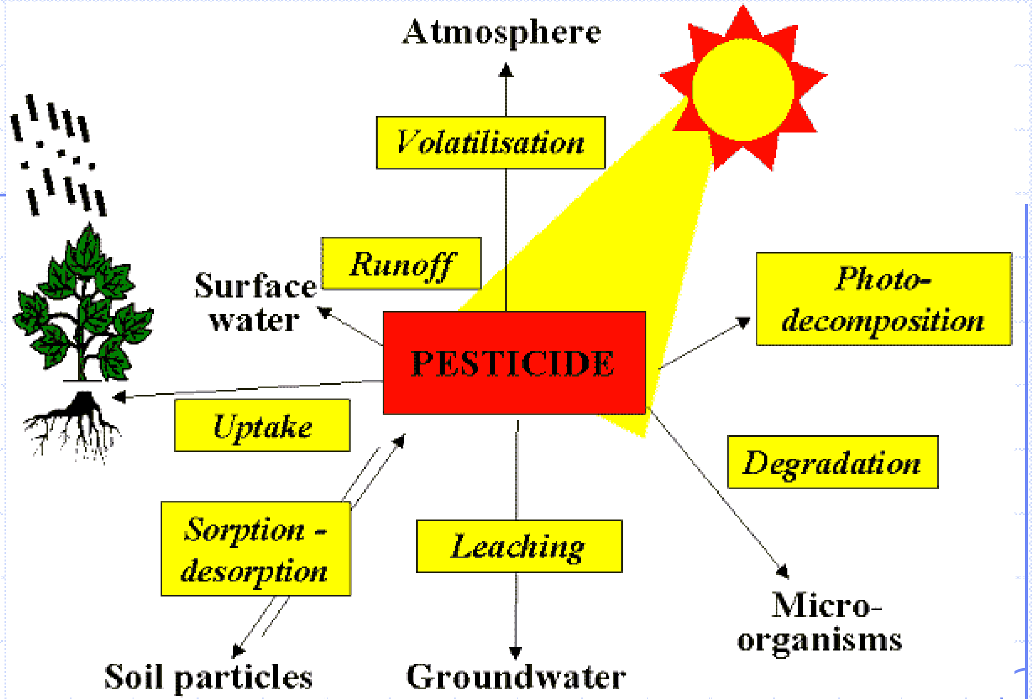
Pesticide Fate and Transport

(a.k.a. Where do pesticides go in the environment?)



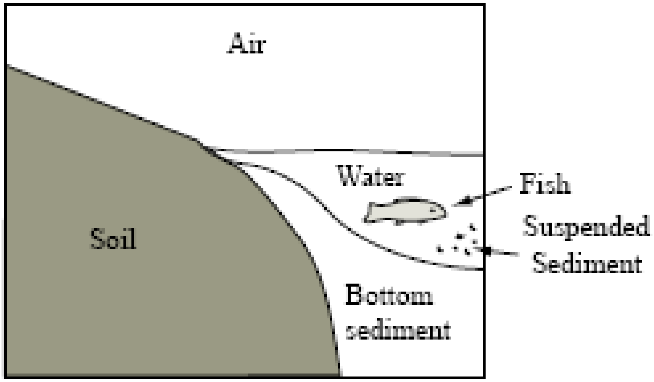
Jay Davis - U.S. Fish & Wildlife Service
ECS 3119 – Pesticides and Fish and Wildlife Resources
Stevenson, WA
June 27-July 1, 2011

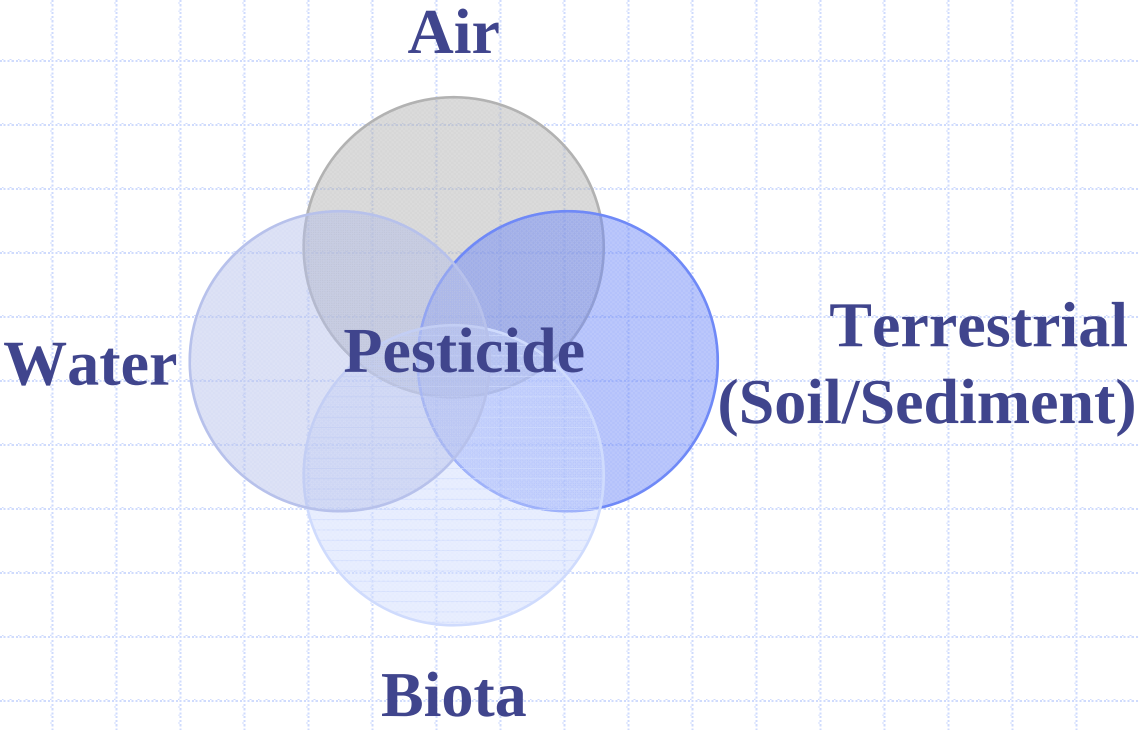
Fate and Transport

- Where and how does a pesticide move in the environment?
  - Major routes of transport
  - Major environmental compartments in which the pesticide resides

Pesticides in the Environment

- Housed in one of 4 major environmental compartments.

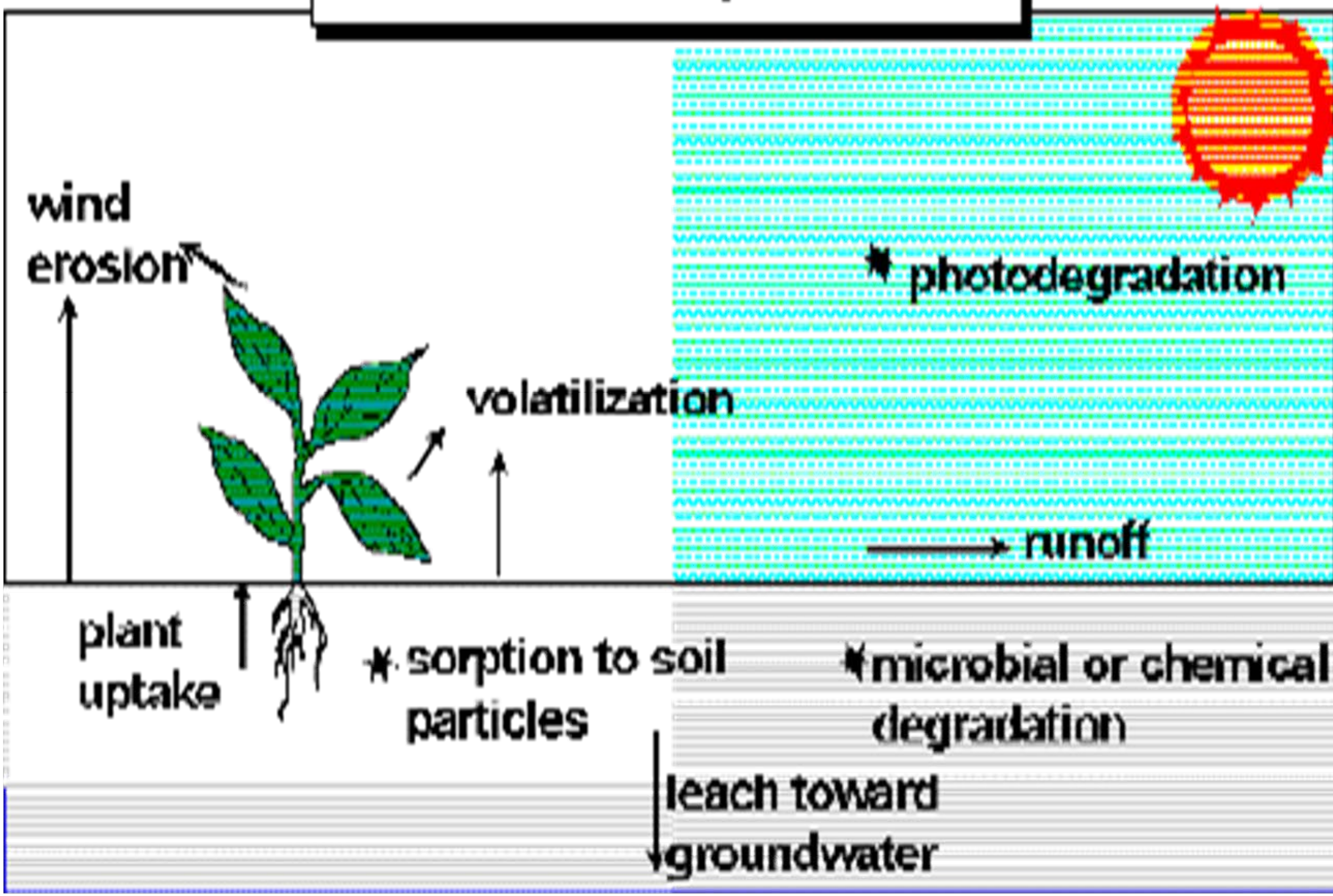




Fate and Transport Processes

- Abiotic and biotic processes within a system
- Pesticides move and reside in a predictable manner based on their physical and chemical properties

Pesticide fate processes

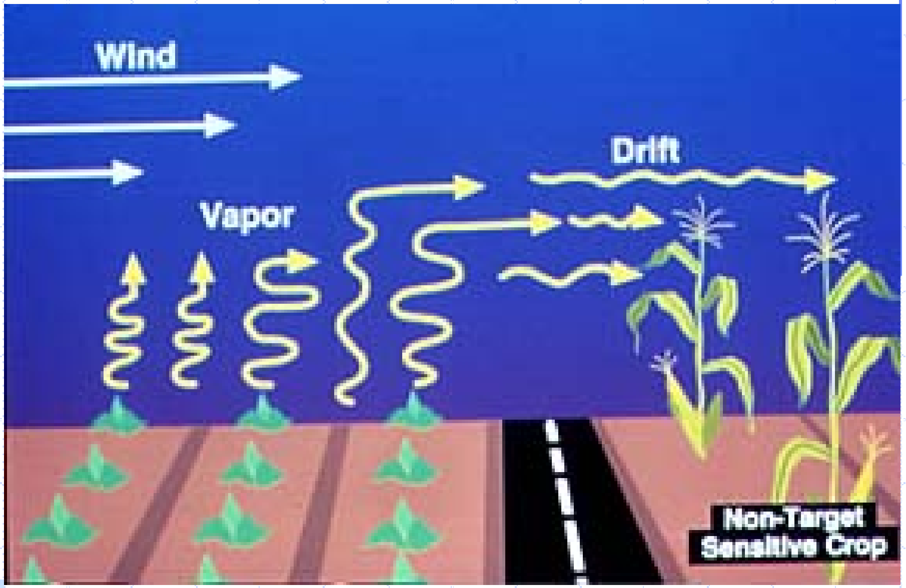


Major Determinants of Pesticide Transport

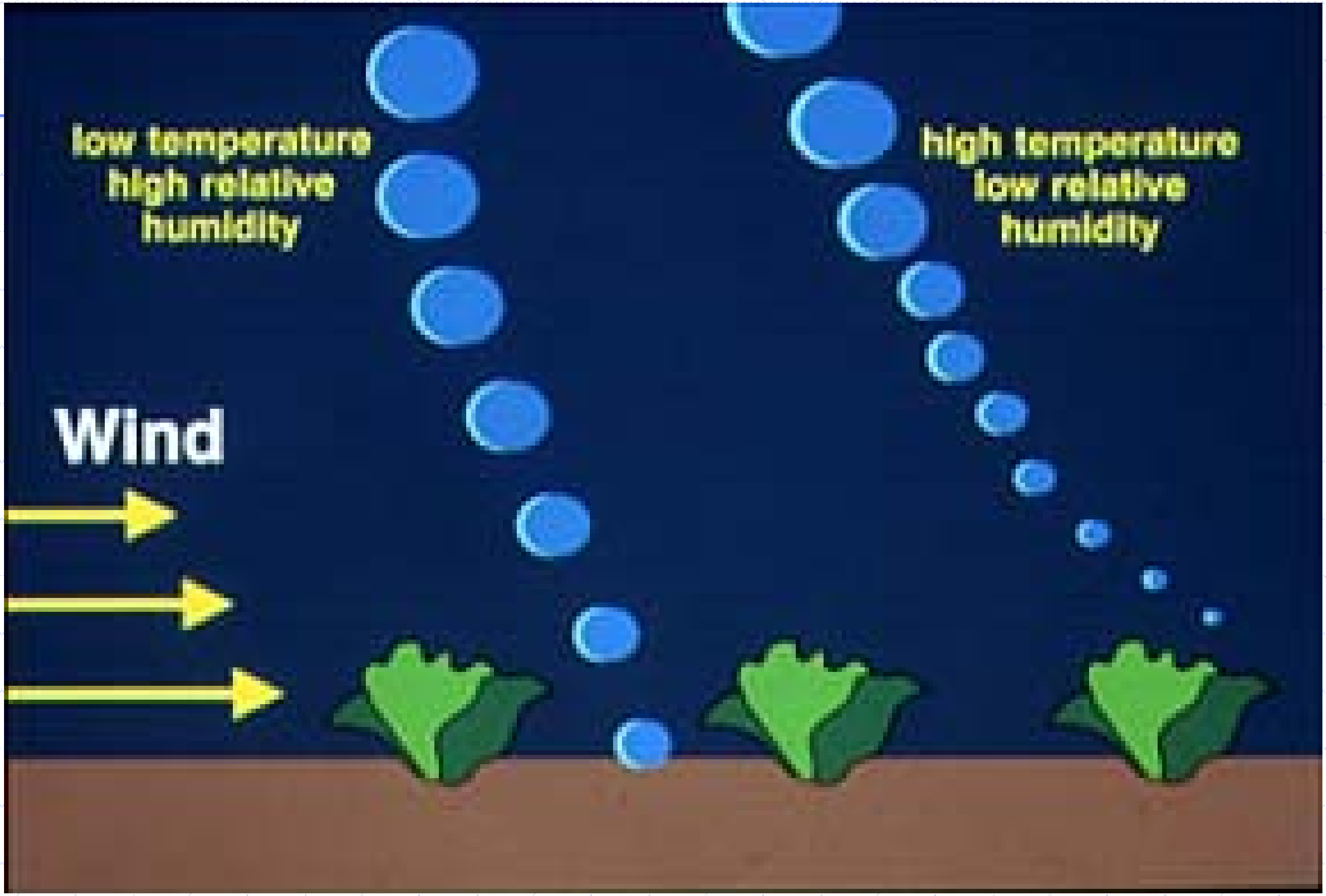
- **Pesticide Application Methods**
  - **Form**: End-use product; major formulations; adjuvants; tank mix
  - **Application**: Maximum proposed rate; frequency; and timing; method

