Technologies for Biogeochemical and Hydrogeologic Characterization and Their Integration for Site Remediation

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• Complex hydrogeology
  • fractured rocks
  • low permeability layers; rock matrix

• Difficult contaminant mix
  • DNAPL
  • dissolved and highly sorbed mix
  • emerging contaminants

• Sensitive habitat or location
  • wetlands
  • bottom sediments
Biogeochemical Characterization-Why?

- Provide the remedy-MNA, bioremediation, biogeochemical reduction
- Secondary effects-alteration of natural biogeochemical conditions, or from presence of secondary contaminants
- Long-term efficiency
  - changes in transmissive plume with remediation
  - low permeability zones
  - “slow” processes key (back diffusion, sorption and desorption, abiotic and biotic degradation reactions)
Biogeochemical Characterization—How?

- MNA protocols provide good framework and tools
- Relevant protocols for organics, radionuclides, and non-radionuclide inorganic
- Three lines of evidence for chlorinated solvents

**Monitored Natural Attenuation (MNA)**

- **Removal of contaminant**
- **Geochem indicators** (DOC, redox, metabolites, pH, Cl)
- **Microbial activity**
Considerations

- History and stage of plume evolution
- DNAPL or LNAPL presence
- Sample key parts of plume, including “transition zones”
- Multilevel sampling-high resolution
- Spatial and temporal variability
- Interaction with and formation of solids

from *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water, Volumes 1 and 2*
Dissolved plumes

Aerobic micro-zones around roots

Evapotranspiration/Phytoremediation

High Organic Carbon Sediment of Wetland (reducing conditions conducive to biodegradation)

Volatilization

Creek

Fe^{2+}

CH_{4}

NH_{3}

S^{2-}

DNAPL

AQUIFER

AQUITARD

WETLANDS- LARGE TRANSITION ZONE
(MODIFIED FROM LORAH ET AL., 2005)

Fig. 1. Possible interactions in the root zone of wetlands for wastewater treatment.
Canal Creek Area, Aberdeen Proving Ground

Chlorinated VOCs- Anaerobic degradation

Parent Contaminants

Chlorinated ethanes:
HCA = hexachloroethane
PtCA = pentachloroethane
1122TeCA = 1,1,2,2-tetrachloroethane

Chlorinated ethenes:
PCE = tetrachloroethene
TCE = trichloroethene

Chlorinated methanes:
CT = carbon tetrachloride
CF = chloroform
West Branch Canal Creek, Natural Attenuation Study Area: Redox

[Diagram showing the study area with various layers and zones marked, including Wetland, Aquifer, and Confining Units.]
West Branch Canal Creek, Natural Attenuation Study Area: VOCs

1,1,2,2-Tetrachloroethane (µg/L)

VERTICAL EXAGGERATION = 2.34X

VC

12DCA

12DCE

TeCA 2.0µM, 90cm
West Branch Canal Creek

Degradation in non-seep areas where relatively slow flow allows strongly reducing conditions.
MNA WBC2 Dechlorinating Consortium, developed to degrade 1,1,2,2-tetrachloroethane (TeCA)

Manchester, et al, 2011

WBC-2 Mole Fract (Daughter/TeCA) vs TeCA Half-life (days)

- VC
- tDCE
- cDCE
- TCE
- 12DCA
- 112TCA
- TeCA
- TeCA t1/2

CC Aquifer CC Wetland (23) CC Wetland (30) CC Aquifer CC Wetland (23) CC Wetland (30)
Standard Chlorine of Delaware, DNAPL Extent

- CB, DCBs, TCBs
- DCBs, TCBs
- Not indicative of DNAPL

USGS Study
- Wetland characterization
- Natural attenuation; enhanced bioremediation
- Feasibility of permeable reactive barrier

State Plane Delaware Transverse Mercator Projection
Chlorobenzenes-
Standard Chlorine of Delaware

- Anaerobic (reductive dechlorination)
  - CB serves as terminal electron acceptor
  - Separate e- donor required
  - rate decreases with decreasing number Cl

- Aerobic (oxidation)
  - O₂ required as electron acceptor
  - CBs utilized as C and e donor
  - Short-lived intermediates
  - rate increases with decreasing number Cl

- Chlorobenzenes
  - Trichlorobenzenes *
    - 135TCB, 124TCB, 123TCB
    - 70 (124TCB)
  - Dichlorobenzenes *
    - 14DCB, 13DCB, 12DCB
    - 75 (14DCB)
  - Chlorobenzene *
    - 100
    - Benzene *
      - 5
      - CO₂, CH₄
    - Drinking Water
      - MCL µg/L

* Parent contaminant
SCD, VOCs in Peepers

Upland Wells, Oct. 2011
Tools to Evaluate Biodegradation

- **Molecular Biological Tools**
  - Quantitative PCR: Counts genes, taxonomic or functional, for specific targets; micro-arrays (QuantArray, MI)
  - Terminal Restriction Fragment Length Polymorphisms (TRFLP): fingerprint of the microbial community
  - Next-generation sequencing (high throughput): in depth profile of the microbial community; Illumina, 454 sequencing

