Lecture

Herbicide/Soil Interactions

1. Fate of herbicides <u>on</u> the soil surface

- volatilization (fate on soil surface)

<u>definitions</u> - volatilization is the process by which a substance changes from a solid or liquid state to a gaseous state. All chemicals have a finite vapor pressure.

Volatilization = evaporation = vaporization e.g. water → steam

Vapor pressure is the pressure exerted by the gas particles of a herbicide when in equilibrium with the liquid or solid state (in the closed container)

<u>vapor pressure influence</u> - the <u>higher</u> the vapor pressure, the <u>greater</u> the volatility

"The herbicide gets up and walks on you".......a farmer's description of off-target movement through volatility.

U**<u>General rule</u>**: If the vapor pressure of a herbicide is >$1x10^{-4}$ (0.0001) mm of Hg at 25C it will need to be incorporated to prevent loss due to volatility/evaporation.

Herbicide	Vapor Pressure in mm of Hg @ 25C
EPTC, Eptam®, Eradicane®	$3.4x10^{-2}$ (0.034)
Vernolate, Vernam®	$1x10^{-2}$ (0.01)
Clomazone, Command®	$1.4x10^{-4}$ (0.00014)
Trifluralin, Treflan/Tri-4	$1.1x10^{-4}$ (0.00011)
Atrazine	$2.9 x10^{-7}$ (0.00000029)
Paraquat, Gramoxone®	TLTL (too low to list)

Note: Command is just barely <u>above</u> the requirement of $1x10^{-4}$ (0.0001 vs. 0.00014) for incorporation; this is the reason that a micro-encapsulated formulation was developed and is now being marketed as Command ME

Note: EPTC approximately 300 times more volatile than trifluralin

Note: Incorporation is required for trifluralin. This is not due to volatilization, but rather to photodegradation (breakdown by sunlight; will be discussed later).

volatilization can be both negative and positive:

negative - herbicide moves off the target (drift); poor weed control on target.

positive - herbicide moves within the soil (as much as 4 inches for EPTC and about 1 inch for trifluralin) filling the pore spaces and promoting distribution and uniformity within the soil; this enhances weed control

factors affecting: (volatilization)

temperature - higher temperature, greater volatility; worst time to apply a volatile herbicide in respect to loss due to volatility is during mid-day (weed control, however, would be expected to increase)

soil moisture - high soil water content increases volatility (water vapor acts as a carrier)

methods to decrease: (volatilization)

soil incorporation (traps herbicide within the soil and prevents loss)

use of special formulations - granular, micro-encapsulated, salt vs. ester formulation (2,4-D); ester formulations most volatile; salt formulation least volatile

apply when conditions are unfavorable for volatilization (e.g., lower temperature)

see Table 7.3 (Vapor pressures of selected soil-applied herbicides arranged according to decreasing vapor pressures; page 10)

- photodecomposition (fate on soil surface)

uv light effect and process - photodecomposition is the break down of herbicide by sunlight, i.e., ultraviolet light, (UV peaks at 400 nm).

If herbicide absorbs light in the UV range, the molecular structure is changed (chemical bonds are broken). All herbicides are susceptible to photodecomposition, but for some, the effect is much greater than others.

Most herbicides in their molecular form are white or nearly white, and peak light absorption would be in the 220-324 nm range.

In contrast, the dinitroaniline herbicides (DNA’s) are yellow in their molecular form (“yellow herbicides”) and peak light absorption is approximately 376 nm, much closer to peak UV (400 nm). This explains why the yellow herbicides are more susceptible to photodegradation.

Herbicides most susceptible to photodecomposition include dinitroanilines (DNA's), s-triazines, and ureas.

<u>methods to decrease</u> (photodecomposition) - incorporation into soil and use of special formulations

- movement into soil - incorporation, rainfall, diffusion (fate on soil surface) - a soil applied herbicide must get into the soil solution to be active. How? rained in or mechanically worked in; how much water required?

