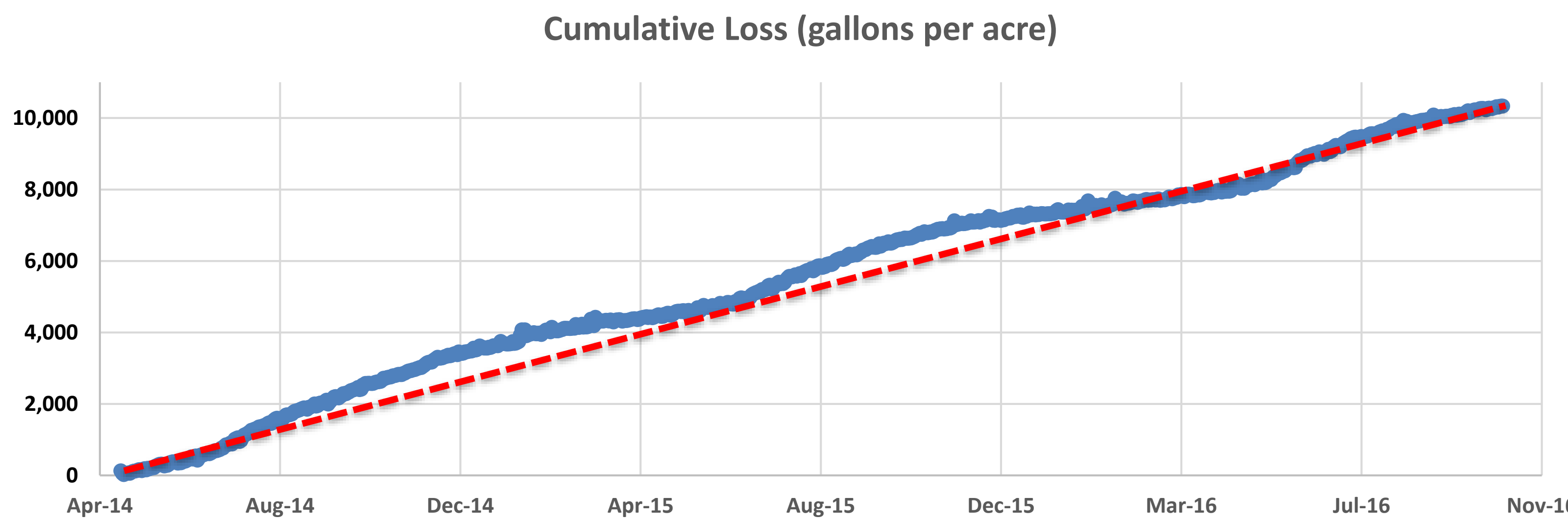
$$LossRate = \frac{-\dot{E}_{RXN}}{\Delta H_r}$$

