MONITORED NATURAL ATTENUATION (MNA) FOR SITE CLEANUP: APPROPRIATE TOOL OR EASY WAY OUT?

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ROAD MAP

• **Intro: Changing Paradigms and MNA Principles**

• **Key Attenuation Processes**
  - Biodegradation
  - Abiotic Processes
  - LNAPL source zone degradation processes
  - Other processes (immobilization, storage, dilution)

• **Field Techniques and Technologies**
  - Groundwater sampling and analytical methods
  - Compound Specific Isotopes Analysis (CSIA)
  - Molecular Biological Tools (MBTs)
  - Natural Source Zone Depletion (NSZD)

• **Should MNA be Used? Data Analysis and Monitoring Tools**
  - Data requirements, LTM, and statistics to understand MNA rates
  - Common Graphics and Calculations
  - Remediation Timeframe Calculations
  - Computer Models

• **Implementation Topics**
SOURCE

PARADIGM

1970s – early 1990s
SOURCE
PARADIGM

1970s – early 1990s
PUMP AND TREAT THE PLUME

Recovery Well Installation

- Well Screen
- Centralizer
- Driller’s knee
- Driller’s helper

Wire-Wrap Well Screen

Sand-Gravel Filter Pack
What Happened?

NRC, 2012
What Happened?

The Good
The Bad
The Ugly
Groundwater contamination: Pump-and-treat remediation

Second of a five-part series

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University of Waterloo
Waterloo, ON, Canada

Organic contaminant plumes
Prior to the passage of the Comprehensive Environmental Response

FIGURE 2
Hypothetical examples of contaminant removal from aquifers

(a) Uniform sand–gravel aquifer

(b) Stratified sand–gravel aquifer

(c) Clay lens in uniform sand–gravel aquifer

(d) Uniform sand–gravel aquifer

* Dense color indicates NAPL contaminant, stippling indicates contaminant in dissolved and sorbed phases (assumed uniformly distributed initially), and arrows indicate relative velocity of groundwater flow. The groundwater is assumed to be extracted from the well at the same rate in the four cases.

*Dotted lines enclose total volume of water that would be pumped to remove contaminant with retardation factor of 2.
DNAPL PARADIGM
Era of In-Situ Innovation
PERFORMANCE:

Geomean Concentration by Site

Remediation Performance: Parent CVOC

- Bioremediation (n=117)
- Chemical Oxidation (n=70)
- Thermal Treatment (n=23)
- Chemical Reduction (n=21)
- Surfactant (n=4)

Site Concentration After Treatment (mg/L) vs Site Concentration Before Treatment (mg/L)

MCL
PERFORMANCE: **Rule of Thumb**

Max. Concs. (Regulatory Drivers)

Middle 50% of Sites Achieved ~ 0.4 to 2 OoM Reduction

![Graph showing Remediation Performance: Parent CVOC](image)
Fig. 3. Leeuwenhoek discovers microbes.
A CARTOON HISTORY OF MICROBIOLOGY, COYNE 1996

Fig. 3. Leeuwenhoek discovers microbes.
DISSOLVED OXYGEN IN GROUNDWATER

Supports Natural Attenuation:
Yes  No  Inconclusive

Benzene Plume

Dissolved Oxygen (mg/L)

LOW  ---  HIGH
FERROUS IRON IN GROUNDWATER

Supports Natural Attenuation:

- Yes
- No
- Inconclusive

Benzene Plume

Ferrous Iron (mg/L)

LOW ---- HIGH
Supports Natural Attenuation:

- Yes
- No
- Inconclusive

SULFATE IN GROUNDWATER

Benzene Plume

Sulfate (mg/L)

LOW    ------    HIGH
METHANE IN GROUNDWATER

Supports Natural Attenuation:

- Yes
- No
- Inconclusive

Benzene Plume

Methane (mg/L)

LOW -- HIGH
EVALUATING MNA IN PLUMES:

**Electron Acceptor Limited Degradation**

- **Biodegradation Capacity**: (17 mg/L)
- **Source Zone Concentration**: (25 mg/L)
- **Observed Source Zone Concentration**: (8 mg/L)

**Groundwater Flow**

**Reaction time**: Days-weeks
**Residence time**: Months/years
**Reactions behave “Instantaneous”**
MNA Protocol for Dissolved Contaminant from Fuels

Draft: 1994

Final: 1999
Most Petroleum Hydrocarbon Plumes Are Under 200 ft Long
Percent of Plumes in California That Are:

- Expanding (I): 8%
- Stable (II): 42%
- Shrinking (III): 33%
- Exhausted (IV): 17%
SCHEMATIC OF PLUME LIFECYCLE

I. EXPANDING  
II. STABLE  
III. SHRINKING  
IV. EXHAUSTED

TIME
Dissolved Hydrogen Is Key Electron Donor For Reductive Dechlorination of Chlorinated Solvents
WHAT ARE NATURAL ATTENUATION PROCESSES?


“A variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, or concentration of contaminants in soil and groundwater.”
WHAT ARE NATURAL ATTENUATION PROCESSES?

Reduction in contaminant mass or concentration in groundwater over time or distance due to natural processes:

**Non-Destructive Processes**
- Dispersion
- Sorption \( k_d = (K_{oc}) \times (foc) \)
- Dilution
- Volatilization

**Destructive Processes**
- Biodegradation
  - Abiotic Reactions (hydrolysis)
  - Oxygen \( (O_2) \)
  - Nitrate \( (NO_3^-) \)
  - Methane \( (CH_4) \)
  - Sulfate \( (SO_4^{2-}) \)
  - Carbon Dioxide \( (CO_2) \)
  - Iron \( (Fe^{+2}) \)
Nature can help!

It is harder and more expensive to clean these sites up than first thought.

Nature is amazing and seems to be degrading or sequestering some of these chemicals.

Let’s let nature do the job.

But you have to do three things:

Protect

Understand

Watch
WHAT EVIDENCE IS NEEDED FOR MNA?

New Trends in LOEs

**LOE 1:** Historical contaminant mass reduction

**LOE 2:** Hydrogeologic or geochemical data

**LOE 3:** Microcosm or Field data

LOE: “Lines of Evidence”
WHAT EVIDENCE IS NEEDED FOR MNA?

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“I Shrink Therefore I Am”

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“Put on the Lab Coat”

LOE: “Lines of Evidence”
## WHAT ARE THE MOST IMPORTANT NEW MNA DEVELOPMENTS?

<table>
<thead>
<tr>
<th>Year</th>
<th>New Contaminant</th>
<th>New Measurement</th>
<th>New Process</th>
<th>New Tools</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000-2005</td>
<td>MTBE-TBA</td>
<td>Two types of rates</td>
<td>Source attenuation of hydrocarbon sites</td>
<td>BIOChlor MAROS NAS SourceDK</td>
</tr>
</tbody>
</table>

Probably the most important “recent” development?
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<th>New Process</th>
<th>New Tools</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010-present</td>
<td>“Emerging Contaminants”</td>
<td>CO₂ traps for NSZD</td>
<td>Natural source zone depletion (NSZD)</td>
<td>PREMChlor Matrix Diffusion Toolkit</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Source attenuation of chlorinated solvent sites</td>
<td>Scenarios for metals/rads</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Attenuation in low-k zones</td>
<td>Source History Tool</td>
</tr>
</tbody>
</table>

**See Also:**

*Development and Validation of a Quantitative Framework and Management Expectation Tool for the Selection of Bioremediation Approaches (MNA, Biostimulation and/or Bioaugmentation) at Chlorinated Solvent Sites*
SOME KEY REFERENCES

1999

Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface

2006

Scenarios Evaluation Tool for Chlorinated Solvent MNA

2011

The Scenarios Approach to Attenuation-Based Remedies for Inorganic and Radionuclide Contaminants

2014

Google: ESTCP MNA FAQ

www.gsi-net.com

www.gsi-net.com
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• Implementation Topics
BIODEGRADATION PROCESSES

It’s all about the electrons...

- **PETROLEUM HYDROCARBONS:** typically serve as electron donors, so you may need more electron acceptor (but not always)

- **CHLORINATED SOLVENTS:** typically serve as electron acceptors, so you may need electron donor

*Important Concepts: biodegradation capacity and mass balances*
BIODEGRADATION OF PETROLEUM HYDROCARBONS

\[ \text{C}_6\text{H}_6 \quad \text{Benzene (oxidized)} \]

\[ \text{O}_2 \quad \text{Oxygen (reduced)} \]

Electrons

Heat

Carbon dioxide \( \text{CO}_2 \)

Water \( \text{H}_2\text{O} \)

Work

\[ \text{C}_6\text{H}_6 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Work} \]
AEROBIC HYDROCARBON BIODEGRADATION

- Highly thermodynamically feasible (it’s a fuel...)
- Hydroxylation (i.e., addition of OH) is often the first step
  - Increases solubility (more susceptible to metabolism)
  - Needs oxygenases (i.e., enzymes that “activate” \( O_2 \) and add it to the hydrocarbon molecule.)
  - Needs \( O_2 \) whose diffusion may be rate-limiting
- Aromatic ring must be di-hydroxylated before fission
• Important natural attenuation mechanism, but tends to occur at slower rates (weaker electron acceptors, $\text{NO}_3^-$, $\text{Fe}^{+3}$, $\text{SO}_4^{2-}$, and $\text{CO}_2$)

• Benzene, the most toxic of the BTEX, is relatively recalcitrant under anaerobic conditions (degrades very slowly – after TEX, or not at all)

