

Factors Impacting the Residual Activity and Off-Target Movement of Soil-Applied Herbicides

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Overview of Fates of Pesticide Compounds in the Environment

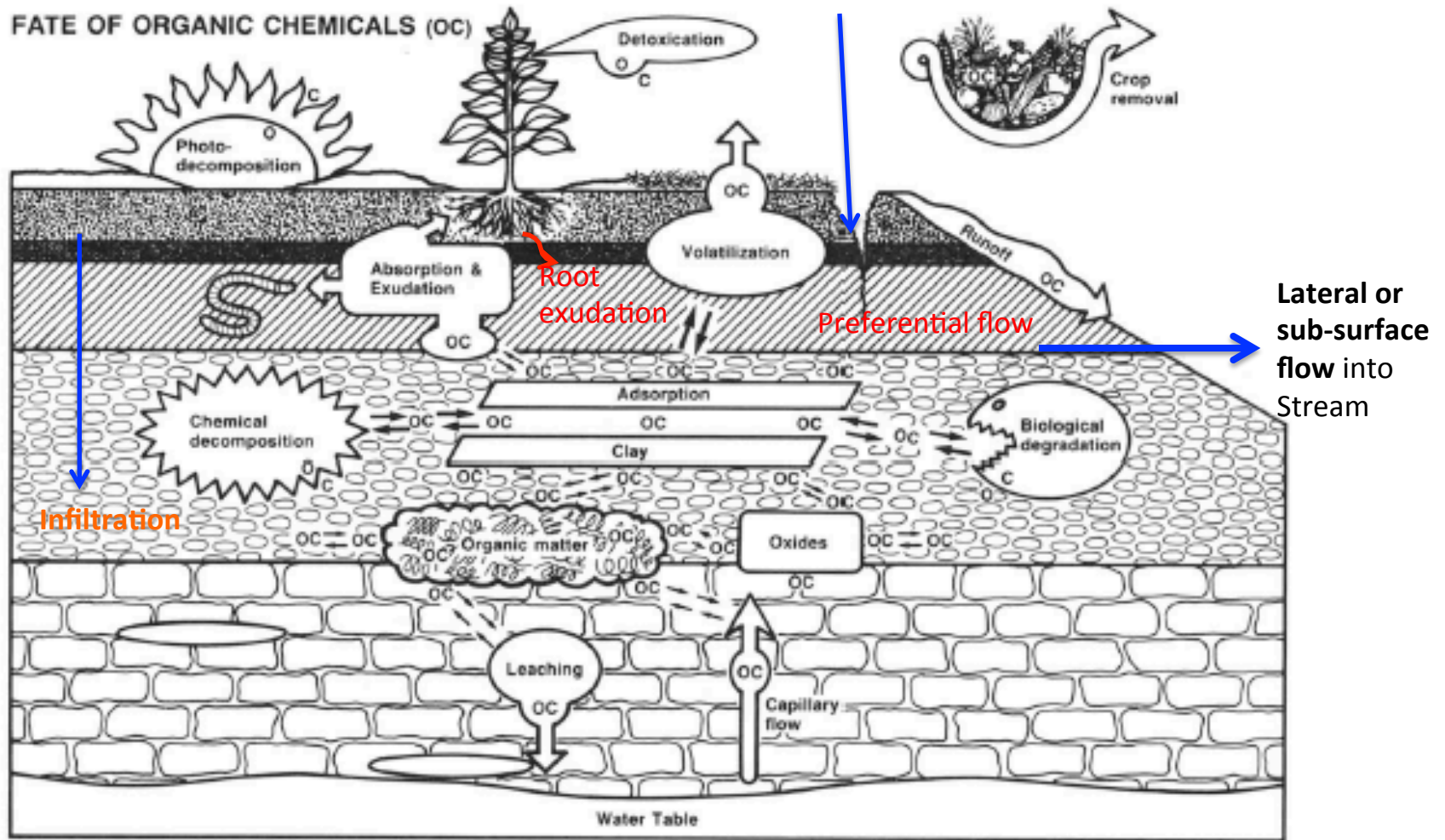


Fig 12-1. Processes affecting the dissipation of organic chemicals (OC) in the environment. Degradation processes are characterized by the splitting of the OC molecule. Transfer processes are characterized by the OC molecules remaining intact.

Fates of Herbicides = **DISSIPATION**:
dispersal of the applied herbicide in the environment

Dissipation of Herbicides in Soil Systems is Dependent on following Processes:

- Chemical decomposition (Degradation)
- Photodecomposition (Photolysis)
- Biological decomposition (Biodegradation)
- Volatilization
- Mobility or movement (Leaching, Erosion, Runoff)
- Plant Absorption and Detoxication / Crop Removal
- Adsorption/Desorption**

Soil chemical system is a **dynamic** system

Chemicals reaching soil become associated with assorted soil particles
During “wetting cycles” (rainfall, irrigation), chemical molecules infiltrate soil and begin dynamic sorption/desorption cycle (continuous process which is subject to any of the other processes i.e., leaching, volatilization, degradation, etc.)

****Adsorption/Desorption – directly affects magnitude of effects of other processes**

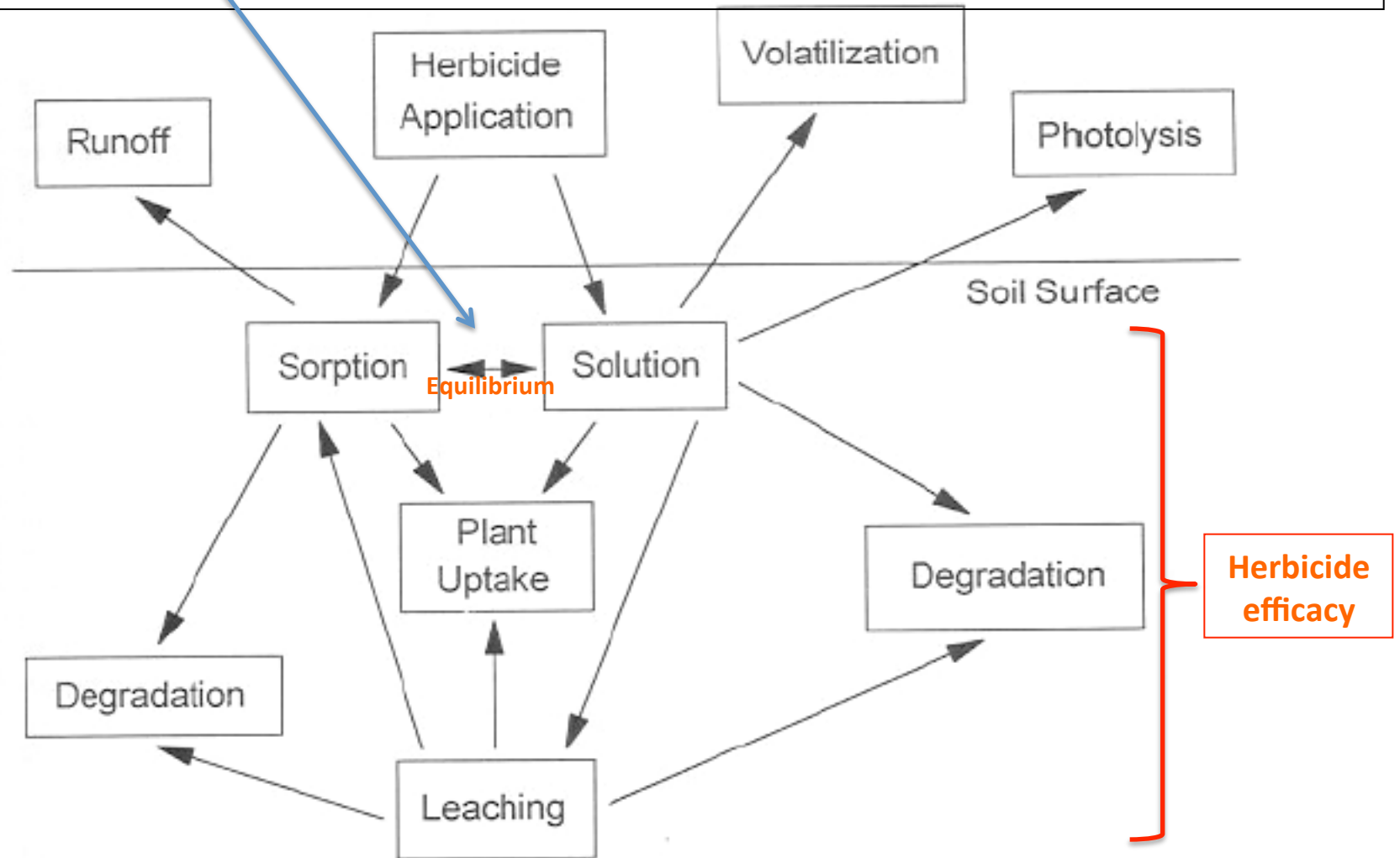


Figure 1. Schematic showing the interaction of herbicide sorption with other processes affecting herbicide dissipation and efficacy.

Source: Harper, S.S. 1994. Sorption-desorption and herbicide behavior in soil. Rev. Weed Sci. 6:207-225.

Adsorption / Desorption:

(Harper. 1994. Reviews of Weed Science. pp. 207-225)

A major process controlling soil-herbicide interactions

Regulates amount of herbicide in soil solution, rates of dissipation, plant uptake

Definitions:

Sorption – surface-induced removal of solutes from solution

Adsorption – attraction and accumulation of molecules at the soil-water or soil-air interface resulting in attachment on the surface of soil particles

Desorption – reverse of sorption; movement from the soil surface into the soil solution

Absorption - physical uptake / ingestion of solute by living organisms

Precipitation – solute concentration exceeds water solubility and falls out of solution

**Most organic molecules are retained by soils, therefore, soil behavior is of interest due to surface and ground water issues

Importance of Adsorption:

Sorption keeps herbicides in the weed control zone

Prevents leaching, reduces volatility losses, reduces biodegradation

Increased sorption: lower weed control because less herbicide available for plant uptake

Sorbed herbicides can contaminate surface waters if soil particles move off site

Sorption Mechanisms

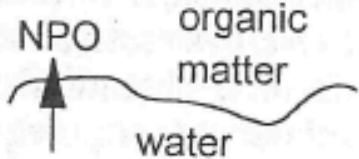
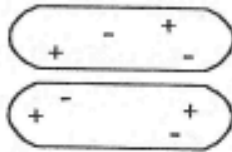
<p>Hydrophobic bonding</p>		<p>Anion exchange</p> $\text{RC}-\overset{\text{O}}{\parallel}{\text{O}}^{-} + \left(\text{clay}\right) + \text{X}^{-}(\text{aq})$
<p>London-van der Waals</p>		<p>Ligand exchange</p> $\text{RC}-\overset{\text{O}}{\parallel}{\text{O}}^{-} + \text{M}^{+} \left(\text{clay}\right) + \text{H}_2\text{O}$
<p>Hydrogen bonding</p>	$\begin{array}{c} \text{R} \\ \\ \text{N}-\text{H} \cdots \text{O}=\text{C} \\ \qquad \qquad \\ \text{H} \qquad \qquad \text{R} \end{array}$	<p>Protonation</p> $\text{RC}=\text{O}-\text{H}^{+} + \text{M}(\text{OH})\text{H}_2\text{O}_{\frac{(m-1)+}{n-1}}$
<p>Cation bridging</p>	$\text{R}^{-} + \text{M}^{+} \left(\text{clay}\right)$	<p>Cation exchange</p> $\text{R}_3\text{NH}^{+} \left(\text{clay}\right) + \text{M}^{+}(\text{aq})$
<p>Water bridging</p>	$\text{R}^{-} - (\text{H}_2\text{O}) - \text{M}^{+} \left(\text{clay}\right)$	<p>Covalent bonding</p> $\text{RC}-\text{O}-\text{CR}$

Figure 2. Examples of sorption mechanisms for herbicides onto soil, where R is a side chain or H atom, M is an exchangeable inorganic cation, X is an exchangeable inorganic anion, and NPO is a nonpolar organic compound.

