Pesticide Properties and Fate in the Environment

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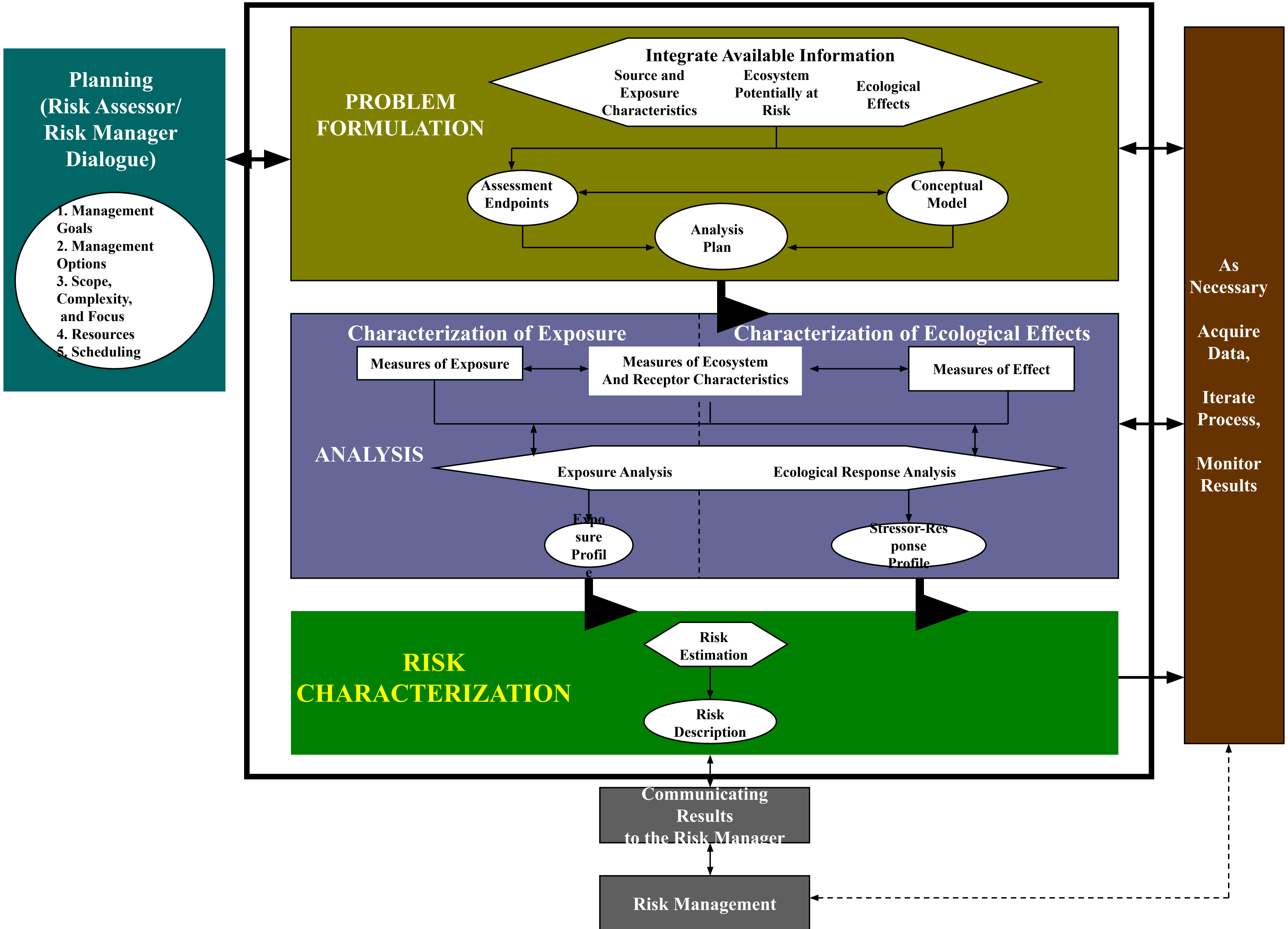
EMT
ENVIRONMENTAL
and
MOLECULAR
TOXICOLOGY

FRAMEWORK FOR ECOLOGICAL RISK ASSESSMENT



Planning
(Risk Assessor/
Risk Manager
Dialogue)

1. Management Goals
2. Management Options
3. Scope, Complexity, and Focus
4. Resources
5. Scheduling

PROBLEM FORMULATION

Integrate Available Information

Source and Exposure Characteristics

Ecosystem Potentially at Risk

Ecological Effects

Assessment Endpoints

Conceptual Model

Analysis Plan

ANALYSIS

Characterization of Exposure

Characterization of Ecological Effects

Measures of Exposure

Measures of Ecosystem And Receptor Characteristics

Measures of Effect

Exposure Analysis

Ecological Response Analysis

Exposure Profile

Stressor-Response Profile

RISK CHARACTERIZATION

Risk Estimation

Risk Description

Communicating Results to the Risk Manager

Risk Management

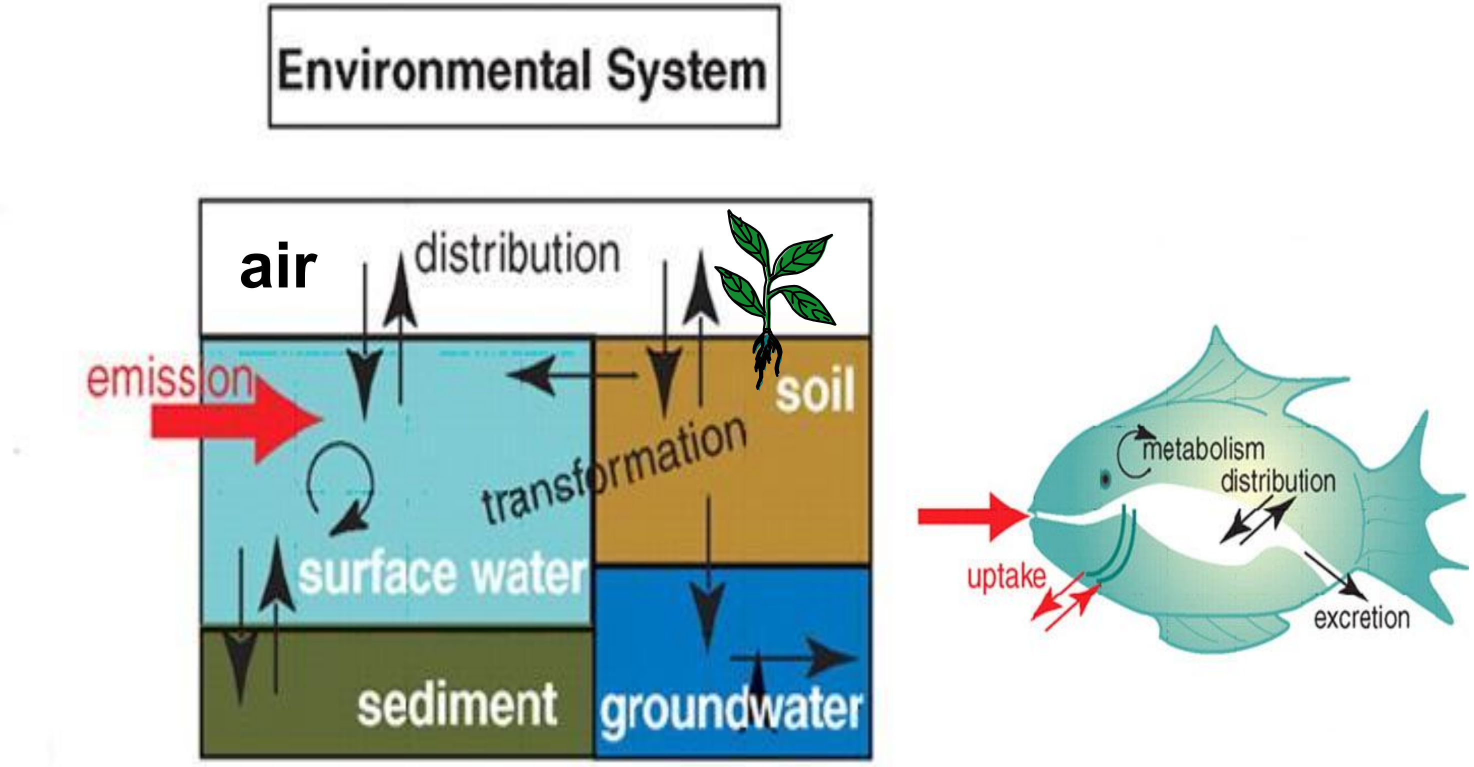
As Necessary

Acquire Data,

Iterate Process,

Monitor Results

Chemical Fate ⟶ Bioavailability ⟶ Exposure



Adapted from R. P. Schwarzenbach et al., Science 313, 1072 -1077 (2006)

THIRD EDITION

ENVIRONMENTAL ORGANIC CHEMISTRY

René P. Schwarzenbach
Philip M. Gschwend
Dieter M. Imboden

with website

WILEY

Chemical fate in the environment

Molecular interactions

(physical-chemical properties, reactivities)

↓

Environmental factors

(Temperature, pH, light intensity, ion composition and strength, microbial activity, natural organic matter, etc.)

↓

Environmental processes

(e.g. air/water exchange, sorption/desorption, chemical, photochemical and biological transformation)

Chemical fate in the environment

Transport and mixing processes

Dynamic behavior in a natural system

(mathematical models and field investigations)

Chemical fate in the environment

Molecular interactions

Desired physical-chemical properties for organics (continued):

Water solubility
Organic solubility
Vapor pressure (V_p)
Henry's Law (K_H)
Acidity constant (pK_a)
Octanol/water partitioning (K_{ow})
Octanol/air partitioning (K_{OA})
Soil sorption (Kd, K_{oc})*

*For various soil types.

Chemical fate in the environment

Physical-chemical properties

Henry's Law constant

Chemical abundance in the gas phase is expressed by it partial pressure, $P_{i.}$

Aqueous phase abundance is expressed as the molar concentration, $C_{w.}$

Therefore:

$$K_H = \frac{P_i}{C_w} (\text{atm} \cdot \text{L} \cdot \text{mol}^{-1})$$

If P_i is expressed as moles per liter then K_H is *dimensionless.*

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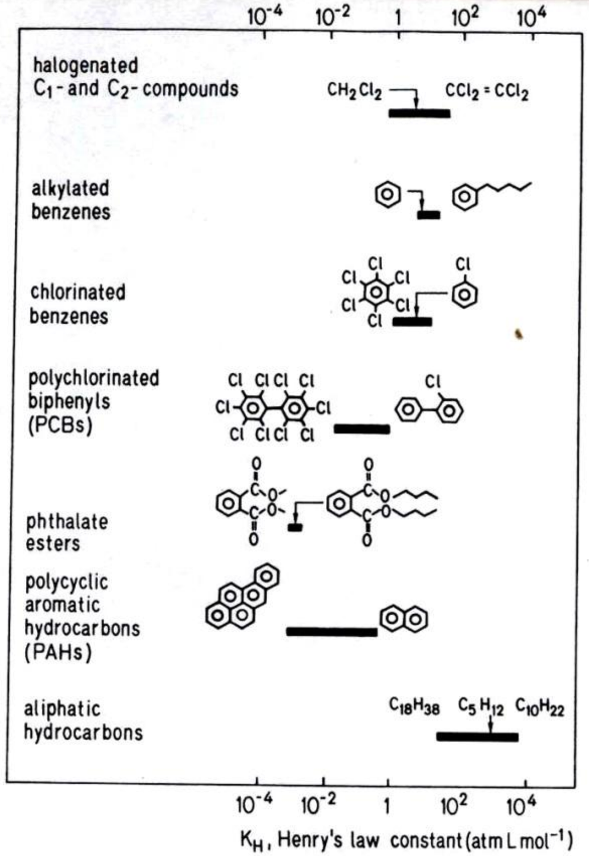


Figure 6.2 Ranges in Henry's Law constants (K_H) for some important classes of organic compounds.

Chemical fate in the environment

Physical-chemical properties

Octanol-water partition coefficient

Around 1900 chemists began to use n-octanol as a surrogate for organisms in studying the uptake of non polar pharmaceuticals.

Today the octanol-water partition coefficient (K_{ow}) is used to estimate equilibrium partitioning of non polar organics between water and organisms.

Chemical fate in the environment

Physical-chemical properties

Octanol-water partition coefficient

The K_{ow} also directly proportional to partitioning into soil humus and other naturally occurring organic phases.

Experimentally, the K_{ow} measures the partition-ing behavior of organic compounds between two immiscible liquids-- water and octanol.

Chemical fate in the environment

Physical-chemical properties

Octanol-water partition coefficient

$$K_{ow} = \frac{C_s}{C_w} \;\; (\mathrm{mol} \cdot L_s^{-1}\ \mathrm{mol}^{-1} \cdot L_w)$$

where: C_s is the concentration in the organic phase

C_w is the concentration in the water

K_{ow} is a *dimensionless* equilibrium constant.

$\text{Log P} = \text{Log}_{10}(K_{ow})$

Octanol-water partition coefficient

$$K_{ow} = \frac{C_{oct}}{C_w} \text{ (quasi-unitless)}$$

where: C_s is the concentration in the organic phase
C_w is the concentration in the water

K_{ow} can be large, reported as log K_{ow} or log P = $\log_{10}(K_{ow})$

- polar compounds $K_{ow} < 10^3$ e.g., ethanol, benzene
- intermediate compounds e.g., naphthalene, HCB
- high mw, non-polar compounds $K_{ow} > 10^5$ e.g., PCBs, DDT

Chemical fate in the environment

Physical-chemical properties
Octanol-air partition coefficient

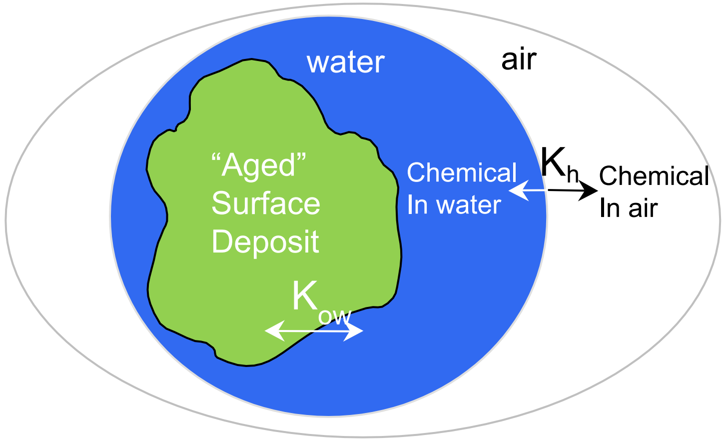
$$K_{OA} = \frac{C_s}{C_A} \ (\mathrm{mol} \cdot L_s^{-1}\ \mathrm{mol}^{-1} \cdot L_A)$$

where: C_s is the concentration in the organic phase
C_A is the concentration in the air

K_{OA} is a *dimensionless* equilibrium constant.

K_{OA} is used to estimate partitioning between plants or particles and the atmosphere.

Source Strength a function of Henry's Law (K_h) or Octanol-air Partition Coefficient K_{OA}



water

air

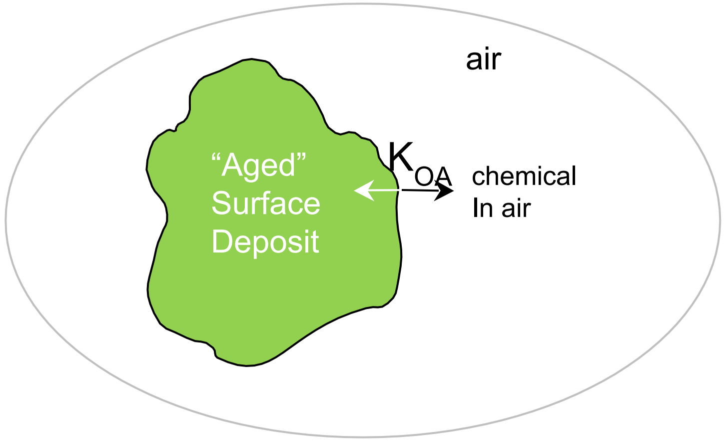
"Aged" Surface Deposit

Chemical In water

K_h

Chemical In air

K_{ow}

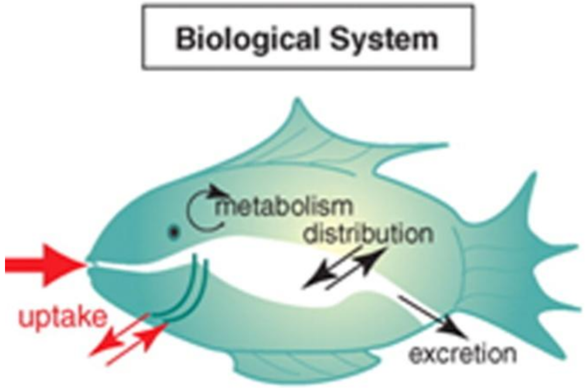


air

"Aged" Surface Deposit

K_{OA}

chemical In air



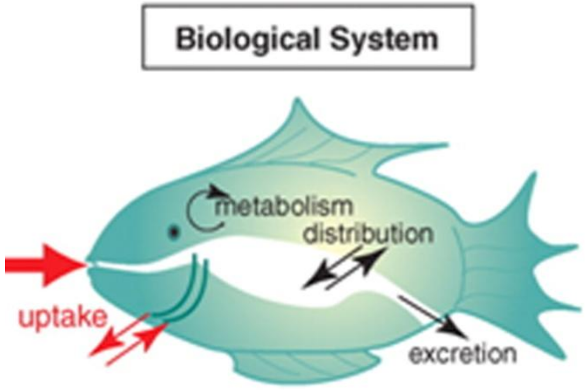
Accumulation in biota

- Bioaccumulation
  - for all exposure routes (partitioning from air, water, soil, sediment, or ingestion)
  - the net amount (after absorption, distribution, metabolism, and elimination - ADME) of a chemical in an organism

- Bioaccumulation factor (BAF) – Ratio of the concentration of a chemical in an organism to the concentration in surrounding media and ingestion.

$$BAF = \frac{C_{organism}}{C_{media}}$$

Accumulation in biota



- Bioconcentration – the net amount (after ADME) in an organism in water (uptake via exposure to water alone).
- Bioconcentration factor (BCF) – ratio of the concentration of a chemical in an organism to its concentration in water.

$$BCF = \frac{C_{\text{organism}}}{C_{water}}$$

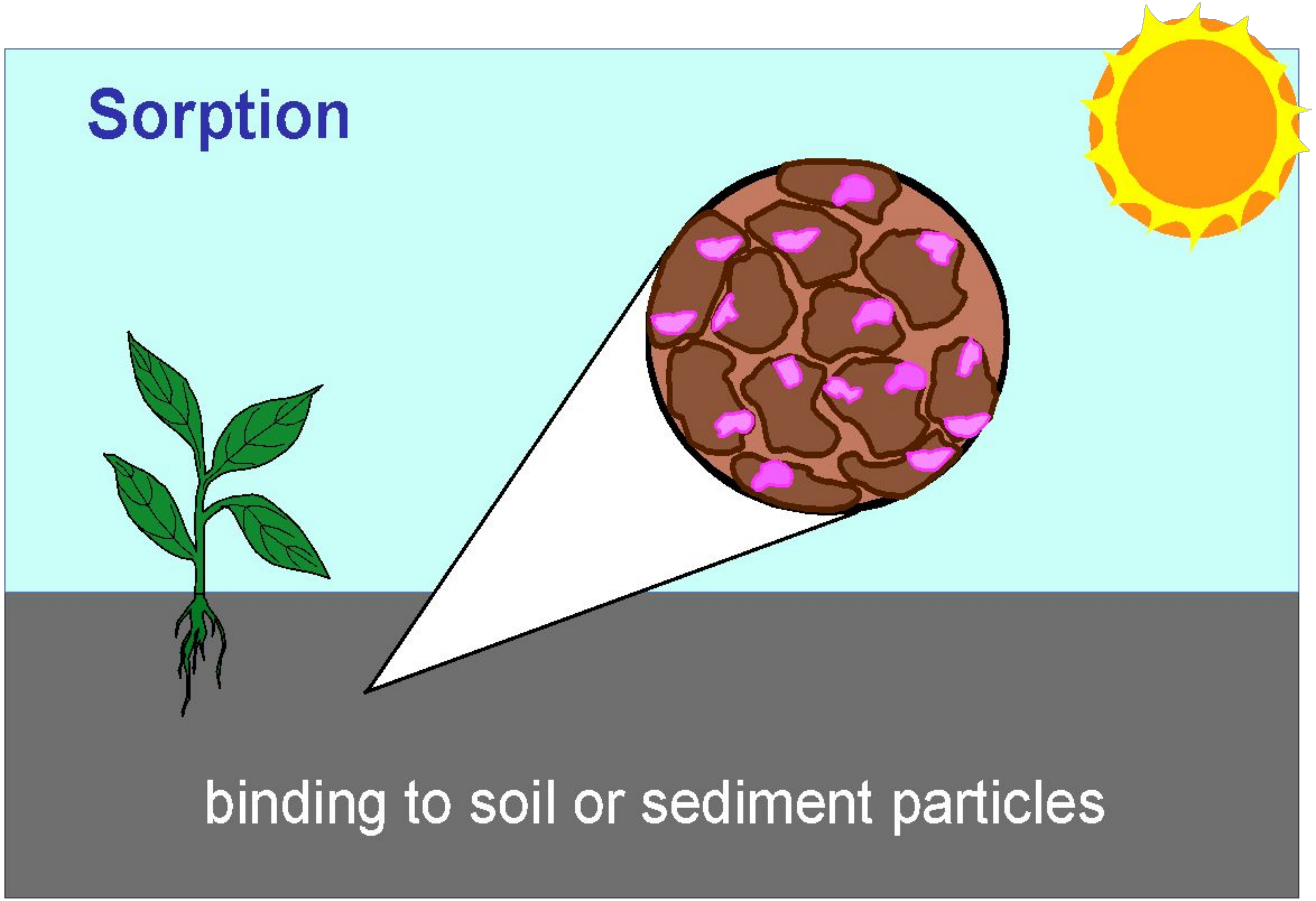
Accumulation in biota

- Biomagnification – A process whereby a chemical becomes increasingly concentrated at successively heigher trophic levels of a food chain or food web.

- Biomagnification factor (BMF) – Ratio of the concentration of a chemical measured in the tissues of organisms in one trophic level to its concentration in tissues of organisms in the next lower trophic level.

