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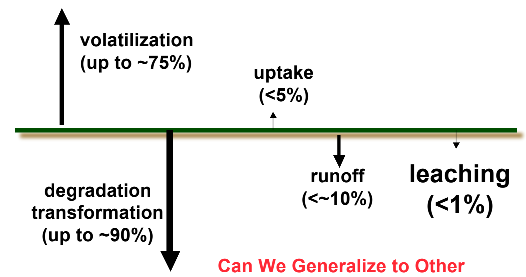
Fall 2005

ES/RP 531
Fundamentals of Environmental Toxicology

Lecture 21
Mass Transfer (Transport)

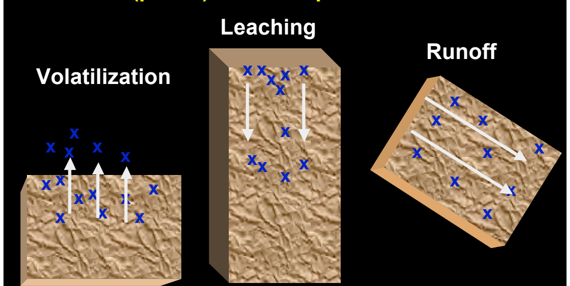
Proportional Disappearance of Pesticides from Soil by Different Pathways



Can We Generalize to Other Contaminants????

Transport Processes

Tendency of molecules to be carried by a medium (phase) from one place to another



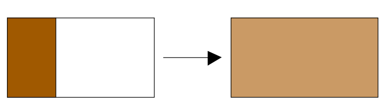
Transport Phenomena

- Diffusion
- Volatilization
- Runoff & Erosion
- Leaching

(Mass Transfer)

Diffusion

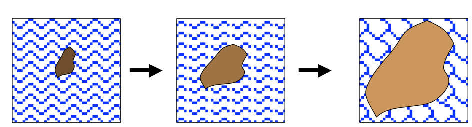
- Molecular scale process
  - Movement of molecules within a medium
  - Movement from higher concentrations to lower concentrations
  - Loss of spatial uneveness in the distribution of mass (concentration, or heat) manifested because of the second law of thermodynamics
    - Entropy increases until equilibrium is reached
    - System at lowest energy state at equilibrium



Diffusivity is related to molecular size of the contaminant and viscosity of the medium

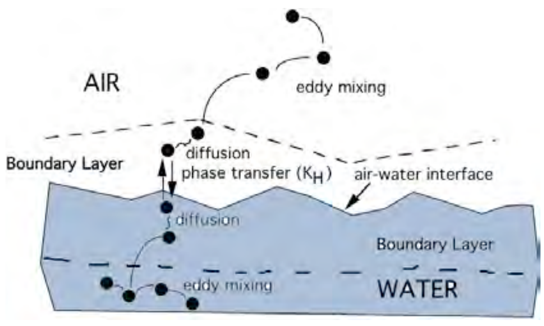
Turbulent Diffusion

- Macroscopic level "diffusion"
  - Movement of medium itself redistributes the contaminant
  - Eddy diffusion

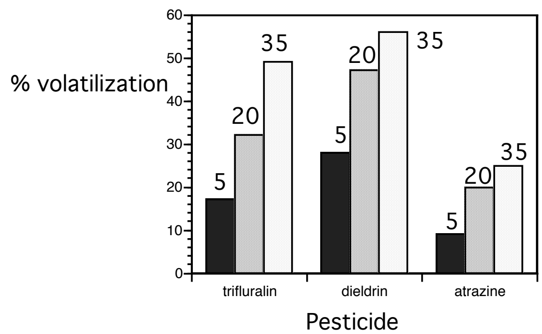


Diffusion occurs quickly over short distances (100 μm) but very slowly over long distances.

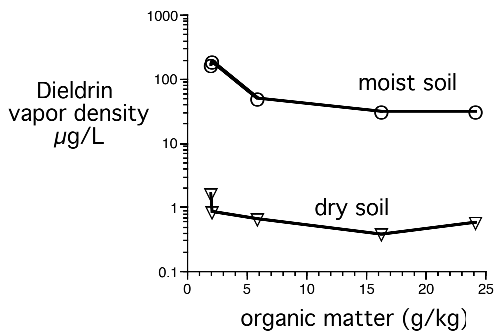
Volatilization



Volatilization is influenced by temperature

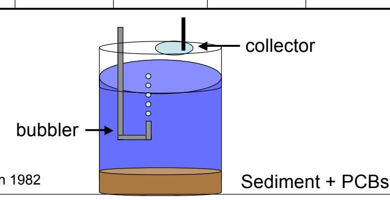


Volatilization is influenced by soil moisture and organic carbon



Effect of Sediment Perturbations on Volatilization of PCBs

System	Sediment 0-5 mm depth (ng/g)	Water (ng/L)	Surface microlayer (ng/cm2)	Jetdrop impactor (ng/cm2)
Midges	123	0	92	16
Worm & Midges	37	6	76	8
Sterile	56	0	0	0
No animals	145	0	0	0



