

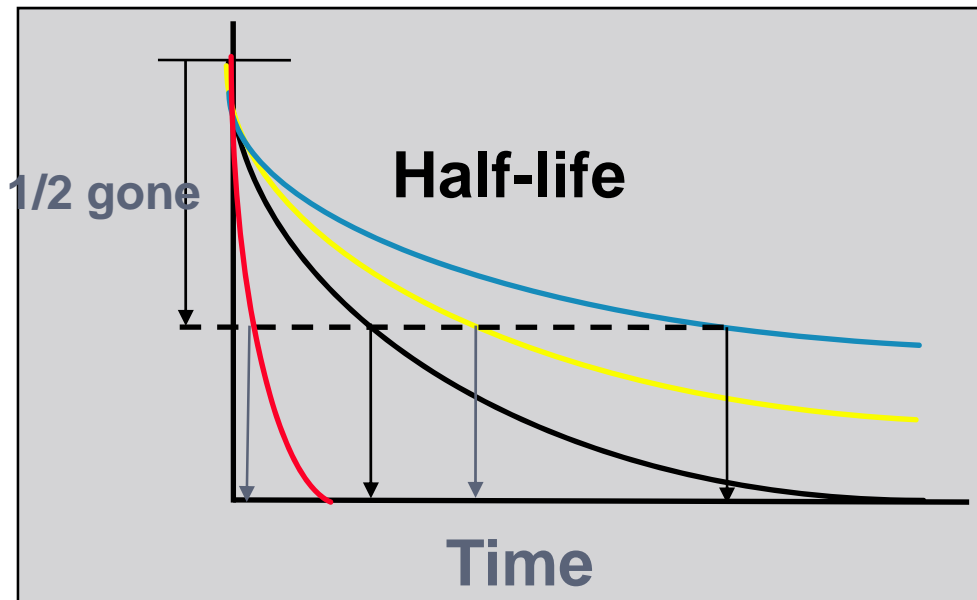
Effect of Soil, Environment, and Chemistry on Herbicide Persistence

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Herbicide Persistence

- The length of time that a herbicide (or its degradation products) remain in biologically significant amounts in the zone of application



Persistence: Why Do We Care?

- Herbicides must:
 - Persist long enough to control weeds
 - Dissipate fast enough to avoid rotational crop injury
 - Degrade fast enough to avoid environmental damage

