Feelin’ the Burn: Thermal Monitoring of Natural Source Zone Depletion (NSZD)

Poonam R. Kulkarni, P.E.
GSI Environmental Inc.

TAEP Meeting
September 15, 2016
Natural Source Zone Depletion (NSZD): Technology Development

CO₂-Efflux Measurements for Evaluating Source Zone Natural Attenuation Rates in a Petroleum Hydrocarbon Contaminated Aquifer

**NATASHA J. SIHOTA, OLGA SINGURINDY, AND K. ULRICH MAYER**
University of British Columbia, Department of Earth and Ocean Sciences, 6339 Stores Rd., Vancouver, BC, V6T 1Z4, Canada

Received September 24, 2010. Revised manuscript received November 29, 2010. Accepted November 30, 2010.

Characterizing Vadose Zone Hydrocarbon Biodegradation Using Carbon Dioxide Effluxes, Isotopes, and Reactive Transport Modeling

Relating subsurface temperature changes to microbial activity at a crude oil-contaminated site

Ean Warren*, Barbara A. Bekins
U.S. Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025, United States

**ARTICLE INFO**
Article history:
Received 26 July 2015
Received in revised form 26 August 2015
Accepted 16 September 2015
Available online 15 September 2015

**ABSTRACT**
Crude oil at a spill site near Bemidji, Minnesota has been undergoing aerobic and anaerobic biodegradation for over 30 years, creating a 150–200 m plume of primary and secondary contaminants. Microbial degradation generates heat that should be measurable under the right conditions. To measure this heat, thermistors were installed in wells in the saturated zone and in water-filled monitoring tubes in the unsaturated zone. In the saturated zone, a thermal groundwater plume originates near the residual oil body with temperatures ranging from 2.9 °C.
Thermal NSZD

Temperature data are uploaded to Thermal NSZD Dashboard for real-time calculation of LNAPL degradation.

1,000 gal/acre/yr LNAPL Degraded

www.ThermalNSZD.com
Thermal NSZD Theory: Heat Released from Biodegradation

KEY POINT: Use heat released from biodegradation to calculate continuous estimates of NSZD rates
KEY POINT: MNA mostly focused on plume, while NSZD describes attenuation within the source zone.
Surprising Result: Vapor transport fluxes much greater than groundwater fluxes!

1-10% vs. 90-99%
Starting Point: **Refinery and Terminal Petroleum Spills Generate Methane from Biodegradation**

Methane bubbles!

Source: Ye et al., 2009

Source: CSU

Water Saturation
Soil Vapor Profile above Diesel Source Zone at Railyard

Typical Condition:

- Biodegradation generates methane gas
- Methane oxidized by aerobic bacteria before reaching ground surface
Methanogenesis in Action

Anaerobic digester

Methane oxidation
NSZD Conceptual Model

**Methane Oxidation**

\[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{Heat} \]

**Anaerobic Biodegradation of LNAPL**

\[ C_{10}H_{22} + 4.5H_2O \rightarrow 2.25CO_2 + 7.75CH_4 \]

Adapted from: ITRC, 2009
## What NSZD Rates are Being Observed?

<table>
<thead>
<tr>
<th>NSZD Study</th>
<th>NSZD Rate (gallons/acre/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Six refinery terminal sites (McCoy et al., 2012)</td>
<td>400 - 18,000</td>
</tr>
<tr>
<td>1979 Crude Oil Spill (Sihota et al., 2011)</td>
<td>500 - 1,700</td>
</tr>
<tr>
<td>Refinery/Terminal Sites in Los Angeles (LA LNAPL Wkgrp, 2015)</td>
<td>300 - 4,000</td>
</tr>
<tr>
<td>Five Fuel/Diesel/Gasoline Sites (Piontek, 2014)</td>
<td>300 - 3,100</td>
</tr>
<tr>
<td>Eleven Sites, 550 measurements (Palia, 2016)</td>
<td>300 – 5,600 (median: 700)</td>
</tr>
</tbody>
</table>

**KEY POINT:** Measured NSZD rates in the *100s to 1000s of gallons per acre per year.*

*Locations across U.S. where carbon traps have been used to measure NSZD rates (E-Flux, 2015).*
Active Remediation vs. NSZD Rates

Active Systems (n=29)
- Minimum: 1.25 gal/ac/yr
- Maximum: 10,200 gal/ac/yr
- Average Rate of Remediation: Median - 1,400 gal/ac/yr

NSZD
- Minimum: 300 gal/ac/yr
- Maximum: 7,700 gal/ac/yr
- Average Site-Wide NSZD Rates: Median - 1,800 gal/ac/yr

Source (active systems): Palia, 2016
Typical LNAPL Recovery Performance

KEY POINTS:
- Recoverability drops but LNAPL thickness remains.
- LNAPL sites very difficult to close.