• Benzoyl-CoA is a common intermediate, and it is reduced prior to ring fission by hydrolysis ($\text{CO}_2$ is still the endproduct).
<table>
<thead>
<tr>
<th>Electron Acceptor</th>
<th>Type of Reaction</th>
<th>Metabolic By-Product</th>
<th>Redox Potential (pH =7 in volts)</th>
<th>Reaction Preference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>Aerobic</td>
<td>CO₂</td>
<td>+ 820</td>
<td>Most Preferred</td>
</tr>
<tr>
<td>Nitrate</td>
<td>Anaerobic</td>
<td>N₂, CO₂</td>
<td>+ 740</td>
<td></td>
</tr>
<tr>
<td>Ferric Iron (solid)</td>
<td>Anaerobic</td>
<td>Ferrous Iron (dissolved)</td>
<td>- 50</td>
<td></td>
</tr>
<tr>
<td>Sulfate</td>
<td>Anaerobic</td>
<td>H₂S</td>
<td>- 220</td>
<td>Least Preferred</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>Anaerobic</td>
<td>Methane</td>
<td>- 240</td>
<td></td>
</tr>
</tbody>
</table>
HYDROCARBON BIODEGRADATION: *Use stoichiometry to estimate biodegradation capacity*

<table>
<thead>
<tr>
<th>Electron Acceptor or By-Product</th>
<th>Utilization Factor *</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Mass E. Acceptor / By-Prod. Consumed per Mass Dissolved Hydrocarbon Degraded)</td>
</tr>
<tr>
<td>Oxygen</td>
<td>3.14 gm/gm</td>
</tr>
<tr>
<td>Nitrate</td>
<td>4.9 gm/gm</td>
</tr>
<tr>
<td>Ferrous Iron</td>
<td>21.8 gm/gm</td>
</tr>
<tr>
<td>Sulfate</td>
<td>4.6 gm/gm</td>
</tr>
<tr>
<td>Methane</td>
<td>0.78 gm/gm</td>
</tr>
</tbody>
</table>

* Based on BTEX
HYDROCARBON BIODEGRADATION: Use stoichiometry to estimate biodegradation capacity

EXAMPLE OF HOW TO CALCULATE UTILIZATION FACTOR:

\[
\text{C}_6\text{H}_6 + 7.5 \text{O}_2 \rightarrow 6 \text{CO}_2 + 3 \text{H}_2\text{O}
\]

Benzene MW = 78 g/mol
Oxygen MW = 32 g/mol

Mass Ratio = \(\frac{\text{Oxygen Mass}}{\text{Benzene Mass}}\)

or “Utilization Factor”

\[
= \frac{32 \text{ g/mol} \times 7.5 \text{ mol}}{78 \text{ g/mol} \times 1 \text{ mol}} = 3.08
\]
### HYDROCARBON BIODEGRADATION:

**Biodegradation capacity example**

<table>
<thead>
<tr>
<th>CONCENTRATIONS (mg/L)</th>
<th>D.O.</th>
<th>NO$_3$</th>
<th>Iron</th>
<th>SO$_4$</th>
<th>CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background</td>
<td>2</td>
<td>0.7</td>
<td>0.5</td>
<td>26.2</td>
<td>0</td>
</tr>
<tr>
<td>Source</td>
<td>0.4</td>
<td>0</td>
<td>36.6</td>
<td>3.8</td>
<td>7.4</td>
</tr>
<tr>
<td><strong>Utilization Factor</strong></td>
<td>3.14</td>
<td>4.9</td>
<td>21.8</td>
<td>4.6</td>
<td>0.78</td>
</tr>
</tbody>
</table>

**BIODEG. CAPAC.**

|          | 0.5 | 0.1  | 1.7  | 4.9   | 9.5   |

Sum to get “Expressed” Biodegradation Capacity = 16.7 mg/L BTEX
BIODEGRADATION OF CHLORINATED SOLVENTS (ANAEROBIC REDUCTIVE DECHLORINATION)

- **H₂** Hydrogen (electron donor)
- **C₂HCl₄** Tetrachloroethene (electron acceptor)
- **Electrons**
- **Heat**
- **Work**
CHLORINATED SOLVENT REDUCTIVE DECHLORINATION: *Electron Donors Are Key*

- **Carbon Source**
  - Fermentation
  - By-Products
- **Dissolved Hydrogen**
  - Is Key Electron Donor
- **Process requires multiple microbial groups and anaerobic conditions**

- **H₂**
  - CO₂
  - PCE
  - Ethene
  - CH₄
  - H₂O
Thermodynamics means that **strongly reducing conditions** are required

- High energy reactions are favored
- Hydrogen will be used first by aerobes and denitrifying bacteria
REDUCTIVE DECHLORINATION: *Chlorinated Ethenes*

Key footprint of PCE, TCE biodegradation: presence of cis 1,2-DCE
REDUCTIVE DECHLORINATION: Pathway for Chlorinated Ethenes

Key footprint of PCE, TCE, cis-1,2-DCE, VC biodegradation: presence of ethene (or ethane)

(Adapted from RTDF, 1997.)
ABIOТИC PROCESSES: How do reactive mineral species contribute to attenuation?

Naturally-occurring minerals can degrade contaminants

- CVOC degradation that is abiotically-mediated by a number of reactive mineral species
  - Iron(II) Sulfide (FeS)
  - Mackinawite – \((\text{Fe})_{1+x}\)S
  - Pyrite (FeS\(_2\))
  - Magnetite (Fe\(_3\)O\(_4\))
  - Goethite (\(\alpha\)-FeO(OH))
  - Hematite (Fe\(_2\)O\(_3\))
  - Lepidocrocite (\(\gamma\)-FeO(OH))
  - Green Rust–(\(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\) cations, \(\text{O}^{2-}\) and \(\text{OH}^-\) anions, with loosely bound \([\text{CO}_3]^{2-}\) groups and \(\text{H}_2\text{O}\) molecules between the layers)

- Basis for ZVI and other PRB designs, but significant evidence of natural attenuation in anaerobic environments

Example of abiotic TCE degradation by magnetite (from ESTCP/AFCEE/NAVFAC, 2007)

Note there is biological component to these reactions!
ABIOTIC PROCESSES: *Unique degradation products when reactive minerals are involved*

**UNIQUE PRODUCTS:**
- If either detected, then this is proof that abiotic attenuation is occurring!

**EASIER SAID THAN DONE...**
- Products are biodegradable (in situ and following sample collection)
- Highly volatile
- Concentration may be low and hard to quantify

**KEY POINT: FALSE NEGATIVES ARE BIG ISSUE**
Compounds may be almost gone by the time the sample reaches the lab, and lab may not be able to measure what’s left
## ABIOTIC PROCESSES:

**Which contaminants and which minerals?**

<table>
<thead>
<tr>
<th></th>
<th>Iron sulfides</th>
<th>Magnetite</th>
<th>Green rust</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorinated Solvents</td>
<td>YES</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td>Pesticides</td>
<td>YES</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Munitions (RDX)</td>
<td>YES?</td>
<td>YES</td>
<td></td>
</tr>
<tr>
<td>Metals (U, As)</td>
<td>YES</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Iron sulfides</th>
<th>Magnetite</th>
<th>Green rust</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum hydrocarbons (BTEX, MTBE)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2,3-trichloropropene</td>
<td></td>
<td>Minor</td>
<td></td>
</tr>
<tr>
<td>PFAS (per- and polyfluorinated alkyl substances)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-nitrosodimethylamine (NDMA)</td>
<td></td>
<td></td>
<td>Maybe?</td>
</tr>
</tbody>
</table>
**ABIOTIC PROCESSES:**

*Hydrolysis*

1,1,1-TCA → Acetic Acid

**Hydrolysis**

Product Yield = 80%

**Dehydrohalogenation**

1,1-Dichloroethene

Product Yield = 20%

*TCA half-lives for Hydrolysis: ~ 1 – 10 yr*
**ABIOTIC PROCESSES:**

*Which contaminants undergo hydrolysis?*

<table>
<thead>
<tr>
<th>Target compound(s)</th>
<th>Undergoes hydrolysis-type reactions?</th>
<th>Product(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1,1-TCA</td>
<td>YES</td>
<td>Acetic acid, 1,1-DCE</td>
</tr>
<tr>
<td>1,1,1,2-TeCA</td>
<td>YES</td>
<td>TCE</td>
</tr>
<tr>
<td>1,2-Dichloropropane</td>
<td>YES</td>
<td>1-Chloropropene</td>
</tr>
<tr>
<td>Chloroethane</td>
<td>YES</td>
<td>Ethanol, ethene</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>YES</td>
<td>CO2</td>
</tr>
<tr>
<td>1,1-DCA</td>
<td>YES</td>
<td>Chloroethene</td>
</tr>
<tr>
<td>1,2-DCA</td>
<td>YES</td>
<td>Chloroethene</td>
</tr>
</tbody>
</table>
• Methods for assessing abiotic degradation capacity are available and/or being developed
  • E.g., magnetite in sediments via magnetic susceptibility testing

• Current research suggests slow but sustainable attenuation rates

EPA, 2009 – detailed descriptions of important methods
LNAPL SOURCE ZONE DEGRADATION:
*Methane production results in ebullition*

Methane bubbles!

Source: CSU

Ye et al., 2009

Day 100

Day 102

Day 106

Day 113

Water Saturation
Methane bubbles!

Source: CSU, Ye et al., 2009

Starting Point: Refinery and Terminal Petroleum Spills Generation

Day 100

Day 102

Day 106

Methane channel!

Water Saturation

Source: CSO 2009
Surprising Result: Vapor transport fluxes much greater than groundwater fluxes!
Carbon Eflux Key Process at LNAPL Sites

Key Point 1: Natural Degradation Occurring >30 Years Later

Key Point 2: 85 - 90% of the carbon biodegradation products outgassed!

Fig. 2. Original pipeline oil composition (solid lines) and most recently measured fate (dashed lines). Boxed constituents on the level directly above dotted horizontal line provided the basis for oil components used in this study. Entries below dotted horizontal line show oil loss pathways. Note that a significant oil mass remains, and oil phase loss includes some dissolved organic carbon (mostly BEX and NVDOC) that has not fully degraded. Components and pathways lacking data constraining are indicated with (?). Data sources: 1Eganhouse et al. (1993), 2Baedecker et al. (2011), 3Thorn and Aiken (1998), 4Bekins et al. (2005), 5Sihota et al. (2011), 6Hostettler et al. (2007), 7Amos et al. (2012).
Current NSZD Conceptual Model

- Methane Oxidation
- Mobile or Residual LNAPL
- Dissolved Phase Plume

Adapted from: CSU, 2016
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CONTAMINANT STORAGE: WHAT IS DIFFUSION?

