Effectively using Natural Source Zone Depletion (NSZD) technology for sustainable management of groundwater impacts at petroleum hydrocarbon sites

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DR. PARISA JOURABCHI, DR. ANWEN HUGHES (PRESENTERS)
AND DR. IAN HERS

Acknowledgments:
British Columbia Contaminated Sites Approved Professionals (CSAP) Society
Dr. Matthew Lahvis (Shell Global Solutions)
Mr. Harley Hopkins (ExxonMobil Environmental Services)
Presentation Overview

NATURAL SOURCE ZONE DEPLETION (NSZD)

• Introduction: NSZD Overview and Guidance
• Part 1: NSZD Tool Kits for Petroleum Hydrocarbon Sites
• Part 2: Case Study of NSZD Methods and Application
• Closing:
  o Incorporation of NSZD in Site Management
  o NSZD in a UK Regulatory Context
• Questions
Natural Source Zone Depletion

**Definition:**
“NSZD is a combination of processes that reduce the mass of LNAPL in the subsurface” ITRC (2009) - Can occur through volatilization, biodegradation and dissolution

**Questions:**
- What is the NSZD rate?
- What are the key processes?
- What are the effects of NSZD on groundwater plumes?
Mass Depletion Processes

**ITRC (2009)**

- Dissolution and flow
- Biodegradation

Lundegaard and Johnson (2006): “Mass loss by dissolution and biodegradation in the saturated zone are currently approximately 2 orders of magnitude slower than mass loss associated with oxygen diffusion through the vadose zone”

- Volatilization
- Biodegradation

Garg et al. (2017): typical saturated zone biodegradation capacity $<^\sim 50$ gal/acre/year.

**Key Point:** Saturated zone NSZD rates typically one to two orders of magnitude less.
Why is NSZD Important?

FOR MANAGEMENT OF PETROLEUM HYDROCARBON SITES

• NSZD is fundamental to understanding LNAPL mobility, distribution, compositional change and longevity; therefore it is an essential component of the LNAPL Conceptual Site Model (CSM).

• NSZD over time reduces LNAPL saturation and mobility; and through LNAPL compositional change may reduce the risks associated with dissolved and vapour plumes.

• Recent science has established the importance of NSZD processes, including rates of LNAPL mass depletion that are often higher than historically understood.

• Recent case studies (e.g., Bemidji) indicate the importance of anaerobic processes and possibility that hydrocarbon components previously thought to be relatively recalcitrant may biodegrade.
NSZD Guidance

Technology Overview

Evaluating Natural Source Zone Depletion at Sites with LNAPL

April 2009

8 July 2016

Toolkits for Evaluation of Monitored Natural Attenuation and Natural Source Zone Depletion

REPORT

Submitted for:
Contaminated Sites Approved Professional Society and Shell Global Solutions

Report Number: 1417511-081-R-Rev0
NSZD in 2017 and Beyond
Overview

Part 1: Toolkits for the Management of Petroleum Hydrocarbon Sites

Part 2: Case Study of NSZD Methods and Application
# Shell-CSAP-Golder MNA and NSZD Toolkits

1. **#1 CSM & Case Study Toolkit**
   - Conceptual Site Model
   - Multi-Site Database Studies
   - BC Case Studies
   - Methods for evaluation of natural attenuation and source depletion
   - Toolkits 1 & 2 (Golder, 2016)*

2. **#2 Monitoring and Prediction Toolkit**
   - Screening criteria for technical feasibility & implementability and comparison to NSZD

3. **#3 Remediation Technology Toolkit**

4. **#4 Sustainability Toolkit**
   - Methods & roadmap for implementing green & sustainable remediation (GSR)

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# Toolkit 1: Plume Lengths and Stability

**Summary of Plume Lengths**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Total Number of sites</th>
<th>Delineation criteria (µg/L)</th>
<th>Weighted mean on 90th and 50th percentile of plume lengths (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>165</td>
<td>5</td>
<td>130 / 55</td>
</tr>
</tbody>
</table>

**Summary of Stability Condition: Concentrations**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Total Number of sites</th>
<th>Decreasing concentrations (%)</th>
<th>“Non-increasing” concentrations (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>905</td>
<td>63</td>
<td>92</td>
</tr>
</tbody>
</table>

**Summary of Stability Condition: Plume lengths**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Total Number of sites</th>
<th>Decreasing plume lengths (%)</th>
<th>“Non-increasing” plume lengths (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>566</td>
<td>32</td>
<td>94</td>
</tr>
</tbody>
</table>

* From review of 13 multi-site or multi-plume studies (Connor et al., 2015)
McHugh et al. 2014

