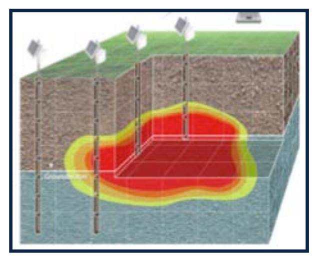
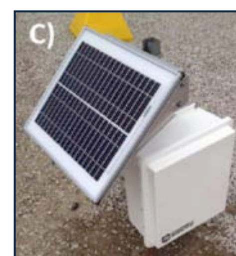
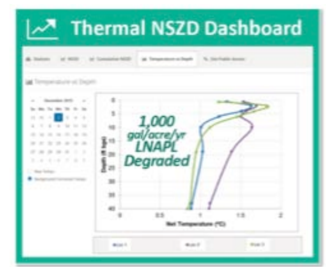
ADVANCES IN MONITORING PETROLEUM CONTAMINATED SITES

Federal Remediation Technologies Roundtable
November 2, 2016 Reston, Virginia



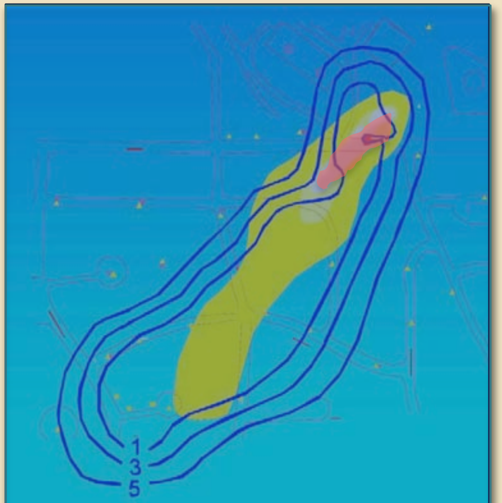




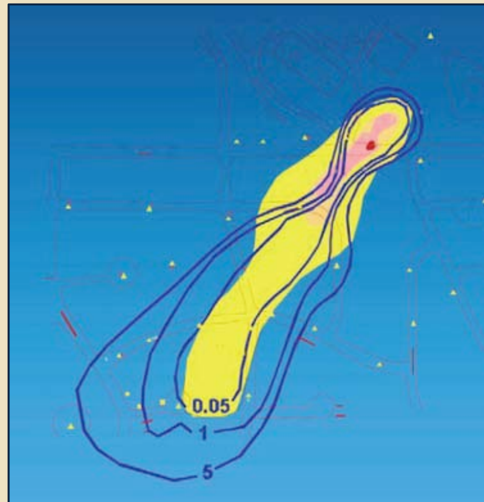
Charles Newell, GSI Environmental
Tom Sale, Colorado State
John Connor, GSI Environmental
Poonam Kulkarni, GSI Environmental
Keith Piontek, TRC Consultants

Key Electron Acceptors For MNA (Yellow/Red Is BTEX Plume) (Concentration: mg/L)

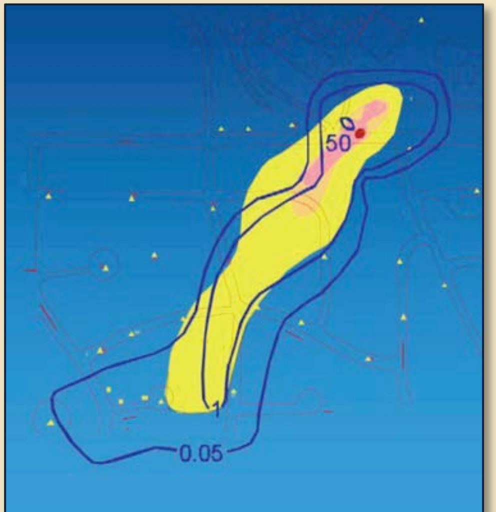
Dissolved Oxygen “Hole”



Nitrate “Hole”

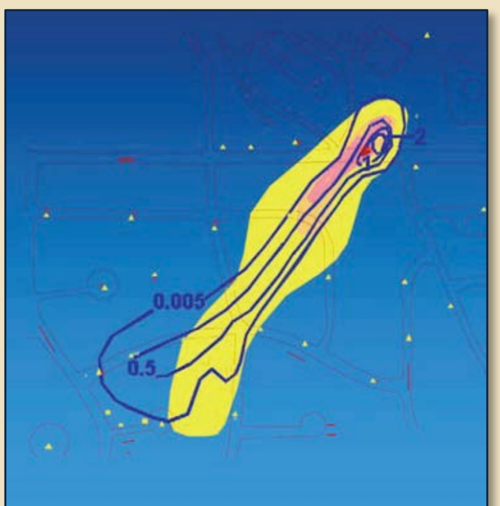


Ferrous Iron “Blob”

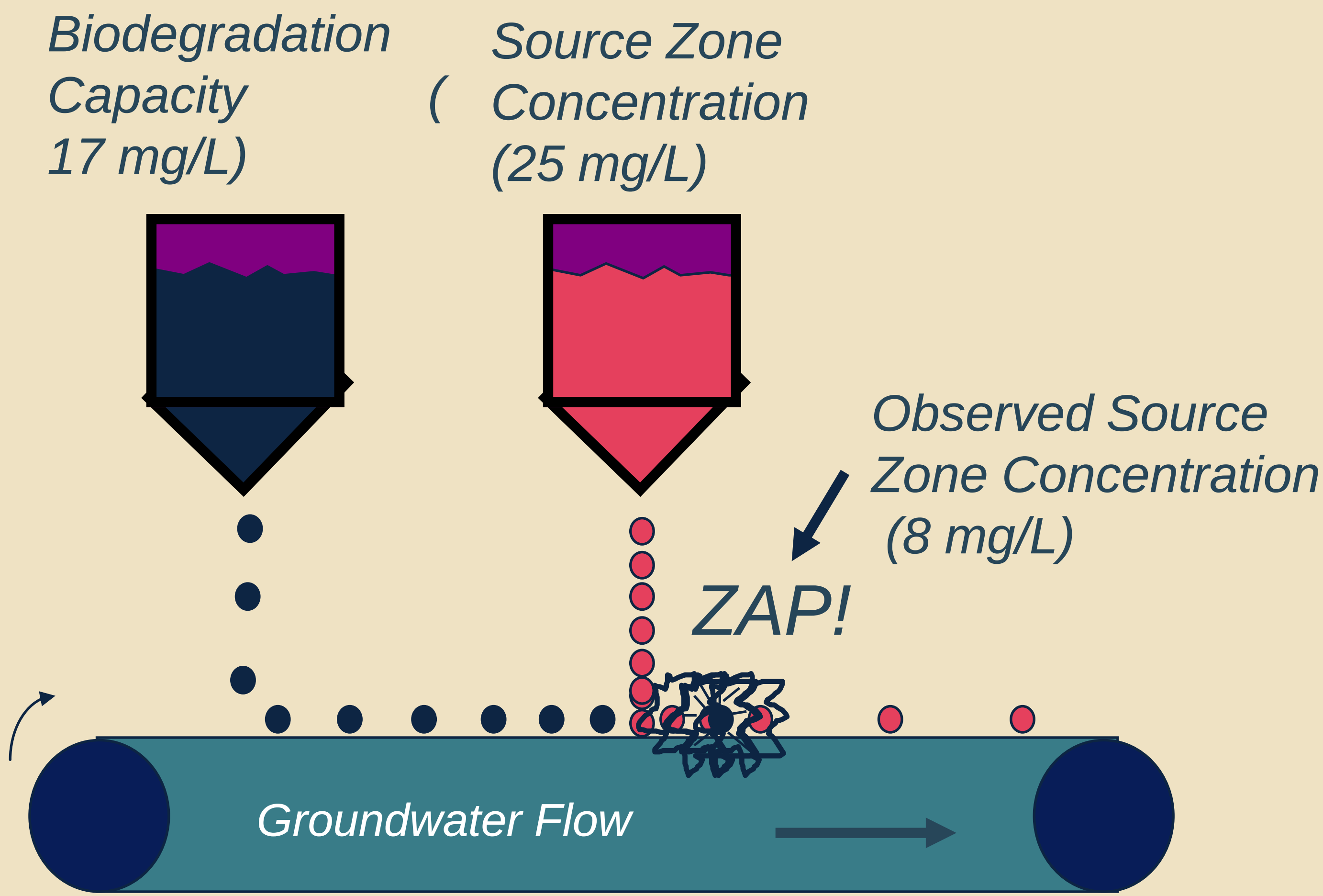


Sulfate “Hole”

Dissolved Methane “Plume”



MNA Mass Balance in Plumes:
Electron-Acceptor-Limited Biodegradation



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

Monitored Natural Attenuation (MNA)

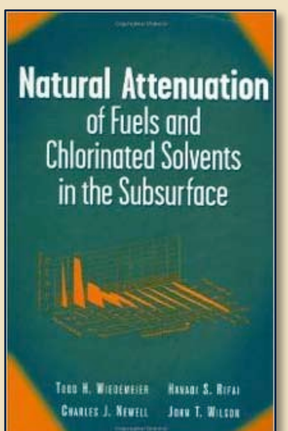
- Mostly focused on plume (“how far”)
- For hydrocarbon plumes, key focus on:

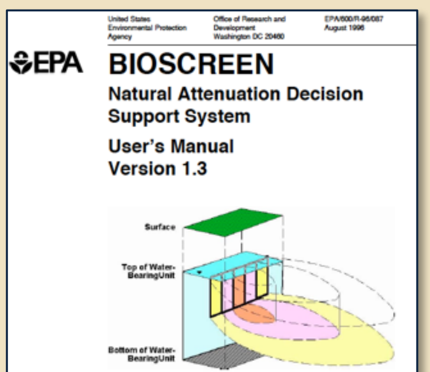
Electron Acceptors

- *Dissolved Oxygen*
- *Nitrate*
- *Ferric iron (solid)*
- *Sulfate*
- *Methanogenesis*

Electron Donors

- *Benzene*
- *Toluene*
- *Ethylbenzene*
- *Xylenes*





WAIT – THERE'S MORE!

Groundwater Mass Flux vs. Vapor Phase Mass Flux

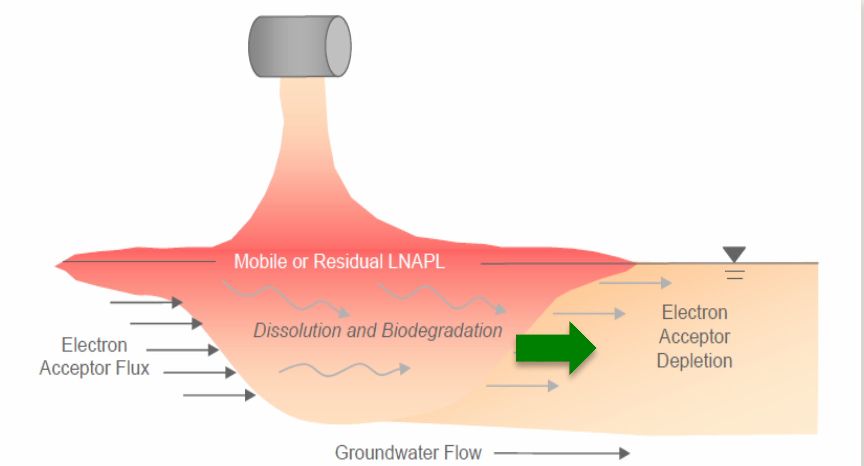


Figure 2-1. Groundwater transport–related NSZD processes.

Original NSZD Conceptual Model

Lundegard and Johnson, 2006; ITRC, 2009

Groundwater Mass Flux vs. Vapor Phase Mass Flux

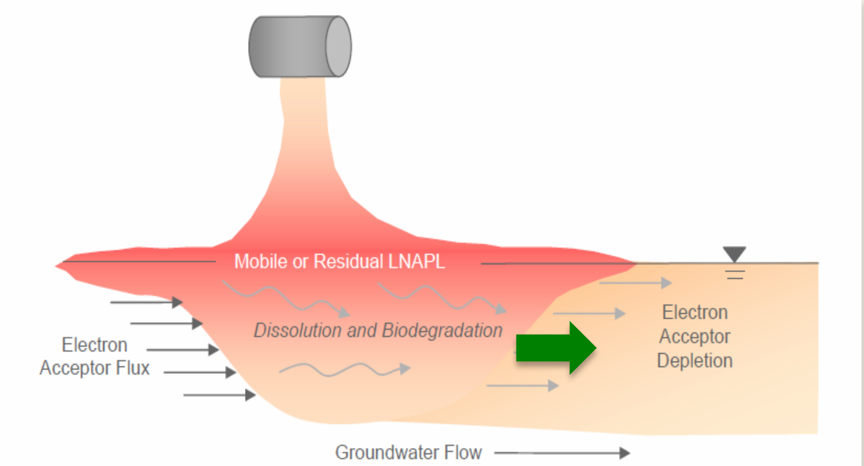


Figure 2-1. Groundwater transport–related NSZD processes.

Original NSZD Conceptual Model

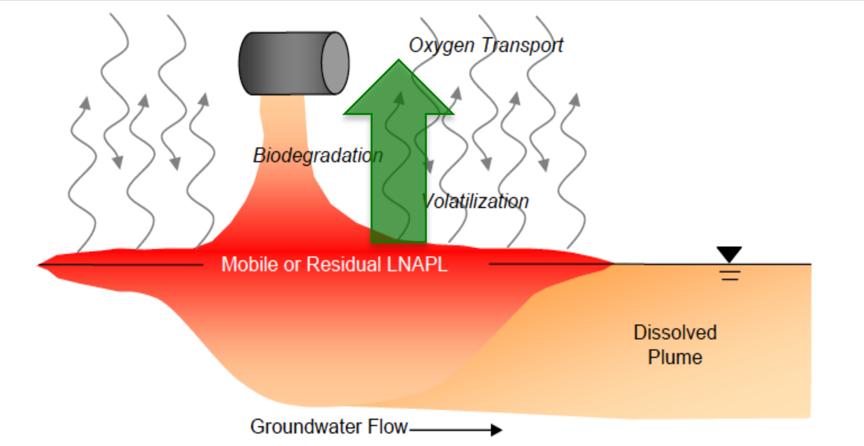
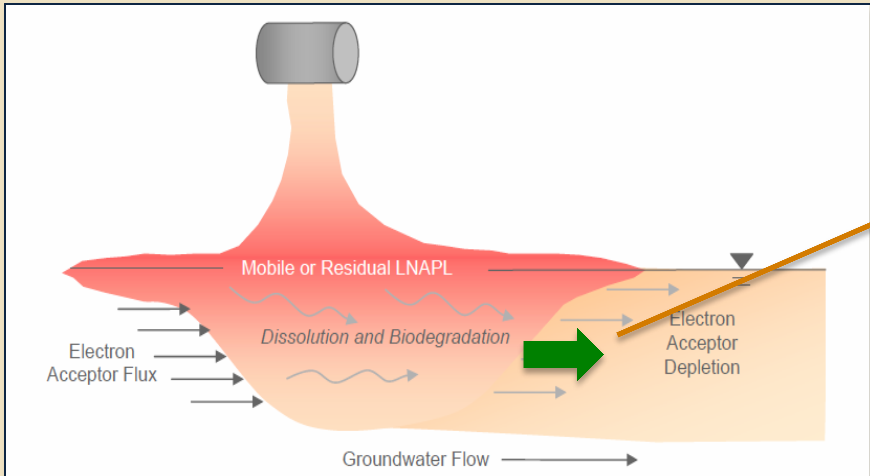


Figure 2-2. Vapor transport–related NSZD processes.

Johnson Lundegard NSZD Conceptual Model:
Include vapor pathway

Lundegard and Johnson, 2006; ITRC, 2009

Groundwater Mass Flux vs. Vapor Phase Mass Flux



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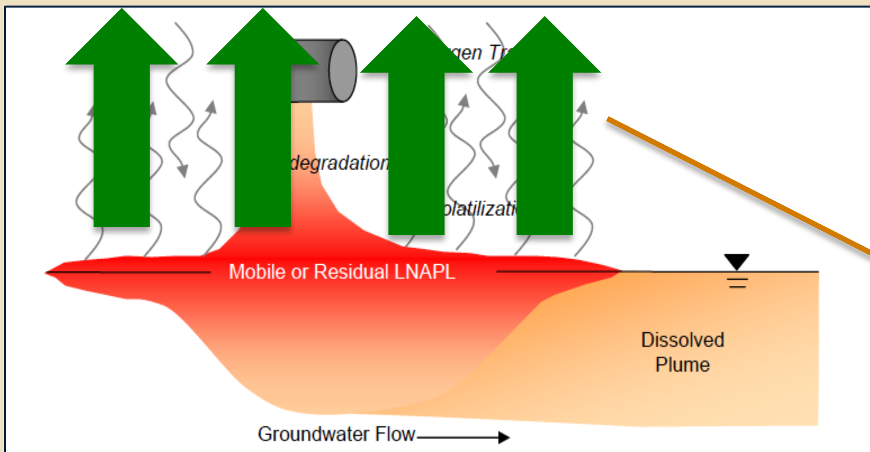


Figure 2-2. Vapor transport–related NSZD processes.

1-10%

90-99%

Surprising Result:
Vapor transport flux is
1 to 2 orders of magnitude
greater than
groundwater flux!

