



Ecotoxicology and Ecological Risk Assessment

**BI01: Environmental Fate and
Possible Effects of Nanoparticles**

The 24th

Jyväskylä Summer School

Jyväskylän yliopisto

Environmental Toxicology

-  Environmental toxicology often used to define the study of environmental contaminants on humans
-  The study of the impacts of pollutants upon the structure and function of ecological systems (from molecular to ecosystem - Landis and Yu, 1995)

Ecotoxicology

-  The branch of toxicology concerned with the study of toxic effects, caused by natural and synthetic pollutants, to the constituents of ecosystems - animals (including human), vegetable, and microbial - in an integrated context. - Truhaut, 1977

Contaminant

A substance released by man's activities

A substance present in greater than natural concentration as a result of human activities.

Contaminant

Anthropogenic - man-made

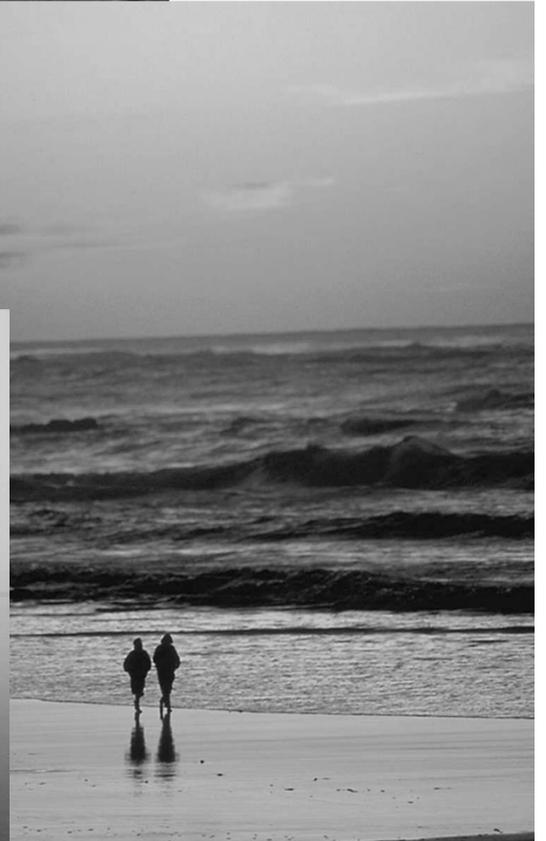
Xenobiotic - foreign chemical or material not produced in nature

Pollutant

A substance that occurs in the environment at least in part as a result of man's activities and which has a deleterious effect on living organisms.