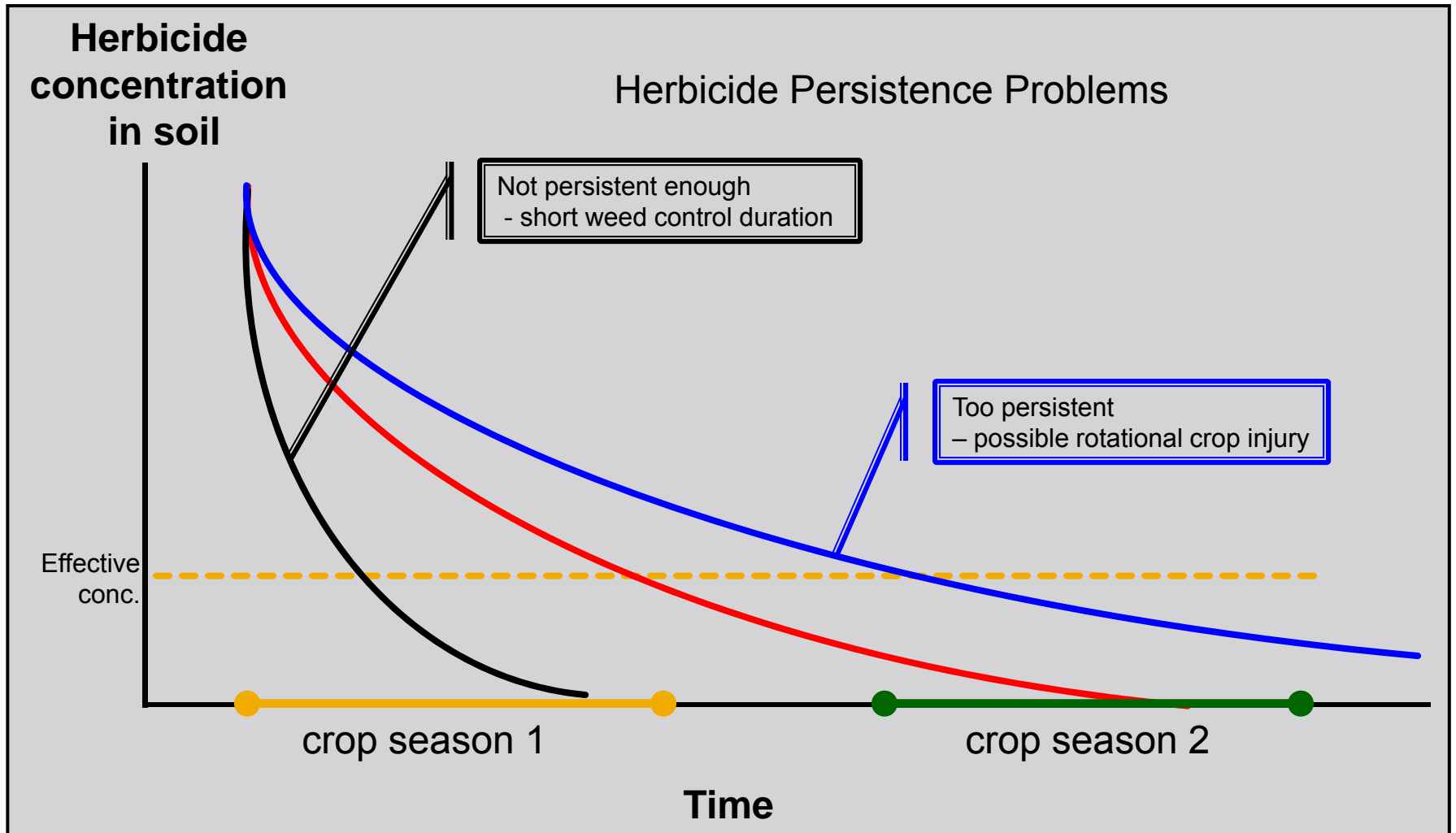


Contact vs soil active – 4 MAT



Carryover in cover crop after vineyard

Soil Active Herbicides



Herbicide Dissipation

- Herbicide dissipation is affected by two types of processes
 - Transfer processes
 - Change in location or availability of the herbicide – NO change in chemical structure or properties
 - Degradation processes
 - Changes in the chemical structure of the compound which alters the potency of the herbicide

Major Transfer Processes

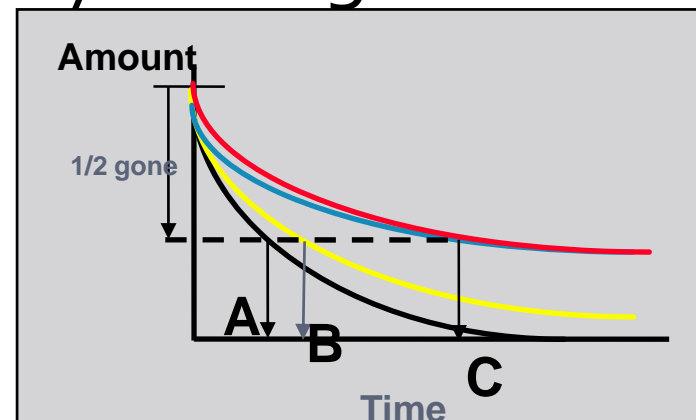
- Physical drift
- Volatilization
- Adsorption to soil
- Leaching in soil
- Surface erosion
- Plant or animal uptake and removal



***Change in location or availability of the herbicide**

Degradation

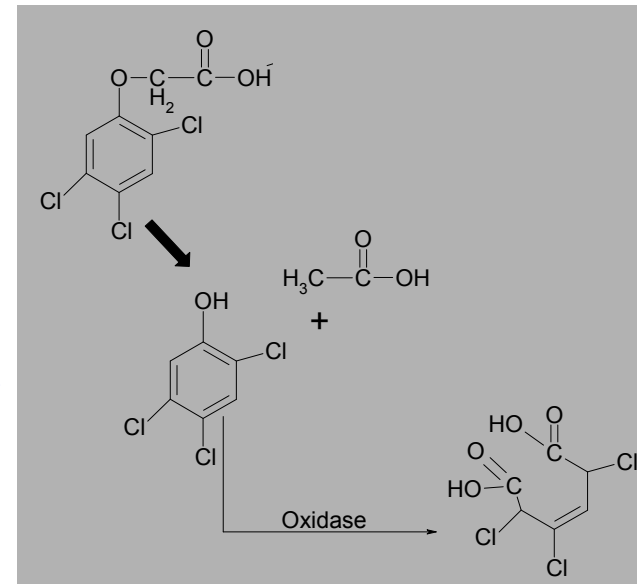
- Begins immediately after application and continues until broken down into molecules like CO_2 and H_2O
- ALL herbicides are degraded in the environment
- The degradation RATE can vary among herbicides or environments



Degradation Processes

- Photochemical
- Chemical (in soil or water)
- Microbial (in soil or water)
- Plant/animal metabolism

