E·FLUX

Easy set-up. Expert results.

THE IMPORTANCE OF NATURAL SOURCE ZONE DEPLETION (NSZD) FOR THE MANAGEMENT OF LNAPL SITES

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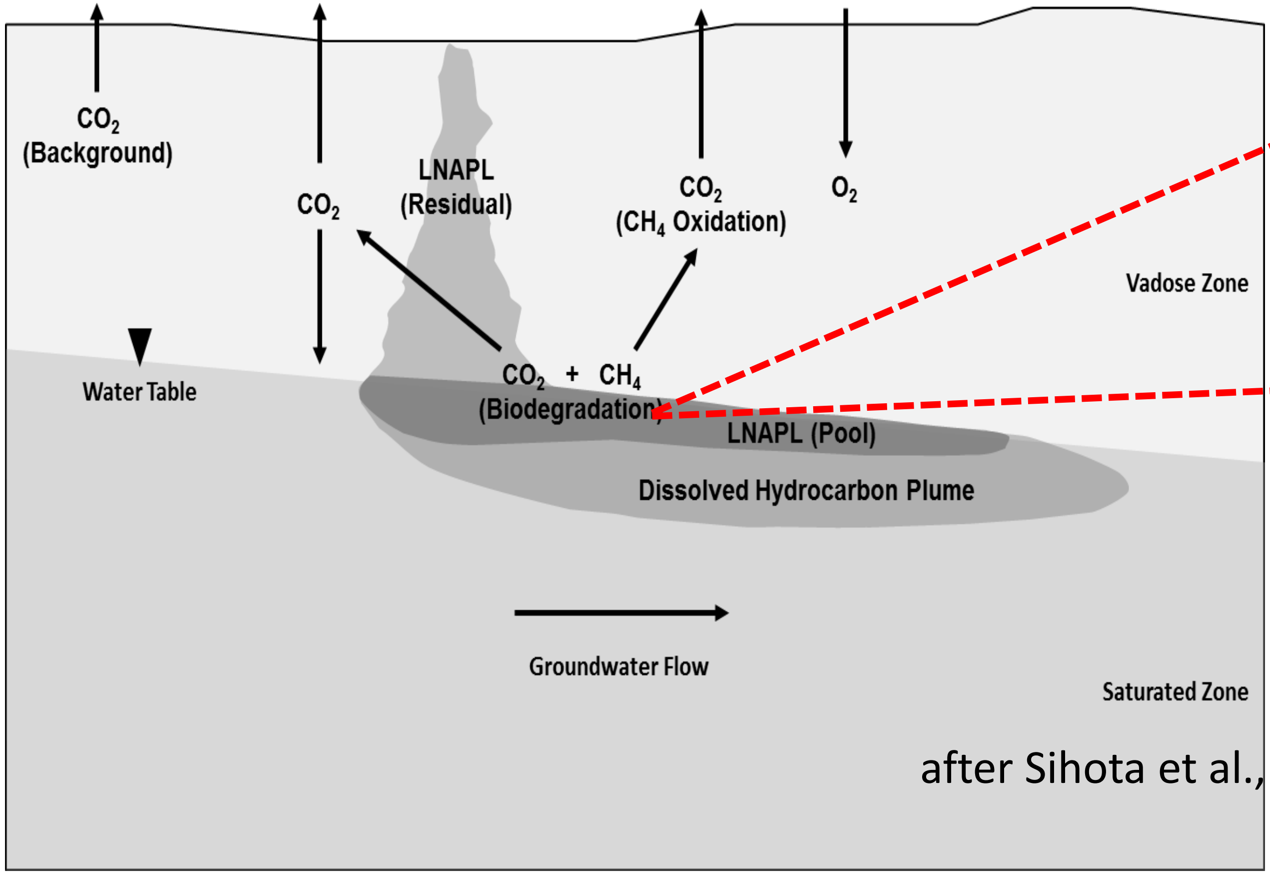
NATIONAL TANKS CONFERENCE WORSHOP

SEPTEMBER 10, 2018

Background



after Sihota et al., 2011

Mechanisms

- Volatilization
- Dissolution
- ***Biodegradation***

Most of the contaminant degradation (~ 98%) is emitted as CO_2 at ground level

Molins et al. 2010 – modeling study

Outline

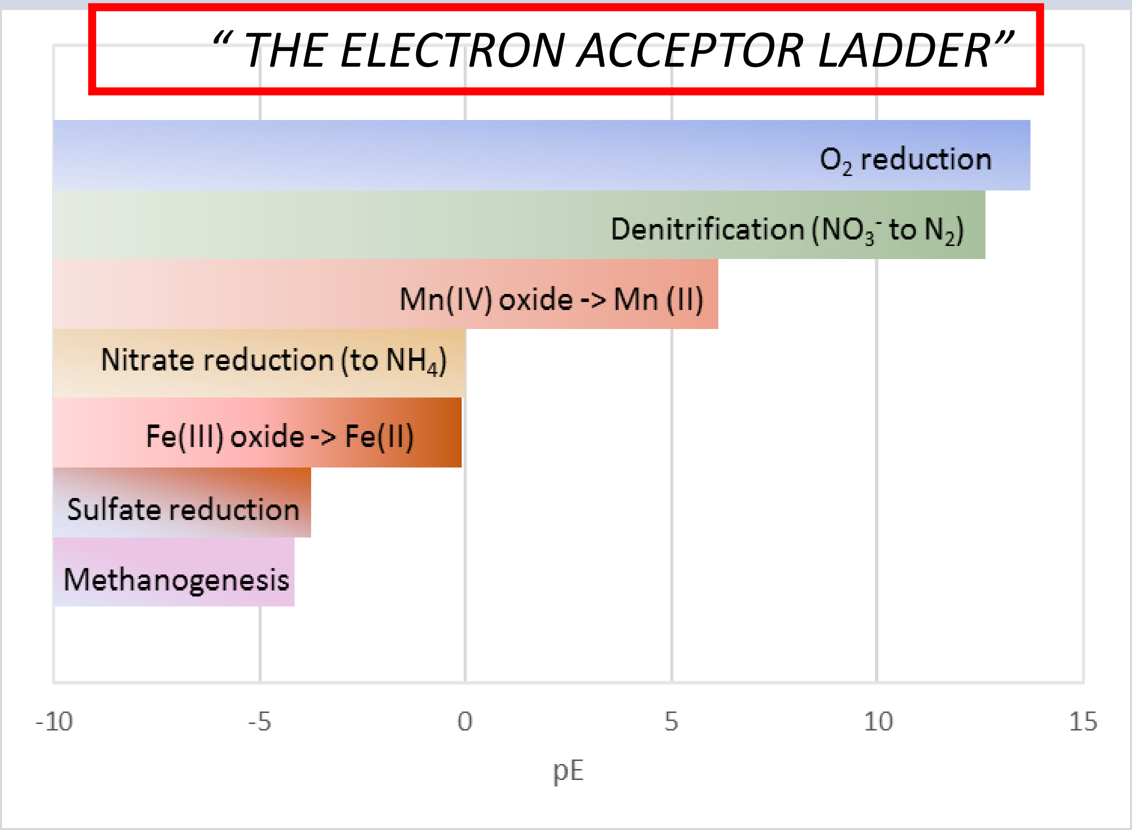
1. Geochemistry overview
2. Rate measurement methods: mass balances
3. Use of carbon isotopes for NSZD rate estimates
4. Case studies
5. Current developments
    - Soil temperatures
    - Other contaminants

Presentation Based on:

2014-2015 ITRC LNAPL Class
2015 Tanks Conference Workshop
2016 ASTSWMO Spring Meeting Workshop

Guidance Documents
2017 API Guidance on NSZD Methodologies
2018 LNAPL ITRC Guidance Document
Soon: RC Care Australian Guidance Document onf SZNA

Electron acceptors for petroleum oxidation

Oxidation (generates e-)	Reduction (accept e-)
$C_nH_{n+2}O_m + \rightarrow n\ CO_2 +$	

From: ITRC 2018 LNAPL Guidance Document, after Stumm and Morgan, 1981

The ITRC framework

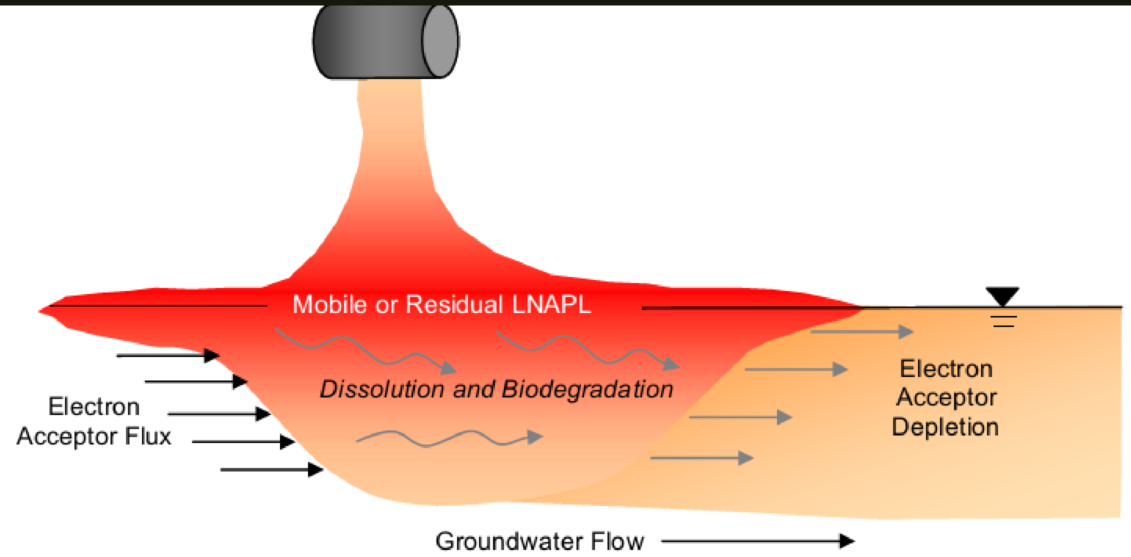


Figure 2-1. Groundwater transport–related NSZD processes.

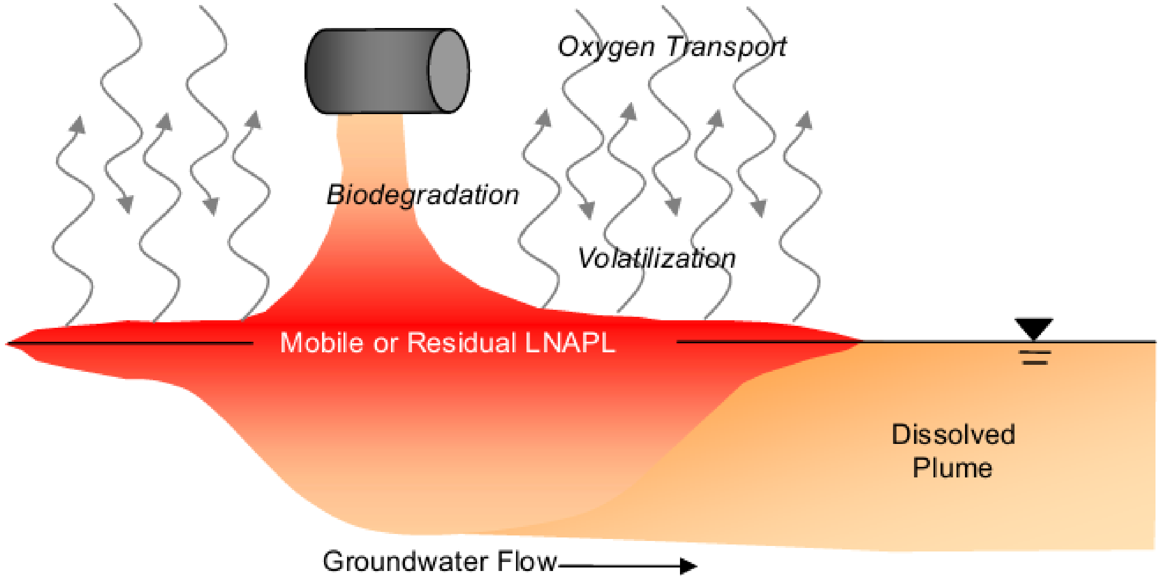
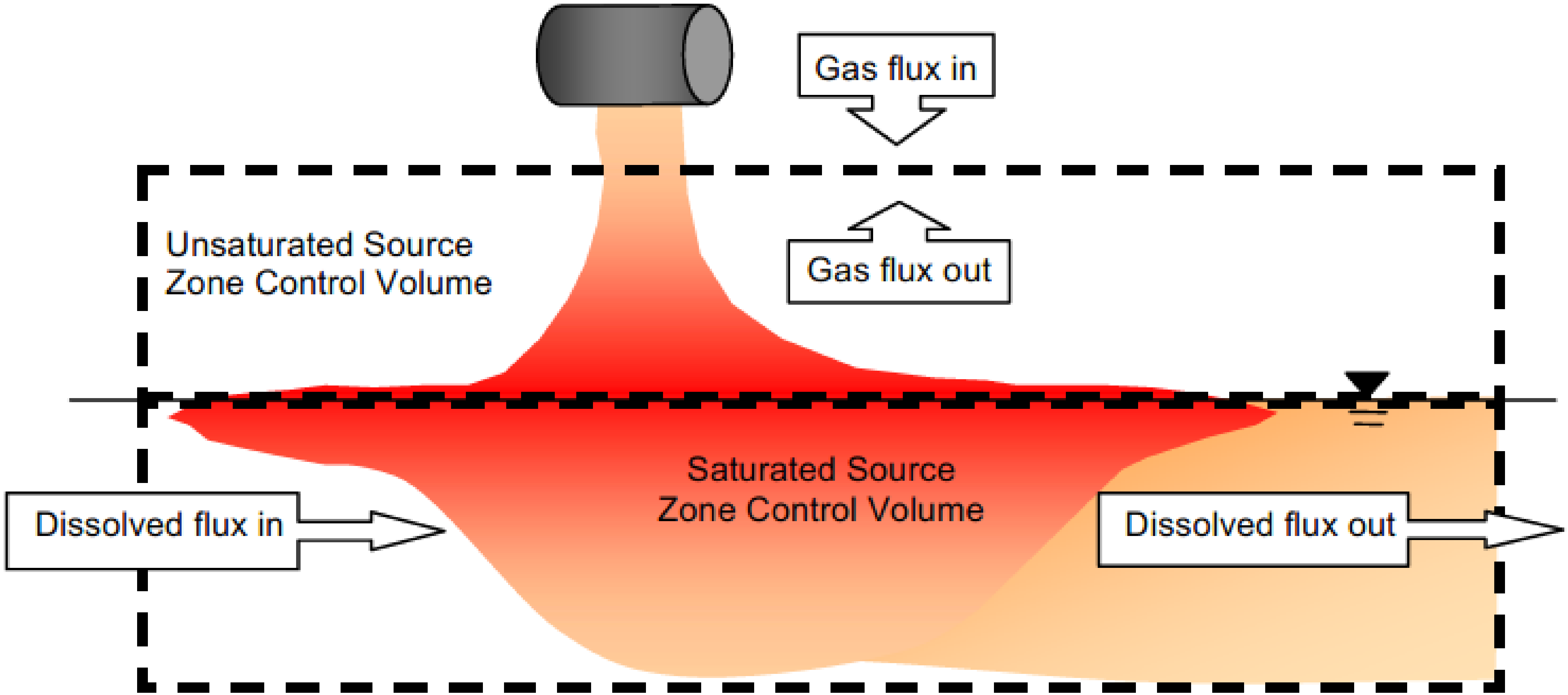


Figure 2-2. Vapor transport–related NSZD processes.

