Environmental Fate of Applied Herbicides

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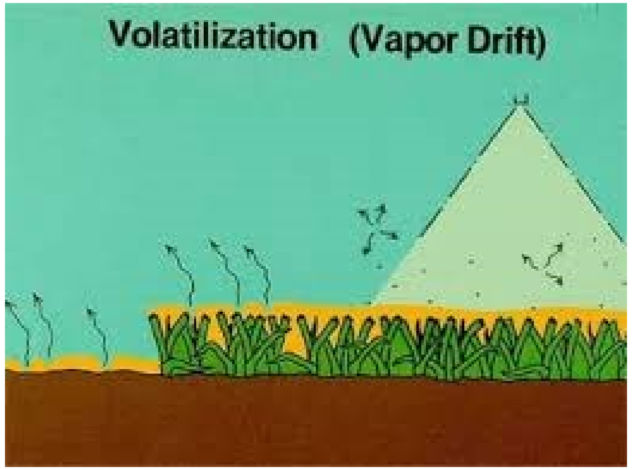
Environmental Fate of Applied Herbicides

- During deposition
  - Movement off target
    - Drift
      - Wind speed & direction
      - Use drift retardants, coarse to extremely coarse sprays, low application heights …
    - volatility
  - Deposited on site – plants & soil
- After deposited on site …



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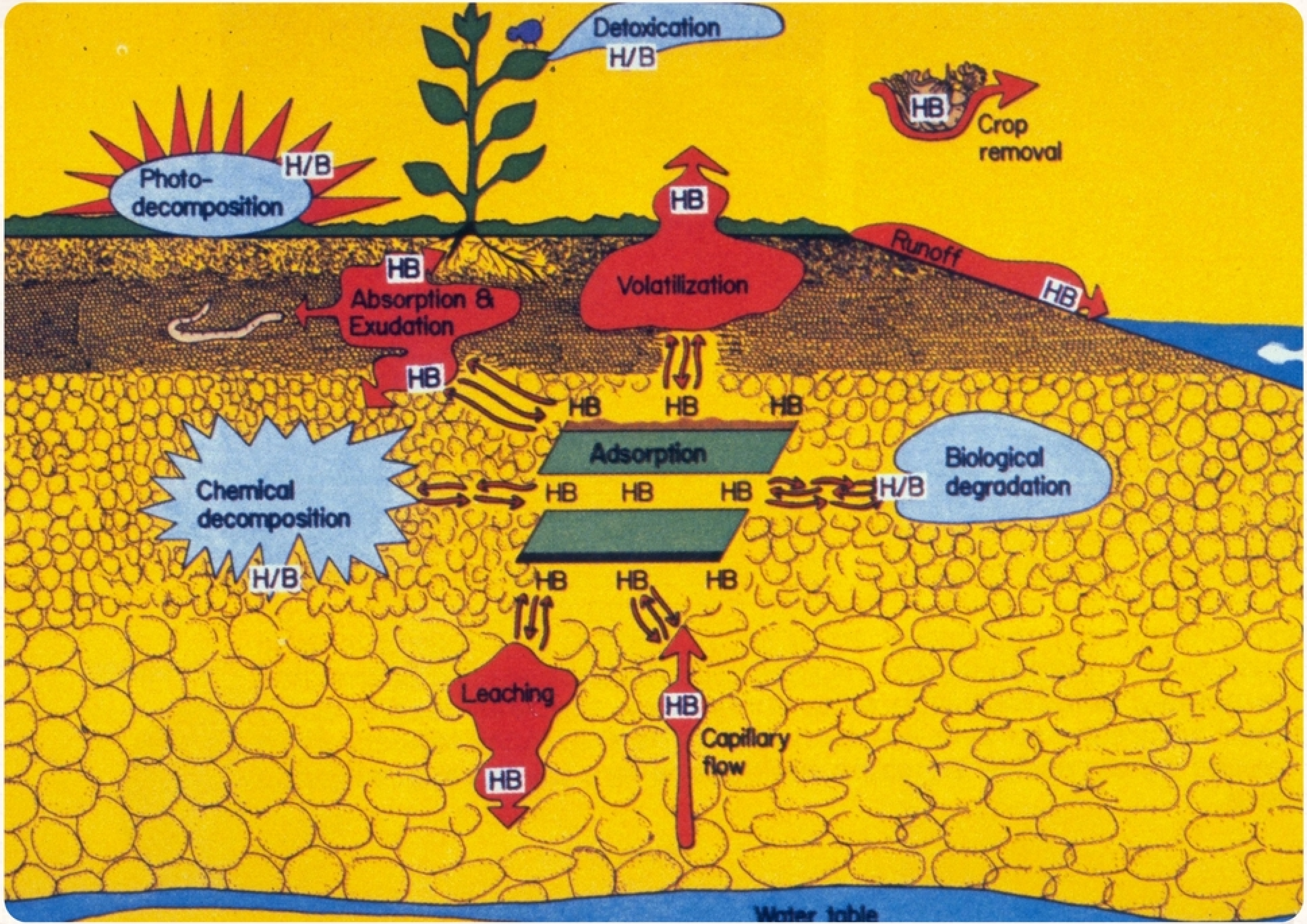
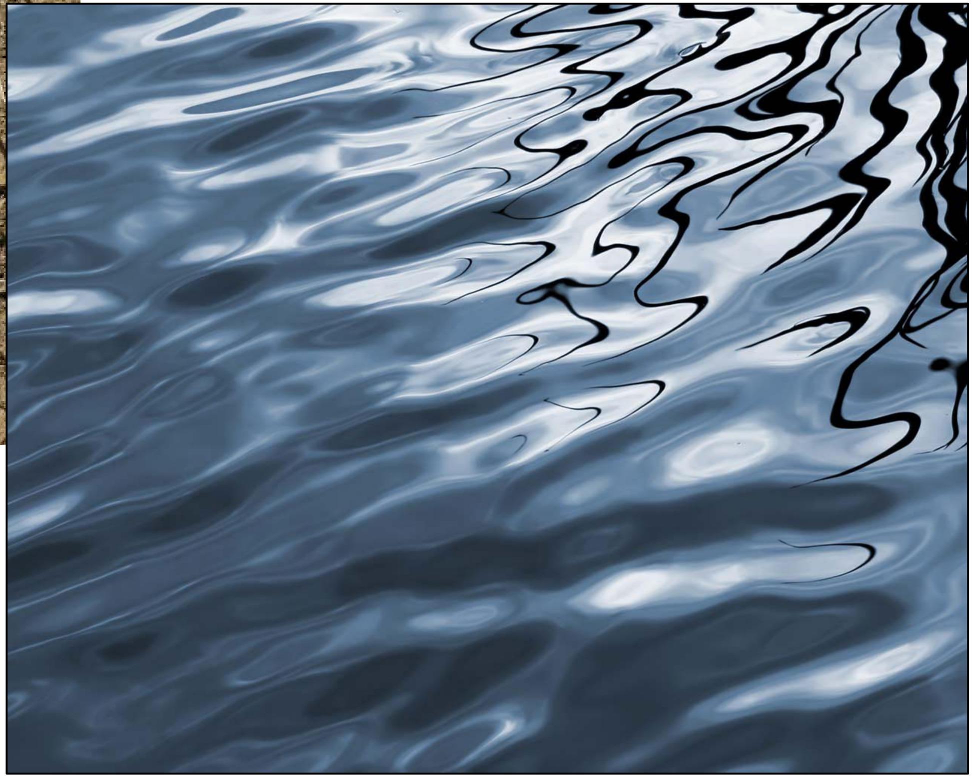
Environmental Fate of Applied Herbicides