Source: Modified from Suthersan et al., 2015
Who Wins?

**Bailer or Interface Probe**
- Sometimes least expensive alternative
- Makes you buff
- But tough to close site

**Thermal Remote Monitoring**
- No site visits, sampling or lab
- Continuous calculation of mass loss
- Convenient web interface

**KEY POINT:**
Geek approach may improve chance of regulatory case closure.
NSZD Site Closure: 3 Case Studies

Kansas Tank Farm
- Active system with negligible LNAPL recovery rates
- NSZD measurements from 2012-2014 (Carbon traps + thermal monitoring)
- KDHE approved system shutdown in 2015

California Pipeline Terminal
- Active system with LNAPL recovery rates ~20 gal/yr
- NSZD rates measured at >3,000 gal/ac/yr
- State Water Board ruling: “Can’t dictate technology”
- NSZD identified as viable remediation technology

Oregon Railyard
- Active systems: skimming, vacuum enhanced fluid recovery, total fluids recovery
- NSZD rates were an order of magnitude higher than current methods
- ODEQ approved conditional NFA for the site
How Can NSZD Rates Be Used?

• To confirm that LNAPL is biodegrading and quantify the rate

• More accurate estimation of remediation timeframe by NSZD

• Evaluate and/or replace an active remediation system
Current NSZD Measurement Methods

- CO₂ flux at Ground Surface
- Methane Oxidation
  - CO₂
  - O₂
  - Heat
- Mobile or Residual LNAPL
  - CO₂
  - CH₄
  - Heat
- Dissolved Phase Plume
- Groundwater

Adapted from: ITRC, 2009
Current NSZD Measurement Methods

- CO$_2$ flux at Ground Surface
- Methane Oxidation
  - Dynamic Closed Chamber (LI-COR)
  - Carbon Traps
- Mobile or Residual LNAPL
- Dissolved Phase Plume

Adapted from: ITRC, 2009
Current NSZD Measurement Methods

- Methane Oxidation
- CO₂ flux at Ground Surface
- Mobile or Residual LNAPL
- Dissolved Phase Plume
- Groundwater

Thermal Monitoring

Adapted from: ITRC, 2009
Biodegradation of LNAPL releases heat

Measure subsurface temperatures with thermocouples

Continuously record temperature data (24/7/365)

Thermal NSZD Dashboard: remote monitoring and calculation of NSZD rates
Heat Signal Over Time: *Kansas Tank Farm*

Source: Stockwell, 2015; Colorado State University
First law of thermodynamics:

\[
\dot{E}_{\text{out}} = \dot{E}_{\text{rxn}}
\]

- Lateral energy loss negligible
- Background location corrects for solar energy input
- Steady-state
- Storage negligible
Fourier’s Law:

Heat flux: \[ \dot{E} = K_T \frac{dT}{dz} \]

(watts/m²)

Where:

- \( K_T \): thermal conductivity (W/m°C)
- \( Z \): depth interval of heat flux (m)
- \( T \): change in net temperature (°C)

Adapted from: ITRC, 2009
Last Step: *Calculate the NSZD Rate*

\[
\text{NSZD Rate} = \frac{\dot{E}_{rxn} \ MW_{LNAPL}}{H_{rxn} \ \rho_{LNAPL}}
\]

Heat Flux (joules/area/time)

Heat of Reaction (joules per mass)

\[H_{rxn} = 45 \text{ kJ/g (diesel)}\]
\[H_{rxn} = 47 \text{ kJ/g (gasoline)}\]
Field Installation: **Thermal Monitoring System**

**A)** Thermocouple on temperature monitoring “stick.”

**B)** Installation of stick using direct push rig.

**C)** Solar power supply and weatherproof box with data logger and wireless communications system.

**SOURCE:** CSU
Thermal NSZD: Continuous Remote Monitoring of Natural Source Zone Depletion (NSZD)

The Thermal NSZD technology (patent pending) measures the rate at which natural biodegradation destroys free-phase product (LNAPL) in the subsurface by measuring the heat released by the microbial reactions.