ITRC, 2009 : Evaluating NAPL NSZD

The ITRC framework



Depletion rate = $f(\text{flux}_{in} - \text{flux}_{out})$

Figure 3-2. Example control volume “box” for quantitative assessment of NSZD.

ITRC, 2009 : Evaluating NAPL NSZD

Units for Vadose Zone NSZD Processes

- CO_2 → µmol/m²/sec

  Unit of raw measurement

- LNAPL → gal/acre/yr

  Unit for remediation metrics

$$\text{Flux}_{\text{total}} = \text{Flux}_{\text{natural}} + \text{Flux}_{\text{NSZD LNAPL}}$$

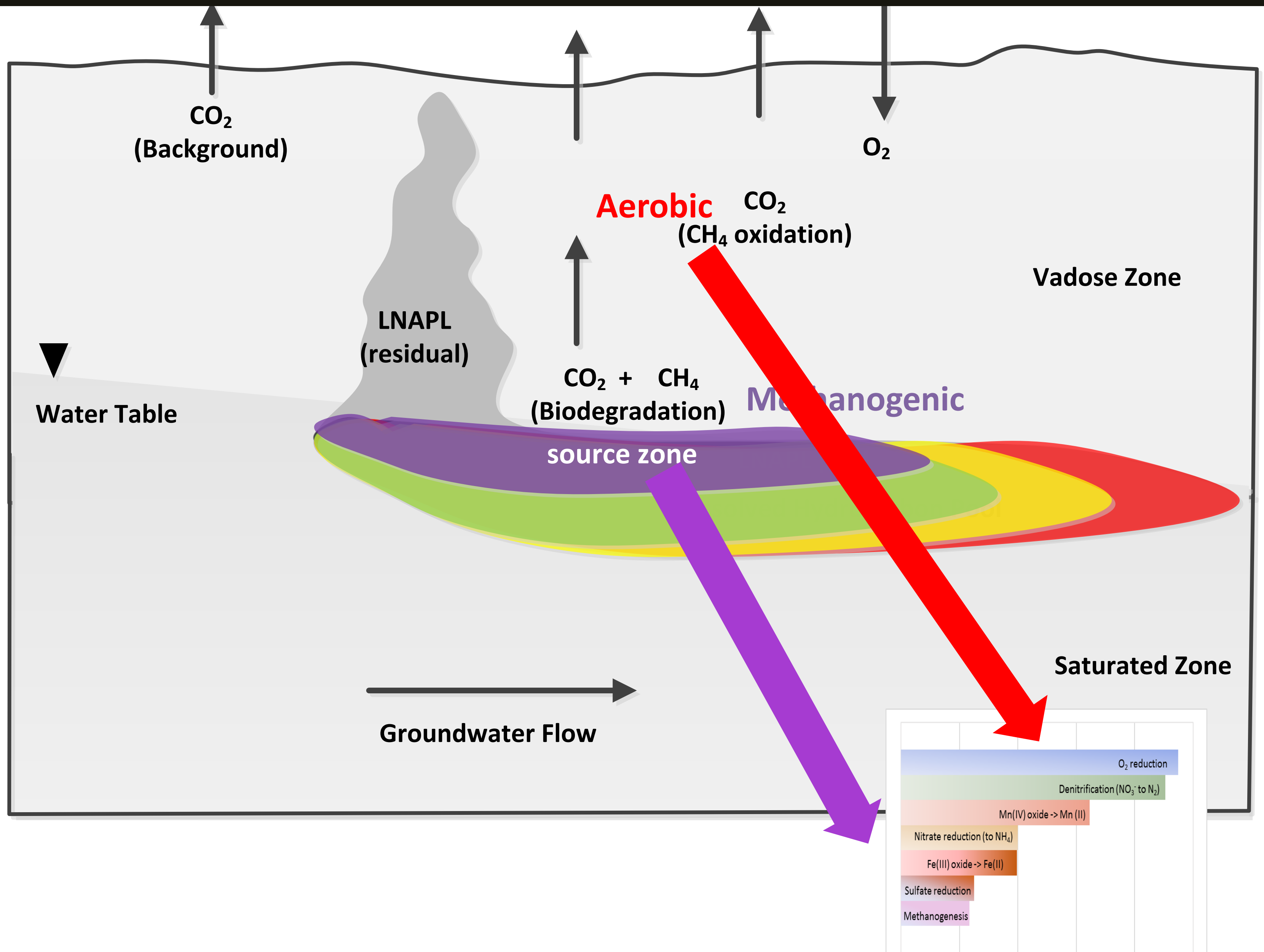
Vadose Zone vs. Groundwater NSZD rates

"mass losses from the submerged part of the source zone and involving ground water transport processes (i.e., dissolution and biodegradation) were estimated to be about approximately **2 orders of magnitude lower**"

Lundegard and Johnson, 2006

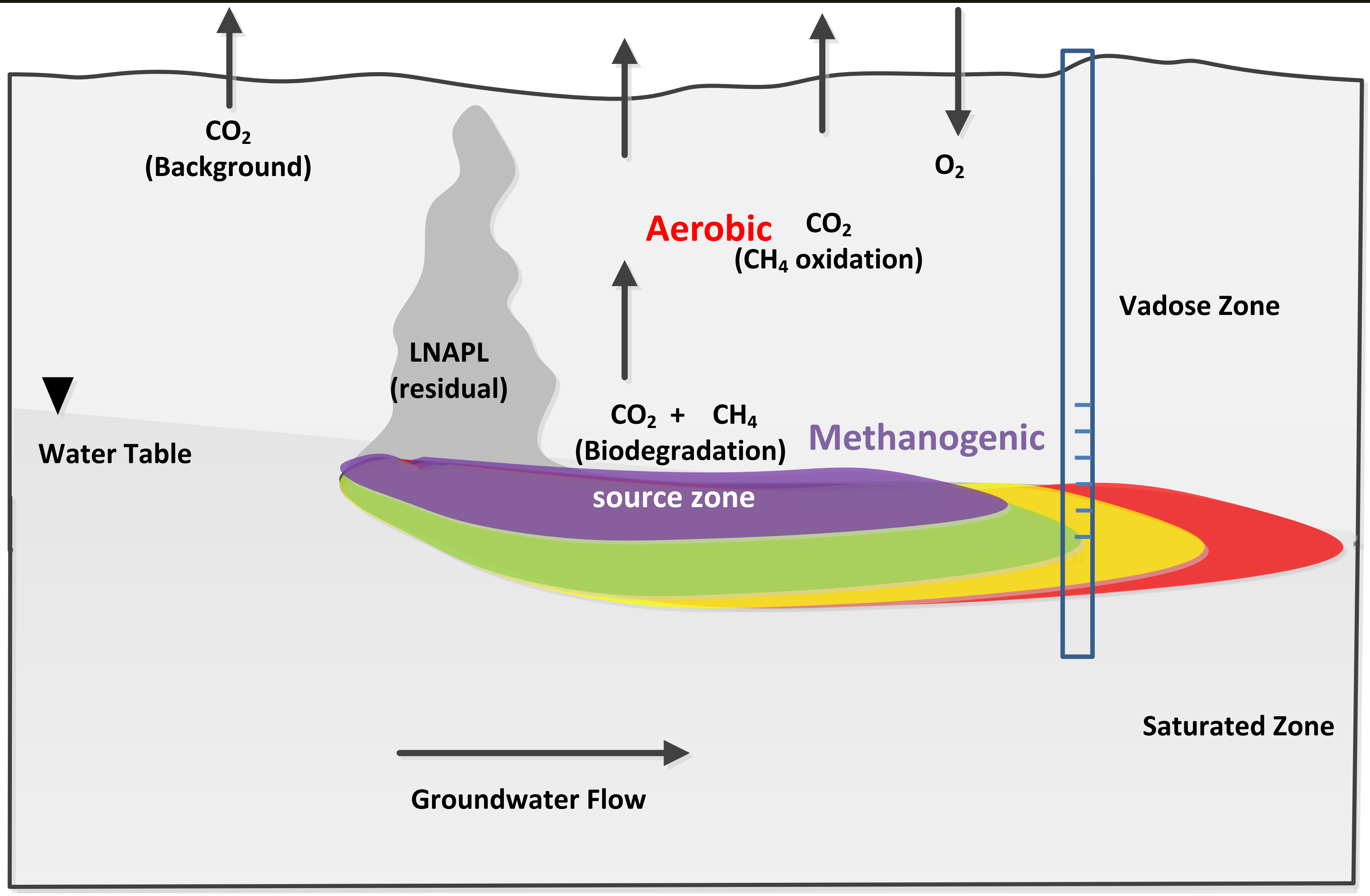
Vadose zone processes seem dominant- biggest bang for the buck

Vadose Zone: Mostly two zones

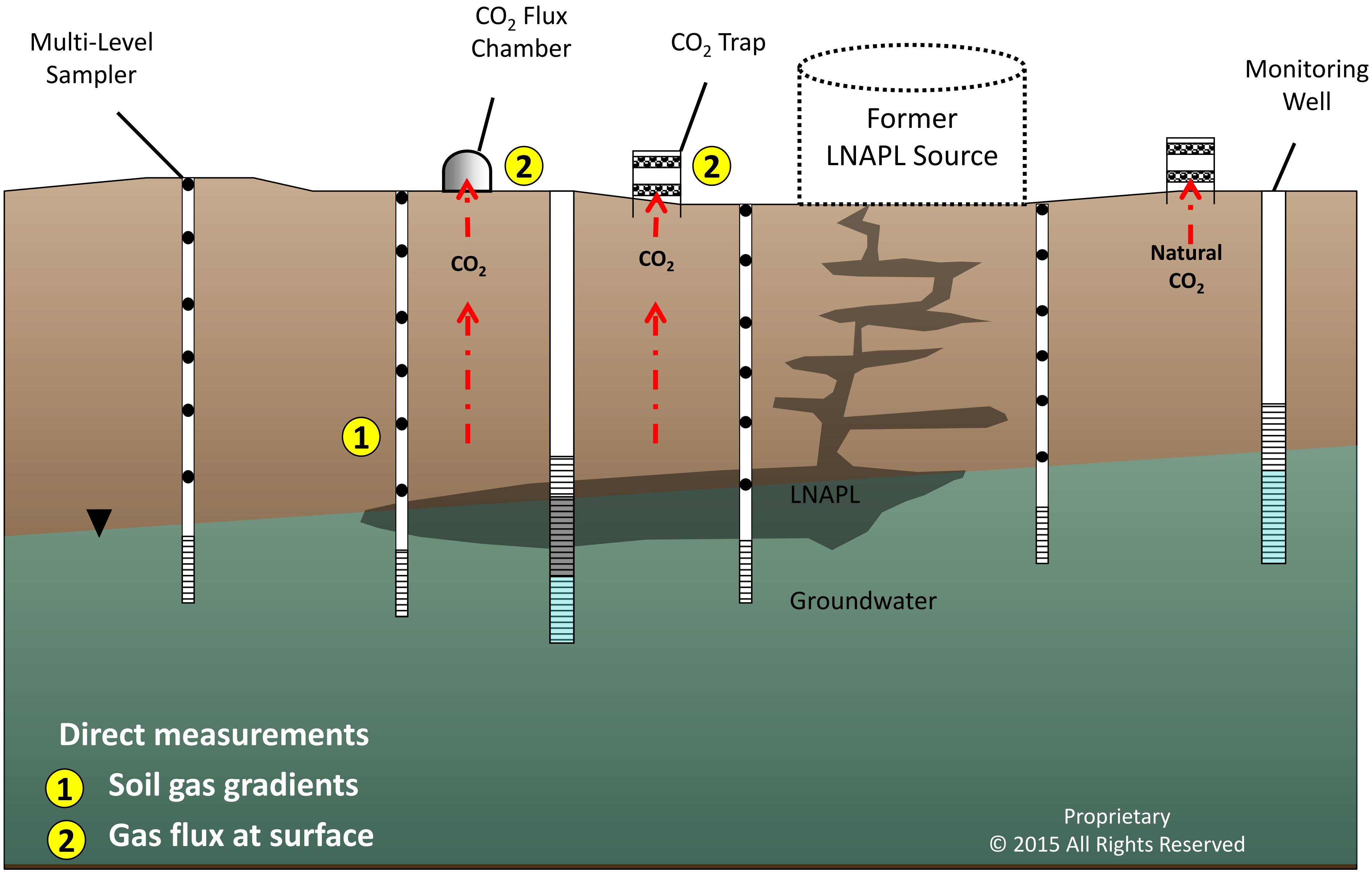


See real example at Lovley et al, 1994

Traditional gw sampling is depth integrated



NSZD Rate Measurement Alternatives

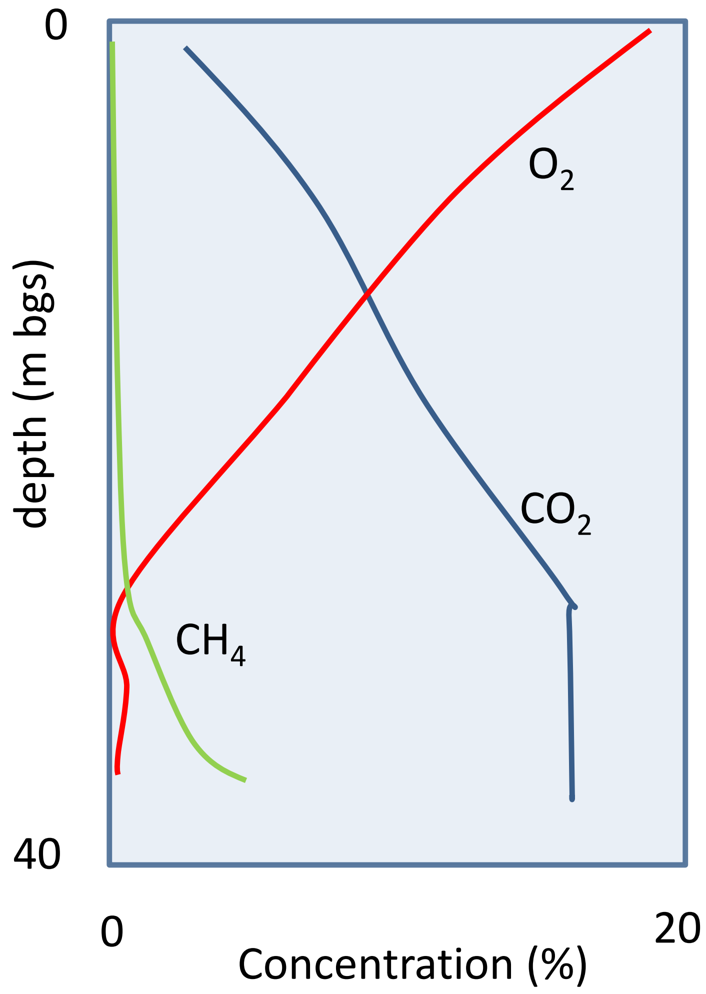


Gradient Method

- Concentration profiles in soil fitted to Fick's 2nd law of diffusion:

$$J = D_{eff,i} \frac{\partial Ci}{\partial z}$$

- Included in ITRC guidance document
- Main advantage: can indicate the location of specific soil processes (i.e., methanogenesis)
- Limitations:
  - Labor intensive: field + post-processing
  - Soil transport properties co-current with concentration profiles
  - Assumes diffusion is only transport mechanism
  - Not for: reactive species, changing conditions, advection important?