Diffusion describes the spread of particles through random motion from regions of higher concentration to regions of lower concentration.

Key people: Fourier (1822), Fick (1855), Einstein (1905), Smoluchowski (1906)

\[ J = D \frac{dC}{dx} \]

- \( J \) = Diffusive flux flowing though a particular cross section (mg/m²/sec)
- \( D \) = Diffusion coefficient (m²/sec)
- \( \frac{dC}{dx} \) = Concentration gradient (mg/liter/meter)

Coffee Cup: convection + diffusion
Laminar Groundwater: Molecular diffusion - movement of molecules only
MATRIX DIFFUSION AS CONTAMINANT STORAGE

Advancing solvent plume  Low permeability silts  Transmissive sand

Expanding diffusion halo in stagnant zone

Simultaneous inward and outward diffusion in stagnant zones

After NRC 2005
Contaminant storage and release processes in low permeability zone is important, but it is governed by concentrations gradients that occur at scales of *centimeters to millimeters*.

**KEY POINT:** *Matrix Diffusion is a Small-Scale Phenomena*

Day 28
Connecticut Site

Source Zone

Groundwater Flow

Transect 1

Chapman and Parker WRR 2005
Image Courtesy of B. Parker
HIGH-RESOLUTION DATA FROM CORE

Chapman and Parker 2005
Image Courtesy of B. Parker

Aquifer

Interface

Aquitard

Aquifer

Aquitard
Connecticut Site

3000 kg TCE present in low-perm zone!

Source Zone

Groundwater Flow

Chapman and Parker WRR 2005
Image Courtesy of B. Parker
CONCENTRATION VS. TIME FROM MONITORING WELLS

Source: Chapman and Parker, 2005 Copyright 2005 American Geophysical Union. Reproduced/modified by permission of AGU.
LIFE CYCLE OF A CHLORINATED SOLVENT SITE

Late Stage

- Vapor Plume
- Matrix Storage (Dissolved and sorbed phases in low flow zones)
- Groundwater Plumes

Sale et al., 2008
(I) Granular Media with Mild Heterogeneity and Moderate to High Permeability (e.g. eolian sands)

(II) Granular Media with Mild Heterogeneity and Low Permeability (e.g. lacustrine clay)

(III) Granular Media With Moderate to High Heterogeneity (e.g. deltaic deposition)

(IV) Fracture Media with Low Matrix Porosity (e.g. crystalline rock)

(V) Fracture Media with High Matrix Porosity (e.g. limestone, sandstone or fractured clays)

After NRC 2005
HETEROGENEITY RULES, EVEN IN “SANDY AQUIFERS”

Matrix Diffusion Paradigm: 
*Remediation Hydraulics (CRC Press)*
Fred Payne, Joseph Quinnan, Scott Potter

Image from Fred Payne /ARCADIS
REMCHLOR-MD MATRIX DIFFUSION MODEL: Game Changer?

Aquifer/Aquitard System

a) transmissive zone
   low permeability confining layer

Layered System

b) low permeability layers
   transmissive zones
   low permeability confining layer

Heterogeneous System

c) transmissive zone
   low permeability confining layer

3D Fractured Porous Media

d)

For REMChlor: google REMChlor USEPA
Soil-to-GW Pathway ($^{GW}_{SOIL}$): Leachate Dilution Factor ($LDF$)

$$LDF = 1 + \frac{U_{gw} \delta_{gw}}{I_f W_s}$$

$$\delta_{gw} = (2\alpha_v W_s)^{0.5} + b_{gw}$$

Must use this equation in Tier 2. (Tier 1 PCLs based on default LDF of 10 or 20.)
Groundwater to Surface Water Pathway ($SW_{GW}$)

$$SW_{GW} = \frac{SW_{RBEL}}{DF}$$

where $DF = $ Dilution factor for affected $GW$ entering $SW$.

$SW_{RBEL} = $ Lowest applicable value for COC per 350.74 (h).

$GW = $ Groundwater
Emerging Conceptual Model:

- Dispersion is very weak process
- Most plumes are long and narrow
- Matrix Diffusion is much more important than dispersion
Dilution in Mass Flux Calculations

Concentration versus Mass Discharge

Site A:
Very wide source
Very fast groundwater

Site B:
Tiny source
Almost stagnant groundwater

But same maximum groundwater Concentration…
Dilution in Mass Flux Calculations
Concentration versus Mass Discharge

- Concentration-based approach may not account for important site characteristics

But same maximum groundwater Concentration...

Mega Site  “Piss-Ant” Site
Definitions

Mass flux, $J$ (mass per area per time)

Integrate

Mass discharge, $M_d$ (Mass per time)

“This plume has a mass discharge of 1.5 grams per day.”

Sir Isaac Newton:
“Method of Fluxions”
Mass Flux / Mass Discharge

Combine flow, size, concentration to get grams per day (mass discharge)
Using Mass Discharge: Estimating Well Impacts

Einarson and Mackay, 2001

Use mass discharge of plume to predict constituent of concern concentration in downgradient water supply well

\[ C_{\text{well}} = \frac{M_d}{Q_{\text{Well}}} \]

- \( C_{\text{well}} \) = Concentration in extraction well
- \( Q_{\text{well}} \) = Pumping rate for extraction well

\[ \frac{2 \text{ grams}}{\text{day}} \times \frac{1}{600 \text{ gpm}} \div \frac{1 \text{ day}}{1440 \text{ min}} \times \frac{1 \text{ gal}}{3.79 \text{ L}} \times \frac{10^6 \text{ ug}}{\text{g}} = < 1 \text{ ug/L} \]
MANAGING SURFACE WATER QUALITY WITH MASS DISCHARGE: *Total Maximum Daily Loads (TMDL)*

“The maximum amount of a pollutant that a water body or water segment can assimilate without exceeding water quality standards.” (1972 CWA)

**EXAMPLES:**

- PCBs into Susquehanna River (Penn.): 0.64 grams per day *(our Mag 4)*
- Copper into Eagle River (Alaska): up to 5450 grams per day *(our Mag 8)*
- Proposed Dioxin into Houston Ship Channel 0.04 grams per day *(our Mag 3)*
# PLUME MAGNITUDE CLASSIFICATION SYSTEM

<table>
<thead>
<tr>
<th>Mass Discharge (grams/day)</th>
<th>Plume Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.001</td>
<td>“Mag 1 Plume”</td>
</tr>
<tr>
<td>0.001 to 0.01</td>
<td>“Mag 2 Plume”</td>
</tr>
<tr>
<td>0.01 to 0.1</td>
<td>“Mag 3 Plume”</td>
</tr>
<tr>
<td>0.1 to 1</td>
<td>“Mag 4 Plume”</td>
</tr>
<tr>
<td>1 to 10</td>
<td>“Mag 5 Plume”</td>
</tr>
<tr>
<td>10 to 100</td>
<td>“Mag 6 Plume”</td>
</tr>
<tr>
<td>100 to 1,000</td>
<td>“Mag 7 Plume”</td>
</tr>
<tr>
<td>1,000 to 10,000</td>
<td>“Mag 8 Plume”</td>
</tr>
<tr>
<td>10,000 to 100,000</td>
<td>“Mag 9 Plume”</td>
</tr>
<tr>
<td>&gt;100,000</td>
<td>“Mag 10 Plume”</td>
</tr>
</tbody>
</table>

Newell et al., 2011
ROAD MAP

• Intro: Changing Paradigms and MNA Principles
• Key Attenuation Processes
  ▪ Biodegradation
  ▪ Abiotic Processes
  ▪ LNAPL source zone degradation processes
  ▪ Other processes (immobilization, storage, dilution)
• Field Techniques and Technologies
  ▪ Groundwater sampling and analytical methods
  ▪ Compound Specific Isotopes Analysis (CSIA)
  ▪ Molecular Biological Tools (MBTs)
  ▪ Natural Source Zone Depletion (NSZD)
• Should MNA be Used? Data Analysis and Monitoring Tools
  ▪ Data requirements, LTM, and statistics to understand MNA rates
  ▪ Common Graphics and Calculations
  ▪ Remediation Timeframe Calculations
  ▪ Computer Models
• Implementation Topics
Characterization/Remedy Selection

MNA MONITORING

<table>
<thead>
<tr>
<th>Line of Evidence 1</th>
<th>Decreasing historical trends in concentration/mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line of Evidence 2</td>
<td>Favorable geochemical and daughter product data</td>
</tr>
<tr>
<td>Line of Evidence 3</td>
<td>Microcosm or field data showing degradation is occurring (and rate)</td>
</tr>
</tbody>
</table>

![Graph showing concentration over time]

Concentration (µg/L)

Sampling Date
CHARACTERIZATION/REMEDY SELECTION: Gathering Better “Lines of Evidence”

Increasingly reliant on new techniques:

- Molecular Biological Tools (MBTs)
- Compound Specific Isotope Analysis (CSIA)
- Natural Source Zone Depletion (NSZD)
- Mass discharge

*We’ll talk more about these in a minute...*
PERFORMANCE MONITORING: 
_Proving that MNA is working_

MNA MONITORING

1. Characterization/Remedy Selection
2. Performance Monitoring

USEPA, 2004
### OBJECTIVES OF LONG-TERM PERFORMANCE MONITORING

<table>
<thead>
<tr>
<th>Objectives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Demonstrate that natural attenuation is occurring</td>
</tr>
<tr>
<td>Detect changes in conditions that reduce attenuation efficiency</td>
</tr>
<tr>
<td>Identify toxic/mobile by-products</td>
</tr>
<tr>
<td>Verify that plume is not expanding</td>
</tr>
<tr>
<td>Verify no impact to downgradient receptors</td>
</tr>
<tr>
<td>Detect new releases</td>
</tr>
<tr>
<td>Confirm institutional controls are working</td>
</tr>
<tr>
<td>Verify attainment of remedial objectives</td>
</tr>
</tbody>
</table>

*Primarily based on sampling groundwater from monitoring wells*

---

**Site-specific**

**REMEDIAL ACTION OBJECTIVES (RAOs)**

**PRELIMINARY REMEDIATION GOALS (PRGs)**
Downgradient transect
Plume transects w/ side gradient wells
Source Area (and recalcitrant zones)
High concentration plume core
Low concentration plume fringe
Plume boundaries
Groundwater Flow Direction

GOALS:
- Assess attenuation rates
- Monitor plume expansion or shrinkage at downgradient locations or transects
- Confirm no risk to receptor(s)
- Establish background, monitor for change in conditions or new releases
TYPICAL ANALYTES FOR LONG-TERM PERFORMANCE MONITORING

Constituents of Concern

Geochemical indicators: oxidation-reduction potential, pH, temperature, methane, sulfate, iron, nitrate

Others:

Transformation products:
daughters products, metals (e.g., Cr, As)

Others:

water level, isotopes, biomarkers, minerals
ISOTOPE ANALYSIS: *Can they prove contaminants are being destroyed?*

Yes, and more

“Stable isotope analyses can provide unequivocal documentation that biodegradation or abiotic transformation processes actually destroyed the contaminant.”

