HOW TO TAKE CREDIT FOR MOTHER NATURE CLEANING UP PETROLEUM IMPACTS

Fritz Krembs, P.E., P.G.

October 15, 2020

HISTORICAL CONTEXT

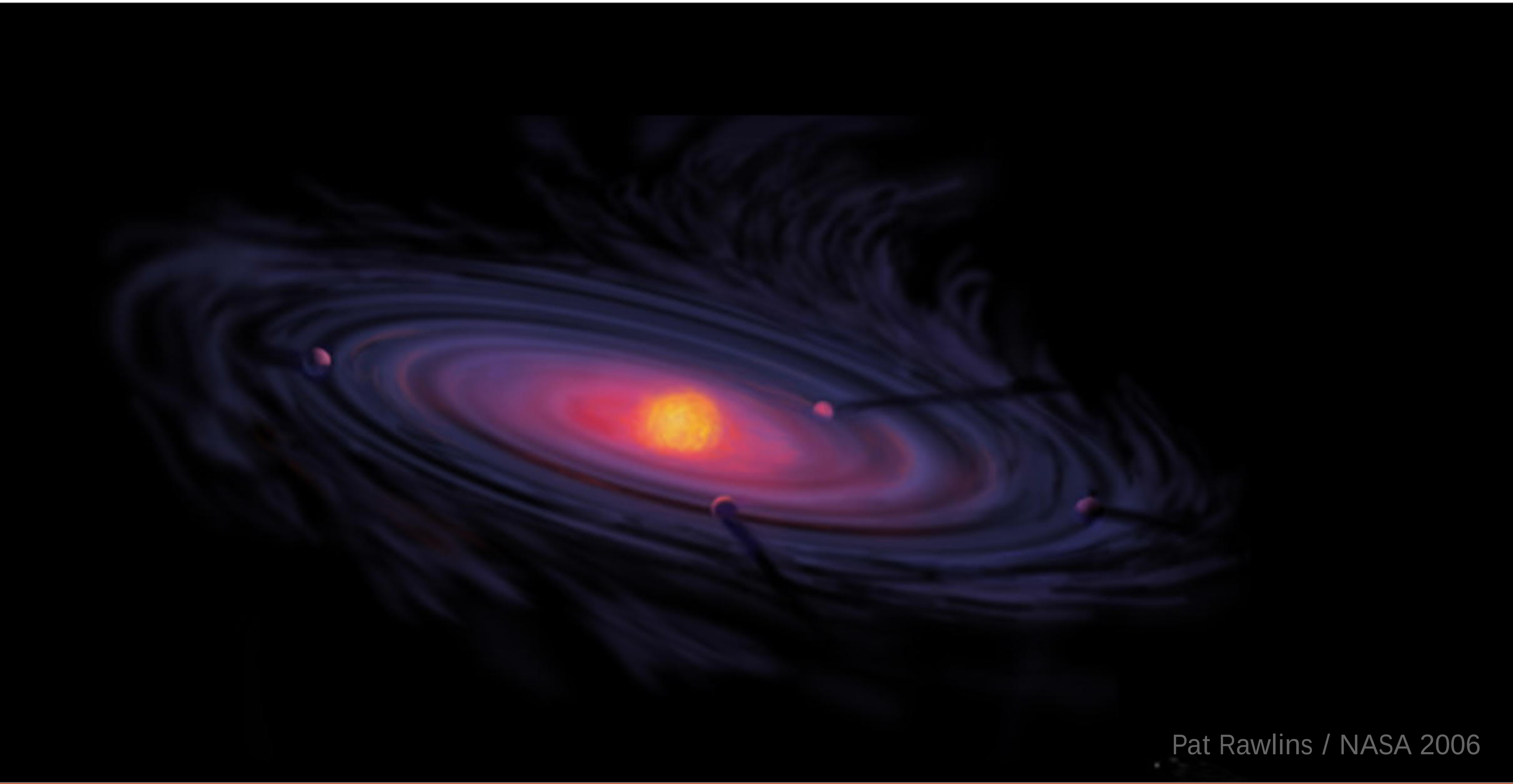
MICROBIAL ECOLOGY AND MONITORED NATURAL ATTENUATION (MNA)

NATURAL SOURCE ZONE DEPLETION (NSZD)

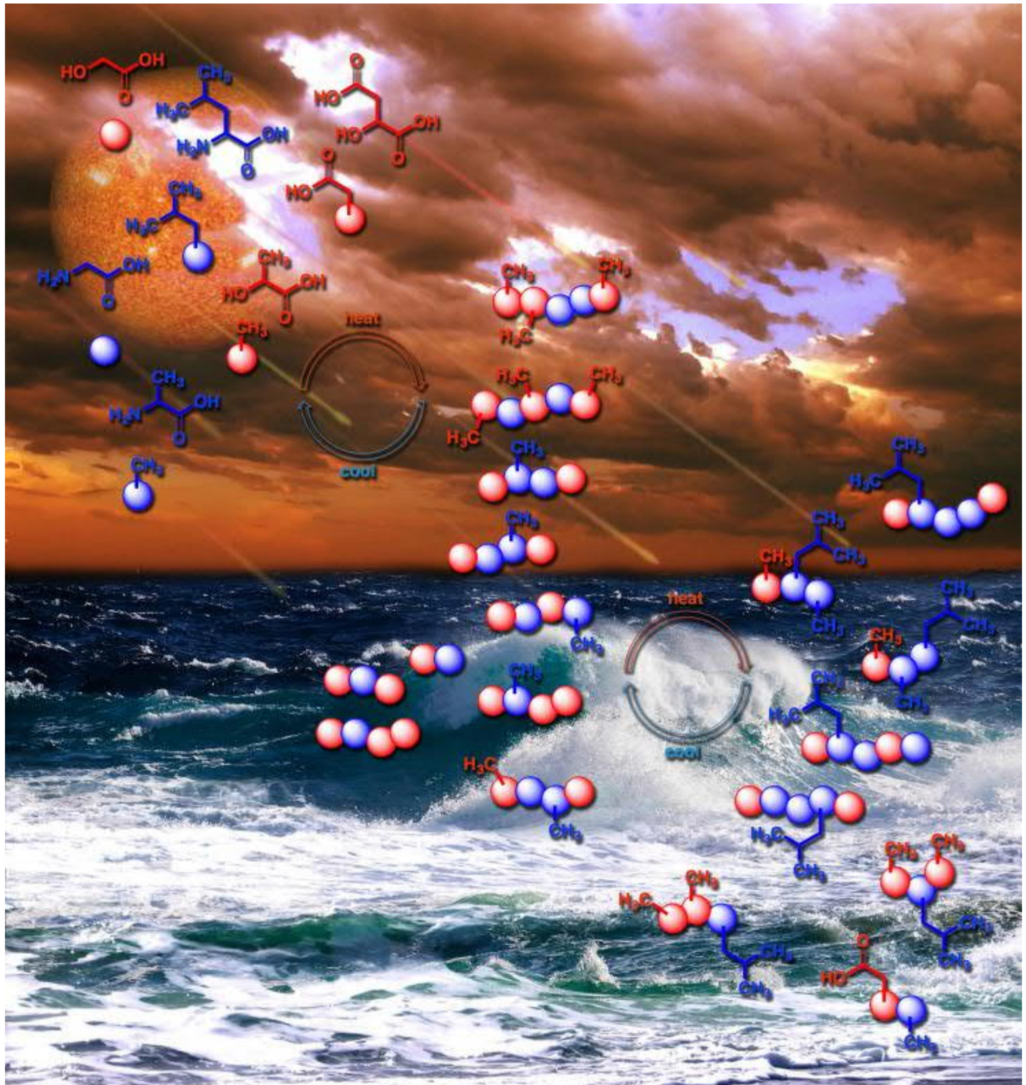
CASE STUDIES

Krembs, 2020

IN THE BEGINNING… UNIVERSE STARTS 13.7 BILLION YEARS AGO



IN THE BEGINNING… SOLAR SYSTEM FORMS 4.6 BILLION



Ram Krishnamurthy / Georgia Tech Center for Chemical Evolution

IN THE BEGINNING... LIFE BEGINS 4.0 BILLION YEARS AGO

“Last Universal Common Ancestor”

