Biogeochemistry of Wetlands
Science and Applications
June 23-26, 2008

Topic: Toxic Organic Compounds (Xenobiotics)

Learning Objectives

- Define xenobiotics
- Ecological significance of xenobiotics
- Sources and common classifications
- Environmental fate of xenobiotics
  - Abiotic pathways
  - Biotic pathways
What is a Xenobiotic?

- Xeno means foreign, Bios means life:
  - Xenobiotic is in essence a compound that is foreign to life
- Synonyms
  - Toxics, toxic [organic] substances, priority organic pollutants [POPs], endocrine disruptors
- Examples:
  - Pesticides, fungicides, herbicides, industrial toxins, petroleum products, landfill leachate

Are Xenobiotics an issue in Wetlands?

- Wetlands are often the receiving bodies of Agricultural and urban drainage
- Extent of xenobiotic contamination in wetlands
  - Approximately 5000 wetlands and aquatic systems impacted by pesticides
Are Xenobiotics an issue in Wetlands?

- Wetlands may be excellent pollutant removers (aerobic - anaerobic interfaces)
- Wetlands are not in the spotlight!
  - No wetland superfund site, etc.
  - Upland (aerobic) and aquifier (anaerobic) soil contamination and remediation is the driving force in our current know-how

Ecological Significance

- Lethal toxicity to biota
- Non-lethal toxicity to biota
  - Endocrine disruptors
  - Hormone mimicry
  - Reproductive disorders
  - Harmful mutation - DNA damage
Types of Xenobiotics

- Petroleum products (BTEX, MTBE)
- Pesticides (DDT, DDE.....)
- Herbicides (2,4D, Atrazine)
- Industrial wastes (PCB’s, aromatics)

Aromatic Compounds

- Benzene
- Toluene
- Napthalene
- Naphthol
- Phenol
- Biphenyl
Halogenated Compounds

- Carbon tetrachloride
- Chloroform
- Vinyl chloride
- 1,2-Dichloroethane
- Trichloroethylene
- Tetrachloroethylene
- Benzoates

Halogenated Aromatic Compounds

- Polychlorinated Biphenyls
  - PCBs
- Organochlorine Insecticides
  - DDT, Toxaphene, ...
- Chlorinated Herbicides
  - 2,4-D, 2,4,5-T, Atrazine.....
- Chlorinated Phenols
  - Pentachlorophenol
  - 2,4-dichlorophenol...2,4-D
  - 2,4,5-trichlorophenol.... 2,4,5-T
  - 2,3, and 4-Nitrophenol
Halogenated Aromatic Compounds

- Chlorobenzene
- 1,3-dichlorobenzene
- PCB
- DDT
- DDE
- DDD

Chlorinated Herbicides
- 2,4-Dichlorophenoxyacetic Acid ([2,4-D])

Chlorinated Phenols
- Pentachlorophenol
Halogenated Aliphatic Compounds

- **Trichloroethylene [TCE]**

- **Ethylene Dibromide [EDB]**

Sources of Xenobiotics

- Wetlands can receive:
  - Drainage from agricultural land [pesticides, herbicides]
  - Drainage from urban areas
  - Discharge from industrial facilities
  - Landfill leachates
  - Undetonated military explosives [TNT, HMX, RDX, etc.] in war zones and training bases
  - Spills [fuels, etc.] due to transportation accidents
  - Atmospheric deposition
Environmental Fate of Xenobiotics

• Need to know constants
• Fugacity Modeling
  – $K_{OW}$ Octanol – water partition coefficient
  – $K_{H}$ Henry’s Law constant
  – $K_{a}$ Dissociation constant
  – $K_{d}$ Partition [sorption] coefficient
  – $K_{r}$ Reaction rate constants
  – $MW$ Molecular weight
  – $S_{w}$ Solubility in water

22/06/2008 WBL 15
Predicting the Fate of Xenobiotics

- Need to know the biogeochemical / environmental conditions in the wetland soils
  - Microbial consortia
  - Redox potential
  - Salinity
  - C content
  - Other e\(^{-}\) acceptors
  - pH
  - Temperature
  - N, P availability
  - Oxygen status
  - Vegetation type

Environmental Fate of Xenobiotics

- Abiotic Pathways
  - Sorption
  - Photolysis
  - Volatilization
  - Export
    - Leaching / surface run-off
Abiotic Pathway: Sorption

For organic chemicals not adsorbed by soils, Kd is equal to zero.

