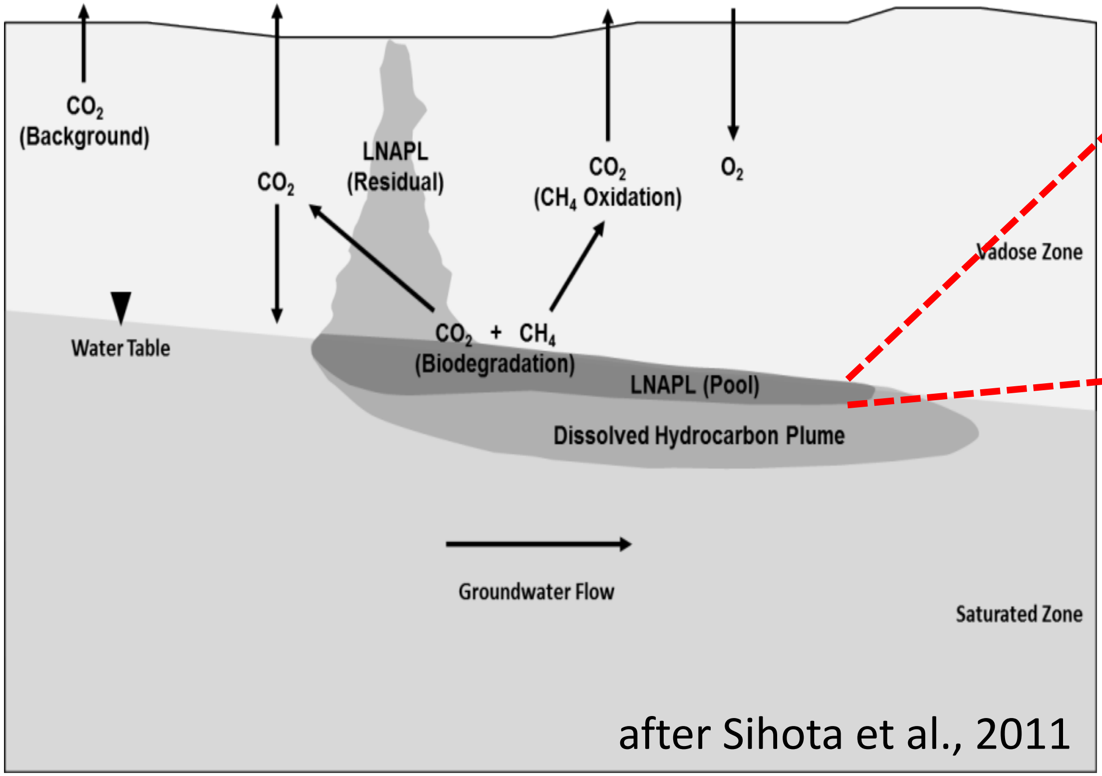
BATTELLE CHLORINATED CONFERENCE
JUNE 5, 2024
DENVER, COLORADO

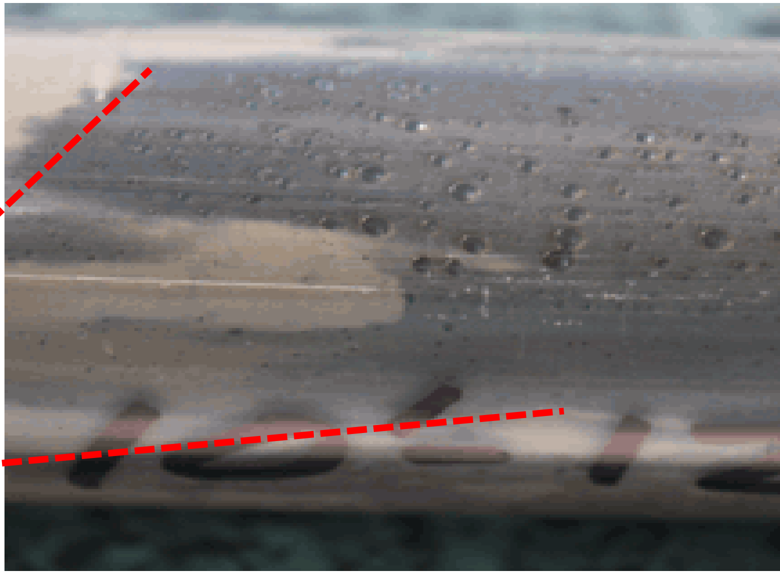
E-FLUX
Easy set-up. Expert results.

USE OF CO_2 PASSIVE CO2 TRAPS TO QUANTIFY THE DEGRADATION RATES OF CHLORINATED SOLVENTS

JULIO ZIMBRON PH.D.
COLLABORATORS:
THOMAS BOYD, PH. D.(SERDP/ESTCP),
GSI ENV,/ORICA

Background: NSZD





Mechanisms

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

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

Molins et al. 2010 – modeling study

The ITRC framework

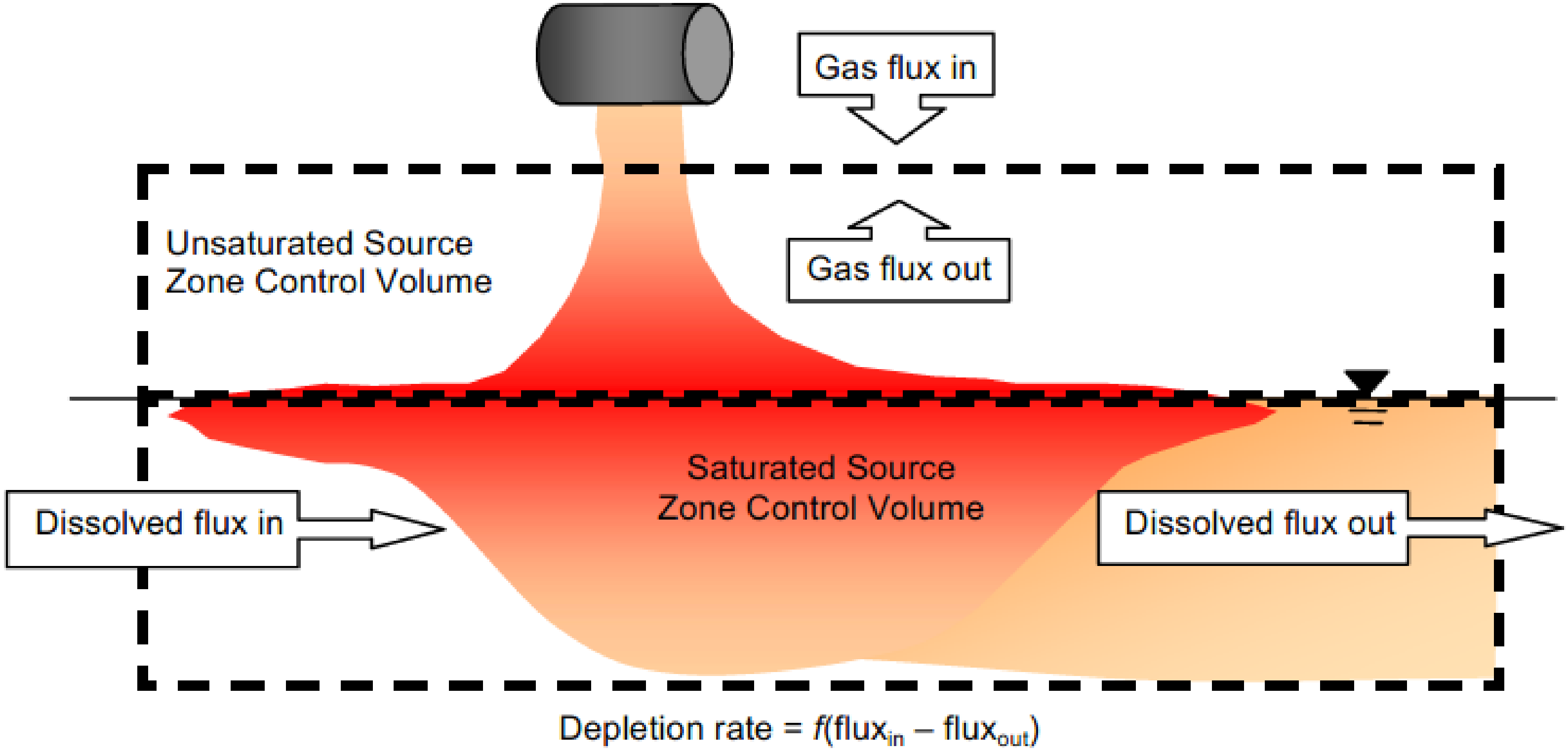


Figure 3-2. Example control volume "box" for quantitative assessment of NSZD.

