Bayer CropScience

Pesticide Behaviour in Soils, Water and Air, York, Sept. 2009

Transformation in Soil and Water
Session Introduction

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PESTICIDE TRANSFORMATIONS IN SOIL & WATER

Soil & Water as a Medium for Pesticide Transformation

- Pesticide transformations can be by both chemical (such as hydrolysis and photolysis) and biological (primarily microbial metabolism).
- Degradation (or decomposition/breakdown) is the result of a change in molecular structure resulting in a lower molecular weight.
- However some mechanisms are additive and the molecular weight can temporarily increase thus transformation is more generic.

The Soil Environment

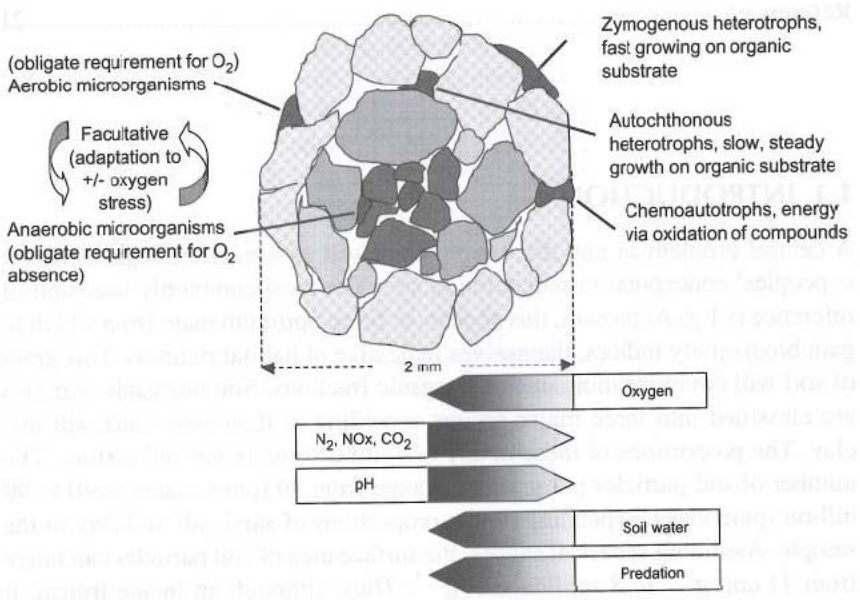


FIGURE 1.1 Schematic of a section through a 2 mm diameter soil aggregate illustrating microsite habitats for bacteria based on physiological requirements. The arrows below show the main directions of diffusion for key processes.

[Dominic Standing and Ken Killham, CRC Press Modern Soil Microbiology, 2007]

Energy Sources for Soil Microorganisms

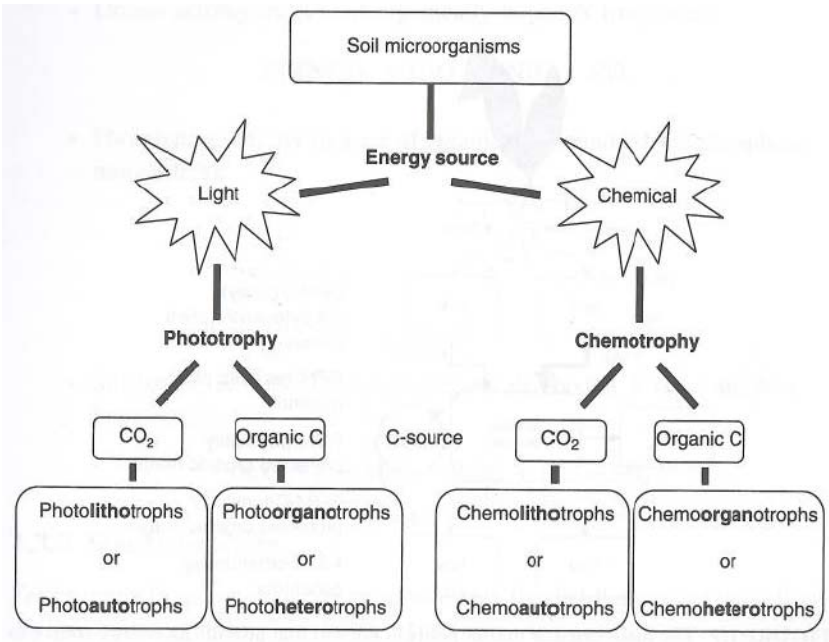


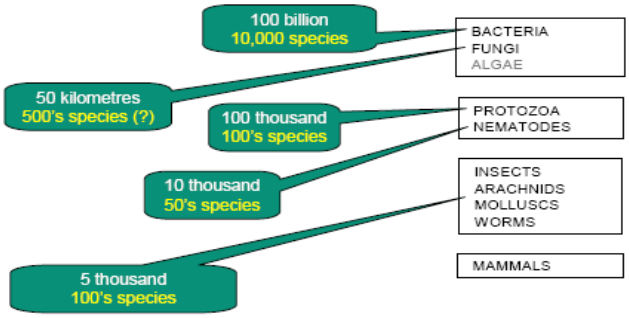
FIGURE 1.6 Classification of soil microorganisms in terms of use of carbon/energy sources.