For a given organic chemical, sorption (Kd) is greater in soils with larger organic matter content. These chemicals move slowly in soils.

For a given soil, organic chemicals with smaller Kd values are sorbed to lesser extent and highly mobile.

Partition coefficient (L/kg) \( K_d = \frac{S \text{ (mg/kg)}}{C \text{ (mg/L)}} \)
Abiotic Pathway: Sorption

- Bioavailability of xenobiotics to degradation is strongly influenced by sorption
- Chemicals with low sorption coefficients are generally more soluble, and are more readily degraded
- Sorption of chemicals increases with amount of soil organic matter

Abiotic Pathway: Sorption

- Sorption may protect biota from toxic levels of chemicals
- High levels of DOM may increase the mobility of chemicals
- Chemicals with high sorption coefficients are generally less mobile
Environmental Fate of Xenobiotics

- Biotic pathways
  - Extracellular enzyme hydrolysis
  - Microbial degradation
  - Plant and microbial uptake
  - Bioaccumulation / magnification

Biotic Pathways:

Microbial ecology: why do microbes degrade Xenobiotics?
1) Derive energy
   i) Electron acceptor
   ii) Electron donor
2) A source of Carbon
3) Substitution for a similar “natural” compound: Cometabolism.

*Cometabolism: organisms mediating the mineralization of a certain compound obtain no apparent benefit from the process*
Energetics of Xenobiotic Biodegradation

- Energetics of aerobic and anaerobic benzoate degradation

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔG (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoate + 7.5O₂ → 2CO₂</td>
<td>-3175</td>
</tr>
<tr>
<td>Benzoate + 6NO₃⁻ → 3N₂ + 7CO₂</td>
<td>-2977</td>
</tr>
<tr>
<td>Benzoate + 8NO₃⁻ → 14NH₄⁺ + 7CO₂</td>
<td>-1864</td>
</tr>
<tr>
<td>Benzoate + 30 Fe³⁺ → 30 Fe²⁺ + 7 CO₂</td>
<td>-303</td>
</tr>
<tr>
<td>Benzoate + SO₄²⁻ → 7CO₂ + 3.75HS⁻</td>
<td>-185</td>
</tr>
<tr>
<td>Benzoate + S⁰ → 7CO₂ + 15HS⁻</td>
<td>-36</td>
</tr>
</tbody>
</table>

Thauer et al. 1977

Biodegradation

- Hydrolysis [ + H₂O ]
- Oxidation [ + O₂ ]
- Reduction [ + e⁻ ]
- Synthesis [ + Functional Groups ]
Biotic Pathway: Hydrolysis

- Extracellular, possibly not compound specific
  - Ether hydrolysis
    - \[ \text{R-C-O-C-R} + \text{H}_2\text{O} \rightarrow \text{R-C-OH} + \text{HO-C-R} \]
  - Ester hydrolysis (Chlorpropham)
    - \[ \text{R-C-O-C=O} + \text{H}_2\text{O} \rightarrow \text{R-C-OH} + \text{HO-C=O} \]
  - Phosphate ester hydrolysis (Parathion)
    - \[ \text{R-C-O-P=O} + \text{H}_2\text{O} \rightarrow \text{R-C-OH} + \text{HO-P=O} \]
  - Amide hydrolysis (Propanil)
    - \[ \text{R-N-C=O} + \text{H}_2\text{O} \rightarrow \text{C=O} + \text{H-N-R} \]
  - Hydrolytic dehalogenation (PCP)
    - \[ \text{R-C-CL} + \text{H}_2\text{O} \rightarrow \text{-C-OH} + \text{HCl} \]

Biotic Pathway: Oxidation

- Key to xenobiotic detoxification and subsequent mineralization through oxidation:
  - Presence of molecular oxygen
  - Presence of selected aerobic or facultative aerobic microbial groups (fungi or bacteria)
  - Aromatic rings without functional groups
    - Benzene, toluene, naphthalene
Biotic Pathway: Oxidation