Sodergren & Larsson 1982

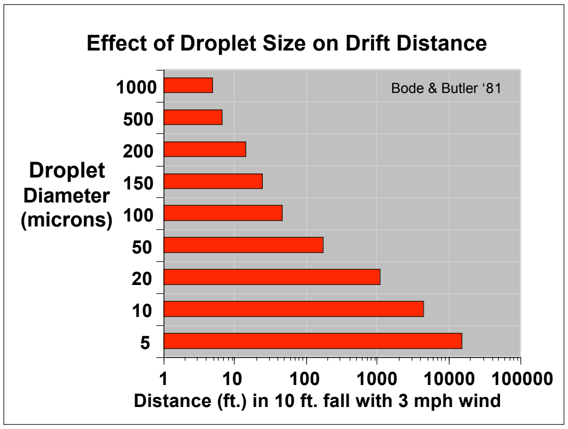
Volatilization

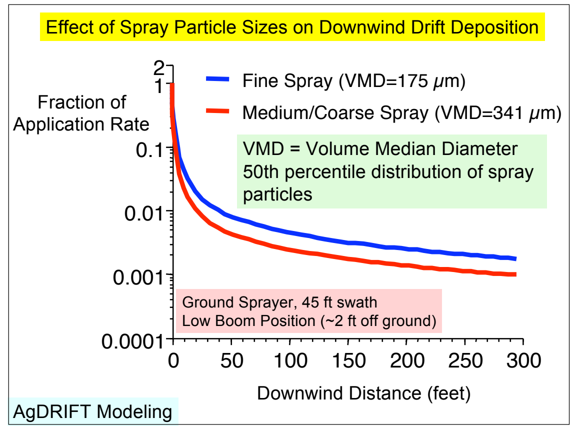
Pesticide	% Volatilized in 24 hours	Crop
alachlor (Lasso)	1.1	fallow
atrazine (Aatrex)	0.1	fallow
simazine (Princep)	0.05	fallow
EPTC (Eradicane)	33.6	alfalfa
2,4-D	4.2	wheat
trifluralin (Treflan)	41.4	fallow (moist)
trifluralin (Treflan)	11.9	fallow (dry)

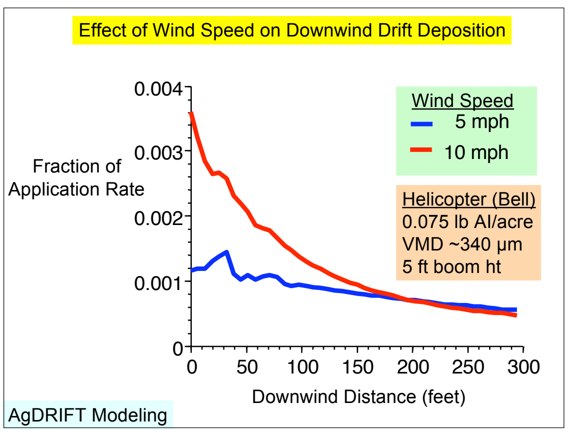
Spencer 1990

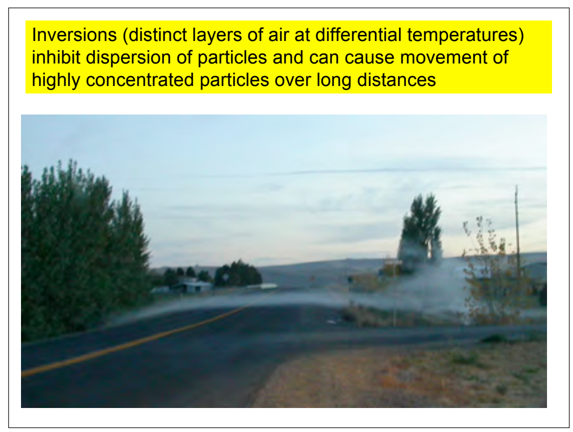
Pesticide Drift: A Direct Route to the Atmosphere