ITRC, 2009 : Evaluating NAPL NSZD

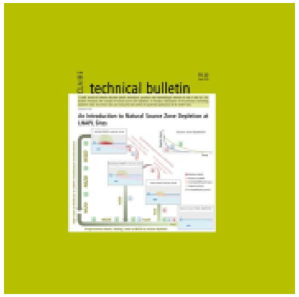
More than a decade of NSZD experience

- NSZD is an important new tool in managing LNAPL contaminated sites
- Many guidance documents describe the methods

2018 NSZD Guidance Document

INTERSTATE TECHNOLOGY REGULATORY COUNCIL ITRC

TECHNICAL REPORT NO. 47



LNAPL Site Management Document

NAVFAC

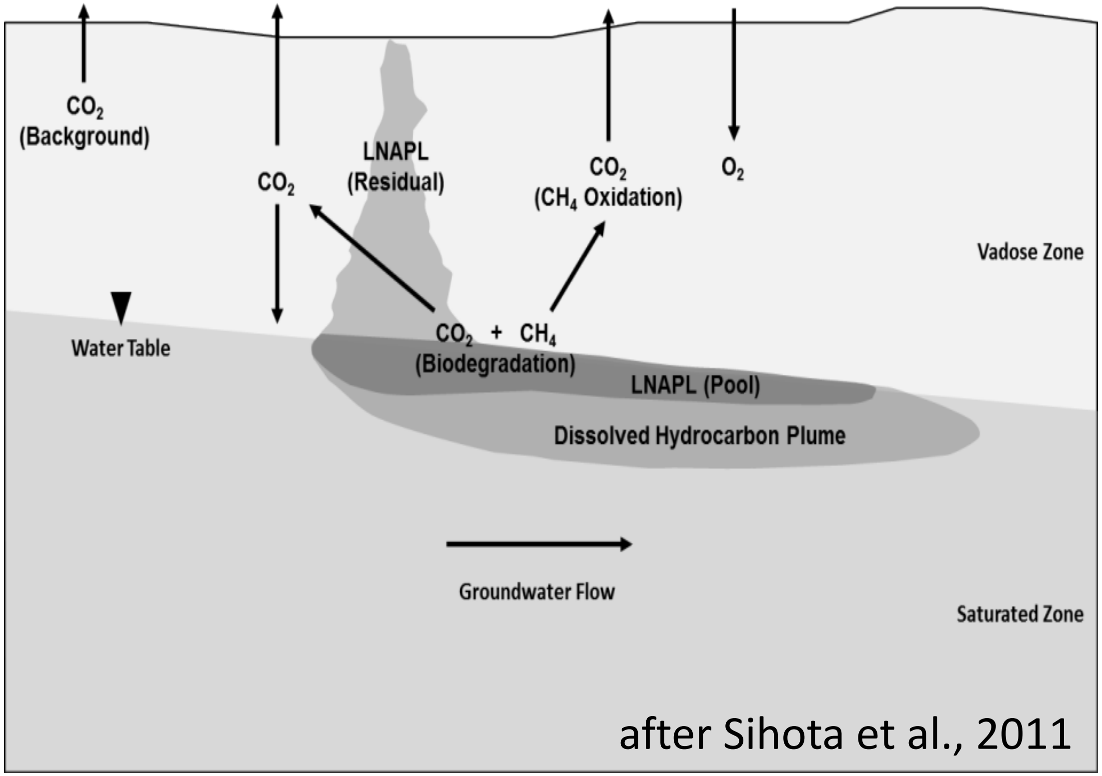
"Currently, it [the CO_2 Trap] is the most common method to obtain NSZD rates"

ASTM INTERNATIONAL

Standards Worldwide

- Many methods available for LNAPL (NSZD)
- This talk focuses on one technique (arguably the most sensitive of the NSZD methods):
  - Long term, time average CO2 fluxes
  - Radiocarbon correction
  - Applied to chlorinated solvents

Chlorinated Solvents Vs. LNAPL



Density differences make DNAPL sources deeper than LNAPL

DNAPL is e-acceptor, LNAPL is e-donor

DNAPL degradation rates are thought to be significantly slower than LNAPL

Degradation Pathways: LNAPL vs DNAPL

(simplified)