- Data from 4,000 sites with monitoring from 2001-2011 with ≥ 4 years of data
- The estimated median attenuation rate for benzene = 0.18 per year (all sites, most active remediation)
- When data analyzed separately for different technologies, only slightly faster attenuation rate, indicating effect of remediation limited

### Toolkit 1: California Multi-Site Study of Retail Gasoline Sites

**CALIFORNIA GEOTRACKER DATABASE**

<table>
<thead>
<tr>
<th>Technology</th>
<th>Constituent</th>
<th>Increase in Source Attenuation Rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SVE</td>
<td>benzene</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>MTBE</td>
<td>11</td>
</tr>
<tr>
<td>Air Sparging</td>
<td>benzene</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>MTBE</td>
<td>22</td>
</tr>
<tr>
<td>Chemical Oxidation</td>
<td>benzene</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>MTBE</td>
<td>17</td>
</tr>
</tbody>
</table>

- MNA-only technology: 72 sites
  - Median benzene attenuation rate of 0.13/year
  - Timeline for attenuation from 10 mg/L to 5 µg/L: 58 years
Step 1: Evaluation of Progress of MNA of Dissolved Plumes

Step 2: Use of Screening Models and Measurements for Estimation of NSZD

Step 3: Use of Multi-Process Models for Evaluation of MNA and Plume Attenuation
Toolkit 2: Quantifying NSZD Rates

Processes
- Biodegradation/Volatilization in unsaturated soil
- Biodegradation in saturated zone
- Dissolution in saturated zone

Tools & Methods
- ITRC Control Volume Model (all 3 processes)
- Gradient Method (VZBL Model)
- CO₂ Efflux Method
- Temperature Method
- GSI Mass Flux Toolkit

• Compare NSZD rate to active remediation rates
• With estimate of source hydrocarbon mass, depletion time can be estimated
Toolkit 2: Methods for Estimation of Unsaturated Zone Biodegradation

• Gradient method
  • Based on vertical soil gas profiles
  • For example, Vadose Zone Biodegradation Loss Model\(^1\)

• Carbon dioxide (CO\(_2\)) efflux methods
  • Dynamic closed chamber
  • Static trap

• Temperature method
  • Heat generation from aerobic biodegradation
  • Measurement of the thermal gradient

\(^1\)Developed by Dr. Parisa Jourabchi and Dr. Ian Hers, Golder and Dr. John Wilson, Scissortail
# Toolkit 2: Comparison of Methods for Estimation of Unsaturated Zone Biodegradation

<table>
<thead>
<tr>
<th>Method</th>
<th>Key Data Required</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gradient</td>
<td>Chemical diffusion gradient, porosity, moisture, water table, native organic carbon</td>
<td>Simple method, uses readily available data</td>
<td>Sensitive to moisture and water table</td>
</tr>
<tr>
<td>CO₂ Efflux</td>
<td>Surface CO₂ efflux, $^{14}$C of CO₂, δ$^{13}$C of CO₂ (optional)</td>
<td>Direct measurement, avoids estimation of diffusive flux</td>
<td>Sensitive to natural soil respiration</td>
</tr>
<tr>
<td>Temperature</td>
<td>Temperature profile, soil thermal conductivity</td>
<td>Direct measurement, provides long-term monitoring</td>
<td>Thermal conductivity difficult to estimate, data analysis complex</td>
</tr>
</tbody>
</table>
Toolkit 3: Remediation Process & Selection Framework

- Determine Remedia Target
- Identify Concerns
- Identify Primary Remediation Mechanism
- Determine Remedial Objectives
- Conduct Remedial Options Screening/Selection
- Identify Performance Metrics and Endpoints
- Conduct Remedial Design
- Operate and Monitor Remediation

Develop CSM in Tiered Framework - Generally increasing data needs with respect to Investigation - Remedial Options Screening - Design
Toolkit 4: Green & Sustainable Remediation*

• Starting with a short-list of applicable remedial technologies (e.g. up to four) selected using Toolki

• Green & Sustainable Remediation (GSR) as the integration of:
  • Sustainable Development: Triple bottom line
  &
  • Green remediation: greater focus on environmental net benefit; lesser focus on social and economic aspects

• Overall impact of remedial activities on human and ecological receptors and society

optimization of triple bottom line = sustainable remediation

*Development of the sustainability Toolkit 4 in collaboration with François Beaudoin (Golder)
Part 2: Case Study of NSZD Methods and Application
CO₂ Efflux Measurement Methods