HERBICIDE SORPTION MECHANISMS

(refer to Fig. 2, Rev. Weed Sci.) - Harper

- *Hydrophobic Partitioning* – based on solubility differences in organic vs water phases
- *London-van der Waal's forces* – short-range bonds developed from correlation in electron movement between ≥ 2 molecules; important for high molecular weight or neutral pesticides
- *Hydrogen-bonding* – dipole-dipole interactions; -OH, -NH groups and exposed electron pairs can interact with SOM → most common herbicide binding mechanism
- *Cation / Water-bridging* – complex between an exchangeable cation or water molecule and anion or polar functional group
- *Anion exchange* – electrostatic attraction of an anion to a positively charged site on the soil surface – significant mainly in soils containing dependent charge from kaolinite or aluminosilicates and iron oxides
- *Ligand exchange* – displacement of an inorganic hydroxyl or water molecule from a metal ion at a hydrous oxide surface by carboxylate or hydroxyl on an organic molecule
- *Protonation* – formation of charge-transfer complex when a functional group such as -NH₂ or carbonyl group forms a complex with a surface proton –significant for compounds with basic functional groups such as amines → Triazines. Occurs at mineral surfaces at low pH and low water content
- *Cation Exchange* – electrostatic attraction involves exchange of cation for cation; important for permanently charged herbicides → paraquat, diquat
- *Covalent bonding* – shared electrons between two atoms – increases stability of bound complex

Soil Organic Matter (SOM) – principle matrix for sorption

"Bound residues" – herbicide residues become unavailable and unextractable with solvents – residues become physically trapped in clay layers, covalently bound, co-metabolized by soil microorganisms; also known as "herbicide ageing" --

herbicide and other pesticide compounds can become part of humic substances

Factors Influencing Sorption:

Various Soil Components

- Soil Organic Matter (SOM) – most important
Humic materials
Plant / animal residues (intercept herbicides – released as residues decay?)
- Clay Fraction (colloidal fraction)
Crystalline and amorphous
Fe, Al oxides
Kaolinite, montmorillonite
Sorption of highly polar / charged molecules (paraquat, diquat)
- Exchangeable Cations
Ca⁺⁺, Fe³⁺, Al³⁺, Cu⁺⁺
Glyphosate sorption is highly influenced by cations;
also acifluorfen, picloram, some triazines
- **Soil P content - glyphosate adsorbs to same sites as phosphate in soil**

Soil Structure

Movement thru large pores => less sorption than thru micropores

Water Potential

Sorption higher in dry soil due to reduced competition with water for sorption sites

Herbicide solubility may be reduced as soil dries

Layer silicate clays expand as moisture increase => more sorption sites available

Water involved in binding mechanisms (water bridging)

Factors Influencing Sorption (continued):

Soil Environmental Factors

Variable relationships – **pH**, Nutrient content (i.e., phosphorus), temperature, moisture content, microbial community

Herbicide Active Ingredient chemical and biological characteristics:

Permanently Ionized – paraquat

Ionizable – (charge changes with change in soil pH)

Phenoxy, Triazines, Sulfonylureas (SU's), Imidazolinones (IMI's), Glyphosate
Acid or $-NH_2$ functional groups

Neutral Compounds – carry little or no charge – i.e., thiocarbamates

Major Conclusion:

Adsorption in soil occurs in a **multi-phasic system** – soil particles, organic matter, water, herbicide, nutrients, metal oxides

Clay particle interacting with organic molecule

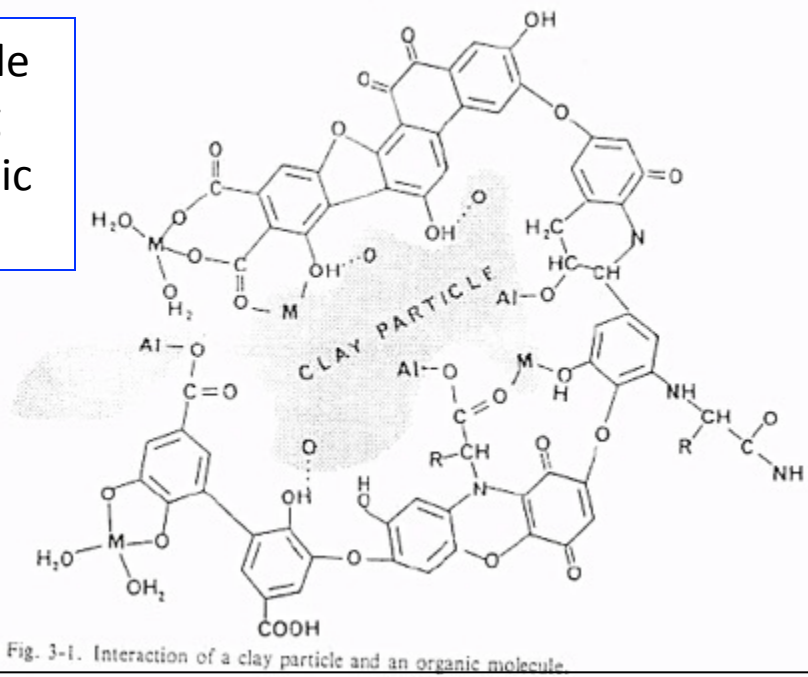
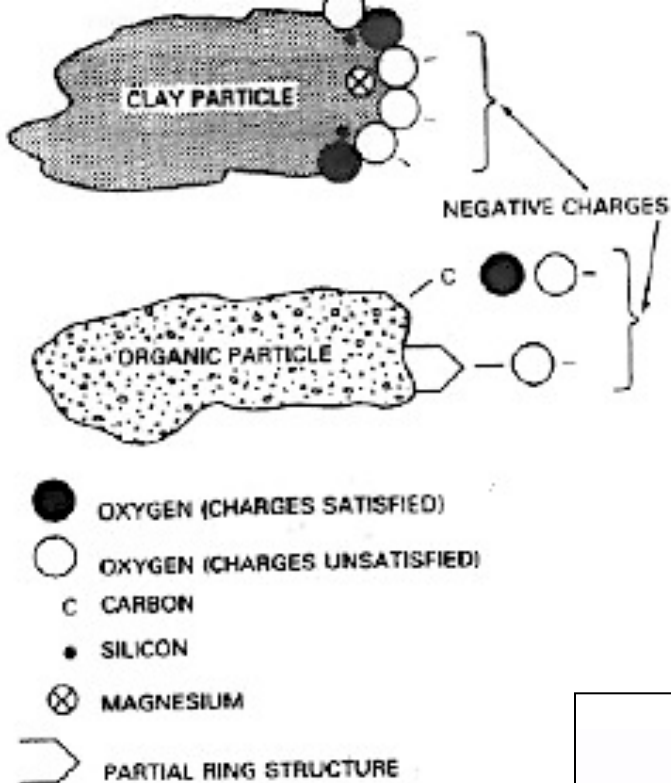


Fig. 3-1. Interaction of a clay particle and an organic molecule.

Hypothetical structure for soil organic matter

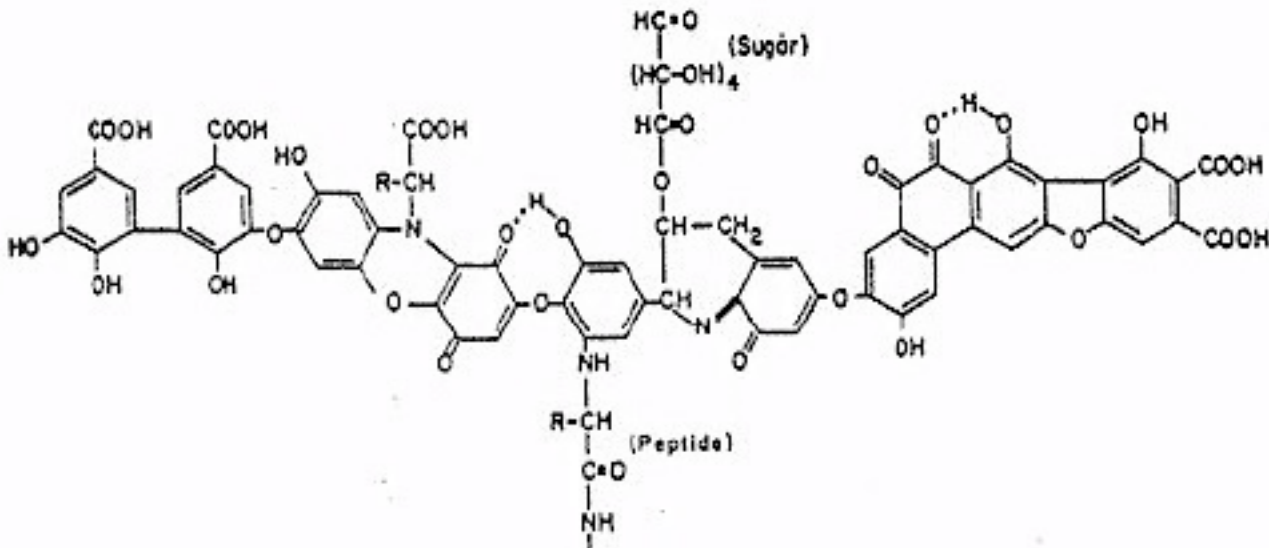


FIGURE 12-7. Diagram of clay and organic matter particles showing the typical negative surface charge gives the colloid its adsorptive ability.

Hypothetical interactions of organic compounds (i.e., herbicides) with soil particles (clay minerals) and organic matter.

Properties of Herbicides Determine Behavior in Soils

Ionizable Compounds - many herbicides are weak acids

Characterized by "**pKa**", the *acid dissociation constant*

this is the negative log of the ratio of dissociated compound (ionized):undissociated compound (non-ionized)

NOTE: soil pH influences herbicide ionization

If herbicide pKa = 2.8, then at soil pH>2.8, herbicide carries a net negative charge

Neutral or Non-polar Compounds - Uncharged, low water solubility, soluble in organic solvents

Characterized by **K_{OW}**, the *octanol:water partition coefficient*

this represents the distribution of herbicide between organic and water phases

Values are high for nonpolar compounds, low for ionizable compounds

Sorption in soils described by **K_d**, coefficient for herbicide distribution between water and soil phases; measured as ratio of concentration of soil-adsorbed herbicide:herbicide in solution

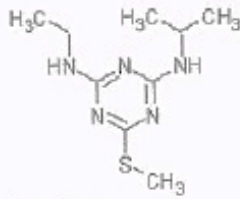
Sorption adjusted for soil carbon (C): described by **K_{OC}**, the ratio of **K_d** to soil organic C content*

Note: soil organic matter (SOM) value can be converted to SOC using SOM=58% C

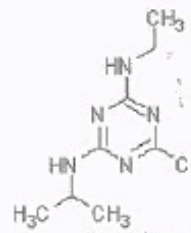
K_{OC} is rather independent of soil soil texture and may be more realistic expression of herbicide adsorption in soils

***These properties used to develop label recommendations for herbicide application, MSDS info, and how to manage for potential residual buildup and non-target effects.**

"Segard"

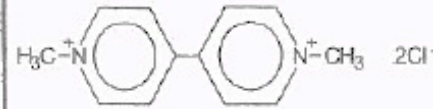


Ametryn
pKa 4.1



Atrazine
pKa 1.7
pKb = 12.3

Paraquat dichloride salt

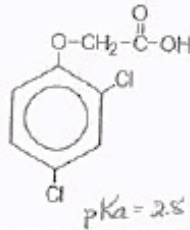


Paraquat
pKa

"Gramoxone"

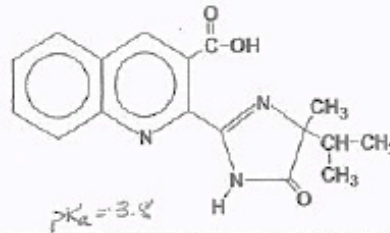
Chemical properties of selected herbicides

2,4-D acid



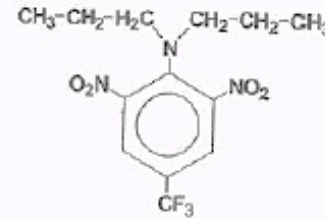
pKa = 2.8

Imazaquin acid **"Scepter"**



pKa = 3.8

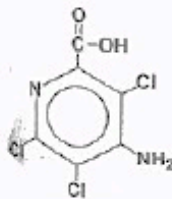
Trifluralin



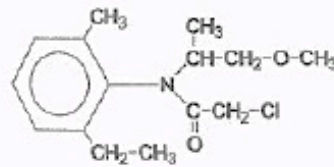
**"Treflan";
"Bayonet";
"Preen"**

**"Tordon";
"Grazon"**

Picloram acid

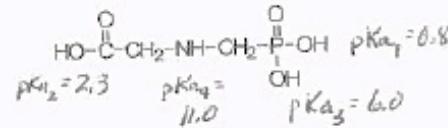


Metolachlor



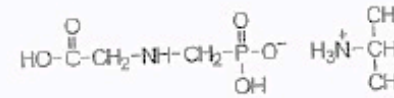
**"Bicep"; "Dual
Magnum"**

Glyphosate acid

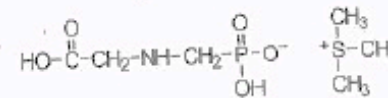


"Roundup"

Glyphosate isopropylamine salt

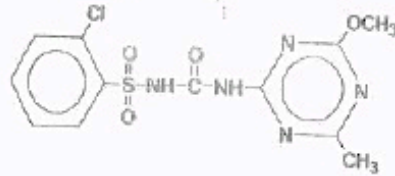


Glyphosate dimethylsulfonium (trimesium) salt



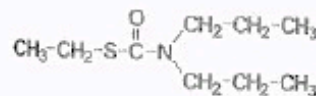
"Glean"

Chlorsulfuron



EPTC

S-ethyl dipropyl carbamothioate



"Eptam"

Glyphosate diammonium salt

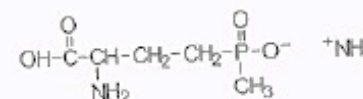


TABLE 12-2. Relative adsorption values of some representative herbicides.

	Herbicide	K_d
"Treflan"	Trifluralin	8000
"Prowl"	Pendimethalin	5000
	Triallate	2400
	Oryzalin	600
	Prometryn	400
"Eptam"	EPTC	200
	Metolachlor	200
	Cyanazine	190
	Atrazine	100
	Metribuzin	60
	2,4-D	20
	Imazaquin	20
"Tordon"	Picloram	16
	Dicamba	2
	Dalapon	1

Source: Data based on Wauchope et al., 1992.

Table 7.2 Water Solubilities and Soil Organic Carbon Sorption Coefficients (K_{oc}) of Selected Soil-Applied Herbicides^a Arranged According to Decreasing Water Solubilities. As water solubility decreases, sorption to organic matter increases.

