TRC

Results you can rely on

Insights into NSZD Rate Measurements at LNAPL Sites

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16th RAILROAD ENVIRONMENT CONFERENCE

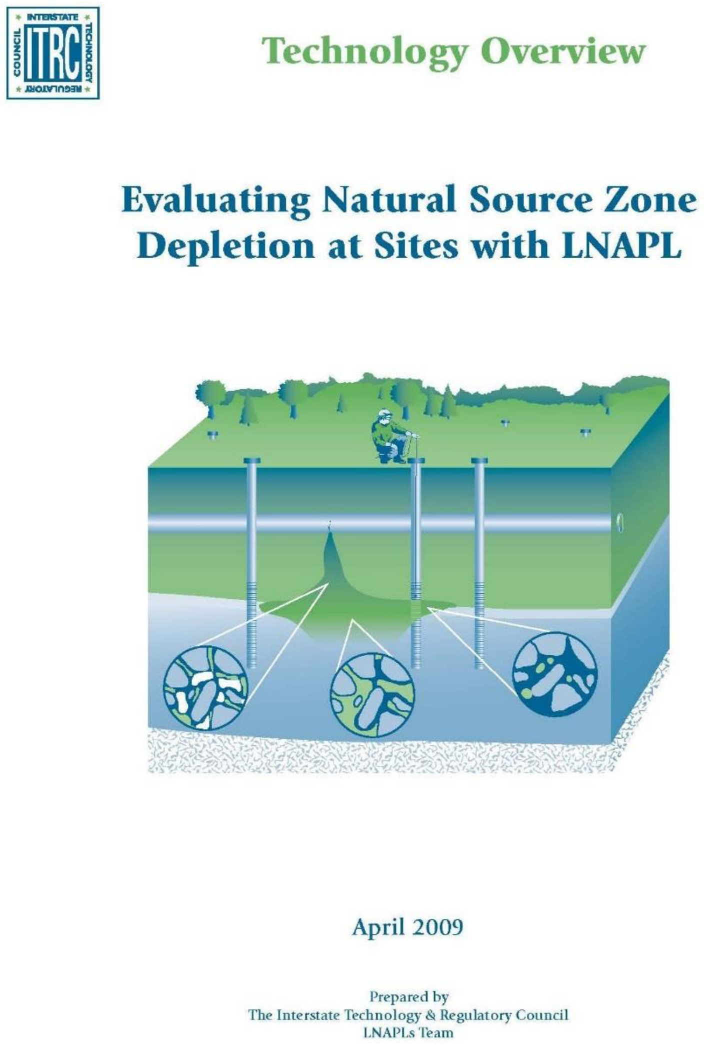
University of Illinois,

Urbana – Champaign, October 29, 2014

Presentation Overview

- Basic Principles
- Carbon Dioxide Trap Methodology
- Results from Various Sites
- Observations and Recommendations
- Thermal Flux Approach
- Case Study – Niche of NSZD in Regulatory Closure

Natural Source Zone Depletion (NSZD)


Technology Overview

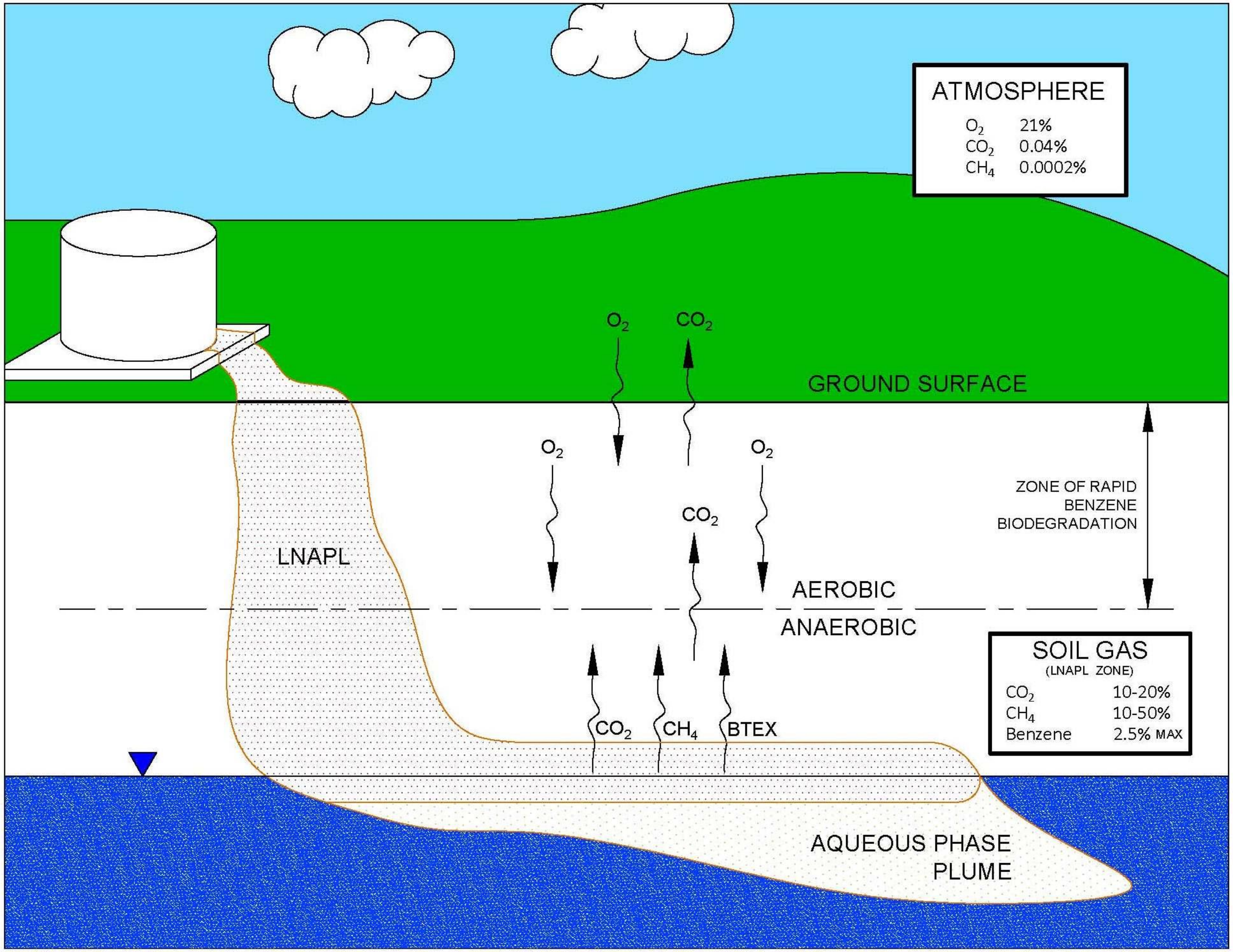
Evaluating Natural Source Zone Depletion at Sites with LNAPL