[Dominic Standing and Ken Killham, CRC Press Modern Soil Microbiology, 2007]

Transformation in Soil and Water

Microbial Transformation

- What influences soil biota?
  - Resources food, water, air
  - Environment temperature, pH, water
- How much is there?
  - In 200 g ca. 0.5 g of fresh biomass
  - In top 30 cm ⇨ arable soil 5.4 tones 100 sheep/ha
    ⇨ grassland 100 tones 2000 sheep/ha
  - In 1 g soil there are 10^7 – 10^9 bacteria
- How diverse is it?



Transformation in Soil and Water

Main Processes of Microbial Transformations

A) Biodegradation

- The pesticide provides substrate for microbial growth.
- All micro-organisms need minerals, plus C, H, O and N with typical C:N:P/S ratios of 100:10:1. Thus it is often the carbon atoms that are required by the organism.
- Mineralisation is the complete transformation into inorganic products e.g. CO_2, H_2O.

B) Cometabolism

The pesticide is transformed by metabolic reactions but does not serve as an energy source. The rate of transformation does not increase with time or with further additions.

C) Addition Reactions

The pesticide or metabolites are transformed by the addition of functional groups, by polymerisation, oxidative coupling or conjugation. This mechanism can be responsible for the formation of unextracted residues.

Transformation in Soil and Water

Transformation pathways:

Oxidation: β Oxidation — Phenoxy alkanoate Herbicides

$RCH_2CH_2COOH \longrightarrow RCOOH$

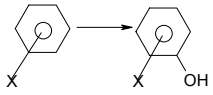
Sulfur Oxidation: $S \longrightarrow SO \longrightarrow SO_2$; $P=S \longrightarrow P=O$ — Organo phosphorus insecticides, oxime carbamates, nematicides with thioether group

Epoxide Formation:  — Cyclododiene Insecticides

Hydrolysis:

$RCN \rightarrow RCONH_2 \rightarrow RCOOH$	Nitrile herbicides
$RNHCOOR' \rightarrow RNH_2 + R'OH + CO_2$	Carbamate insecticides and herbicides
$ROPX \rightarrow ROH + HOPX$	Organophosphorus Insecticides
$RCOOR' \rightarrow RCOOH + R'OH$	Benzoicacid ester herbicides
$RCONH_2 \rightarrow RCOOH + NH_3$	Amide herbicides

Reduction:	$NO_2 \rightarrow NH_2$	e.g. Parathion Trifluralin
Dechlorination	$RCCl_3 \rightarrow RCHCl_2$	Organohalogen compounds
Decarboxylation:	$RCOOH \rightarrow RH+CO_2$	Wide Variety
N-dealkylation:	$NR,RZ \rightarrow -NHR \rightarrow -NH_2$	Urea herbicides Amides and Triazines

Aromatic Ring Hydroxylation:  — Phenoxy alkanoate herbicides

O-dealkylation: Ar-O-R ⟶ ArOH — Phenoxy alkanoate herbicides

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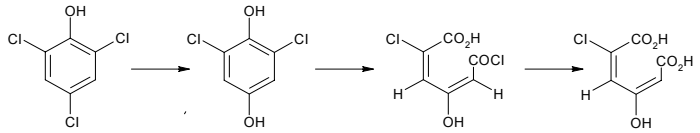
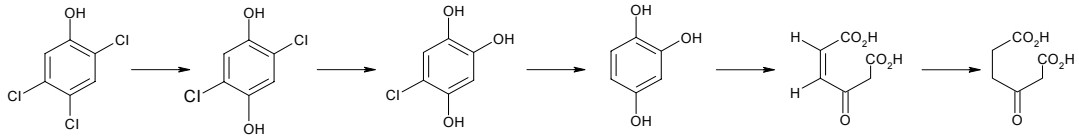
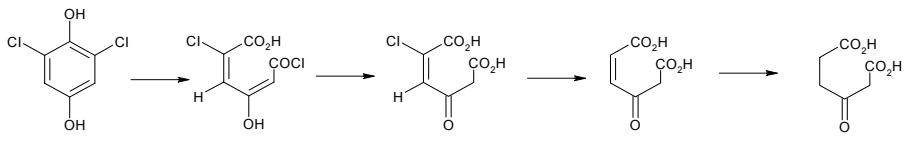
Degradation of a) 2,4,6-trichlorophenol, b) 2,4,5-trichlorophenol and c) 2,6-dichlorohydroquinone

a) 

b) 

c) 

Environmental Degradation and Transformation of Organic Chemicals A. H. Nielson & A-S Allard, CRC Press Taylor and Francis 2008 p.485

