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ES/RP 531
Fundamentals of Environmental Toxicology

Lecture 23
Biotic Phase Transfers
Bioconcentration, Bioaccumulation, Biomagnification, Bioavailability

Bioconcentration

- Originally referred to the amount of chemical residue accumulated by an organism by adsorption (I.e., through the integument) or other routes of entry (including food ingestion)
- Results in increased concentration of pesticide relative to environmental matrix (includes food, water, & air)

A Negative Context

- Bioconcentration is commonly thought of as being adverse
- Bear in mind that all nutrients and secondary metabolites are 'bioconcentrated'

Modern Usage

- Bioconcentration strictly should be used only when referring to accumulation of residues in tissues by uptake from an environmental phase through surface sorption or absorption
- Does not include dietary exposure
- Commonly used to refer to aquatic organisms, but also includes terrestrial organisms, especially if soil dwelling and plants

Bioaccumulation

- Uptake of contaminants via bioconcentration as well as by food ingestion
- Most appropriately used if cannot distinguish between the two mechanisms of uptake

Expression of Bioconcentration & Bioaccumulation Potential

- Ratio of concentration of contaminant in the tissue (or whole body or biochemical compartment, like lipids) relative to the concentration of contaminant in environmental phase (or matrix)

$$\text{BCF or BAF} = \frac{[C]_{organism}}{[C]_{phase}}$$

Equilibrium Partitioning Theory

- BCF & BAF can largely be explained by invoking the same thermodynamic "rules" used to explain physicochemical properties and other phase transfers
- Thus, uptake of contaminants by aquatic organisms from water and sediment is often explained by invoking the phrase "equilibrium partitioning theory"

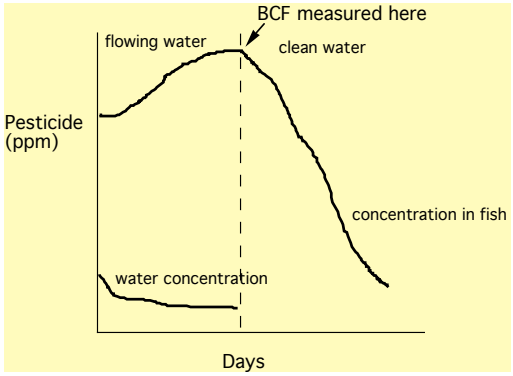
Think About It

- Given chemical **x** & **y**, **x** has a lower fugacity than y in water
  - Is the BCF in the common test invertebrate, *Daphnia*, higher for **x** or lower than for **y**

In fact, this question cannot be definitively answered until an important piece of the puzzle is placed on the board!

Measuring the BCF

- BCF (or BAF) should only be determined when the 'system' is at equilibrium (or for field measurements, at least in an empirical steady state)



Must Consider Rate of Depuration

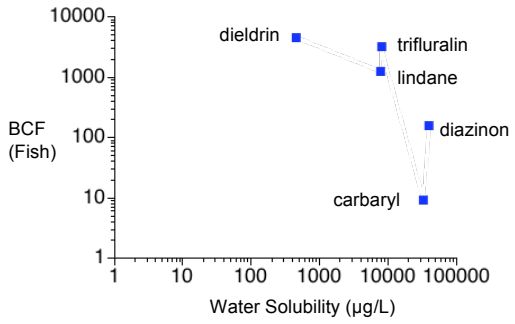
- In other words, chemicals are metabolized at different rates, which will affect their actual BCF or BAF
  - DDT
    - Log Kow ~ 5.7 - 7; Log BCF(water) ~ log 5
  - Permethrin
    - Log Kow ~3 - 6; Log BCF (water) ~ log 2

$$\frac{dC_A}{dt} = k_1 \bullet C_w - k_2 \bullet C_A$$

$$C_{AS} = \frac{k_1}{k_2} \bullet C_w = BCF \bullet C_w$$

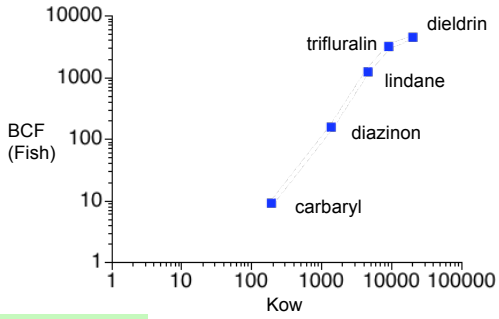
Where,
C_A = concentration in the animal;
C_{AS} = concentration in animal at steady state;
C_w = concentration in water;
k_1 = rate constant for uptake from water (day^{-1});
k_2 = rate constant for elimination from animal (day^{-1}))

