HOW TO TAKE CREDIT FOR MOTHER NATURE
CLEANING UP PETROLEUM IMPACTS

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IN THE BEGINNING... UNIVERSE STARTS 13.7 BILLION YEARS AGO
IN THE BEGINNING... SOLAR SYSTEM FORMS 4.6 BILLION
IN THE BEGINNING... LIFE BEGINS 4.0 BILLION YEARS AGO
IN THE BEGINNING... LIFE BEGINS 4.0 BILLION YEARS AGO

“Last Universal Common Ancestor”
IN THE BEGINNING... 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
HISTORICAL CONTEXT

NATURAL SOURCE ZONE DEPLETION (NSZD)

MICROBIAL ECOLOGY AND MONITORED NATURAL ATTENUATION (MNA)

CASE STUDIES
- Carbon source ("food")
  - Organic carbon
  - Petroleum
  - CO₂
- Terminal electron acceptor
  (what they "breathe")
  - Oxygen, nitrate etc. (see next slide)
<table>
<thead>
<tr>
<th>ORP (mV)</th>
<th>Reaction</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>+800</td>
<td>$\text{O}_2 \rightarrow \text{H}_2\text{O}$</td>
<td>Aerobic Respiration</td>
</tr>
<tr>
<td></td>
<td>$\text{NO}_3 \rightarrow \text{N}_2$</td>
<td>Denitrification</td>
</tr>
<tr>
<td></td>
<td>$\text{Mn}^{3+} \rightarrow \text{Mn}^{2+}$</td>
<td>Manganese Reduction</td>
</tr>
<tr>
<td></td>
<td>$\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$</td>
<td>Iron Reduction</td>
</tr>
<tr>
<td></td>
<td>$\text{SO}_4 \rightarrow \text{HS}$</td>
<td>Sulfate Reduction</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_2\text{HCl}_3 \rightarrow \text{Cl}$</td>
<td>Reductive Dechlorination</td>
</tr>
<tr>
<td>-250</td>
<td>$\text{CO}_2 \rightarrow \text{CH}_4$</td>
<td>Methanogenesis</td>
</tr>
</tbody>
</table>
MICROBIAL ECOLOGY - REDOX LADDER IN SUBSURFACE

Image from USEPA clu-in.org after Parsons 2004
Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water

Images from ITRC (left) and Apkarian & Taylor, Emory Univ. (right)
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
Natural Source Zone Depletion (NSZD) is monitored natural attenuation for petroleum free product.
Lundegard and Johnson (2006) report mass loss measured by vapor flux (10^{-1} to 10^2 \text{ g TPH/m}^2\text{-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.
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.)
Dynamic Closed Chamber Method

- 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.
CO₂ Trap Method

- Install soil collars at ground surface, and allow to equilibrate.
- Place CO₂ trap for extended period (2 to 4 weeks).
- Repeat in uncontaminated area.
- Send traps to lab. Quantify sorbed CO₂ concentration and calculate CO₂ flux.
- Convert CO₂ flux to hydrocarbon flux by subtracting background from contaminated area values. Alternatively, supplier offers measurement of CO₂ radiocarbon content to estimate flux attributable to hydrocarbon biodegradation.
NSZD in the Saturated Zone

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

Images from Michalski et al. (2011)
**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 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.
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.
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](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](https://global.ihs.com) for $204 (multi-user pdf)
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

NATURAL SOURCE ZONE DEPLETION (NSZD)

MICROBIAL ECOLOGY AND MONITORED NATURAL ATTENUATION (MNA)

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 - GUADALUPE DUNES
CASE STUDY - GUADALUPE DUNES

Images from guadalupedunes.com

California Red-legged Frog

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

by Paul D. Lundegard and Paul C. Johnson
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 Sable

Table 3
Examples of Site-Wide Average NSZD Rate Measurements at Field Sites

<table>
<thead>
<tr>
<th>NSZD Study</th>
<th>Number of Sites</th>
<th>Site-Wide NSZD Rate (All Sites) (Gallons/Acre/Year)</th>
<th>Site-Wide NSZD Rate (Middle 50%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery terminal sites</td>
<td>6</td>
<td>2100–7700</td>
<td>2400–3700</td>
<td>McCoy 2012</td>
</tr>
<tr>
<td>1979 crude oil spill</td>
<td>1</td>
<td>1600</td>
<td>—</td>
<td>Sihota et al. 2011</td>
</tr>
<tr>
<td>Seasonal range</td>
<td></td>
<td>310–1100</td>
<td>—</td>
<td>Sihota et al. 2016</td>
</tr>
<tr>
<td>Diverse petroleum sites</td>
<td>11</td>
<td>300–5600</td>
<td>600–800</td>
<td>Palaia 2016</td>
</tr>
<tr>
<td>All studies</td>
<td>25</td>
<td>300–7700</td>
<td>700–2800</td>
<td></td>
</tr>
<tr>
<td>Saturated zone electron acceptor biodegradation capacity</td>
<td>9</td>
<td>0.4–53</td>
<td>1.7–19</td>
<td>This paper (see Appendix S1)</td>
</tr>
</tbody>
</table>

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 – PIPELINE RELEASE

- Site-Specific NSZD Rate of 94 bbls oil / yr
- Comparable to ongoing recovery
- 75th Percentile of Garg et al.
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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References (1 of 2)

References (2 of 2)