***Changes in the chemical structure of the compound**



Degradation Reactions

- Numerous types of reactions

- Dehalogenation 

- Dealkylation

- Decarboxylation

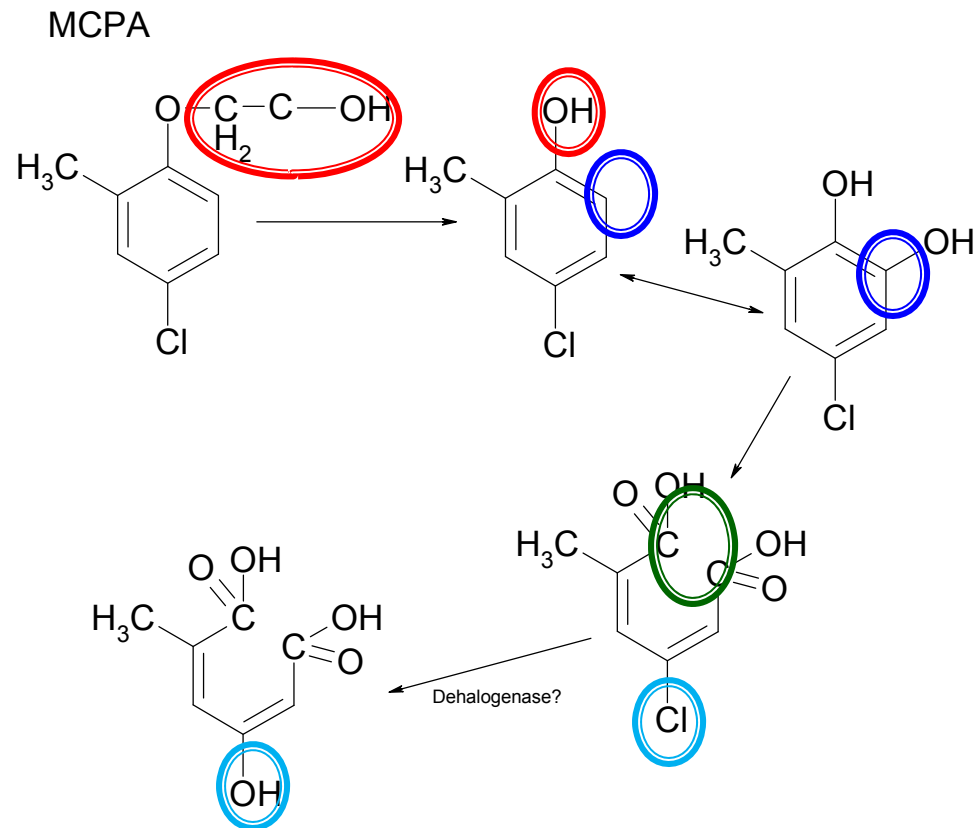
- Oxidation 

- Hydrolysis 

- Conjugation

- Ring cleavage 

- etc



Photochemical Degradation

- Occurs due to destruction of chemical bonds by UV radiation
- On soil surface or in water
 - Some products formulated with “sunscreen” to minimize this
- Affected by:
 - Herbicide structure
 - Duration of exposure
 - Time of year



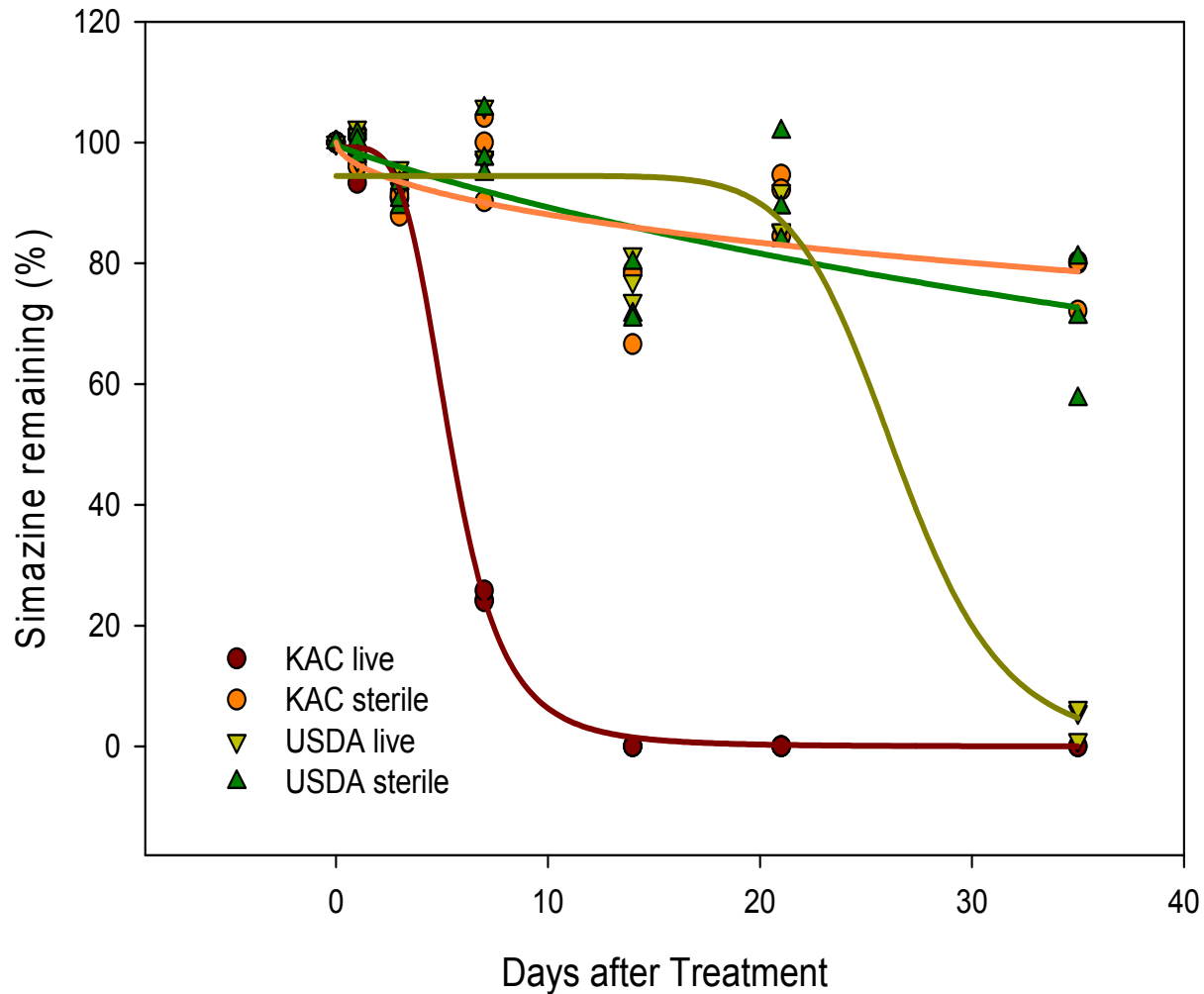
Chemical Degradation

- Change in structure due to non-biological factors in soil or water
 - Ex. Hydrolysis: molecule reacts with water
- Factors affecting:
 - Soil or water pH
 - Temperature
 - Clay and organic matter content
 - Water content of soil
 - Chemical structure
 - Rings vs chains, functional groups