- surface movement in water (fate on soil surface) - runoff of herbicide can be detrimental to the environment (non point source pollution)

- adsorbed (bound/tied up) to organic matter (fate on soil surface)

  <u>electrical attraction</u> - organic matter has a strong negative (-) charge and attracts cations which are positive (+); the charge status of a herbicide may be positive, negative, or neutral

  <u>adsorptive capacity (CEC)</u> - is the measure of the ability of soil to attract cations - the higher the CEC the more binding sites available for the herbicide.

  High organic matter on the soil surface can result in binding of herbicide and lack of weed control; this is common with some herbicides used in sugarcane in Florida on muck soils

2. Fate of herbicides in the soil

   - leaching (fate in soil)

     <u>definition</u> - leaching is the downward movement of herbicide into a soil profile; movement can be lateral and reverse leaching (upward movement) can occur when a wet soil dries

     <u>results can be positive and negative</u> - leaching is necessary for soil applied herbicides to move into the zone where weed seeds are present

     leaching can result in herbicide movement out of the zone where weed seed will germinate (loss of herbicide activity) and may increase crop injury if moved too deep (reason for planting corn 2 inches deep when using Lasso/Dual).

     In some cases (depending on herbicide) leaching may result in groundwater contamination. This is determined by the solubility of the herbicide and the absorptive capacity of the soil and the herbicide (will be discussed later).

     Discuss problems with atrazine in the Midwest.

<u>factors influencing</u>: (leaching)

<u>soil texture, permeability, rainfall, adsorption</u> - sandy soil would have a higher leaching potential than a clay soil (larger pore spaces and lower CEC)

soil permeability would be affected by the presence or absence of a hardpan that could restrict leaching (discuss the soils of the Crowley rice area)

greater the rainfall the greater the potential for leaching; herbicide adsorbed to soil or organic matter would not be susceptible to leaching

<u>herbicide solubility in water and adsorptive capacity</u> - the more water soluble the herbicide the greater the likelihood for leaching. This would also be affected by adsorptive capacity of the herbicide (will be discussed later)

<u>see Table 7.2</u> (Water solubilities and soil organic carbon sorption coefficients (K_{OC} values of selected soil-applied herbicides; page 11)

- adsorption/desorption to soil particles/organic matter (fate in soil)

<u>electrical attraction and effect on uptake</u> - adsorption is the association of a herbicide with the surface of a soil particle. An equilibrium exists between the soil particle and the soil solution and adsorption and desorption are both occurring.

Because of the electrical attraction, a positively charged herbicide (+) will be adsorbed onto the negatively charged clay particle (-) and immobilized.

Adsorbed herbicide is not available for weed control. Herbicide must be in the soil solution to provide weed control.

Adsorptive capacity varies depending on the herbicide. The soil organic carbon sorption coefficient (K_{OC} value) is used to compare herbicides.

The greater the adsorptive capacity the lower the potential for leaching. **Why?** herbicide is bound to soil or organic matter and not in soil solution where it can be leached

As solubility of the herbicide decreases, sorption increases.

<u>see Table 7.2</u> (Water solubilities and soil organic carbon sorption coefficients (K_{OC}) of selected soil-applied herbicides; page 11); discuss relationship between the two values

adsorptive capacity (CEC) clay vs. sand vs. organic matter - CEC is the ability of soil to attract cations - the higher the CEC the more binding sites available. Clay soils have a higher CEC than a sandy loam soil.

A soil with a high organic matter content [a lot of negative sites(-)] will also bind herbicides and prevent them from being present in soil solution.

Discuss the "nontraditional" antidote for paraquat ingestion

effect of soil texture/organic matter on herbicide rate - For some herbicides, a higher herbicide rate is required for effective weed control for clay soils when compared with sandy loam soils.

For the clay soil, herbicide concentration must be high enough to "saturate" all the binding sites and still have enough left over in the soil solution to provide weed control.

