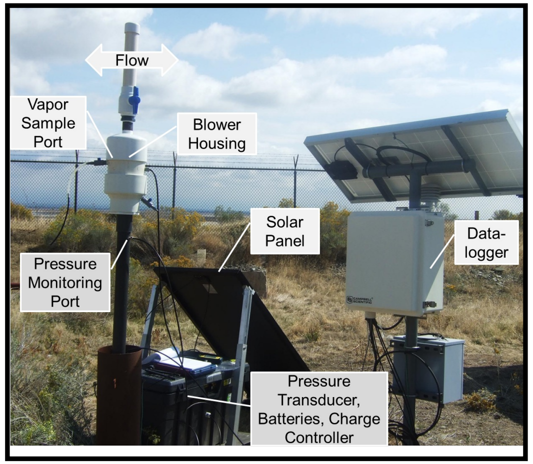
Methods to Enhance *Natural Source Zone Depletion (NSZD)* Rates: Heat, Oxygen, and More

Workshop on Nature-Based Solutions for Contaminated Sites



Sept 27, 2023

Charles Newell
Kayvan Karimi Askarani

GSI Environmental Inc.
cjnewell@gsi-net.com

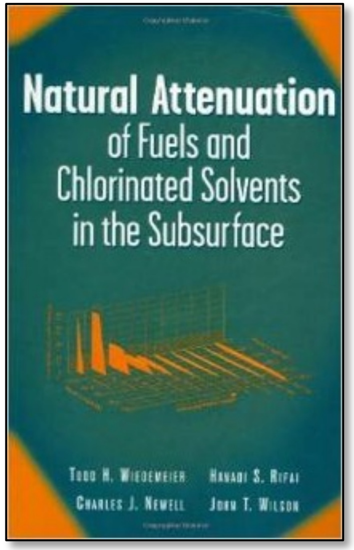
Road Map

- Natural Source Depletion (NSZD): How it was Discovered and How it Works
- Adding Heat to Enhance NSZD
- Adding Oxygen to Enhance NSZD
- Experimental Concepts to Enhance NSZD

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

MNA typically focuses on plumes:

- Is plume stable?
- What is ultimate plume length?



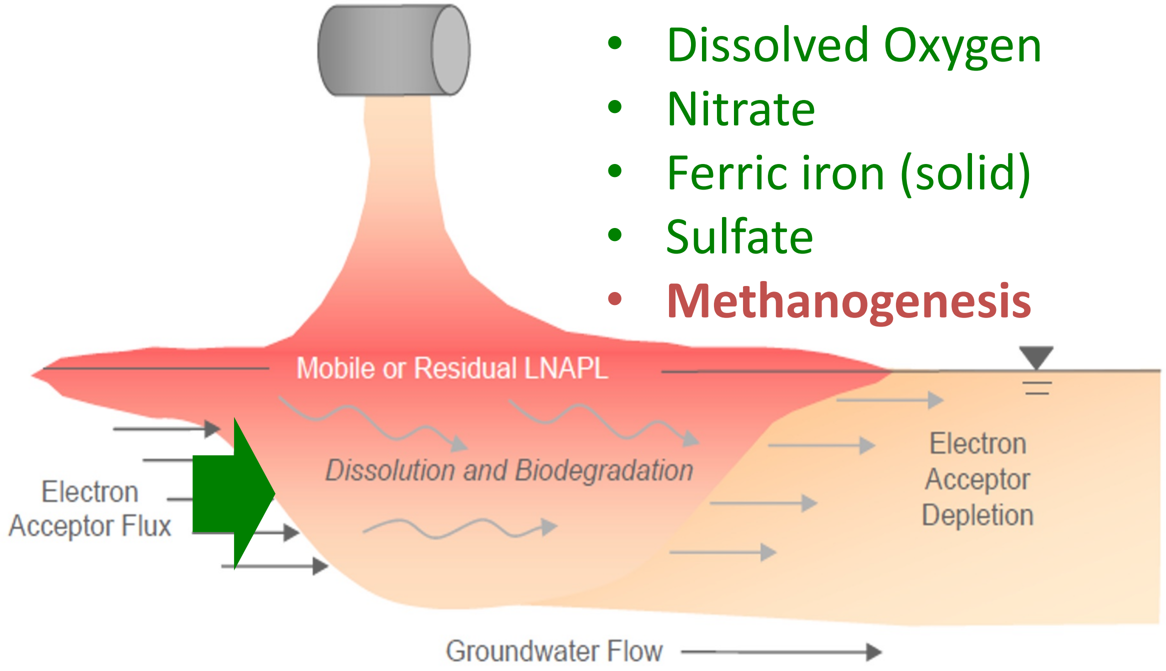


Figure 2-1. Groundwater transport–related NSZD processes.

Groundwater Mass Flux vs. Vapor Phase Mass Flux
Horizontal Flux vs. Vertical Flux

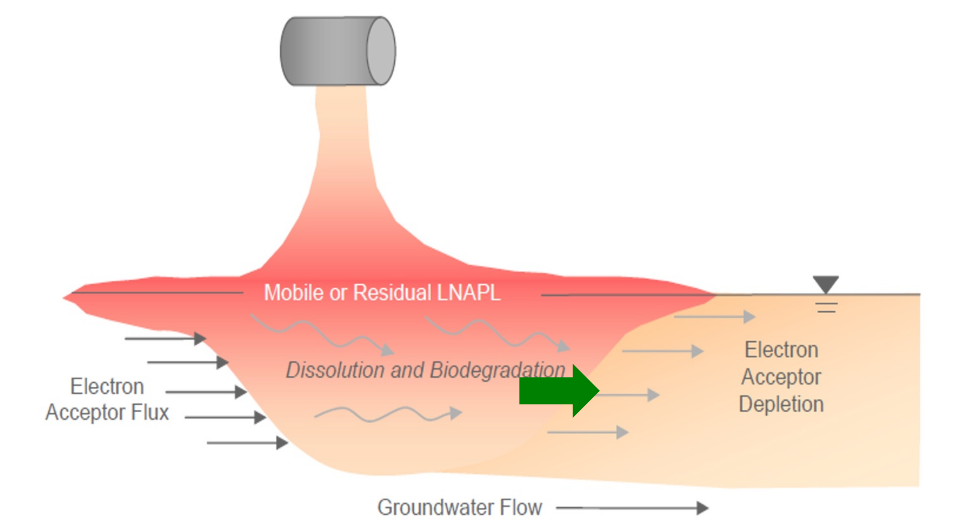
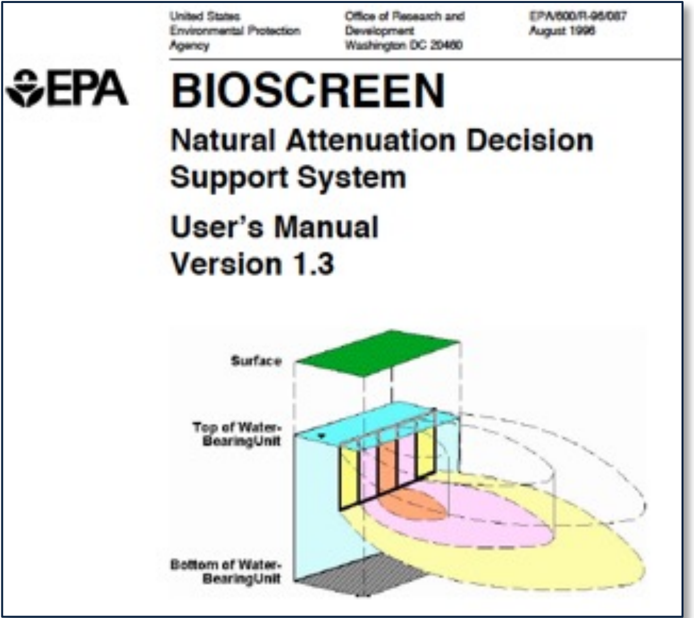


Figure 2-1. Groundwater transport–related NSZD processes.


United States Environmental Protection Agency
Office of Research and Development Washington DC 20460
EPA/600/R-96/087 August 1996

EPA

BIOSCREEN

Natural Attenuation Decision Support System

User's Manual Version 1.3

Old NSZD Conceptual Model: It's all Horizontal Flux

NSZD is mostly from dissolution to groundwater

And it is very very slow….

Lundegard and Johnson (2006) Guadalupe Oil Field
An Amazing Discovery

The vertical NSZD signal is **10x to 100x larger** than the horizontal NSZD signal!

Johnson & Lundegard:

- Idea: lets find pits using CO_2 flux
- It didn't work out as planned
- There is large upward vertical flux of CO_2 throughout the entire LNAPL zone!

Photos: M. Johnson, Cali. Dept. Fish and Wildlife

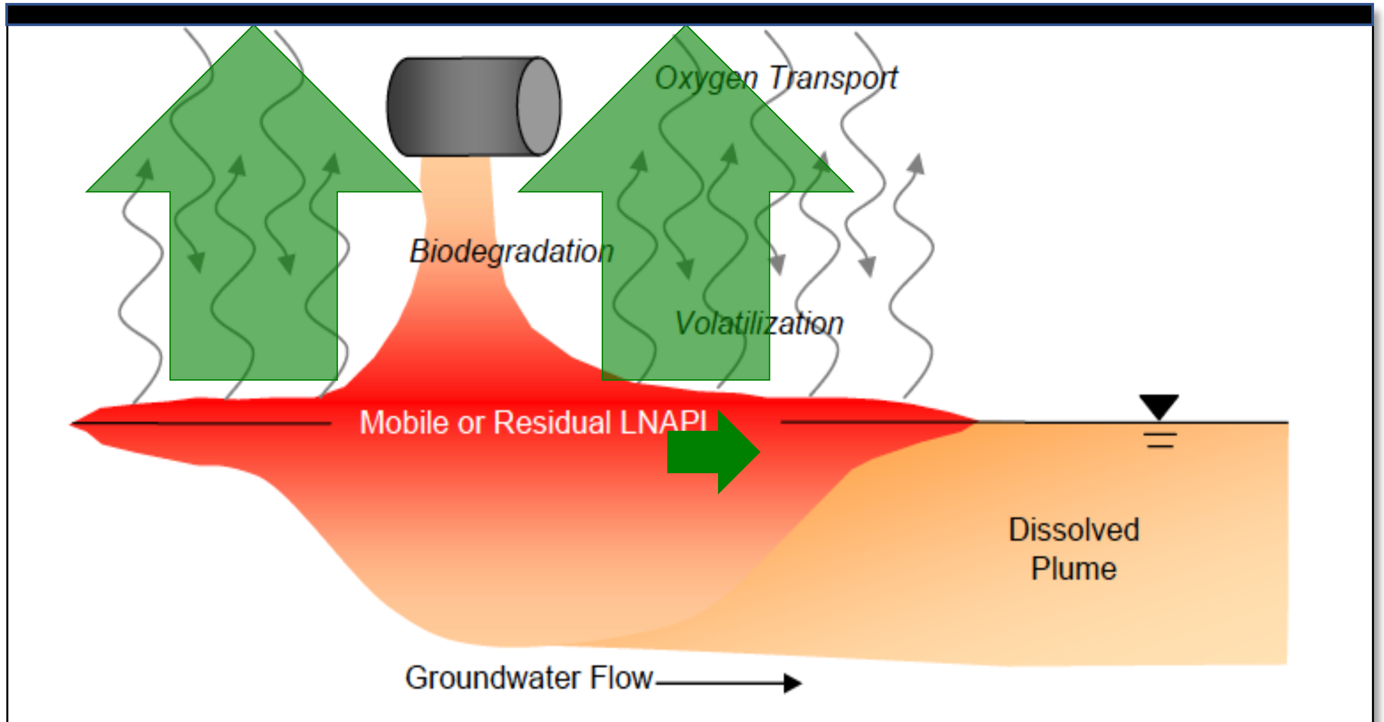


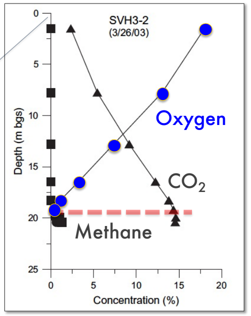
Figure 2-2. Vapor transport–related NSZD processes.

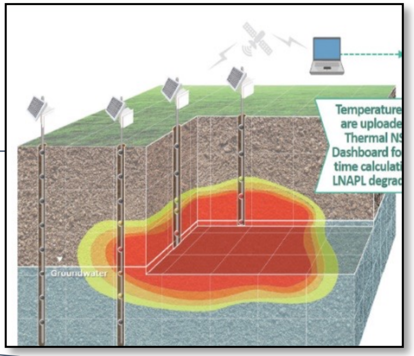
Johnson et al., 2006; Lundegard and Johnson, 2006; ITRC, 2009

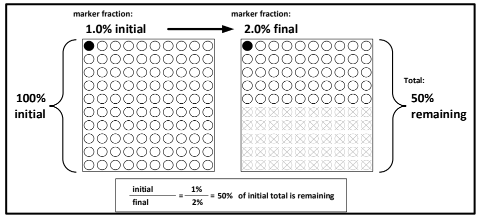
NSZD Applications: Five Methods

Five Methods

1. The Gradient Method
2. Dynamic Closed Chambers
3. Carbon Dioxide Traps
4. Thermal NSZD Methods
5. LNAPL Compositional Analysis







Acknowledgements: Poonam Kulkarni, GSI and Sanjay Garg, Shell

NAVFAC (2021) 10 Sites: Does the LNAPL Type Matter?

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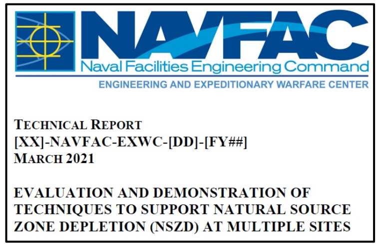
“With the exception of fuel-grade ethanol, the differences in median NSZD by fuel type (nat. gas liquid; mixed LNAPL; crude; gasoline, diesel/jet) were relatively small: **470 -1,310 gal/acre/yr**”

“The range of NSZD rates within each fuel type (>10x) was higher than the range of median attenuation rates between fuel types (<4x) ***suggesting that site factors other than fuel type are more important determinants of the NSZD rate at the site.***”



NAVFAC
Naval Facilities Engineering Command
ENGINEERING AND EXPEDITIONARY WARFARE CENTER

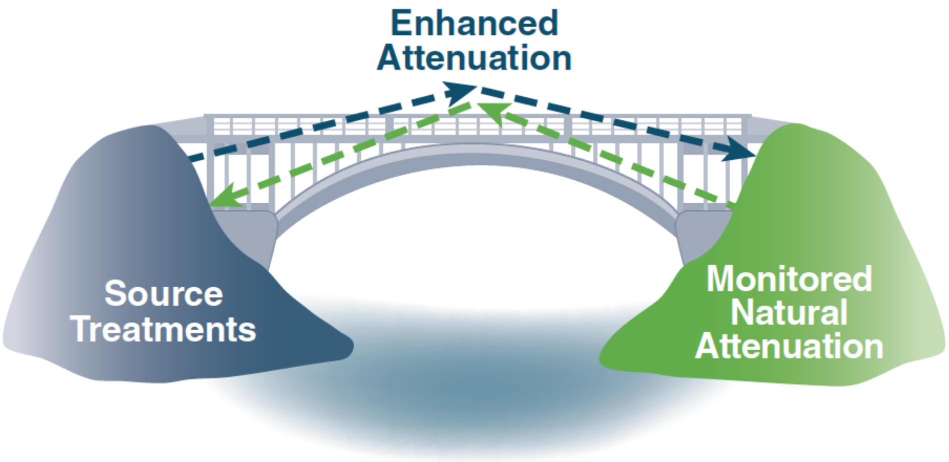
TECHNICAL REPORT
[XX]-NAVFAC-EXWC-[DD]-[FY##]
MARCH 2021