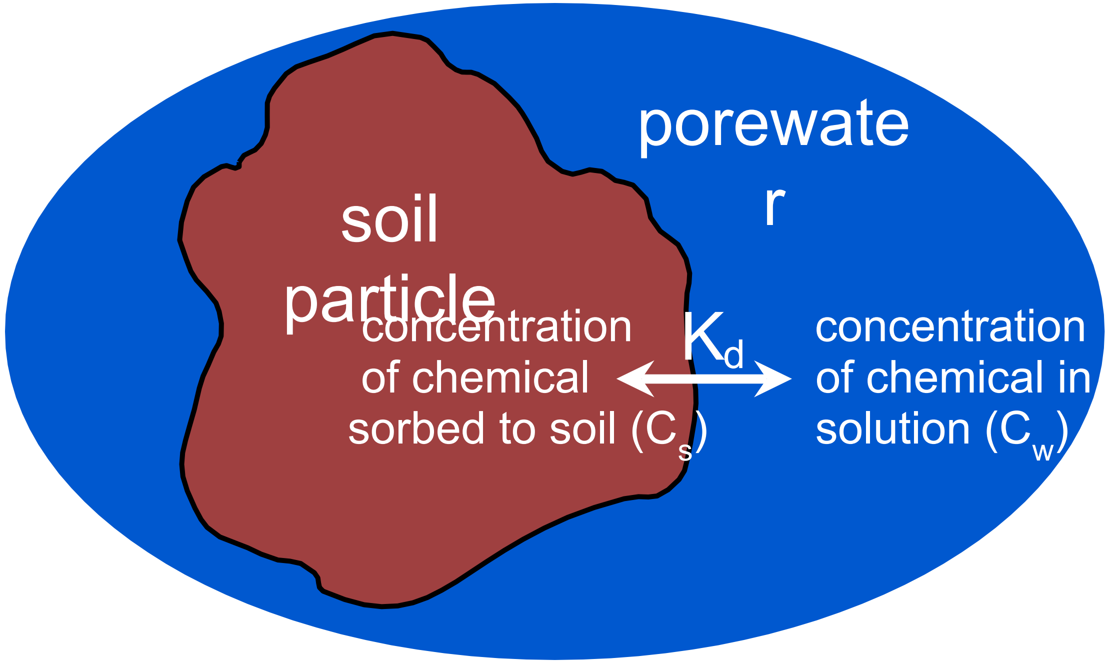
Pesticide Fate in Soil

Sorption



binding to soil or sediment particles

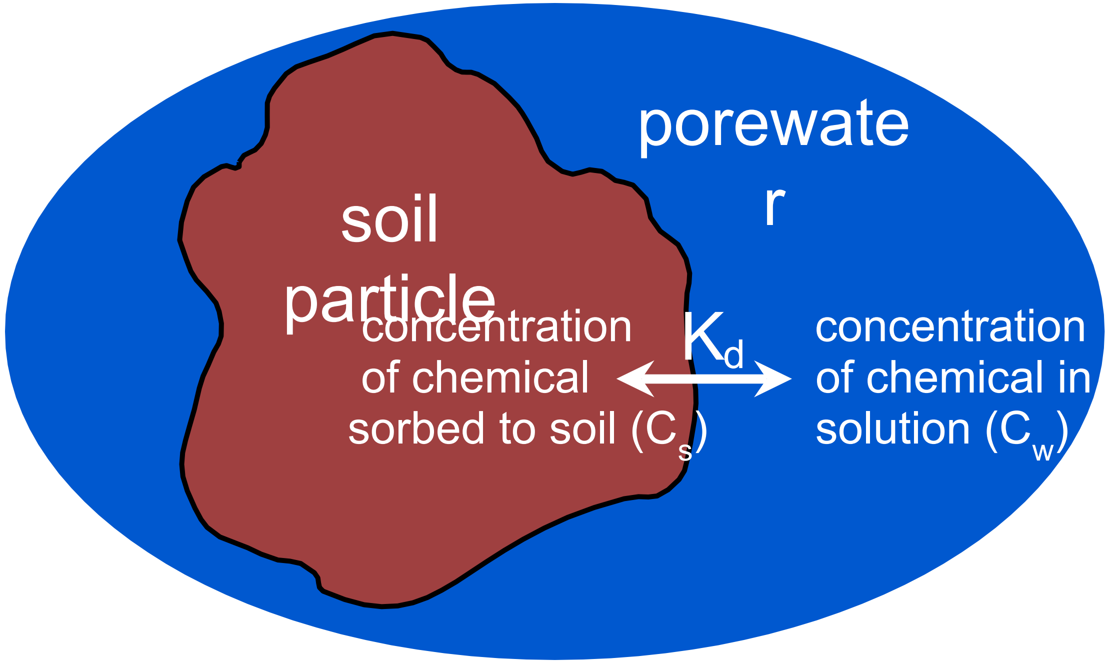
Soil sorption



Sorption involves a phase transfer process of vapor or dissolved molecules with adjacent solid phases.

Sorption is extremely important because it can dramatically affect chemical fate in the environment (transport and transformation).

Sorption to Soils/Sediment



soil particle

porewate
r

concentration of chemical sorbed to soil (C_s)

K_d

concentration of chemical in solution (C_w)

$$K_d = \frac{C_s\left(\frac{moles}{kg}\right)}{C_w\left(\frac{moles}{L}\right)} = \frac{\mathrm{L}}{\mathrm{kg}}$$

- K_d typically applies to only low concentrations and is treated as a constant
- non-linear sorption often observed so use K_d with caution
- for hydrophobic (low water solubility and high K_{ow}), neutral chemicals, K_d is related to the fraction of organic matter (or carbon) in soils and sediments (next slide)

Soil Distribution coefficient K_d

$$K_d = \frac{C_s}{C_w}$$

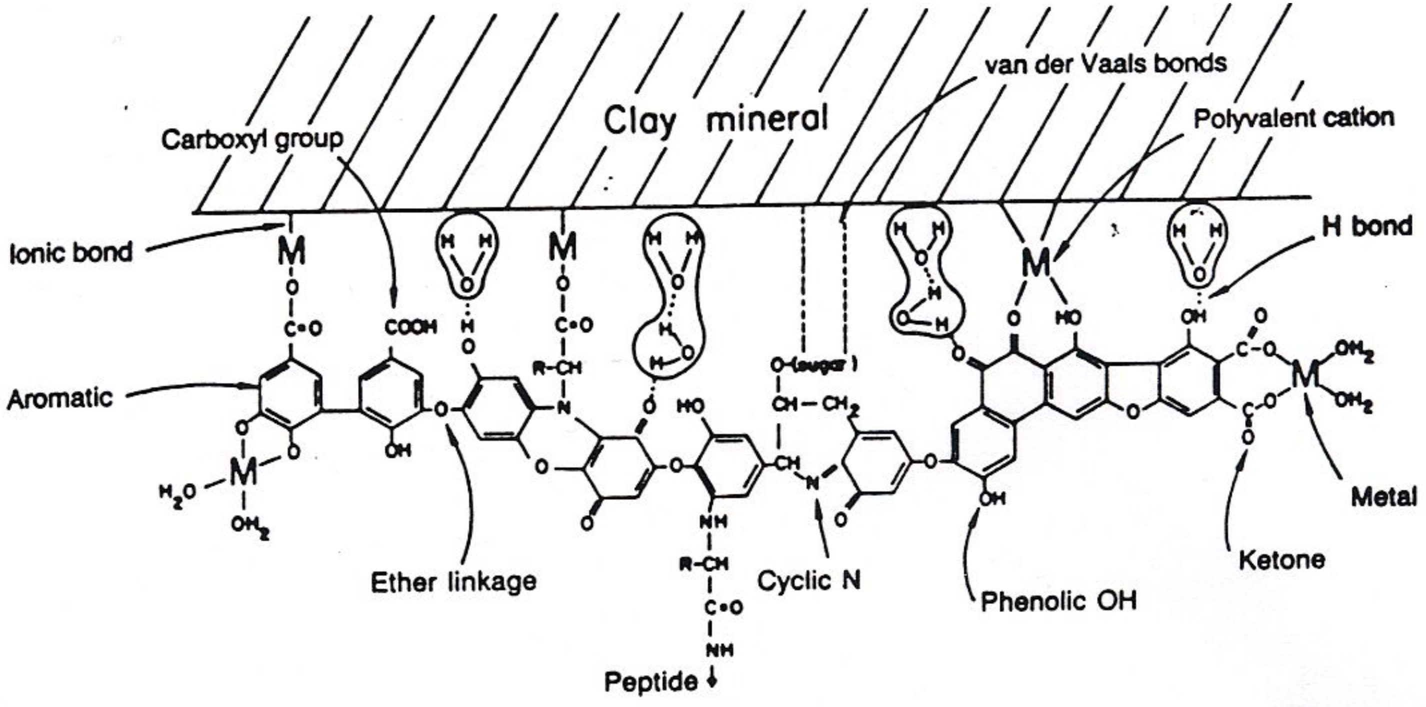
Where: C_s = concentration in the solid phase- soil
C_w = concentration in water

Pesticide	Kd
aldicarb	10
carbofuran	29
atrazine	172
carbaryl	229
malathion	1178
Parathion	7161

Soil sorption

clay

organic matter

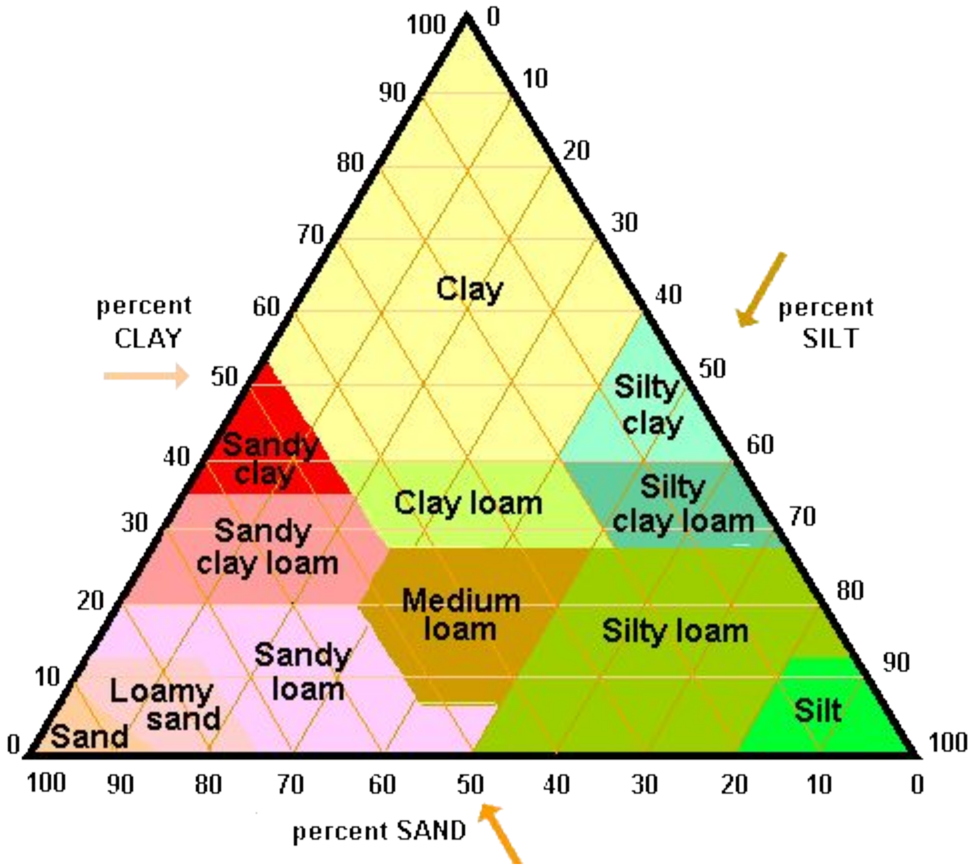


Soil sorption is highly dependent of the soil type and particularly soil organic matter (OM) content.

Generally, soils higher in clay and organic matter have a higher sorption capacity.

Soils

- A porous media composed of minerals - sand, silt, clay - and organic matter.
- Each soil has unique properties that influence:
  - Chemical sorption
  - Flux of air and water
  - Chemical transport in air or water



Clay Crystal Structure

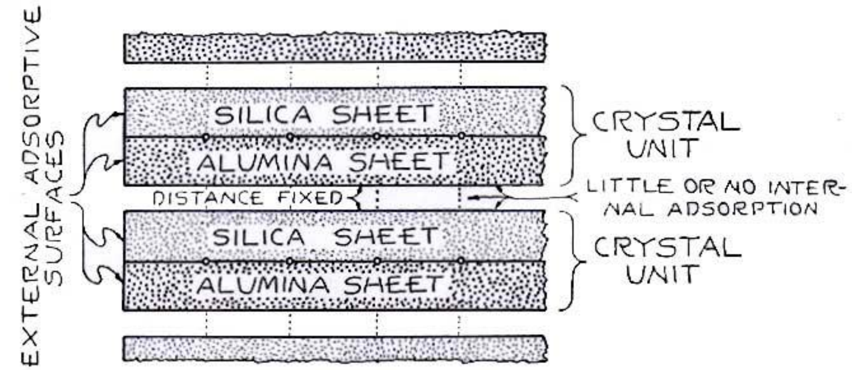
Lattice structure

Dense negative surface charge

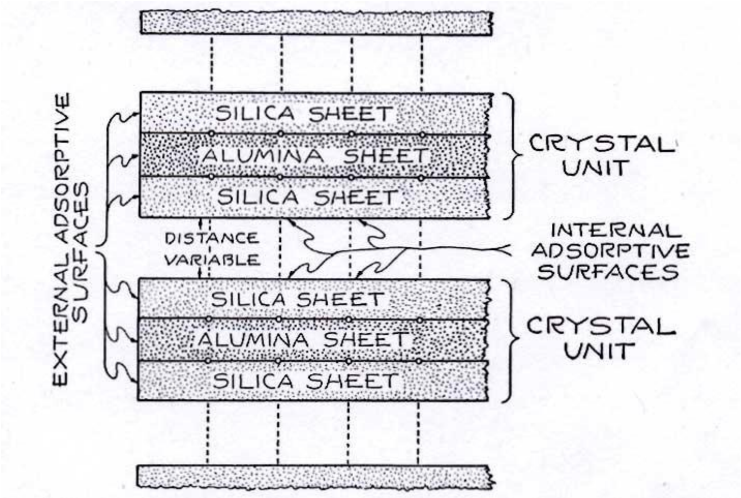
Expanding clays allow binding to internal surfaces

Cation exchange capacity (CEC) and organic matter content much greater (10-15 X) for expanding clays.

Kaolinite (non-expanding)



Montmorillontie, illite (expanding)



Sorption v. Clay Type

Non-linear sorption:

1,3,5-trinitrobezene planar
with electronegative centers

Binding by electron
donor-acceptor interactions,
not H-bonding

Montmorillonite and Illite are
expanding clays – more surface
area,

Montmorillonite greater
charge density

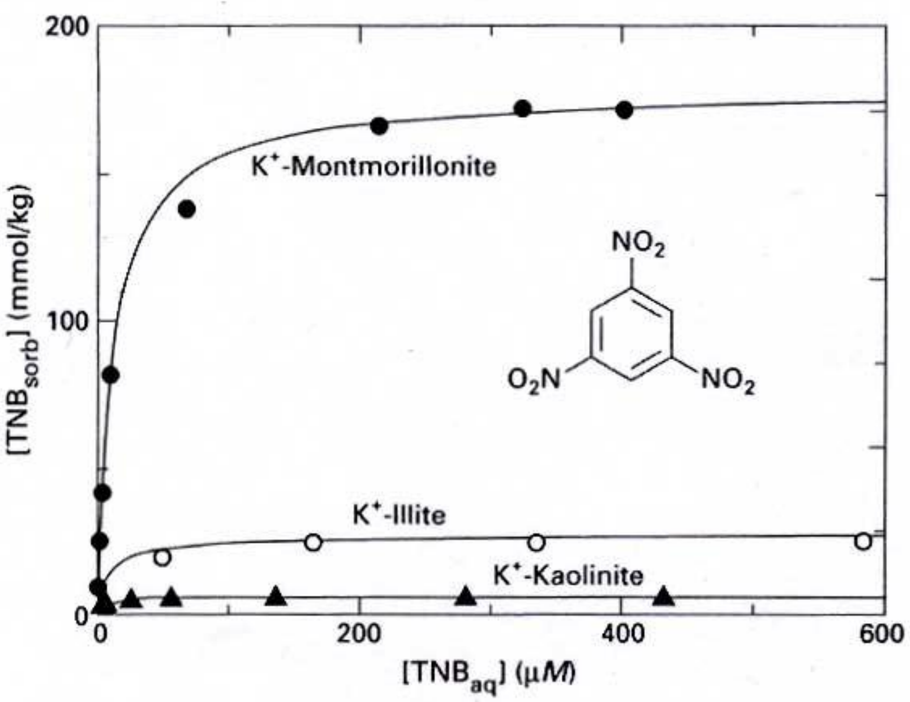


Figure 7.27 Adsorption of 1,3,5-trinitrobenzene by homoionic K⁺-exchanged clays in aqueous suspensions. [Data from Haderlein et al. (1996). Reproduced with permission.]

Soil Organic Matter

Humic and Fulvic acids

Soil analysis:

instantaneous oxidation by "flash combustion" which converts all organic C to CO_2. % organic matter (OM) expressed as % organic carbon (OC). OM ~58% OC

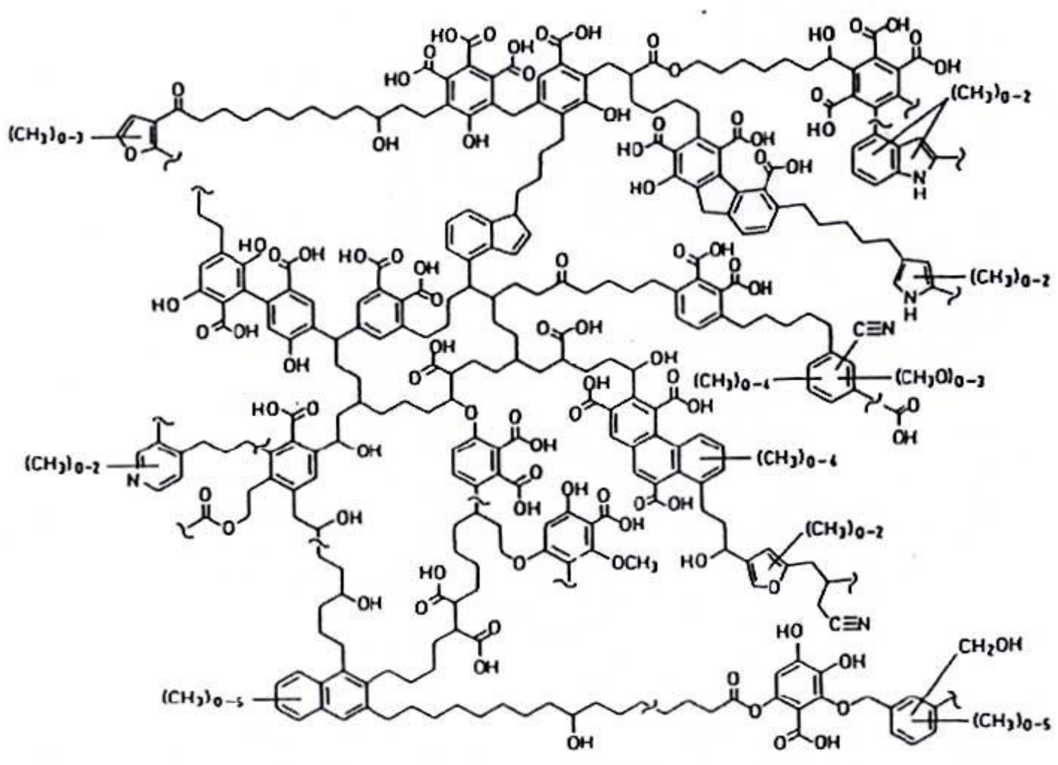
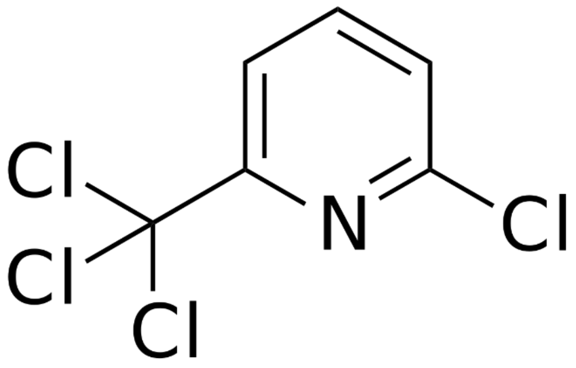


Figure 3.3 A structure proposed for fulvic acid. [Reproduced with permission from J. Buffle et al., *Environ. Sci. and Technol.* **32**, 2887 (1998). Copyright © 1998, American Chemical Society.]

Soil sorption



Nitrapyrin sorption on several soils

Soil	% O.C.	Kd	Koc
1	0.081	0.40	491
2	0.62	3.18	514
3	0.86	5.39	627
4	0.97	4.43	457
5	1.45	9.09	627
6	3.80	15.90	417
7	5.76	44.00	764
8	21.70	132.00	611
mean		26.90	564
CV		167%	20%

Chemical characteristics

Soil sorption

To account for different soil types and organic matter content the K_d is normalized for % organic carbon (OC) or organic matter (OM).

$$K_{OC} = \frac{K_d}{\%\ \text{organic carbon}^*} \qquad K_{OM} = \frac{K_d}{\%\ \text{organic matter}^*}$$

* decimal equivalent

pH effects on partitioning

Acidity constant

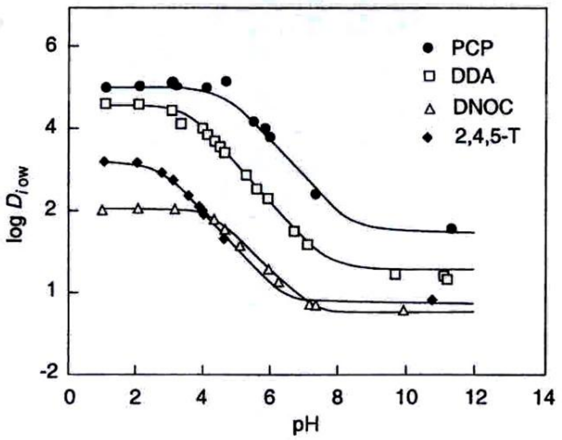
The pK_a is the measure of the strength of an acid (or conjugate acid, BH^+) relative to water, and tells us at what pH that the acid is present in equal parts in the dissociated (A^-) and associated (HA) forms.

$$[A^-] = [HA] \quad \text{at} \quad pH = pK_a$$

pH effects on partitioning

- The fraction of the acid or base in its HA or B form is the fraction that partitions into air or into octanol.
- By analogy, the HA and B forms of organic acids and bases have K_{oc}s (and K_{om}s) that are an order of magnitude higher than that of their A^- and BH+ forms

Figure 8.9 The pH dependence of the *n*-octanol–water distribution ratio of pentachlorophenol (PCP, pK_{ia} = 4.75), 4-chloro-α-(4-chlorophenyl) benzene acetic acid (DDA, pK_{ia} = 3.66), 2-methyl-4,6-dinitrophenol (DNOC, pK_{ia} = 4.46), and 2,4,5-trichlorophenoxy acetic acid (2,4,5-T, pK_{ia} = 2.83). (from Jafvert et al., 1990).