Microbial Degradation

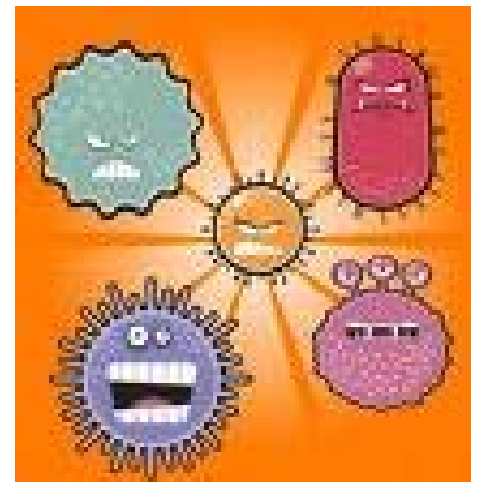
- Change in structure due to activity of microorganisms
 - Microbes produce enzymes that degrade the compounds
 - Organisms use the molecule as food source
- Usually not specific, but sometimes can be
 - Enhanced degradation
- Overall, the most important degradation process for herbicides

Effect of Soil Sterilization on Herbicide Degradation



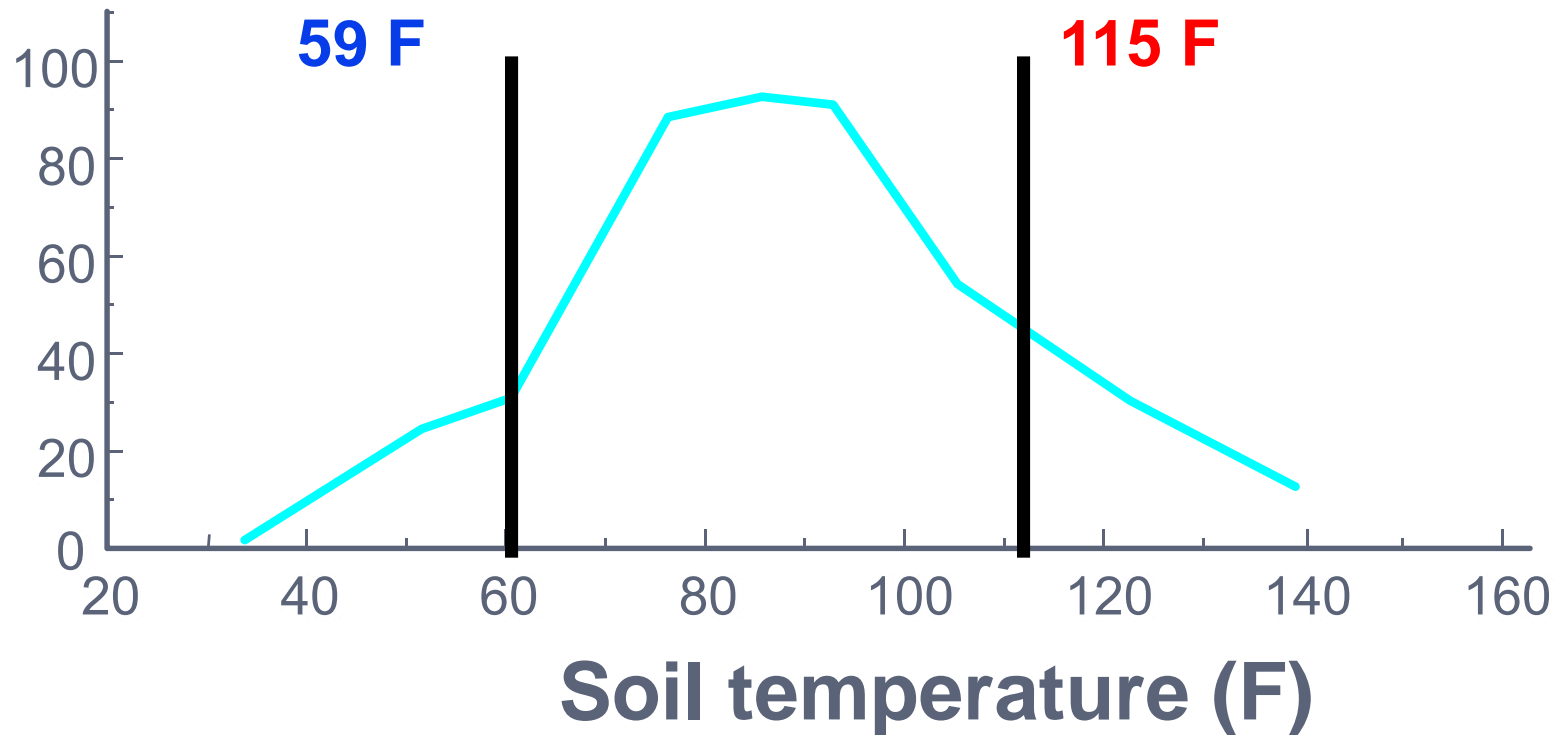
Microbial, cont.