Inverse Correlation Between BCF and Water Solubility



Kanazawa (1981)

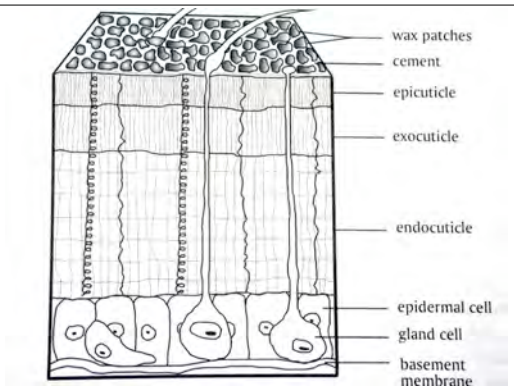
Positive Correlation Between BCF and Kow



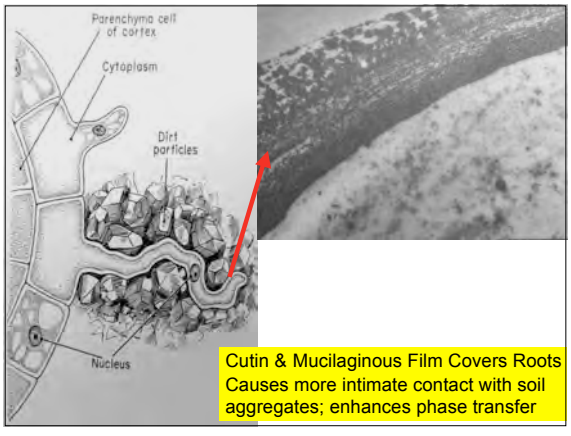
Kanazawa (1981)

Mechanistic Considerations

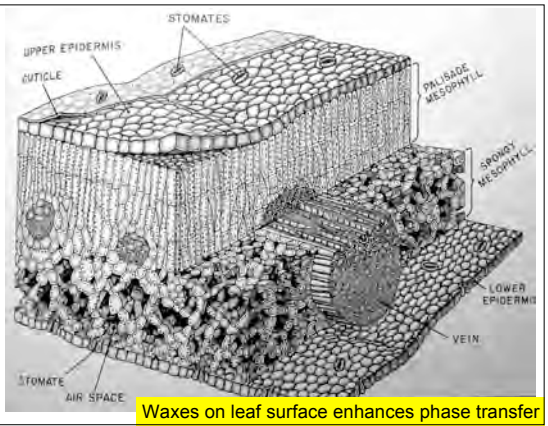
- Waxy layers on invertebrate cuticle & plant leaves
- Mucilaginous layers on plant roots
- Lipid bilayer of cell membranes
- Possible movement along junctions between cells into interstitial spaces
- Gastrointestinal physiology of animals



Wax on Arthropod cuticle enhances phase transfer



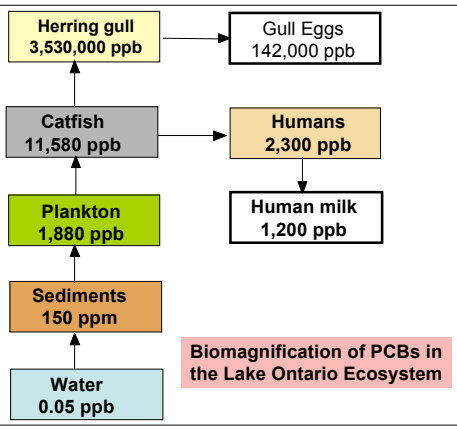
Cutin & Mucilaginous Film Covers Roots
Causes more intimate contact with soil aggregates; enhances phase transfer



Waxes on leaf surface enhances phase transfer

Dazed & Confused

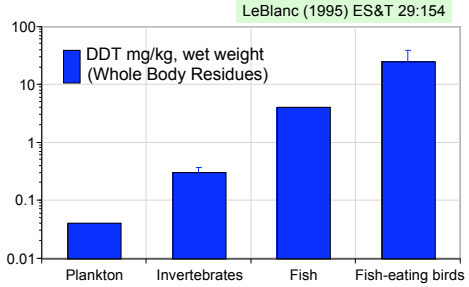
- Probably as a result of early work with DDT, the term biomagnification seems commonly thought to be a major mechanism that explains comparatively higher concentrations of contaminants in organisms from higher trophic levels than in lower levels
- However, biomagnification should be used only when contaminants have bioaccumulated and experiments have proven increasingly higher concentrations in tissues as trophic level increases
  - i.e., food chain magnification