AERIAL DRIFT

APPLICATION FACTORS/CONDITIONS INFLUENCING DRIFT



- high application height
- droplet sizes <200 µm
- high winds
- lack of thatch or vegetative cover
- high wind shear or pressure &/or small droplet size


low temperature
high relative
humidity
high temperature
low relative
humidity
Wind

Drift from Broadcast Methods: Fixed Wing > Helicopter>Air blast> Chemigation>Ground Spray

Drift is typically 15x greater at 25 ft from treatment site by fixed wing vs. ground boom

Major Determinants of Pesticide Transport (cont.)

- **Site Characteristics**
  - **Site description**: geographic/physical location, landscape/watershed location, slope/gradient, overall topography and hydrology
  - **Soil characteristics**: physical/chemical properties, description, classification
  - **Weather**: temperature, precipitation and irrigation (historical, actual), overall climate
  - **Management**: crops grown, pesticide usage (especially similar pesticides), crop/agronomic management history
  - **Catastrophic events**: prone to flooding or fire

Major Properties that Determine Fate

- **Physicochemical Properties**
  - Solubility (Water)
  - Volatility (Air)
  - Adsorption/Leachability (Water/Soil/Sediment)
  - Partitioning/Bioaccumulation (Biota & Soil)
  - Persistence/Degradation/Dissipation (All)

Connectivity of Aquatic Landscapes

Persistence/Degradation/Dissipation

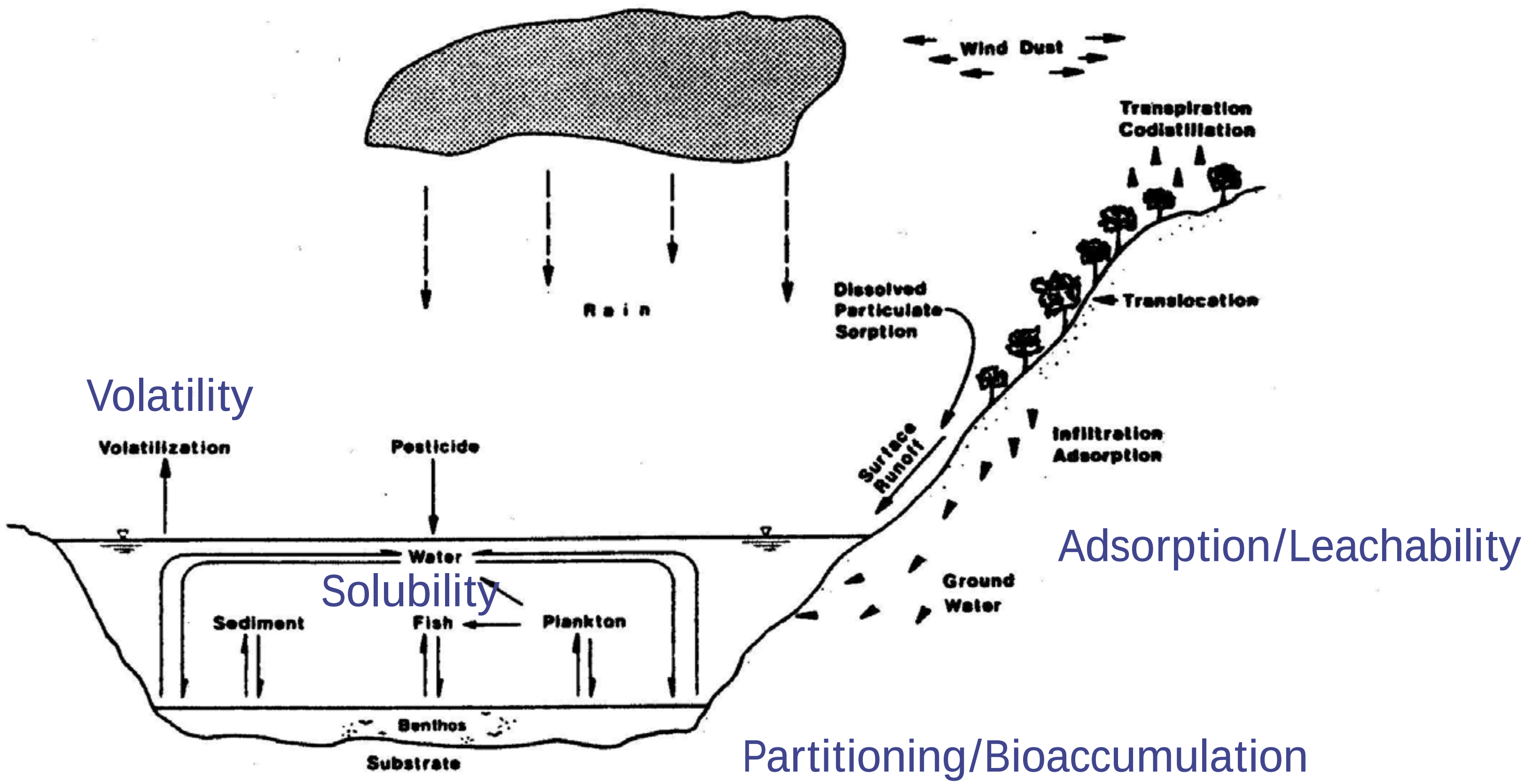


Figure 1 Movement of pesticides into and through aquatic ecosystems.

Solubility: a pesticide’s ability to dissolve in water

Mobility Class	**Water Solubility (ppm)**	**Examples (ppm, mg/L)**	
Very High	3,000 – 1,000,000	Diquat	700,000
High	300 – 3,000	2,4-D	890
Medium	30 - 300	Carbaryl	40
Low	2 - 30	Parathion	24
Slight	0.5 - 2	Ethion	1
Immobile	<0.5	DDT	0.0012

Solubility – Mobility Relationship

Low solubility ~ immobility ~ hydrophobic

High solubility ~ mobility ~ hydrophilic

Insoluble: < 0.1 ppm

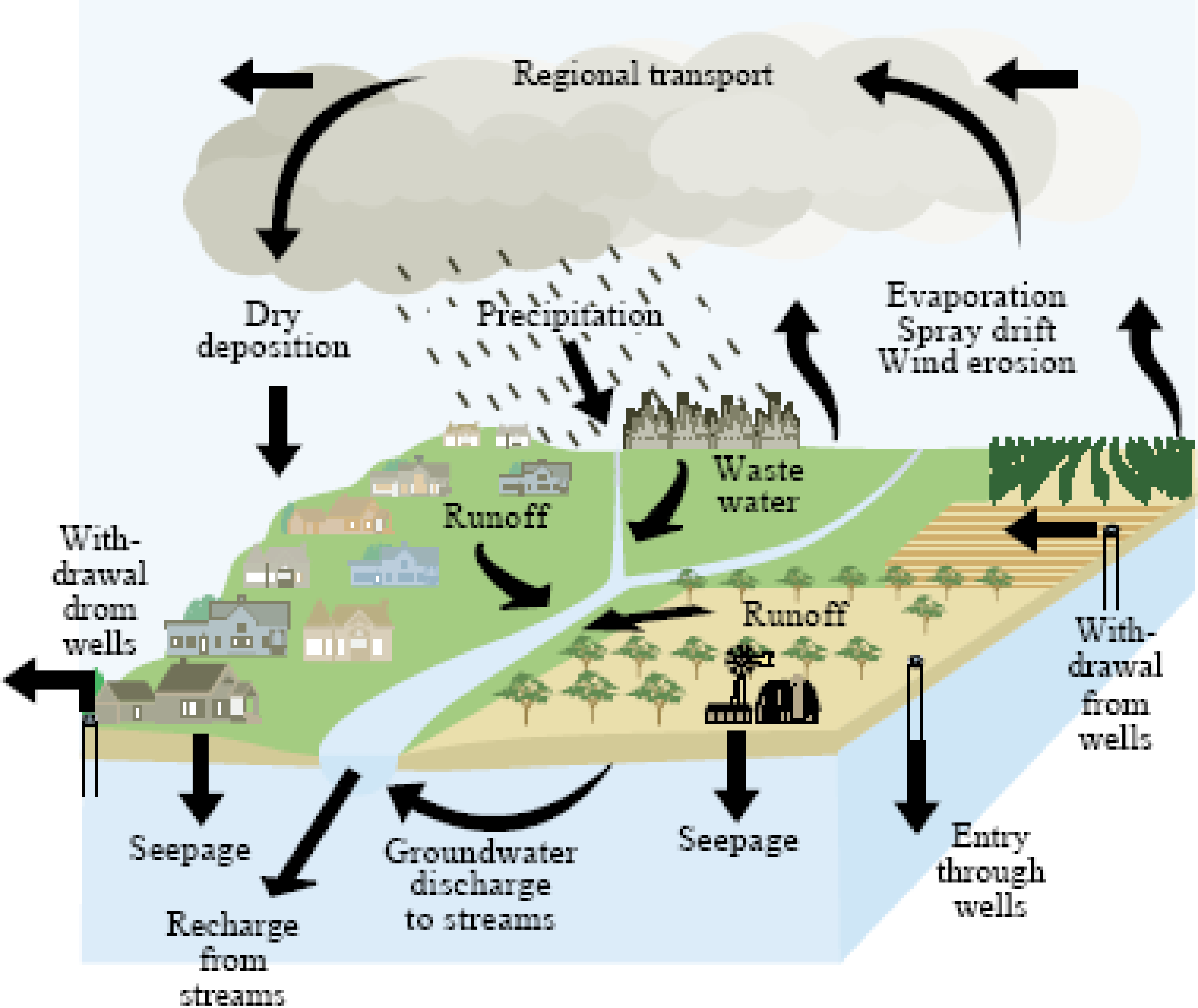
Moderately soluble: 100 to 1,000 ppm

Very soluble: > 10,000 ppm

Factors that Affect Runoff to Surface Waters of Soluble Pesticides

- ***high rainfall or storm events***
- ***no/sparse vegetation***
- ***heavy irrigation***
- ***saturated soil***
- ***non-pervious soils***
- ***sloped topography***
- ***soil disturbances***

- ***no or low rainfall***
- ***vegetated buffer (grass>shrubs>trees)***
- ***moist soil***
- ***pervious soils***
- ***no or low slope***
- ***no soil disturbances***



Pesticide movement in the hydrological system (Barbash and Resek 1996).

