Natural Attenuation at a High Energy GSI, St. Joseph, MI

Peter Adriaens, Ph.D.
Professor

Environmental and Water Resources Engineering
Dept. of Civil and Environmental Engineering
www.engin.umich.edu/dept/cee/research/adriaens/index.html
From Flask to Field (and Back Again!)

Research Themes
Monitored Natural Attenuation
Remediation System Design
Microbial Sensing and Control

ONR
EPA
NSF
NIEHS

Mike McCormick
Angela Lindner
Shiang Fu
Andrei Barkovskii
Aksay Kumar

Noemi Barabas
Hirotaka Saito
Cyndee Gruden
Babu Fathepure
Tim Towey

Jack Lendvay
Sean Dean
Peter Yung
Erik Petrovskis

DEQ
EPA
Navy
St. Joseph MI Superfund Site: Groundwater-Surface Water Interface (GSI)

- Chlorinated solvents (> 500 mg/kg); vinyl chloride at > 16 mg/kg; Hydrocarbons (< 1 mg/kg)
- Contaminant flux in Lake Michigan estimated at 8.4-17 kg/yr.
Hydrodynamic Processes at the GSI

1. Recharge and infiltration.
2. Hydraulically driven flow.
3. Wave setup and infiltration.
4. Ebullition processes.
5. Hydraulically driven flow into surface water.
Hypothesis

“Biogeochemical changes resulting from hydrological interactions between anaerobic groundwater and aerobic surface water facilitate in situ (bio)transformation processes.”

Specific Objective: demonstrate vinyl chloride attenuation at GSI or “Are the biogeochemical processes sufficient to mitigate contaminant fluxes into L.M.?”
Groundwater Analyses
Offshore Sampling Procedures
Geophysical Characterization:
Ground Penetrating Radar

Principle: Short term emission of electro-magnetic pulses, and longer term reception of reflected waves results in "reflection patterns" from the interaction of the pulses with features of the subsurface.

Electrical conductivity ($\sigma$) of the subsurface controls the wave attenuation; the higher the conductivity, the less is the penetration.

Electrical permittivity ($\varepsilon_r$) in the subsurface varies from 2-5 for soils and rocks, to ~9 for moist sand and to ~25 for saturated sand. The water table is thus a clear conductivity boundary.

Magnetic permeability ($\mu_r$) becomes relevant when minerals exhibit magnetic properties, e.g. magnetite.
Contaminant Plume GPR Profiles
Macroscale Phenomena: Respiratory Depletion of Iron (III) Minerals

Bioavailable Iron(III) Extracted from Sediment

Iron(II) Extracted from Sediment

Surface Water

Dry well

GW Flow (±0.5 m/d)

Fe(II)

CH$_4$/SH$^-$
Iron Transformation as a Consequence of Microbial Iron Reduction

2 am-Fe(OH)$_3$ (s) + Fe$^{2+}$ (aq) $\rightarrow$ Fe$_3$O$_4$ (s) + 2 H$_2$O + 2 H$^+$

Fe$^{2+}$

Fe$^{2+}$ Fe$^{2+}$ Fe$^{2+}$

Fe$^{II}$Fe$^{III}$$_2$O$_4$
(magnetite)

am-Fe(OH)$_3$
Specific Conductance and Chloride Scatter-grams

Transect-I

\( \rho = 0.90 \)

\(|t| = 10.6 \)

\( t\)-stat = 2.49

Transect-II

\( \rho = 0.96 \)

\(|t| = 11.7 \)

\( t\)-stat = 2.68

Transect-III

\( \rho = 0.93 \)

\(|t| = 13.5 \)

\( t\)-stat = 2.46
Contaminant & Geochemical Profiles for 55-AE

Transect-I

Elevation (MAMSL)

Concentration (μM)

TCE

c-DCE

t-DCE

VC

Ethene

Oxygen

Nitrogen

Iron(aq)

Sulfate

Methane

Redox Potential (mV)

Piezometric Surface at 176.8 MAMSL
Contaminant & Geochemical Profiles for Barge-2

Transect-III

Elevation (MAMSL)

Concentration (μM)

Concentration (mM)

Concentration (mM)

Redox Potential (mV)

Lake Bottom at 172.7 MAMSL

TCE

cis-DCE

trans-DCE

VC

Oxygen

Nitrogen

Iron (aq)

Sulfate

Methane

Redox against Ag/AgCl

Barge-2

A

B

C

D
Conceptual Diagram of Plume

- Mil-Slotted Geoprobe Screen
  - 5-foot screen
- Iron(III)-Reducing Zone
- Sulfate-Reducing Zone
- Methanogenic Zone
- Uncontaminated Aerobic Zone