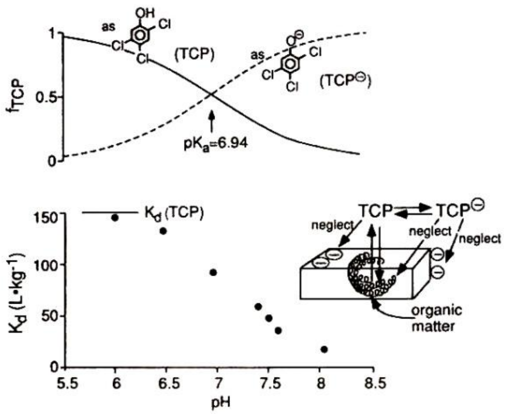


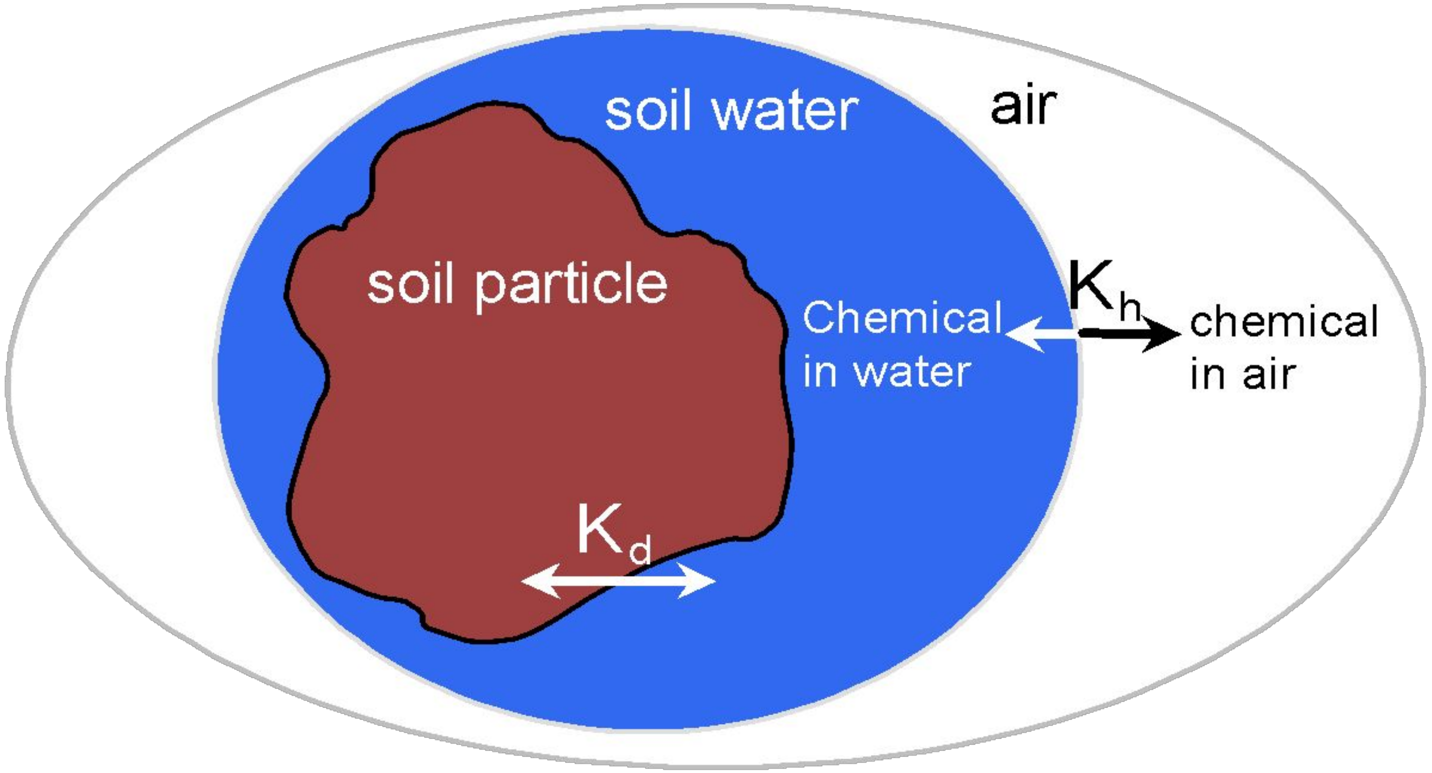
Figure 11.17 2,4,5-Trichlorophenol ionization (upper) and sorption to a lake sediment (lower) as a function of solution pH (data from Schellenberg et al., 1984). Inset indicates the importance of TCP interaction with particulate organic matter, in this case, relative to other sorption processes for TCP or TCP⁻.

Distribution ratio $D_{ow} = K_{ow}$ f(pH)

For acids: $\log D_{OW} = \log K_{OW} - \log[1 + 10^{(pH - pK_a)}]$

For bases: $\log D_{OW} = \log K_{OW} - \log[1 + 10^{(pK_a - pH)}]$

Partitioning between soil compartments (soil, water air)



K_h describes the relationship between pesticide concentration in soil water and pesticide concentration in air.

Partitioning between soil compartments (soil, water air)

K_d, K_H, and V_p describe the potential for exchange of organic compounds between soil, water, and air over short distances by diffusion.

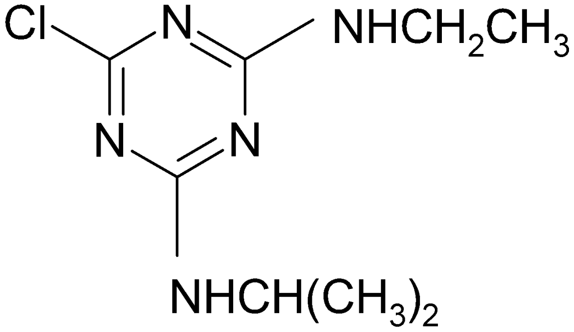
Transport over longer distances involves mass transfer – chemical movement with air or water bulk flow.

Chemical movement in soils

- Chemical solutes move with water bulk flow or convection.

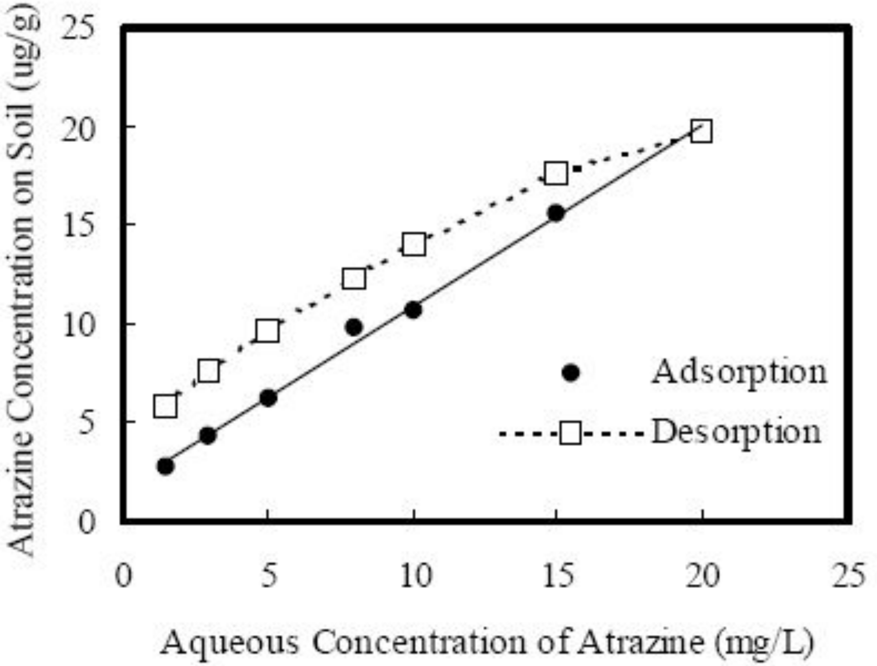
- The porous soil creates a tortuous path resulting in solute hydrodynamic dispersion

- Unique soils and conditions create unique patterns of chemical convection-dispersion; difficult to predict water and solute flux.



Atrazine sorption-desorption

Soil desorption isotherm showing hysteresis typical of organic contaminants



W. M. Wang, X. M. Liang. 2001.A New Method for Determination of Adsorption and Desorption Coefficients of Pesticides with Soil Column Liquid Chromatography, Chinese Chemical Letters Vol. 12, No. 2, pp. 157−160.

Sandy loam soil LUFA Speyer, Germany

Chemical movement in porous media (soil)

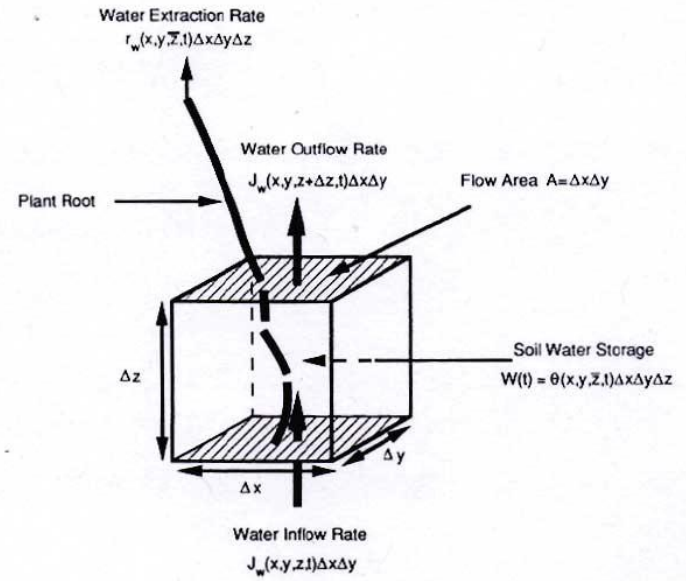
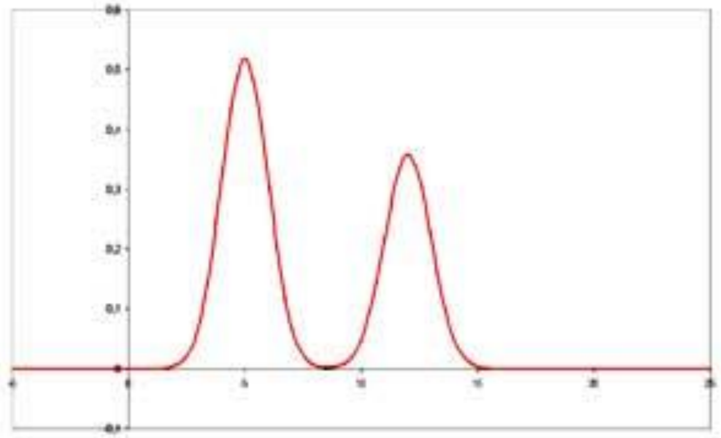
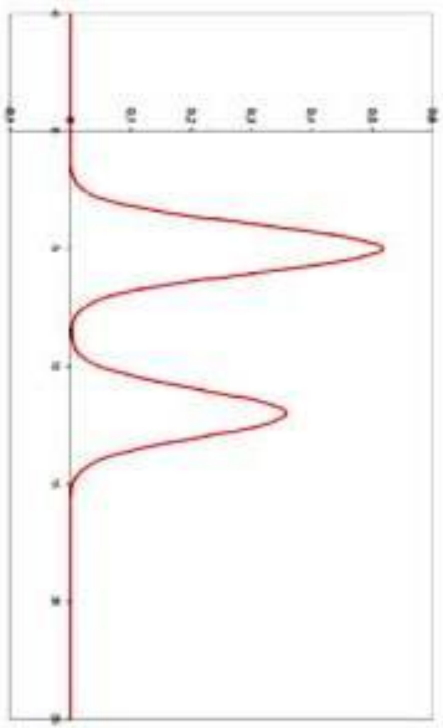


Figure 3.19 Unit volume of soil used to calculate the water mass balance equation.

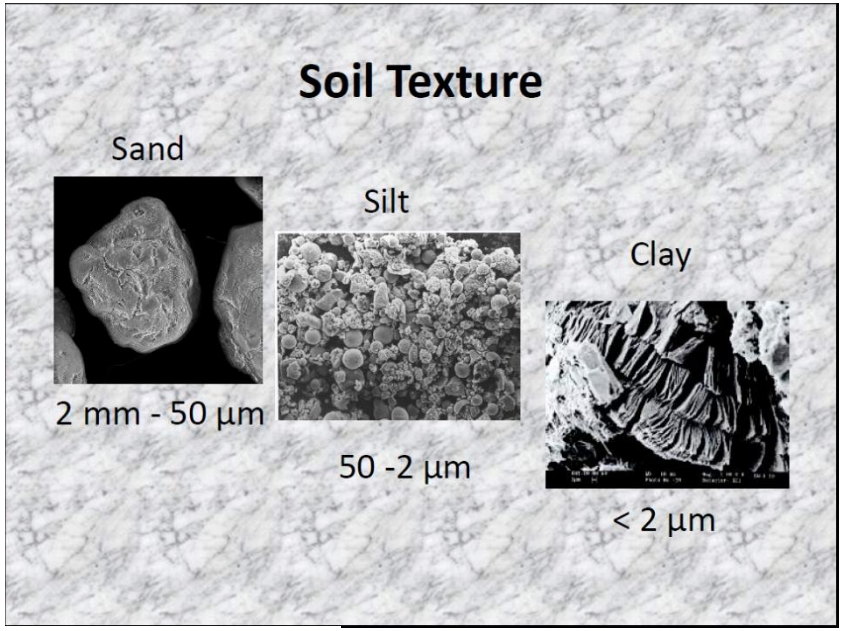




Water conservation eq. for unsaturated flow (above)
Darcy's law – saturated hydraulic conductivity
Capillary flow – unsaturated hydraulic conductivity

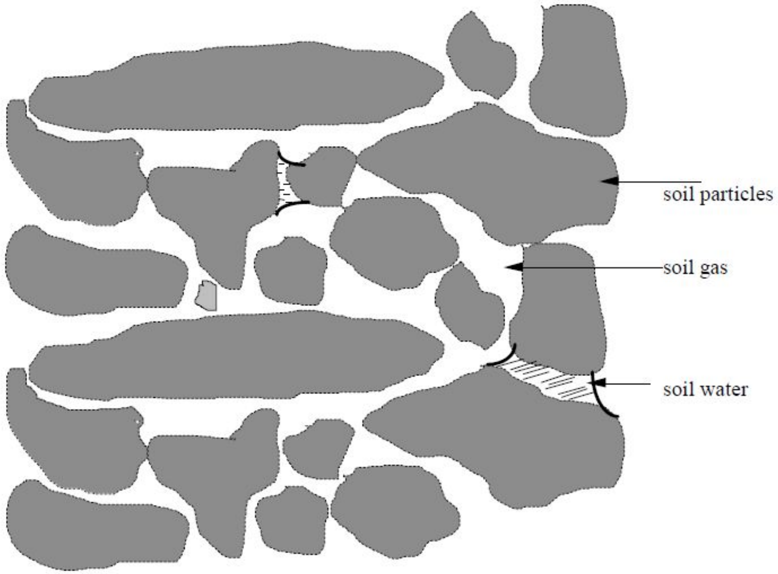
Describe convection-dispersion of non absorbing solutes and sorbing chemicals

Soil texture and Permeability



Soil solid phase characterized by:

- Soil texture - size distribution of particles
- Chemical and mineralogical (clay) properties
- Shape and surface area of soil particles
- Soil structure - arrangement of soil particles



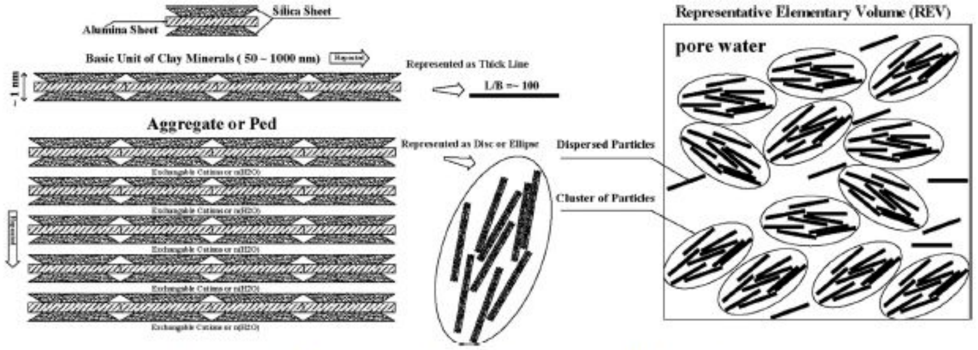


Fig. 1. Basic unit cell, sheet and cluster of montmorillonite particles for REV and different pore sizes.

Montmorillonite theoretical specific surface area ~800 m^2 per gram

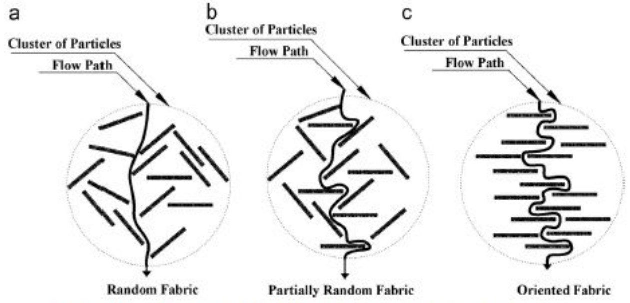


Fig. 3. Tortuous flow path through intra-particle pores for different particle arrangements.

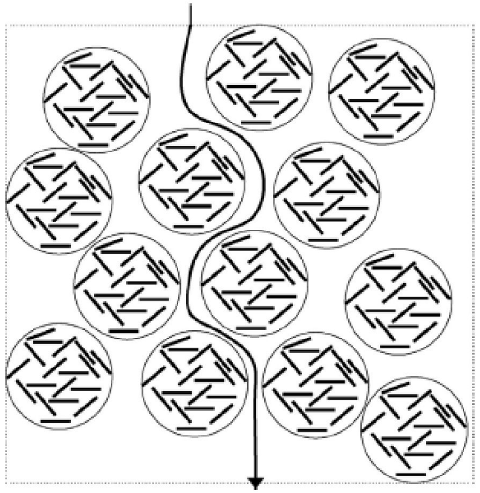
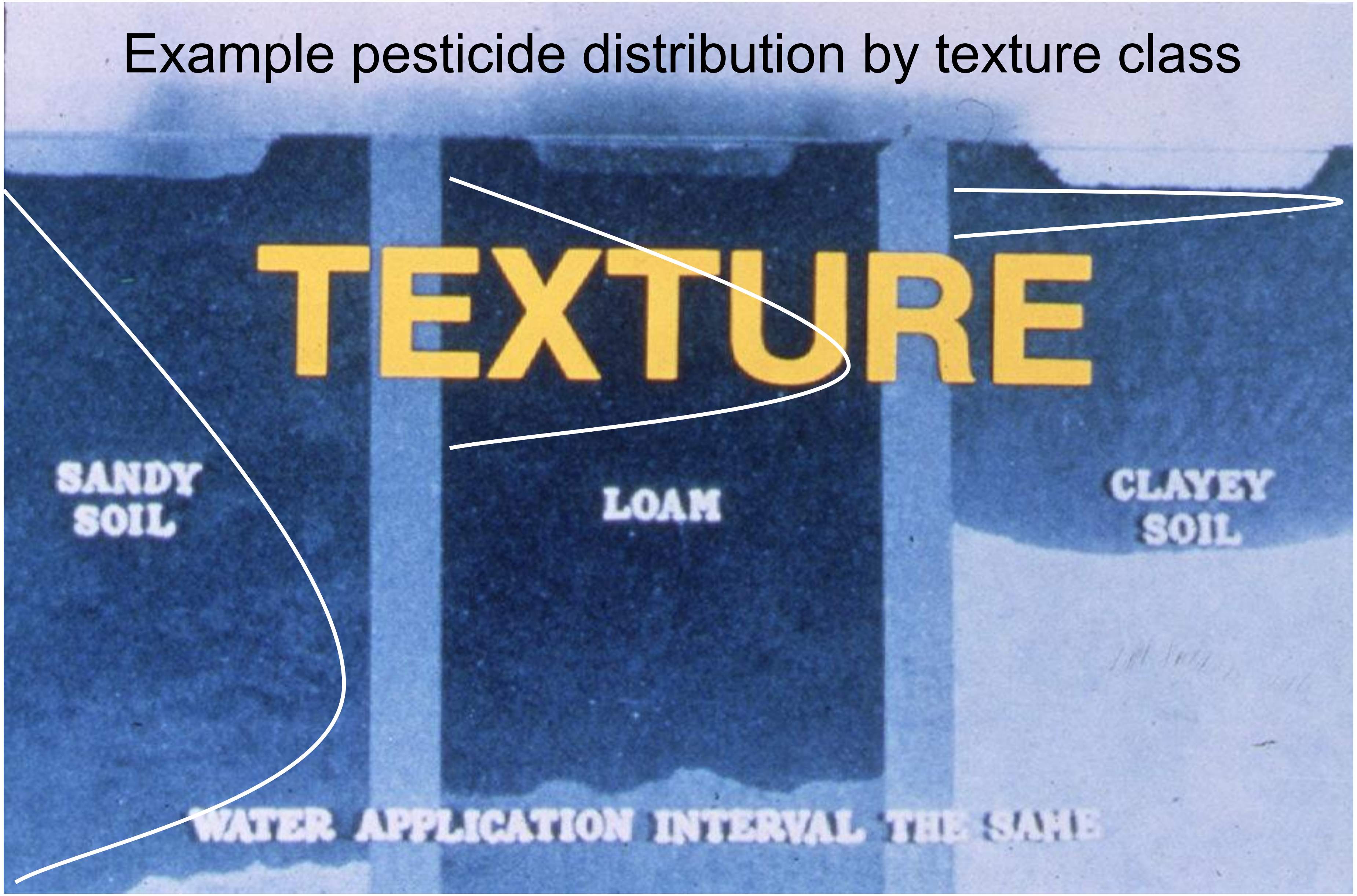


Fig. 2. Tortuous flow path between clusters.

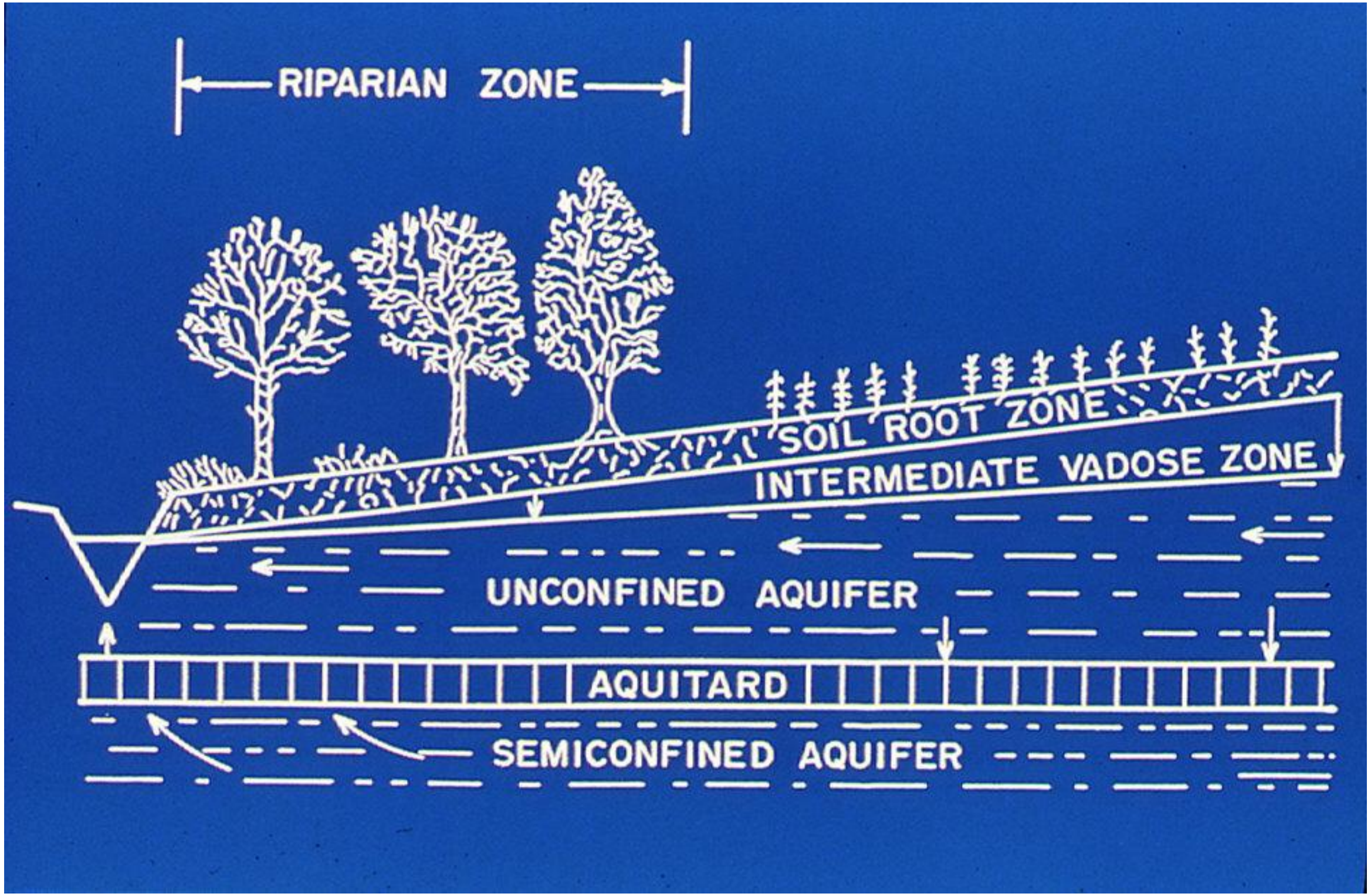
Inter-particle and intra-particle pores

Example pesticide distribution by texture class



Course textured soils and other soil conditions that result in preferential flow paths must also be considered.