Temperatures Influence on Solubility

- Effects on chemical behavior:

No single pattern, change T in a given direction may ↑, ↓, or not change toxicity, but…

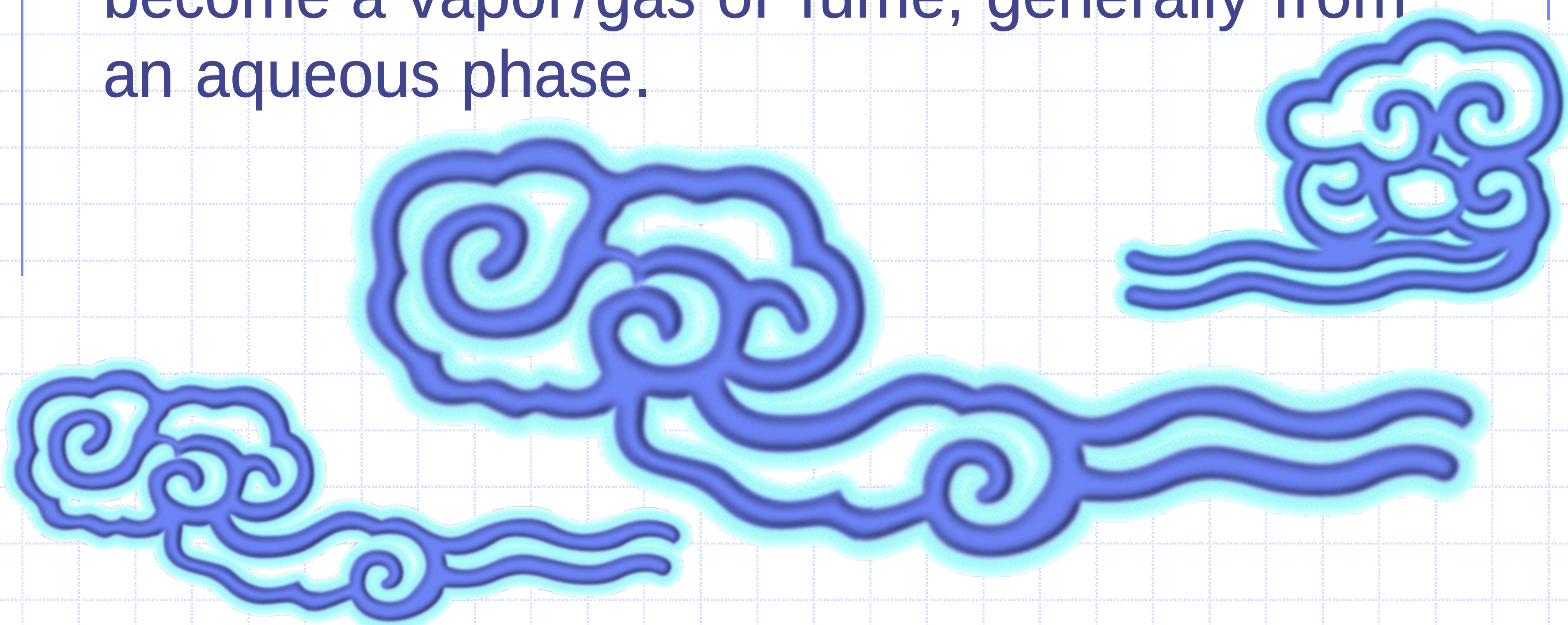
As T ↑, biodegradation usually ↑

As T ↑, solubility of organics ↑

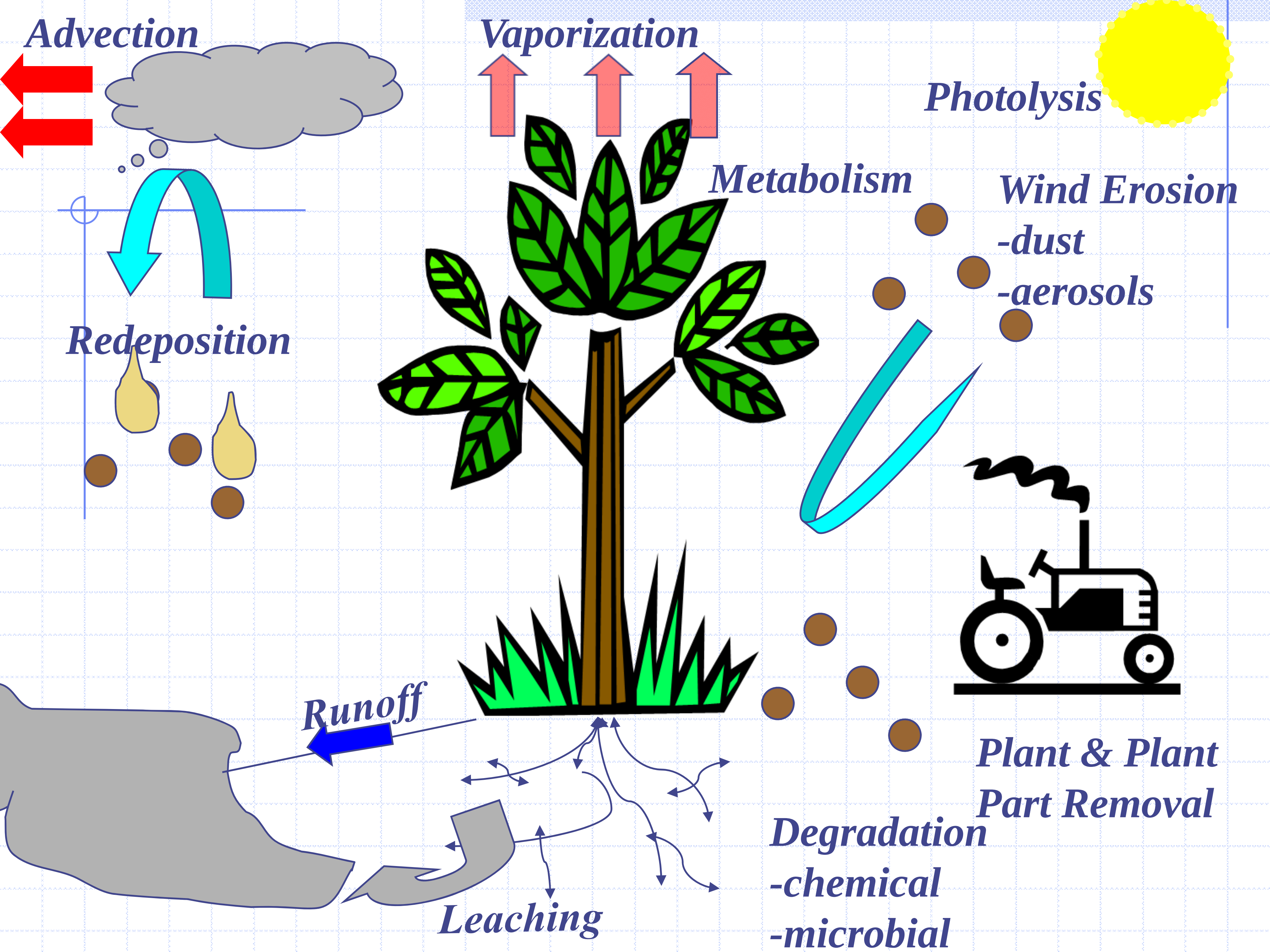
T ↑ generally ↑ toxicity if there is an effect

Volatility

- The ability to transform into a gaseous state, become a vapor/gas or fume, generally from an aqueous phase.



Fugacity: A measure of the tendency of a substance, often a fluid, to move from one phase to another or from one site to another.


Advection
Vaporization
Photolysis
Metabolism
Wind Erosion
-dust
-aerosols
Redeposition
Runoff
Plant & Plant
Part Removal
Degradation
-chemical
-microbial
Leaching

FACTORS FAVORING VOLATILIZATION OR AERSOL FORMATION OF COMPOUNDS

Highly Volatile:

Trifluralin

Atrazine

Butylate

Quinclorac

Esters of 2,4-D, MCPA & Triclopyr

Bensulide

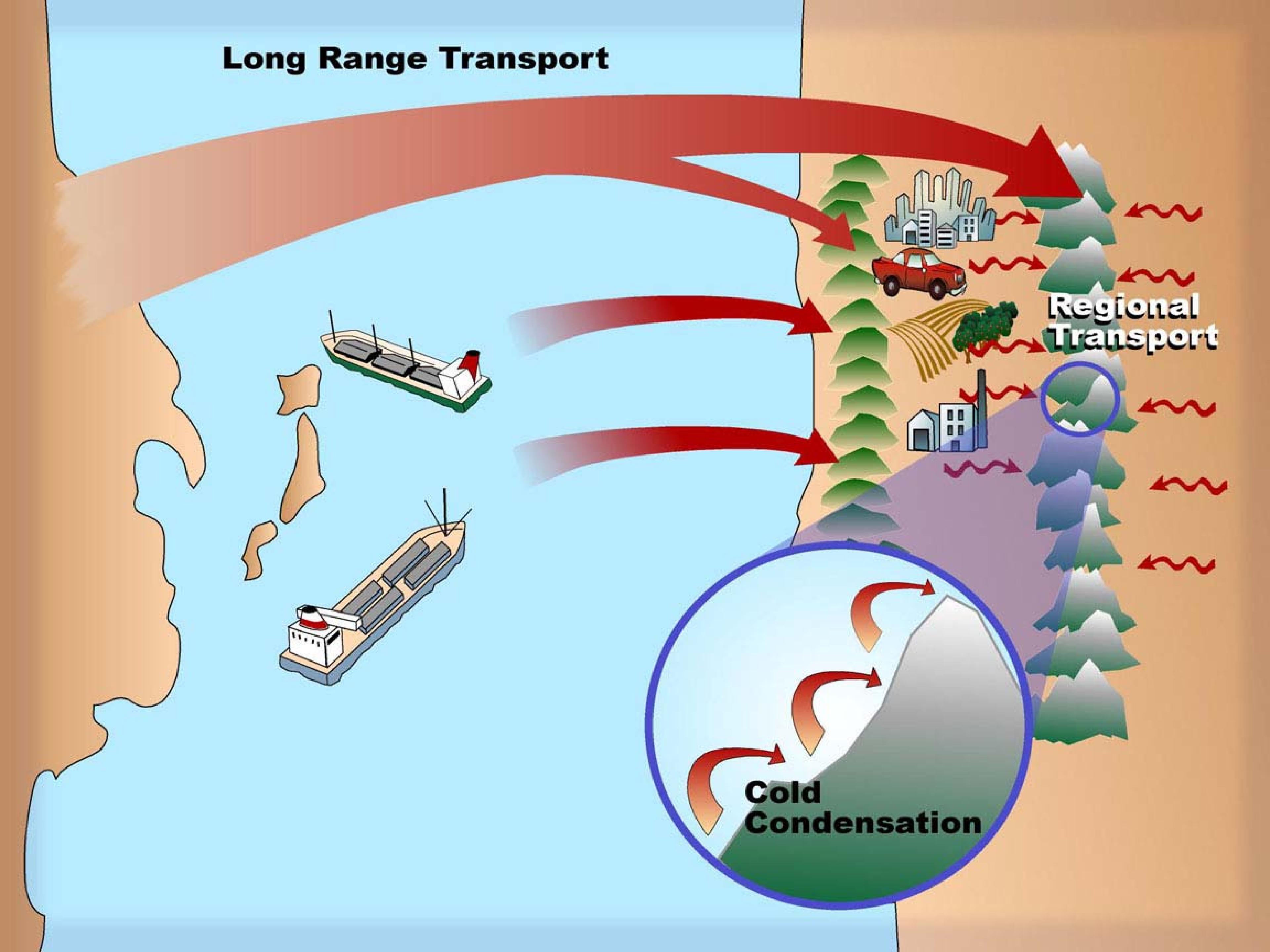
1,3 Dichloropropene

- high H, VP
- low solubility
- low specific gravity
- low boiling point
- high air/soil temperature
- low humidity
- fine, powdery soils
- high winds
- lack of thatch or vegetative cover
- high application height
- droplet sizes <200 µm
- high wind shear or pressure &/or small droplet size

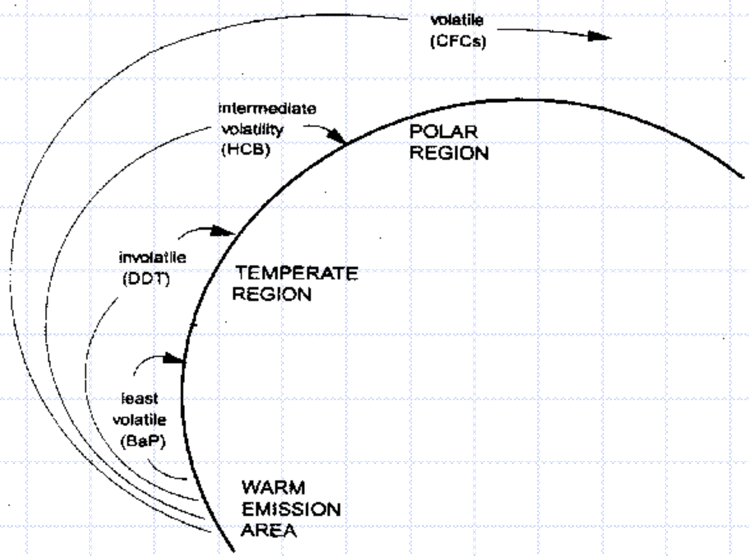
Tendency to Vaporize based on Vapor Pressure Index (=VP*10^7)

- <10 = low
- 10-1000 = moderate
- >1000 = high

Henry's Law Constant (H or HLC) = VP/S


Long Range Transport
Regional
Transport
Cold
Condensation

Global Long-Range Transport and Deposition



Global Distillation Depends On:

- Volatility (Vapor Pressure, Henry's Law Constant)
- Hydrophobicity (K_{ow})
- Persistence in the Atmosphere (half-life > 2 days)