April 2009

Prepared by
The Interstate Technology & Regulatory Council
LNAPLs Team

- *"NSZD is a combination of processes that reduce the mass of LNAPL in the subsurface"*
- Naturally occurring biodegradation is typically the dominant process

LNAPL Biodegradation and Soil Gas Composition



Carbon Dioxide Trap Methodology

Groundwater

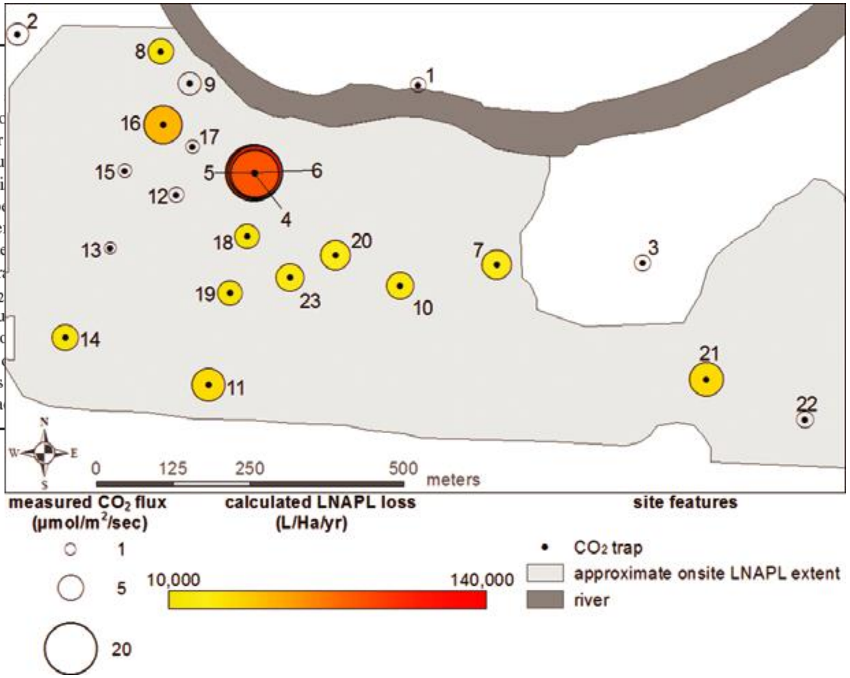
Methods Note/

Measurement of Natural Losses of LNAPL Using CO_2 Traps

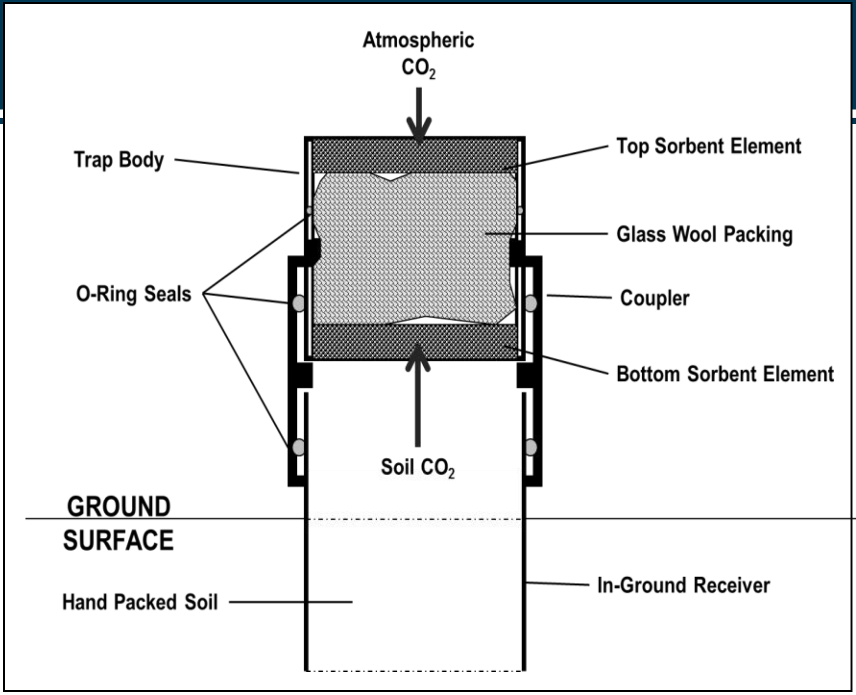
by Kevin McCoy[1], Julio Zimbron[1], Tom Sale[2], and Mark Lyverse[3]