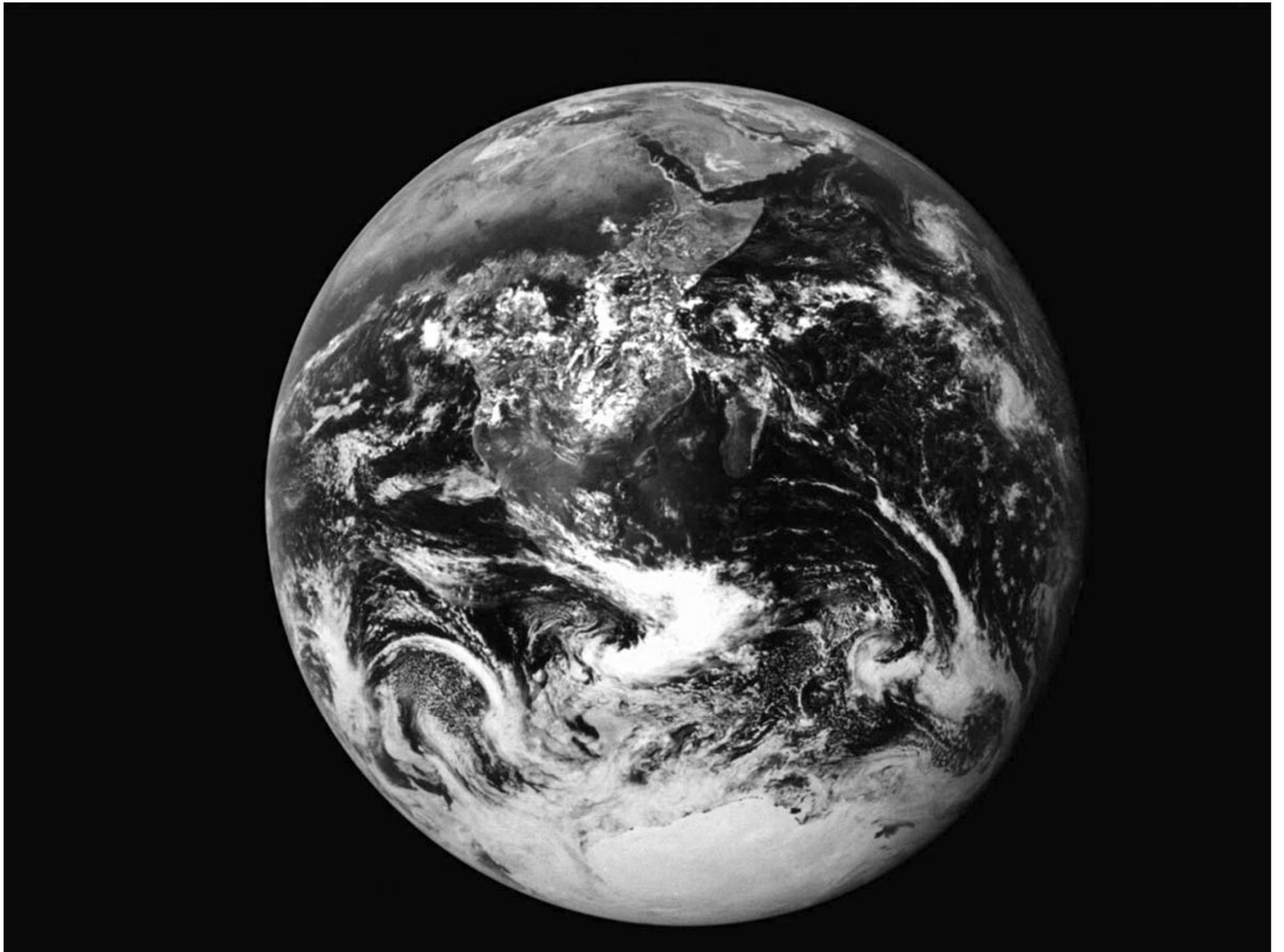
Dilution Paradigm

- 🌐 “the solution to pollution is dilution”
- 🌐 Pre World War II philosophy that stemmed from a parochial view of our world.



Dilution Paradigm

Post World War II era made people aware of the interconnectedness of our world



Boomerang Paradigm

“what you throw away can
come back and hurt you”

Historical Tragedies

- 🌐 **Minimata Bay - nearly 1000 people died from methylmercury poisoning before Chisso Corporation halted discharge of mercury into Minimata Bay.**

Historical Tragedies

-  Itai-Itai Disease - Irrigation water originating from metal mine waste caused high levels of cadmium in rice. Itai-Itai means “ouch-ouch” and refers to the extreme joint pain associated with the disease.

Historical Tragedies

- 🌐 **Radionuclides - 1945 open air testing of nuclear weapons began. In 1954, the Bravo bomb was exploded at Bikini Atoll dropping fallout on thousands of square kilometers of ocean, vessels, and islands. Human body burden of $^{137}\text{Cesium}$ increased worldwide through 1965 then decreased as the US, USSR, France, and China ceased open air-testing.**

Historical Tragedies

- 🌐 **DDT (dichlorodiphenyltrichloroethane) - the first of the chlorinated organic insecticides, was originally prepared in 1873, but it was not until 1939 that Paul Muller of Geigy Pharmaceutical in Switzerland discovered the effectiveness of DDT as an insecticide he was awarded the Nobel Prize in medicine and physiology in 1948 for this discovery).**

Historical Tragedies

- 🌐 **DDT use increased enormously after WWII**
- 🌐 **Controlled mosquitoes that spread malaria**
- 🌐 **Controlled lice that carried typhus**
- 🌐 **WHO estimates that over 25 million lives were saved**

Historical Tragedies

- DDT has low mammalian oral LD50 value (300-500 mg/kg).
- In late 1940s problems began to appear
- Insect resistance; fish toxicity - DDT accumulated in the brain until enough was present to cause axonic dysfunction and death
- High lipid solubility and high o/w partition coefficient lead to high accumulation in fat tissues.
- From 1957-1960 Hunt and Bischoff (1960) reported deaths of Western grebes resulting from bioaccumulation of DDT.

Historical Tragedies

- 1962 - *Silent Spring*, book by Rachel Carson raised awareness to the issue of recalcitrant pesticides.
- Eggshell thinning - accumulated in foodchain until concentrations in the shell gland of birds became sufficient to inhibit Ca-dependent ATPases resulting in a reduction of Ca deposition in the shells.
- Birds at higher trophic levels were most susceptible.
- Caused large population declines
- Use of DDT banned in US in 1973
- By 1978 EPA reported a 90% reduction of DDT in Lake Michigan fish