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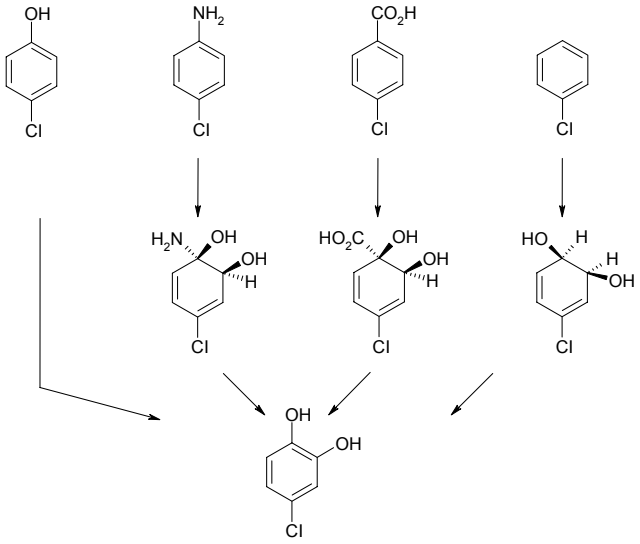
Outline of the biodegradation of 4-chlorophenol, 4-chloroaniline, 4-chlorobenzoate and chlorobenzene



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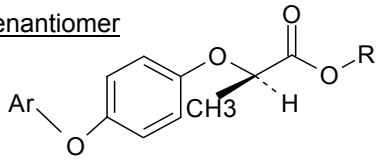
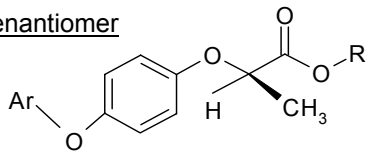
Transformation in Soil and Water

Stereo-chemical Transformations
Aryloxy Phenoxy Propionate Herbicides
General Structure

R enantiomer



S enantiomer



Diclofop-methyl (RS), Quizalofop-ethy (RS), Fenoxaprop-ethyl (RS), Fuazifop-butyl (RS), Fenthiaprop-ethyl (RS)

S-Fluazifop-butyl → S-Fluazifop-acid

R-Fluazifop-buty → R-Fluazifop-acid → Further Degradation

R-Fluazifop-acid has twice the herbicidal activity of S-Fluazifop-acid

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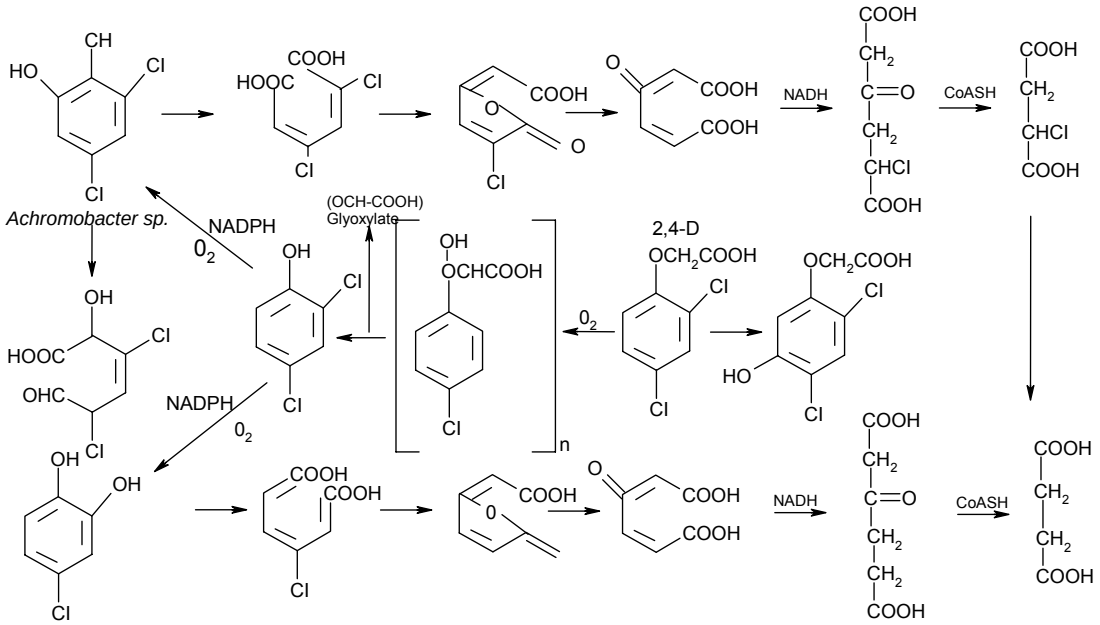
Pathways for microbial metabolism of 2,4-D (after Kaufman, 1974)



Summary

- **Soil and to a lesser extent water contain a high number and diversity of microorganisms which have remarkable capabilities to transform pesticides into non-toxic fragments.**
- **Microbial, hydrolytic and photolytic transformation processes all occur simultaneously, pesticides and their metabolites generally don't accumulate in soil either they are fully degraded between applications or reach a plateau following repeated use.**
- **Metabolic pathways of transformation are almost always identical irrespective of the continent, country soil or water type.**
- **Soils and waters have an inherent capacity and capability to mineralize to CO_2 and H_2O both natural and anthropogenic compounds.**

Thank you very much for your kind attention.