Abstract

Efflux of CO_2 above releases of petroleum light nonaqueous phase liquids (LNAPLs) has emerged parameter for resolving natural losses of LNAPLs and managing LNAPL sites. Current approaches fo CO_2 efflux include gradient, flux chamber, and mass balance methods. Herein a new method for CO_2 efflux above LNAPL bodies, referred to as CO_2 traps, is introduced. CO_2 traps involve an u lower solid phase sorbent elements that convert CO_2 gas into solid phase carbonates. The sorbent i an open vertical section of 10 cm ID polyvinyl chloride (PVC) pipe located at grade. The lower sorbe captures CO_2 released from the subsurface via diffusion and advection. The upper sorbent eleme atmospheric CO_2 from reaching the lower sorbent element. CO_2 traps provide integral measureme efflux based over the period of deployment, typically 2 to 4 weeks. Favorable attributes of CO_2 tr simplicity, generation of integral (time averaged) measurement, and a simple means of capturing CO_2 isotope analysis. Results from open and closed laboratory experiments indicate that CO_2 traps qu capture CO_2. Results from the deployment of 23 CO_2 traps at a former refinery indicate natural lo LNAPL (measured in the fall, likely concurrent with high soil temperatures and consequently high rates) ranging from 13,400 to 130,000 liters per hectare per year (L/Ha/year). A set of field triplicates coefficient of variation of 18% (resulting from local spatial variations and issues with measurement a



CO_2 Traps
Credit: Kevin McCoy/CSU

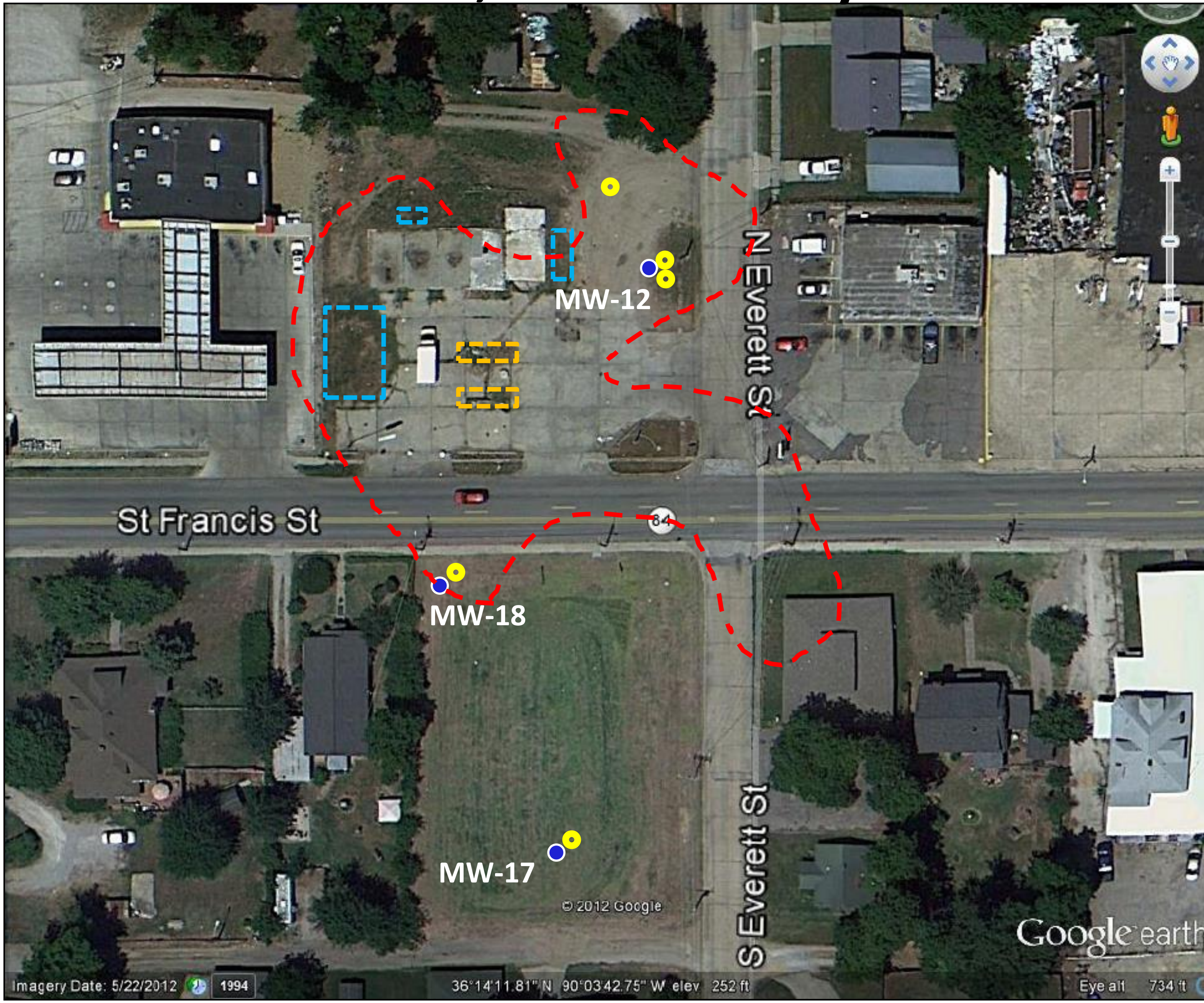


- Integral CO_2 flux measurement
- 2 sorbent elements
  - Sodalime media
  - Bottom element → soil CO_2
  - Top element → atmospheric CO_2
- Travel blank for QC
- Lab analysis for total carbonate

