Transport and Fate of Contaminants in the Subsurface

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Mike Wireman
National Ground-Water Expert
US Environmental Protection Agency
Natural Ground-Water Quality

- Nearly all GW originates as rain or snow that infiltrates to the saturated zone.
- Infiltration through soil zone / vadose zone & flow in saturated zone influences chemistry of water.
- Soil generates carbonic acid ($H_2CO_3$) and consumes dissolved oxygen.
Natural Ground-Water Quality

- Chemistry of GW is controlled by rock-water interaction that occur as gw flows from areas of recharge to areas of discharge
  - Increases in total dissolved solids and major ions
  - Changes in dominant anions - $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$
  - Cation concentrations vary due to reactions
Dissolved Constituents in GW

- **Major constituents**
  - (> 5mg/l)
    - Bicarbonate (HCO₃⁻)
    - Calcium (Ca)
    - Chloride (Cl)
    - Magnesium (Mg)
    - Silicon (Si)
    - Sodium (Na)
    - Sulfate (SO₄²⁻)
    - Carbonic Acid (H₂CO₃)

- **Minor constituents**
  - (> 0.01 -10mg/l)
    - Boron (B)
    - Carbonate (CO₃²⁻)
    - Fluoride (F⁻)
    - Iron (Fe)
    - Nitrate (NO₃⁻)
    - Potassium (K)
    - Strontium (Sr)
Dissolved Constituents in GW

Trace constituents (< 0.1 mg/l)

- Aluminum
- Antimony
- Arsenic
- Barium
- Cadmium
- Chromium
- Copper
- Lead
- Manganese
- Lithium
- Phosphate
- Radium
- Selenium
- Silver
- Uranium
- Zinc
Dissolved Constituents in GW Organics and gases

- Organic constituents
  - Important species
    - $\text{H}_2\text{CO}_3$, $\text{CO}_2$, $\text{HCO}_3^-$, $\text{CO}_3^-$
  - Ubiquitous
  - Mostly fulvic & humic acid

- Atmospheric gases
  - $\text{N}_2$, $\text{O}_2$, $\text{CO}_2$

- Gases produced by anaerobic biochemical processes
  - $\text{CH}_4$, $\text{H}_2\text{S}$, $\text{N}_2\text{O}$
Contaminant transport & fate refers to the physical, chemical, and biological processes that impact the movement of the contaminants from point A to point B and how these contaminants may be altered while they are transported.
Contaminant Transport & Fate

- Physical processes move mass from point to point

- Chemical and biological processes redistribute mass among different phases and chemical forms
  - This controls concentration at a given location
Transport & Fate

- Simple View: Contaminants move with the ground water (and are not altered)
- In fact: Contaminants rarely move at the rate of ground water due to a variety of processes and they generally are altered when moving through aquifer materials due to various processes
Controls on Contaminant Transport & Fate

- Physical & chemical characteristics of earth materials
- Hydraulics of the flow system
- Nature of the contaminant
- Natural processes that tend to remove or degrade
Controls on Contaminant Distribution

Physical & chemical characteristics of earth materials
- Porosity
- Permeability
- Organic carbon content
- Cation exchange capacity
Controls on Contaminant Distribution

Hydraulics of the flow system

- Groundwater velocity (Advection)
  - Hydraulic conductivity
    - Permeability (property of the aquifer)
    - Fluid density, specific gravity, dynamic viscosity
  - Hydraulic gradient
HYDRAULIC PROPERTIES

- $Q = K_i A$
- $K =$ hydraulic conductivity (fluid dependent)
  - $K = \frac{k p g}{u}$
  - $k =$ intrinsic permeability
  - $p =$ fluid density
  - $g =$ gravity constant
  - $u =$ fluid viscosity
- $T$ (transmissivity) = $K_b$
  - $b =$ aquifer /saturated thickness)
Controls on Contaminant Distribution