C_nH_{2n+2}

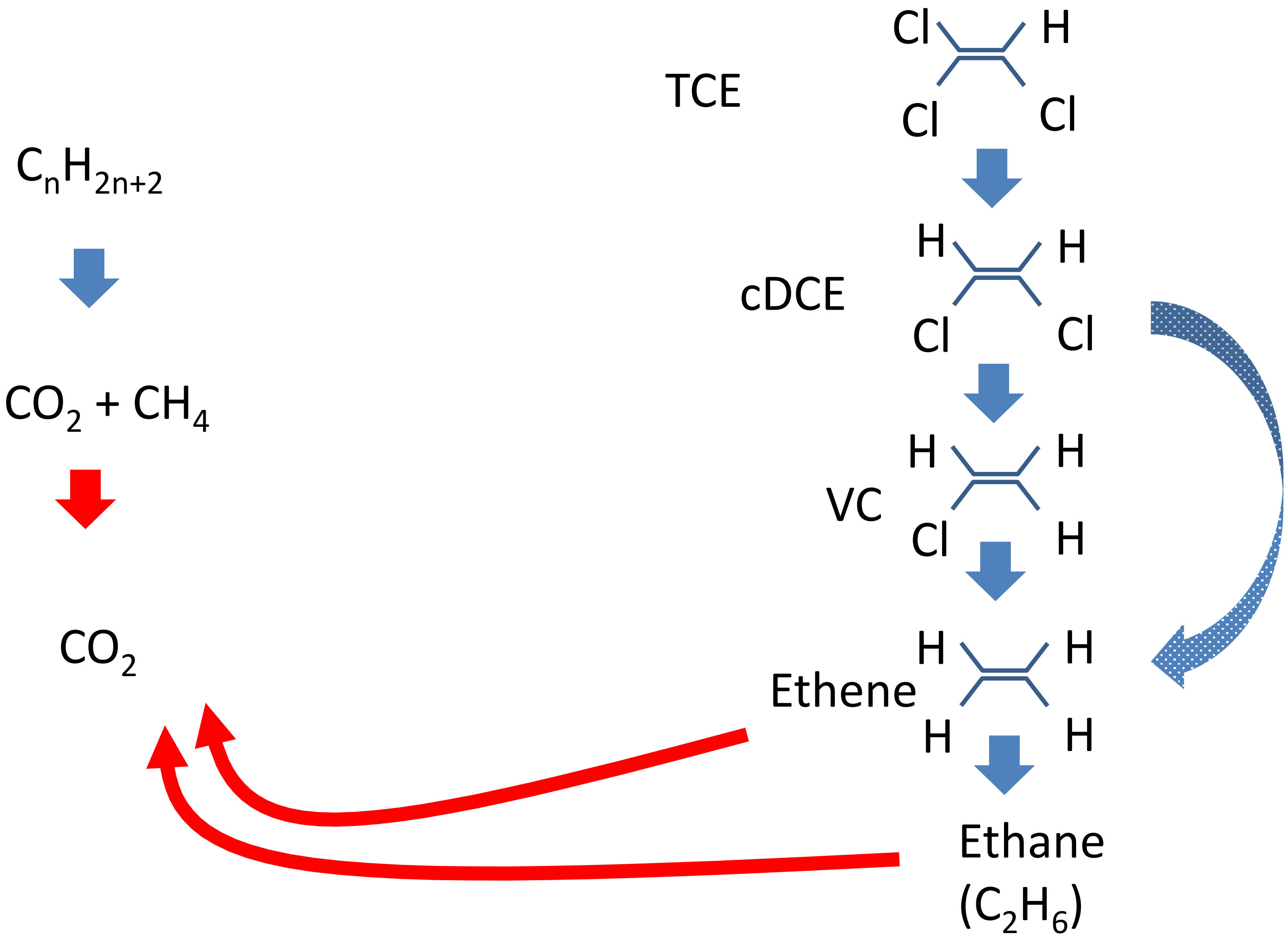
$\downarrow$

$CO_2 + CH_4$

$\downarrow$

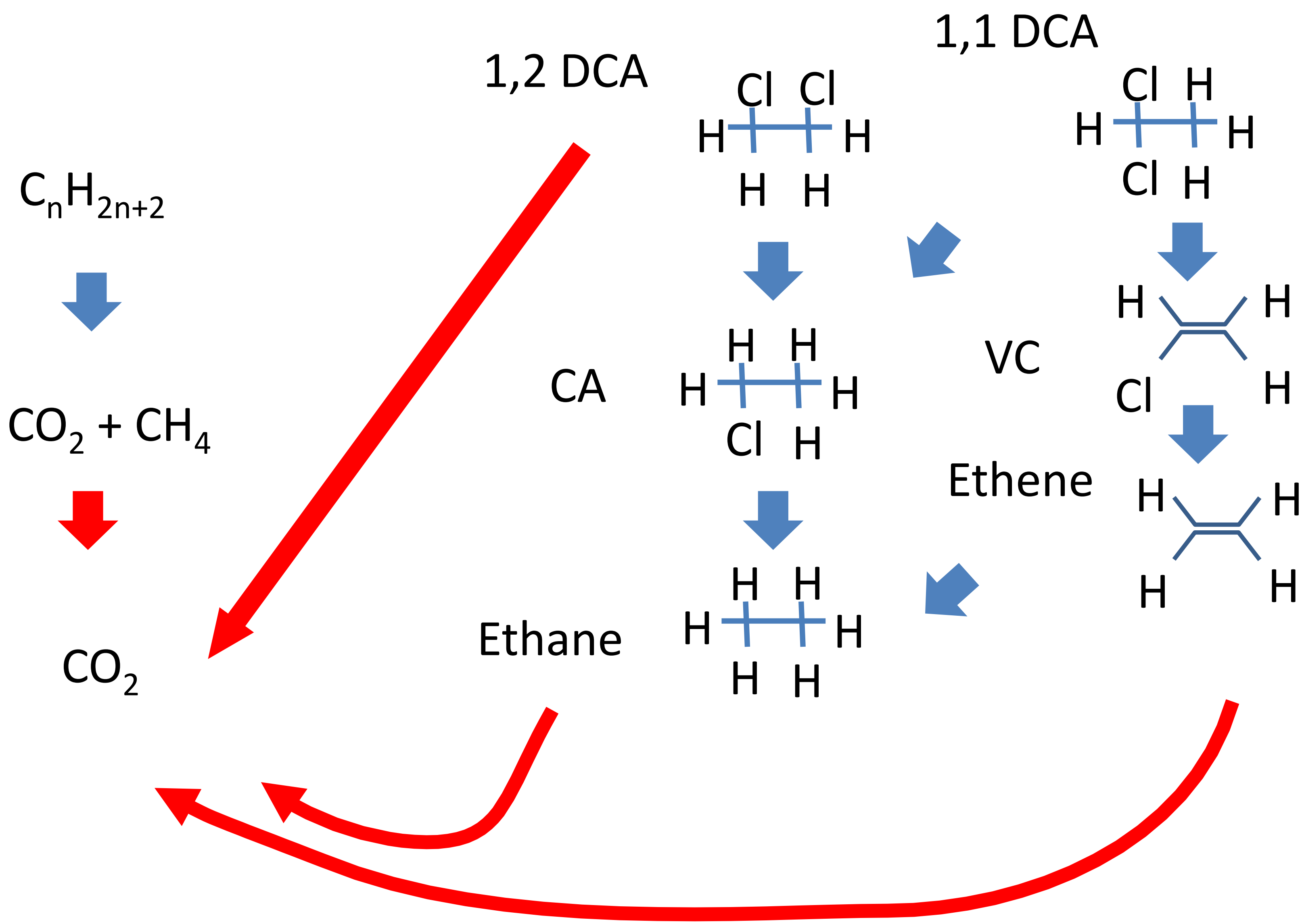
CO_2

Degradation Pathways: LNAPL vs DNAPL
(simplified)



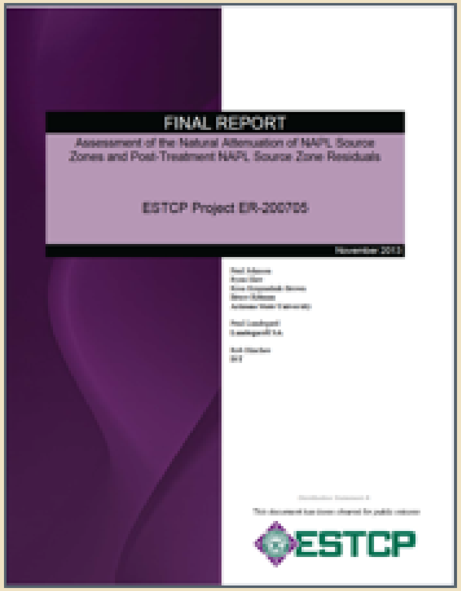
Degradation Pathways: LNAPL vs DNAPL

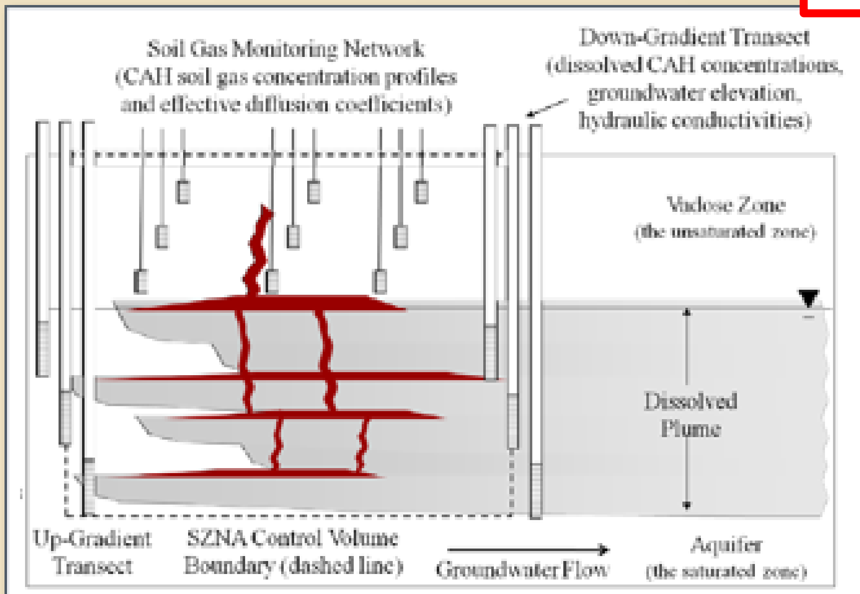
(simplified)



Is There NSZD at Chlorinated Sites?