Lundegard and Johnson, 2006

Deff from Johnson et al, 1998

Gradient Method

- Estimating in-situ diffusion coefficients (D_{eff})
- Similar to push-pull test, but for gases
- Inject a tracer gas into the soil
- Recover it
- Fit the recovery curve to a diffusion model

- Limitations
  - Point estimation (in time and space)
  - D_{eff} changes with
    - Soil properties (including moisture)
    - Temperature
    - Location/time

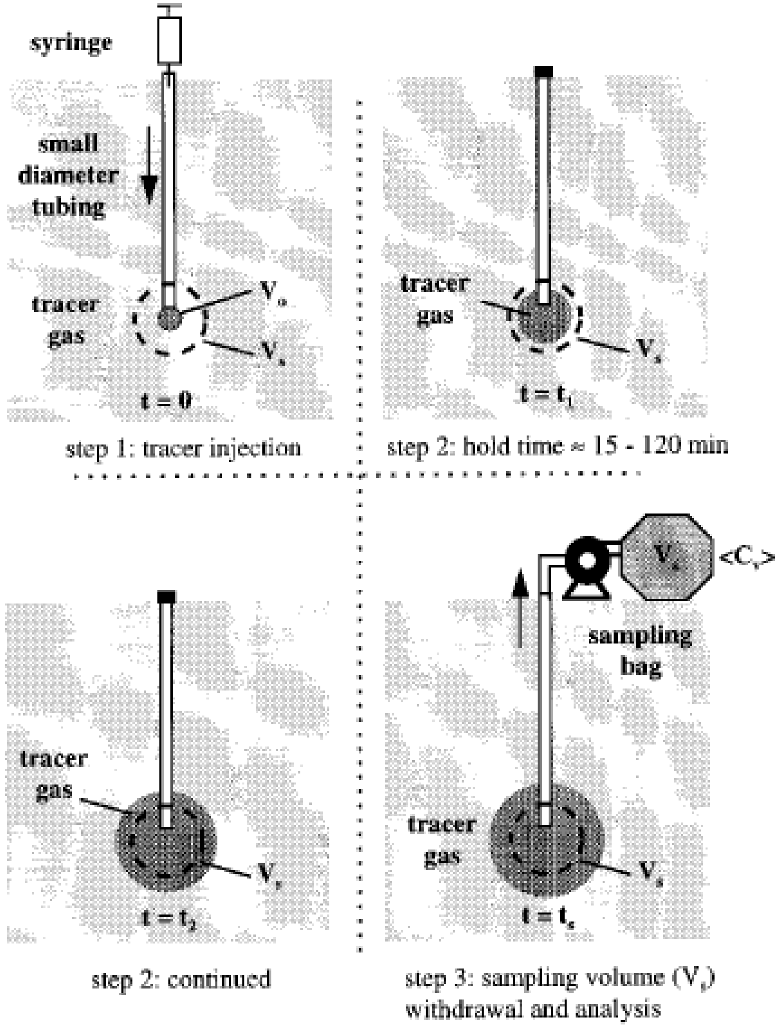
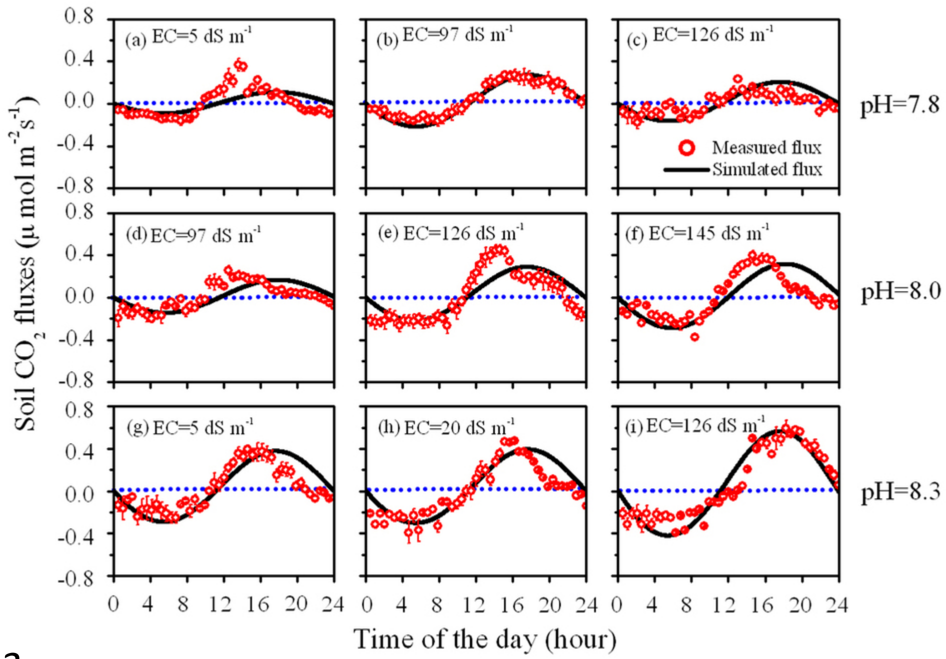


FIGURE 1. Generalized schematic of in situ measurement approach.

Deff from Johnson et al, 1996

Dynamic Flux Chambers

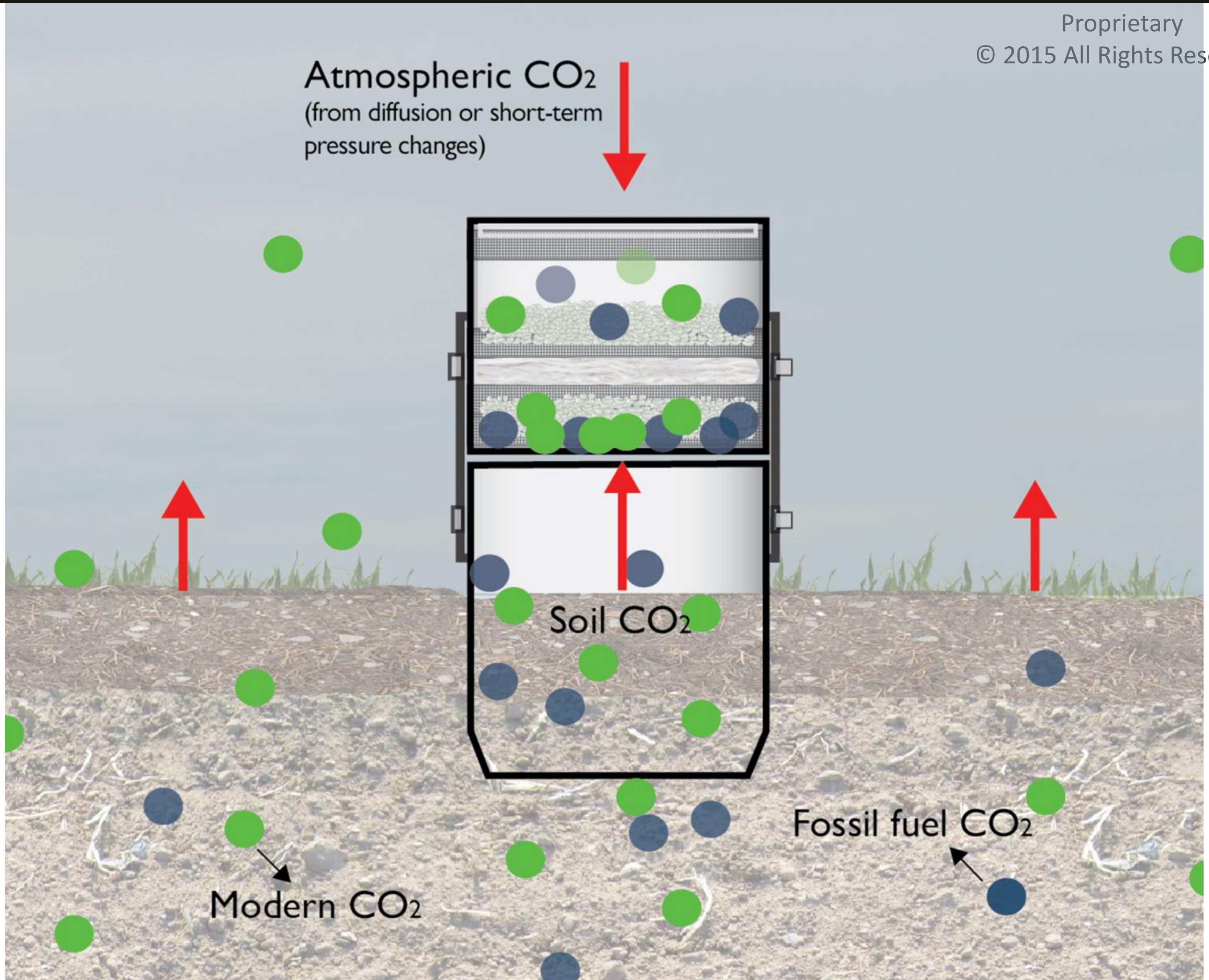
- Developed as short term measurement (although fluxes change rapidly)
- Full time series needed for long term estimates
- Not carbon isotope friendly (field method)
- Best suited as screening tool?
- Mostly for CO_2,
  - but adaptable to other soil gases (need real time sensor)
- Diffusion + advection



Ma et al, 2013,
used with permission

CO_2 traps

CO_2 traps



Proprietary
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Atmospheric CO2
(from diffusion or short-term pressure changes)
Soil CO2
Fossil fuel CO2
Modern CO2

CO_2 traps

- Field efforts are minimal
- No power nor moving parts
- Field method but lab analysis (easy to do carbon isotopes)
- Time integrated flux (long term)
- Diffusion + advection (sorbent is porous and allows free air flow)
- Longer turnaround time (i.e., 4 weeks)

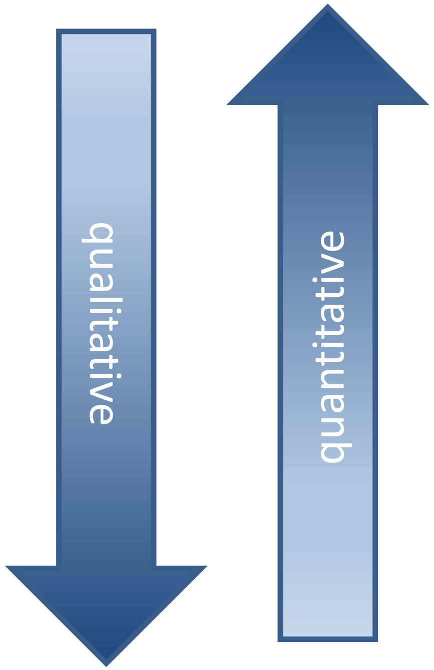
Comparison of Methods for CO_2 flux

	Gradient Method	Passive CO_2 Traps	Dynamic CO_2 Chambers
Field Design	Wells/vapor points in vadose zone	Install soil pipe collar into shallow soils	Install soil pipe collar into shallow soils
Measurement period	Few hours	1-4 weeks	5-15 min
Total Field time	2-5 days	2 days	2 days
Advantages	Insight into depth-dependent processes	Long term average ^{14}C- corrected data Easiest to implement	Fast turnaround time
Data Analysis	Fick's law of diffusion	Lab-based analysis	Software
Correction for non-LNAPL related CO_2	Compare to unimpacted, or ^{14}C-corr. analysis (multiple samples)	^{14}C-corrected analysis	Compare to unimpacted, or ^{14}C-corr. analysis (multiple samples)
Cost (assume 10 locations)	$$$	$$	$