- Highest microbial levels in upper soil layers
- Factors affecting microbial activity (and thus degradation)
 - Temperature
 - Organic matter
 - Nutrient content
 - Soil or water pH
 - Water content of soil



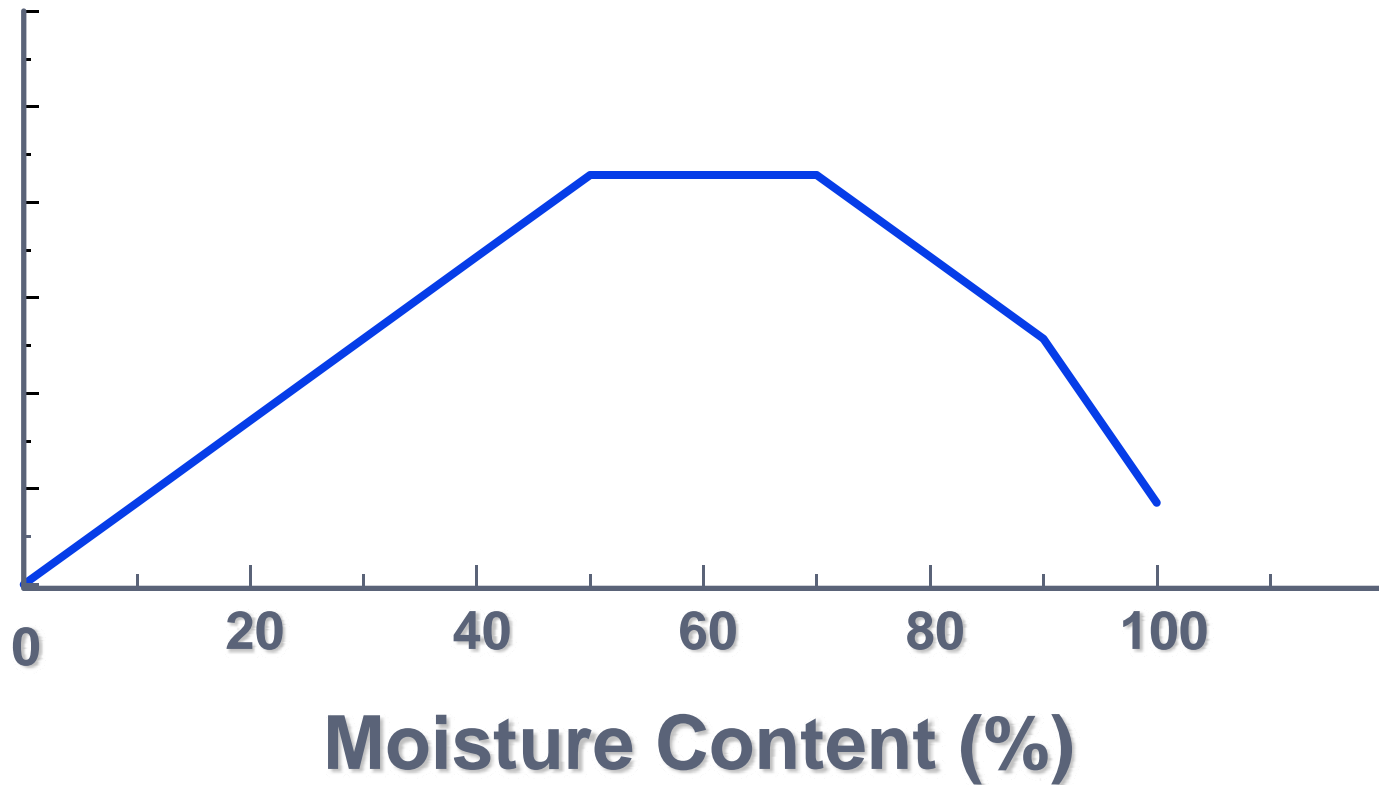
Temperature and Microbial Activity

General Microbial Activity (%)



Soil Moisture and Microbial Activity

General Microbial Activity (%)



Relative Persistence - Interactivity

- Consider how soil, environmental, and herbicide chemistry affect chemical and microbial degradation and transfer processes

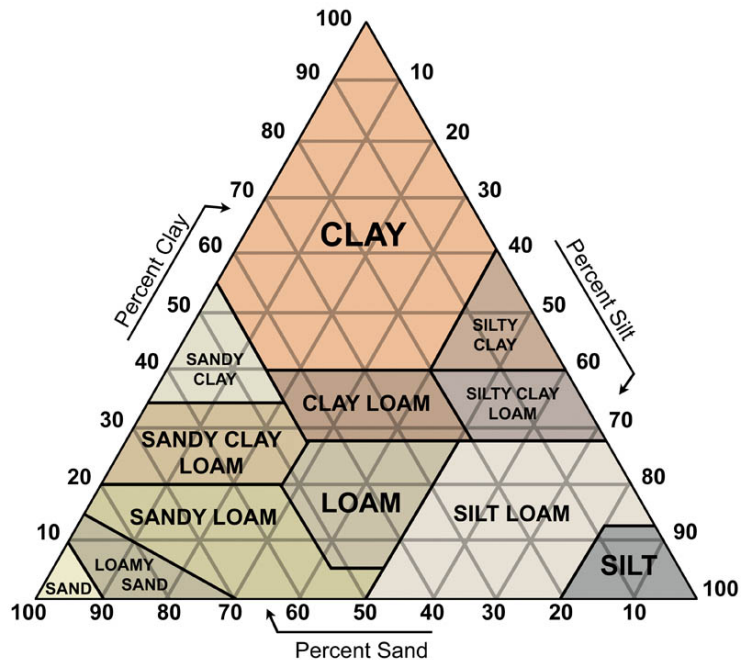


Soil Factors

- Soil is a complex matrix with physical and chemical properties that affect herbicide dissipation
- Made up of various physical fractions
 - Mineral (soil texture)
 - Organic (living and decaying)
 - Water
 - Air space