Boomerang Paradigm

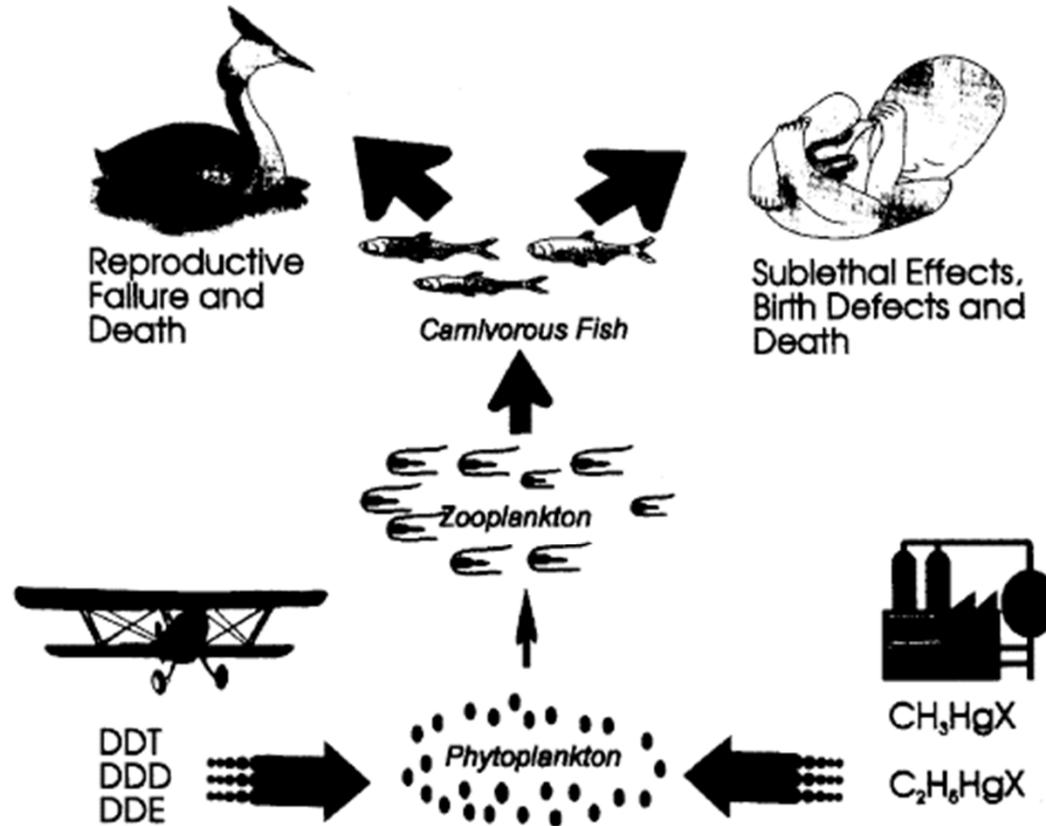
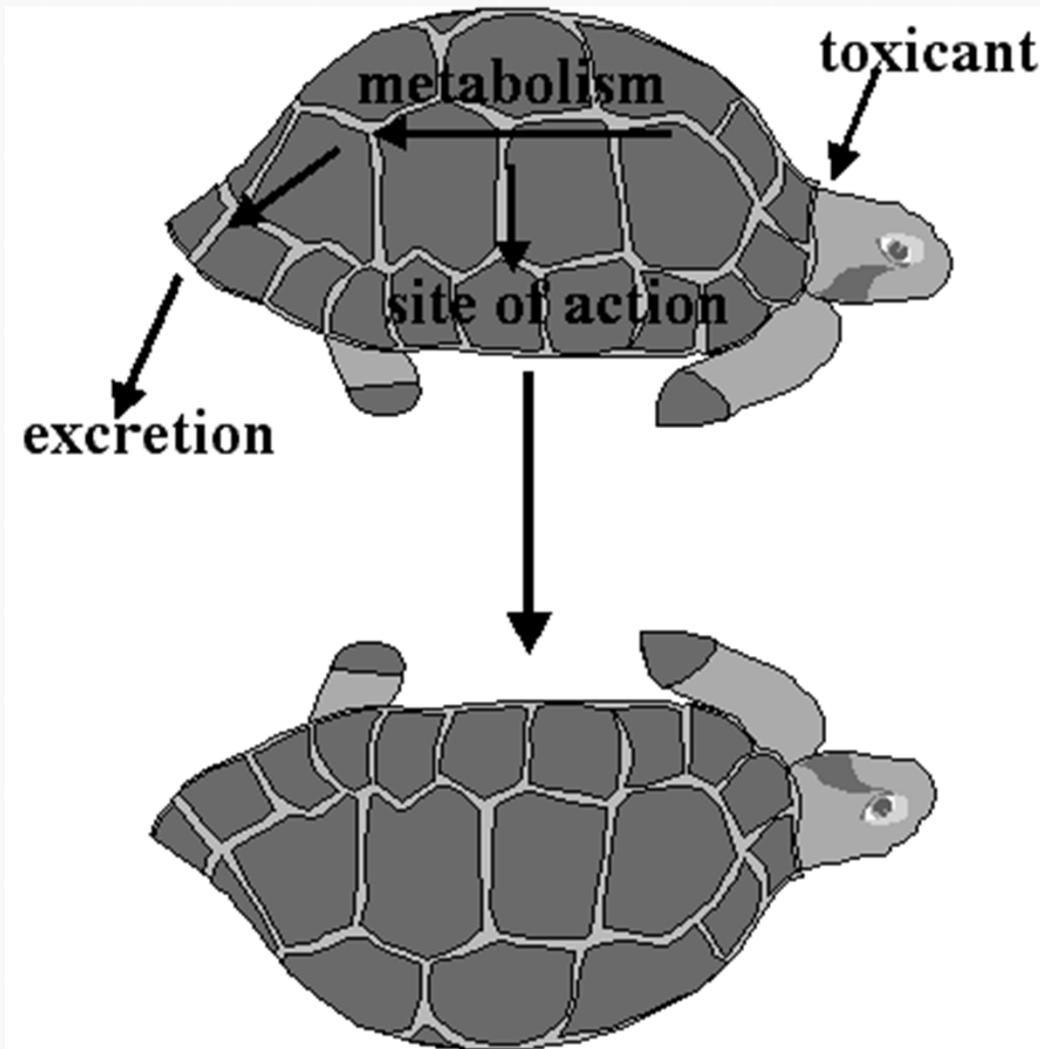


FIGURE 1.2. Two of the first contaminants to draw attention to the inadequacies of the dilution paradigm were DDT and methylmercury. They became watershed examples of the boomerang paradigm. Both were returned to humans and to valued wildlife species by transfer through foodwebs.