Nature of the contaminant
- Water solubility
- Vapor pressure
- Henry’s Law Constant
- Valence (inorganics)
- Organic partition coefficient (organics)
- Viscosity, interfacial tension, wettability (NAPLs)
Controls on Contaminant Distribution

Natural processes that tend to remove or degrade

- Advection
- Dispersion
- Partitioning
  - Sorption
  - Dissolution/Precipitation
  - Volatilization

- Biological transformation

- Abiotic transformation
  - Complexation
  - Acid-base reactions
  - Redox reactions
Basic Fate and Transport Processes in the Unsaturated Zone

- Infiltration
- Atmospheric Losses
- Volatilization
- Dissolution into Soil Water
- Degradation
- Sorption with Soil
- Diffusion
- Dense Vapor Flow
- Residual Product

Water table
Basic Fate and Transport Processes in the Saturated Zone

- Dissolution
- Volatilization
- Leachate
- Mixing
- LNAPL
- DNAPL
- Advection
- Dispersion
- Sorption
- Degradation
- Aquifer
- Confining Unit
Contaminant Transport Processes

Mass Transport

– Advection: Displacement by ground water flow ("go with the flow")
– Dispersion: Spreading of contaminant mass in three dimensions during flow
– Retardation: Reduction of the average velocity of the contaminant mass relative to the ground water velocity due to sorption of the contaminant by the geologic materials
Advection

- Solutes (e.g. dissolved contaminants) are transported by bulk portion of the flowing ground water.

- Non-reactive (i.e. conservative) solutes are carried at an rate equal to the average linear velocity of the water.

- Function of groundwater velocity
Advection

Distance from **Slug-Release** Contaminant Source

Relative Concentration

Advection
Advection II

Distance from Continuous Contaminant Source

Relative Concentration

Advection
Molecular Diffusion

Process by which molecules move under the influence of their kinetic activity in the direction of their (decreasing) concentration gradient.

- Occurs whether or not there is bulk flow of groundwater
- Ceases only when concentration gradients become nonexistent
- Main process for contaminant exchange between fractures and rock matrix, or between fine-grained and coarse-grained sediment.
Mechanical Dispersion

- Mixing that occurs as a consequence of pore-scale variations in groundwater velocity

- Results in spreading of the solute

- Function of groundwater velocity and a measure of the “dispersivity” of the aquifer medium
What causes Dispersion?

**Mechanical Dispersion** due to water moving results when:
- Flow lines have different lengths, diverging and mixing with each other
- Velocity varies across individual pores due to friction in the pore
- Pore sizes vary

Mechanical dispersion usually greater than diffusion
Dispersion is an **attenuating** process.
Advection & Dispersion II

Distance from Continuous Contaminant Source

Relative Concentration

$A$ Advection

$D$ Dispersion

$A + D$
Transport in Fractured Porous Rock

Diffusion Into Rock Matrix

Fracture Flow
Partitioning

Changes in phase without a change in composition, usually reversible.

- Sorption: Transfer between contaminant and solids. Leads to “Retardation”
- Dissolution/precipitation: Transfer between liquid (e.g. water) and contaminant
- Volatilization: Transfer from liquid phase (or solid) of contaminant to gas phase
Sorption & Retardation

- Mass adsorbed is a function of the dissolved concentration
- Relationship between adsorbed and dissolved mass may be linear or non-linear
- Process may be reversible or non-reversible
- Commonly expressed in terms of a partition coefficient (Kd)
  - Assumes a linear reversible relationship
  - Not always adequate
Determining Partition Coefficients

- Laboratory experiments

- Comparing distribution of non-sorbing (e.g., tracer) contaminants relative to sorbing contaminants

- Modeling
Sorption of Organic Chemicals

- Dominant mechanism of sorption for hydrophobic organic chemicals is the bond between contaminant and natural organic matter associated with the aquifer.

