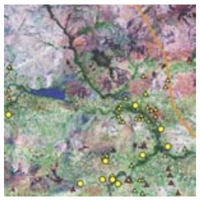
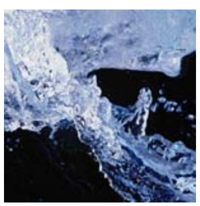
Identifying Appropriate Pesticide Environmental Fate and Application Parameters for Surface Water Modeling





Pesticides and the Environment

- Now that we have an understanding of the hydrologic and sediment transport processes that move water and soil in and out of an agricultural field, we need to understand how pesticides are affected by these processes

Matter can Neither be Created nor Destroyed

A key concept is that pesticide mass balance is preserved

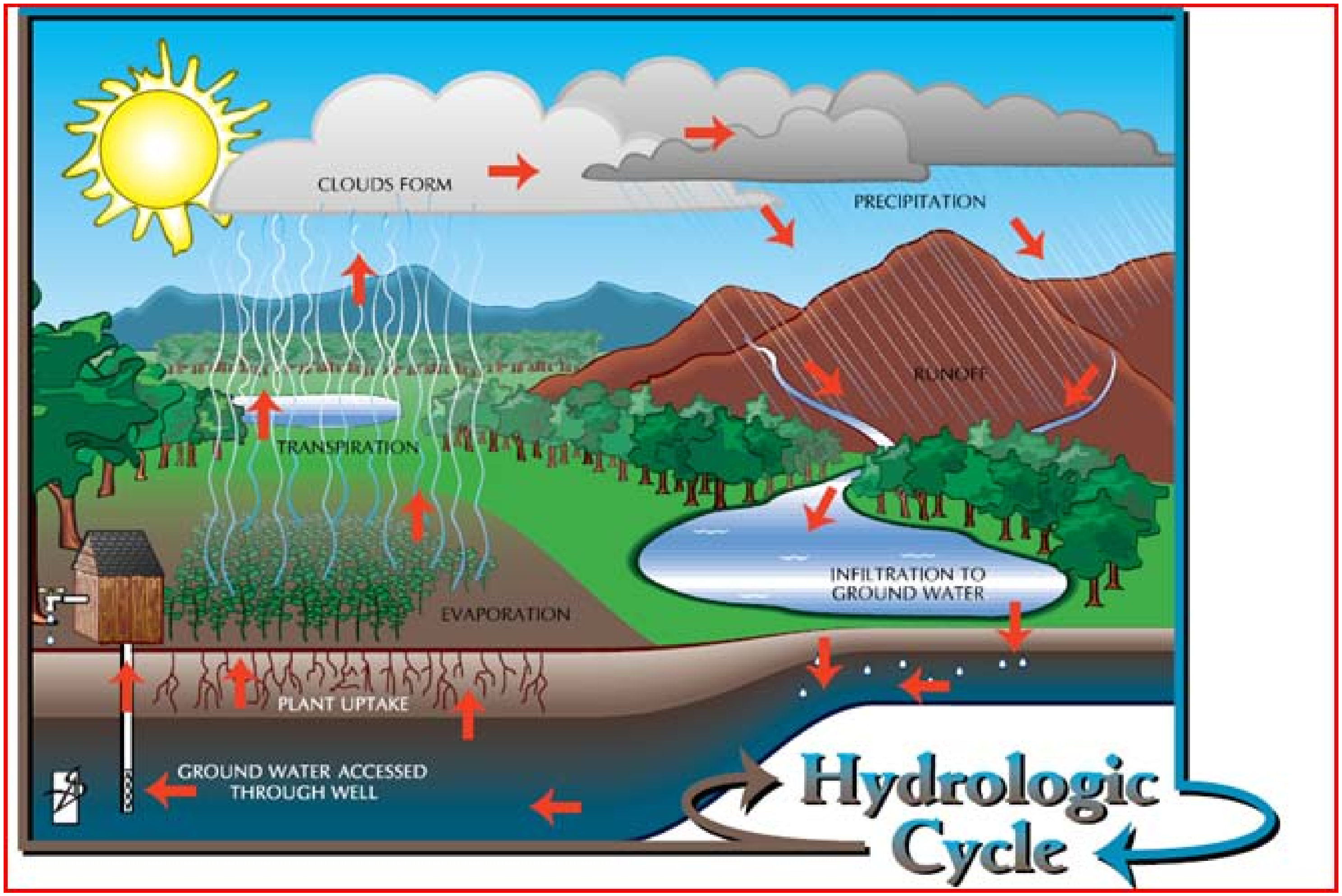
- Law of Conservation of Matter—a fundamental principle of classical physics that matter cannot be created or destroyed in an isolated system

