Learning about Secondary Water Quality Impacts from the Bemidji Oil Spill

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Crude-oil pipeline broke in August, 1979

- Spilled 1.7 million L (441,000 gallons) light crude oil onto glacial outwash deposits
- After cleanup efforts in 1980, 400,000 L remain
- North and South oil pools along water table
Learning about BTEX from the Bemidji Oil Spill

BTEX = Benzene, Toluene, Ethylbenzene, and Xylene

- Volatile organic carbons found in petroleum products
- Adverse health effects: sensory irritant and carcinogen (benzene)
- Highest solubility, easily spread through groundwater (benzene)

Misconceptions about BTEX plumes at the time of the Bemidji Oil Spill

- BTEX biodegradation requires **oxygen**
- **Oxygen** is plentiful in shallow aquifers
- Plumes mix readily with **oxygen** in background water
Research at the Bemidji Oil Spill Site: Focus on the North Oil Pool and Plume

Spray zone
Oil flowed over land surface

Cross section line

North pool
Middle pool
South pool

100 m

2010
3.3 µg/L

1996
10 µg/L Benzene

Lake

Bekins et al., 2016
DOI:10.1111/gwat.12419
Bemidji North Pool Well Transect

Anaerobic conditions

Lessons Learned About BTEX Degradation from Bemidji

**Naturally: BTEX degrades anaerobically**

- 1993: Eganhouse et al., Bennett et al., Baedecker et al.

- **First demonstration of BTEX degradation coupled to iron reduction** [Lovely et al. Nature 1989]

- Anaerobic metabolites (non-volatile DOC) present in plume [Cozzarelli et al. 1994]

- CH$_4$ in plume indicates (anaerobic) methanogenesis [Amos et al. 2005]

- Models indicate 60% of degradation is anaerobic [Essaid et al, 1995]

- Natural attenuation established as an effective BTEX remediation strategy [National Research Council, 2000]
What can we learn about BEYOND BTEX degradation from the Bemidji Oil Spill Site?
Emerging Concern: Secondary Water Quality Impacts (SWQI's) of Anaerobic Bioremediation?
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- Spill Site
- (oil, soluble, mulch biowall, mixed)
- Biostimulation
- Degradation of e.g. chlorinated solvents
- Spill Site groundwater flow
- Secondary groundwater contaminants!
Emerging Concern: Secondary Water Quality Impacts (SWQI's) of Anaerobic Bioremediation?

Organic substance (oil, soluble, mulch biowall, mixed)

Spill Site

Biostimulation

Degradation of e.g. chlorinated solvents

Secondary groundwater contaminants!

CH₄, H₂S, Fe⁺², Mn⁺², N₂, O₂

Sequence of Redox Processes

e- acceptor

Oxidation State | Oxidized | Reduced | Oxidation State
--- | --- | --- | ---
0 | O₂ | H₂O | -II
V | NO₃⁻ | N₂ | 0
IV | MnO₂ | Mn²⁺ | II
VI | SeO₄²⁻ | HSO₄⁻ | Cr(OH)₃ | IV | III
VI | CrO₄²⁻ | Se | 0
III | Fe(OH)₃ | Fe²⁺ | IV
V | HAsO₄²⁻ | H₃AsO₄ | III
IV | SO₄²⁻ | H₂S | -II
IV | HCO₃⁻ | CH₄ | -IV

Electron Flow

Propagation of oxidation reactions

Bioremediation site monitoring: some (limited) data

Intensively monitored analogue: Bemidji oil spill

Long-term secondary water quality impacts of Bemidji oil spill?
Observations beyond BTEX at Bemidji: Composition of Degrading Oil

Significant degradation of \( n \)-alkanes 1983-1999

Hostettler et al, 2008, DOI:10.1080/15275920802115738
Observations beyond BTEX at Bemidji: Methane

Oil degradation produces methane

Dissolved CH\textsubscript{4} (SWQI)

Amos et al, 2005, DOI:10.1029/2004WR003433
Observations beyond BTEX at Bemidji:
Surface CO$_2$ gas efflux

Elevated surface efflux of CO$_2$ measured above oil body
[Sihota et al. 2011]
**Dissolved and Sediment Fe**

Coupled to anaerobic oil degradation:

- Fe(III) reduction

Sediment-bound Fe(II)

+ Dissolved Fe(II) (SWQI)

Tuccillo et al. 1999
30 years after oil body emplacement

Observed Long-Term SWQIs at Bemidji

Cozzarelli et al., 2015
Observed Long-Term SWQIs at Bemidji

30 years after oil body emplacement

What controls production and limit of secondary plumes $(\text{Fe}^{2+}, \text{CH}_4)$?
Data Compiled to Constrain SWQI Processes

<table>
<thead>
<tr>
<th><strong>Sources</strong></th>
<th><strong>Sinks</strong></th>
</tr>
</thead>
</table>
| - Oil components and saturation  
  • Initial oil\(^a\,b\,c\), 2008\(^d\,e\,f\) | - Inorganic and CH\(_4\) aqueous chemistry  
  • Initial\(^c\), 1987\(^g\,i\), 1993\(^c\,h\), 2008\(^c\,k\) |
| - BTEX  
  • 1987\(^a\,g\), 1993\(^h\), 2008\(^c\) | - Sediment Fe  
  • Initial\(^l\), 1993\(^l\), 2008\(^c\,i\) |
| - Nonvolatile organic carbon  
  • 1987\(^a\,g\), 1993\(^h\), 2008\(^i\) | - CO\(_2\) surface efflux  
  • 2008\(^m\,n\) |

\(^a\)Eganhouse et al. [1993]  
\(^b\)Essaid et al. [2003]  
\(^c\)Ng et al. [2014]  
\(^d\)Baedecker et al. [2011]  
\(^e\)Thorn and Aiken [1998]  
\(^f\)Bekins et al. [2005]  
\(^g\)Baedecker et al. [1993]  
\(^h\)Cozzarelli et al. [2001]  
\(^i\)Amos et al. [2012]  
\(^j\)Bennett et al. [1993]  
\(^k\)Amos et al. [2011]  
\(^l\)Tuccillo et al. [1999]  
\(^m\)Sihota et al. [2011]  
\(^n\)Sihota et al. [2014]

Requires extensive and complete data on plume sources and sinks  

*Ng et al. 2014 (JCH)*
Synthesize Extensive Data: Geochemical Mass Balance and Reactive Transport Modeling

**PHT3D: 3D Reactive Multicomponent Transport Model**
[Prommer and Post 2010]

- Suitable for complex hydrologic, geochemical apps
- Incorporates well-established models

**Coupling**
Flow / Transport  
Geochemical Reactions

**MODFLOW/ MT3DMS v5.3**
[Zheng and Wang, 1999]
- Groundwater flow (MODFLOW)
- Advective-dispersive transport

**PHREEQC-2** [Parkhurst and Appelo, 1999]
- Geochemical processes (equilibrium, kinetic)

<table>
<thead>
<tr>
<th>Element or element valence state</th>
<th>PHREEQC notation</th>
<th>Formula used for default gram formula weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity</td>
<td>Alkalinity</td>
<td>Ca\textsubscript{2+}(CO\textsubscript{3})\textsubscript{3}^-</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>Al</td>
</tr>
<tr>
<td>Barium</td>
<td>Ba</td>
<td>Ba</td>
</tr>
<tr>
<td>Boron</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>Bromide</td>
<td>Br</td>
<td>Br</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cd</td>
<td>Cd</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca</td>
<td>Ca</td>
</tr>
<tr>
<td>Carbon</td>
<td>C</td>
<td>HCO\textsubscript{3}</td>
</tr>
<tr>
<td>Carbon(IV)</td>
<td>C(4)</td>
<td>HCO\textsubscript{3}</td>
</tr>
<tr>
<td>Carbon(IV), methane</td>
<td>C(4)-</td>
<td>CH\textsubscript{4}</td>
</tr>
<tr>
<td>Chloride</td>
<td>Cl</td>
<td>Cl</td>
</tr>
</tbody>
</table>
Example Plume Simulation

Normalized change in concentration

TDOC, $t=1500d$

CH$_4$, $t=1500d$

Fe$^{2+}$, $t=1500d$

DO, $t=1500d$
Overview of Site Processes

\[ CH_4 + O_2 \rightarrow CO_2 + 2H_2O \]