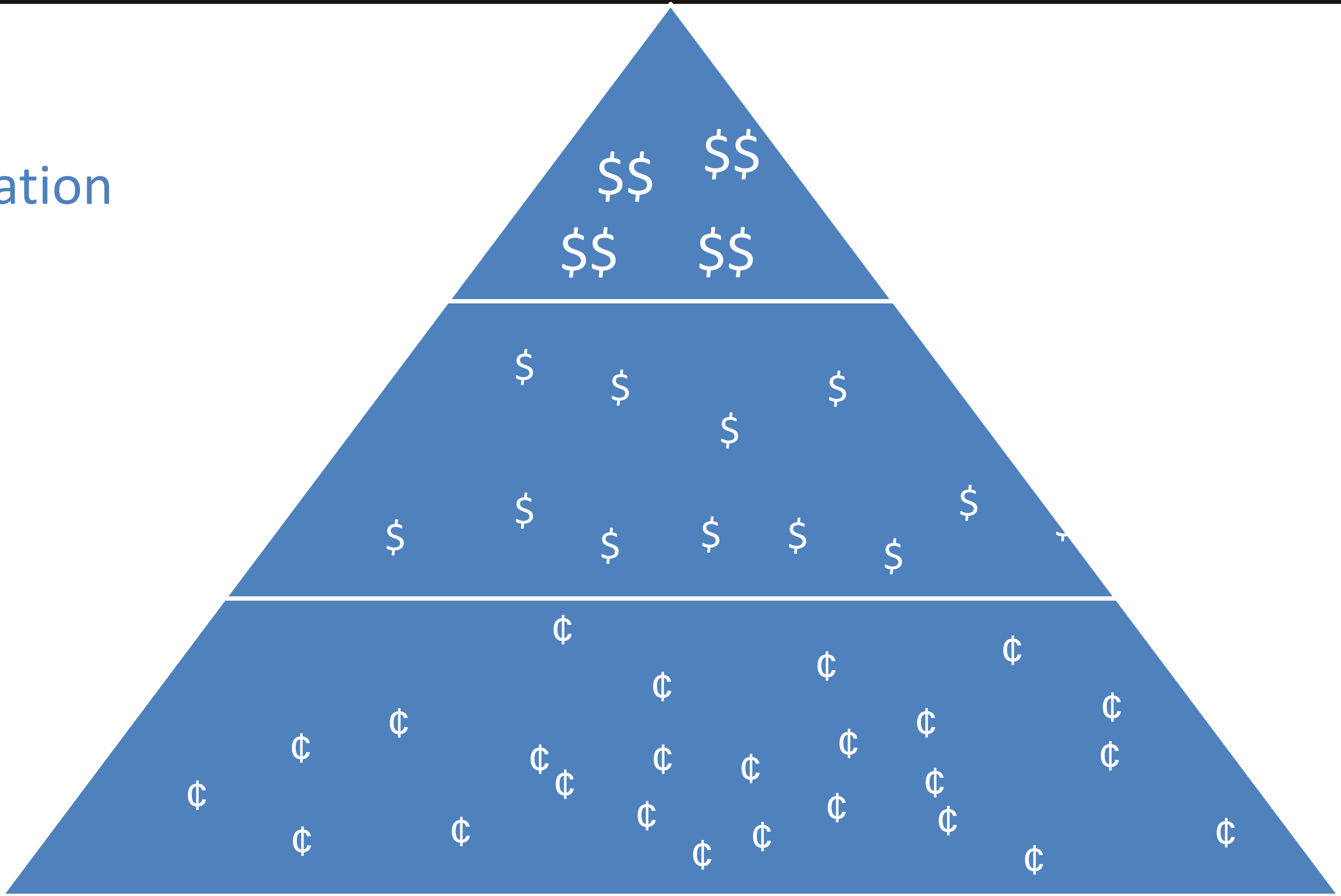
Adapted from de Courcy-Bauer et al, 2015

NSZD data quality

NSZD rate quantitation



Line of evidence



Accounting only from LNAPL-derived CO_2 flux

- Accounting for fluxes associated with NSZD (not natural processes)
  - Background correction

$$J_{CSR} = J_{TSR} - J_{NSR}$$

  - ^{14}C analysis

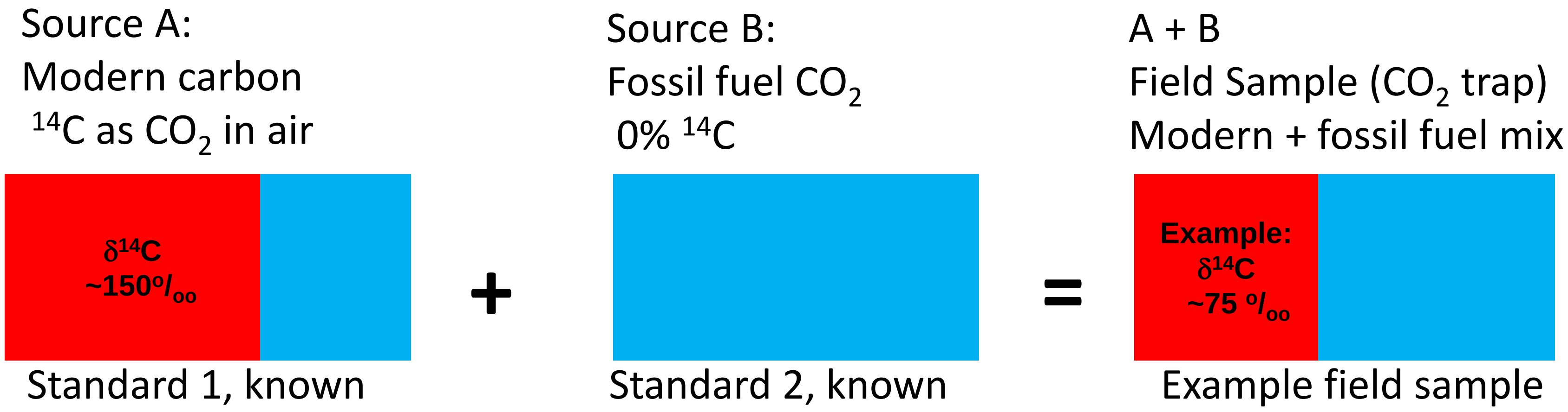
Sihota et al 2011

total carbon = modern + fossil fuel

ASTM C6866-12

^{14}C-based two source model (fossil fuel vs. modern)

ASTM Method D6866-12 is a 2-source model based on ^{14}C analysis



In the example sample with half the ^{14}C than a modern one, fossil fuel contribution is 50% and 50% modern (i.e., from natural soil and plant activity).

^{14}C analysis allows to determine the fossil fuel contribution in the captured CO_2 in the traps.

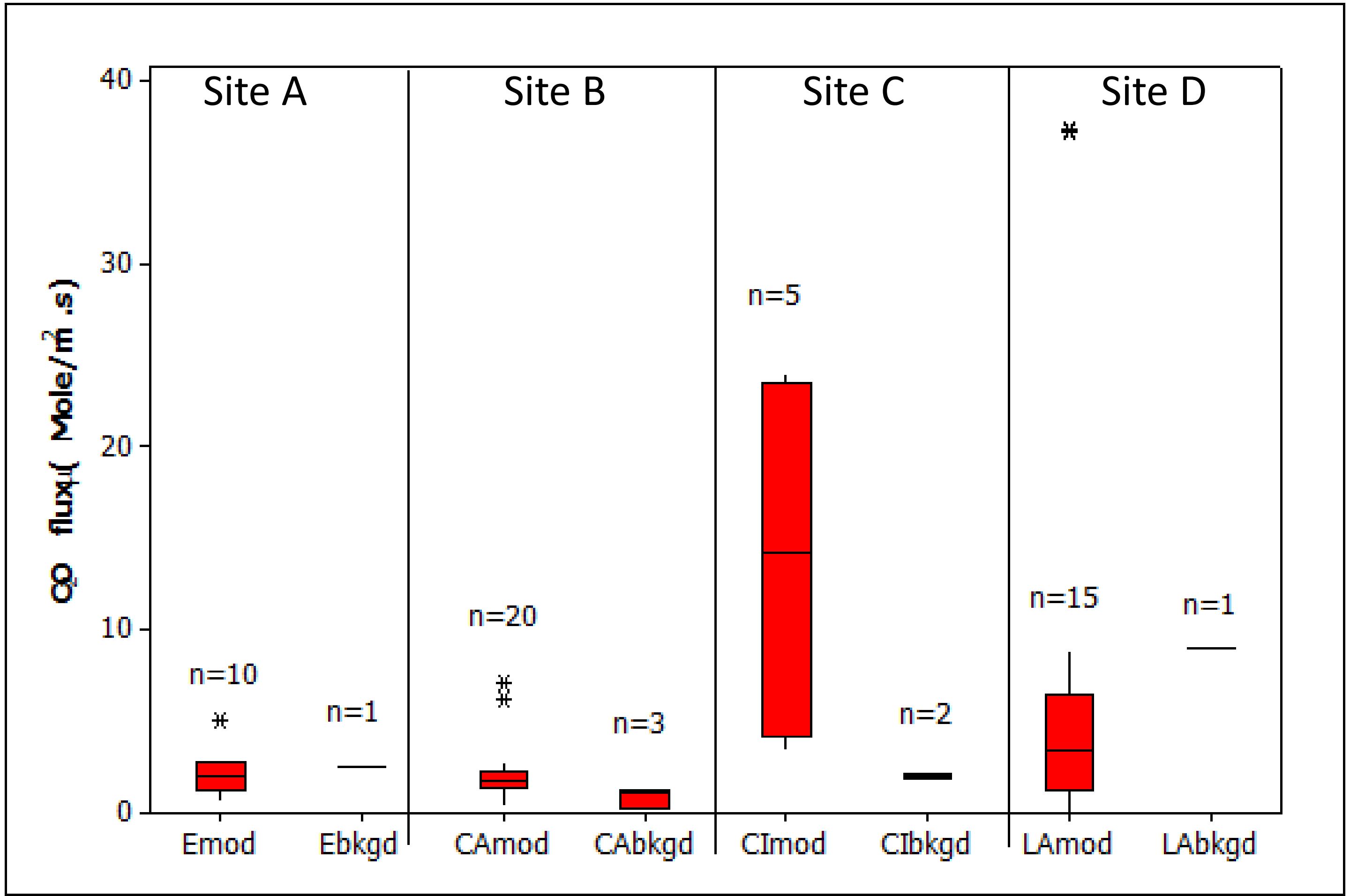
^{14}C analysis vs Background: signal not related to LNAPL

- ^{14}C analysis total carbon = modern + fossil fuel

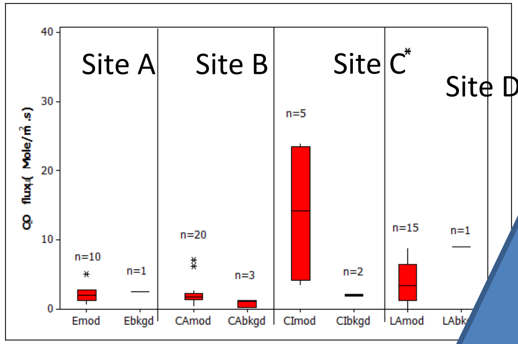
ASTM C6866-12

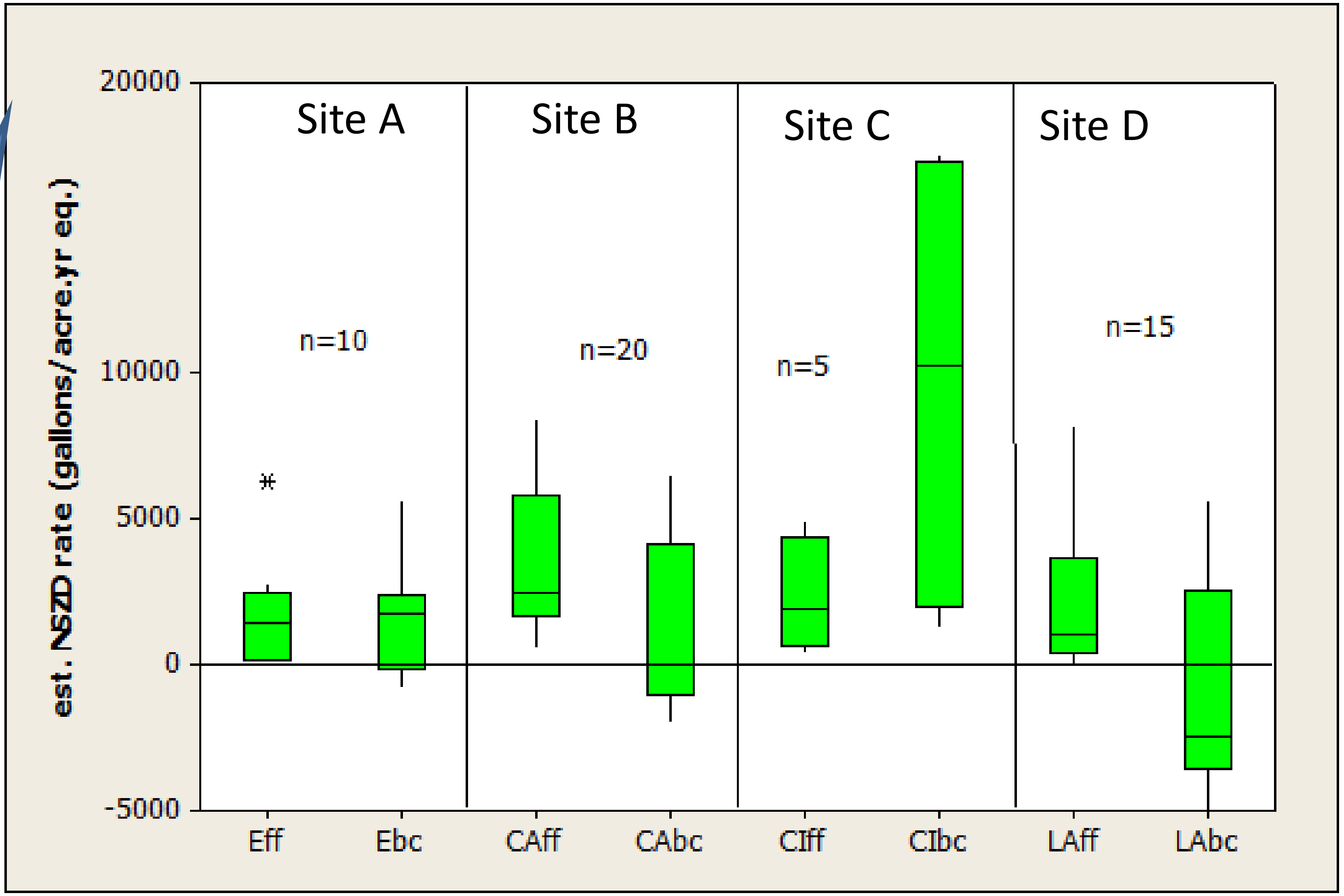
- Background correction $J_{CSR} = J_{TSR} - J_{NSR}$

Sihota et al 2011



^{14}C analysis vs Background: NSZD Rate Estimates





Background correction assumes vegetation and other modern CO_2 generating processes are similar between impacted and unimpacted locations

^{14}C analysis allows location specific measurement of fossil fuel derived CO_2 fluxes

Background correction results in larger variability estimates than those using ^{14}C analysis

