Fate and Behaviour of Chemicals in the Environment

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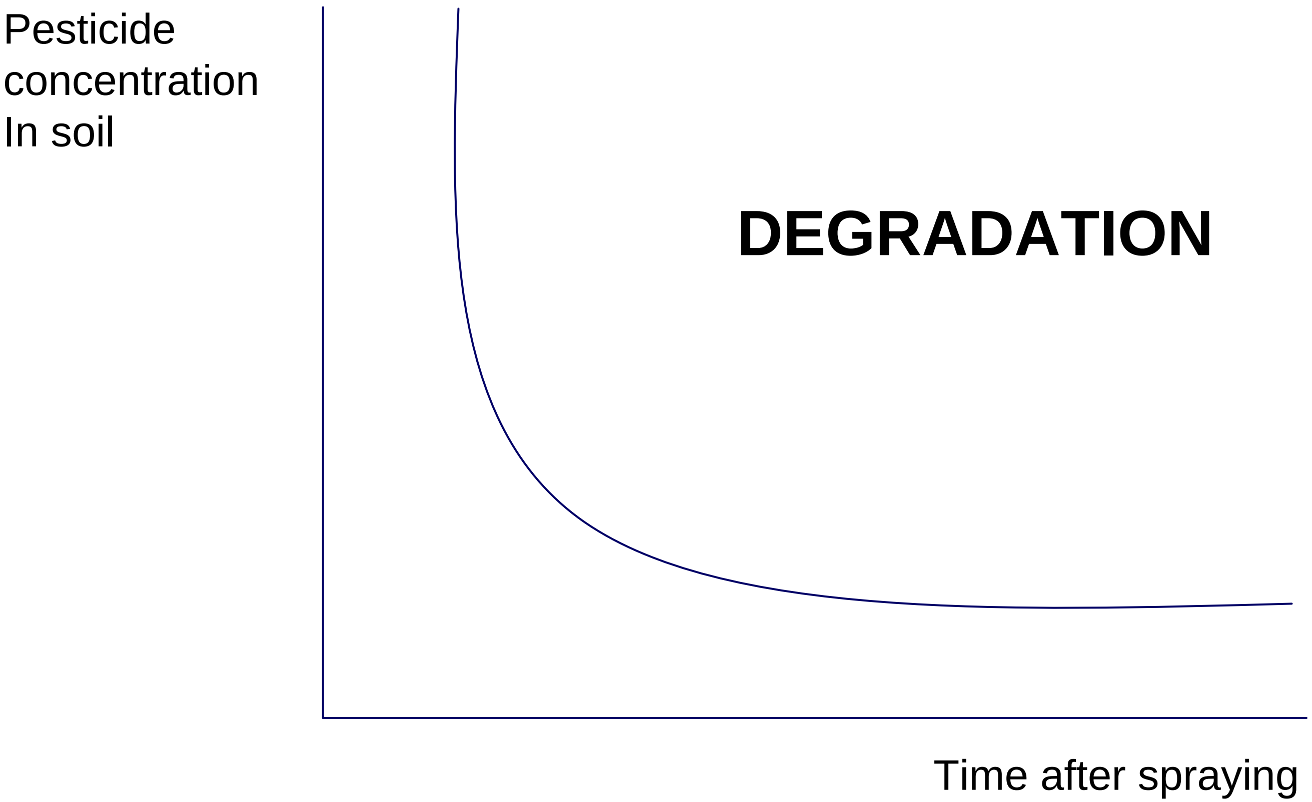
e.g. Pesticide sprayed onto a crop