Temperature Data Input ➔ Energy Balance Model ➔ NSZD Rate Output

TRC
Results you can rely on





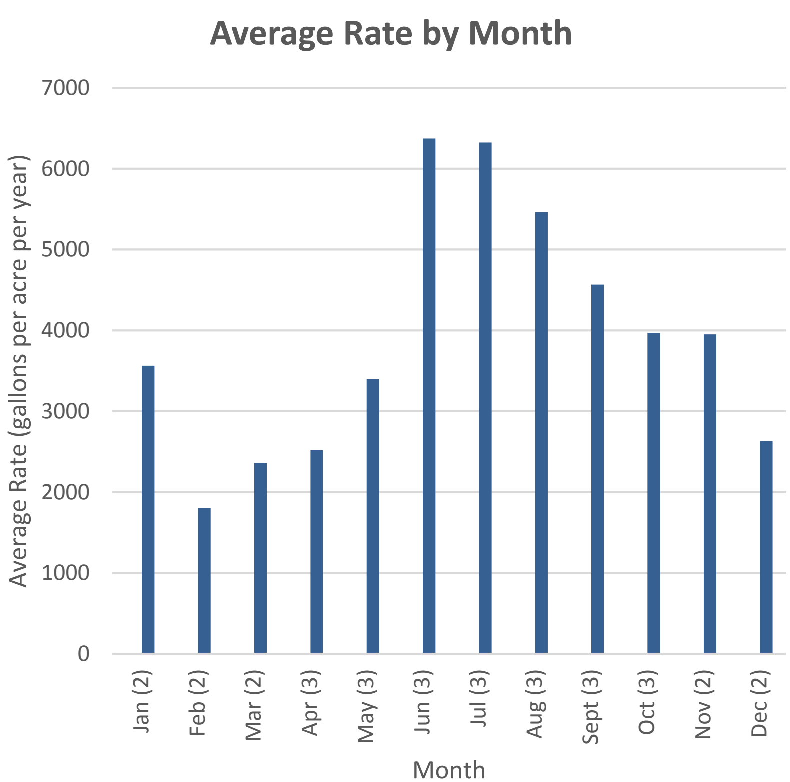


Method Comparison
(All Measurements at 3 Locations Along a Transect)

Passive CO2 Flux	Biogenic Heat
September 2012 through December 2014	April 2014 through October 2016
Six events	Continuous Monitoring
^{14}C Correction for Background CO_2	Cumulative Loss of 10,300 gallons per acre
Average: 4,900 gallons per acre per year	Average: 4,000 gallons per acre per year

What is the Cause of Temporal Variability?