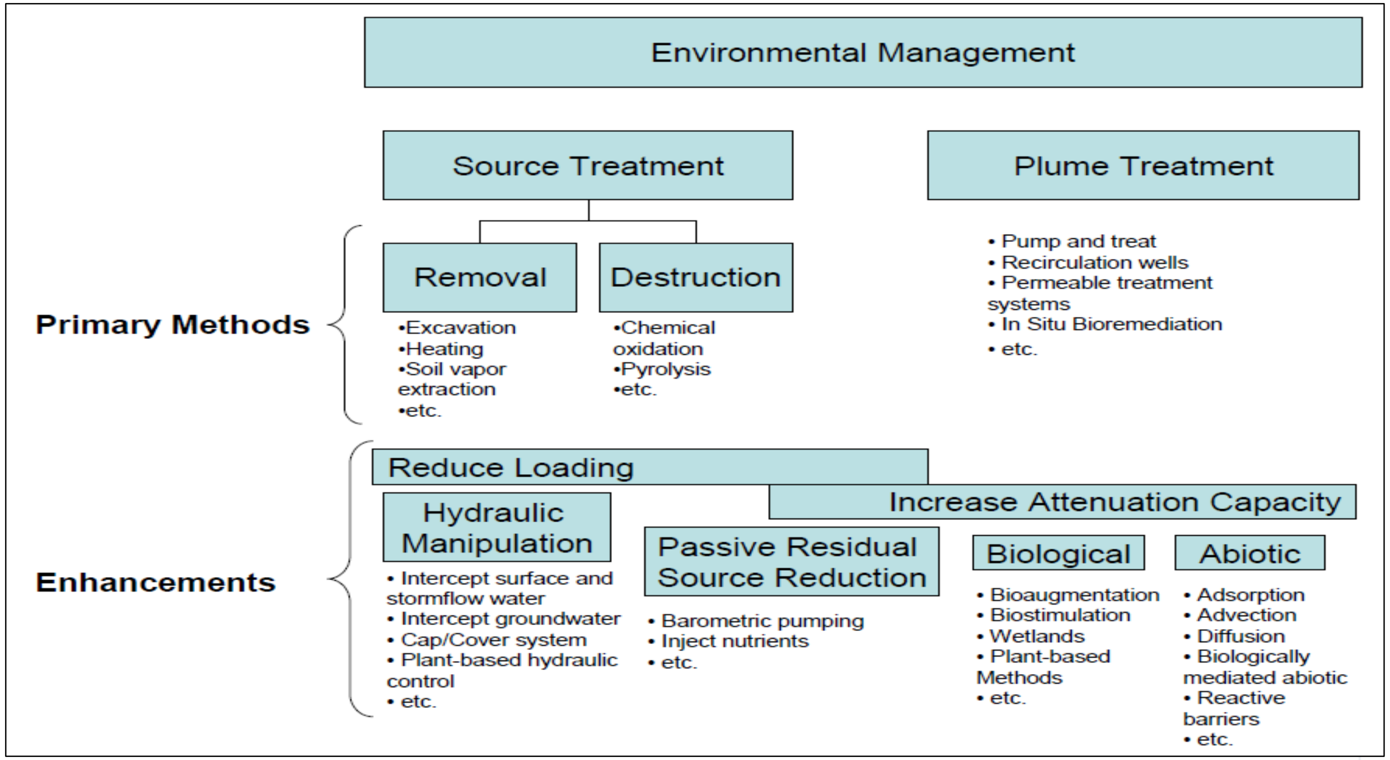
EVALUATION AND DEMONSTRATION OF TECHNIQUES TO SUPPORT NATURAL SOURCE ZONE DEPLETION (NSZD) AT MULTIPLE SITES

Fuel Type	Range of NSZD Rates Measured (gal/acre/yr)	Median NSZD Rate (gal/acre/yr)
Natural Gas Liquid	170 - 5,860	500
Mixed	190 - 6,100	470
Crude Oil	240 - 2,560	820
Gasoline	300 - 4,440	1,050
Diesel and Jet Fuel	70 - 10,630	1,310
Fuel-Grade Ethanol	13,200 - 16,300	14,700
Total	**Median**	**935**

NAVFAC, 2021

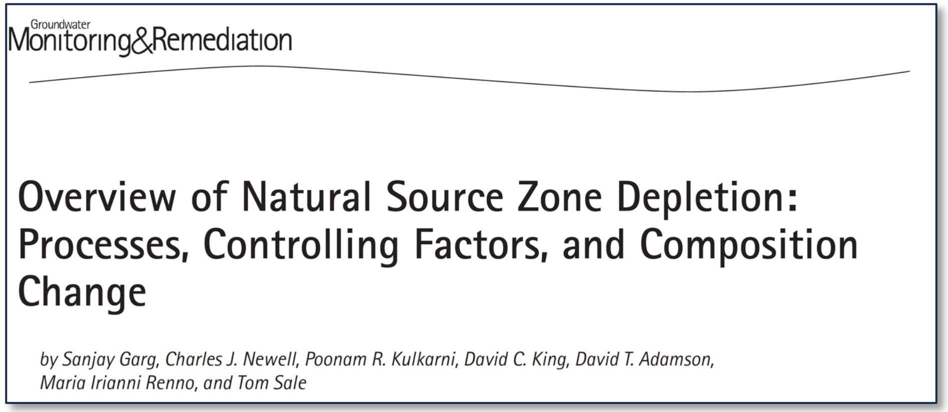
One Vision for "Enhanced Attenuation"





ITRC, 2008

NSZD Conceptual Model (Most Sites)

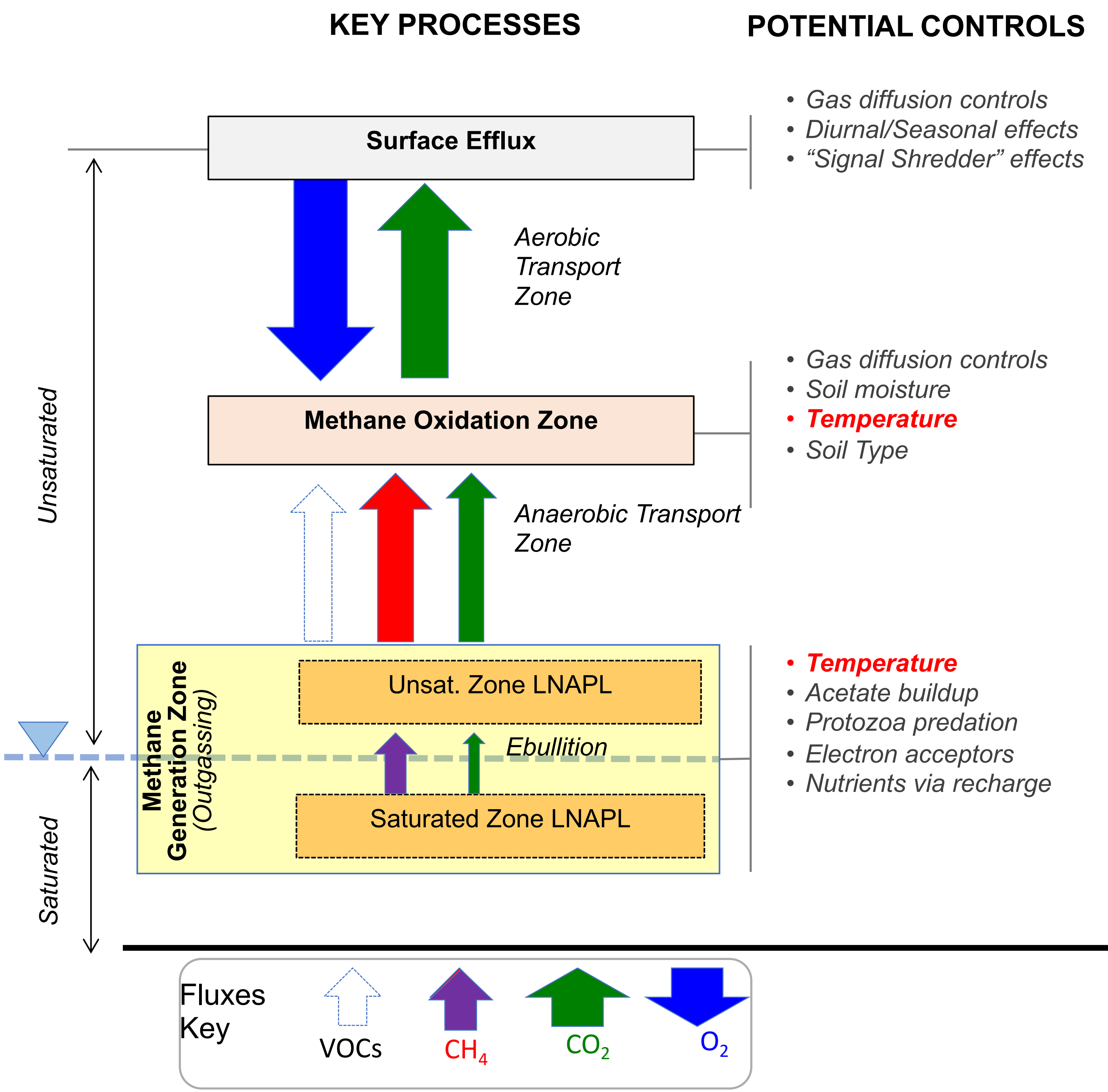


Groundwater Monitoring&Remediation

Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change

by Sanjay Garg, Charles J. Newell, Poonam R. Kulkarni, David C. King, David T. Adamson, Maria Irianni Renno, and Tom Sale

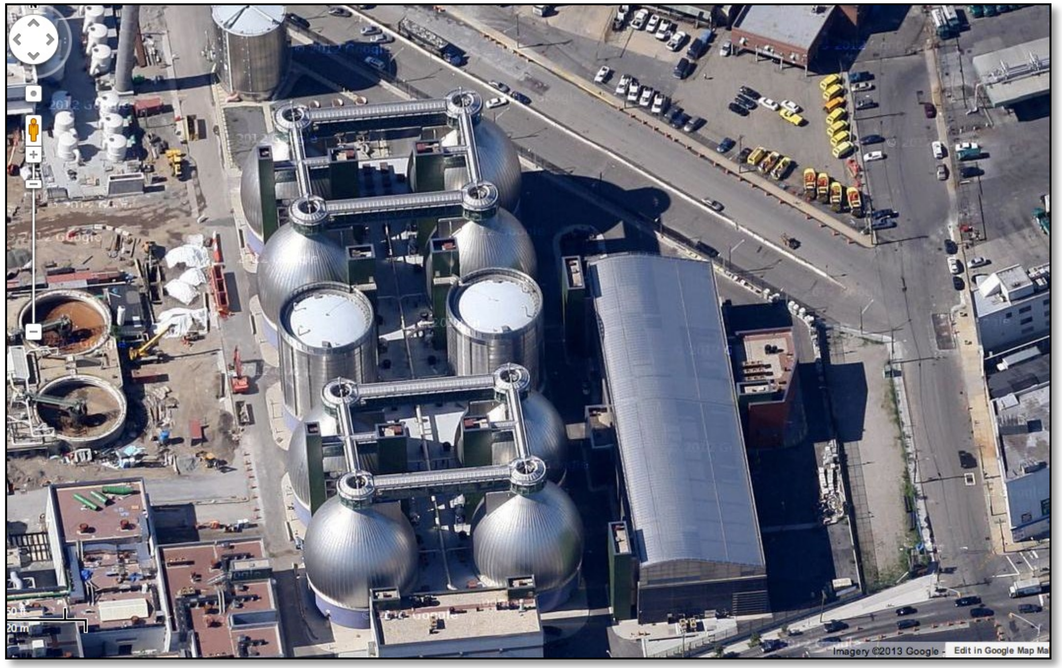
Garg et al. (2017)

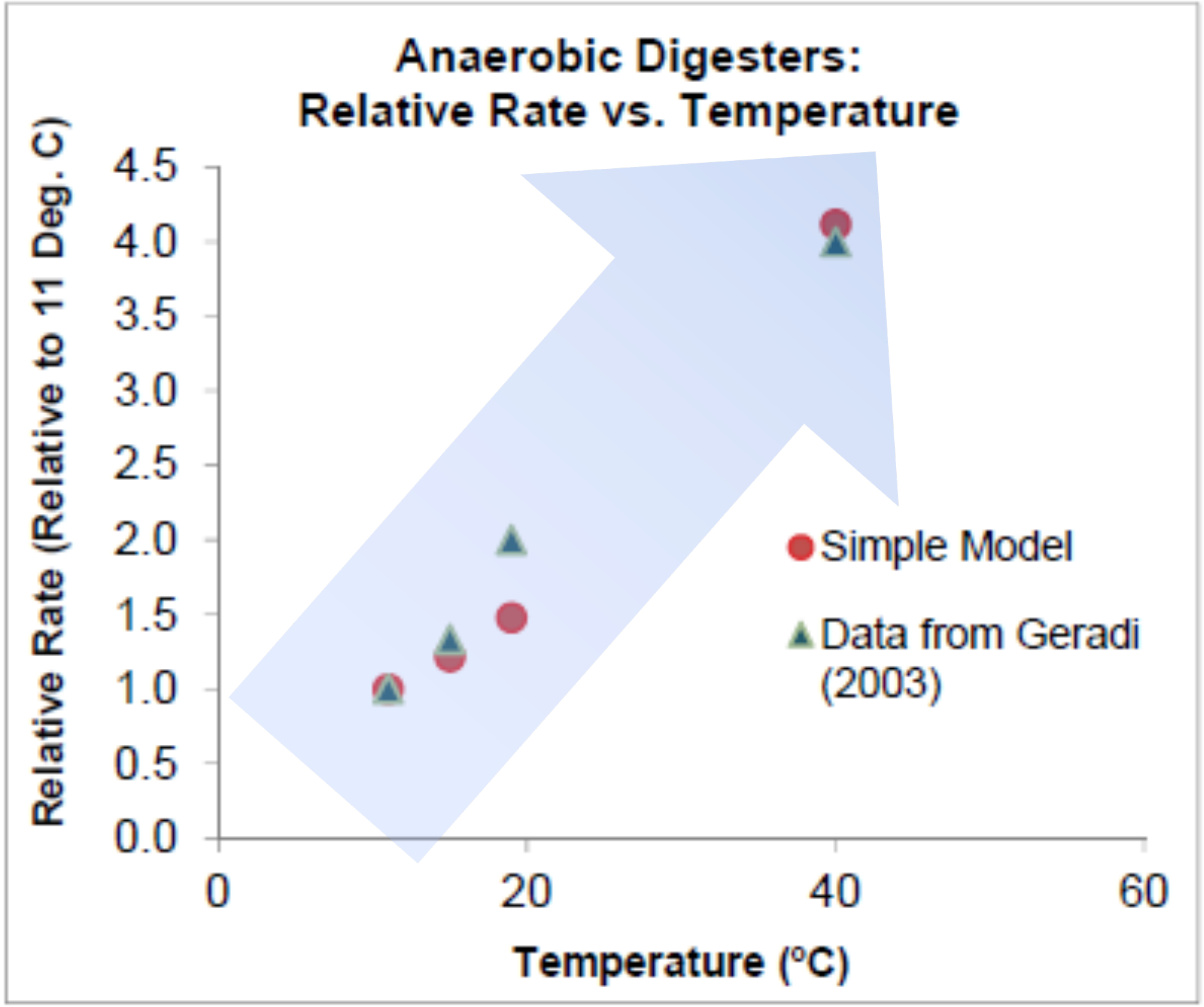


Wastewater Treatment Plant in Brooklyn, NY using anaerobic digesters

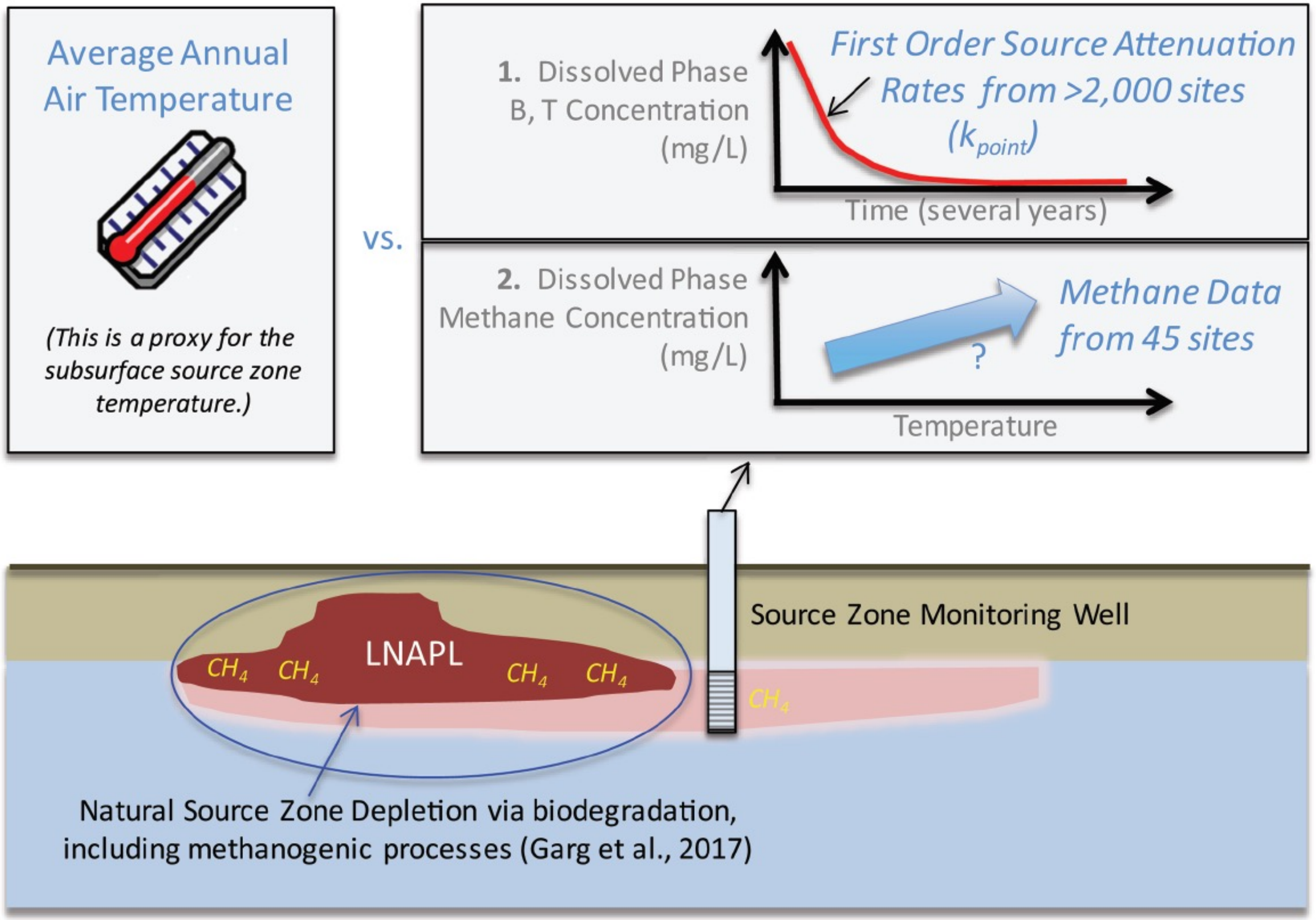
"The blue color is a symbol for calm, cleanliness, and purity, but it also serves to contrast the light of the city, which is predominantly amber or bright white"