Sorption and chemical movement

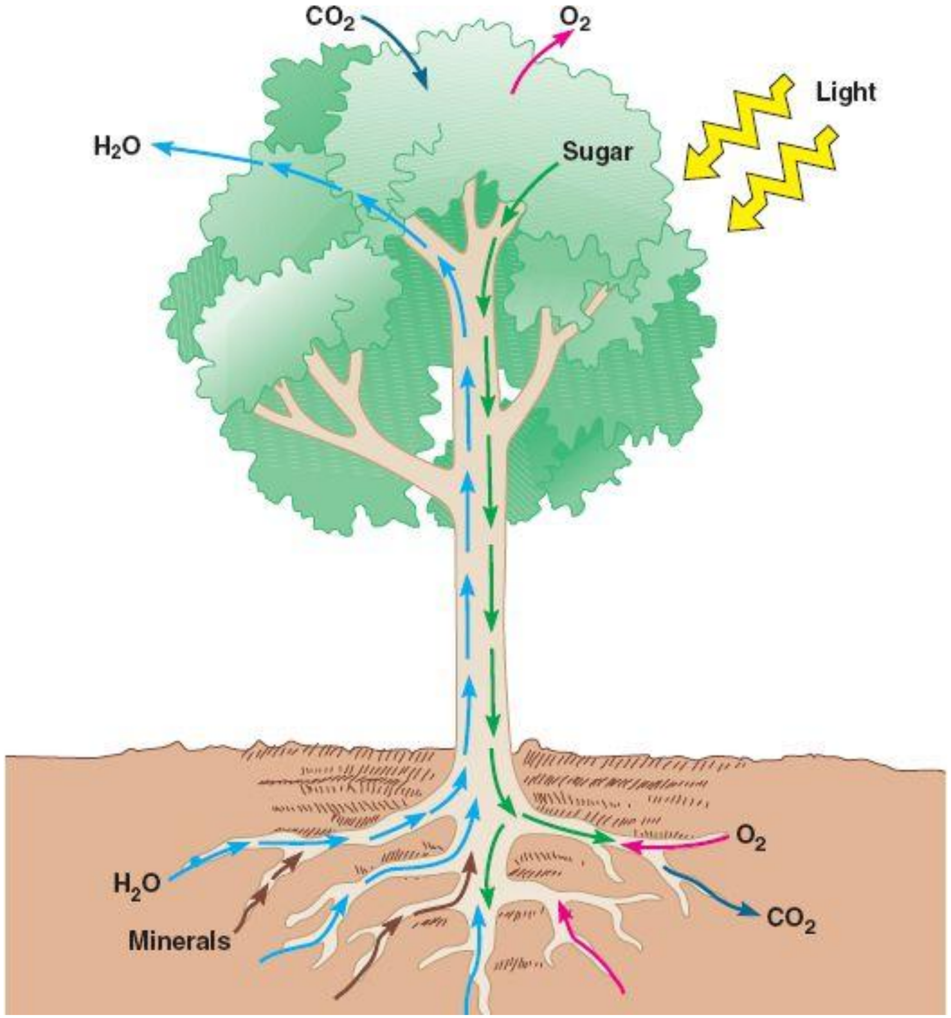


Systemic Pesticides

Systemic pesticides are soluble enough in water that they can be absorbed by a plant and moved around in its tissues.

Systemic pesticides can be applied to the soil beneath a plant and transported in the xylem to reach pests that are otherwise hard to kill.

When systemic pesticides are applied to the soil, beneficial insects, birds, pets, and people are much less likely to encounter the pesticide in the form of residues or spray drift.



Systemic Pesticides

Guttation - loss of liquid water from uninjured leaf margins due to root pressure, may contain dissolved substances, only occurs in some plants (grasses, tomato).

Pollen and Nectar

- EPA 2016[1] - numerous field studies have demonstrated that imidacloprid applied via foliar, soil or seed treatment methods can result in residues in pollen and nectar of blooming plants.

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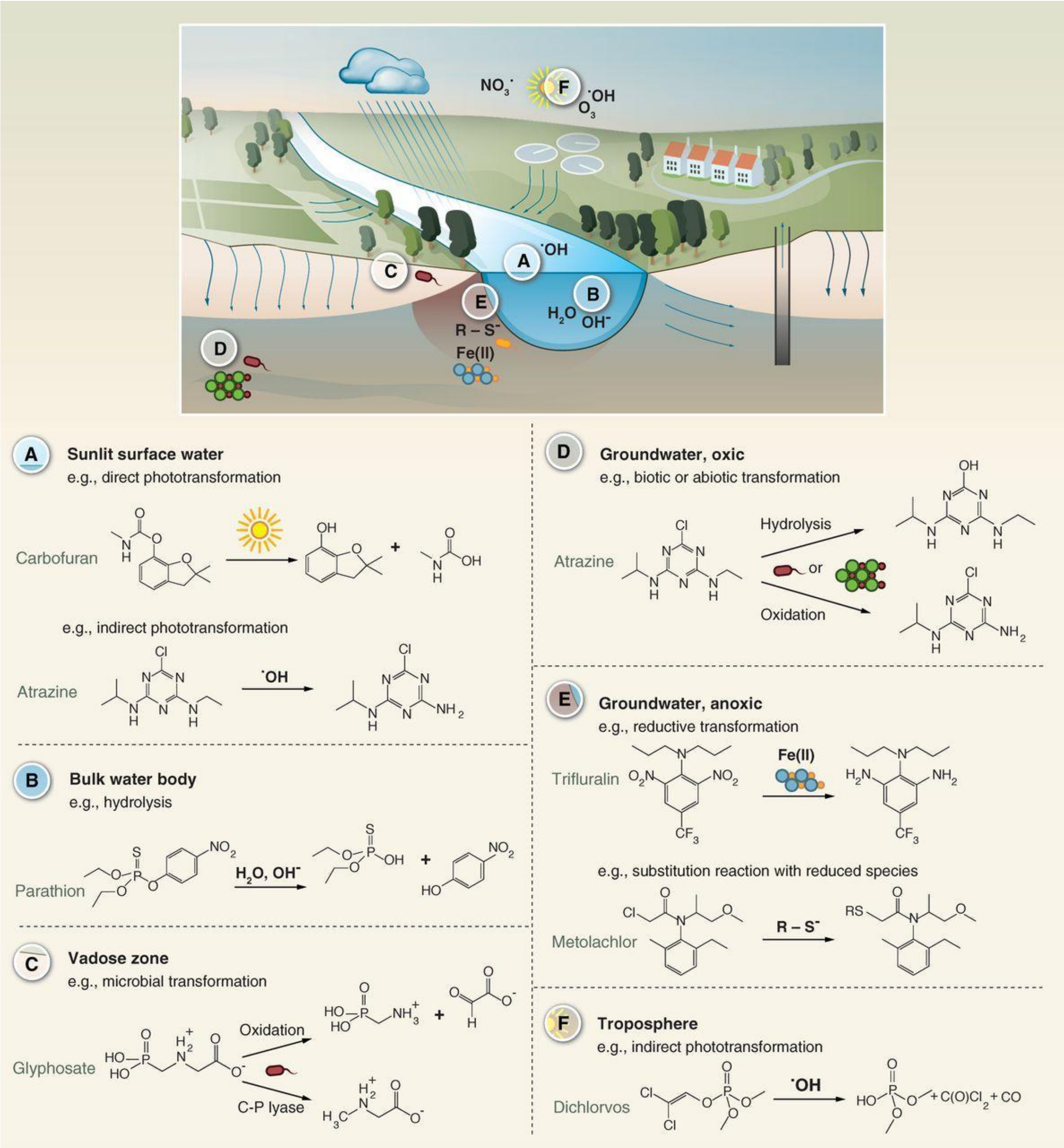
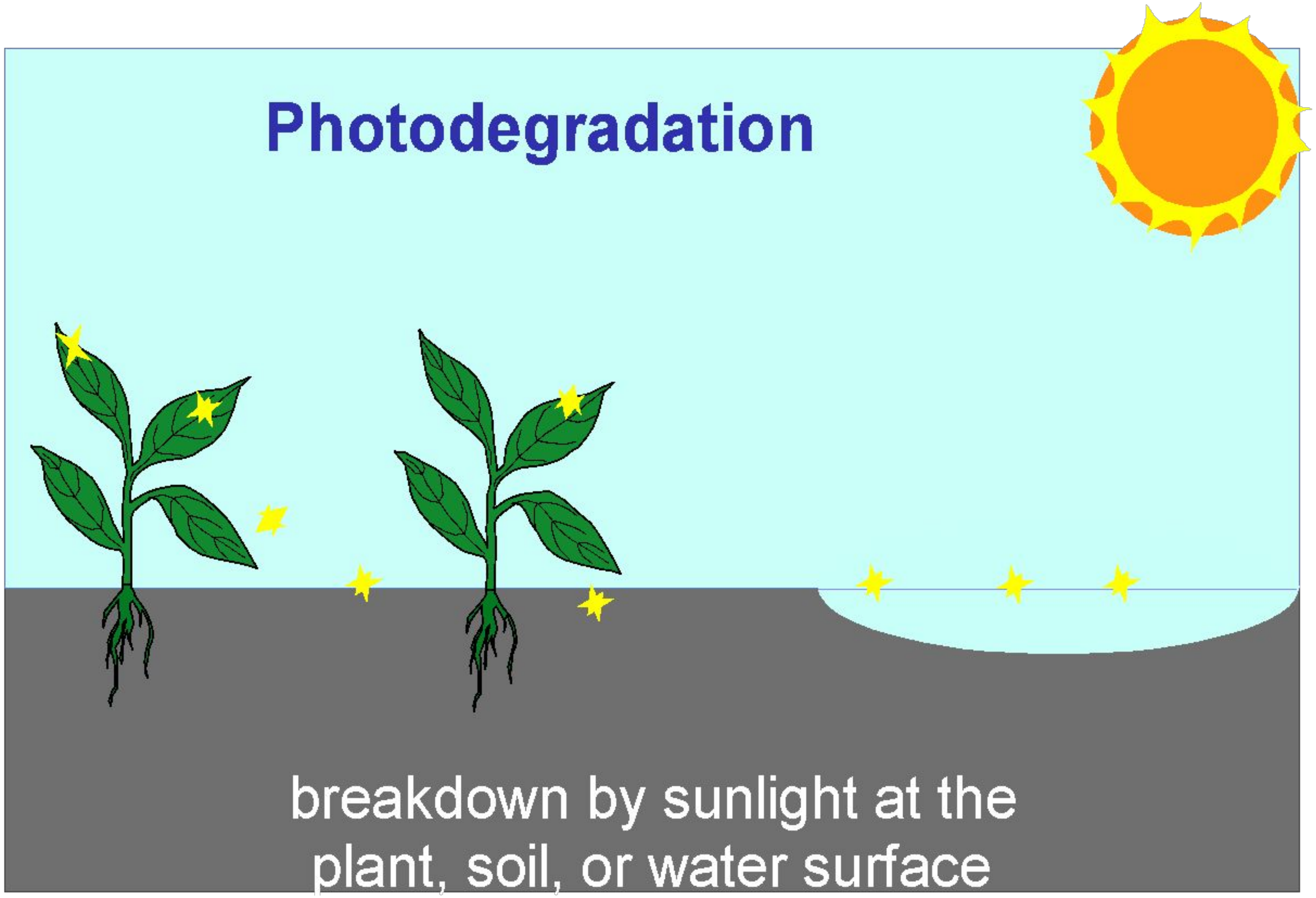
[1] Preliminary Pollinator Assessment to Support the Registration Review of Imidacloprid EPA-HQ-OPP-2008-0844-0140

Pesticide Degradation in the Environment



K Fenner et al. Science 2013;341:752-758

Photodegradation



breakdown by sunlight at the plant, soil, or water surface

Pesticide fate in the environment

Photochemical reactions

Direct photolysis- chemical absorbs light and is transformed (bonds break or conformational change).

Indirect photolysis- energy transfer from another excited species, or reaction with short lived species ($OH^{\cdot}$, $OOR^{\cdot}$, $^{1}O_2$) that are formed in the presence of light.

Pesticide fate in the environment

Photochemical reactions

Direct photolysis: 1st order reaction

$$\frac{dC}{dt} = -\Phi k_a C$$

where: C = chemical concentration

$k_a = \sum k_{a\lambda}$ = the sum of the rate constants for light absorbed at each wavelength.

Φ = quantum yield

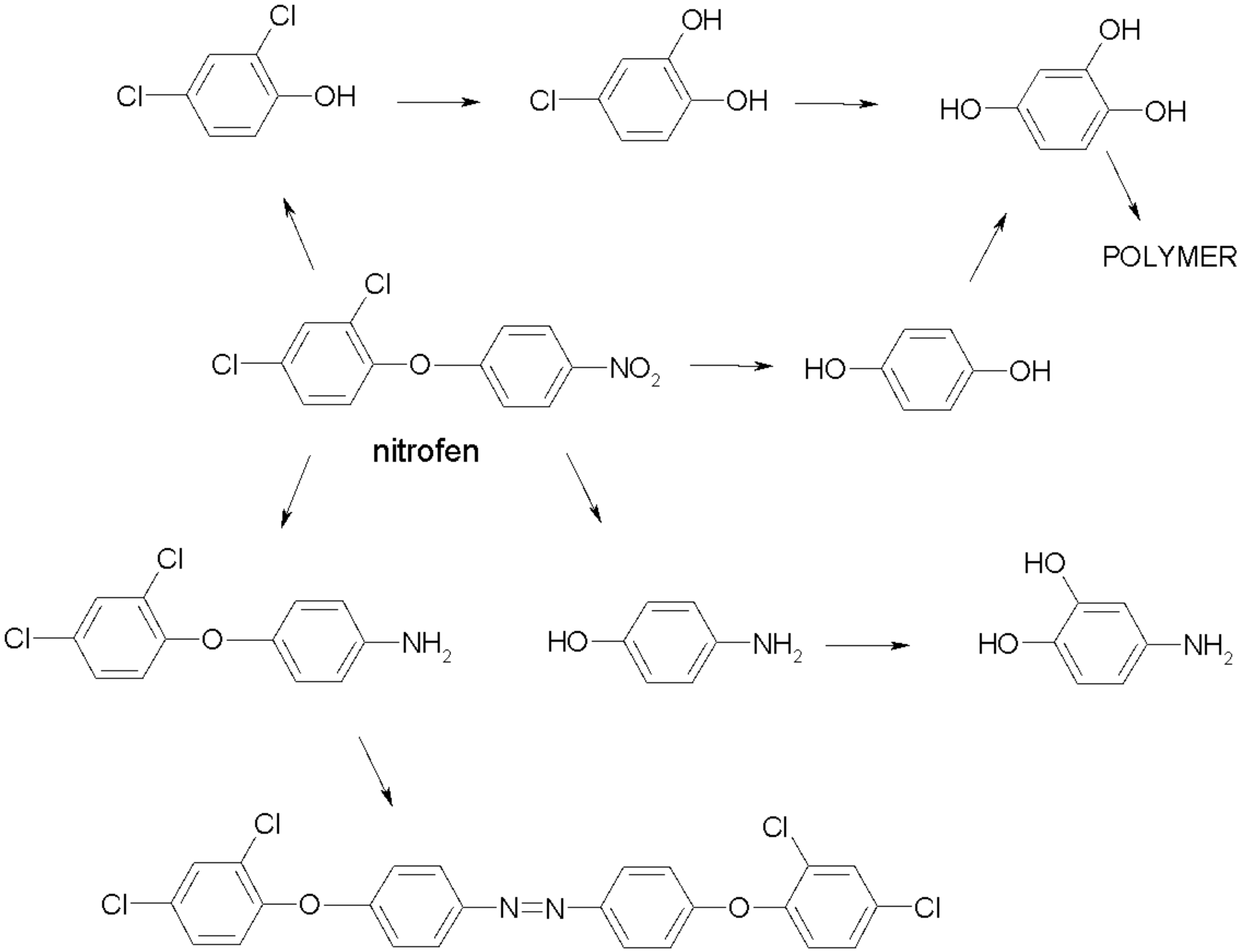
Pesticide fate in the environment

Photochemical reactions

Quantum yield, $\Phi(\lambda)$ is:

$$\Phi\ (\lambda) = \frac{\text{number of molecules transformed}}{\text{total number of photons at wavelength } \lambda \text{ absorbed}}$$

Sunlight photolysis of an aqueous suspension of nitrofen



Pesticide fate in the environment

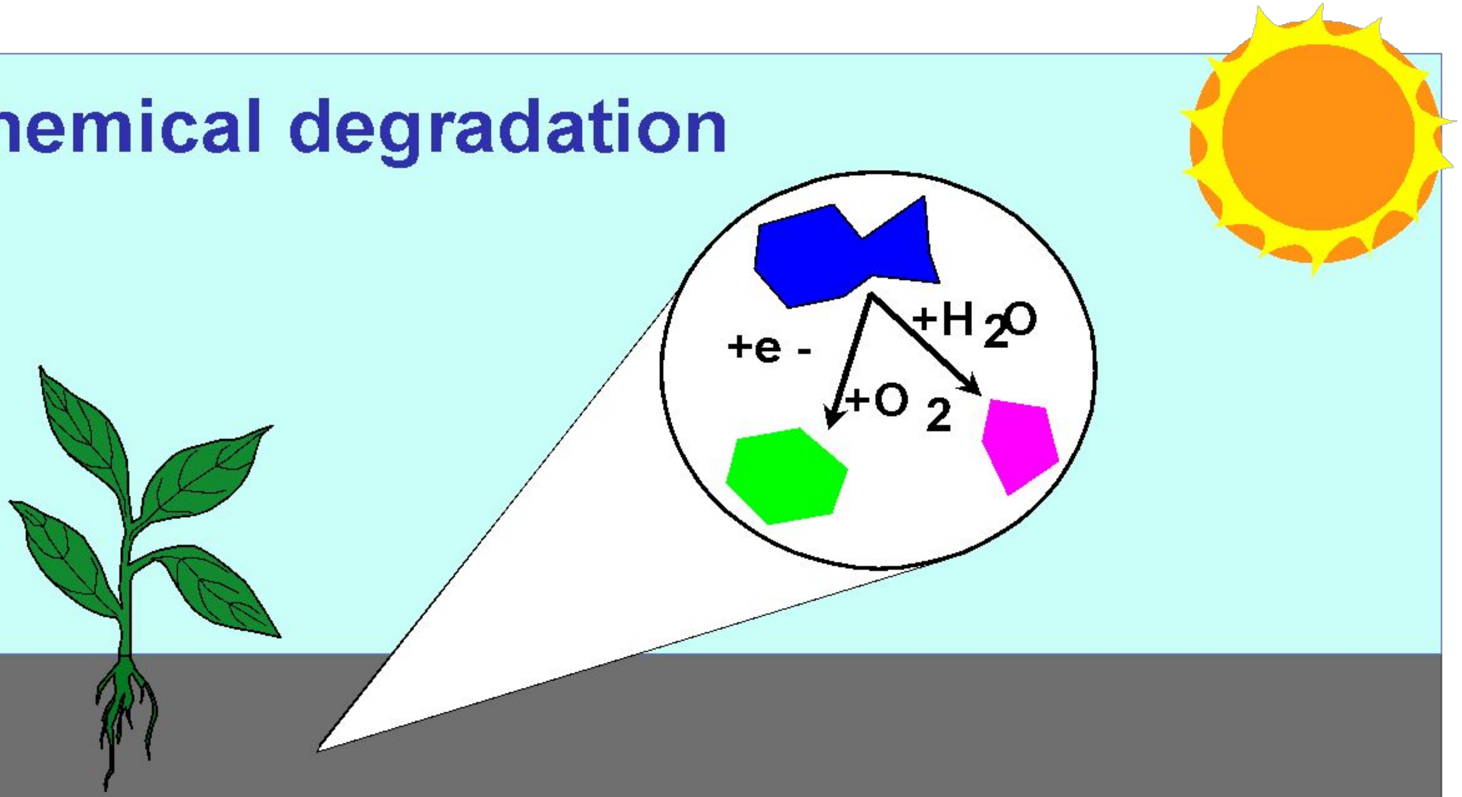
Indirect photolysis: photo-oxidation

Many compounds do not directly absorb sunlight, but are transformed by reaction with oxidizers formed by sunlight.

Free radical oxidation requires a series of reactions:

initiation
propagation
termination

Chemical degradation



breakdown by processes not involving living organisms (abiotic)

Chemical fate in the Environment

For certain chemical classes, hydrolysis may be the predominant mechanism of chemical degradation in soil, sediments or water.

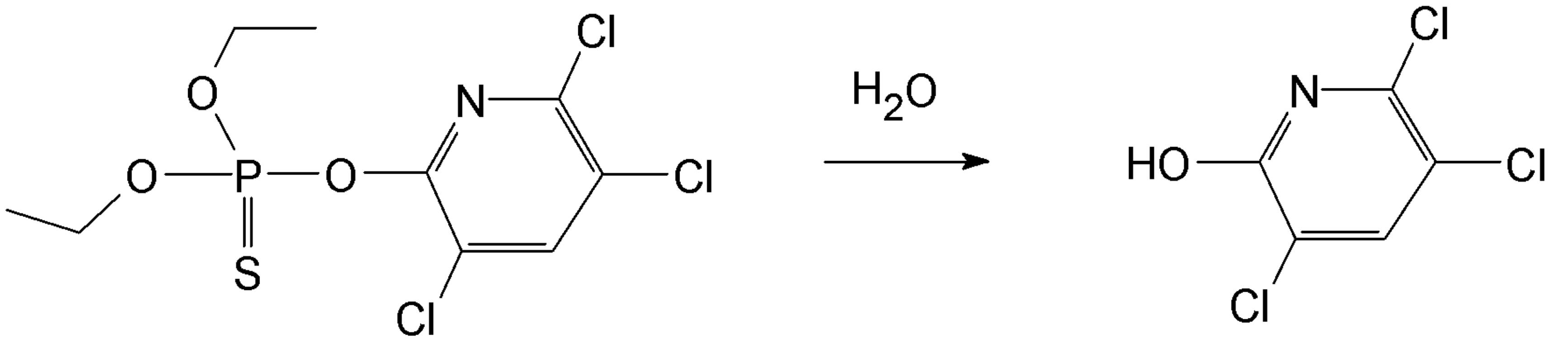
Chemicals containing the following functional groups are known to be susceptible to hydrolysis:

- Amides
- Carbamates
- Epoxides
- Esters
- Halides
- Nitriles
- Phosphate esters

Hydrolysis reaction

$$\mathrm{RX} + \mathrm{HO}^- \xrightarrow{\mathrm{H_2O}} \mathrm{ROH} + \mathrm{X}^-$$

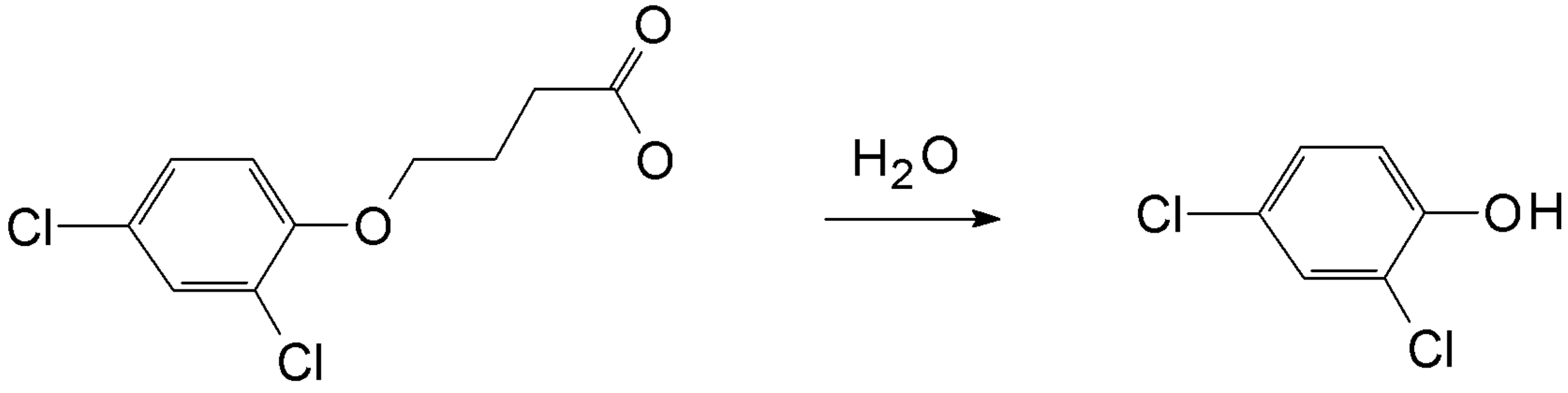
Hydrolysis of Dursban



chlorpyrifos

3,5,6 Trichloro-2-pyridinol

Hydrolysis of 2,4 DB



2,4 D butyl ester

2,4 dichlorophenol

How does pH affect the hydrolysis of pesticides?