2018, Battelle Conference Flashback
Source: GSI, used with permission


FINAL REPORT
Assessment of the Natural Attenuation of NAPL Source Zones and Post-Treatment NAPL Source Zone Residuals
ESTCP Project ER-200705
November 2013
ESTCP



Paul Johnson:

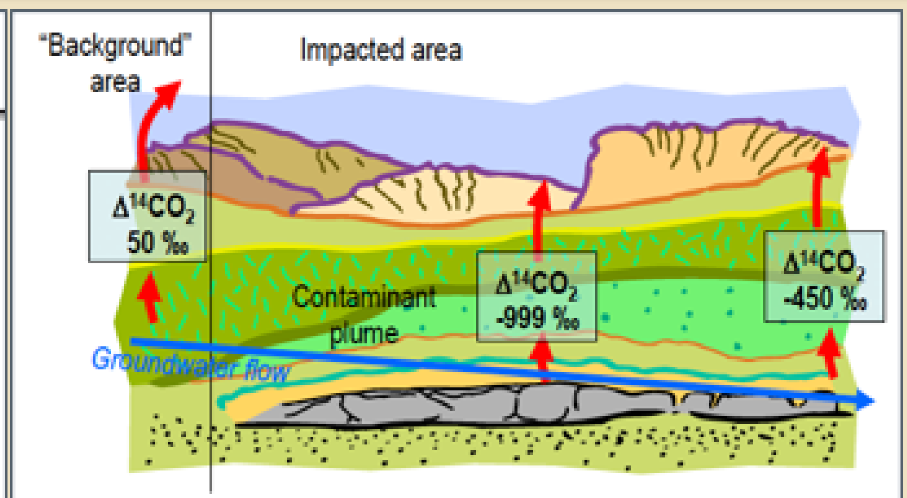
NSZD Rate Between 1 & 10 Kilograms PCE per Year (but no CO_2 measurement)


Naval Research Laboratory
Washington, DC 20375-5320

CO₂ Radiocarbon Analysis to Quantify Organic Contaminant Degradation, MNA, and Engineered Remediation Approaches

Thomas J. Boyd
Michael Montgomery
Chemical Dynamics and Diagnostics Branch
Chemistry Division

Richard H. Cuenca
Yutaka Hagimoto
Oregon State University
Corvallis, Oregon



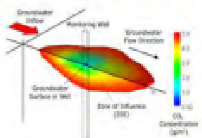
Tom Boyd:

GW Recirc to measure ^{14}C

Cross-Checking CO_2 Trap Data:

- **In-well traps**
  - CO_2 is trapped directly within monitoring a well headspace.
  - Traps are suspended in the well, then headspace sparged with Ar gas.

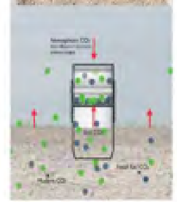
- CO_2 is quantified after 4-8 week deployment by coulometry (high precision).
- CO_2 is analyzed for natural abundance radiocarbon (AMS lab – NOSAMS).
- Sampled volume calculated using Zone of Influence (ZOI) model.



Boyd et al, 2014, 2014a, 2015, 2016

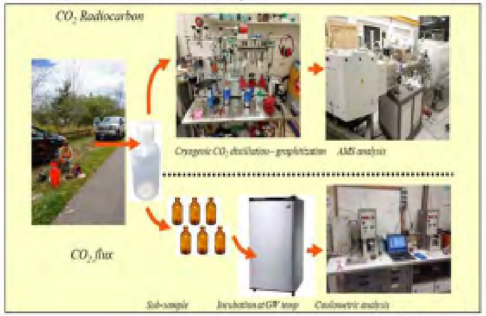
- **E-Flux soil:atmosphere traps**
  - CO_2 is trapped as it passes from soil to atmosphere. Interference from ambient CO_2 eliminated by trap double layer design.
  - Traps are deployed on soil surface.

- CO_2 is quantified after ~2 week deployment.
- CO_2 is analyzed for natural abundance radiocarbon.
- CO_2 flux is the basis to estimate footprint losses. Assuming source depth enables estimating volumetric losses.



McCoy et al, 2015; Carroll et al., 2017

- **Short-term incubations**
  - Groundwater samples transferred to serum bottles (triplicates). Controls killed at t_0 ($CuSO_4$, NaOH).
  - Samples incubated, then killed. Respiration measured by difference.
  - Subsample sent for radiocarbon analysis.



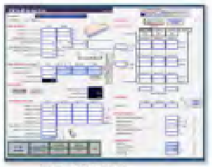
Boyd et al, 2018

Four seasonal samplings at two sites (ESTCP)

Use REMChlor-MD to Obtain Independent Attenuation Rates

- New ESTCP Modeling Tool (ER-201426) developed by Dr. Ron Falta with GSI Environmental assisting in interface development and case studies.
- Simulates source attenuation, matrix diffusion, plume biodegradation, remediation.
- GSI will calibrate REMChlor-MD to the study sites for these parameters:
  - Initial source mass
  - source "gamma" term
  - source decay term
  - plume decay
  - Other parameters if necessary

Key Point: *Calibrated REMChlor-MD model will provide key data to obtain attenuation rates that can be compared to measured CO_2 fluxes.*



ER-201426

Data inter-compared; within context of REMChlor-MD

Approach: CO_2 traps

- Field efforts are minimal
- No power need, 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)
- Turnaround time: 4 weeks

^{14}C Correction (a.k.a. radiocarbon)

- "Two source model": way of allocating contribution from two sources of known isotopic composition

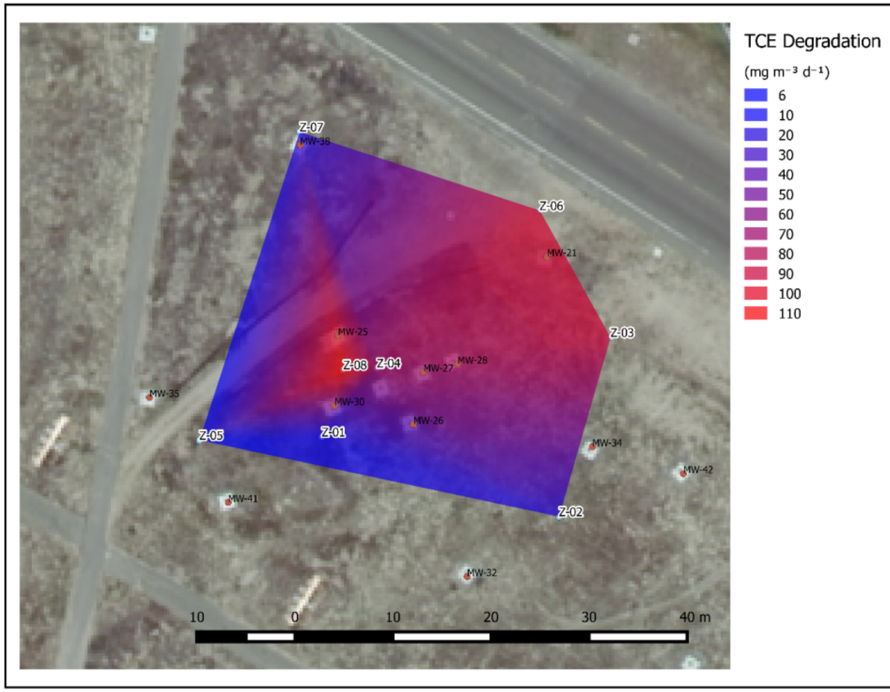
  Modern carbon

  Old (fossil fuel, or f.f.) carbon

- By measuring radiocarbon, the contribution from modern carbon to the soil respiration rate can be eliminated
- Fossil fuel CO_2 is stoichiometrically converted into mass loss units of the contaminant source
- Expressed on a footprint basis, μmole fossil fuel $CO_2/m^2/s$ (or equivalent, like gallons/acre/yr, or kg/Ha/yr)