USEPA, 2008
WHAT ARE STABLE ISOTOPES?

$^{12}\text{C}$

“LIGHT”

6 neutrons + 6 protons
Abundance = 98.9%

$^{13}\text{C}$

“HEAVY”

7 neutrons + 6 protons
Abundance = 1.1%

$^{14}\text{C}$ is subject to radioactive decay and not considered stable
WHAT ARE “COMPOUND-SPECIFIC” STABLE ISOTOPES?

Process is called FRACTIONATION – the isotopic ratio is changing due to degradation.

Lighter isotopes are degraded preferentially (more rapidly)

Degradation causes remaining PCE to become enriched in heavier isotope
HOW DO YOU EXPRESS ISOTOPIC DATA?

Ratio = \( R = \left(\text{“heavy”}\right) / \left(\text{“light”}\right) \)

e.g., \(^{13}\text{C}\) measured in TCE

e.g., \(^{12}\text{C}\) measured in TCE

\[ \delta_{\text{TCE}} = \text{“del”} = \frac{R_{\text{TCE}} - R_{\text{std}}}{R_{\text{std}}} \times 1000 \]

Units are “per mil” or ‰
HOW TO USE CSIA:

**Evidence for degradation of parent compound**

Increased Fractionation ("Heavier") vs. $\delta^{13}C$ (%o)

- $\delta_0$
- $\delta_{\text{parent}}$

Reflects extent of parent degradation

Need > 2‰ for to confirm C fractionation (EPA, 2008)
HOW TO USE CSIA:

Evidence for degradation of daughter compound

DEGRADATION OF DAUGHTER PRODUCT:
\[ \delta_{\text{daughter}} \text{ exceeds } \delta_{0,\text{parent}} \]
as \( C_{\text{parent}} \) approaches 0
KEY BENEFITS OF CSIA

- Demonstrating that parent compound is being degraded
- Estimating the extent of degradation
- Differentiating between destructive and non-destructive pathways
- Differentiating between various destructive pathways
- Demonstrating that complete degradation has occurred
- Estimating rate of degradation
- Source identification and differentiation
- Can be incorporated into reactive transport modeling

**Easy protocol:** collect groundwater from monitoring wells and send to lab.

- Carbon ($^{13}$C/$^{12}$C)
- Oxygen ($^{18}$O/$^{16}$O)
- Nitrogen ($^{15}$N/$^{14}$N)
- Chlorine ($^{37}$Cl/$^{35}$Cl)
- Hydrogen ($^{2}$H/$^{1}$H)
MOLECULAR BIOLOGICAL TOOLS: Can they prove contaminants are being destroyed?

MBTs provide strong, but not definitive evidence of MNA

1. Show that key organisms are present (e.g., Dehalococcoides, Dehalobacter)

2. Show that key enzymes are present (e.g., vcrA, oxygenase-encoding genes)

3. Establish relative abundance of key microbial populations

KEY ISSUE: Most tests focus on presence, not activity!
Evaluating chlorinated solvent degradation using PCR-based methods for tracking \textit{Dehalococcoides (Dhc)}

<table>
<thead>
<tr>
<th>Tools</th>
<th>MNA Application</th>
<th>MNA Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCR / qPCR</td>
<td>• Identify if key organisms / enzymes</td>
<td>• Many techniques cannot differentiate between live and inactive cells</td>
</tr>
<tr>
<td></td>
<td>• Determine if abundance of key biomarkers is increasing</td>
<td>• Attempts to correlate in situ activity and gene expression still in infancy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Target mostly well-known pathways (others in development)</td>
</tr>
</tbody>
</table>

\textit{Others:}

\textit{Stable Isotope Probing (SIP), microbial fingerprinting, microarrays, enzyme activity probes}
• Groundwater or Soil using established procedures
  • starting at about $200 per sample/target)

• Quantitative Rules for MNA.
  • Specific recommendations for MNA
  • Lu et al., 2006: “generally useful” attenuation rates of cis-1,2-DCE and VC (> 0.3/yr) were associated with sites where \( Dhc \) was detected, while no attenuation was observed at sites where it was absent

\[ Dhc \text{ at } 10^4 \text{ to } 10^6 \text{ gene copies/L can support MNA} \]
\[ Dhc \text{ at } > 10^6 \text{ gene copies/L is the target threshold for ensuring ethene production} \]

*Guidance also included in “BioPIC” discussed later in this presentation*
TYPICAL APPLICATION: “Passive microbial sampling devices”, e.g., BioTraps, are installed in monitoring well for 30 days or more

Calculating Mass Discharge: Transect Method Simple Example

Step-by-step approach assuming uniform groundwater velocity

1. Characterize plume (C)
2. Characterize flow (q)
3. Draw transect: with simple approach, just build cross-sectional polygons (“window panes”) for each well across flow
4. Determine area (W • b = A)
5. Multiply and sum together:

\[ M_d = \sum (C_n \cdot A_n \cdot q) \]

\[ M_d = \text{Mass discharge} \]
\[ C_n = \text{concentration in polygon } n \]
\[ A_n = \text{Area of segment } n \]

Nichols and Roth, 2004
Tools for Transect Method: Calculator

Mass Flux Toolkit
To Evaluate Groundwater Impacts, Attenuation, and Remediation Alternatives

Lead author: Shahla Farhat, Ph.D.
free at www.gsi-net.com
Microsoft Excel-based

Calculate Flux
Impact of Flux
Learn About Flux

Version 1.0 Beta
## Input Data and Grid

### Site Location and I.D.: 
- **Texas**  
- **MTBE**

### Data Input Instructions:
- **Enter value directly.**
- **Value calculated by model.**

#### 4. CHOOSE TRANSECT
- **Transect 1**

#### 5. CHOOSE TIME PERIOD
- **1**

#### 6. ENTER TRANSECT DATA
- **Distance of Transect 1 from Source:** 192 (ft)
- **Darcy Velocity**
- **Hydraulic Conductivity**
- **Sampling Interval**
- **Mid Point of Sampling Interval**

#### Hydraulic Conductivity Units
- **Uniform Hydraulic Conductivity?** Yes
- **Uniform Hydraulic Gradient?** Yes

#### Monitoring Point

<table>
<thead>
<tr>
<th>Monitoring Point</th>
<th>Distance from Edge of Transect (ft)</th>
<th>Sampling Interval (ft bgs)</th>
<th>Plume Top (ft bgs)</th>
<th>Plume Bottom (ft bgs)</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Top</td>
<td>Bottom</td>
<td>Top</td>
<td>Bottom</td>
</tr>
<tr>
<td>1</td>
<td>TR1-2</td>
<td>10</td>
<td>5</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>TR1-2</td>
<td>10</td>
<td>5</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>TR1-4</td>
<td>27.5</td>
<td>5</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>TR1-4</td>
<td>27.5</td>
<td>15</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>TR1-4</td>
<td>27.5</td>
<td>15</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>TR1-6</td>
<td>45</td>
<td>5</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>TR1-6</td>
<td>45</td>
<td>10</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>8</td>
<td>TR1-6</td>
<td>45</td>
<td>15</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>9</td>
<td>TR1-8</td>
<td>62.5</td>
<td>5</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>10</td>
<td>TR1-8</td>
<td>62.5</td>
<td>10</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>11</td>
<td>TR1-8</td>
<td>62.5</td>
<td>15</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>12</td>
<td>TR1-12</td>
<td>80</td>
<td>5</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>13</td>
<td>TR1-12</td>
<td>80</td>
<td>10</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### 7. CHOOSE GRID
- **Orig mean cell width (x-axis) (ft):** 14.0
- **Orig cell thickness (y-axis) (ft):** 1.5
- **Refine cell width by:** 1
- **Refine cell thickness by:** 1

#### 8. SELECT CONSTITUENT FOR CALCULATIONS
- **MTBE**
- **Constituent B**
Method 3 – Passive Flux Meter

► Permeable sorbent
  • Accumulates contaminant based on flow and concentration

► Soluble tracers
  • Loses tracer based on groundwater velocity and flux convergence calculations

1. Contaminant adsorbed onto passive flux meter over time to get Concentration

   \[ t_1 \quad \stackrel{\text{Dye intercepted in a meter}}{\longrightarrow} \quad t_2 \quad \stackrel{\text{Dye intercepted in a meter}}{\longrightarrow} \quad t_3 \]

2. Tracer desorbs from passive flux meter over time to get Flow (Q)

   \[ K >> K_0 \]

Source: Hatfield and Annable
CURRENT NATURAL SOURCE NSZD CONCEPTUAL MODEL

CO₂ flux at Ground Surface

Methane Oxidation

Heat

Mobile or Residual LNAPL

Dissolved Phase Plume

Adapted from: CSU, 2016
CO₂ flux at Ground Surface

Methane Oxidation

Mobile or Residual LNAPL

Dissolved Phase Plume

Groundwater

CO₂ Flux Measurement at Surface

Measure Inward Diffusion of Oxygen

Adapted from: CSU, 2016
NSZD STUDIES: Johnson et al, 2006; Lundegard and Johnson, 2006; Sihota et al., 2011; McCoy et al., 2013

![Graph showing concentrations of Oxygen, CO₂, and Methane over depth.](image)

Lundegard and Johnson, 2006
## WHAT NSZD RATES ARE BEING OBSERVED?