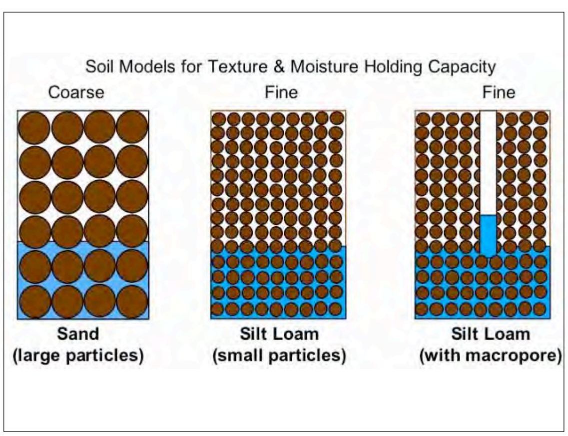
- Movement of spray droplets during application of pesticides
  - Phenomenon can be applied to any application of any chemical in which a liquid is sheared under pressure and released into the environment

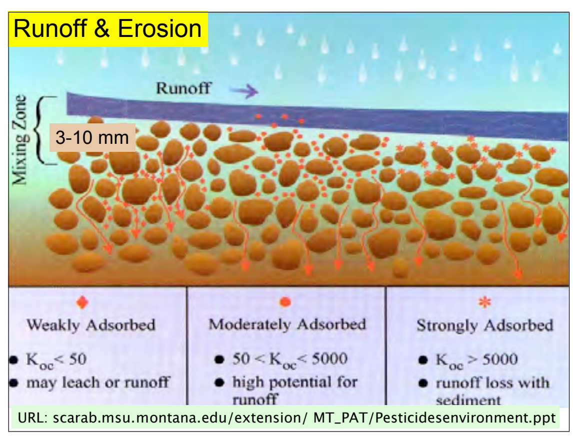

Effect of Droplet Size on Drift Distance
Bode & Butler '81
Droplet Diameter (microns)
1000
500
200
150
100
50
20
10
5
1
10
100
1000
10000
100000
Distance (ft.) in 10 ft. fall with 3 mph wind


Effect of Spray Particle Sizes on Downwind Drift Deposition
Fraction of Application Rate
2
1
0.1
0.01
0.001
0.0001
Fine Spray (VMD=175 µm)
Medium/Coarse Spray (VMD=341 µm)
VMD = Volume Median Diameter
50th percentile distribution of spray particles
Ground Sprayer, 45 ft swath
Low Boom Position (~2 ft off ground)
0
50
100
150
200
250
300
Downwind Distance (feet)
AgDRIFT Modeling

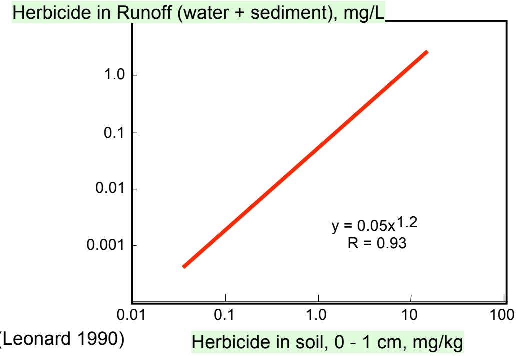

Effect of Wind Speed on Downwind Drift Deposition
Fraction of Application Rate
0.004
0.003
0.002
0.001
0
Wind Speed
5 mph
10 mph
Helicopter (Bell)
0.075 lb AI/acre
VMD ~340 µm
5 ft boom ht
0
50
100
150
200
250
300
Downwind Distance (feet)
AgDRIFT Modeling


Inversions (distinct layers of air at differential temperatures) inhibit dispersion of particles and can cause movement of highly concentrated particles over long distances


Soil Models for Texture & Moisture Holding Capacity
Coarse
Fine
Fine
Sand
(large particles)
Silt Loam
(small particles)
Silt Loam
(with macropore)