Basic Scope of Work - NSZD Rate Measurement

- "Snapshot" of LNAPL Intrinsic Bioremediation Rate
- Plant 5 Traps + travel blank
  - 3 locations
  - 1 duplicate
  - 1 background
- Leave in place two weeks
- Analyze for carbon dioxide and ^{14}C
- Associated measurements
  - Groundwater temperature
  - Vadose zone oxygen, methane and carbon dioxide

Kennett, MO Site – Layout



○ CO_2 Trap Locations
● Monitoring Well Locations
Former UST Pit
Former Fueling Island
Consistent LNAPL

Kennett MO – Q1 Results

Sample	Location	CO_2 Flux Rate (GPAY)
TRC-CO2-05	MW-17	819
TRC-CO2-01	MW-18	1,220
TRC-CO2-02	MW-12	738
TRC-CO2-03		480
TRC-CO2-04	NW of MW-12	2,083
Average for Three Locations in LNAPL Zone		***1,304***

[1] **Values are corrected for ^{14}C**

Duplicate	(orange)
Background	(green)

Technical Findings - Methodology

- ^{14}C Method a More Reliable Method than Background Location for Determining Background
  - Significant ^{14}C flux at the background location
  - Method based on background location can significantly underestimate the rate
- Overall Rate Estimation is Conservative
  - Traps give flux at a specific location (units of GPAY)
  - Multiple traps give average flux over the LNAPL zone
  - Average flux x LNAPL footprint = overall rate (gallons per year)
  - Does not account for CO_2 flux from the ground surface outside the LNAPL footprint

Results

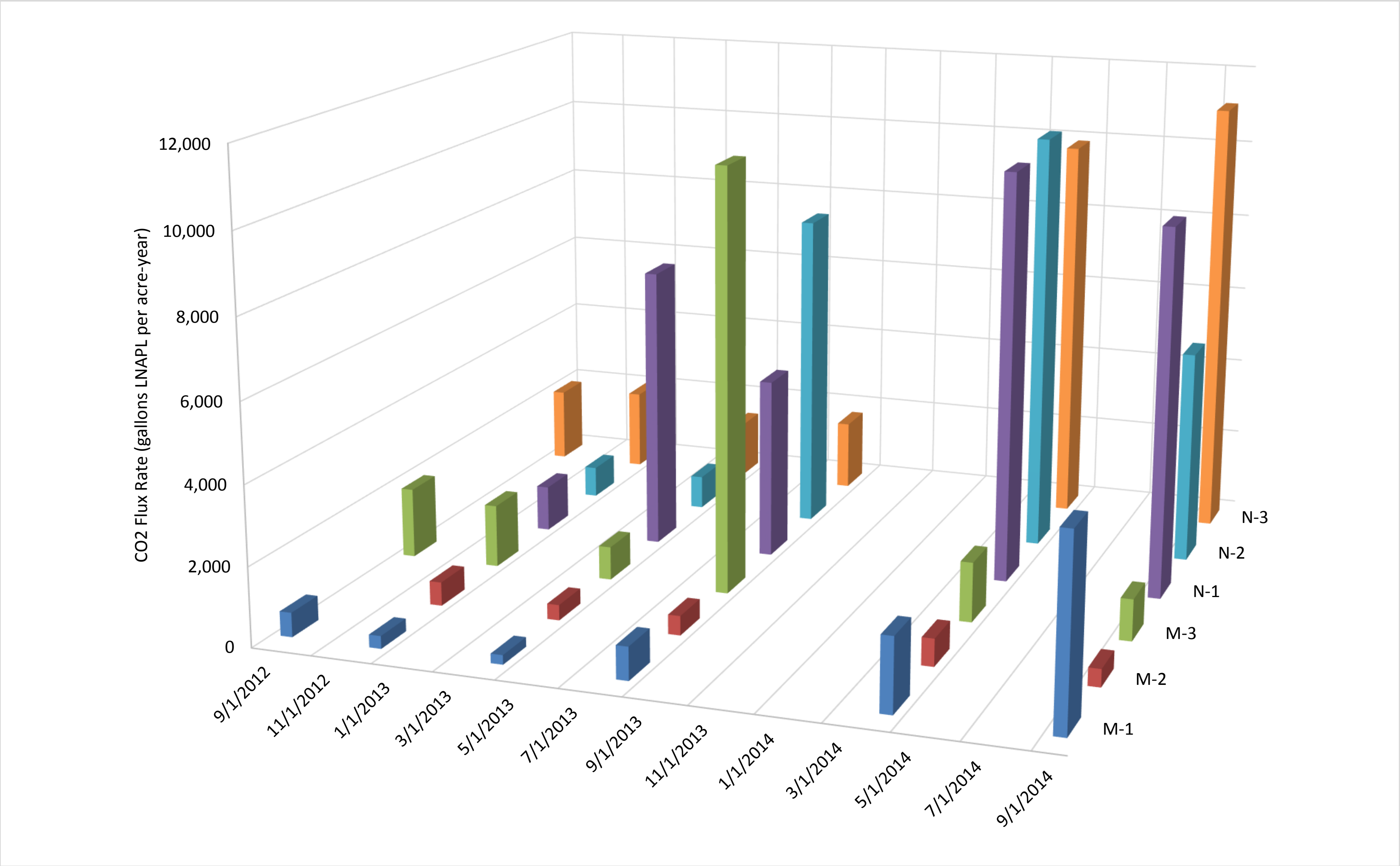
Location	Fuel Type	LNAPL Zone (acres)	Methodology		NSZD Rate (GPAY)
			Trap Locations (LNAPL Zone)	Frequency	
Kansas City, KS	Weathered Fuel Mixture (Predominantly C_{12} to C_{16})	22	3 to 6	Quarterly, 6 events total to date	3,100
Kennett, MO	Gasoline	1.3	3	Quarterly - One Year	1,050
Klamath Falls, OR	Diesel	5.5	4	Once	1,800
Spanish Lake, MO	Gasoline	0.6	3	Once	300
West Quincy, MO	Diesel	0.9	3	Once	2,700