Biomagnification of PCBs in the Lake Ontario Ecosystem

Evidence for Biomagnification
LeBlanc's Analysis of Woodwell et al. 1967

LeBlanc (1995) ES&T 29:154



Note the "consistent" increase in DDT residues from one trophic level to the next

Woodwell's Hypothesis

- DDT and PCBs efficiently ingested and absorbed in association with food
- However, contaminants depurated at a rate slower than the consumption of biomass needed for energy requirements
- Thus, the contaminants are stored in lipophilic tissues at much higher concentrations than occur in the food

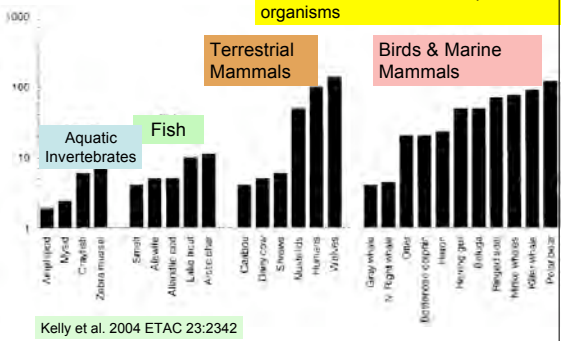
Seminal observations for the hypothesis reported in Woodwell et al. (1967) "DDT residues in an East Coast estuary: A case of biological concentration of a persistent insecticide." Science 156:821-824.

Effect of Trophic Level and Depuration Rate on Biomagnification of a Hypothetical Contaminant

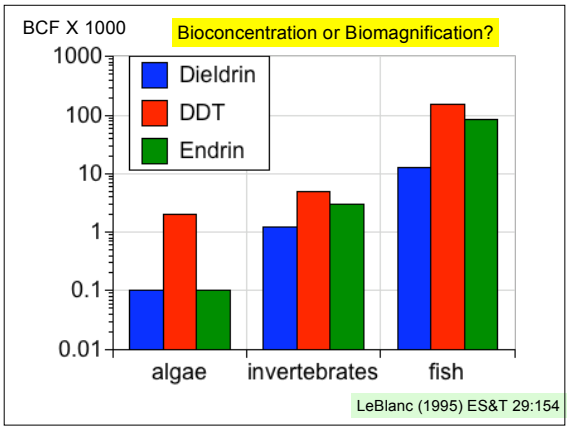
Trophic Level	Daily food Intake as Proportion of Body Weight	Steady-state Concentration for T1/2 (days) of:			Concentration Factors for T1/2 (days) of:		
		10	50	150	10	50	150
1	1.00	1	1	1	-	-	-
2	0.04	0.58	2.9	8.7	0.58	2.9	8.7
3	0.20	0.17	4.2	37.5	0.29	1.4	4.3
4	0.10	0.024	3.0	81.1	0.14	0.72	2.2
5	0.05	0.0017	1.1	87.8	0.07	0.36	1.1

BMF_{max}
(biomagnification factors)

Note the magnitude differences between the terrestrial organisms or marine mammals and the aquatic organisms

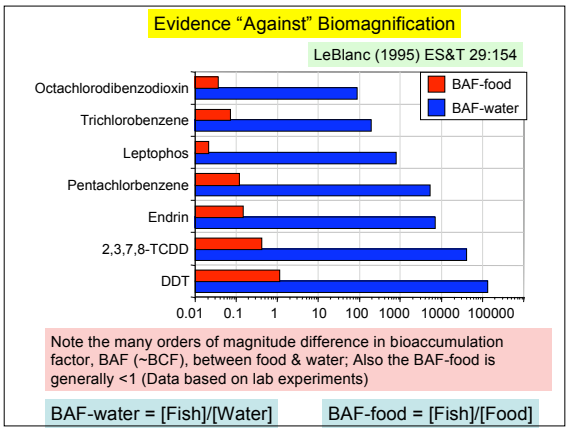


Kelly et al. 2004 ETAC 23:2342



Biomagnification De-Mythified?