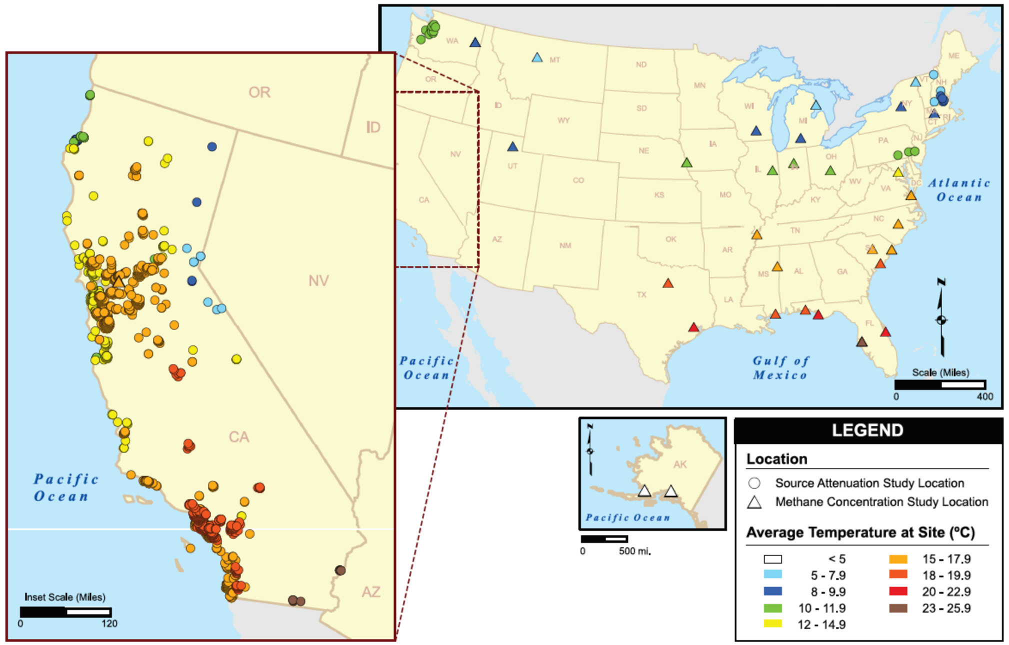
Anaerobic Digesters: Set the Oven to 40 °C

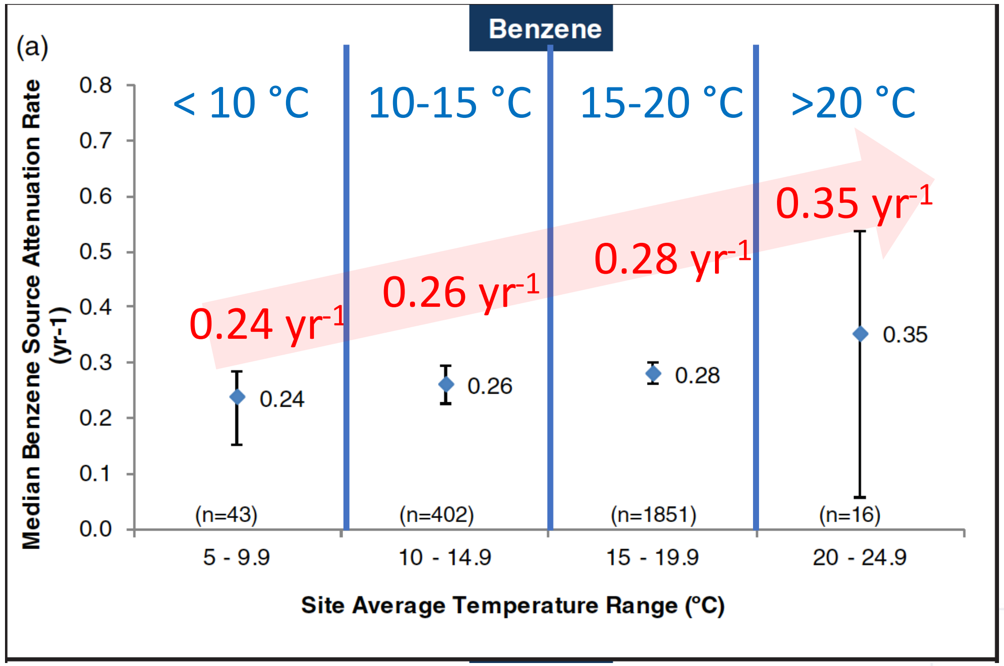




Biodegradation Rates at ~ 2,000 Hydrocarbon Groundwater Sites

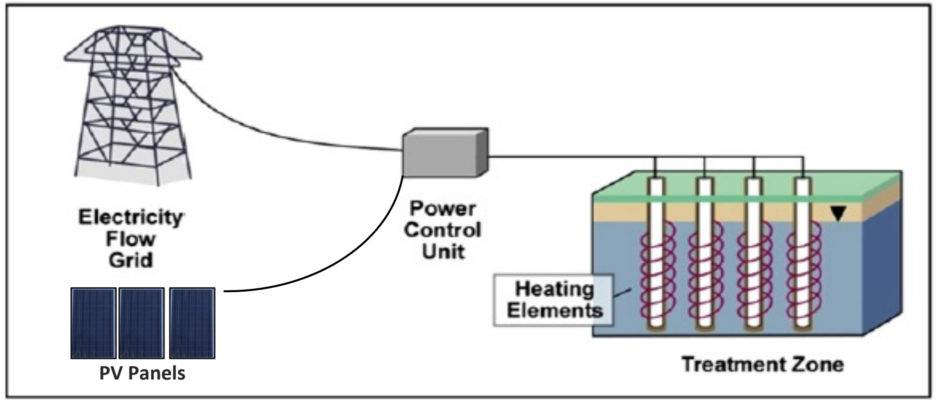




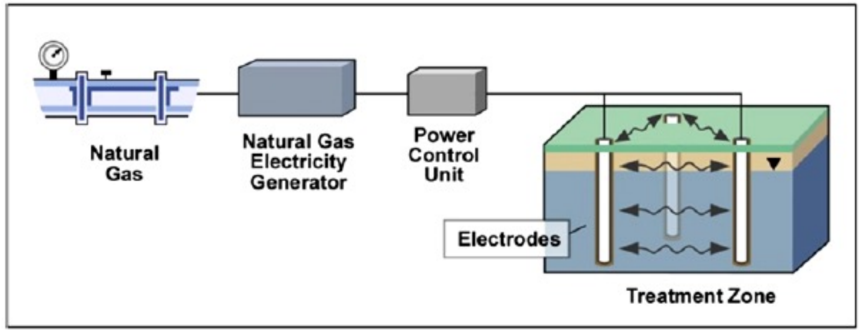


Kulkarni et al., 2021.

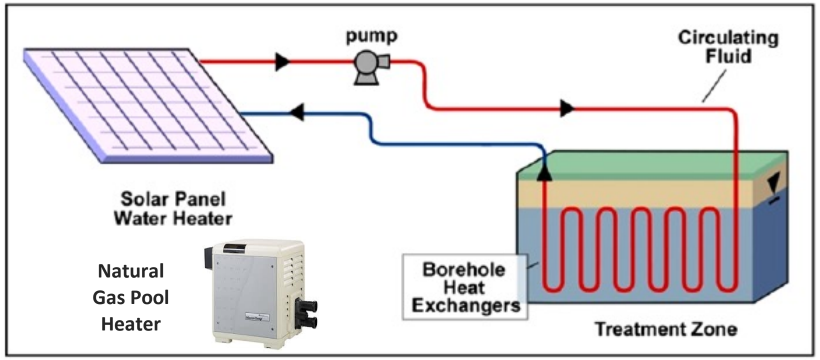
Sustainable Thermally Enhanced LNAPL Attenuation (STELA)
Active Methods to Add Heat to the Shallow Subsurface



Thermal Conductance Heating

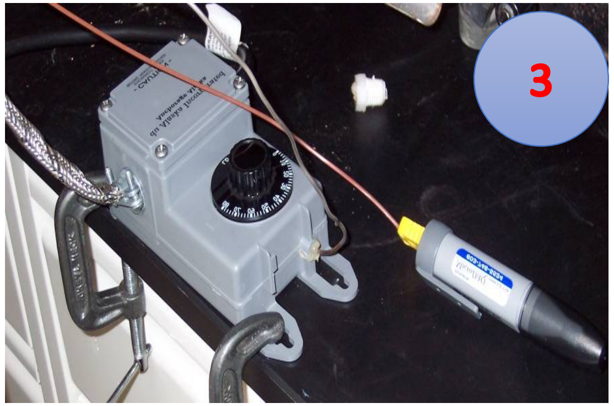


Electrical Resistance Heating



Borehole Heat Exchangers

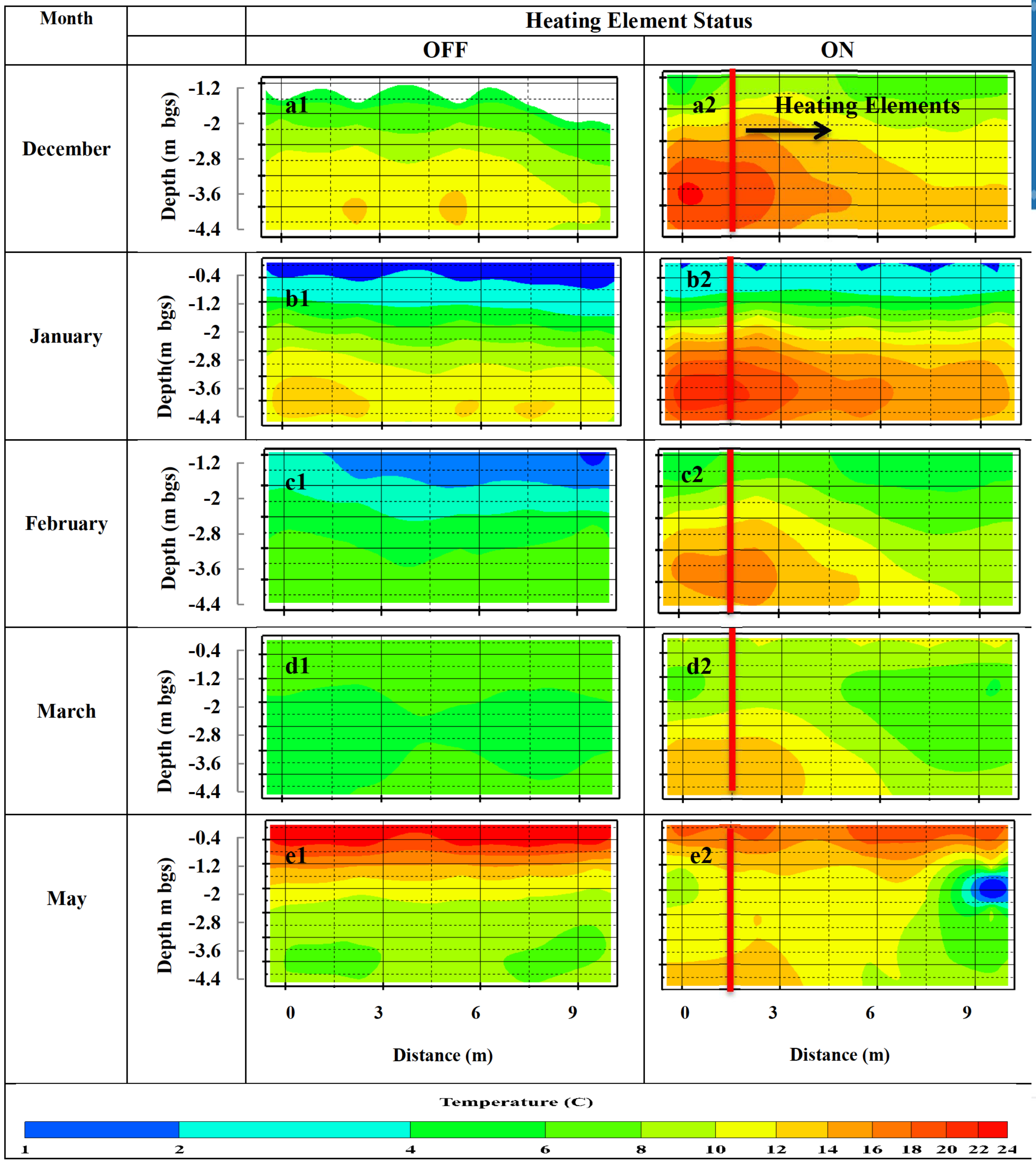
Colorado State Soil Heating via Vertical Resistance Heating Points



Photos courtesy of
Dr. Tom Sale

CSU Wyoming STELA Pilot Test

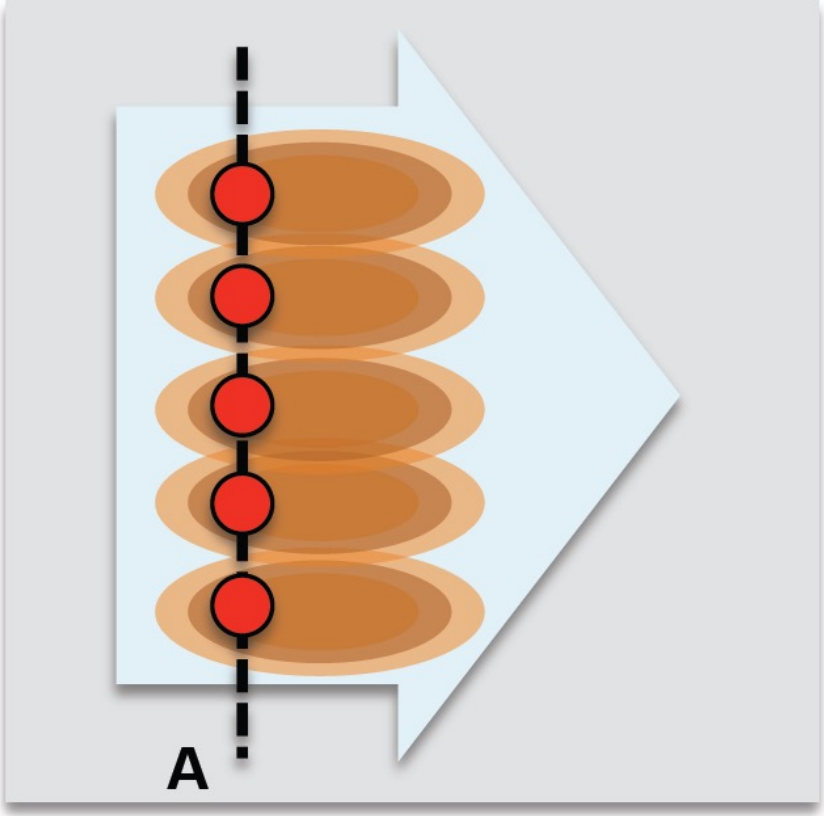
STELA Pilot Test for LNAPL Refinery Site



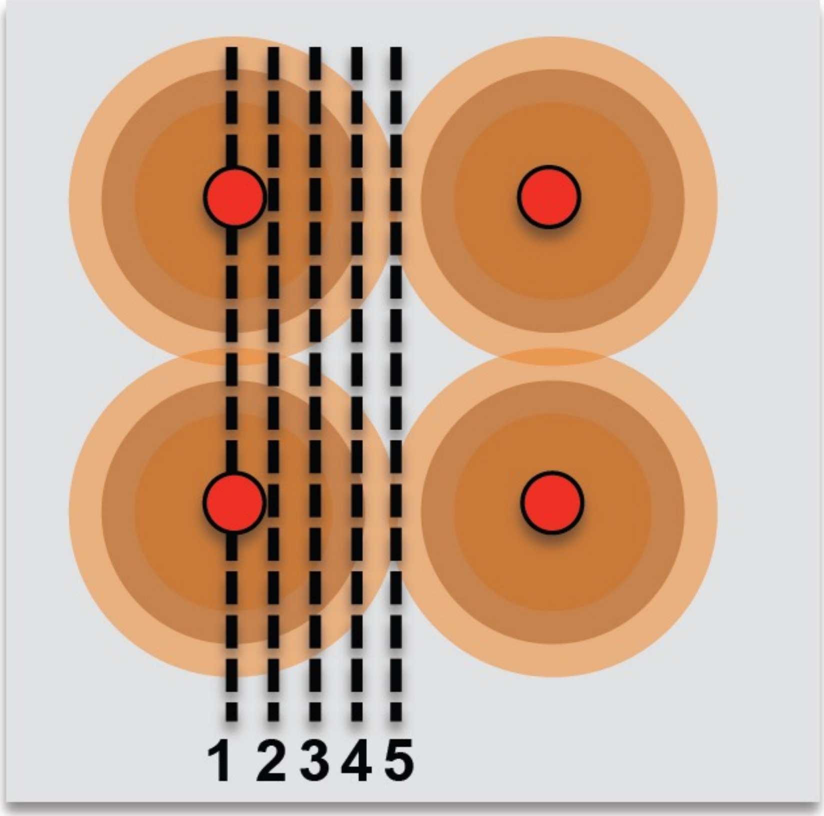
Source: Sale, 2011, Akhbari, 2013.

