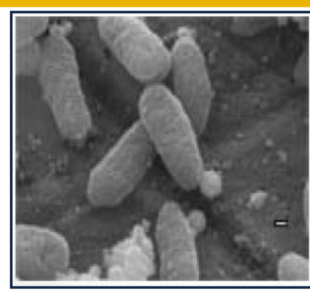
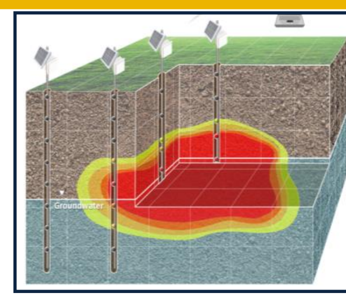
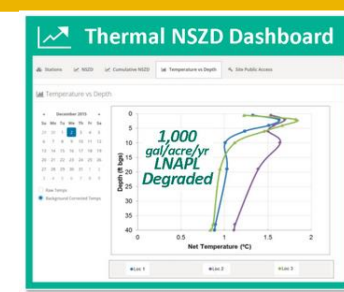
Feelin' the Burn: Thermal Monitoring of Natural Source Zone Depletion (NSZD)







Poonam R. Kulkarni, P.E.
GSI Environmental Inc.

TAEP Meeting
September 15, 2016

Natural Source Zone Depletion (NSZD): *Technology Development*

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]

CO_2-Efflux Measurements for Evaluating Source Zone Natural Attenuation Rates in a Petroleum Hydrocarbon Contaminated Aquifer

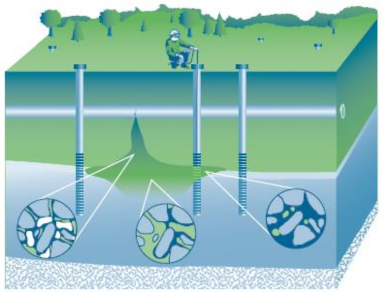
NATASHA J. SIHOTA, OLGA SINGURINDY, AND K. ULRICH MAYER*

University of British Columbia, Department of Earth and Ocean Sciences, 6339 Stores Rd., Vancouver, BC, V6T 1Z4, Canada

Received September 24, 2010. Revised manuscript received November 29, 2010. Accepted November 30, 2010.

Technology Overview

Evaluating Natural Source Zone Depletion at Sites with LNAPL



April 2009

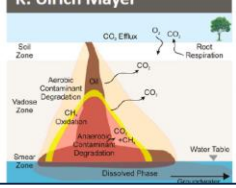
Prepared by
The Interstate Technology & Regulatory Council
LNAPLs Team

Groundwater Monitoring&Remediation

Temperature as a Tool to Evaluate Aerobic Biodegradation in Hydrocarbon Contaminated Soil

by Robert E. Sweeney and G. Todd Ririe

Natasha J. Sihota*
K. Ulrich Mayer



Characterizing Vadose Zone Hydrocarbon Biodegradation Using Carbon Dioxide Effluxes, Isotopes, and Reactive Transport Modeling

Naturally occurring biodegradation of hydrocarbon compounds may offer a sustainable management option at contaminated sites. However, a sound understanding of contaminant mass loss rates is required to enable estimation of source zone longevity, serving to alleviate public concerns and inform decision makers. Under some conditions, surficial CO_2 efflux measurements can be useful to delineate petroleum hydrocarbon containing source zones, and to provide estim
tion rates. However, the accu
separate CO_2 effluxes associa
to naturally occurring soil res
within the vadose zone, this

Ground Water Monitoring&Rem

Source Zone Natural Attenuation at Petroleum Hydrocarbon Spill Sites—I: Site-Specific Assessment Approach

by Paul Johnson, Paul Lundegard, and Zhuang Liu

Relating subsurface temperature changes to microbial activity at a crude oil-contaminated site

CrossMark

Ean Warren *, Barbara A. Bekins

U.S. Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025, United States

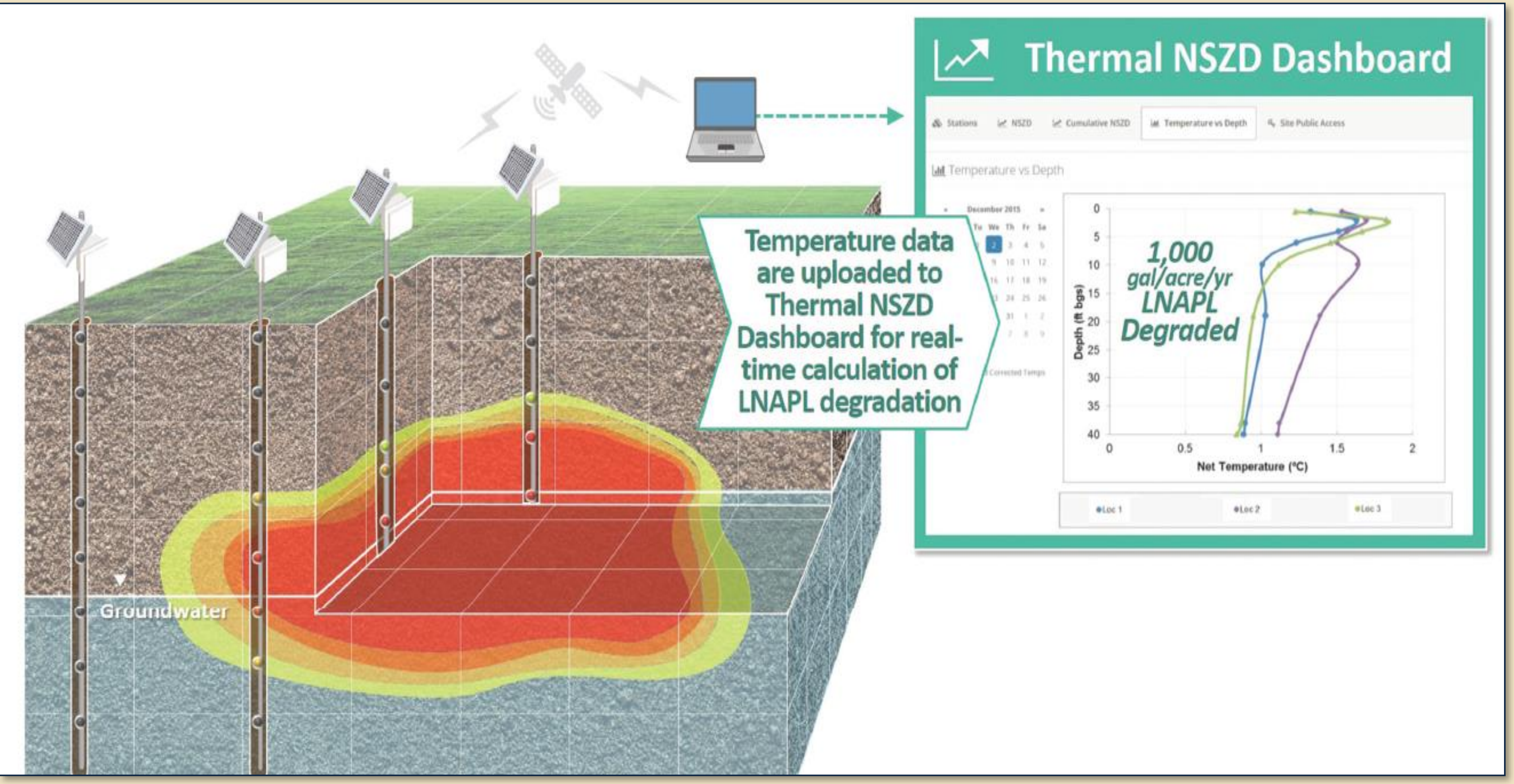
ARTICLE INFO

Article history:
Received 29 July 2015
Received in revised form 26 August 2015
Accepted 10 September 2015
Available online 15 September 2015

ABSTRACT

Crude oil at a spill site near Bemidji, Minnesota has been undergoing aerobic and anaerobic biodegradation for over 30 years, creating a 150–200 m plume of primary and secondary contaminants. Microbial degradation generates heat that should be measurable under the right conditions. To measure this heat, thermistors were installed in wells in the saturated zone and in water-filled monitoring tubes in the unsaturated zone. In the saturated zone, a thermal groundwater plume originates near the residual oil body with temperatures ranging from 2.9 °C

Thermal NSZD



www.ThermalNSZD.com

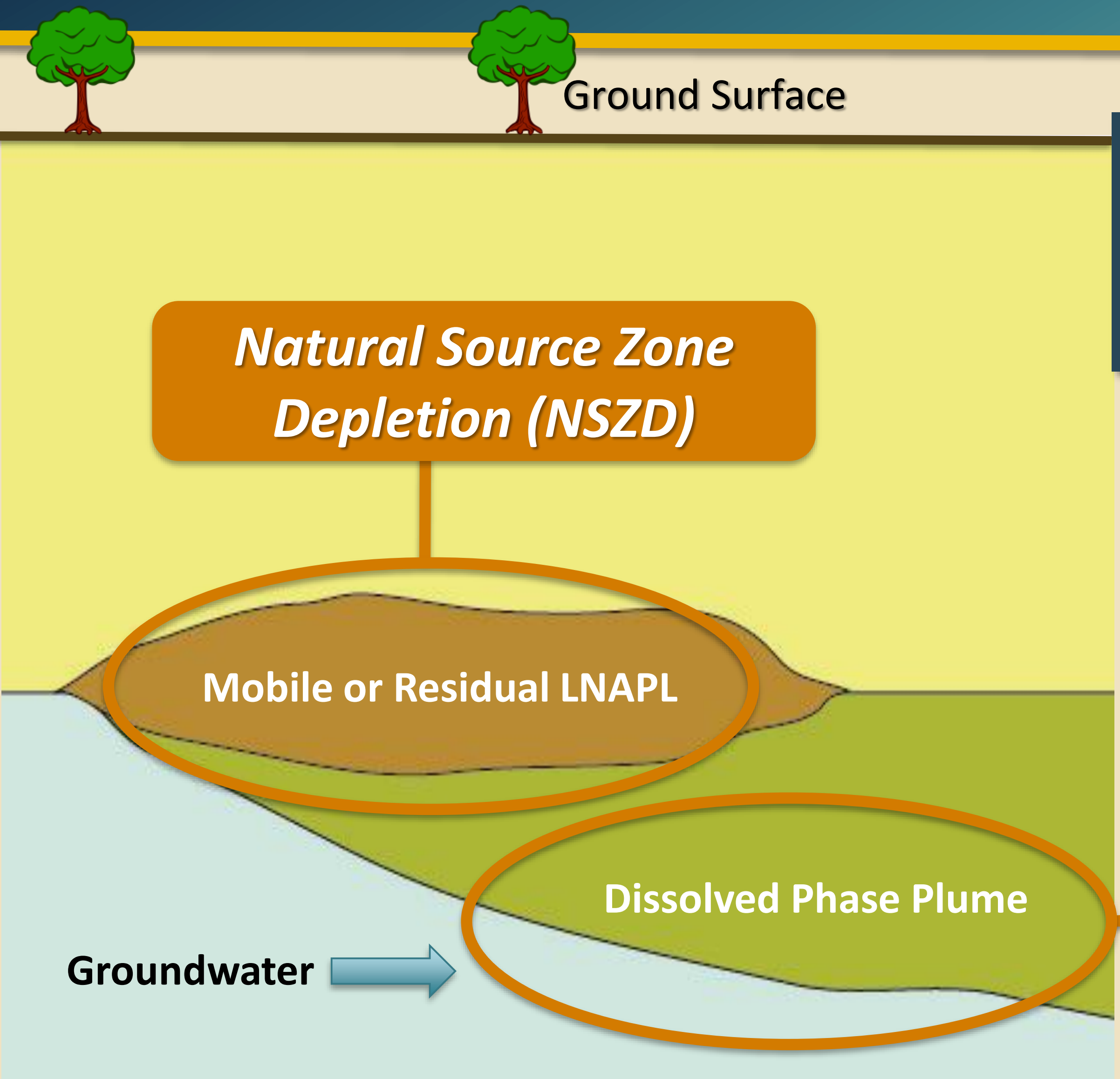
Thermal NSZD Theory:
Heat Released from Biodegradation

COMPOST PILE

KEY POINT: **Use heat released from biodegradation to calculate continuous estimates of NSZD rates**

Monitored Natural Attenuation (MNA) *versus* Natural Source Zone Depletion (NSZD)

KEY POINT: ***MNA mostly focused on plume, while NSZD describes attenuation within the source zone.***



Monitored Natural Attenuation (MNA)

Adapted from: ITRC, 2009

Groundwater Mass Flux vs. Vapor Phase Mass Flux

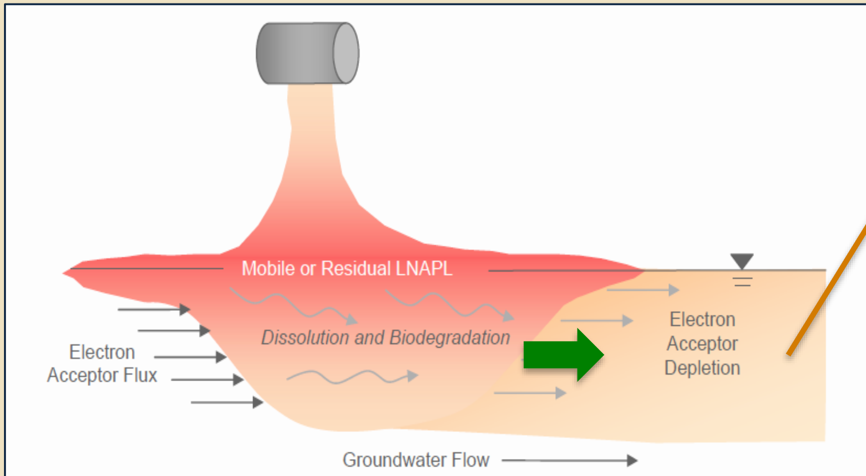


Figure 2-1. Groundwater transport–related NSZD processes.

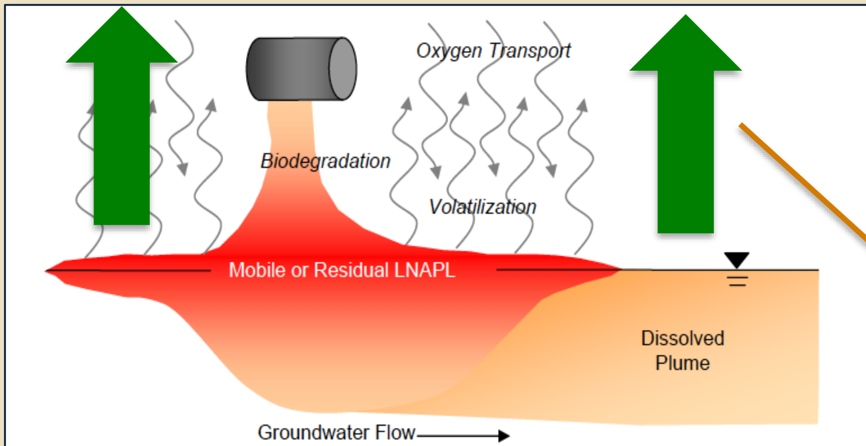


Figure 2-2. Vapor transport–related NSZD processes.