Soil Texture

- Water holding capacity
- Hydraulic conductivity
- Macro and micropore spaces

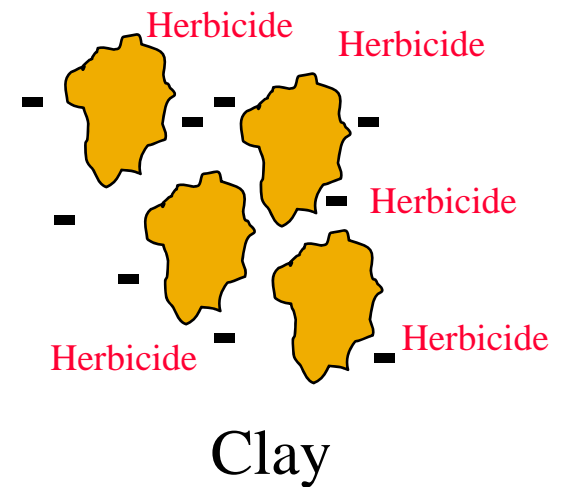
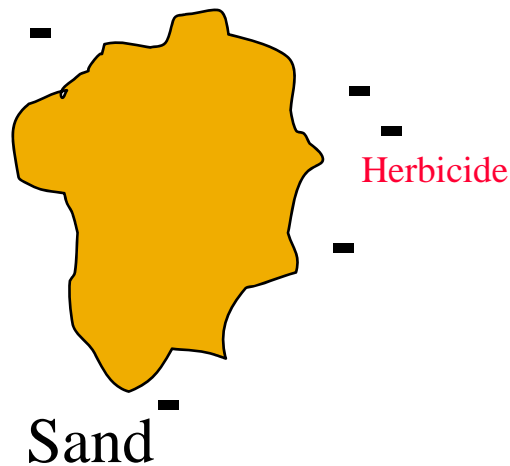


Soil Chemistry

- pH (pKa of herbicides)
- CEC (cation exchange capacity)
 - Negative charge of soil
 - Clay and OM have more than sand
 - Influenced by type and amount of clay

Chemistry and Texture

- Surface area of soil particles
 - Sand ~ 90 cm² / gram
 - Silt ~ 450 cm² / gram
 - Clay ~ 8,000,000 cm² / gram



Reactive Sites

Carbon-seeding grass seed, then treating with diuron



Examples:

- Carbon-seeding
- Fly ash applic.
- burn piles
- high OM soils

Soil Moisture and Temperature

- Moisture
 - Irrigation vs dryland
 - Wetting and drying cycles
 - Saturated zones (anaerobic)
- Temperature
 - Application timing
 - Weather events
 - Mulches?