Herbicide	Solubility in Water (ppm) ^b	Average K_{oc} (ml/g)
Dicamba (amine salt)	720,000	2
Clopyralid (amine salt)	300,000	6
Picloram (potassium salt)	200,000	16
Hexazinone	33,000	54
Chlorsulfuron	31,800	40
Tebuthiuron	2500	80
Metribuzin	1100	60
Clomazone	1100	300
Molinate	970	190
Triasulfuron	815	65-191
2,4-D (amine salt)	796	20
Prometon	720	150
Terbacil	710	55
Bromacil	700	32
Propachlor	613	112
Metalachlor	488	200
Chlorimuron	450	110
EPTC	370	200
Sulfometuron	300	78
Alachlor	242	124
Ametryn	200	300
Cyanazine	171	190
Fluometuron	110	100
Vernolate	108	260
Cycloate	85	600
Linuron	75	400
Napropamide	73	700
Pebulate	60	430
Imazaquin	60	20
Butylate	45	400
Diuron	42	480
Prometryn	33	400
Atrazine	33	100
Norflurazon	28	700
Bensulide	25	1000
Butachlor	23	700
Dichlobenil	21.2	400
Siduron	18	420
Pronamide	15	800
Fluridone	12	1000
Simazine	6.2	130
Triallate	4	2400
Oryzalin	2.6	600
Isoxaben	1	190-570
Oxadiazon	0.7	3200
DCPA	0.5	5000
Trifluralin	0.3	7000
Ethalfuralin	0.3	4000
Pendimethalin	0.275	17,200
Oxyfluorfen	0.1	100,000
Benfen	0.1	9000
Prodiamine	0.013	13,000

^aData from *Herbicide Handbook* of the Weed Science Society of America,

DESORPTION – reverse of sorption – controls the level of weed control efficacy after rainfall, application, or irrigation → equilibrium in soil is governed
In an ideal system, every herbicide molecule is available to plants; Reality – some herbicides become irreversibly retained

HERBICIDE MOBILITY

Important in determining herbicide efficacy, suitability, use as selective herbicide, groundwater contamination potential, runoff potential

Dependent of several factors:

Water solubility and herbicide sorption

(Predict environmental fate)

PKa of ionizable herbicide and soil pH

Vapor pressure of herbicide

Soil texture – high SOM, high clay content => less mobility, high adsorption

Soil permeability – porosity, structure

Intensity / frequency of rainfall

Large amounts of water applied continuously can move ≤80% of a relatively mobile herbicide

Logic diagram to determine mechanism of herbicide sorption in soils or other media.

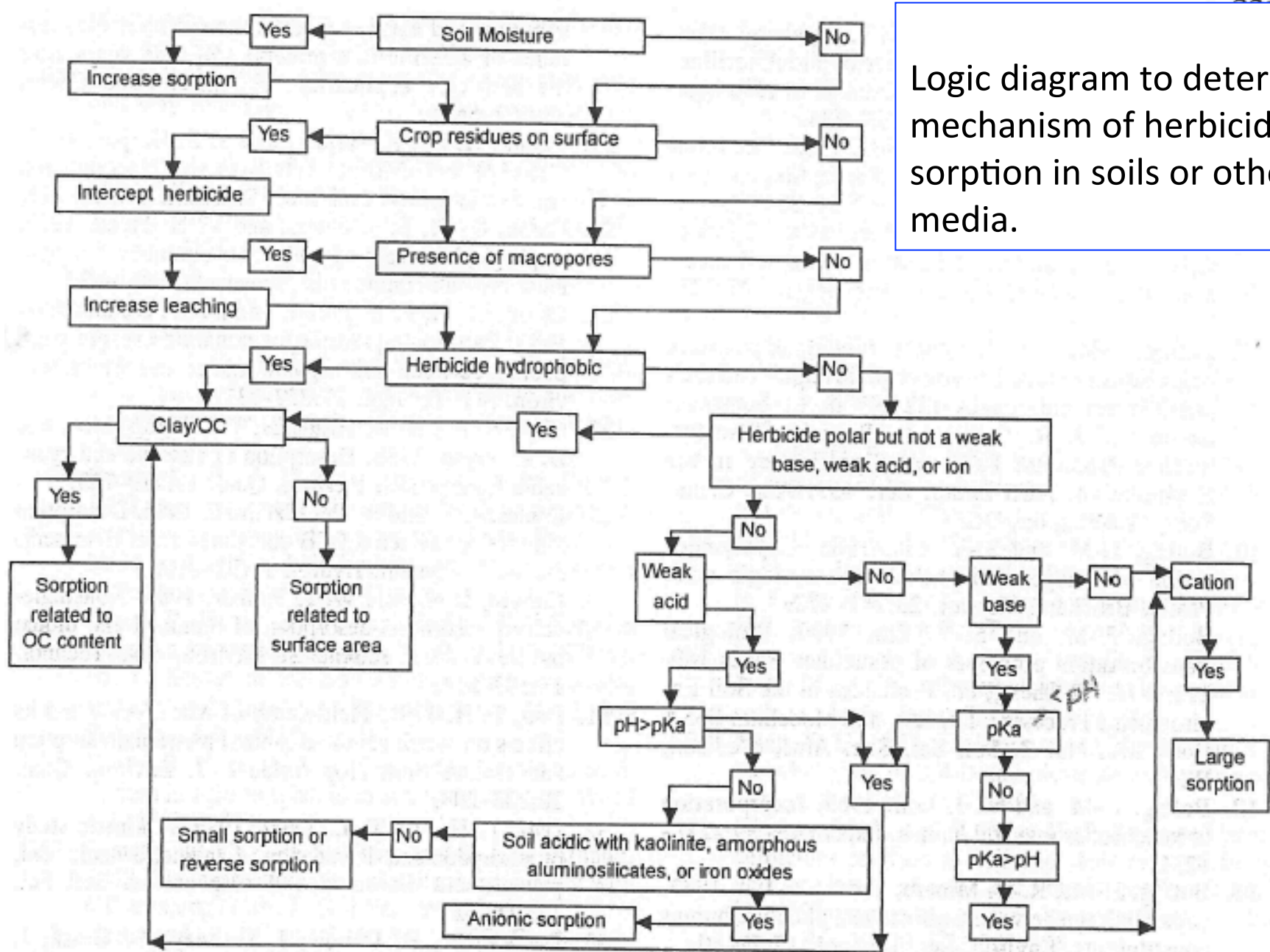


Figure 4. Schematic for determining the factors affecting sorption of herbicides in soil (Adapted from Green and Karickhoff (50); by permission)

Source: Harper, S.S. 1994. Sorption-desorption and herbicide behavior in soil. Rev. Weed Sci. 6:207-225.

VOLATILIZATION

Physico-chemical process that controls dispersion of herbicide in environment.

1. Evaporation of herbicide introduced in air from liquid solution
2. Dispersion-dilution of resulting vapor in the air

Liquid or soil transformed to gas phase by temperature elevation or pressure reduction.

Vapor pressure = tendency of substance to volatilize

$\geq 10^{-4}$ mm Hg, volatile compound – i.e., thiocarbamates, trifluralin, therefore, these herbicides must be soil-incorporated

See Table 12-3

Most ionizable compounds are considered non-volatile.

Factors:

1. Vapor pressure
2. Herbicide concentration
3. Transport rate to soil surface
4. Soil sorption
5. Soil temperature
6. Velocity of air above soil surface
7. Soil moisture

VP - equilibrium pressure of a vapor above a solid

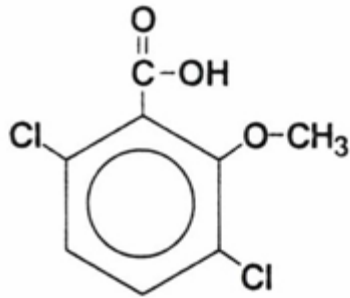
Volatility - tendency of a substance to vaporize; direct relationship to VP

>1 mPa

(100 bars = 1 mPa;

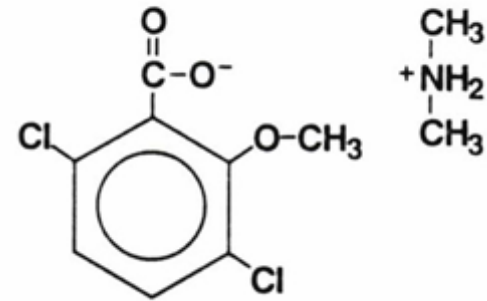
mm Hg = 133,000 mPa)

Dicamba acid



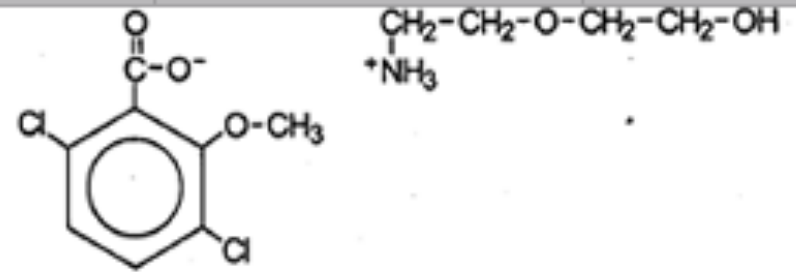
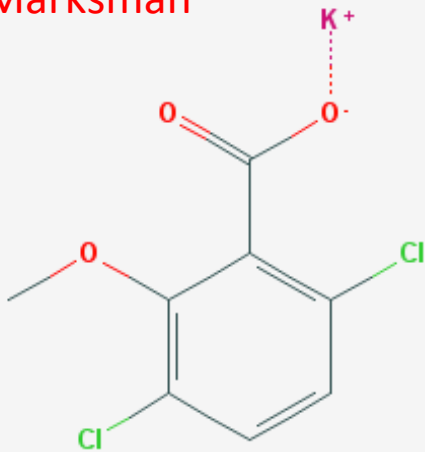
Most volatile molecule

Dicamba dimethylamine salt



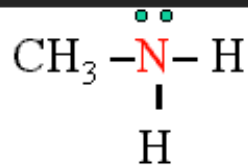
Banvel

Marksman



dicamba diglycolamine salt

Clarity



Methylamine

Salt added for *Engenia* modification
[Xtendimax ? Fexepan?]

Air sampler



Indicator plants



Why is dicamba problematic?
Low volatility does not mean **no** volatility
Most broadleaf plants very sensitive
(*crop and non-crop*)
Large acreages are applied with dicamba
Applications originally in spring but now often
during summer temperatures

Table 7.3 Vapor Pressures of Selected Soil-Applied Herbicides^a Arranged According to Decreasing Vapor Pressures

Older, soil-incorporated herbicides

Herbicide	Vapor Pressure (mm Hg) ^b
EPTC	3.4×10^{-2}
Butylate	1.3×10^{-2}
Vernolate	1.0×10^{-2}
Pebulate	8.9×10^{-3}
Cycloate	6.2×10^{-3}
Molinate	5.6×10^{-3}
Dichlobenil	1×10^{-3}
Clomazone	1.4×10^{-4}
Triallate	1.1×10^{-4}
Trifluralin	1.1×10^{-4}
Pronamide	8.5×10^{-5}
Ethalfuralin	8.2×10^{-5}
Propachlor	7.9×10^{-5}
Benefin	7.8×10^{-5}
Metalachlor	3.1×10^{-5}
Linuron	1.7×10^{-5} (20°C)
Alachlor	1.6×10^{-5}
Pendimethalin	9.4×10^{-6}
Dicamba (amine salt)	9.2×10^{-6}
Prometon	7.7×10^{-6}
Butachlor	4.5×10^{-6}
Napropamide	4×10^{-6}
Ametryn	2.7×10^{-6}
DCPA	2.5×10^{-6}
Oxyfluorfen	2×10^{-6}
Clopyralid (amine salt)	1.3×10^{-6}
Prometryn	1.2×10^{-6}
Fluometuron	9.4×10^{-7}
Bensulide	8×10^{-7}
Oxadiazon	7.76×10^{-7}
Isoxaaben	$<3.9 \times 10^{-7}$
Bromacil	3.1×10^{-7}
Terbacil	3.1×10^{-7}
Atrazine	2.9×10^{-7}
Hexazinone	2×10^{-7}
2,4-D (amine salt)	1.4×10^{-7}
Metribuzin	1.2×10^{-7} (20°C)
Tebuthiuron	1×10^{-7}
Fluridone	$<1 \times 10^{-7}$
Diuron	6.9×10^{-8}
Norflurazon	2.9×10^{-8}
Prodiamine	2.51×10^{-8}
Simazine	2.2×10^{-8}
Imazaquin	$<2 \times 10^{-8}$ (45°C)
Triasulfuron	$<1.5 \times 10^{-8}$
Oryzalin	$<1 \times 10^{-8}$
Siduron	4×10^{-9}
Cyanazine	1.6×10^{-9} (20°C)
Chlorsulfuron	2.3×10^{-11}
Chlorimuron	4×10^{-12}
Sulfometuron	5.5×10^{-16}
Picloram (potassium salt)	Negligible

^aData from *Herbicide Handbook of the Weed Science Society of America*, Lawrence, Kansas (1994).

^bVapor pressures at 25°C unless otherwise indicated.

Photolysis / Photodecomposition

Direct – pesticide absorbs light directly and is transformed

Indirect – another compound absorbs light and transfers energy to pesticide or serves as oxidant that transfers electrons to pesticide.

Factors:

- Intensity and spectra of light
- Presence / absence of sensitizer or quencher (absorbs light)
- Inherent tendency of compound to be photodecomposed

Energy required for breakage of chemical bonds:

C-C	88 Kcal/mole
C-H	98 Kcal/mole
O-H	119 Kcal/mole
O-O	52 Kcal/mole

Energy of selected radiation wavelengths:

200 nm	143 Kcal/mole
300 nm	95 Kcal/mole
400 nm	68 Kcal/mole

≈ 98% of UV light is absorbed within 1 Å of soil surface, therefore, shallow incorporation into soil protects most herbicides from photodecomposition; however, trifluralin is not very photo-stable.