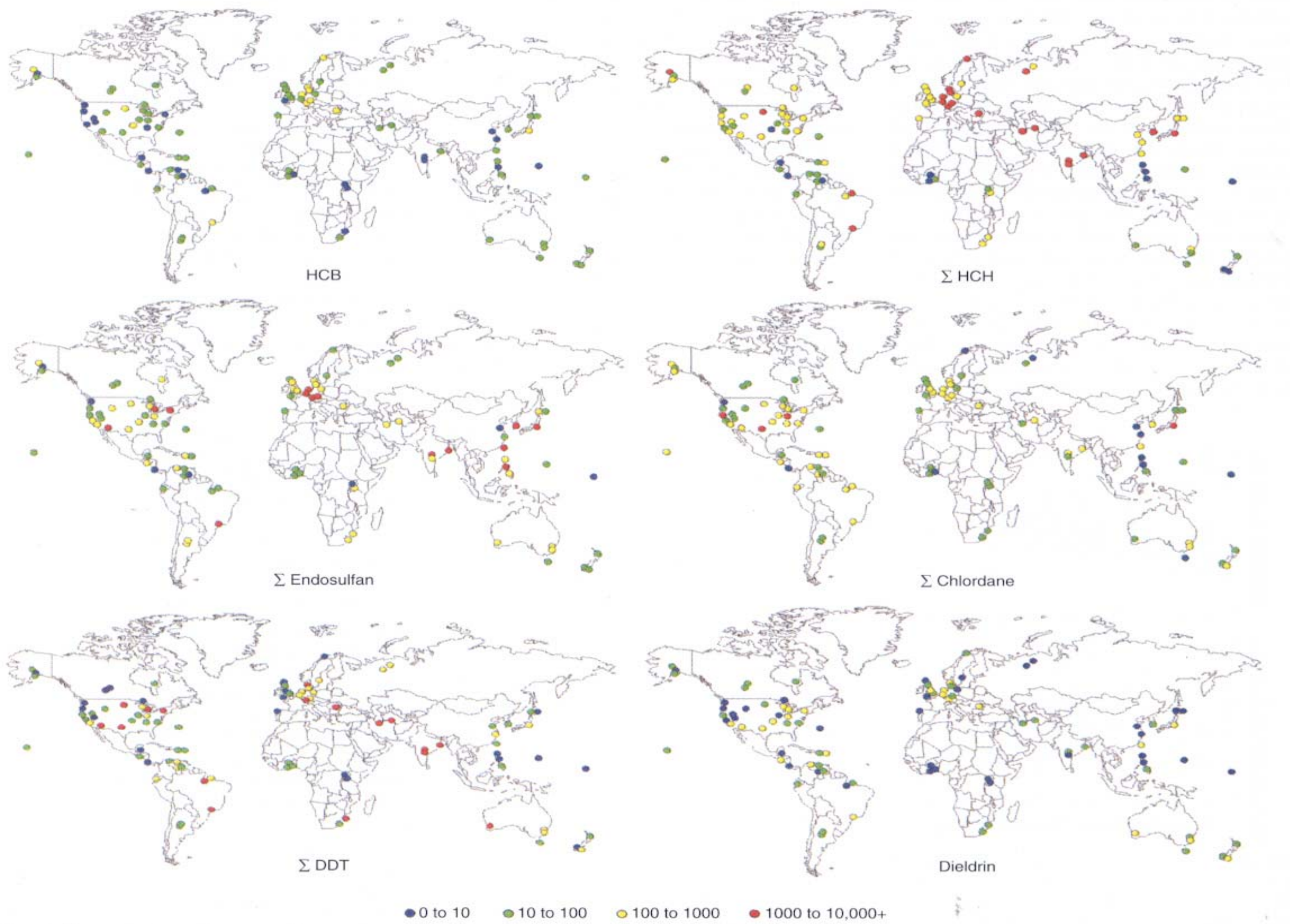
Wania, F. and Mackay, D. *Ambio* **1993**, *22*, 10-18

Global Importance of Semi-Volatile Organic Compounds

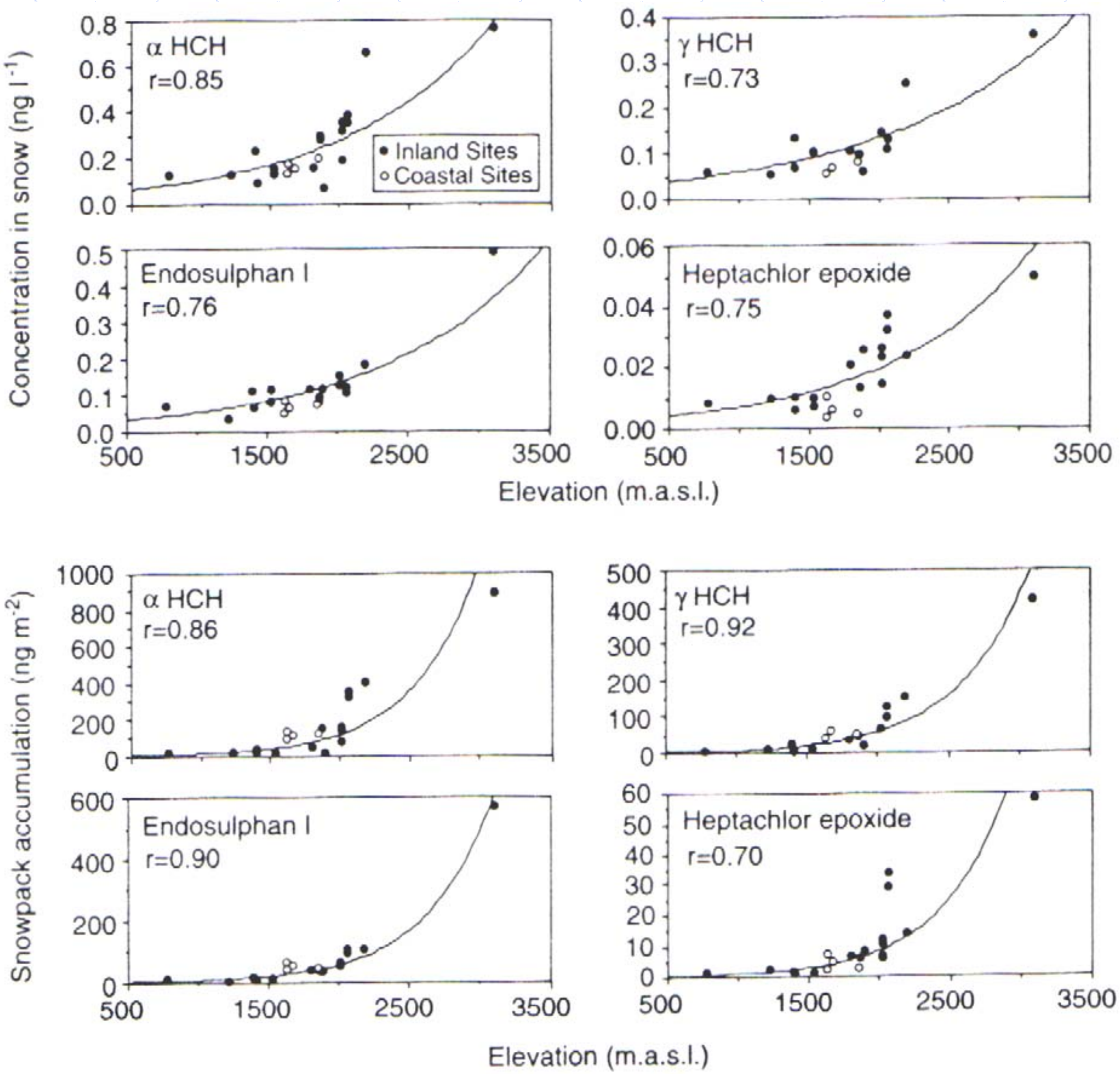
- Wide range of phys-chem properties (VP, K_{ow}, HLC) and biodegradability. Vapor pressure less than 10 Pa.
- Potential to partition to/from all environmental compartments (including biota and humans)
- Products of incomplete combustion (PAHs, PCDD/F) and industrial activities (PCBs), **pesticides (DDT, Lindane),** and commercial products (fragrance materials)
- Historical **(OC pesticides like DDT)** and current use (Polybrominated diphenyl ethers and perfluorinated chemistries) compounds

➢ New focus on volatilization to the atmosphere, atmospheric fate and transport, and deposition from atmosphere to aquatic and terrestrial ecosystems worldwide.

Global Distribution of Pesticides in Tree Bark

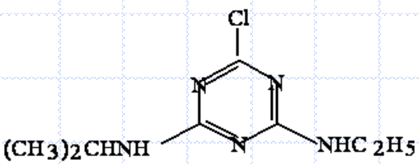


Regional Deposition: Canadian Rockies

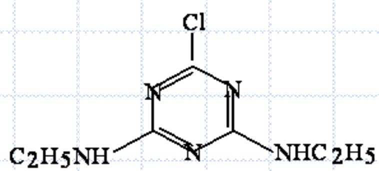


Blais, J.M., et al *Nature* **1998**, *395*, 585-588.

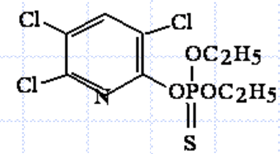
Growing Evidence: Long Range Transport of Current Use Pesticides



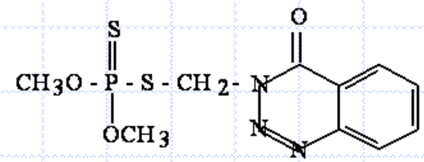
Atrazine



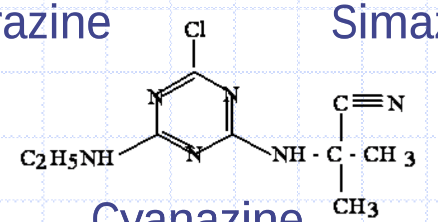
Simazine



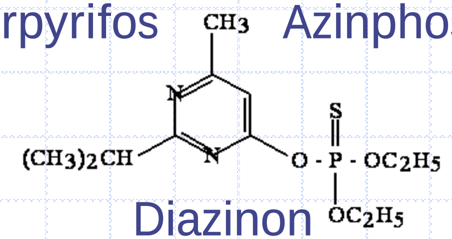
Chlorpyrifos



Azinphos-methyl



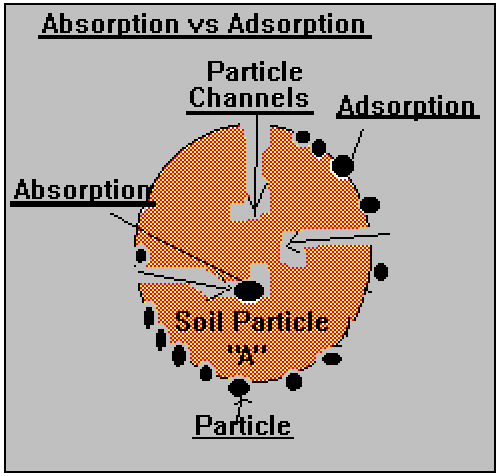
Cyanazine



Diazinon

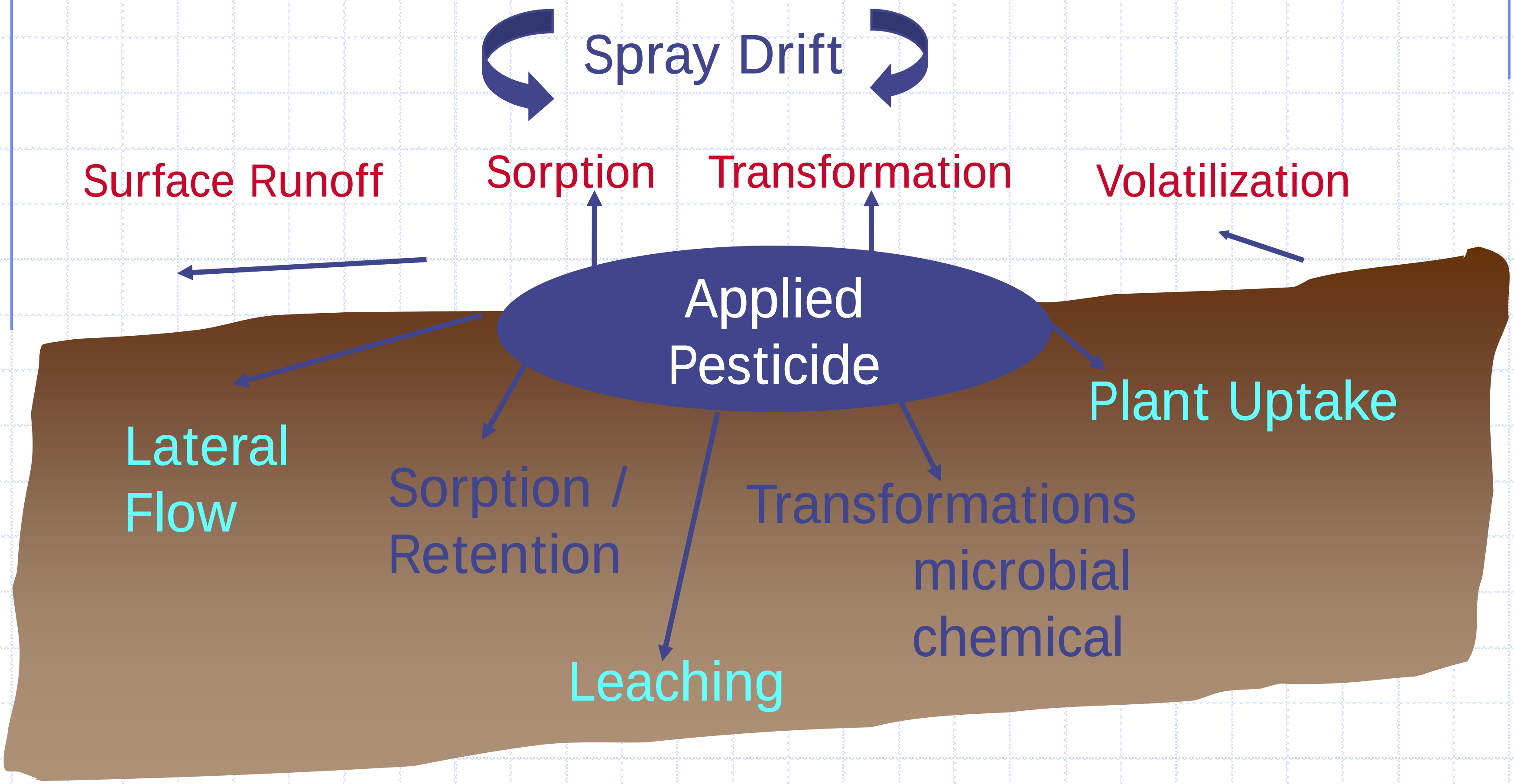
- Less persistent, less volatile, less hydrophobic than traditional organochlorine pesticides
- Important to also look for atmospheric degradation products
- Atmospheric transport during use periods (April – September)
- Markers for North American (regional) sources

Adsorption



- Process by which a pesticide is bound/adhered to a surface via chemical or physical attraction
  - **Kd = DISTRIBUTION COEFFECIENT:**
    concentration of chemical sorbed to soil/ concentration in aqueous solution
    High Kd=pesticide more strongly sorbed to soil
    Low Kd = pesticide more in solution
- An indication/measure of a pesticide's leachability
  - **Leachable** – the ability of a pesticide to dissolve & move through soils generally via the process of percolation by water.