Lundegard and Johnson, 2006; ITRC, 2009; Suthersan 2015

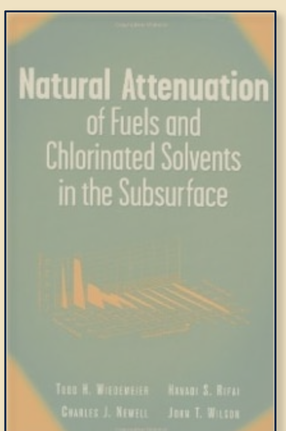
Monitored Natural Attenuation (MNA) versus Natural Source Zone Depletion (NSZD)

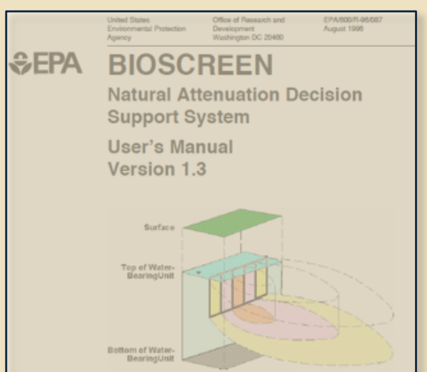
Monitored Natural Attenuation (MNA)

- Mostly focused on plume
- For hydrocarbon plumes, key focus on:

Electron Acceptors
- Dissolved Oxygen
- Nitrate
- Ferric iron (solid)
- Sulfate
- Methanogenesis

Electron Donors
- Benzene
- Toluene
- Ethylbenzene
- Xylenes





Natural Source Zone Depletion (NSZD)

Focused on source attenuation ("how long")

For hydrocarbon sites, key focus LNAPL

Key reactions:

LNAPL ⇨ CO_2 + Methane

Methane ⇨ CO_2

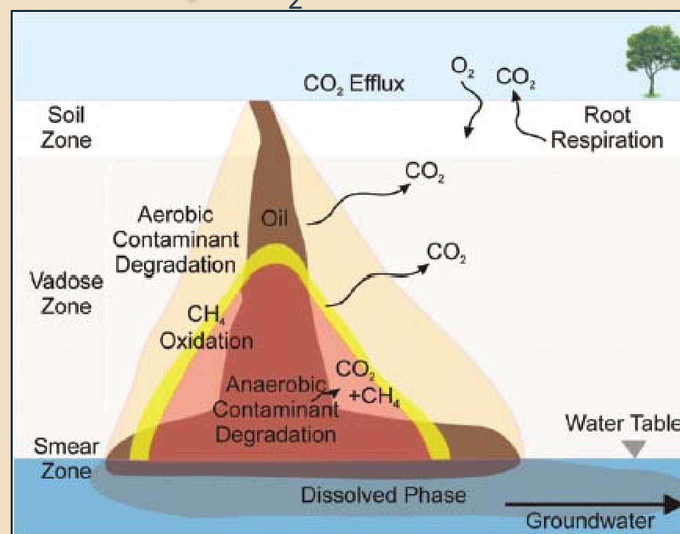


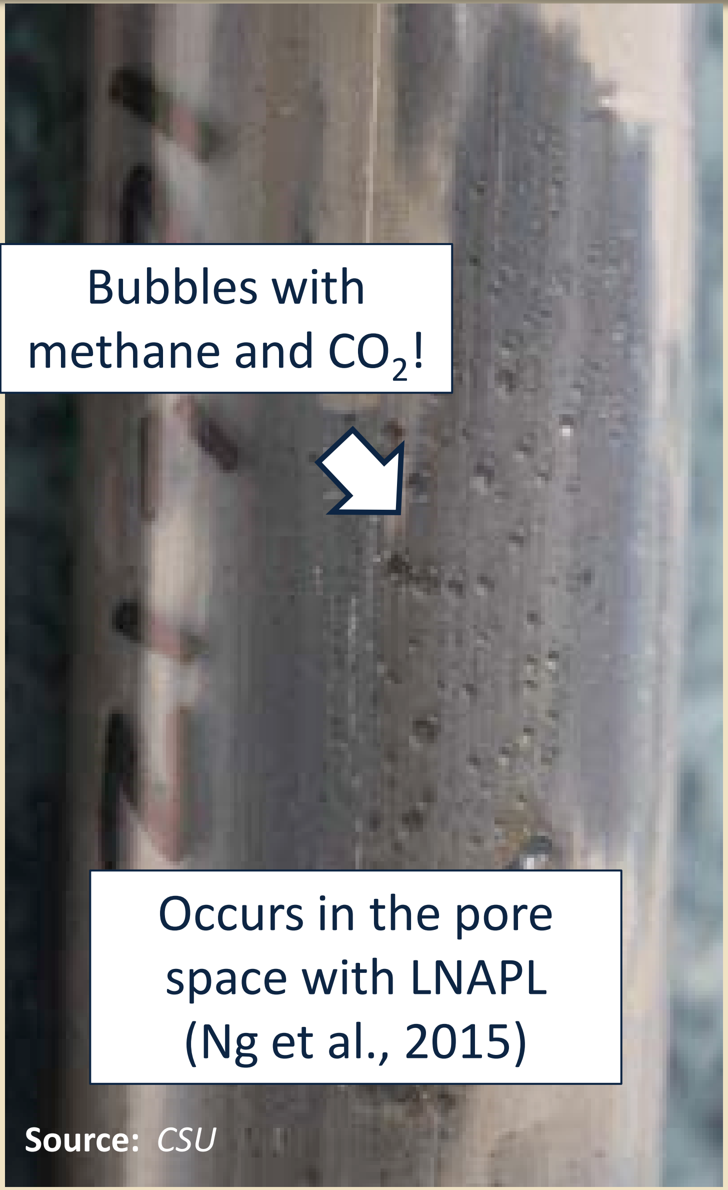
Fig. 1. Conceptual model of contamination in the vadose zone at the Bemidji site.

Sihota and Mayer, 2011

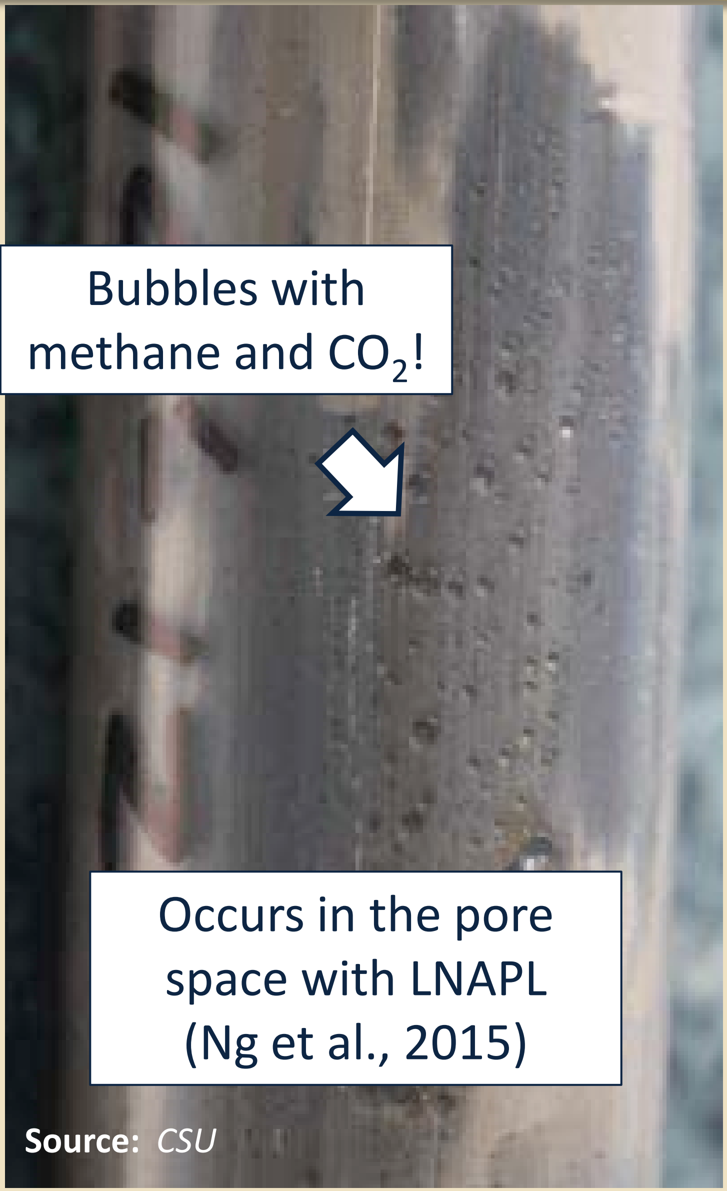
Direct Offgassing and Ebullition of Biodegradation Gases

Source: *CSU*

Direct Offgassing and Ebullition of Biodegradation Gases



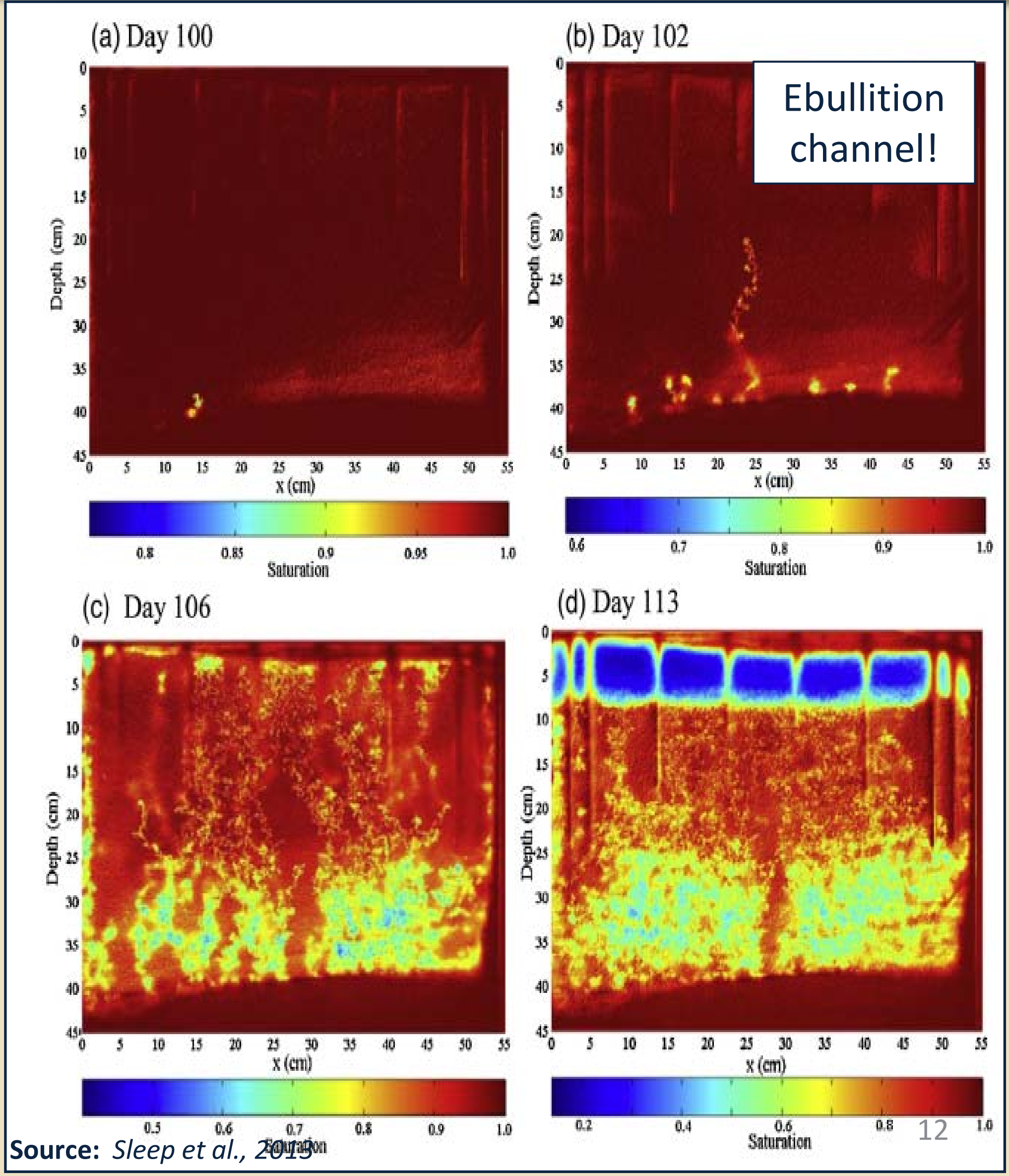
Direct Offgassing and Ebullition of Biodegradation Gases



Bubbles with methane and CO_2!

Occurs in the pore space with LNAPL (Ng et al., 2015)

Source: *CSU*



Ebullition channel!

Source: *Sleep et al., 2015*

Day 100

Day 102

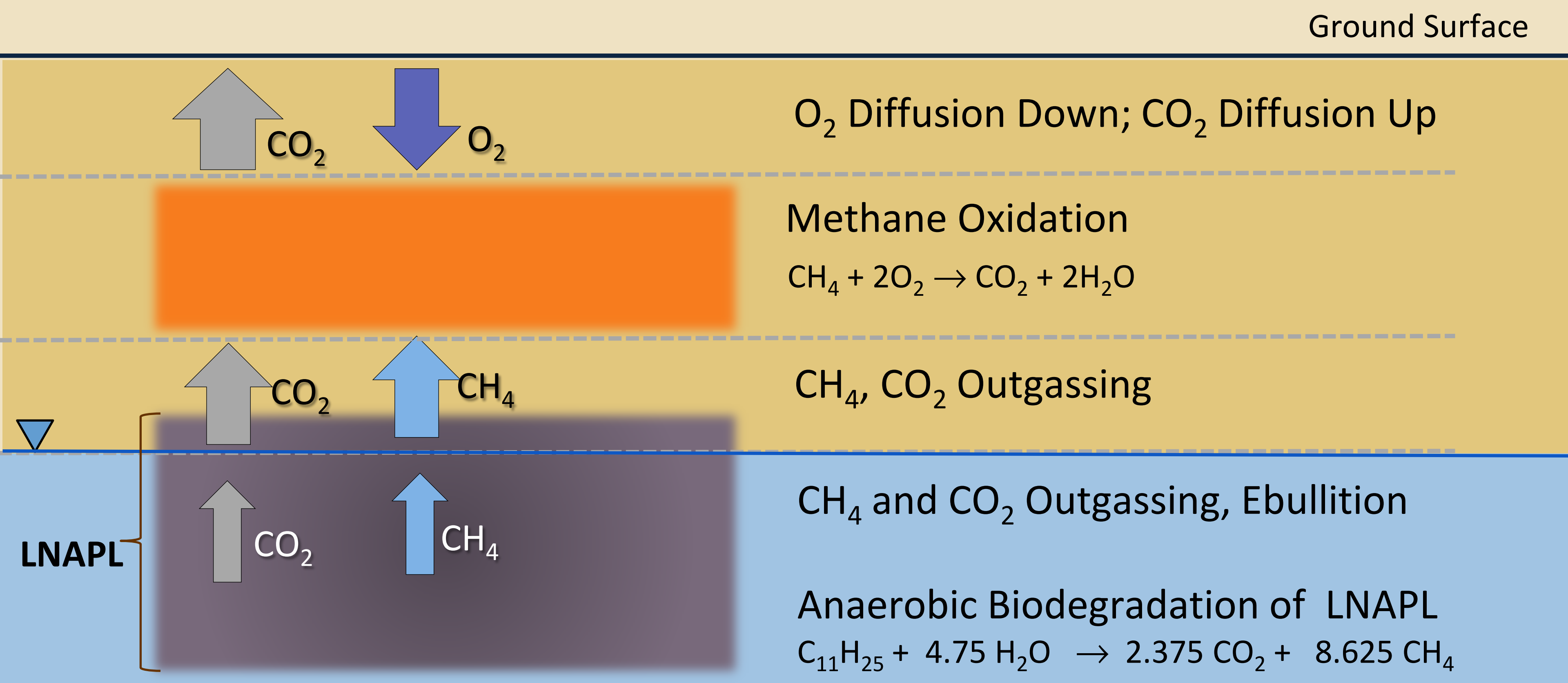
Methane channel!