**ADMSE:
Absorption, Distribution, Metabolism, Storage, Excretion**



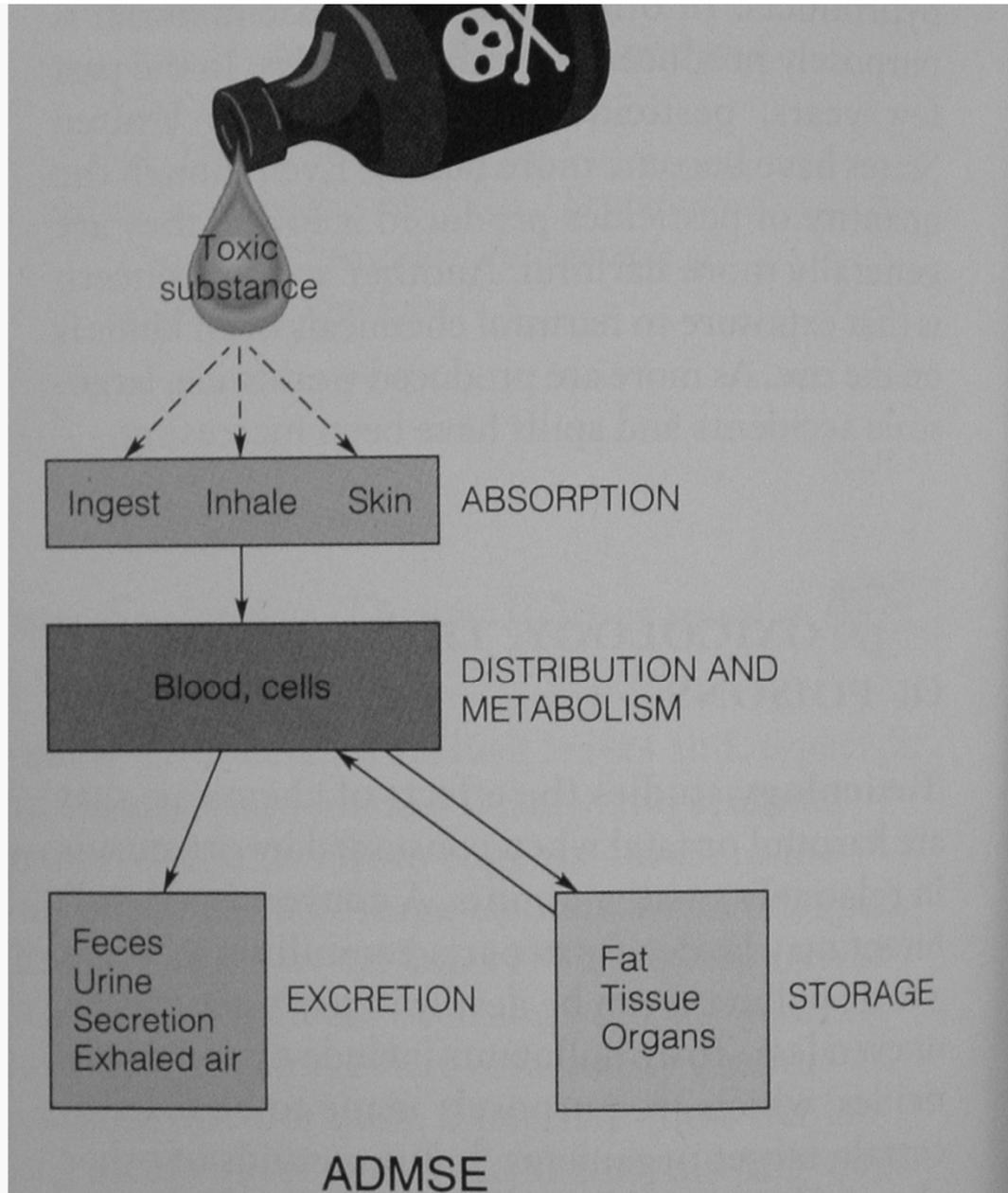
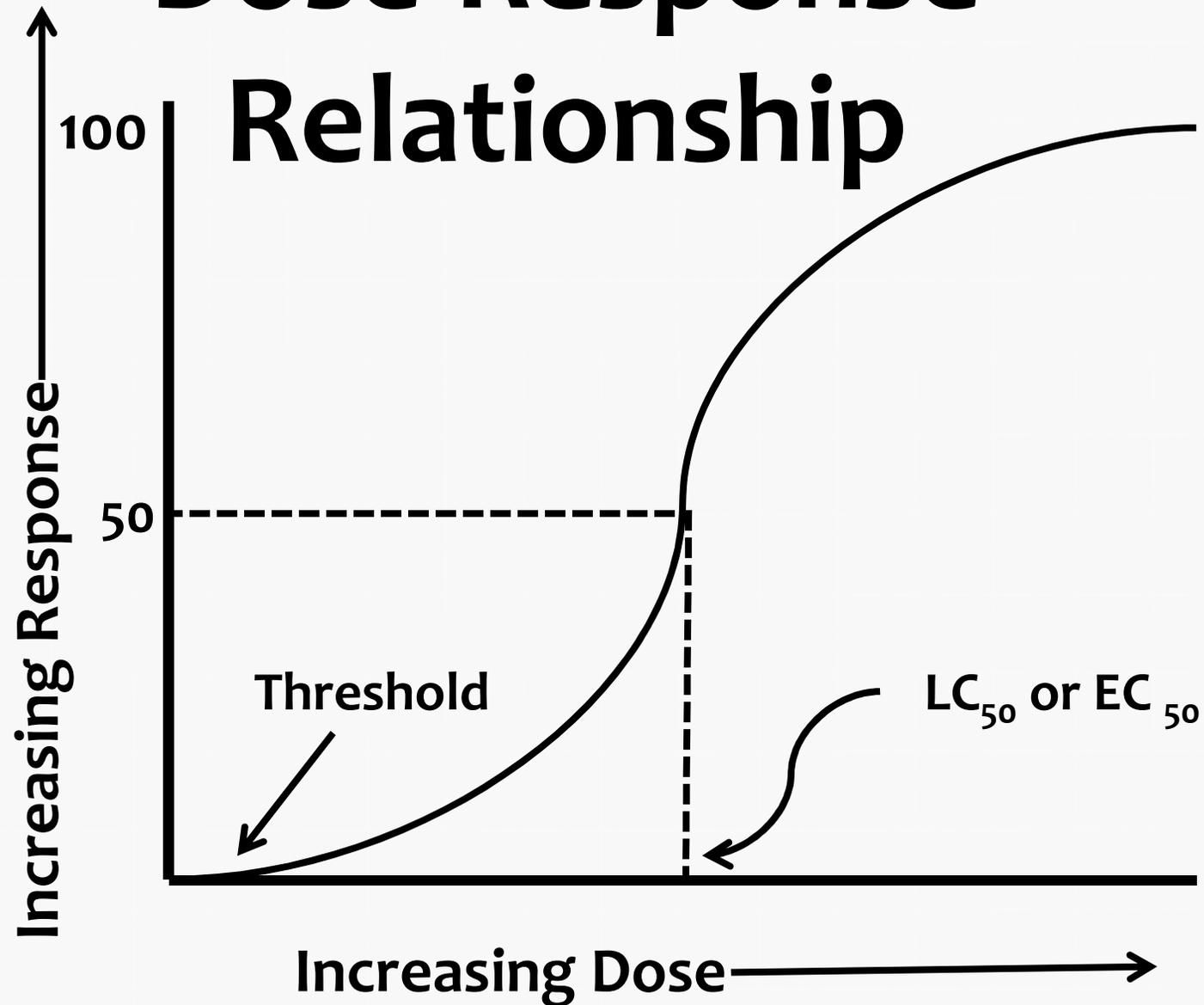