Soil and Water Quality Influences on Herbicide Environmental Fate



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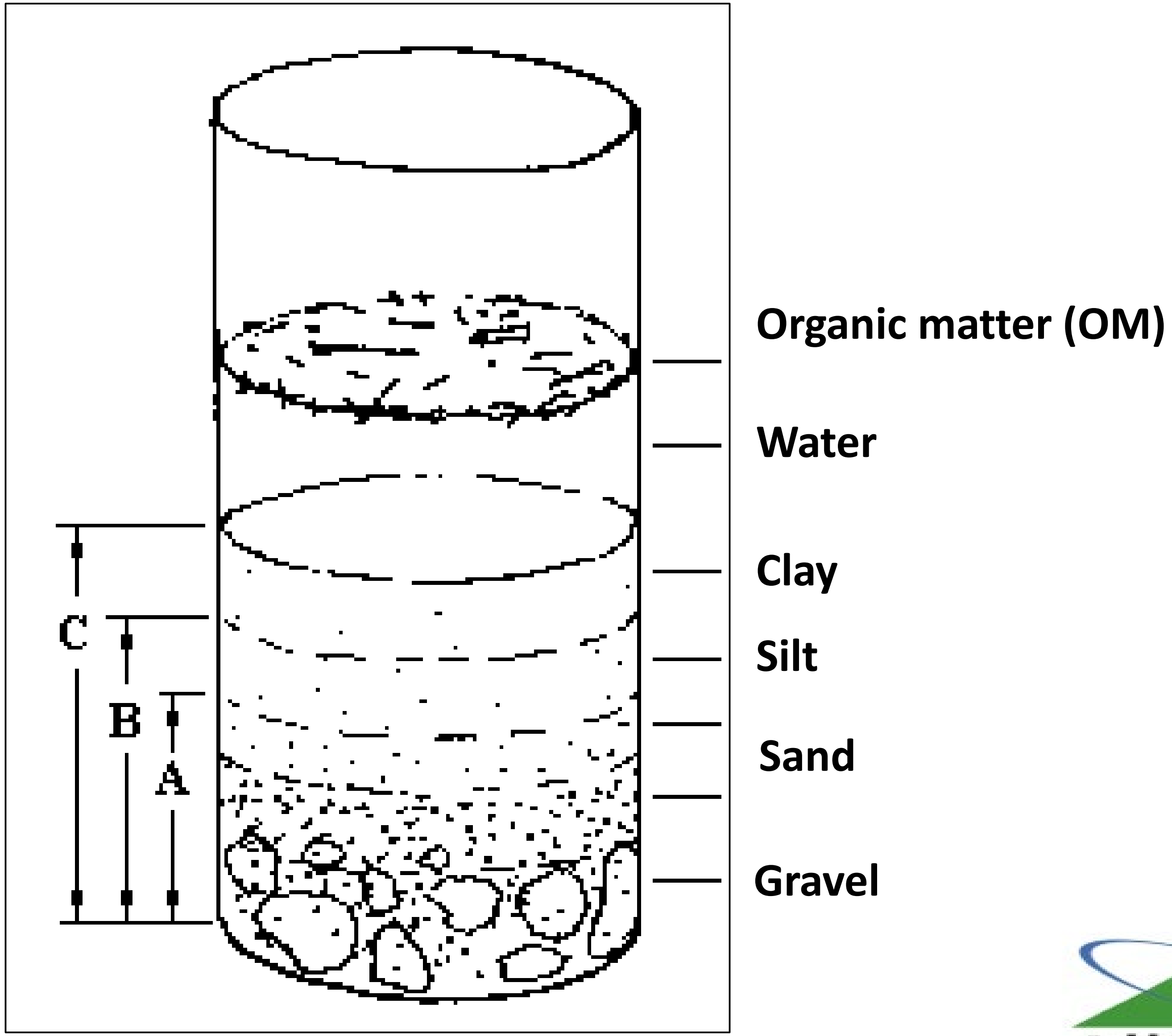
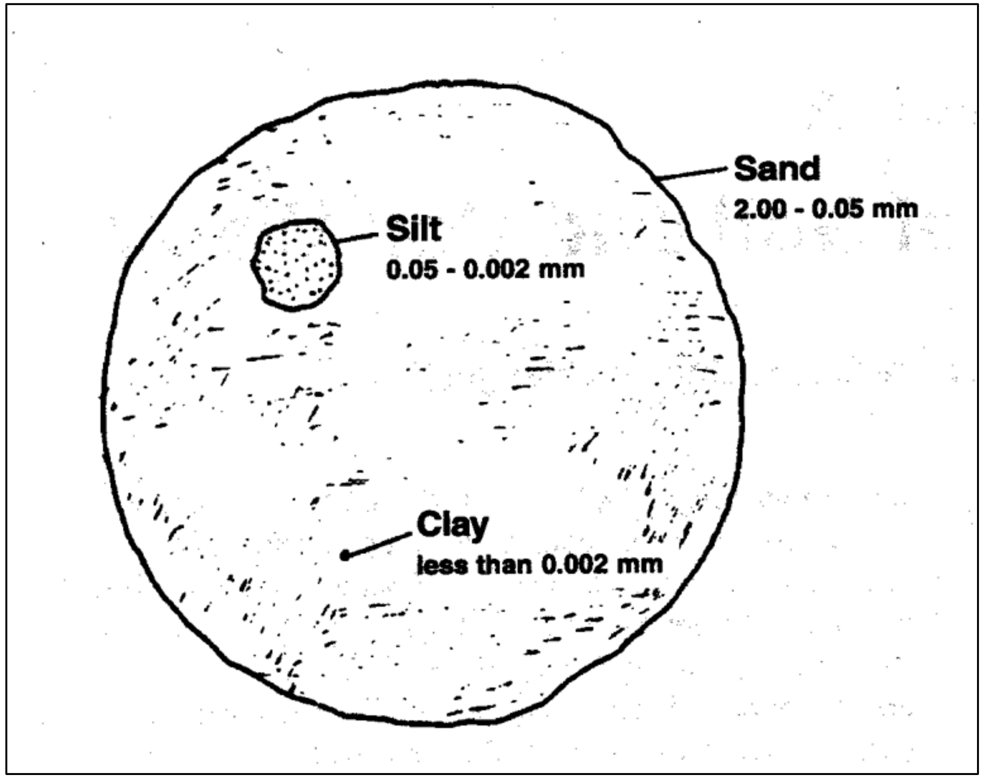
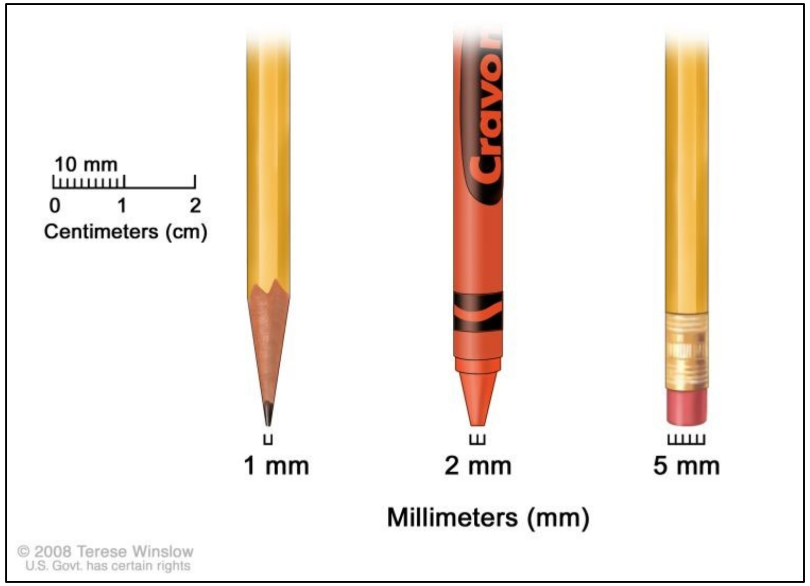
Soils

