DEFINITIONS

<u>BIODEGRADATION</u> - biologically catalyzed reduction in complexity of a chemical.

$$\underset{\text{cellulose}}{(C_6H_{10}O_5)n} + H_2O \xrightarrow{\text{enzymes}} \ldots \longrightarrow \underset{\text{glucose}}{nC_6H_{12}O_6}$$

<u>MINERALIZATION</u> - conversion of organic compound into inorganic product

$$\underset{\text{glucose}}{nC_6H_{12}O_6} \xrightarrow[\text{aerobic}]{\text{enzymes}} CO_2 + H_2O$$

BIOREMEDIATION - 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 immissible 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

	Species adversely affected				
Element	Humans	Animals	Aquatic organisms	Birds	Plants
Cd	*	*	*	*	*
As, Pb, Hg, Cr, Se	*	*	*	*	
Cu, Ni, Zn			*		*
Mo, F, Co		*			
B					*

Source: Page, 1992.

HUMAN HEALTH

CD TOXICITY - RENAL DYSFUNCTION,

ITAI-ITAI DISEASE (BONE LOSS)

PB TOXICITY - MENTAL IMPAIRMENT,

ANIMAL HEALTH

MO TOXICITY - MOLYBDENOSIS

SE TOXICITY - SELENOSIS

PHYTOTOXICITIES

RESULT IN SPARSE GROUNDCOVER,

INCREASED WIND AND WATER EROSION,

AND FURTHER SPREAD OF CONTAMINATION

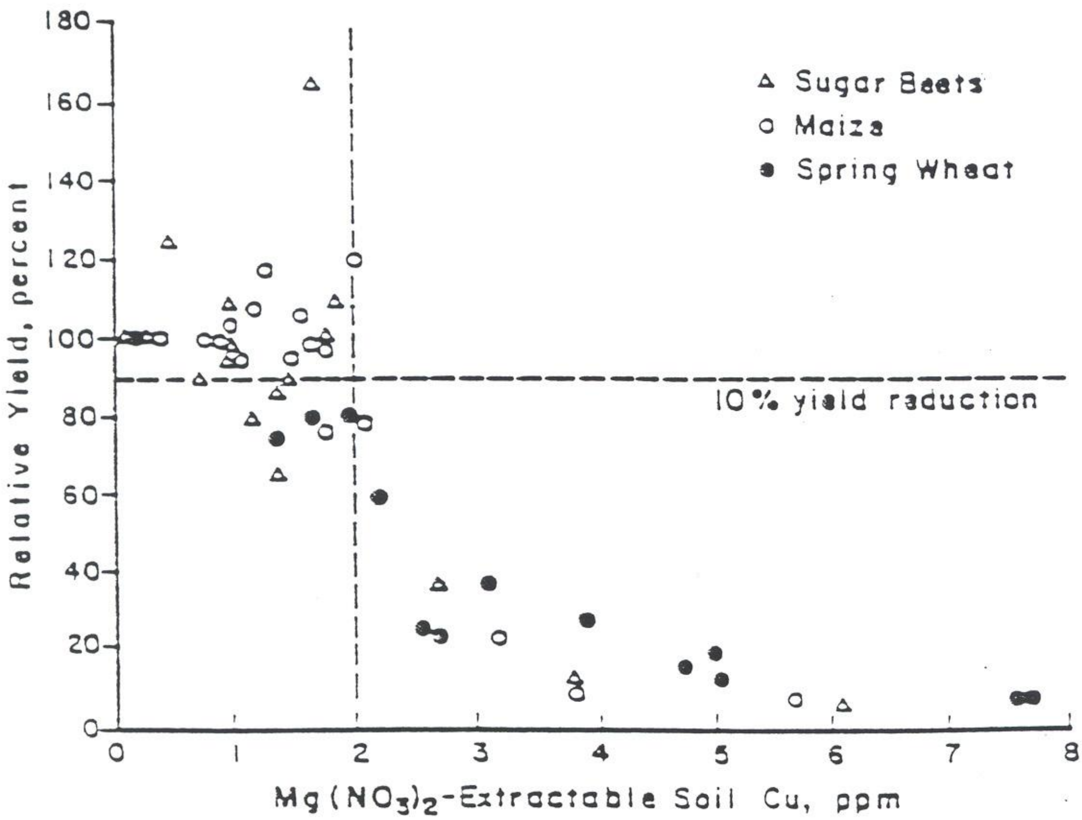

Figure 7-4 Relationships between Mg $(NO_3)_2$-extractable Cu in soil and crop yield. (Reprinted from Lexmond and deHaan, 1977. With permission.)