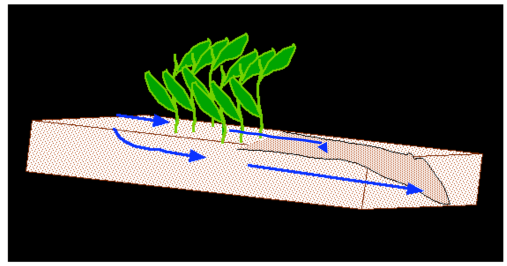

Runoff & Erosion
Runoff
Mixing Zone
3-10 mm
Weakly Adsorbed
Koc < 50
may leach or runoff
Moderately Adsorbed
50 < Koc < 5000
high potential for runoff
Strongly Adsorbed
Koc > 5000
runoff loss with sediment
URL: scarab.msu.montana.edu/extension/ MT_PAT/Pesticidesenvironment.ppt

Only Pesticide in Top Centimeter Is Susceptible To Runoff But Amount Moving Is Concentration Dependent

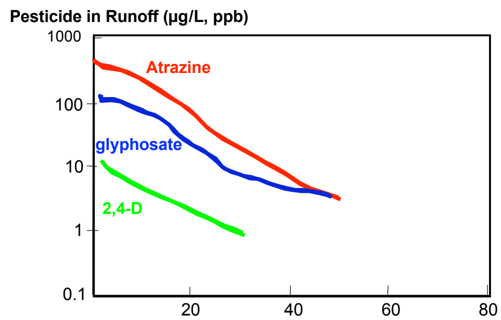


(Leonard 1990)

Effect of Rills On Pesticide Runoff



Combination of Pesticide Degradation & Aging Reduces Surface Runoff Over Time

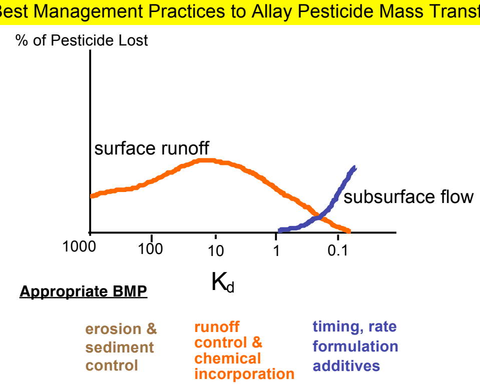


(Leonard 1990)

Factors Affecting Surface Transport

- Rainfall timing & intensity
- Location of contaminant
- Contaminant properties
- Topography

Relationship Between Phase Transfer Properties and Appropriate Best Management Practices to Allay Pesticide Mass Transfer



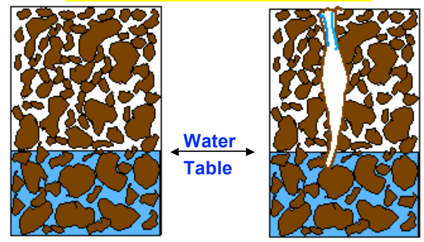
Contaminant Properties Affecting Leaching

- Water solubility
- Sorption potential
- Volatilization potential
- Reactivity

Field Factors Affecting Leaching

- Precipitation & Irrigation
  - Volume
  - Intensity
- Soil Properties & Structure
  - Organic matter content
  - Clay content
  - pH
  - Macropores

Reality is Irregular



Soil particles are irregular, creating small and large pores.

Old root channels or earthworm burrows create macropores.

Macropores

- Large continuous openings in field soils
- May be continuous for distances of several meters in both vertical and lateral directions
- Characteristic of structured soils
- Cause preferential flow
  - aka macropore flow
  - flow velocities ~0.3 mm/sec -- 20 mm/sec

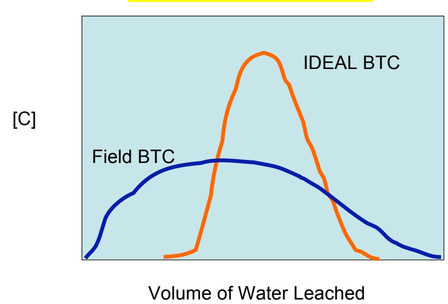
Macropores

- Pores formed by soil fauna
  - ~1 mm - >50 mm
- Pores formed by plant roots
  - < 1 mm
- Pores formed by cracks & fissures
  - variable sizes

Preferential Flow

- Rapid movement of water along facilitated pathways resulting in water movement through only a fraction of the available pore space
  - macropores
  - heterogeneous pore sizes