IN THE BEGINNING... LIFE BEGINS 4.0 BILLION YEARS AGO

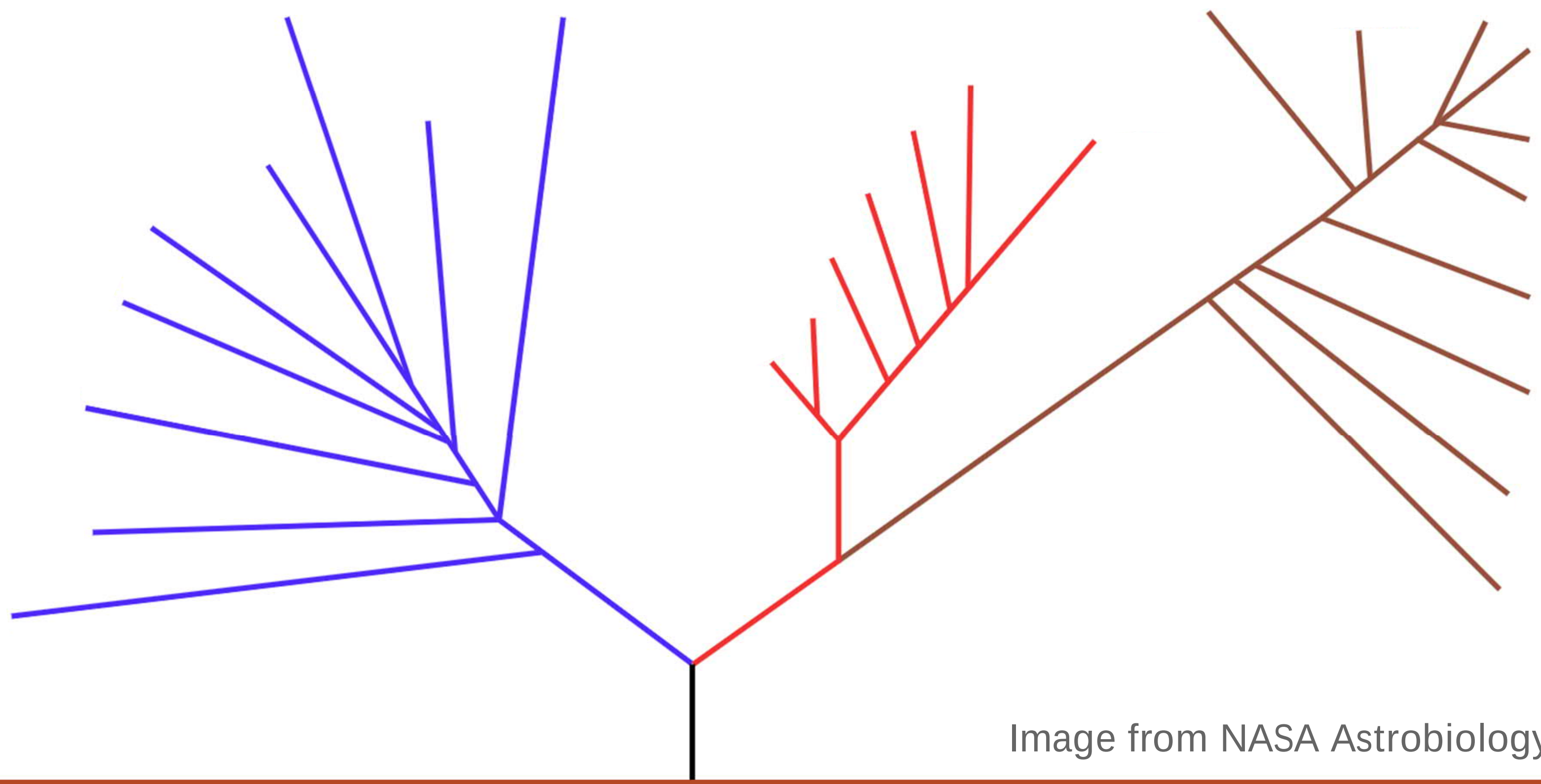


Image from NASA Astrobiology Institute

IN THE BEGINNING... PHYLOGENETIC TREE OF LIFE

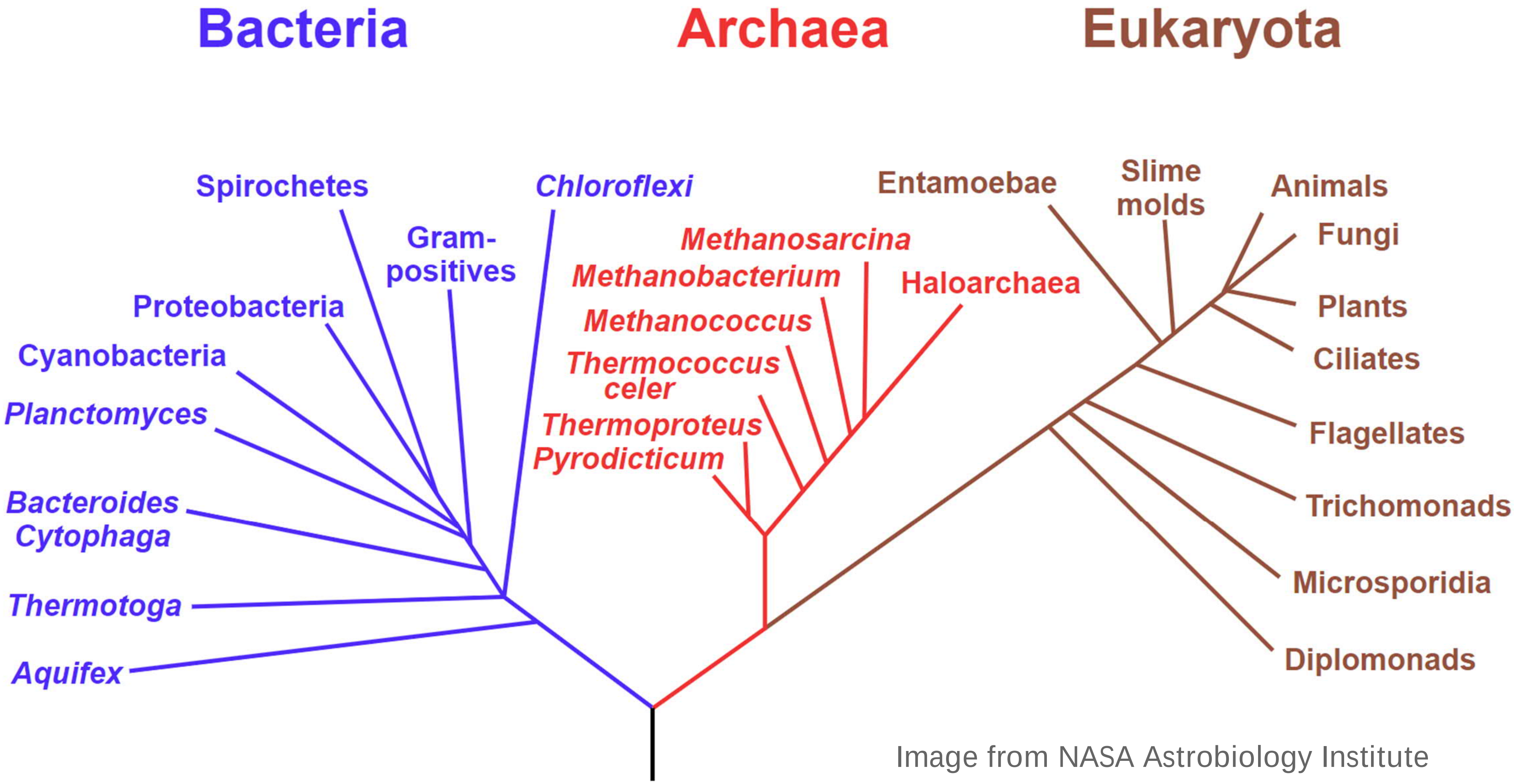
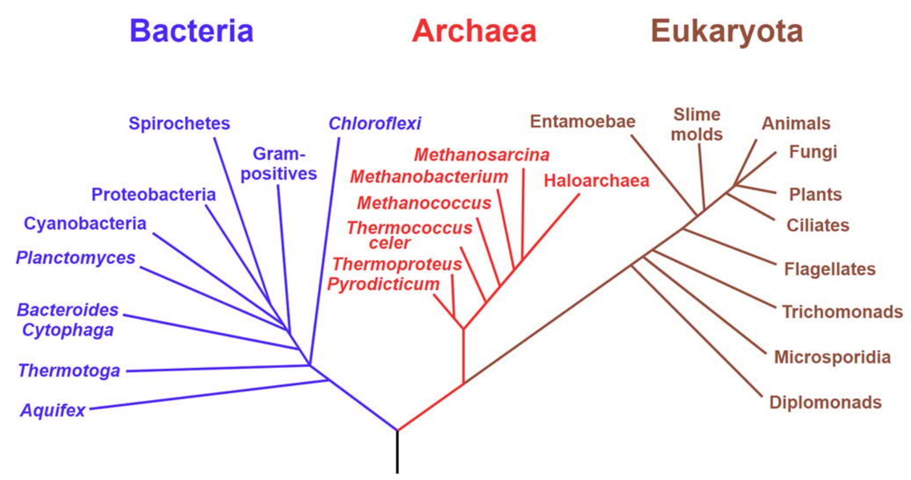