Rates are ^{14}C Corrected, No Additional Corrections (Background Location)

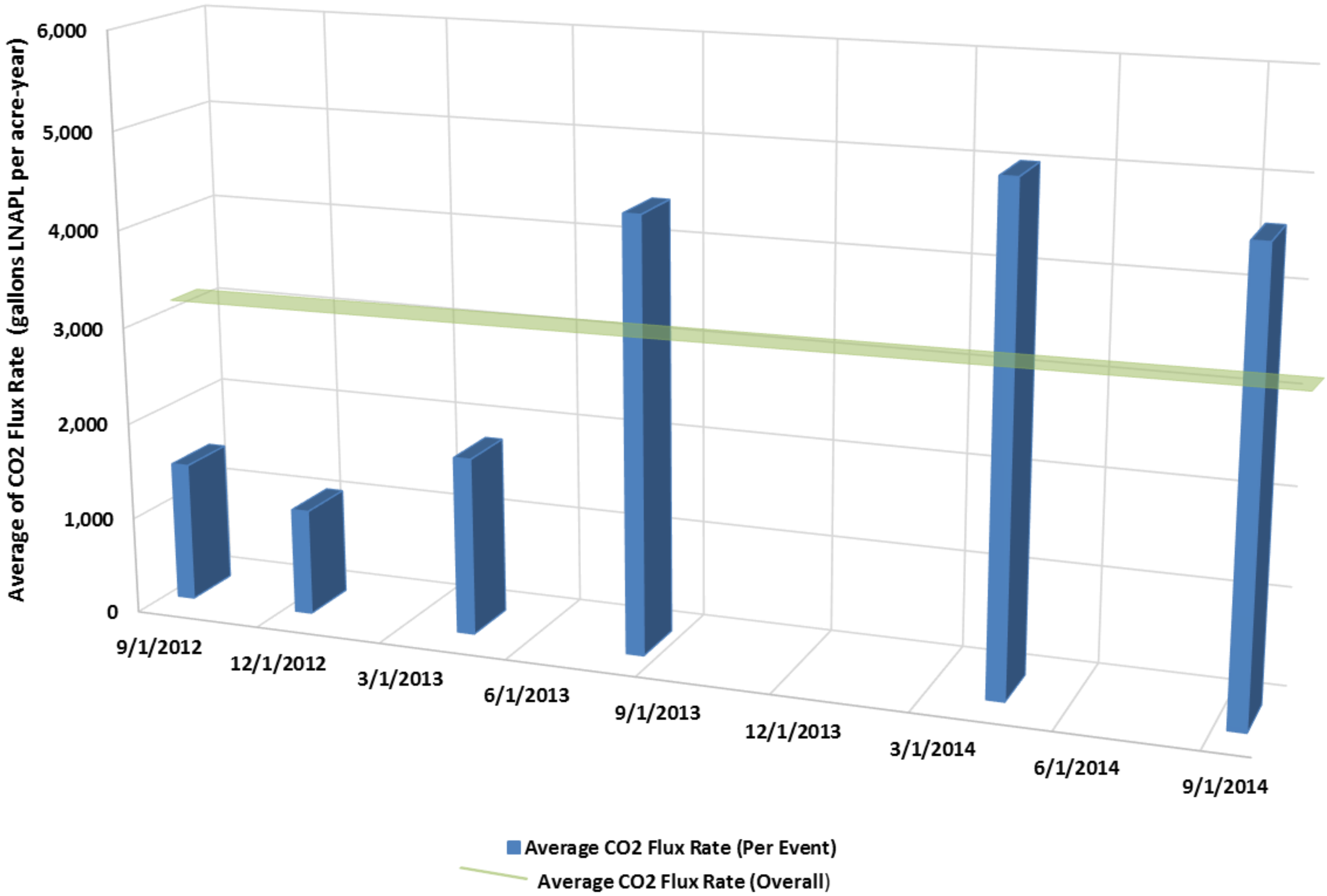
Technical Findings – NSZD Rate

- Rates ranged from 300 to 3,000 GPAY
- Consistent with range of rates reported in ITRC LNAPL Training (Kansas City, MO – April 2014): "***hundreds to thousands of gallons per acre per year***"

Kansas City, KS – Variability in Measured Rate by Location



Kansas City, KS – Variability in Average Rate



Factors Potentially Impacting Carbon Dioxide Flux Measurements

- Temperature
- Rainfall, soil moisture content, and soil gas diffusion
- Variability in soil profile
- Wind (Bernoulli's Principle and Stack Effect)
- Water table fluctuations
  - Rising water table and displacement of soil gas
  - Falling water table and influx of atmospheric gas
  - Rate = f (submergence)?