Day 106

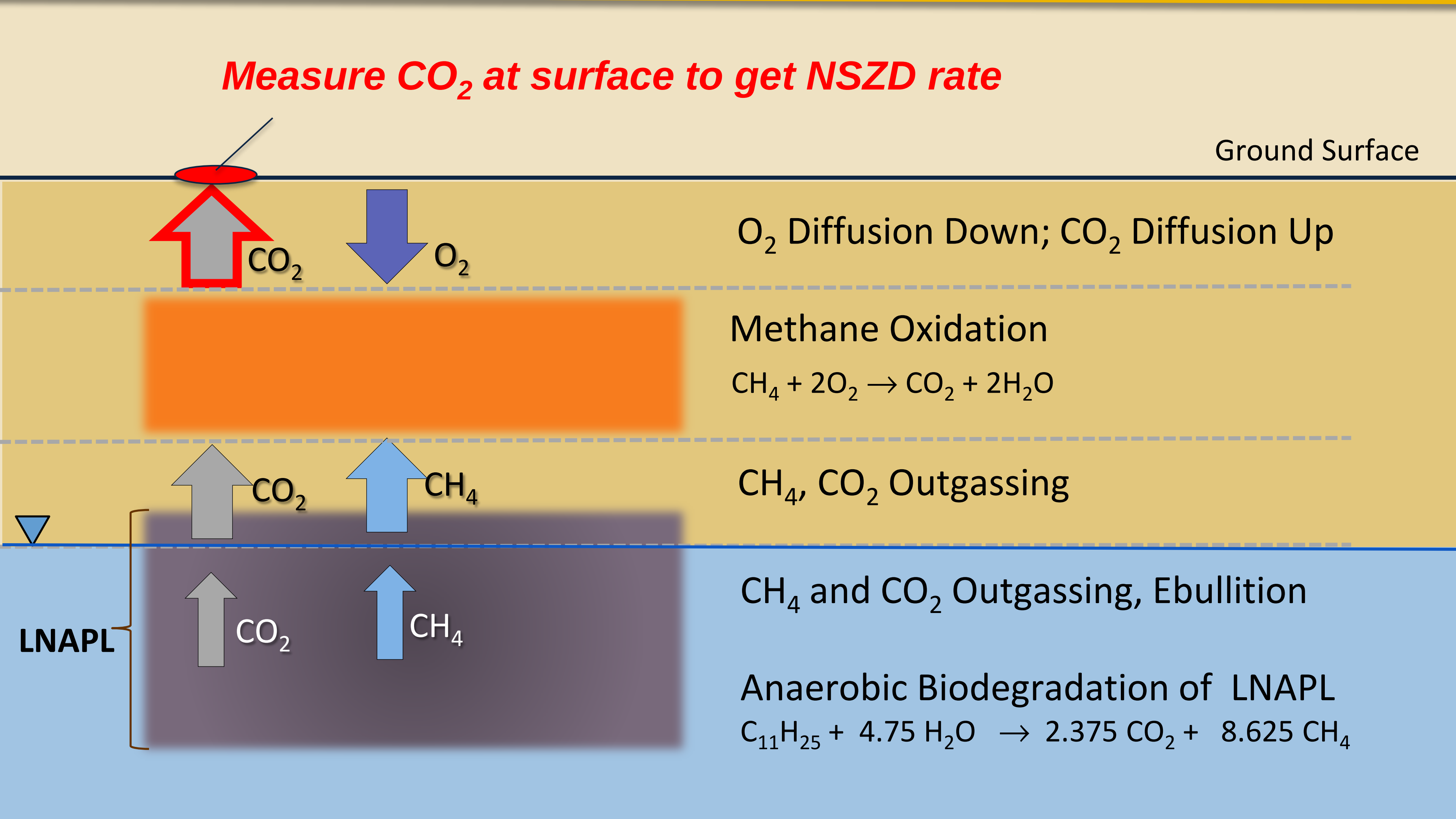
Water Saturation

Source: CSU

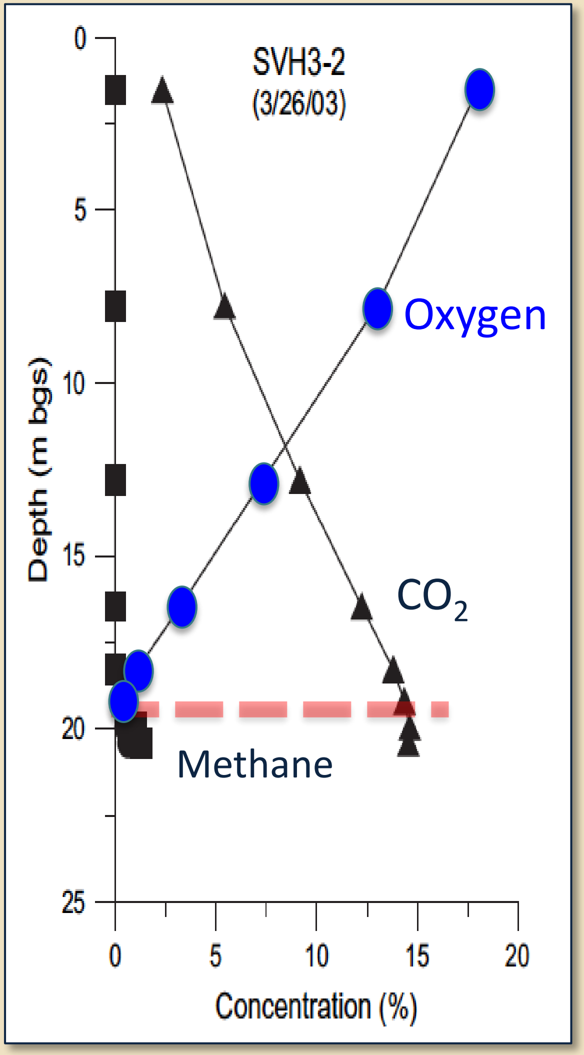
NSZD Conceptual Model



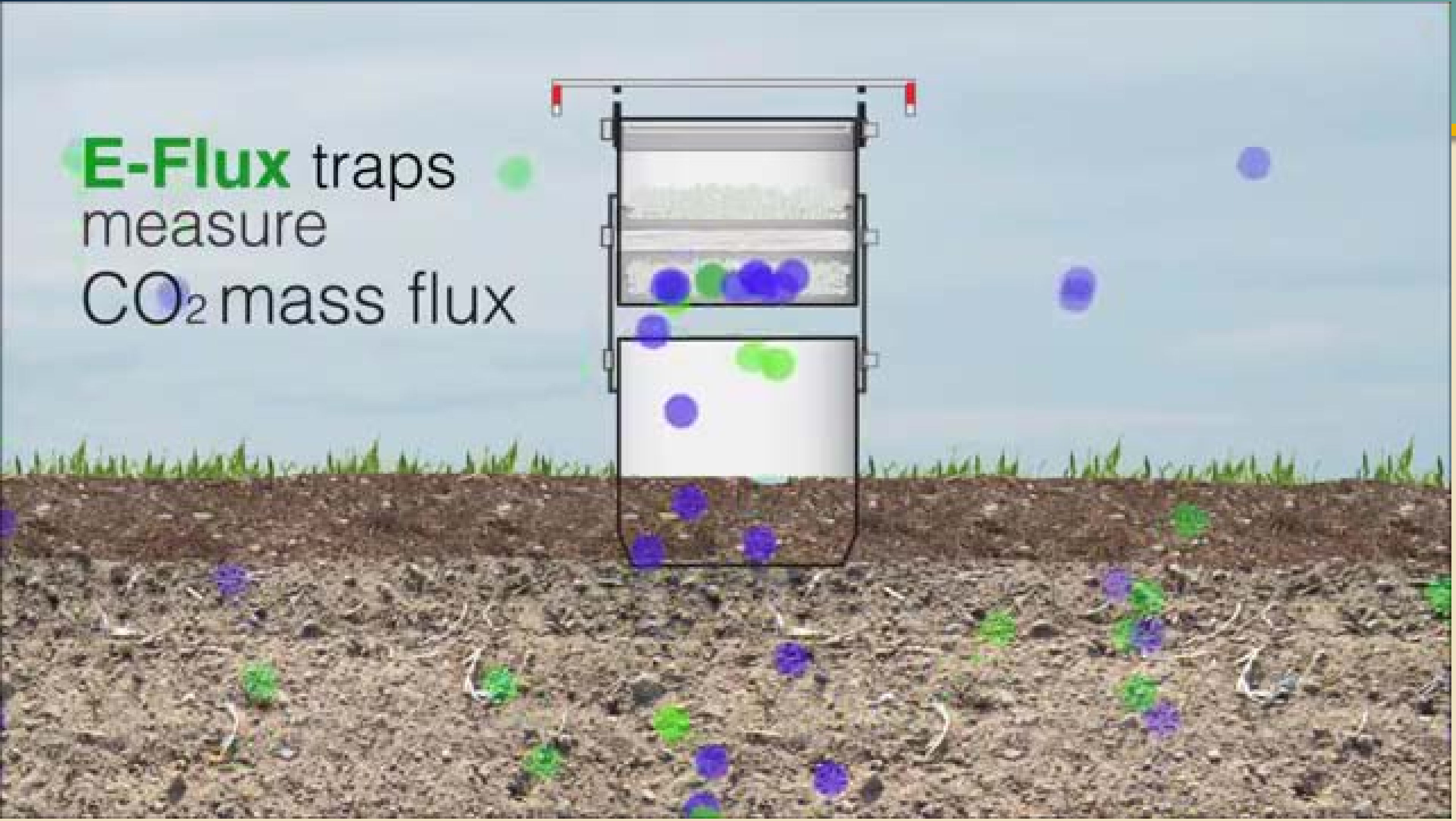
NSZD Conceptual Model



NSZD STUDIES: *Johnson et al, 2006; Lundegard and Johnson, 2006; Sihota et al., 2011; McCoy et al., 2013*



Lundegard and Johnson, 2006


E-Flux traps
measure
CO2 mass flux

What NSZD Rates are Being Observed?

NSZD Study	Site-wide NSZD Rate (gallons/ acre /year)
Six refinery terminal sites (McCoy et al., 2012)	2,100 – 7,700
1979 Crude Oil Spill (Sihota et al., 2011)	1,600
Refinery/Terminal Sites in Los Angeles (LA LNAPL Wkgrp, 2015)	1,100 – 1,700
Five Fuel/Diesel/Gasoline Sites (Piontek, 2014)	300 - 3,100
Eleven Sites, 550 measurements (Palaia, 2016)	300 – 5,600

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.**

Reactive transport modeling of geochemical controls on secondary water quality impacts at a crude oil spill site near Bemidji, MN

Gene-Hua Crystal Ng[1,2], Barbara A. Bekins[2], Isabelle M. Cozzarelli[3], Mary Jo Baedecker[3], Philip C. Bennett[4], Richard T. Amos[5], and William N. Herkelrath[2]

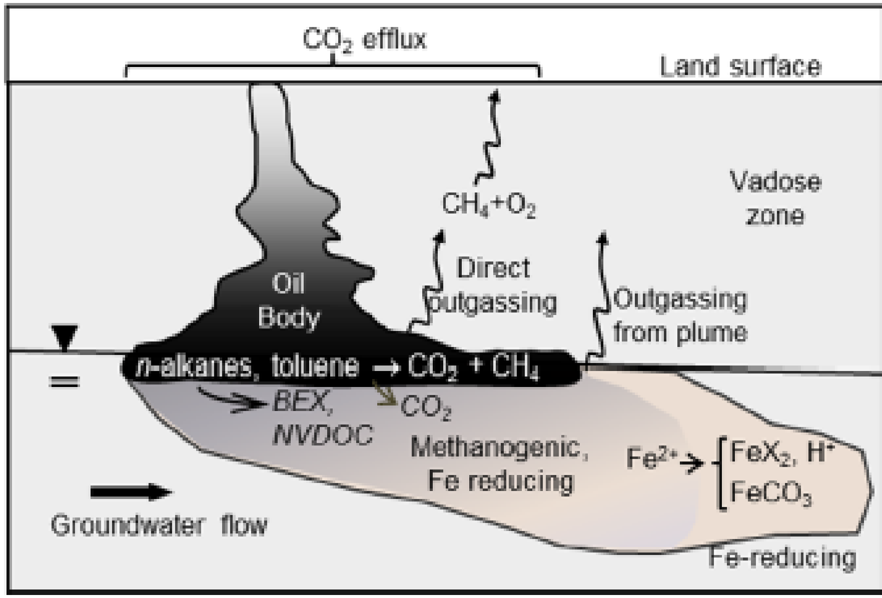
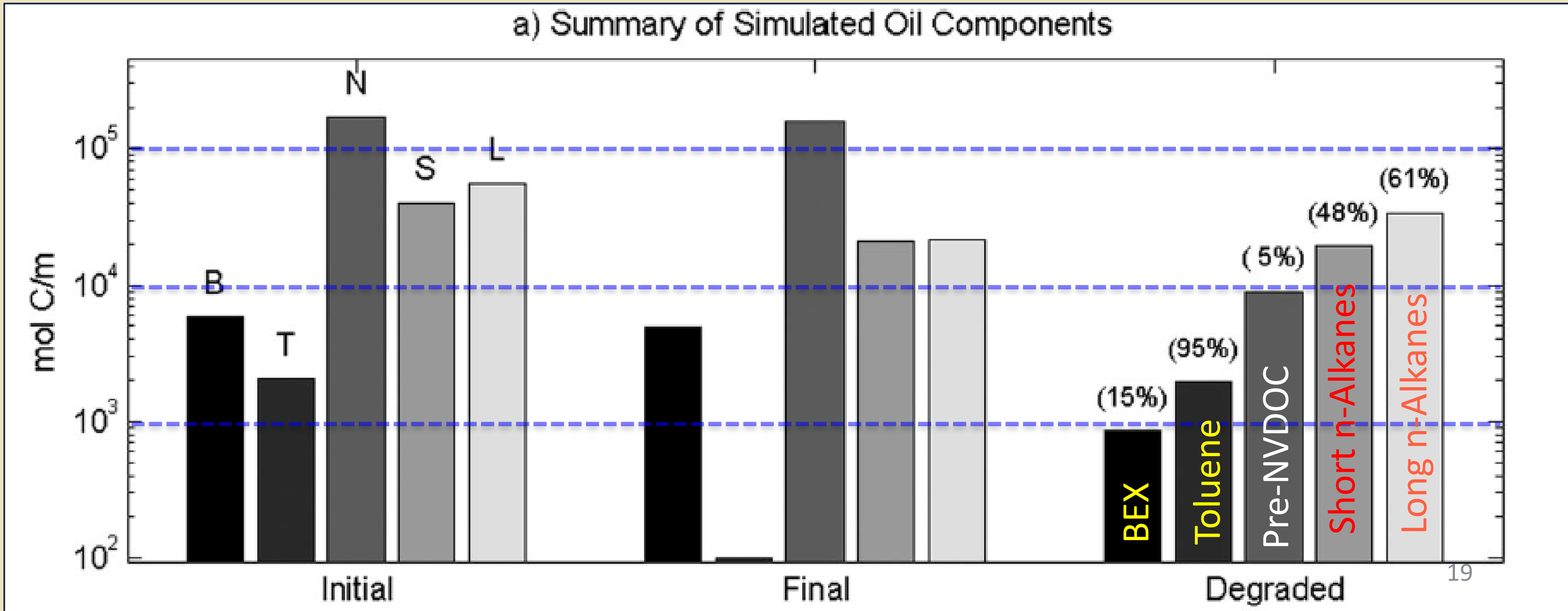


Figure 1. New conceptual model of the Bemidji north pool implemented with the reac-



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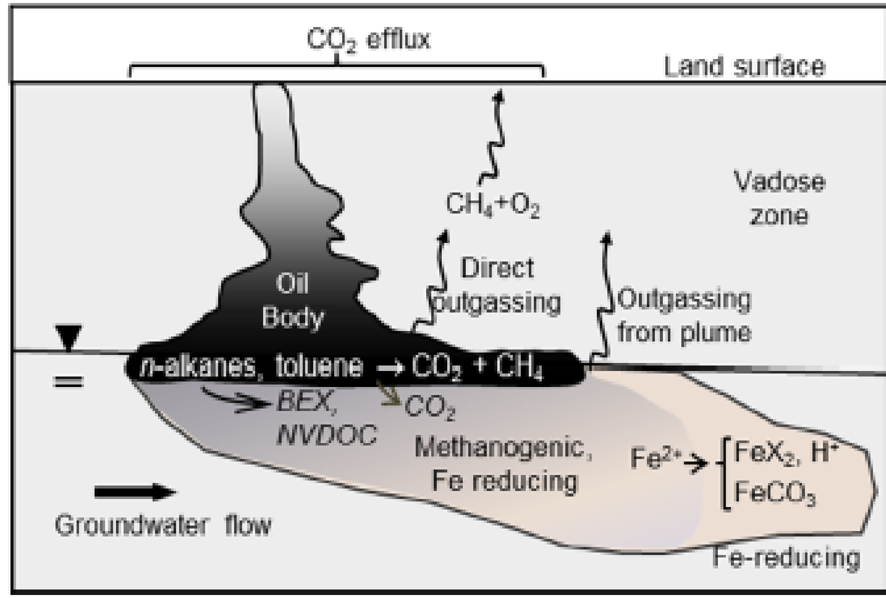

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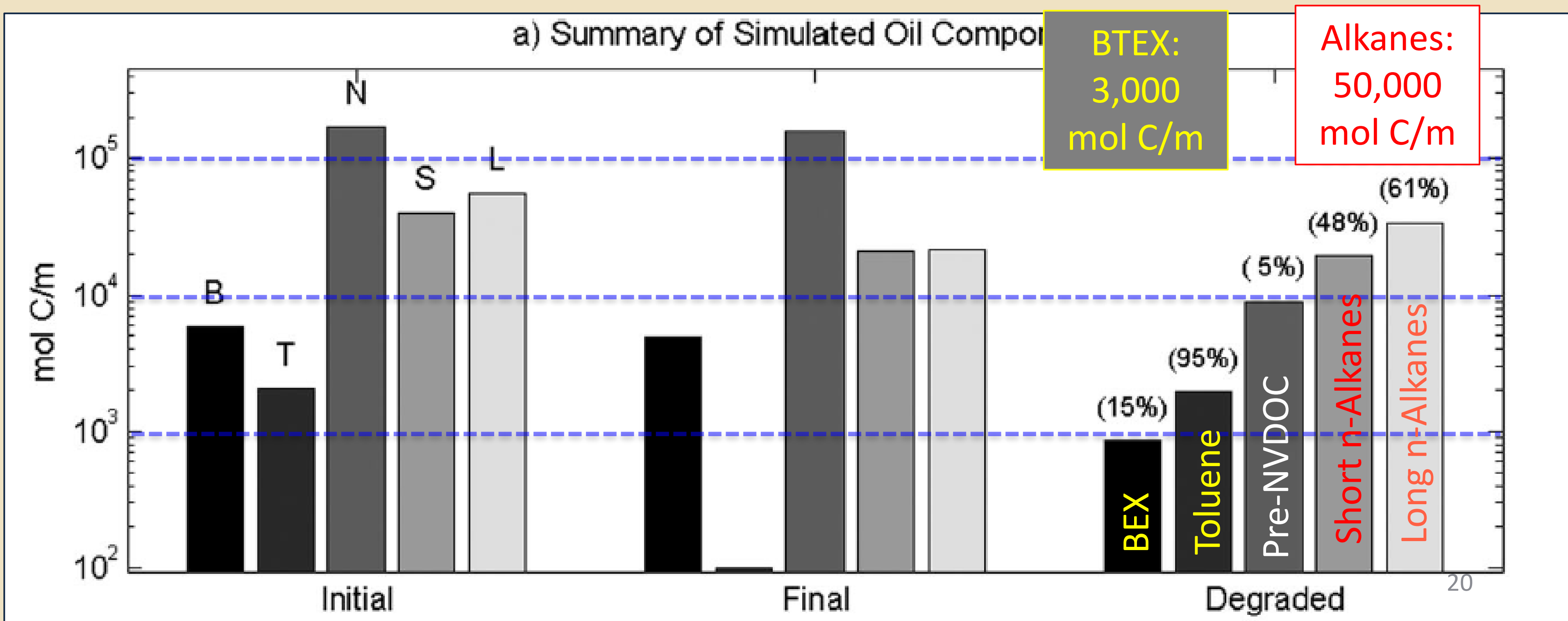
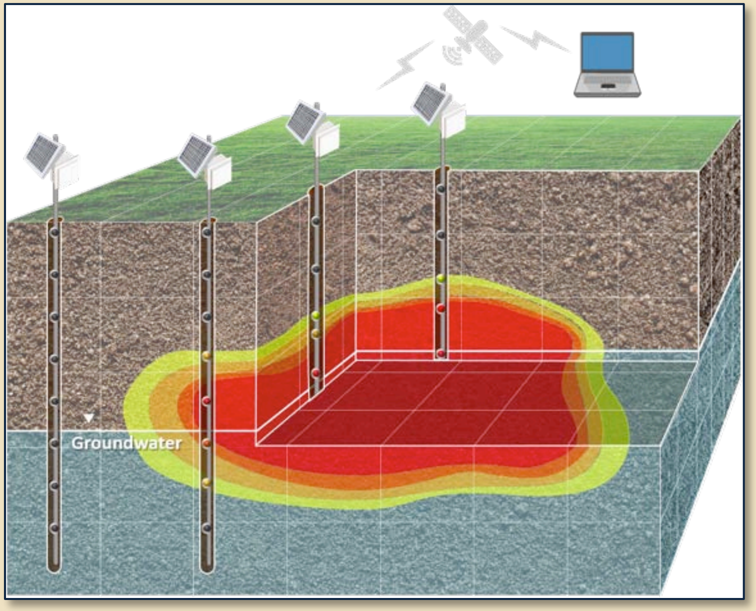
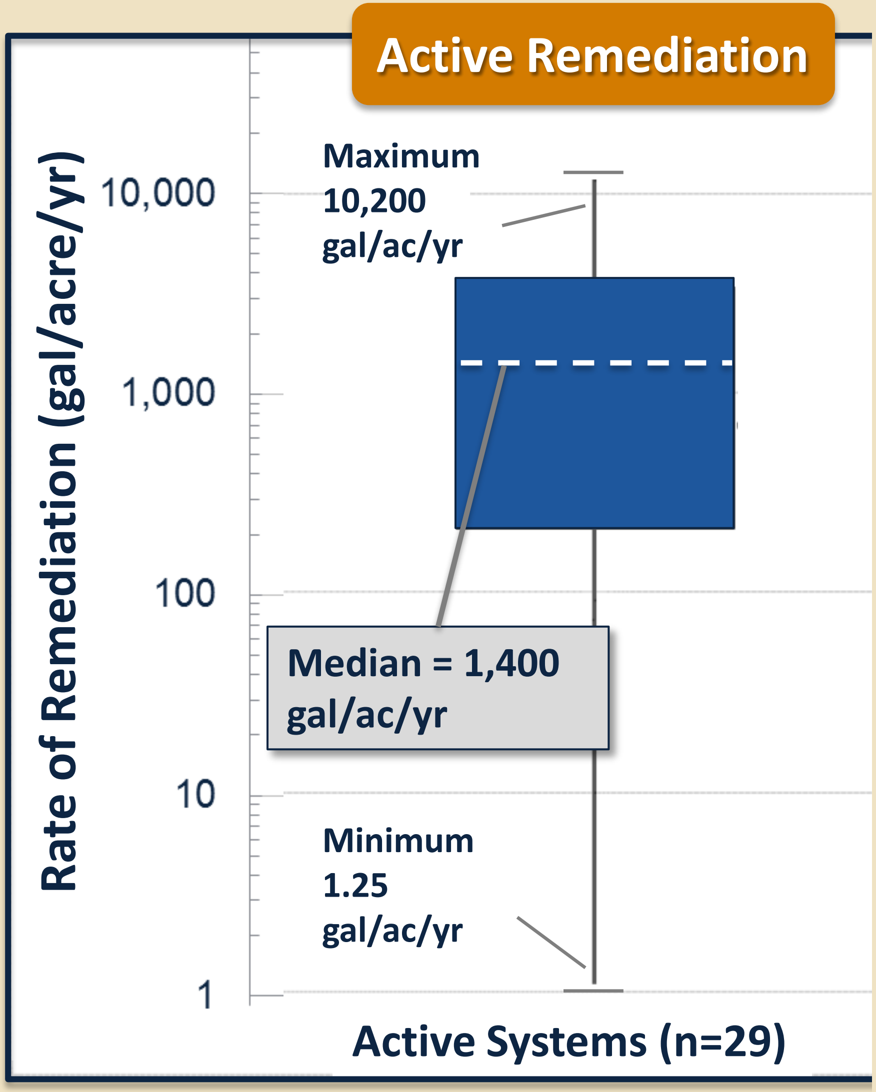


How Can NSZD Rates Be Used?