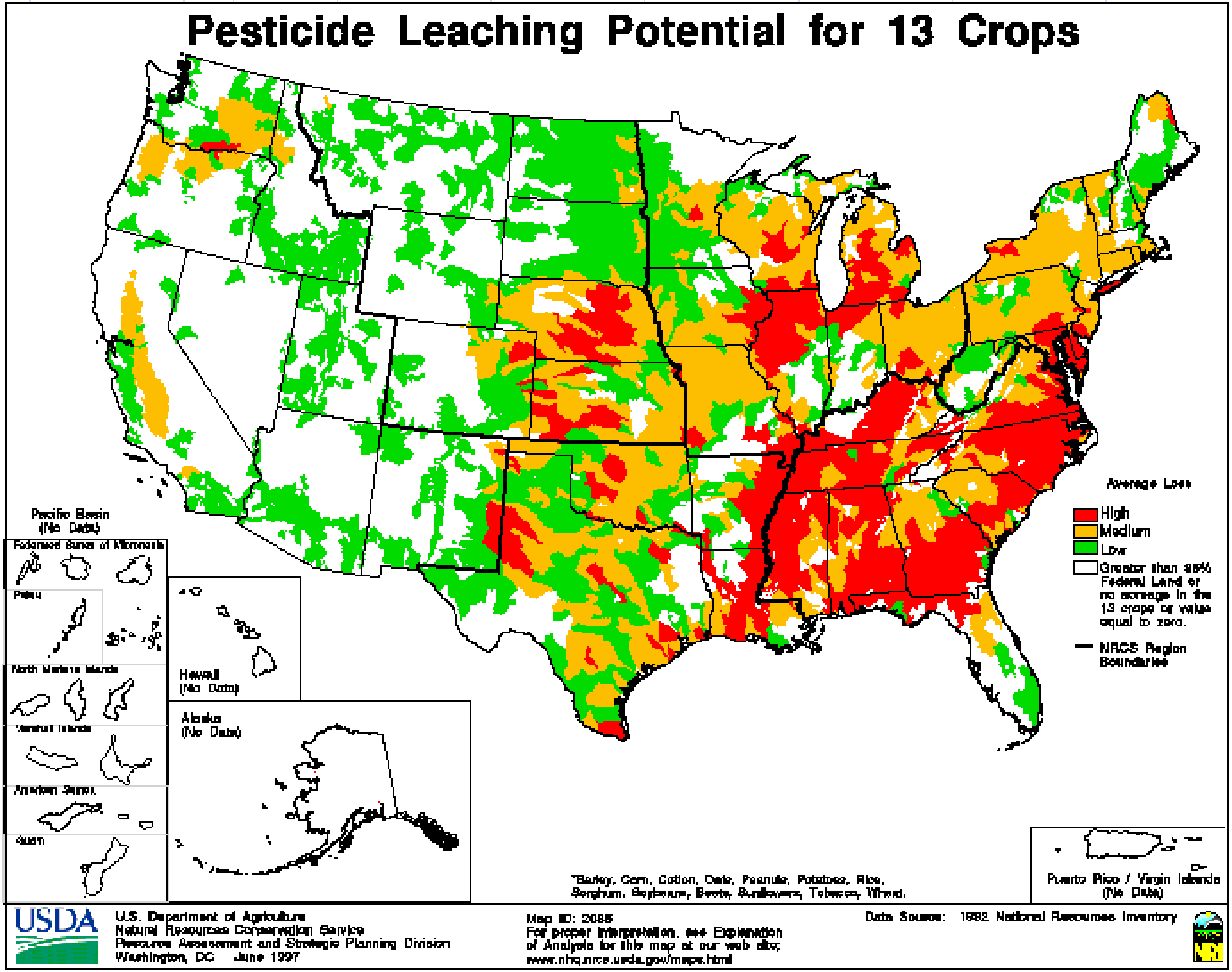
Conceptual Model



Leachability of Various Soil Types

Gravel > Sand > Sandy Loam > Loam > Silty Loam > Silt > Clay > Peat

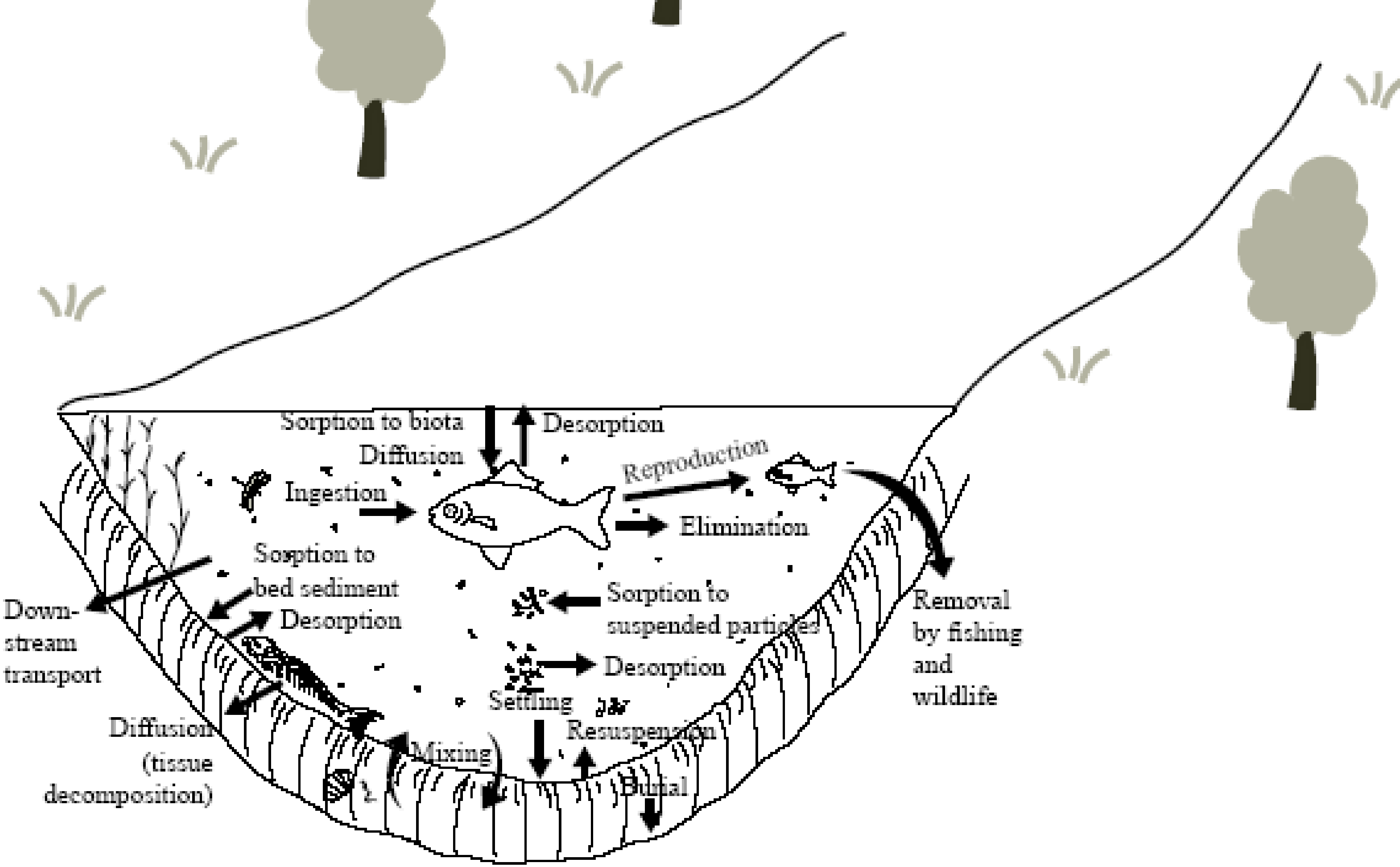
Soil Type	**Grain Size**
Clay	<2 µm
Silt	2 to 50 µm
Sand	50 – 2000 µm
Gravel	>2000 µm



http://www.nrcs.usda.gov/technical/land/meta/m2085.html

Partitioning

- **K_{oc}** - Organic carbon-normalized partitioning coefficient: a measure of a pesticide's differential solubility between the sediment and interstitial (pore) water. [adsorption to organic matter]
- **K_{ow}**- Octanol/water partitioning coefficient: a measure of the pesticide's differential solubility in organic (octanol) and aqueous (water) solutions. [absorption in lipid]



Pesticide movement to, from and within sediment and aquatic biota in surface waters (Nowell et al. 1999)

Qualitative Mobility Assessment Based on K_{oc}

ASTM recommendations (ASTM, 1996)

K_{oc}	Mobility Class
0 - 50	very high
50 - 150	high
150 - 500	medium
500 - 2000	low
2000 - 5000	slight
5000 +	immobile

Log K_{oc} is used as an indication of a chemical's tendency to leach

Classification of Chemical Mobility in Soil

Mobility Class	Example	K_{oc} in Soil
Very High	Ethylene dibromide	32
High	Monuron	83
Medium	Atrazine	170
Low	Lindane	1,300
Slight	Trifluralin	3,900
Immobile	Parathion	10,000
	Chlorpyrifos	14,000
	DDT	240,000

High K_{oc} ~ immobile in soil ~ low leachability

Low K_{oc} ~ mobile in soil ~ high leachability

Octanol-Water Partition Coefficient

K_{ow}– ratio of a compound's solubility in n-octanol and water at equilibrium (on a log scale)

The log Kow is used as an indicator of a chemical's tendency to bioaccumulate

...so if DDT was dissolved in a beaker of equal volumes octanol and water and you measure:

3 micrograms / liter in the water phase and

3 grams / liter in the octanol phase...

K_{ow}– ratio of solubility in n-octanol and water at equilibrium (on a log scale)

DDT:

3 micrograms / liter in the water phase and

3 grams / liter in the octanol phase...

= 3,000,000 micrograms / liter

K_{ow} = log ([DDT in octanol] \ [DDT in water])

= log (3,000,000 / 3)

= log (1,000,000)

= 6

K_{ow} for DDT = 6.19

Application:

So if DDT is highly lipophilic (K_{ow} = 6.19), which of the following would likely be the best to measure to document avian exposure to DDT?

A) feathers

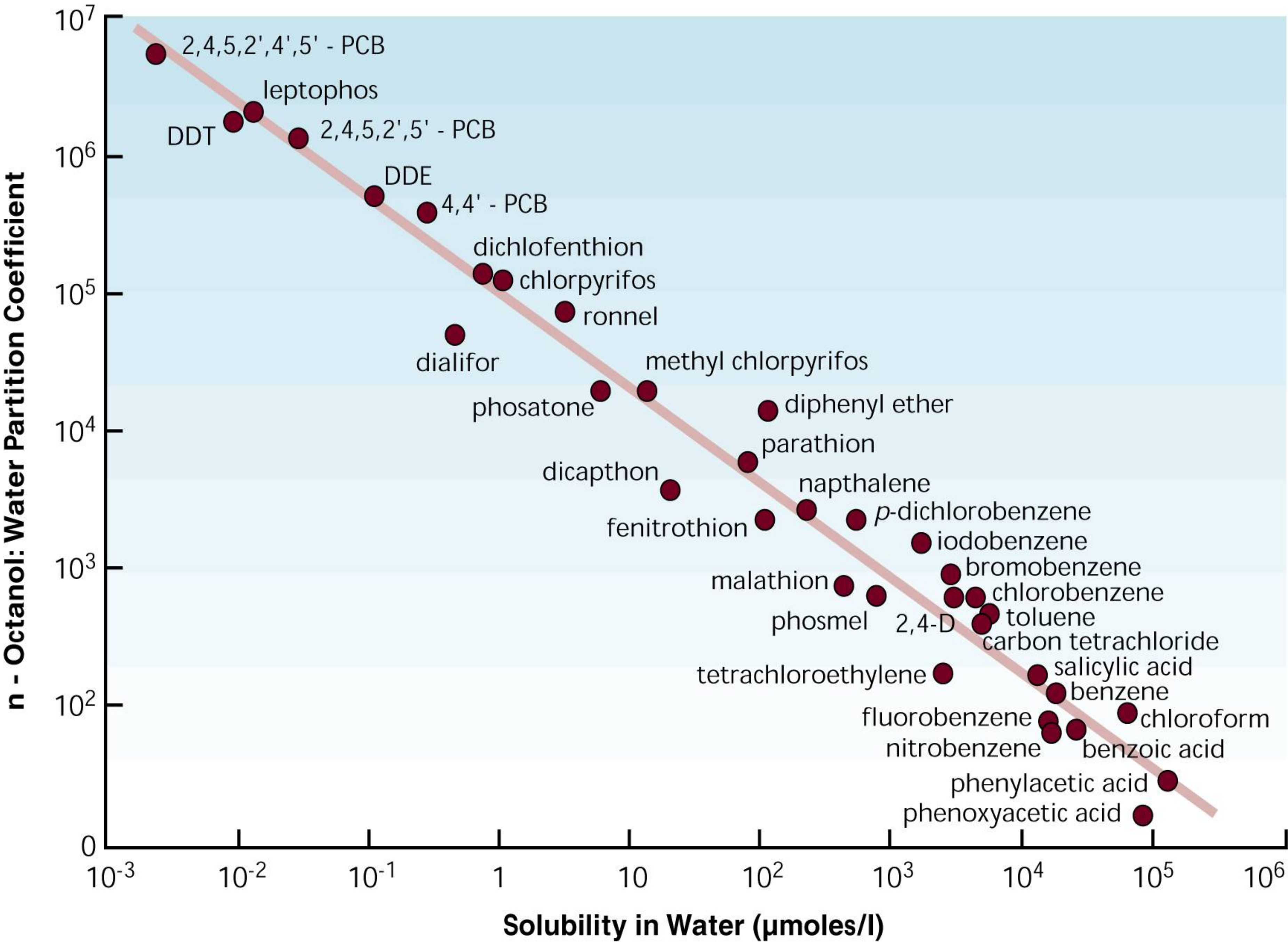
B) adipose

C) excreta (uric acid)