- Kd for organic chemicals can be estimated:
  - \( Kd = Koc \times foc \)

  - \( Koc = \) organic carbon partition coefficient (related to \( Kow = \) octanol water partition coefficient)

  - \( foc = \) fraction organic carbon content of sediment (if \( foc > 0.001 \))
Retardation Factor

- Measure of the amount of the contaminant is slowed by sorption.
  - Function of Kd, bulk density, and porosity

- Ratio of average groundwater velocity to average contaminant velocity
Dispersion and sorption are **attenuating** processes.

**Retardation I**

- **A** Advection
- **D** Dispersion
- **S** Sorption

**Distance from Slug-Release Contaminant Source**

**Relative Concentration**

- **A + D + S**
- **A + D**
Retardation II

- A Advection
- D Dispersion
- S Sorption

Distance from Continuous Contaminant Source vs. Relative Concentration

- $A + D + S$
- $A + D$

Retardation processes remove contaminants from the groundwater during transport. Thus the contaminant concentration arriving at a certain point at a certain time is less than it would have been for a conservative (non-retarded) contaminant.
Biodegradation

- Reactions involving the degradation of organic compounds --- rate is controlled by the abundance of microorganisms as well as the ground-water geochemistry.
- Important mechanism for contaminant reduction, but can lead to undesirable daughter products.
- Geochemical changes may result in mobilization of certain inorganics such as As, Mn and Fe.
- More successful for gasoline products (BTEX) than chlorinated solvents.
Dispersion, Sorption and degradation are attenuating processes.
Degradation II

Distance from Continuous Contaminant Source

Relative Concentration

A Advection
D Dispersion
S Sorption
B Biodegradation

A + D + S
A + D + S + B
A + D
Rates of contaminant movement are determined by ground-water flow rates, chemical/physical interactions with aquifer materials and changes in water chemistr.

Shape and size of a contaminant plume depends on geologic framework, ground-water flow system, type and concentration of contaminants and variations in their release.

Contaminants in ground water tend to be removed or reduced in concentration with time and distance due to various attenuation mechanism.
Contaminant Transformation
Chemical and Biological Processes

- Acid-base reactions
- Phase change reactions (Solution, Volatilization, & Precipitation)
- Complexation reactions
- Reactions on surfaces
- Radioactive Decay
- Oxidations-reduction reactions
- Groundwater Microbiology
Equilibrium vs Kinetic Reactions

Equilibrium reactions

- Fast relative to groundwater transport rates
- \( cC + dD = yY + zZ; \quad K = \frac{[Y]^y [Z]^z}{[C]^c [D]^d} \)

Kinetic reactions

- Slow relative to groundwater transport rates
- \( cC + dD = yY_{\frac{k_1}{k_2}} zZ; \quad r_C = -k_1(C)^{n_1}(D)^{n_2} \)
Acid-Base Reactions

Consume or produce hydrogen ions $H^+$

$\text{Fe}_2\text{S} + \text{O} + \text{H}_2\text{O} > \text{Fe(OH)}^+ + \text{SO}_4^{2-} + \text{H}^+$
Phase Change

Gas solution and exsolution (e.g., CO$_2$):

- Henry’s Law (equilibrium):
  \[ K_H = \frac{P_{gas}}{C_{water}} \]

May be mass transfer rate limited
Phase Change

Volatilization (e.g., VOCs):

- Henry’s Law (equilibrium):

\[ K_H = \frac{P_{air}}{C_{water}} \]

\[ K_{H'} = \frac{C_{air}}{C_{water}} \]

May be mass transfer rate limited
Phase Change, Cont’d

Dissolution and precipitation of solids

- Carbonates: \( \text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-} \)

- Sulfates: \( \text{CaSO}_4 = \text{Ca}^{2+} + \text{SO}_4^{2-} \)
Phase Change’ Cont’d

Solution of organic solutes in water (i.e., NAPL dissolution)

– $K_{ow} = \frac{C_{octanol}}{C_{water}}$

– May be mass transfer rate limited
Complexation

Metal + Ligand = Metal-Ligand Complex

Metals: Ca^{2+}, Cu^{2+}, Zn^{2+}, Cr^{3+}, etc.