Biodegradation of Herbicides & Xenobiotics

TERMINOLOGY

Xenobiotic – compound not found in ‘natural systems’ – often refers to human-made or synthetic compounds; resistant to biodegradation or decomposition

Dissipation - dispersal of the applied herbicide in the environment

Degradation - conversion or 'breakdown' of the compound to simpler components or by removal of one or more parts (i.e., functional groups) of the herbicide molecule

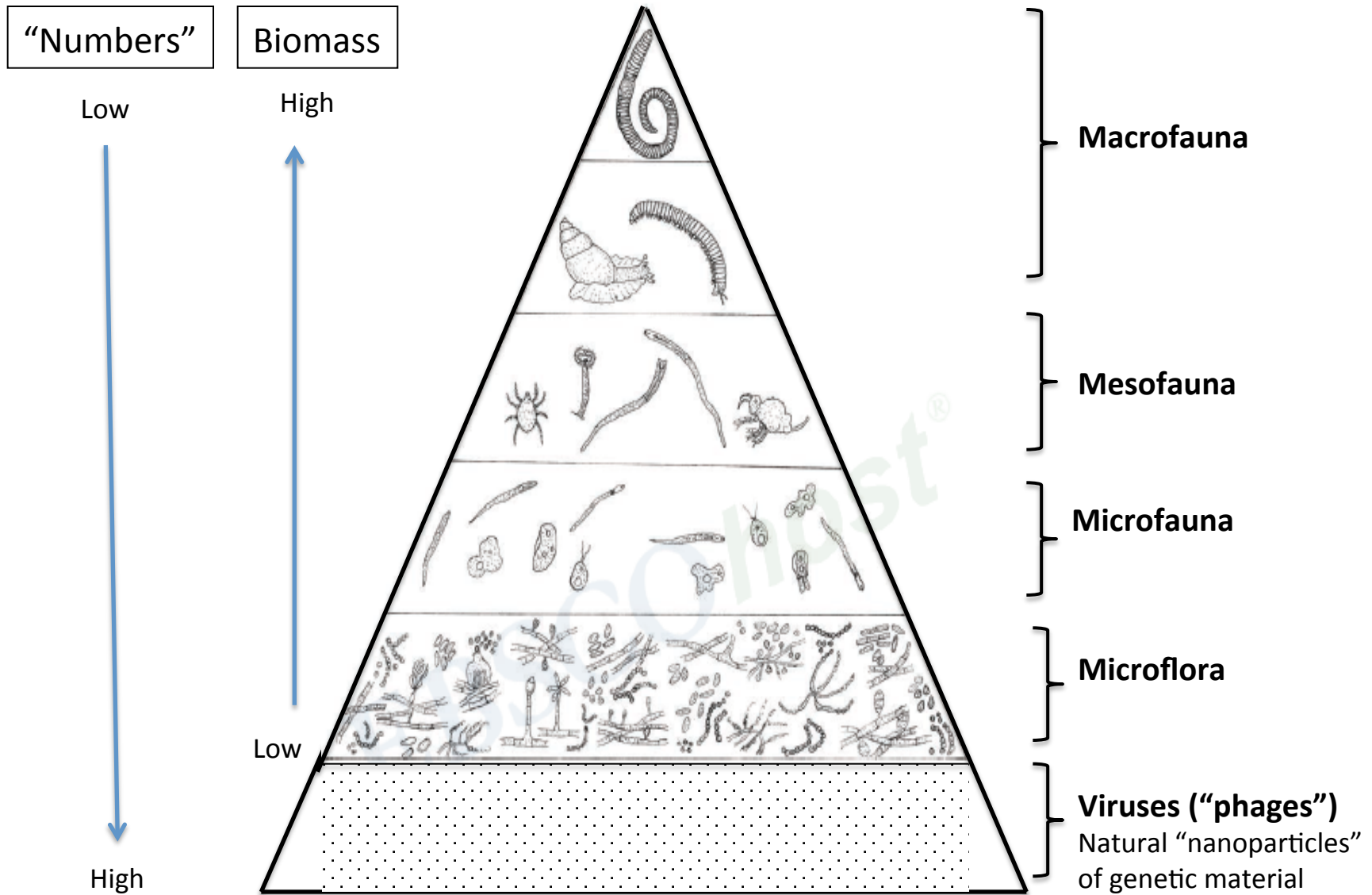
Chemical degradation - in absence of biological mediation, "abiotic hydrolysis"

Biodegradation (Biological degradation) - leads to organic metabolites ("breakdown products") or complete mineralization to inorganic components mediated by soil microorganisms capable of metabolizing naturally-occurring C substrates

➔ The most important route of herbicide dissipation in the environment

Biological transformations of herbicides (xenobiotics) are mediated by the soil microbial biomass through the action of enzymes. [a limited number of enzymes specific for xenobiotic degradation have been isolated and identified]

Diversity, Abundance and Distribution of Organisms in Soils



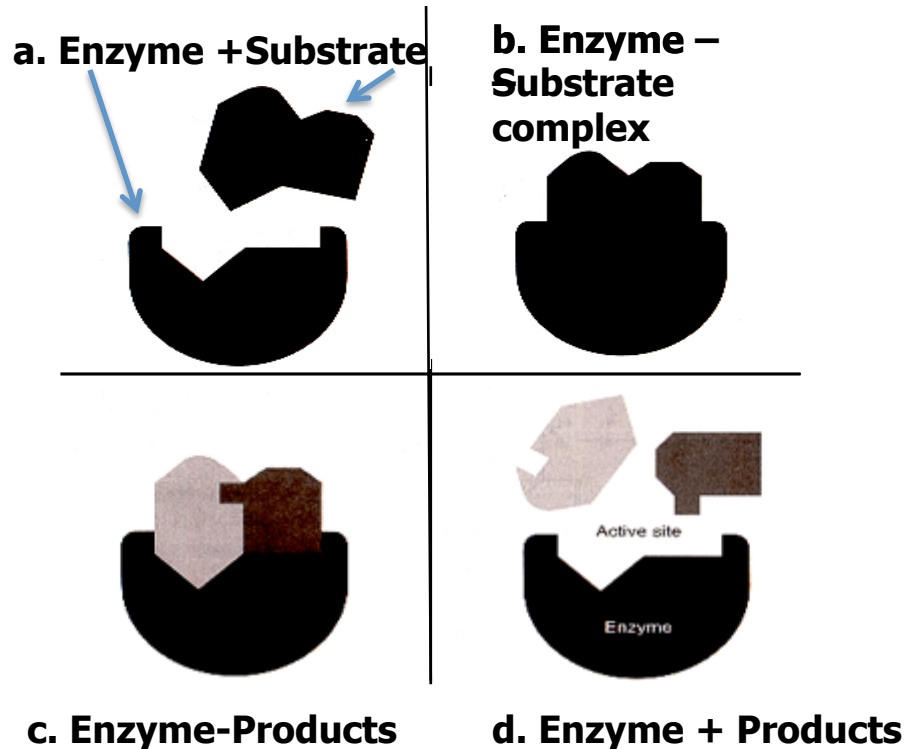
(Modified from Stirling et al., 2016. “Soil Health, Soil Biology, Soilborne Diseases and Sustainable Agriculture”, CSIRO Publishing, Clayton South, Victoria, Australia)

ENZYMES (Biocatalysts):

- a. Proteins – organic catalysts in biochemical reactions
 1. thermo-labile – denatured by high temperatures
 2. substrate-specific
 3. intracellular – primarily those involved in basic metabolic pathways
 4. Exocellular (extra-cellular) – important in degradation of complex, organic compounds
 5. Many have ‘co-factor’ requirements for activity - these are mainly “micro-nutrients”
- b. **Mechanism:** Enzyme combines with specific portion of substrate at the enzyme *active or catalytic site*
The formation of the *enzyme-substrate complex* is first step in the enzymatic reaction.
Reaction is carried out and degradation products are formed in next steps.

“Catabolic enzyme”:

Herbicide = “Substrate”
Herbicide breakdown
fragments or “metabolites” =
“Products”



Example:

Enzyme: glyphosate oxidoreductase; reaction: Glyphosate \rightarrow aminomethylphosphonic acid (AMPA) + glyoxalate

Conditions Required for Microbial Degradation:

1. Organism(s) effective in metabolizing herbicides must be present in soil or develop therein. **[Biodegradation rate is highly correlated to quantity and activity of microbial biomass]** - ***Microorganisms with appropriate enzymes!!***
2. Compound must be in a form suitable for degradation (chemical structure, solubility)
3. Chemical must be available to organism (adsorption - desorption) -- **“Bioavailability”**
4. Compound must be vulnerable to enzymes necessary for degradation (concentration, solubility optima, ability to induce enzyme synthesis)
5. Environmental conditions (pH, temp, moisture, SOM, ***micronutrients***) must be suitable for microbial proliferation and enzyme activation as well as herbicide molecule availability.

Metabolism of Herbicides:

1. **Support Microbial Growth (Catabolism/Anabolism):**

Herbicide serves as source of Energy, C, N, S, P

Microbial population and activity increases

Herbicide disappearance proportional to microbial growth rate

2. **Cometabolism** = incomplete metabolism and degradation of a compound; microbe unable to metabolize compound far enough to yield C & E for growth;

Microbe population presumably grows on another substrate while performing transformations on the herbicide compound

Also known as "*Incidental Metabolism*" - no gain for microbe yet modification of herbicide occurs - no increase in microbial population

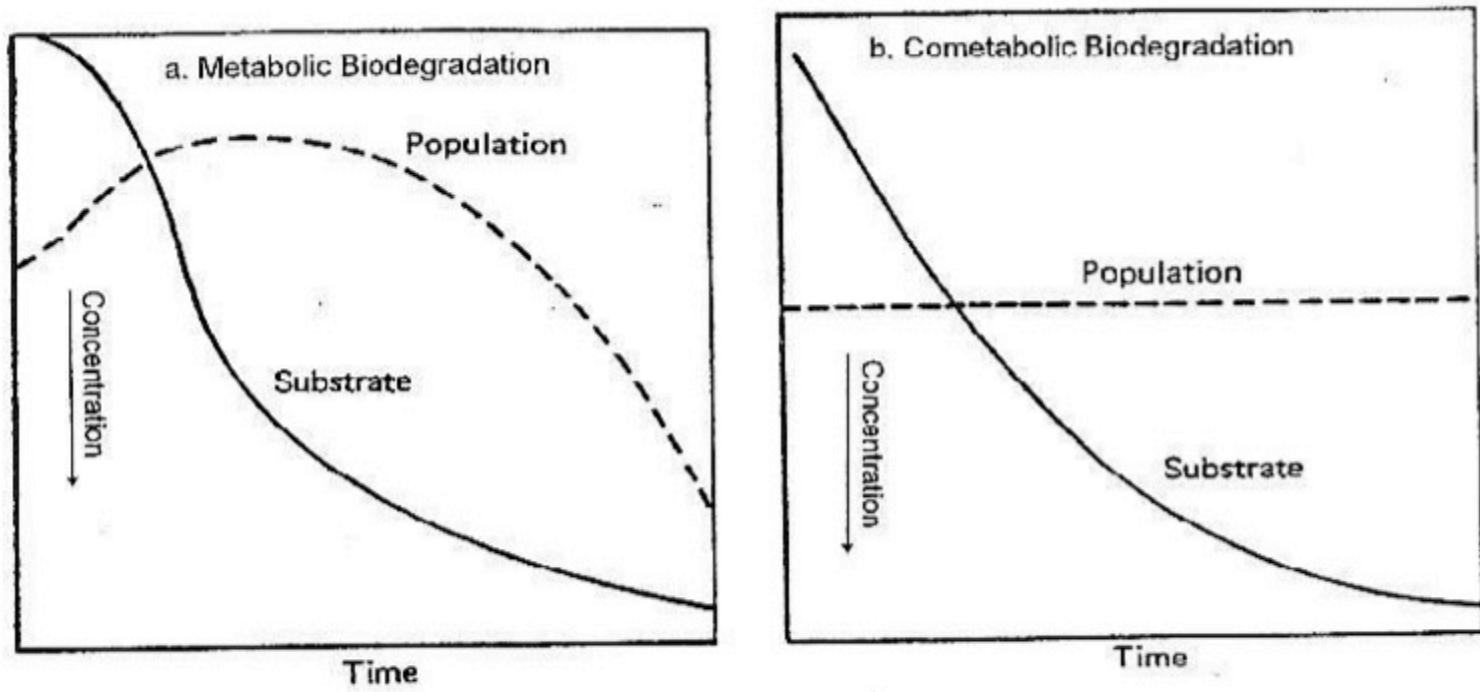
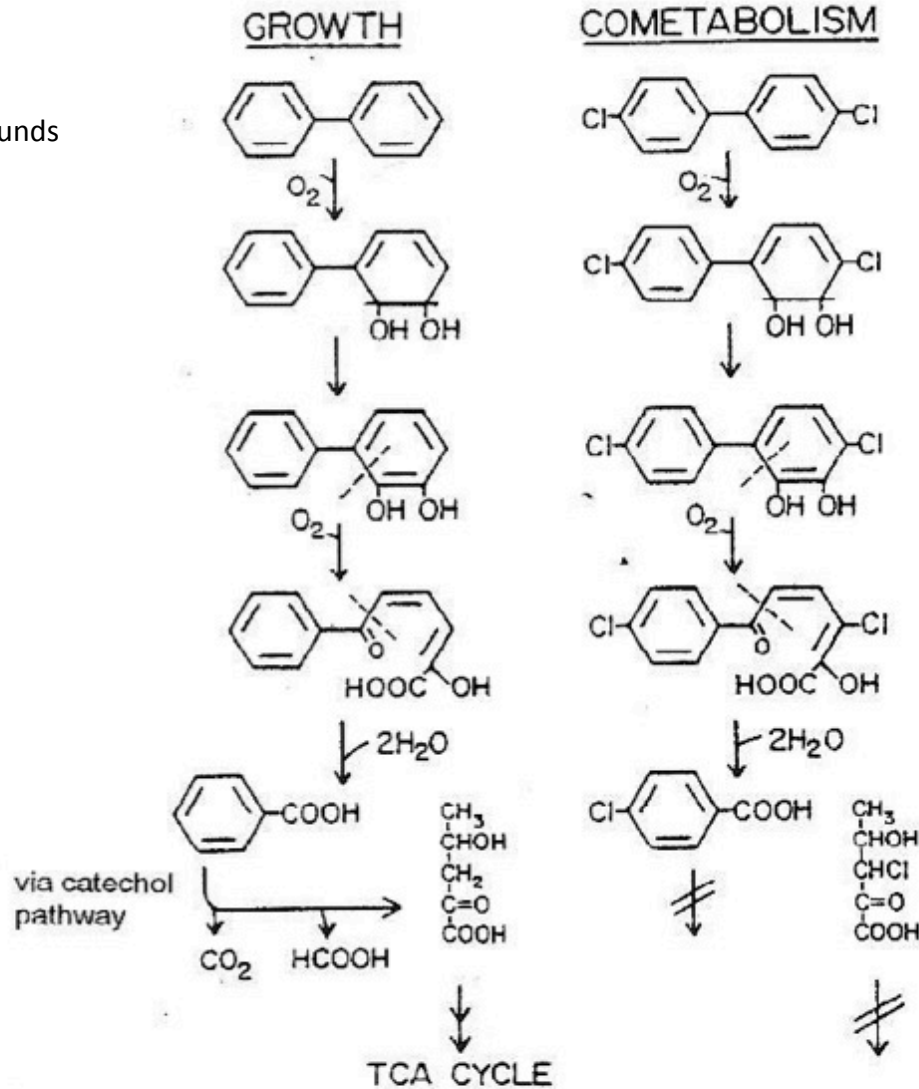