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: AsO_4^{3-}, CrO_4^{2-}, MoO_4^{2-}, $HSeO_3^{1-}$, SeO_4^{2-}

SOURCES OF METAL CONTAMINANTS:

TABLE 18.6
Sources of Selected Inorganic Soil Pollutants

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

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

Element	"Normal" range (mg/kg)	Metal-rich range (mg/kg)
As	<5–40	Up to 2,500
Cd	<1–2	Up to 30
Cu	2–60	Up to 2,000
Mo	<1–5	10–100
Ni	2–100	Up to 8,000
Pb	10–150	10,000 or more
Se	<1–2	Up to 500
Zn	25–200	10,000 or more

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

	Percentage of elements in each form					
Forms	*Cd*	*Cr*	*Cu*	*Ni*	*Pb*	*Zn*
Exchangeable/adsorbed	1	1	2	5	1	2
Organically bound	20	5	34	24	3	28
Carbonate/iron oxides	64	19	36	33	85	39
Residual[a]	16	77	29	40	12	31

From Chang et al. (1984).
[a] Sulfides and other very insoluble forms.

FIG. 11 EFFECT OF pH ON ADSORPTION

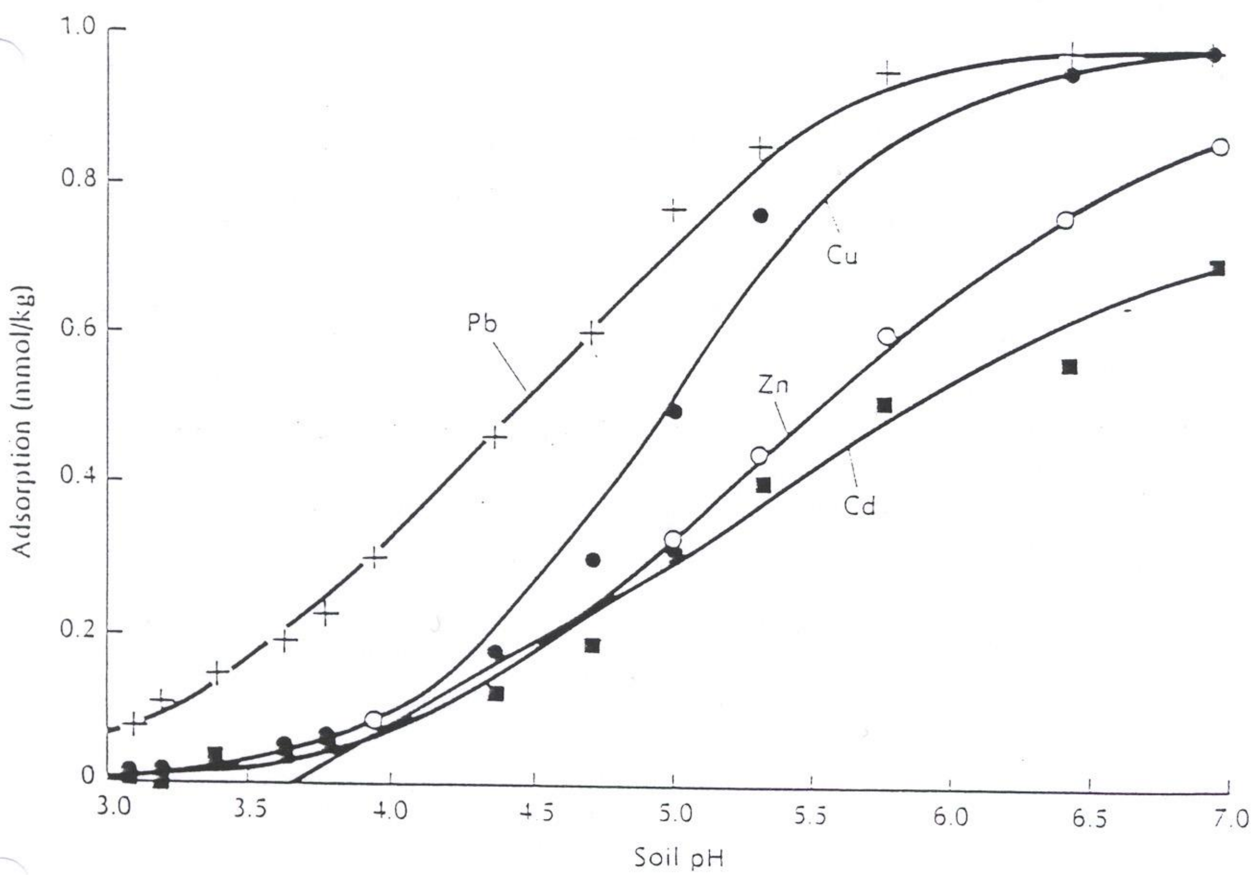

Figure 18.11
The effect of soil pH on the adsorption of four heavy metals. Maintaining the soil near neutral provides the highest adsorption of each of these metals and especially of lead and copper. The soil was a Typic Paleudult (Christiana silty clay loam). [From Elliot et al. (1986)]

FIG. 7-3 DISTRIBUTION FROM SOURCE

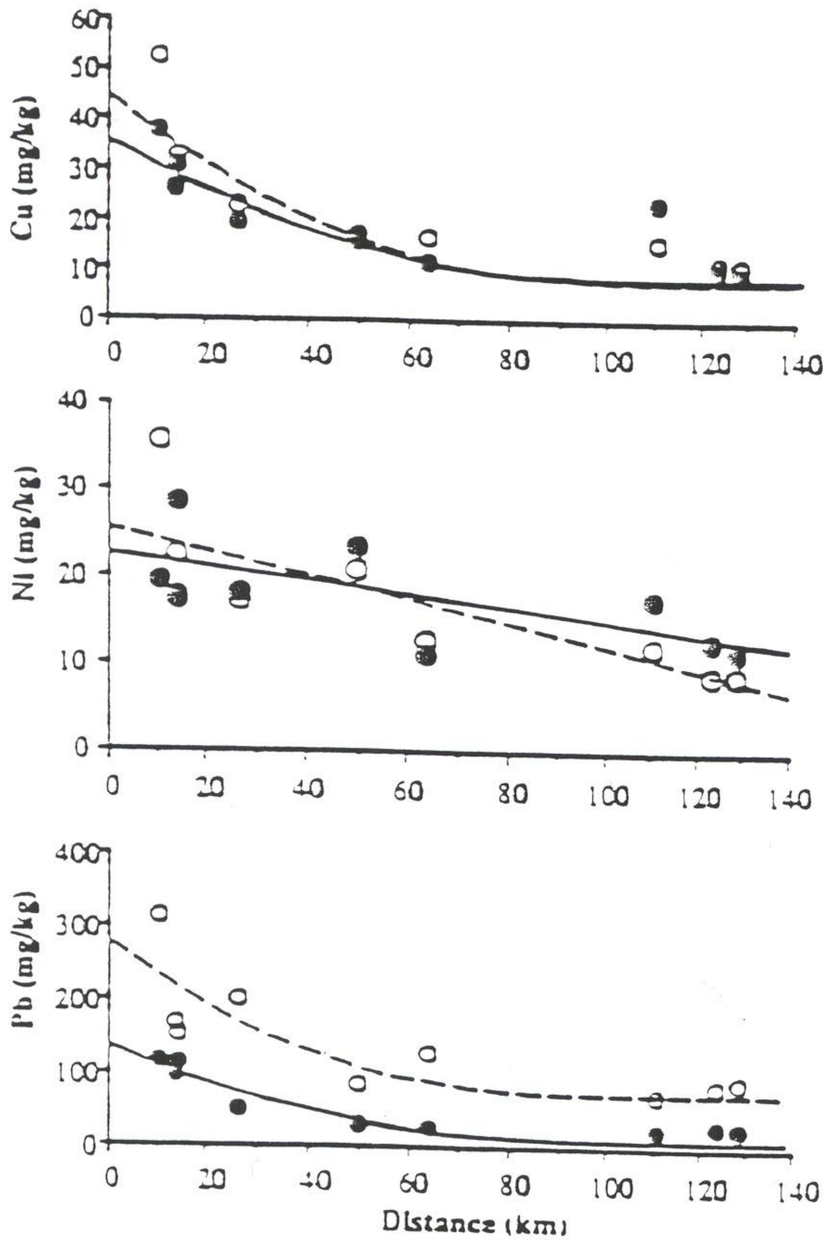

Figure 7-3 Forest floor and soil heavy metal concentrations as a function of distance from Central Park, Manhattan, New York City. Open circles represent forest floor and closed circles represent soil values. (Reprinted from Pouyat and McDonnell, 1991. With permission.)

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