Advantages of Thermal NSZD

- One-time field installation of remote monitoring system with minimal O&M, no site visits, no sampling and no lab.
- Daily temperature readings from vertical profiles of thermocouples.
- Secured, read only access to site data for regulators.

www.ThermalNSZD.com
Thermal NSZD Dashboard:
Continuous Subsurface Temperatures Updated Daily

- Temperature (deg. Celsius)
- Date: Aug to Apr 2016
- Depth markers: 0.5 ft, 2 ft, 4 ft, 6 ft, 10 ft, 19 ft, 38 ft, 40 ft
- Options: Raw Temps, Background Corrected Temps
Thermal NSZD Dashboard:

**Cumulative NSZD Per Location**

![Cumulative NSZD Graph](image.png)

- **X-axis:** Months from Aug to Apr 2016
- **Y-axis:** Cumulative NSZD (gallons/acre)
- **Lines:**
  - L10
  - L2
  - L4
  - L8
  - L9

The graph shows the cumulative NSZD for different locations from August 2016 to April 2017.
Thermal NSZD Dashboard:
Cumulative Sitewide NSZD Updated Daily

Amount of LNAPL Degraded Since NSZD Monitoring Began: 36,475 gallons LNAPL
Natural Source Zone Depletion Rate Over Past 30 Days: 239 gallons/acre/year
Current Status of Technology Rollout 2012 - 2016

Source: CSU

- In Place (5 sites)
- Pending (5 sites)
Wrap Up: **Key Advantages**

- **One-time installation** for continuous measurement of NSZD rates
- **Remote monitoring** via secure Dashboard
- **Thermal NSZD method** less susceptible to surface conditions compared to other CO$_2$ efflux methods
- **Off-the-shelf components**
Related and On-going Work: **Enhancing NSZD Rates**

Subsurface Low-Level Heating Using Plastic
Questions?

FOR MORE INFORMATION:

Poonam R. Kulkarni, P.E.
prk@gsi-net.com

Source: CSU
# Advantages/Disadvantages

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface E-Flux Methods</td>
<td>- Simpler installation</td>
<td>- High variability in results</td>
</tr>
<tr>
<td></td>
<td>- Non-invasive</td>
<td>- One-time measurement requires repeat sampling</td>
</tr>
<tr>
<td>Temperature Method</td>
<td>- Real-time, continuous readings</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- One-time installation, no sampling, no lab</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Off-the-shelf components</td>
<td></td>
</tr>
</tbody>
</table>
## Biodegradation Reactions

<table>
<thead>
<tr>
<th>Aqueous Phase Process</th>
<th>Decane Redox Reaction</th>
<th>$\Delta H_r$ (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic Respiration</td>
<td>$15.5O_2 + C_{10}H_{22} \rightarrow 10CO_2 + 11H_2O$</td>
<td>-6792</td>
</tr>
<tr>
<td>Denitrification</td>
<td>$12.4NO_3^- + 12.4H^+ + C_{10}H_{22} \rightarrow 10CO_2 + 17.2H_2O + 12.4N_2$</td>
<td>-6316</td>
</tr>
<tr>
<td>Manganese Reduction</td>
<td>$62H^+ + 31MnO_2 + C_{10}H_{22} \rightarrow 10CO_2 + 31Mn^{2+} + 42H_2O$</td>
<td>-6561</td>
</tr>
<tr>
<td>Iron Reduction</td>
<td>$124H^+ + 62Fe(OH)<em>3 + C</em>{10}H_{22} \rightarrow 10CO_2 + 62Fe^{2+} + 166H_2O$</td>
<td>-5162</td>
</tr>
<tr>
<td>Sulfate Reduction</td>
<td>$15.5H^+ + 7.75SO_4^{2-} + C_{10}H_{22} \rightarrow 10CO_2 + 7.75H_2S + 11H_2O$</td>
<td>-232</td>
</tr>
<tr>
<td>Methanogenesis</td>
<td>$4.5H_2O + C_{10}H_{22} \rightarrow 2.25CO_2 + 7.75CH_4$</td>
<td>-25</td>
</tr>
<tr>
<td>Methane Oxidation</td>
<td>$7.75CH_4 + 15.5O_2 \rightarrow 7.75CO_2 + 15.5H_2O$</td>
<td>-6766</td>
</tr>
</tbody>
</table>
NSZD Conceptual Model **With Heat**