Ionization of water

$$H_2O \rightleftharpoons H^+ + OH^-$$

Equilibrium constant for water

$K_w = [H^+] [OH^-] = 10^{-14}\ mol^2/liter^2$

$pH = -\log [H^+]$

$-\log 10^{-14} = 14$

At pH 7 $[H^+] = [OH^-]$

pH 7 means water is neutral
because there are equal concentrations of hydrogen [H^+] and hydroxyl [OH^-] ions

Waters with pH less than 7 are acidic

Waters with pH greater than 7 are basic (alkaline)

pH of natural waters range between 4 and 9

Some pesticides are weak acids or bases

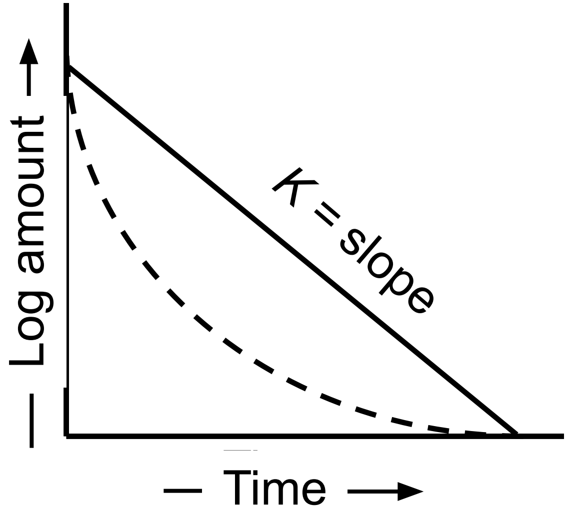
- Weak acids
  - 2,4 D
  - triclopyr
- Weak bases
  - atrazine
  - dicamba
  - simazine

Chemical reaction rate
how fast?

$$dC/dt = -k\,C$$

C = concentration

k = 1st order rate constant



The rate constant *k* determines how fast the pesticide degrades

- Hydrolysis rate can be influenced by
  - pH of the water
  - water hardness (carbonate and bicarbonate)
  - dissolved organic matter
  - dissolved metal ions
  - Temperature

Half-life = the amount of time it takes the parent compound to decay to half its original concentration

Hydrolysis *Half-life*

$$C_t/C_0 = 0.5 = e^{-kt_{1/2}}$$

$$t_{1/2} = 0.639/k$$

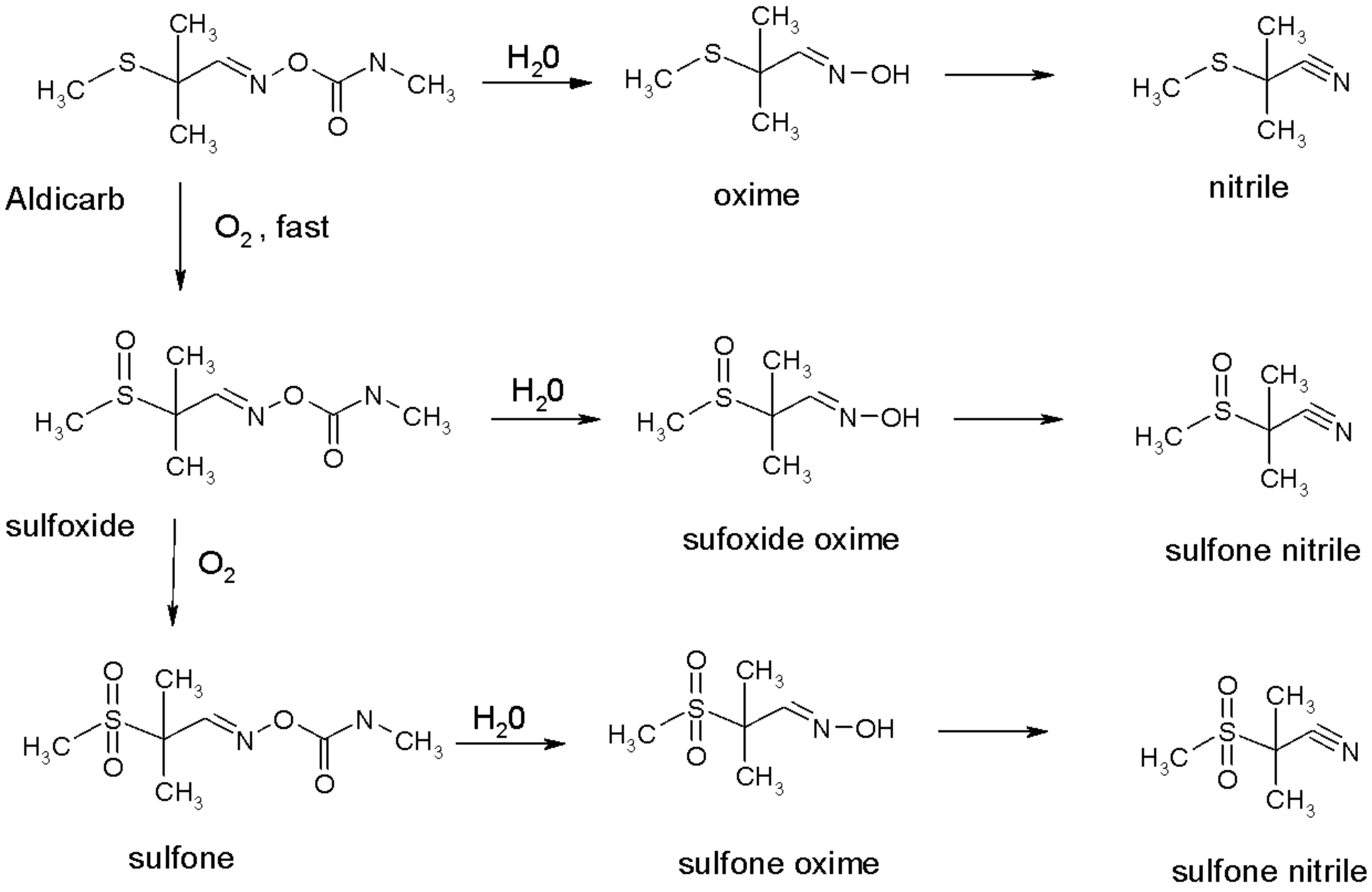
Where: C_t = concentration at time t

C_0 = concentration at time 0

Pesticide hydrolysis 1/2 life ($t_{1/2}$)

Cythion	pH 9, $t_{1/2}$ = 12 hours
Imidan	pH 7, $t_{1/2}$ = 9.4 hours pH 9, $t_{1/2}$ = 5.5 min.
Fusilade	pH 9, $t_{1/2}$ = 9 hours
Captan	pH 7, $t_{1/2}$ = 8 hours pH 9, $t_{1/2}$ = 4 min.
2,4 D ester	pH 6, $t_{1/2}$ = 4 years pH 9, $t_{1/2}$ = 37 hours

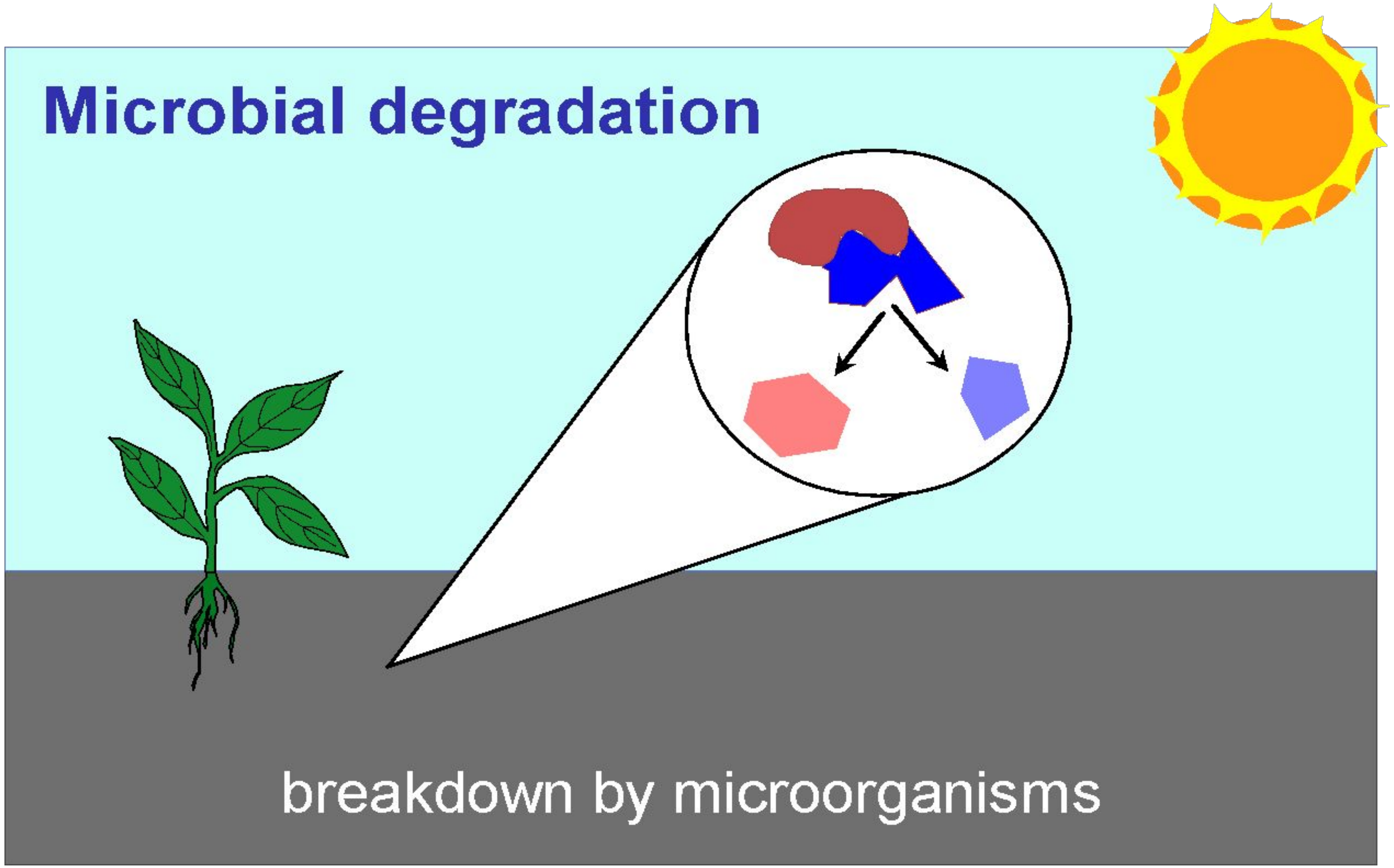
Aldicarb degradation pathways



Aqueous Half-life (days) of Aldicarb sulfoxide and sulfone (1:1)

	pH			
	5.5-7	7.5	8	8.5
Temp °C				
5	1000	733	236	76
10	633	402	122	37
15	415	219	62	18
20	239	112	31	9
25	138	57	15	4

Microbial degradation



breakdown by microorganisms

Pesticide fate in the environment
Microbial degradation

- Microorganisms have evolved as key agents in the transformation of the vast array of organics in terrestrial and aquatic environments.

- Among biological processes, microbial metabolism is the primary pathway of synthetic organic transformation.

- The microorganisms that are responsible for the majority of xenobiotic transformations are bacteria and fungi.

Table 2 Abundance of microbial groups in different subsurface habitats

Group	Habitat	Contamination	Abundance (cells cm^{-3})	Reference
Prokaryota				
Bacteria	Water from karst and cave systems	No	10^2–10^5	Gounot (1994); Farnleitner *et al*. (2005)
	Sediment from cave waters	No	10^4–10^8	Gounot (1994); Rusterholtz & Mallory (1994)
	Water from granite and basalt systems	No	10^2–10^5	Stevens & McKinley (1995); Pedersen (1997)
	Ground water	No	10^3–10^6	Ghiorse & Wilson (1988); Madsen & Ghiorse (1993); Pedersen (2000); Griebler (2001)
		Yes	10^3–10^7	
	Groundwater-saturated porous sediment	No	10^5–10^8	
		Yes	up to 10^{10}	
	Vadose zone sediment	No	10^4–10^8	Brockman *et al*. (1992); Kieft *et al*. (1993)
Archaea		Yes or no	up to 20% of total cell counts	Detmers *et al*. (2004)
Protozoa				
Heterotrophic Flagellata	Ground water	No	10^0–10^2	Hirsch *et al*. (1992); Madsen & Ghiorse (1993); Novarino *et al*. (1997)
		Yes	up to 10^5	Novarino *et al*. (1997); Zarda *et al*. (1998)
	Groundwater-saturated porous sediment	No	10^3–10^5	Novarino *et al*. (1997)
		Yes	up to 10^8	Novarino *et al*. (1997)
Amoebae	Ground water	Yes or no	10^{-1}–10^1	Hirsch *et al*. (1992); Madsen & Ghiorse (1993); Novarino *et al*. (1997)
Ciliata	Ground water (near surface)	Yes or no	10^{-1}–10^0	
Heliozoa	Ground water (near surface)	No	10^{-1}–10^0	

Distribution of different microbial groups in the subsurface

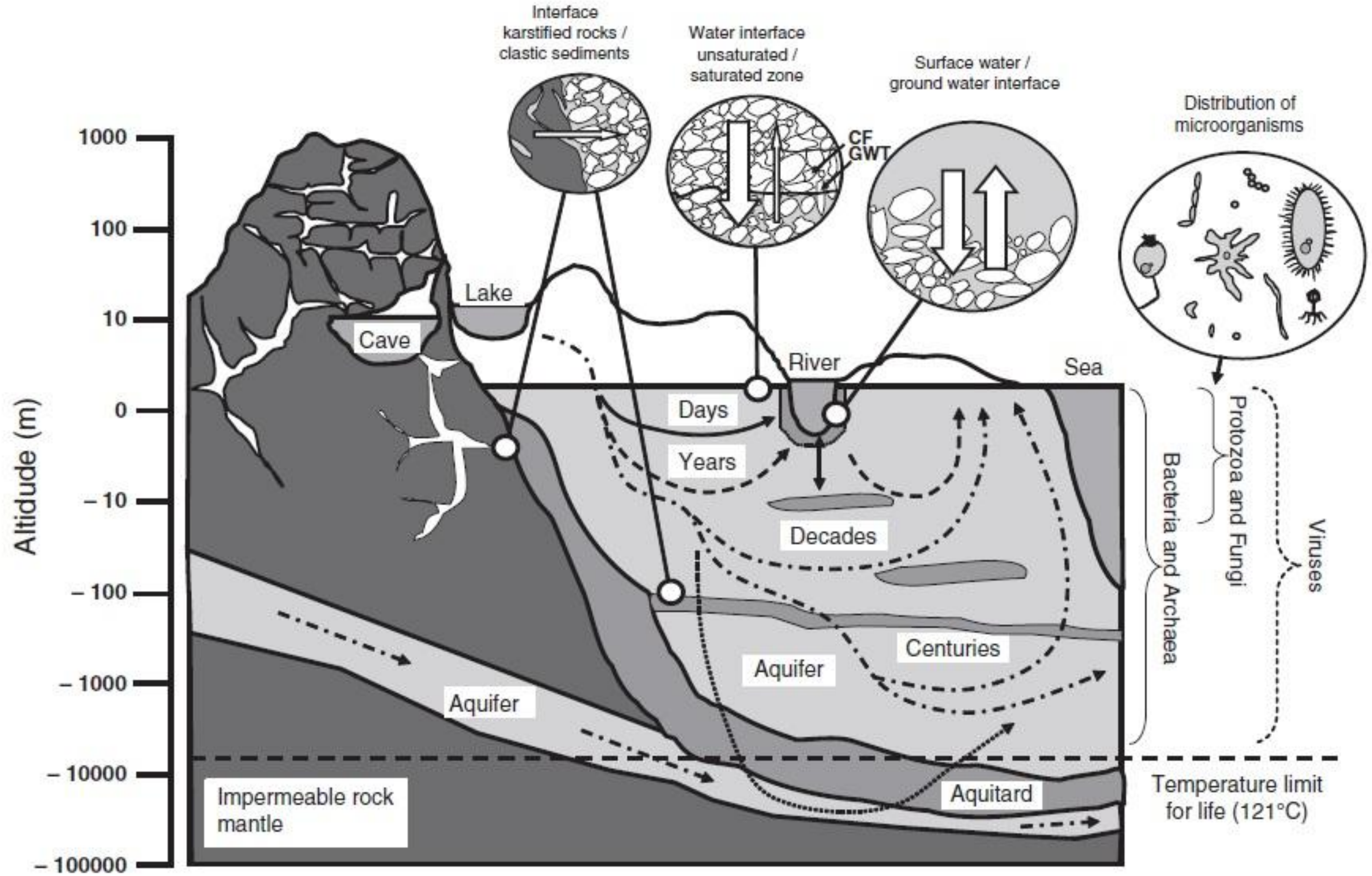


Fig. 1 Schematic view of aquatic surface and subsurface habitats. Arrows depict the flow of water carrying energy and matter through the subsurface, with boxes next to arrows indicating typical groundwater residence times. Circles highlight transition zones between habitat types. Curly braces indicate the distribution of different microbial groups in the subsurface. CF, capillary fringe; GWT, groundwater table.

Pesticide fate in the environment
Microbial degradation

Five processes can be involved in xenobiotic biotransformation:

1. Biodegradation: xenobiotic serves as substrate for growth (energy source).

2. Cometabolism: xenobiotic is transformed by metabolic reactions but does not serve as an energy source.

Pesticide fate in the environment
Microbial degradation

3. Polymerization and conjugation: xenobiotics are linked with themselves or other organics, ie., incorporation into soil organic matter.

4. Accumulation: xenobiotics are incorporated into the microorganism.

5. Secondary effects: xenobiotics are transformed due to changes in pH or redox conditions, or reactive products brought about by micro-organisms.

Pesticide fate in the environment
Microbial degradation

Mineralization: complete biodegradation; metabolism by one or more interacting micro-organisms to yield CO_2, H_2O, and inorganics (minerals).

Mineralization of xenobiotics is desired to avoid the potential for reactive or toxic intermediates.

Pesticide fate in the environment
Microbial degradation

Rates of microbial degradation are largely determined by environmental conditions that will support microbial growth, such as:

temperature, pH, redox conditions, moisture, oxygen, organic matter and other substrates.

Microbial degradation: reaction rates

Microbial metabolism follows Michaelis-Menten enzyme kinetics:

$$K_b = \frac{\hat{\mu} X}{Y(K_M + C)}$$

where: K_b = biological transformation rate

$\hat{\mu}$ = maximum growth rate

X = viable microbial biomass concentration

Y = cell yield: cells / xenobiotic conc. (C) utilized

K_M = Michaelis - Menten half saturation constant

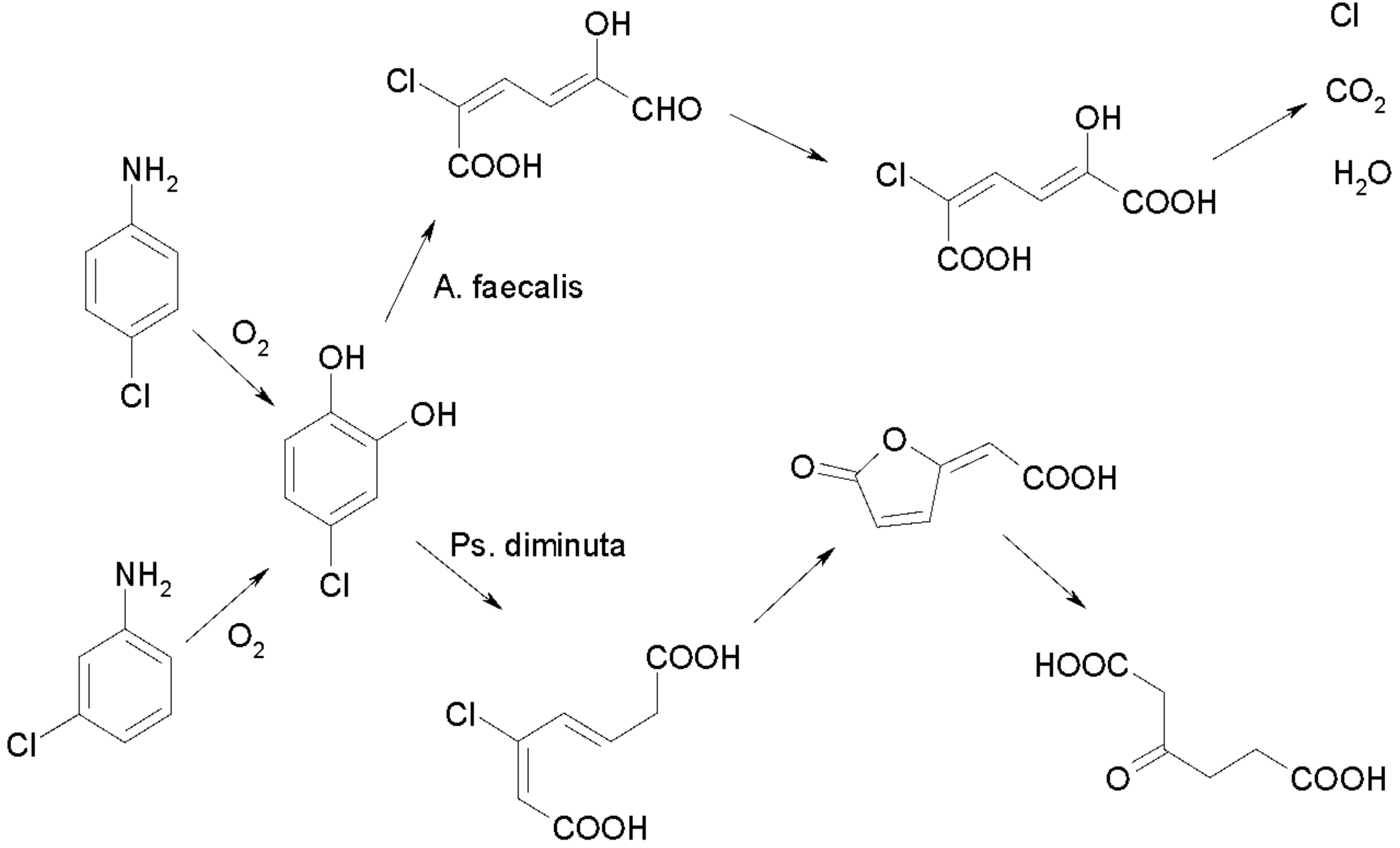
Microbial degradation: reaction rates

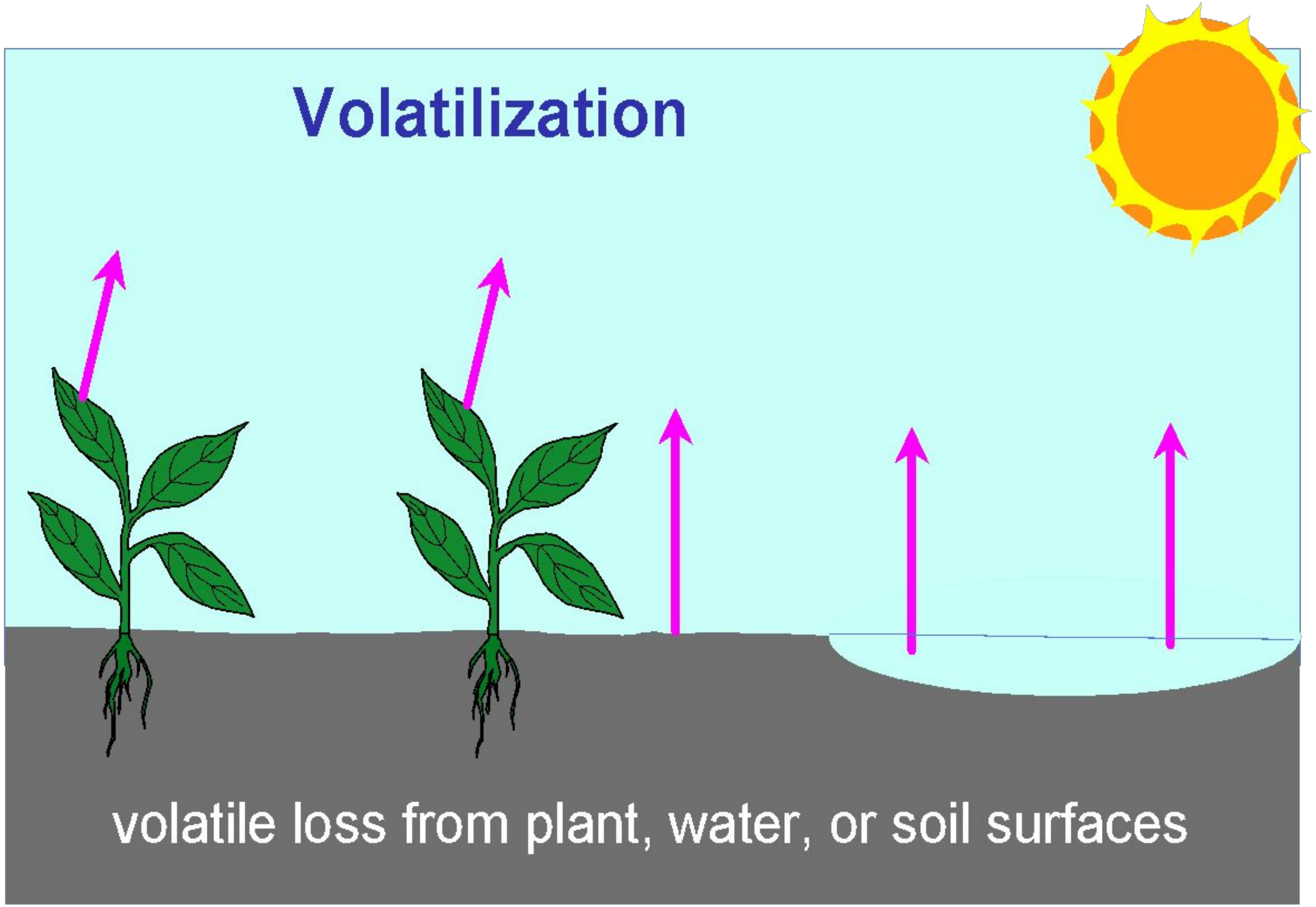
When the xenobiotic concentration, C, is <10 μg/l, and much less than K_M (~0.1-10 mg/l), then:

$$K_b = \frac{\hat{\mu}}{YK_M} X$$

This results in a pseudo first order reaction with respect to microbial biomass (X) and xenobiotic concentration (C).