Discuss cost factor

pH effect on certain herbicides and adsorption - pH is a measure of soil acidity.

Soil pH can change the ionic characteristics of a herbicide and affect adsorption.

In low pH (acid) soil, atrazine will be cationic (+ charge), therefore, it will be adsorbed onto soil particles and unavailable to provide weed control.

Consequently, atrazine will be more active in higher pH soils (pH 6 to 8 compared with 5), since it will not be negatively charged and therefore available in the soil solution for root uptake.

- plant uptake (fate in soil) - herbicide must be in the soil solution to be taken up by the plant; herbicide would be either anionic (- charge) or not charged

- chemical reactions/degradation of herbicides (fate in soil) - breakdown of herbicides by chemical processes or reactions in the absence of a living organisms vs. biochemical breakdown - in a living organism

oxidation / reduction (Redox) - results in the ionization of compounds; involves the transfer of electrons (LEO says GER)

<u>hydrolysis</u> - the reaction of the herbicide with water (H-OH). A hydrogen ($-H^+$) or more commonly a hydroxyl group (-OH) is added to the molecule. The structure of the herbicide is changed chemically, e.g.,

Simazine o hydroxysimazine (chlorine replaced with OH group and toxicity decreased 1000X)

It doesn't take much change in a chemical structure to significantly affect activity

<u>formation of insoluble salts</u> - e.g., Ca^{++}, Mg^{++} e.g. soils with high Ca^{++} may react with herbicide to form water insoluble calcium salts

<u>formation of chemical complexes</u> - chelation, e.g.,
glyphosate + metal ions, e.g., Fe^{+3} o glyphosate ●Fe complex

- microbial metabolism/decomposition (fate in soil) - primary means of degrading herbicides in soil; microbes utilize organic herbicides as a energy source

3. See Figure 7.1 (Processes that determine the fate of herbicides in the environment; page 12)

   - review of herbicide fate

4. Microbial decomposition of herbicides (fate in soil)

   - organisms involved

   <u>bacteria</u> - procaryotes single cell microrganisms; no organized nucleus

   <u>actinomycetes</u> - bacteria that form branching filaments (higher level of development compared with bacteria)

   <u>fungi</u> - eukaryotes and higher development level than bacteria or actinomycetes

   These microorganisms are all present in the soil. They are not plants and do not carry on photosynthesis; they require food for energy in the form of organic compounds

   in the process of degradation O_2 is required and CO_2 is released (called respiration)

- mechanism of herbicide degradation

  microbes have enzymes that are secreted and act as catalysts to drive specific reactions

- reactions (microbial / biochemical)

  dehalogenation - removal of halogen from the herbicide molecule. Halogens are those elements toward the right side of the Periodic Table, Fluorine (F), Chlorine (Cl), Bromine (Br), and Iodine (I)

  dealkylation - removal of an alkyl group (C-H aliphatic chain)

  amide hydrolysis - cleavage of a bond of an amide (contains NH_2 group) by addition of water; a weak acid and NH_3 is produced

  ester hydrolysis - cleavage of a bond of an ester by addition of water; a weak acid is produced

  beta-oxidation - a normal pathway for degradation of long chain fatty acids; 2 carbons are removed when a compound goes through the pathway once

  ring hydroxylation - reaction with water whereby a OH group is added to the ring structure

  ring cleavage - the bonds within the ring structure of the herbicide molecule are split or cleaved

  reduction of nitro groups in anaerobic conditions - NO_2 is reduced to NH_2 and O_2 is released

  specific examples of these reactions will be covered later

- environmental factors affecting microbial decomposition of herbicides

  moisture - 50% to 100% of field capacity is optimum. Field capacity is the amount of water a soil will hold against the force of gravity.