1-10%

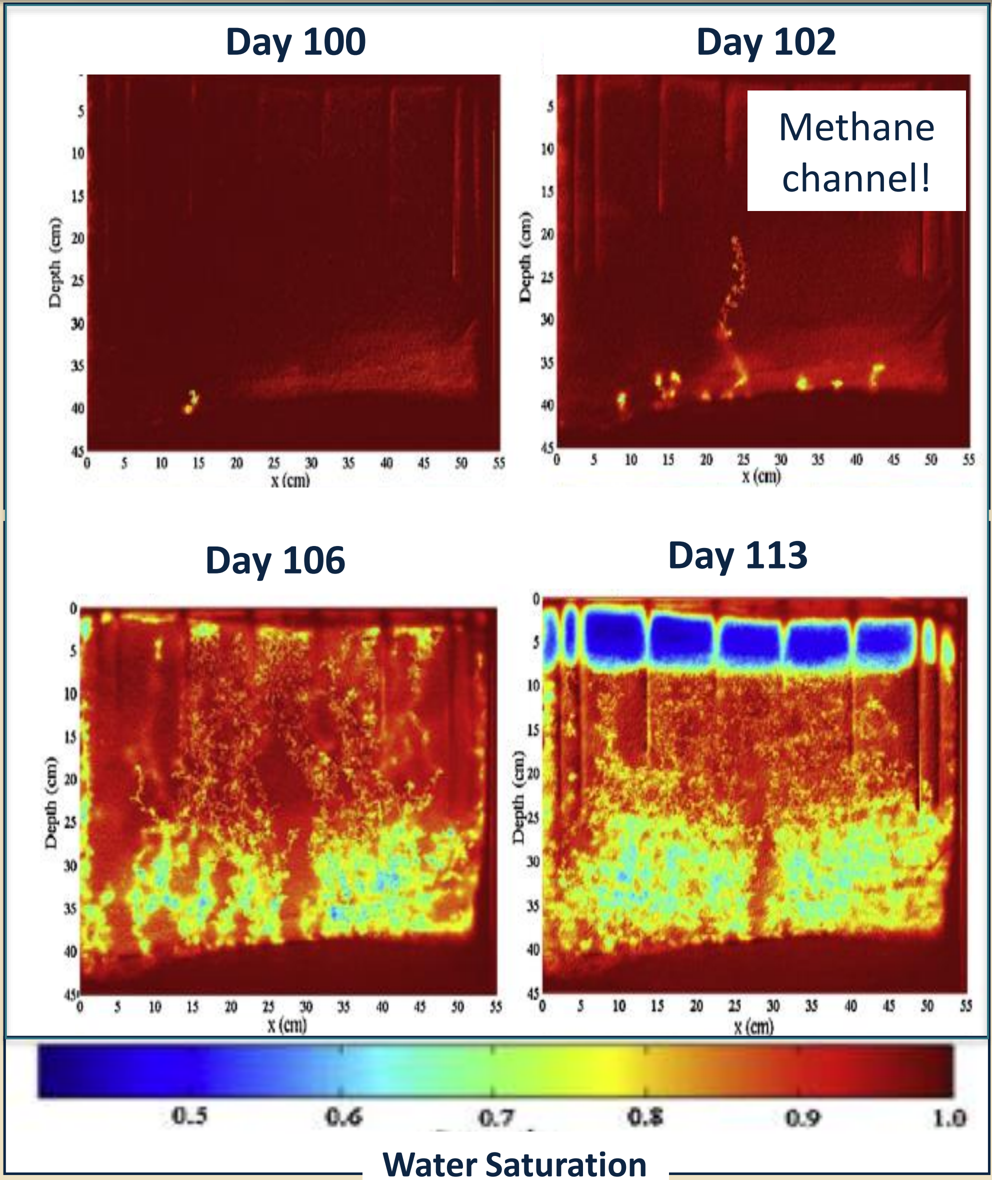
90-99%

Surprising Result: **Vapor transport fluxes much greater than groundwater fluxes!**

ITRC, 2009; Suthersan 2015

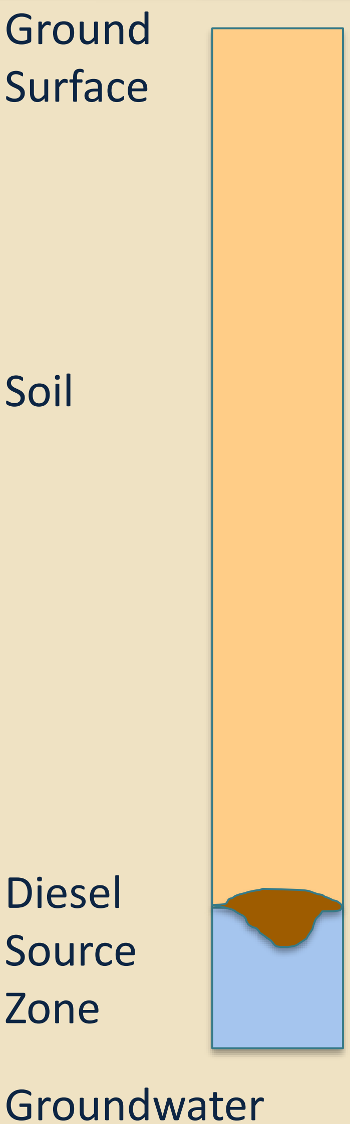
Starting Point: *Refinery and Terminal Petroleum Spills Generate Methane from Biodegradation*

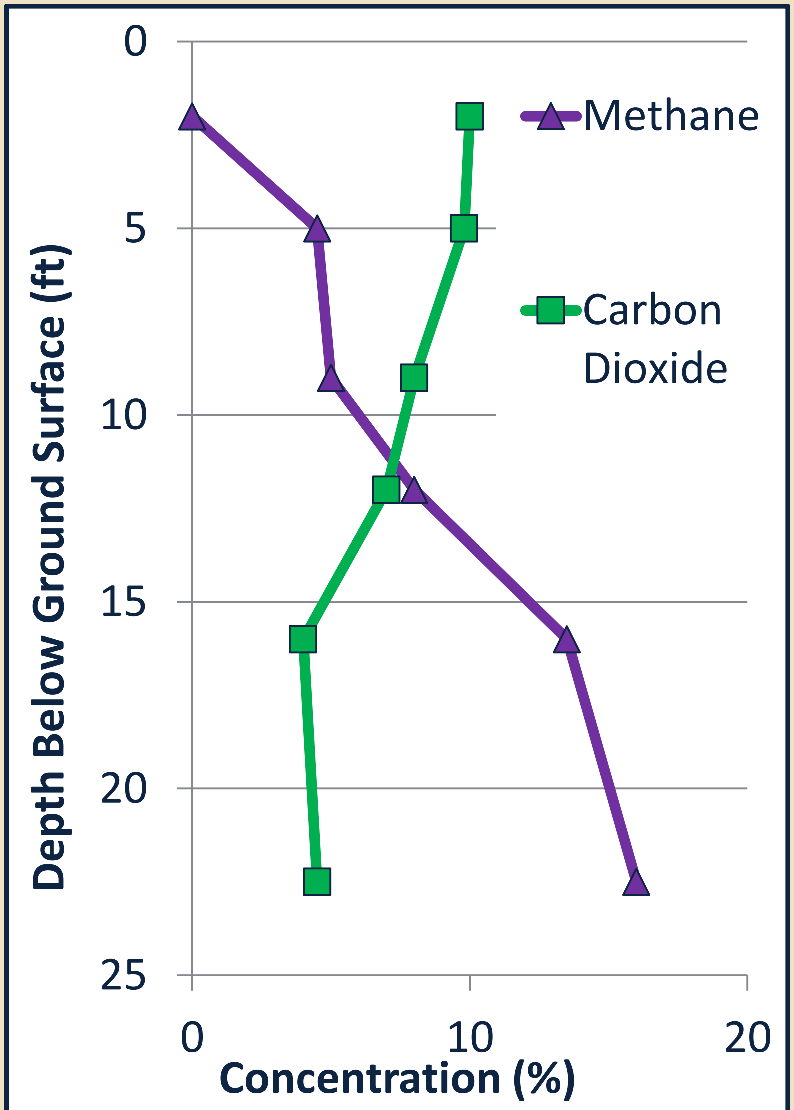
Source: *CSU*



Source: *Ye et al., 2009*

Soil Vapor Profile above Diesel Source Zone at Railyard

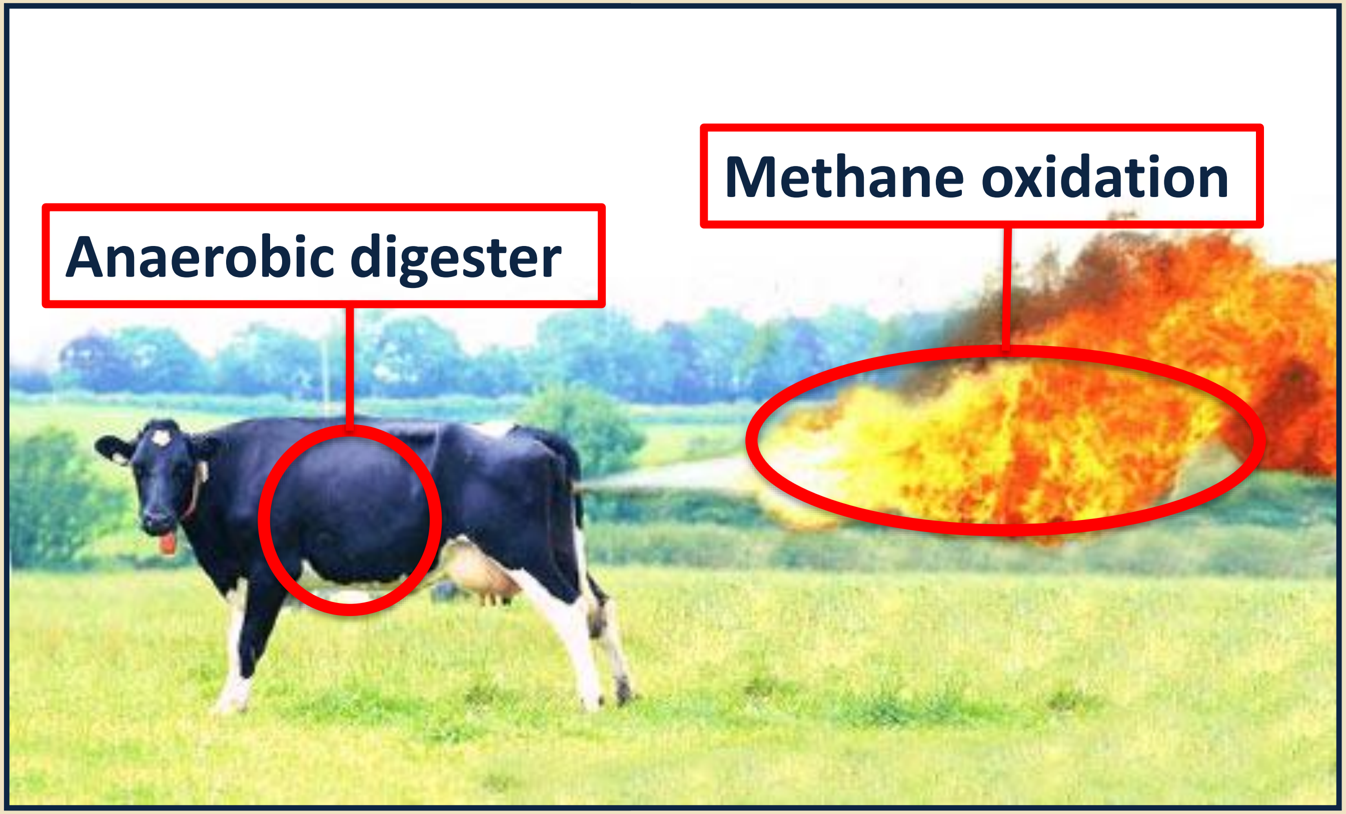




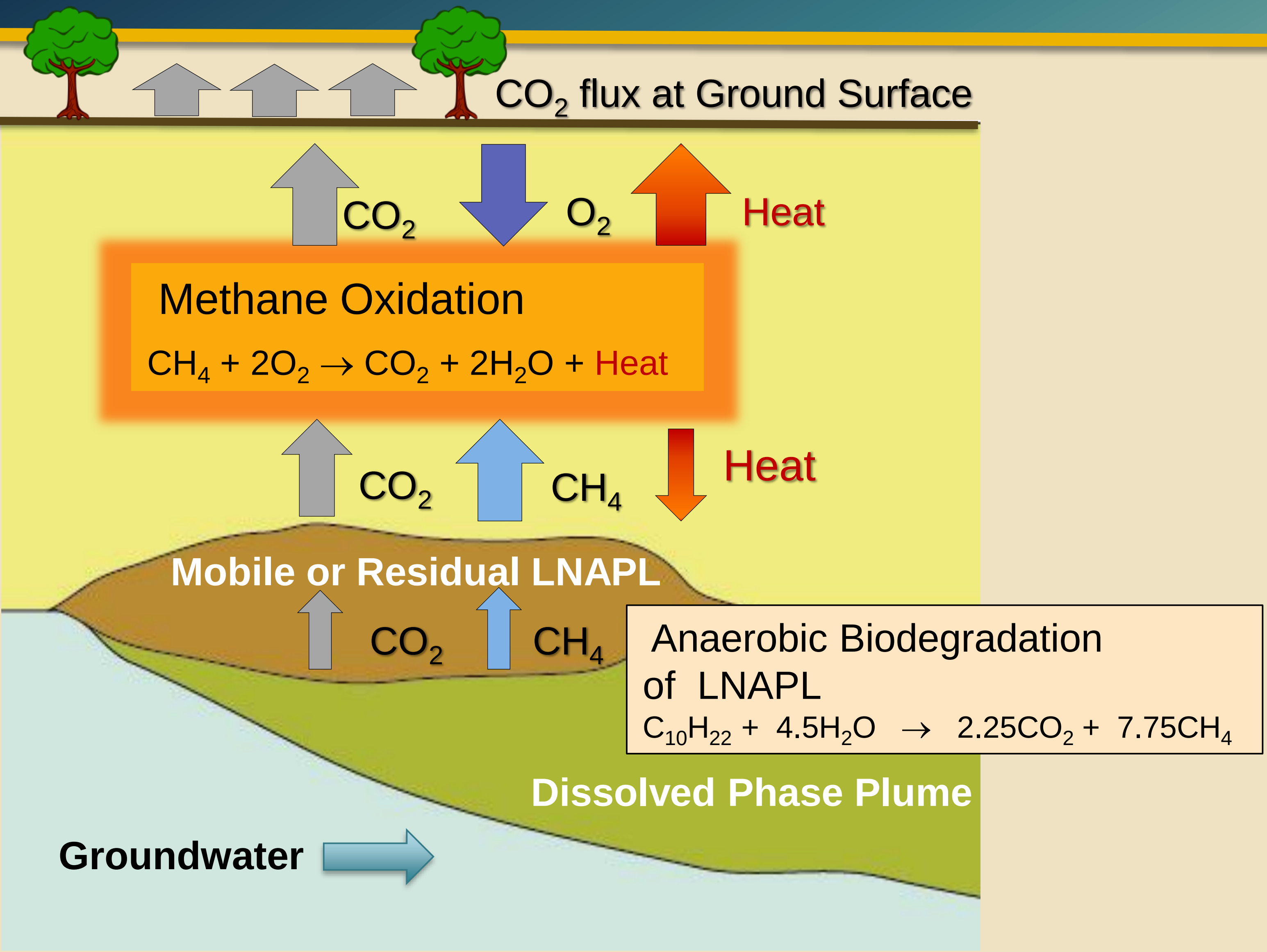
Typical Condition:

- **Biodegradation generates methane gas**
- **Methane oxidized by aerobic bacteria before reaching ground surface**

Methanogenesis in Action



NSZD Conceptual Model



Adapted from: ITRC, 2009

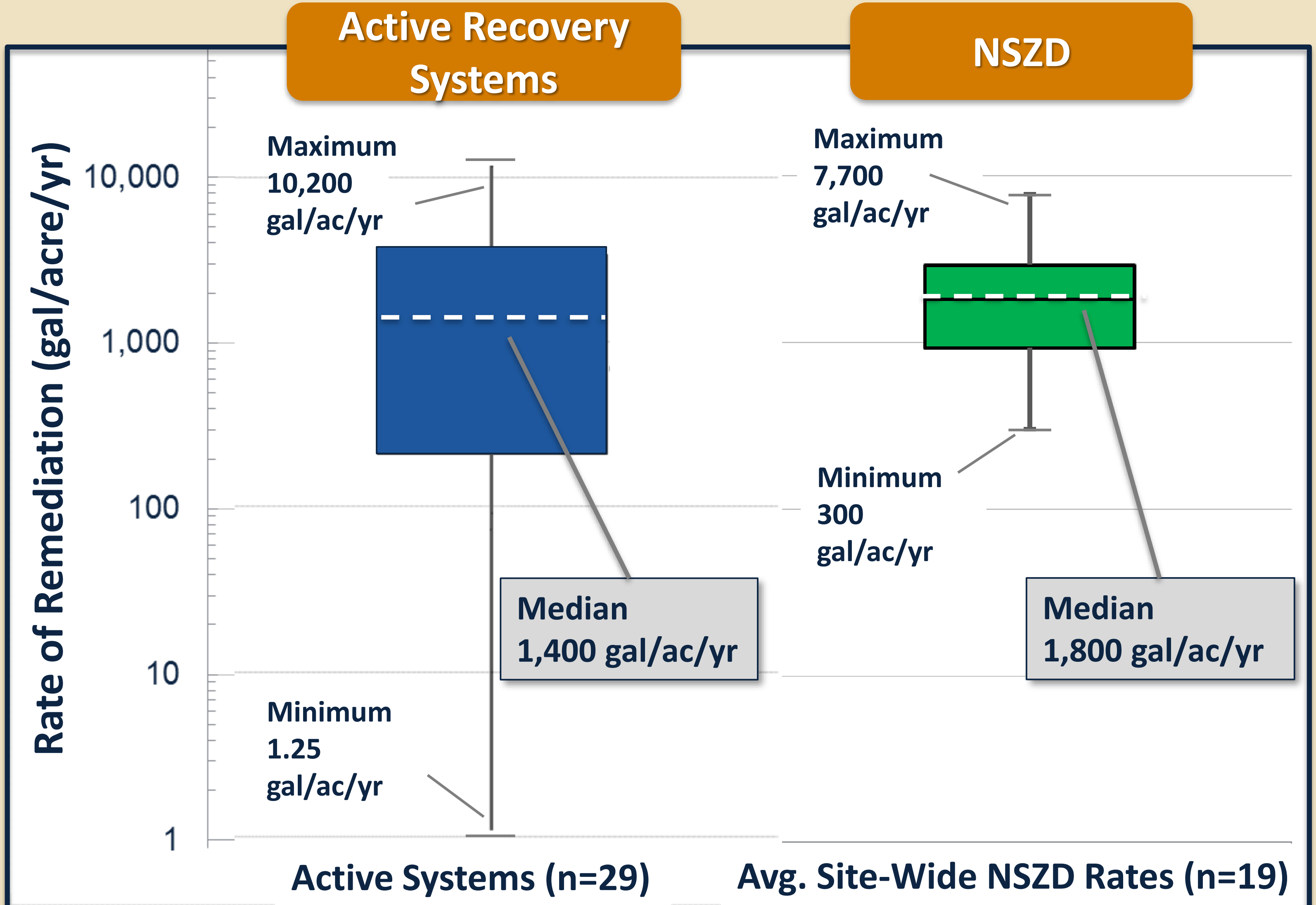
What NSZD Rates are Being Observed?

NSZD Study	NSZD Rate (gallons/ acre /year)
Six refinery terminal sites (McCoy et al., 2012)	400 - 18,000
1979 Crude Oil Spill (Sihota et al., 2011)	500 - 1,700
Refinery/Terminal Sites in Los Angeles (LA LNAPL Wkgrp, 2015)	300 - 4,000
Five Fuel/Diesel/Gasoline Sites (Piontek, 2014)	300 - 3,100
Eleven Sites, 550 measurements (Palia, 2016)	300 – 5,600 (median: 700)

Locations across U.S. where carbon traps have been used to measure NSZD rates (E-Flux, 2015).