Pesticide Modeling and Mass Balance

Mass Balance

- The total mass of the pesticide into the model must be accounted for in the output from the model. The total mass does not increase or decrease but it can change from or redistribute within the system of the model

Pesticide Behavior in the Environment



Purdue University provides an excellent summary of pesticide behavior in the environment in their document, "PESTICIDES AND WATER QUALITY PRINCIPLES, POLICIES, AND PROGRAMS"

Pesticide Fate Processes

Comprehending the fate of pesticides requires an understanding of three processes:

- Transformation
- Transfer
- Transport

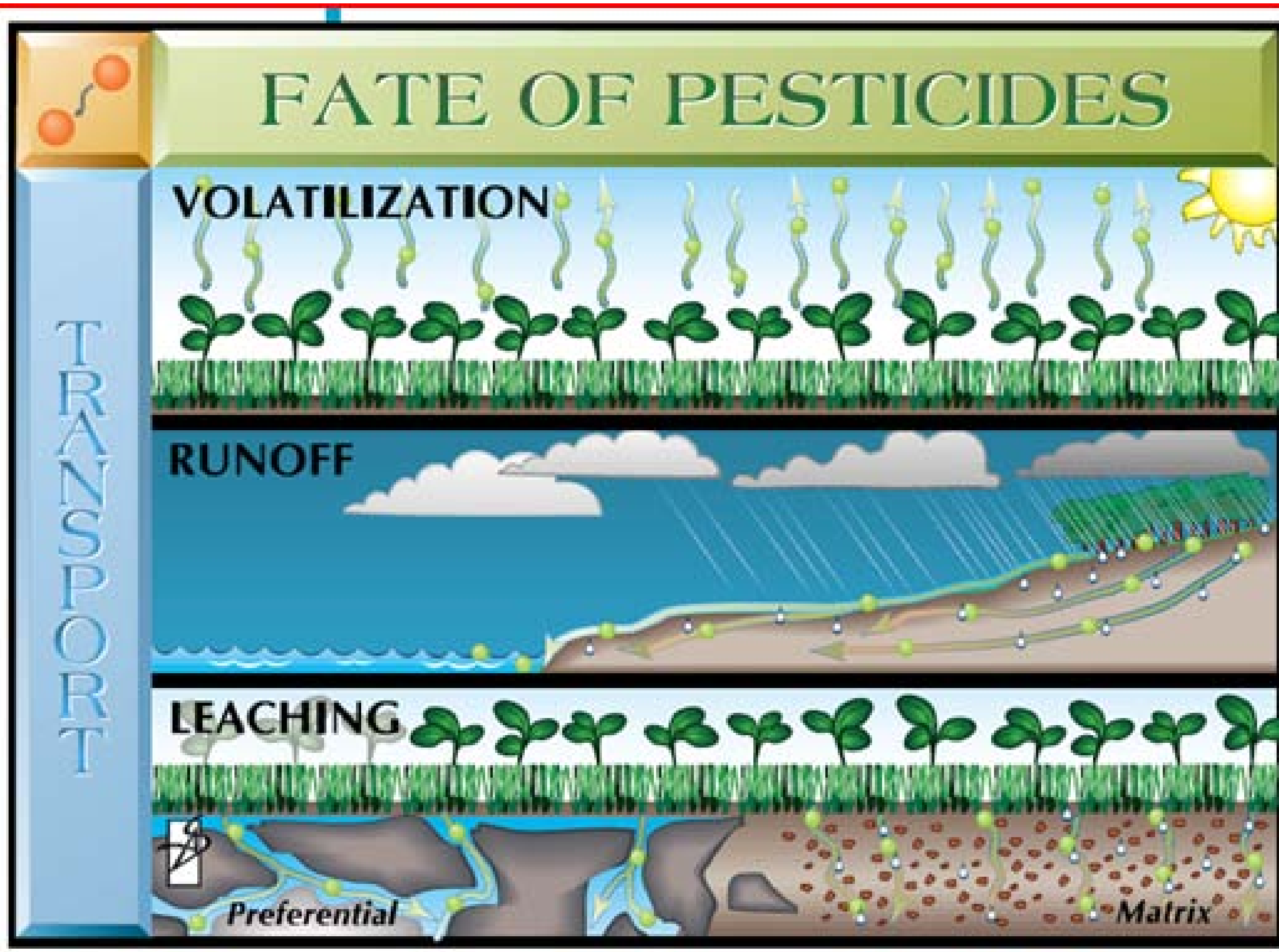
Pesticide Fate Processes (continued)

- Transformation refers to biological and chemical processes that change the structure of a pesticide or completely degrade it
- Transfer refers to the way in which a pesticide is distributed between solids and liquids (e.g., between soil and soil water) or between solids and gases (as between soil and the air it contains)
- Transport is the movement from one environmental compartment to another, such as the leaching of pesticides through soil to ground water, volatilization into the air, or runoff to surface water