<table>
<thead>
<tr>
<th>NSZD Study</th>
<th>Site-wide NSZD Rate (gallons/acre/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Six refinery terminal sites (McCoy et al., 2012)</td>
<td>2,100 – 7,700</td>
</tr>
<tr>
<td>1979 Crude Oil Spill (Sihota et al., 2011)</td>
<td>1,600</td>
</tr>
<tr>
<td>Refinery/Terminal Sites in Los Angeles (LA LNAPL Wkgrp, 2015)</td>
<td>1,100 – 1,700</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).
CURRENT NATURAL SOURCE NSZD CONCEPTUAL MODEL

CO₂ flux at Ground Surface

Methane Oxidation

CO₂ Flux Measurement at Surface

Measure Inward Diffusion of Oxygen

Subsurface Temperature Measurement

Adapted from: CSU, 2016
Key Objective: Use heat released from biodegradation to calculate continuous estimates of NSZD rates.
CONCEPTUAL MODEL

Surface heating and cooling

LNAPL degradation

Heat Source

Groundwater Flow

Geothermal gradient

Source: CSU
FIELD INSTALLATION: *Thermal Monitoring System*
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
Most of heat released by methane oxidation (conversion to CO$_2$) in vadose zone, not by the methane generation itself
HEAT SIGNAL OVER TIME: *Kansas Tank Farm*

*Source: Stockwell, 2015; Colorado State University*
Temperature data are uploaded to Thermal NSZD Dashboard for real-time calculation of LNAPL degradation.
THERMAL NSZD DASHBOARD:
Cumulative Sitewide NSZD Updated Daily

Amount of LNAPL Degraded Since NSZD Monitoring Began: 61,966 gallons LNAPL

Natural Source Zone Depletion Rate Over Past 30 Days: 518 gallons/acre/year

Sitewide NSZD (gallons)

Cumulative NSZD (gallons)

<table>
<thead>
<tr>
<th>May</th>
<th>Jul</th>
<th>Sep</th>
<th>Nov</th>
<th>2017</th>
<th>Mar</th>
<th>May</th>
<th>Jul</th>
<th>Sep</th>
<th>Nov</th>
</tr>
</thead>
</table>

Sitewide NSZD Value
ROAD MAP

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  ▪ Remediation Timeframe Calculations
  ▪ Computer Models
• Implementation Topics
WHY DO WE NEED TREND ANALYSIS?

- Answers important questions!
- Short-term variability can make this challenging, so need statistical methods
- Linear regression has limitations

Source: McHugh et al., 2015
LONG-TERM ATTENUATION RATES VS. SHORT-TERM VARIABILITY

KEY POINTS:

• Short-term variability makes it harder to determine trend and increases the amount of monitoring needed to evaluate progress in remediation

• Long-term trend apparent over longer monitoring period
WHY SHOULD WE USE MANN-KENDALL FOR TREND ANALYSIS?

- Mann-Kendall only cares about relative magnitudes of the concentrations, not the actual concentrations.
- Easier to establish trend even with a modest slope.
- Non-detects are more easily handled.
- Simple method – can use existing software tools.
## HOW DO YOU PERFORM MANN-KENDALL ANALYSIS?

<table>
<thead>
<tr>
<th>CALCULATE 3 DIFFERENT METRICS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>S Statistic (S)</strong></td>
</tr>
<tr>
<td><strong>Confidence Factor (CF)</strong></td>
</tr>
<tr>
<td><strong>Coefficient of Variation (COV)</strong></td>
</tr>
</tbody>
</table>

*For description of how each are calculated, see User’s Guide for Mann-Kendall Toolkit (GSI, 2012): Also see MAROS (www.gsi-net.com/en/software)*
HOW DO YOU PERFORM MANN-KENDALL ANALYSIS?

<table>
<thead>
<tr>
<th>S Statistic</th>
<th>Confidence in Trend</th>
<th>Trend</th>
</tr>
</thead>
<tbody>
<tr>
<td>S &gt; 0</td>
<td>CF &gt; 95%</td>
<td>Increasing</td>
</tr>
<tr>
<td>S &gt; 0</td>
<td>95% ≥ CF ≥ 90%</td>
<td>Probably Increasing</td>
</tr>
<tr>
<td>S &gt; 0</td>
<td>CF &lt; 90%</td>
<td>No Trend</td>
</tr>
<tr>
<td>S ≤ 0</td>
<td>CF &lt; 90% and COV ≥ 1</td>
<td>No Trend</td>
</tr>
<tr>
<td>S ≤ 0</td>
<td>CF &lt; 90% and COV &lt; 1</td>
<td>Stable</td>
</tr>
<tr>
<td>S &lt; 0</td>
<td>95% ≥ CF ≥ 90%</td>
<td>Probably Decreasing</td>
</tr>
<tr>
<td>S &lt; 0</td>
<td>CF &gt; 95%</td>
<td>Decreasing</td>
</tr>
</tbody>
</table>

2 other options:  
ND = locations w/ all non-detect values  
N/A = locations w/ < 4 datapoints
HOW DOES MONITORING FREQUENCY AFFECT CONFIDENCE AND ACCURACY OF THE RATE?

Increasing the time between monitoring events will increase the CONFIDENCE and ACCURACY of your long-term attenuation rate...

But by how much?
### Accuracy/Confidence Cost

<table>
<thead>
<tr>
<th>Medium Confidence:</th>
<th>Medium Accuracy:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Statistically-significant; decreasing concentration trend ( (p &lt; .1) ) for 80% of monitoring wells</td>
<td>Determine the long-term attenuation rate with an accuracy (i.e., 95% confidence interval) of +/- 50% or +/- 0.1 yr(^{-1}) (whichever is larger) for 80% of monitoring wells</td>
</tr>
</tbody>
</table>

20 sites were examined to see how much data was needed to meet these thresholds.
### HOW MUCH DATA IS NEEDED TO DEFINE TREND WITH CONFIDENCE AND ACCURACY?

<table>
<thead>
<tr>
<th>Accuracy/Confidence Cost</th>
<th>Best Site</th>
<th>Median Site</th>
<th>Worst Site</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Medium Confidence:</strong> Statistically-significant; decreasing concentration trend ( p &lt; .1 ) for 80% of monitoring wells</td>
<td>2.8 years</td>
<td><strong>7.3 years</strong></td>
<td>30 years</td>
</tr>
<tr>
<td><strong>Medium Accuracy:</strong> Determine the long-term attenuation rate with an accuracy (i.e., 95% confidence interval) of +/- 50% or +/- 0.1 yr(^{-1}) (whichever is larger) for 80% of monitoring wells</td>
<td>4.0 years</td>
<td><strong>7.4 years</strong></td>
<td>14.5 years</td>
</tr>
</tbody>
</table>
1) It commonly takes **seven years or more of quarterly monitoring data** to characterize the attenuation rate with even a medium level of accuracy (i.e., +/- 50%).

2) Making decisions (e.g., remedy effectiveness; remediation timeframe) based on insufficient data can result in incorrect decisions.
WHAT IS THE TRADE-OFF BETWEEN MONITORING FREQUENCY AND DURATION?

The answer is the same

4 yrs quarterly monitoring
5 yrs semiannual monitoring
7 yrs annual monitoring

Trade Off Between Time and Money

All points on the line provide the same accuracy and confidence as 16 quarterly monitoring events.
What is the trade-off between monitoring frequency and duration?

START

Is data "cleanup" required?  
Yes  Do you have historical well data for the site?  
No  
No  
Yes  
Go to a Data Management Tool to clean up your data (e.g., MAROS)

Monitoring Variability Tool

Question 1: When will this site meet the groundwater clean-up goal?
Question 2: Do any individual wells appear to be attenuating more slowly than the source as a whole?

Monitoring Optimization Tool

Question 1: How much monitoring data do I need to determine a site’s long-term source attenuation rate with a defined level of accuracy or confidence?
Question 2: What are the trade-offs between monitoring frequency and time required for trend identification?

Free Help in Answering Questions: Monitoring Optimization and Trend Analysis Toolkit
### Monitoring Optimization – Question #2:

*What are the trade-offs between monitoring frequency and time required for trend identification*

<table>
<thead>
<tr>
<th>Option</th>
<th>Sample Frequency</th>
<th>Total Sampling Events</th>
<th>Cost Per Well ($K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Option 1</td>
<td>Sample weekly for 1.6 years</td>
<td>82</td>
<td>123</td>
</tr>
<tr>
<td>Option 2</td>
<td>Sample monthly for 2.7 years</td>
<td>33</td>
<td>49</td>
</tr>
<tr>
<td>Option 3</td>
<td>Sample quarterly for 4.1 years</td>
<td>16</td>
<td>25</td>
</tr>
<tr>
<td>Option 4</td>
<td>Sample semiannually for 5.0 years</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Option 5</td>
<td>Sample annually for 6.5 years</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>Option 6</td>
<td>Sample every 2 years for 9.0 years</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>Option 7</td>
<td>Sample every 5 years for 18.4 years</td>
<td>4</td>
<td>6</td>
</tr>
</tbody>
</table>
MONITORING REQUIREMENTS: **KEY POINTS**

- Short-term variability makes it harder to determine trend and increases the amount of monitoring needed to evaluate progress in remediation.
- It commonly takes seven years or more of quarterly monitoring data to characterize the attenuation rate with even a medium level of accuracy.
- Less frequent monitoring over longer periods of time may be more cost appropriate for determining trends during MNA.
Define groundwater plume status as stable, shrinking, or expanding.