Site 1

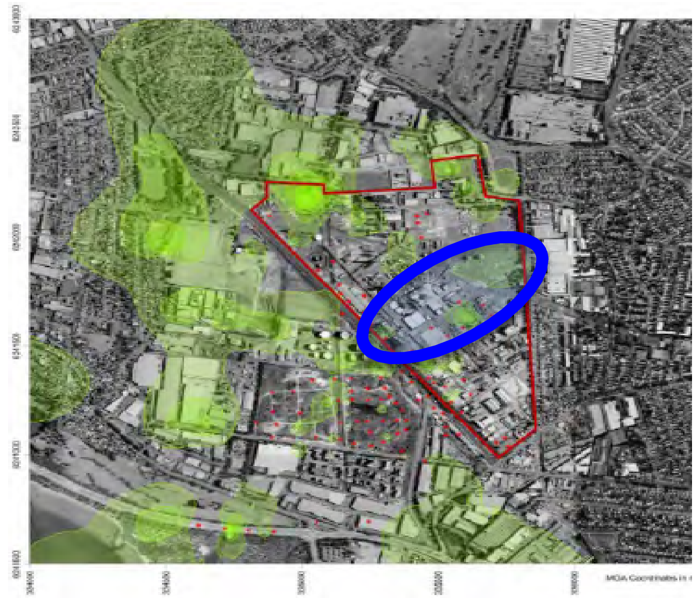
- IR Site 5 at N Island, Coronado, CA, USA
- ~1,000 m^2 = 0.1 Ha = 0.25 ac
- Sampling in 2015
- 10 traps deployed
- Former landfill (1,000-2,000 ton of hazardous waste disposal)
- EVO and ZVI remediation efforts
- Average fossil fuel flux: 0.49 micromole $CO_2/m^2.s$
- This translates into about 500 kg TCE/yr at a site ~0.1 Ha

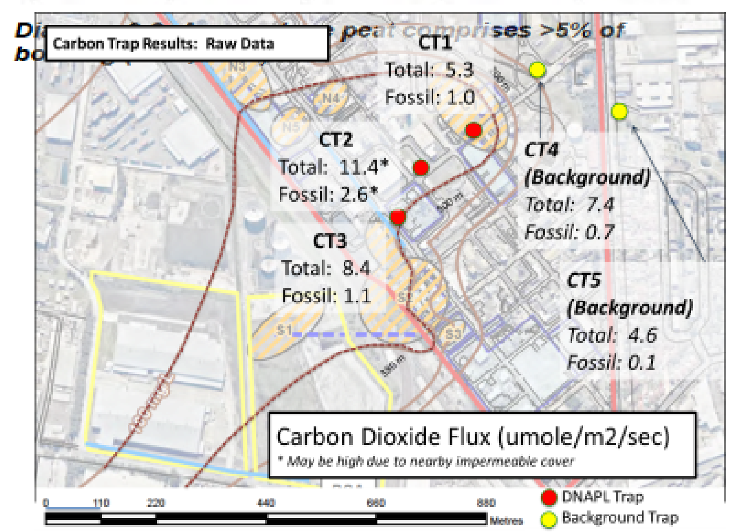


Site 2

Source: GSI, 2018, Battelle Conference, used with permission

- Orica, Sydney, Australia
- Sampling 2017, 5 CO2 traps deployed (3 at impacted locations, COC: 1,2 DCA)
- Complication: Natural peat in soils
- Used a modified 2-source model (3-source model using background locations for ^{14}C content attributable to peat)
- Equivalent to ~10-15 ton/Ha/yr of 1-2 DCE degraded

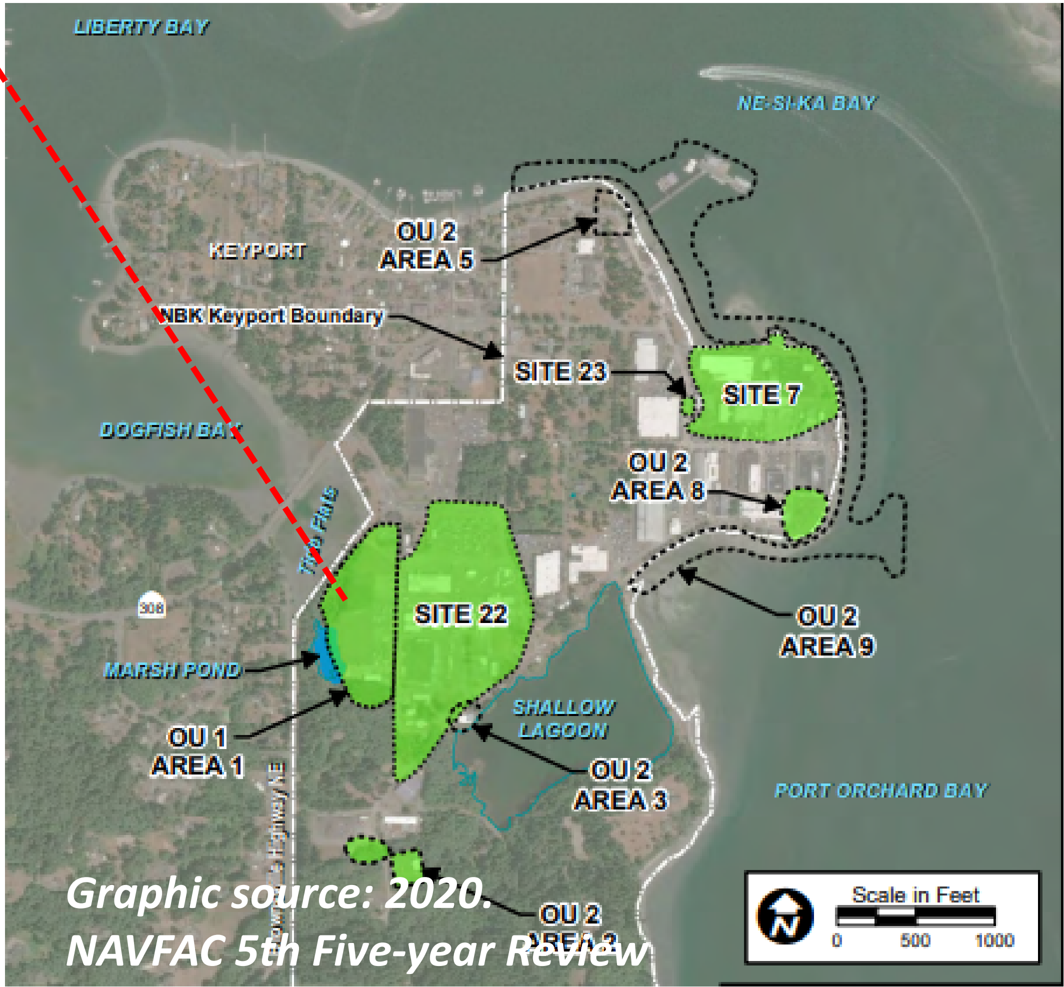




Site 3

- OU-1 Keyport, WA
- Two Rounds of Sampling, 10 samples each, 2019-2020

Non Detectable (ND) results after 2 rounds of sampling. CO_2 trap data consistent with other measurements