Soil at field capacity is ideal growing conditions. Generally, whatever is good for plant growth is good for microbes.

aeration - a well aerated soil (O_2) is favorable to microbial development and degradation

temperature - 80 - 90 F ideal

pH - bacteria/actinomycetes predominate at pH >5.5; fungi predominate at pH < 5.5 competition can occur among microorganisms

organic matter - enhances microbial populations since it provides a carbon source for the microbes to utilize

soil nutrients - enhances microbial populations since microbes utilize nutrients for growth

Louisiana has high microbial action in soil due to the ideal conditions for their growth during much of the year. Our mild winters and abundant rainfall stimulate microbial degradation of herbicides.

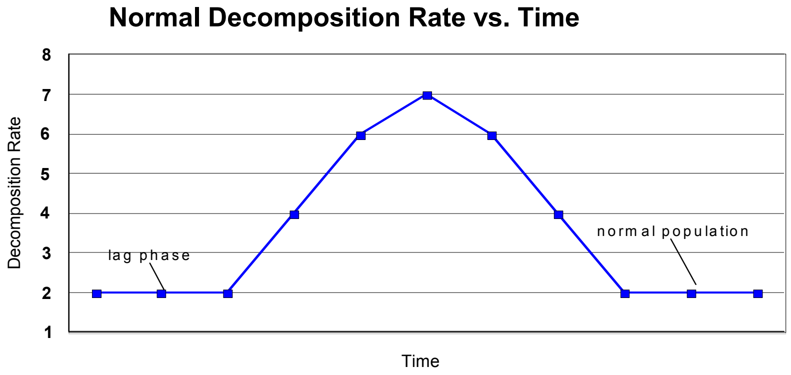
Consequently herbicide persistence is generally short compared with other areas of the U.S. We have had much fewer problems with herbicide carryover from one crop to the next than in other southern states.

- herbicide x microbe interaction

EPTC in Midwest (graphs are shown on page 9)

Herbicides will remain toxic in soil when conditions are not favorable for microbes. Degradation of the herbicide follows the population growth of the microbes. The normal decomposition rate for a herbicide over time is shown below.

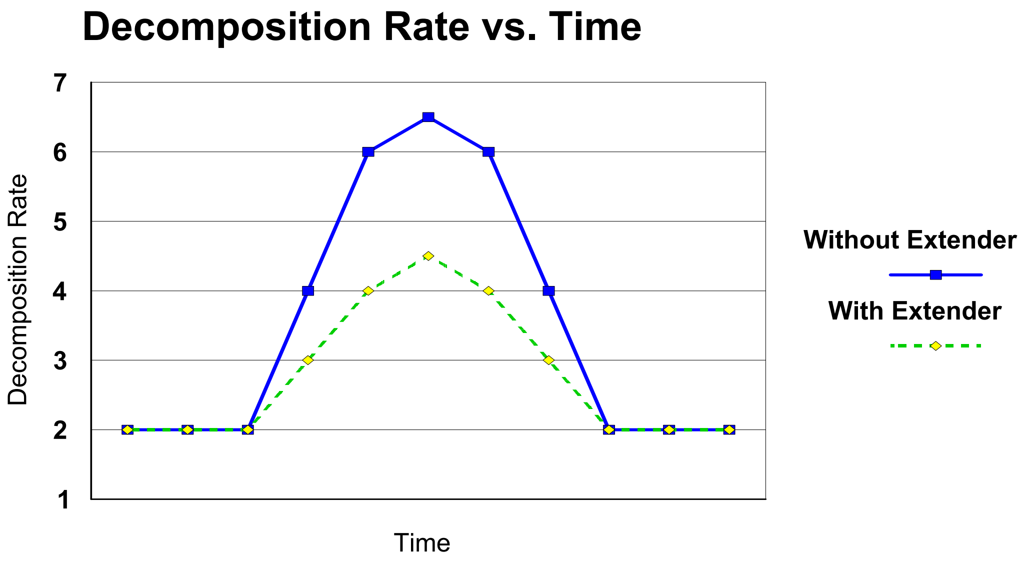
During the lag phase the microbial population increases in response to food source and rapid decomposition occurs. The rate levels off and then begins to decrease since no more substrate is available. A normal population level is then established.