- **Stable Isotopes**
  - SIP, Stable Isotope Probing: $^{13}$C used as a tracer
  - CSIA, Compound Specific Isotope Analysis: isotopic fractionation in parent and metabolites

**Bio-Traps, Microbial Insights**

- **GEO**
  - GEO anions, VFAs

- **COC**
  - COCs, redox

- **MICRO**
  - Bio-sep beads, microbes

- **13C Amendments donor**

**Bio-Sep® beads**
- Bio-Sep® beads provide a large surface area for microbial attachment
In situ microcosms with Bio-Traps (Microbial Insights)

- Two each northwest and northeast sites
- Three standard treatments and three $^{13}$C-labeled treatments
  - MNA, monitored natural attenuation (no amendments)
  - Lactate, biostimulated with lactate + chitin
  - WBC-2, bioaugmented
- $^{13}$C-labeled chlorobenzene
- QuantArray analysis of species and functional genes for aerobic and anaerobic biodegradation
**ISM Results:**

- Complete degradation of DCBs evident in WBC-2 treatment in standard ISMs.
- $^{13}$C-labeled ISMs showed complete degradation of monochlorobenzene in MNA and WBC-2.

**Results:**

<table>
<thead>
<tr>
<th></th>
<th>WBC-2 $^{13}$C</th>
<th>MNA $^{13}$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$ (per day)</td>
<td>0.019</td>
<td>0.021</td>
</tr>
<tr>
<td>Half life (days)</td>
<td>37.1</td>
<td>33.5</td>
</tr>
</tbody>
</table>

- Pre-Deployment:
  - 66% for WBC-2 $^{13}$C
  - 69% for MNA $^{13}$C
Bio-Traps: 13C-labeled Chlorobenzene

Incorporation in dissolved inorganic carbon = Mineralization

Incorporation in PLFA = Metabolism (C for growth)

13C Utilized for CO2, 13C Chlorobenzene

13C Utilized for Biomass, 13C Chlorobenzene

aerobic metabolism
QuantArray Microbial Analysis - Anaerobic

---Reductive dechlorination---

Reductive dechlorination:
DHC, Dehalococcoides spp.
TCE, tceA reductase
VCR, vinyl chloride reductase
BV1, vinyl chloride reductase
DHBt, Dehalobacter spp.
DHG, Dehalogenimonas spp.

BTEX, PAHs and alkanes:
BCR, Benzoyl coenzyme A reductase
bssA, benzylsuccinate synthase
assA, alkylsuccinate synthase
QuantArray Microbial Analysis- Aerobic

- **pMMO**, particulate methane monooxygenase
- **sMMO**, soluble methane monooxygenase
- **TCBO**, trichlorobenzene dioxygenase
- **RDEG**, toluene monooxygenase 2
- **RMO**, toluene monooxygenase
- **PHE**, phenol hydroxylase
- **EDO**, ethylbenzene/isopropylbenzene dioxygenase
- **PM₁**, *Methylibium petrophilum* PM₁
- **ALKB**, alkane monooxygenase
Changing Paradigm

Previous paradigm for chlorinated VOCs:

- Anaerobic reductive dechlorination only process in apparent low redox zones
- Aerobic oxidation requires measurable oxygen
- Anaerobic oxidation responsible for losses of lower VOCs at anaerobic plume fringes

**Perils of Categorical Thinking: “Oxic/Anoxic” Conceptual Model in Environmental Remediation**

**Isolation of an aerobic vinyl chloride oxidizer from anaerobic groundwater**

**Sustained Aerobic Oxidation of Vinyl Chloride at Low Oxygen Concentrations**

**Concurrent and Complete Anaerobic Reduction and Microaerophilic Degradation of Mono-, Di-, and Trichlorobenzenes**

Fullerton et al. 2014

Bradley 2012

Gossett 2010

Bradley and Chapelle 2011

Burns et al. 2013
Bioaugmentation: Fractured sedimentary rock aquifer, former Naval Air Warfare Center (NAWC)

USGS
Toxic Substances Hydrology Program
New Jersey Water Science Center
National Research Program

VOCs vs Time Injection Well - 36BR-A

“stall”? 
Matrix diffusion/
DNAPL dissolution

Chloride vs Time
Injection Well 36BR-A

Currently investigating
changes in native and
bioaugmented microbial
communities-
toxicity/inhibition effects
cause growth of “partial
dechlorinators”?

(Modified from Tom Imbrigiotta)
Use of laboratory testing to characterize microbial communities and biodegradation processes

- Site characterization
- Feasibility evaluation
- Technology development
- Pilot test remediation

Native Bioreactor
Bioaugmented Bioreactor

Polyethylene and polyurethane support matrix for building biofilm of native or bioaugmented microorganisms
SCD Bioreactors - Aerobic vs. Anaerobic

- occurrence of aerobic and anaerobic degradation by native bacteria
- aerobic degradation faster than anaerobic biodegradation
- WBC-2 able to degrade chlorinated benzenes and benzene anaerobically
- accumulation of daughter products not evident
Questions?
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