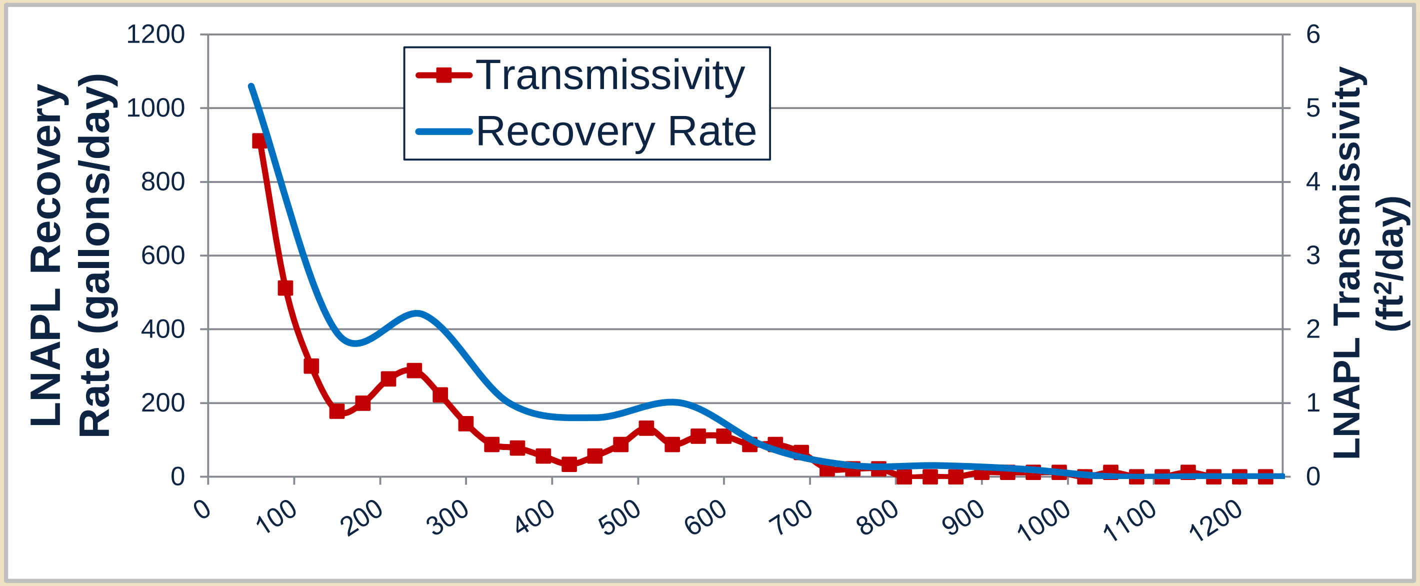
KEY POINT: Measured NSZD rates in the **100s to 1000s of gallons per acre per year.**

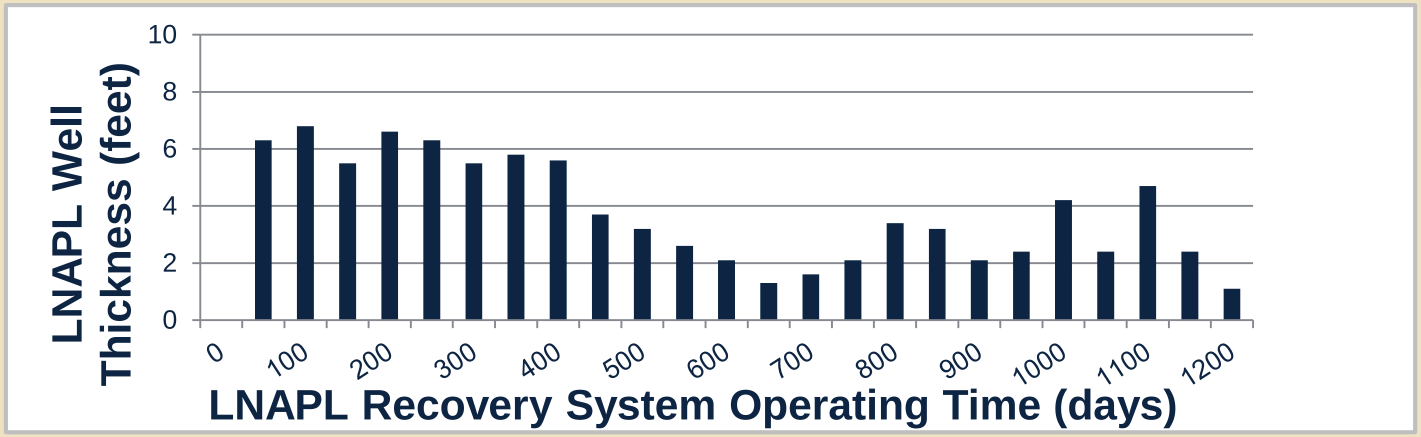
Active Remediation vs. NSZD Rates



Source (active systems): Palia, 2016

Typical LNAPL Recovery Performance





KEY POINTS:

- ***Recoverability drops but LNAPL thickness remains.***
- ***LNAPL sites very difficult to close.***

Source: Modified from Suthersan et al., 2015

Technology Smackdown: *Going Geeky*

Thermal NSZD

Who Wins?

Bailer or Interface Probe

- Sometimes least expensive alternative
- Makes you buff
- But tough to close site

Thermal Remote Monitoring

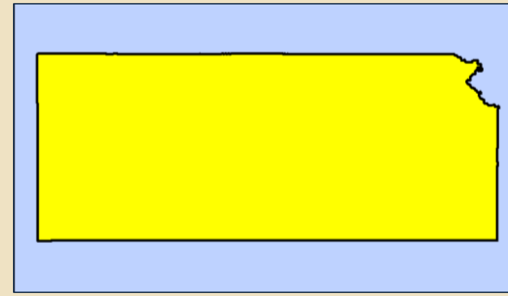
- No site visits, sampling or lab
- Continuous calculation of mass loss
- Convenient web interface

KEY POINT: *Geek approach may improve chance of regulatory case closure.*

GSI ENVIRONMENTAL

NSZD Site Closure: *3 Case Studies*

Kansas Tank Farm

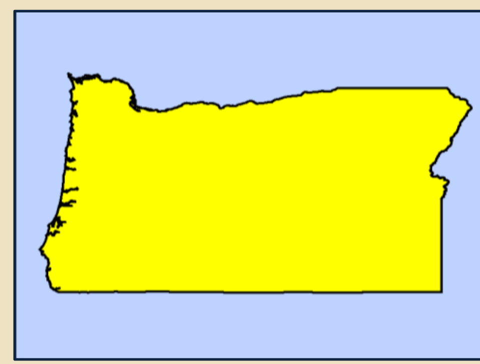


- Active system with negligible LNAPL recovery rates
- NSZD measurements from 2012-2014 (Carbon traps + thermal monitoring)
- KDHE approved system shutdown in 2015

California Pipeline Terminal

- Active system with LNAPL recovery rates ~20 gal/yr
- NSZD rates measured at >3,000 gal/ac/yr
- State Water Board ruling: “Can’t dictate technology”
- NSZD identified as viable remediation technology

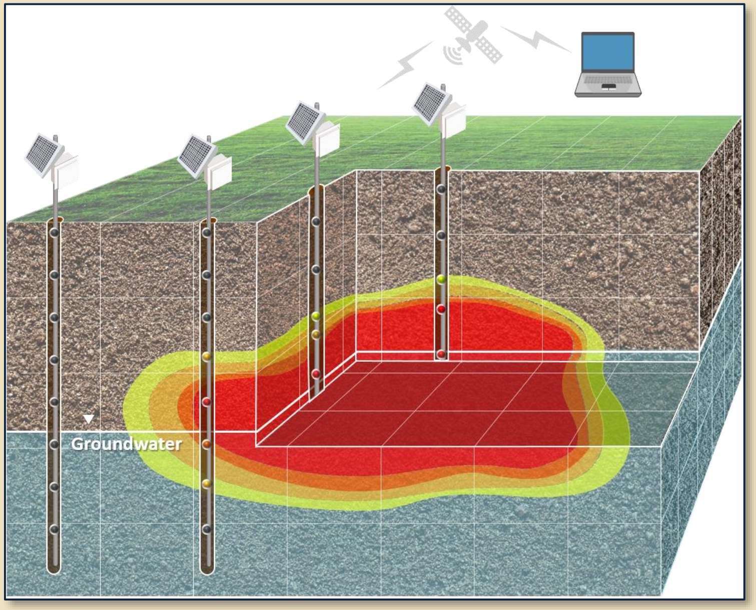
Oregon Railyard



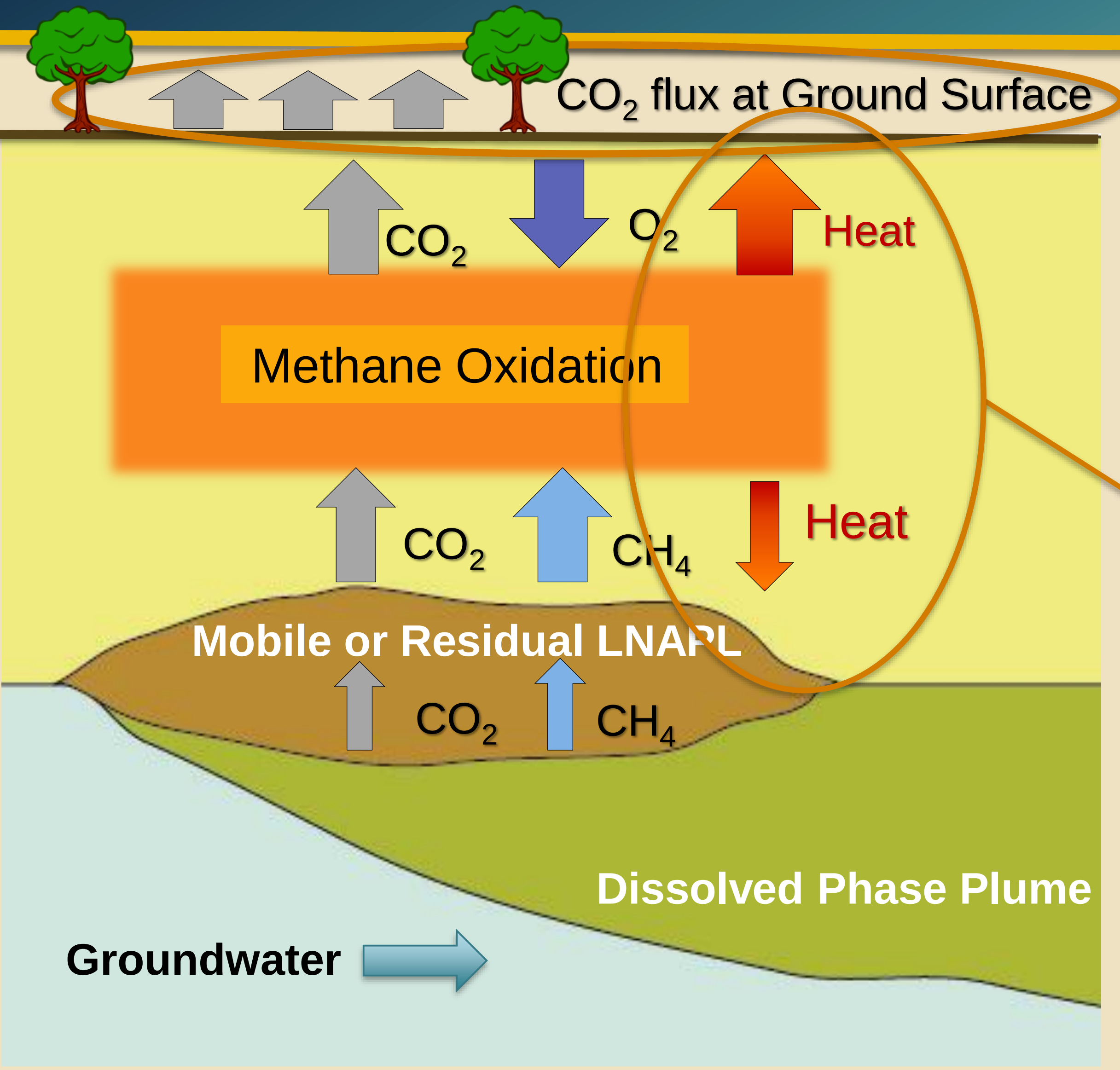
- Active systems: skimming, vacuum enhanced fluid recovery, total fluids recovery
- NSZD rates were an order of magnitude higher than current methods
- ODEQ approved conditional NFA for the site

How Can NSZD Rates Be Used?

- To confirm that **LNAPL is biodegrading and quantify the rate**
- More accurate **estimation of remediation timeframe by NSZD**
- **Evaluate and/or replace** an active remediation system