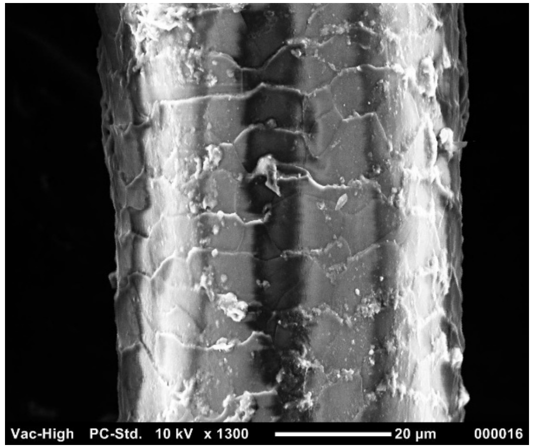


Soil Particle Size & Surface Area





Human hair ~ 20 microns



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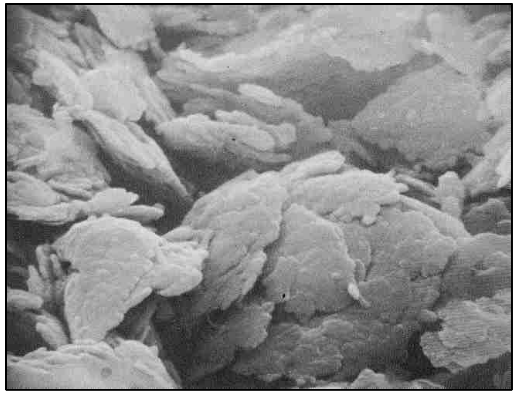
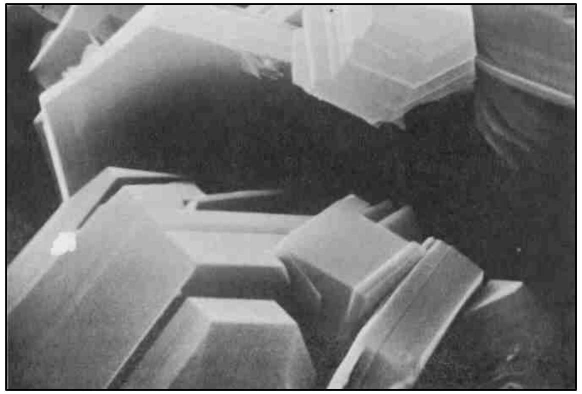
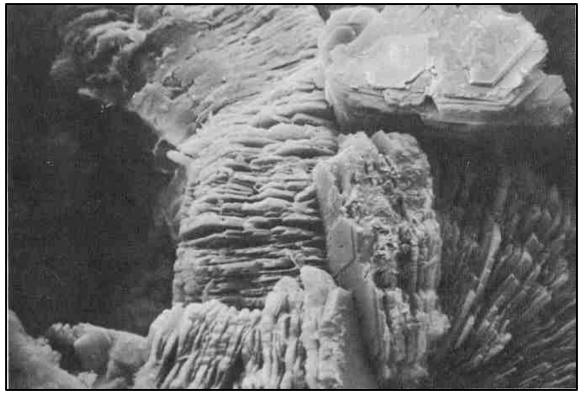
Cation Exchange Capacity (CEC) & Soil Particle Surface Area

Exchange Surface	CEC (meq/ 100 g)	Surface area (cm^2/g)
Organic matter	100 - 300	500 - 800
Montmorillonite	100	600 - 800
Illite	30	65 - 100
Kaolinite	10	7 - 30







Soil Factors Influencing Fate of Applied Herbicides

1. Volatilized
2. Absorbed by plants
    1. Exudation
    2. Detoxication
    3. Removed with harvest
3. Adsorbed to soil
4. Leached
5. Runoff with surface water
6. Degraded

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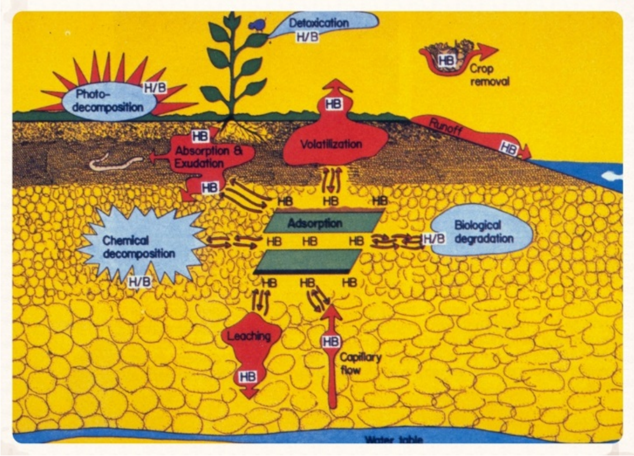
Soil factors:
- Texture
- Organic matter
- pH
- Temperature
- Moisture



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Environmental Fate of Applied Herbicides

- Herbicides in runoff;
  - Can be prevented:
    - Herbicides short half-life
      - Not always advantageous
    - Herbicides little or no soil activity
      - Not always possible or desirable
    - Use short half-life, minimal soil activity near sensitive areas
      - Or other types of buffers
- Herbicides removed with harvest;