K_{ow}s for a Few Pesticides

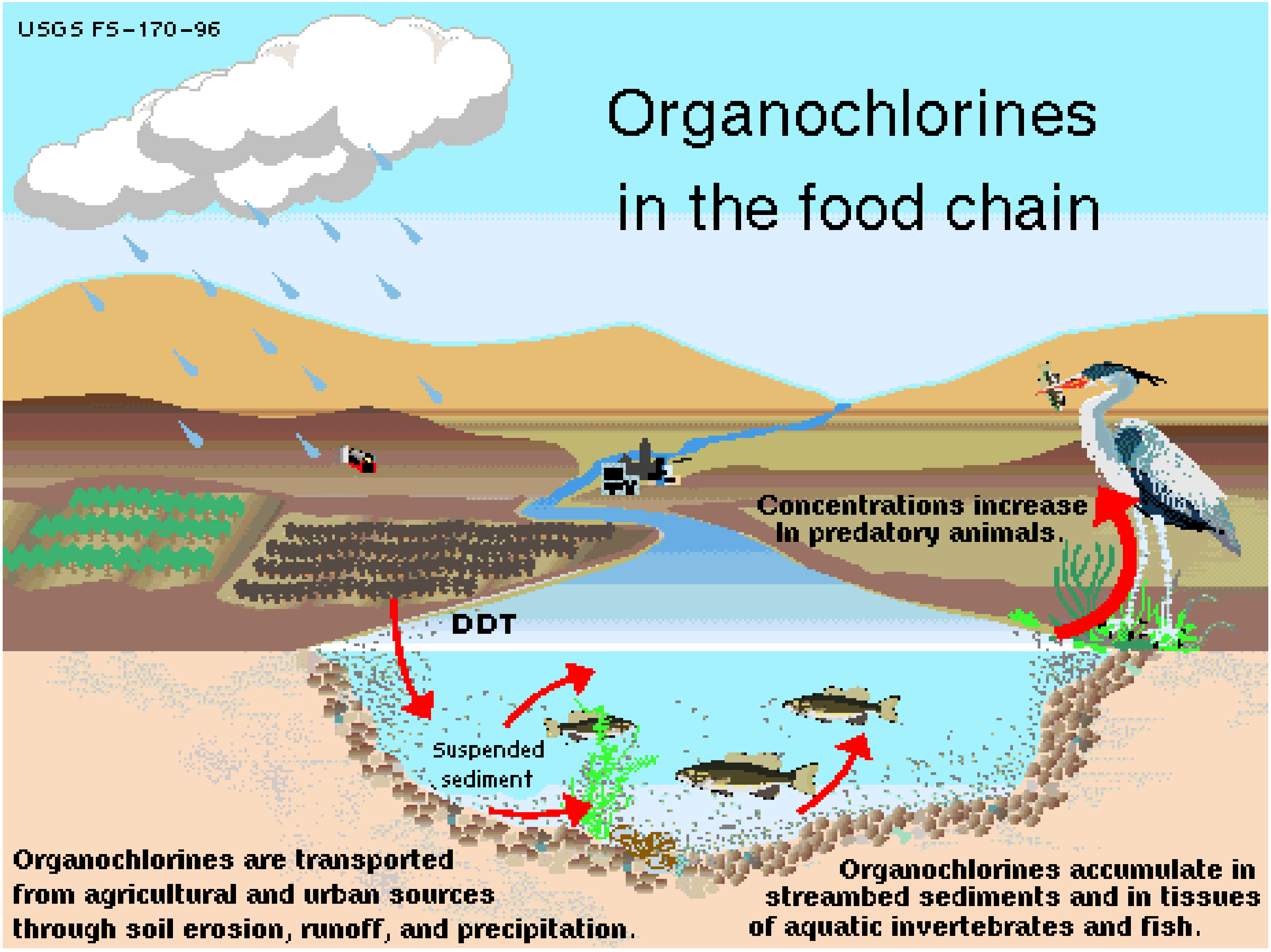
Pesticide	**K_{ow}**	**Log K_{ow}**
parathion	~1,000 : 1	3.8
chlorpyrifos	~50,000 : 1	4.7
DDT	>1,000,000 : 1	6.2

High log K_{ow} ~ more hydrophobic ~ more bioaccumulative
Low log K_{ow} ~ more hydrophilic ~ less bioaccumulative


n - Octanol: Water Partition Coefficient
Solubility in Water (µmoles/l)
10^7
10^6
10^5
10^4
10^3
10^2
0
10^-3
10^-2
10^-1
1
10
10^2
10^3
10^4
10^5
10^6
2,4,5,2',4',5' - PCB
leptophos
DDT
2,4,5,2',5' - PCB
DDE
4,4' - PCB
dichlofenthion
chlorpyrifos
ronnel
dialifor
methyl chlorpyrifos
phosatone
diphenyl ether
parathion
dicapthon
napthalene
p-dichlorobenzene
fenitrothion
iodobenzene
bromobenzene
malathion
chlorobenzene
toluene
phosmel
2,4-D
carbon tetrachloride
salicylic acid
tetrachloroethylene
benzene
fluorobenzene
chloroform
nitrobenzene
benzoic acid
phenylacetic acid
phenoxyacetic acid

"BIO" - TERMS

- **Bioconcentration** - Uptake across the membranes (i.e. through non-dietary routes like the gills) and generally used in reference to waterborne exposures.
- **Bioaccumulation** – Accumulation through the food chain (i.e. consumption of food, water/sediment) or direct water and/or sediment exposure.
- **Biomagnification** – Transfer of chemicals via food chain through two or more trophic levels as a result of the former two processes.
  - Residue levels increase (usually an order of magnitude) from one trophic level to the next.


USGS FS-170-96
Organochlorines in the food chain
Concentrations increase in predatory animals.
DDT
Suspended sediment
Organochlorines are transported from agricultural and urban sources through soil erosion, runoff, and precipitation.
Organochlorines accumulate in streambed sediments and in tissues of aquatic invertebrates and fish.

"BIO" – TERMS – Part 2

- **<u>Bioconcentration Factor</u> (BCF)** - A ratio of the concentration of a chemical in an organism to the concentration in the surrounding medium.
  - Most commonly used as a measure of direct partitioning from water to aquatic organisms.

$$\text{BCF (unitless)} = \frac{[\text{chemical in the organism}]}{[\text{chemical in the water}]}$$

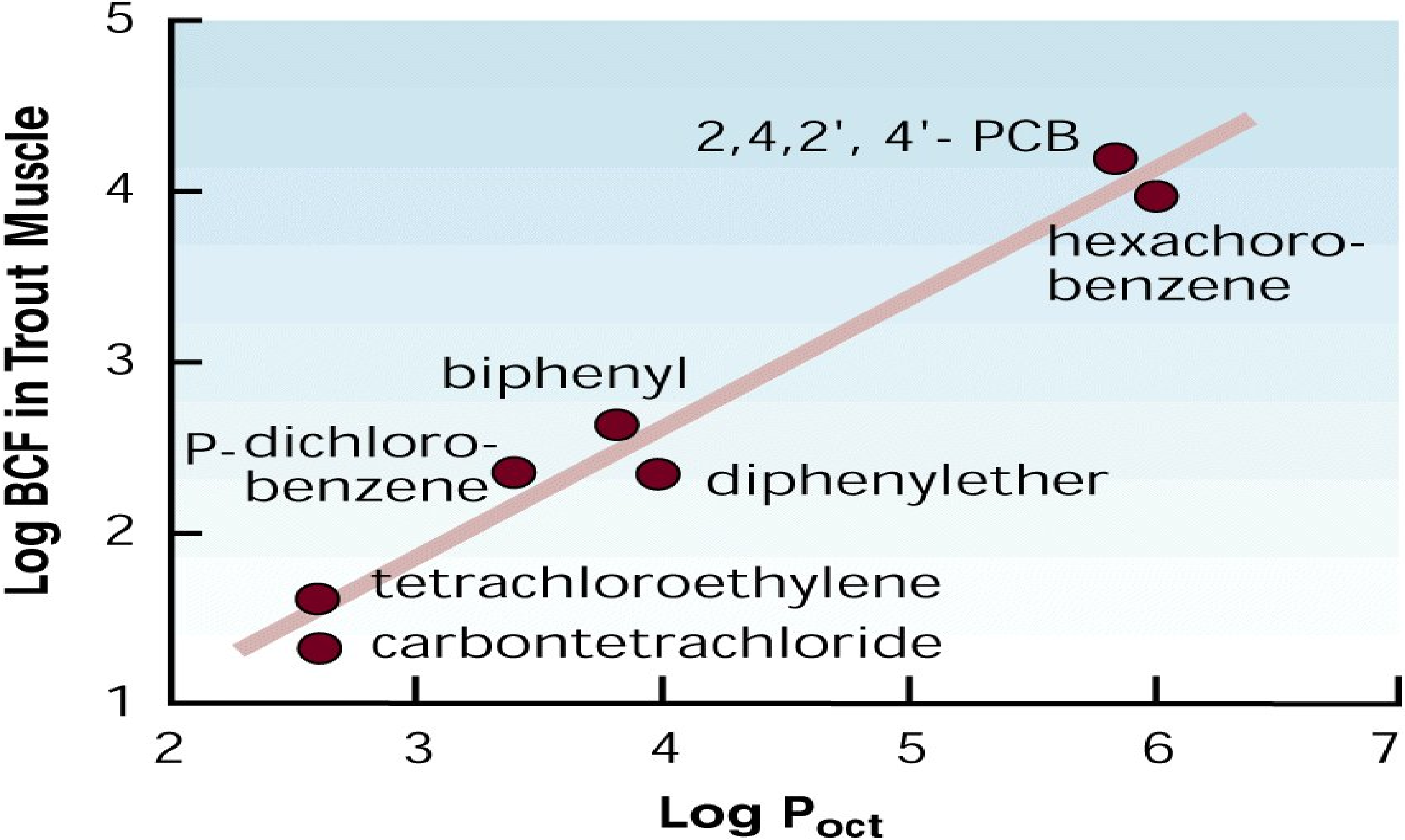


Fig. 2.25 — Relationship between octanol/water partition (P oct) coefficient and bioaccumulation factor (BCF) in trout muscle. Water quality can be inferred by the accumulation of contaminants in fish tissue.
In Stream Corridor Restoration: Principles, Processes, and Practices (10/98).
Interagency Stream Restoration Working Group (15 federal agencies)(FISRWG).

Persistence

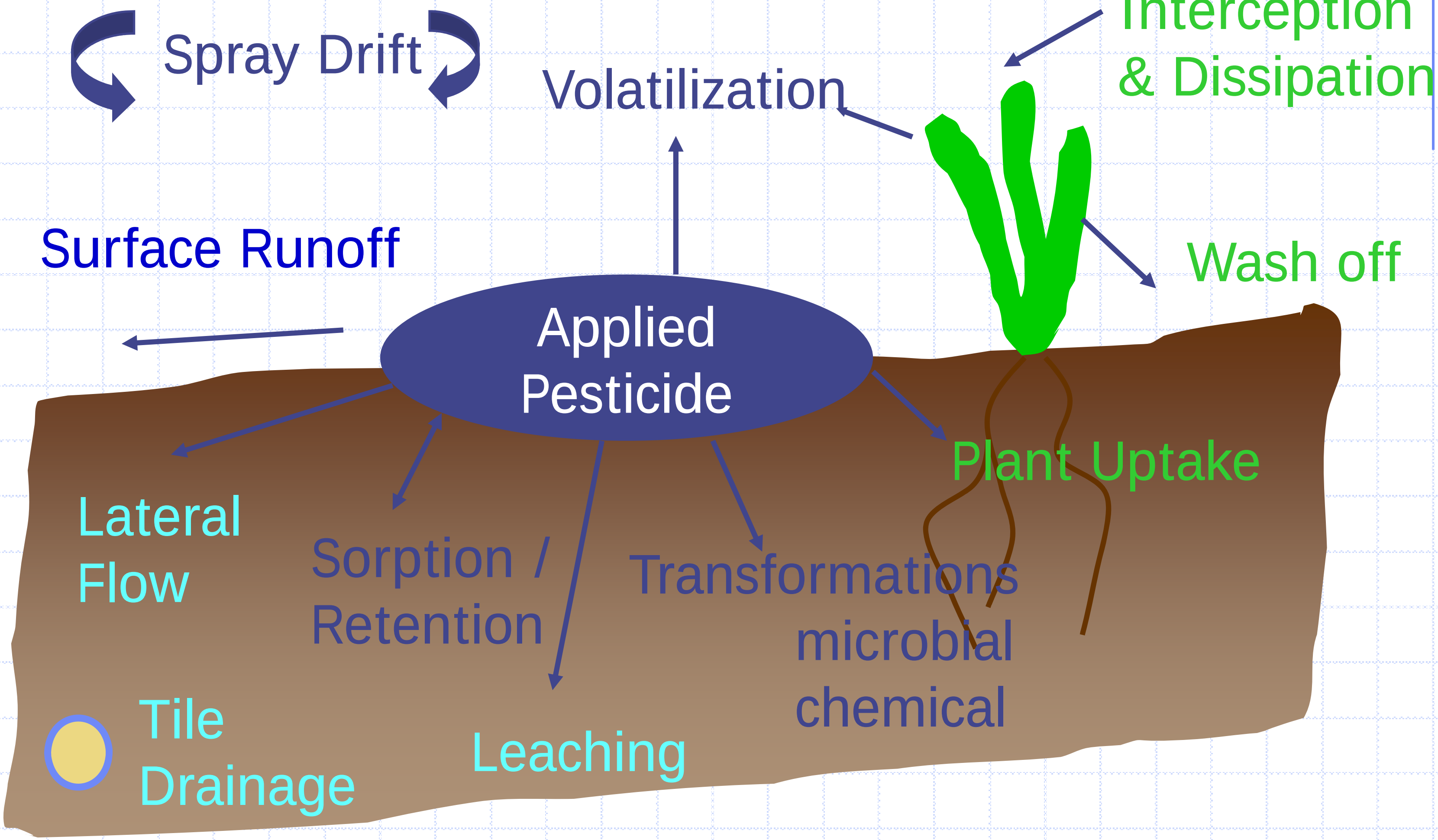
- Persistence or Longevity of a pesticide depends upon several factors:
  - Degradation of parent compound (stability)
  - Environmental conditions (temperature, pH, anaerobic/aerobic habitat, UV light)
    - As T ↑, biodegradation usually ↑
  - Dissipation/Volatilization

