DEFINITIONS

BIODEGRADATION - biologically catalyzed reduction in complexity of a chemical.

\[(C_6H_{10}O_5)_n + H_2O \rightarrow \cdots \rightarrow nC_6H_{12}O_6\]

cellulose \hspace{1cm} \text{enzymes} \hspace{1cm} \text{glucose}

MINERALIZATION - conversion of organic compound into inorganic product

\[nC_6H_{12}O_6 \rightarrow CO_2 + H_2O\]

glucose \hspace{1cm} \text{enzymes} \hspace{1cm} \text{aerobic}
BIOREMEDICATION - technology based on biodegradation/mineralization

- Composting, Slurry Reactors, Biofilters, etc.

BIOAVAILABILITY - an access of a chemical to microorganisms.

- Presence in water phase, close contact, absence of sorption to solid surfaces.

NAPLs - organic solvents immiscible with water:

- petroleum products
- crude oils
- industrial solvents

SURFACTANTS - agents reducing the surface tension of a liquid

- artificial surfactants (detergents, shampoos, industrial cleaning products, etc.)
- microbial biosurfactants
ORGANIC CHEMICALS IN THE ENVIRONMENT

SYNTHETIC ORG. CHEM. 60 MTONS/yr MANUFACTURED IN US

PESTICIDES USED IN AGRICULTURE IN US 0.5 MILLION MTONS/yr

GROUNDWATER SURVEY (1988):
- 67 PESTICIDES FOUND IN 33 STATES
- 17 PESTICIDES AT LEVELS ABOVE EPA HEALTH ADV. LEVELS IN 17 STATES
- 0 TO 10% GROUNDWATER CONTAMINATION
Pesticides used in the US:

Herbicides 60%
Insecticides 25%
Fungicides 6%
Others 9%
(Includes Bactericide, Nematicide, Acaricides, Rodenticide)

Adverse effects due to:
Lack of specificity
Bioaccumulation

Pesticide impacts on plants:
Growth irregularity
Loss in biomass
Death
Sorption - Desorption

Van der Waals forces

H bonding

Dipole-dipole interaction

Ion exchange

Covalent bonding

Protonation

Ligand exchange

Cation bridging

Water bridging

Hydrophobic partitioning
FATE AND TRANSPORT IN SOILS

1. Plant uptake and metabolisis to non-toxic levels by:
   - Redox reactions
   - Hydrolysis
   - Hydroxylation
   - Dehalogenation
   - Dealkylation
   - Conjugation
2. Volatilization

Depends on volatility and proximity to soil surface

Volatility: measured in terms of half-life (time required for one half of reactant to be converted to product)
3. Abiotic and Biotic Transformation

**Abiotic:**

*In aquatic env.:* Hydrolysis, Redox, Photolysis

*In soil env.:* Hydrolysis, Redox

**Biotic:**

Biodegradation - Contaminant used as substrate for metabolism

Cometabolism - Contaminant is transformed by metabolic reactions without being used as energy source

Accumulation - in the microorganism
POLYMERIZATION OR CONJUGATION - BOUND TO ANOTHER ORGANIC MOLECULE
SECONDARY EFFECTS OF BIOLOGICAL ACTIVITY CAUSING TRANSFORMATION

4. Leaching by movement with soil water - strongly influenced by sorption characteristics
ADVERSE EFFECTS

Table 7-4 A Summary of Species Most Commonly Affected by Toxicities of Selected Trace Elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Humans</th>
<th>Animals</th>
<th>Aquatic organisms</th>
<th>Birds</th>
<th>Plants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>*</td>
<td>*</td>
<td></td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>As, Pb, Hg, Cr, Se</td>
<td>*</td>
<td>*</td>
<td></td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Cu, Ni, Zn</td>
<td>*</td>
<td></td>
<td></td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>Mo, F, Co</td>
<td>*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


HUMAN HEALTH

Cd toxicity - Renal dysfunction, itai-itai disease (Bone loss)

Pb toxicity - Mental impairment,

ANIMAL HEALTH

Mo toxicity - Molybdnenosis

Se toxicity - SeLENOSIS
PHYTOTOXICITIES

RESULT IN SPARSE GROUNDCOVER, INCREASED WIND AND WATER EROSION, AND FURTHER SPREAD OF CONTAMINATION

Figure 7-4  Relationships between Mg(NO₃)₂-extractable Cu in soil and crop yield. (Reprinted from Lexmond and deHaan, 1977. With permission.)