Eradicane (EPTC) at one time was widely used for weed control in corn in the Midwest. This herbicide is very susceptible to microbial degradation. It was observed that after several seasons of use, decreased weed control was observed.

It was learned later that the microbial population specific to this herbicide had built up to such high numbers that degradation occurred before weeds could be controlled.

To help alleviate this problem an "extender (dietholate)" was added to the herbicide formulation to inhibit accelerated breakdown.



- herbicide persistence and half life

Most herbicides retain their biological activity for 4-6 weeks, some herbicides may retain activity for a year. Half-life values (time required for half of the herbicide to degrade) for the majority of herbicides is less than 6 months.

<u>see Table 7.5</u> (Half lives selected herbicides; page 13)

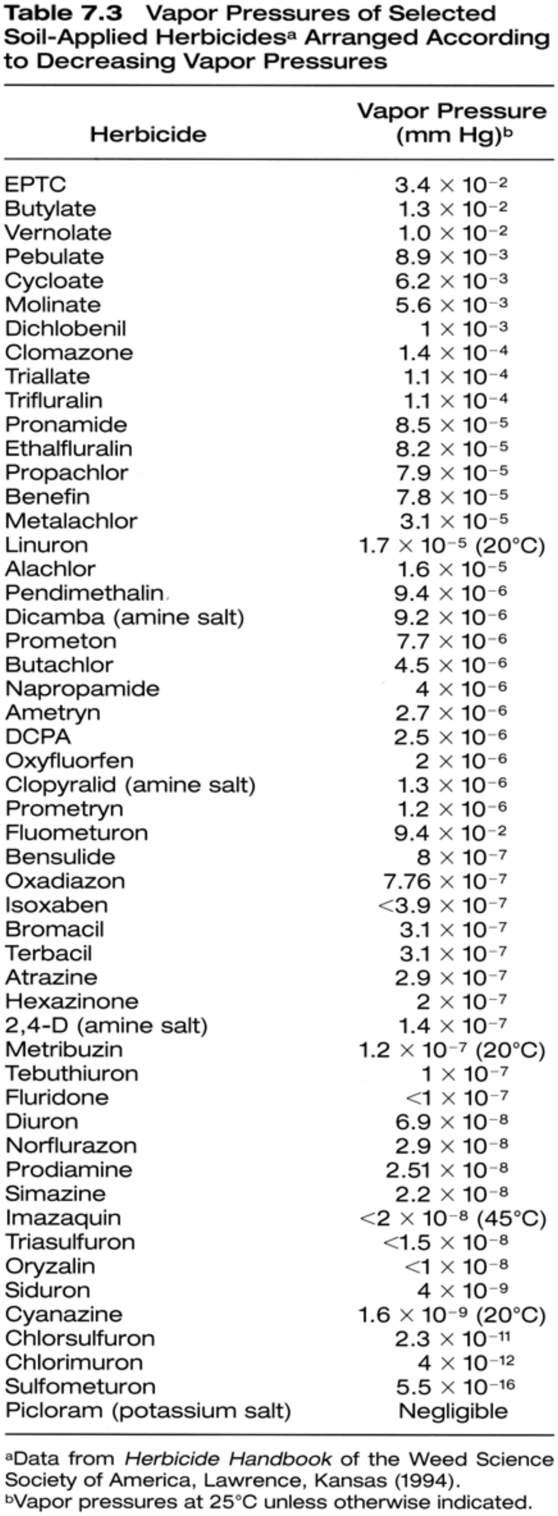


Table 7.3 Vapor Pressures of Selected Soil-Applied Herbicides[a] Arranged According to Decreasing Vapor Pressures

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}
Ethalfluralin	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^{-2}
Bensulide	8×10^{-7}
Oxadiazon	7.76×10^{-7}
Isoxaben	$<3.9 \times 10^{-7}$
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

[a] Data from *Herbicide Handbook* of the Weed Science Society of America, Lawrence, Kansas (1994).