- 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

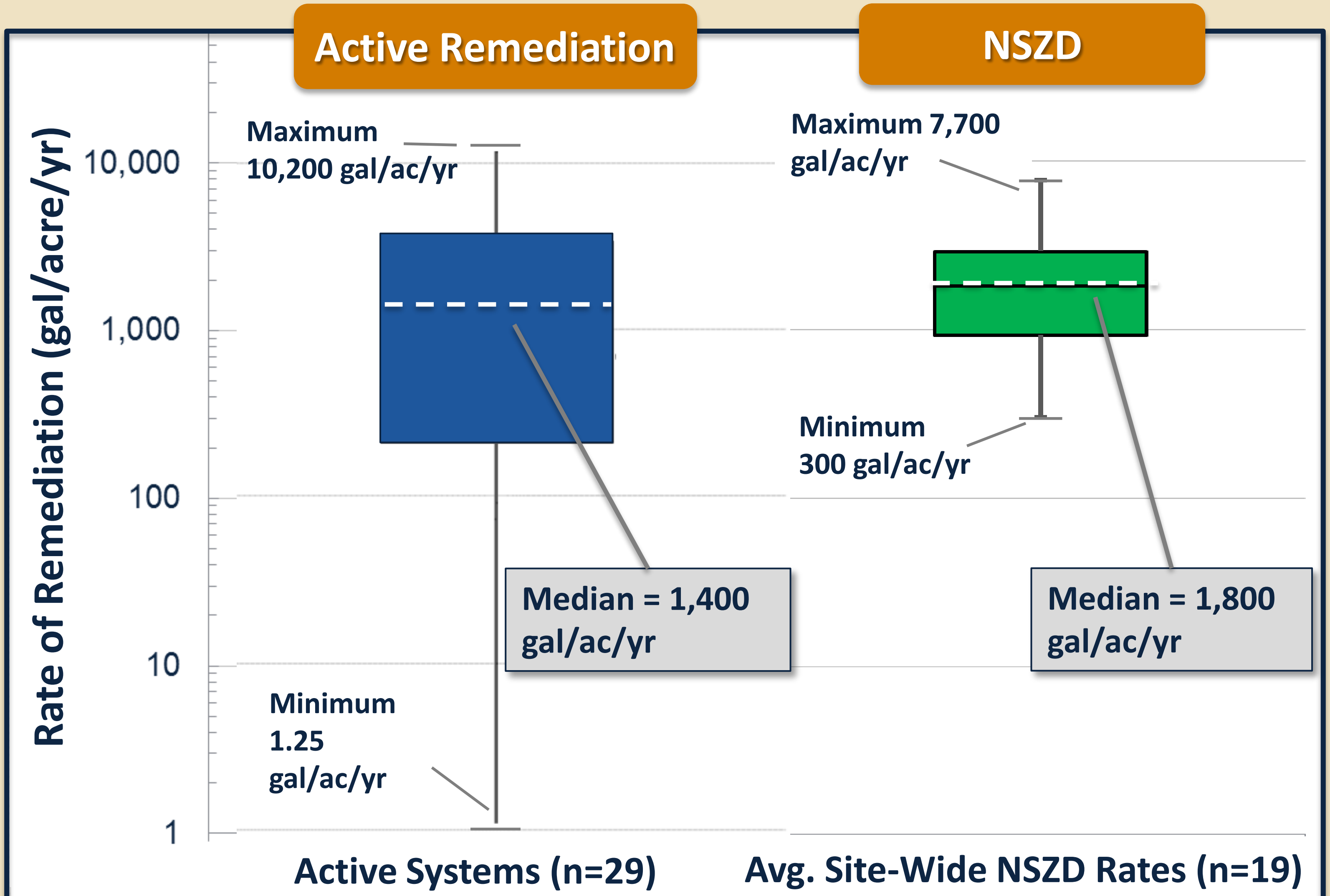


Optimizing Active LNAPL Remediation Compare to NSZD



Source (active systems): Palia, 2016

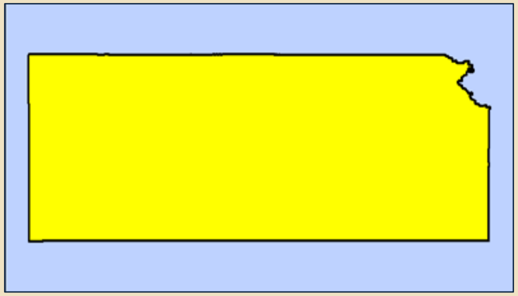
Active Remediation vs. NSZD Rates
Palaia, 2016



Source (active systems): Palia, 2016 Multiple Sources

NSZD Site Closure: *3 Case Studies*

Kansas Tank Farm

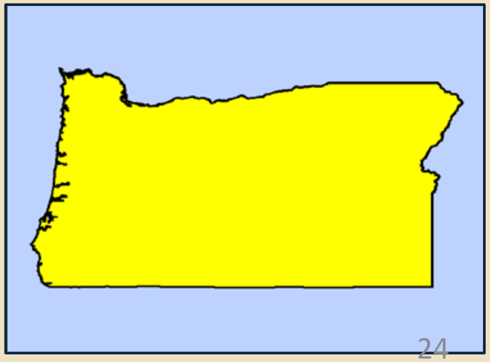


- Active system with negligible LNAPL recovery rates
- NSZD measurements from 2012-2014 (Carbon traps + thermal monitoring)
- KDHE approved system shutdown in 2015

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

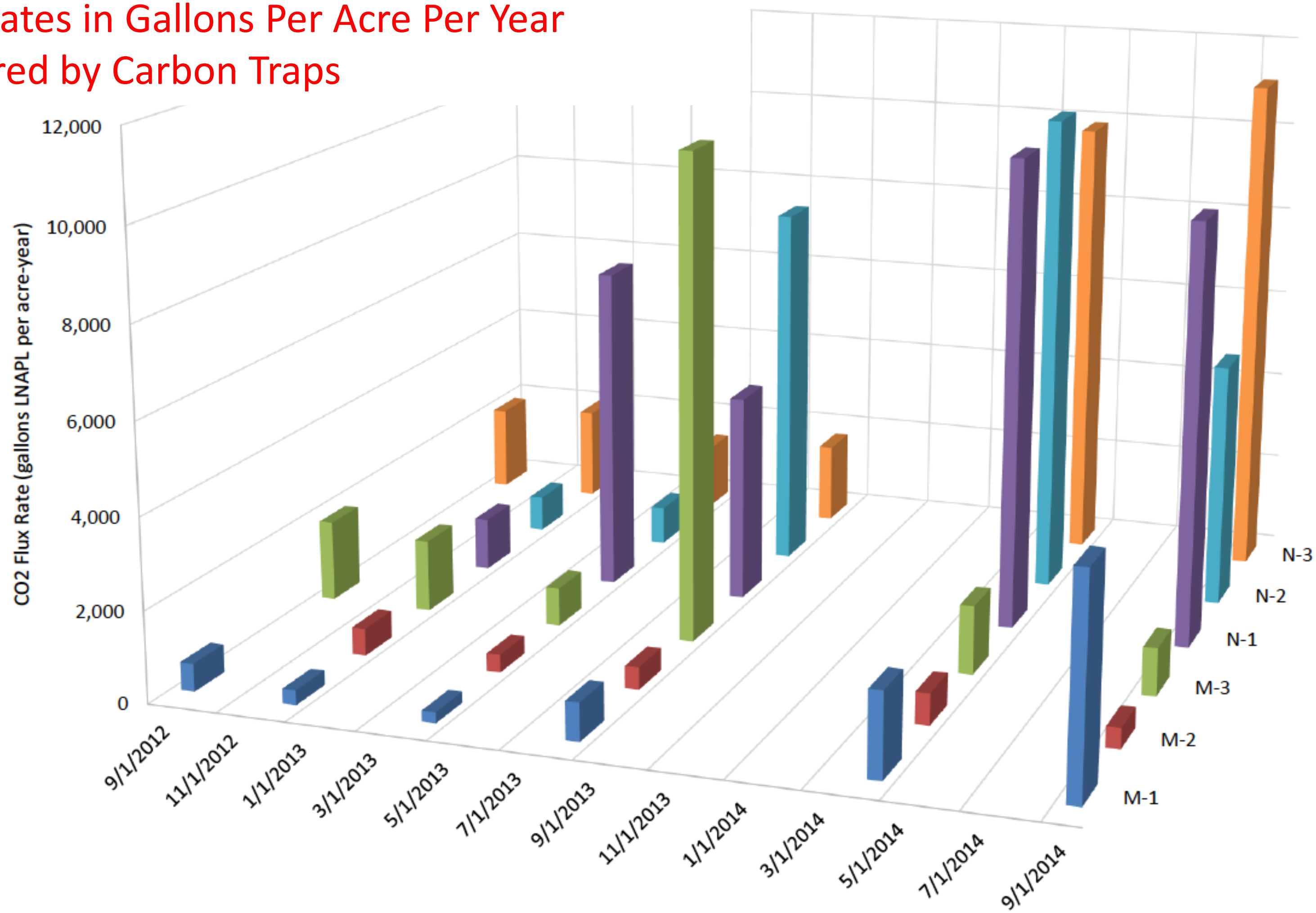
Oregon Railyard



- 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

Kansas City, KS – Variability in Measured Rate by Location

NSZD Rates in Gallons Per Acre Per Year
Measured by Carbon Traps



Source: Keith Piontek, TRC Consultants

Can We Optimize How We Measure NSZD?

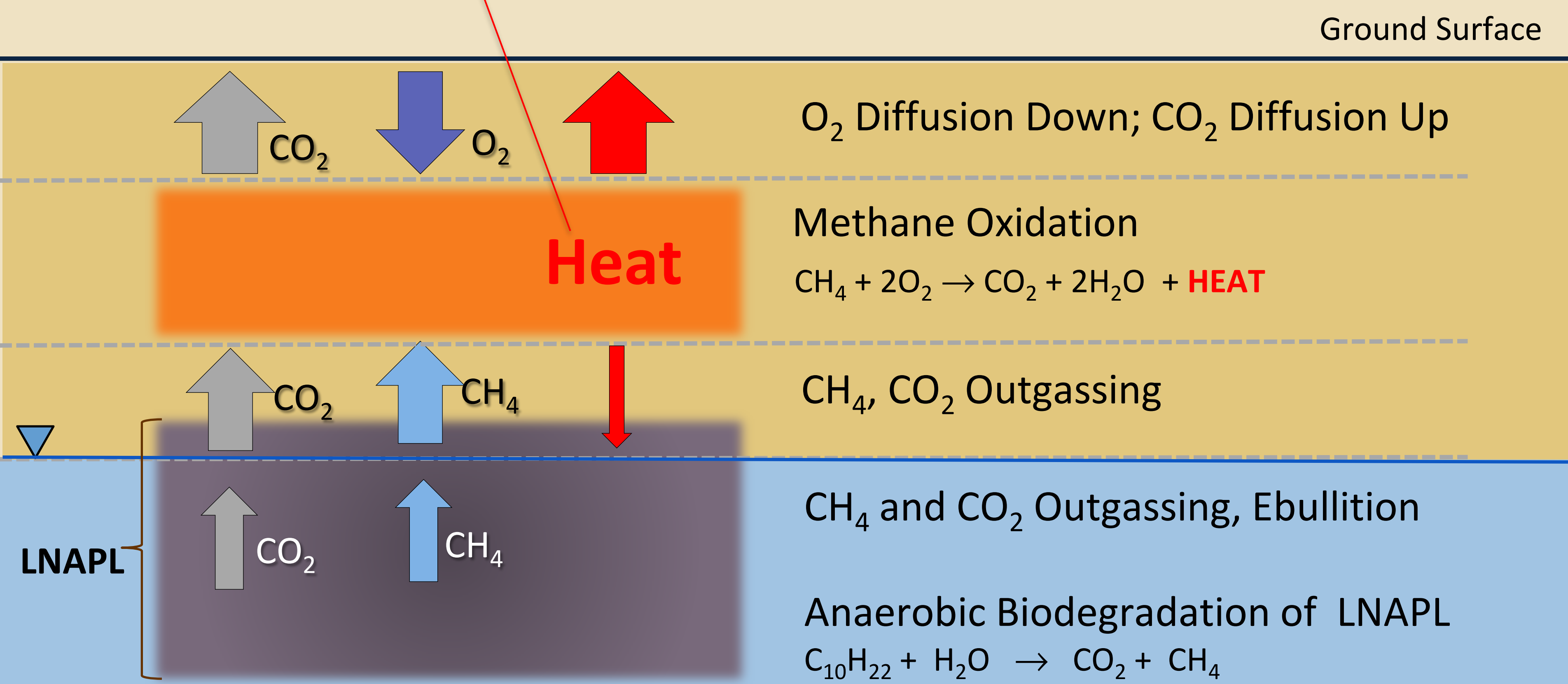
Source: SB Johnny

“Turning a Hot Compost Pile”

Source: SB Johnny

NSZD Conceptual Model

Measure Heat Generation in Subsurface to get NSZD Rates



*Note: size of arrows indicate degree of release

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

Ean Warren *, Barbara A. Bekins

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

E. Warren, B.A. Bekins / Journal of Contaminant Hydrology 182 (2015) 183–193

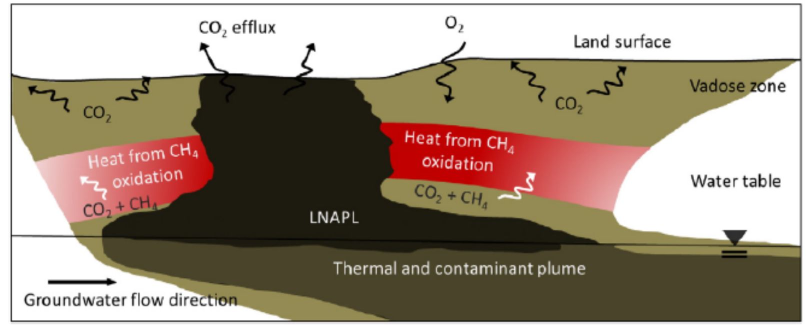


Fig. 4. Conceptual model of methane generation and oxidation in the unsaturated zone above the light non-aqueous phase liquid (LNAPL). Adapted with permission from Sihota et al. (2011). Copyright 2011 American Chemical Society.

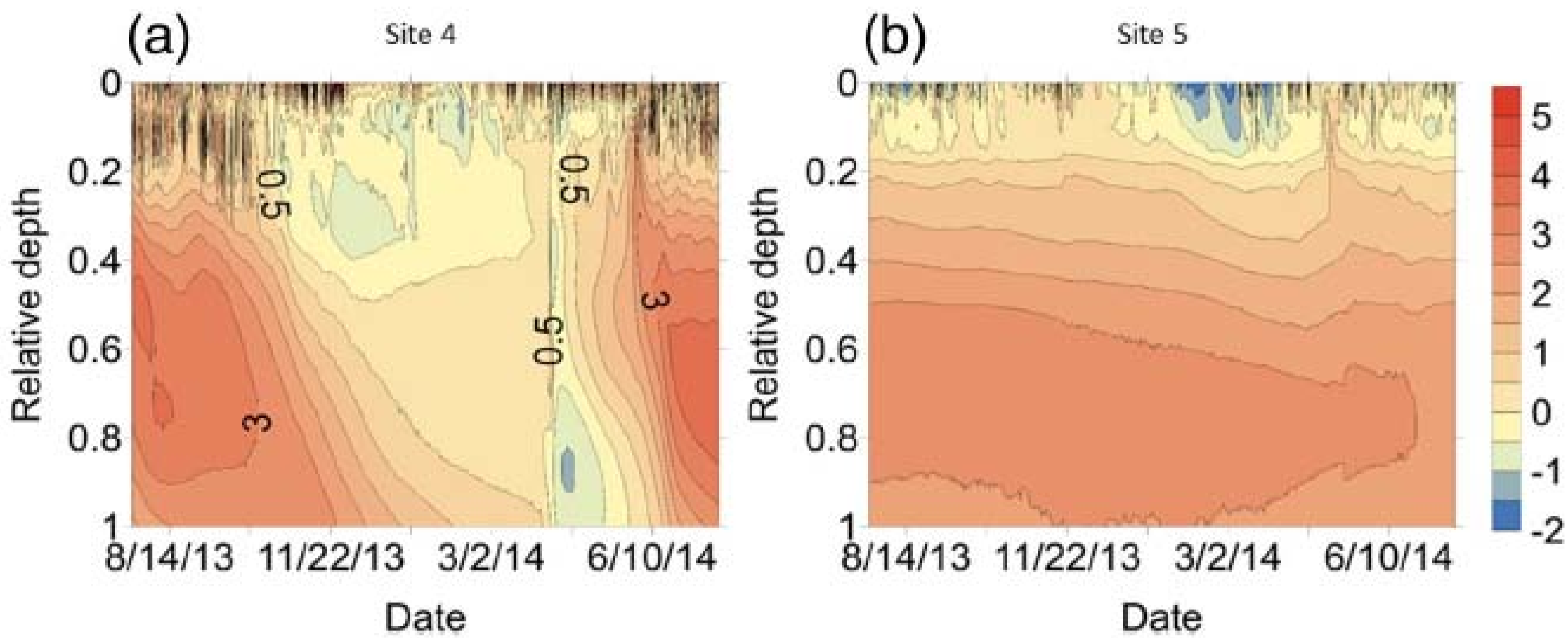


Fig. 10. Contours of temperatures above background from 22 July 2013 to 21 July 2014 for sites 4 (a) and 5 (b).