- What causes degradation?
- Predicting degradation rate

Hydrolysis

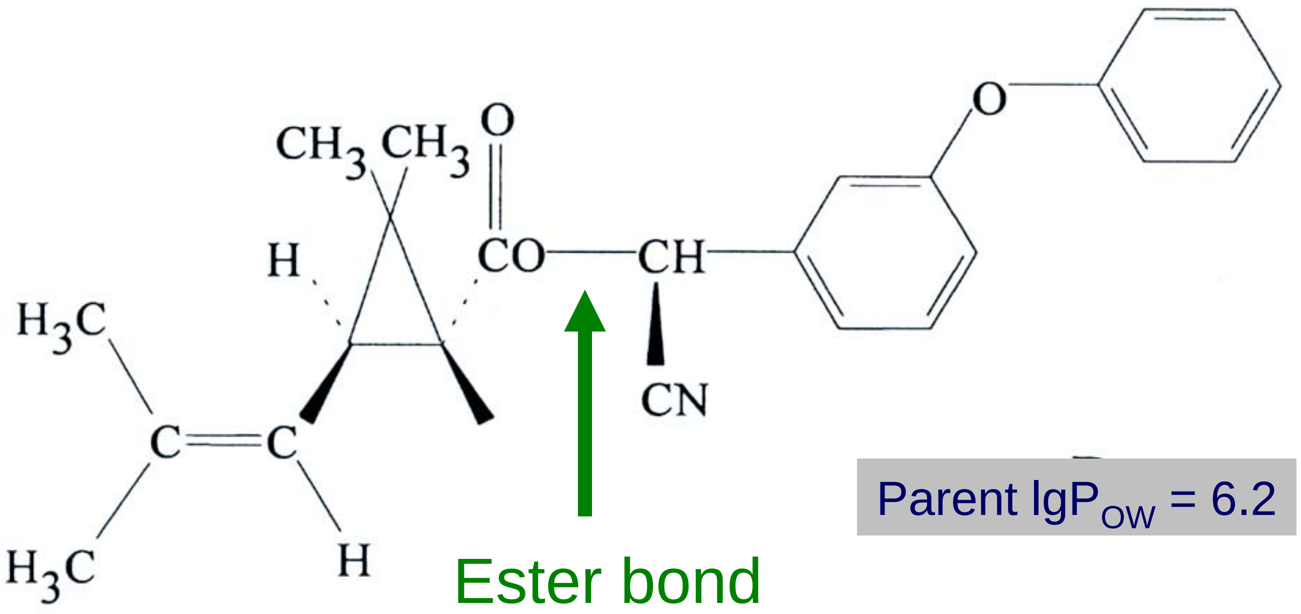
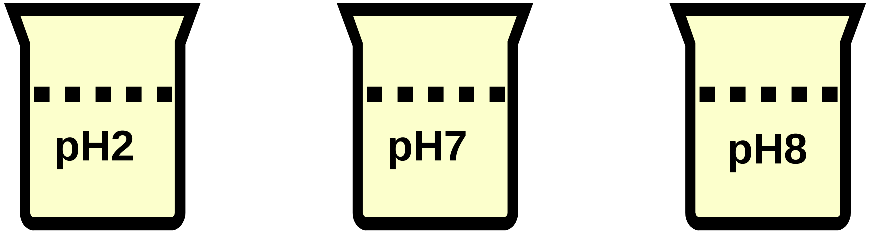
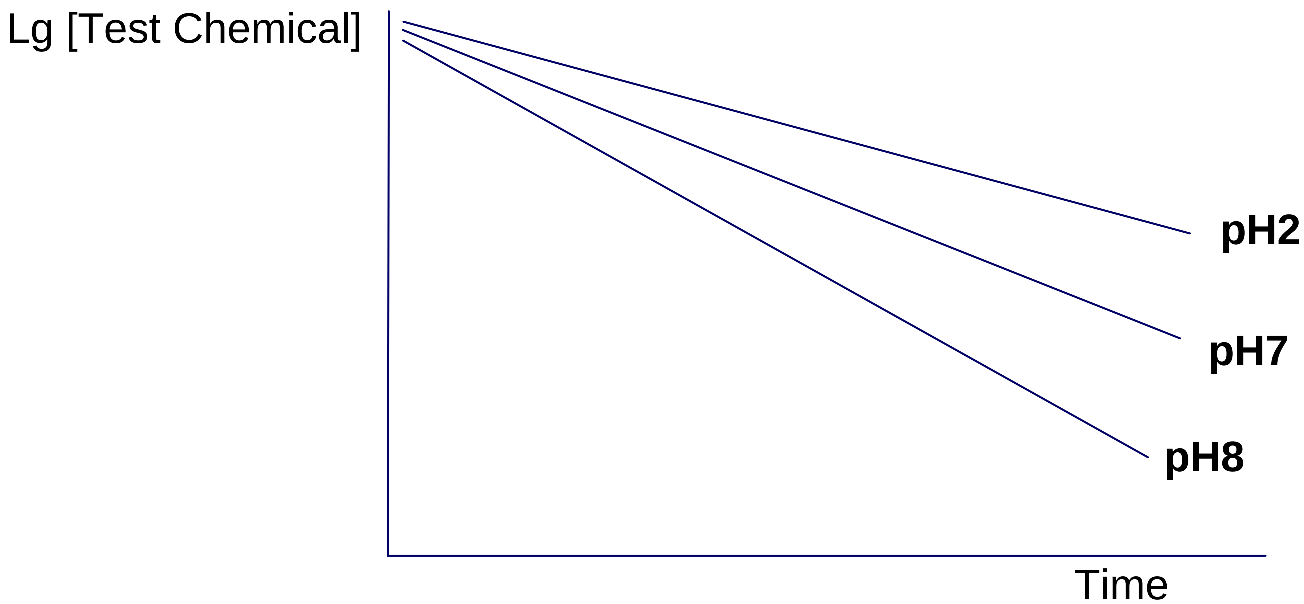


Figure 2.11 Molecular structures of Decamethrin (A), one of the first pyrethroid insecticides to be synthesised, and Cypermethrin (B), a modern insecticide which can be used to replace OPs in sheep dips and as a crop insecticide.