**O₂ Diffusion Down; CO₂ Diffusion Up**

**Methane Oxidation**

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + \text{heat} \]

**CH₄, CO₂ Outgassing**

**CH₄ and CO₂ Ebullition**

**Anaerobic Biodegradation of LNAPL**

\[ \text{C}_{10}\text{H}_{22} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{CH}_4 \]

*Note: size of arrows indicate degree of release*
Thermal NSZD: Continuous Remote Monitoring of Natural Source Zone Depletion (NSZD)

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Advantages of Thermal NSZD

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- Daily temperature readings from vertical profiles of thermocouples.
- Secured, read only access to site data for regulators.

www.ThermalNSZD.com

Patent Pending
Kansas Site

LNAPL Locations

Background Location
### NSZD Rate Comparison: Temp vs. Traps

**California Site (gallons per acre per year)**

<table>
<thead>
<tr>
<th>Method</th>
<th>Averaging Period</th>
<th>Loc. 2</th>
<th>Loc. 4</th>
<th>Loc. 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Trap</td>
<td>14 days</td>
<td>710</td>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td>Thermal NSZD</td>
<td>315 days</td>
<td>430</td>
<td>380</td>
<td>390</td>
</tr>
</tbody>
</table>
### NSZD Rate Comparison: Temp vs. Traps

**California Site**

<table>
<thead>
<tr>
<th>Method</th>
<th>Avg. of 3 NSZD Locations</th>
<th>SVE-Impacted Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Trap</td>
<td>280</td>
<td>50*</td>
</tr>
<tr>
<td>Thermal NSZD</td>
<td>400</td>
<td>3180</td>
</tr>
</tbody>
</table>

*Not representative of actual rate due to effect of negative pressure from SVE system*
Seasonal Change, Background Correction vs. Depth

Naturally-Occurring Seasonal Temperature Changes

Heat Signal from Biodegradation = Temp. in LNAPL – Background Temp.
# Compare and Contrast the Different Methods

The Where, How, When can be Different

<table>
<thead>
<tr>
<th>Method</th>
<th>Where is Measurement?</th>
<th>How Get NSZD Rate?</th>
<th>Over What Time Period?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gradient Method</td>
<td>Point in Vadose Zone with No Oxygen</td>
<td>If Shallow, Subtract Background</td>
<td>Snapshot</td>
</tr>
<tr>
<td>CO₂ Efflux: Dynamic Closed Chamber</td>
<td>Surface</td>
<td>Subtract Background or ¹⁴C</td>
<td>Snapshot, or many readings</td>
</tr>
<tr>
<td>CO₂ Efflux: Carbon Traps</td>
<td>Surface</td>
<td>Mostly ¹⁴C Now</td>
<td>14 Days</td>
</tr>
</tbody>
</table>
## Advantages/Disadvantages

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gradient Method</td>
<td>- Provides info. based on entire vadose zone</td>
<td>- Snapshot measurement</td>
</tr>
<tr>
<td></td>
<td>- Less sensitive to near-surface conditions</td>
<td>- Invasive and labor-intensive to install</td>
</tr>
<tr>
<td>DCC LI-COR</td>
<td>- Both short-term and long-term measurements</td>
<td>- Uncertainties in diffusion coefficient</td>
</tr>
<tr>
<td></td>
<td>- Real-time data availability</td>
<td>- Additional field deployments needed for &gt;1 sampling event</td>
</tr>
<tr>
<td></td>
<td>- Not invasive installation</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Method</td>
<td>Advantages</td>
<td>Disadvantages</td>
</tr>
<tr>
<td>-----------------------</td>
<td>----------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Carbon Traps</td>
<td>- Time-averaged measurement over two weeks</td>
<td>- Snapshot measurement</td>
</tr>
<tr>
<td></td>
<td>- 14C analysis for background correction</td>
<td>- Surface type may impact measurements</td>
</tr>
<tr>
<td></td>
<td>- Less labor intensive</td>
<td>- Expensive analytical (~$1,700) per location per sampling event</td>
</tr>
<tr>
<td></td>
<td>- Not invasive installation</td>
<td>- Additional field deployments needed for &gt;1 sampling event</td>
</tr>
<tr>
<td>Temperature Method</td>
<td>- Real-time, continuous readings of NSZD rate</td>
<td>- Requires field installation</td>
</tr>
<tr>
<td></td>
<td>- Client sees daily results on webpage (data analysis centralized on webpage)</td>
<td>- Complex calculation</td>
</tr>
<tr>
<td></td>
<td>- One-time field installation with minimal O&amp;M and no additional field deployments required for additional sampling events</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Off-the-shelf components</td>
<td></td>
</tr>
</tbody>
</table>
NSZD: **Measurement Methods**