Image from NASA Astrobiology Institute

PHYLOGENETIC TREE OF LIFE

KEY POINTS ON HISTORICAL CONTEXT

- Life on Earth is very diverse
- Most of that diversity is things that are very small
- Very small things can perform many different functions



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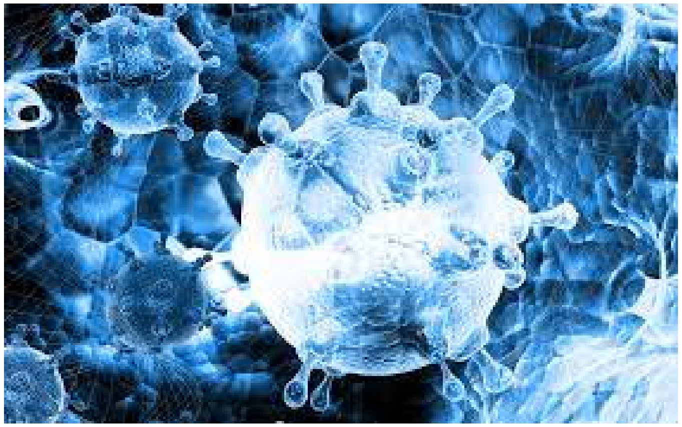
HISTORICAL CONTEXT

MICROBIAL ECOLOGY AND MONITORED NATURAL ATTENUATION (MNA)

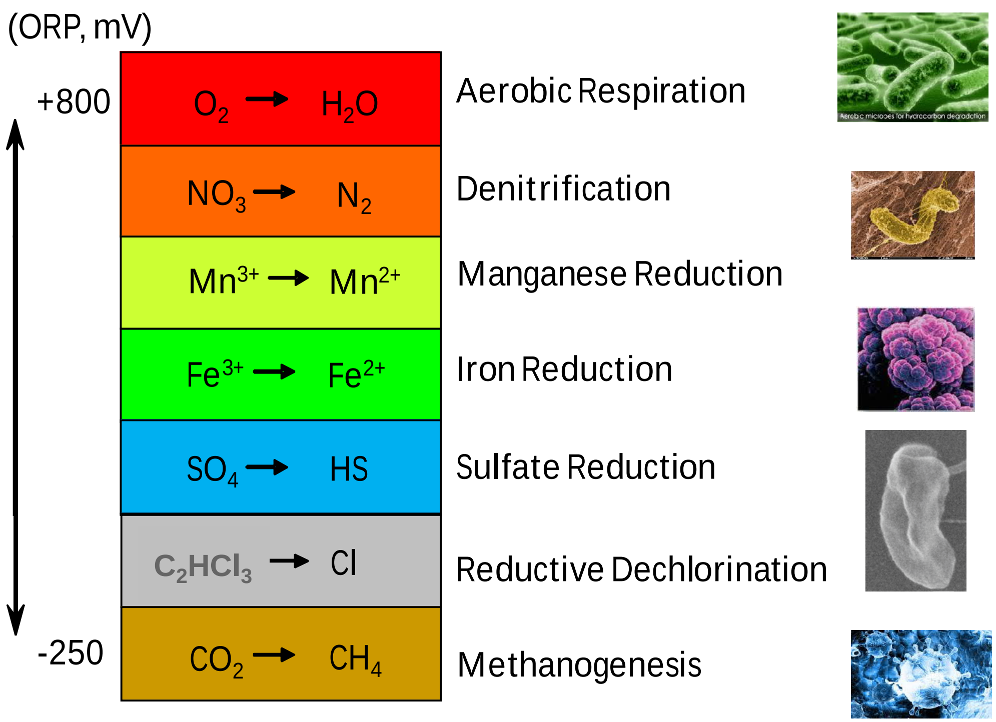
NATURAL SOURCE ZONE DEPLETION (NSZD)

CASE STUDIES

- Carbon source ("food")
  - Organic carbon
  - Petroleum
  - CO_2
- Terminal electron acceptor (what they "breathe")
  - Oxygen, nitrate etc. (see next slide)



MICROBIAL ECOLOGY – GROWTH REQUIREMENTS



MICROBIAL ECOLOGY – REDOX LADDER (WHAT THEY “BREATHE”)

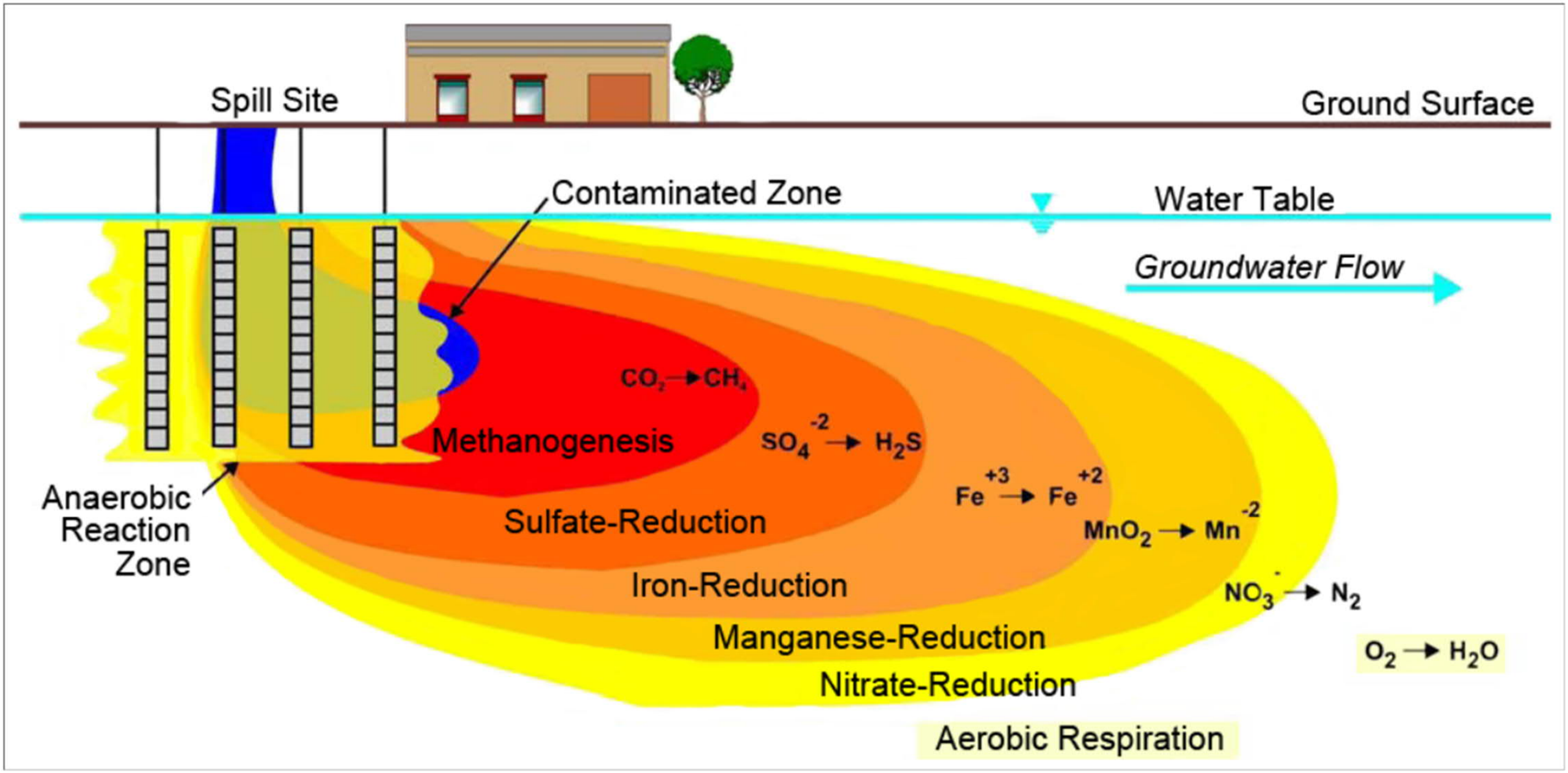
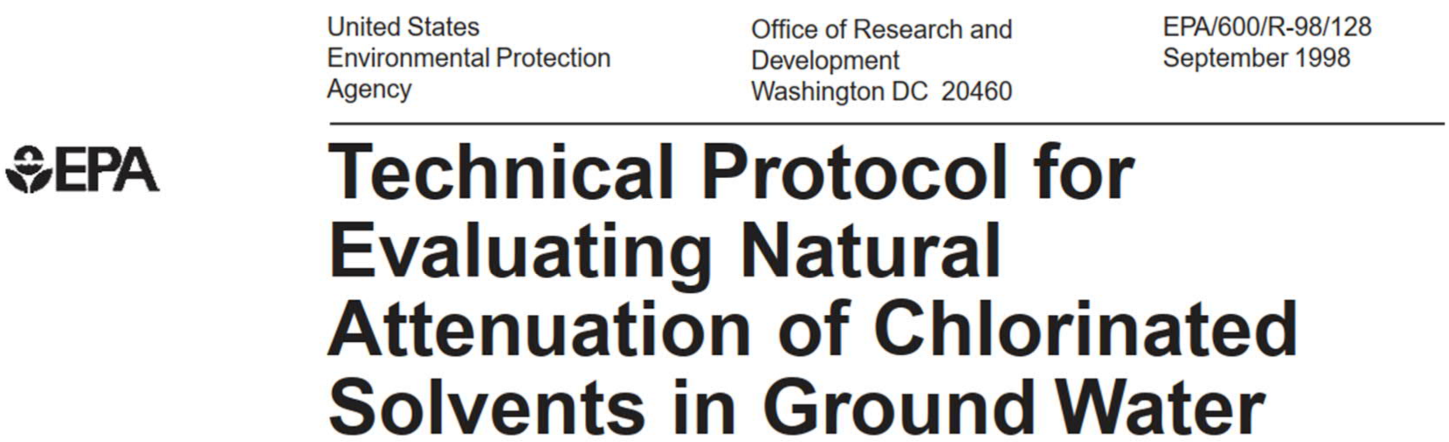