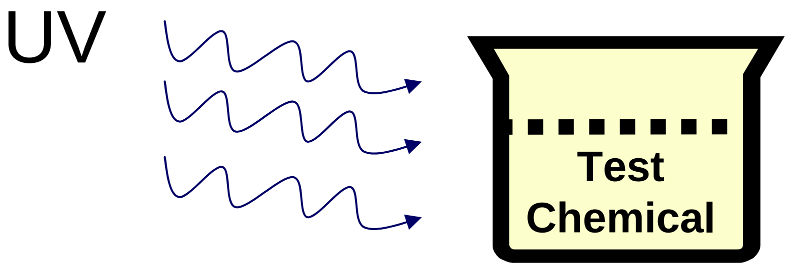
Testing Hydrolysis

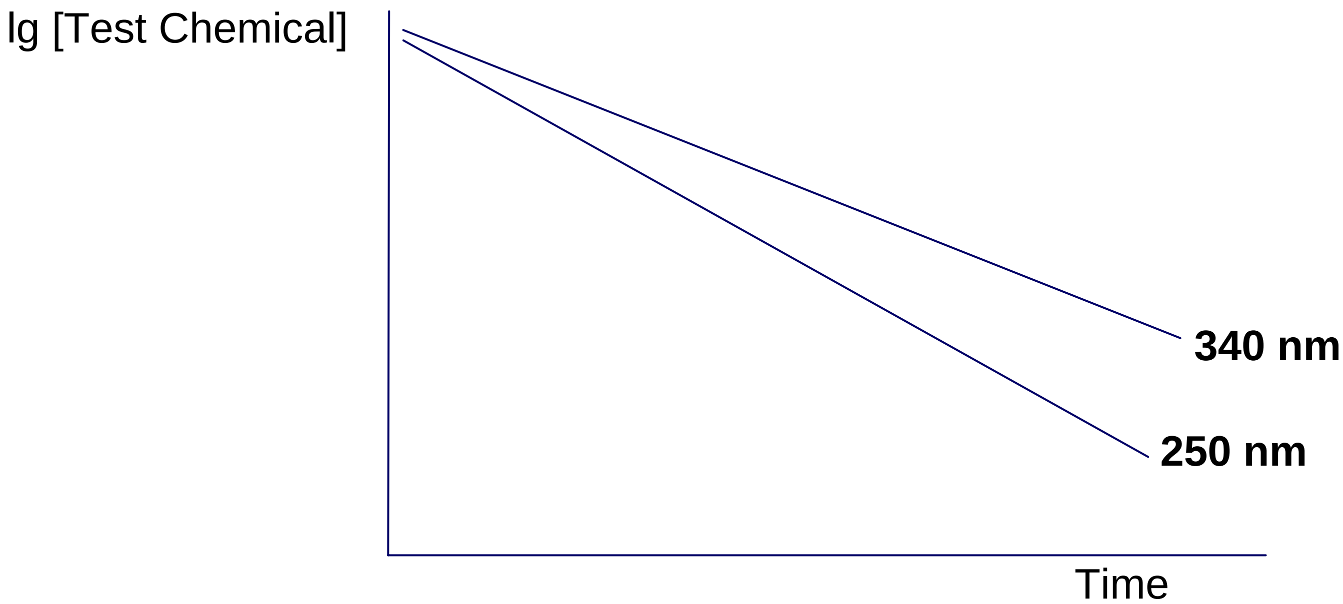




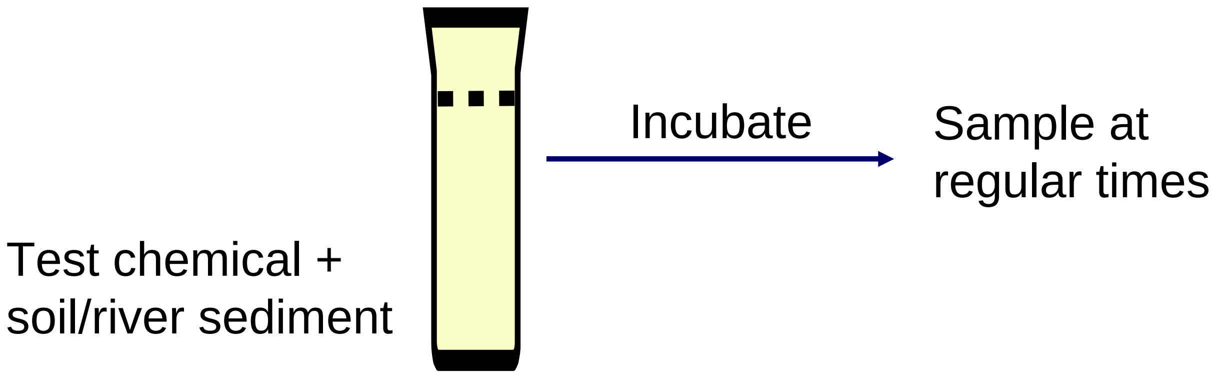
Photolysis

Light catalysed degradation
Particularly ultra violet
E.g. pesticides on leaves and stems