Non-persistent = half-life < 30 days

Moderately Persistent = half-life > than 30 days, < than 100 days

Persistent = half-life > 100 days

Dissipation is...simply lose



Expression of Persistence: Half-life

Example - Malathion

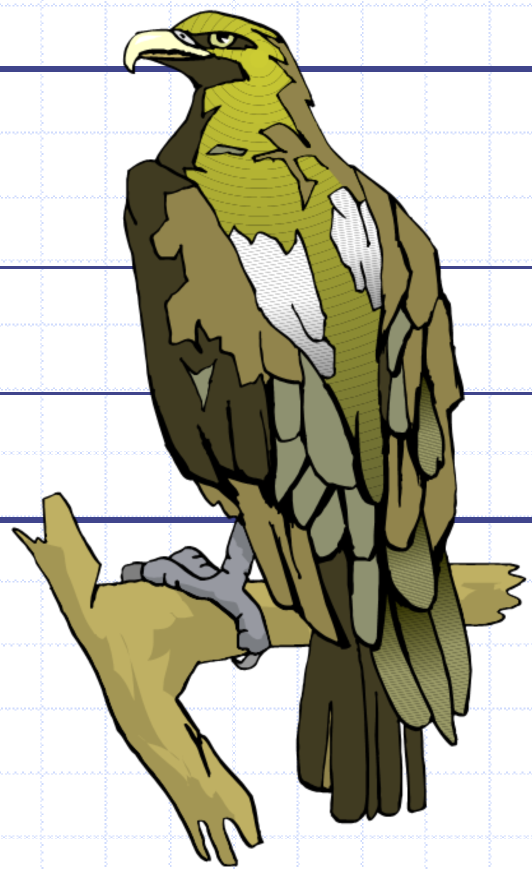
- Half-Life in Soil 24 hrs to 6 days
- Half-Life in Water 1.5 days to 21 wks
- Half-Life in Air 1.5 days
- Log K_{OW} 2.36 (moderately lipophilic)
- Boiling Point 156-157 C
- Solubility in Water 143 ppm at 20 C

Half-life (t ½) is the time required to reduce by half the amount of toxicant in an environmental compartment.

Less **Stability/Persistence** More

Lesser **Bioaccumulation** Greater

Carbamates and OPs		OCs
Malathion		DDT
Carbaryl		Endrin



Persistence of Pesticides in Rainbow Trout (Macek 1970).

Persistence	Pesticide
<1 day	Malathion
<2 days	Lindane
<3 days	Simazine
<1 week	Diazinon, Dursban, Azinphos-methyl, Parathion, 2,4-D, Methoxychlor
<2 weeks	Dichlorobenil
<3 weeks	Diquat, Endothal
1 month	Heptachlor, Dieldrin
4 months	Sodium arsenate
>5 months	DDT
>6 months	DDD, Camphechlor

Degradation

The process by which a chemical is reduced to a less complex compound via:

- Microorganisms/Biota (Metabolism)
- Water (Hydrolysis)
- Sunlight (Photolysis)
- Air or Other Agents (Degradates)

Processes of Degradation/Transformation

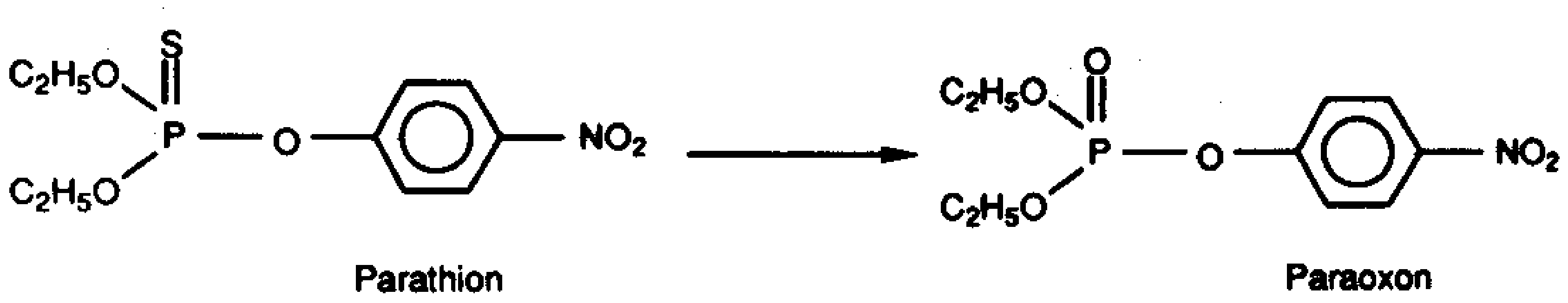
Structural changes to parent compounds "generally" result in lower toxicity and more hydrophilic secondary products

- **Reduction:** adding H molecule to reactive group (gain electron).

$$CCl_4 \longrightarrow CHCl_3$$

Chemical Degradation Processes (cont.)

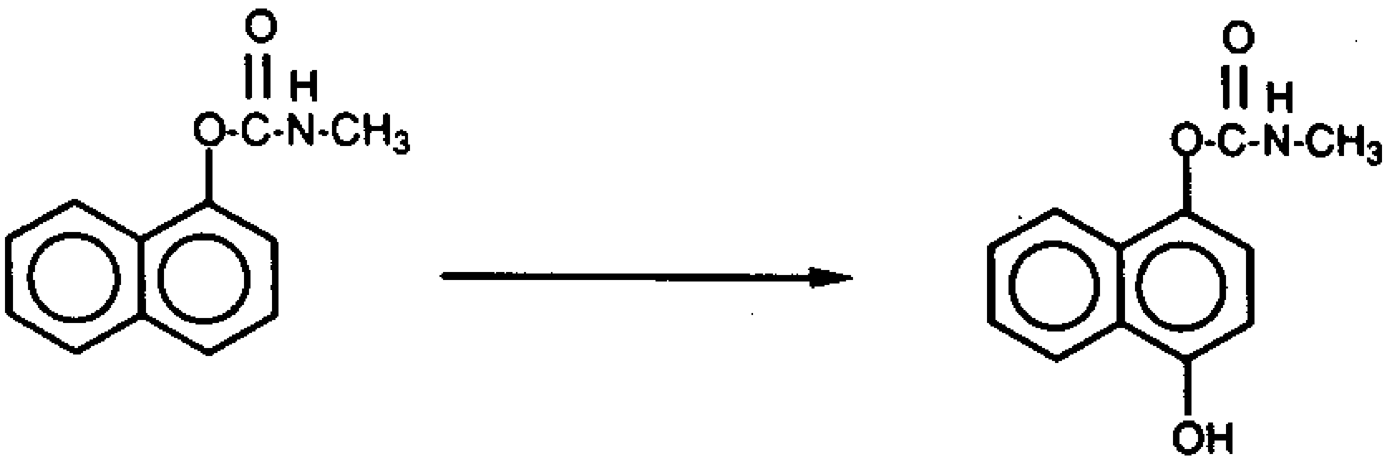
- **Oxidation:** adding or replacing reactive portions of the compound with oxygen (lose electron)



10 X more toxic

Chemical Degradation Processes (cont.)

- **Hydrolysis:** Adding an OH^- group to the reactive portion of a compound



carbaryl

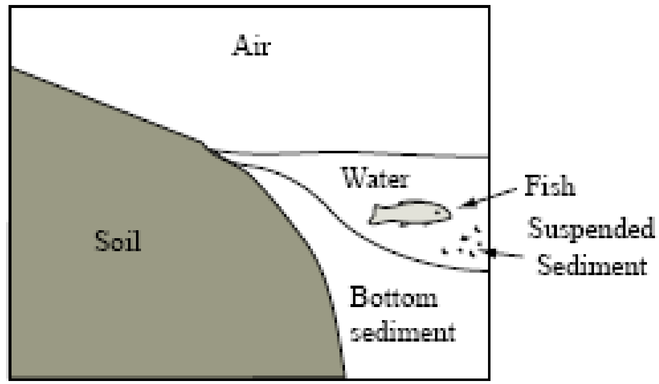
4-hydroxy carbaryl

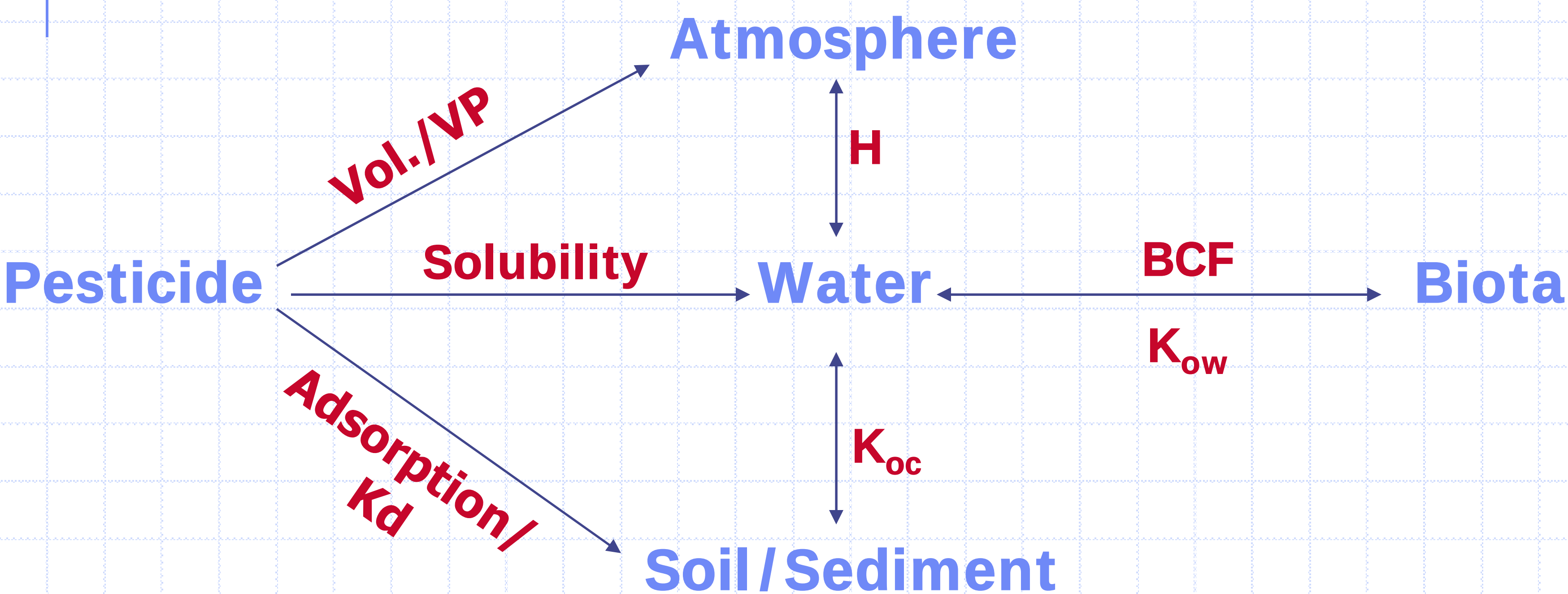
Hydrolysis is an important breakdown pathway for many pesticides, especially OPs, so pH of the water helps determine pesticide persistence

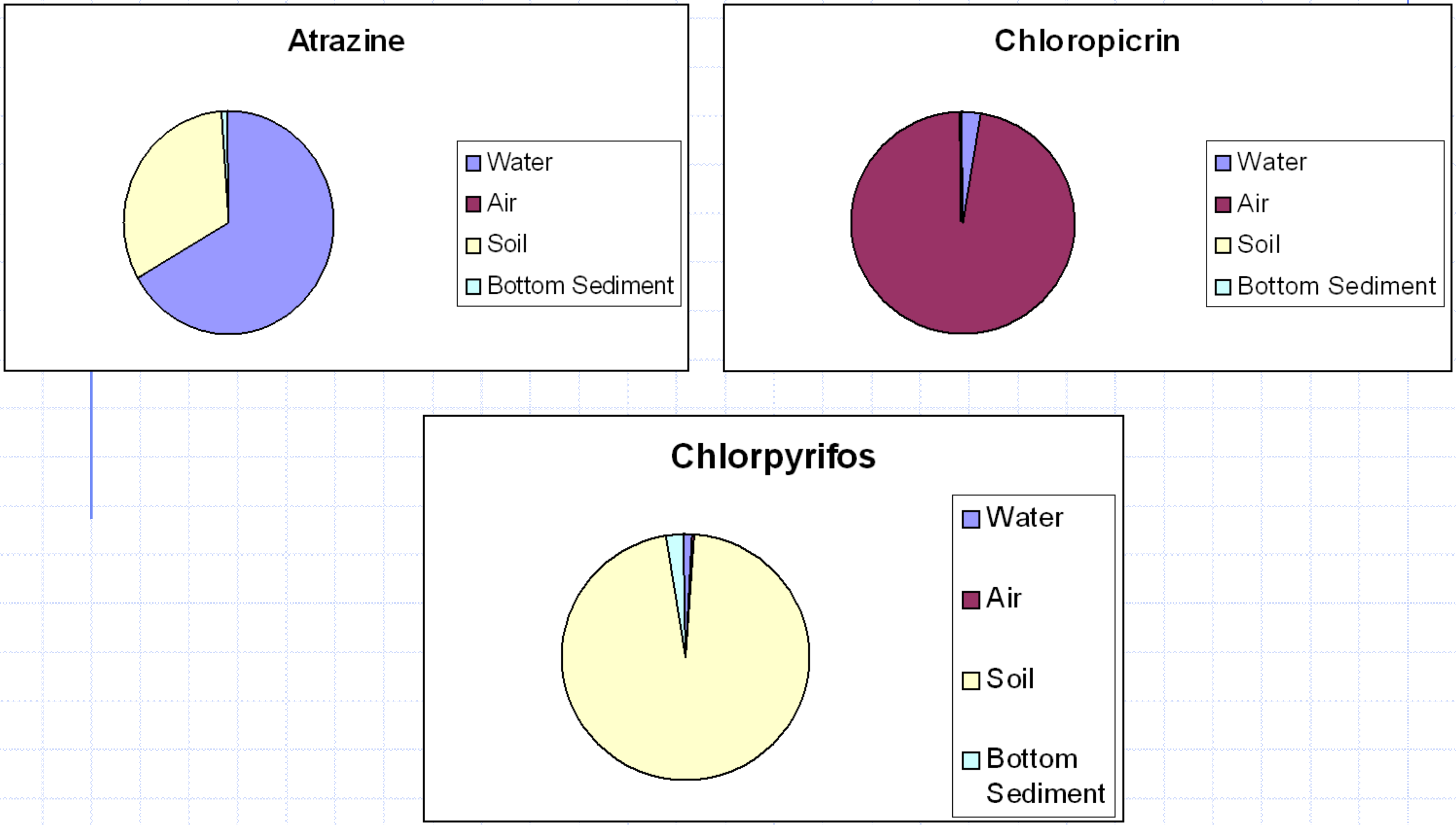
Pesticide Half-Lives in Weeks at Different Water pHs