FIGURE 15-2

ADMSE traces the path of toxic substances through the body: absorption, distribution, metabolism, storage, and

Dose-Response Relationship



Terms

-  **Adsorption**
-  **Absorption**
-  **Bioconcentration**
-  **Bioaccumulation**
-  **Biomagnification**

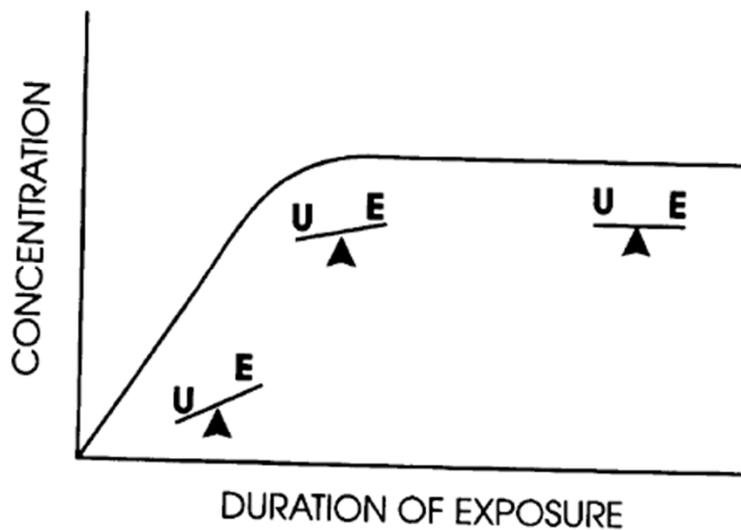
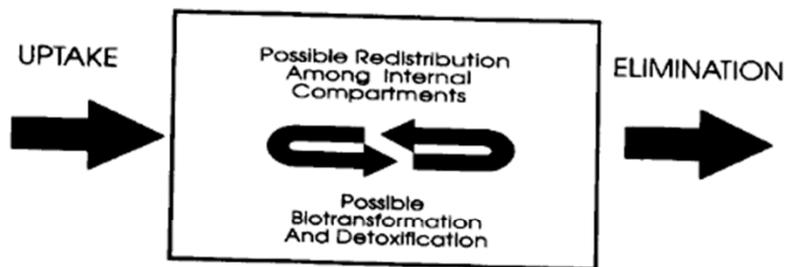
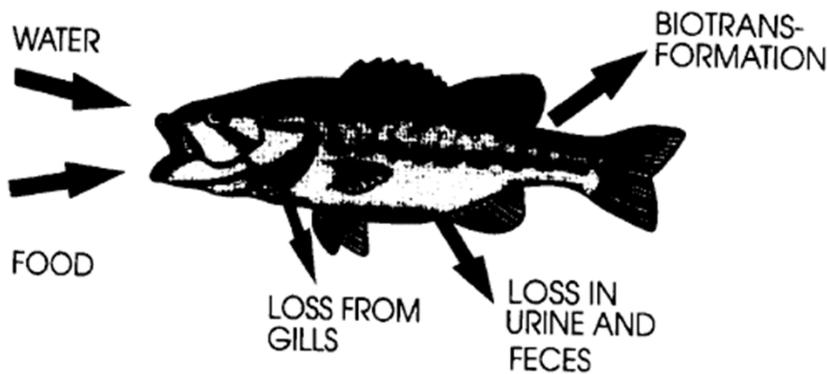