Evaluate historical concentration measurements in groundwater.

Always apply based on sufficient historical data.
Define groundwater plume status as **stable, shrinking, or expanding**.

**WHAT?**

Evaluate historical concentration measurements in groundwater.

**HOW?**

**WHEN?**
PRIMARY LINES OF EVIDENCE: *Mass Loss and Plume Stability*

**WHAT?**
Define groundwater plume status as *stable, shrinking, or expanding.*

**HOW?**
Evaluate historical concentration measurements in groundwater.

**WHEN?**
Always apply based on sufficient historical data.
LINE OF EVIDENCE 1: *Demonstrate Mass Loss, Plume Stability With Two Common Graphs*

**Plume Outer Contour vs. Time**

**Concentration vs. Distance at Different Times**

- **TCE Concentration (mg/L)**
- **Downgradient Distance from Source (ft)**
DEMONSTRATE MASS LOSS AND PLUME STABILITY: 2 Graphical Methods

METHOD 1

METHOD 2

Well Concentration vs. Distance

Well Concentration vs. Time
**Ground Water Issue**

Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies

Charles J. Newell\(^1\), Hanadi S. Rifai\(^2\), John T. Wilson\(^3\), John A. Connor\(^4\), Julia A. Aziz\(^5\), and Monica P. Suarez\(^6\)

---

### Rate Constant Table

<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Method of Analysis</th>
<th>Significance</th>
<th>Use of Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Point Attenuation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rate (Fig. 1)</td>
<td>C vs. T Plot</td>
<td>Reduction in contaminant concentration over time at a single point</td>
<td>Plume Attenuation: NO(^*)</td>
</tr>
<tr>
<td><strong>Bulk Attenuation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rate (Fig. 2)</td>
<td>C vs. D Plot</td>
<td>Reduction in dissolved contaminant concentration with distance from source</td>
<td>Plume Attenuation: YES</td>
</tr>
</tbody>
</table>

---

**Figure 1.** Determining concentration vs. time rate constant ($k_{\text{point}}$).

**Figure 2.** Determining concentration vs. distance rate constant ($k$).
CONTROL REMEDY: Deriving Attenuation Action Levels (AALs)

Option 1: Graphical Method

1. Plot C vs. D whisker plot showing range of historical COC concentrations.
2. Draw AAL line connecting max conc. at point near source to PCL conc. at POE.
3. Determine AAL for each AMP as the intersect of well distance with AAL line.

AAL = Attenuation Action Level
AMP = Attenuation Monitoring Point
POE = Point of Exposure
LINE OF EVIDENCE 2: **Appropriate Geochemical Conditions – Dissolved Oxygen Example**

**Supports Natural Attenuation:**
- ✔ Yes
- □ No
- □ Inconclusive

**Dissolved Oxygen (mg/L)**

- Benzene Plume
  - LOW
  - HIGH

**Example:**
- Dissolved Oxygen Example
LINE OF EVIDENCE 2: **Appropriate Geochemical Conditions – Dissolved Oxygen Example**

- **Key Patterns for MNA**
  - Dissolved oxygen “hole” in BTEX plume location.
  - Same for NO$_3$, SO$_4$.
  - “Mountain” of Fe(II) and methane
How Far Will Plume Migrate?

How Long Will Source Be There?
Adveective-dispersive-degradation equation:

\[
\text{rate of change in conc. at any point} = \text{net rate of advective transport to that point} + \text{net rate of dispersive transport to that point} - \text{net rate of degradation at that point}
\]
\textbf{1-DIMENSIONAL ADVECTION DISPERSION EQUATION}

Concentration at Downgradient Location \( X \)

\[
\text{Conc} (x) = \text{Co} \cdot \exp \left\{ \frac{x}{2 \alpha_x} \left[ 1 - \left( 1 + \frac{4 \lambda \alpha_x}{V_s/R} \right)^{1/2} \right] \right\} \text{erf} \left[ \frac{S_w}{4 \alpha_y x} \right] \text{erf} \left[ \frac{S_d}{4 \alpha_z x} \right]
\]

- Source Concentration
- Longitudinal Dispersivity
- Groundwater Seepage Velocity
- Hydraulic Conductivity
- Effective Soil Porosity
- Hydraulic Gradient
- First-Order Decay Constant
- Retardation Coefficient
- Error Function
- Transverse Dispersivity
- Vertical Dispersivity
- Groundwater Source Width and Depth
**HOW FAR? Using a Model to Evaluate if MNA Can/Will Stabilize a Plume**

**KEY POINT:**

*Calibrate, then Predict*

---

**Step 1**

Calibrate model to existing monitoring data.

**Step 2**

Increase time to some time in the future.

**Step 3**

See if plume gets larger or smaller or becomes stable.
HOW LONG? HOW LONG WILL SOURCE BE THERE?

Source Term Mass Balance

$C_0$ ?

$?\ ?$

$t$
APPROACH: **Assume Source Zone is a Box**

- $M_\text{o} = \text{Total Mass of BTEX in Source Zone}$
- $Q = \text{Flow Rate Through Source Zone}$
- $C_\text{o} = \text{Concentration in Source Zone at Time } t = 0$

**IF CONSTANT SOURCE CONCENTRATION:**

\[
t = \frac{M_\text{o}}{Q C_\text{o}}
\]
BETTER SOURCE DECAY MODEL:

Concentration Declines with Tailing Effect

\[ C_t = C_0 \times \exp(-k_s t) \]
HOW LONG? Example assuming first-order decay of source

\( Q = \) Flow Rate Through Source
(Assume 500 L/Day)

\( M_0 = \) Total Mass in Source
(Assume 10 kg)

\( C_0 = \) Concentration in Source Zone at Time = 0
(Assume 2 mg/L)
HOW LONG? Example assuming first-order decay of source

\( Q = \text{Flow Rate Through Source} \)

(Assume 500 L/Day)

\( M_0 = \text{Total Mass in Source} \)

(Assume 10 kg)

\( C_0 = \text{Concentration in Source Zone at Time} = 0 \)

(Assume 2 mg/L)

IF DECLINING SOURCE CONCENTRATION:

\( k_s = \)
**Example assuming first-order decay of source**

**Q** = Flow Rate Through Source  
(Imagine 500 L/Day)

**Mo** = Total Mass in Source  
(Assume 10 kg)

**Co** = Concentration in Source Zone at Time = 0  
(Assume 2 mg/L)

**IF DECLINING SOURCE CONCENTRATION:**

\[ k_s = \frac{Q \cdot C_o}{M_o} = \frac{(500) \cdot (2)}{10,000,000} = 0.0001 \text{ day}^{-1} \]

\[ C_t = C_o \times e^{-0.0001 \cdot t} \]
WHY USE MODELS?

- Method for Predicting Something Precisely?  
  - No

- System to Organize Site Data
  - Yes

- Tool to Help Understand Site Processes
  - Yes

- Additional Line of Evidence
  - Yes

- Screen for Applicability of MNA
  - Yes
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>BIOSCREEN</td>
<td>Hydrocarbons</td>
<td>No</td>
<td>No</td>
<td>Excel</td>
</tr>
<tr>
<td>BIOCHLOR</td>
<td>Chlorinateds</td>
<td>No</td>
<td>No</td>
<td>Excel</td>
</tr>
<tr>
<td>REMChlor</td>
<td>Chlorinateds</td>
<td>Source – yes</td>
<td>Yes</td>
<td>Stand alone</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Plume – no</td>
<td></td>
<td></td>
</tr>
<tr>
<td>REMFuel</td>
<td>Hydrocarbons, MTBE</td>
<td>Source – yes</td>
<td>Yes</td>
<td>Stand alone</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Plume – no</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Matrix Diffusion Toolkit</td>
<td>Any</td>
<td>Yes</td>
<td>Yes*</td>
<td>Excel</td>
</tr>
<tr>
<td>Model</td>
<td>Contaminant?</td>
<td>Contaminant Type</td>
<td>Matrix Diffusion?</td>
<td>Analyze Remediation?</td>
</tr>
<tr>
<td>-------------</td>
<td>--------------</td>
<td>------------------</td>
<td>-------------------</td>
<td>---------------------</td>
</tr>
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<td>No</td>
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</tr>
<tr>
<td>Matrix Diffusion Toolkit</td>
<td>Any</td>
<td>Yes</td>
<td>Yes*</td>
<td>Excel</td>
</tr>
</tbody>
</table>
REMChlor
Remediation Evaluation Model for Chlorinated Solvents
Beta Version 1.0

Developed by
Dr. Ron Falta,
Clemson University
Analytical model for source behavior

Mass balance model on source zone predicts discharge including effects of remediation

Couple Models At the Edge of the Source Zone to Provide Contaminant Discharge to Plume Model

Plume model simulates mass balance based on advection, dispersion, retardation, and degradation reactions + plume remediation (but all with simple flow field)
HOW GAMMA ($\Gamma$) MIGHT FIT THESE DATA

- $\Gamma < 1$
- $\Gamma = 1$
- $\Gamma > 1$

Normalized Concentration vs. Time Since Beginning of Temporal Record (years)
RESULTS OF SEQUENTIAL REACTIONS

Distance from Source

Concentration

Distance from Source

TCE

DCE

VC
Divide space and time into “reaction zones”, solve the coupled parent-daughter reactions for chlorinated solvent degradation in each zone.

Example:

Each of these space-time zones can have a different decay rate for each chemical species.
ROAD MAP

• **Intro: Changing Paradigms and MNA Principles**

• **Key Attenuation Processes**
  - Biodegradation
  - Abiotic Processes
  - LNAPL source zone degradation processes
  - Other processes (immobilization, storage, dilution)

• **Field Techniques and Technologies**
  - Groundwater sampling and analytical methods
  - Compound Specific Isotopes Analysis (CSIA)
  - Molecular Biological Tools (MBTs)
  - Natural Source Zone Depletion (NSZD)

• **Should MNA be Used? Data Analysis and Monitoring Tools**
  - Data requirements, LTM, and statistics to understand MNA rates
  - Common Graphics and Calculations
  - Remediation Timeframe Calculations
  - Computer Models

• **Implementation Topics**
MOTIVATION FOR BIOPIC: 
*Obtaining better rate data for MNA*

To select MNA, you need lines of evidence (often within several tiers) to demonstrate it will be effective.