Pesticide Principle Processes

To understand how pesticides behave in the environment, we need to understand the environmental fate parameters that characterize their behavior. There are three principle processes:

- Adsorption / desorption to soil particles
- Degradation
- Volatility


FATE OF PESTICIDES
TRANSPORT
VOLATILIZATION
RUNOFF
LEACHING
Preferential
Matrix

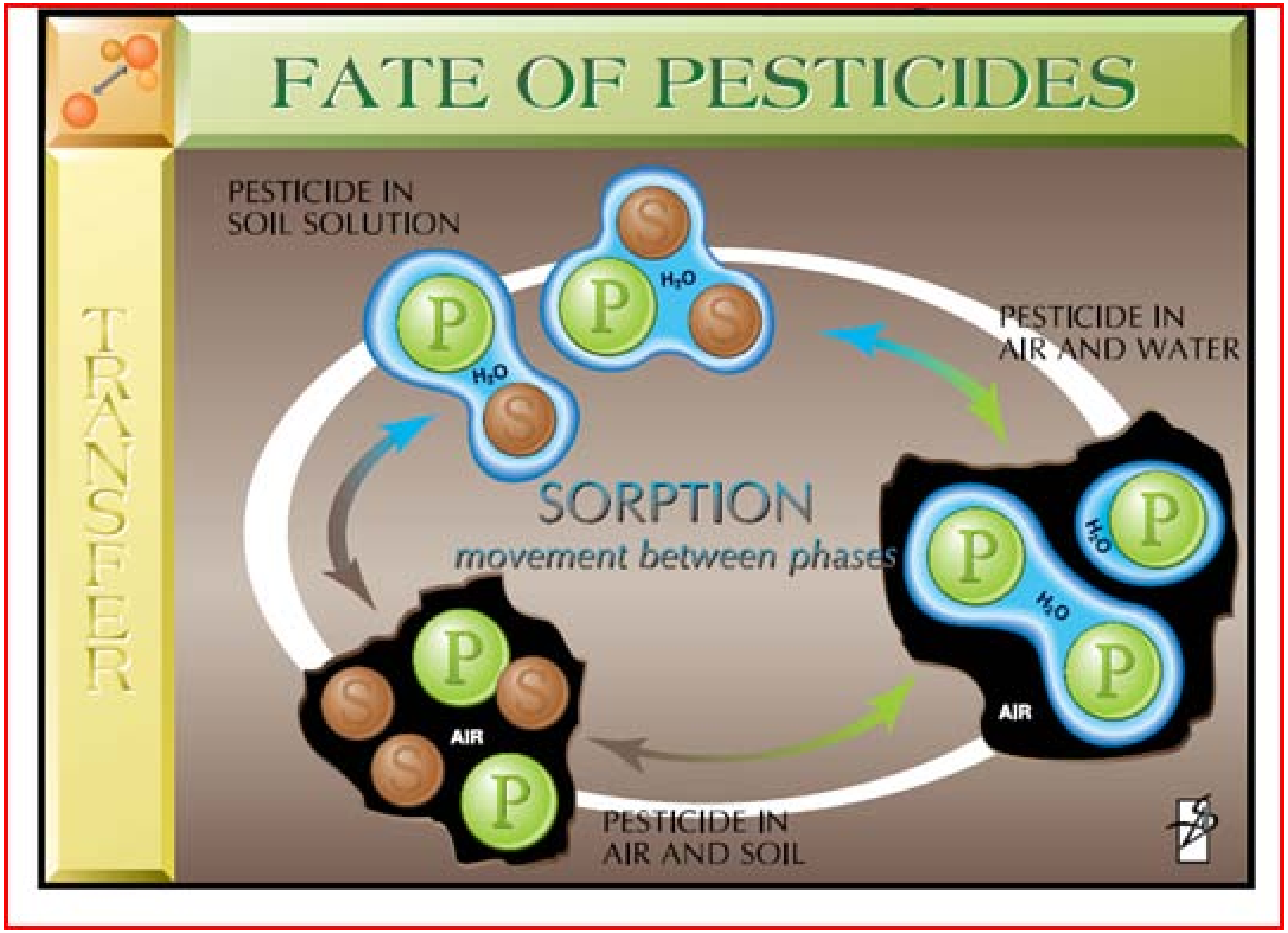
Molecular Weight

- The sum of the atomic weights of all the atoms in a molecule
- Also called formula weight (answers.com)

Water Solubility

Solubility is a physical property of a liquid, multi-component system describing its ability to dissolve a substance, the solute, at a specific temperature and pressure from another phase. Solubility is measured as the solute concentration the liquid (or solvent) contains when equilibrium is reached between the liquid and a second phase that consists mainly of the solute. The resulting solution is called a saturated solution.