AQUATIC ENVIRONMENTS

MOBILITY IS DIFFICULT TO ASSESS. SOURCE IS SEDIMENT DUE TO EROSION. EFFECT: CONT. WATER OR CONT. SOIL?
HEAVY METALS IN SOILS

CATIONIC METALS: Cd 2+, Cr 3+, Cu 2+
Hg 2+, Ni 2+, Pb 2+, Zn 2+
OXYANIONS: AsO4 3-, CrO4 2-, MoO4 2-
HSeO3 1-, SeO4 2-

SOURCES OF METAL CONTAMINANTS:

Table 18.6
Sources of Selected Inorganic Soil Pollutants

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Major uses and sources of soil contamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>Pesticides, plant desiccants, animal feed additives, coal, and petroleum; mine tailings and detergents</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Electroplating, pigments for plastics and paints, plastic stabilizers, and batteries</td>
</tr>
<tr>
<td>Chromium</td>
<td>Stainless steel, chrome-plated metals, pigments, and refractory brick manufacture</td>
</tr>
<tr>
<td>Copper</td>
<td>Mine tailings, fly ash, fertilizers, wind blown copper-containing dust</td>
</tr>
<tr>
<td>Lead</td>
<td>Combustion of oil, gasoline, and coal; iron and steel production</td>
</tr>
<tr>
<td>Mercury</td>
<td>Pesticides, catalysts for synthetic polymers, metallurgy, thermometers</td>
</tr>
<tr>
<td>Nickel</td>
<td>Combustion of coal, gasoline, and oil; alloy manufacture, electroplating, batteries</td>
</tr>
<tr>
<td>Zinc</td>
<td>Galvanized iron and steel, alloys, batteries, brass, rubber manufacture</td>
</tr>
</tbody>
</table>

Data selected from Moore and Ramamoorthy (1984).
# Table 7-1 Concentrations in Soils

Table 7-1 Selected Trace Element Concentrations in Soils at Normal and Geochemically Anomalous Levels

<table>
<thead>
<tr>
<th>Element</th>
<th>&quot;Normal&quot; range (mg/kg)</th>
<th>Metal-rich range (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>&lt;5–40</td>
<td>Up to 2,500</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;1–2</td>
<td>Up to 30</td>
</tr>
<tr>
<td>Cu</td>
<td>2–60</td>
<td>Up to 2,000</td>
</tr>
<tr>
<td>Mo</td>
<td>&lt;1–5</td>
<td>10–100</td>
</tr>
<tr>
<td>Ni</td>
<td>2–100</td>
<td>Up to 8,000</td>
</tr>
<tr>
<td>Pb</td>
<td>10–150</td>
<td>10,000 or more</td>
</tr>
<tr>
<td>Se</td>
<td>&lt;1–2</td>
<td>Up to 500</td>
</tr>
<tr>
<td>Zn</td>
<td>25–200</td>
<td>10,000 or more</td>
</tr>
</tbody>
</table>

*Source: Bowie and Thornton, 1985.*
Table 18.9  Forms of Heavy Metals

Table 18.9  
Forms of Six Heavy Metals Found in a Greenfield Sandy Loam (Coarse Loamy, Mixed, Thermic Typic Haloxeralf) That Had Received 45 Mg/ha Sewage Sludge Annually for 5 Years

<table>
<thead>
<tr>
<th>Forms</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable/adsorbed</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>5</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Organically bound</td>
<td>20</td>
<td>5</td>
<td>34</td>
<td>24</td>
<td>3</td>
<td>28</td>
</tr>
<tr>
<td>Carbonate/iron oxides</td>
<td>64</td>
<td>19</td>
<td>36</td>
<td>33</td>
<td>85</td>
<td>39</td>
</tr>
<tr>
<td>Residual(^a)</td>
<td>16</td>
<td>77</td>
<td>29</td>
<td>40</td>
<td>12</td>
<td>31</td>
</tr>
</tbody>
</table>

From Chang et al. (1984).

\(^a\) Sulfides and other very insoluble forms.

**Fig. 11 Effect of pH on Adsorption**

Figure 18.11
The effect of soil pH on the adsorption of four heavy metals. Maintaining the soil near neutral provides the highest adsorption of each of these metals and especially of lead and copper. The soil was a Typic Paleudult (Christiana silty clay loam). [From Elliot et al. (1986)]
Figure 7-3  Forest floor and soil heavy metal concentrations as a function of distance from Central Park, Manhattan, New York City. Open circles represent forest floor and closed circles represent soil values. (Reprinted from Pouyat and McDonnell, 1991. With permission.)
REMEDIATION OPTIONS

TREATMENT TECHNOLOGIES:
Removal and treatment by-
High temperature treatment
Addition of solidifying agents
Washing processes

Disadvantages: costly for large quantities of soil

On-site Management:
Isolation-
Vitrification by electric current
Addition of solidifying agents
Reduce bioavailability-
Alter soil pH
Increase sorption capacity
Precipitation of metals