STELA Vertical Heating Elements – Configuration Options

DRIFT
(may be less effective)



GRID



STELA Passive Methods to Add Heat: *Soil Solarization*

Figure 1. Overview of solarization in a field.

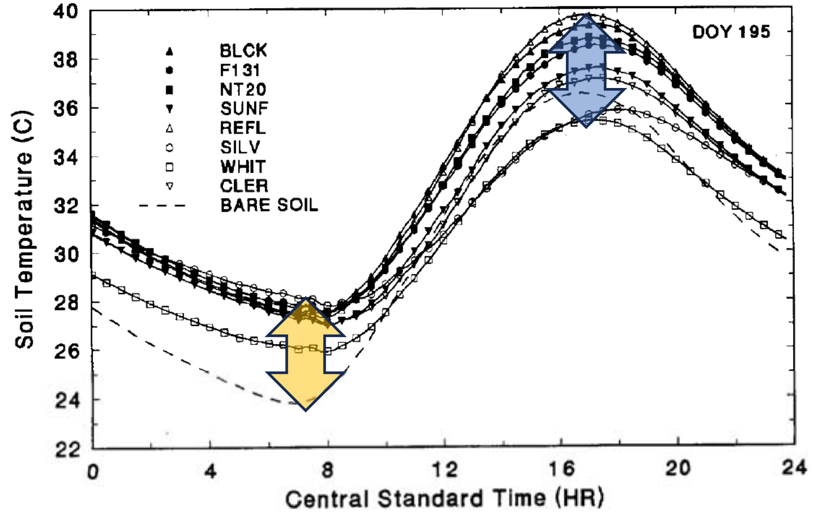
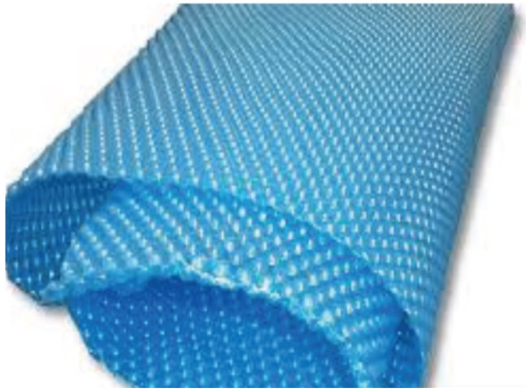


Fig. 1. Diurnal patterns of soil temperature at the 10-cm depth on DOY 195. Data are shown for each of the plastic mulches and the bare soil plot. Skies were clear.

Key Points:

- They want to kill weeds, pests.
- The agricultural field calls this plastic covering ”mulch”
- Lots of technology on the placement and kinds of plastic

Personal field trial of soil solarization



Updates on Solarization Research

CSU: Maria Renno, Emily Stockwell, Daria Ahkbari, Nolan Platt, Christina Ankrom, Jay Ham and Tom Sale

GSI: Poonam Kulkarni and Charles Newell

07/17/2015

CSU Soil Solarization "Temperature Only" Research

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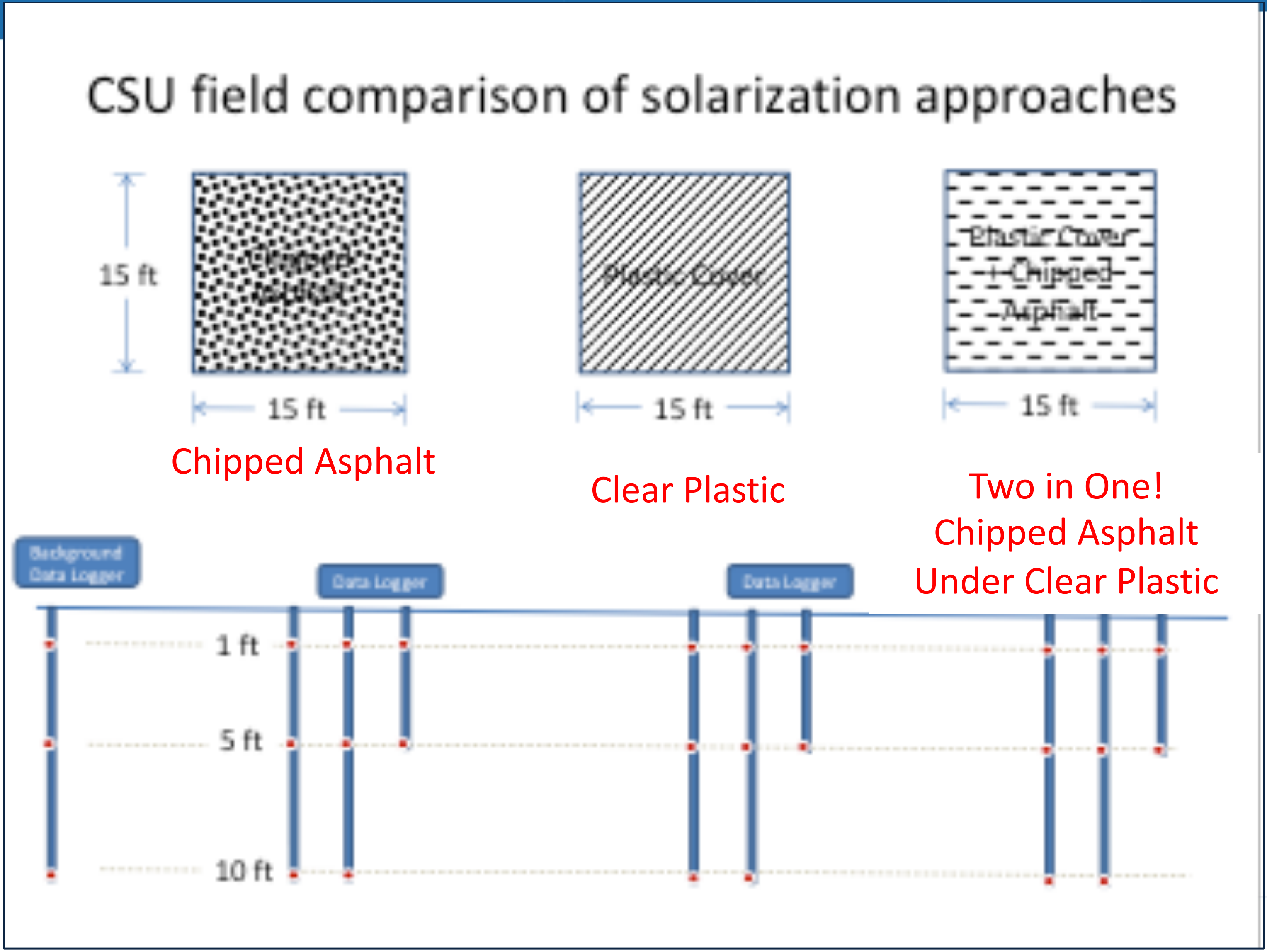
Chipped Asphalt



CSU Soil Solarization Experiment Over 1 Year Subsurface Heating 1 ft bgs ~ 8 °C for Plastic.

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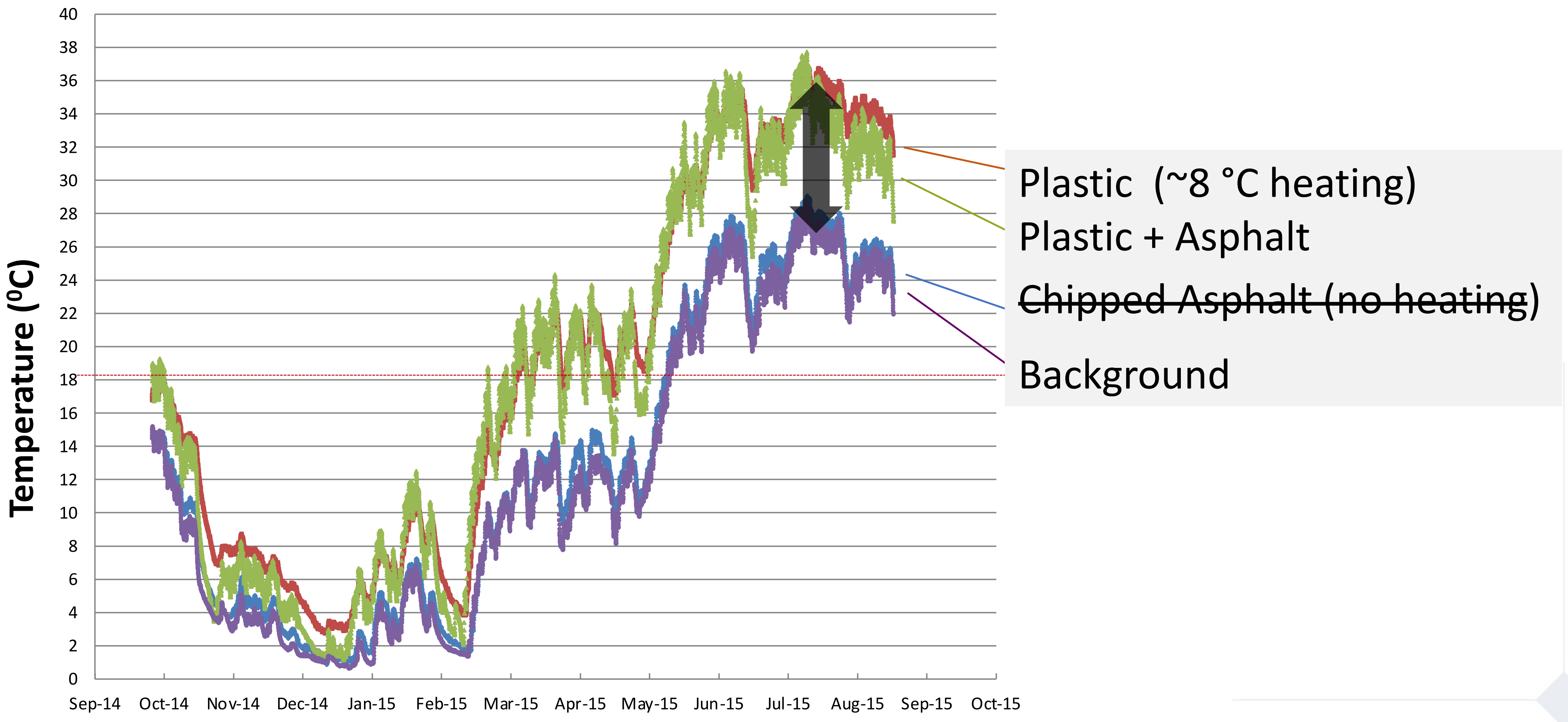

CSU Research: Effective Seasonal Benefits from Solarization

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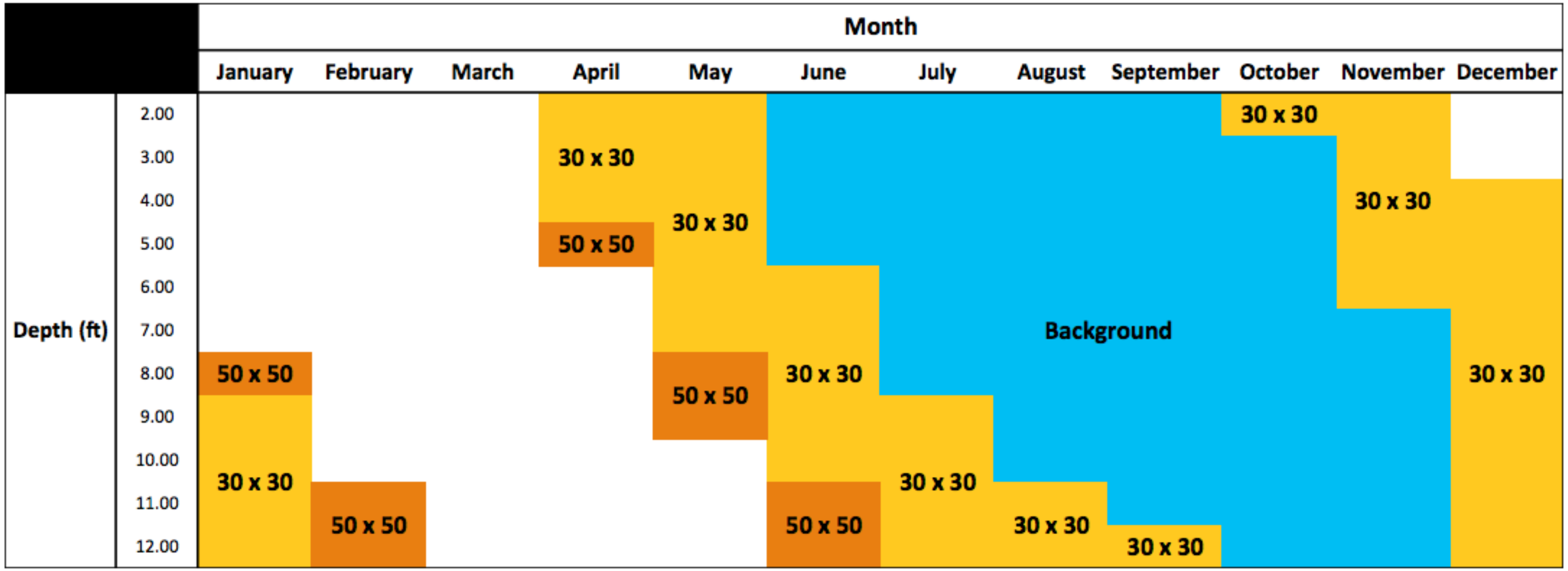
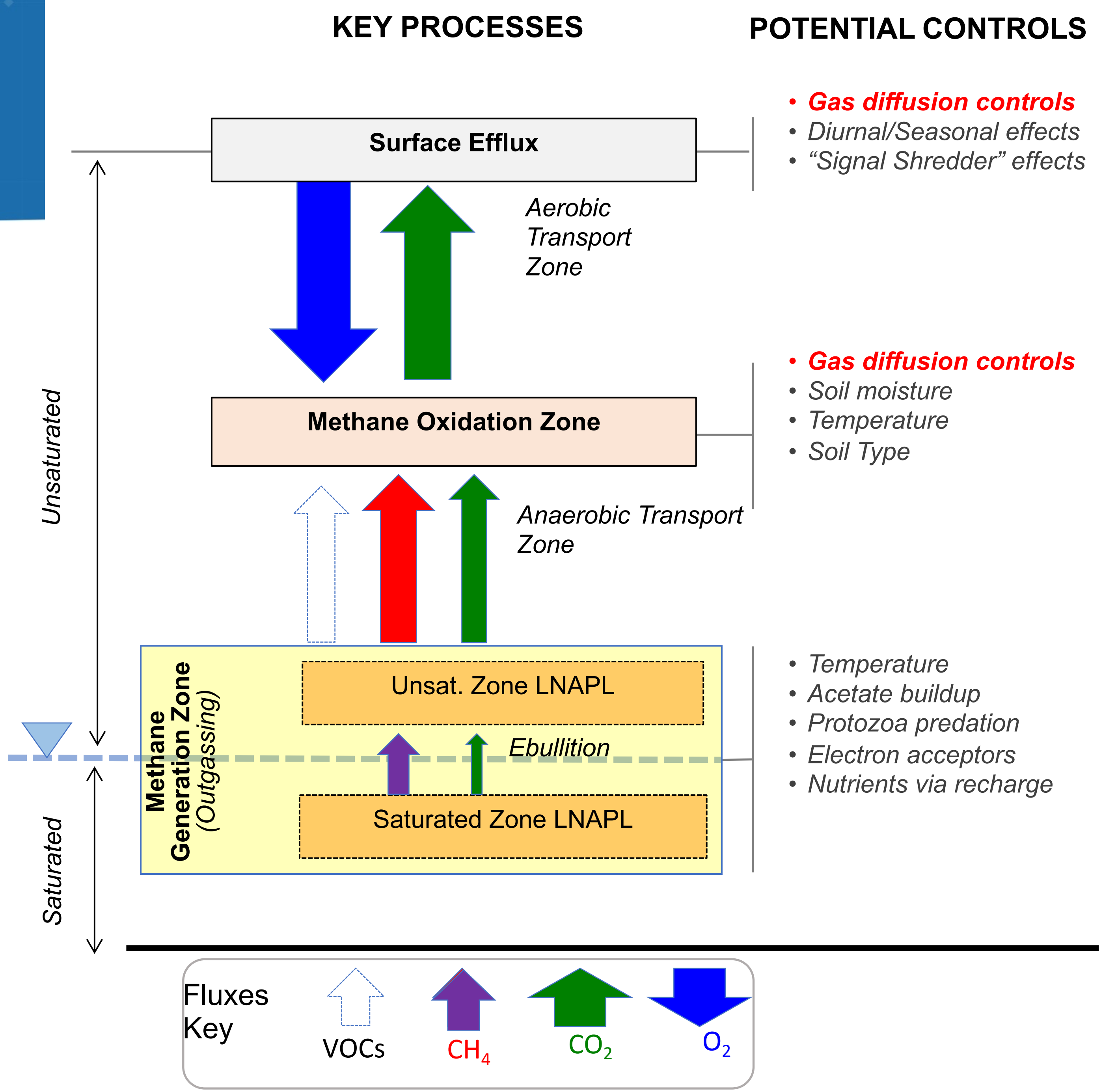


Figure 2. Effective Season for enhanced LNAPL biodegradation (> 18°C) by month and depth for two sizes of a combined Asphalt Chip + Clear Plastic cover: 30 ft by 30 ft (yellow squares) and 50 ft by 50 ft cover (orange squares). Blue squares show times/depths with soil temperatures exceeding 18°C under background (no cover) conditions. Source: Akhbari et al., 20140.