Ligands: Cl^-, SO_4^{2-}, CO_3^{2-}
Surface Reactions

Hydrophobic sorption of organic compounds:

\( K_d = K_{oc} \times f_{oc} \)
Surface Reactions

- Cation-Exchange
  - Clay minerals
  - Hydroxides
    (charge and capacity vary with pH)

Midvale Slag
Radioactive Decay

- Irreversible decline in the activity of a radionuclide through a nuclear reaction.
- Partial or complete transmutation of the radionuclide.
- Daughter nuclides may be more toxic than parent.
- Important mechanism for contaminant attenuation if half-life for decay is short.
- Timeframes required for complete decay may be large.
Oxidation/Reduction

- Involve electron transfer from one atom to another
- Usually mediated by microorganisms
- Important for pollution problems
  - Acid mine drainage (Fe II, Fe III)
  - Chromium & arsenic fate
  - Biodegradation of organic compounds
Eh

- Oxidation potential expressed in terms of Eh (volts)
- Measure of the electrical potential for reaction relative to standard state hydrogen oxidation
- Poor correlation between field data and calculated Eh values
Redox reactions typically are a function of Eh and pH.
Acid Mine Drainage

**Sulfide Oxidation**

\[ 2O_2 + HS^- = SO_4^{2-} + H^+ \]

**Iron Oxidation**

\[ O_2 + 4Fe^{+2} + 4H^+ = 4Fe^{3+} + 2H_2O \]
Groundwater Microbiology

- Microbial presence in aquifers
- Biodegradation mechanisms
Microbial Presence in Aquifers

- Total microbial counts in shallow aquifers range 100,000 to 10,000,000 per gram dry weight

- Types vary with depth

- Diverse communities
Biodegradation Mechanisms

- Indigenous microorganisms use organic matter (including contaminants) as electron donors to support respiration.

- Aerobic bacteria use $O_2$ as electron acceptor.

- Anaerobic bacteria use $NO_3$, Mn, Fe, $SO_4$, and $CO_2$ as electron acceptors.
## Biodegradation Mechanisms

<table>
<thead>
<tr>
<th>Microbial Process</th>
<th>Electron Acceptor</th>
<th>Products</th>
<th>Eh (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic respiration</td>
<td>O₂</td>
<td>H₂O</td>
<td>+810</td>
</tr>
<tr>
<td>Denitrification</td>
<td>NO₃, etc</td>
<td>N₂</td>
<td>+750</td>
</tr>
<tr>
<td>Manganese reduction</td>
<td>Mn⁴⁺</td>
<td>Mn²⁺</td>
<td>+396</td>
</tr>
<tr>
<td>Iron reduction</td>
<td>Fe³⁺</td>
<td>Fe²⁺</td>
<td>-182</td>
</tr>
<tr>
<td>Sulfate reduction</td>
<td>SO₄²⁻</td>
<td>H₂S</td>
<td>-220</td>
</tr>
<tr>
<td>Methanogenesis</td>
<td>CO₂</td>
<td>CH₄</td>
<td>-240</td>
</tr>
</tbody>
</table>
Biodegradation Mechanisms

Increasingly reducing conditions

Inhibition by Substrates

Anaerobic Heterotrophs
- Tolerate low oxygen

Sulfate Reducing Bacteria
- Inhibited by high nitrate levels
- Inhibited by oxygen

Methanogens
- Inhibited by high levels of sulfate and nitrate
- Totally inhibited and killed by low oxygen

Facultative Heterotrophic Anaerobes

Aerobic

Landfill Site
Relative Importance of Biodegradation Mechanisms

- Sulfate Reduction: 29%
- Methanogenesis: 39%
- Iron (III) Reduction: 8%
- Denitrification: 14%
- Aerobic Respiration: 10%
Biodegradation of Chlorinated Hydrocarbons

[Diagram showing the biodegradation pathway of chlorinated hydrocarbons, including PCE, TCE, 1,1,1-TCA, 1,1-DCA, Chloroethane, Ethane CH₃CH₃, Cis-1,2-DCE, Trans-1,2-DCE, 1,1-DCE, Vinyl Chloride, Ethene CH₂CH₂.]