Adapted from ITRC, 2009 and Suthersan et al., 2015

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Observed NSZD Contribution

- 90-99%
- 1-10%

---

Adapted from ITRC, 2009 and Suthersan et al., 2015
## GSI CAPABILITIES AND EXPERIENCE:
### GSI OVERVIEW

### Who We Serve
- Government Agencies
- R&D Organizations
- Oil and Gas Industry
- Chemical Industry
- Law Firms

### What We Do
- Environmental strategic planning
- Environmental site investigations
- Risk assessments and modeling studies
- Corrective action design/implementation
- Data management and data analysis
- Software development
- Training courses
- Litigation support services

---

**BOTTOM LINE:** International reputation as high-quality, innovative firm.
GSI OVERVIEW: GSI PROJECTS AROUND THE WORLD

North America
- U.S.
- Canada

Latin America
- Brazil
- Colombia
- Argentina
- Venezuela
- Paraguay
- Guatemala
- Dominican Republic
- Chile
- Puerto Rico
- Ecuador
- Mexico
- Bolivia
- Peru

Middle East / Asia
- Saudi Arabia
- Yemen
- Japan
- Malaysia
- Singapore

Europe
- Spain
- United Kingdom
- Italy
- Bulgaria
- Germany
- Belgium
- Denmark

Australia
**RELATED WORK: Pushing the Frontiers of Science...**

**LNAPL Conceptual Model**

- New field methods to develop understanding of LNAPL conceptual model
- Assess NSZD rates using existing methods
- Large-scale ("big-data") studies to assess source attenuation

**Partners and Collaborators**

- Universities
- Large Oil and Gas Companies
- Technology developers
### Who We Are

<table>
<thead>
<tr>
<th>WHO</th>
<th>Consultants in environmental science and engineering</th>
</tr>
</thead>
<tbody>
<tr>
<td>WHERE</td>
<td>Offices in Houston and Austin, TX, Irvine and Oakland, CA with projects worldwide</td>
</tr>
<tr>
<td>WHEN</td>
<td>Founded 1986; completed &gt;3,500 projects throughout the US and worldwide</td>
</tr>
<tr>
<td>WHAT</td>
<td>M.S. and Ph.D. Engineers/ Scientists, Hydrogeologists, Software Developers, Database/GIS Professionals, Field Techs, Expert Witness Staff</td>
</tr>
</tbody>
</table>

**KEY POINT:** Focus on environmental engineering projects for industry, Chemical manufacturers, transportation, law firms, R&D organizations, and Government agencies.
Background-corrected Temperature (Heat Signal)

(Stockwell, 2015; Colorado State University)
Calculating LNAPL Mass Loss by NSZD

After Background Correction:

\[ \dot{E}_{out} = \dot{E}_{rxn} \]
Both Combustion and Biodegradation Generate Heat

*Heat of combustion for diesel: 45 kilojoules per gram*

**Burn 1 gram diesel:**
45 kilojoules

**Biodegrade 1 gram diesel (decane):**
45 kilojoules
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Chronology of Key Publications

Sale et al., 2014
Provisional Patent

Sweeney and Ririe, 2014
Basic theory to estimate rate

Warren and Bekins, 2015

Sihota et al., 2016 CO₂ Efflux Methods (CSR): 1.1
Warren and Bekins, 2015 Temperature Method: ~0.82