• Dynamic Closed Chamber (DCC)
• LI-COR Instrument: LI-8100A
  Automated Soil Gas Flux System
• Infrared Detector
• Survey System with 20 cm
diameter chamber

• E-Flux Low Profile Static
  Trap Units
• Sorbent material made
  from calcium and sodium
  hydroxides
Vadose Zone Biodegradation Loss (VZBL) Model*

- Method calculates the biodegradation rate based on:
  - \(O_2\) flux estimated from \(O_2\) gradient and effective \(O_2\) diffusion coefficient
  - Methane flux from TPH degradation under methanogenic conditions based on decrease in soil gas \(N_2\) concentration

- Simple to use model with several features to improve estimation process
  - Variable water table
  - Multi-layered soil
  - Optional baseline \(O_2\) respiration
  - Mass balance for depletion

* Model is available upon request.

TPH = total petroleum hydrocarbon
VZBL Predicted TPH Profiles in Soil - example

TPH = total petroleum hydrocarbon
Case Study – Former Refinery and Distribution Terminal

- Field trial conducted in area of former refinery and distribution terminal
- Petroleum hydrocarbon plume: weathered middle distillate with lesser amounts of lube oil
- Silty sand and silt (1.8 to 4.0 m thick) over coarse sand
- Depth to corrected water table: 2.7 - 4.7 m
- Apparent in-well LNAPL thickness 0.01 to 0.6 m
- Relatively high organic carbon content near ground surface
# Case Study – Former Refinery and Distribution Terminal

<table>
<thead>
<tr>
<th>Objectives</th>
<th>Approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compare CO$_2$ efflux methods</td>
<td>CO$_2$ efflux - DCC and Static Trap</td>
</tr>
<tr>
<td>Better understand spatial and temporal variability</td>
<td>DCC repeat measurements short term and seasonal monitoring</td>
</tr>
<tr>
<td>Develop new method of correction for natural soil respiration</td>
<td>Use of radiocarbon ($^{14}$C) analyses &amp; air sample collection</td>
</tr>
<tr>
<td>Compare CO$_2$ efflux to Gradient method for estimation of NSZD rates</td>
<td>Average DCC estimates to gradient method estimates (VZBL model)</td>
</tr>
<tr>
<td>Estimate NSZD rates for study area</td>
<td>Combination of vadose zone estimates (CO$_2$ efflux) plus saturated zone processes</td>
</tr>
</tbody>
</table>
Method Comparison – Total CO₂ Efflux by DCC and Static Trap

Key Points:
• Relatively high spatial variability in DCC effluxes
• Low temporal variability in DCC effluxes (measured over several days and during one day)
• Relatively good correlation between static trap and DCC total effluxes ($R^2 = 0.73$)
**Key Points:**

- Very large seasonal variability in CO$_2$ efflux measurements
- NSZD rates based on this data are considered to span the likely seasonal range, however, the lowest values represent an extreme short term, wet condition.

Note different scales are used for each plot.
Radiocarbon Estimation of Contaminant Soil Respiration

CO₂ Efflux = Contaminant Soil Respiration + Natural Soil Respiration

\[ J_{CO2} = J_{CSR} + J_{NSR} \]

Objective: to estimate \( J_{CSR} \) or the fraction of \( J_{CSR} \) to \( J_{NSR} \)

\[ F_{CSR} \equiv \frac{J_{CSR}}{J_{CO2}} \]

- Radiocarbon or \(^{14}\)C analysis has been used to differentiate between CO₂ derived from fossil fuel and natural sources of atmospheric CO₂. Method builds on research studies conducted by Sihota and Mayer (2012).
- Technique relies on \(^{14}\)C analysis, a carbon isotope with a half-life of approximately 5,700 years generated by cosmic rays in the atmosphere.
- Fraction of \(^{14}\)C content of carbon (F\(^{14}\)C) is measured by accelerator mass spectrometry.

**Key Point:** Contemporary (modern) organic carbon is \(^{14}\)C-rich, while fossil fuel carbon is \(^{14}\)C-depleted

Radiocarbon Estimation of Contaminant Soil Respiration

- Novel method based on two-component mass balance developed for ExxonMobil
  - Sample A: Ambient air
  - Sample B: Mixture air and soil gas

\[ F_{CSR} = 14F_A - \frac{14F_B [CO_2]_B - 14F_A [CO_2]_A}{[CO_2]_B - [CO_2]_A} \]

- Assumes \( F^{14}C \) associated with CSR is zero
- Decrease in \( F^{14}C \) in Sample B represents fraction of CSR
## NSZD Estimates – CO₂ Efflux & $^{14}$C Data