Current NSZD Measurement Methods

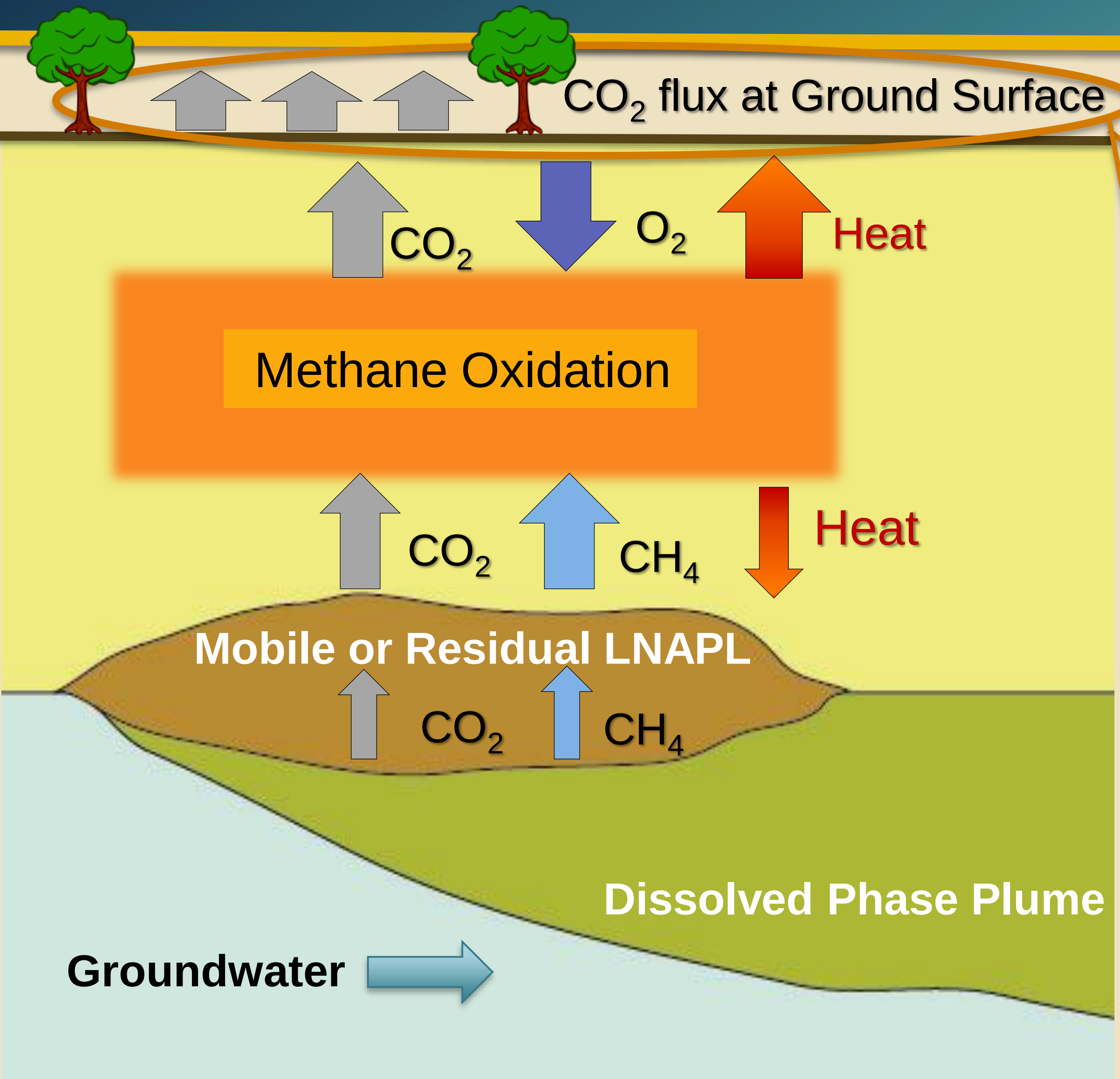


CO_2 Flux Measurement at Surface

Subsurface Temperature Measurement

Adapted from: ITRC, 2009

Current NSZD Measurement Methods

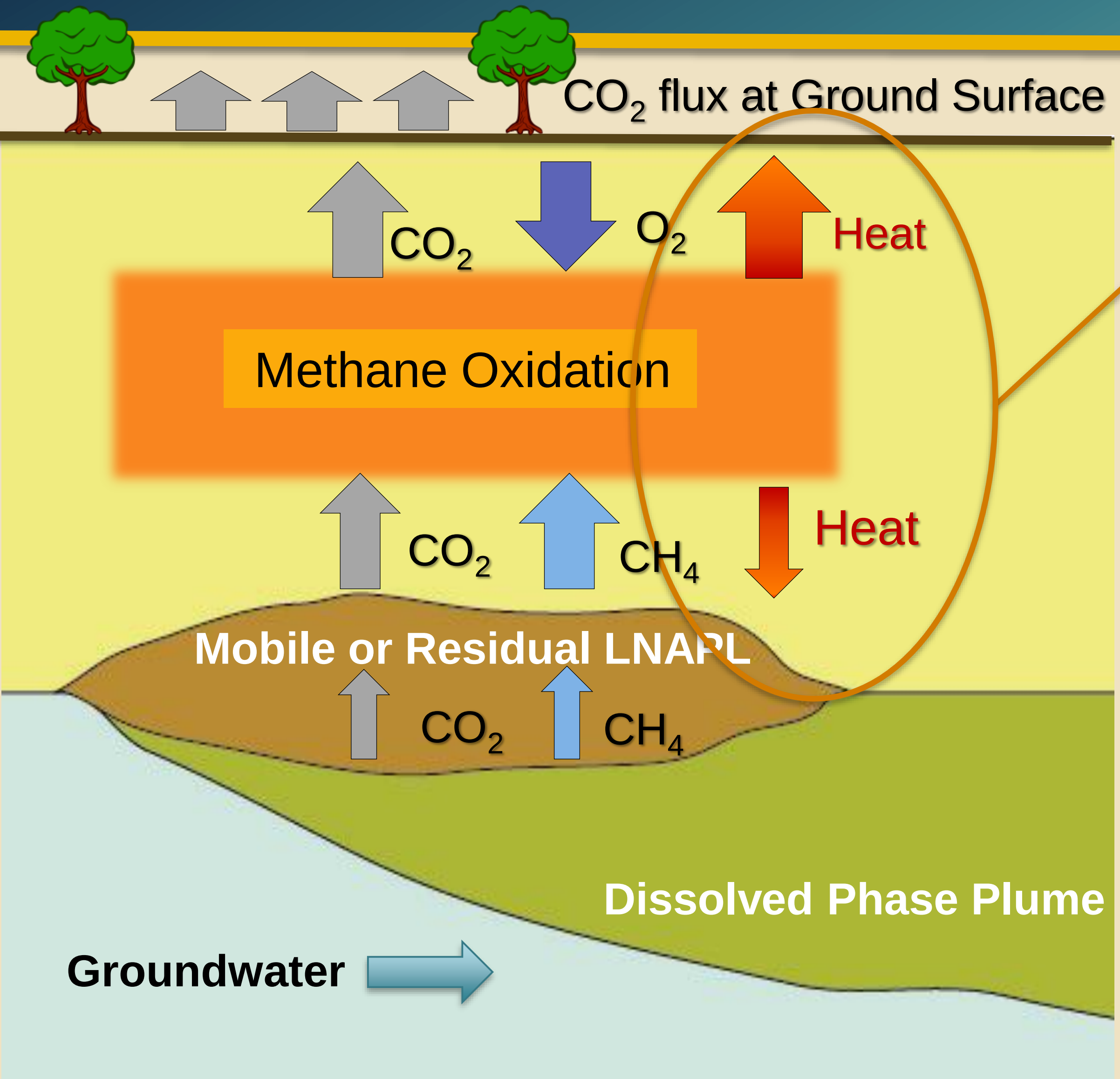


Dynamic Closed Chamber (LI-COR)

Carbon Traps

Adapted from: ITRC, 2009

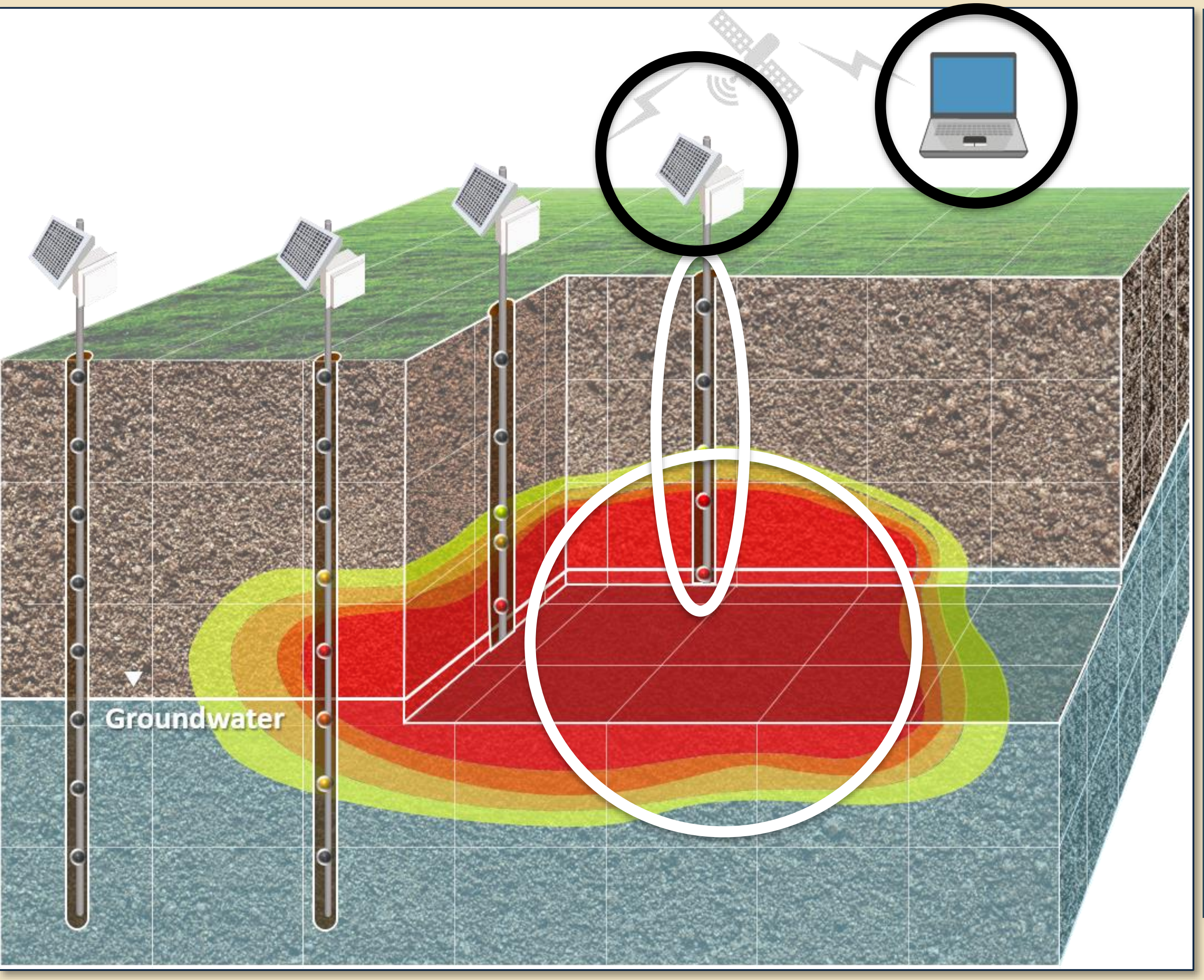
Current NSZD Measurement Methods



Thermal Monitoring

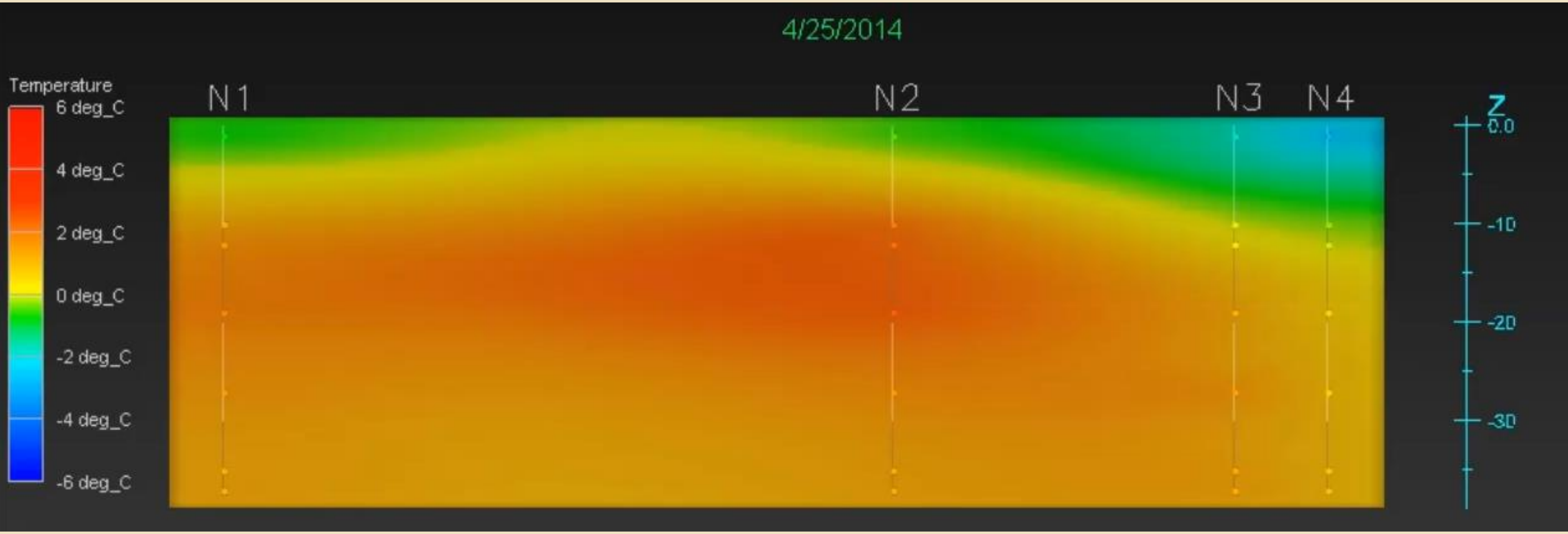
Adapted from: ITRC, 2009

Thermal NSZD: *Basic Principles*

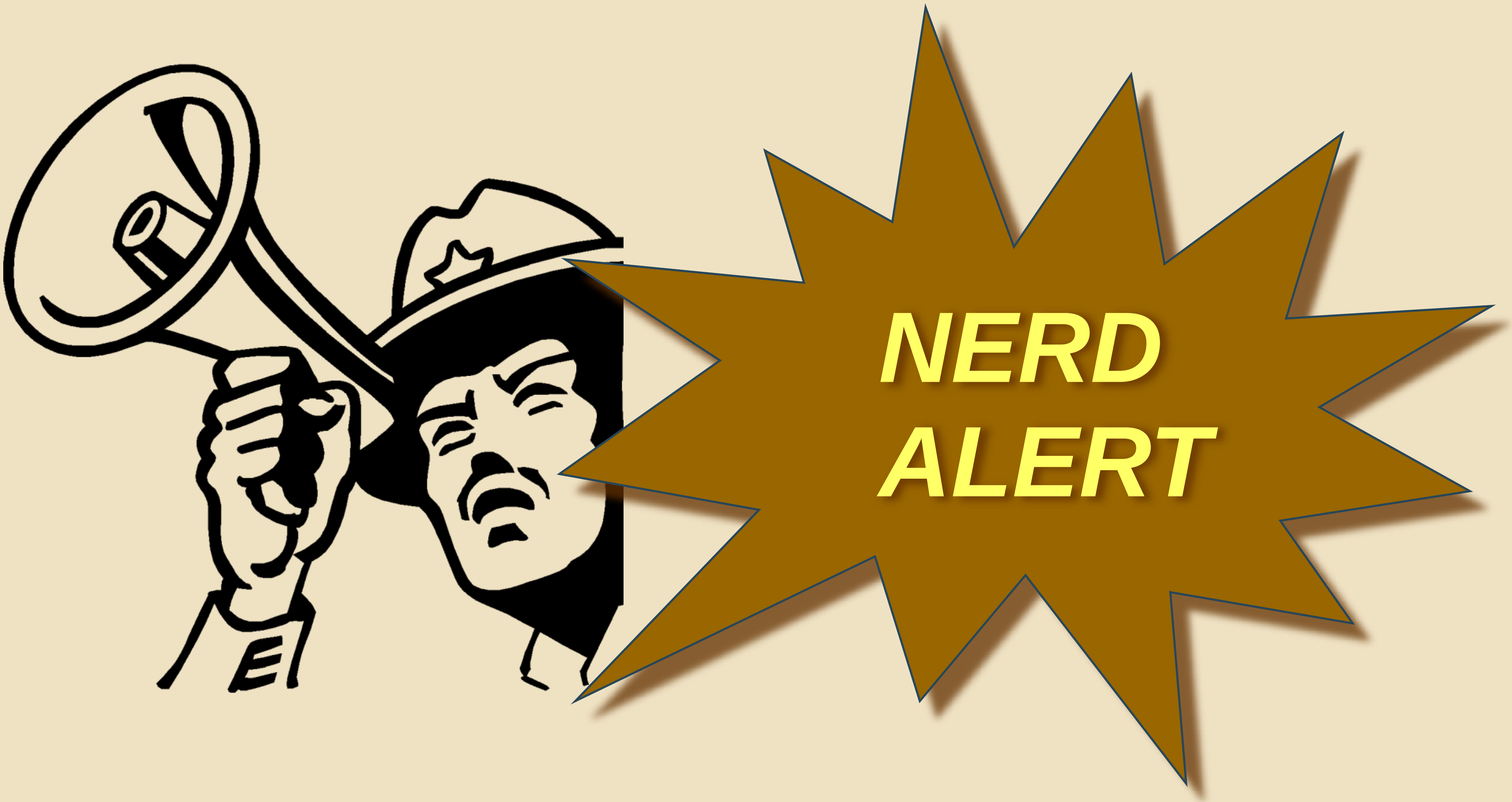


- Biodegradation of LNAPL releases heat
- Measure subsurface temperatures with thermocouples
- Continuously record temperature data (24/7/365)
- Thermal NSZD Dashboard: remote monitoring and calculation of NSZD rates

Heat Signal Over Time: *Kansas Tank Farm*



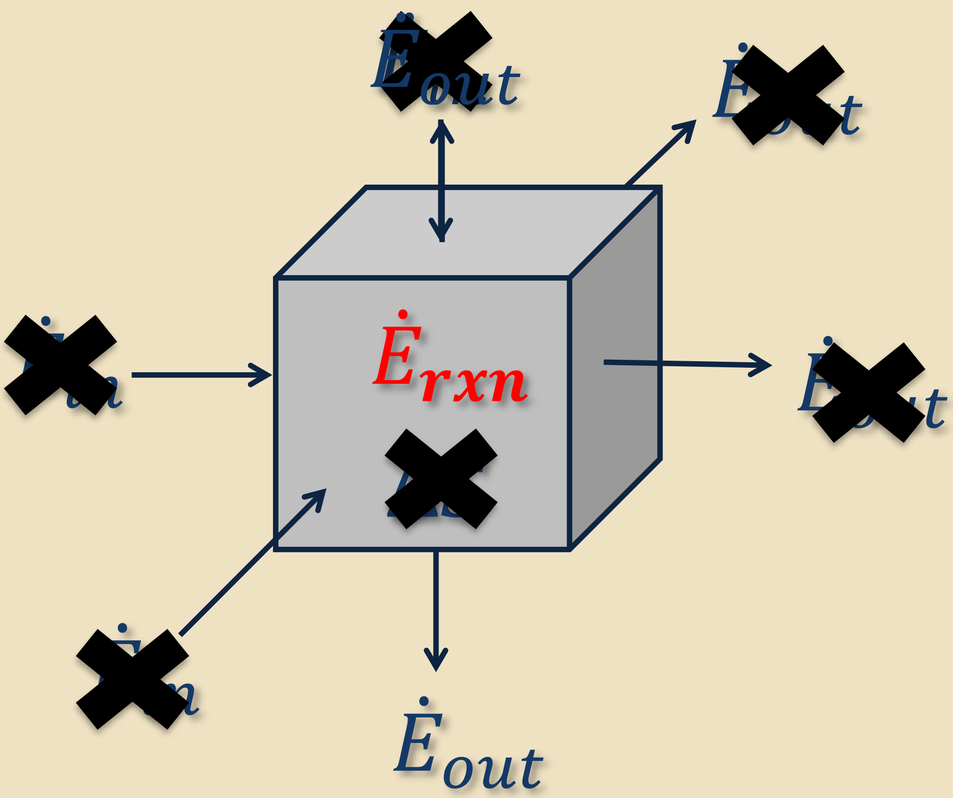
Source: Stockwell, 2015; Colorado State University


NERD
ALERT

Calculating LNAPL Mass Loss by NSZD

First law of thermodynamics:

$$\dot{E}_{out} = \dot{E}_{rxn}$$



- **Lateral energy loss negligible**
- **Background location corrects for solar energy input**
- **Steady-state**
- **Storage negligible**

NSZD Conceptual Model

Fourier's Law:

Heat flux: $\dot{E} = K_T \frac{dT}{dz}$

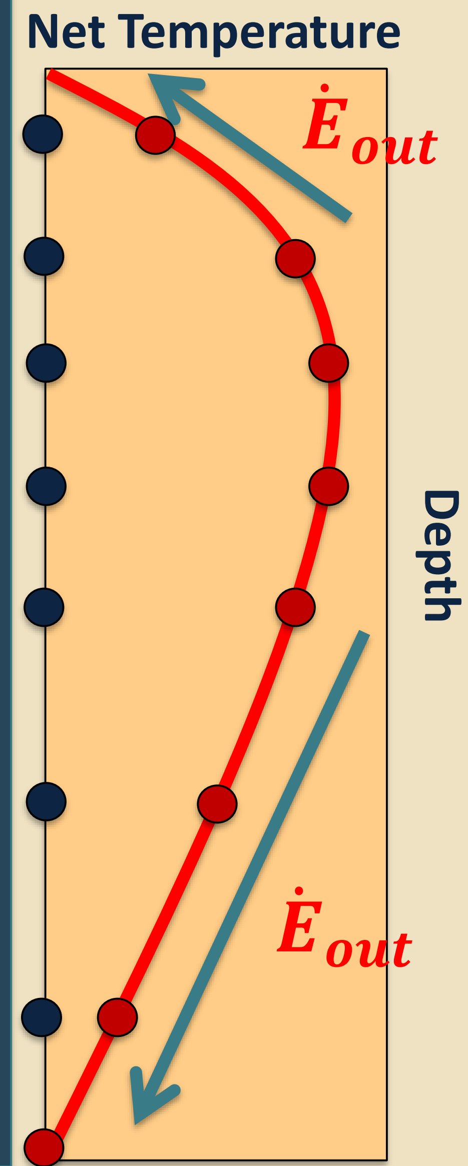
(watts/m^2)

Where:

K_T thermal conductivity (W/m°C)

Z depth interval of heat flux (m)

T change in net temperature (°C)



Last Step: *Calculate the NSZD Rate*

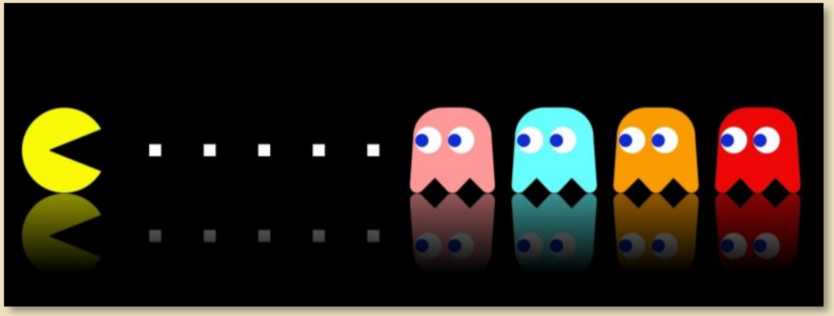
$$\textbf{NSZD Rate} = \frac{\dot{E}_{rxn}}{H_{rxn}} \frac{MW_{LNAPL}}{\rho_{LNAPL}}$$

(gallons/acre/year)

Heat Flux (joules/area/time)

Heat of Reaction (joules per mass)

H_{rxn} = 45 kJ/g (diesel)
H_{rxn} = 47 kJ/g (gasoline)



Field Installation: *Thermal Monitoring System*

Thermocouple on temperature monitoring "stick."