Chemical and microbial degradation of chloroanilines





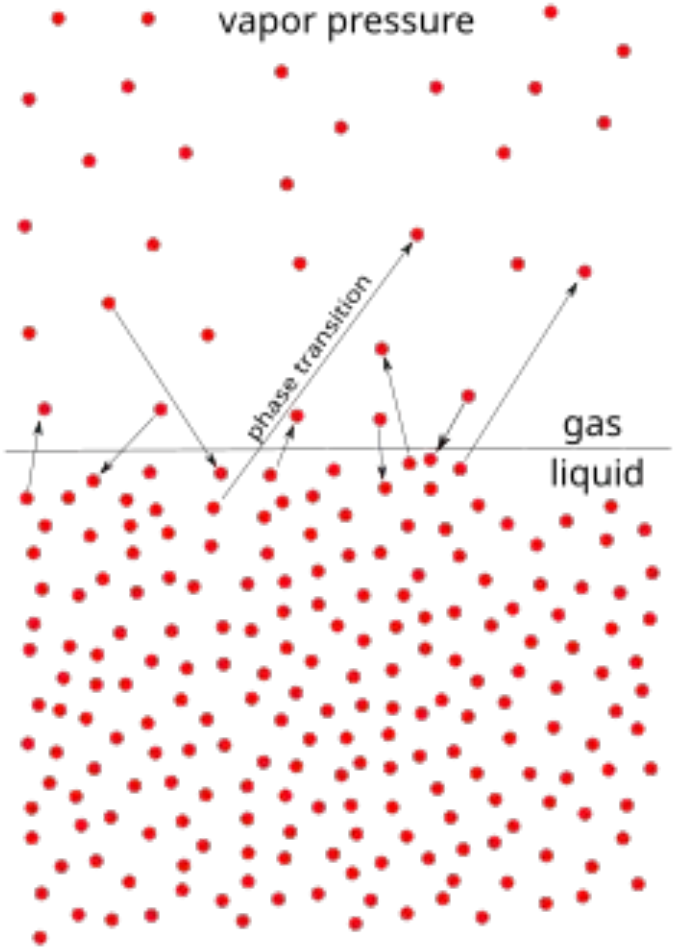
Volatilization

volatile loss from plant, water, or soil surfaces

Vapor Pressure

- Vapor pressure or equilibrium vapor pressure is the pressure exerted by a vapor in thermodynamic equilibrium with its condensed phases (solid or liquid) at a given temperature in a closed system.

- Measure of a pesticide’s tendency to volatilize from itself.



Volatilization from soil surface

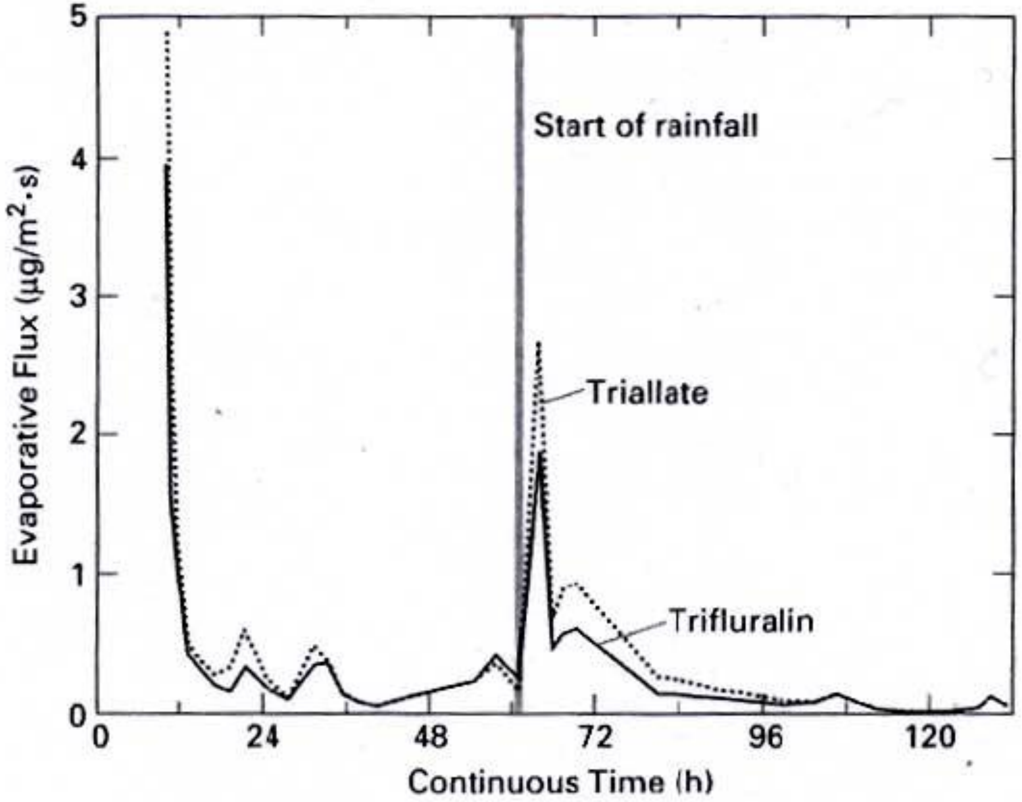
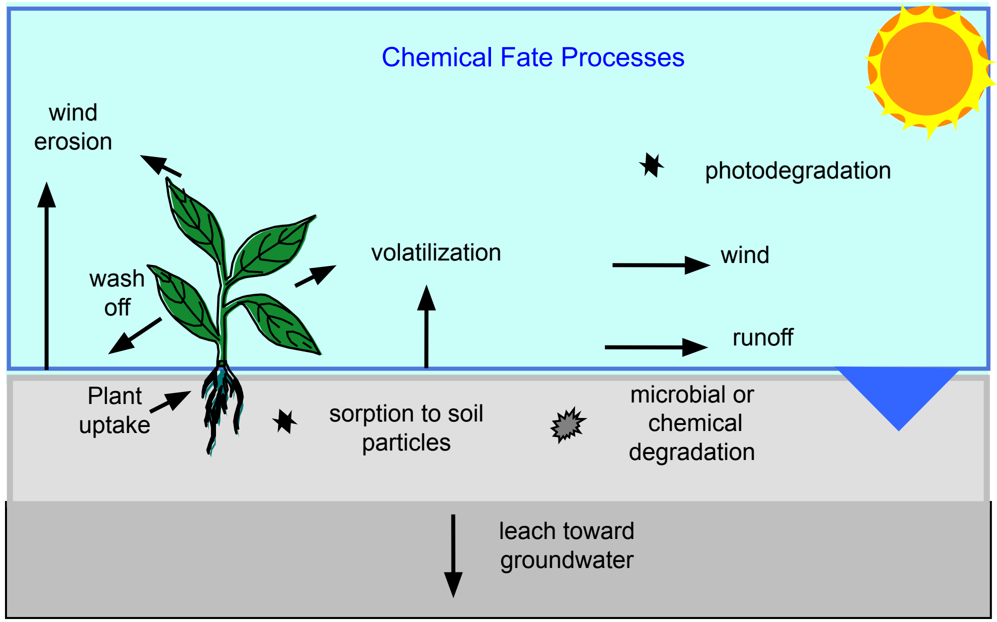
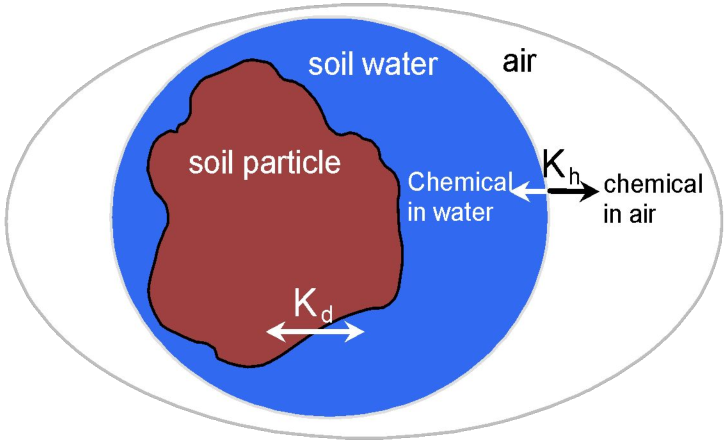


Figure 7.48 Evaporative fluxes of triallate and trifluralin herbicides with time, showing the effect of a rainfall after the spray of herbicides to a field site in Ottawa, Canada. [Data from Majewski et al. (1993). Reproduced with permission.]

Volatilization from soil surface

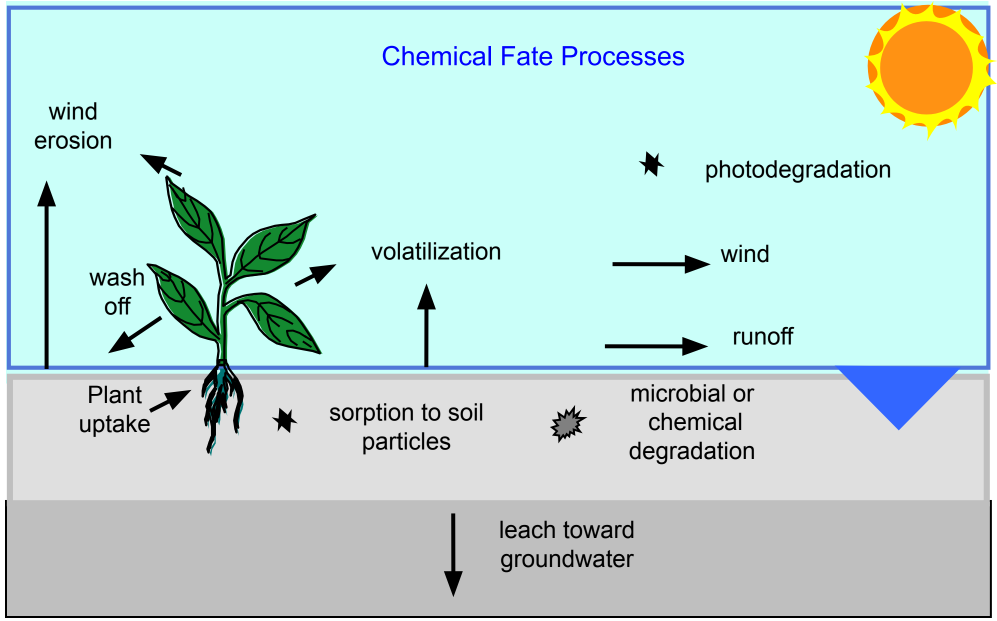


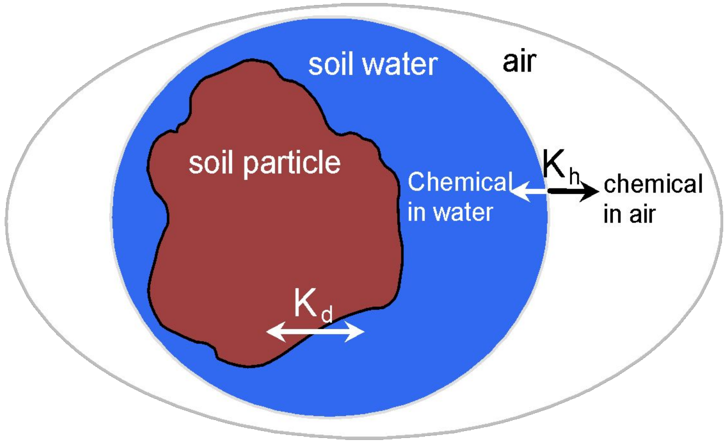


K_h describes the relationship between pesticide concentration

Capillary flow – unsaturated hydraulic conductivity
Convection-dispersion of sorbing chemicals

Volatilization from soil surface





K_h describes the relationship between pesticide concentration

Capillary flow – unsaturated hydraulic conductivity
Convection-dispersion of sorbing chemicals

Pesticide volatilization from dry and moist soils

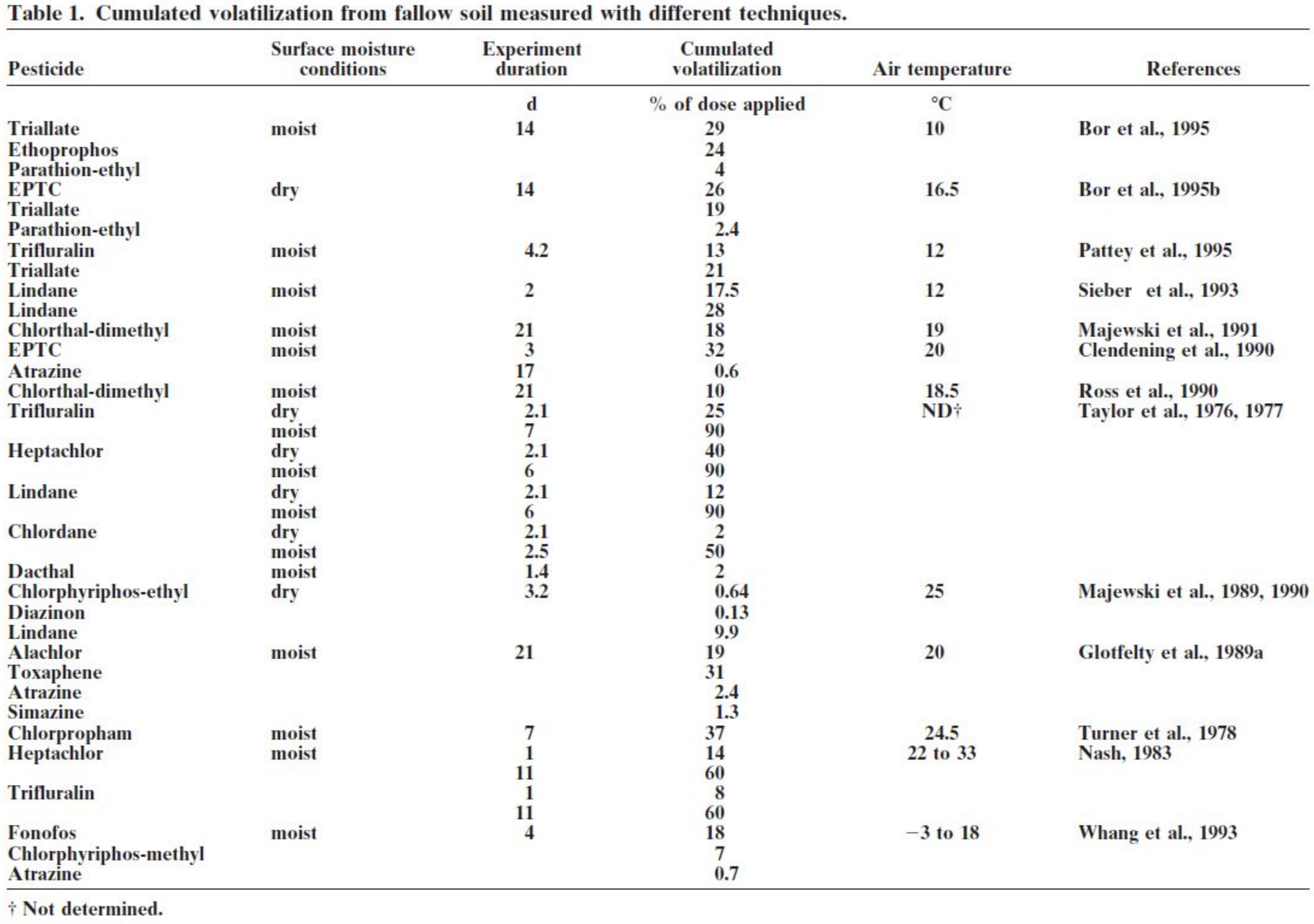


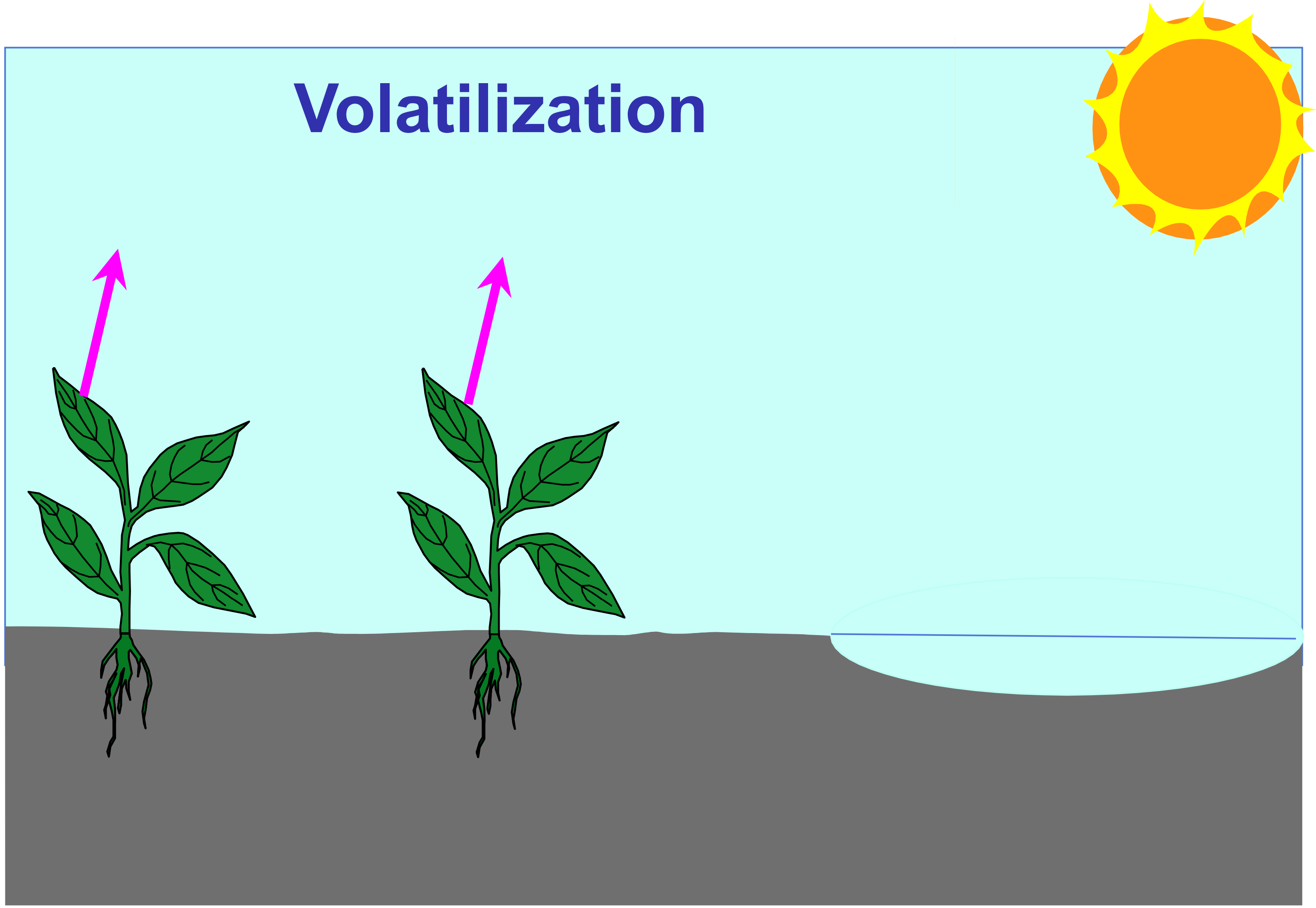
Table 1. Cumulated volatilization from fallow soil measured with different techniques.