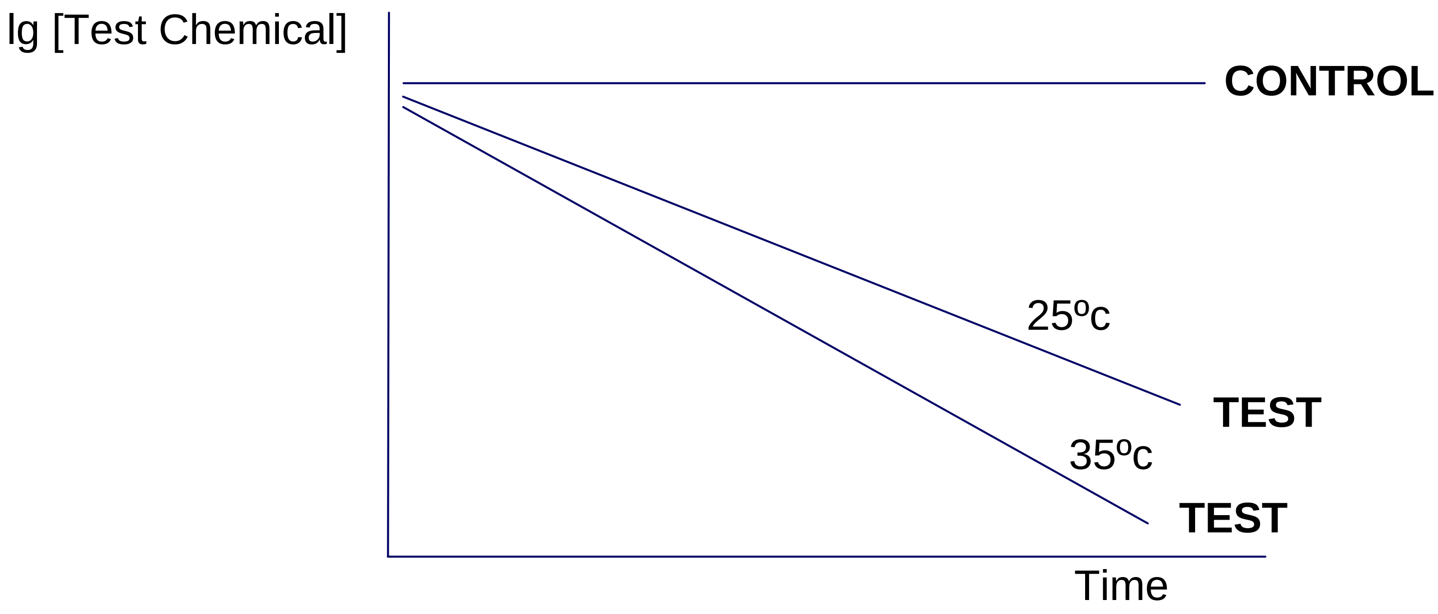




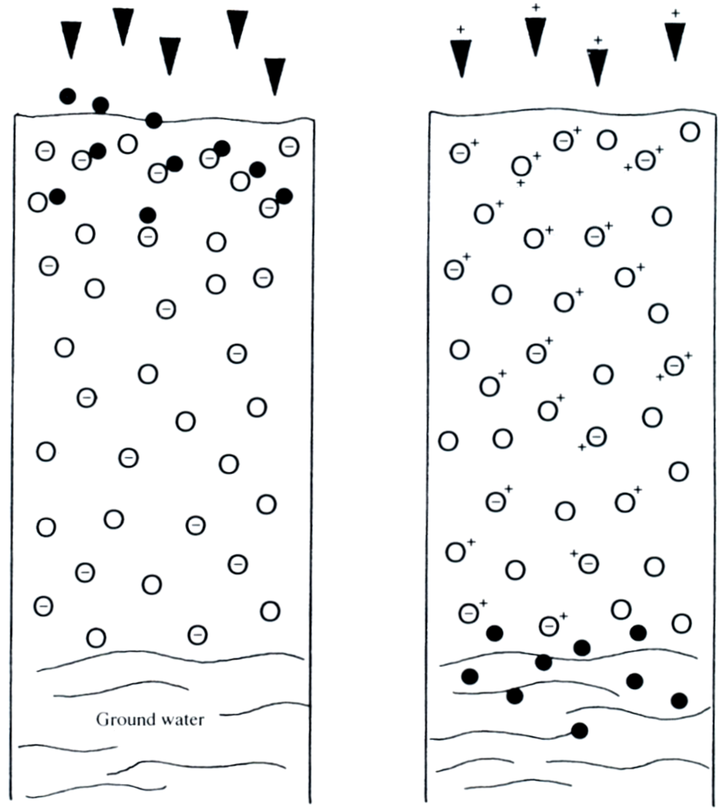
Bacterial degradation



- **CONTROL = Sterilised soil/sediment**



Flow of chemicals through soil



Positively charged molecules (●) will be electrostatically attracted to the negatively charged soil particles (⊖).

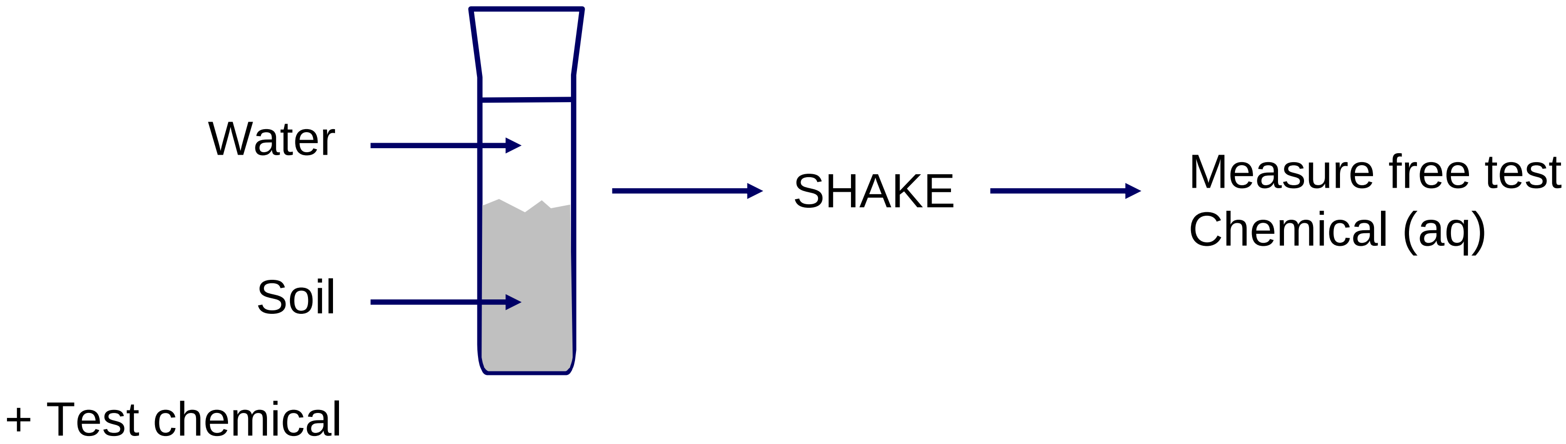
pH change (towards acid +) can either displace positively charged contaminants from their electrostatic interaction with soil particles or alter the molecule's intrinsic charge (dependent upon pKa value). This results in the once bound contaminant leaking through the soil into groundwater.

Figure 6.3 Schematic representation of the flow of molecules through soil (or silt), showing the effects of pH and the intrinsic charge of the molecules.

Quantifying flow through soil –

- Absorption/desorption
- Mobility

Absorption/Desorption



Express as $$\frac{\text{[Free Test Chemical]}}{\text{[Bound Test Chemical]}}$$

- Effect of pH?

Mobility

1. Binding to soil particles

Soil/water distribution coefficient -K_d

$$K_d = \frac{[\text{Test chemical in aq. phase}]}{[\text{Total chemical}] - [\text{Chemical in aq. phase}]}$$

K_d >2 likely to leach from soil

Mobility

2. Binding to organic soil components (humus)

Organic binding constant - K_{OC}

$$K_{OC} = \frac{K_d}{\text{\% organic carbon in sample}}$$

% organic carbon determined by combustion

K_{OC} >500 Mobile test chemical

Bacterial degradation

Types of metabolic pathways in bacteria:

Hydroxylation

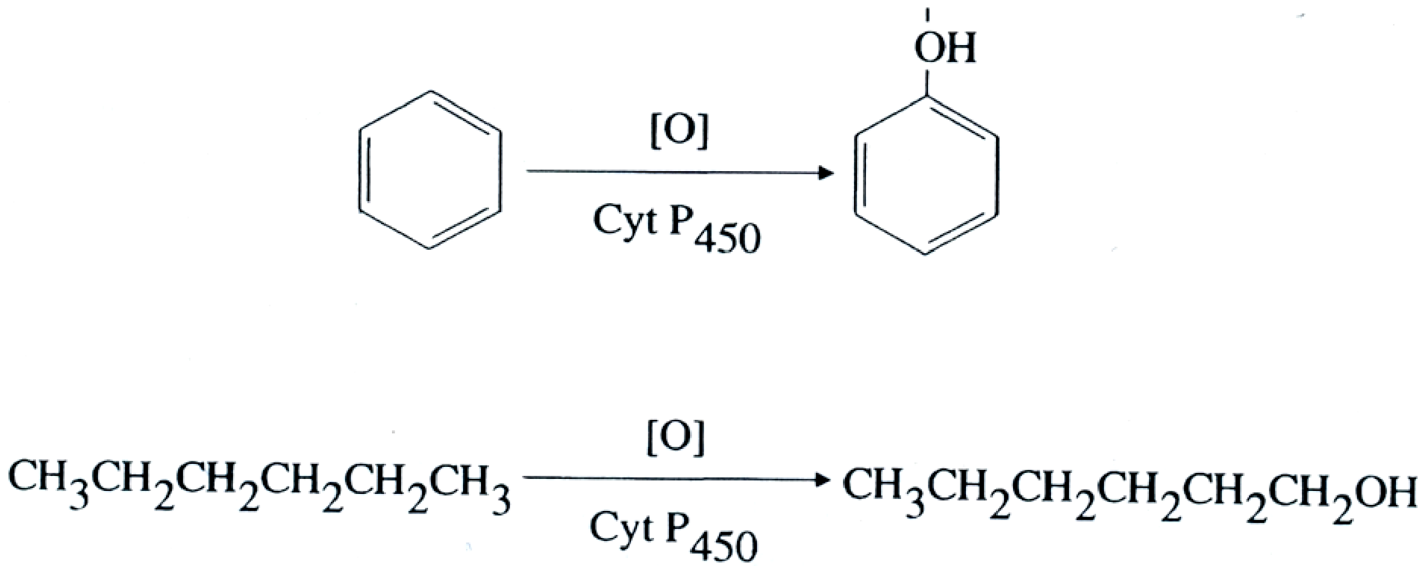


Figure 6.7 Cytochrome P_{450}-catalysed hydroxylation of benzene (above) to form phenol and hexane (below) to form hexan-1-ol.

Bacterial degradation

Types of metabolic pathways in bacteria:

Oxidative dealkylation

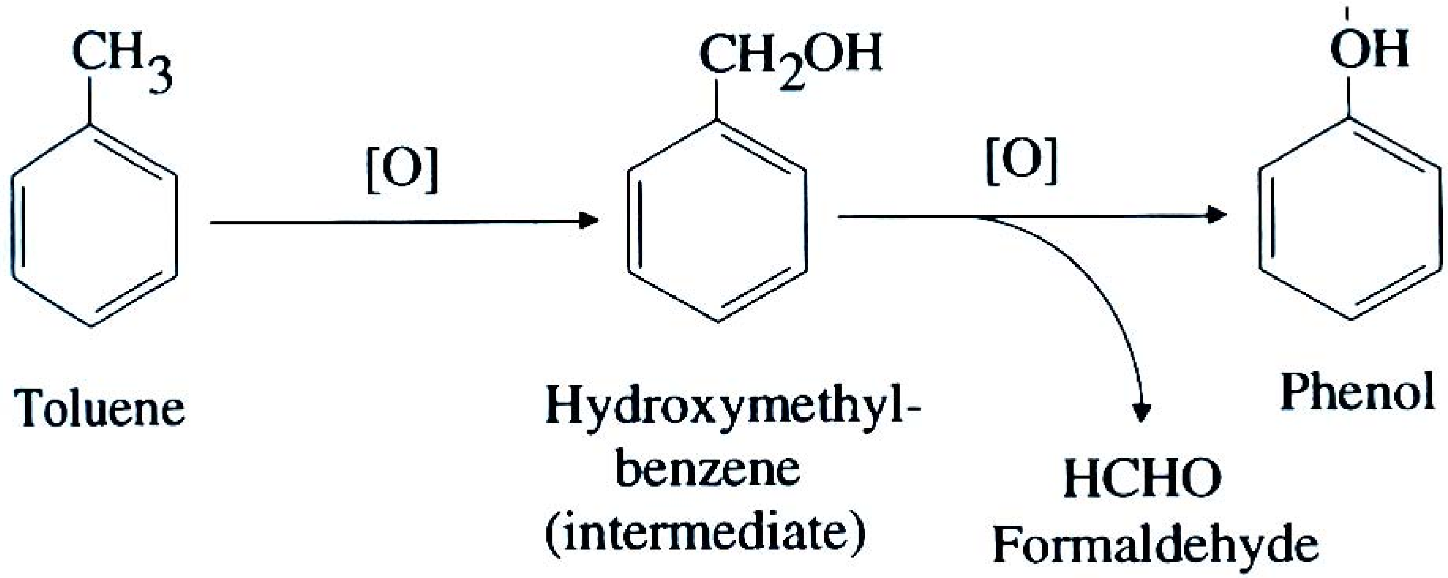


Figure 6.8 Cytochrome P_{450}-catalysed oxidative demethylation of toluene to form phenol.