<table>
<thead>
<tr>
<th>Time Period</th>
<th>Average Contaminant CO₂ Efflux, $J_{CSR}$ (µmol/m²/s)</th>
<th>Average NSZD Rate (US gal/acre/yr)</th>
<th>Minimum NSZD Rate (US gal/acre/yr)</th>
<th>Maximum NSZD Rate (US gal/acre/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jun 23 - Jul 10, 2015 (dry &amp; warm)</td>
<td>2.0</td>
<td>1,100</td>
<td>200</td>
<td>4,000</td>
</tr>
<tr>
<td>Oct 12 - 14, 2016 (moist &amp; cool)</td>
<td>0.44</td>
<td>246</td>
<td>3.3</td>
<td>6,200</td>
</tr>
<tr>
<td>Oct 26 - Nov 1, 2016 (very wet &amp; cool)*</td>
<td>0.010</td>
<td>5.5</td>
<td>2.5</td>
<td>9.4</td>
</tr>
</tbody>
</table>

*Short-term unseasonably high precipitation and essentially saturated conditions*
# NSZD Estimates with VZBL Spreadsheet Tool

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Estimated NSZD Rate</th>
<th>Soil Moisture Condition</th>
<th>Baseline Soil Respiration (mg O$_2$/g-OC/day)</th>
<th>Surficial Soil Type</th>
<th>US gallons/acre/year</th>
<th>CO$_2$ (µmol/m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet Fall (Oct 17-19)</td>
<td></td>
<td></td>
<td>0.11</td>
<td>Measured soil properties</td>
<td>1.1</td>
<td>510</td>
</tr>
<tr>
<td>Dry Summer</td>
<td>0.35</td>
<td></td>
<td></td>
<td>Assuming sandy loam</td>
<td>13</td>
<td>5,600</td>
</tr>
<tr>
<td>Dry Summer</td>
<td>0.35</td>
<td></td>
<td></td>
<td>Assuming loam</td>
<td>3.6</td>
<td>1,600</td>
</tr>
</tbody>
</table>

**Key Points**: The site-wide estimate of mass loss from the VZBL model higher than estimates from contaminant CO$_2$ efflux measurements, but within the same order of magnitude.
Summary of NSZD Processes & Rate Estimates

**Key Point**: While vadose zone biodegradation rates largest, potentially important to quantify all depletion mechanisms.

- **Saturated Zone Biodegradation**: 35 gal/acre/year (approximately 60% from CH$_4$ production)
- **Vadose Zone Biodegradation**: Seasonal range ~250 to 1,000 gal/acre/year
- **Saturated Zone Dissolution & Flow**: 72 gal/acre/year
Vadose Zone Biodegradation Loss Rates

Hers et al. (Battelle 2016)
Incorporation of NSZD in Management of Petroleum Hydrocarbon Sites

• NSZD rate measurements serve as basis for assessing NSZD as a remedy and can be compared to measured or estimated rates for other technologies

• Typically NSZD should be considered as a secondary remedy after primary active remediation is no longer effective or sustainable

• Recent case studies including the study presented here indicate that NSZD rates, though seasonally variable, can be significant and exceed rates for later stage active remediation

• Sustainability and lifecycle principles can aid in assessment of technologies and evaluation of technology transition – this is key – A life cycle analysis within a sustainability framework can aid in evaluation of remedial options and technology transition.

• Emerging focus is on evaluating compositional changes associated with NSZD and relative depletion rates
NSZD in a UK Context

- New contamination (accidental) vs. historical legacy (passive)
- Planning and Part 2A Regimes
- Water Framework Directive
- Site Specific Risk Management Approach (CLR11)
- Sustainable Remediation (SuRF-UK Framework)
NSZD in a UK Context

• Understanding role and importance of NSZD processes in CSM with respect to both LNAPL source and implications for dissolved phase plume

• Relationship between LNAPL NSZD and plume MNA:
  o NSZD as a passive remediation technology for the long-term natural depletion of LNAPL source zone (e.g. ITRC, 2009 assessment guidelines);
  o MNA relates to the long-term stability /attenuation of the dissolved phase plume (e.g. EA, 2000 lines of evidence approach)

• Existing NAPL contamination: minimize further entry of hazardous substances, remove or control mobile and residual NAPL, stabilize and reduce plume expansion – risk based approach (EA guidance, www.gov.uk)

• Challenges of UK Drift and Bedrock aquifers and requirements for site-specific risk based approach with site-specific evaluation of NSZD rates and potential...
Thank You!

Parisa Jourabchi (pjourabchi@golder.com)
Anwen Hughes (ahughes@golder.com)
Ian Hers (ihers@golder.com)