Pesticide	Surface moisture conditions	Experiment duration	Cumulated volatilization	Air temperature	References
		d	% of dose applied	°C	
Triallate	moist	14	29	10	Bor et al., 1995
Ethoprophos			24		
Parathion-ethyl			4		
EPTC	dry	14	26	16.5	Bor et al., 1995b
Triallate			19		
Parathion-ethyl			2.4		
Trifluralin	moist	4.2	13	12	Pattey et al., 1995
Triallate			21		
Lindane	moist	2	17.5	12	Sieber et al., 1993
Lindane			28		
Chlorthal-dimethyl	moist	21	18	19	Majewski et al., 1991
EPTC	moist	3	32	20	Clendening et al., 1990
Atrazine		17	0.6		
Chlorthal-dimethyl	moist	21	10	18.5	Ross et al., 1990
Trifluralin	dry	2.1	25	ND†	Taylor et al., 1976, 1977
	moist	7	90		
Heptachlor	dry	2.1	40		
	moist	6	90		
Lindane	dry	2.1	12		
	moist	6	90		
Chlordane	dry	2.1	2		
	moist	2.5	50		
Dacthal	moist	1.4	2		
Chlorphyriphos-ethyl	dry	3.2	0.64	25	Majewski et al., 1989, 1990
Diazinon			0.13		
Lindane			9.9		
Alachlor	moist	21	19	20	Glotfelty et al., 1989a
Toxaphene			31		
Atrazine			2.4		
Simazine			1.3		
Chlorpropham	moist	7	37	24.5	Turner et al., 1978
Heptachlor	moist	1	14	22 to 33	Nash, 1983
		11	60		
Trifluralin		1	8		
		11	60		
Fonofos	moist	4	18	−3 to 18	Whang et al., 1993
Chlorphyriphos-methyl			7		
Atrazine			0.7		

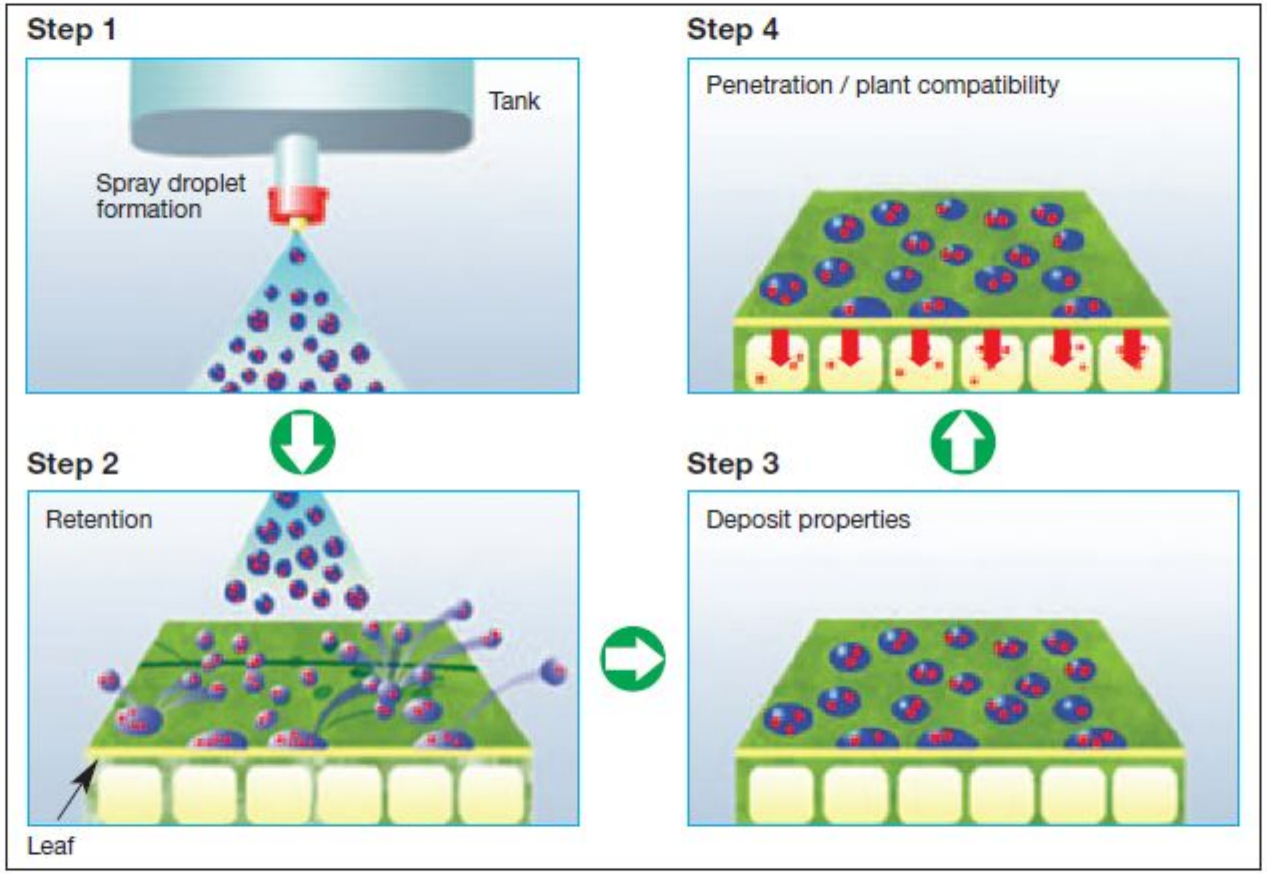
† Not determined.

Frederico et. al, Predicting and Measuring Environmental Concentration of Pesticides in Air after Soil Application – JEQ 2003

Volatile loss from Plant Surfaces

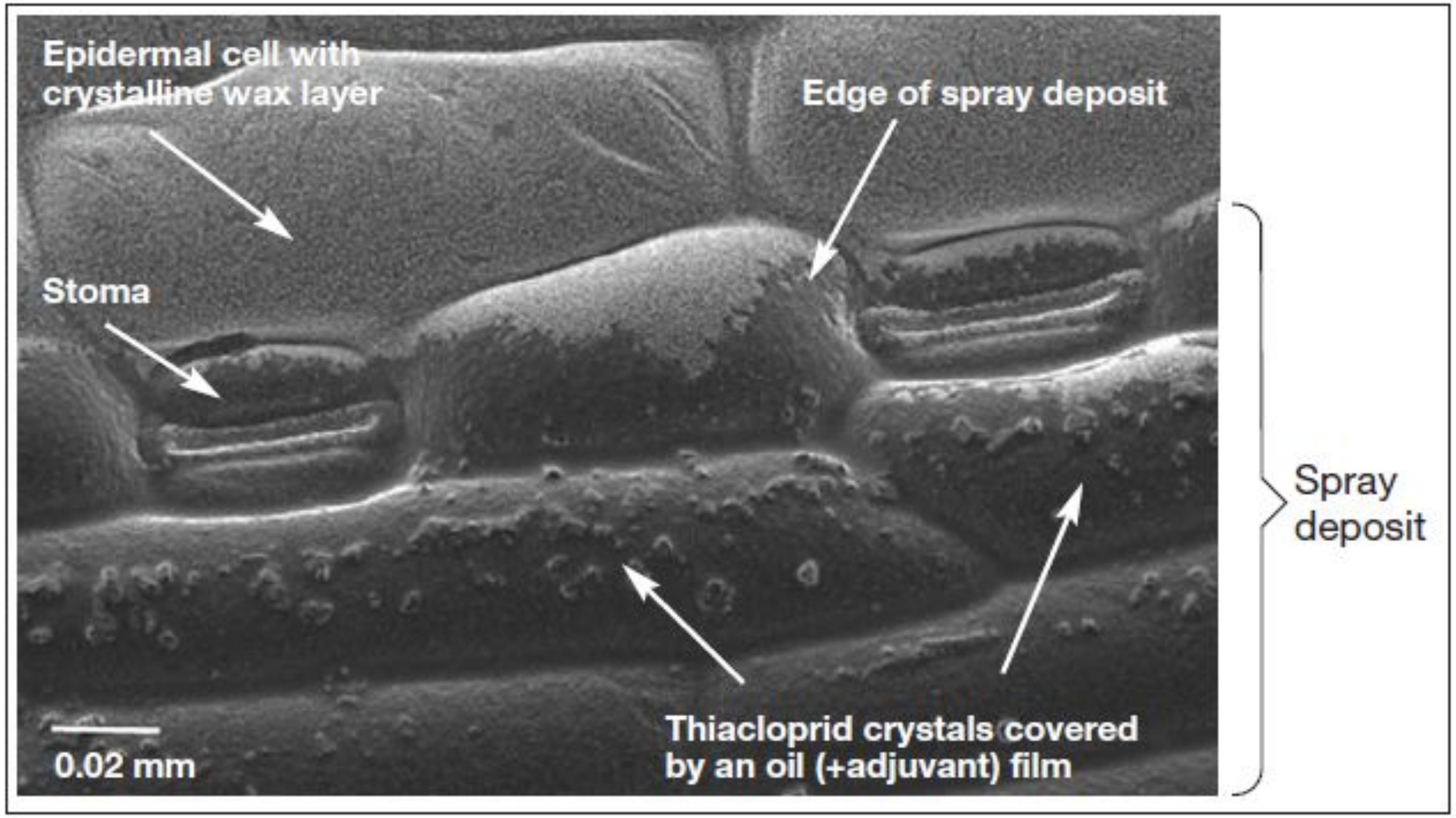


Transfer of agrochemicals to the target



R. Pontzen, Pflanzenschutz-Nachrichten Bayer 59/2006, 1, p 63-72

Spray deposit of thiacloprid on a barley leaf (electron micrograph).



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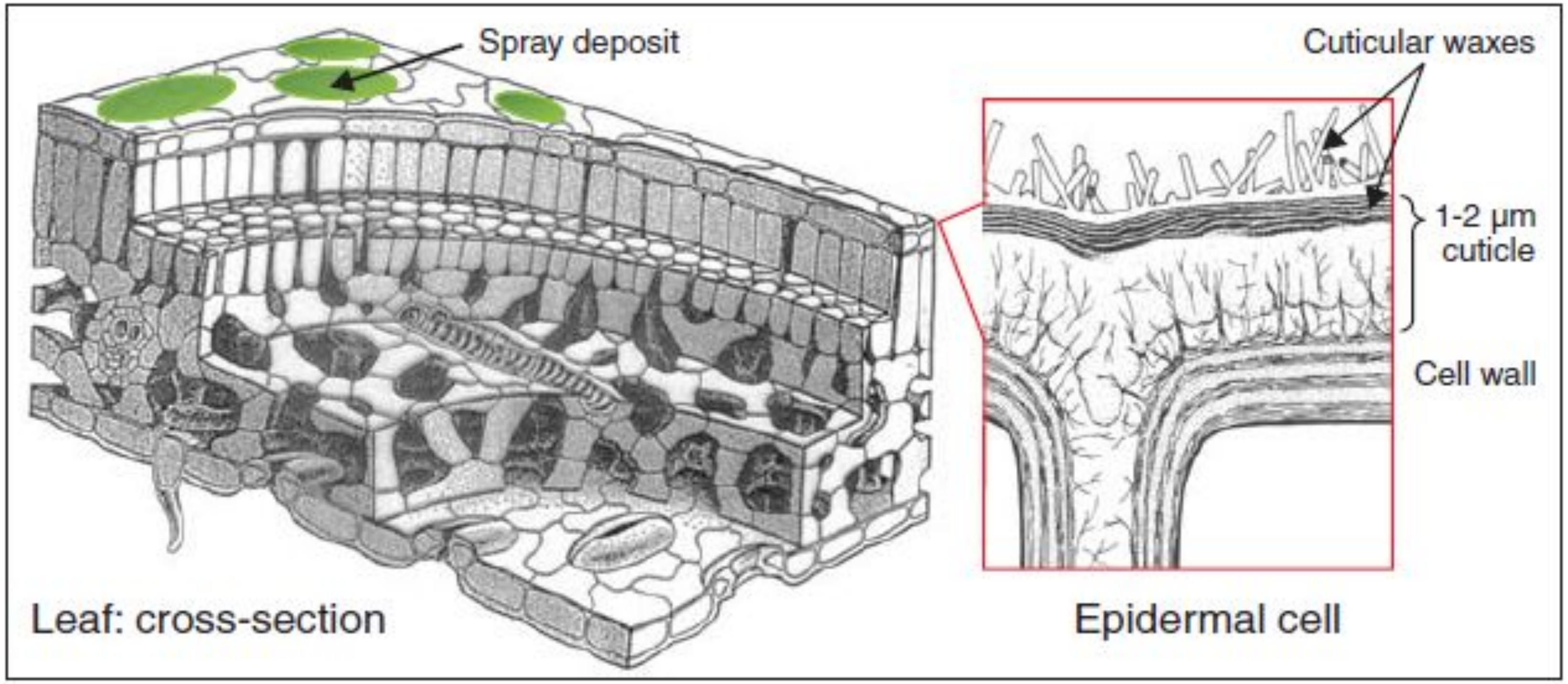
Agrochemical Spray deposit on the leaf surface



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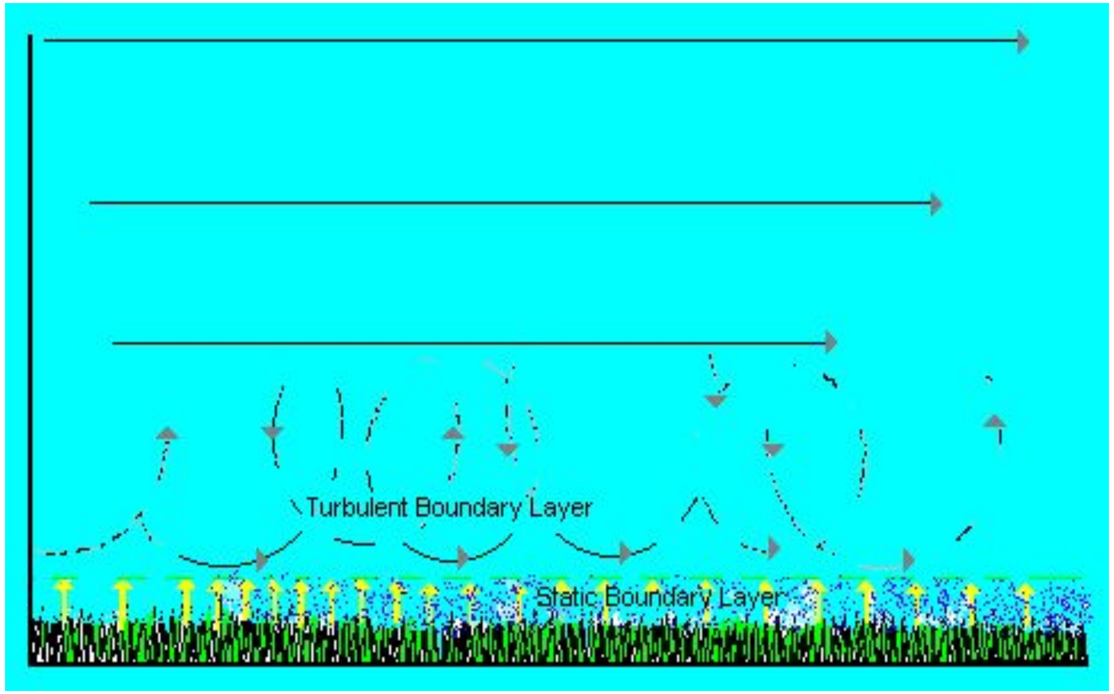
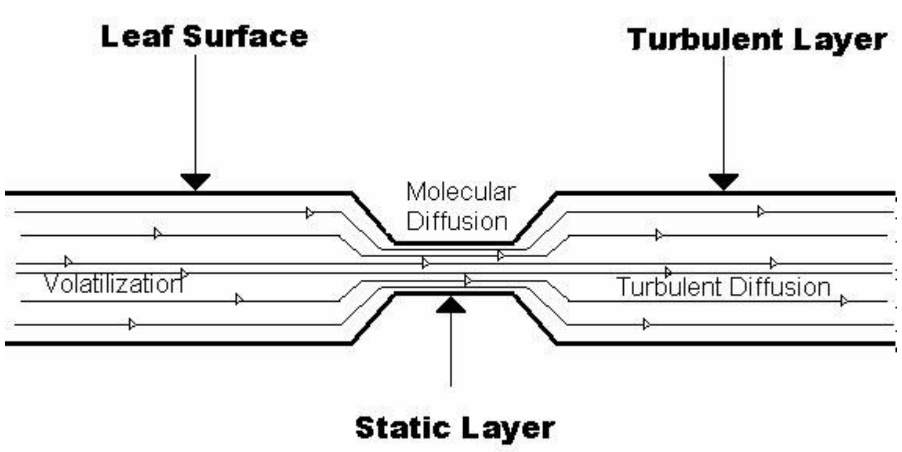
Atmospheric Transport Zones



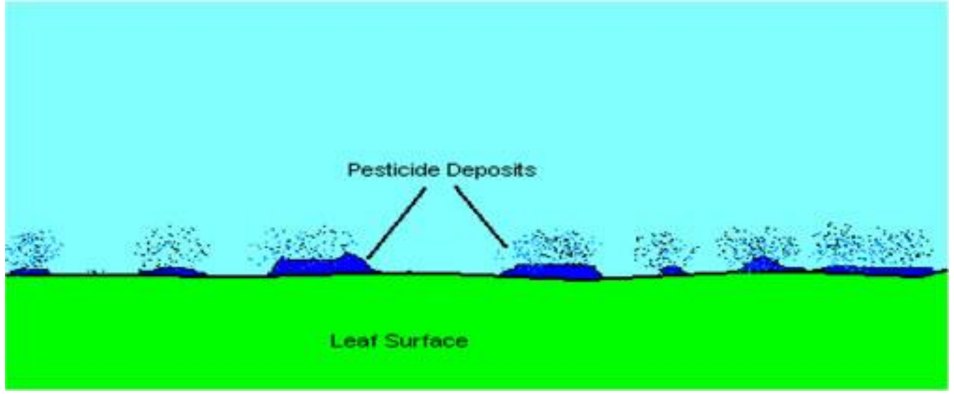
The *diffusivity* of a solute defines the rate of transfer of the solute in a given fluid under the driving force of a concentration gradient.



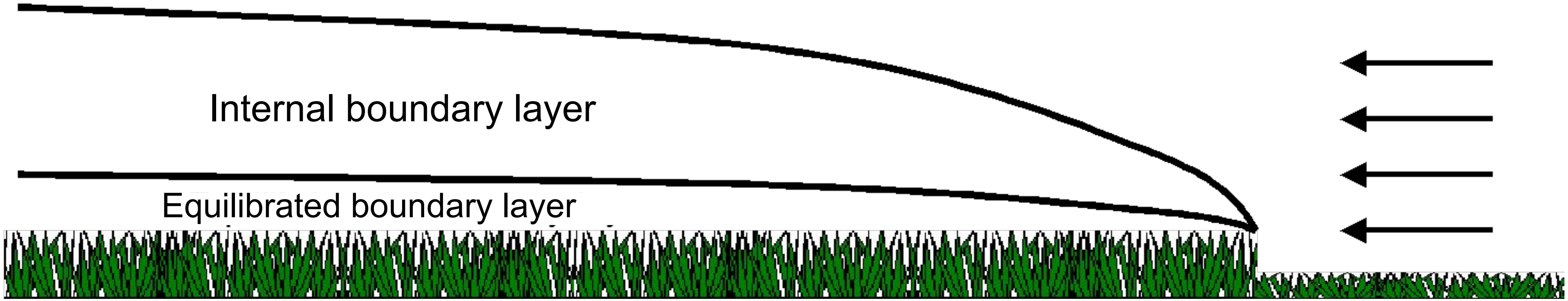
Follows the concentration gradient:

Leaf surface to atmosphere

Atmospheric deposition to leaf surface



Atmospheric Boundary: region of air whose properties are affected by features of the surface below



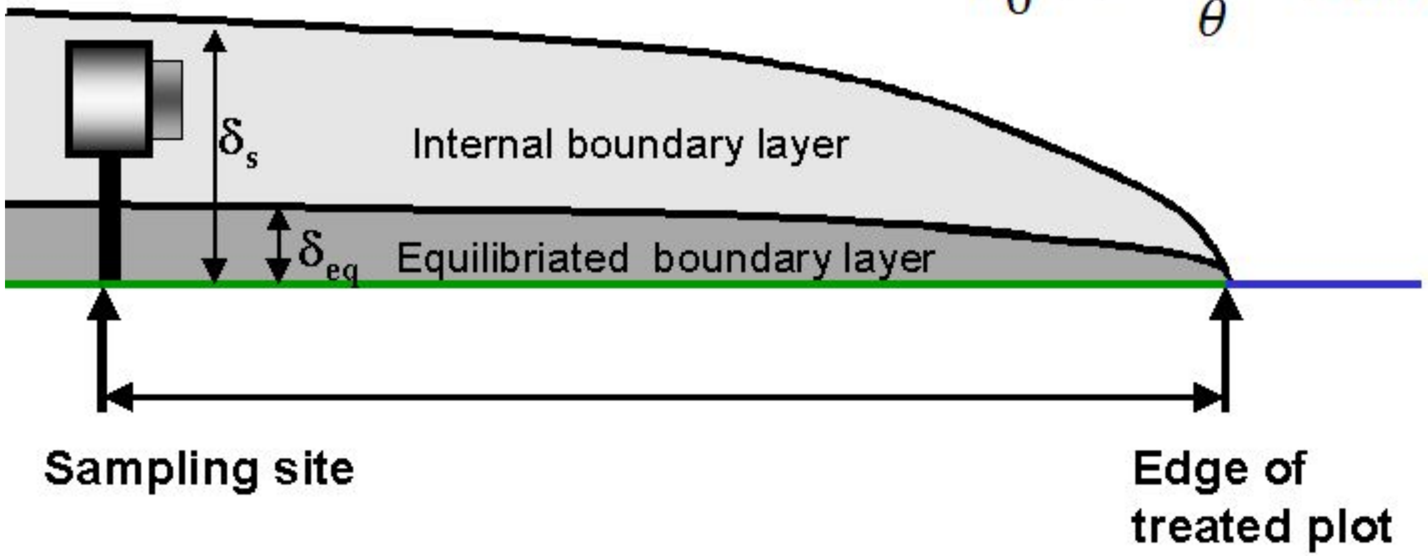
Internal boundary layer

Equilibrated boundary layer

Boundary layer formation over a transition in roughness length.
The internal boundary layer flow features are affected by the roughness features of the surface.
The equilibrated boundary layer has fully adjusted to the roughness features of the surface.

Theoretical Shape Profile method

$$F_0 = \frac{u_Z\, c_Z}{\theta}\, 3600\, (\frac{s}{hr})$$

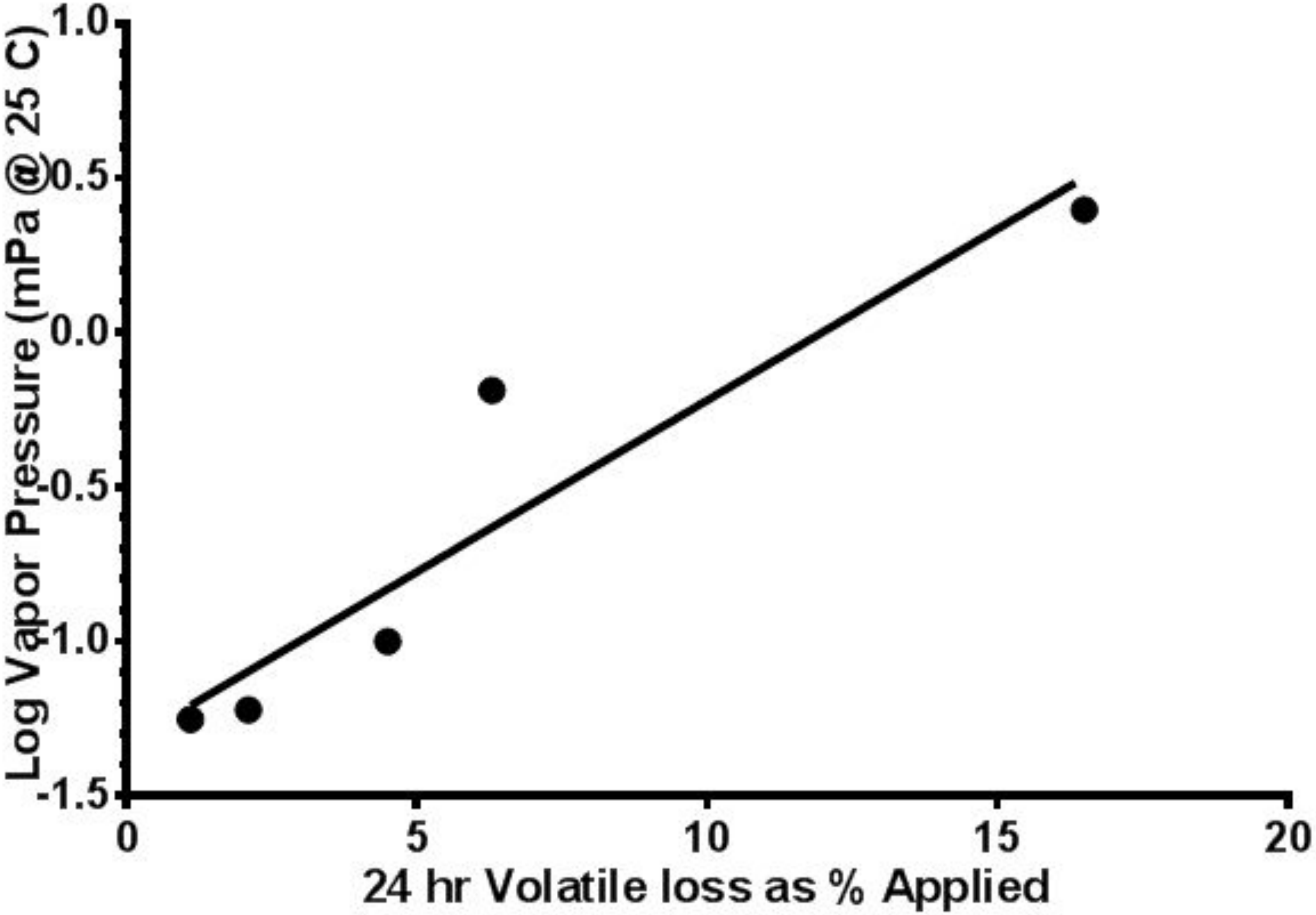


F_0 - (ug/m^2/hr) flux of pesticide vapor from the turf grass.
c_z - (ug/m^3) airborne concentration of pesticide vapor at the sampling height, above the turf plot.
u_z - (m/s) the average cup wind speed at the sampling height during the air sampling interval.
Θ - normalized horizontal flux (unitless), estimated using the TPS method (Wilson et al, 1982) or the Backward-Time Lagrangian Stochastic Dispersion (BTLSD) method (Flesch et al., 1995);
Sampling height chosen to minimize Θ error (on the order of 20%)

Volatile Loss From Turfgrass as Percent Applied

Pesticide	Application Rate (kg a.i./Ha)	24 hr volatile loss % Applied	Vapor Pressure (mPa, 25 °C)	Enthalpy of vaporization (kJ/mol)	Diffusion Coefficient (cm^2/s)
Chlorpyrifos	1.9	16.5	2.50		?
Ethofumesate	2.5	6.3	0.650		?
Triclopyr	1.1	4.5	0.170		?
Triadimefon	3.1	2.1	0.060		?
Propiconazole	2.2	1.1	0.056		?
Cyfluthrin	0.2	ND	0.004		?