Vadose zone

Oil Body

\[ n\text{-alkanes} \rightarrow CO_2 + CH_4 \]

Direct outgassing

Aqueous phase outgassing

Methanotrophic zone

BTEX Nonvolatile DOC

Fe-reducing zone

Methanogenic zone

Groundwater flow

Ng et al., 2015, DOI: 10.1002/2015WR016964
CH$_4$ Plume Production and Fate

- Direct outgas: 91.8%
- Outgas from plume: 7.4%
- Dissolved in plume: 0.8%

Compare: Diluent spill in Guadalupe Oil Field (CA)

C Mass flux in
- Groundwater: 1-10%
- Vapor: 90-99%

[Lundegard and Johnson, 2006]
Fe(II) Plume Production and Fate

Dissolved in plume 0.8%
Precipitated FeCO$_3$ 7.4%
Sorbed 91.1%

Ng et al. 2014 (JCH); Ng et al. 2015 (WRR)
Learning about Secondary Water Quality Impacts from modeling the Bemidji Oil Spill

- **Secondary Water Quality Impacts:**
  - 30+ yrs Fe$^{2+}$, (early!) CH$_4$

- **Secondary Water Quality Controls:**
  - **CH$_4$ Plume -**
    - Driven by diverse degrading oil components
    - Attenuated by out-gassing
      (>99% of CH$_4$ exits as surface CO2 efflux)
  - **Fe plume -**
    - Driven by reduction of (depleting) Fe(III) oxide minerals
    - Attenuated by immobilization on sediments
      (>99% of reduced Fe is attenuated on sediments)

*Ng et al. 2014 (JCH); Ng et al. 2015 (WRR)*
Learning about oil degradation from the SWQI model

Fate of oil lost from pool (e\textsuperscript{-} balance):

- Direct \(\text{CH}_4\) outgas: 86%
- Outgas from \(\text{CH}_4\) plume: 7.0%
- Dissolved in \(\text{CH}_4\) plume: 0.7%
- Sorb Fe(II): 5.7%
- Diss Fe(II): <0.1%
- \(\text{FeCO}_3\): 0.5%

(Aerobic Degradation: 0.09%)
Ongoing Lessons: Groundwater Plume

- Arsenic immobilization*
- Heat generated from biodegradation
- Fate of oil metabolites**
- Mixed BTEX ethanol plume experiments

*Cozzarelli et al., 2015, Arsenic Cycling in Hydrocarbon Plumes: Secondary Effects of Natural Attenuation, Groundwater, doi: 10.1111/gwat.12316

**Bekins et al., 2016, Crude Oil Metabolites in Groundwater at Two Spill Sites, Groundwater, doi: 10.1111/gwat.12419
Ongoing Lessons: Oil

Hydrophobic soils:
• Mapped areas of hydrophobic soils*
• Pilot remediation plots

Source Zone
• Seasonal gas efflux cause
• Oil composition changes

*Adams et al., 2016, International Journal of Environmental Science and Technology.
Ongoing Lessons: Methods Development

- Biogeophysics
- Freezing drive shoe
- Colloidal boroscope flowmeter
- Optical fluorescence probe
- Hydraulic conductivity profiling
- Low cost $^{14}\text{C}$ analysis
Collaborative Agreement

- Maintain the research site
- Promote/advance science, research, education related to the fate, transport, and natural attenuation of crude oil contamination in the subsurface
- Make results widely available to researchers, industry, consultants, regulators, teachers, and students

Beltrami County, Minnesota

Continuing to learn from Bemidji oil spill

Use the site’s capabilities to develop new methods and understanding about oil degradation and beyond

Groundwater
- 255 Monitoring wells

Oil
- 35 Oil monitoring wells

Gases
- 22 Vapor wells
- Surface CO2 efflux
- 14 continuous CO2 and O2

Geophysics
- Self potential
- Magnetic susceptibility
- Electrical resistivity

Recharge
- 4 Moisture probe arrays
- 4 Suction lysimeter arrays
- 6 Temperature profile arrays

Spatially referenced database
- DO, pH, SpCond
- Water levels
- Oil thicknesses

http://mn.water.usgs.gov/projects/bemidji/