Carbon Dioxide Traps
Paired with Monitoring Wells

Site Screening – Soil Gas Measurements

Ground Water Monitoring & Remediation

A New Screening Method for Methane in Soil Gas Using Existing Groundwater Monitoring Wells

by Kenneth P. Jewell and John T. Wilson

Soil Gas Composition (% v/v)

Site	Average CO_2 Flux Rate (gallons LNAPL per acre per year)	Most Anaerobic Location			Average for All LNAPL Zone Wells		
		O_2	CO_2	CH4	O_2	CO_2	CH_4
Spanish Lake, MO	300	0.1	14.5	0.2	5.9	9.2	0.1
Kennett, MO	1,050	0.7	14.4	6.4	1	13.8	5.3
Klamath Falls, OR*	1,800	0	14.2	2.3	4.8	11.1	2.4
Kansas City, KS	3,100	0	9.6	48	0.7	13.7	25.3

* Average does not include apparently anomalous results for MW-7

Methane Measurements
Kansas City, KS

Well	Method	Methane (%)
RW-209	Laboratory (Summa)	32.0
	Field (Meter)	29.3
RW-229	Laboratory (Summa)	19.0
	Field (Meter)	18.5
MW-15	Laboratory (Summa)	11.0
	Field (Meter)	24.3
RW-234	Laboratory (Summa)	12.0
	Field (Meter)	16.4

Technical Findings - Methodology

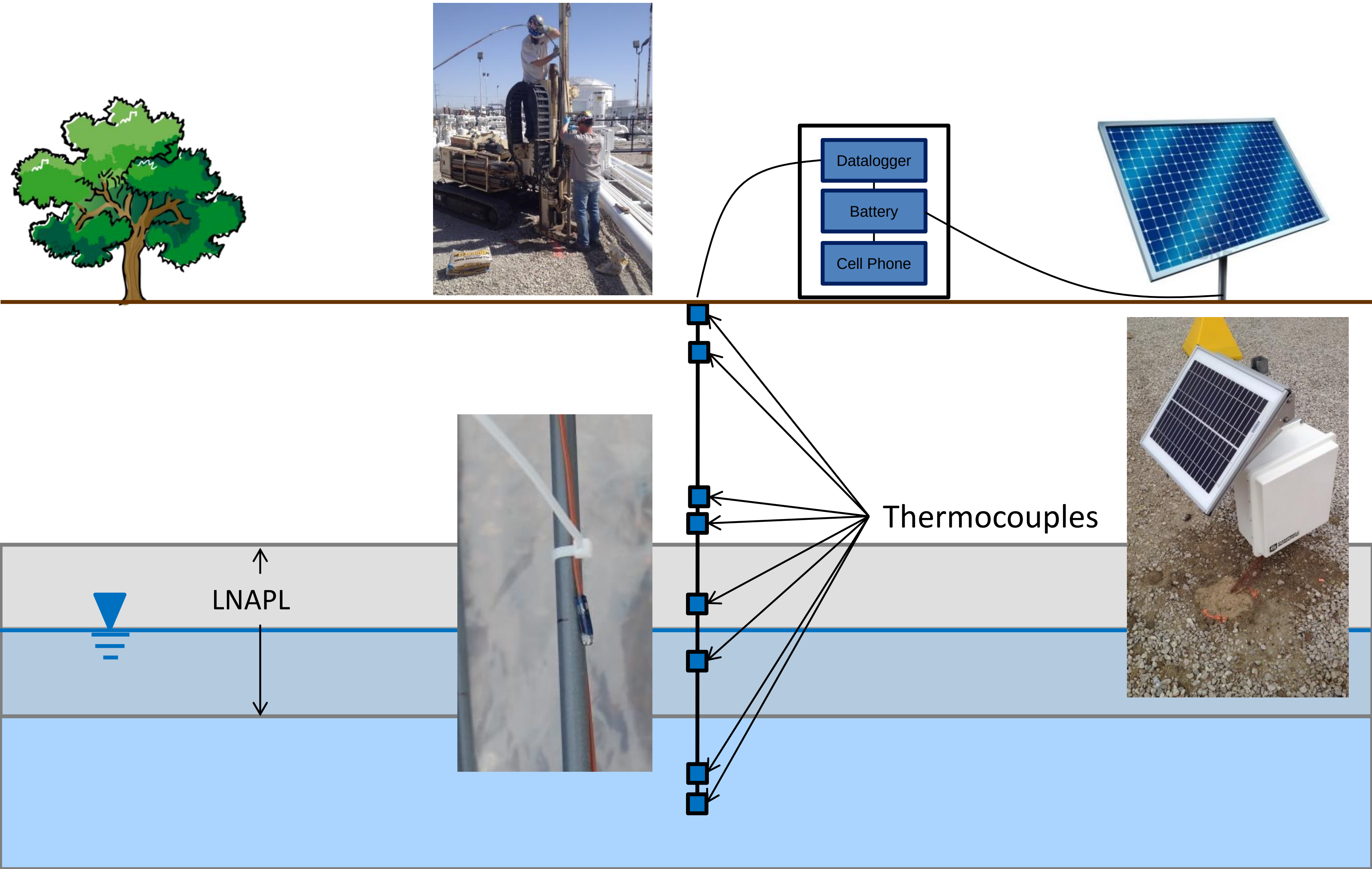
- Soil gas measurements a useful screening step
- Duplicate results indicate small-scale variability in measurement is within reasonable limits
- Two sites allow assessment of accuracy based on a single measurement versus average based on quarterly measurements:
  - Kennett, MO: +/- 30 percent
  - Kansas City, KS: Underestimate by a factor of 3, overestimate by a factor of 2
- A single round of measurements provides a value “in the ballpark”