Installation of stick using direct push rig.

Solar power supply and weatherproof box with data logger and wireless communications system.

SOURCE: *CSU*

ThermalNSZD

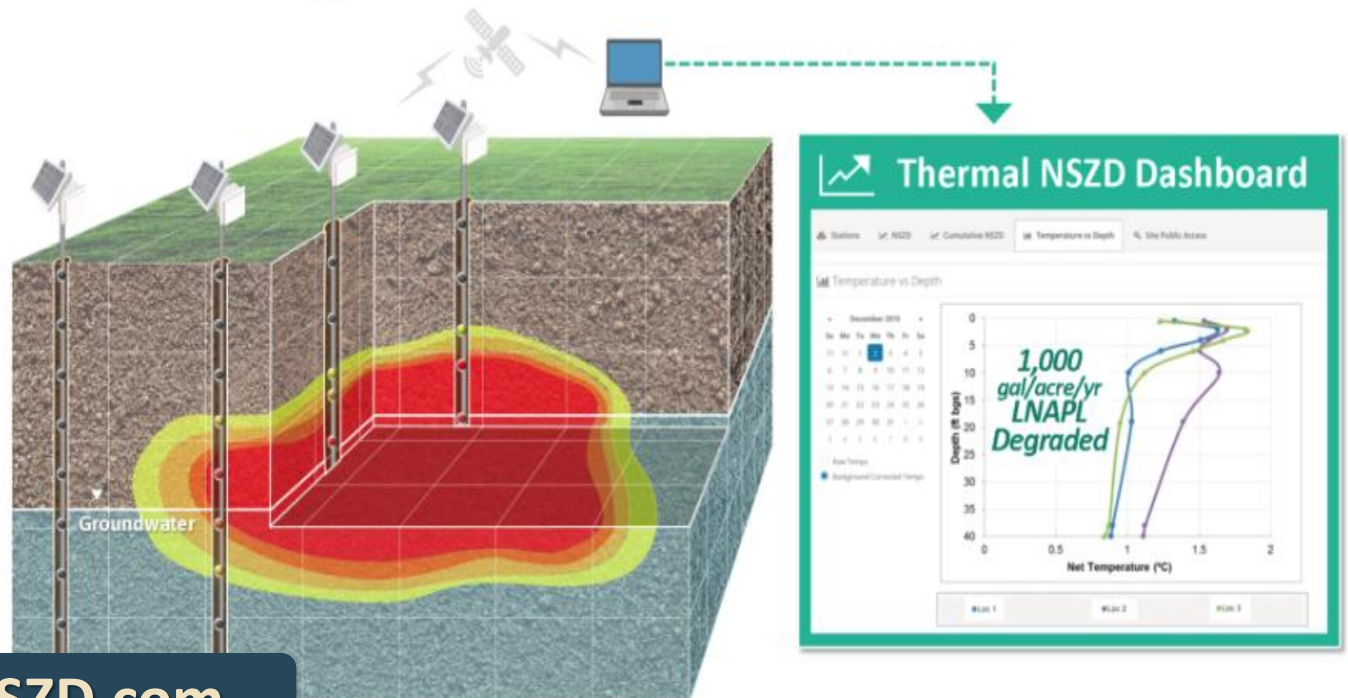
HOME TECHNOLOGY DEMO IMPLEMENT CONTACT CUSTOMER LOGIN

Thermal NSZD: Continuous Remote Monitoring of Natural Source Zone Depletion (NSZD)

The Thermal NSZD technology (patent pending) measures the rate at which natural biodegradation destroys free-phase product (LNAPL) in the subsurface by measuring the heat released by the microbial reactions.

Advantages of Thermal NSZD

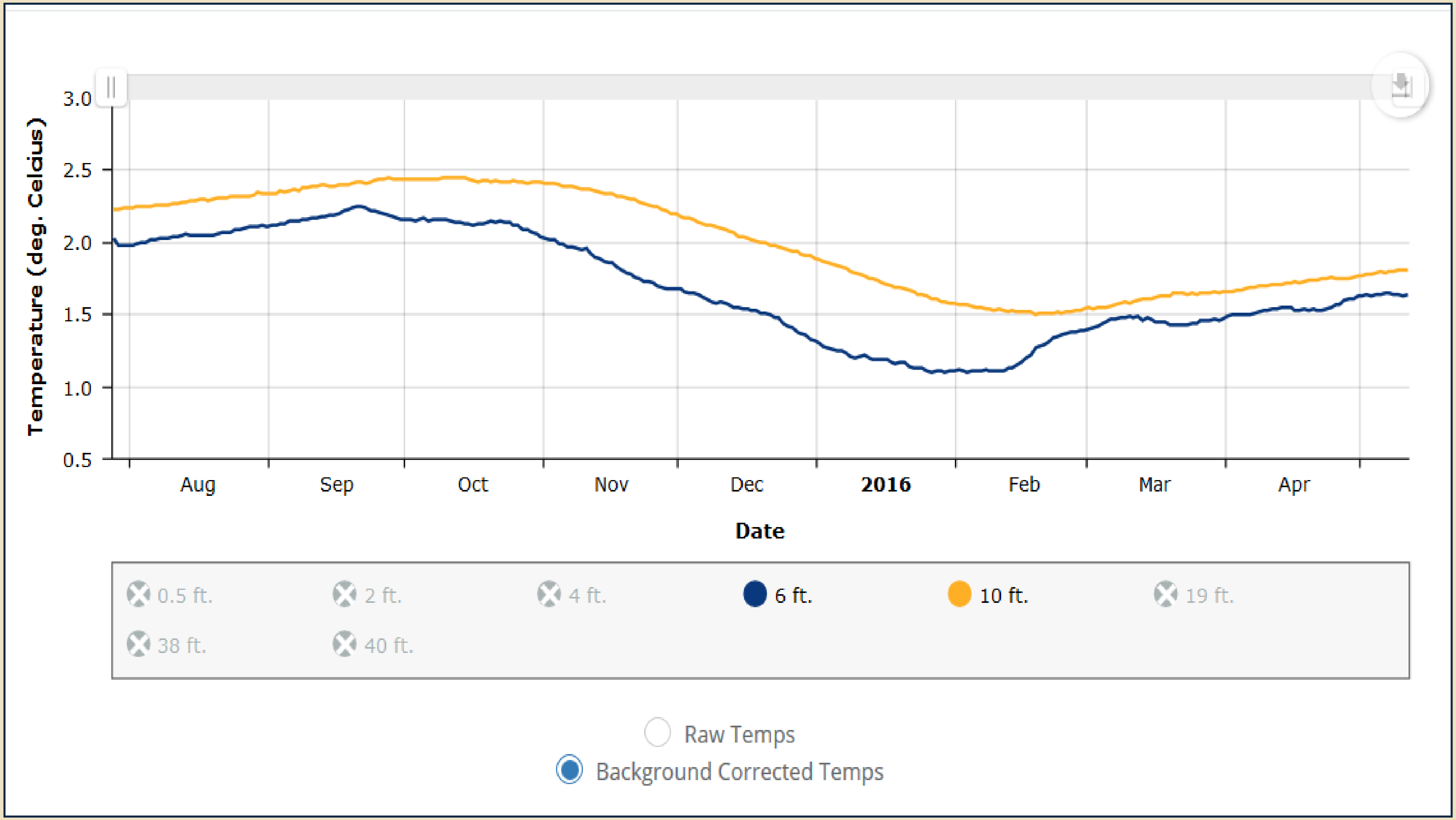
- One-time field installation of remote monitoring system with minimal O&M, no site visits, no sampling and no lab.
- Daily temperature readings from vertical profiles of thermocouples.
- Secured, read only access to site data for regulators.



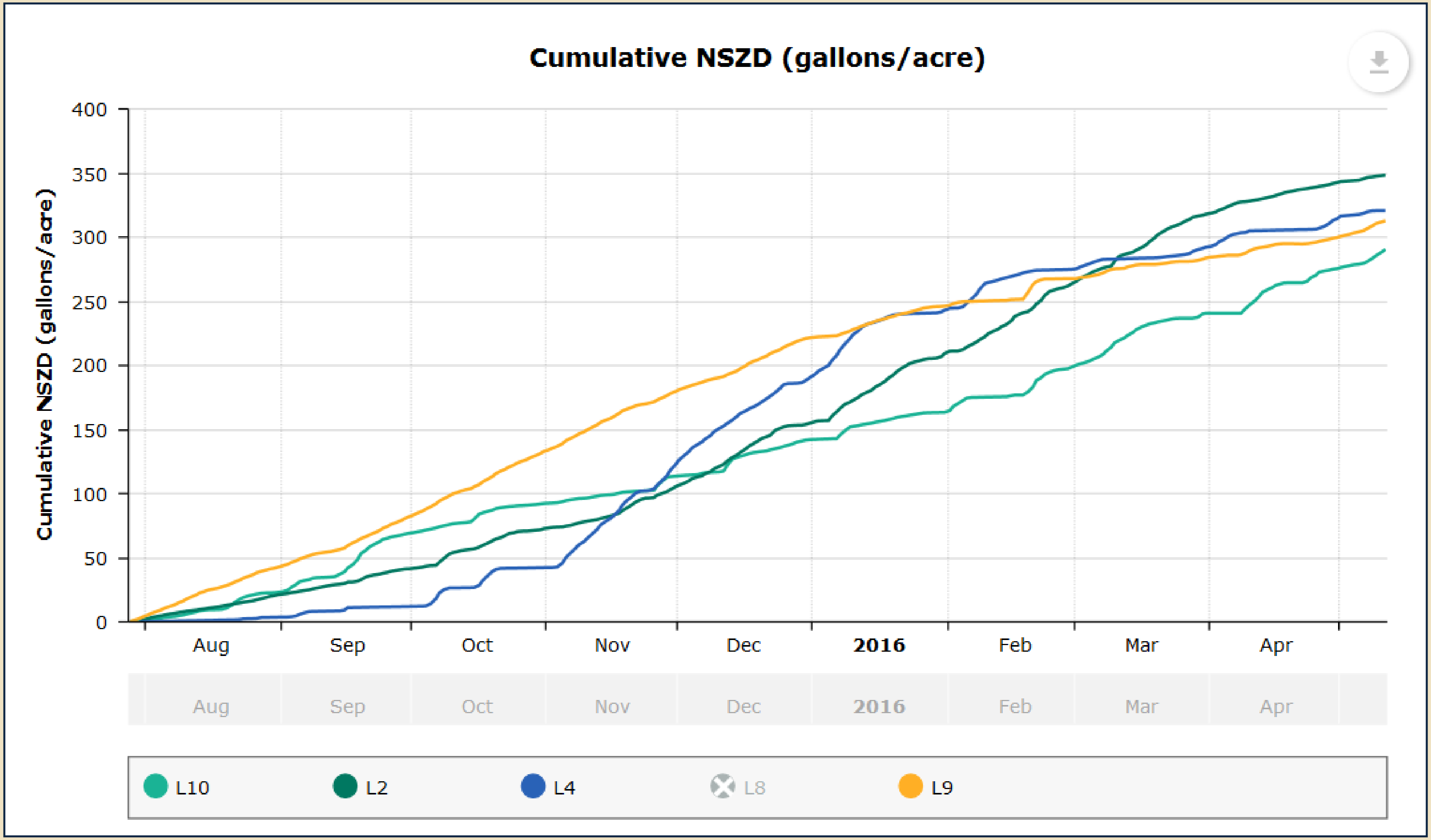
www.ThermalNSZD.com

Patent Pending

Thermal NSZD Dashboard:
Continuous Subsurface Temperatures Updated Daily



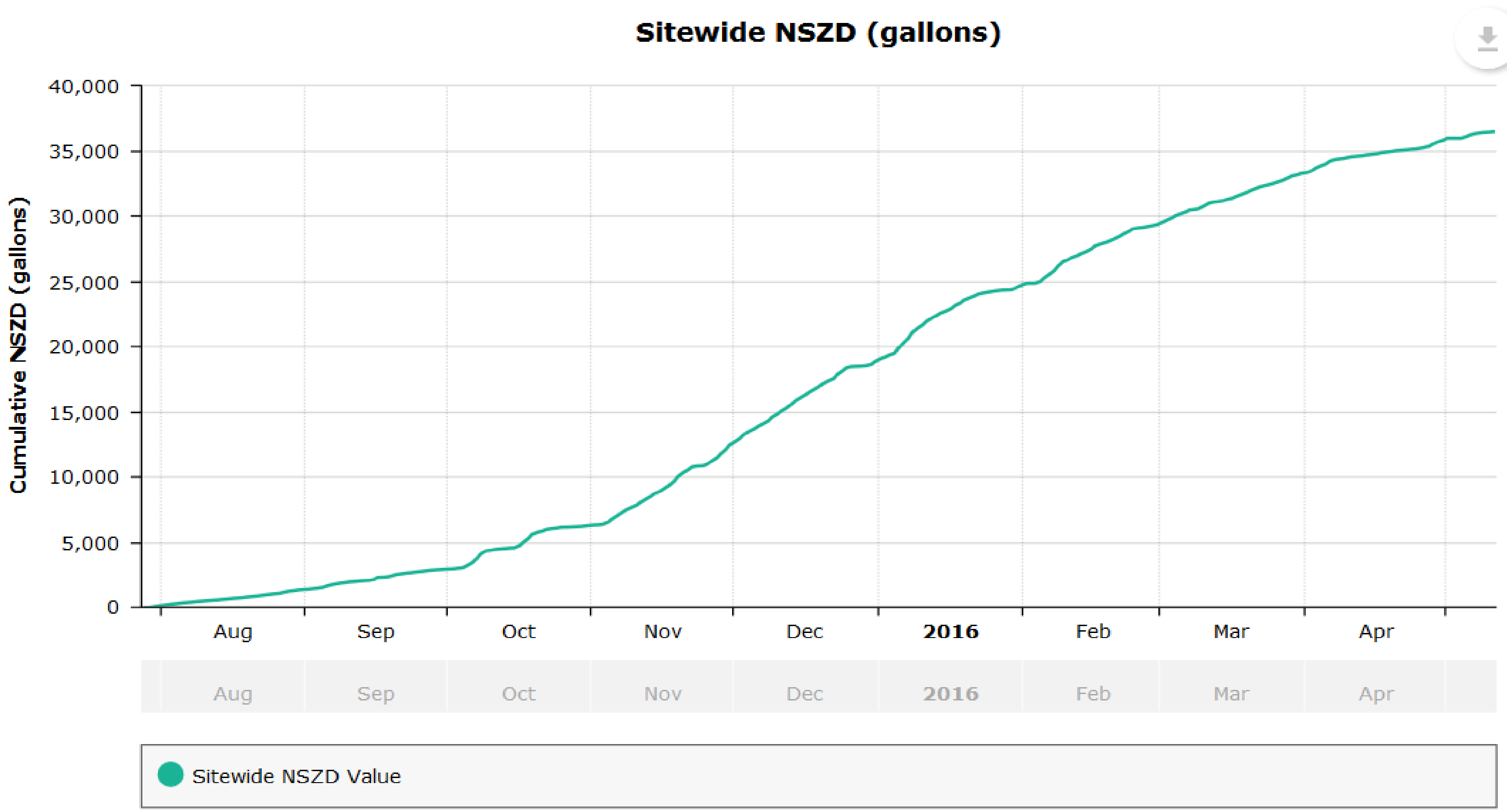
Thermal NSZD Dashboard:
Cumulative NSZD Per Location