1. Historical groundwater...data that demonstrate a clear and meaningful trend of decreasing contaminant...concentration over time at appropriate monitoring locations.

2. Hydrogeologic and geochemical data that can be used to demonstrate indirectly the types of natural attenuation processes and the rate at which such processes will reduce...to required levels.
QUANTITATIVE FRAMEWORK: “A systematic approach to evaluate whether MNA is an appropriate remedy based on site-specific conditions”

BioPIC: Pathway Identification Criteria
A Decision Guide to Achieve Efficient Remediation of Chlorinated Ethenes

Notes: Click the "Start" button above to begin the process. Answer the pop-out questions. If the "Yes" or "No" buttons are selected, the next question will appear on the screen. "Decision Criterion" and "Help" buttons provide explanations of the various Decision Criteria and guidance for answering a given question. An overview of the processes automated by BioPIC is displayed in the form of a flowchart under the tab "Overview." The Report SELECTION OF BIOREMEDIATION APPROACHES, Development and Validation of a Quantitative Framework and Management Expectation Tool for the Selection of Bioremediation Approaches (Monitored Natural Attenuation [MNA], Biostimulation and/or Bioaugmentation) at Chlorinated Ethene Sites provides further support and

Another way to think about it: basis for choosing between 3 options for chlorinated ethene sites

1. Biostimulation
2. Bioaugmentation
3. MNA

Search “ESTCP ER-201129” for tool download and guidance
HOW BIOPIC WORKS

Framework is designed to help answer question of: “Will a plume impact a receptor?”

**FIRST:** Use GW Fate and Transport model to extract rate constants from field data to determine the necessary rate of degradation to achieve goal.
Framework is designed to help answer question of: “Will a plume impact a receptor?”

**SECOND:** Use BioPIC to confirm if that rate is consistent with rates that have been observed in other studies for any potentially-applicable pathways (2nd Line of Evidence)
How Biopic Works

### Attenuation Pathways that are included

<table>
<thead>
<tr>
<th>Pathway</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete Anaerobic Reductive Dechlorination</td>
</tr>
<tr>
<td>Partial Anaerobic Reductive Dechlorination</td>
</tr>
<tr>
<td>Aerobic Biological Oxidation</td>
</tr>
<tr>
<td>Abiotic Degradation</td>
</tr>
</tbody>
</table>

### Parameters found to have direct correlation on attenuation rate

<table>
<thead>
<tr>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dehalococcoides density (for TCE, cDCE, and VC)</td>
</tr>
<tr>
<td>Magnetic susceptibility</td>
</tr>
<tr>
<td>Iron sulfide (FeS)</td>
</tr>
<tr>
<td>Methane (CH₄)</td>
</tr>
<tr>
<td>Ferrous iron (Fe(II))</td>
</tr>
</tbody>
</table>

*EPA Directive (1999) only included reductive dechlorination*

*Lots of other parameters were evaluated but no correlation could be established*
HOW BIOPIC WORKS: Example using abiotic degradation pathway

- Magnetic susceptibility = $2.6 \times 10^{-7} \text{ m}^3/\text{kg}$
- Rate coefficient estimated from field data = 0.25/yr

RESULT:
- Your data fall within blue shaded area of high confidence
- Abiotic degradation explains observed rate
- SERVES AS LINE OF EVIDENCE FOR MNA
Can I apply MNA to contaminants besides chlorinated solvents and BTEX?

**YES - CONSIDER MTBE AS AN EXAMPLE**

- Not promising in early protocols
  
  MTBE had been found to “…migrate large distances and threaten downgradient water supplies at the same sites where the BTEX component of a plume has either stabilized or diminished due to natural attenuation” and included MTBE among compounds “…that tend not to degrade readily in the subsurface”.

- Lots of research and field work in the following 5-10 years, and we ended up with a completely different story!
CAN I APPLY MNA TO METALS, INORGANICS, AND RADIONUCLIDES?

YES, says USEPA

Tiered Lines-of-Evidence Approach
(similar to protocols for organics)

1. Plume is not expanding and sorption is occurring
2. ID the attenuation mechanism and estimate rate
3. Determine capacity and sustainability
4. Develop monitoring and contingency measures
CAN I APPLY MNA TO METALS, INORGANICS, AND RADIONUCLIDES?

- Primary attenuation pathway for many inorganics is transformation to less mobile forms through coprecipitation or sorption
- Reactions are generally more complex and highly influenced by geochemical conditions

USEPA’s 2015 policy document
<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Biological Reaction</th>
<th>Abiotic Reaction</th>
<th>Sequestration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anaerobic</td>
<td>Aerobic</td>
<td></td>
</tr>
<tr>
<td>Nitrate</td>
<td>Yes, degradation</td>
<td>No</td>
<td>Yes (reactive iron)</td>
</tr>
<tr>
<td>Perchlorate</td>
<td>Yes, degradation</td>
<td>No</td>
<td>Conflicting Data</td>
</tr>
<tr>
<td>Chromium (Cr), Selenium (Se), Copper (Cu), Cadmium (Ca), Lead (Pb), Nickel (Ni), Zinc (Zn), Beryllium (Be), Arsenic (As) (metalloid)</td>
<td>Valence change, generally favorable</td>
<td>Valence change, generally unfavorable</td>
<td>Valence change, generally favorable</td>
</tr>
<tr>
<td>Uranium, Technetium, Strontium, Cesium, Radium, Iodine</td>
<td>Valence change, generally favorable</td>
<td>Valence change, generally unfavorable</td>
<td>Valence change, generally favorable</td>
</tr>
</tbody>
</table>
CAN I APPLY MNA TO METALS, INORGANICS, AND RADIONUCLIDES?

ADDITIONAL GUIDANCE: “SCENARIOS FOR METALS, RADS” (Truex et al., 2011)
WHICH EMERGING CONTAMINANTS ARE CANDIDATES FOR MNA?

1,4-Dioxane, 1,2,3-TCP, NDMA, Phthalates, and Maybe Others?

- DoD general goal for emerging contaminants:
  “Identify chemicals or materials that either lack human health standards or have an evolving science and regulatory status.”

- Other problems
  - Prevalence at individual sites is largely unknown
  - Absence of well-established treatment technologies
  - Absence of tools for establishing MNA (e.g., CSIA, MBTs)
<table>
<thead>
<tr>
<th>Emerging Contaminant</th>
<th>Biological Degradation</th>
<th>Abiotic Degradation</th>
<th>Sequestration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anaerobic</td>
<td>Aerobic</td>
<td></td>
</tr>
<tr>
<td><strong>1,4-Dioxane</strong></td>
<td>Limited</td>
<td><strong>YES</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(mostly lab studies; can be cometabolic or used as a carbon source)</td>
<td>Not documented</td>
<td><strong>No</strong> (poor sorption)</td>
</tr>
<tr>
<td><strong>Per- and polyfluoroalkyl substances (PFAS)</strong></td>
<td>Very limited (incomplete pathway)</td>
<td>Very limited (incomplete pathway)</td>
<td>Limited (a reliable light+Fe(III) reaction has been established)</td>
</tr>
<tr>
<td><strong>N-Nitrosodimethylamine (NDMA)</strong></td>
<td><strong>YES</strong></td>
<td><strong>YES</strong></td>
<td><strong>No</strong> (several ex situ methods, including UV photolysis)</td>
</tr>
<tr>
<td></td>
<td>(cometabolic)</td>
<td>(reactive iron, base hydrolysis)</td>
<td></td>
</tr>
<tr>
<td><strong>1,2,3-Trichloropropane</strong></td>
<td><strong>YES</strong></td>
<td><strong>YES</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(slow, often incomplete pathyway)</td>
<td>(slow, incomplete pathway)</td>
<td>Very limited (reactive iron, base hydrolysis)</td>
</tr>
</tbody>
</table>
MNA FOR OTHER CONTAMINANTS: **KEY POINTS**

- USEPA has detailed guidance for MNA of inorganics “metals and rads”
- Example of how scientific knowledge advances: MNA of MTBE and other oxygenates
- Lots of research on MNA for emerging contaminants: some contaminants look promising, others not so much
MNA AT DRY CLEANER SITES: **Regulatory Perspective**

- Most states have guidance on MNA, but don’t differentiate between dry cleaners and other sites in their guidance
- Many states have dry cleaner cleanup programs, and some specifically discuss MNA
- State Coalition for Remediation of Drycleaners has case studies for 36 sites where MNA has been implemented
MNA AT DRY CLEANER SITES:

**Performance**

- Published study of 137 dry cleaner sites in Texas (Suarez et al., 2004)
  - Average half lives for PCE = 1 to 3 yr
  - Dry cleaner plumes (median = 100 m) were shorter than plumes from industrial sites (median = 300 to 500 m)
  - Industrial sites ~ 300 to 500 m
  - Dry cleaning sites ~ 100 m
MNA AT DRY CLEANER SITES: 

**Performance**

- Remediation performance survey for ESTCP ER-1120 (2016):
  - Similar performance for sites with PCE compared to sites with TCE or other chlorinated solvents
  - MNA performance for PCE was slightly lower than other technologies
USING MATRIX DIFFUSION TO EVALUATE SOURCE HISTORY: *Comparing a PCE Site vs. a TCE Site*

**Process:**

- Soil profile reflects style of source loading over time

---

**Transmissive Zone**

GW flow

**Diffusion into/out of low k zone based on concentration gradient**

**Low k Zone**

**Mass transport dominated by diffusion**

---

**CONSTANT SOURCE**

**SOURCE REMOVAL**

- Concentration History at Low K Zone Interface
- Profiles in Low K Zone

- $t = 20 \text{ yr}$
- $t = 25 \text{ yr}$
**Possible Solution?**

- At sites with low-k intervals, high-resolution data from soil cores provides a way to do this.
FIELD DEMONSTRATION:  
2 Different Source Areas at NAS Jacksonville