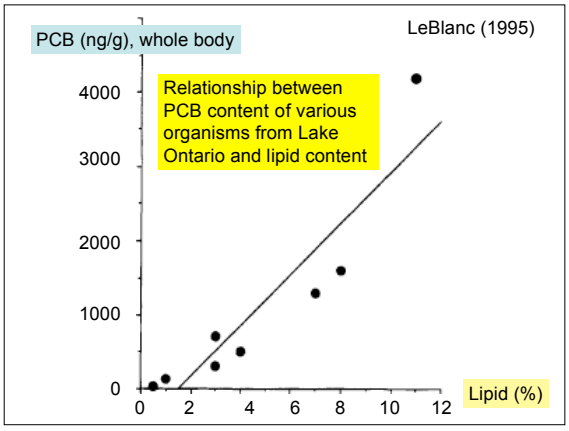
- LeBlanc (1995) argues that lab experiments show few substances actually biomagnify
- Differences in lipophilic contaminant concentration between trophic levels can be explained by lipid content differences from one trophic level to the next
- Larger organisms (fish) have slower depuration rates than smaller organisms (phytoplankton, invertebrates)
- The so-called food chain effect has a low probability of occurrence relative to passive diffusion from the environment
  - Differences in lipid content and depuration among organisms at different trophic levels can account for differences in BCF or BAF

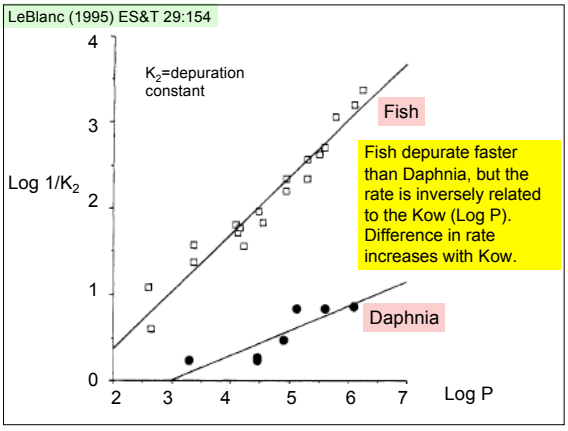


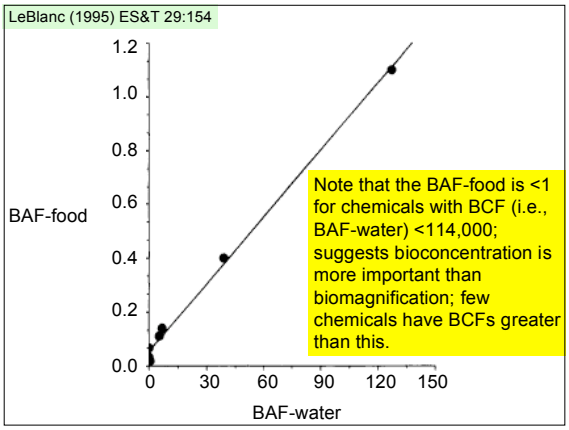
Relationship Between Trophic Level and Lipid Content

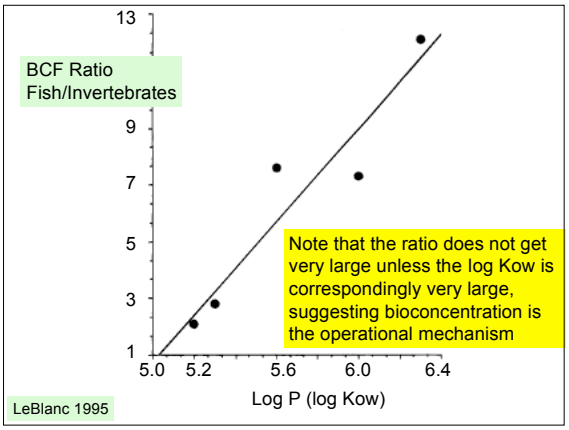
Organism	% Lipid ± StdDev	N (number of organisms)
Phytoplankton	0.5	1
Invertebrates	1.8 ± 0.9	8
Fish	5.4 ± 1.9	10