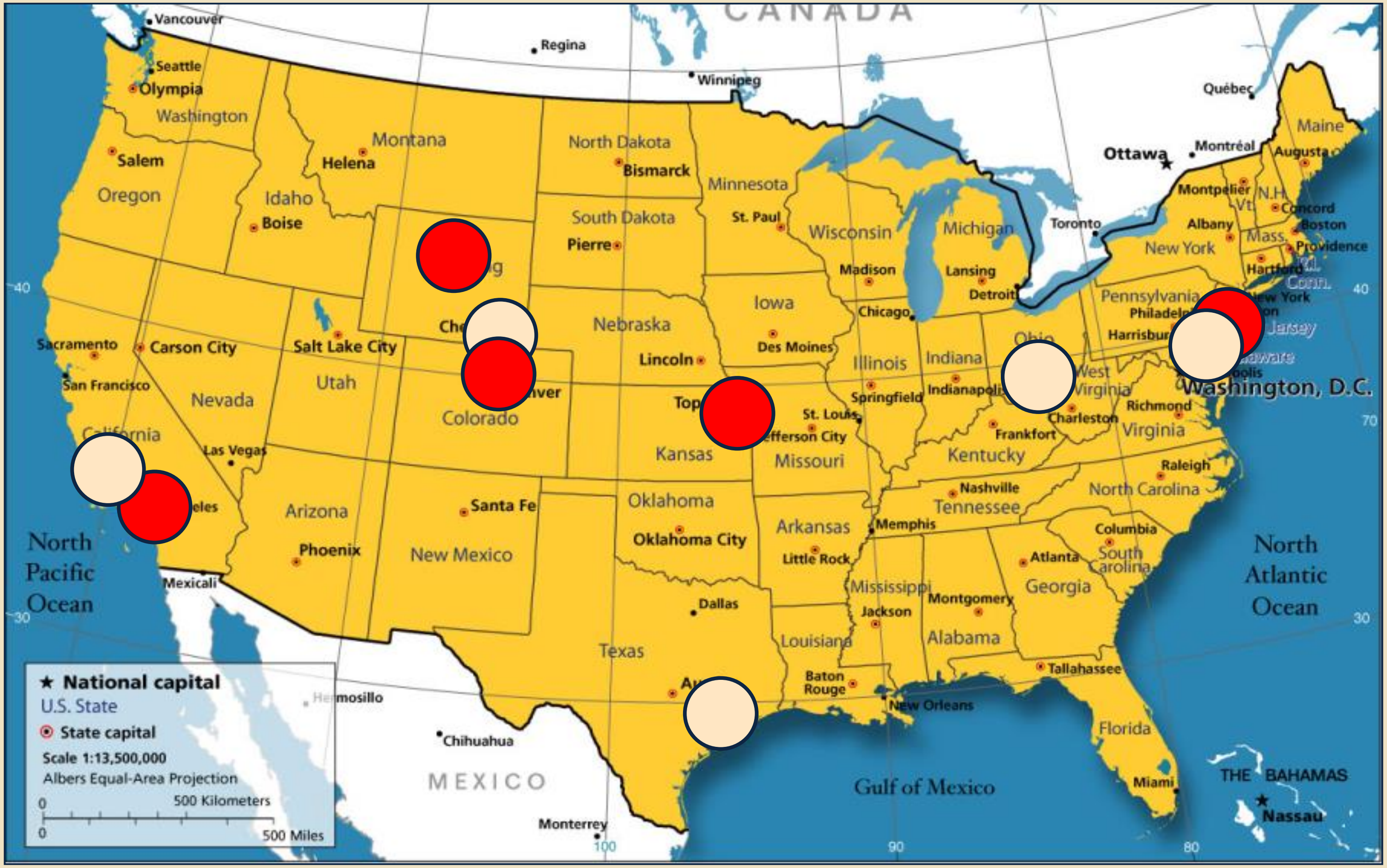
Thermal NSZD Dashboard:
Cumulative Sitewide NSZD Updated Daily

Amount of LNAPL Degraded Since NSZD Monitoring Began: 36,475 gallons LNAPL

Natural Source Zone Depletion Rate Over Past 30 Days: 239 gallons/acre/year



Current Status of Technology Rollout 2012 - 2016



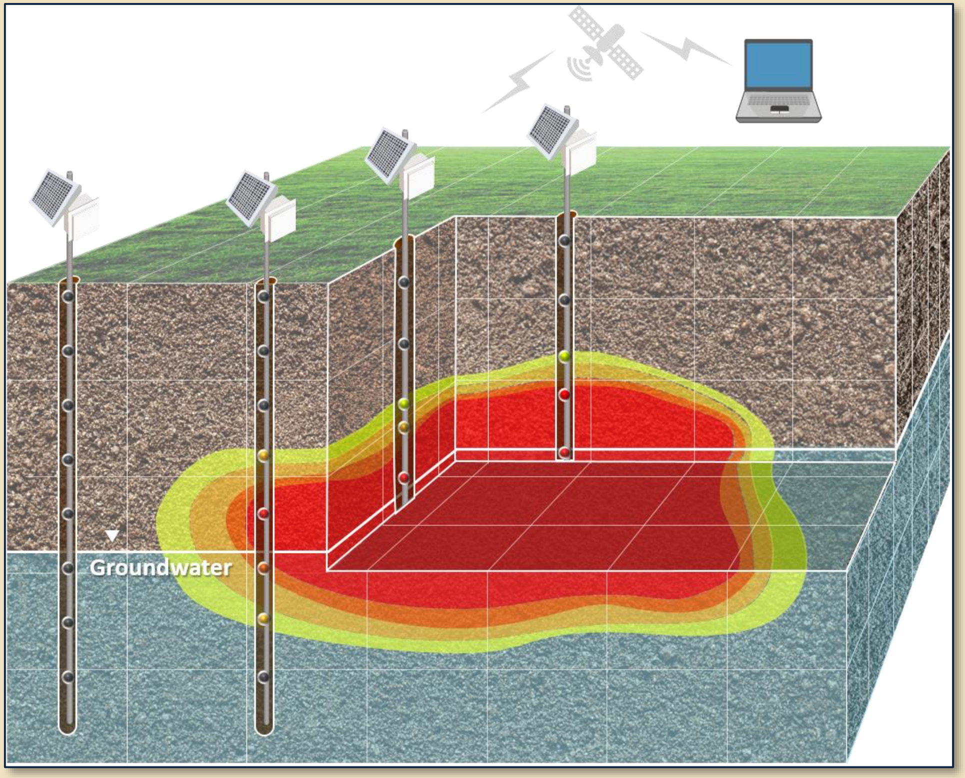
In Place (5 sites)

Pending (5 sites)

Source: *CSU*

Wrap Up: *Key Advantages*

- ✓ **One-time installation** for continuous measurement of NSZD rates
- ✓ **Remote monitoring** via secure Dashboard
- ✓ **Thermal NSZD method less susceptible to surface conditions** compared to other CO_2 efflux methods
- ✓ **Off-the-shelf components**



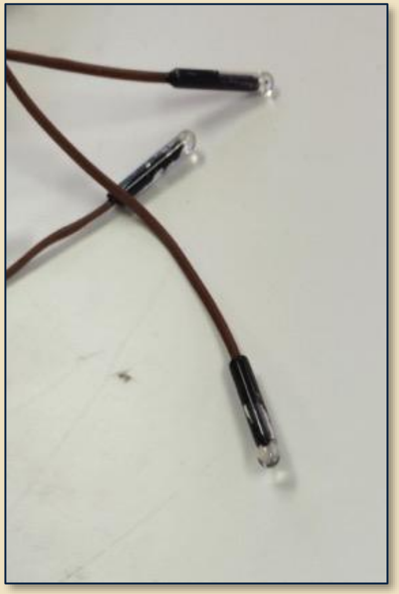
Related and On-going Work: *Enhancing NSZD Rates*

Subsurface Low-Level Heating Using Plastic

Questions?

FOR MORE INFORMATION:

Poonam R. Kulkarni, P.E.
prk@gsi-net.com



Source: *CSU*

BACK-UP

Advantages/Disadvantages

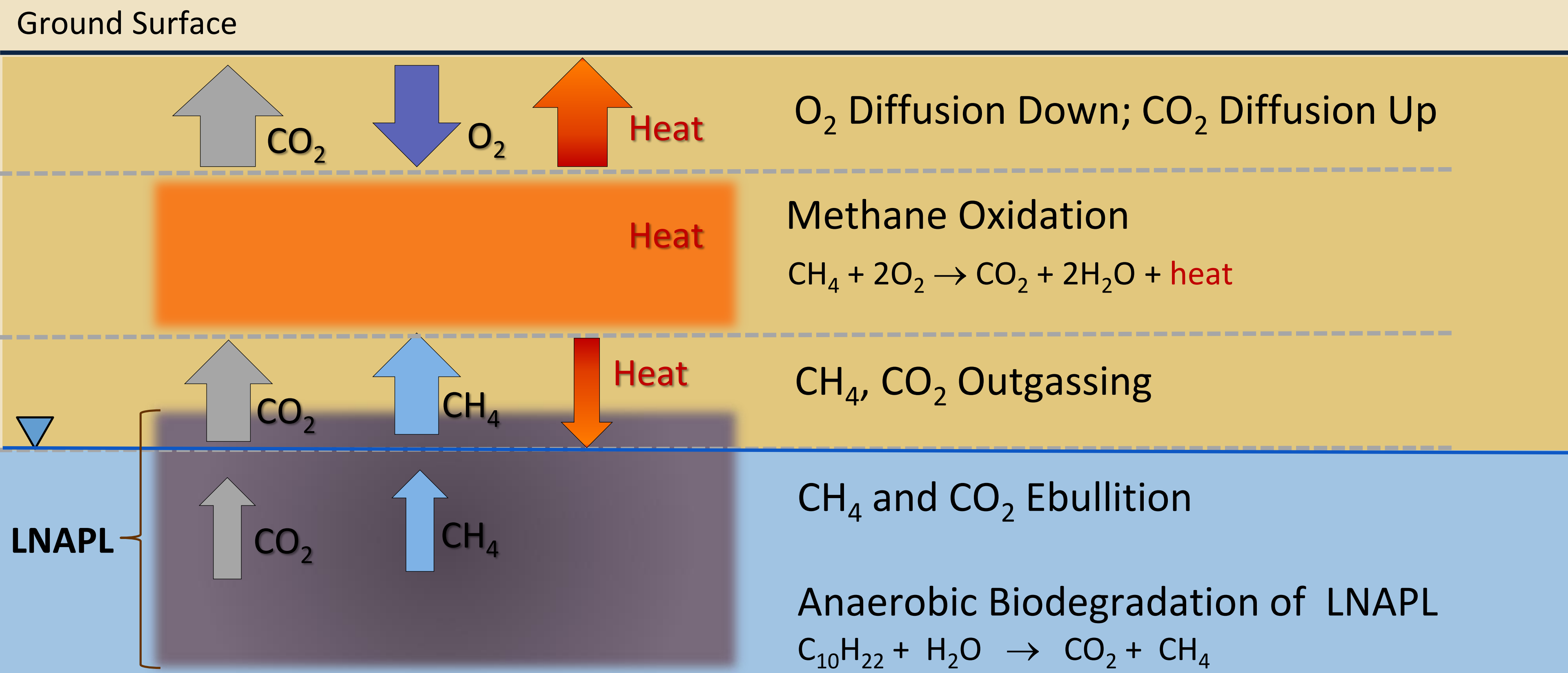
Method	Advantages	Disadvantages
Surface E-Flux Methods	- Simpler installation - Non-invasive	- High variability in results - One-time measurement requires repeat sampling

Biodegradation Reactions

Aqueous Phase Process	Decane Redox Reaction	ΔHr (kJ/mole)
Aerobic Respiration	$15.5O_2 + C_{10}H_{22} \rightarrow 10CO_2 + 11H_2O$	-6792
Denitrification	$12.4NO_3^- + 12.4H^+ + C_{10}H_{22} \rightarrow 10CO_2 + 17.2H_2O + 12.4N_2$	-6316
Manganese Reduction	$62H^+ + 31MnO_2 + C_{10}H_{22} \rightarrow 10CO_2 + 31Mn^{2+} + 42H_2O$	-6561
Iron Reduction	$124H^+ + 62Fe(OH)_3 + C_{10}H_{22} \rightarrow 10CO_2 + 62Fe^{2+} + 166H_2O$	-5162
Sulfate Reduction	$15.5H^+ + 7.75SO_4^{2-} + C_{10}H_{22} \rightarrow 10CO_2 + 7.75H_2S + 11H_2O$	-232
Methanogenesis	$4.5H_2O + C_{10}H_{22} \rightarrow 2.25CO_2 + 7.75CH_4$	-25
Methane Oxidation	$7.75CH_4 + 15.5O_2 \rightarrow 7.75CO_2 + 15.5H_2O$	-6766

NSZD Conceptual Model With Heat

Add box of where energy balance is happening



*Note: size of arrows indicate degree of release

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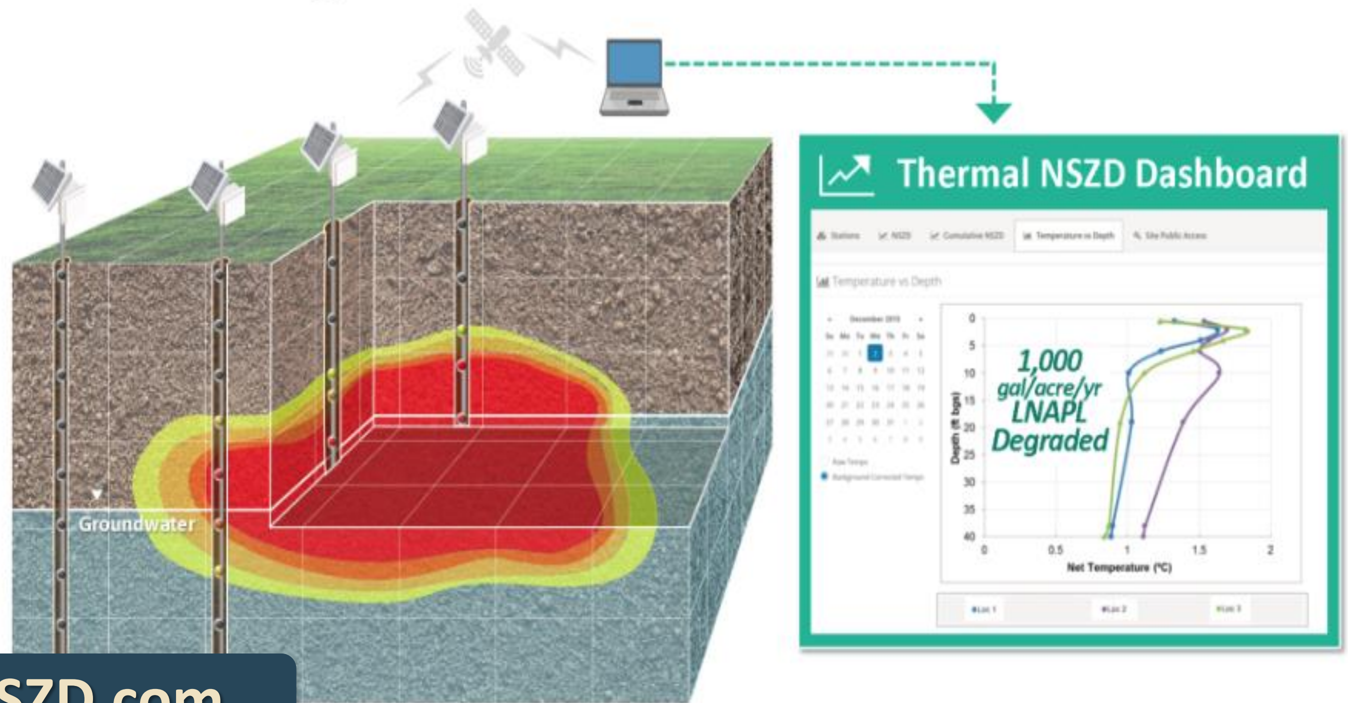


www.ThermalNSZD.com

Patent Pending

Kansas Site

LNAPL Locations

Background Location

NSZD Rate Comparison: Temp vs. Traps
California Site (gallons per acre per year)

NSZD Rate (gallons per acre per year)

Method	Averaging Period	Loc. 2	Loc. 4	Loc. 9	
Carbon Trap	14 days	710	80	60	
Thermal NSZD	315 days	430	380	390	

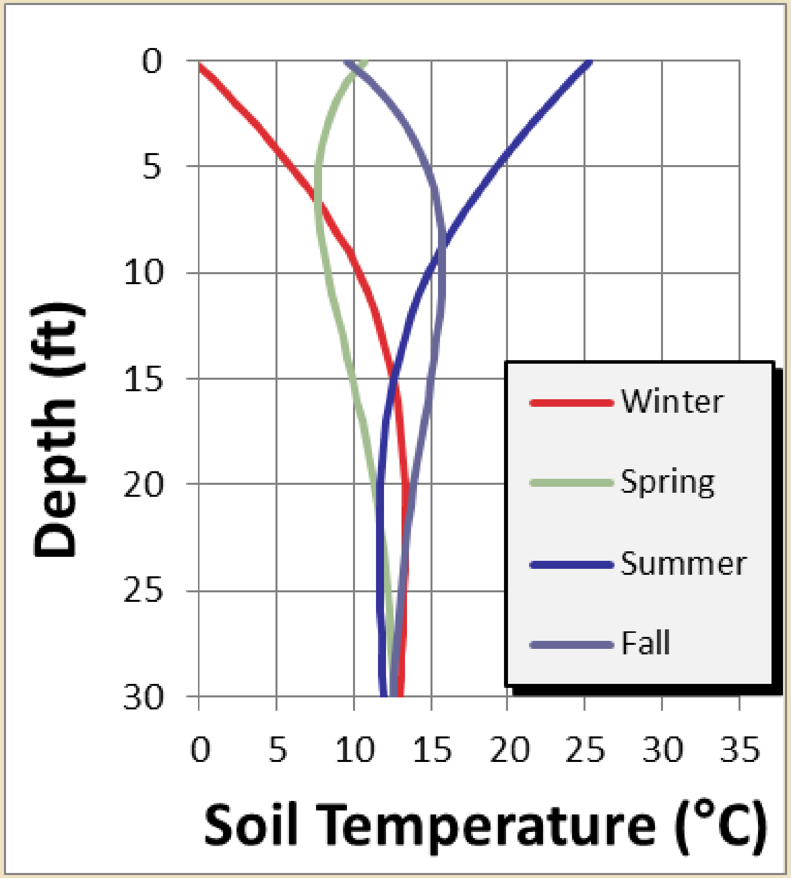
NSZD Rate Comparison: Temp vs. Traps
California Site