NSZD Conceptual Model (Most Sites) (Garg et al.,2017)

What about oxygen addition?



Bioventing Initiative Study Early 1990s

GSI ENVIRONMENTAL

- Air Force Bioventing Study
- 178 Sites
- 1988-1995

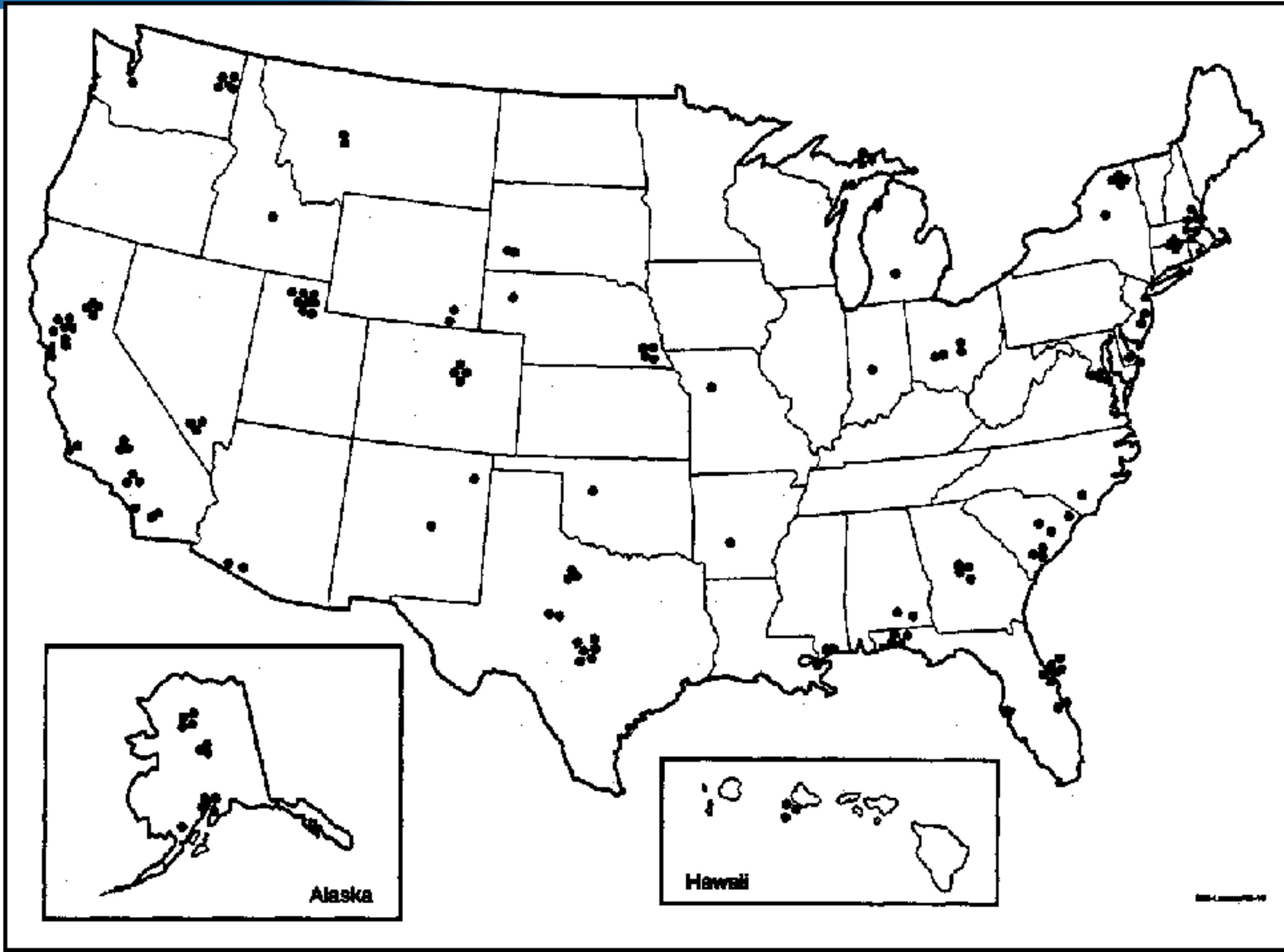
PRINCIPLES AND PRACTICES OF BIOVENTING

VOLUME I: BIOVENTING PRINCIPLES

by
Andrea Leeson and Robert E. Hinchee
Battelle Memorial Institute
Columbus OH

with contributions by

Bruce A. Alleman, Douglas C. Downey, Gregory Headington,
Jeffrey A. Kittel, Priti Kumar, Lt Colonel Ross N. Miller, Say Kee Ong,
Gregory D. Sayles, Lawrence Smith, Catherine M. Vogel



Bioventing Principle of Operation

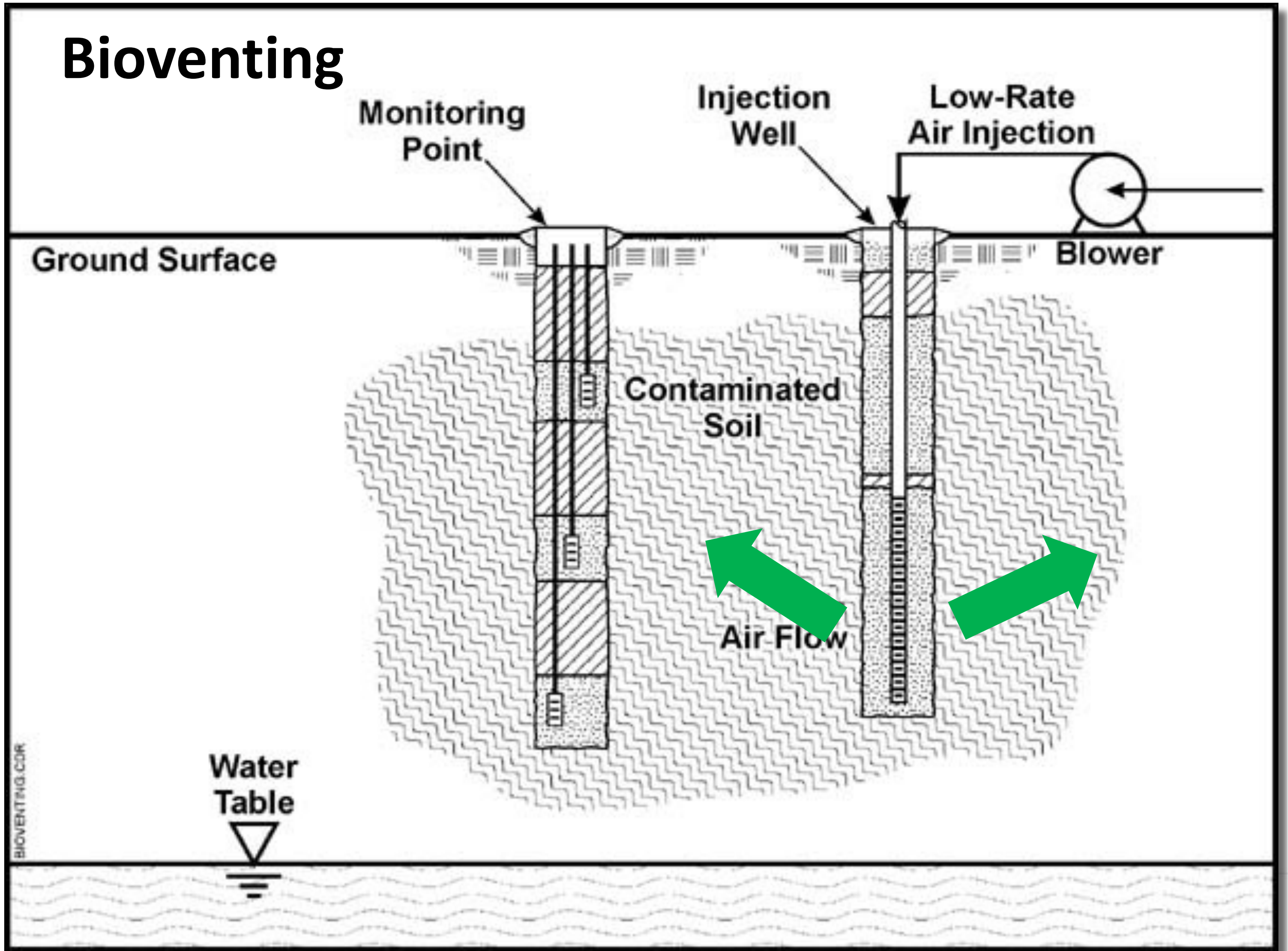
GSI ENVIRONMENTAL

Soil Vapor Extraction (SVE)

1. Suck air out of the ground
2. You treat the vapors

Bioventing

1. Pump air *into* the ground
2. **Nature treats the vapors**



Biodegradation Rates at 178 Bioventing Sites

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Zero-order biodegradation rates calculated from oxygen utilization rates

	Initial (mg/kg-day)	After ~One Year (mg/kg-day)
Median	**5.3**	**1.5**
Mean	10.6	3.1
Minimum	0.1	0.1
Maximum	91.4	16.0

Bioventing Correlations And Oxygen Utilization Model

$$\log(O_2) = -2.7 + 0.39 \log(NIT) - 0.108 (MOI) + 0.017 \log(TPHsg) * MOI - 0.004 \log(TPHsg) * TMP$$

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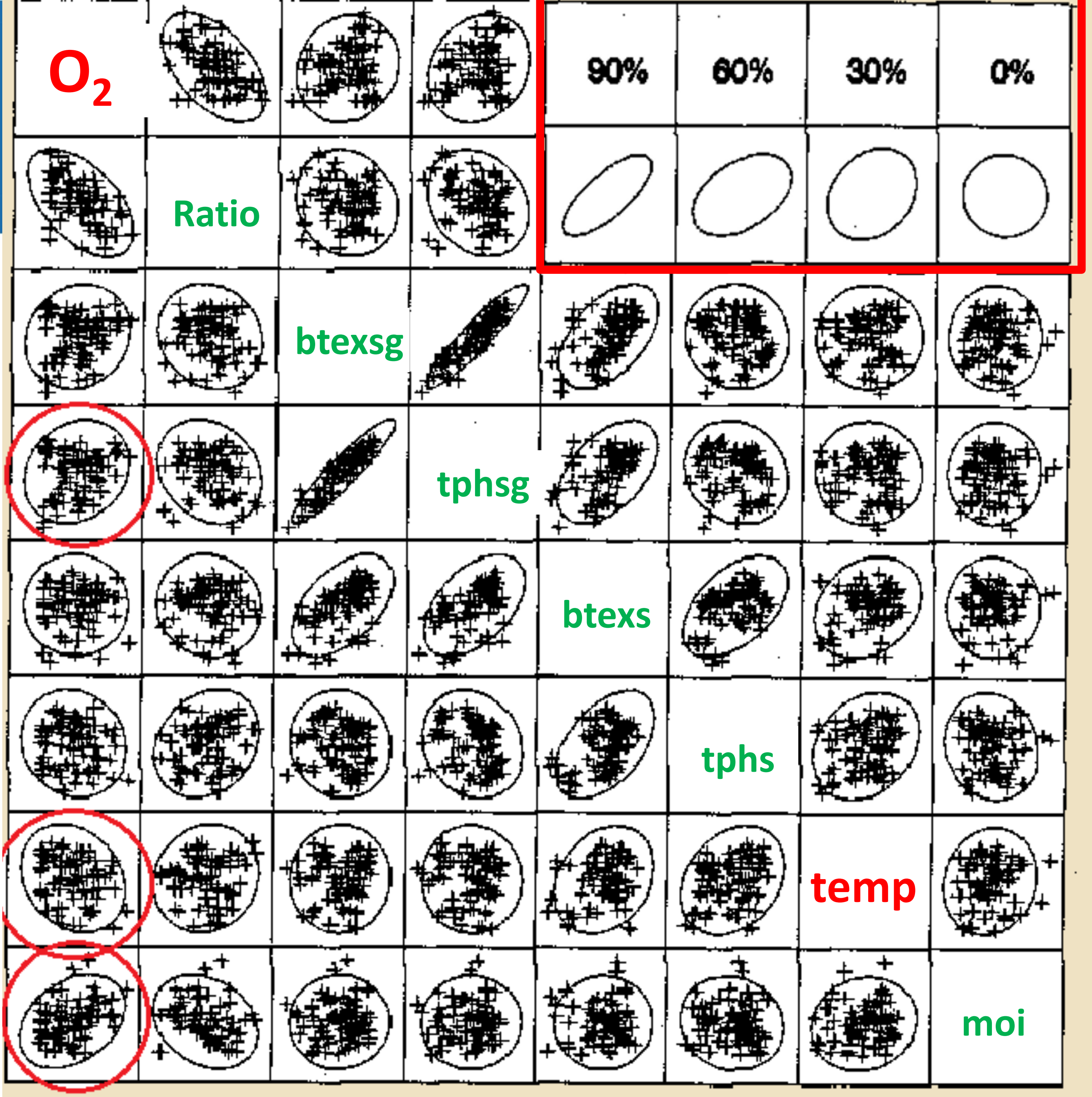
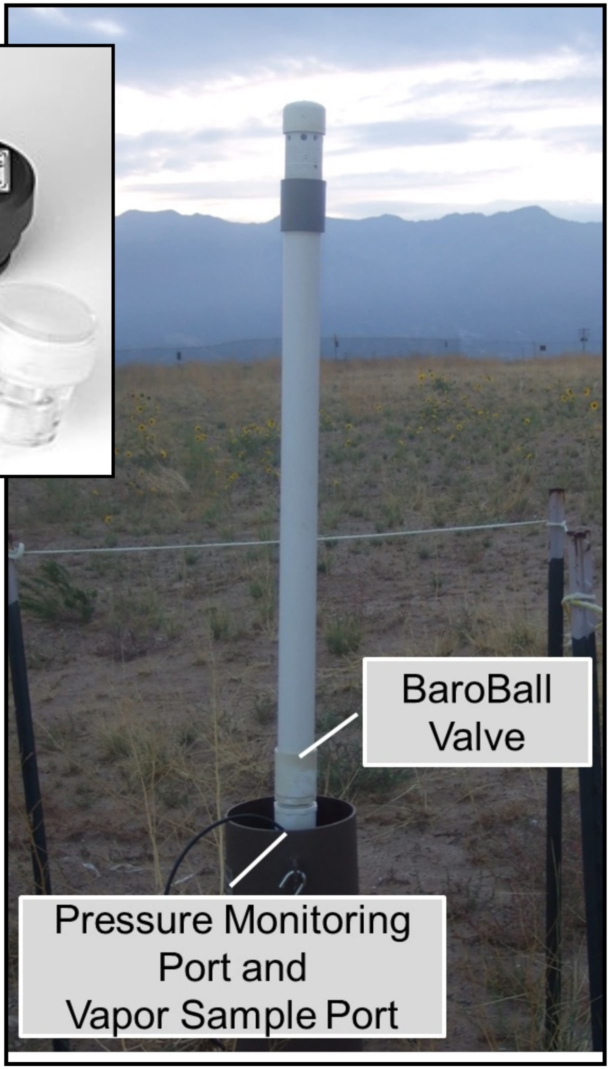
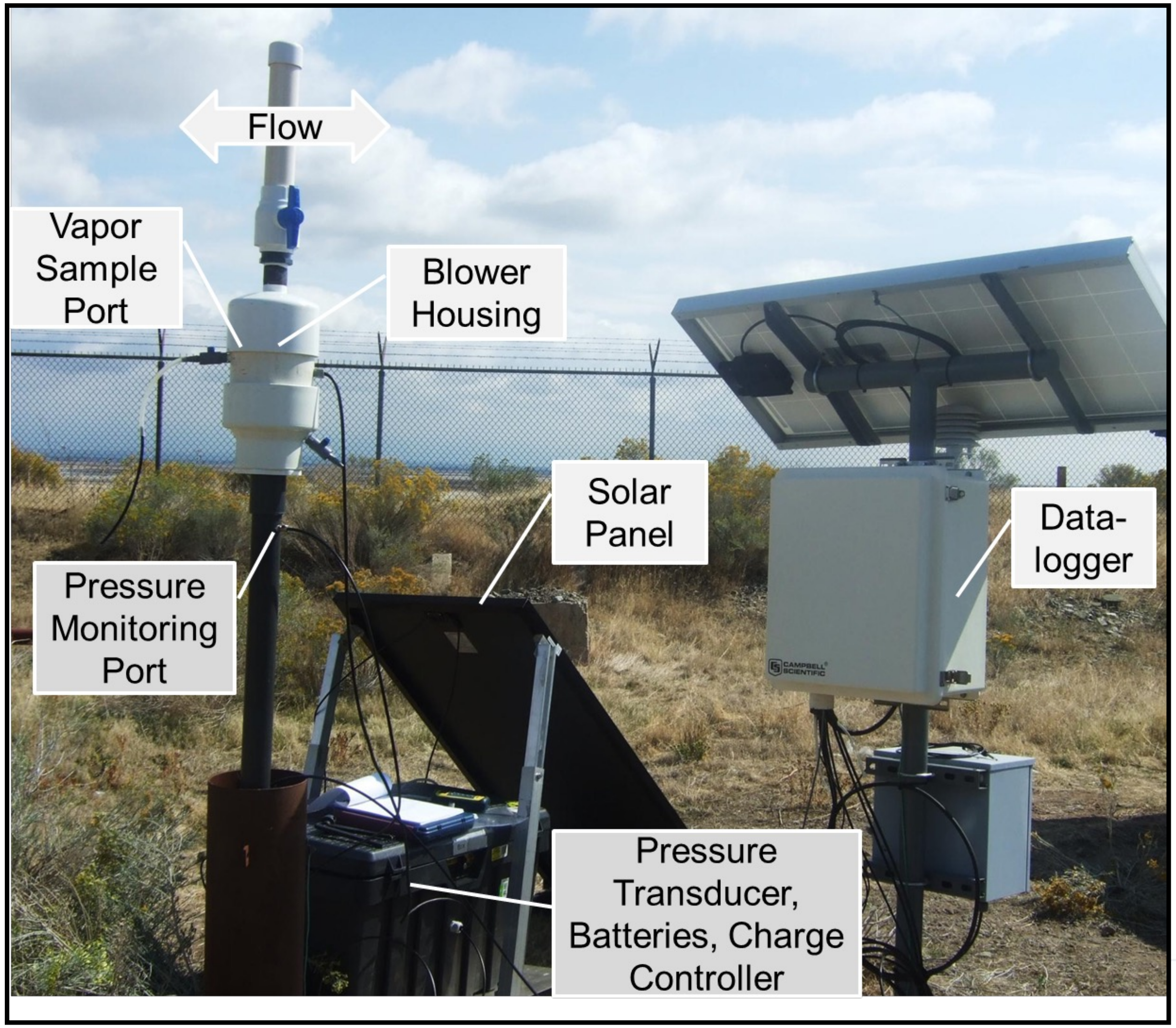