Benzene + O₂ → HO₂⁻ + O₂ → HO₂⁻ + O₂ → CO₂ + H₂O

Monooxygenase

Dioxygenase

Muconic Acid

Biotic Pathway: Reduction

- Reductive dechlorination
  - (TCE, PCB, PCP)
- Reduction of the aromatic ring
  - (BTEX)

6 H⁺ + 6 e⁻ →

- Reduction of the Nitro group
  - (Parathion)
  - R-C-NO₂ + 6H⁺ + 6e⁻ → C-C-NH₂
Reductive Dechlorination

Sequential replacement of Cl⁻ ions with H atoms
Usually results in accumulation of toxic intermediates
Promoted under highly reducing conditions (low redox potential) and high microbial activity

Acetate Oxidation with Different Electron Acceptors

<table>
<thead>
<tr>
<th>Electron acceptor</th>
<th>ΔG°' (kJ/mol Ac)</th>
<th>ATP (mol/mol Ac)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ / H₂O</td>
<td>-858</td>
<td>28</td>
</tr>
<tr>
<td>PCP / TeCP</td>
<td>-557</td>
<td>18</td>
</tr>
<tr>
<td>NO₃⁻ / NO₂⁻</td>
<td>-556</td>
<td>18</td>
</tr>
<tr>
<td>SO₄²⁻ / HS⁻</td>
<td>-56</td>
<td>2</td>
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</tbody>
</table>
Reductive Dechlorination of PCP in Methanogenic Everglades Soils

Reductive Dechlorination by Anaerobic Microorganisms

Van Dort and Bedard, 1991; Appl. Environ. Micro. 57:1576-1578

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Biotic Pathway: Reduction

\[
\text{NO}_2^- + 6e^- + 6H^+ \rightarrow \text{NH}_2^- + H_2O
\]

**p-nitrophenol** \[ \text{OH} \] \[ \text{OH} \]

**p-aminophenol**

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Anaerobic Degradation of 2,4,6-trinitrotoluene [TNT]

Boopathy et al. 1993  Water Environ. Res. 65:272-275

![Graph showing degradation of TNT with different electron acceptors](image-url)

- No electron acceptors
- Sulfate Reducing
- Nitrate Reducing
- \( H_2 + CO_2 \)

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Fate Processes of Chlorophenols in Soil

- Microbial transformations
  - Reductive dechlorination
  - Aerobic catabolism
- Sorption

Coupled Anaerobic-Aerobic PCP Degradation

Anaerobic: Cl⁻ removal

Aerobic: Cl⁻ removal and ring cleavage

PCP + O₂ → CO₂ + H₂O + 2Cl⁻
Biotic Pathway: Polymerization

- Oxidative coupling under aerobic conditions
- Recalcitrant humic-like polymers. Example TNT

2,4,6-trinitrotoluene $\rightarrow$ 2,2',6,6'-tetranitro-4,4'-azoxytoluene

Field et al. 1995. Antonie van Leeuwenhoek 67:47-77

Biotic Pathway: Polymerization

2, 4-dichlorophenol $\rightarrow$ 2,3,7,8-dibenzo-p-dioxin

Field et al. 1995. Antonie van Leeuwenhoek 67:47-77
Case Study: Lake Apopka

- 1940’s marshes of lake Apopka drained for agricultural use (19,000 acres)
- 1950-1990 extensive eutrophication and numerous fish / alligator kills
- 1992 alligator / turtle population crash
  - Reproduction problems, gender definition
  - 1980 Dicofol spill (90% gator die-off)
Case Study: Lake Apopka

- 1997 muck farm buy out by state ($100m)
- 1998 marsh restoration and reflooding begins (July)
- November 1998 massive wading bird kill on Apopka with dispersion (est. 1000+ birds)
- Necropsy found DDT, Diedrin, Toxaphene

Contaminant Exposures and Potential Effects on Health and Endocrine Status for Alligators in the Greater Everglades Ecosystem

Xenobiotics in Wetlands

- Sources and examples
- Aerobic-Anaerobic interfaces
- Fate dictated by partitioning
- Abiotic pathways
  - Sorption, photolysis, volatilization
- Biotic pathways
  - Hydrolysis, Oxidation, Reduction, Synthesis
  - Mediated by microbial consortia
  - Biogeochemical controls
  - Environmental controls