Herbicide Availability

Henry's Law Constant

- Related to **solid:gas** phase equilibrium

K_H

Sorption (distribution) Coefficient

- Related to **liquid:solid** phase equilibrium

K_D

K_{OW}

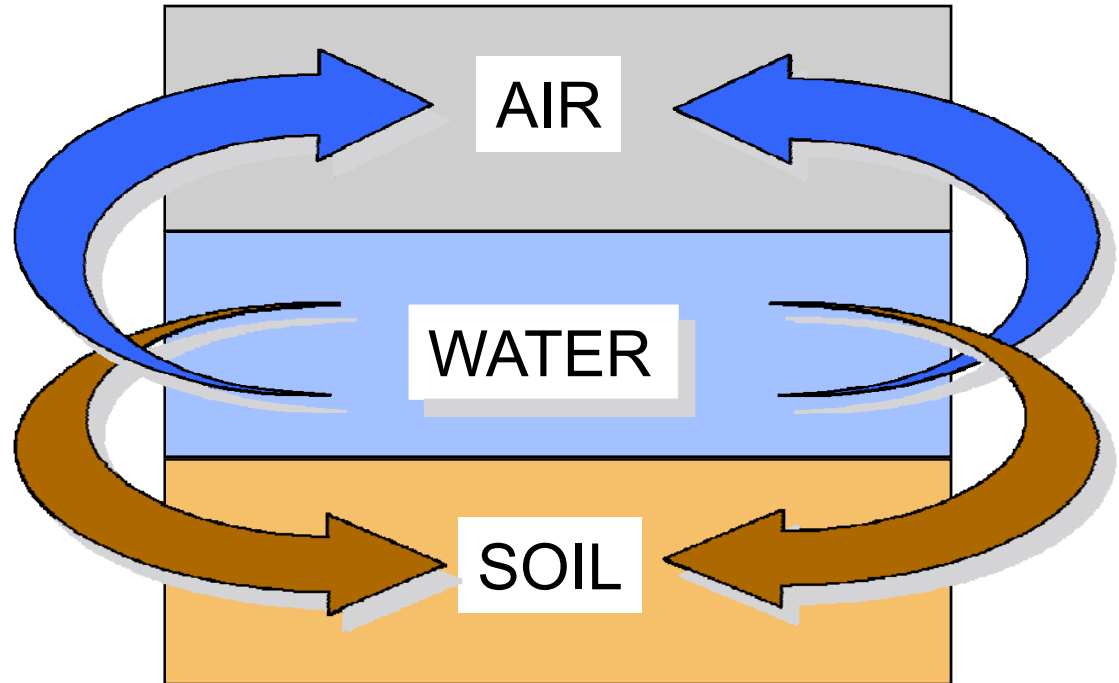
Octanol:Water Coefficient

- Related to **polar:non-polar** equilibrium
Hydrophobic vs lipophilic

K_{OC}

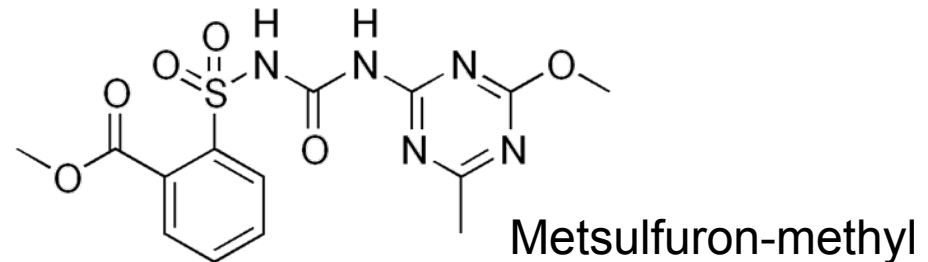
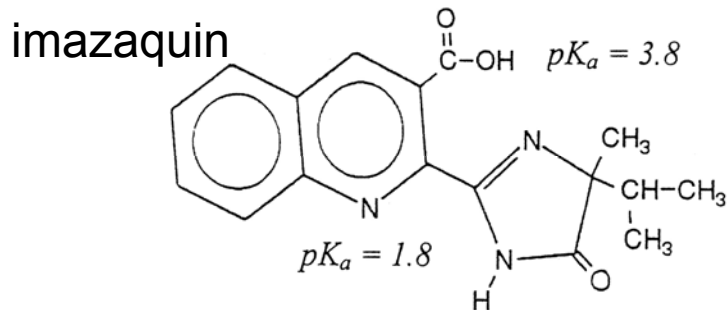
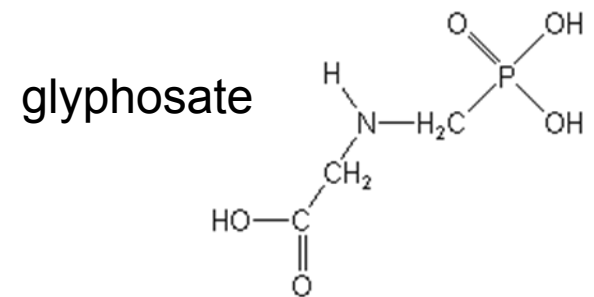
Organic Carbon:Water Partitioning Coefficient

- Related to **liquid:solid** phase equilibrium (K_d) but normalized for carbon content



Herbicide Chemistry / Structure

- Structure affects availability (sorption) and stability
 - Some molecules are inherently more/less stable than others
 - Ionizable groups
 - Rings vs chains
 - Various side chains????



Adsorption

- Binding of herbicide to clay or OM
 - May be permanent or reversible
 - Can increase or decrease persistence
 - If strongly sorbed, not available for plant uptake OR degradation
- Affected by:
 - Herbicide structure
 - Charge, ionizable groups, Koc
 - Organic matter content
 - Reactive sites
 - Clay type and content
 - Soil pH and moisture

Herbicide pKa

- Some herbicides are “charged” – weak acids or weak bases
 - At a certain pH (ie it's pKa value) the molecule can shift to the “uncharged” form
 - Acid to neutral, base to neutral, or vice versa
 - Can affect persistence
- Example: prometryn (Caparol)
 - Weak base. pKa at pH 4.09
 - Relatively stable at neutral pH
 - Slight positive charge at low pH, so more tightly sorbed