Insecticide	**pH 4.5**	**pH 6.0**	**pH 8.0**
Chlorpyrifos	11	7	3
Diazinon	0.5	8	10
Malathion	18	6	0.5

Summary


Air
Water
Fish
Soil
Suspended
Sediment
Bottom
sediment


Atmosphere
Vol./VP
H
Pesticide
Solubility
Water
BCF
Biota
K_{ow}
Adsorption/
Kd
K_{oc}
Soil/Sediment



Distribution of pesticides among air, surface water, soils, and aqueous sediments based on fugacity calculations (Mackay et al. 1997).

Potential Threats to Surface and Groundwater - Summary

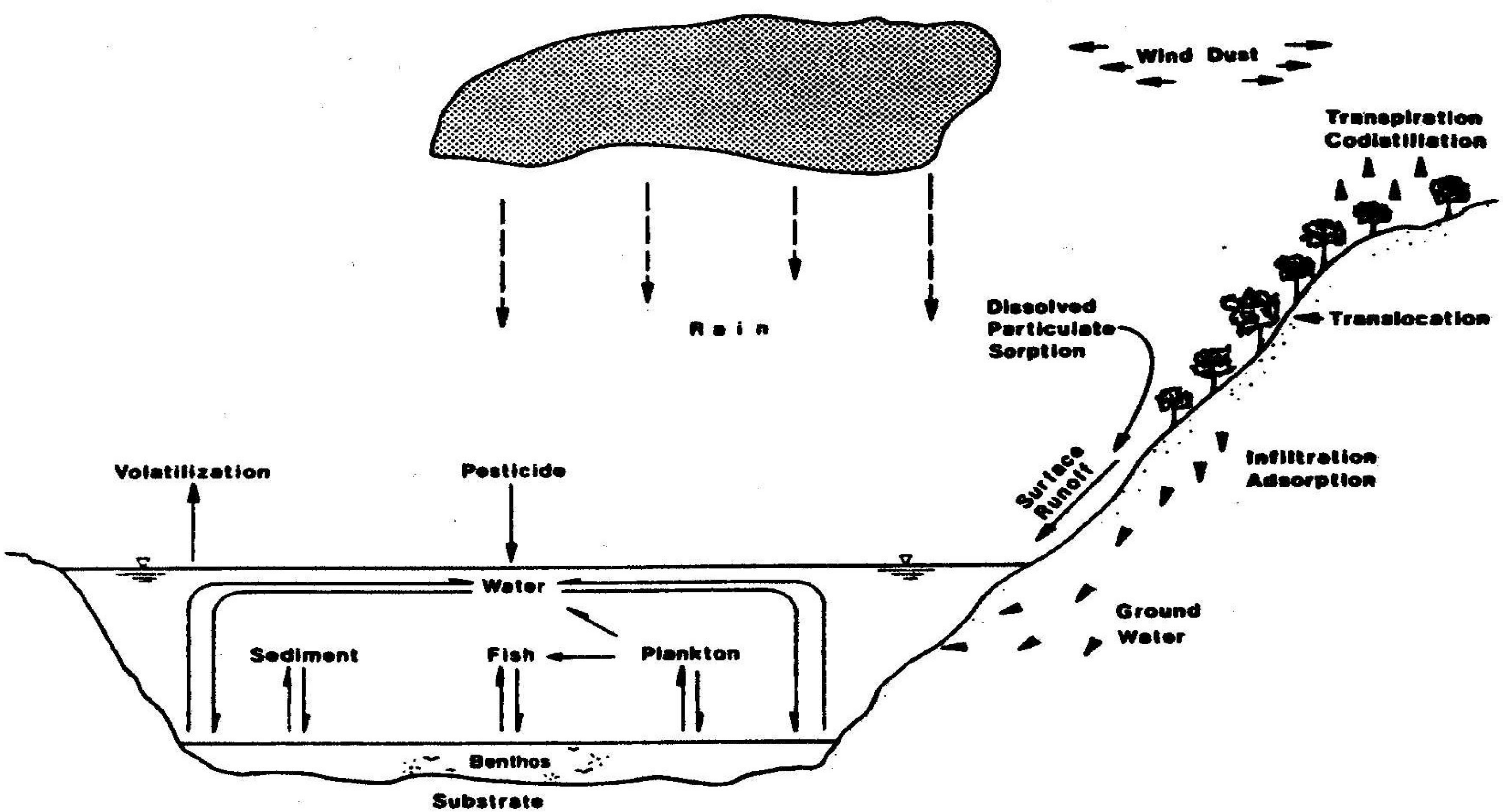
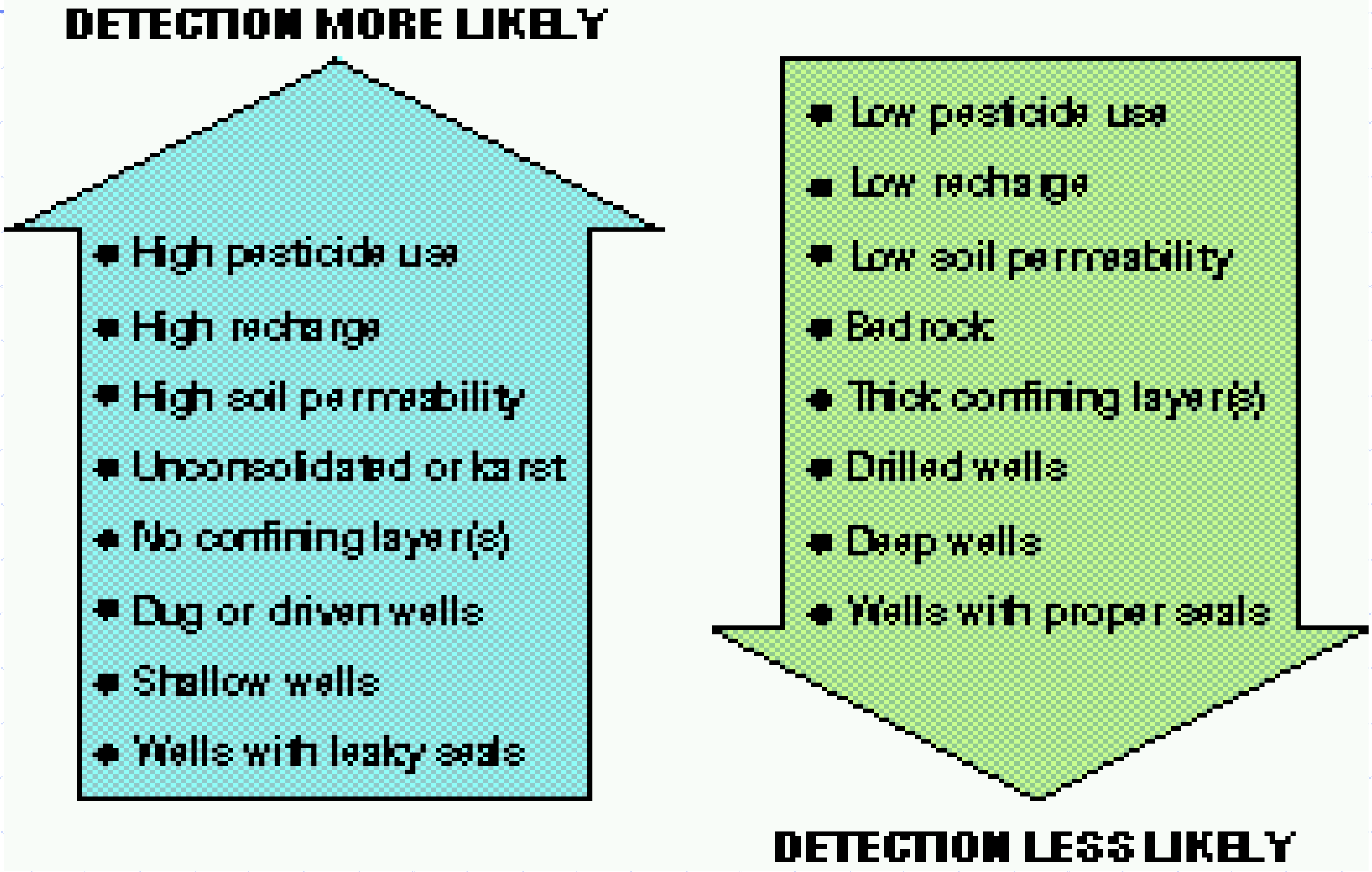


Figure 1 Movement of pesticides into and through aquatic ecosystems.

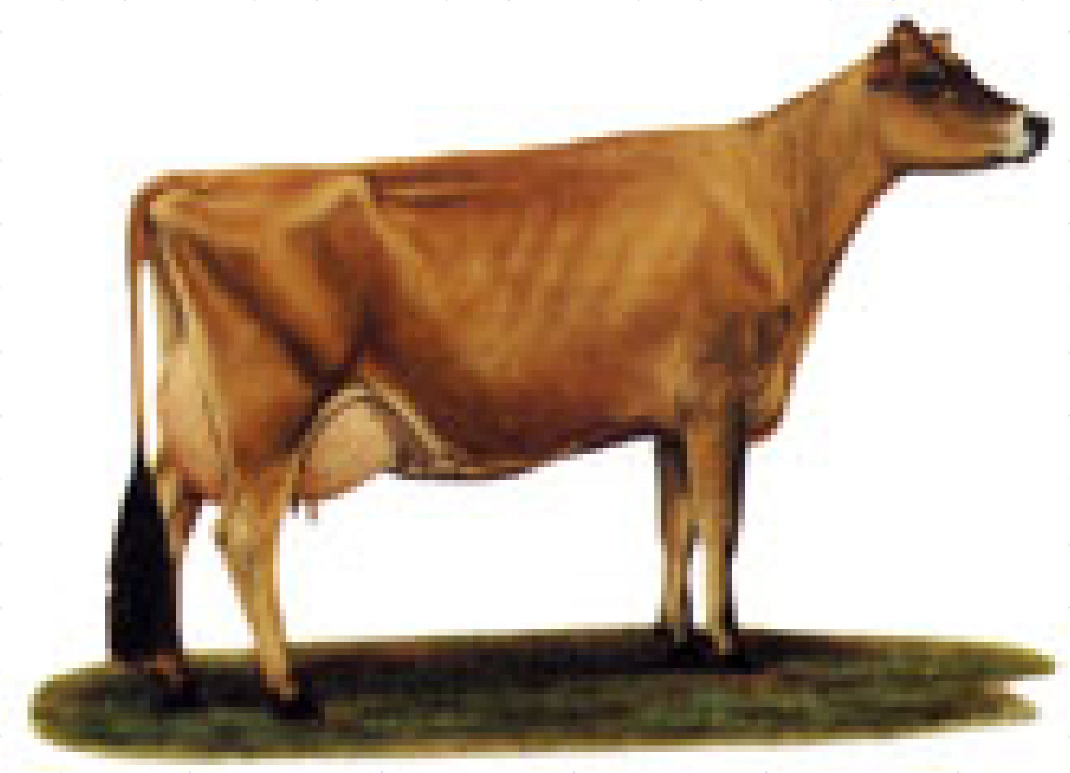
Assessing Threats to Groundwater and Surface Waters



Characteristics of Pesticides Likely to Contaminate Groundwater

- **Pesticide Characteristics:**
  - Water Solubility > 30 ppm (medium to high)
  - K_{oc} < 500 (mobility medium to high)
  - Hydrolysis Half-life >25 weeks
  - Photolysis Half-life >1 week
  - Soil Half-life >2 weeks
- **Field Conditions:**
  - Precipitation or irrigation >25cm/yr
  - Porous/leachable soils that drain quickly (sand)
  - Soil pH that promotes chemical stability

Miscellaneous Transport Mechanisms



- clopyralid in urine & manure, remains phytotoxic at 1 ppb

Miscellaneous Transport Mechanisms

Fire ➡ Oust on rangeland ➡ High Winds ➡
➡ Dust ➡ >100,000 acres crop damage
100 farmers, $100,000,000 in claims
(Damage on crops from soil residues of 31 pptr - 11 ppb)

Questions?