FIGURE 3.1. A simplified conceptualization of bioaccumulation. At the top of this figure, the fish (largemouth bass) is thought to potentially take in contaminants from its food and water, and lose contaminants via the gills, urine, and feces. There may be internal redistribution or biotransformation of the contaminant. This process is rendered to a simple box and arrow diagram. Here, only uptake from water is assumed to be significant, and all elimination processes are described by one elimination process. The most common mathematical description of this model predicts a gradual increase in contaminant in the fish until a steady state concentration is obtained as depicted in the graph at the bottom of this figure.

Absorption

 Ingestion

 Inhalation

 Dermal absorption

 Injection

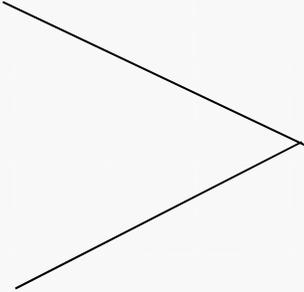
 IV

 IP

 IM

 SC

Membrane
Transport



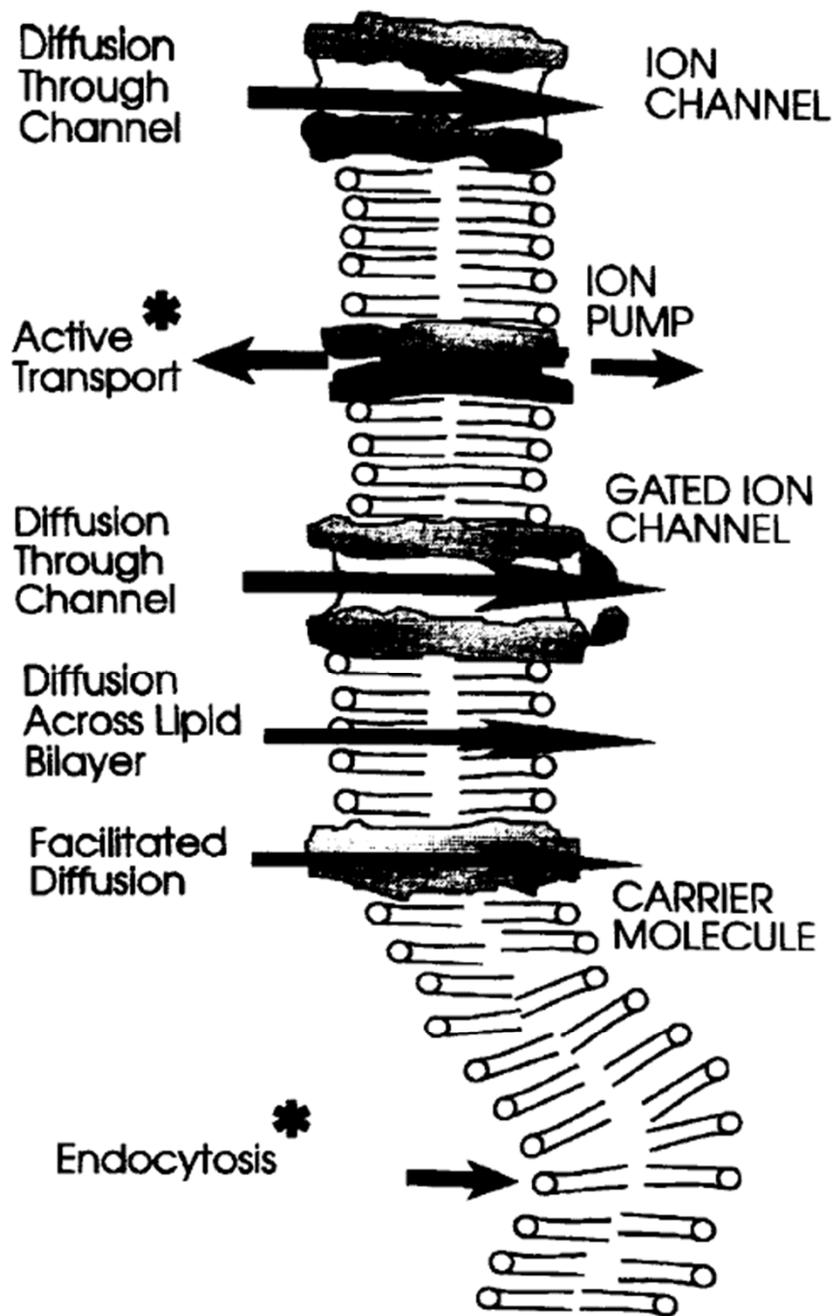


FIGURE 3.2. Mechanisms of uptake of contaminants into cells. Simple diffusion can occur across the lipid bilayer or through an ion channel formed by a channel protein. Channels may be gated and their functioning influenced by chemical and electrical conditions. Facilitated diffusion occurs via a carrier protein. Active transport passes the solute up an electrochemical gradient. Here the Na^+ , K^+ ATPase pump ion pump is illustrated. Potassium is pumped in as sodium is pumped out of the cell. The last mechanism for cellular uptake is endocytosis. As indicated by an *, endocytosis and active transport require energy.

Weak acid/base (influence of pH)