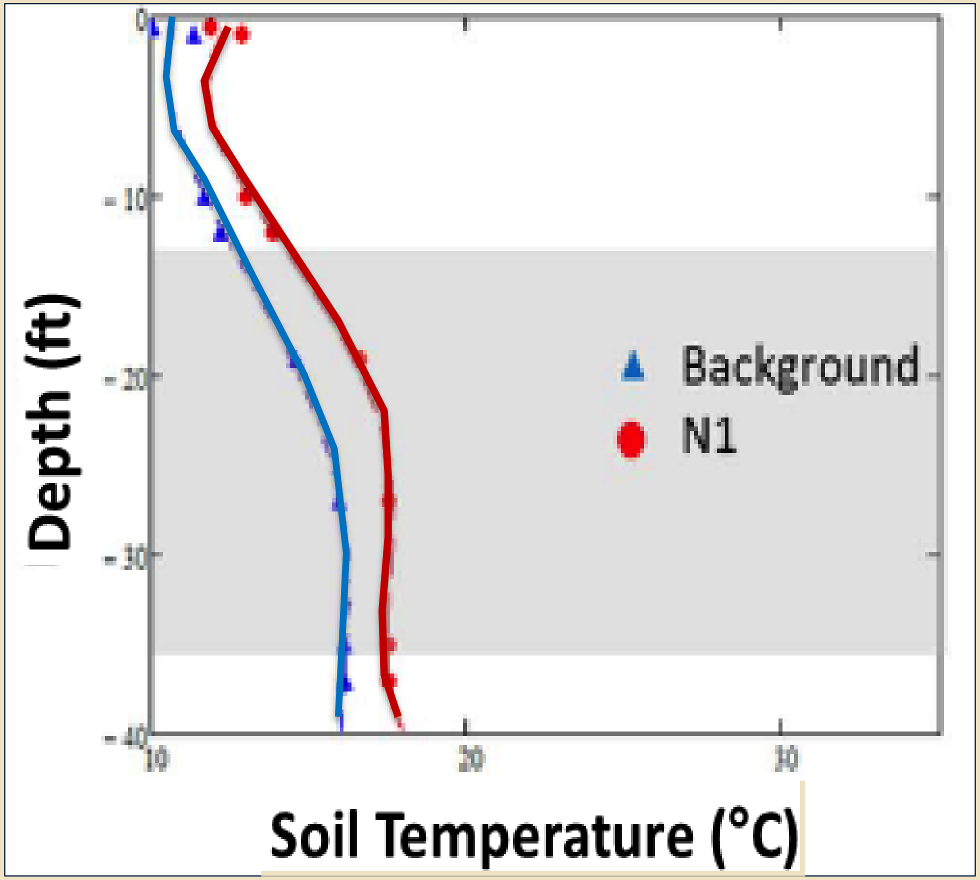
NSZD Rate (gallons per acre per year)

Method	Avg. of 3 NSZD Locations	SVE-Impacted Location
Carbon Trap	280	50*
Thermal NSZD	400	3180

* Not representative of actual rate due to effect of negative pressure from SVE system

Seasonal Change, Background Correction vs. Depth



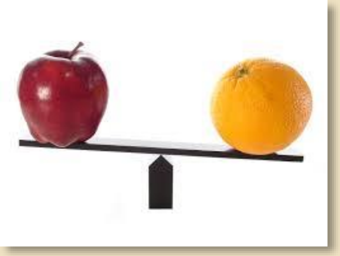


Naturally-Occurring Seasonal Temperature Changes

Heat Signal from Biodegradation = Temp. in LNAPL – Background Temp.

Compare and Contrast the Different Methods

The Where, How, When can be Different



	Where is Measurement?	How Get NSZD Rate?	Over What Time Period?
Gradient Method	Point in Vadose Zone with No Oxygen	If Shallow, Subtract Background	Snapshot
CO_2 Efflux: Dynamic Closed Chamber	Surface	Subtract Background or ^{14}C	Snapshot, or many readings
CO_2 Efflux: Carbon Traps	Surface	Mostly ^{14}C Now	14 Days

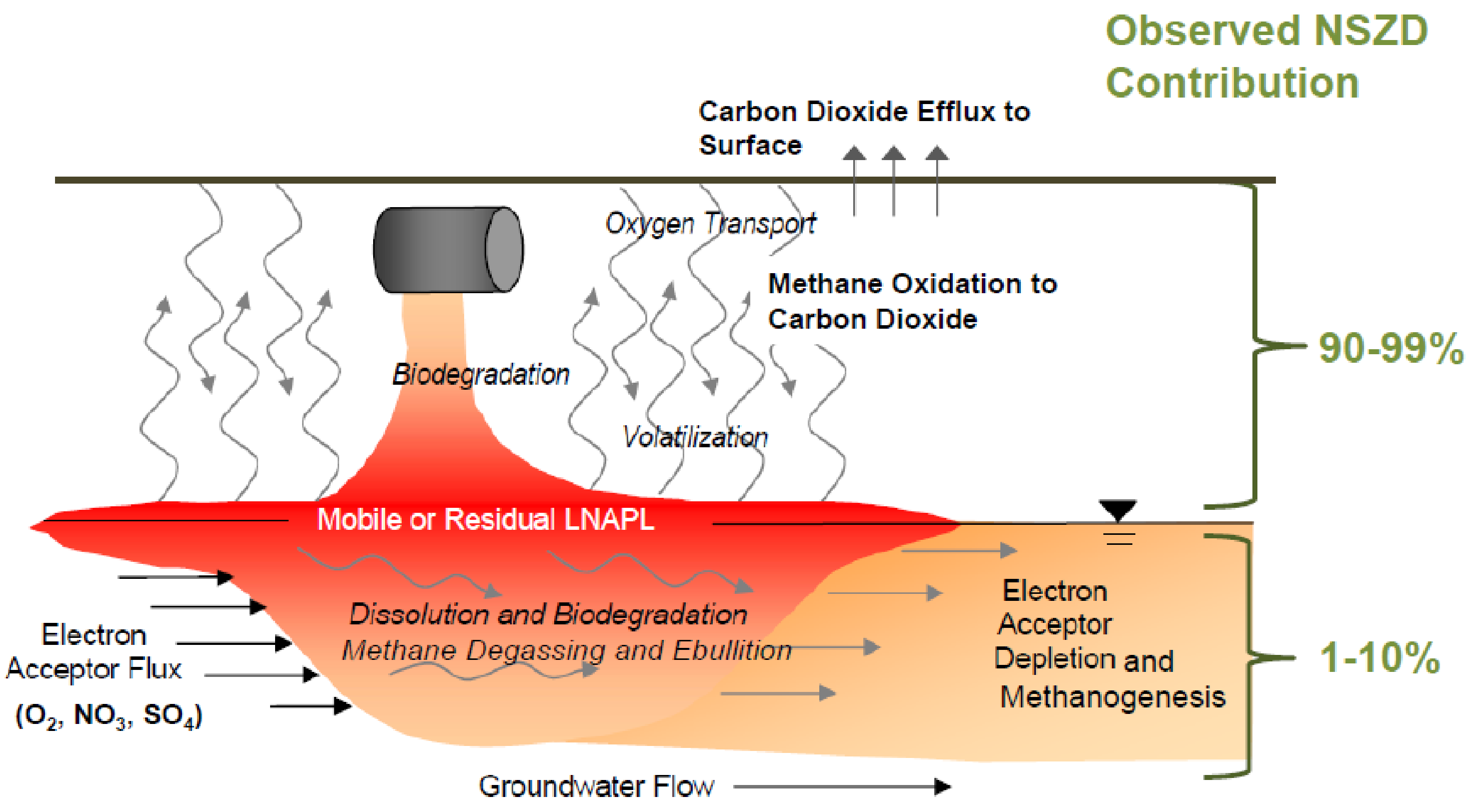
Advantages/Disadvantages

Method	Advantages	Disadvantages
Gradient Method	- Provides info. based on entire vadose zone - Less sensitive to near-surface conditions	- Snapshot measurement - Invasive and labor-intensive to install - Uncertainties in diffusion coefficient - Additional field deployments needed for >1 sampling event
DCC LI-COR	- Both short-term and long-term measurements - Real-time data availability - Not invasive installation	- Snapshot measurement - Requires background correction - Surface type may impact measurements - Longer-term data collection requires power source - Expensive equipment (~$20K) - Additional field deployments needed for >1 sampling event

Advantages/Disadvantages *(Cont'd)*

Method	Advantages	Disadvantages
Carbon Traps	- Time-averaged measurement over two weeks - 14C analysis for background correction - Less labor intensive - Not invasive installation	- Snapshot measurement - Surface type may impact measurements - Expensive analytical (~$1,700) per location per sampling event - Additional field deployments needed for >1 sampling event
Temperature Method	- **Real-time, continuous readings of NSZD rate** - **Client sees daily results on webpage (data analysis centralized on webpage)** - **One-time field installation with minimal O&M and no additional field deployments required for additional sampling events** - **Off-the-shelf components**	- **Requires field installation** - **Complex calculation**

NSZD: *Measurement Methods*



Adapted from ITRC, 2009 and Suthersan et al., 2015

GSI CAPABILITIES AND EXPERIENCE:
GSI OVERVIEW

Who We Serve

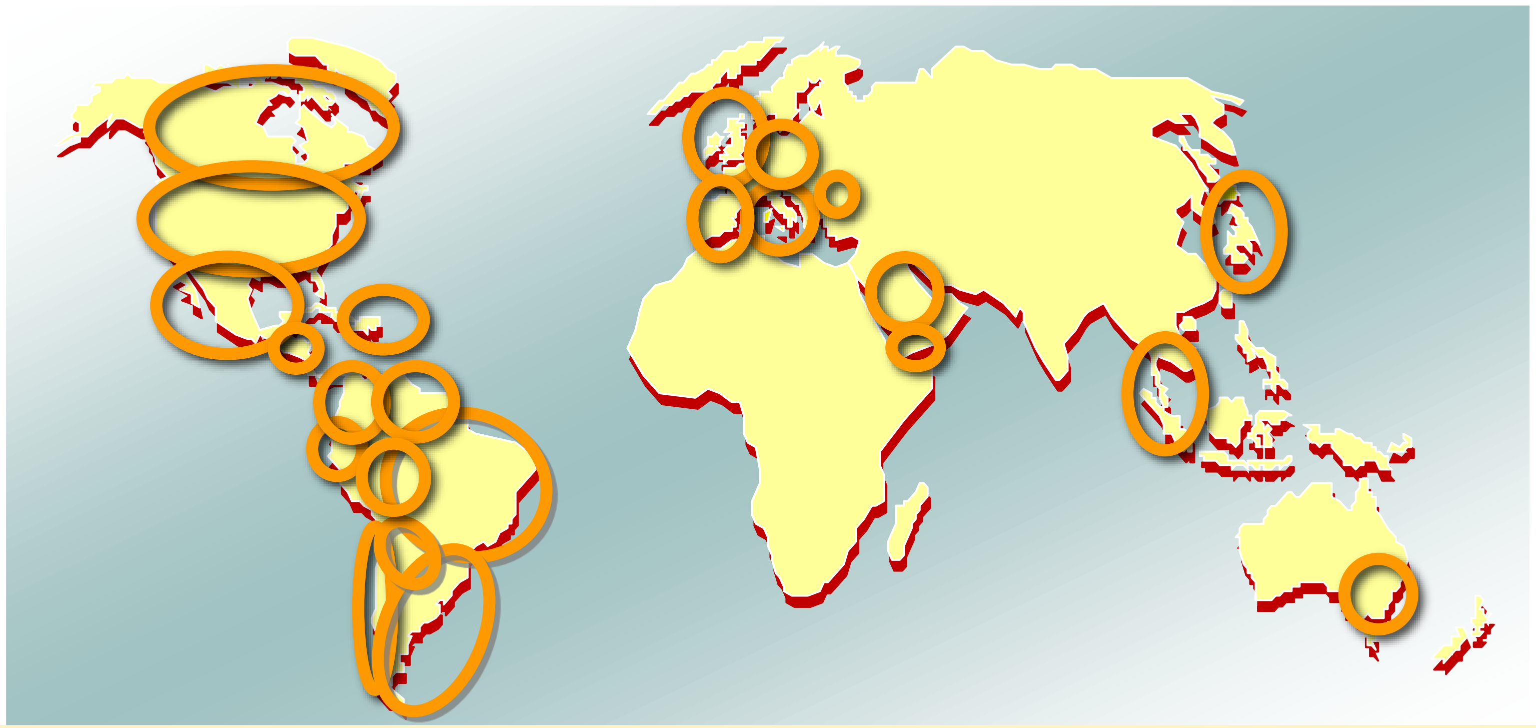
- *Government Agencies*
- *R&D Organizations*
- *Oil and Gas Industry*
- *Chemical Industry*
- *Law Firms*

What We Do

- Environmental strategic planning
- Environmental site investigations
- Risk assessments and modeling studies
- Corrective action design/ implementation
- Data management and data analysis
- Software development
- Training courses
- Litigation support services

BOTTOM LINE: **International reputation as high-quality, innovative firm.**

GSI OVERVIEW: *GSI PROJECTS AROUND THE WORLD*



North America

- U.S.
- Canada

Australia

Latin America

- Brazil
- Colombia
- Argentina
- Venezuela
- Paraguay
- Guatemala
- Dominican Republic
- Chile
- Puerto Rico
- Ecuador
- Mexico
- Bolivia
- Peru

Middle East / Asia

- Saudi Arabia
- Yemen
- Japan
- Malaysia
- Singapore

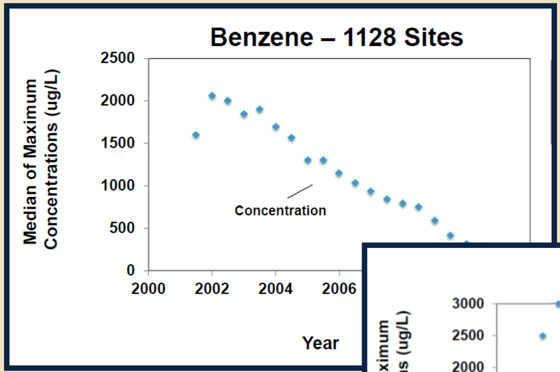
Europe

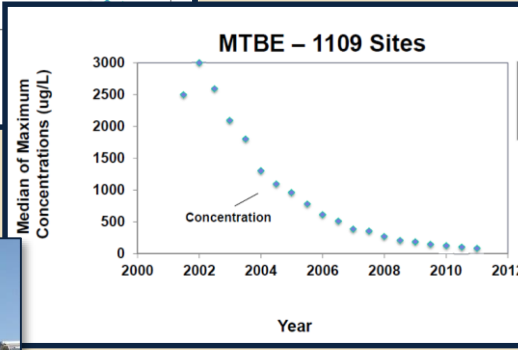
- Spain
- United Kingdom
- Italy
- Bulgaria
- Germany
- Belgium
- Denmark

RELATED WORK: *Pushing the Frontiers of Science…*

LNAPL Conceptual Model

- New field methods to develop understanding of LNAPL conceptual model
- Assess NSZD rates using existing methods
- Large-scale (“big-data”) studies to assess source attenuation