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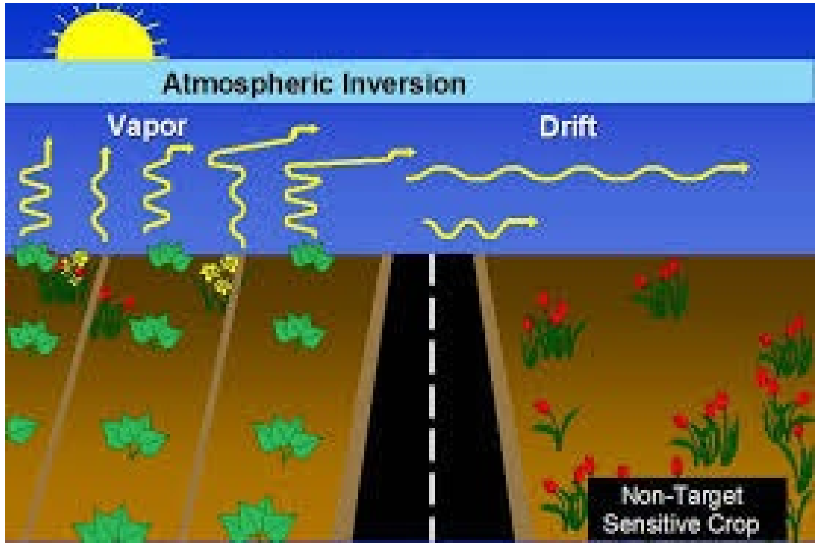
Applied Herbicides Volatilize

- Tendency of herbicide to move from liquid to gaseous phase;
  - Measured as vapor pressure (mm Hg)
    - Influenced primarily by chemistry of parent acid
    - Also influenced by soil characteristics
      - Temperature mostly
      - Also soil moisture
      - Lesser extent OM, pH, texture



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Relative Volatility of Some Herbicides

Herbicide	Vapor Pressure (mm Hg)	Relative Volatility
Benefin (Balan)	7.8×10^{-3}	High
Pendimethalin	9.4×10^{-6}	Low
2,4-D acid	1.4×10^{-6}	Low
2,4-D dimethylamine salt	1×10^{-7}	Very low
2,4-D butoxyethyl ester	2.4×10^{-6}	Low
Dicamba	1.25×10^{-5}	Moderate
Triclopyr triethylamine salt	3.6×10^{-7}	Very low
Triclopyr butoxyethyl ester	3.6×10^{-6}	Low
Picloram	6.0×10^{-16}	Negligible
Aminopyralid	7.14×10^{-11}	Negligible
Clopyralid	9.98×10^{-6}	Low
Sulfometuron	5.48×10^{-16}	Negligible
Metsulfuron	2.5×10^{-12}	Negligible
Imazapyr	1.79×10^{-11}	Negligible
Imazapic	7.75×10^{-12}	Negligible

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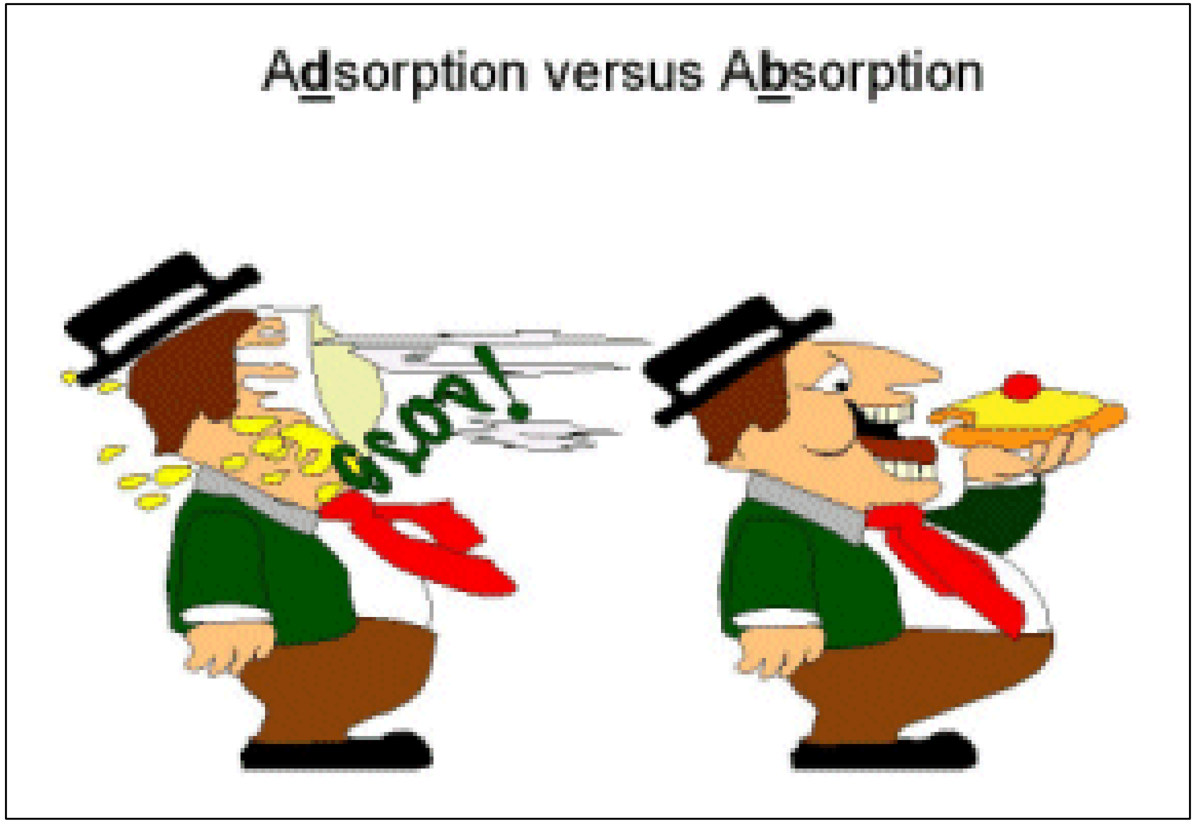
Absorption & Adsorption

- Absorption is passage through an interface
- Adsorption is accumulation at an interface