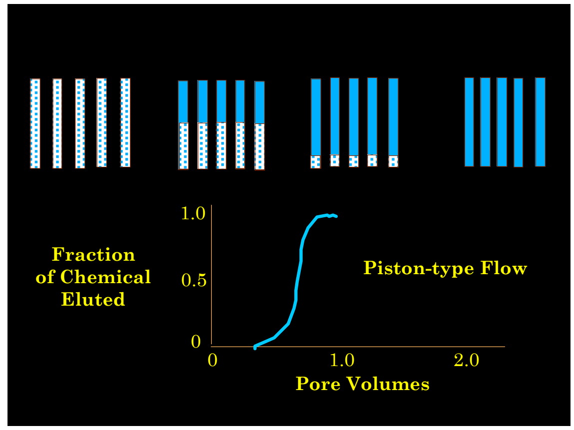
Breakthrough Curves (BTC)

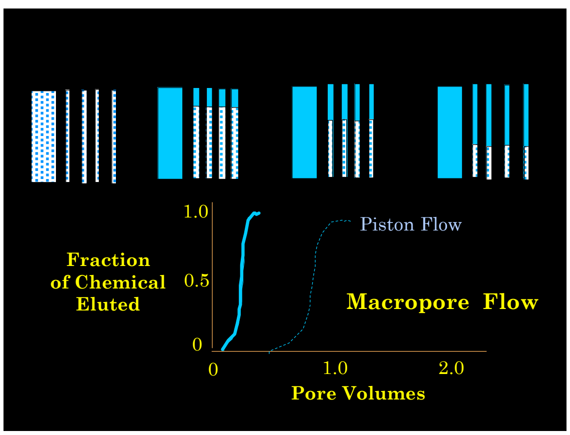


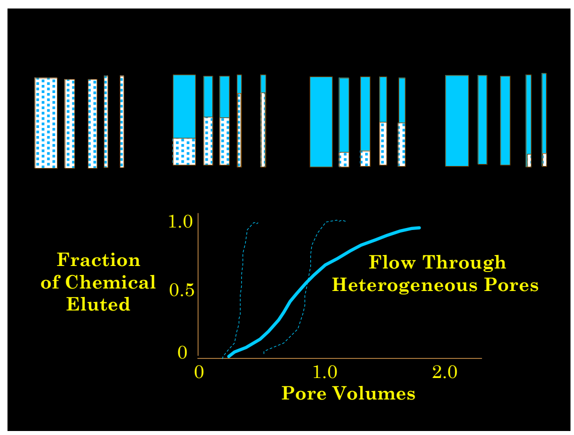
Note early elution of chemical C under field conditions owing to preferential flow

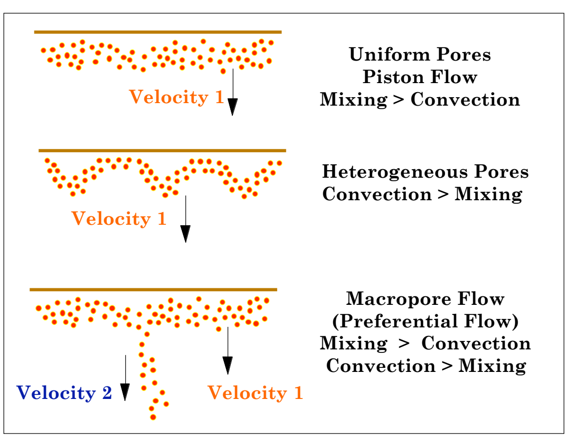
Importance of Precipitation Rate & Infiltration Rate

- When precipitation rate is slow relative to infiltration rate, flow occurs through micropores
- When precipitation rate is close to infiltration rate, macropore flow occurs
- When precipitation rate exceeds infiltration rate, surface runoff occurs

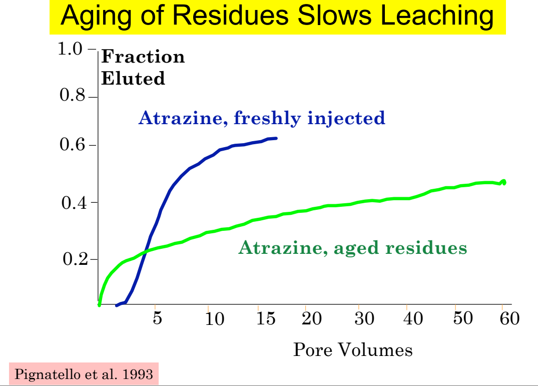








Aging of Residues Slows Leaching

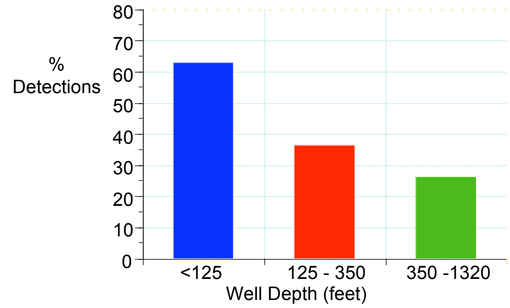


Operational Factors Affecting Leaching

- Depth of Well
- Well Maintenance
- Timing of Application
- Waste Disposal Practices
- Irrigation System