Fig. 3-3. Population and substrate concentrations during (a) metabolic and (b) cometabolic biodegradation (Scow, 1982).

Comparison of Metabolic **Biodegradation vs Cometabolism** of a Xenobiotic Compound by Soil Microorganisms

Bi-phenyl compounds



Comparison of Metabolic (growth) vs Cometabolic pathways for two similar xenobiotic compounds

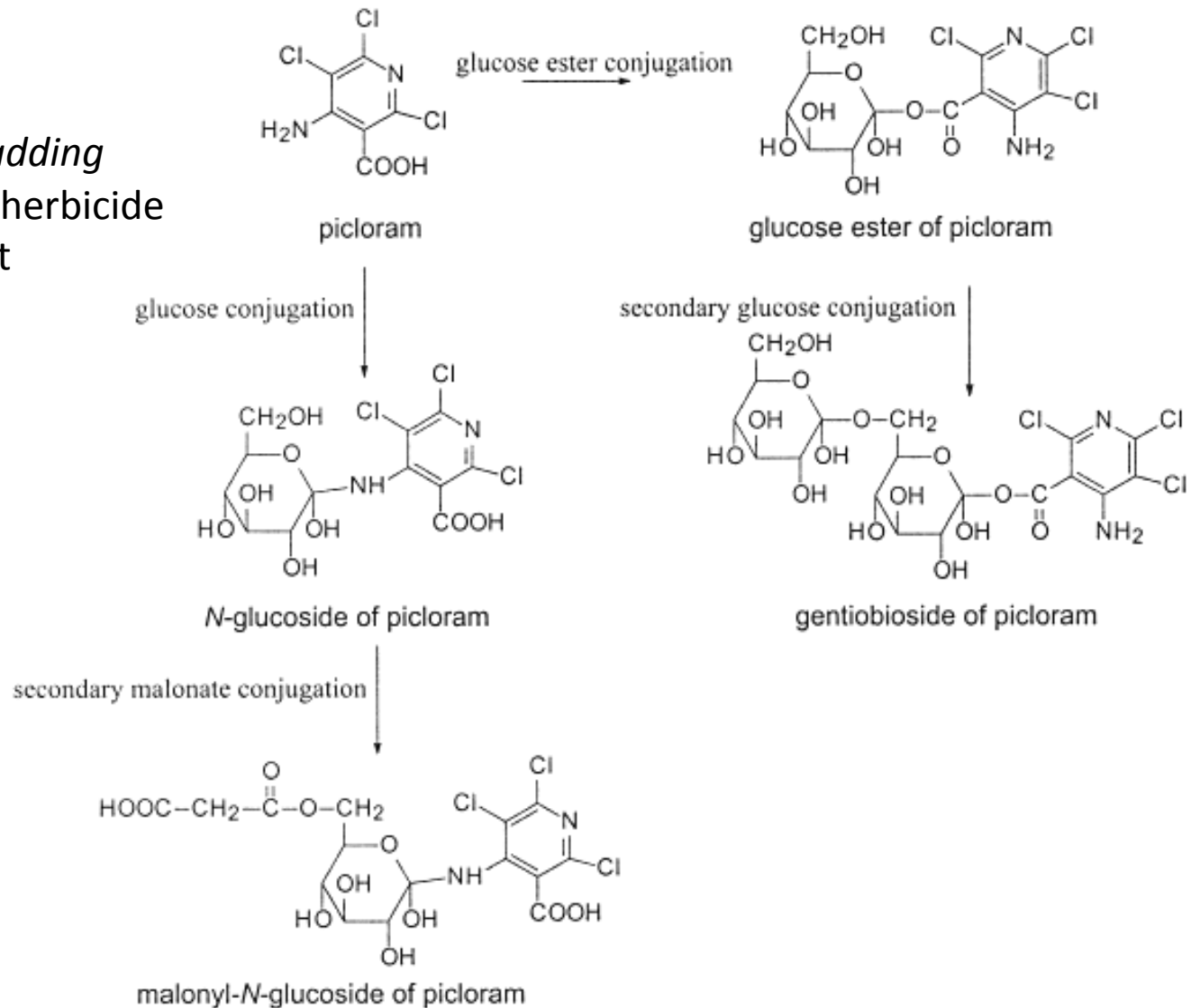
Fig. 3-4. Metabolism (mineralization) and cometabolism (no mineralization) of aromatic compounds by pure cultures, using biphenyl and 4,4'-dichlorobiphenyl as an example (Focht, 1993).

Herbicide Transformations by Soil Microorganisms:

1. **Biodegradation** - destructive changes of chemical to simpler components
"Decomposition", "Breakdown" - also considered as biodegradation
"Mineralization" - complete degradation
2. **Accumulation** -- herbicide molecule directly incorporated into biomass
i.e., norflurazon in bacterial exopolysaccharides
3. **Detoxification** - toxicity of herbicide is decreased due to chemical alteration
4. **Activation** - conversion of nontoxic molecule to toxic form
5. **Defusing** - conversion of a potentially toxic molecule to a product not able to be activated any further
6. **Conjugation/Polymerization** - making herbicide more complex by addition of new chemical groups (from SOM; i.e., lignin metabolites); condensation of herbicide molecules into polymer-like compounds; conjugation with glutathione (GHS) [i.e., alachlor-GHS pathway in rhizosphere environment]; various sugars
7. **Change in Spectrum of Toxicity** - change in toxicity toward one organism to a product toxic toward a different type of organism
8. **Secondary Effects** - microbial activity indirectly transforms herbicides due to changes in pH, redox, reactive products, etc. in soil

Conjugation Type Reaction -

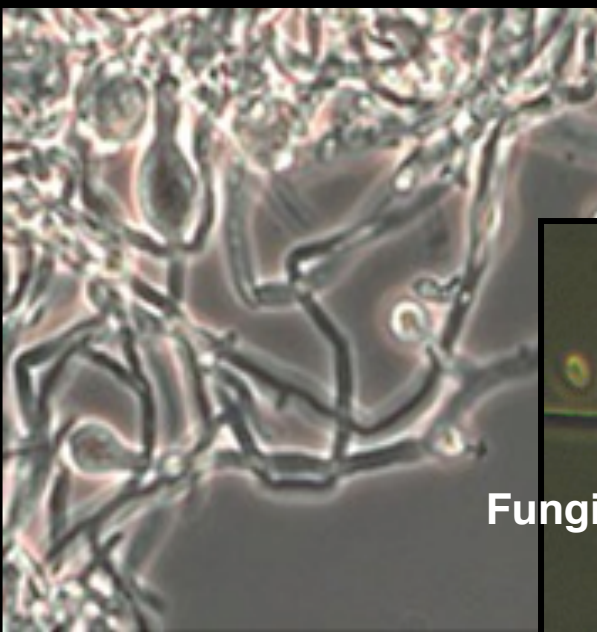
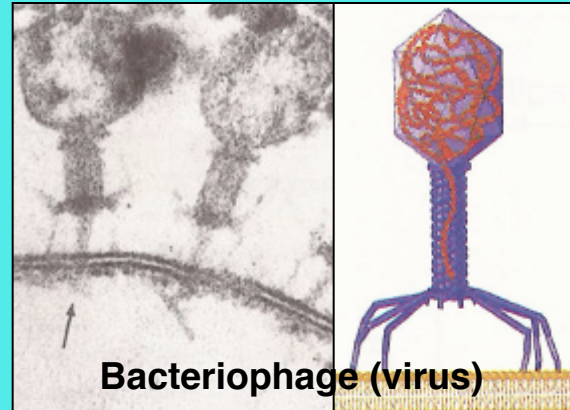
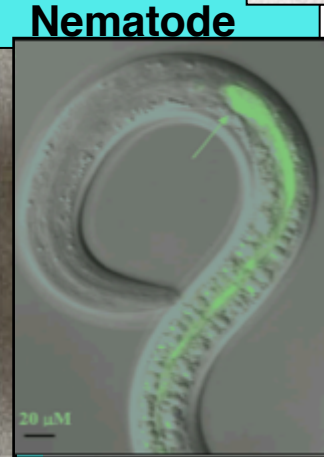
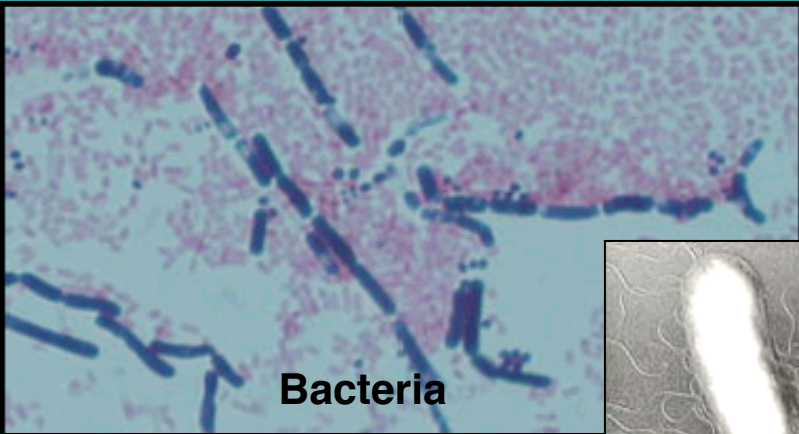
Alternative to degradation - *adding* compounds to herbicide to immobilize it



Conjugation and secondary conjugation of picloram in leafy spurge (*Euphorbia esula* L.) as proposed by Frear et al. (1989).

Why is a highly diverse microbial community important to degrade herbicides?