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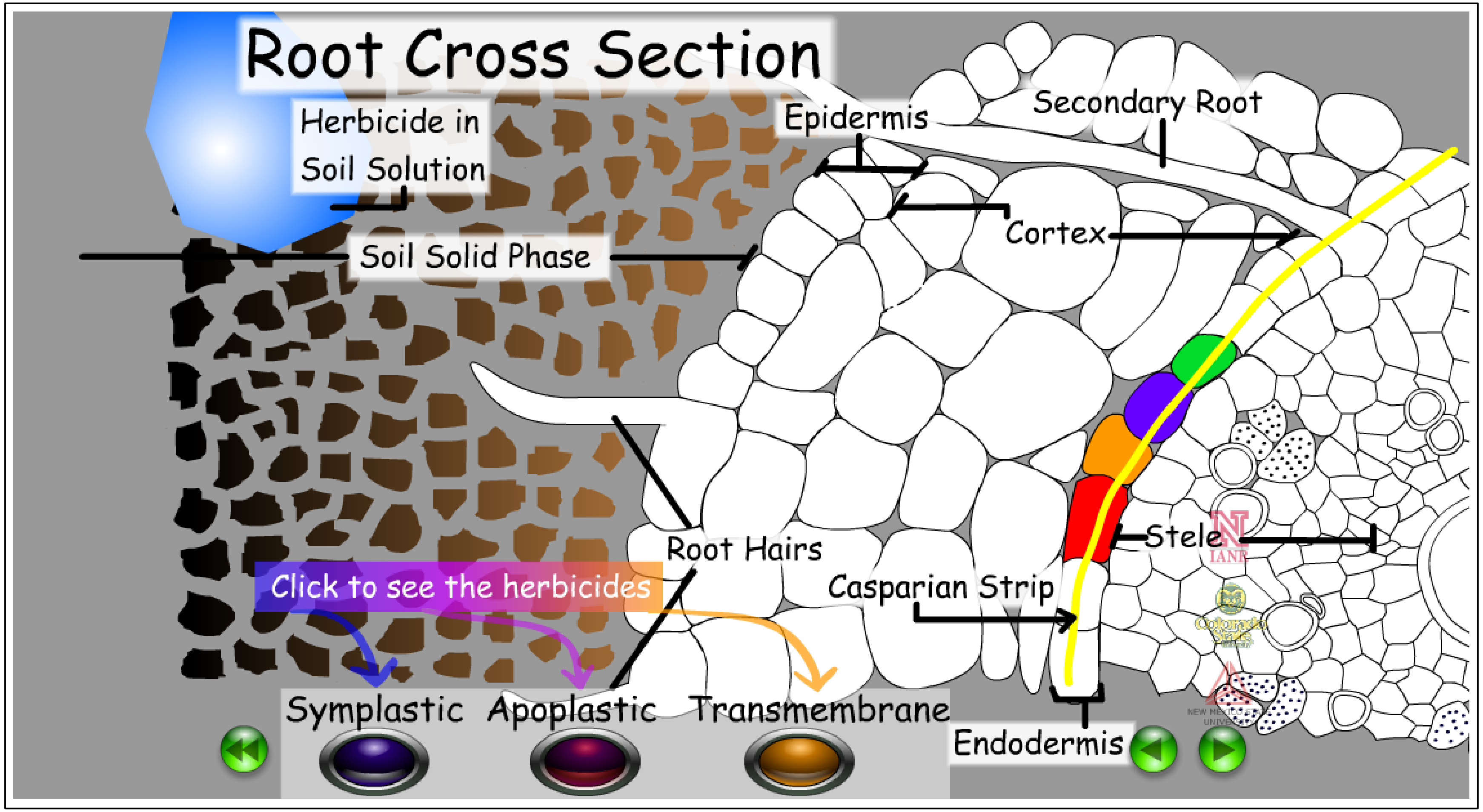
Absorption & Adsorption



(plantandsoil.unl.edu)

Plant and Soil Sciences eLibrary

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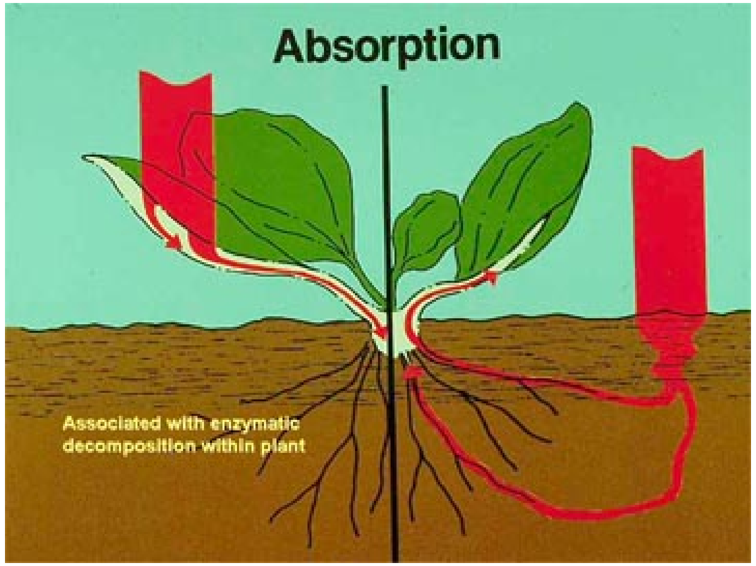
Applied Herbicide Are Absorbed by plants

Absorption by plants decreases availability of herbicide for soil adsorption, leaching, or degradation;

- target weed(s) v non/off-target plants

Influenced by soil:

- Moisture & temperature primarily;
- pH of the soil solution



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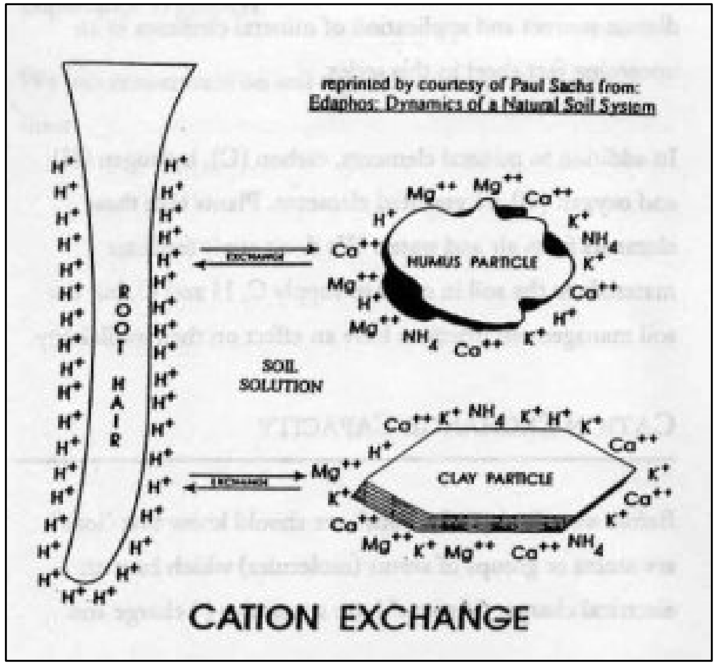
Applied Herbicides Adsorb to Soil Particles

- Particles in the soil
  - Strong bonds: magnetic (cationic, anionic)
  - Weak bonds: hydrogen bonds

- Adsorption decreases availability of herbicide absorption, leaching, volatilization …
  - Influenced by herbicide

    binding affinity, soil moisture, pH, texture



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Soil Factors Influencing Adsorption of Herbicides

- Soil factors:
  - Organic matter, texture, soil moisture and pH;
    - pH (determines ionic state of herbicide) primarily;
- We measure:
  - Extent of binding: *(distribution coefficient)*

$$K_d = \frac{\text{Herbicide sorbed (mg/kg)}}{\text{Herbicide in solution (mg/L)}}$$

  - Strength of binding: *(soil organic carbon sorption coef.)*

$$\text{Koc} = \frac{K_d}{\text{weight fraction of organic C in soil}}$$

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Adsorption Strength of Some Herbicides

Adsorption Strength	Herbicide
Very Strong; K_{oc}>5,000	e.g. glyphosate, paraquat
Strong; K_{oc}500-4,999	e.g. diuron, atrazine, flumioxazin
Moderate; K_{oc}100-599	e.g. most phenoxies, imazapyr, tebuthiuron, topramazone
Weak; K_{oc}0.5-99	e.g. dicamba, picloram, clopyralid, aminopyralid, imazapic, sulfometuron, chlorsulfuron, metulfuron

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Practical Implications of Herbicides in the Soil