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

Ean Warren *, Barbara A. Bekins

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

Site	Total depth, m	f_{depth}	ΔZ, m	ΔT, °C	q_H, W m^{-2}	Rate, mol m^{-2} y^{-1}
2	5.8	0.4	2.3	0.7	0.38	18
3	5.6	0.9	5.1	1.6	0.38	18
4	5.5	0.6	3.3	1.7	0.63	30
5	7.6	0.7	5.3	3.2	0.76	36

Temperature Method:
30 mol/m^2/year

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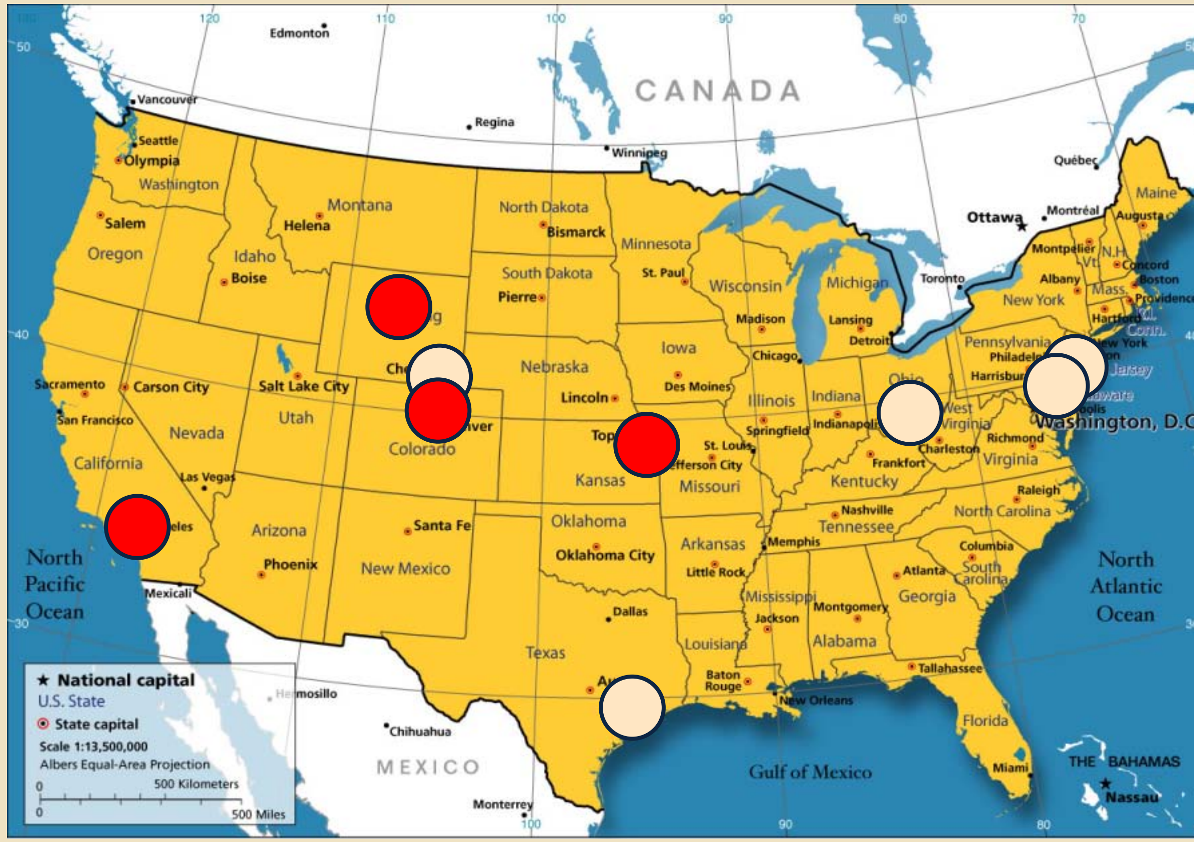
3	5.6	0.9	5.1	1.6	0.38	18
4	5.5	0.6	3.3	1.7	0.63	30
5	7.6	0.7	5.3	3.2	0.76	36

Temperature Method:
0.95 um/m2/sec
600 gal/acre/yr

Sihota et al., 2016: LI-COR
1.1 um/m2/sec
690 gal/acre/yr

CSU/GSI/TRC Thermal NSZD Technology Rollout 2012 - 2016

- 416 Thermo-couples
- 38 Wireless Modems
- ~8 million temperature values



In Place

Planned

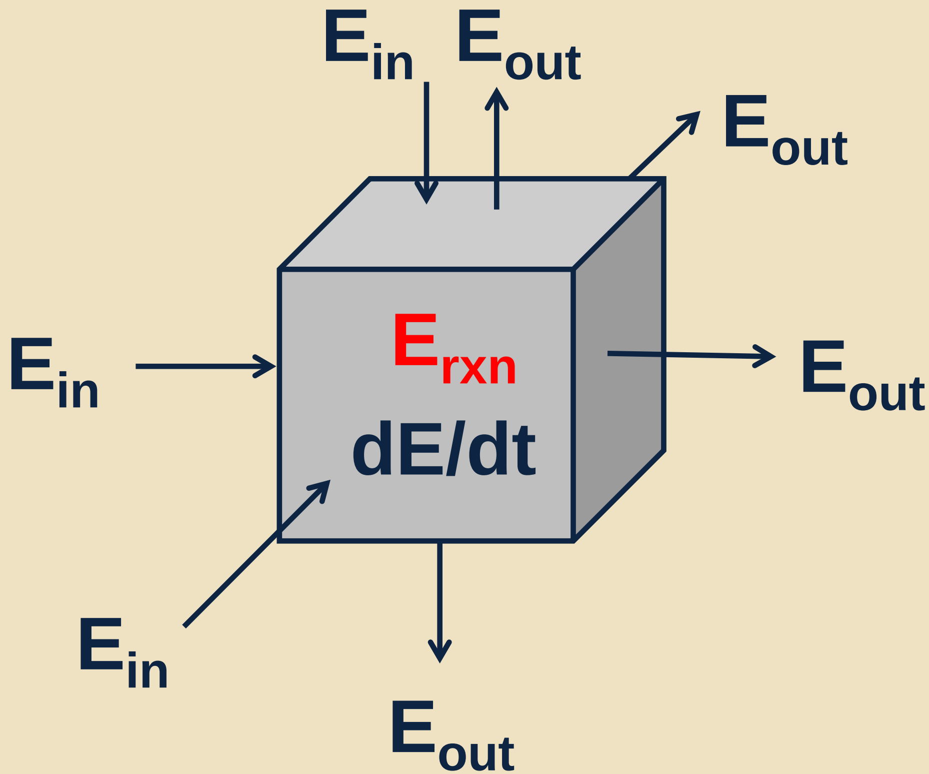
Sale et al., Feb. 2014
Provisional Patent

Source: *CSU*

Calculating LNAPL Mass Loss by NSZD

First Law of Thermodynamics

$$E_{in} - E_{out} + E_{rxn} = dE/dt$$



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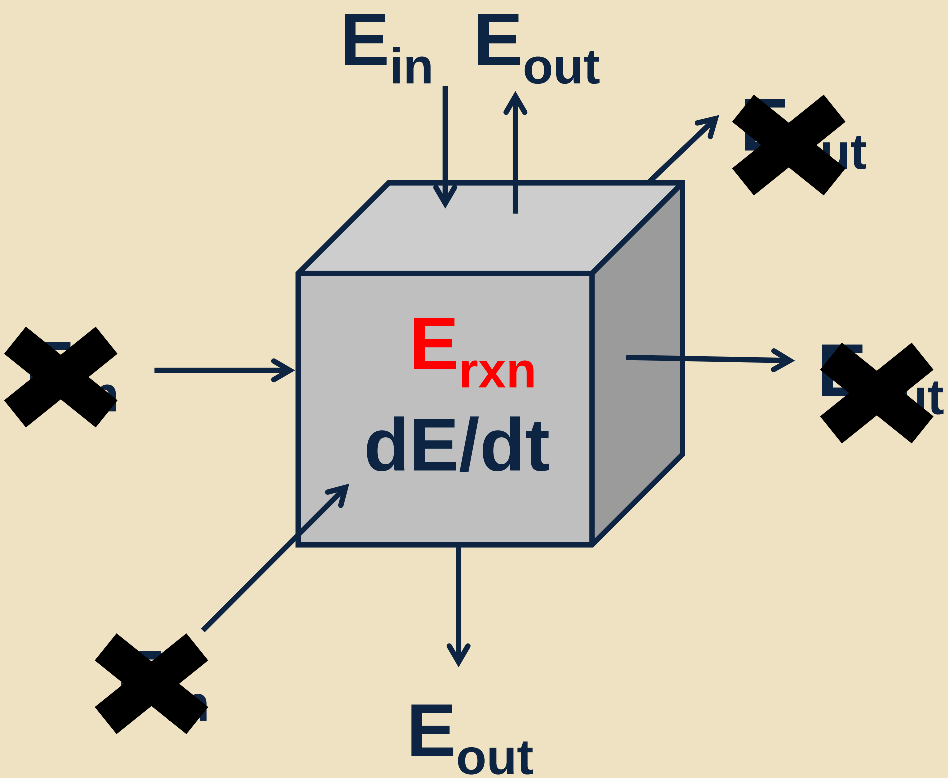
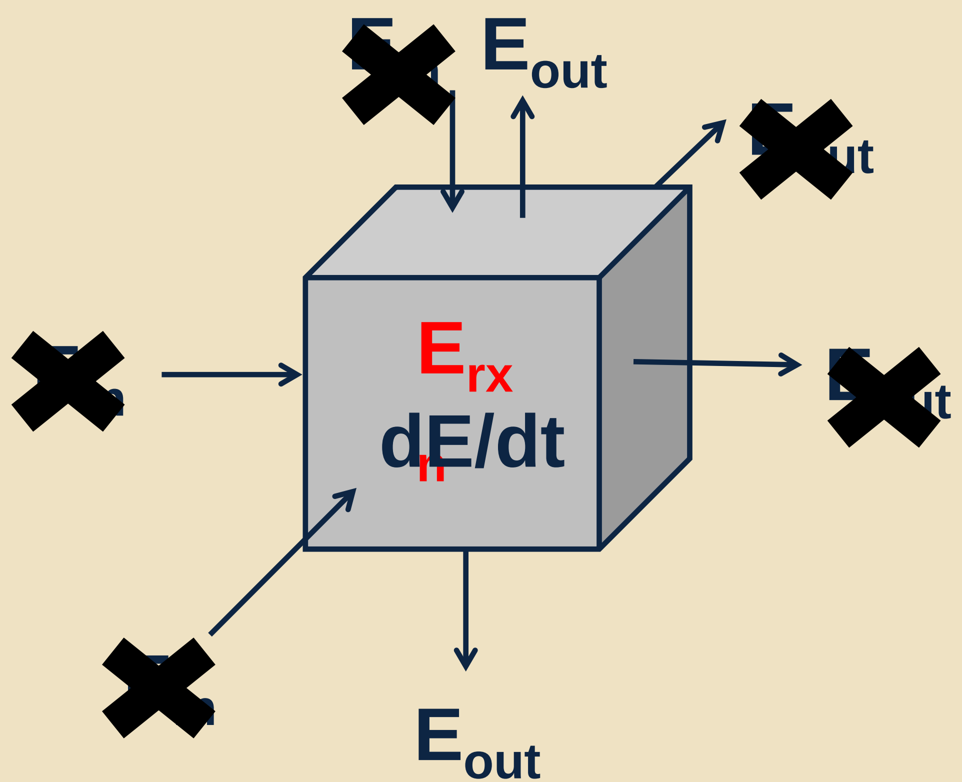


- **Lateral energy loss negligible**

Calculating LNAPL Mass Loss by NSZD

First Law of Thermodynamics

~~E_{in}~~ - E_{out} + E_{rxn} = dE/dt

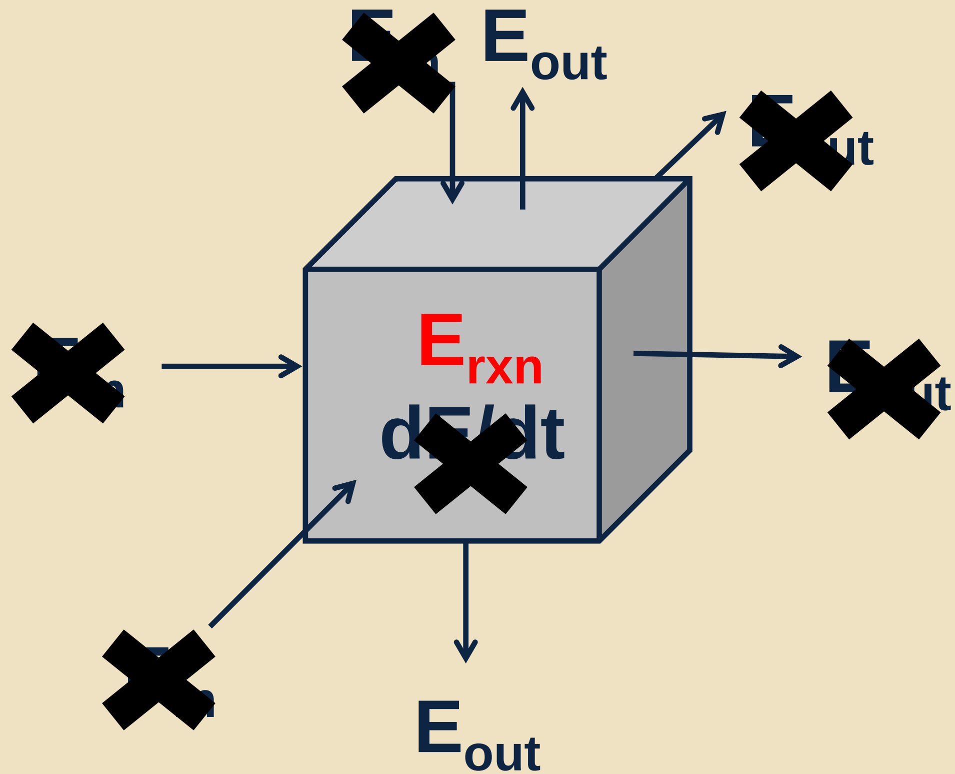


- Lateral energy loss negligible
- Background location corrects for solar energy input

Calculating LNAPL Mass Loss by NSZD

First Law of Thermodynamics

$$\cancel{E_{in}} - E_{out} + E_{rxn} = \cancel{dE}/dt$$

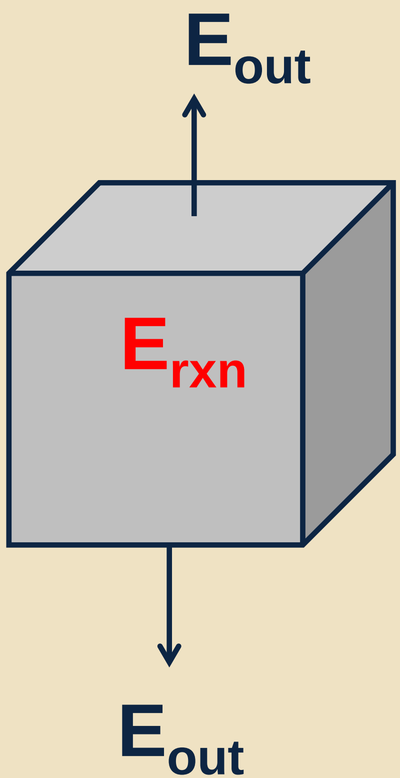


- Lateral energy loss negligible
- Background location corrects for solar energy input
- Steady-state; no change in storage

Calculating LNAPL Mass Loss by NSZD

First Law of Thermodynamics

$$E_{out} = E_{rxn}$$



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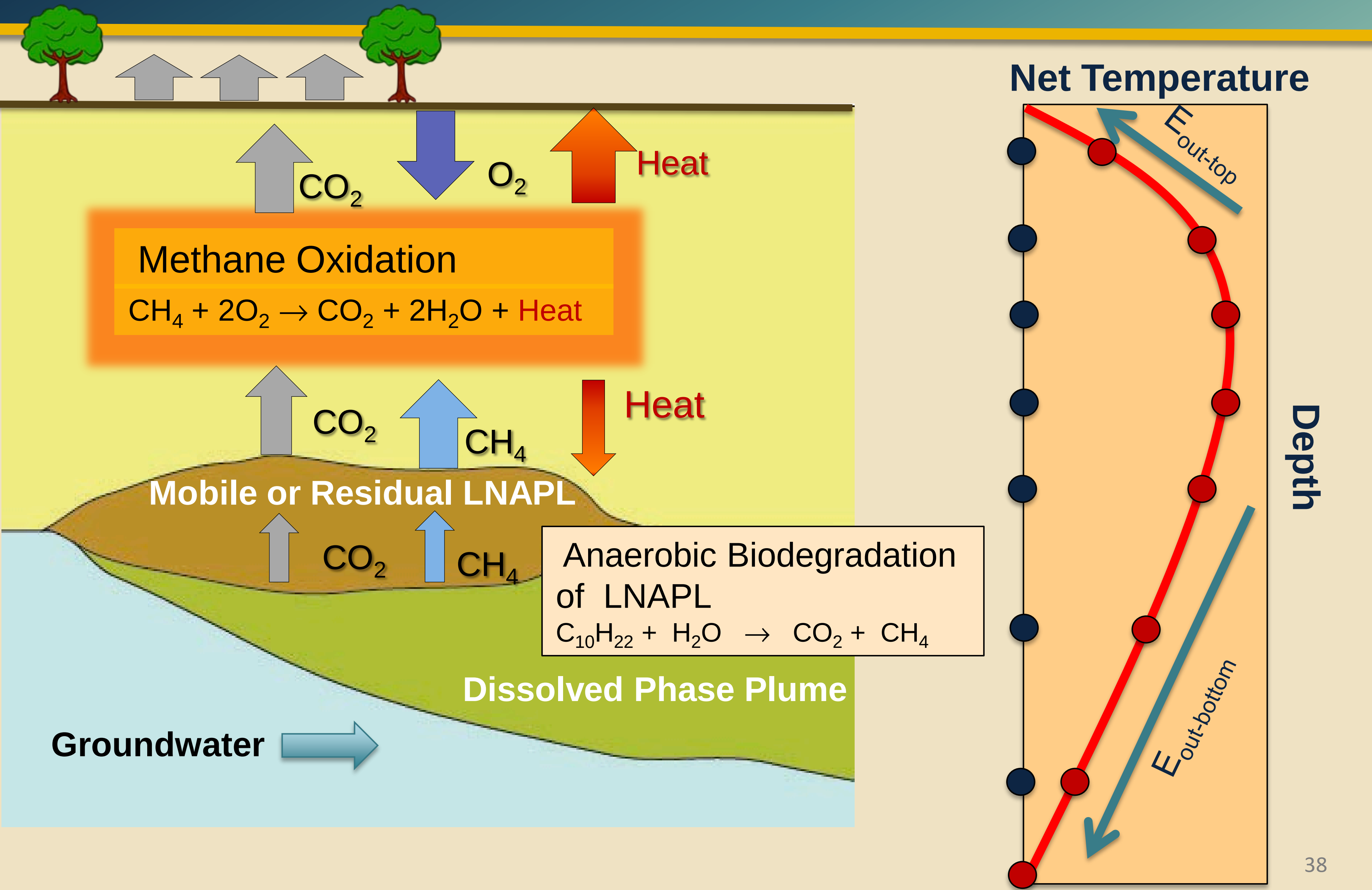
NSZD Conceptual Model



NSZD Conceptual Model

Fourier's Law: $E_{out} = K_T \, dT/dz$

Heat flux:

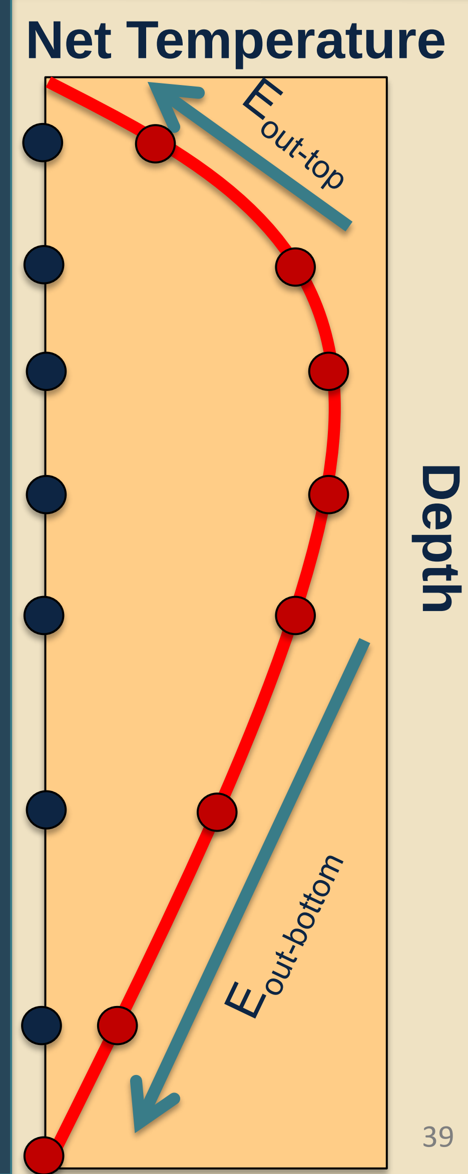
(watts/m^2)

Where:

K_T thermal conductivity (W/m°C)

Z depth interval of heat flux (m)

T change in net temperature (°C)



Both Combustion and Biodegradation Generate Heat

Heat of combustion for gasoline:
45 kilojoules per gram

Burn 1 gram gas:
45 kilojoules

Biodegrade 1 gram gas:
45 kilojoules

Last Step: Calculate the NSZD Rate

$$\text{NSZD Rate (Mass degraded per area per time)} = \frac{E_{rxn}}{H_{rxn}}$$

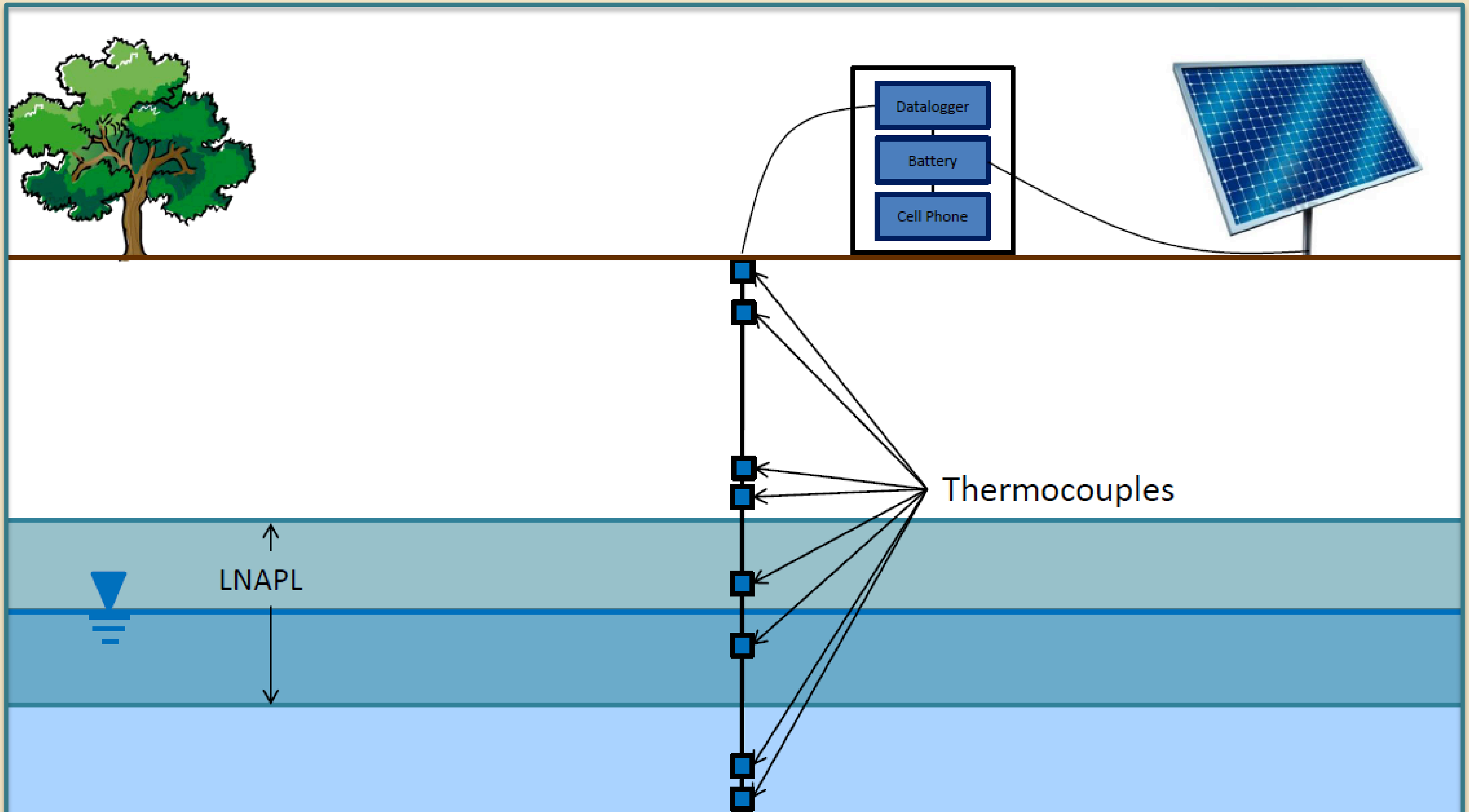
Heat Flux (joules/area/time)

Heat of Reaction (joules per mass)

H_{rxn} = 45 kilojoules per gram

NSZD Rate can be converted to *gallons per acre per year*

Field Installation for Thermal NSZD



SOURCE: *CSU*

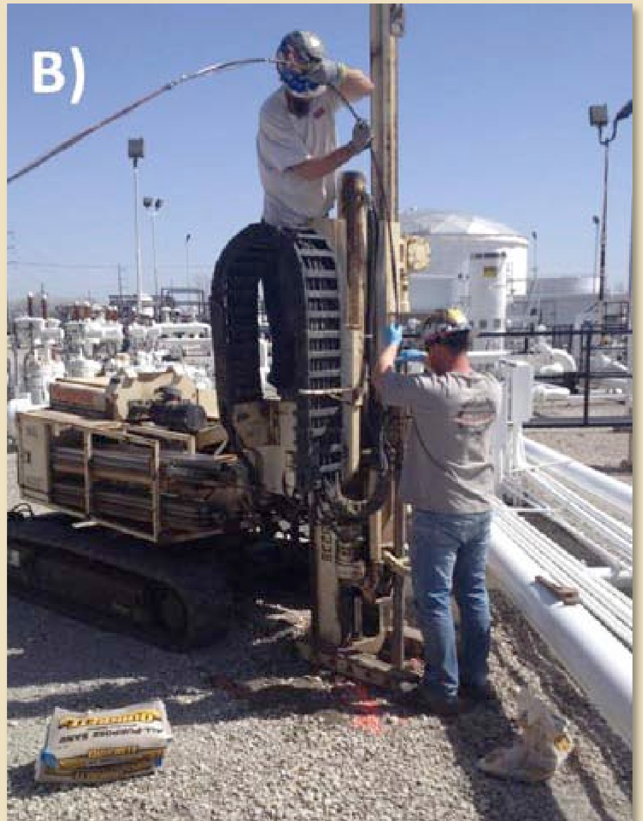
Field Installation: Thermal Monitoring System

Thermocouple on temperature monitoring "stick."

SOURCE: *CSU*

Field Installation: Thermal Monitoring System

Thermocouple on temperature monitoring "stick."



Installation of stick using direct push rig.

SOURCE: *CSU*

Field Installation: Thermal Monitoring System

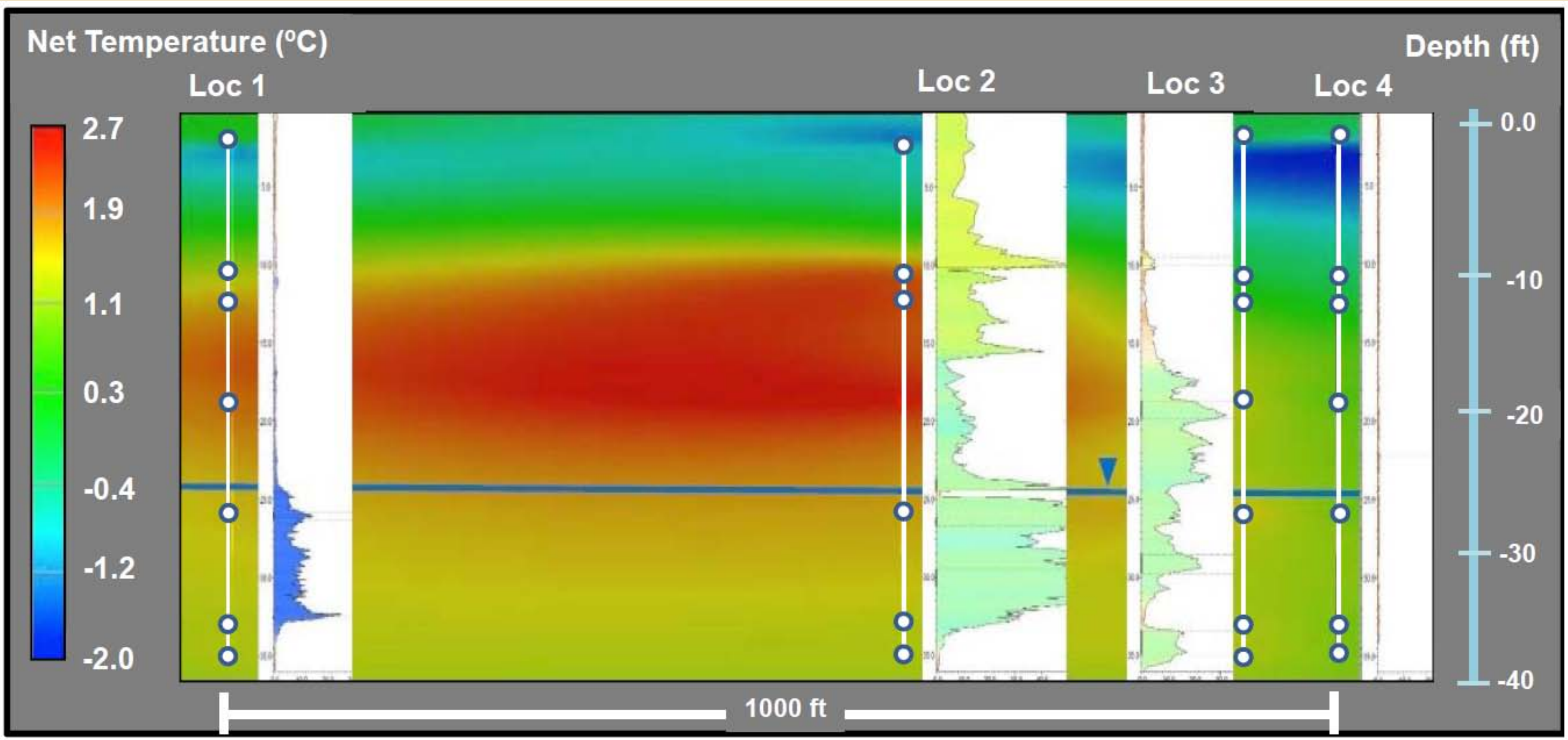
Thermocouple on temperature monitoring "stick."

Installation of stick using direct push rig.

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

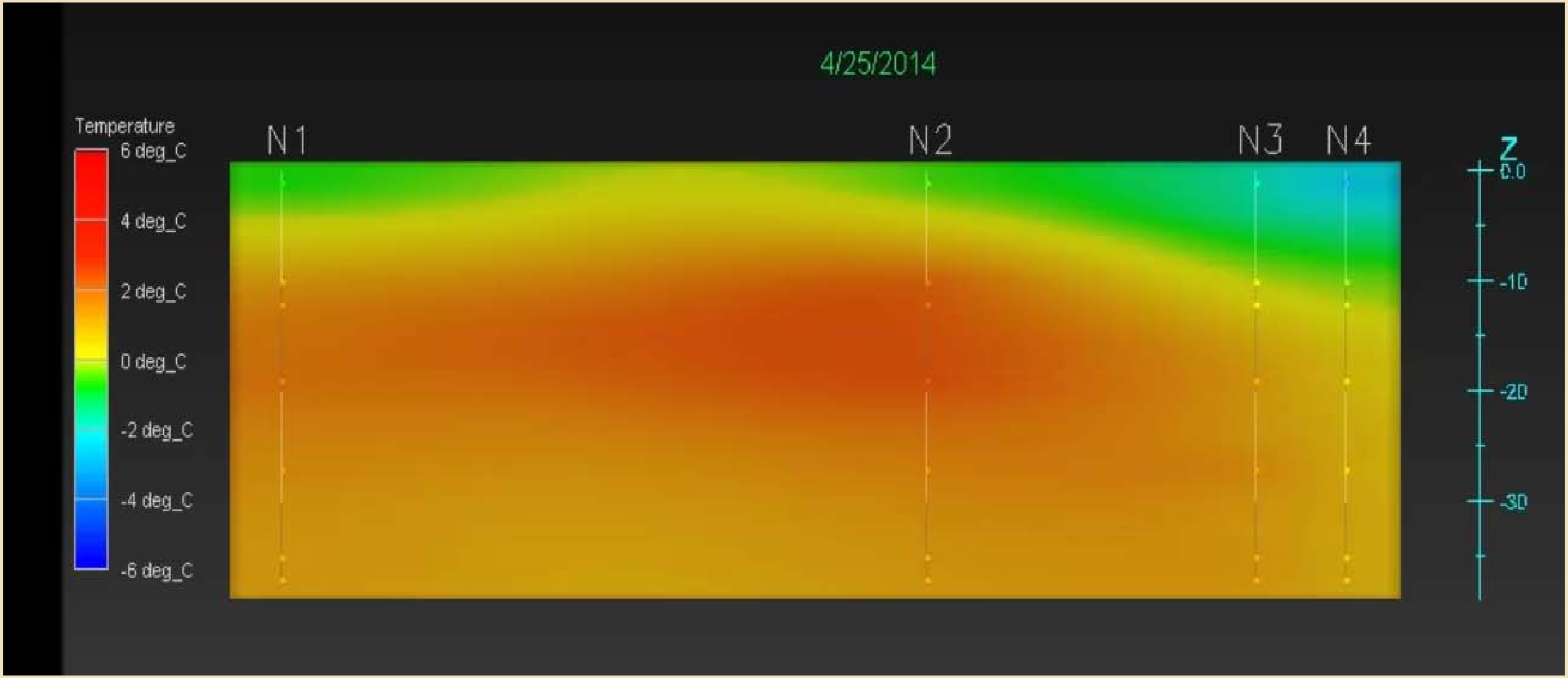
SOURCE: *CSU*

Results from One Site: Background-Corrected Temperature



(Stockwell, 2015; Colorado State University)

HEAT SIGNAL OVER TIME



(Stockwell, 2015; Colorado State University)

ThermalNSZD

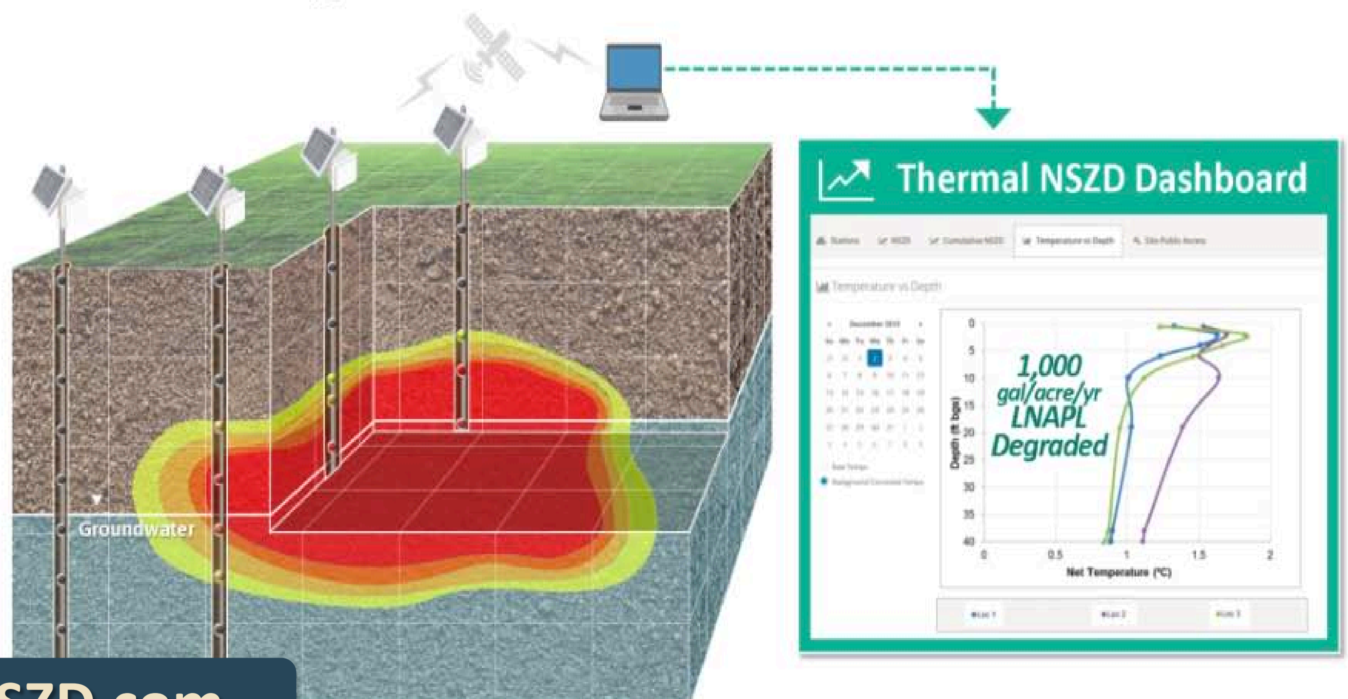
HOME TECHNOLOGY DEMO IMPLEMENT CONTACT CUSTOMER LOGIN