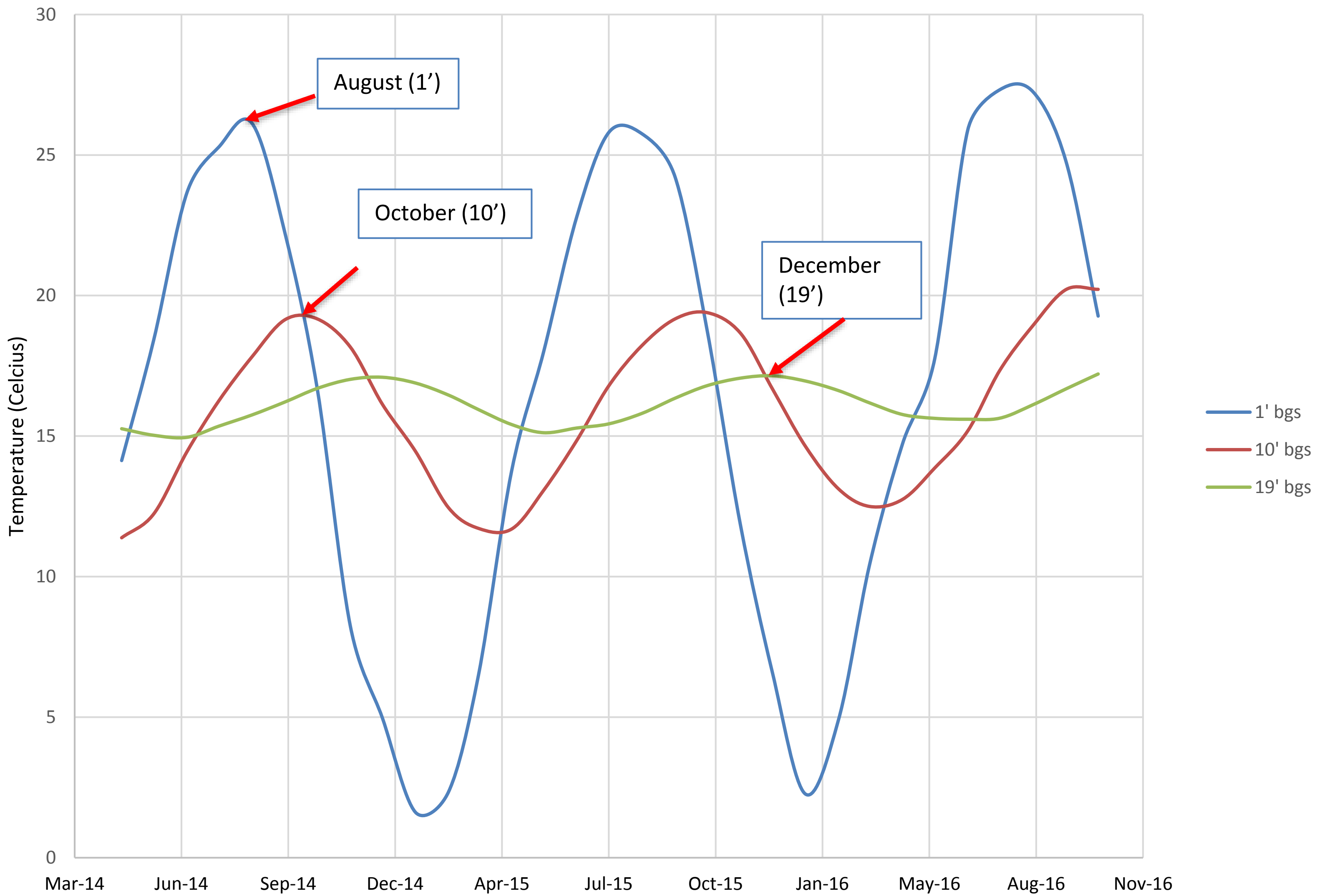
Seasonal Pattern



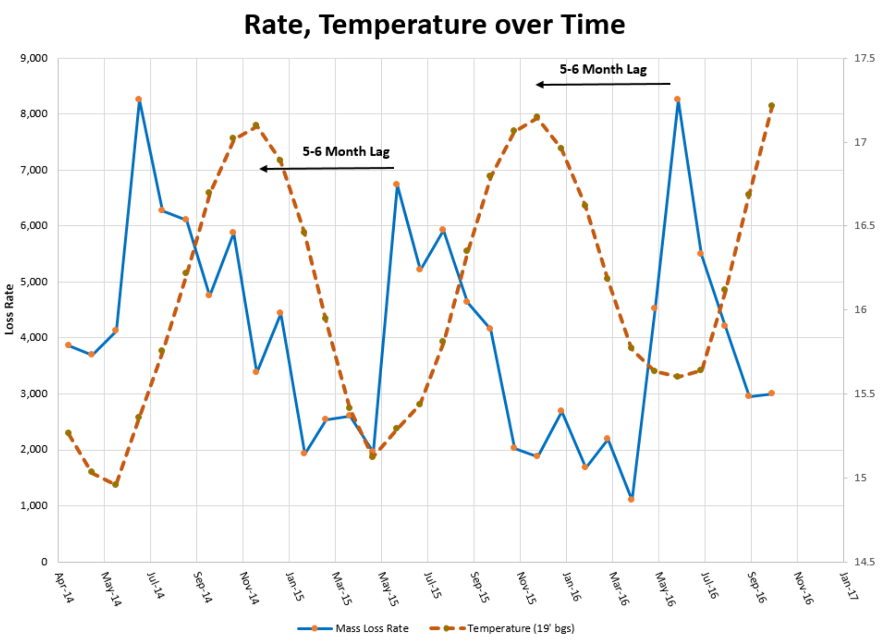
Potential Cause

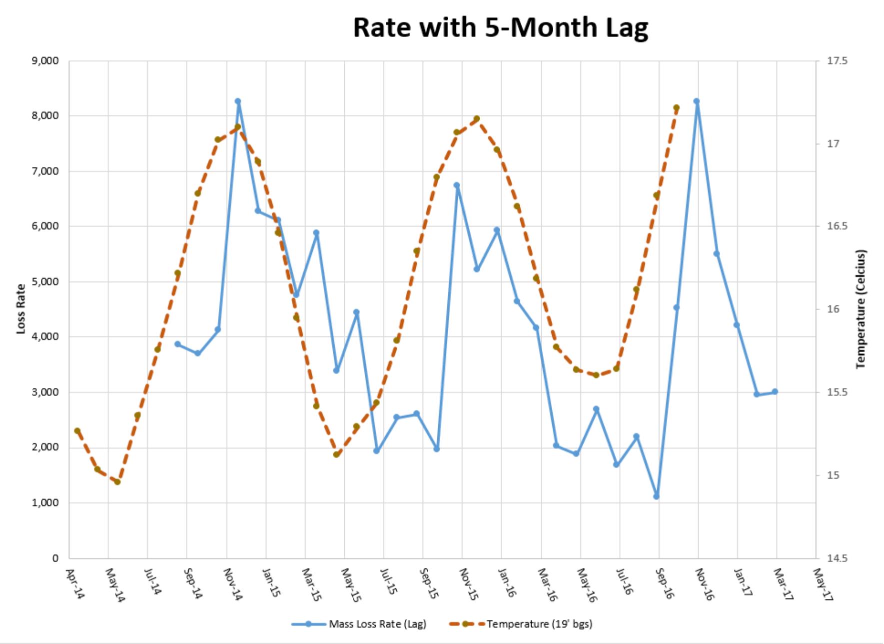
- Temperature
  - Proven relationship between temperature and rate
- Water Table Fluctuations
  - Hypothesis of faster rate in unsaturated portion of smear zone
- Soil Moisture
  - Both gas diffusion and advection a function of air-filled porosity