Graphic source: 2020. NAVFAC 5th Five-year Review

Site 4: Saint Juliens Creek Annex, VA

- Site 2, Saint Juliens Creek Annex

Chesapeake, VA

Impacted area ~2,200 m2

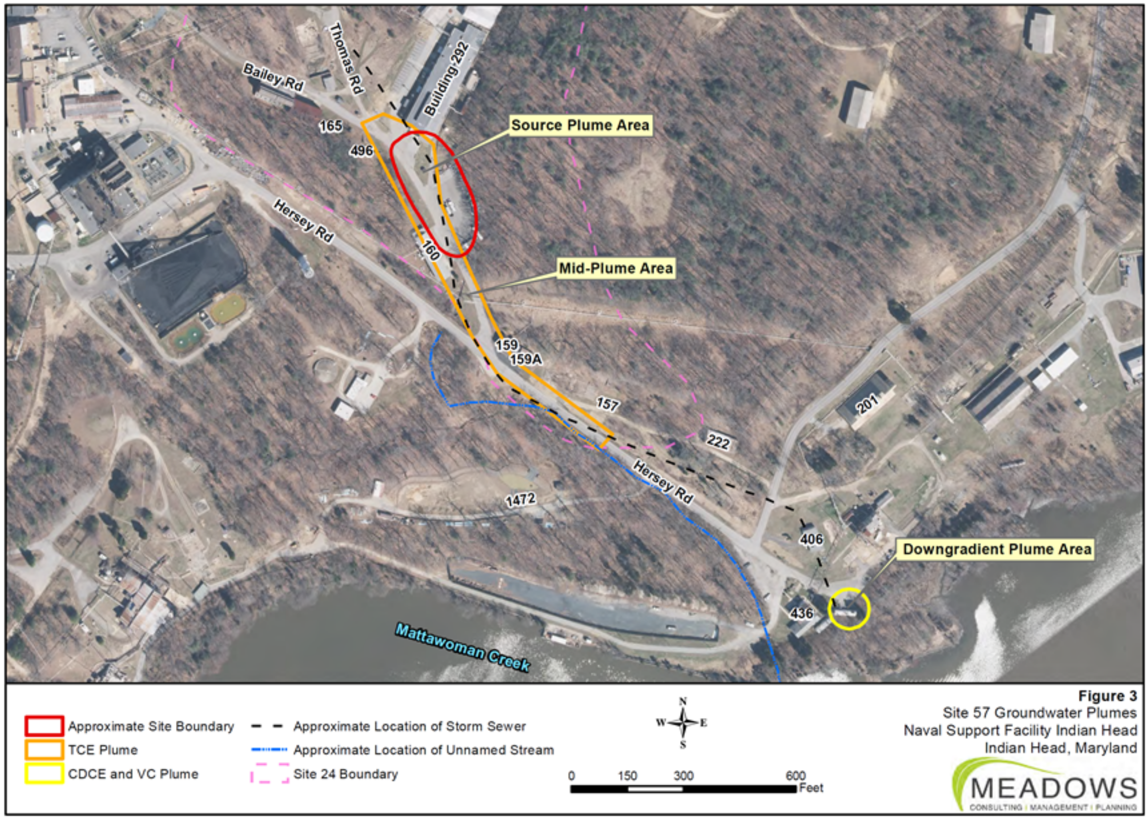
Replacement for OU-1 Keyport

- Site has chlorinated solvent contamination
- On-going assessment underway. Long term monitoring
- EVO injection at source area in 2019

Quarterly measurements ranged from ND (winter) to ~700 kg TCE yr (average ~250 kg TCE /yr)

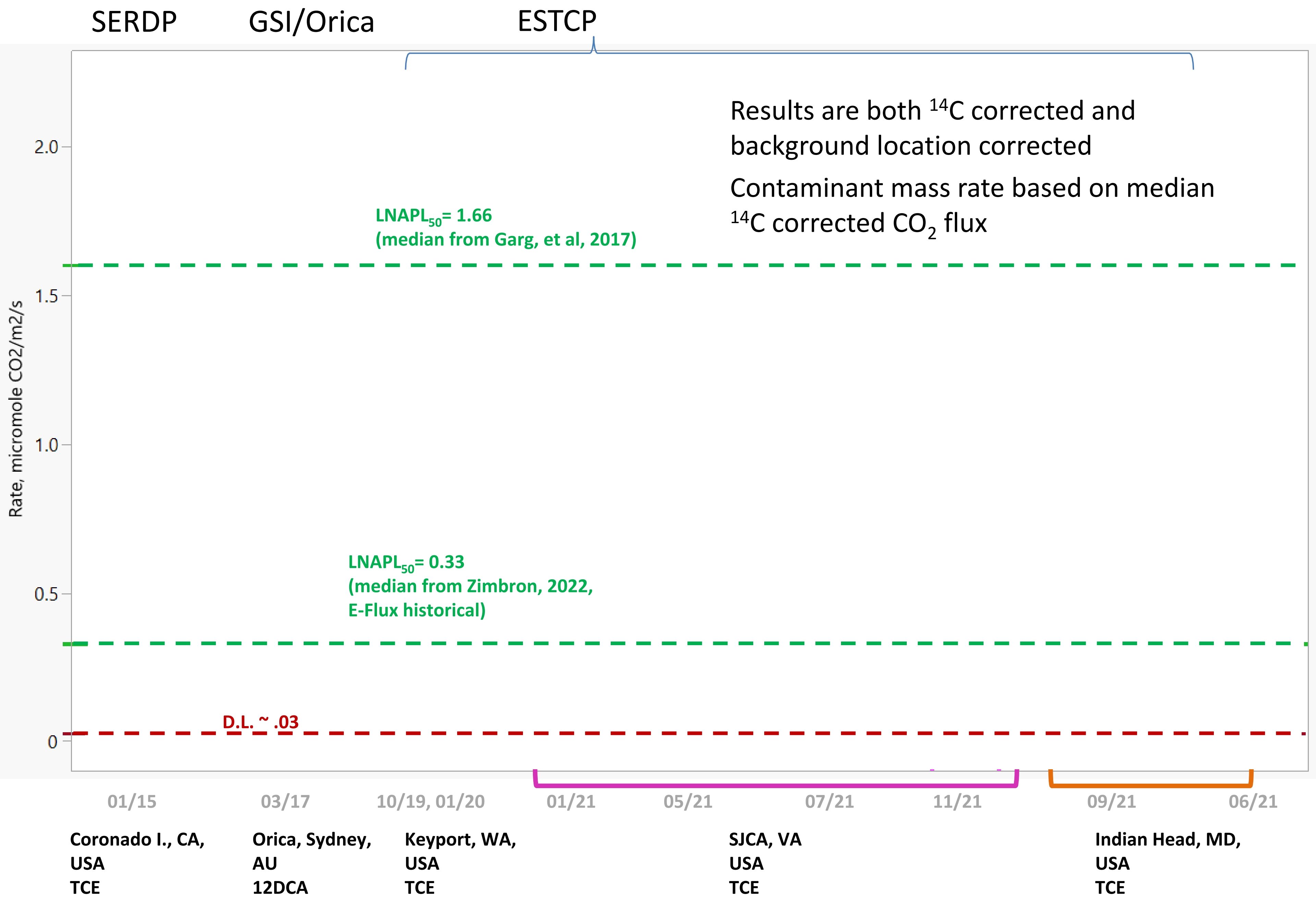
Site 5

- IR-57 at Indian Head NSWC, MD
- Source Plume ~3,800 m^2
- Site has chlorinated solvent contamination
- On-going assessment underway
- EVO injection at source area in April 2018