Source Area #1: OU3 Building 106

- Former dry cleaner (1962 – 1990): PCE and TCE released to shallow aquifer

Source Area #2: OU3 Building 780

- Former paint stripping/solvent recycling facility (1970s – 1980s): PCE, TCE, and 1,1,1-TCA released to shallow aquifer
EXAMPLE: Soil core VOC profile from OU3-9 shows reasonable match with declining source

OTHER MODEL RUNS COMPLETED (not shown): 1,1,1-TCA, 1,2-DCA
EXAMPLE: Soil core VOC profile from OU3-3 shows good match with constant source

NOTE: GW conc. used to calibrate transmissive zone due to loss of soil mass in sands

MODEL TESTING: Source Area #1 – Building 106

Median RPD = 12%
RMS Error = 2.9 mg/L
<table>
<thead>
<tr>
<th>SITES THAT ARE WELL-SUITED FOR MNA</th>
</tr>
</thead>
<tbody>
<tr>
<td>No receptors impacted</td>
</tr>
<tr>
<td>Decreasing concentration trends w/ reasonable remediation timeframe</td>
</tr>
<tr>
<td>Shrinking or stable plume</td>
</tr>
<tr>
<td>Slow groundwater velocity (or long travel time)</td>
</tr>
<tr>
<td>Attenuation mechanisms have been established</td>
</tr>
<tr>
<td>Geochemical conditions favor continued attenuation</td>
</tr>
<tr>
<td>Weak source</td>
</tr>
</tbody>
</table>
**SITES THAT ARE **NOT** WELL-SUITED FOR MNA**

<table>
<thead>
<tr>
<th>Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Receptors impacted</td>
</tr>
<tr>
<td>Increasing concentration trends w/ long timeframe</td>
</tr>
<tr>
<td>Expanding plume (or imminent threat)</td>
</tr>
<tr>
<td>Attenuation mechanisms poorly understood</td>
</tr>
<tr>
<td>Geochemical conditions won’t sustain attenuation</td>
</tr>
<tr>
<td>Strong or uncontrolled source (some states won’t allow free or residual product to remain)</td>
</tr>
<tr>
<td>Monitoring limitations (can’t ensure it’s protective)</td>
</tr>
</tbody>
</table>
“We are all Keynesians now”

“We are all MNA implementers now”
SCHEMATIC OF PLUME LIFECYCLE

I. EXPANDING
II. STABLE
III. SHRINKING
IV. EXHAUSTED

TIME
LOW RISK SITES AND MATRIX DIFFUSION

• If site is “Late Stage”
  – Different source process
  – Mass discharge % from NAPL is low
  – Matrix Diffusion % is high
  – Not “Principal Threat Waste”

• Conceptual Model
  – No potential source migration
  – Further source remediation difficult
  – Not practicable to remove mass in low-permeability zones

Late Stage Site (Sale, 2008)
WHAT IS A LOW RISK SITE?

• Low-Risk means MNA the rest of the way
• Recognition that complete closure is difficult/unattainable
• Concentrations low
• Example NOT low risk: mobile NAPL
• Example YES low risk: matrix diffusion

Air Force “LoRSC” Guidance
I. Do You Have a Complete CSM that Reflects Key Low-Risk Closure Concepts?

1. Have all of the components of the Conceptual Site Model (CSM) been evaluated?  
   (Section 3.1.1)

   - Answer: YES

2. Are there no significantly mobile source materials?  
   (Section 3.2.1)

   - Answer: NO

3. Is the source zone free of any environmentally significant quantity of NAPL?  
   (Section 3.2.2)

   - Answer: YES

4. Is it possible that any further source zone cleanup will be constrained by matrix diffusion processes?  
   (Section 3.2.3)

   - Answer: NO

5. Are sources relatively small?  
   (Section 3.2.4)

   - Answer: YES

6. Are source zone concentrations stable or decreasing?  
   (Section 3.2.5)

   - Answer: NO

7. Is there evidence of on-going natural attenuation processes in the source zone?  
   (Section 3.2.6)

   - Answer: NO

II. Are Sources Controlled?

8. Will future source remediation only marginally improve site conditions?  
   (Section 3.2.7)

   - Answer: NO
III. Will Residual Contamination Have No Adverse Effect on Present and Future Land and Water Uses?

1. Is the groundwater plume stable or shrinking? (Section 3.3.1)  
   - YES  
   - NO

2. Is there evidence of on-going natural attenuation processes in the plume? (Section 3.3.2)  
   - YES  
   - NO

3. Are conditions protective of potential and future receptors? (Section 3.3.3)  
   - YES  
   - NO

4. Is there no near-term need for the impacted groundwater resource or any impacted land uses? (Section 3.3.4)  
   - YES  
   - NO

**KEY:**

**MUST HAVE DATA:** Critical Line of evidence for low-risk site closure - necessary to demonstrate these criteria at almost all sites if applicable.

**SUPPORTING DATA:** Supporting line of evidence, with 0-4 of the supporting lines recommended for low-risk site closure.

**WHAT IT MEANS**

LoRSC Site Type A (strongest case for low-risk closure or reduced monitoring)
- All “Must Have” Questions = Yes
- AND 3 or 4 of the “Supporting” Questions = Yes

LoRSC Site Type B (Moderately good case for low-risk closure or reduced monitoring)
- All “Must Have” Questions = Yes
- AND 0 to 2 of the “Supporting” Questions = Yes

LoRSC Site Type C (More difficult for low-risk closure or reduced monitoring)
- Any “Must Have” Question = No

**“Must Have” Questions**  
- All “YES”?  
  - YES  
  - NO

**“Supporting” Questions**  
- Number of “YES”  
  - 4
LOW THREAT SITES

CALIFORNIA’S CRITERIA FOR UNDERGROUND STORAGE TANK
LOW-THREAT CLOSURE

1. Site must be in service area of public water system
2. Release must consist of “petroleum”
3. Release has been stopped
4. Free product removed to the extent practicable
5. Conceptual Site Model prepared and validated
6. “Secondary Source” removal has been addressed
7. MTBE testing requirement
California Low-Threat Petroleum UST Closure Policy – Scenario 1

Scenario Characteristics:
1. Contaminated Groundwater Plume is <100' in Length.
2. There is no free-product.
3. The nearest existing water supply well and/or surface water body is >250' from defined plume boundary.
California Low-Threat Petroleum UST Closure Policy – Scenario 3

Scenario Characteristics:
1. Contaminated Groundwater Plume is <250’ in Length.
2. Free-product may be present below the site and not extend off-site.
3. The Plume has been stable or decreasing for a minimum of five years.
4. The nearest existing water supply well and/or surface water body is >1000’ from the defined plume boundary.
5. The property owner is willing to accept a deed restriction if the regulatory agency requires a deed restriction as a condition of closure.

Groundwater Pathway Scenario 3:
- Groundwater Elevation
- Groundwater
- Contaminated Groundwater Plume
- Soil
- Water Supply Well
- Defined Plume Boundary
- Confining Layer
- >1000’
California Low-Threat Petroleum UST Closure Policy – Scenario 4

Scenario Characteristics:
1. Contaminated Groundwater Plume is <1000' in Length.
2. The nearest existing water supply well and/or surface water body is >1000' from the defined plume boundary.
3. Dissolved concentration of benzene and MTBE are <1 ppm and <1 ppm, respectively.

Groundwater Pathway Scenario 4:
- Groundwater Level
- Groundwater
- Contaminated Groundwater Plume
- Soil
- Water Supply Well
- Water supply well screened in deeper aquifer
- Defined Plume Boundary
- Confining Layer
- >1000'
- <1000'
CLOSURE FOR “LOW RISK” SITES: Key Points

• MNA is likely to be a component of almost all remedies at some time during the site life cycle

• Examples: California Chlorinated Low Threat Closure, Air Force Low Risk Guidance, National Research Council Transition Assessment

• Not a matter of if, but when MNA is applied
LOW THREAT SITES

SAN FRANCISCO RWQCB’S LOW-THREAT SITE CLOSURE PROGRAM

- Regional Water Quality Control Board
- 9-Point Process
- Must demonstrate residual pollution will not adversely affect:
  - Groundwater plumes
  - Cleanup Standards
  - Risk Management Measures

[Graph showing Maximum PCE Concentration in Groundwater at Case Closure (46 Cases Surveyed)]
MNA TRANSITION

- 1999 EPA Directive:
  - MNA should not be considered a default or presumptive remedy, and that it should be applied “very cautiously as the sole remedy” and that “source control will be fundamental components of any MNA remedy.”

- MNA being used extensively
  - Sole remedy
  - Sole groundwater remedy

- States have specific criteria
Are the risks acceptable? 
Is the plume stable or shrinking? 
Are conditions sustainable? 
Is the remediation timeframe acceptable? 
Are the cost-benefits acceptable?

NO?

Enhanced Attenuation (instead of MNA)
“If the effectiveness of site remediation reaches a point of diminishing returns prior to reaching cleanup goals and optimization has been exhausted, the transition to monitored natural attenuation or some other active or passive management should be considered”

NATIONAL RESEARCH COUNCIL, 2012
ROAD MAP

• Intro: Changing Paradigms and MNA Principles

• Key Attenuation Processes
  ▪ Biodegradation
  ▪ Abiotic Processes
  ▪ LNAPL source zone degradation processes
  ▪ Other processes (immobilization, storage, dilution)

• Field Techniques and Technologies
  ▪ Groundwater sampling and analytical methods
  ▪ Compound Specific Isotopes Analysis (CSIA)
  ▪ Molecular Biological Tools (MBTs)
  ▪ Natural Source Zone Depletion (NSZD)

• Should MNA be Used? Data Analysis and Monitoring Tools
  ▪ Data requirements, LTM, and statistics to understand MNA rates
  ▪ Common Graphics and Calculations
  ▪ Remediation Timeframe Calculations
  ▪ Computer Models

• Implementation Topics