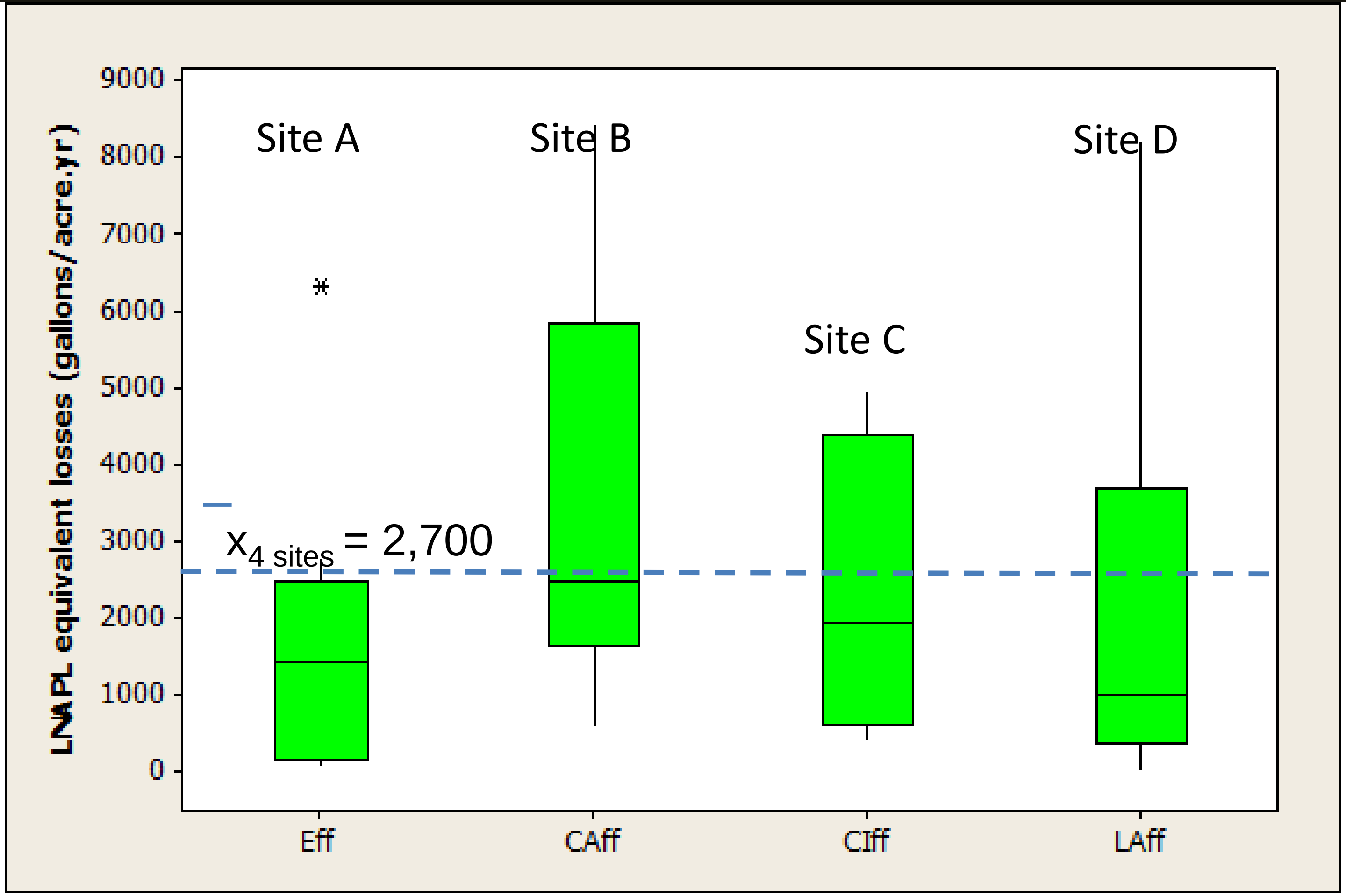
Assuming a site wide noise is unrealistic

- Interference (modern CO_2 flux):
  - assumed to be site dependent
  - data suggests is location dependent

“The use of ^{14}C is arguably the best, most quantitative means for background correction and it should be considered of utmost reliability.”

2017, API Guidance Document

Fossil Fuel LNAPL degradation rates



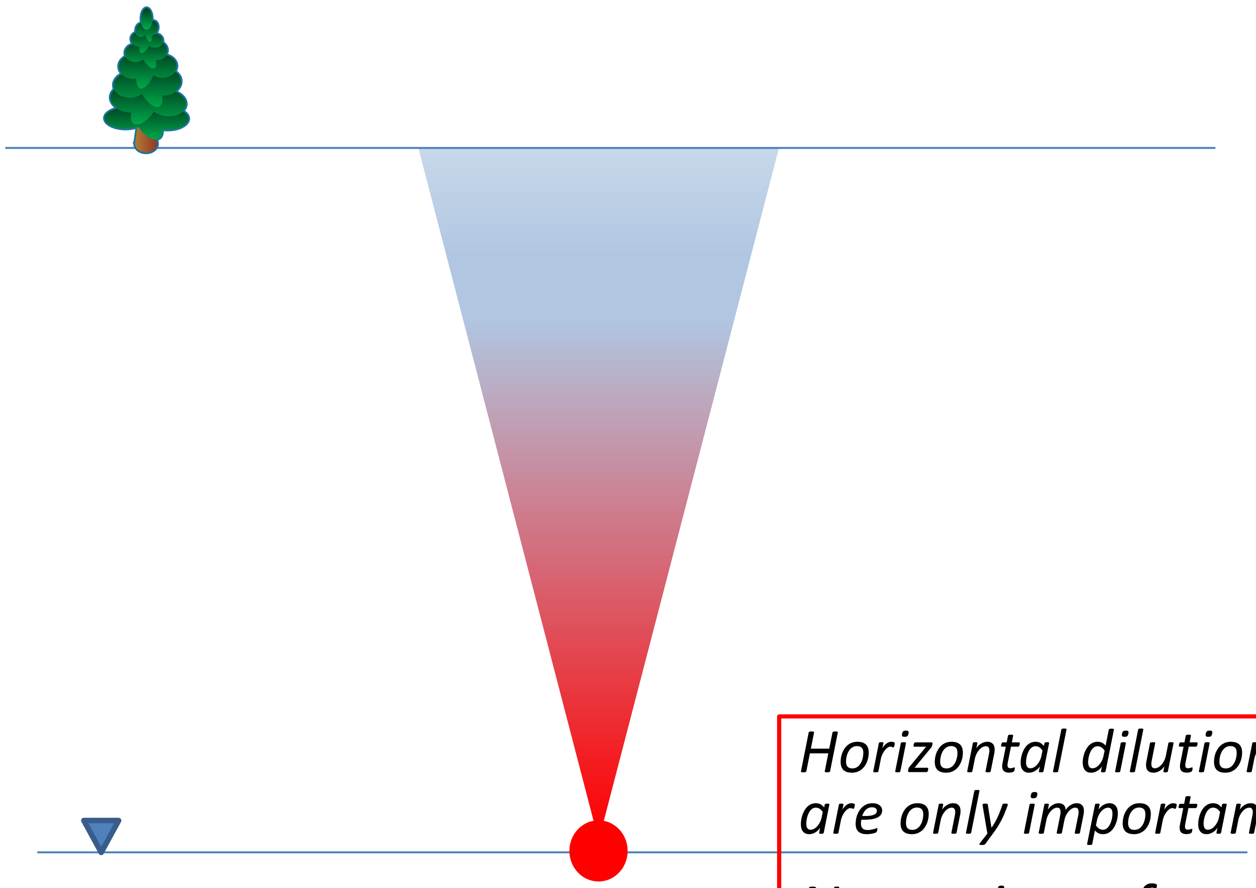
Petroleum NSZD is widespread throughout sites
Measurements in the order of 1,000s gallons/acre.year are common
NSZD should be accounted for in management plans

One dimensional gas transport?

- What would be the flux under this condition?
- How long would this last?
- Is it worth doing a measurement here?

Photo by K. McCoy

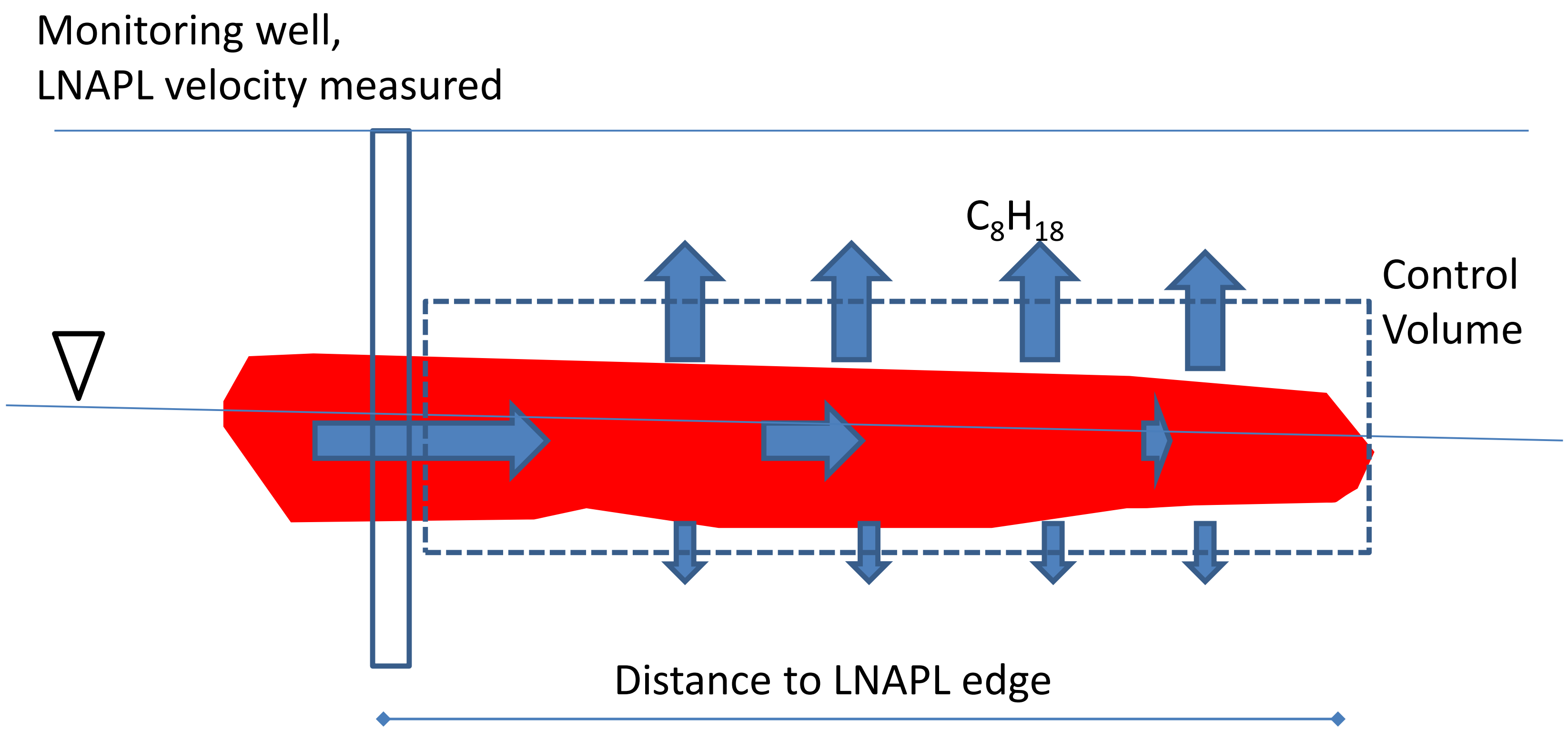
Deep aquifers and 1-D transport?



Horizontal dilution effects due to depth to water table are only important on control volume edges.

Not an issue for most sites (even at 35 m depth to water table)