Partners and Collaborators

- Universities
- Large Oil and Gas Companies
- Technology developers

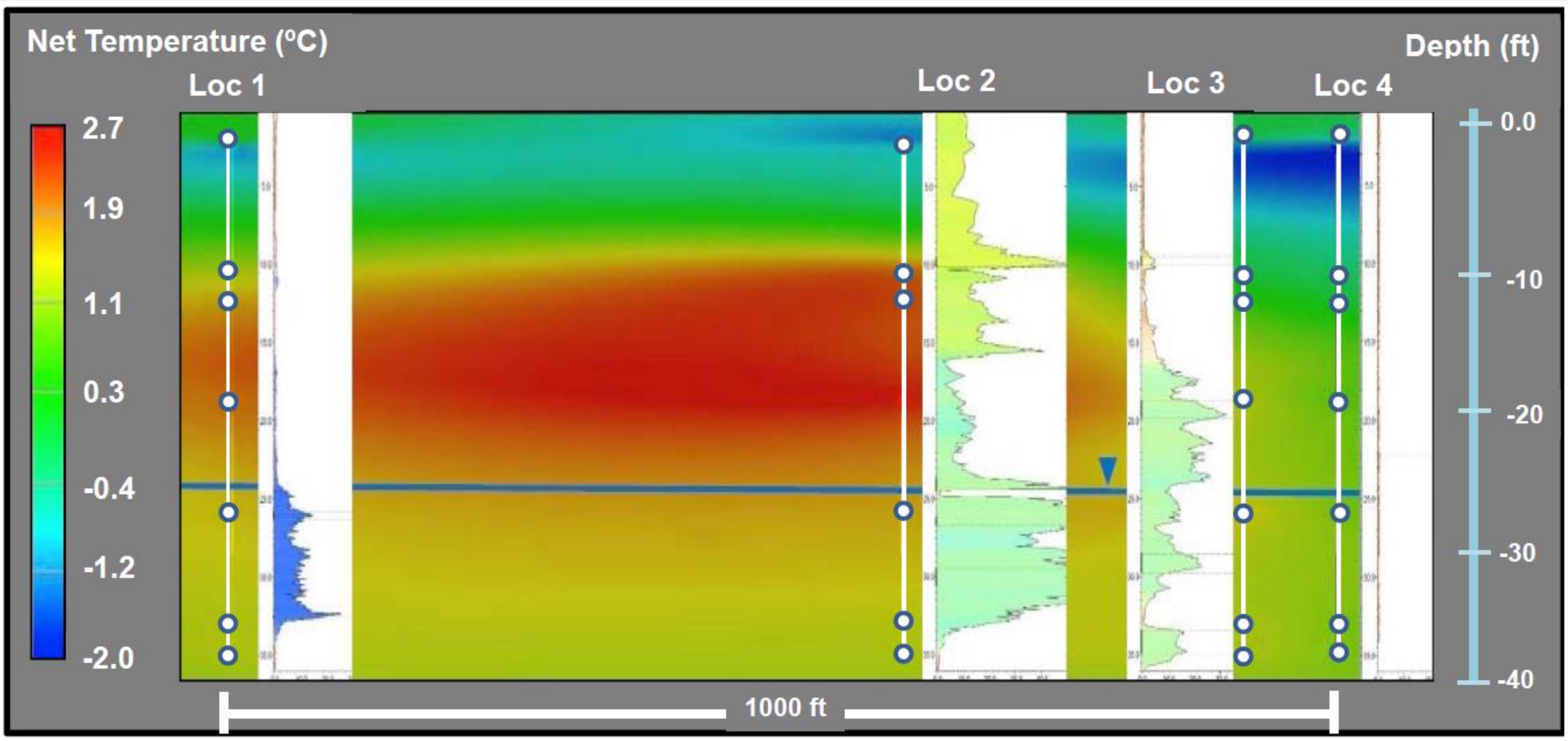
Who We Are

GSI ENVIRONMENTAL

WHO	Consultants in environmental science and engineering
WHERE	Offices in Houston and Austin, TX, Irvine and Oakland, CA with projects worldwide
WHEN	Founded 1986; completed >3,500 projects throughout the US and worldwide
WHAT	M.S. and Ph.D. Engineers/ Scientists, Hydrogeologists, Software Developers, Database/GIS Professionals, Field Techs, Expert Witness Staff

KEY POINT: *Focus on environmental engineering projects for industry, Chemical manufacturers, transportation, law firms, R&D organizations, and Government agencies.*

Background-corrected Temperature (Heat Signal)

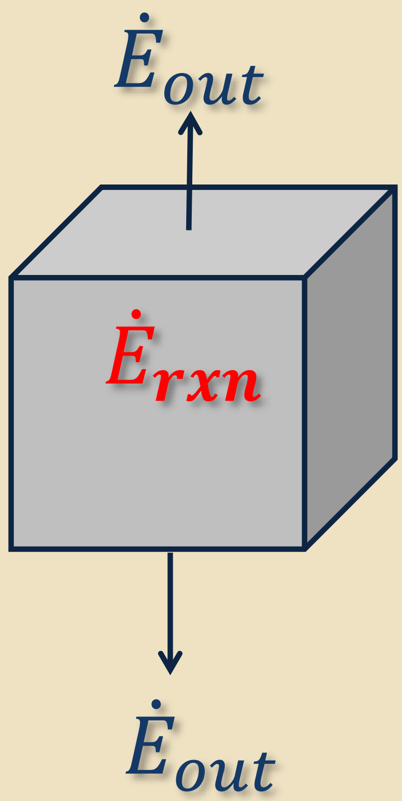


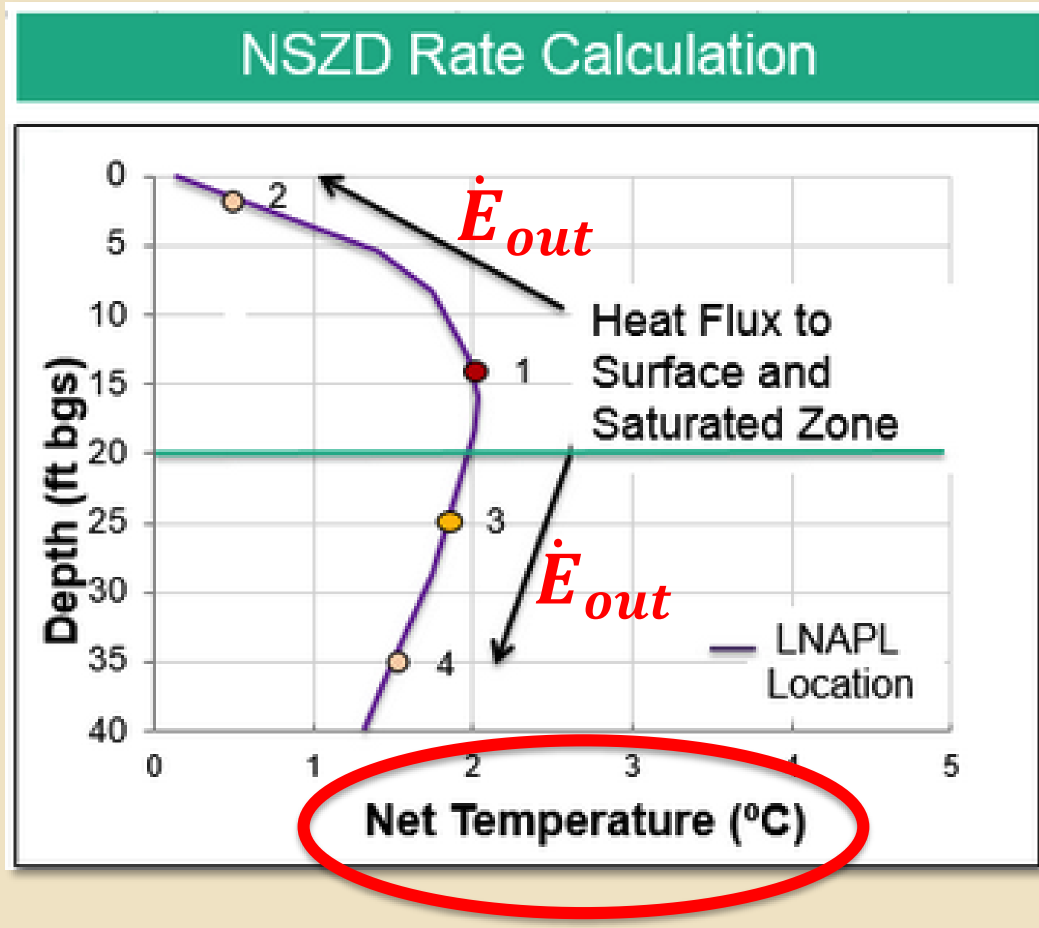
(Stockwell, 2015; Colorado State University)

Calculating LNAPL Mass Loss by NSZD

After Background Correction:

$$\dot{E}_{out} = \dot{E}_{rxn}$$

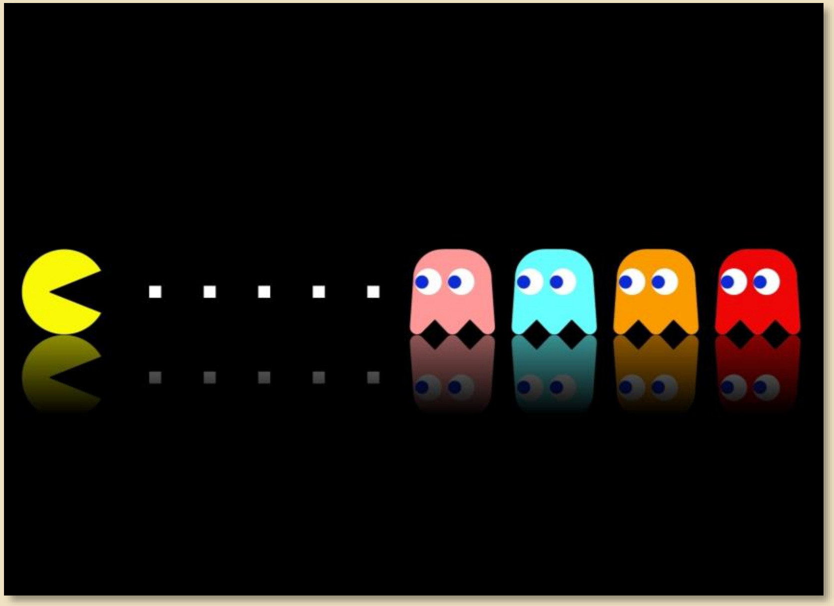




Both Combustion and Biodegradation Generate Heat

Heat of combustion for diesel:
45 kilojoules per gram

Burn 1 gram diesel:
45 kilojoules



Biodegrade 1 gram diesel (decane):
45 kilojoules

ThermalNSZD

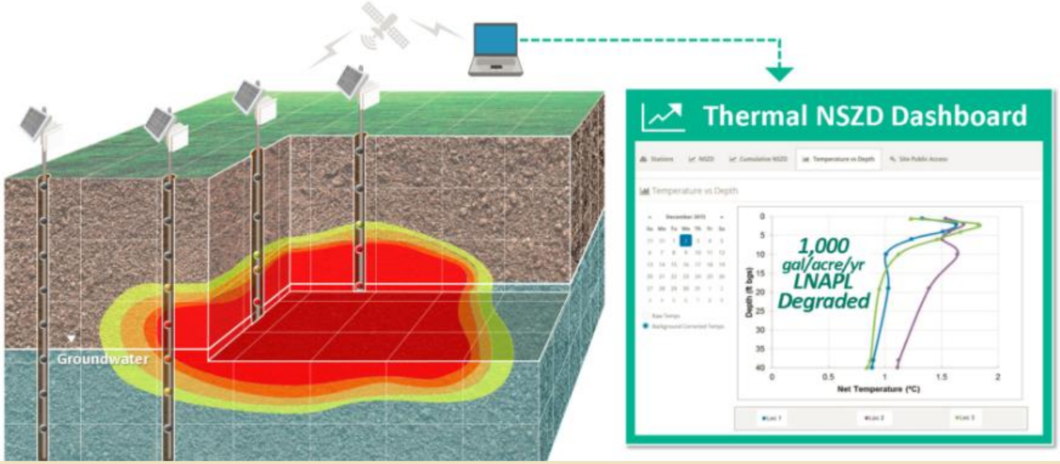
HOME TECHNOLOGY DEMO IMPLEMENT CONTACT CUSTOMER LOGIN

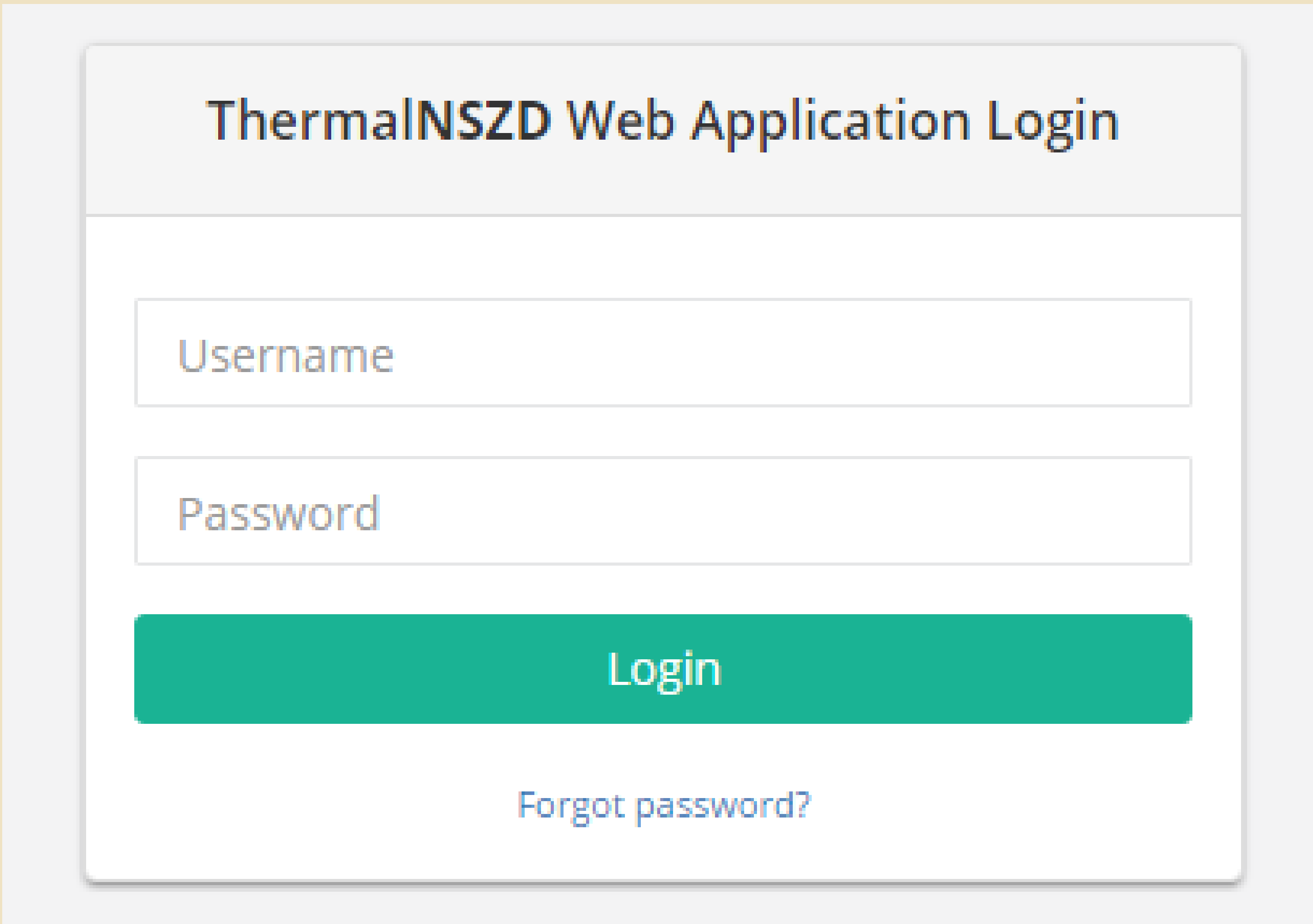
Thermal NSZD: Continuous Remote Monitoring of Natural Source Zone Depletion (NSZD)

The Thermal NSZD technology (patent pending) measures the rate at which natural biodegradation destroys free-phase product (LNAPL) in the subsurface by measuring the heat released by the microbial reactions.

Advantages of Thermal NSZD

- ✔ One-time field installation of remote monitoring system with minimal O&M, no site visits, no sampling and no lab.
- ✔ Daily temperature readings from vertical profiles of thermocouples.
- ✔ Secured, read only access to site data for regulators.




ThermalNSZD Web Application Login
Username
Password
Login
Forgot password?

Chronology of Key Publications

US 20150233773A1

(19) **United States**
(12) **Patent Application Publication**
Sale et al.

(10) **Pub. No.: US 2015/0233773 A1**
(43) **Pub. Date: Aug. 20, 2015**

(54) DEVICES AND METHODS FOR MEASURING THERMAL FLUX AND ESTIMATING RATE OF CHANGE OF REACTIVE MATERIAL WITHIN A SUBSURFACE FORMATION

(71) Applicants: **Colorado State University Research Foundation**, Fort Collins, CO (US); **GSI Environmental, Inc.**, Houston, TX (US)

(72) Inventors: **Thomas C. Sale**, Bellvue, CO (US); **Emily B. Stockwell**, Fort Collins, CO (US); **Charles J. Newell**, Houston, TX (US); **Poonam R. Kulkarni**, Houston, TX (US)

(73) Assignees: **Colorado State University Research Foundation**, Fort Collins, CO (US); **GSI Environmental, Inc.**, Houston, TX (US)

(21) Appl. No.: **14/625,570**

(22) Filed: **Feb. 18, 2015**

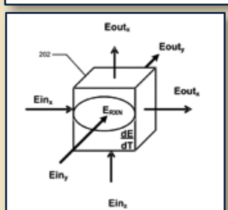
Related U.S. Application Data

(60) Provisional application No. 61/941,194, filed on Feb. 18, 2014.

Publication Classification

(51) **Int. Cl.**
G01K 17/08 (2006.01)
E21B 47/06 (2006.01)

(52) **U.S. Cl.**



Sale et al., 2014
Provisional Patent

Groundwater Monitoring&Remediation

Temperature as a Tool to Evaluate Aerobic Biodegradation in Hydrocarbon Contaminated Soil

by Robert E. Sweeney and G. Todd Ririe

Sweeney and Ririe, 2014
Basic theory to estimate rate

Relating subsurface temperature changes to microbial activity at a crude oil-contaminated site

CrossMark

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A R T I C L E   I N F O

Article history:
Received 29 July 2015
Received in revised form 26 August 2015
Accepted 10 September 2015
Available online 15 September 2015

A B S T R A C T

Crude oil at a spill site near Bemidji, Minnesota has been undergoing aerobic and anaerobic biodegradation for over 30 years, creating a 150–200 m plume of primary and secondary contaminants. Microbial degradation generates heat that should be measurable under the right conditions. To measure this heat, thermistors were installed in wells in the saturated zone and in water-filled monitoring tubes in the unsaturated zone. In the saturated zone, a thermal groundwater plume originates near the residual oil body with temperatures ranging from 2.9 °C

Warren and Bekins, 2015

	umoles $CO_2/m^2/sec$
Sihota et al., 2016 CO_2 Efflux Methods (CSR):	1.1
Warren and Bekins, 2015 Temperature Method:	~0.82