Image from USEPA clu-in.org after Parsons 2004

MICROBIAL ECOLOGY – REDOX LADDER IN SUBSURFACE

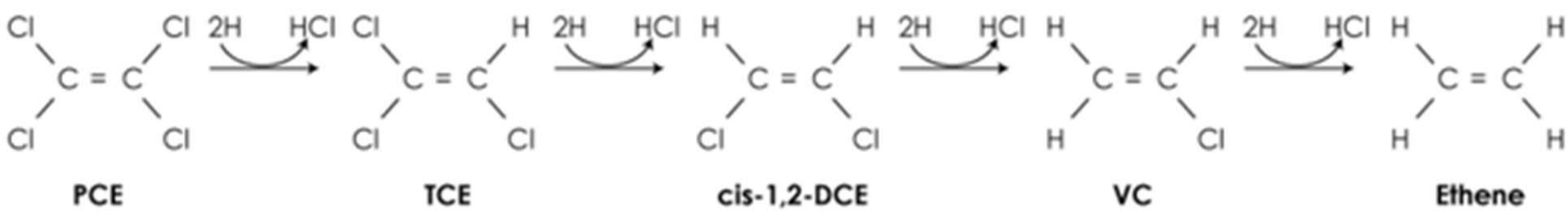

United States
Environmental Protection
Agency

Office of Research and
Development
Washington DC 20460

EPA/600/R-98/128
September 1998

EPA

Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water

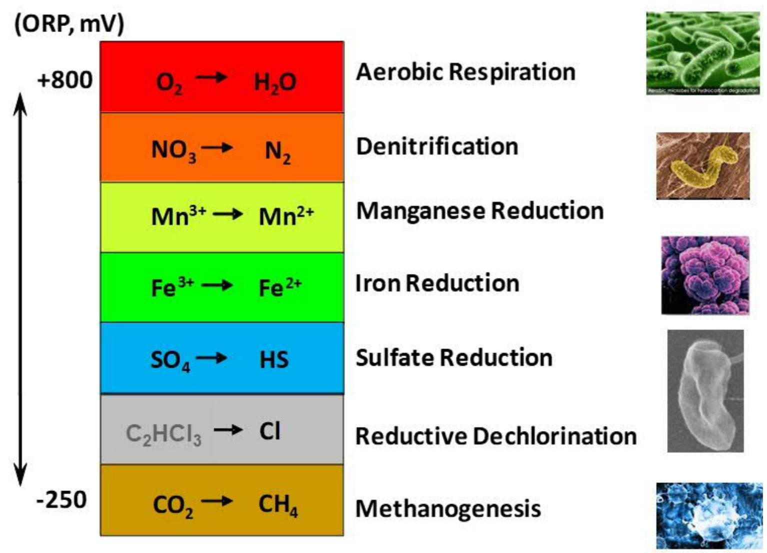


Images from ITRC (left) and Apkarian & Taylor, Emory Univ. (right)

NATURAL ATTENUATION OF CHLORINATED SOLVENTS

KEY POINTS ON MICROBIAL ECOLOGY

- Bacteria need a carbon source and terminal electron acceptor
- The order in which TEAs are consumed is quite predictable
- There is a long, well-understood track record for natural attenuation of chlorinated compounds



HISTORICAL CONTEXT

MICROBIAL ECOLOGY AND MONITORED NATURAL ATTENUATION (MNA)

NATURAL SOURCE ZONE DEPLETION (NSZD)

CASE STUDIES

Natural Source Zone Depletion

- Natural Source Zone Depletion (NSZD) is monitored natural attenuation for petroleum free product

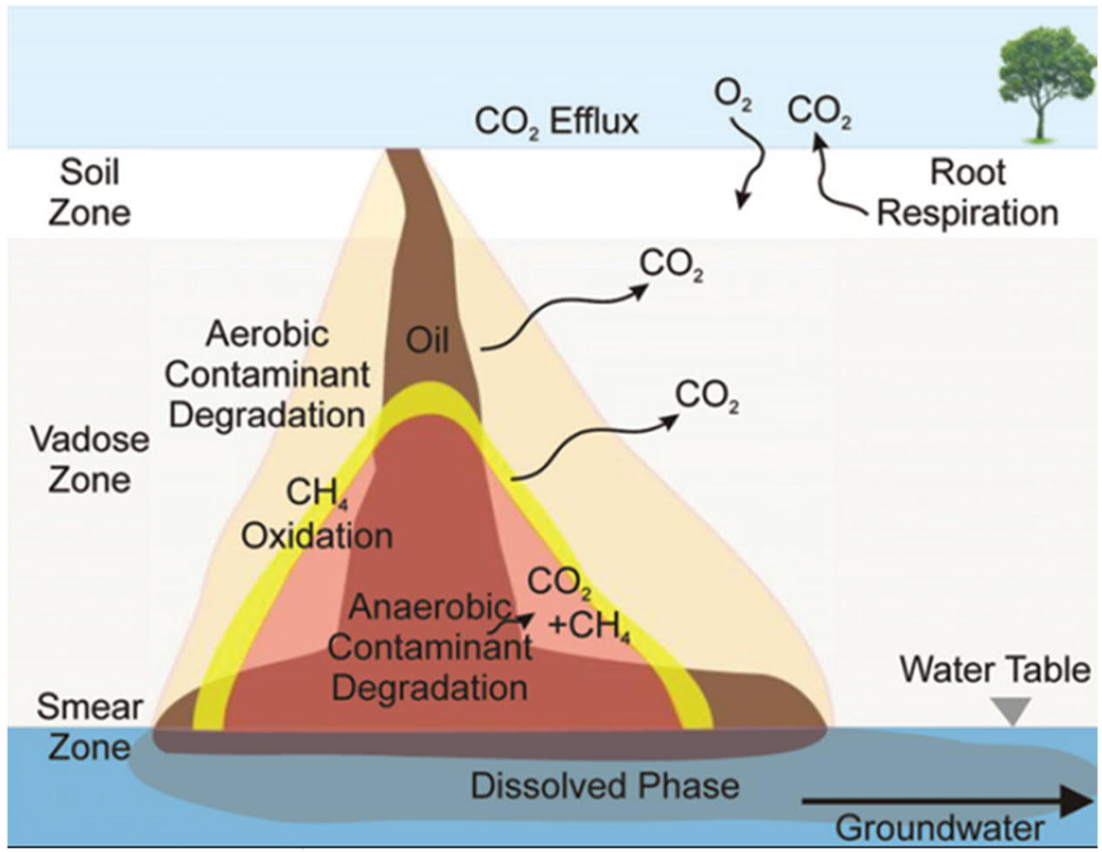


Image from Sihota and Mayer (2012)