O_2 = log O_2 Rate   Ratio = (CO_2 Rate/O_2 Rate)^x btexsg = log BTEX in Soil Gas   tphsg = log TPH in Soil Gas
btexs = log BTEX in Soil   tphs = log TPH in Soil   TMP = Soil Temperature   MOI = Moisture

Passive / Semi Passive Bioventing Approaches
Baroballs (left) and Microblowers (right)





Experimental Concept: A Geotechnical ”Sewing Machine” for Accessing the Subsurface: Wick Drains

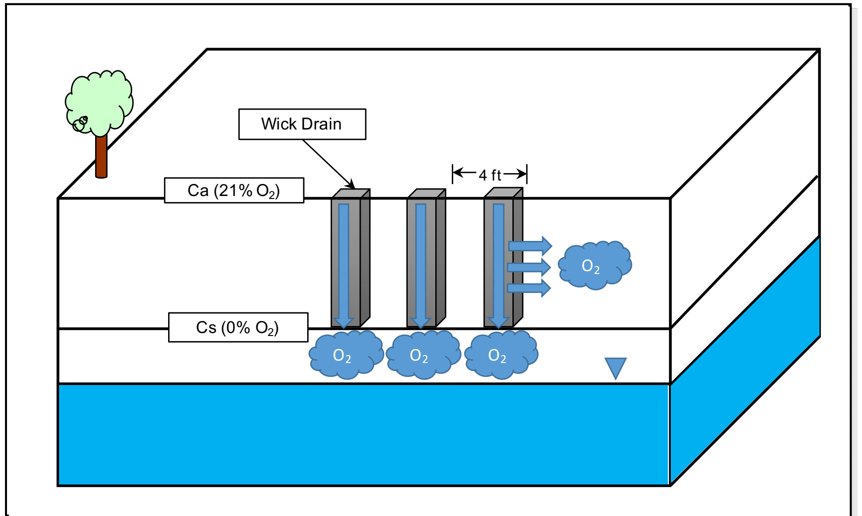
Wick Drains for Geotech Applications

- Used to dewater soils such as hydraulic fill
- Can put in 100s of these vertical sleeves (wick drains) per day
- Water travels up the channels between the wick drain fabric and the corrugated center piece.

Wick Drains for Passive Bioventing?

- Put hundreds of wick drains, that increases diffusion of oxygen into tight soils

Figure 7. GSI Environmental Engineer Luz Rocha with the section of wick drain. *Inset:* Duck-bill connector attached to the top of the wick drain.



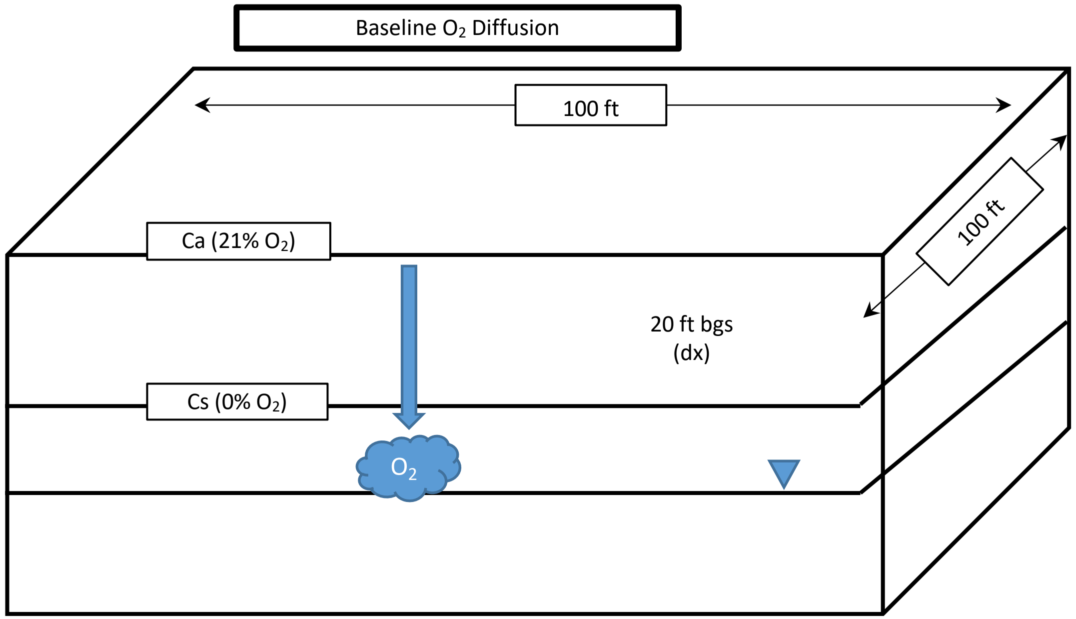
Comparison of Passive/Semi-Passive Bioventing Technologies

Assuming 100 ft x 100 ft plot....

Preliminary- may change significantly

Table 1: Additional O2 Injected in Subsurface

Technology	Baseline O2 Diffusion (kg/yr)	Estimated Flow Rate (scfm)	Additional O2 Injection (kg/yr)	Increase Factor
Wick Drains	847	--	6,500	6.7
MicroBlowers	847	5	110,000	133
BaroBalls	847	0.5	9,400	10.1

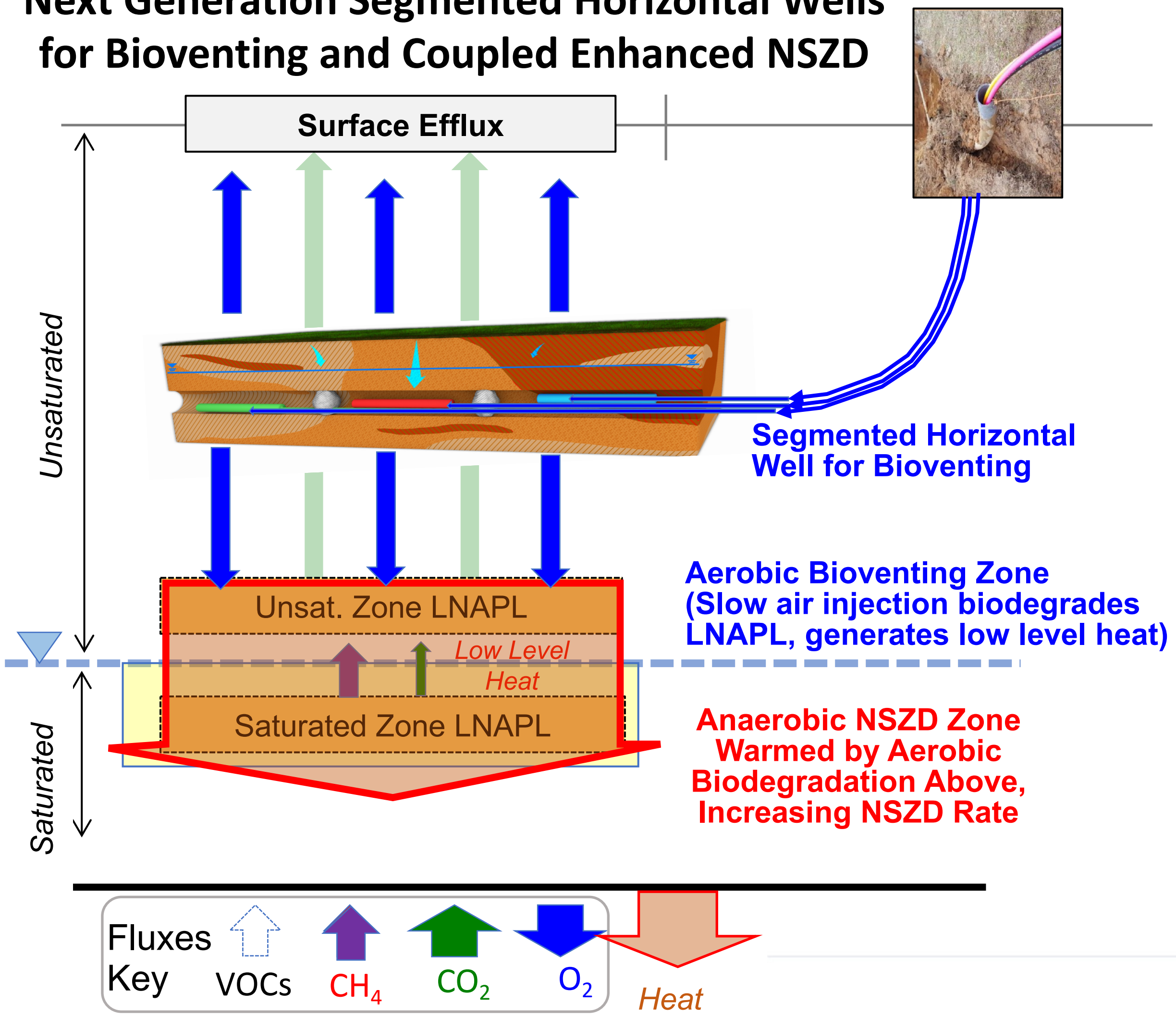


625 Wick Drains: 4 foot spacing
6 Microblower Wells: 20 ft spacing
11 Baroball Wells: 15 foot spacing

Bioventing's Beneficial Side Effect?

1. Bioventing Heats the Unsaturated Zone,
2. Which Warms the Saturated Zone,
3. Which Can Increase Methanogenesis

Next Generation Segmented Horizontal Wells for Bioventing and Coupled Enhanced NSZD



Technology Development Pyramid (Cherry et al., 1996)
Stages in the Evolution of New Remediation Technologies
Proven Technology: *"Known Performance for a Known Price"*

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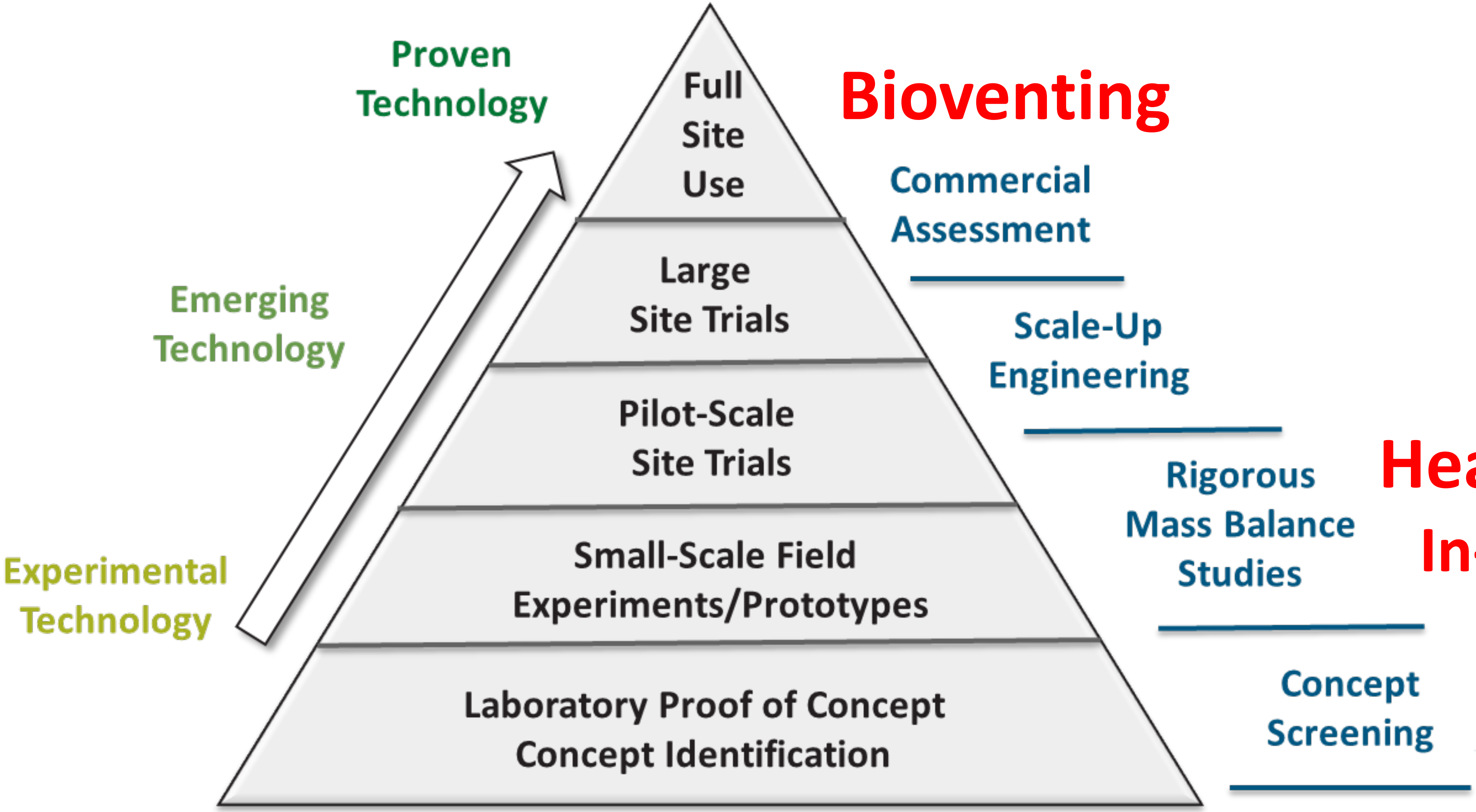