Background Temperature Over Time at Various Depths



NSZD Rate vs Background Soil Temperature (19' bgs)

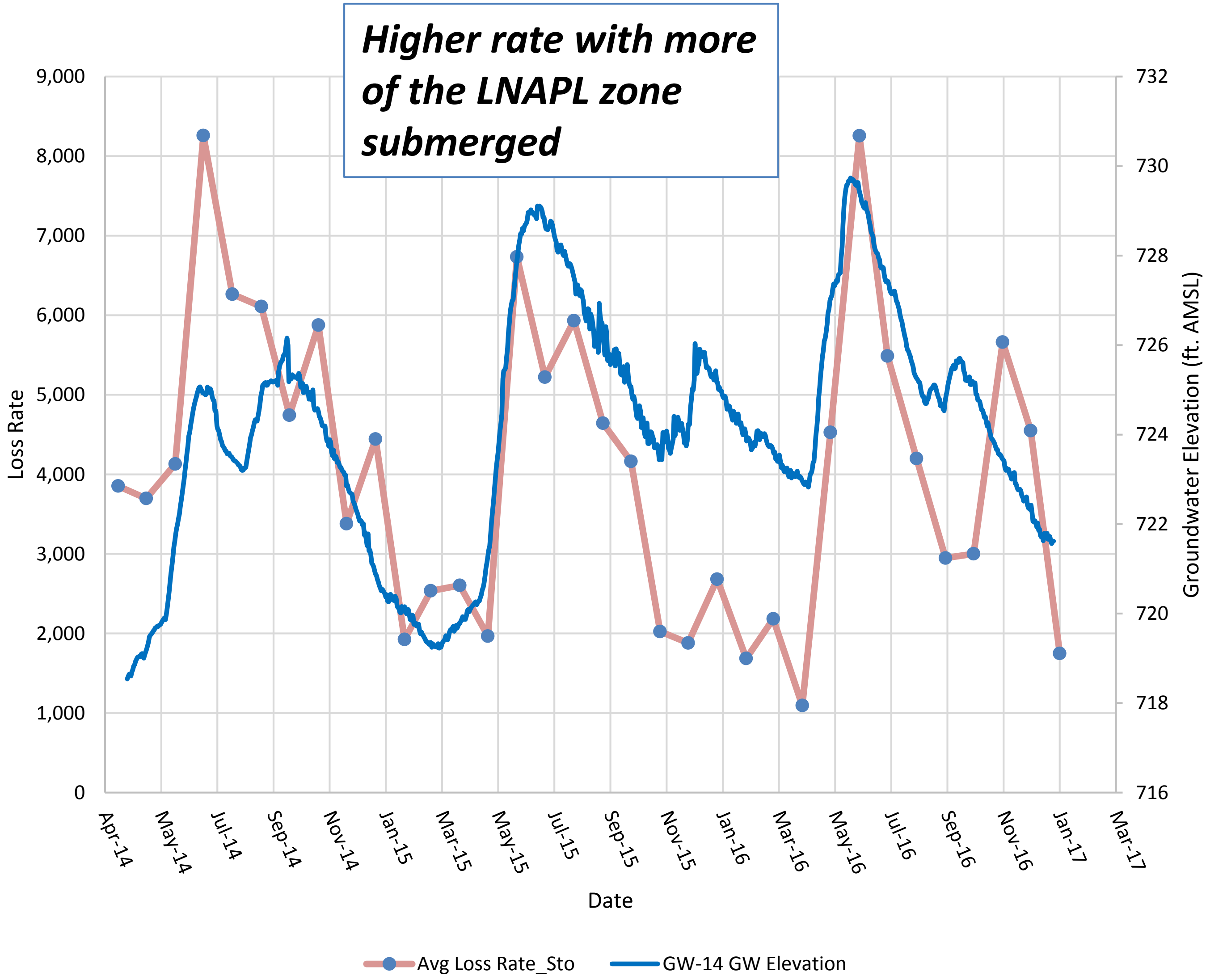




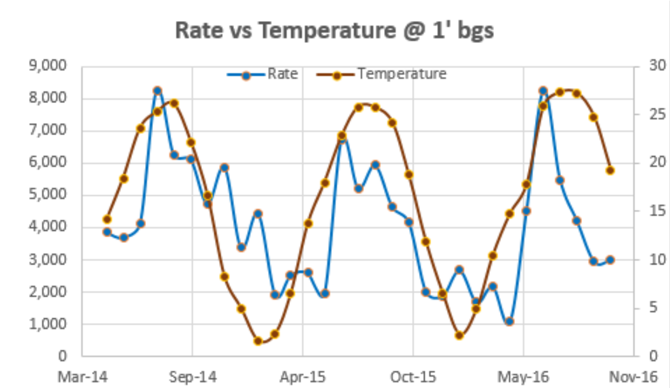
Is the assumption of a 5 month lag reasonable?