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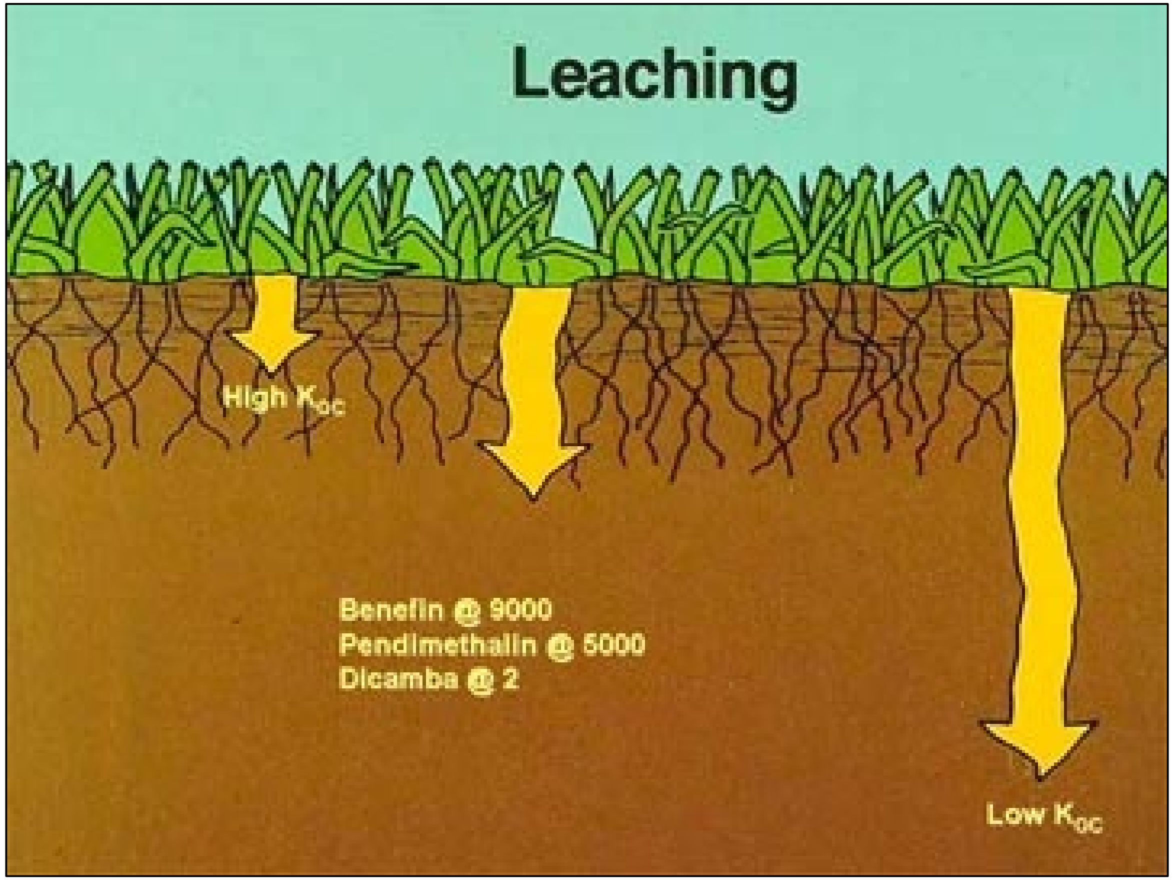
Applied Herbicides Can Leach



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Relative Mobility of Herbicides in Soils

5	4	3	2	1
Dicamba	Picloram	Atrazine	Diuron	Roundup
Method	MCPA	Chlorsulfuron	Pendimethalin	Paraquat
	2,4-D	Imazapyr	Flumioxazin	
	Aminopyralid	Topramazone	Indaziflam	
** 5 = very mobile; 1 = essentially immobile*				

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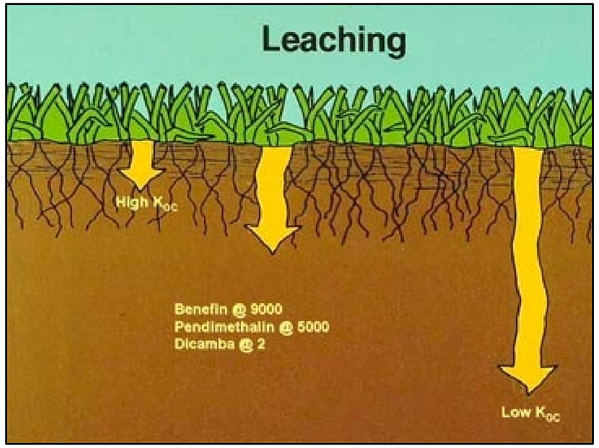
Soil Factors Influencing Leaching & Mobility

- Adsorption … leaching inversely related to % OM & clay content
- Moisture … leaching increases as more water moves through soil profile
- pH … at low pH levels adsorption increases, decreasing leaching
- Temperature … theoretically > at higher temp as sorption increases



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Herbicide Factors Influencing Leaching

- Water solubility …
  - – more soluble in water > potential to leach
- Binding affinity & ionic state of herbicide …
  - – pka is pH where half of the herbicide molecules are neutral (non-dissociated) and half are ionized or charged
    - **higher pKa, greater the potential to leach or move**