[b] Vapor pressures at 25°C unless otherwise indicated.

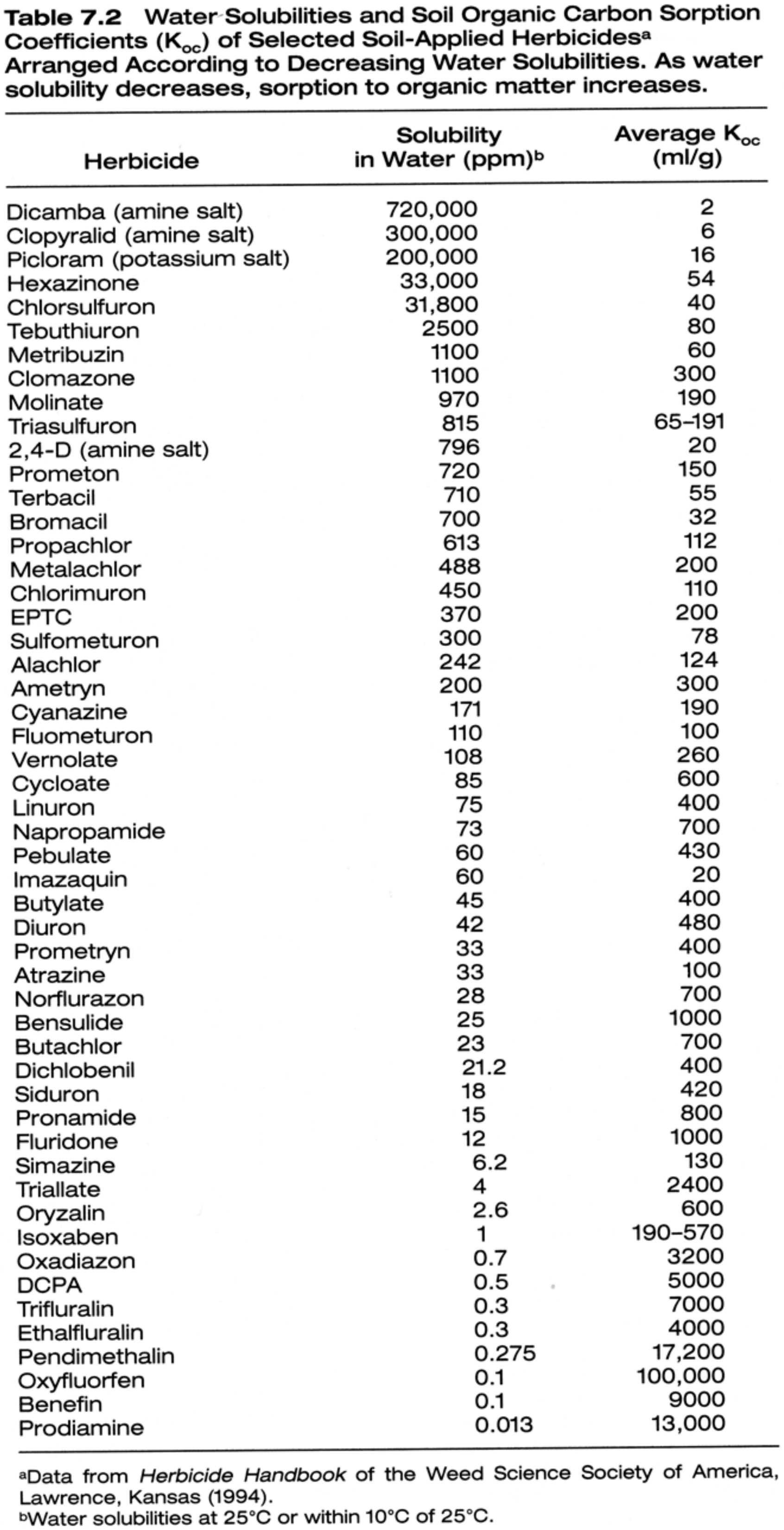


Table 7.2 Water Solubilities and Soil Organic Carbon Sorption Coefficients (K_{oc}) of Selected Soil-Applied Herbicides[a] Arranged According to Decreasing Water Solubilities. As water solubility decreases, sorption to organic matter increases.