Soil Microbial Diversity (Soil Biodiversity) - variety of living microorganisms at species, inter-species and intra-species levels in soil ecosystem



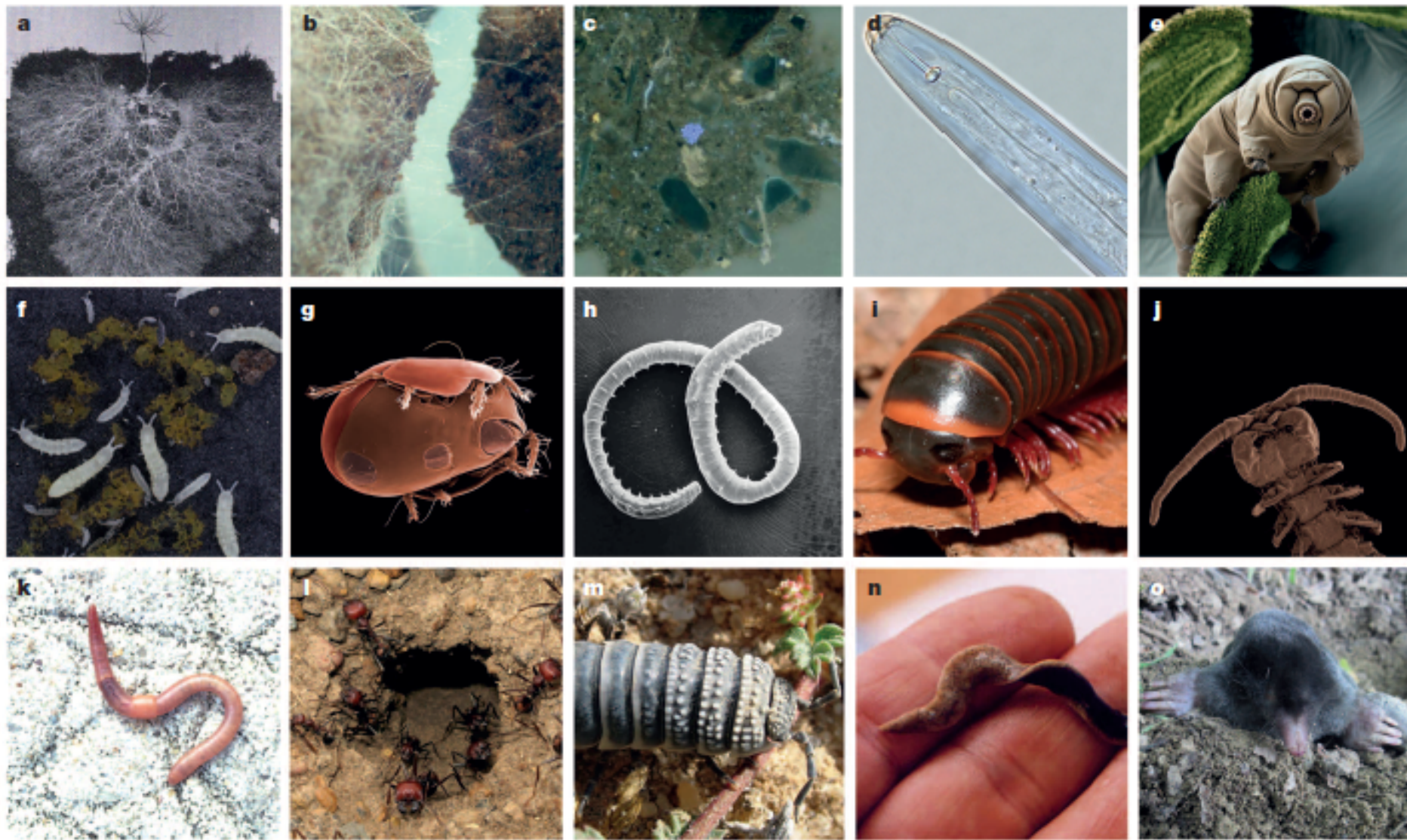
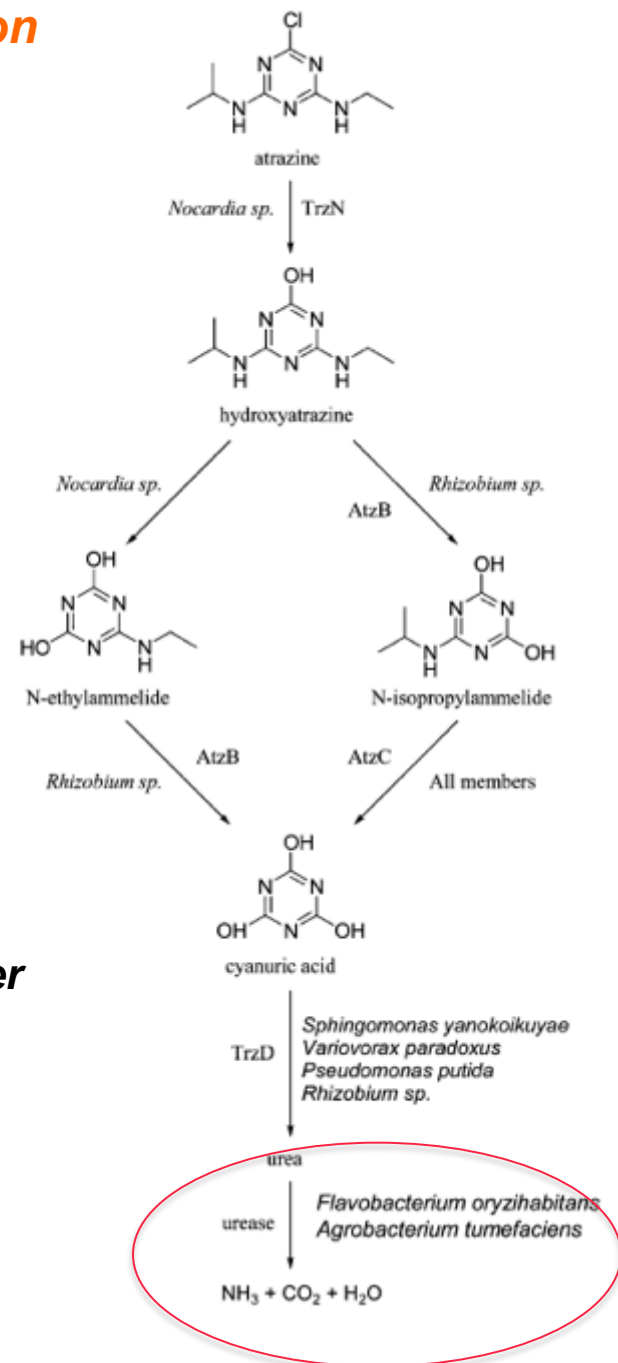


Figure 1 | A selection of organisms of the soil food web. a–o, The selection of organisms includes ectomycorrhizal (a) and decomposer fungi (b), bacteria (c), nematode (d), tardigrade (e), collembolan (f), mite (g), enchytraeid worm (h), millipede (i), centipede (j), earthworm (k), ants (l), woodlice (m), flatworm (n) and mole (o). All photographs are from the European Soil Biodiversity

Atlas, courtesy of A. Jones; individual photo credits are K. Ritz (b, c); H. van Wijnen (d); Water bear in moss, Eye of Science/Science Photo Library (e); P. Henning Krog (f); D. Walter (g); J. Rombke (h); J. Mourek (i, j); D. Cluzeau (k); European Soil Biodiversity Atlas, Joint Research Centre (l, n); S Taiti (m); and H. Atter (o).

Why Microbial Diversity is Critical for Biodegradation of Herbicides in the Environment

Role of microbial consortia in biodegradation of Atrazine



Proposed atrazine degradation pathway for an **eight-member microbial consortium** each of which contribute specific enzymes to complete biodegradation to mineralization.

Source: Smith et al. 2005. *FEMS Microbiol. Ecol.* 53:265-273.

Highly diverse microbial community (**consortia**) needed to completely degrade glyphosate in the soil environment - well-managed soils is key to success -

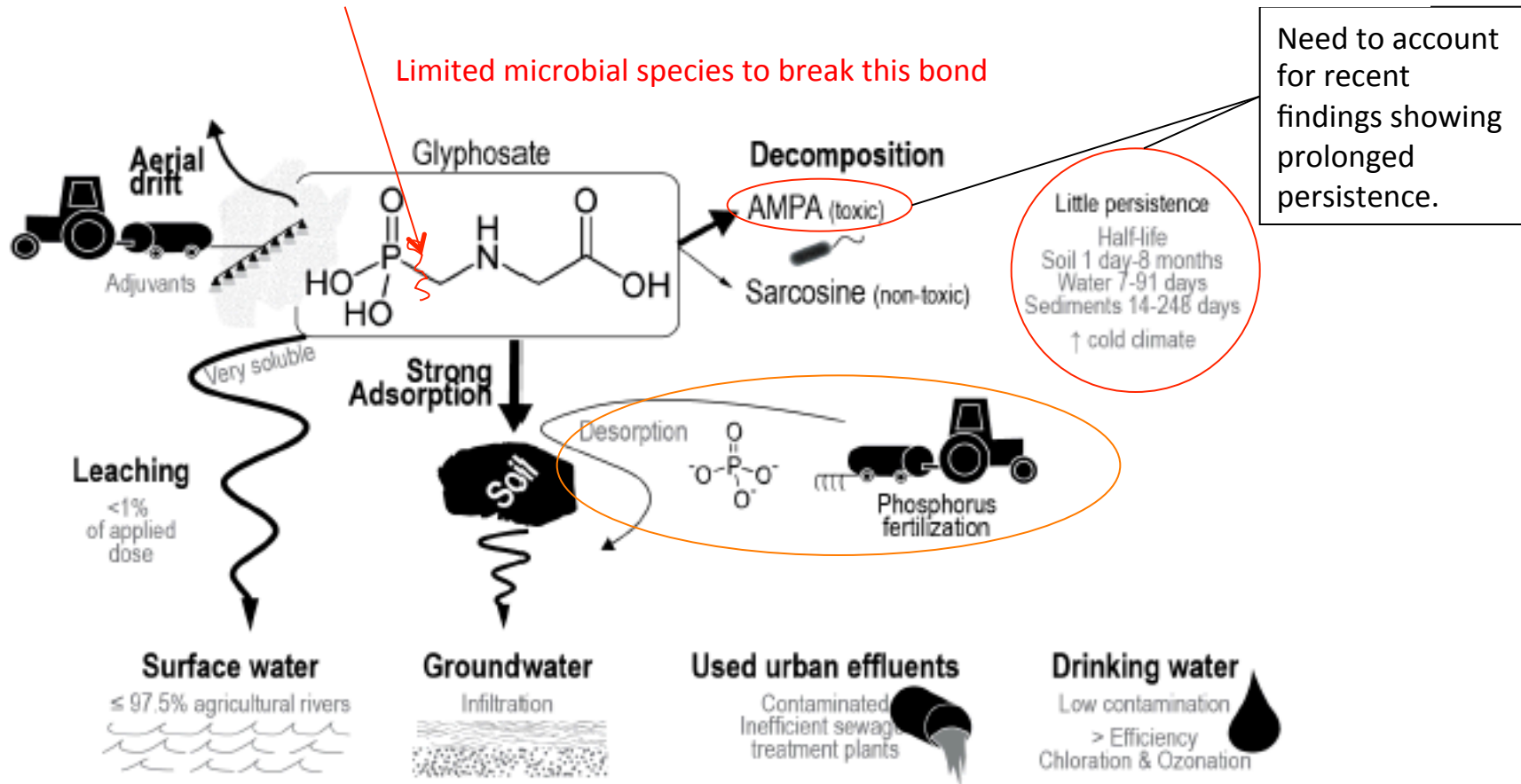
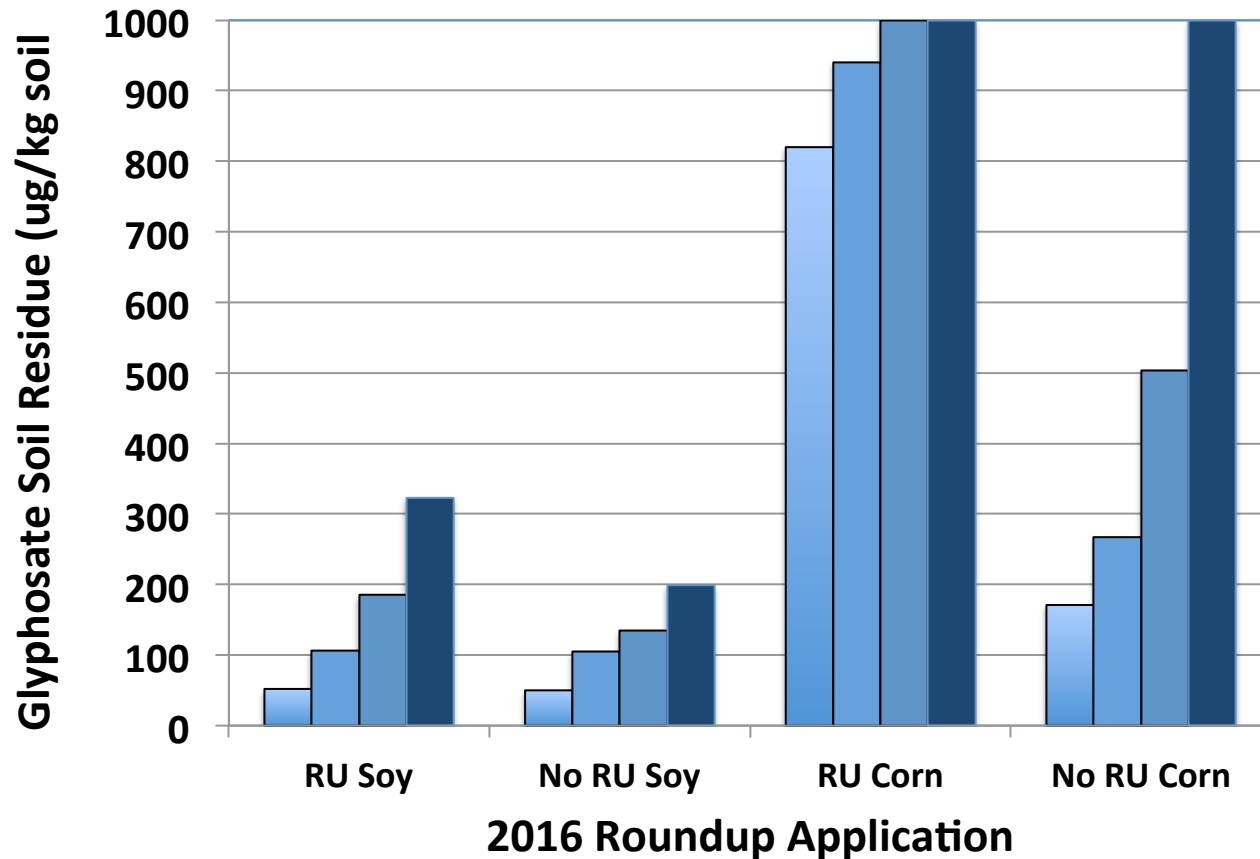


Figure 3: Glyphosate movement and environmental persistence.