Oxidative deamination

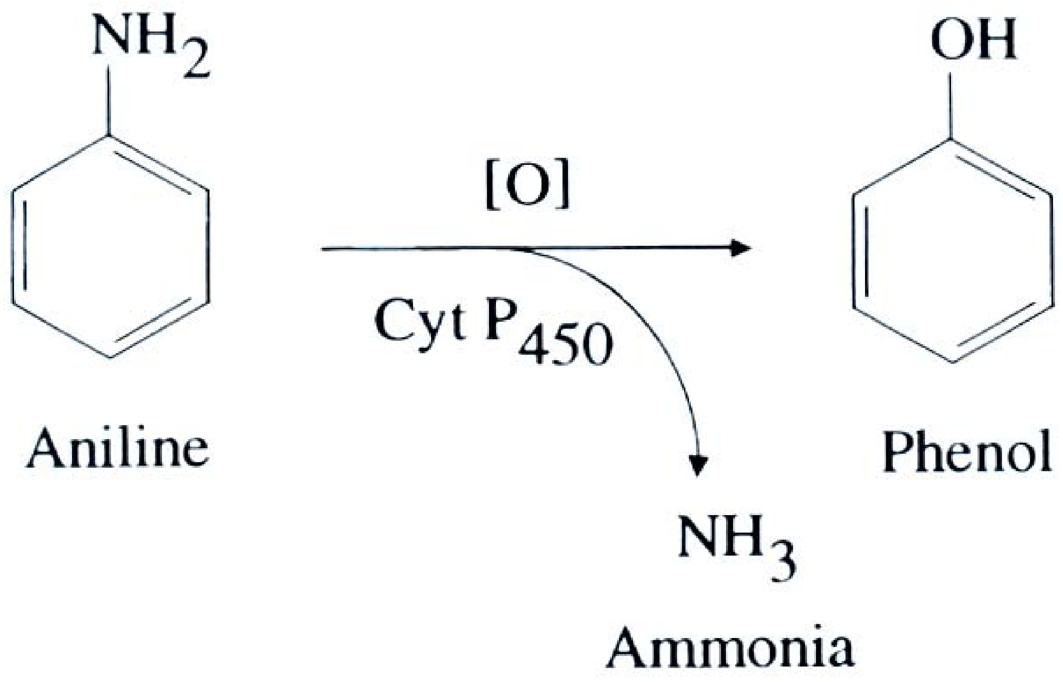


Figure 6.9 Cytochrome P_{450}-catalysed oxidative deamination of aniline to form phenol.

Cypermethrin – a pyrethroid insecticide

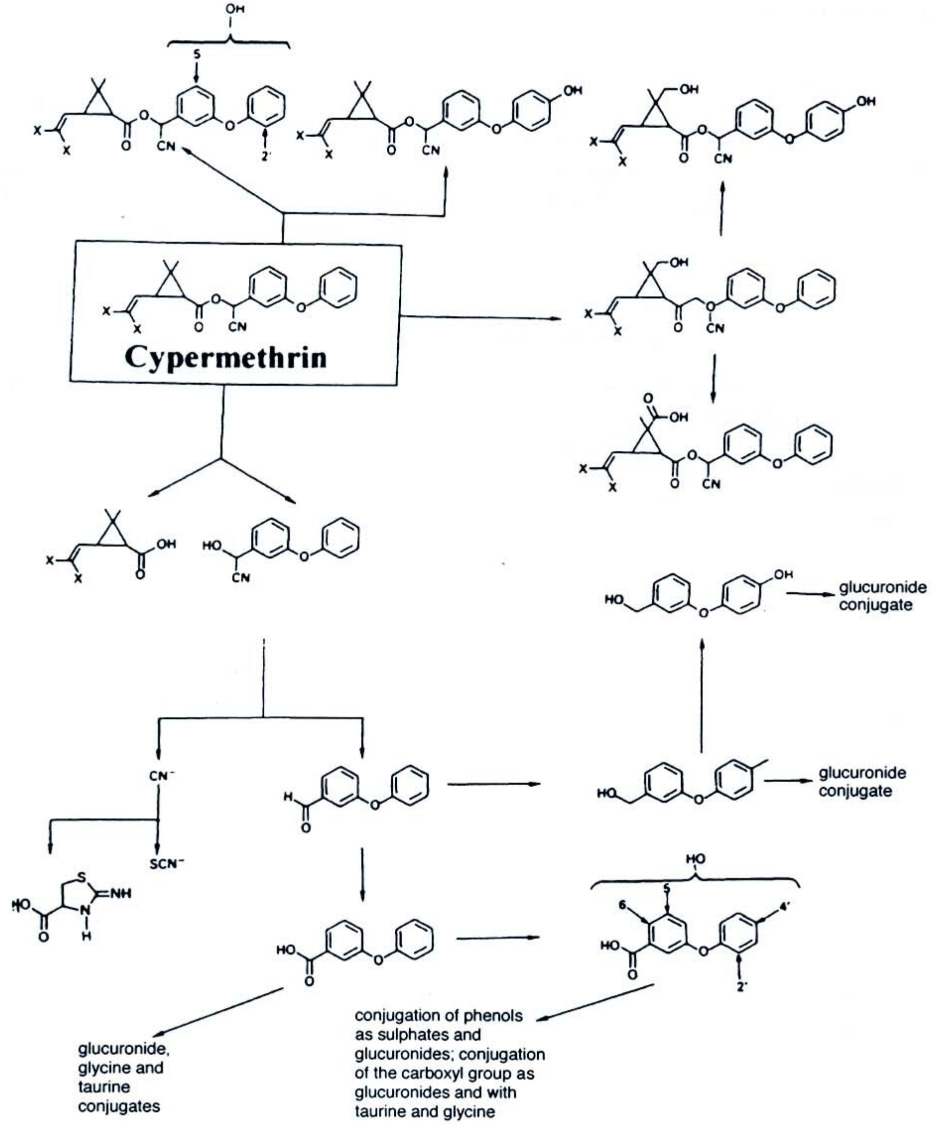


Figure 2.12 Generalised metabolic pathway for Cypermethrin. Elements of the pathway occur in mammals, insects and plants; the pathway is, however, based on the metabolism in mammals. Adapted from Cremlyn (1990), *Agrochemicals*, Wiley.