Pesticide 24 Hr Volatile loss from Turfgrass



Properties of Common Herbicides

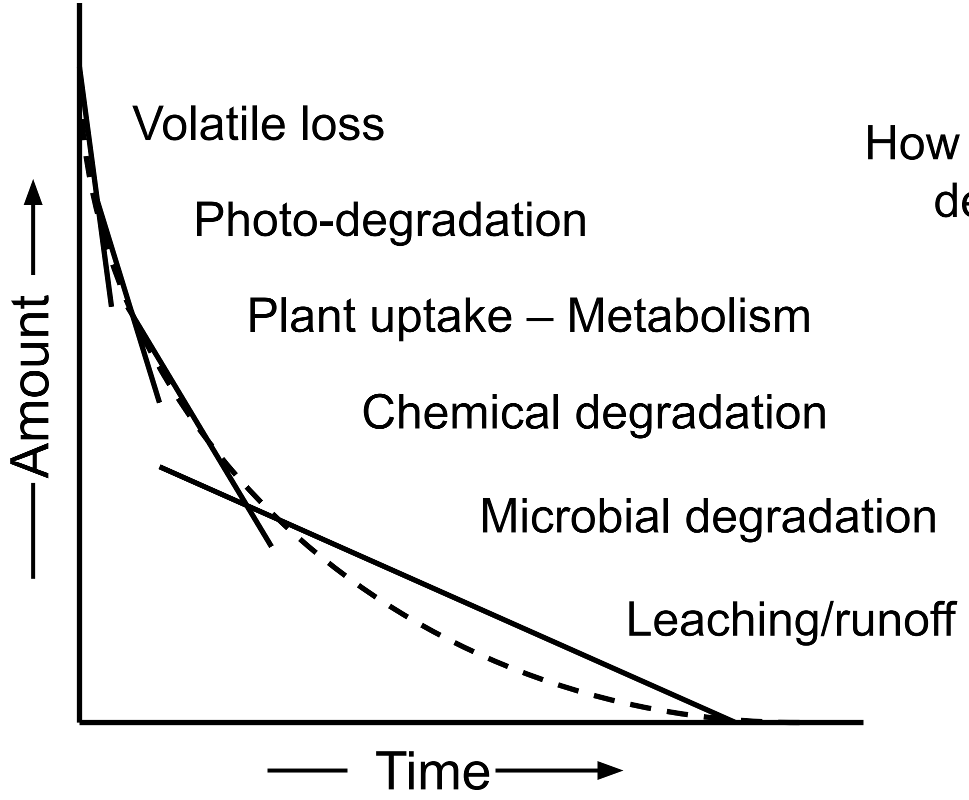
Trade name	Common name	½ life (days)	Koc	water sol mg/L	vapor pressure (mm Hg)
Sencor	metribuzin	40	60	1220	1.0x10-5
Banvel	Dicamba (acid)	14	2	400000	3.4x10-5
Milestone	aminopyralid	35	11	2480	7.1x10-11
Garlon	trichlopyr	30	210	260	3.0x10-8
Dual	metolachlor	90	200	530	3.1x10-5
Roundup	glyphosate	47	24000	530000	0
2,4-D	2,4 D acid	10	20	89	1.1x10-7
2,4-D ester	2,4-D butoxyethyl ester	7	500	100	1.0X10-7
Chopper	imazapyr	90	100	1100	1.3x10-11
Velpar	hexazinone	90	54	3300	8.2x10-11
Kerb	pronamide	60	800	15	8.5x10-5
Oust	Sulfometuron methyl	28	78	70	1.7x10-16
Goal	oxyfluorfen	35	100000	0.1	2.0x10-7
Prowl	pendimethalin	90	500	0.3	9.4x10-6
Buctril	bromoxynil	7	10000	0.8	4.8x10-6
Dachthal	DCPA	100	5000	0.5	2.5x10-6

OSU Extension Pesticide Properties Database EM 8709

Pesticide Fate in the Field

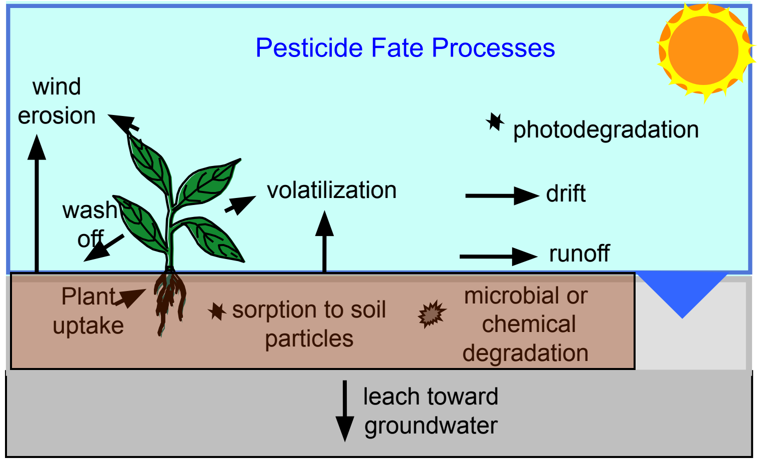
- Field dissipation: sum of chemical and biological processes including:
  - Chemical degradation[1]
  - Biological degradation (microbial + plant)[1]
  - Photodegradation[2]
  - Volatilization
- [1] Approximated with a 1st order rate constant
- [2] Approximated with a psuedo 1st order rate constant

Pesticide Field Dissipation From a Soil Compartment

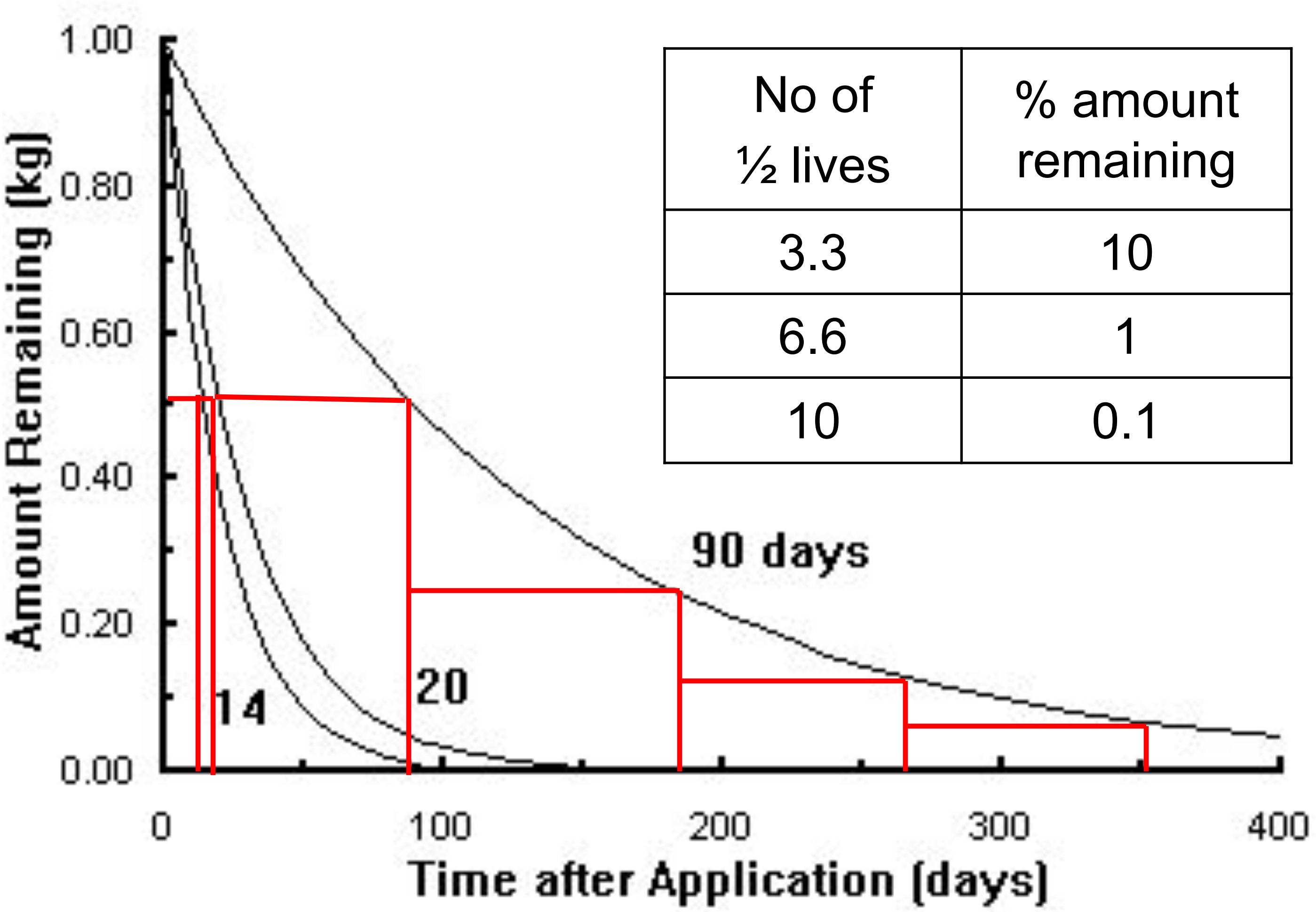


Assumption: competing dissipation processes roughly conform to 1st order degradation kinetics

How fast and which pathway predominates depends on chemical properties and environmental conditions



Pesticide dissipation half-life

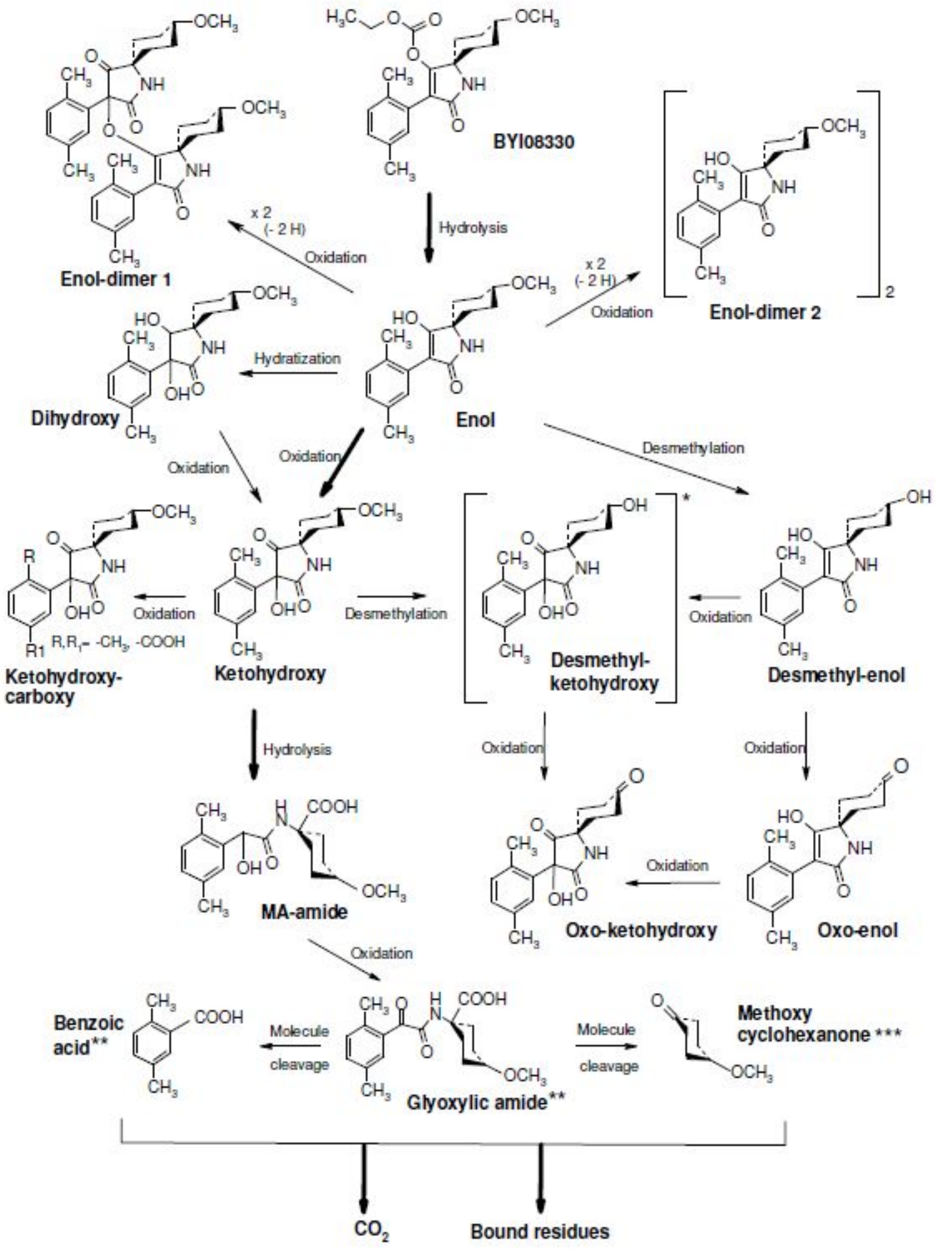


No of ½ lives	% amount remaining
3.3	10
6.6	1
10	0.1

Proposed metabolic/degradation pathway for Spirotetramat in soil (^{14}C ring labeled).

Parent hydrolyzed to enol (fast),
Enol to degradates (slow)
  oxidation
  desmethylation
  hydratization

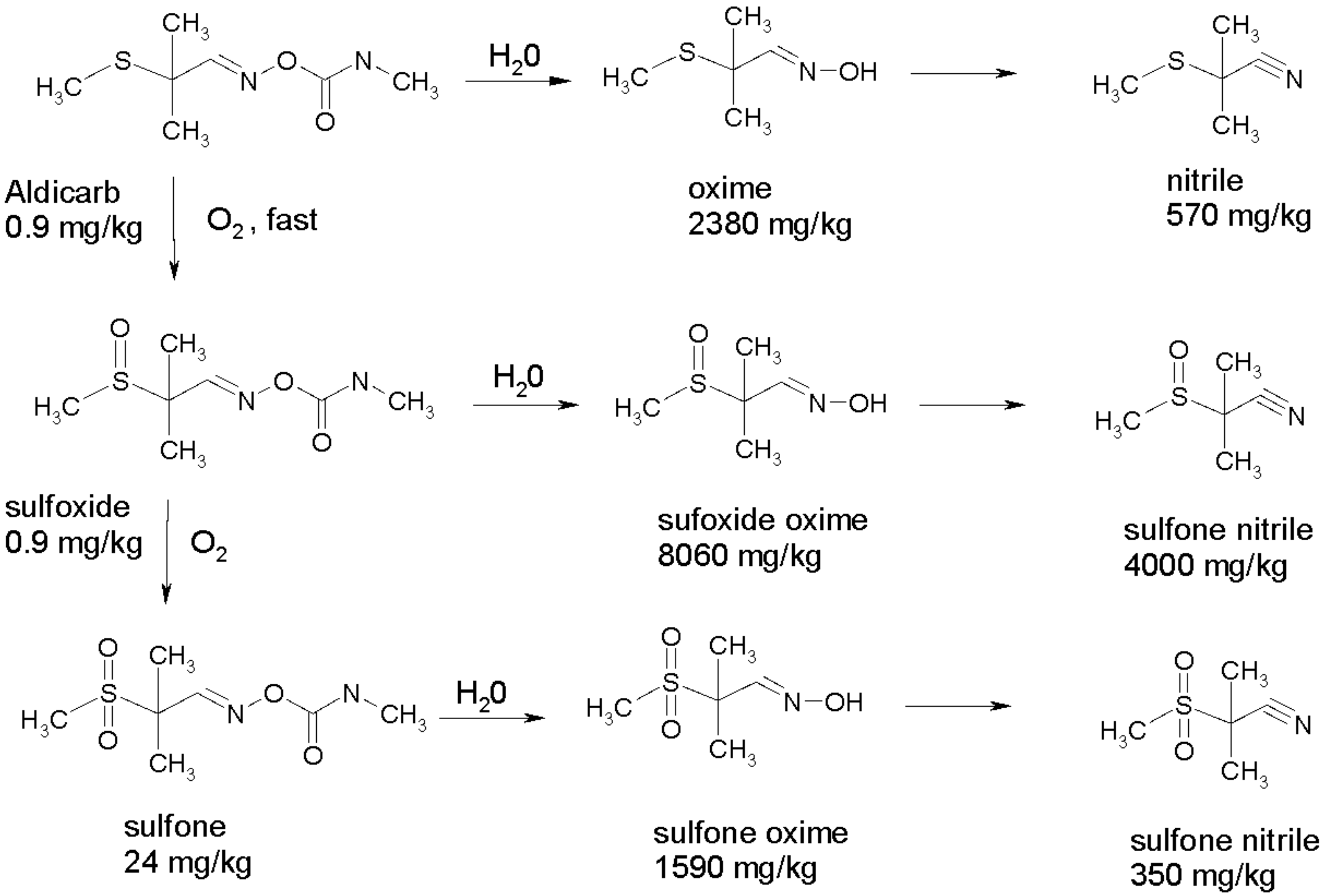
Identify all metabolic/degradation products of toxicological concern



*: postulated intermediate; ** and *** were identified in studies including light (dependent on radiolabel used)

Figure 8: Proposed Metabolic/Degradation Pathway for Spirotetramat (BYI08330) in Soil

Aldicarb degradation pathways and LD$_{50}$ values (rat acute oral)



Aldicarb
0.9 mg/kg

oxime
2380 mg/kg

nitrile
570 mg/kg

sulfoxide
0.9 mg/kg

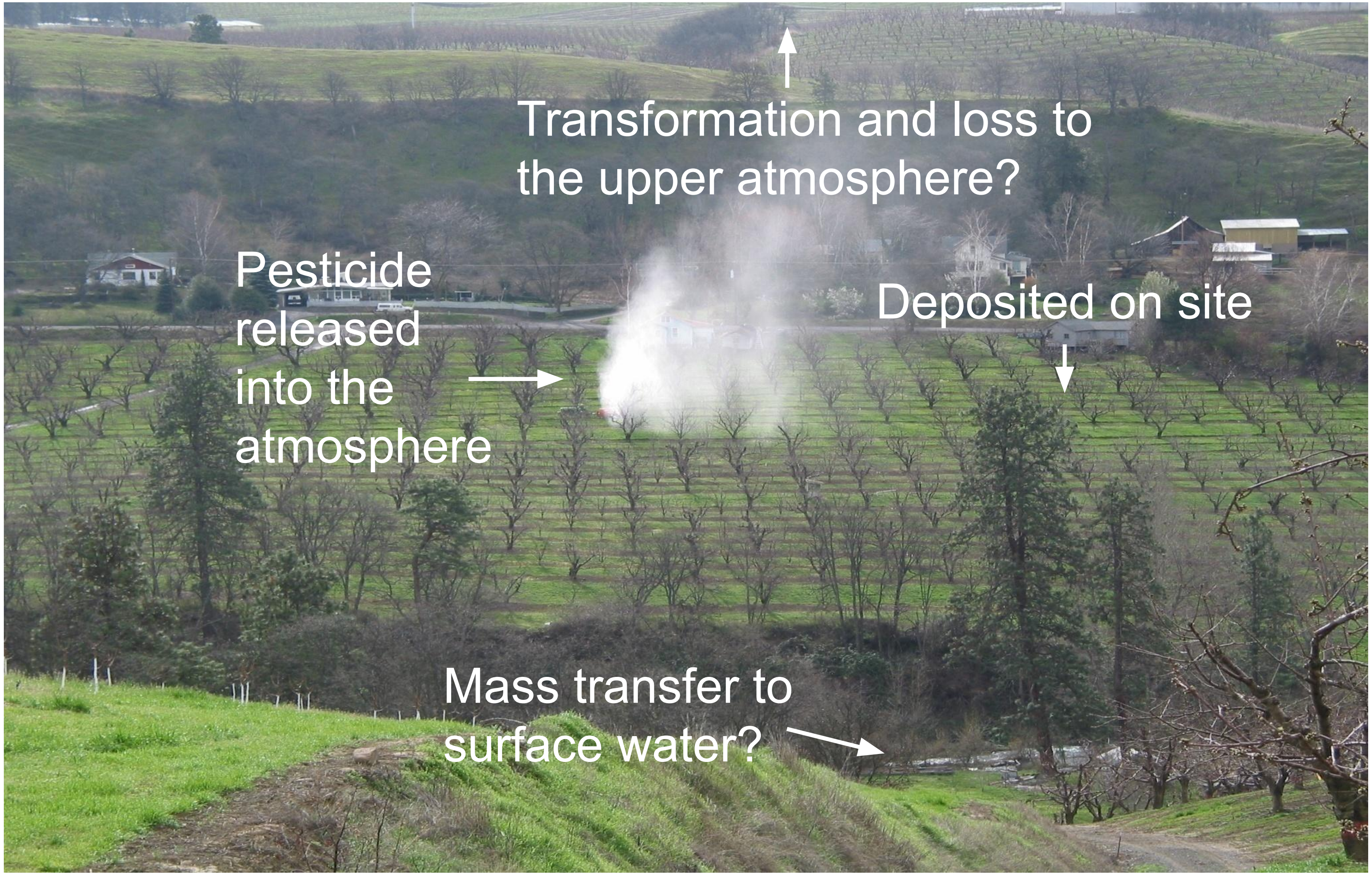
sufoxide oxime
8060 mg/kg

sulfone nitrile
4000 mg/kg

sulfone
24 mg/kg

sulfone oxime
1590 mg/kg

sulfone nitrile
350 mg/kg


Transformation and loss to the upper atmosphere?

Pesticide released into the atmosphere

Deposited on site

Mass transfer to surface water?

Summary

- Characterizing chemical fate is important to understanding human and wildlife exposure.
- Chemical fate is determined by phys-chem properties, initial distribution, and environmental conditions.
- Exposure estimates rely on existing data, measurements, or models.