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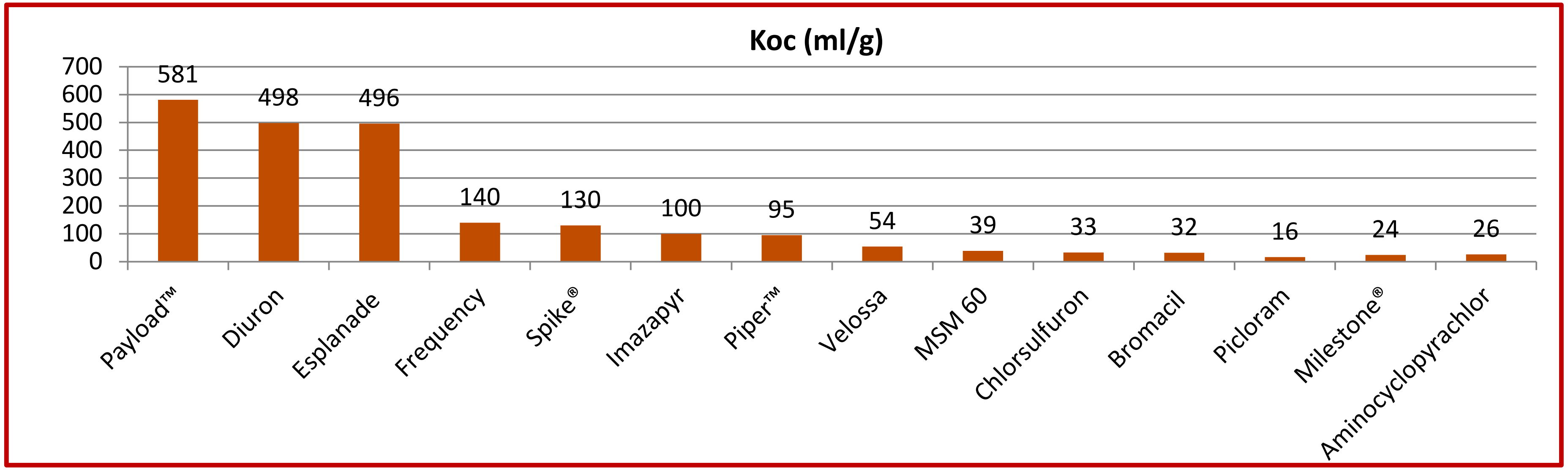
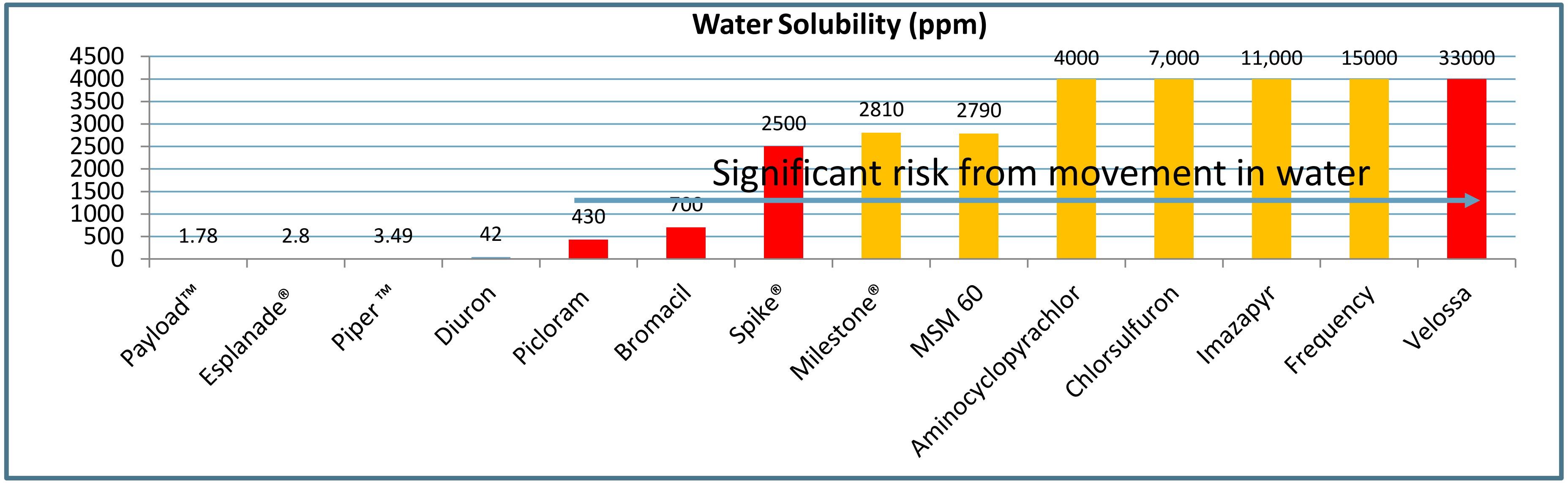
Common Herbicide
Water Solubility and Koc Comparison





High risk of movement in water

Very High risk of movement in water

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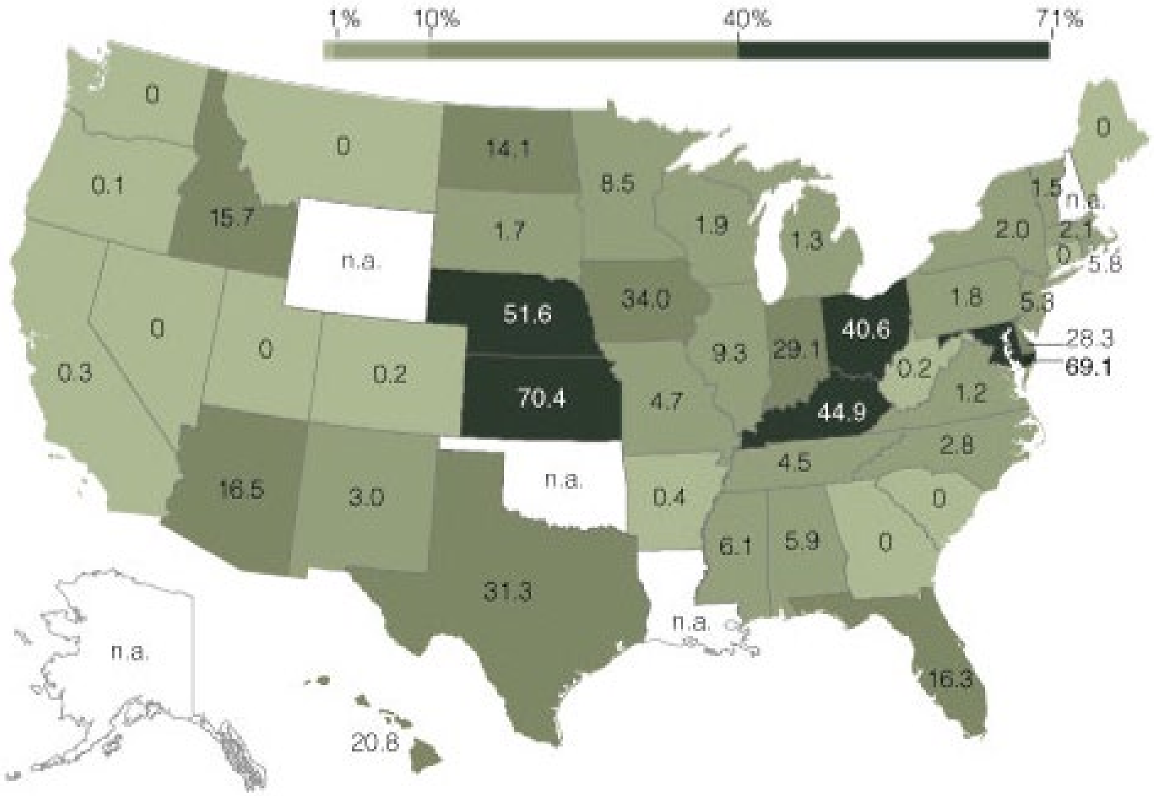
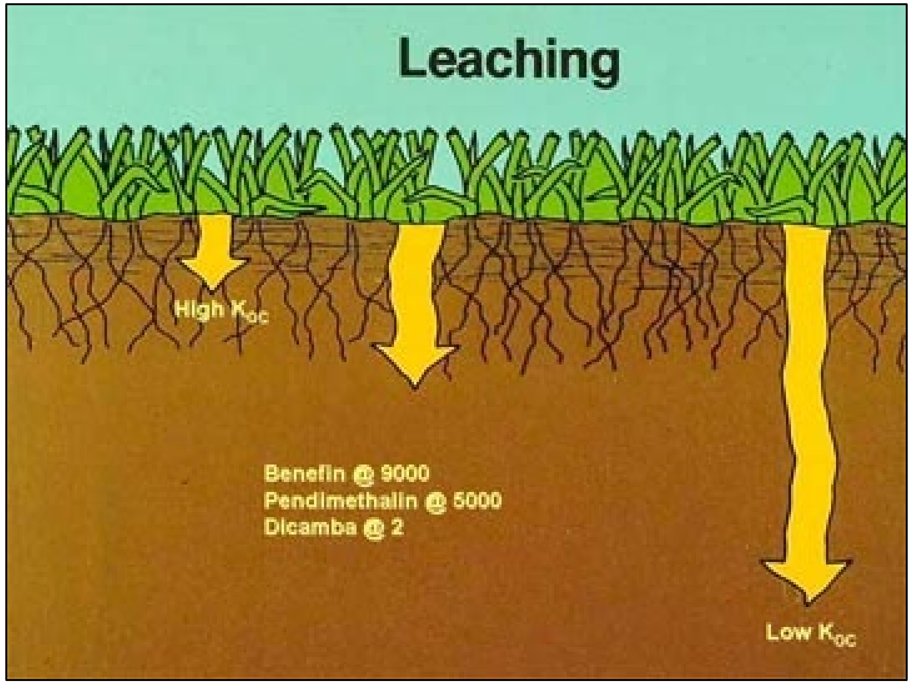
Practical Implications of Herbicides in the Soil

Atrazine K_{oc} = 100 g/ml





The New York Times

"Debating how much weedkiller is safe in your water class. August 22, 2009."