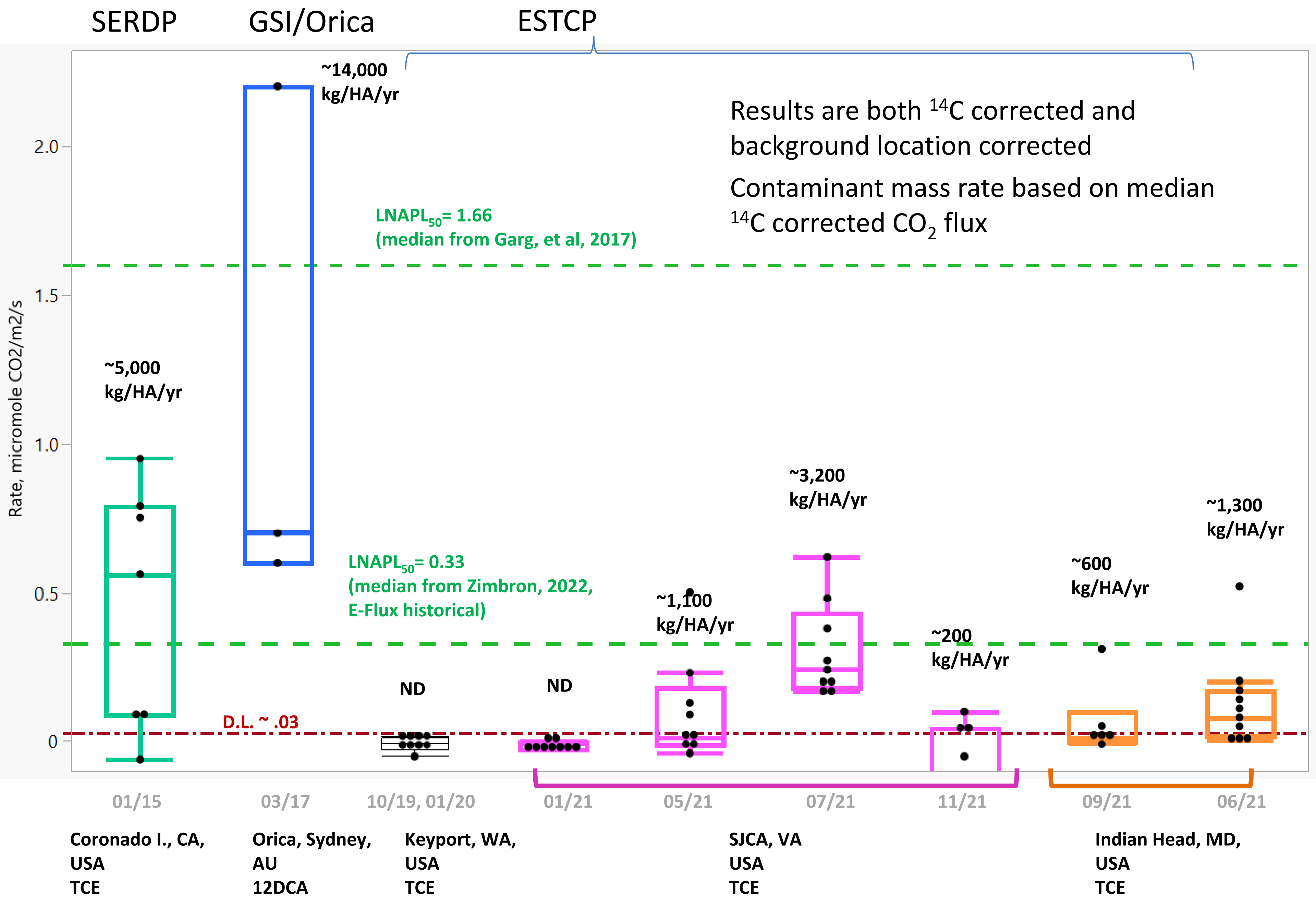


Two quarterly measurement (so far) ~230-400 Kg TCE/yr

Five Site Results



Five Site Results



Summary

- Fossil fuel CO_2 efflux signal pervasive at contaminated “hot spots” for all sites, except for one
- Current DL=0.03 micromole/m^2.s (equivalent to ~320 kg TCE/Ha.yr, or ~50 lb TCE/ac.yr)
- This sensitivity sufficient for “hot spots”, but higher sensitivity might be needed (easy to get)
- Co-contamination with petroleum can be an issue

  bot have fossil fuel carbon backbone
- Respirometry methods require adequate soil respiration

  impervious covered sites have been a challenge

Limitations

- Presentation limited on order of magnitude (OM) measurements using one technique (passive sampling using CO_2 traps)
- ESTCP projects will offer fuller view of each site (2+ sites)
- Discussion using multiple “lines of evidence” pending final ESTCP report
    - Geospatial correlations (source, dissolved plume)
    - Other techniques
    - Lab incubations (microcosm studies)
    - In well gas stripping + ROI model
    - RemChlor MD
- Other?

Conclusions

- Management of LNAPL contaminated sites revolutionized by NSZD through respirometry methods
- Applications: source mapping, remedy transition, NSZD as remedy…
- ^{14}C correction needed to see past modern carbon noise
- Long term (seasonal) variability
- First five sites of CO_2 Traps described today show remarkable consistency
- CO_2 Traps:
  - Multi-day deployment and 14C corrections
  - User friendly
  - Easy direct field quantification of chlorinated contaminant degradation rates
  - Sensitivity unmatched by other soil respiration methods
- Simple approach ready to help chlorinated solvent sites

E-FLUX

Easy set-up. Expert results.

Julio Zimbron, Ph.D.

www.soilgasflux.com

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Conclusions

- Most sites present measurable "^{14}C corrected respiration rates" using CO_2 traps
- CO_2 Traps:
  - User friendly
  - Easy direct field quantification of contaminant degradation rates
  - Sensitivity unmatched by other respirometry methods
- Partial results: first five sites of CO_2 Traps show consistency for chlorinated solvents
- Lessons from NSZD experience

  NSZD has revolutionized management of LNAPL sites through respirometry methods

  Applications: source mapping, remedy transition, NSZD as remedy…

  ^{14}C correction needed to see past modern carbon noise
- Simple approach ready to help chlorinated solvent sites

In Situ Microcosm: Overcoming Impervious Limitations

NSZD rate measurements rely on 1-D transport assumption

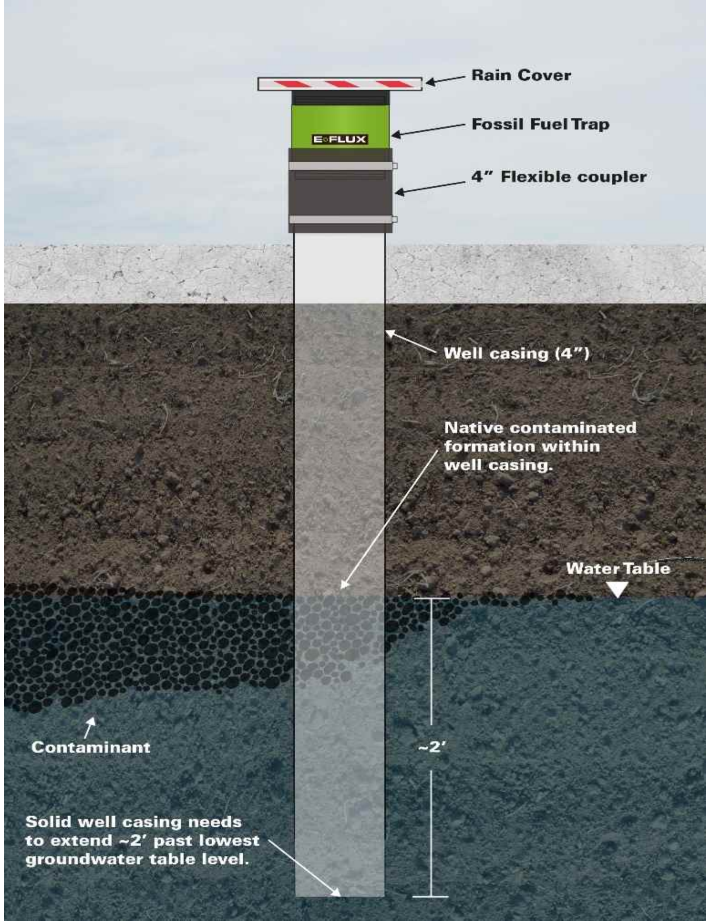
- Capped sites do not meet this condition
- Alternative: make a large opening

  ~6x6 ft
- Novel solution: closed system to force 1-D behavior. CO_2 monitoring as in an open system. All **native** local conditions are preserved:

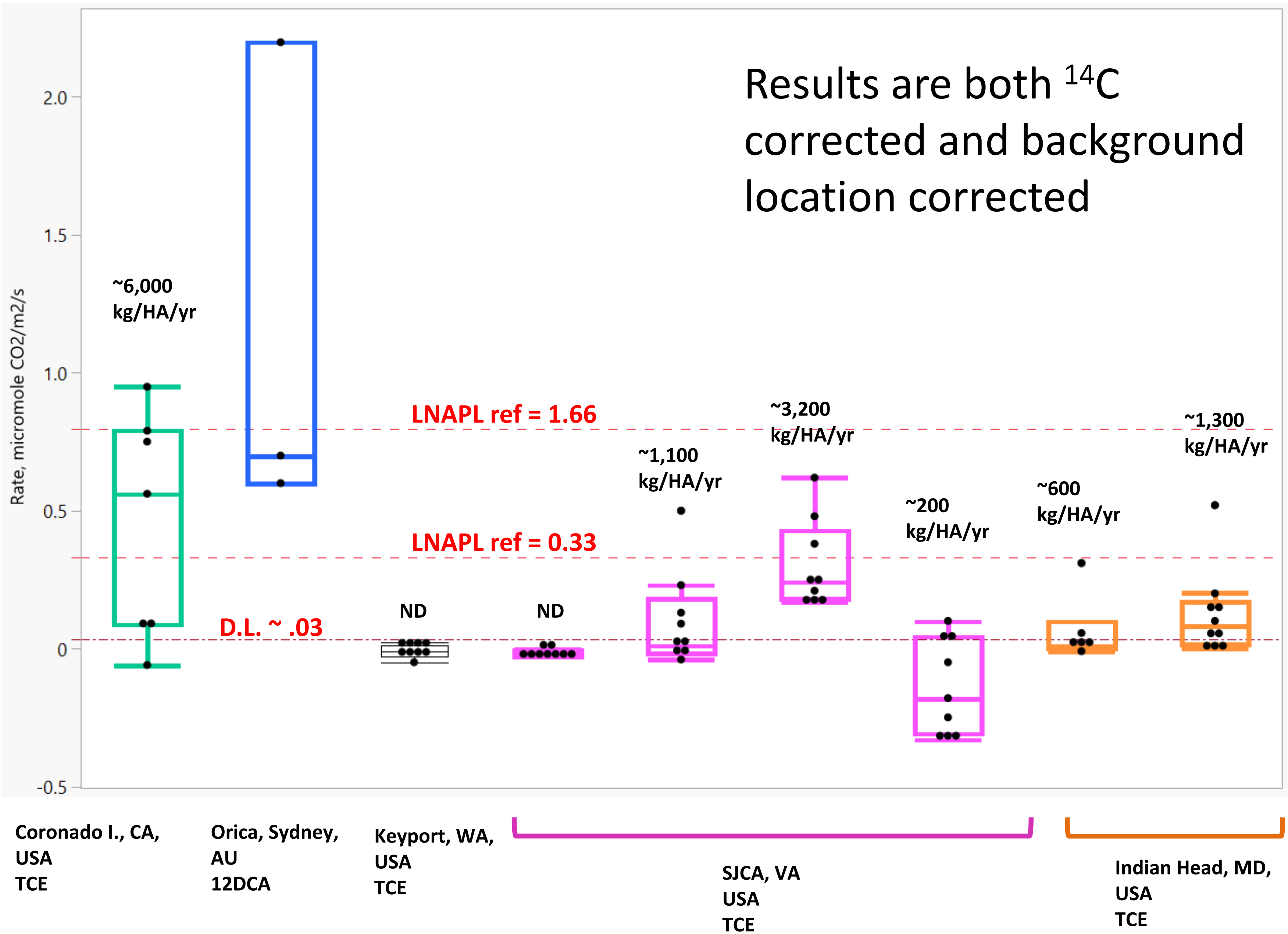
geochemistry	lithology
microbes	contaminant mass and distribution
temperature	

Limitation: shallow, direct push installation

So far tested at 2 LNAPL sites with excellent results



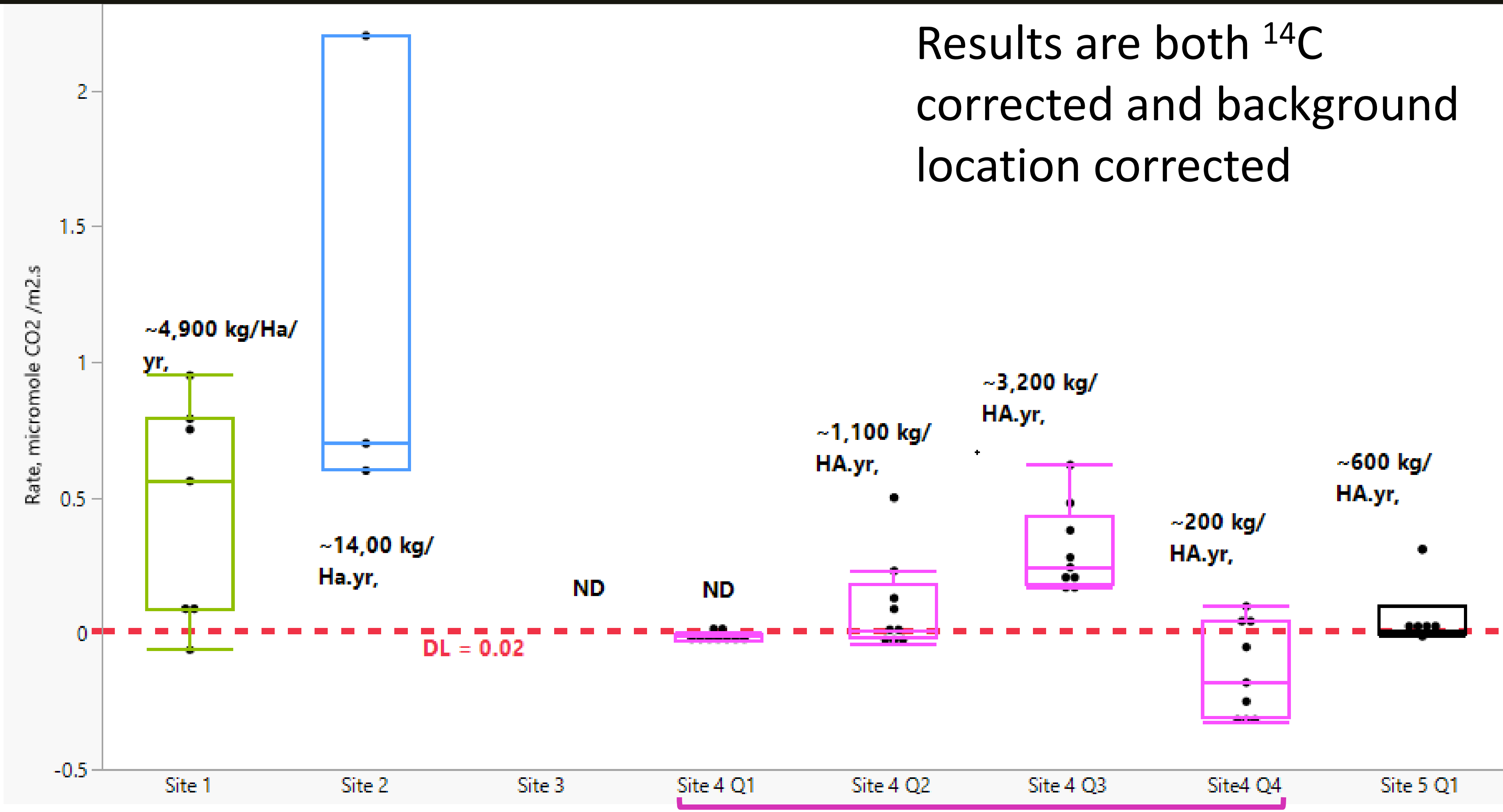
Five Site Results



Results are both ^{14}C corrected and background location corrected

Five Site Results

Results are both ^{14}C corrected and background location corrected



Coronado Island, CA, USA TCE

Orica, Sydney, AU 12DCA

Keyport, WA, USA TCE

SJCA, VA USA TCE

Indian Head, MD, USA TCE