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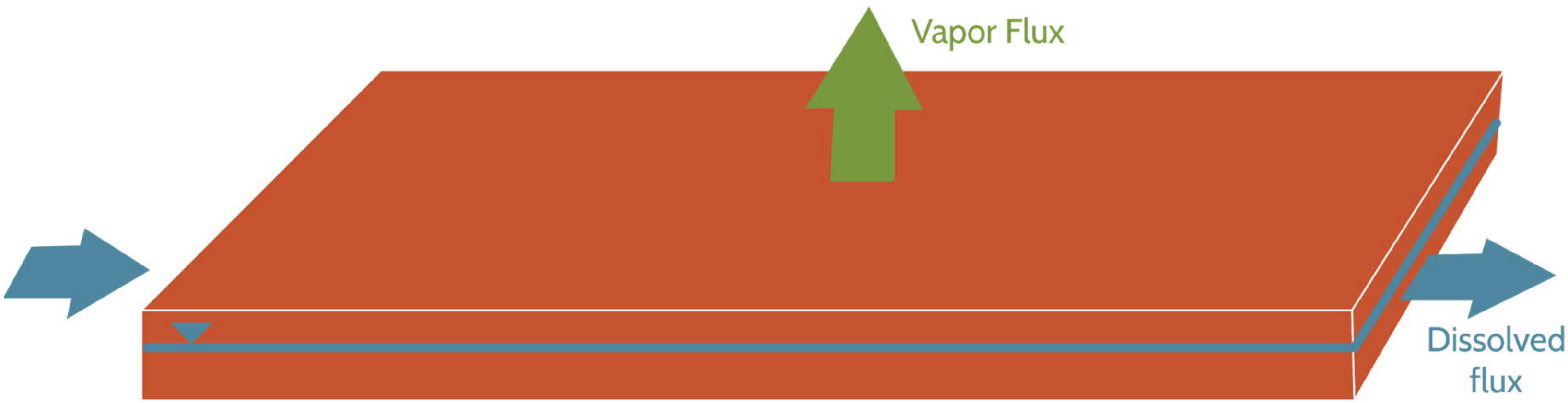
NSZD Rates



- Lundegard and Johnson (2006) report mass loss measured by vapor flux (10^{-1} to 10^{2} g TPH/m^{2}-day) as 2 orders of magnitude greater than mass loss measured by dissolved flux.
- Others report similar vapor loss rates (summarized in Sihota et al. 2011).
- Relatively high vapor loss rates are consistent with a typically large flux plane for volatilization and subsequent biodegradation.

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NSZD Measurement Methods

Concentration Gradient Method

- Install nest of vapor wells above LNAPL smear zone
- Measure O_2, CH_4, and hydrocarbons in soil gas
- Measure vapor diffusion coefficient
- Plot soil gas profiles
- Determine flux planes
- Calculate O_2, CH_4, and hydrocarbon flux
- Convert O_2 and CH_4 flux to hydrocarbon flux

  (Note – some practitioners use CO_2 profiles for calculation. Some others use temperature.)

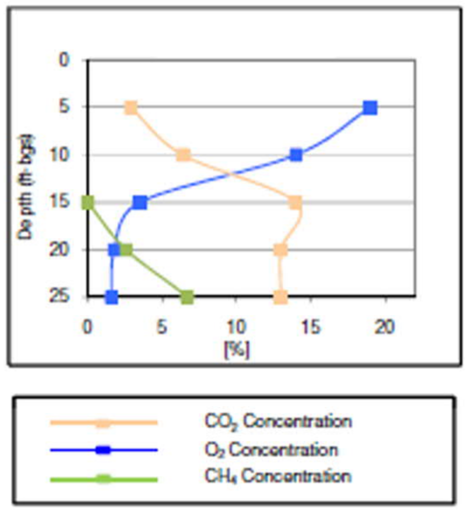


Image from Michalski et al. (2011)

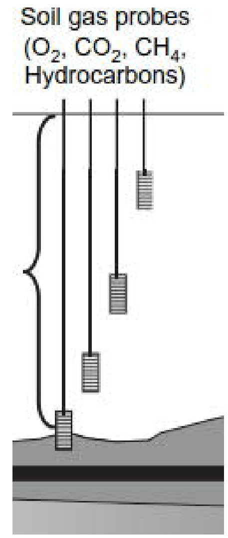
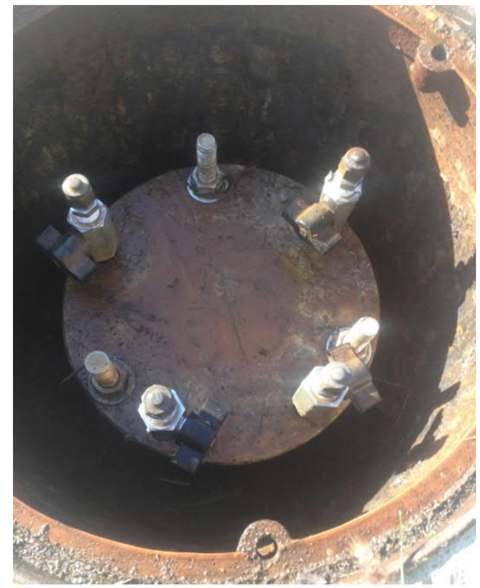


Image from Lundegard and Johnson (2006)



Dynamic Closed Chamber Method

Image from www.licor.com

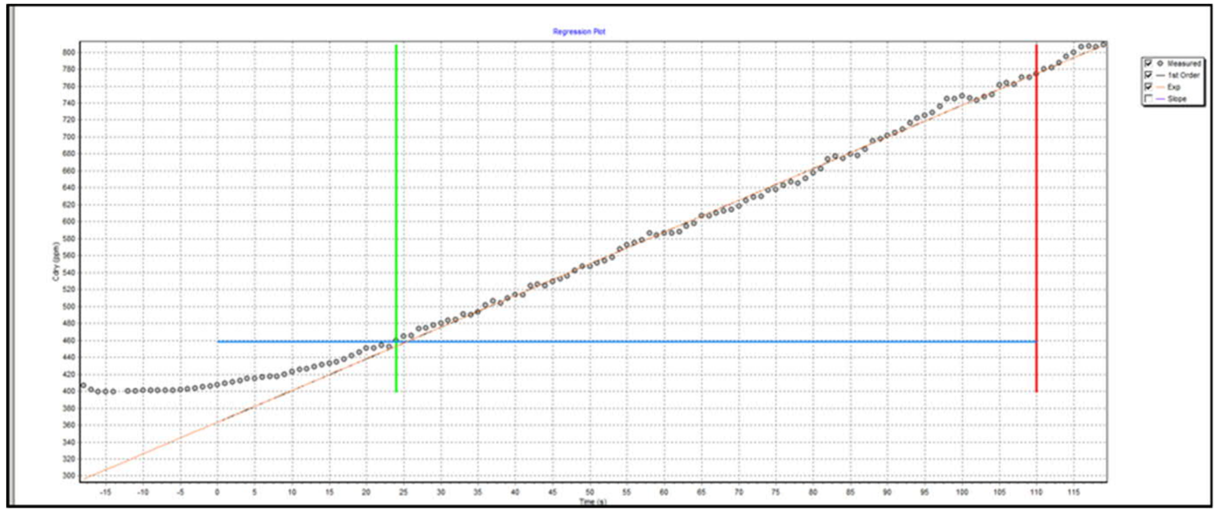


Image from LI-COR data file

- Install soil collars at ground surface, and allow to equilibrate.
- Place dynamic chamber and measure CO_2 concentration for short period (minutes).
- Convert CO_2 time trend to flux.
- Repeat in uncontaminated area.
- Convert CO_2 flux to hydrocarbon flux by subtracting background from contaminated area values, or using radiocarbon (^{14}C) correction.

CO_2 Trap Method

Images from www.soilgasflux.com

- Install soil collars at ground surface, and allow to equilibrate.
- Place CO_2 trap for extended period (2 to 4 weeks).
- Repeat in uncontaminated area.
- Send traps to lab. Quantify sorbed CO_2 concentration and calculate CO_2 flux.
- Convert CO_2 flux to hydrocarbon flux by subtracting background from contaminated area values. Alternatively, supplier offers measurement of CO_2 radiocarbon content to estimate flux attributable to hydrocarbon biodegradation.