Approximate Elevation (MAMSL):
- 190
- 185
- 180
- 175
- 170
- 165

Lake Michigan

Groundwater Flow

Clay Layer
Temporal Effects: Storm Activity

Lake Michigan Wave Data
(NOAA Buoy 45007)

Average Wave Height (m)

Month 1996
Computational Grid and Boundary Conditions

Lake Michigan

Specified Head

Specified Flux

Clay Layer

1408 Nodes

1325 Elements
Predicted Oxygen Profiles in Response to Storm/Wave Activity

Dissolved Oxygen Contours

Initial Conditions: Oxygen present at 12 mg/l throughout aquifer.
Boundary Conditions: Aerobic lake water (12 mg/l).
Aerobic rainwater infiltration (12 mg/l).
Anaerobic groundwater inflow from inland (0 mg/l).

Velocity Field: 4 day cycle - 1 stormy day followed by 3 calm days
Storm: 1.5 meter waves
0.75 meter rise in lake level
Installation of Multilevel Samplers on the Beachhead
Contaminant & Geochemical Profiles at the GSI

Chloroethene

Oxygen

Methane
Redox and Hydrogen Profiles

A

Redox (mV)

Elevation (MAMSL)

August
September
November
December

Shallow Zone
Deep Zone

B

[Hydrogen] (nM)

Elevation (MAMSL)

August
September
November
December

Shallow Zone
Deep Zone
Construction of Quantile-Quantile (q-q) Plot

Histograms for Chloroethene

Cumulative Histograms for Chloroethene

Temporal Variation in Chloroethene
Temporal Variations

A. Temporal Variation in Methane

B. Temporal Variation in cis-DCE

C. Temporal Variation in Chloroethene

[Diagrams showing temporal variations of Methane, cis-DCE, and Chloroethene with markers for Shallow and Deep levels]
**Activity of Aquifer Solid-Eluted Cell Suspensions: Methanotrophs**

- **cis-DCE:** > zero relative to Control
- **Chloroethene:** -2.94 nMoles / (day-mg protein)
- **Ethene:** -0.85 nMoles / (day-mg protein)
• **Effect of Oxidation:**
  - Chloroethene Flux at Transect-5 is 0.86g/(yr-m²).
  - Oxidative Flux by Field Measurement is 0.063g/(yr-m²) (~7%).
  - Oxidative Flux by Lab Measurement is 0.0007g/(yr-m²) (~0.1%).
Modeling Bioremediation at the GSI:

*Methanotrophic Vinyl Chloride Oxidation at GSI During Storm Events*

Vinyl Chloride Contours Assuming No Degradation

Vinyl Chloride Contours With Degradation in the Anoxic Zone

Degradation: If \( \text{oxygen} > 0.1 \text{ mg/l} \) \( k = 1.5/\text{day} \)
If \( \text{oxygen} < 0.1 \text{ mg/l} \) \( k = 0. \)
Implications for Intrinsic Bioremediation at GSI

- The contaminant plume has migrated to the lake and discharges into Lake Michigan between the shoreline and 100 meters from shore.

- Surface water activity oxidizes the shallow and deep portions of the GSI, however, this effect is greatest in the shallow zone.

- Contaminants are transformed via oxidative processes in the shallow zone and reductive processes in the deep zone.

- Aerobic natural attenuation is insufficient to prevent flow of chloroethene into Lake Michigan.
“Heads Up”: CLEANER (NSF Collaborative Large-Scale Engineering Assessment Network for Environmental Research)

- **Backbone**: A series of well-instrumented field facilities (EFFs) representing distinctive stressed environments or environments that are representative of a common set of conditions or anthropogenic stressors.

- **Enabling Technologies**: Remote and on-site sensors, as well as local and off-site sample analysis. Real-time data acquisition and wireless transmission. Distributed parameter models. Geostatistical integration of monitoring data and GIS layers.

- **Objective**: Systematic and dynamic evaluation of ecosystems conditions and flows across and within media. Improved management strategies for ecosystems by controlling anthropogenic inputs and applying remediation techniques.
Layered Information Approach for Contaminated Sediments: Incorporating Uncertainty Analysis in Remedial Unit Design

Concentrations

Dechlorination contribution

Interpolated Dechlorination Map

$H_2, p$

$RU-s$

PVA: Polytopic Vector Analysis – An Environmental Forensics Tool for Source Apportionment
Contaminated Sediment Sites

- Naval Station San Diego
- 12/12/00 Sampling
- Surface Grab Samples
- Gravity Core Samples
- Saginaw Bay, MI
- New York Harbor, NY
- Passaic River, NJ
- San Diego Bay, CA
- Pearl Harbor, HI