PCE = Perchloroethene, TCE = Trichloroethene, TCA = Trichloroethane, DCA = Dichlorethane, DCE = Dichloroethene.

BIOCHLOR: http://www.epa.gov/ada/csmos/models/biochlor.html
Biodegradation of Chlorinated Hydrocarbons

Reductive transformation of chlorinated ethenes.

BIOCHLOR: http://www.epa.gov/ada/csmos/models/biochlor.html
### Natural Attenuation Screening Protocol

The following is taken from the USEPA protocol (USEPA, 1998). The results of this scoring process have no regulatory significance.

**Natural Attenuation Interpretation Score**

<table>
<thead>
<tr>
<th>Interpretation</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inadequate evidence for anaerobic biodegradation* of chlorinated organics</td>
<td>0 to 5</td>
</tr>
<tr>
<td>Limited evidence for anaerobic biodegradation* of chlorinated organics</td>
<td>6 to 14</td>
</tr>
<tr>
<td>Adequate evidence for anaerobic biodegradation* of chlorinated organics</td>
<td>15 to 20</td>
</tr>
<tr>
<td>Strong evidence for anaerobic biodegradation* of chlorinated organics</td>
<td>&gt; 20</td>
</tr>
</tbody>
</table>

### Concentration in Points

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Concentration in Most Contam. Zone</th>
<th>Interpretation</th>
<th>Yes</th>
<th>No</th>
<th>Points Awarded</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen*</td>
<td>&lt;0.5 mg/L</td>
<td>Tolerated, suppresses the reductive pathway at higher concentrations</td>
<td>●</td>
<td>●</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>&gt; 5 mg/L</td>
<td>Not tolerated; however, VC may be oxidized aerobically</td>
<td>●</td>
<td>●</td>
<td></td>
</tr>
<tr>
<td>Nitrate*</td>
<td>&lt;1 mg/L</td>
<td>At higher concentrations may compete with reductive pathway</td>
<td>●</td>
<td>●</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>&gt;1 mg/L</td>
<td>Reductive pathway possible; VC may be oxidized under Fe(III)-reducing conditions</td>
<td>●</td>
<td>●</td>
<td>3</td>
</tr>
<tr>
<td>Sulfate*</td>
<td>&lt;20 mg/L</td>
<td>At higher concentrations may compete with reductive pathway</td>
<td>●</td>
<td>●</td>
<td>2</td>
</tr>
<tr>
<td>Sulfide*</td>
<td>&gt;1 mg/L</td>
<td>Reductive pathway possible</td>
<td>●</td>
<td>●</td>
<td>0</td>
</tr>
<tr>
<td>Methane*</td>
<td>&gt;0.5 mg/L</td>
<td>Ultimate reductive daughter product, VC Accumulates</td>
<td>●</td>
<td>●</td>
<td>0</td>
</tr>
<tr>
<td>Oxidation Reduction Potential* (ORP)</td>
<td>&lt;50 millivolts (mV)</td>
<td>Reductive pathway possible</td>
<td>●</td>
<td>●</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>&lt;-100 mV</td>
<td>Reductive pathway likely</td>
<td>●</td>
<td>●</td>
<td></td>
</tr>
<tr>
<td>pH*</td>
<td>5 &lt; pH &lt; 9</td>
<td>Optimal range for reductive pathway</td>
<td>●</td>
<td>●</td>
<td>0</td>
</tr>
<tr>
<td>TOC</td>
<td>&gt;20 mg/L</td>
<td>Carbon and energy source; drives dechlorination; can be natural or anthropogenic</td>
<td>●</td>
<td>●</td>
<td>0</td>
</tr>
</tbody>
</table>

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BIOCHLOR: [http://www.epa.gov/ada/csmos/models/biochlor.html](http://www.epa.gov/ada/csmos/models/biochlor.html)