Bioventing

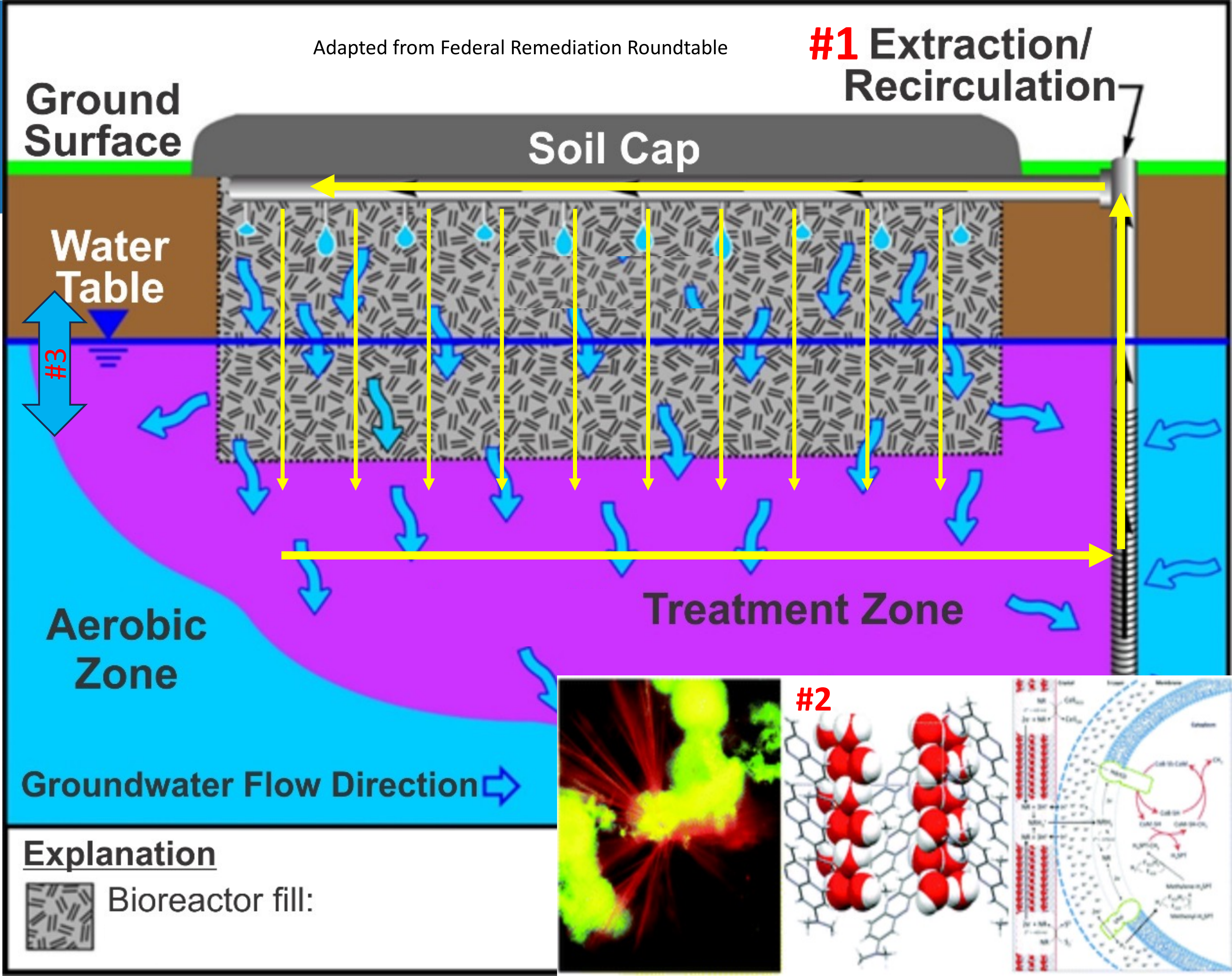
Heating

In-situ bioreactors

3 Experimental Technologies?

Three More Experimental Concepts to Enhance NSZD

1. Start with Anaerobic Bioreactors: Could Recirculation Alone Help Mix Acetate, control pH?
2. Add “neutral red” to enhance methanogenesis? (Beckmann et al., 2016; Manefield lab)
3. Fluctuate water table to help methane bubble to surface?



Wrap Up: How to Enhance NSZD

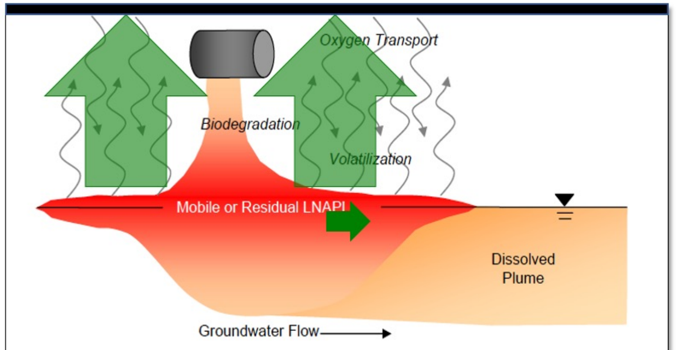
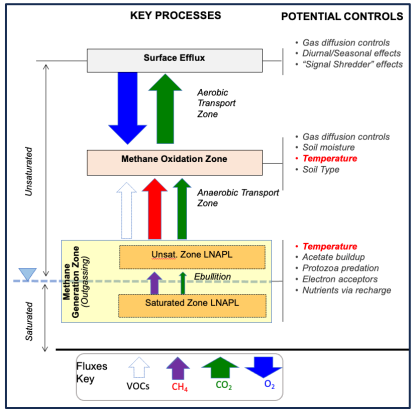
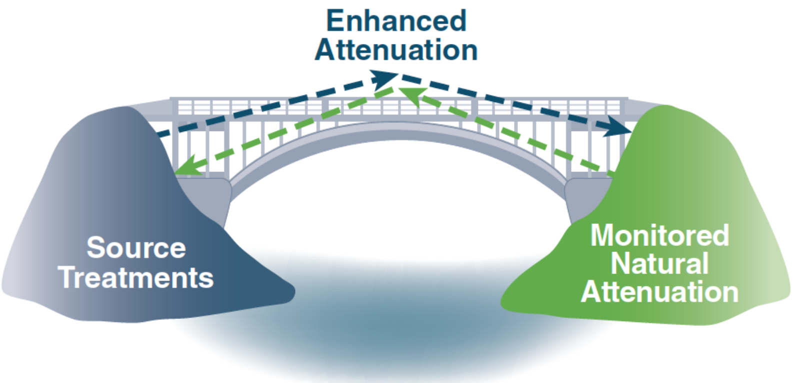
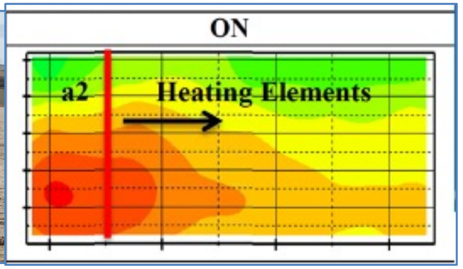
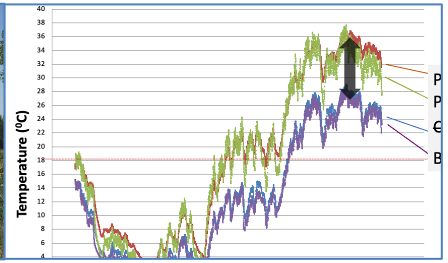


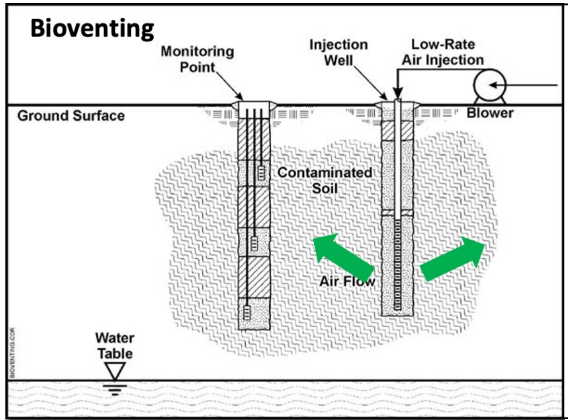
Figure 2-2. Vapor transport–related NSZD processes.

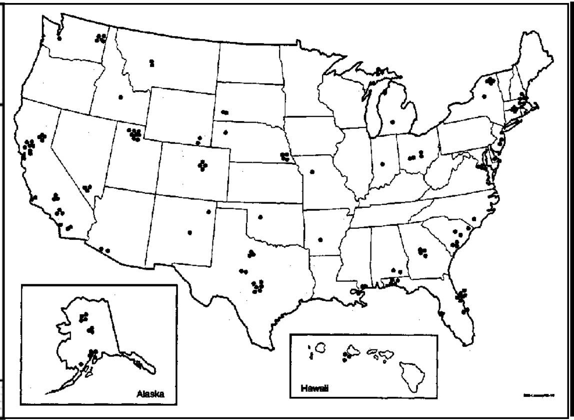


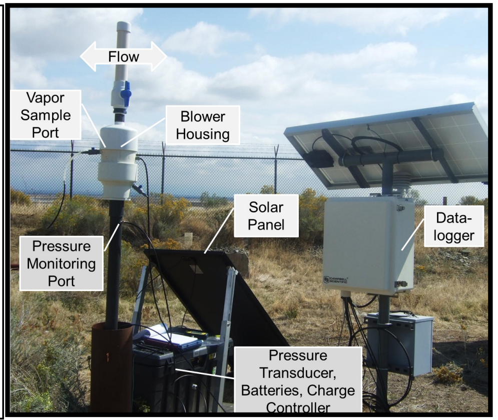


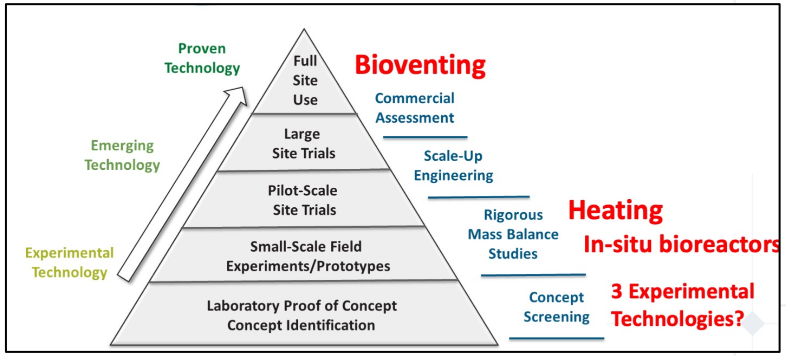












SPARE SLIDES

Traditional Bioventing Configuration

GSI ENVIRONMENTAL

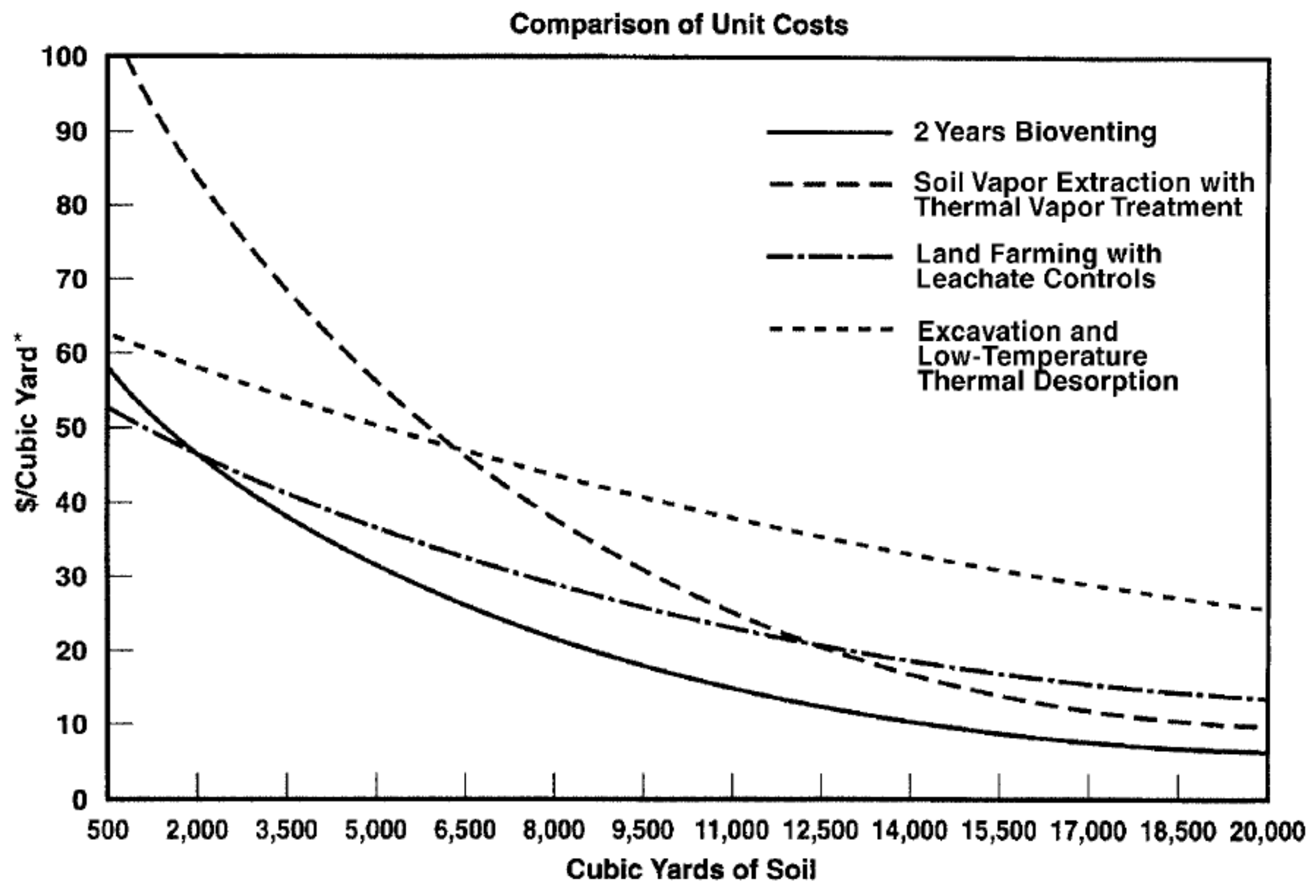
United States Environmental Protection Agency | Office of Research and Development Washington, DC 20460 | EPA/625/XXX/001 September 1995

EPA

Manual

Bioventing Principles and Practice

Volume II: Bioventing Design

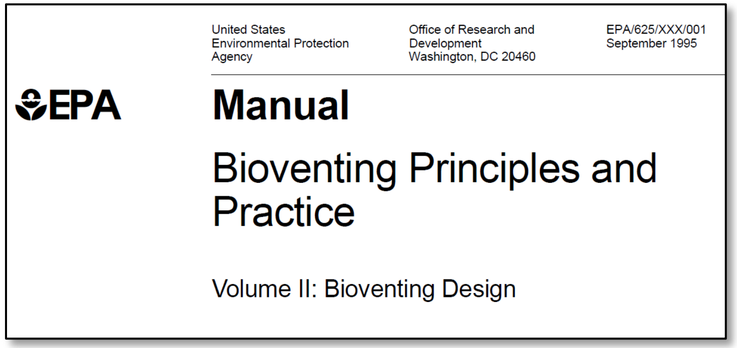


* Based on treatment of soil contaminated with 3,000 mg of JP-4 jet fuel per kg of soil. Costs do not include the cost of reconstructing excavated sites.

Figure 5-1. Comparison of costs for various remedial technologies for fuel-contaminated soils (Downey et al., 1994b).