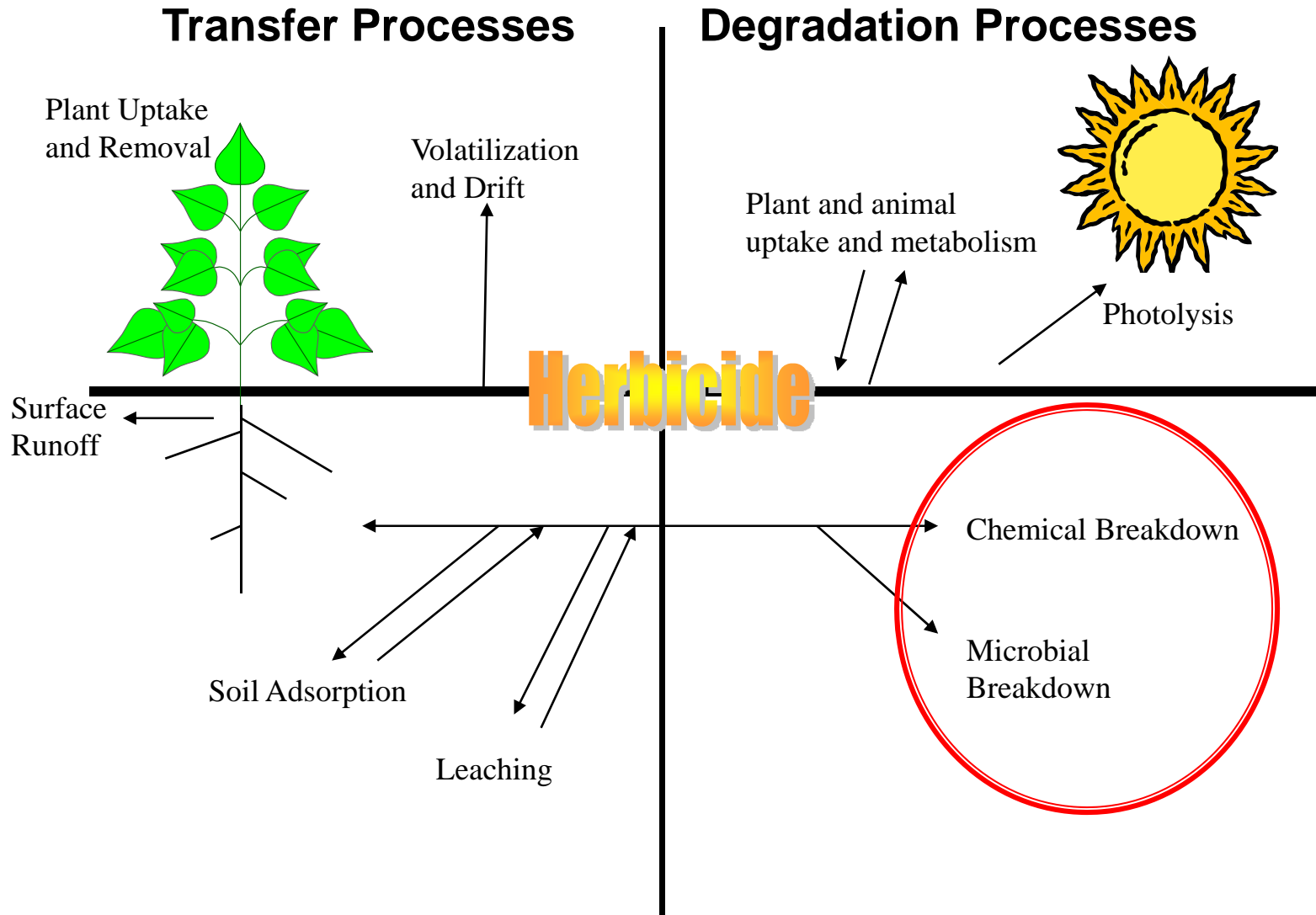
Koc values

- Koc is the ratio of herbicide sorbed to soil vs amount in water in a water/soil slurry (adjusted for organic carbon content of the soil)
 - Low Koc value indicates weak binding
 - High Koc value indicates strong binding
 - Koc examples:

■ 2,4-D	~20 ml g ⁻¹
■ Atrazine	~100
■ Pronamide	~800
■ Trifluralin	~7,000
■ Glyphosate	~24,000
■ Paraquat	~1,000,000

 - Antidote for paraquat poisoning = eat dirt

Herbicide Dissipation



What (Unusual) Environmental Factors Affect Persistence?

- Unusual (or uneven) moisture
 - Drought
 - Excess moisture
 - Near drippers or micros
 - Pockets of standing water (low spots)
- Unusual soils
 - pH, texture, microbial communities
- Fumigation?
- Micro climate or soil factors

Causes of Excessive Herbicide Persistence

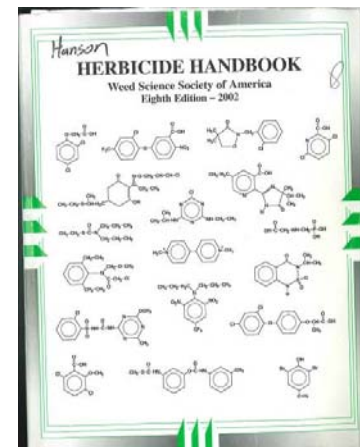
- Herbicide labels are the product of a lot of research to maximize efficacy and minimize crop injury
- Common causes of crop injury include:
 - Over application (miscalc., overlaps)
 - Crop failure and/or early replant
 - Late application timing
 - Adverse weather (esp. drought)
 - Unusual soil conditions (pH, texture)

Rotational Crop Injury

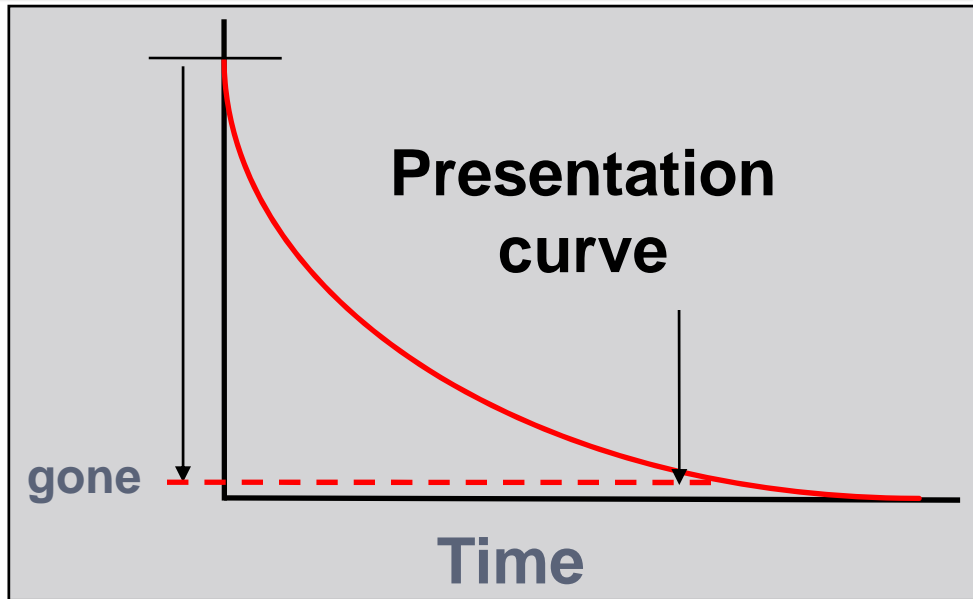
- Some crops are more sensitive than others
 - Read herbicide labels!
 - No restrictions, or very short
 - 30 days
 - 3-6 months
 - 48-60 months!
- Important consideration in some areas
 - Esp. rented or newly purchased land in diverse cropping areas

Herbicide Persistence Summary

- Herbicides are affected by transfer and degradation processes
- All herbicides are eventually degraded in the soil environment
- Persistence varies considerably depending on chemical properties and environmental factors
 - Microbial and chemical degradation are the most important degradation processes



Questions?



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