- Bemidji Site (Sihota, et. al., 2016): Yes
- Site-specific assessment: No

Water Table Fluctuation

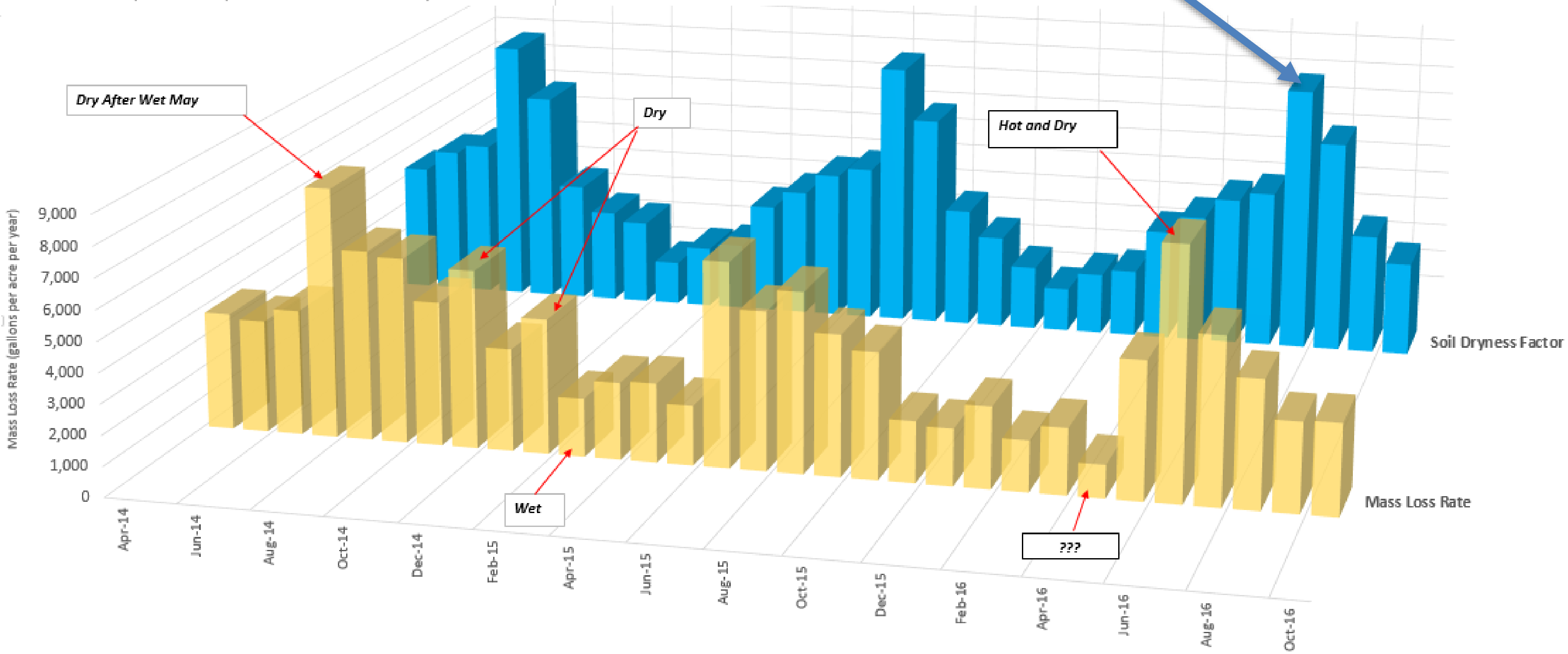


Rate vs Annual Soil Moisture Cycle



Derivation of monthly soil dryness factor based on long-term averages of:

- Pan evaporation
- Precipitation



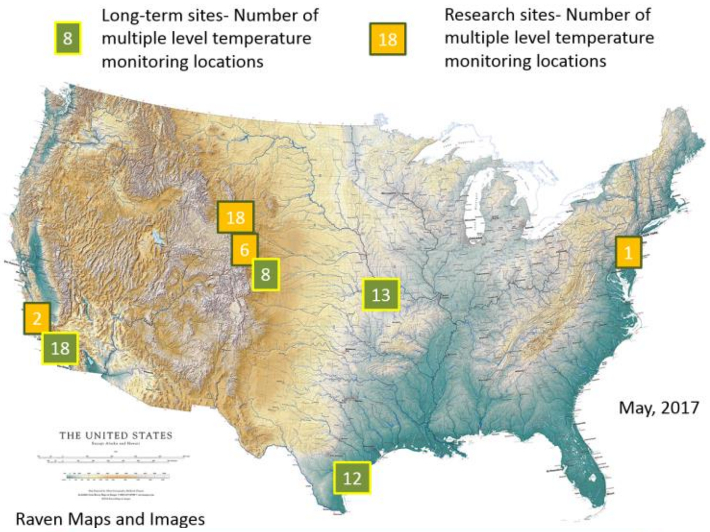
Findings for Terminal Site

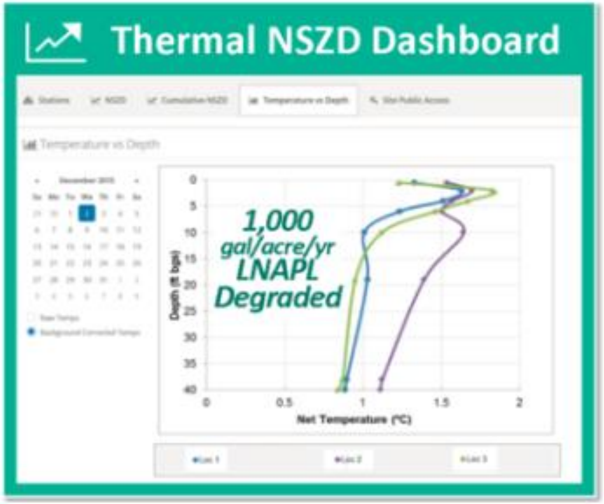
- Engineering: the biogenic heat monitoring system worked, and its still going
- NSZD Rate (northern transect):
  - CO_2 flux method: 4,900 gallons per acre per year
  - Thermal method: 4,000 gallons per acre per year
  - **Validation of the CSU energy balance model for rate derivation**
- Regulatory:
  - NSZD is the approved remedy for LNAPL zone and aqueous phase plume
  - Continued tracking of LNAPL mass loss and plume status required

“Limitation” of the Biogenic Heat Monitoring Method	TRC’s Experience with the CSU System
Background correction needed.	Yes…but not that hard.
Top and bottom of oxidation zone must be known.	Not with any precision.
Downward heat flux an uncertainty	Easily accounted for.
Must be careful of thermal anomalies.	Yes!
Unless the site is in an equatorial zone, need monitoring throughout the year.	A system for continuous monitoring exists.
Its complicated - have to account for the heat generated by all biological reactions, variable heat production.	Its not that complicated to derive a rate that has less uncertainty than other methods.

Findings for Broader Consideration

- Rate measurements based on biogenic gas efflux at the ground surface
  - Significant temporal variability
  - Cause of variability?
- Biogenic heat monitoring approach
  - Continuous monitoring accounts for temporary variability
  - The hardware and energy balance model has been validated
  - More cost-effective than surface efflux methods for:
    - "True annual average" LNAPL mass loss
    - Long-term monitoring





http://www.gsi-net.com/en/services/thermal-nszd.html

Thank you

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