NSZD Rate from Thermal Flux

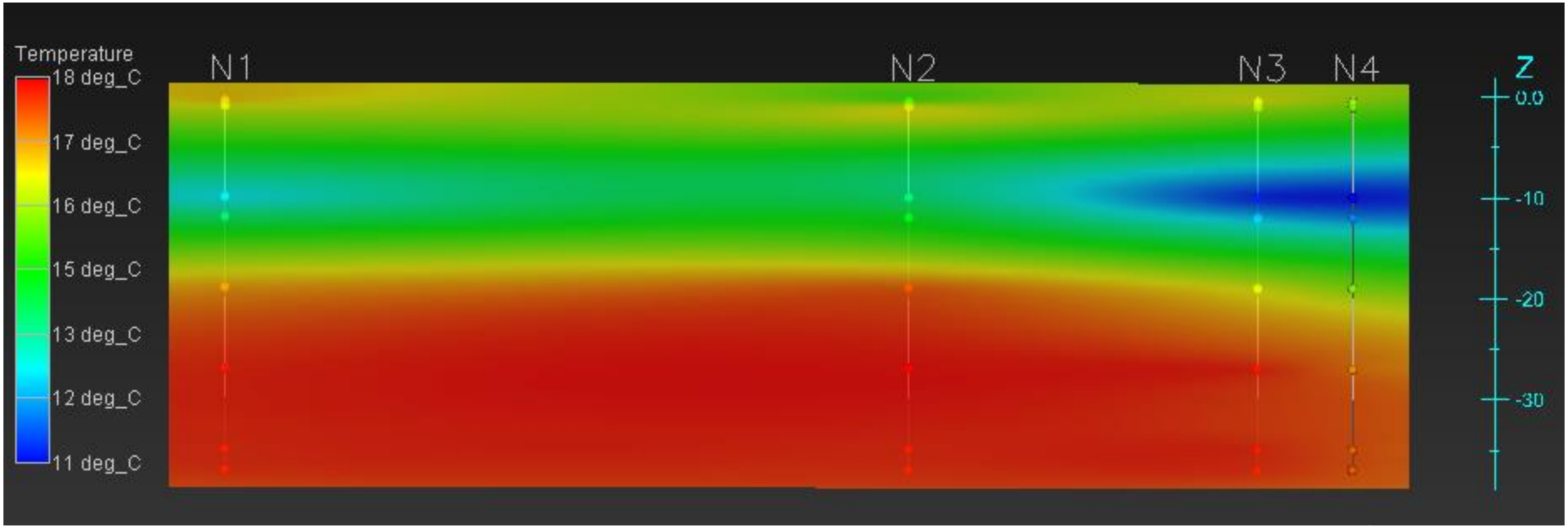
- Hypothesis
  - Fuel oxidation is exothermic
  - Heat of reaction can be used to derive NSZD rate measurement
  - Continuous temperature monitoring can yield real-time rate monitoring

- Objectives
  - Provide another line of evidence for NSZD rate measurement.
  - Continuous rate measurement to better quantify annual natural LNAPL losses, assess longevity of impacts.
- Application (in progress)
  - Kansas City, KS Site
  - Collaboration with CSU Center for Contaminant Hydrology