Traditional Bioventing Configuration

GSI ENVIRONMENTAL


United States Environmental Protection Agency
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Base	Site Type	Air Injection Depth (ft)	Air Injection Rate (cfm)	Area of Influence (ft^2)
Beale AFB, CA	Fire Training Pit	10 - 25	30	6,500
Bolling AFB, DC	Diesel Spill	10 - 15	20	5,100
Eielson AFB, AK	JP-4 Spill	6.5 - 13	30	43,600
Fairchild AFB, WA	JP-4 Spill	5 - 10	15	5,100
McClellan AFB, CA	JP-4 Spill	10 - 55	50	9,700
Plattsburgh AFB, NY	Fire Training Pit	10 - 35	13	11,500

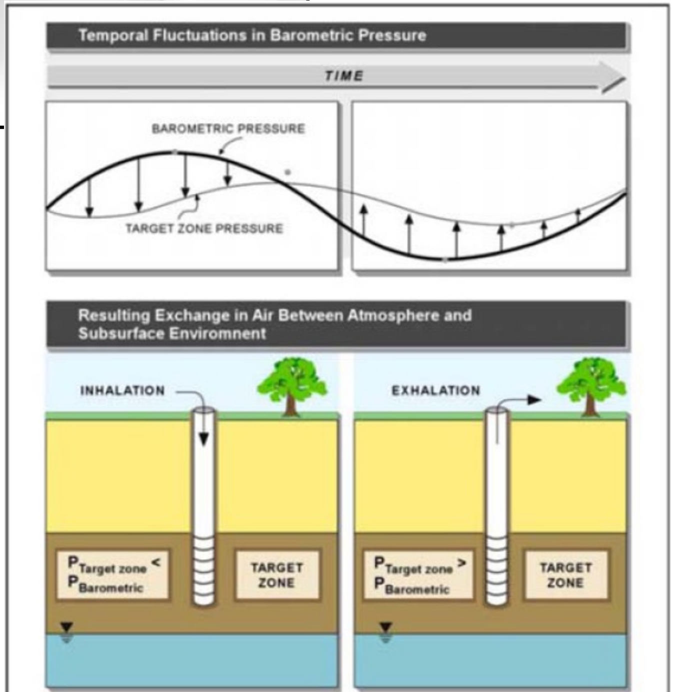
NSZD Five Methods: A Quick Subjective Compare and Contrast

GSI ENVIRONMENTAL

	Advantages?	Disadvantages?
1. The Gradient Method	Two ways: O_2 and CO_2	Need vapor probes, sensitive to soil D_e, need background correction, vertical 1D assumption not always valid
2. Dynamic Closed Chambers	Quick, good for spatial snapshot	Spatial, temporal variability, not applicable on paved surfaces, need background correction
3. Carbon Dioxide Traps	Easy to use, ^{14}C analysis (background correction)	Spatial, temporal variability, more difficult to apply to paved surfaces
4. Thermal NSZD Methods	Good temporal coverage, likely can use existing wells	Equipment cost, thermal conductivity estimate, need background correction if < 1 year of data
5. LNAPL Composition	No drilling needed, no background correction	Need LNAPL compositions from same location over long periods of time intervals (>5-10 yrs)

Comparison of Four NSZD Methods (Kulkarni et al., 2020)

BaroBalls



Kamath et al., 2010

Inverted BaroBall

- Typical flowrates: 0.1 - 1.0 scfm
- Relies on atmospheric pressure gradients – one way flow expected 50% of time
- Cost per Unit: ~$200

"Application of Four Measurement Techniques for NSZD" (Kulkarni et al., 2020)

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Groundwater Monitoring&Remediation

Check for updates

Application of Four Measurement Techniques to Understand Natural Source Zone Depletion Processes at an LNAPL Site

by Poonam R. Kulkarni, Charles J. Newell, David C. King, Lisa J. Molofsky and Sanjay Garg

Table 1
Measurement Methods and Time Period of Installation at Each Location

Location	Carbon Trap	Gradient Method[1]	DCC LI-COR[1]	Thermal NSZD[1]	IsoFlask Sampling
L2	2 events + Duplicate	2 events	2 events	Continuous 1 year	2 events
L4	2 events	2 events	2 events	Continuous 1 year	n/a
L5	2 events	2 events	2 events	Continuous 1 year	2 events
L8[2]	—	—	—	—	2 events
L9[2]	—	—	—	—	2 events

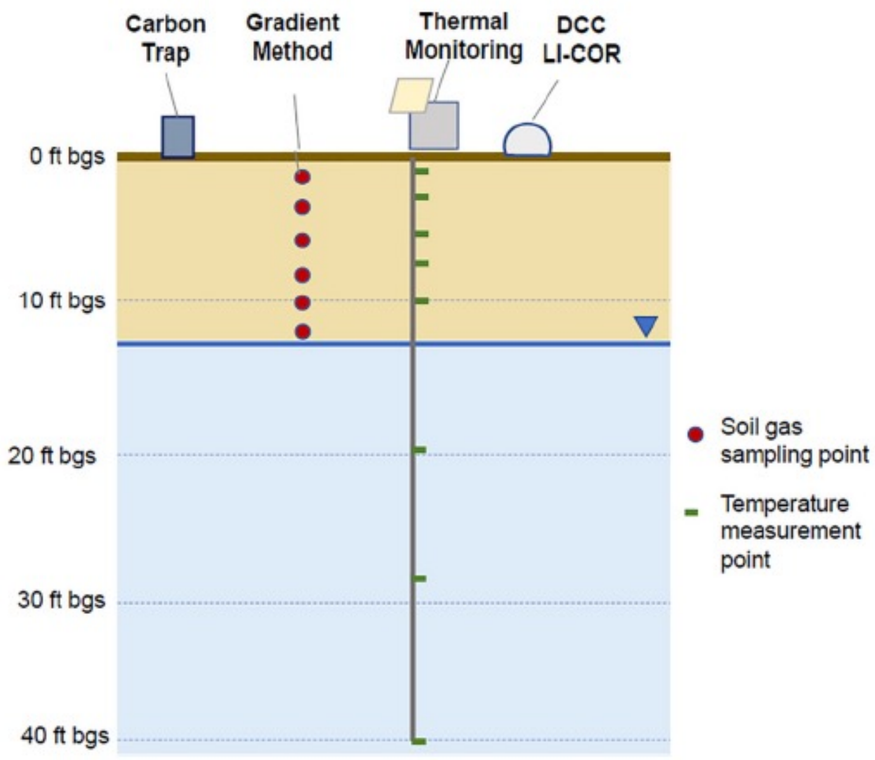


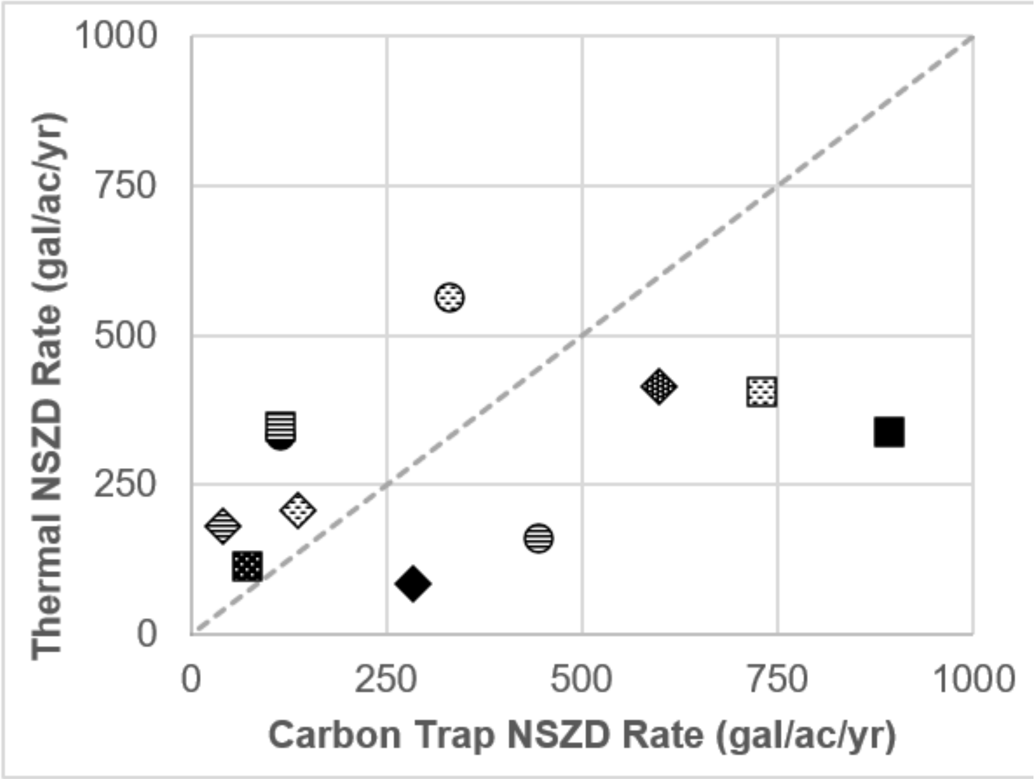
Figure 3. Conceptual diagram of measurement methods installed at locations.

Kulkarni et al. (2020)

Shell / GSI Environmental "Spatio-Temporal" NSZD Research Project: *What is Correlated to NSZD Rates?*

Correlation NSZD Rates for Two NSZD Methods

$r^2 = 0.4$

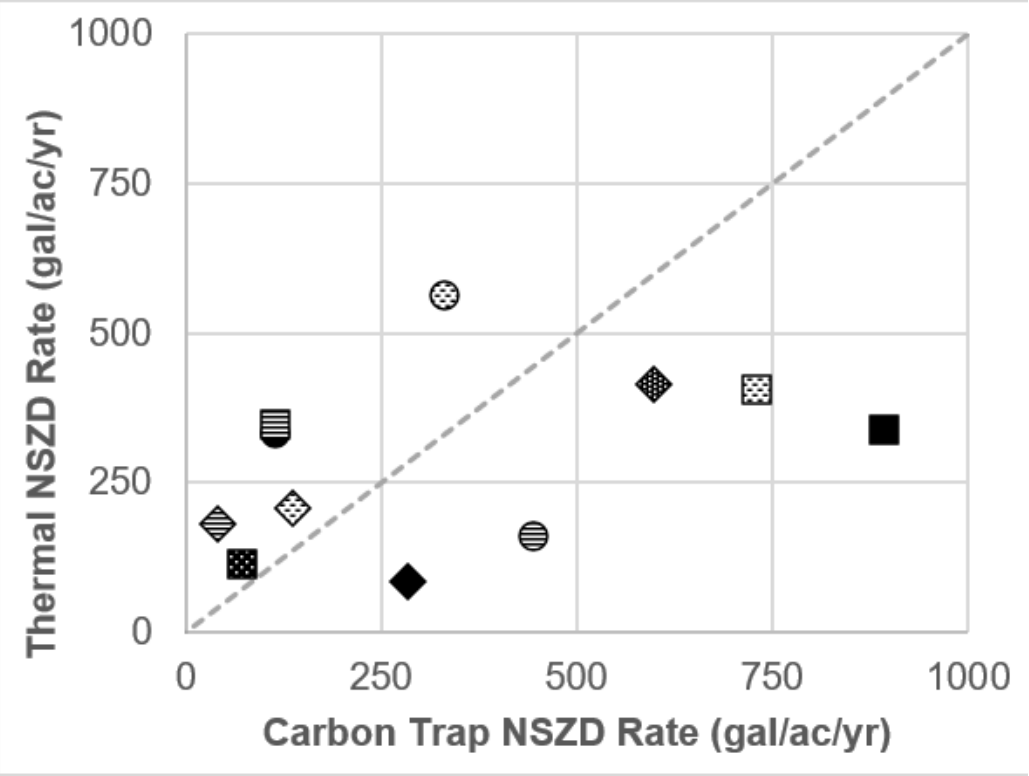


	THERMAL NSZD		CARBON TRAPS	
Variable	*Spearman's r and p-value*	*Confidence in Trend*	*Spearman's r and p-value*	*Confidence in Trend*
Maximum TPH Concentration in Soil	(0.7) 0.05	**High**	(0.2) 0.55	Low
Depth of Maximum TPH	(0.5) 0.17	Limited	(0.7) 0.06	**High**
Benzene Concentration in Groundwater	(0.5) 0.10	Limited	(0.7) 0.01	**High**
% ROST Signal in Unsaturated Zone	(-0.6) 0.05	**High**	(-0.6) 0.04	**High**
Specific Volume	(0.3) 0.40	Low	(0.4) 0.27	Limited
Lithology: % Fines (Silts and Clays)	(-0.3) 0.45	Low	(-0.4) 0.19	Limited
Lithology: % Clay	(-0.6) 0.07	**High**	(-0.7) 0.02	**High**
nC17: Pristane Ratio	(0.3) 0.46	Low	(0.6) 0.08	**High**
Portion of TPH with >nC12 (%)	(0.5) 0.15	Limited	(-0.1) 0.91	Low

Shell / GSI Environmental "Spatio-Temporal" NSZD Research Project: *What is Correlated to NSZD Rates?*

Correlation NSZD Rates for Two NSZD Methods

$r^2 = 0.4$



	THERMAL NSZD		CARBON TRAPS	
Variable	*Spearman's r and p-value*	*Confidence in Trend*	*Spearman's r and p-value*	*Confidence in Trend*
Maximum TPH Concentration in Soil	(0.7) 0.05	High	(0.2) 0.55	Low
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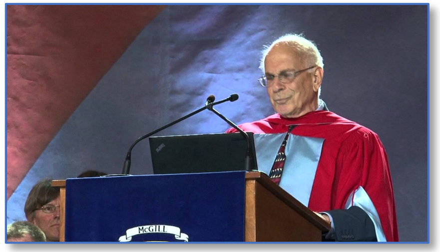
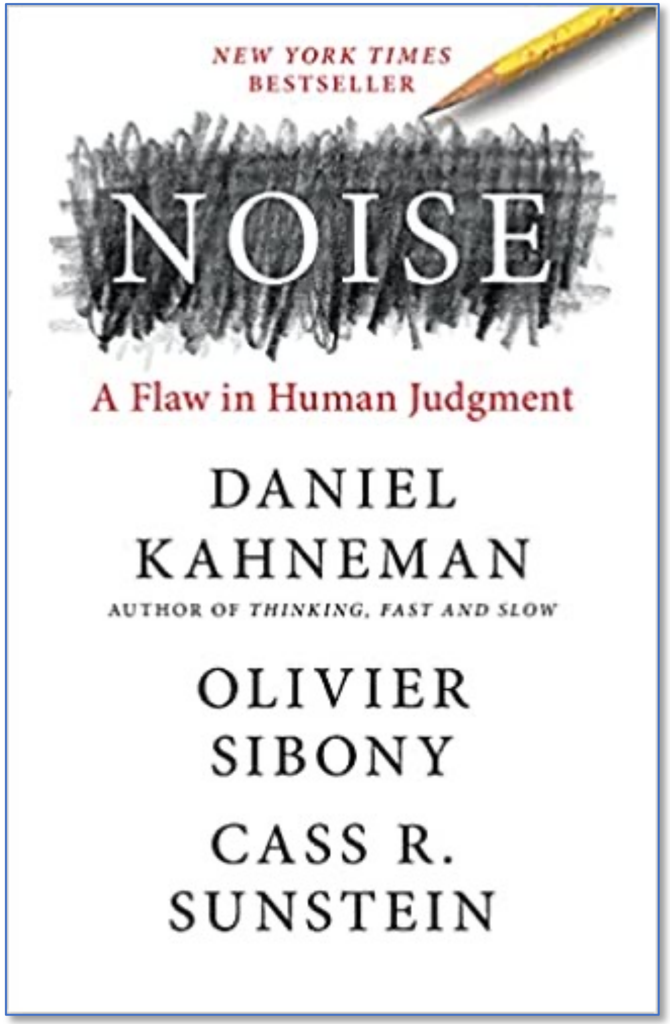
Benzene Concentration in Groundwater	(0.5) 0.10	Limited	(0.7) 0.01	High
% ROST Signal in Unsaturated Zone ***Negative Correlation***	(-0.6) 0.05	High	(-0.6) 0.04	High
Specific Volume	(0.3) 0.40	Low	(0.4) 0.27	Limited
Lithology: % Fines (Silts and Clays)	(-0.3) 0.45	Low	(-0.4) 0.19	Limited
Lithology: % Clay in Log ***Negative Correlation***	(-0.6) 0.07	High	(-0.7) 0.02	High
nC17: Pristane Ratio	(0.3) 0.46	Low	(0.6) 0.08	High
Portion of TPH with >nC12 (%)	(0.5) 0.15	Limited	(-0.1) 0.91	Low

Noise: A Flaw In Human Judgment (Kahneman, Sibony, and Sustein, 2021)



Kahneman, Sibony and Sunstein argue that noise in human judgment is a thoroughly prevalent and insufficiently addressed problem in matters of judgment. They write that noise arises because of factors such as cognitive biases, mood, group dynamics and emotional reactions. While contrasting statistical bias to noise, they describe cognitive bias as a significant factor giving rise to both statistical bias and noise. (Wikipedia)



NSZD Conceptual Model (Most Sites)

(Garg et al.,2017)