Deeper Wells--Less Detections

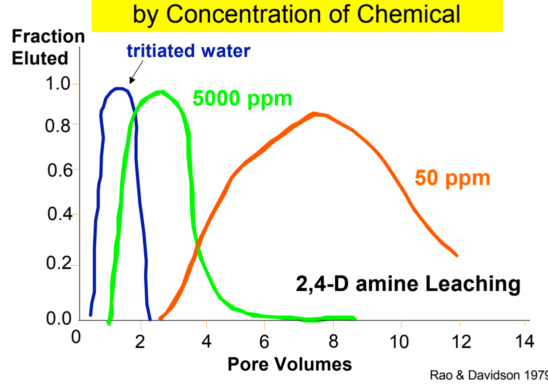
USGS Analysis of Public Water Supply Wells
(Central Columbia Plateau -- 1994)



Waste Disposal & GW Contamination

- Many agrichemical facilities with contaminated soil & wells
- Historical “dumping” prior to Congressional mandated waste regulations
  - RCRA; CERCLA
- High concentrations favor
  - persistence
  - leaching

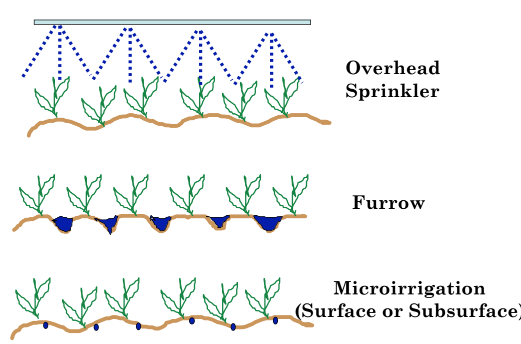
Velocity of Leaching Is Affected by Concentration of Chemical

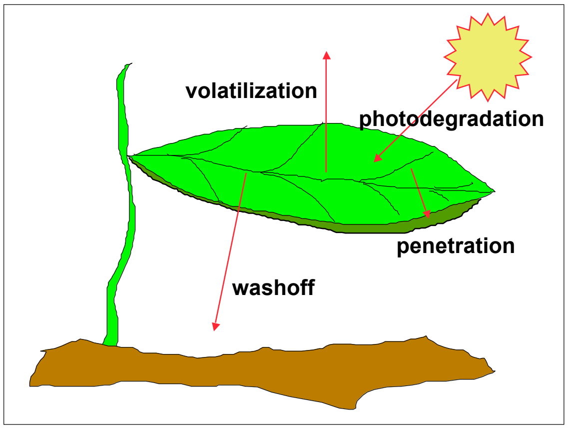


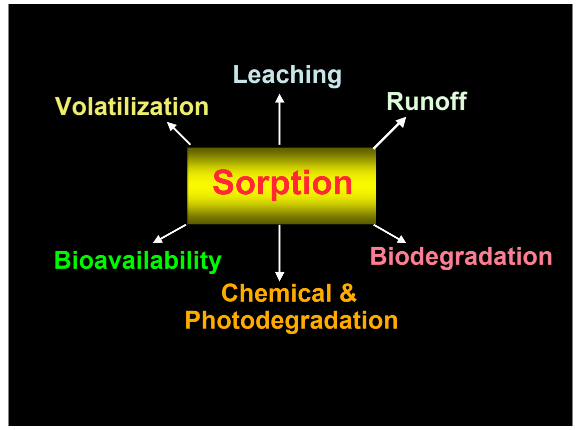
Recharge

- Irrigation in the Columbia Basin has raised the water table and the yearly recharge rate
  - Whitman Co.
    - 2 - 5 inches per yr
  - Franklin Co.
    - >10 inches per yr

Irrigation Style Affects Leaching




volatilization
photodegradation
penetration
washoff


Leaching
Volatilization
Runoff
Sorption
Bioavailability
Biodegradation
Chemical &
Photodegradation