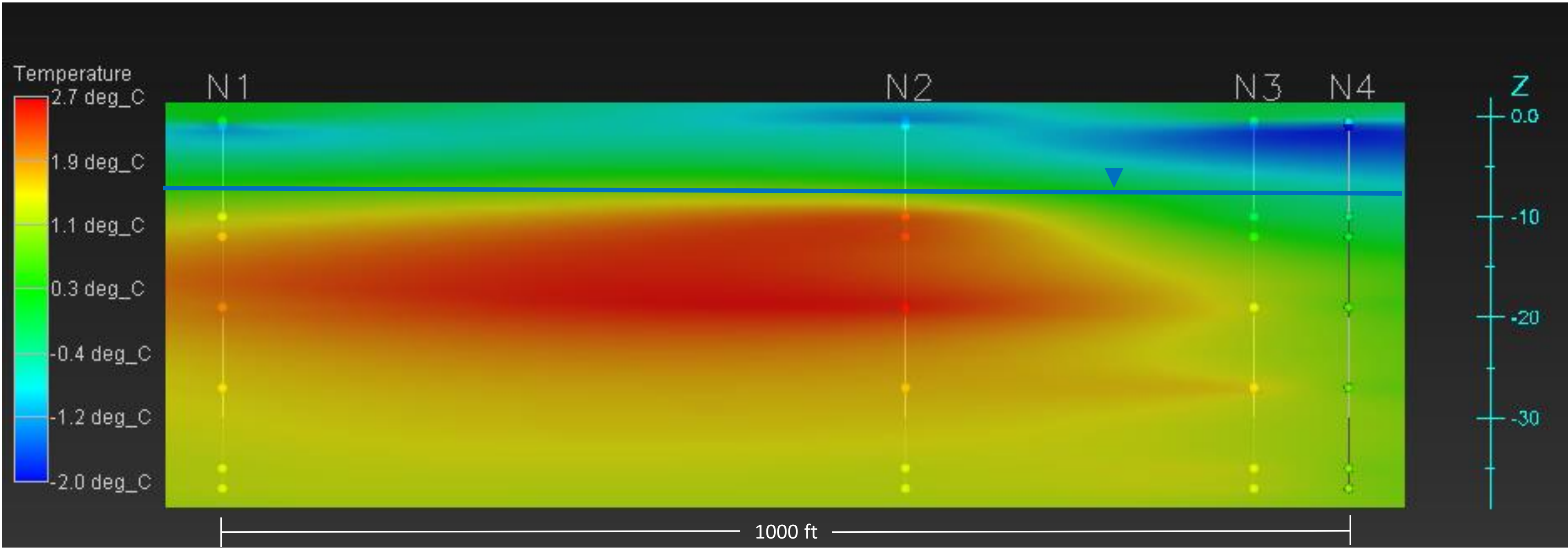
Kansas City, KS Field Setup



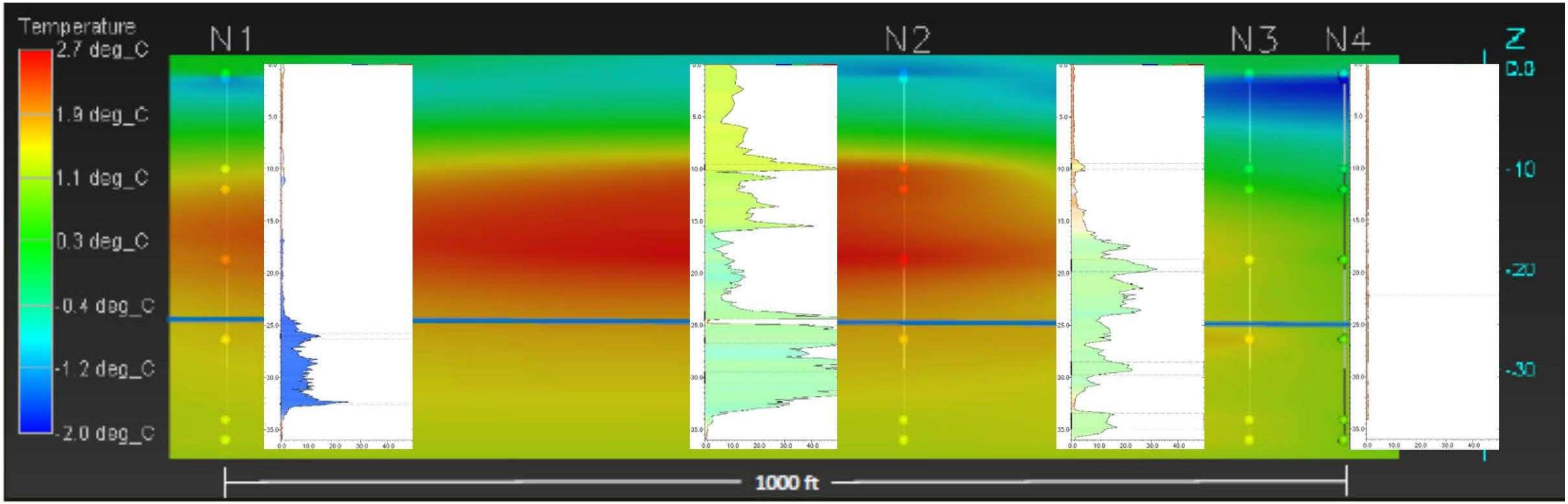
Kansas City, KS Temperature Profile



With Background Correction



With LIF LNAPL Profile



Regulatory and LNAPL Recovery Implications

- Requirement to "*remove free product to the maximum extent practicable as determined by the implementing agency*" (40 CFR 280.64, 1988)
  - Assumption: Any free product posed a particularly significant hazard; e.g., migration to nearby sewers
- Things we have learned since 1988:
  - "Free product" is often a small fraction of total LNAPL, particularly with an aged release
  - "Accumulation in a well" does not equal macro-scale mobility, NOT a good metric for recoverability
  - <u>NSZD rate will often far exceed rate of free product recovery, particularly with an aged release</u>

BNSF Yard – Klamath Falls, Oregon

- **Key Site Issues:**
  - Dissolved-phase diesel plume stability
  - Persistent occurrence of LNAPL in several wells
- **Historical LNAPL Recovery Efforts**
  - Hand bailing
  - Operation of belt skimmer system between 1997 and 2005
  - Skimmer system efficiency decreased due to the decrease in recoverable LNAPL
  - Seven Vacuum Enhanced Fluid Recovery (VEFR) events conducted in 2012

Phase Approach to NSZD Evaluation

Phase I - Characterize biogeochemistry and determine dominant intrinsic bioremediation processes through groundwater and soil gas sampling

Phase II – Implement NSZD evaluation to provide site-specific intrinsic rate of LNAPL removal

BNSF Yard – Klamath Falls, Oregon

Historic LNAPL Removal

- Total of 589 gallons of LNAPL recovered via hand bailing and skimmer system operation between 1997 and 2005
- Estimate approximately 1,000 gallons of LNAPL recovered during seven VEFR events in 2012

vs.

LNAPL Removal via NSZD

- Approximately 2,500 gallons per year via intrinsic rate of NSZD (based on conservative flux rate)

BNSF Yard – Klamath Falls, Oregon

- ***June 2013*** - TRC awarded project
- ***September - October 2013*** – TRC implemented NSZD field evaluation
- ***December 2013*** – Site-specific intrinsic rate of NSZD established
- ***February 2014*** – TRC submitted Summary Technical Report of NSZD Results and Findings
- **August 2014** – Targeted project outcome achieved

Oregon
John A. Kitzhaber, MD, Governor

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August 4, 2014

Scott MacDonald
BNSF Railway Company
2454 Occidental Ave. S, Suite 1A
Seattle, WA 98134

Re: Conditional No Further Action Determination, BNSF Midland Market Rail Yard, Klamath Falls, ECSI No. 1732

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  - "Accumulation in a well" does not equal macro-scale mobility, NOT a good metric for recoverability
  - NSZD rate will often far exceed rate of free product recovery, particularly with an aged release
- For regulatory agencies, the most readily acceptable niche for NSZD: "*a polishing step at the end of an active remediation effort*"

For More Information

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