Residual Activity and Off-Target Movement of Herbicides

Source: Henault-Ethier, 2016. Backgrounder: Glyphosate: Ubiquitous and Worrisome. Technical Report, Canadian Association of Physicians for the Environment. DOI: 10.13140/RG2.2.3511.5129

Residual glyphosate in rhizosphere soil of GE soybean and corn with and without Roundup* in 2016 (Mexico silt loam, Knox County Missouri)**



* Application rate = 0.75 lb a.i./A

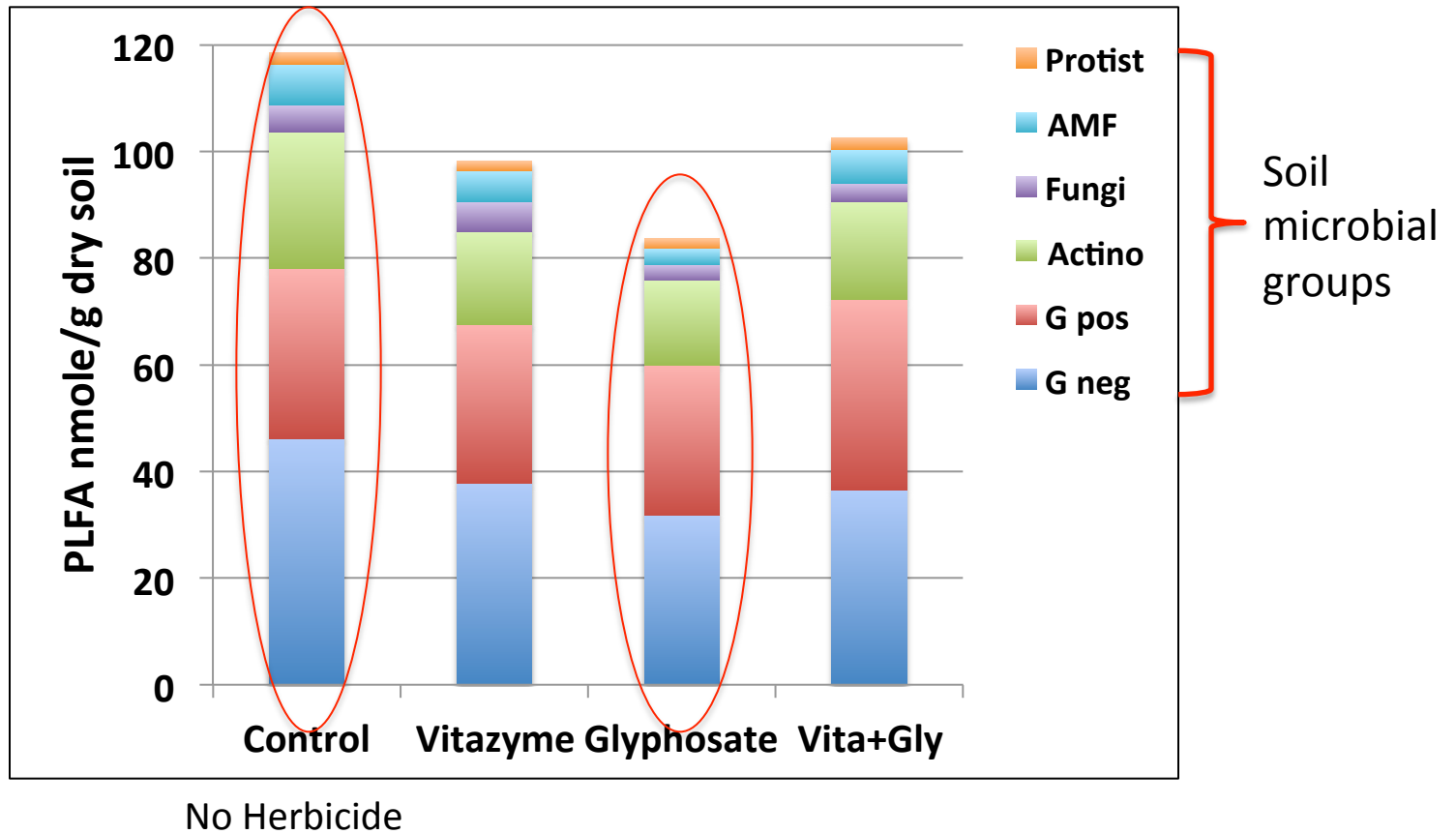
** Roundup applied at field site periodically thru 2015

Residual Glyphosate Damage to Pumpkins after a RR Soybean – corn rotation



Photo: Frank Dean

Impact of Herbicide on Rhizosphere Soil Microbial Community



Factors interact with biodegradation to affect persistence, residual activity and off-target effects of herbicides in soils:

1. Soil pH
2. Soil mineralogy - composition i.e., MnO_4 content
3. Soil texture (>20,000 soil series in U.S.!)
4. Soil organic matter content
5. Reaction with soil plant nutrients (P, Mg, Ca, K, Mn, Fe, etc.)
6. Plant root reabsorption thru exchange on soil sites with nutrients
7. Soil nutrient status (cationic nutrient content)
8. Herbicide formulation and components (i.e., *surfactants*)
9. Soil surface vegetative residue cover
10. Soil oxygen status; compaction (anoxic conditions may prolongs persistence)
11. Composition of soil microbial community (adequate **diversity** [consortium] to completely degrade molecule?) - metabolic diversity assures required enzymes present
13. Bioaccumulation in some soil/sediment meso- & macro-fauna
14. Offsite movement in surface runoff, contaminate surface waters
15. Offsite movement of sediment, accumulation in catchments

Rate-Determining Factors of Microbial Transformations of Herbicides:

1. Soil Characteristics:

Adsorption-desorption equilibria

- a. Some herbicides strongly adsorbed to soil particles and SOM fractions affecting availability of compounds to microbes;
- b. *Sorption of specific enzymes to compound* - may inhibit biodegradation process

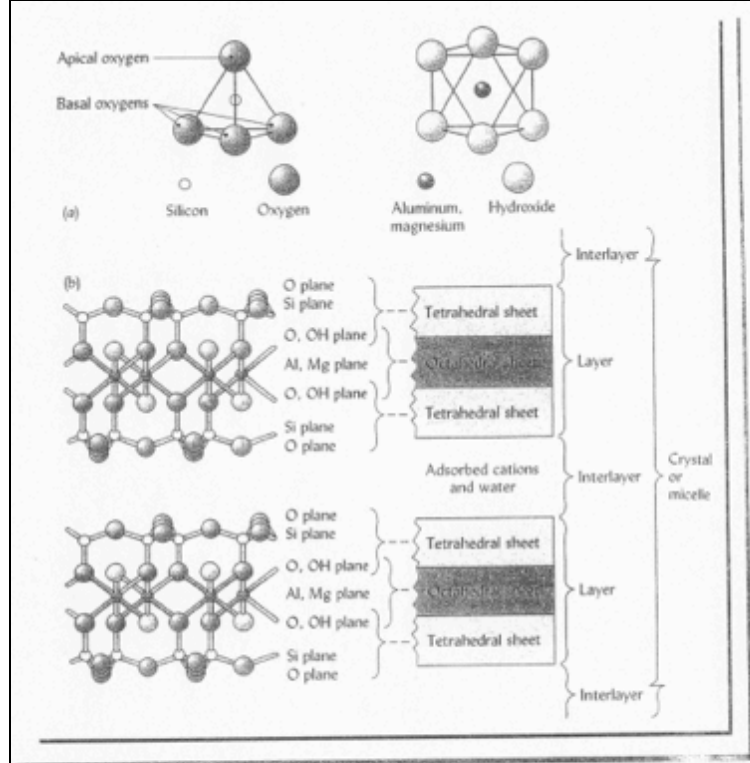


FIGURE 8.4 The basic molecular and structural components of silicate clays. (a) A single tetrahedron, a four-sided building block composed of a silicon ion surrounded by four oxygen atoms; and a single eight-sided octahedron, in which an aluminum (or magnesium) ion is surrounded by six hydroxy groups or oxygen atoms. (b) In clay crystals thousands of these tetrahedral and octahedral building blocks are connected to give planes of silicon and aluminum (or magnesium) ions. These planes alternate with planes of oxygen atoms and hydroxy groups. Note that apical oxygen atoms are common to adjoining tetrahedral and octahedral sheets. The silicon plane and associated oxygen-hydroxy planes make up a tetrahedral sheet. Similarly, the aluminum-magnesium plane and associated oxygen-hydroxy planes constitute the octahedral sheet. Different combinations of tetrahedral and octahedral sheets are found. In some silicate clays these layers are separated by interlayers in which water and adsorbed cations are found. Many layers are found in each crystal or micelle (microcell).

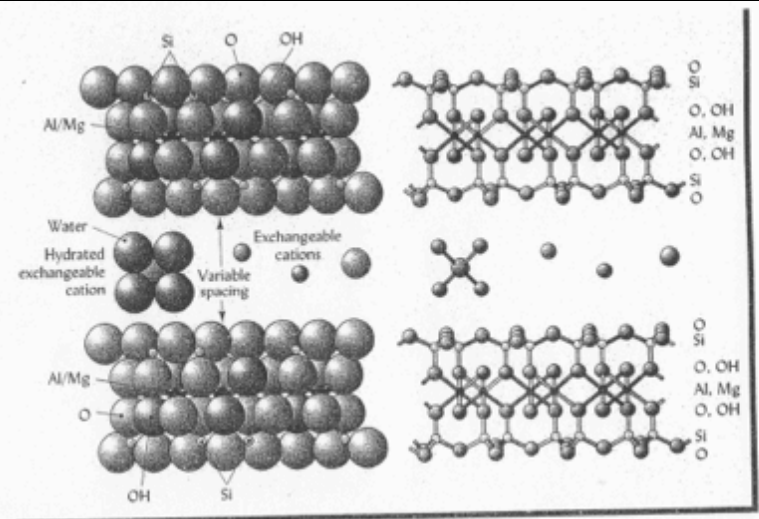


FIGURE 8.7 Model of two crystal layers and an interlayer characteristic of montmorillonite, a smectite expanding-lattice 2:1-type clay mineral. Each layer is made up of an octahedral sheet sandwiched between two tetrahedral sheets with shared apical oxygen ions that hold the sheets together. There is little attraction between oxygen atoms in the bottom tetrahedral sheet of one unit and those in the top tetrahedral sheet of another. This permits a variable space between layers, which is occupied by water and exchangeable cations. The internal surface area thus exposed far exceeds the surface around the outside of the crystal. Note that magnesium has replaced aluminum in some sites of the octahedral sheet. Likewise, some silicon atoms in the tetrahedral sheet may be replaced by aluminum (not shown). These substitutions give rise to a negative charge, which accounts for the high cation exchange capacity of this clay mineral. A ball-and-stick model of the atoms and chemical bonds is at the right.

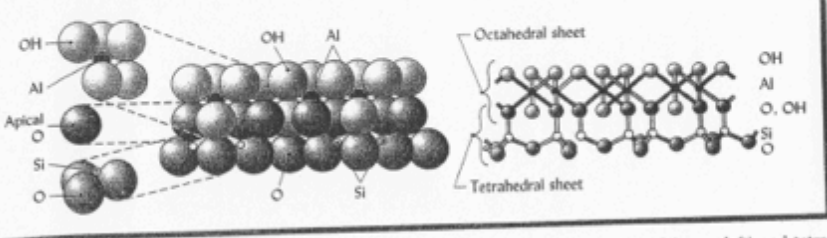


FIGURE 8.6 Models of the 1:1-type clay kaolinite. The primary elements of the octahedral (upper left) and tetrahedral (lower left) sheets are depicted as they might appear separately. In the crystal structure, however, these sheets are held together by common apical oxygen atoms. Note that each layer consists of alternating octahedral and tetrahedral sheets—hence, the designation 1:1. Aluminum ions surrounded by six hydroxy groups and/or oxygen atoms constitute the octahedral sheet (upper left). Smaller silicon ions associated with four oxygen atoms constitute the tetrahedral sheet (lower left).

2. Management Practices:

a) Type of Application – (for soil-applied herbicides)

Soil incorporation vs surface application

Adsorption & volatilization affect amount available for transformation

b) Rate & Frequency of Application

Higher levels always result in higher amount of the pesticide transformed, thus, when product is subjected to microbial enzymes, each successive application is degraded at a faster rate until a maximum rate is attained -- “**Accelerated or Enhanced Biodegradation**”

Essentially an increase in numbers and/or activity of microbes capable of metabolizing pesticides following multiple additions to soil = ***Enrichment culture of soil microbial degraders***

Carbofuran

2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate

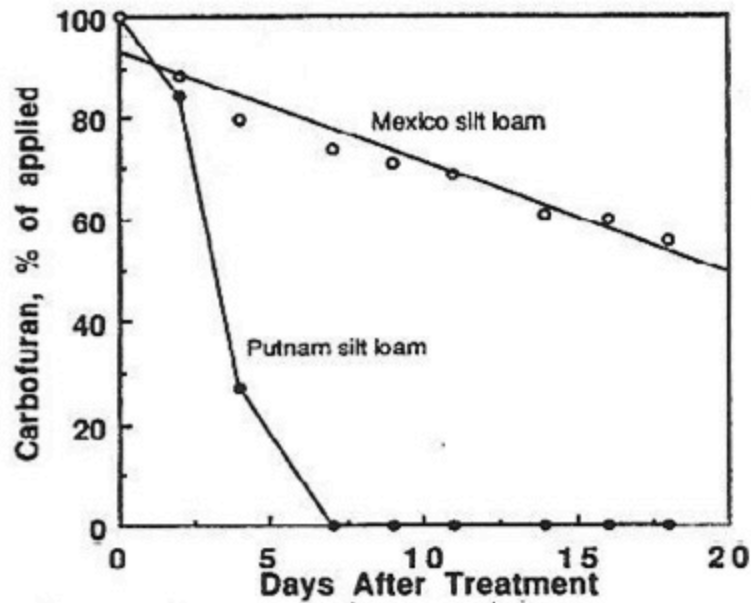
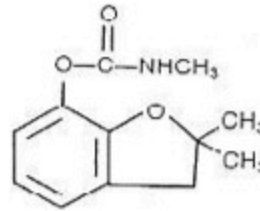


FIGURE 4

Recovery of carbofuran from Putnam and Mexico soils following treatment with 20 mg/kg carbofuran.