Dichlorodiphenyltrichloroethane (DDT)

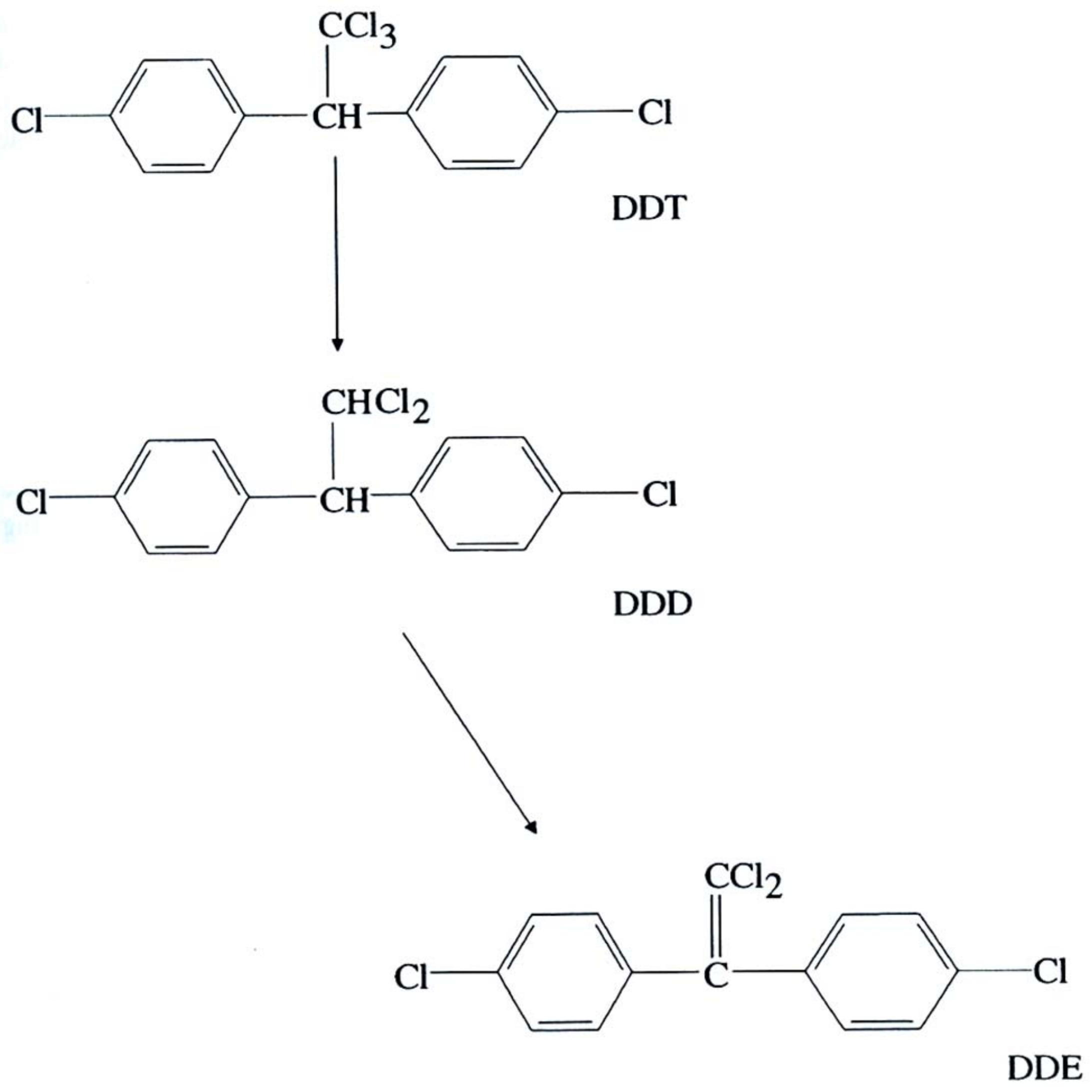


Figure 6.11 Biotransformation of DDT showing the formation of DDD and DDE.