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

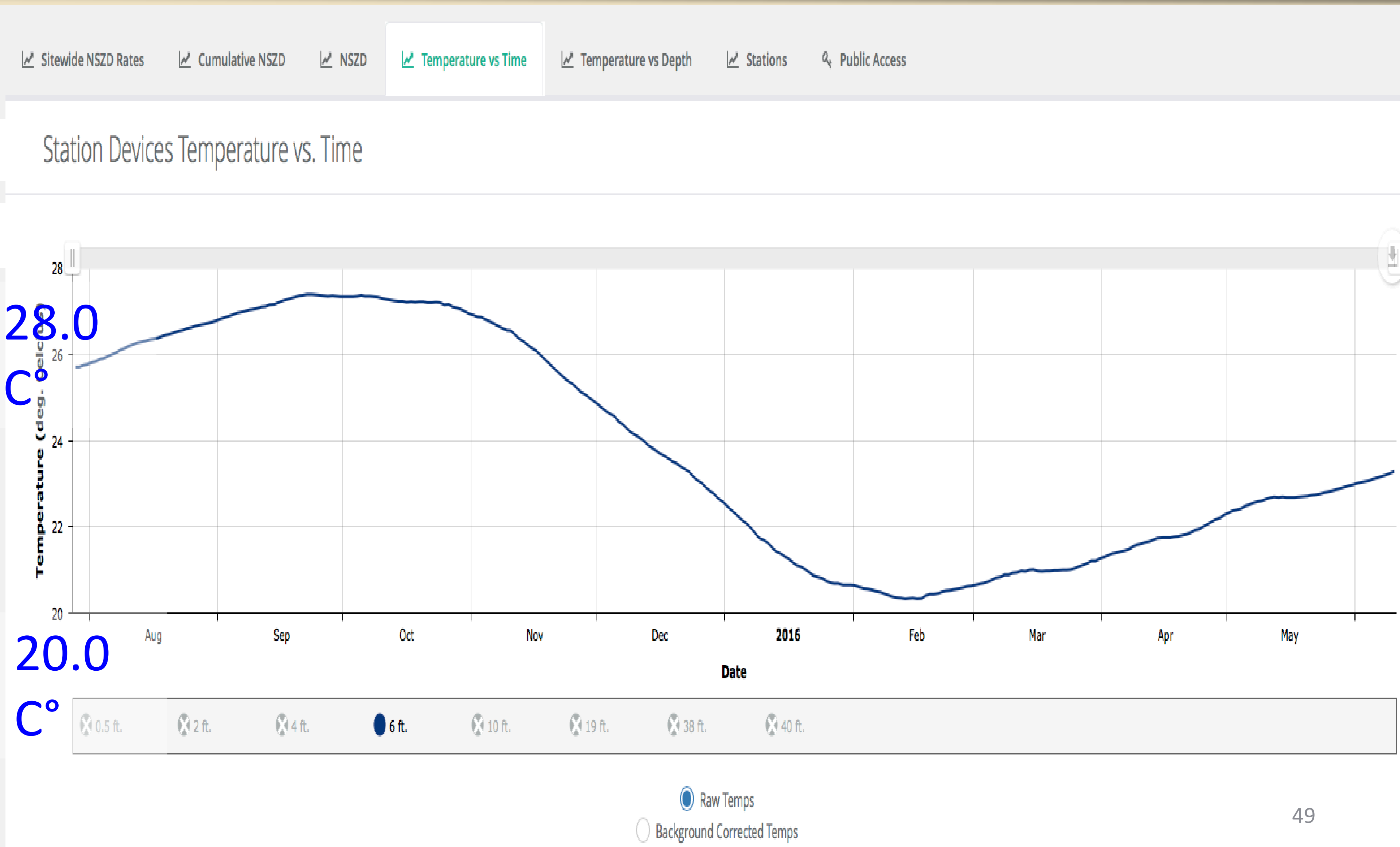
- One-time field installation of remote monitoring system with minimal O&M, no site visits, no sampling and no lab.
- Daily temperature readings from vertical profiles of thermocouples.
- Secured, read only access to site data for regulators.



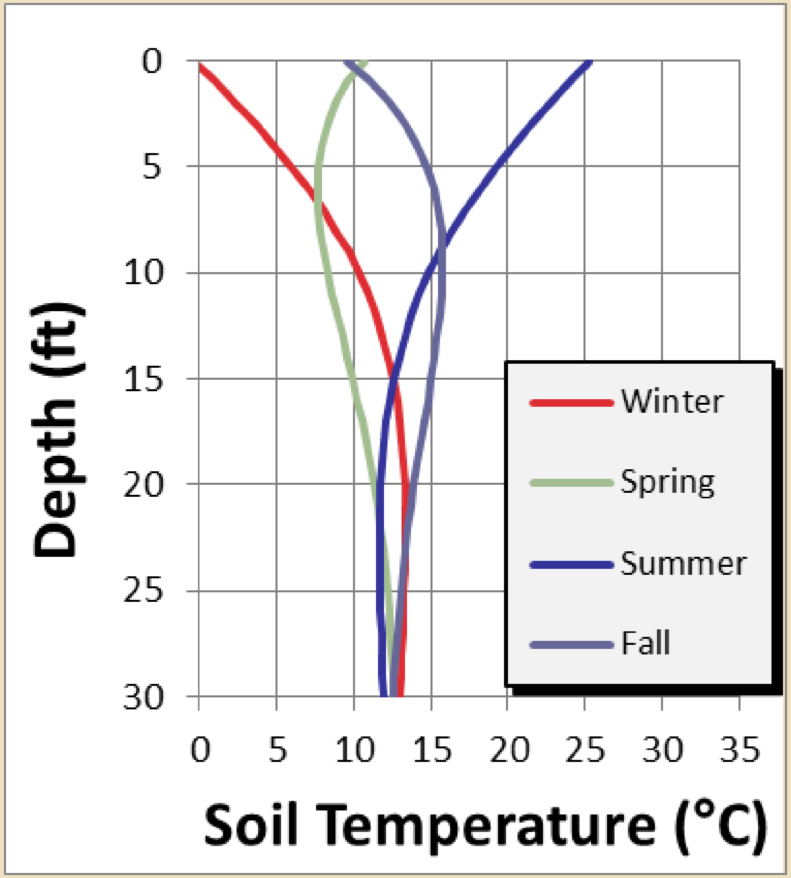
www.ThermalNSZD.com

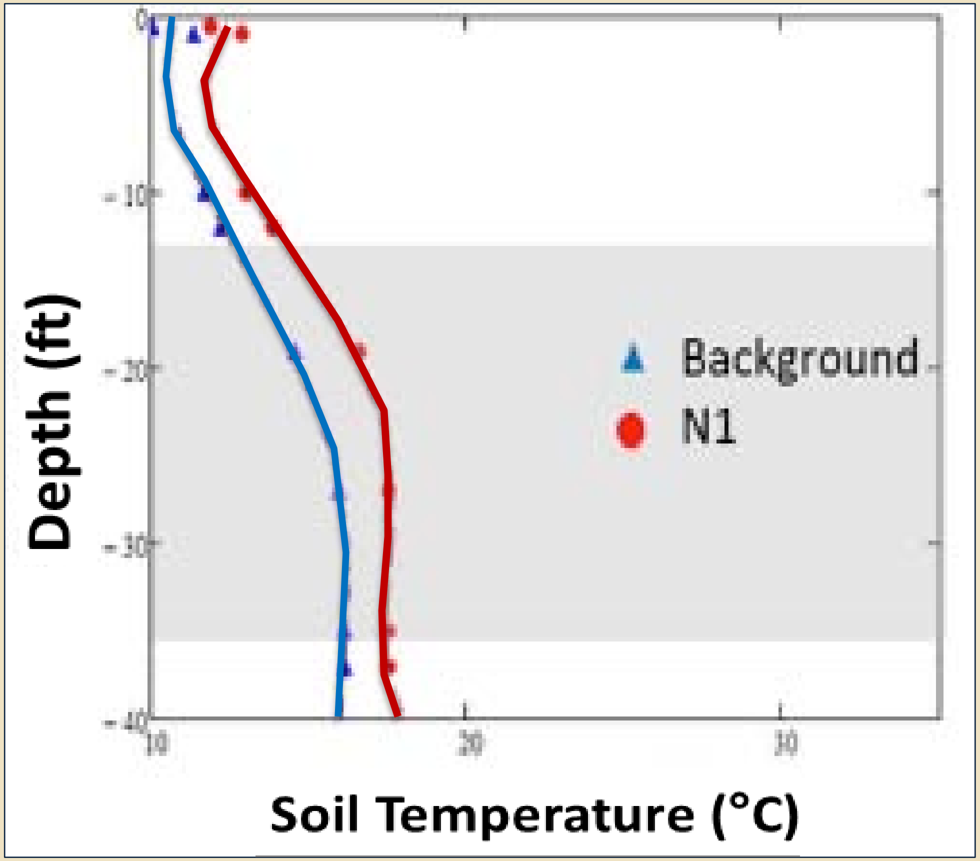
Patent Pending

But Natural Variation in Soil Temperature Complicate this Energy Balance



Seasonal Change, Background Correction vs. Depth

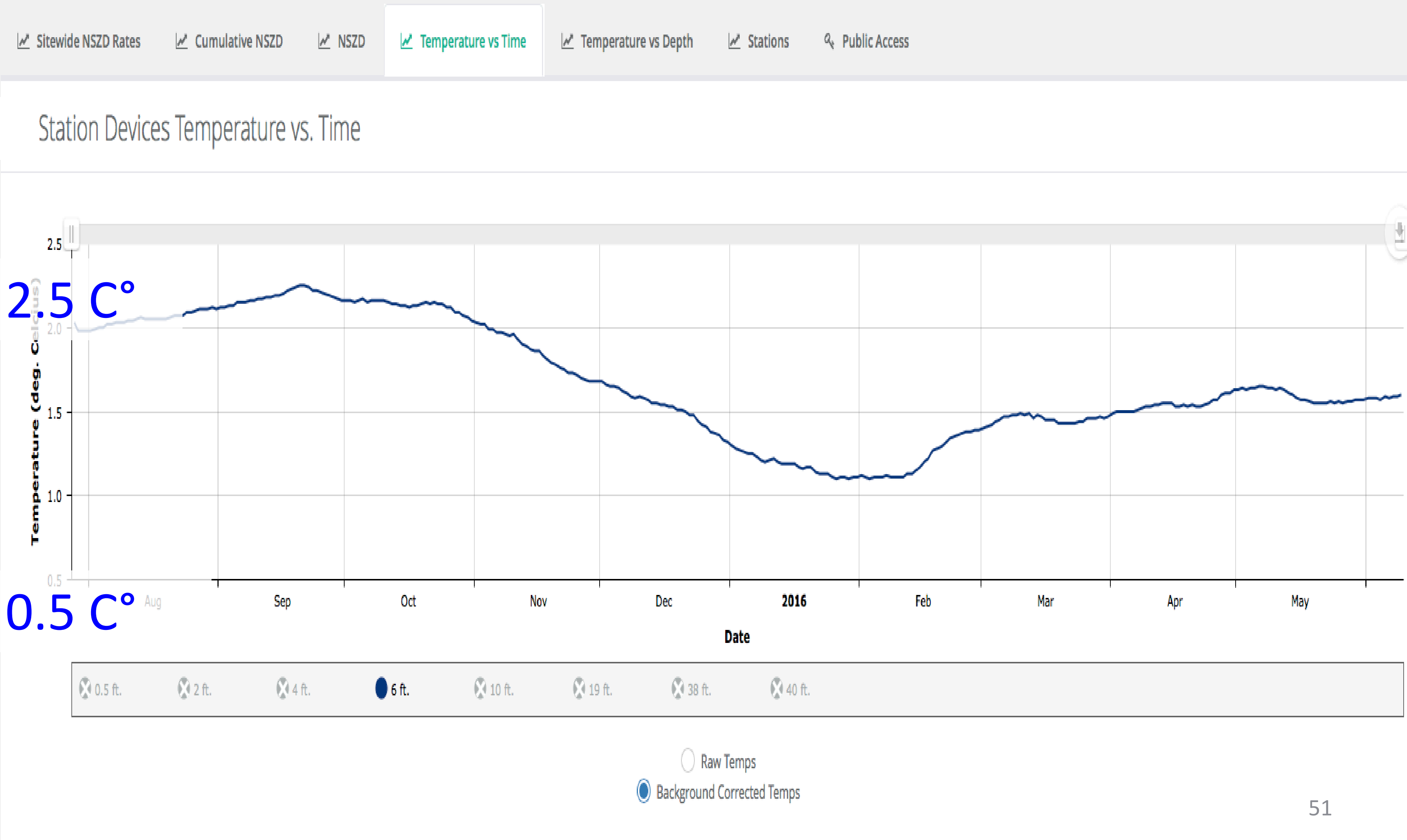




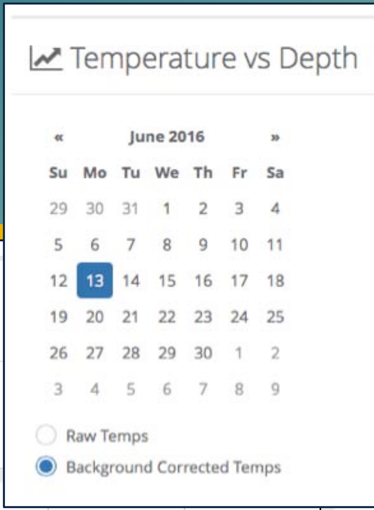
Natural Seasonal Temperature Changes

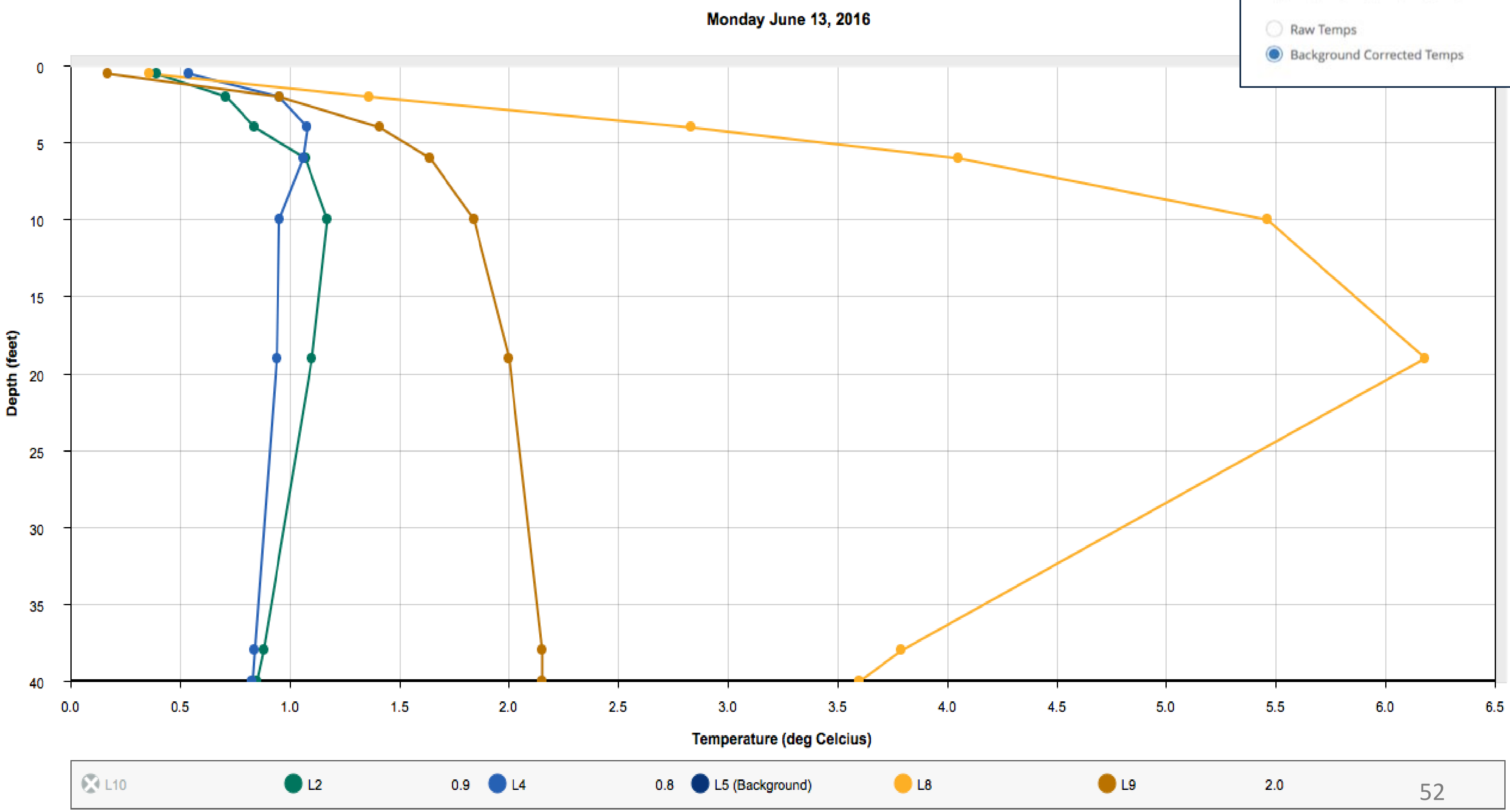
Heat Signal from Biodegradation = Temp. in LNAPL – Background Temp.

Subtract Out Background Soil Temperature



Thermal NSZD Dashboard Temperature vs. Depth





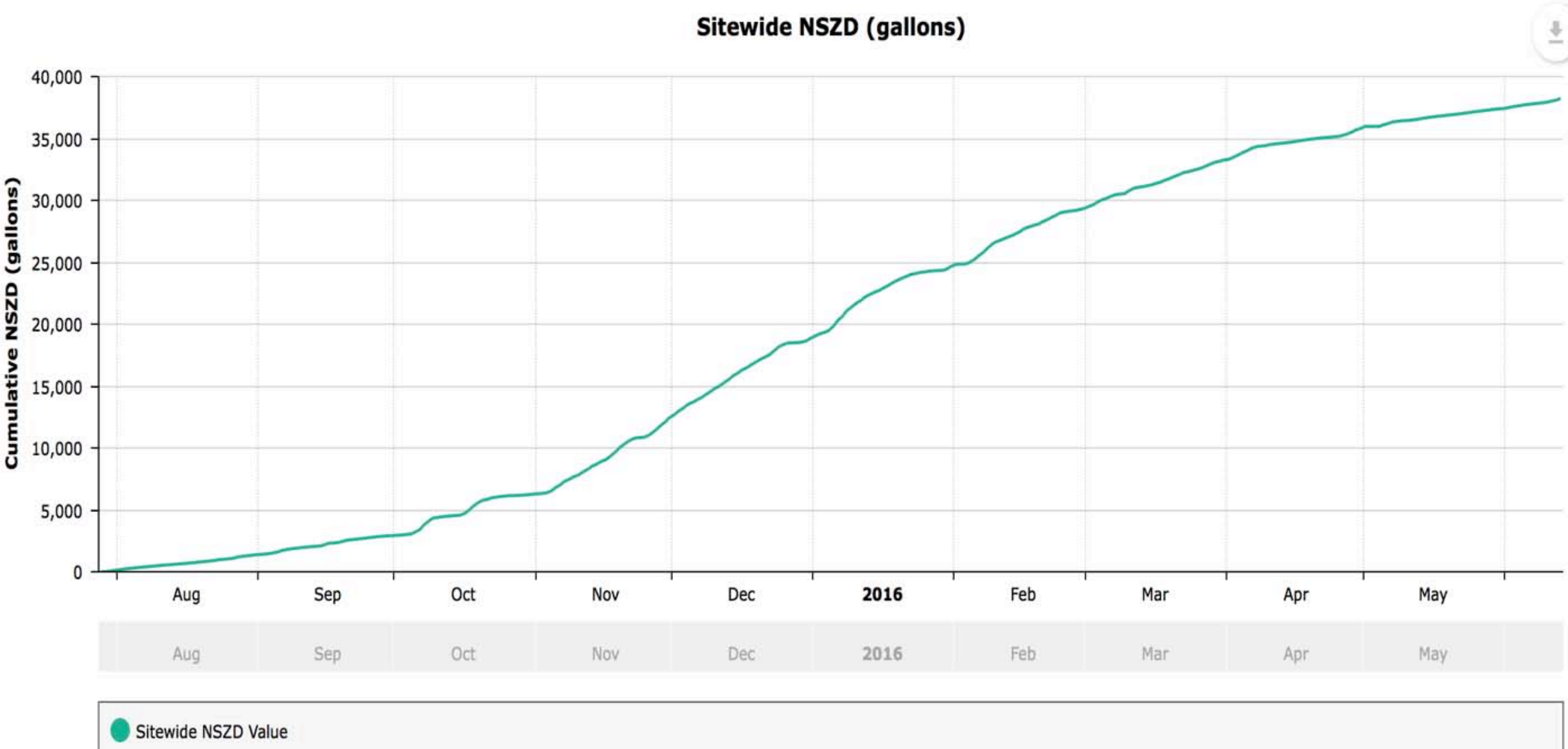
Sitewide NSZD Rates

Sitewide NSZD

Amount of LNAPL Degraded Since NSZD Monitoring Began: 38,227 gallons LNAPL

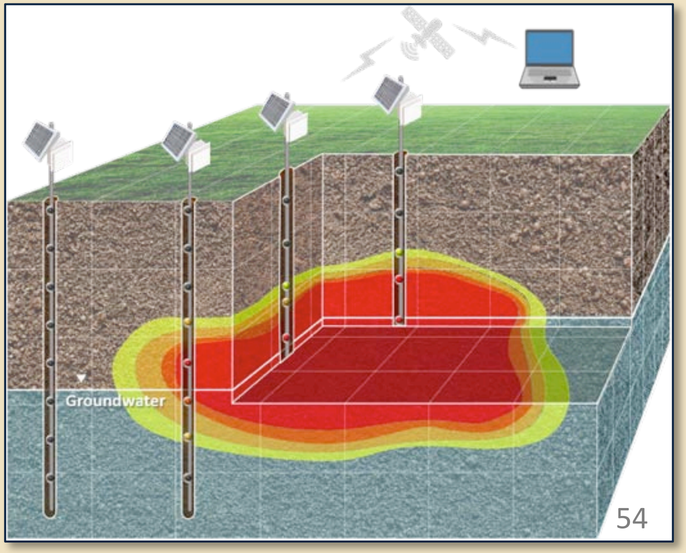
Natural Source Zone Depletion Rate Over Past 30 Days: 177 gallons/acre/year