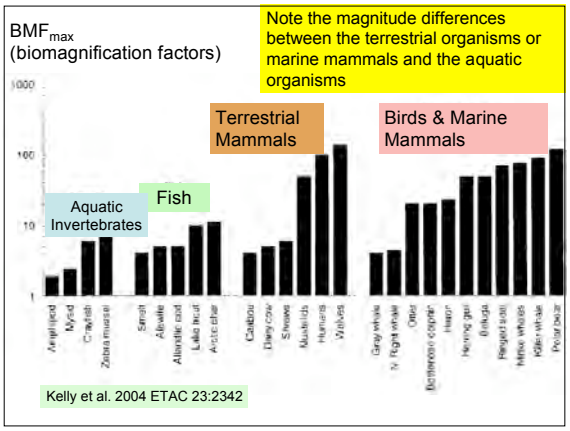
LeBlanc (1995) ES&T 29:154









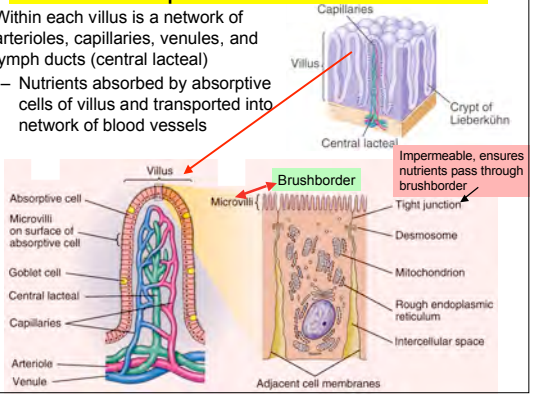


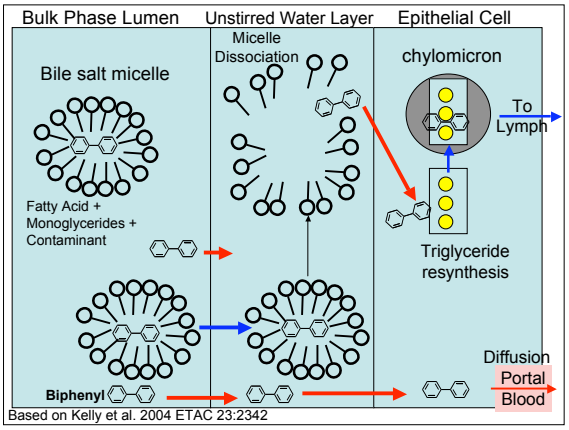
Mechanistic Explanation of Gastrointestinal Uptake of Hydrophobic Contaminants

- Applicable to mammals: bile salt micelles secreted through gall bladder associate with hydrophobic contaminants in gut lumen
  - This mechanism normally isolates monoglycerides and free fatty acids from undigested fat globules
- Micelles move to a water boundary layer near brush border membrane (i.e., gut tissue cell evaginations) with a higher pH than in the lumen
- Micelles break up and contaminant is 'released' close to the cell wall where it diffuses along a concentration gradient into the cell and from there the general circulation

Intestinal Epithelium: Brush Border

- Within each villus is a network of arterioles, capillaries, venules, and lymph ducts (central lacteal)
  - Nutrients absorbed by absorptive cells of villus and transported into network of blood vessels

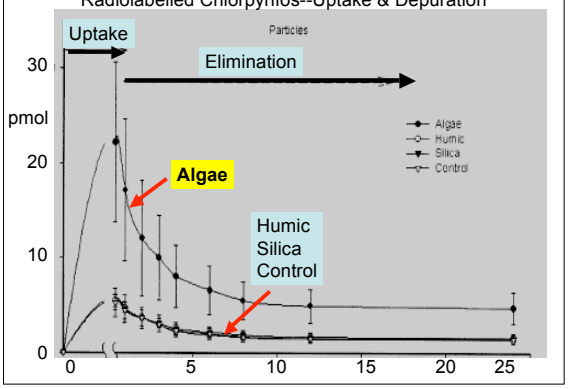




Bioavailability

- The fraction of the contacted dose that is transferred from the site of contact (or administration) into the general circulation or tissues
- In soil and/or water, because of sorption of contaminants to particulate matter, not all of the chemical present will be taken up (or cross the integument of the organism)

Bivalve Clams Feeding on Different Particulates Containing Radiolabelled Chlorpyrifos--Uptake & Depuration



Bioavailability of Metals

- Many metals occur as cations in soil and water
  - Thus metals can bind intensely to soil or sediment particles, especially if they are rich in clays
  - Binding makes them less bioavailable than just an elemental analysis of total concentration would suggest
- Note however, that as concentration of metal in soil/water goes up, BCF would not go up (it may decrease
  - Reason: metals have specific membrane transport systems such as carrier proteins