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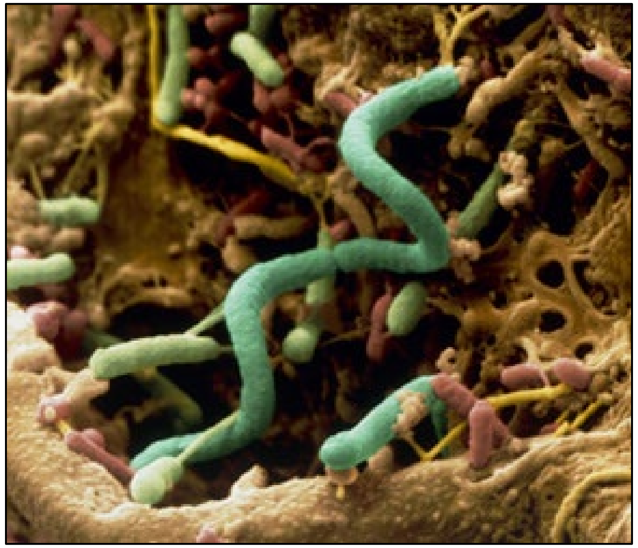
Microbial Decomposition

- Major route of herbicide degradation
  - Soil microbes use herbicide as nutritional substrate
  - Influenced by all soil properties, but especially moisture and temperature …
  - increases microbially-mediated enzymatic reactions



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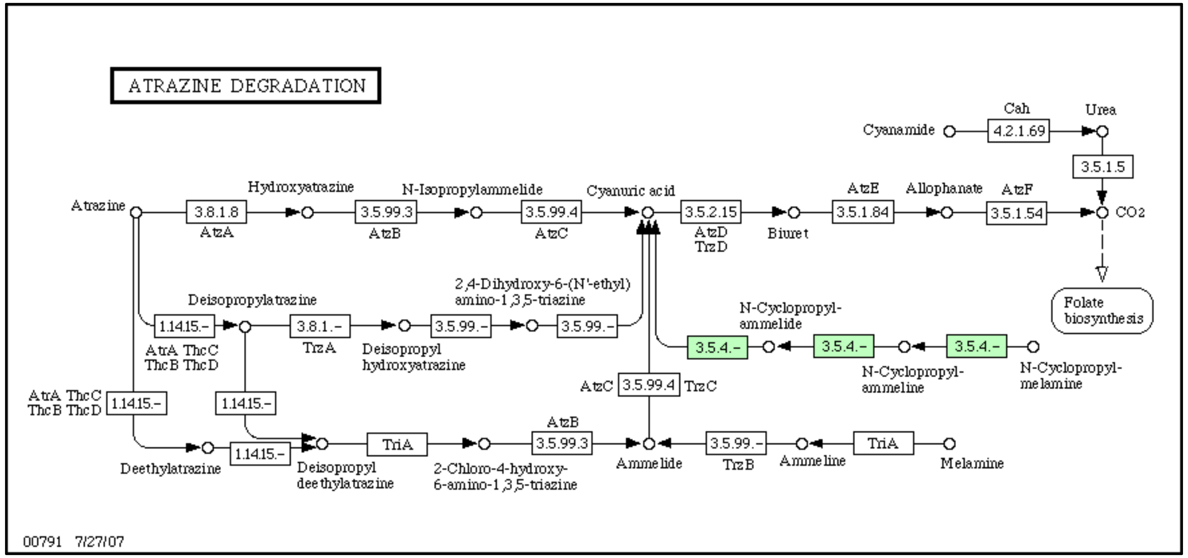
Chemical Decomposition

- Degradation by purely chemical, non-enzymatic means
  - Includes: dehalogenation, dealkylation, decarboxylation, oxidation, hydrolysis, hydroxylation, ester cleavage, conjugation, ring cleavage
    - Influenced by soil temperature and pH



Photodecomposition of Herbicides

- Effect of radiation on internal chemical bonds
  - type of chemical degradation
  - changes bonds, releases energy stimulating reactions
- Effect on herbicide soil residues is (generally) negligible, much more significant in aquatic environments

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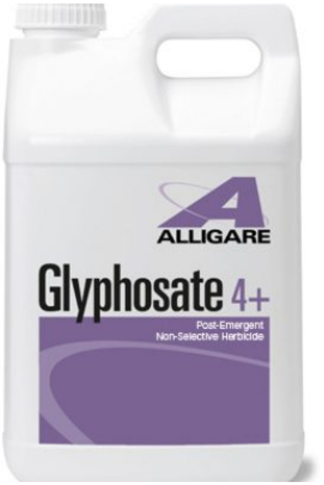
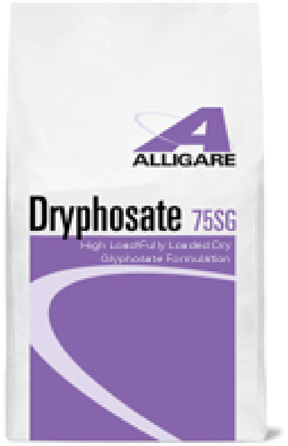
Water Quality & Herbicides

- “water quality”; amount of soil sediment, suspended plant material, dissolved salts (cations & anions), pH
  - can bind some herbicides
  - also create physical problems (plugging) of sprayer parts, especially screens & tips
- Avoid using poor quality water when applying herbicides or other pesticides





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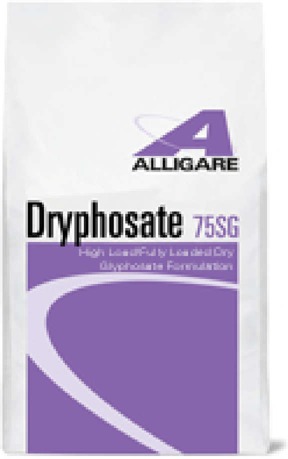
Water Quality & Glyphosate

- Glyphosate is a strong acid & forms metal and onium salts
- Glyphosate exists as mono or dianions in soils or at physiological pHs
  - One or two negative charges
  - In plants, readily bound by zinc and copper
- In spray solution suspended soil, cations (e.g. Ca^{++}, Mg^{++}) or OM will bind with glyphosate making it unavailable to plants
- Addition of spray grade ammonium sulfate (AMS) helps prevent complexing with divalent cations in spray solution



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Questions?