38,000 gallons of LNAPL degraded since NSZD monitoring began



Render Time: 0.2584 Memory: 1MB Security Level: 1

Advantages	Disadvantages
- One-time installation for getting continuous NSZD rates - Remote monitoring via secure Dashboard - Can be “silent sentinel” for change of conditions - One way to optimize NSZD by replacing frequent site visits	- Indirect measure of NSZD - Requires oxidation of methane - Limited comparisons with other NSZD methods



Wrap Up

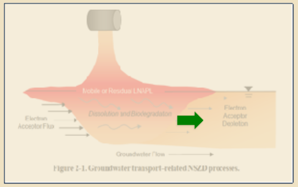
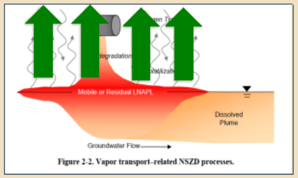
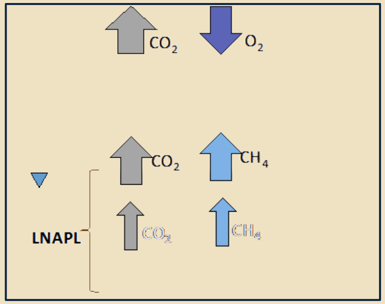


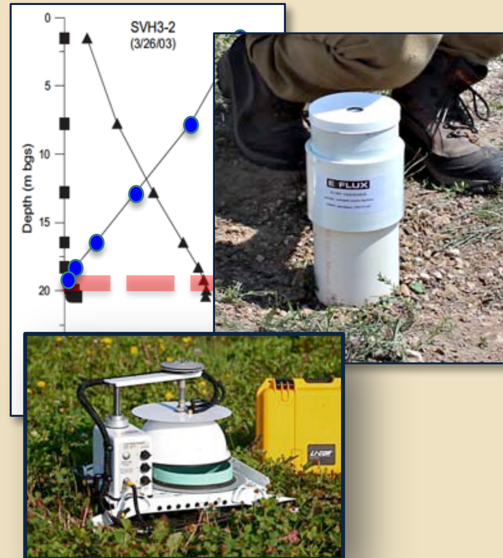
Figure 2-1. Groundwater transport-related NSZD processes.



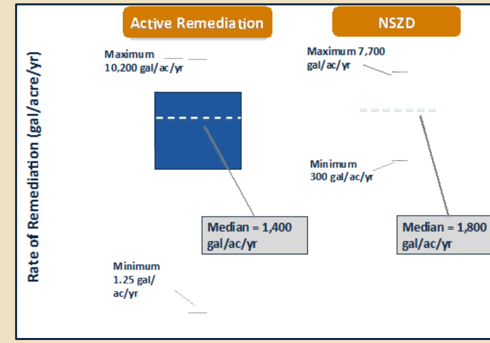
Mobile or Residual LNAPL
Dissolved Plume
Groundwater Flow
Figure 2-2. Vapor transport-related NSZD processes.



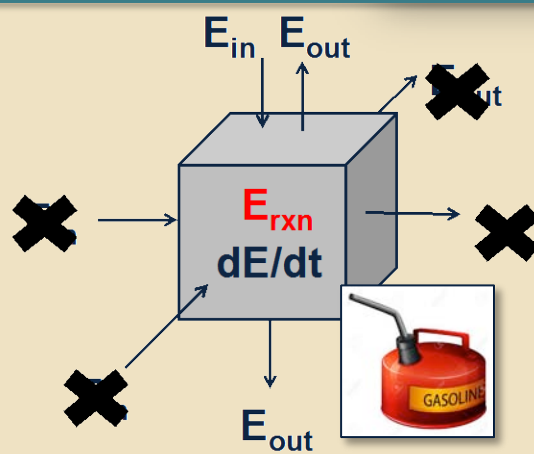
CO_2
O_2
CO_2
CH_4
LNAPL
CO_2
CH_4



SVH3-2
(3/26/03)
Depth (m bgs)
0
5
10
15
20
E-FLUX
LI-COR

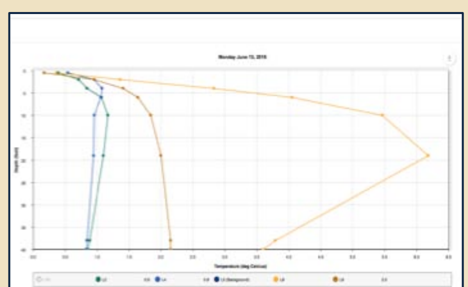


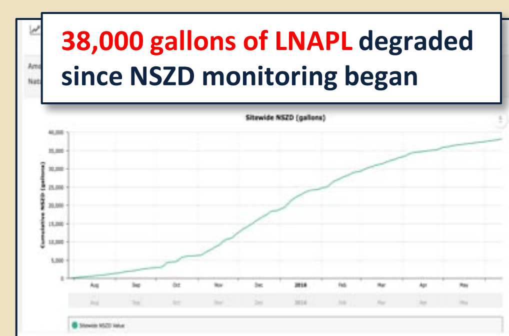
Active Remediation
NSZD
Rate of Remediation (gal/acre/yr)
Maximum 10,200 gal/ac/yr
Maximum 7,700 gal/ac/yr
Minimum 300 gal/ac/yr
Median = 1,400 gal/ac/yr
Median = 1,800 gal/ac/yr
Minimum 1.25 gal/ac/yr



E_{in}
E_{out}
E_{rxn}
dE/dt
E_{out}
GASOLINE

A)
B)
C)





38,000 gallons of LNAPL degraded since NSZD monitoring began
Sitewide NSZD (gallons)

QUESTIONS?

FOR MORE INFORMATION:

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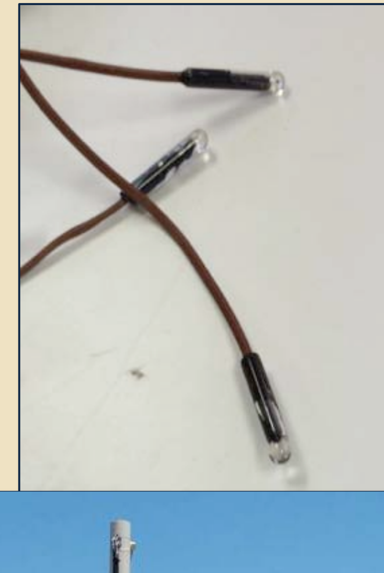
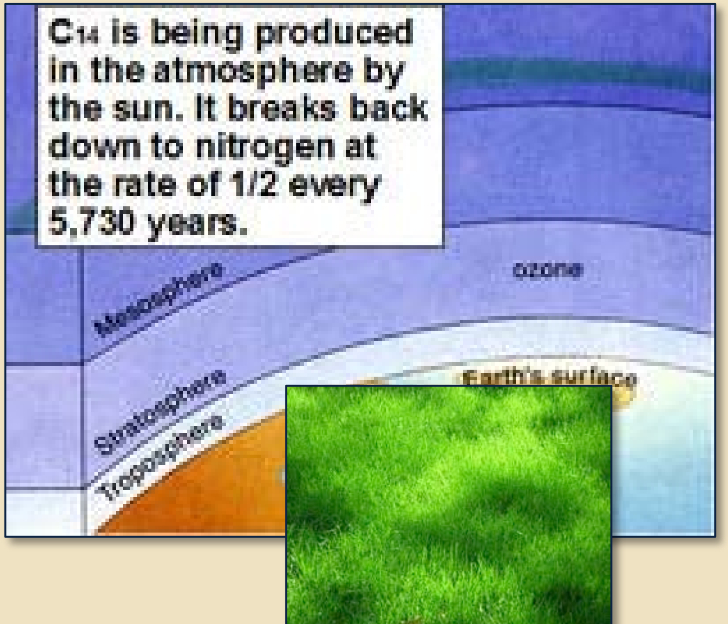
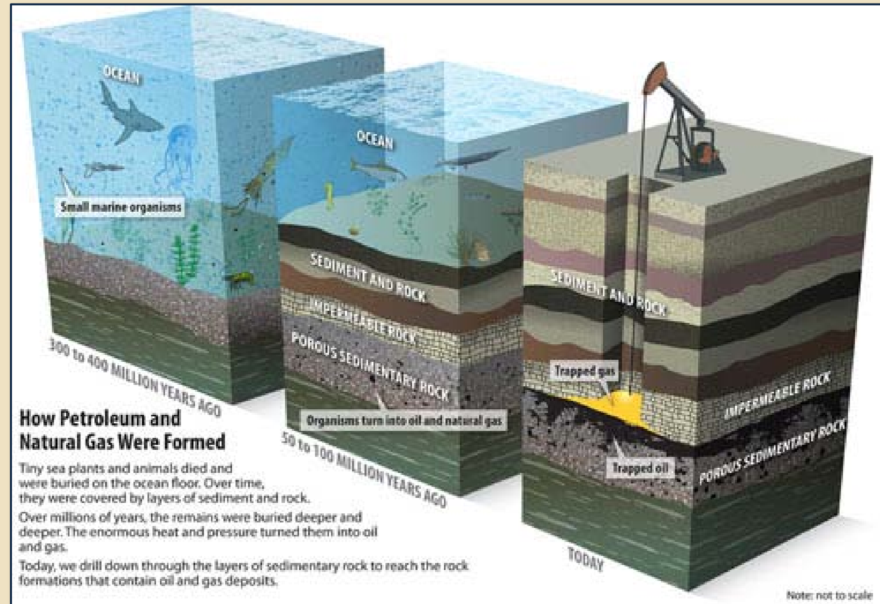
prk@gsi-net.com



- **Spare Slides**

^{14}C Method: When was the Carbon Removed from Atmosphere?





Modern Carbon is from….
plants that removed carbon from atmosphere recently, ^{14}C has not broken down yet…

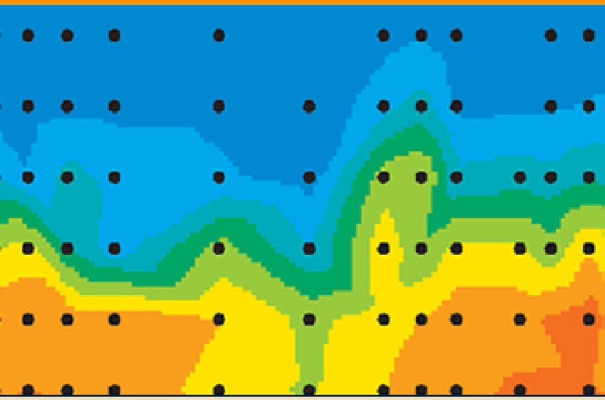
LNAPL Carbon is from….
Plants that removed carbon from atmosphere by plants millions of years ago – all ^{14}C is gone by now.

"Modern" CO_2

Dividing Line: 60,000 years ago

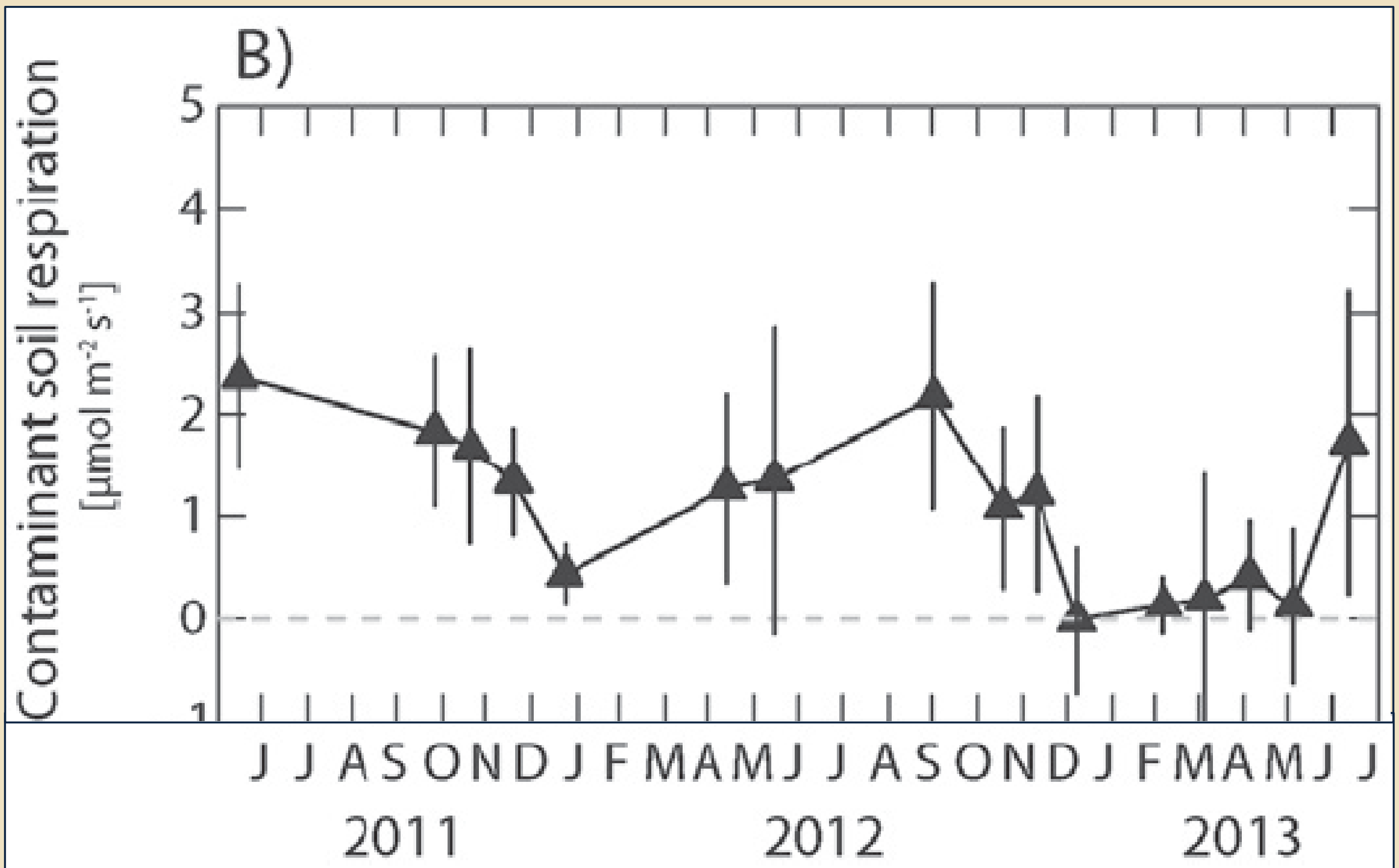
"Hydrocarbon" CO_2

Original Research



Seasonal Variability in Vadose Zone Biodegradation at a Crude Oil Pipeline Rupture Site

N.J. Sihota,* J.J. Trost,* B.A. Bekins, A. Berg, G.N. Delin, B. Mason, E. Warren, and K.U. Mayer



1 um/m2/sec =
626 gal/acre/year

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

Groundwater Monitoring&Remediation

by Robert E. Sweeney and G. Todd Ririe

$$\text{G-bio} = \text{ku} * (dT_u / dz) + \text{kd} * (dT_d / dz_d)$$

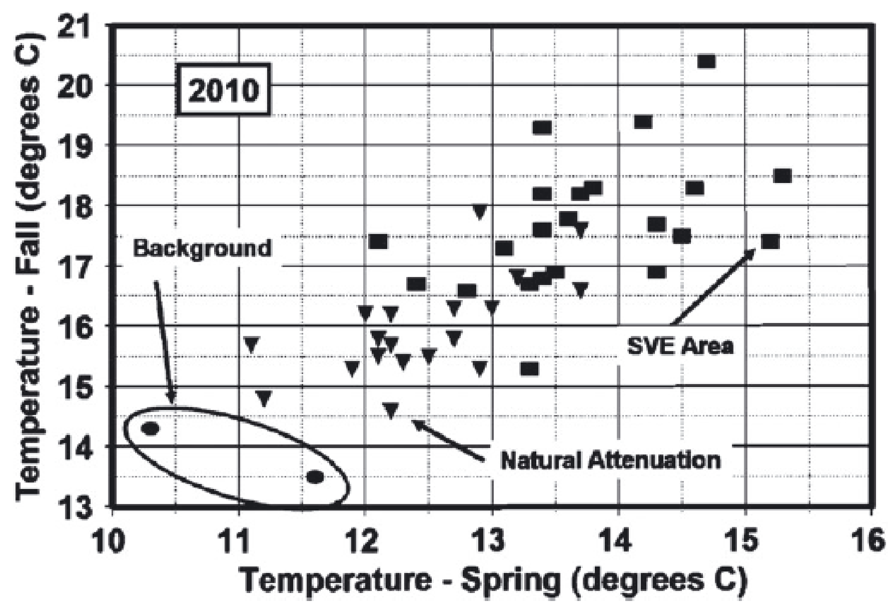


Figure 9. Plot of 2010 spring vs. fall in situ groundwater temperature for wells within the background, natural attenuation, and SVE areas at site in North-Central United States.