$$K = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]} \longrightarrow [\text{H}^+] = \frac{K [\text{HAc}]}{[\text{Ac}^-]}$$

$$\longrightarrow \text{pH} = \text{pK} - \log \frac{[\text{HAc}]}{[\text{Ac}^-]}$$

$[HA]/[Ac^-]$
 -2 -> 99/1
 -1 -> 90/10
 pH = pK -> 50/50
 +1 -> 10/90
 +2 -> 1/99

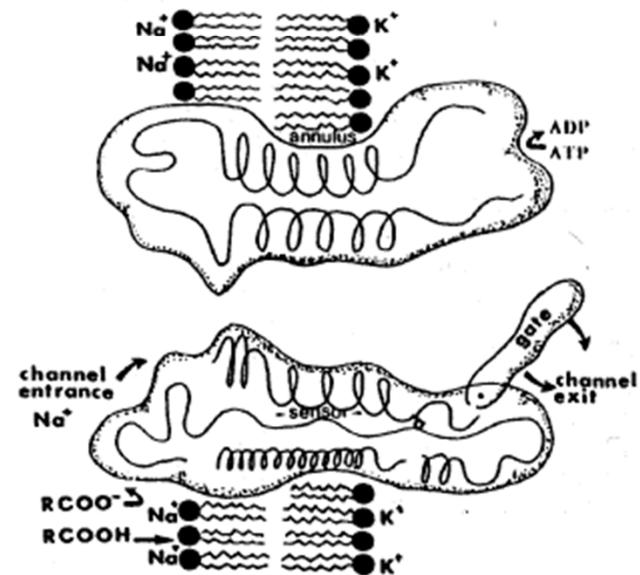
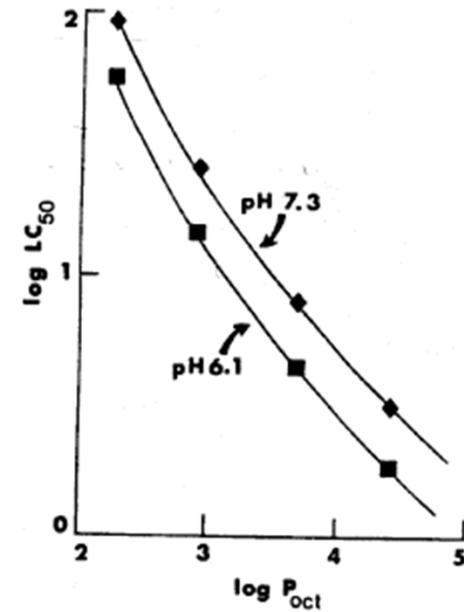


Figure 3 The effect of a fall in pH on the concentration necessary to kill 50% (LC₅₀) of the guppies exposed to these chlorophenols (top). Note that the increased acidity increases the lipid solubility. An interpretation of this data for a generalized acid is given in the membrane model (bottom).

Distribution

- 🌐 Protein binding
 - 🌐 Albumin
 - 🌐 Ionic bonds
 - 🌐 Van der Waals forces
 - 🌐 Hydrogen bonding
 - 🌐 Metalothionein
 - 🌐 SH bonds

Distribution and Storage

Tissue Partitioning

Lipids

Partitioning due to lipophilicity

O/W partitioning coefficient

Bone

Partitioning due to ion exchange and ligand binding

Biotransformation & Detoxification



Leads to:



enhanced elimination,



detoxification,



sequestration,



redistribution,



or activation.

Excretion

Feces

-  Incompletely digested food
-  Biliary excretion
 -  Enterohepatic recirculation

Urine

-  Renal excretion
 -  Molecular sieve
 -  Membrane exchange

Excretion

-  **Other**
 -  **Exhalation**
 -  **Sweat**
 -  **Hair**
 -  **Saliva**

Ecological Risk Assessment

-  Ecological risk assessment is a quantitative or semi-quantitative process to characterize the probability of harmful effects from actions or chemicals.