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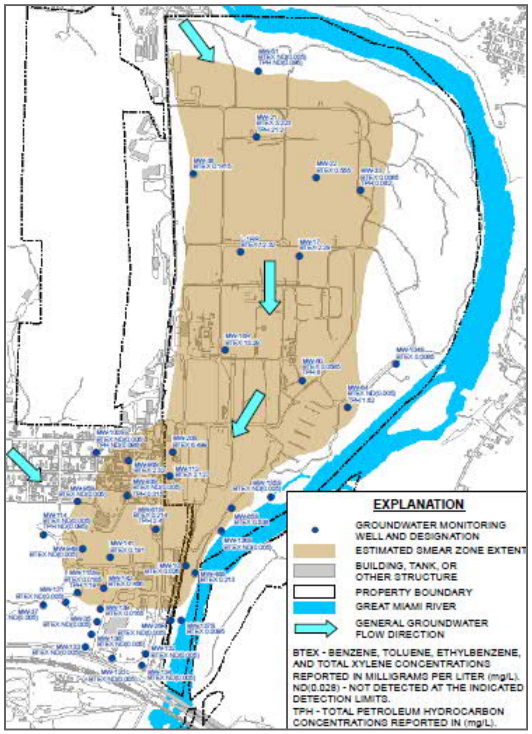
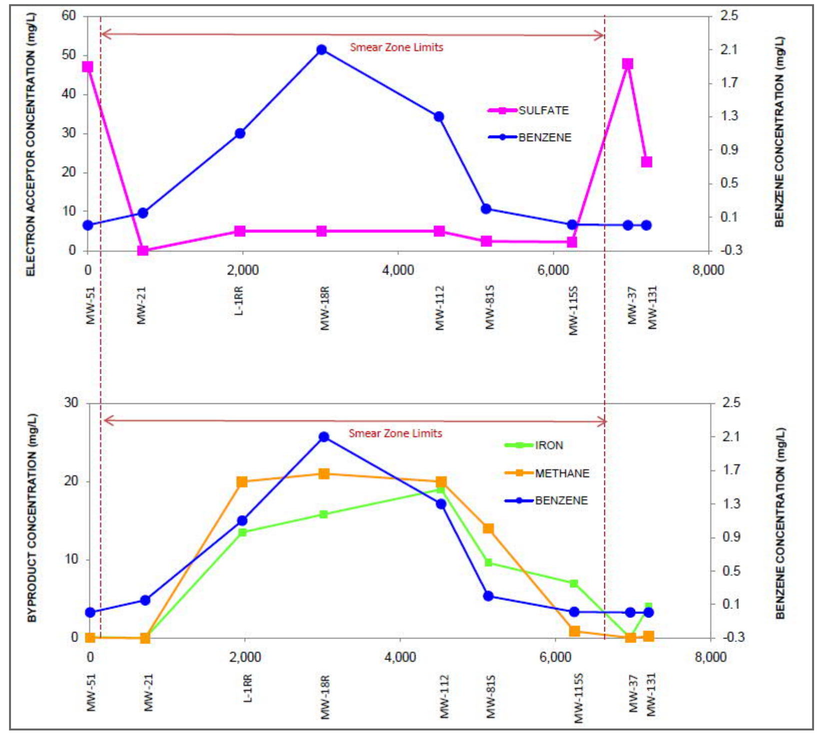
NSZD in the Saturated Zone





Images from Michalski et al. (2011)

Concentration versus distance plots indicate hydrocarbon dissolution and biodegradation within the source zone

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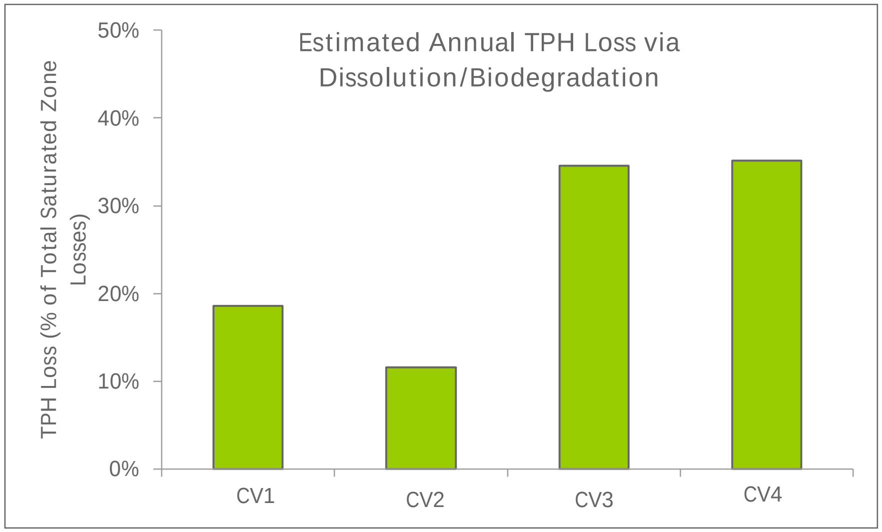
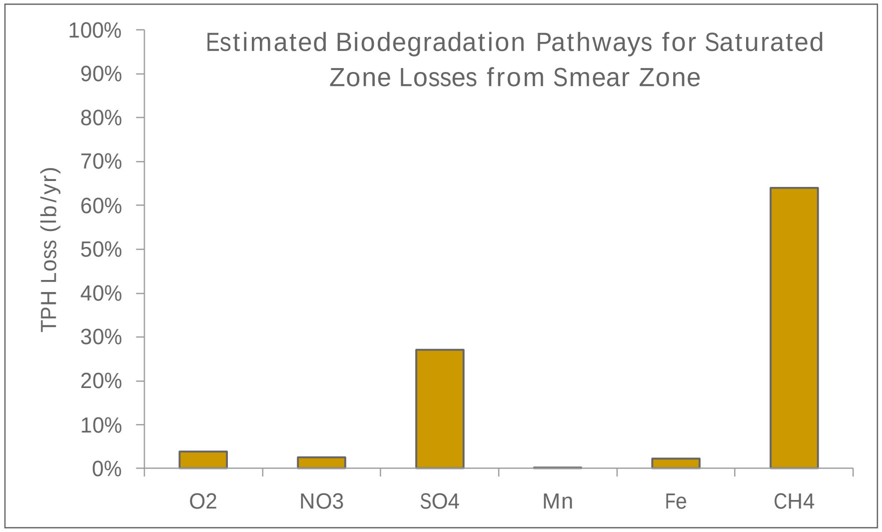
NSZD in the Saturated Zone

- Typical MNA data (i.e., biodegradation reactants and products) can be used to estimate NSZD rates.
- Identifies dominant attenuation mechanisms in saturated zone.
- Provides information on viable enhancements should natural rates be lower than expected.





Images from Michalski et al. (2011)

Thermal Monitoring of NSZD Rates

- Two articles are currently available for using heat profiles in the subsurface to estimate NSZD rates.
  - Sweeney and Ririe (2014)
  - Warren and Bekins (2015)
- Multiple entities are developing mathematical models that use the heat is generated by hydrocarbon / methane biodegradation in the vadose zone to estimate NSZD rates.
- Even without those models it is possible to collect robust temperature data to support NSZD evaluations.

Groundwater Monitoring&Remediation

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

by Robert E. Sweeney and G. Todd Ririe

Journal of Contaminant Hydrology 182 (2015) 183–193

Contents lists available at ScienceDirect

Journal of Contaminant Hydrology

journal homepage: www.elsevier.com/locate/jconhyd

ELSEVIER

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

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Why Measure NSZD?

- “Polishing” step
- Indicator to end active remediation
- Higher resolution site characterization
- In support of green remediation
- In support of conventional remediation

NSZD as a "Polishing" Step

- ITRC guidance (December 2009): NSZD effective at:
  - Decreasing LNAPL saturations
  - Changing LNAPL composition
  - Improving groundwater concentrations
  - Improving vapor concentrations
- NSZD generally considered useful, but not the first step in remediation because of the long timeframe.

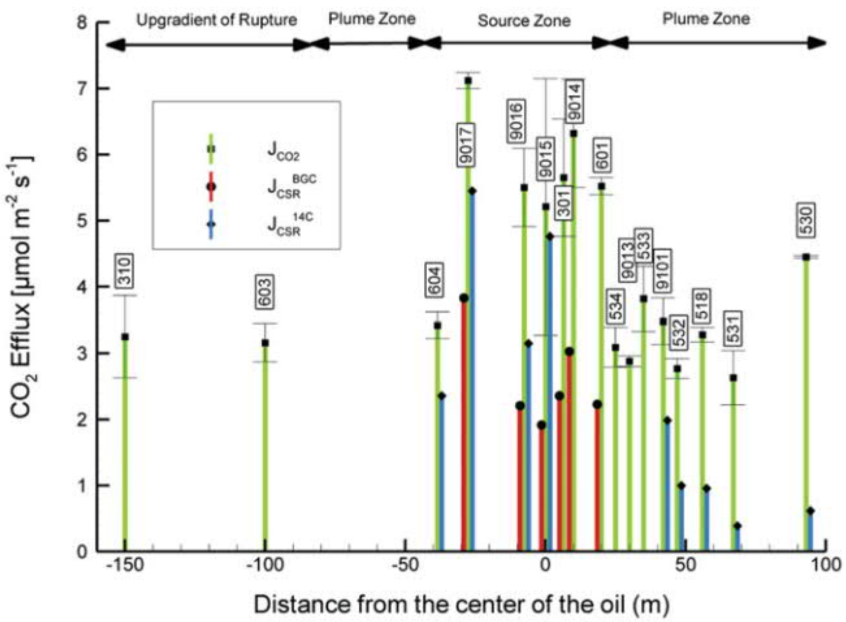
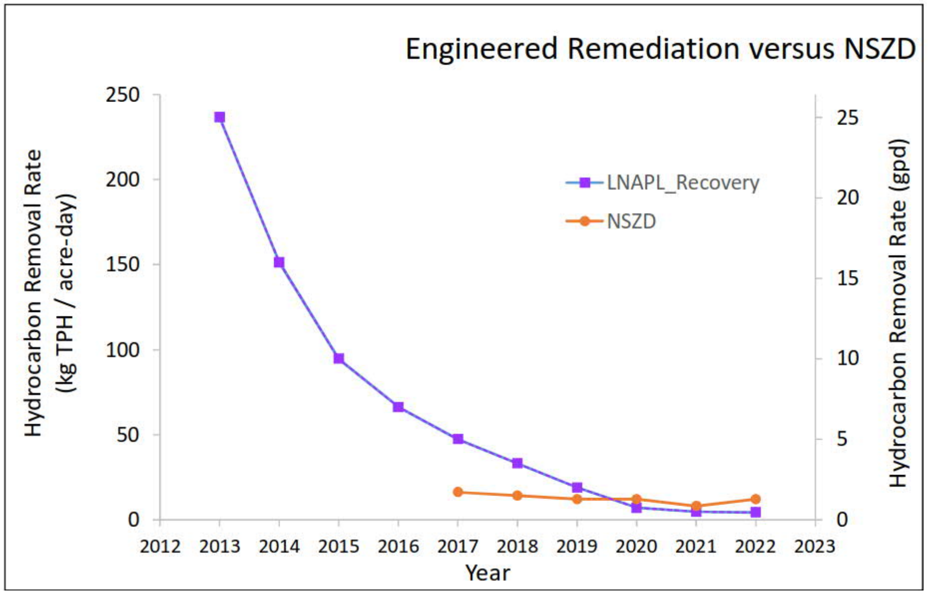