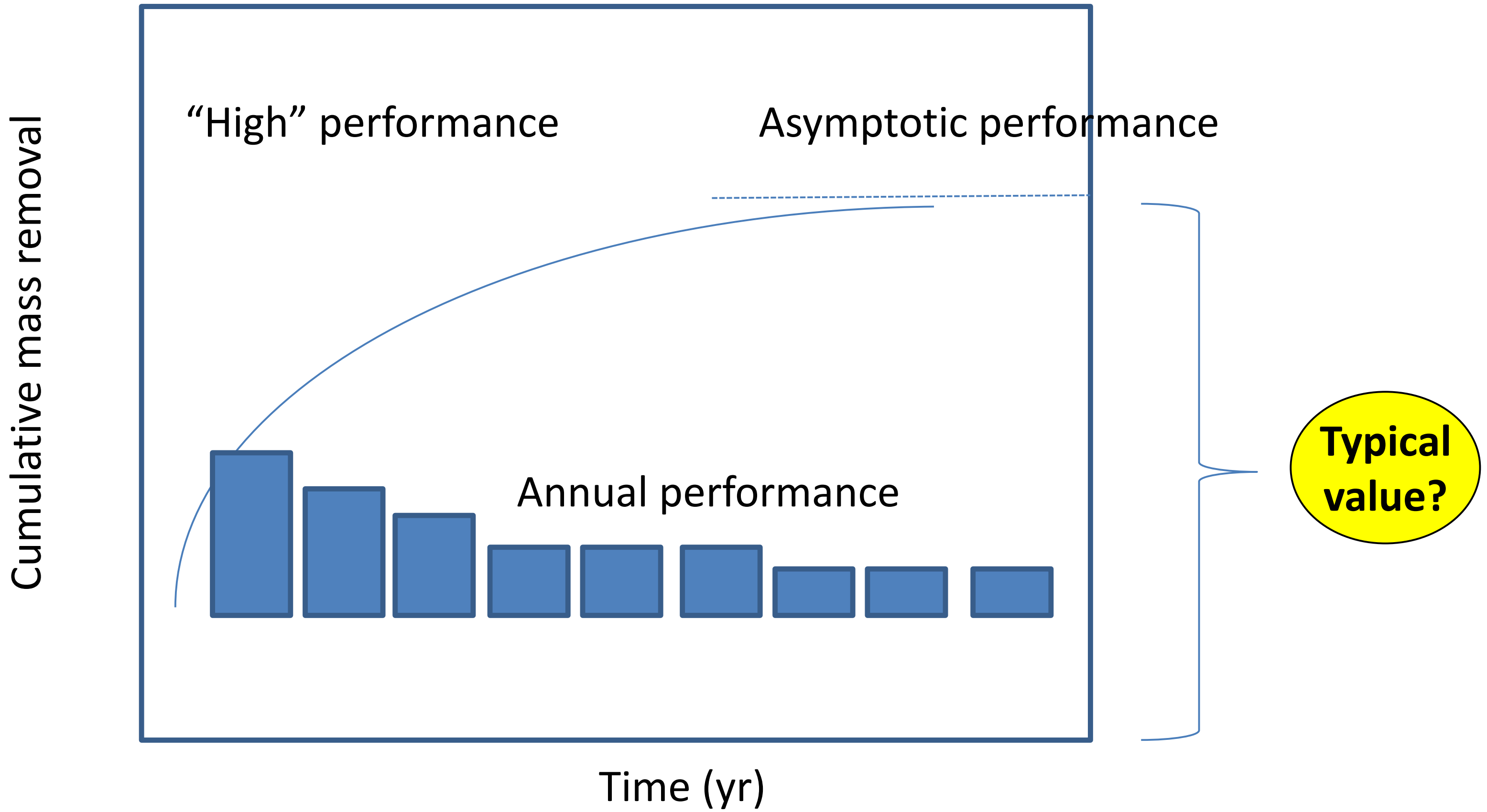
Mobility, Risk, and NSZD



Approach from Mahler et al., 2012

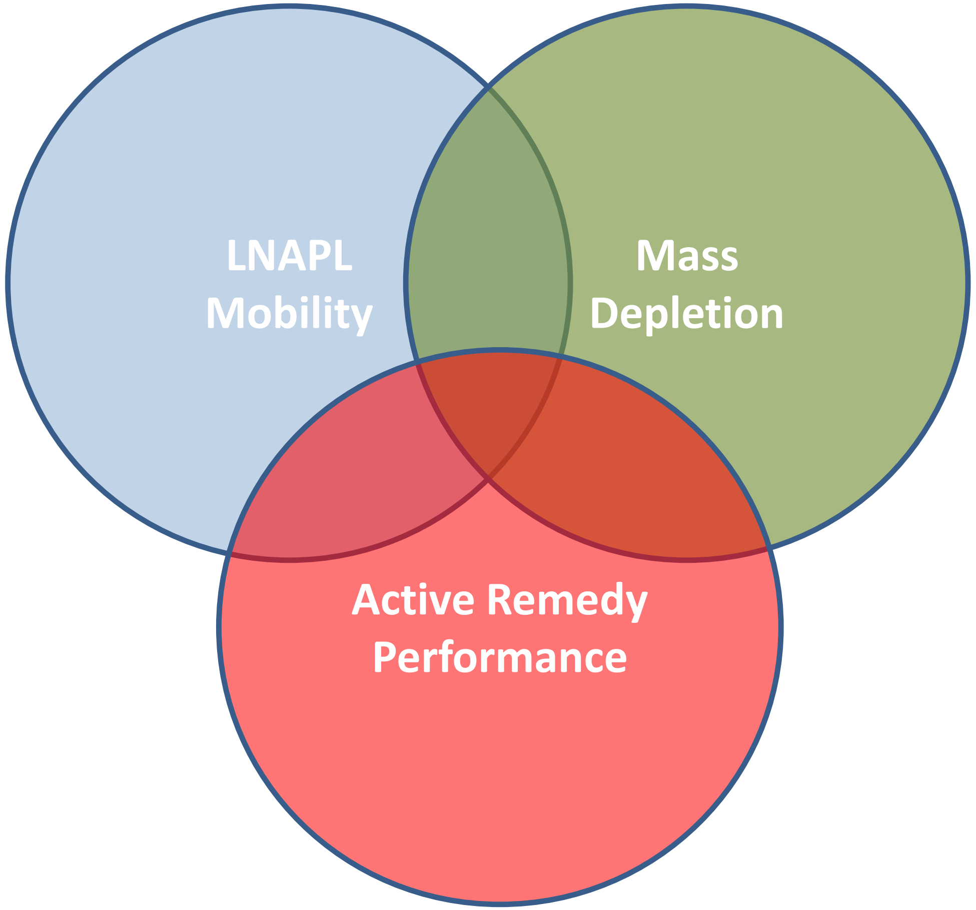
LNAPL velocity is typically 2 orders of magnitude lower than groundwater velocity

Mass Depletion and Active Remedies



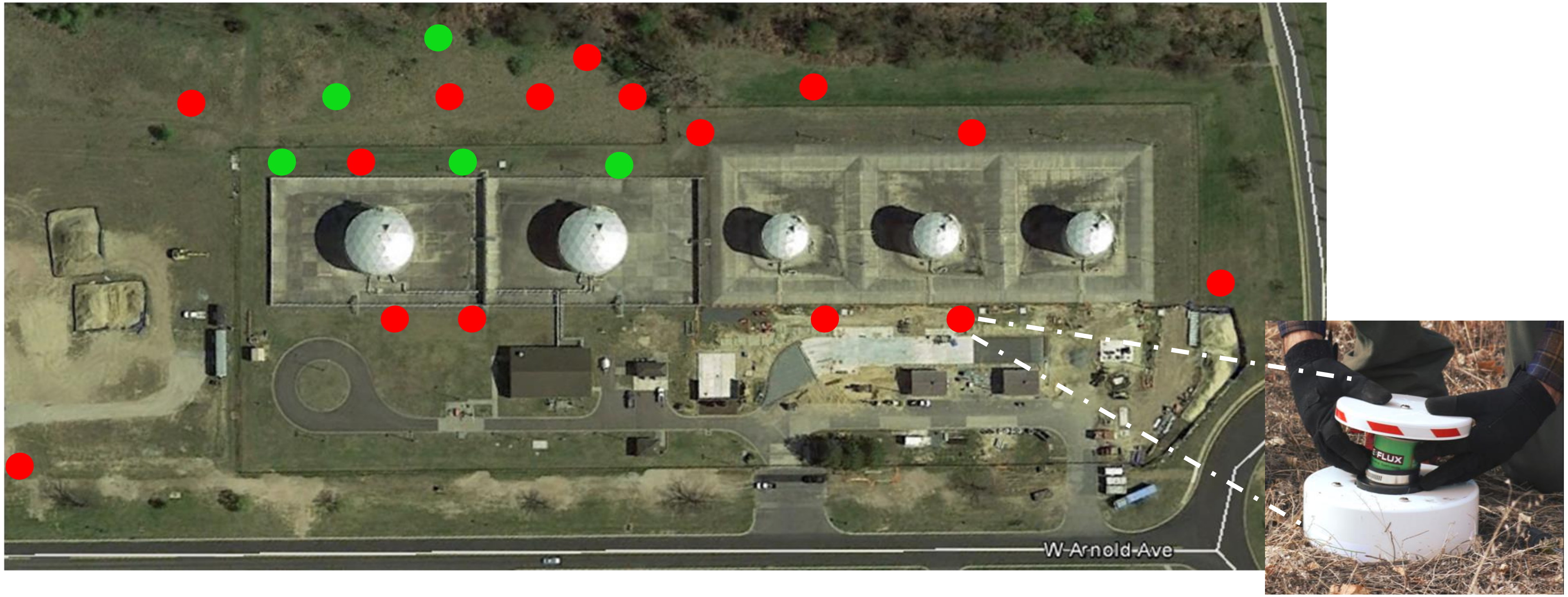
- Specific values depend on many things: remedy, stage (early/late), but …
- late stage sites with conventional remedies might reach asymptotic performance levels < 100s gallons/acre.yr

NSZD as a remedy? NSZD and Risk Assessment



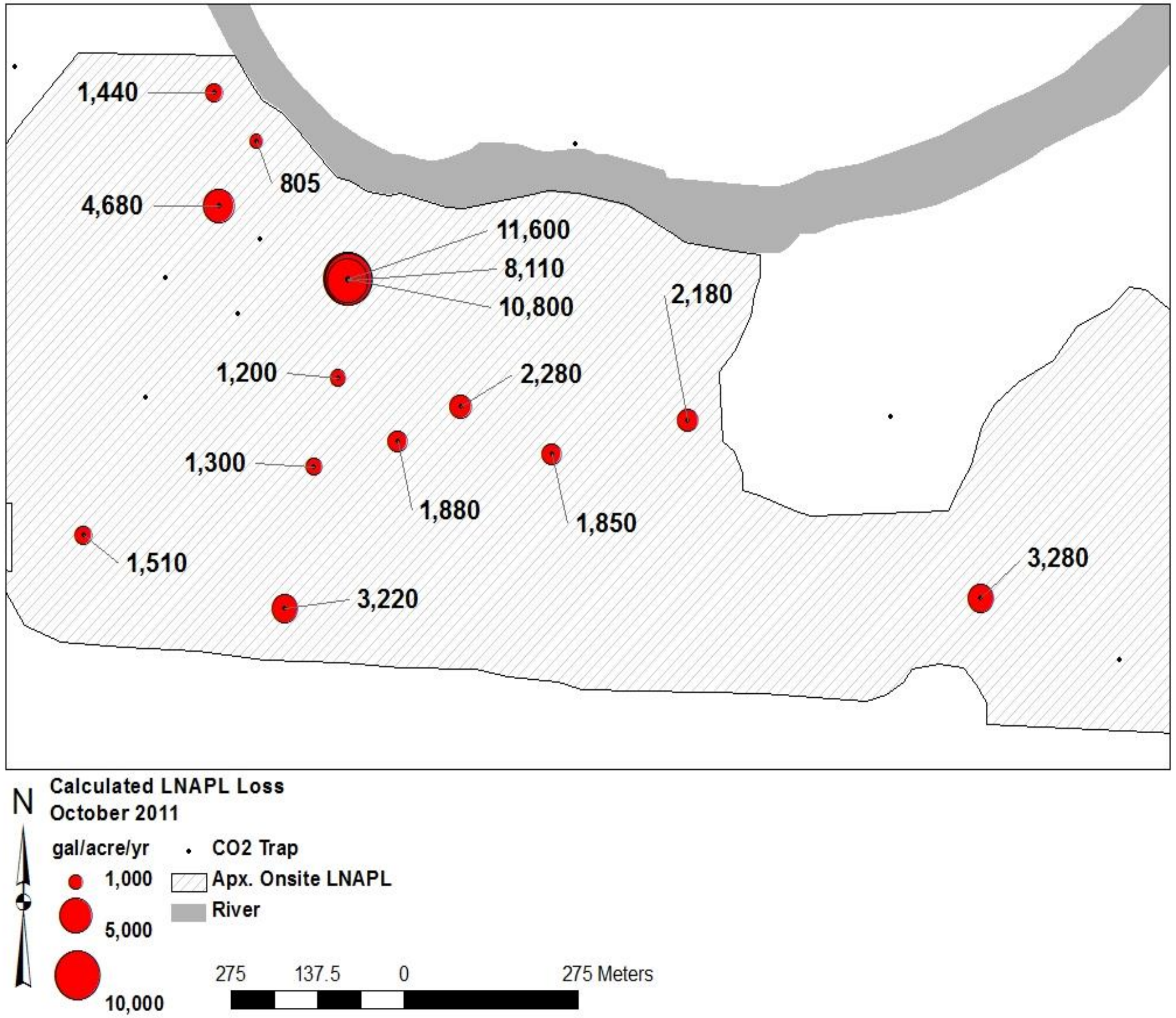
- Other risk assessment considerations
  - Composition (benzene, naphthalene)

Case Study: Delineating LNAPL sources



- Map Traps usef for delineation of LNAPL sources
- Results
  - Time integrated total CO_2 flux
  - Qualitatitive carbon isotopic analysis reveals fossil fuel signature
- Technology designed to offer higher data density than Fossil Fuel Traps
- Screening-level tool before other remedial investigations (well installation, high density investigations, etc)

Case Study: Calculated LNAPL Losses

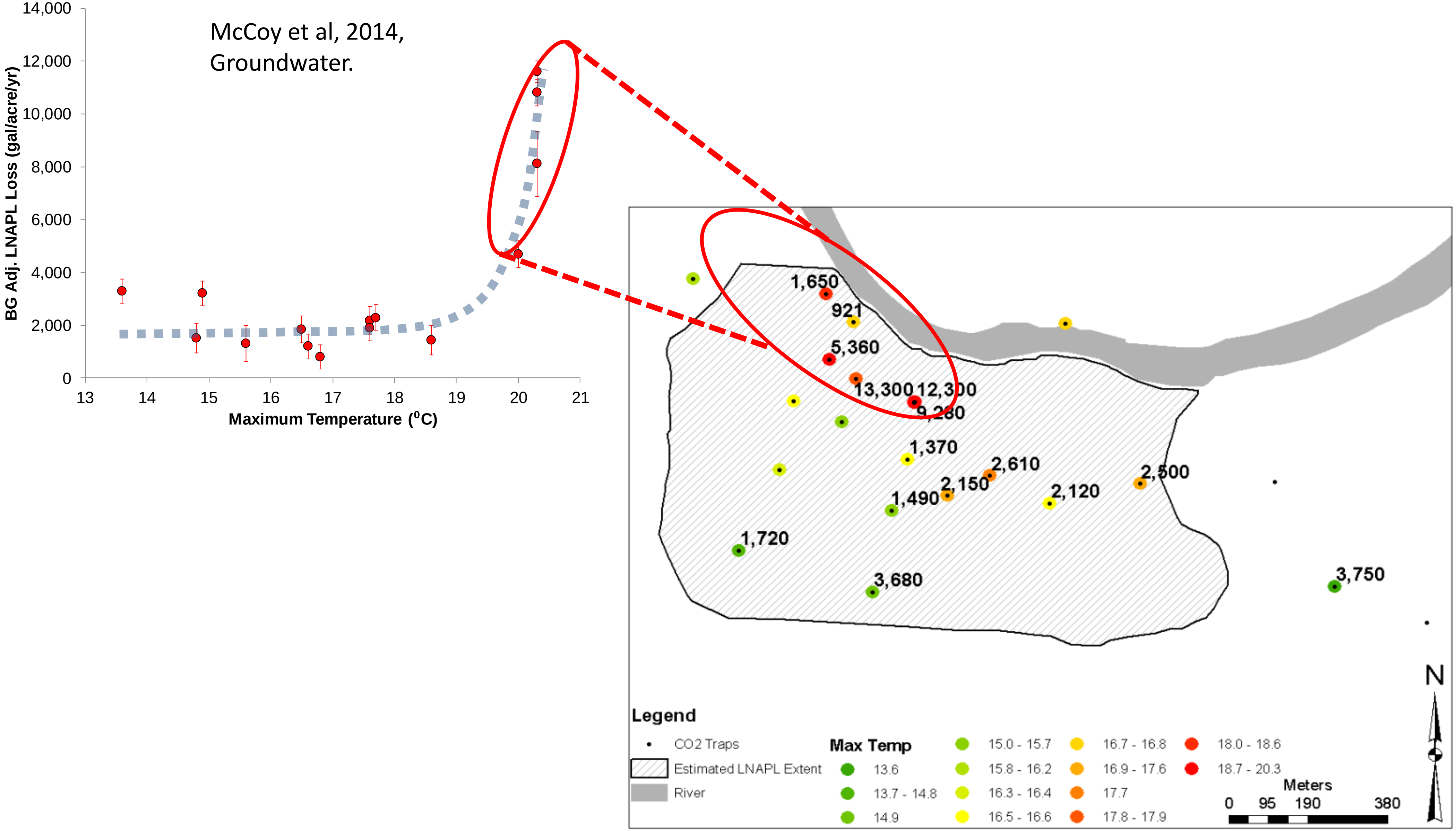


- Symbol size proportional to background corrected LNAPL loss rate (gallons/acre/yr).
- Calculated LNAPL loss rates (as C_6H_6) range from 921 – 13,300 gal/acre/yr.
- Uncolored symbols are not significantly different from background.