Corn soil insecticide carbofuran (Furadan) applied to same field on Putnam soil continuously for several years resulted in buildup of soil microorganisms able to rapidly degrade the insecticide before it was able to attack its target pest, the corn rootworm. Soil microorganisms in a 'native soil' from Tucker Prairie (Mexico soil) did not have ability to rapidly degrade carbofuran, therefore, the compound remained in soil longer. (From Edwards et al. 1993).

Conclusions

- Specific properties of herbicides are useful to understand their behavior in the environment
- Complete dissipation of herbicides is dependent on many soil and environmental factors
- The soil microbial community mediates multiple transformations of herbicides
- Biodegradation of herbicides is driven by level of microbial diversity in soils, which determines if complete mineralization occurs or not
- Biodegradation (extent and rate) is affected by multiple soil and environmental factors
- Biodegradation is affected by interaction with various properties of herbicides with microorganisms and enzymes
- Continuous use of herbicides may lead to residual buildup affecting microbial communities in soils and growth of subsequent vegetation OR lead to accelerated biodegradation whereby the herbicide is ineffective

10.29.2014

Resources serving as basis for lecture:

1. Camper, N.D. (ed.) 1986. Research Methods in Weed Science. 3rd ed. Southern Weed Science Society. Champaign, IL.
2. Harper, S.S. 1994. Sorption-desorption and herbicide behavior in soils. *Reviews of Weed Science* 10:207-224.
3. Walker, A. 1987. Herbicide persistence in soil. *Reviews of Weed Science* 3:1-17.
4. Roma-Burgos, N. & S.O. Duke (eds.) 2015. Research Methods in Weed Science. *Weed Science Special Issue 1*. DOI:10.1614/wees-13-00-13.1
5. Shaner, D.L. (ed.) 2014. *Herbicide Handbook*, 10th ed. Weed Science Society of America. Lawrence, KS.
6. Sawhney, B.L. & K. Brown. 1989. Reactions and Movement of Organic Chemicals in Soils. Soil Science Society of America, Madison, WI Special Publication 22.

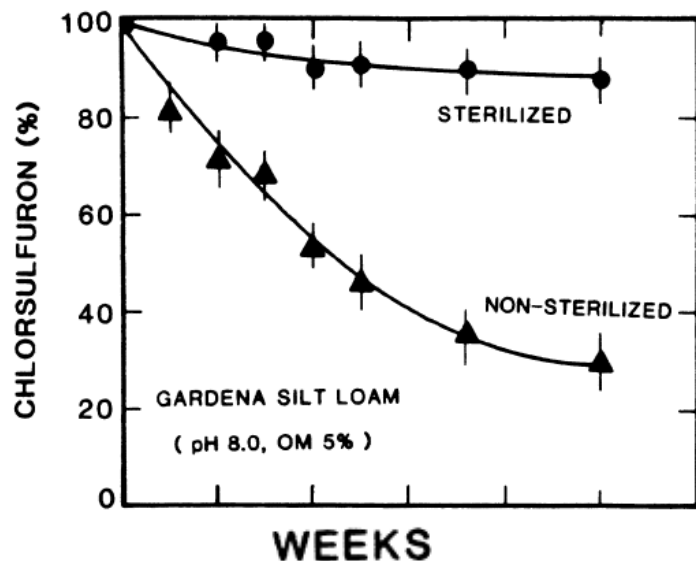


Table 3. Emergence of peas as influenced by chlorsulfuron in sterilized (Et0) and nonsterilized Gardena silt loam soil after 4 weeks at different temperatures^a.

Temperature (C)	Chlorsulfuron (ppb)	Pea emergence (% of untreated)	
		Nonsterilized soil	Sterilized soil
5	0	100 b	100 a
	4	58 bc	0 d
	8	0 d	0 d
	12	0 d	0 d
15	0	100 a	100 a
	4	100 a	58 bc
	8	50 c	0 d
	12	0 d	0 d
30	0	100 a	100 ab
	4	100 a	57 c
	8	100 a	10 d
	12	100 a	0 d

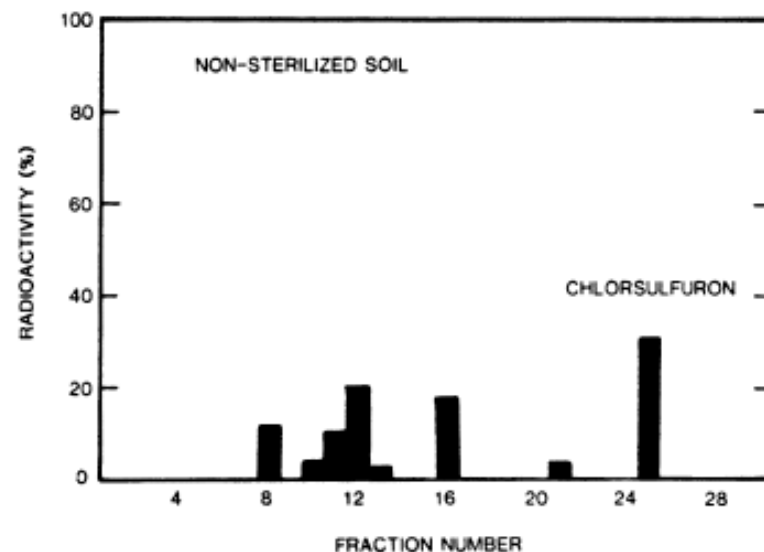
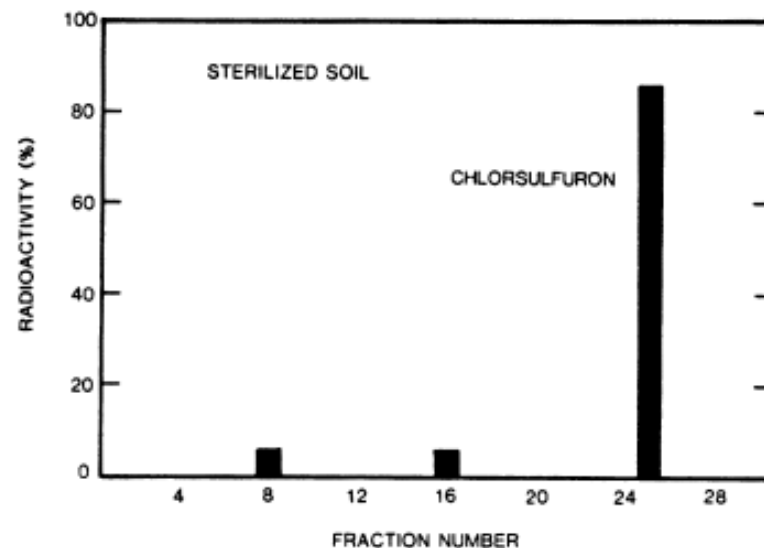
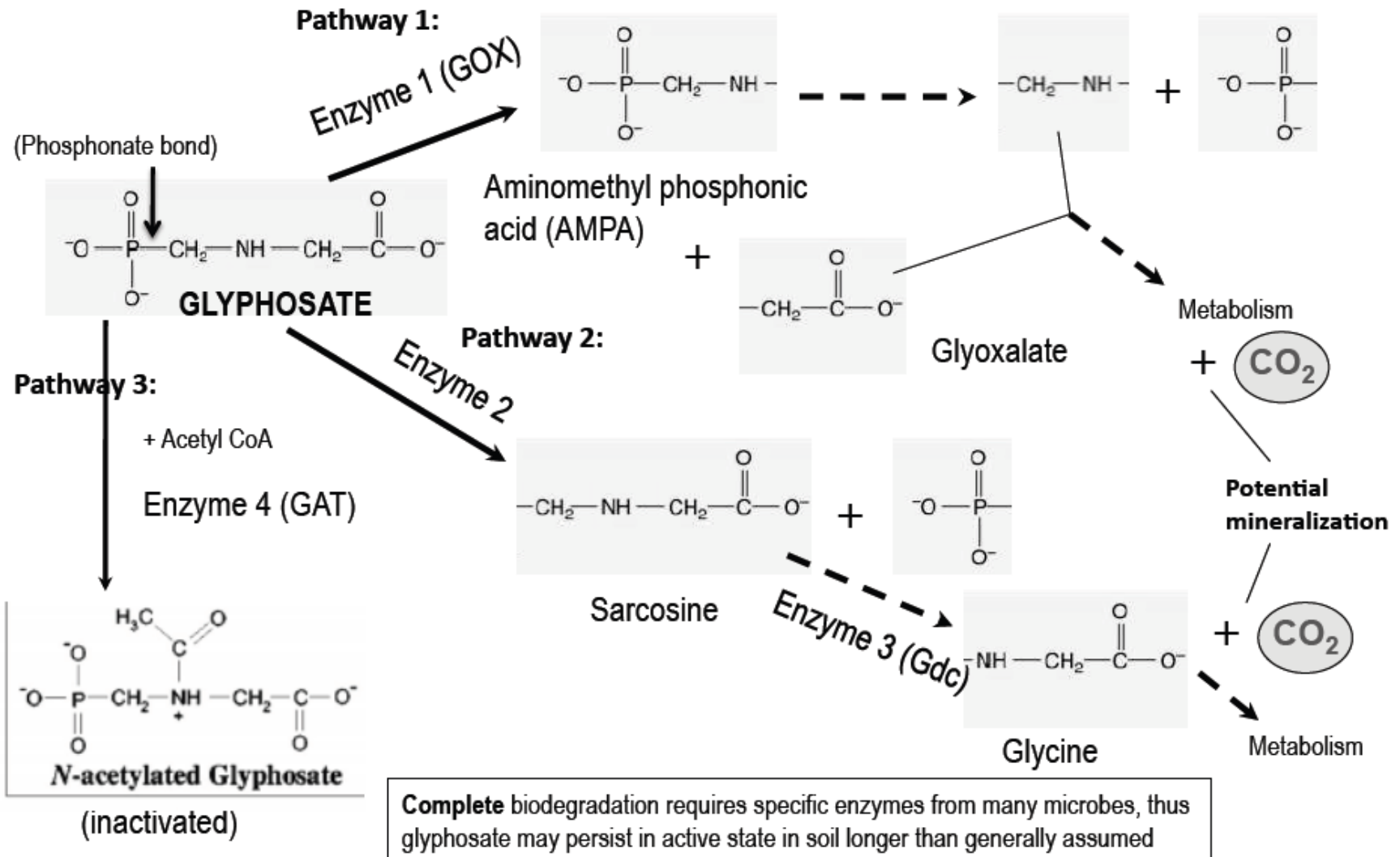


Figure 2. Reconstructed reverse-phase HPLC radiochromatograms of ¹⁴C-chlorsulfuron and its degradation products extracted from sterilized and nonsterilized Gardena silt loam soil after 10 weeks' incubation at 30 C. Column eluate was collected as 1.4-ml (1-min) fractions and the fractions were counted by liquid scintillation spectrometry. Data is expressed as the percent per fraction of the total chromatographed radioactivity.

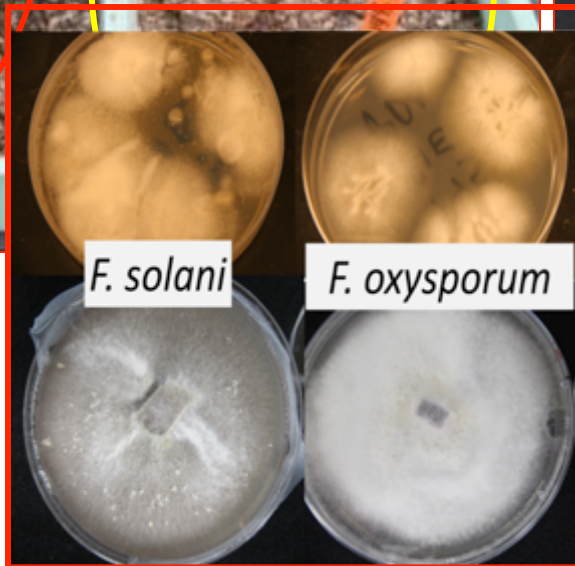
Glyphosate as example herbicide substrate in microbial biodegradation pathway:
 Highly diverse microbial community (**consortia**) needed to completely degrade glyphosate in the soil environment - well-managed soils is key to success -



Enzymes: 1, Glyphosate oxidoreductase; 2, C-P Lyase; 3, Glyphosate decarboxylase complex; 4, Glyphosate acetyl transferase

Response of Resistant & Susceptible Waterhemp to Soil Sterilization Following Treatment with Glyphosate

Fresh Soil: Resist+ Gly Suscept+ Gly



Glyphosate may predispose BOTH S and R biotypes to root colonization by *Fusarium* - soil community?

However, microbial diversity as determined by PLFA changed little regardless of biotype or glyphosate use. (Rosenbaum et al. 2014)

Sterile Soil: Resist & Suscept