Image from Sihota and Mayer (2012)

NSZD as Indicator to End Active Remediation

- Engineered remediation systems eventually reach diminished returns, but regulators can be reluctant to approve shutdown.
- If NSZD rates are similar to or even higher than what high-footprint systems are achieving, this can be an argument to suspend operations.



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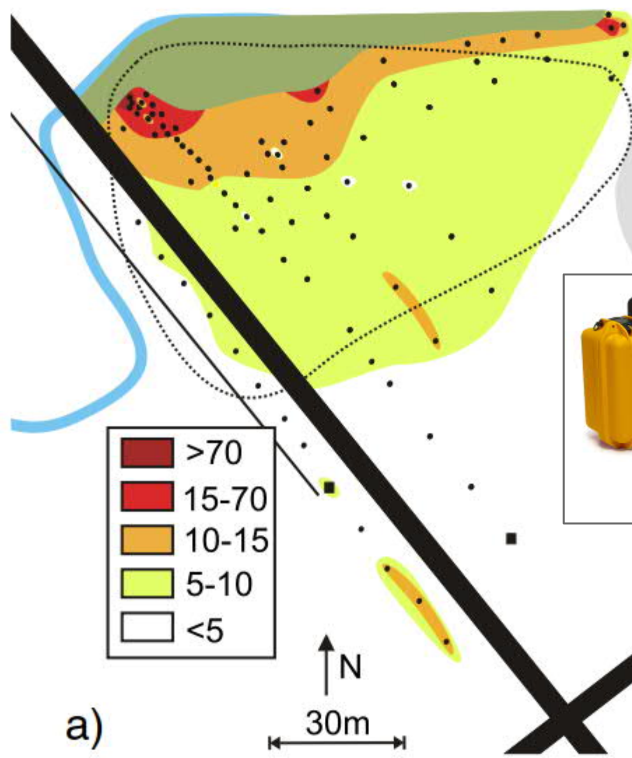
NSZD for Higher Resolution Site Characterization

- Dynamic closed chamber in particular can provide many measurements in a short time.
- Can help identify smear zone hot spots.
- Team can “take credit” for areas with high NSZD rates, and target remediation to areas with lower rates.



Map image from Sihota et al. (2013), instrument image from licor.com

New Guidance Documents

- NSZD is covered in Appendix C to the Interstate Technology Regulatory Council (ITRC 2018) LNAPL Guidance Document
  - Describes the alignment of NSZD data collection to LNAPL management objectives
  - Available at https://www.itrcweb.org
- NSZD is covered in API Publication 4784 (2017): Quantification of Vapor Phase-related Natural Source Zone Depletion Processes
  - Describes field methods for several of the NSZD approaches
  - Available at https://global.ihs.com for $204 (multi-user pdf)

Printed from: Interstate Technology & Regulatory Council (ITRC). 2018. *Light Non-Aqueous Phase Liquid (LNAPL) Site Management: LCSM Evolution, Decision Process, and Remedial Technologies.* LNAPL-3. Washington, D.C. https://lnapl-3.itrcweb.org.

Appendix B-Natural Source Zone Depletion (NSZD) Appendix

Executive Summary

Numerous sites across the country are impacted with light, nonaqueous-phase liquids (LNAPL). LNAPL Natural Source Zone Depletion (NSZD) occurs through the combined action of natural processes that reduce the mass of LNAPL in the subsurface. Key NSZD processes include volatilization, dissolution, and biodegradation; these processes reduce LNAPL mass, saturation, and mobility over time. NSZD rates (i.e., the rates of bulk LNAPL mass depletion) are often higher than historically acknowledged.

This document updates and supersedes earlier ITRC guidance on NSZD (ITRC 2009b), reflecting advances in the intervening years in understanding NSZD mechanisms (including direct biodegradation of LNAPL) and methods to confirm the occurrence and/or quantify the rate of NSZD. This appendix discusses key mechanisms and several frequently-used NSZD assessment methods, including:

- The **gradient method**, based on soil gas composition,
- **Carbon dioxide flux based-methods**, including CO_2 traps and flux chambers, and
- The **biogenic heat monitoring method**.

This appendix discusses the importance of incorporating NSZD into the three stages of the LNAPL Conceptual Site Model (LCSM) development process (the Initial LCSM, Remedy Selection LCSM, and Design and Performance LCSM). NSZD is a fundamental aspect of understanding issues such as LNAPL mobility, distribution, and longevity, and thus is a key part of the Initial LCSM. In later LCSM stages, NSZD can be evaluated as a remedial alternative, with NSZD serving in one or more of the following roles:

- A **baseline** to evaluate the relative benefit of other technologies (e.g., by comparing an LNAPL skimming system's removal rates to NSZD rates);
- A **stand-alone remedy** at sites where LNAPL-related impacts are stable, potential receptors are not at risk, and NSZD timeframes are consistent with the goals of the site owner and with regulatory requirements;
- A **component of a remedy,** where NSZD is primary remedy component for portions of the LNAPL zone, and engineered remediation systems are focused on those portions of the LNAPL footprint where more aggressive removal is appropriate to meet remedial goals; and
- A final step in a treatment train, where there is **remedy transition** to NSZD as a long-term risk management approach after other remedial technologies have achieved their design objectives.

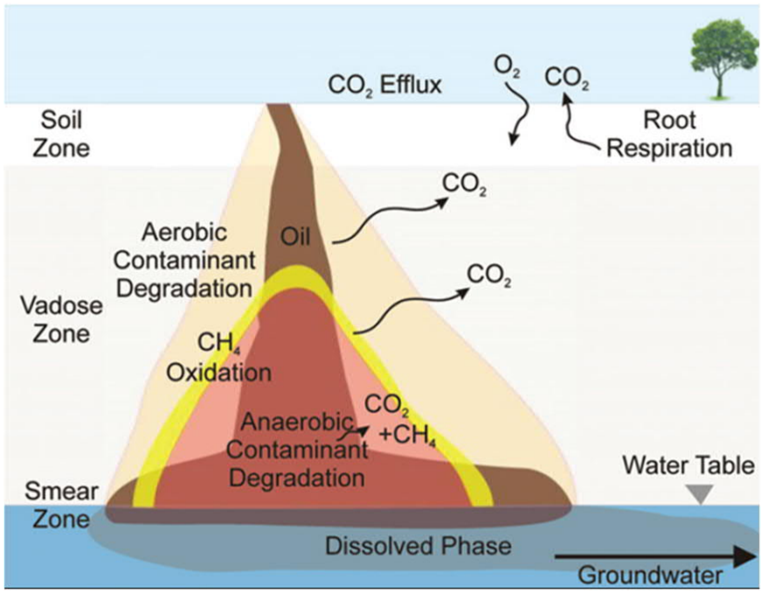
NSZD is an underlying driver of progress toward remedial goals at almost all LNAPL sites, through reductions in LNAPL mobility and LNAPL body longevity, and changes in LNAPL composition. Research continues into developing and refining methods to confirm NSZD activity and quantify NSZD rates.

1.0 Introduction

Numerous sites across the country are impacted with light, nonaqueous-phase liquids (LNAPL). LNAPL Natural Source Zone

KEY POINTS ON NSZD

- NSZD is a demonstrated technology
- NSZD processes occur without human intervention
  - They can also be enhanced
- Multiple methods are available for quantifying NSZD rates



HISTORICAL CONTEXT

MICROBIAL ECOLOGY AND MONITORED NATURAL ATTENUATION (MNA)

NATURAL SOURCE ZONE DEPLETION (NSZD)

CASE STUDIES

Aerial view of surface oil contamination from the pipeline rupture at the Bemidji Crude Oil Spill Research Site, Minnesota (circa 1979). Much of the black area was caused by oil spraying from the rupture.