McCoy et al, 2014, Groundwater.

Mc Coy, K. 2012. CSU. M.Sc. Thesis

Case Study: Temperature Dependence of LNAPL Loss



Data Uses

- Contaminant source mapping
- NSZD as benchmark for active remedies
- NSZD as a remedy
  - Provided other criteria are met

Data quality needs to be commensurate to data use

Current Developments

- CO_2 flux to quantify degradation of other contaminants
- Soil temperatures

CO_2 flux to quantify degradation of chlorinated solvents

$$C_2C_3H \quad \rightarrow \quad C_2H_4 + C_2H_6 + CH_4 \quad \rightarrow \quad CO_2$$

CO_2 flux to quantify degradation of chlorinated solvents

$$C_2C_3H \quad \rightarrow \quad C_2H_4 + C_2H_6 + CH_4 \quad \rightarrow \quad CO_2$$

- Boyd, et al. 2018. *Coupled Radiocarbon and Short-Term Incubations Measure In Situ Hydrocarbon Degradation Rates.* ***2018 Battelle Chlorinated Conference***

- Newell, et al, 2018. *Natural Source Zone Depletion Studies at the Botany Groundwater Cleanup Program*. ***2018 Battelle Chlorinated Conference***

NSZD Rates in Perspective: Site Longevity

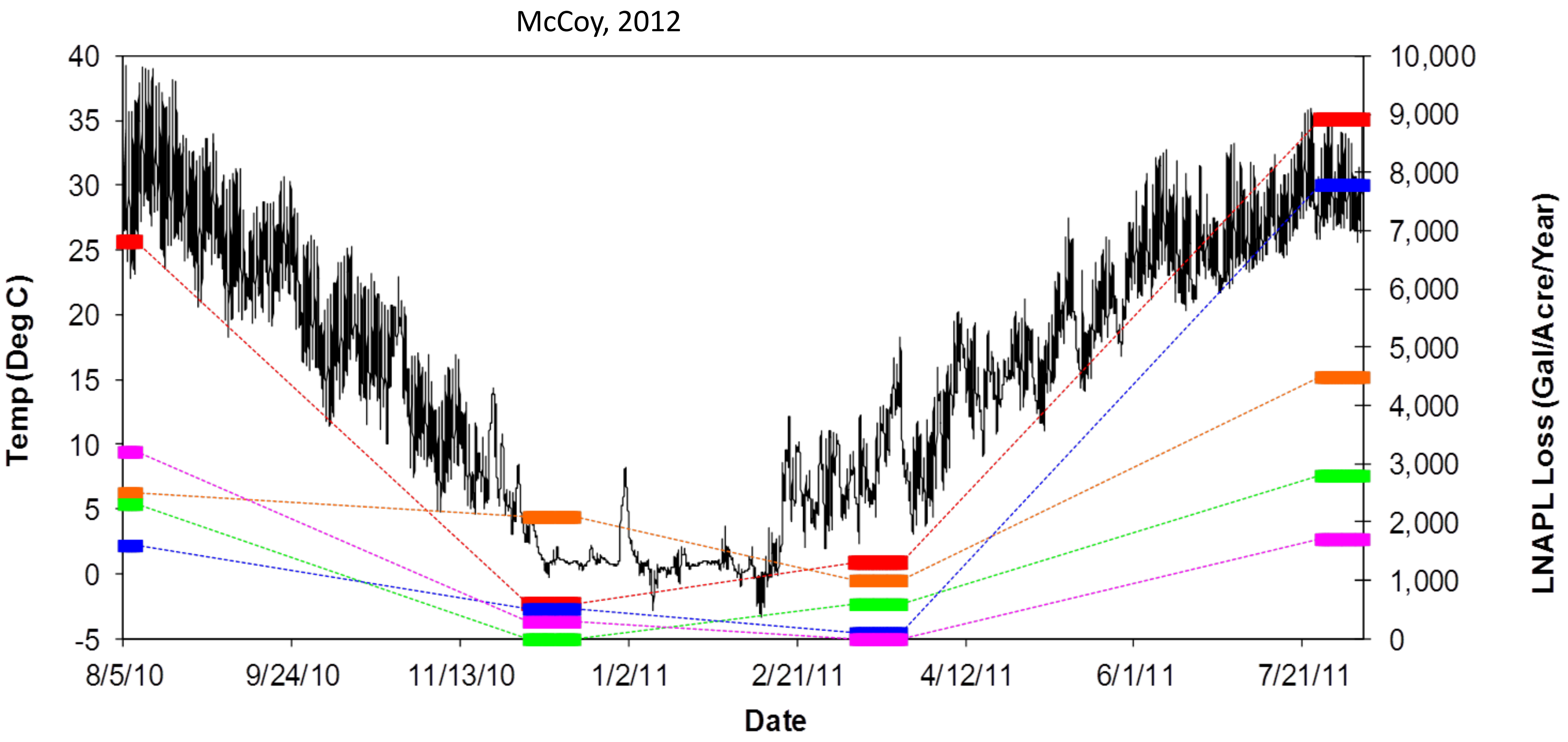
- Hypothetical Case: Compare a high NSZD rate to a given LNAPL thickness (6" = 150 mm)

$$1{,}000\,\frac{gallons}{acre\,.yr}\,x\,\frac{3.75\,L}{1\,gallon}\,x\,\frac{1m^3}{1000L}\,x\,\frac{1\,acre}{4{,}046m^2}\,x\,\frac{1000\,mm}{1m}=\frac{0.9\,mm\,of\,free\,LNAPL}{yr}$$

$$\frac{\frac{0.9\,mm\,of\,free\,LNAPL}{yr}}{150\,mm}=\frac{0.7\%}{yr}$$

Measured NSZD rates are consistent with site longevities of multiple decades

Temperature Dependence of LNAPL Loss

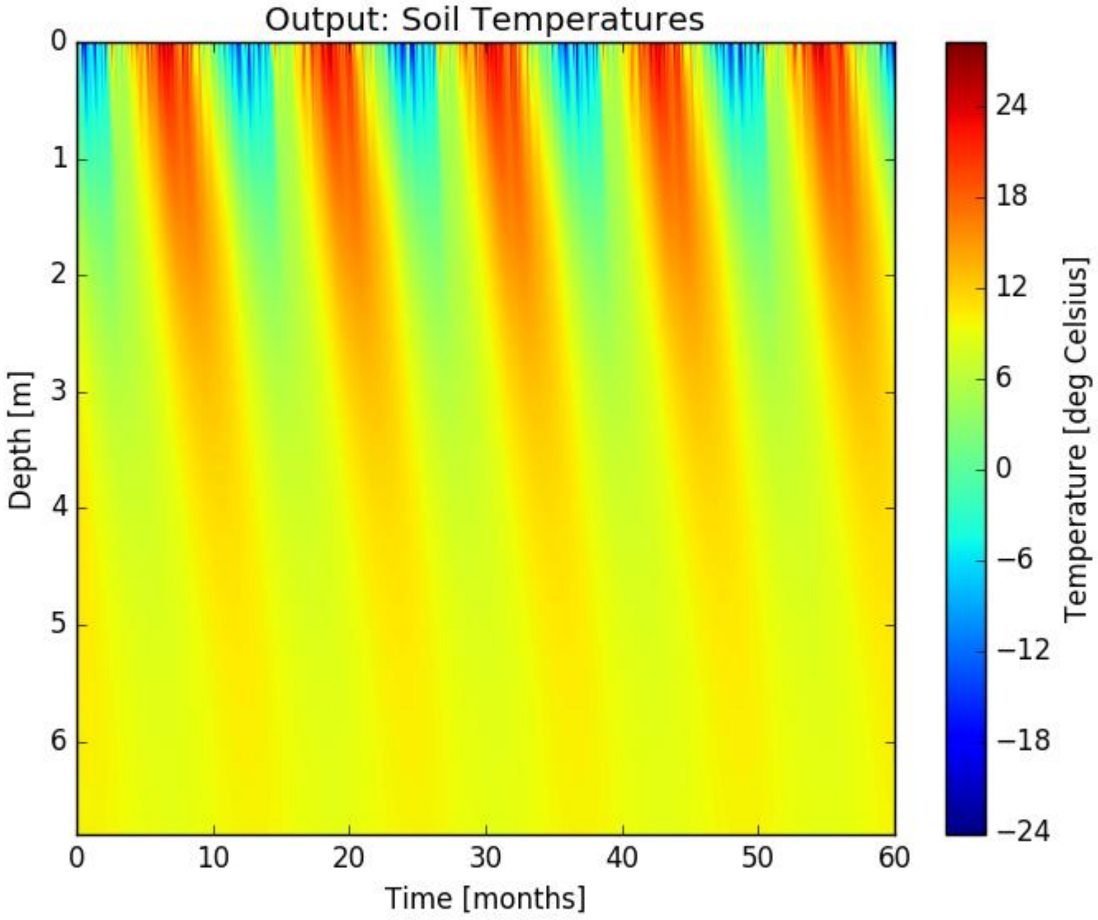


Loss rates are seasonally variable (within a < 5x factor)

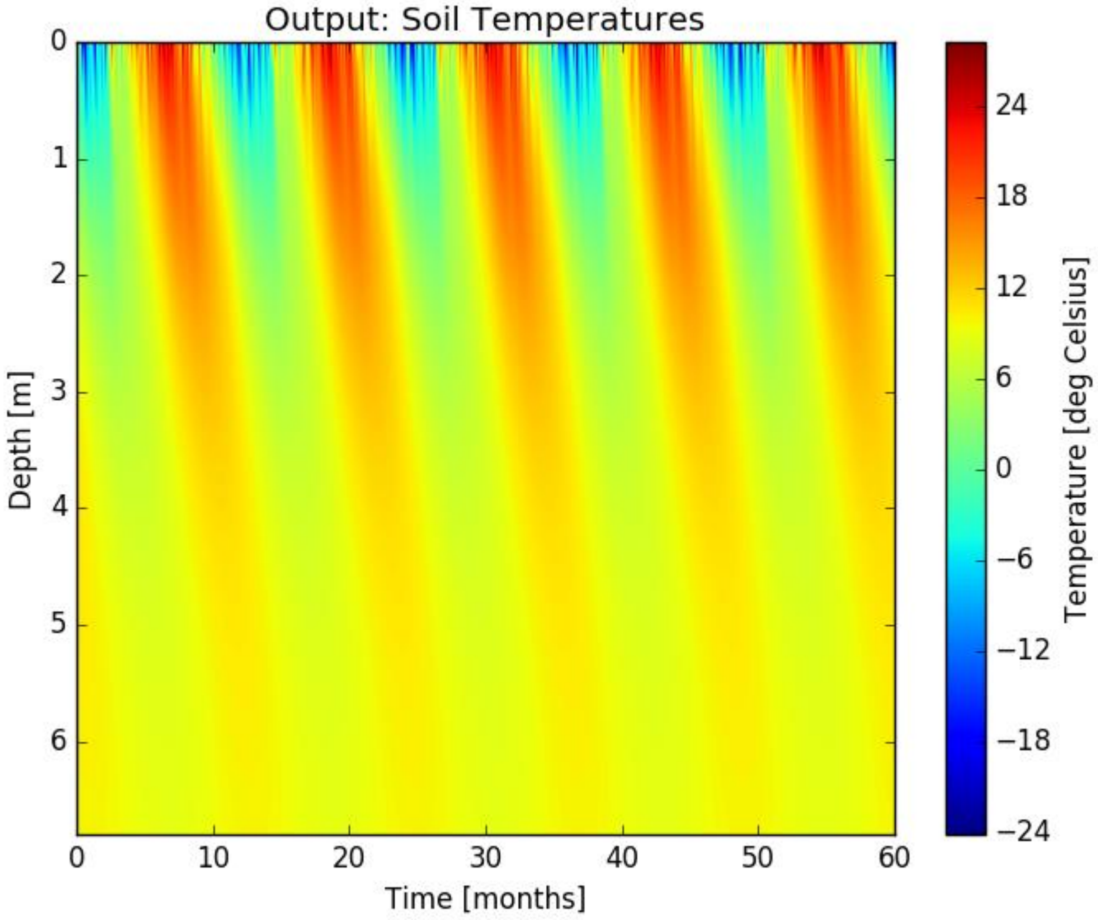
Median within each sampling event correlates with ambient temperatures

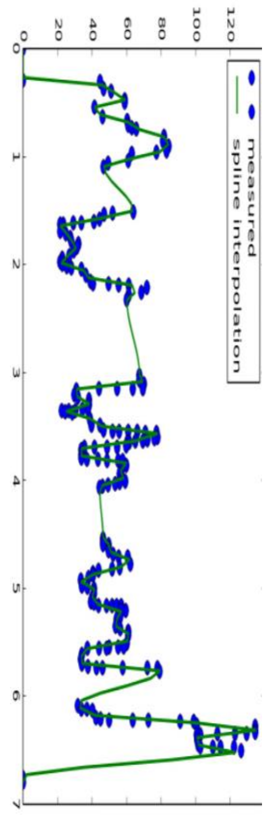
Ranking of locations within each event remains constant