Solomon et al. 1996.
Ecological Risk
Assessment of
Atrazine in North
American Surface
Waters.
ET&C 15: 31-76

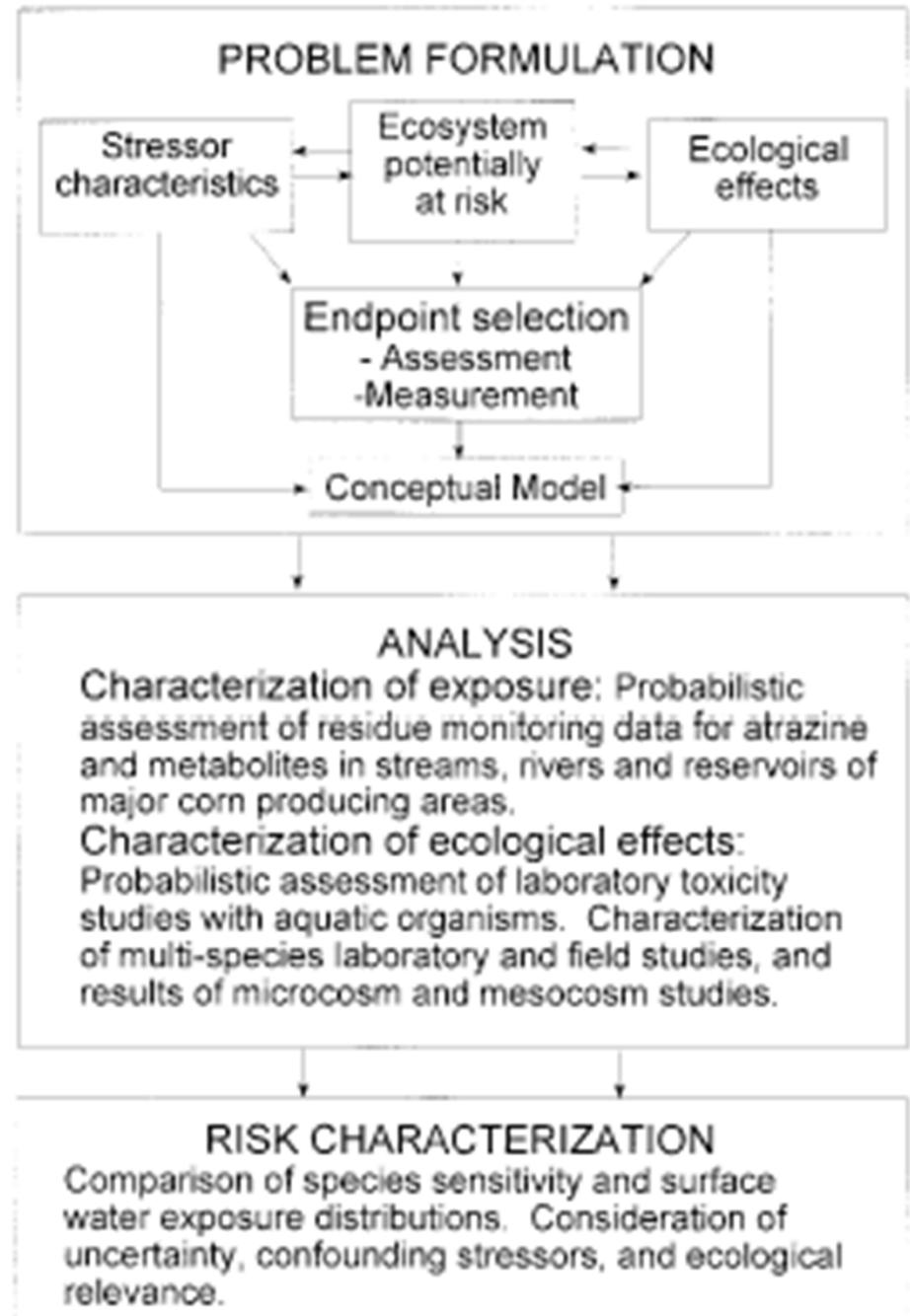


Fig. 1. Structure for risk assessment of atrazine in aquatic ecosystems.

Tiered Approach

- 🌐 **Tier 1: Screening-level risk assessment**
 - 🌐 **Worst case exposure scenario**
 - 🌐 **All chemical is bioavailable**
 - 🌐 **Ho: toxic chemicals in water body will have adverse effects on survival, growth, or reproduction of aquatic species, or will be significantly bioaccumulated**
 - 🌐 **Risk characterization estimated by risk quotient**
 - 🌐 **Exposure (EEC)/Toxicity (often LC50 for acute, NOAEC for chronic)**
 - 🌐 **If > 1 significant risk exists -> Contaminant of Potential Concern (COPC)**

Tiered Approach

- 🌐 **Tier 2: Risk quantification with existing data**
 - 🌐 **COPCs identified in Tier 1**
 - 🌐 **Probabilistic risk estimate**
 - 🌐 **Aquatic ecorisk quantified as percent of species or genera affected by toxic chemical or chemicals**
 - 🌐 **May be site-specific**
 - 🌐 **Includes estimates of uncertainties**
 - 🌐 **Ho: EECs of chemicals have adverse effects on the survival, growth, or reproduction of aquatic organisms and the structure of the aquatic community**

Tiered Approach

- 🌐 **Tier 3: Risk quantification with new and existing data**
 - 🌐 Same approach as Tier 2
 - 🌐 New, site-specific data used
 - 🌐 These data generated to reduce uncertainties identified in Tier 2 or fill in data gaps