Images from USGS Toxic Substances Hydrology Program

CASE STUDY – BEMIDJI SITE

Image from Interactive Planning and Management 2001

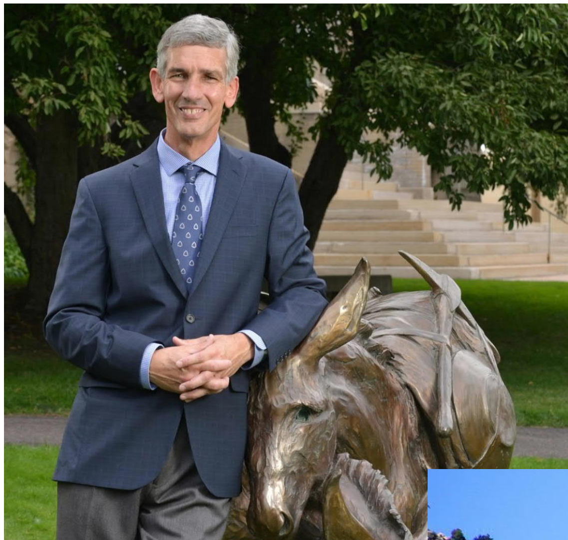
CASE STUDY – GUADALUPE DUNES

California
Red-legged
Frog

Images from guadalupedunes.com

Silvery Legless Lizard

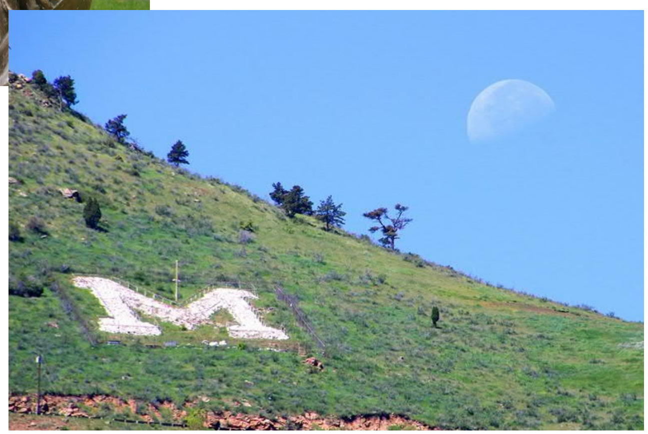
CASE STUDY – GUADALUPE DUNES



Ground Water Monitoring&Remediation

Source Zone Natural Attenuation at Petroleum Hydrocarbon Spill Sites—II: Application to a Former Oil Field

by Paul D. Lundegard and Paul C. Johnson



CASE STUDY – GUADALUPE DUNES

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

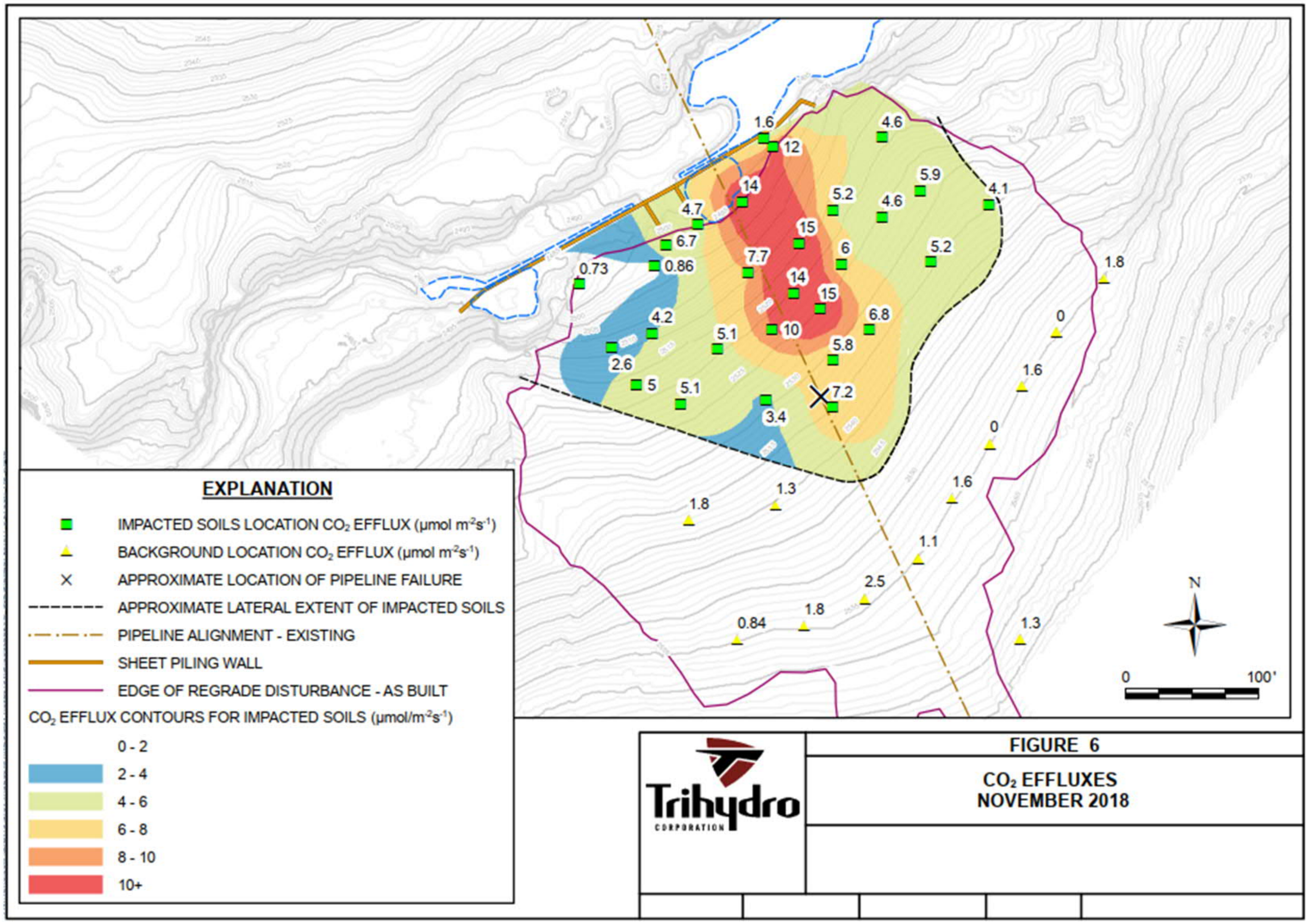
Table 3

Examples of Site-Wide Average NSZD Rate Measurements at Field Sites

NSZD Study	Number of Sites	Site-Wide NSZD Rate (All Sites) (Gallons/Acre/Year)	Site-Wide NSZD Rate (Middle 50%) (Gallons/Acre/Year)	Reference
Refinery terminal sites	6	2100–7700	2400–3700	McCoy 2012
1979 crude oil spill	1	1600	—	Sihota et al. 2011
Seasonal range		310–1100	—	Sihota et al. 2016
Refinery/terminal sites	2	1100–1700	1250–1550	Workgroup, L.A. LNAPL 2015
Fuel/diesel/gasoline	5	300–3100	1050–2700	Piontek et al. 2014
Diverse petroleum sites	11	300–5600	600–800	Palaia 2016
All studies	25	300–7700	700–2800	
Saturated zone electron acceptor biodegradation capacity	**9**	**0.4–53**	**1.7–19**	This paper (see Appendix S1)

Notes: Middle 50% column shows the 25th and 75th percentile values. To demonstrate the significance of methanogenesis, NSZD rates calculated from the biodegradation capacity of electron acceptors in the saturated zone, ignoring methanogenesis, are shown in the last row.

CASE STUDY – DATA MINING



- Site-Specific NSZD Rate of 94 bbls oil / yr
- Comparable to ongoing recovery
- 75th Percentile of Garg et al.

CASE STUDY – PIPELINE RELEASE

Summary

- NSZD is becoming an accepted remedial technology, especially as a "polishing step" following active remediation.
- Measuring NSZD has considerably more application than just "MNA for smear zones." The available tools open up possibilities for:
  - Setting remedial endpoints
  - Increased spatial coverage for characterizing smear zones
  - Demonstrating effectiveness of green and sustainable remediation
  - Supporting conventional remediation (when desired)
- Recent advances include guidance documents, CO2 efflux evaluations, and thermal monitoring approaches.

Questions?

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WHAT WHY WHERE WHEN WHO HOW

References (1 of 2)

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