Diazinon – an organophosphorus (OP) insecticide

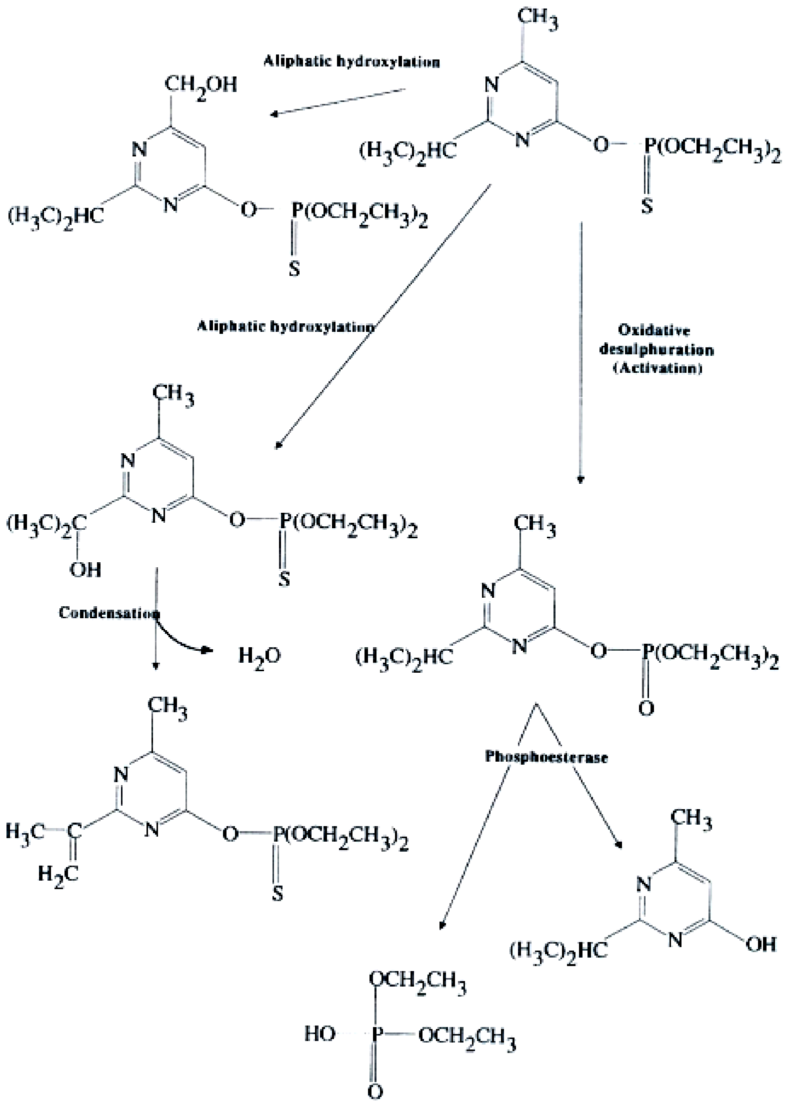
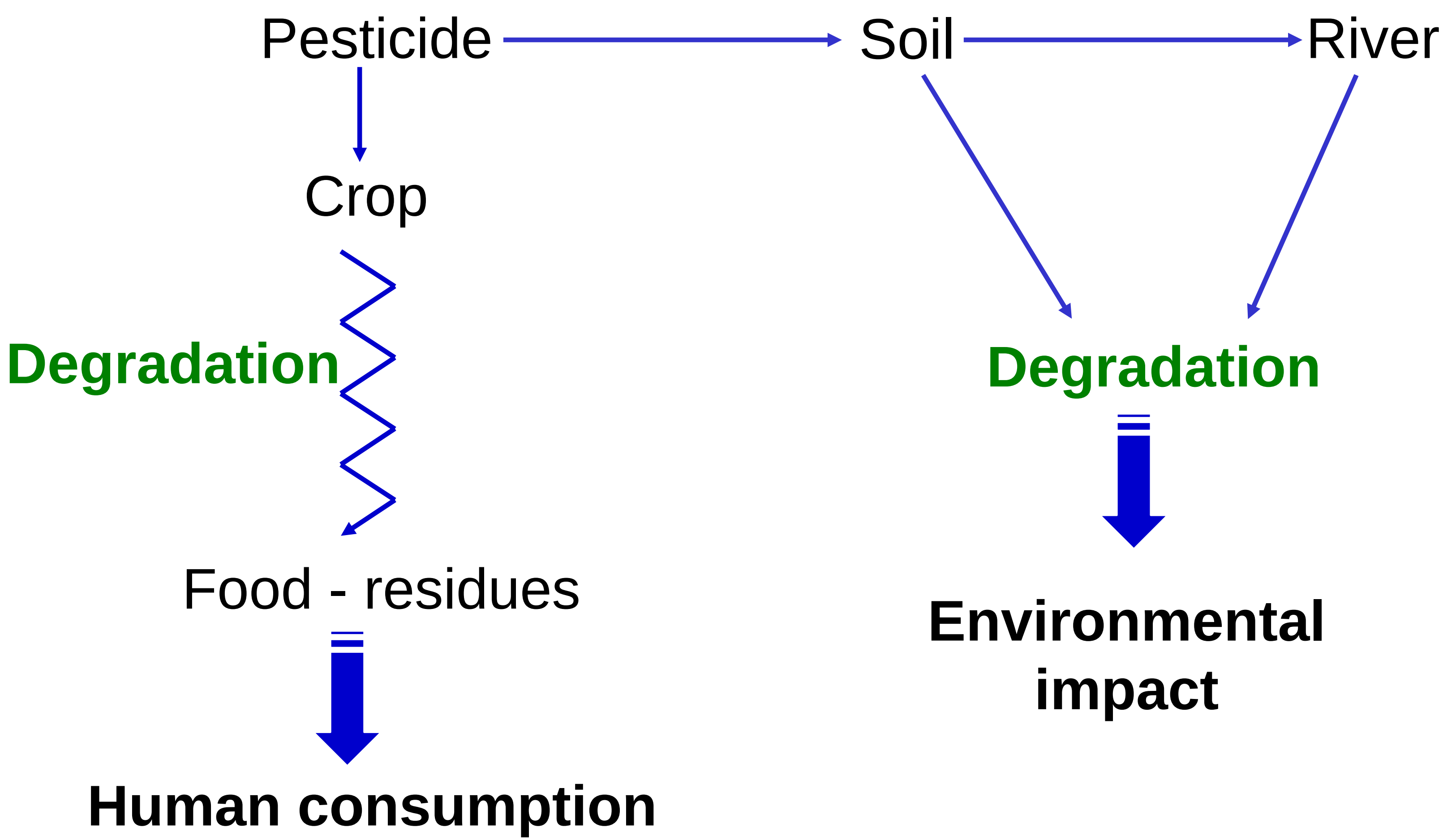


Figure 6.12 Part of environmental degradative pathway of the OP Diazinon showing its activation to the OXO compound.

The Fate of a Chemical in the Environment



Monitoring human exposure

- Residues analysis in food
- Human tissue residues
- Human milk levels
  e.g. DDT in human milk

Table 2: Examples of *p,p'*-DDT and HCB residues in human milk fat from around the world

Country/City	*p,p'*-DDT (mg/kg)	HCB (mg/kg)	Reference
USA			
Arkansas	0.039	0.045	[18]
New York	0.023	0.022	[19]
Jordan			
Amman		0.29	[20]
Germany			
E. Berlin	2.28		[21]
W. Berlin	0.81		[21]
Thailand			
Bangkok	0.734	0.007	[19]
S. Vietnam	4.22 - 7.3	0.01	[19]
Ho Chi Minh	0.023	0.003	[19]
Papua New Guinea	0.42		[9]
India (Punjab)			
Ludhiana	7.18		[17]
Faridkot	13.81		[17]

Bringing the package together

K_{OC} / K_d

Hydrolysis rate

Photolysis rate

Toxicity profile – EC_{50}

Degradation – $t_{½}$

lg P_{OW}

↓

DECISION