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
Ethalfluralin	0.3	4000
Pendimethalin	0.275	17,200
Oxyfluorfen	0.1	100,000
Benefin	0.1	9000
Prodiamine	0.013	13,000

[a] Data from *Herbicide Handbook* of the Weed Science Society of America, Lawrence, Kansas (1994).

[b] Water solubilities at 25°C or within 10°C of 25°C.

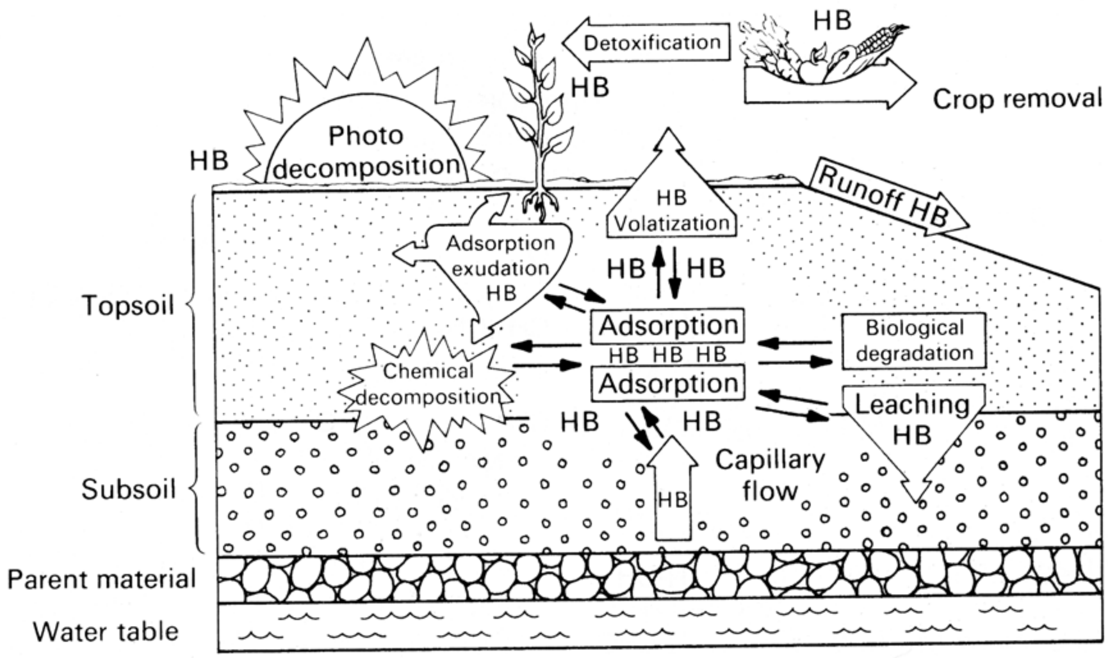


Figure 7.1 Processes that determine the fate of herbicides in the environment (HB=herbicide) (redrawn from Weber et al. 1973).