Soil Temperatures and NSZD

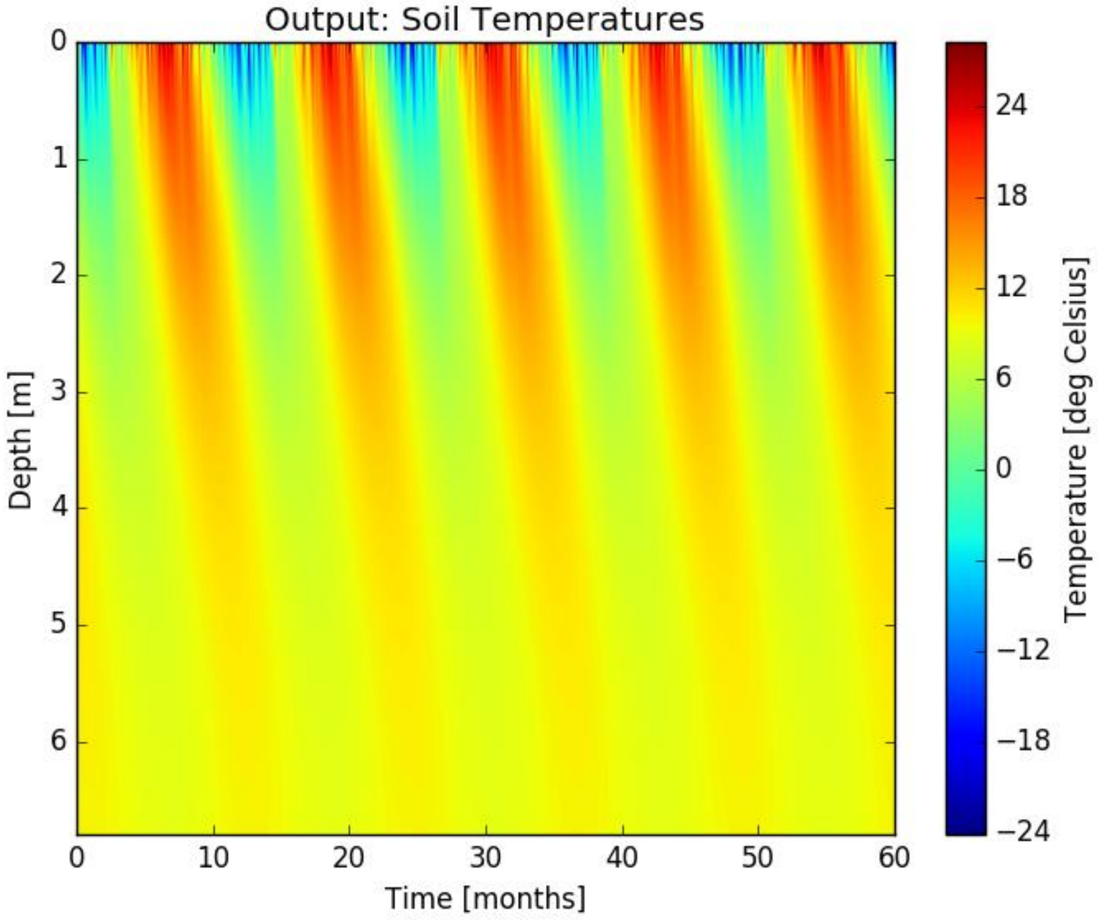


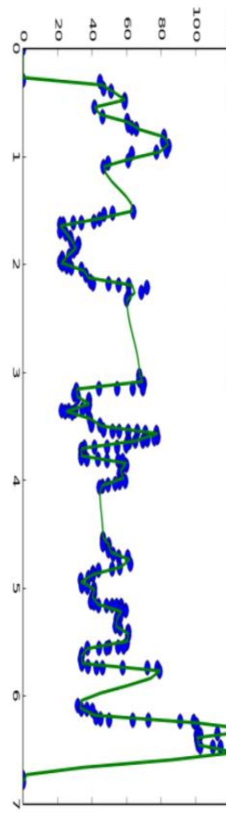
Soil Temperatures and NSZD

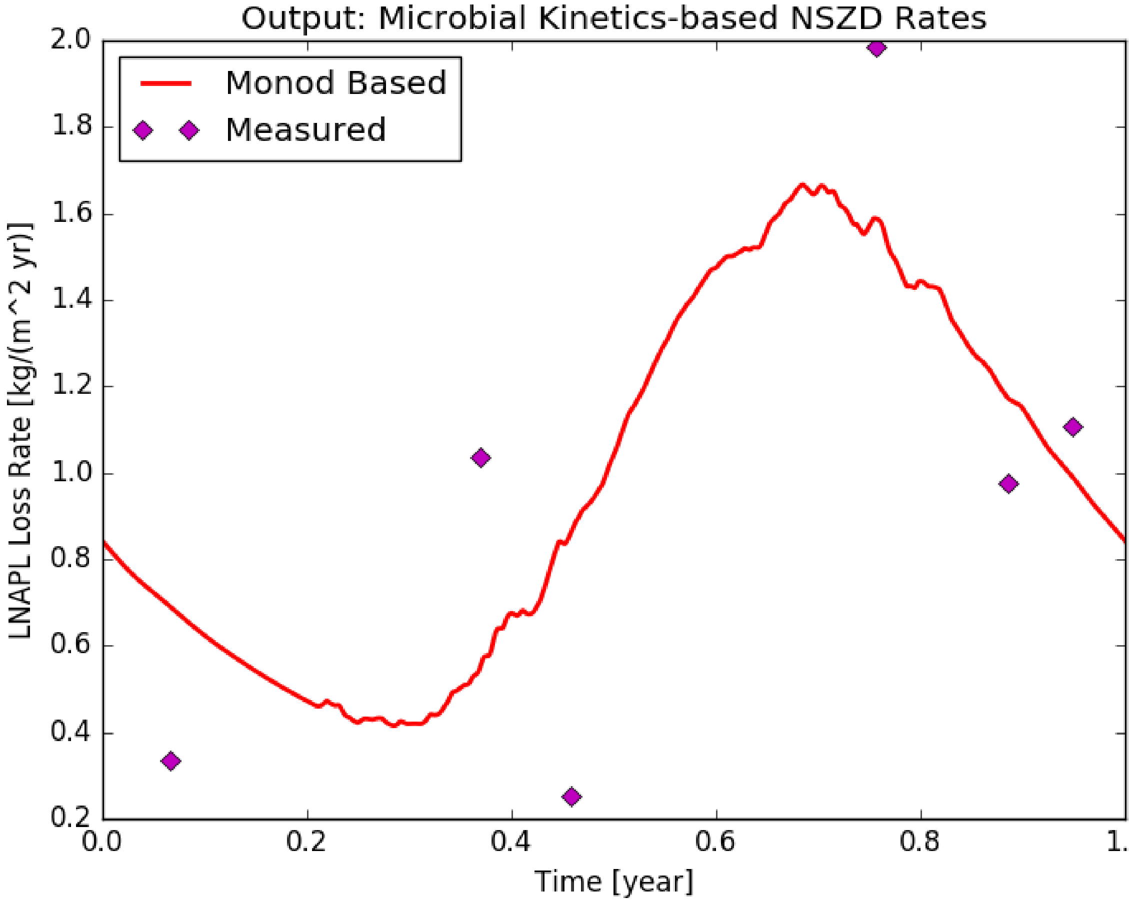




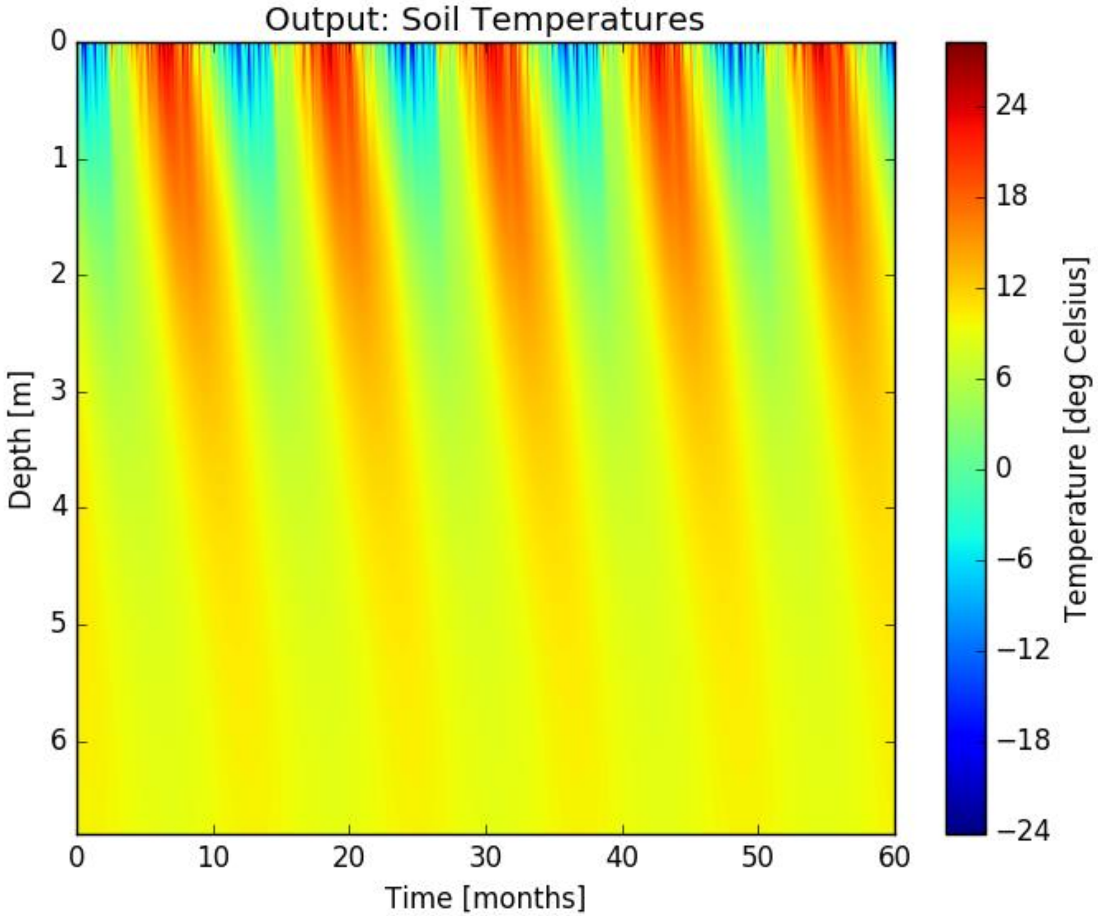
Soil Temperatures and NSZD

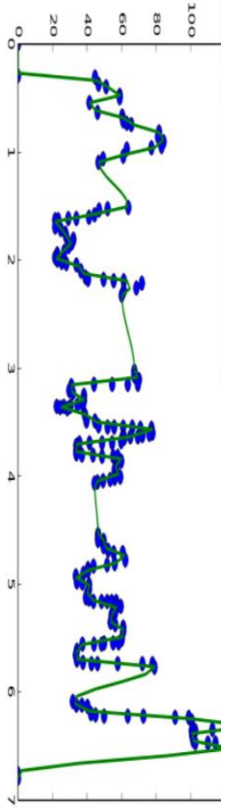


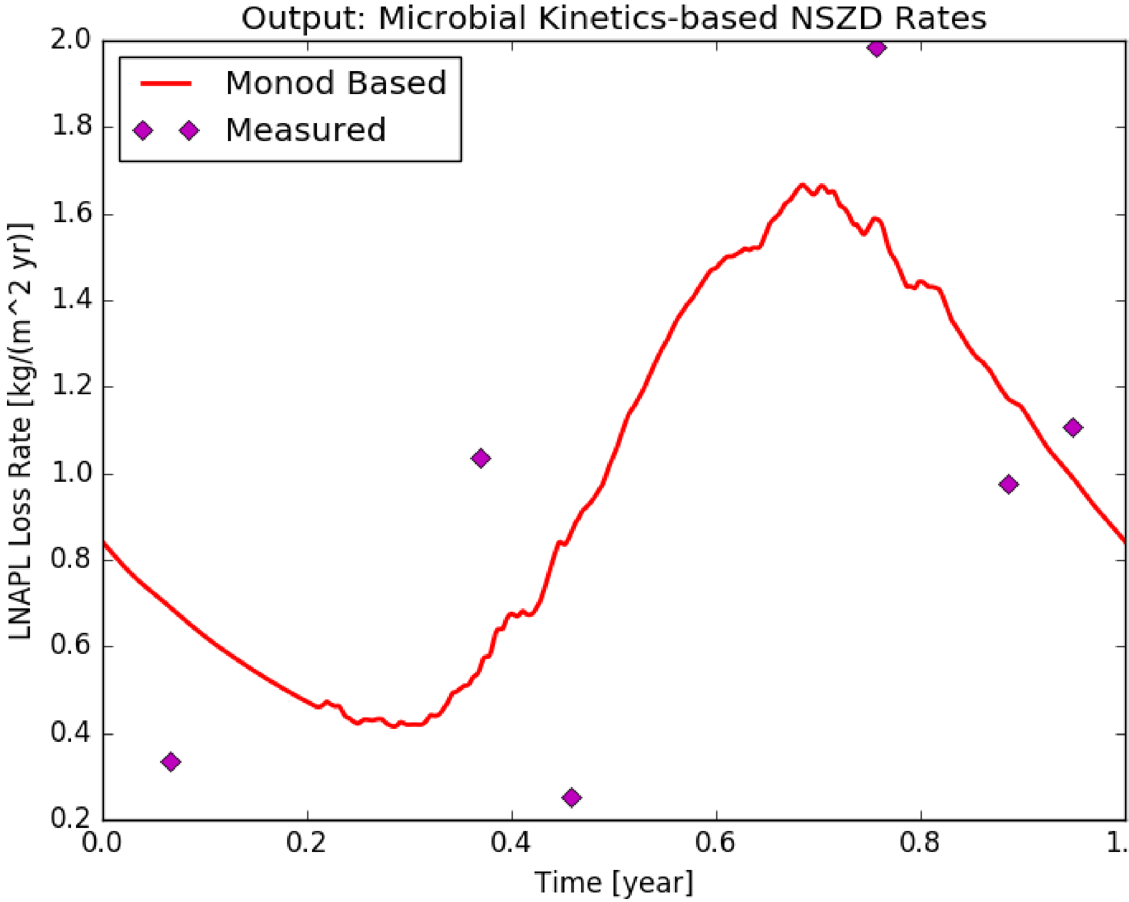




Soil Temperatures and NSZD







www.BiogenicHeat.com

Experiences from 100+ sites

- Vadose zone processes seem dominant- biggest bang for the buck

"mass losses from the submerged part of the source zone and involving ground water transport processes (i.e., dissolution and biodegradation) were estimated to be about approximately 2 orders of magnitude lower"

Lundegard and Johnson, 2006

- Methods to measure CO_2 flux at ground level are easier to implement
- Eliminating interference modern carbon CO_2 flux is key: ^{14}C
- Major limitation to all available methods is gas transport

Summary

- NSZD is an important process at most LNAP sites
- NSZD management requires quantification. Quantification requires vadose zone processes
- Three well accepted vadose zone methods
- NSZD rates consistent with active remediation rates, site longevity
- NSZD importance:
  - API guidance document on methods
    - Mass balance methods: Gradient, Dynamic Closed Chamber, CO2 Traps
    - Innovative Methods: Temperature, ^{14}C for DCC
  - ITRC LNAPL Guidance Document updated to include new methods for NSZD
  - CRCCare guidance document (in progress)

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Q & A

Limitations of NSZD rate measurement through gas transport

- One dimensional gas transport
- Accounting for fluxes associated with NSZD (not natural processes)

NEXT PRESENTATION