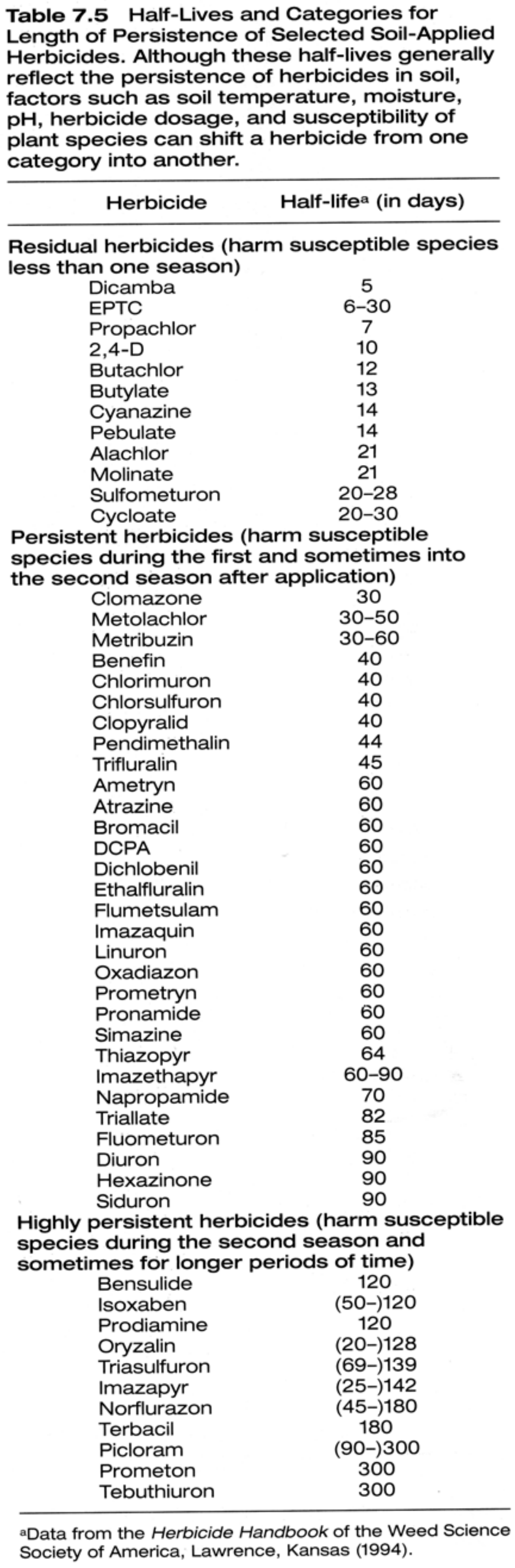


Table 7.5 Half-Lives and Categories for Length of Persistence of Selected Soil-Applied Herbicides. Although these half-lives generally reflect the persistence of herbicides in soil, factors such as soil temperature, moisture, pH, herbicide dosage, and susceptibility of plant species can shift a herbicide from one category into another.

Herbicide	Half-life[a] (in days)
Residual herbicides (harm susceptible species less than one season)	
Dicamba	5
EPTC	6–30
Propachlor	7
2,4-D	10
Butachlor	12
Butylate	13
Cyanazine	14
Pebulate	14
Alachlor	21
Molinate	21
Sulfometuron	20–28
Cycloate	20–30
Persistent herbicides (harm susceptible species during the first and sometimes into the second season after application)	
Clomazone	30
Metolachlor	30–50
Metribuzin	30–60
Benefin	40
Chlorimuron	40
Chlorsulfuron	40
Clopyralid	40
Pendimethalin	44
Trifluralin	45
Ametryn	60
Atrazine	60
Bromacil	60
DCPA	60
Dichlobenil	60
Ethalfluralin	60
Flumetsulam	60
Imazaquin	60
Linuron	60
Oxadiazon	60
Prometryn	60
Pronamide	60
Simazine	60
Thiazopyr	64
Imazethapyr	60–90
Napropamide	70
Triallate	82
Fluometuron	85
Diuron	90
Hexazinone	90
Siduron	90
Highly persistent herbicides (harm susceptible species during the second season and sometimes for longer periods of time)	
Bensulide	120
Isoxaben	(50–)120
Prodiamine	120
Oryzalin	(20–)128
Triasulfuron	(69–)139
Imazapyr	(25–)142
Norflurazon	(45–)180
Terbacil	180
Picloram	(90–)300
Prometon	300
Tebuthiuron	300

[a] Data from the *Herbicide Handbook* of the Weed Science Society of America, Lawrence, Kansas (1994).