Pesticide Sorption



Sorption Adsorption/Desorption Definition

- Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (the adsorbate)
- It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution
- The term sorption encompasses both processes, while desorption is the reverse process

Sorption Definition (continued)

- "Sorption is a transfer process by which pesticides are dispersed between solid matter and water
- In soil: it is important in regulating the concentration of pesticides in soil water
- One important environmental sink (retention or storage site) for many pesticides is organic matter in the soil
- The transfer—called 'partitioning'—of a pesticide into organic matter in soil is a somewhat nonspecific mechanism"

Sorption and Organic Matter

- For pesticides, the pesticide residues adsorb and desorb to organic matter on the surface of soil particles
- The quantity of pesticides that sorb to the soil is usually a function of the amount of organic matter in the soil
- This is usually reported in terms of % Organic Matter, which is the percent of the soil which is composed of organic matter

The Convention of “like dissolves like” holds for Pesticide Interactions with Organic Matter in Soil.

Nonionic (noncharged or neutral) pesticides escape from soil solution into the hydrophobic interior and a pesticide equilibrium is set up between organic matter and soil solution

Pesticides move between organic matter and water in soil:

- Pesticides that are water soluble tend to remain at the surface of soil organic matter
- Pesticides that are insoluble tend to penetrate to the hydrophobic interior

Organic Matter and Pesticide Transfer

- The amount of pesticide sorbed is largely a function of the total amount of organic matter (sorption regions) in the soil and the pesticide’s water solubility
- Pesticides strongly sorbed to soil particles travel primarily with eroded soil to enter surface water
- Weakly sorbed pesticides that are more water soluble may be released into soil water solution and enter surface water as runoff

What is Organic Matter?

- Substances of or derived from plant or animal matter, as opposed to inorganic matter derived from rocks and minerals
- Characterized by its carbon-hydrogen structure
- Typically highest at the surface of a soil and decreases with depth

What is Organic Matter? (continued)

- Much organic matter (humus) is made up of a series of organic polymers (long chains or mats of molecules)
- Consists of two systems:
  - hydrophilic (water-loving) surface
  - hydrophobic (water-hating) interior

Organic Carbon (OC)

- A measure of organic matter present in aqueous solution, suspension, or bottom sediment
- May be reported as dissolved organic carbon (DOC), particulate organic carbon (POC), or total organic carbon
- Many of the models require % Organic Carbon instead of % Organic Matter as an input parameter for each soil layer
- % Organic Carbon can be estimated from % Organic Matter by:

  % Organic Carbon = % Organic Matter/1.72

Kd and K_{OC}

- Adsorption (binding) tests are performed on soils of several textural classes prior to pesticide registration
- The soil/water equilibrium partition coefficient (Kd) can be used to estimate the adsorbed fraction for any chemical
- The organic carbon normalized soil/water equilibrium partition coefficient (K_{oc}) is preferred for pesticides for which there is a strong positive correlation between the organic carbon and rate of adsorption
- Kd value and the organic carbon content of the soils on which the adsorption tests were performed. If there is no correlation, use of the Kd is preferable.
- Kd and K_{OC} are correlated with water solubility
- Units are L/kg

K_{OC} - Octanol/Carbon Partitioning Coefficient

- K_{OC} basically is an indicator of whether a pesticide “prefers” to remain dissolved in soil pore water or sorb to organic carbon on the soil particles in a soil profile
- K_{OC} can be estimated from a pesticide’s water solubility by

  $$\text{Log } K_{oc} = 3.64 - (0.55 \times \text{Log SOL})$$

  where SOL = water solubility, mg/L
- Direct K_{OC} values are usually available from laboratory data

Relationship between Kd and K_{OC}

The relationship between Kd and K_{OC} is estimated as follows:

- Kd = (%Organic Carbon * K_{OC}) / 100.0
- Note: Most adsorption/desorption modeling assumes that adsorption/desorption occurs in chemical equilibrium as a linear function
- Some models can perform non-linear adsorption/desorption
- Care needs to be taken when parameterizing these models since this is a function of a user-supplied fraction of pesticide available for instantaneous desorption and a user-supplied rate of desorption
- Both of these parameters require lots of data to estimate

Pesticide Concentration in Soil and Kd/K_{OC}

The relationship between Kd and K_{OC} is estimated as follows:

- The pesticide residues flow through the soil profile dissolved in rain and irrigation water
- Residues sorb to soil particles as a function of K_{OC} (or Kd) and the % Organic Carbon in soil

Let Cw = concentration of pesticide in soil pore water

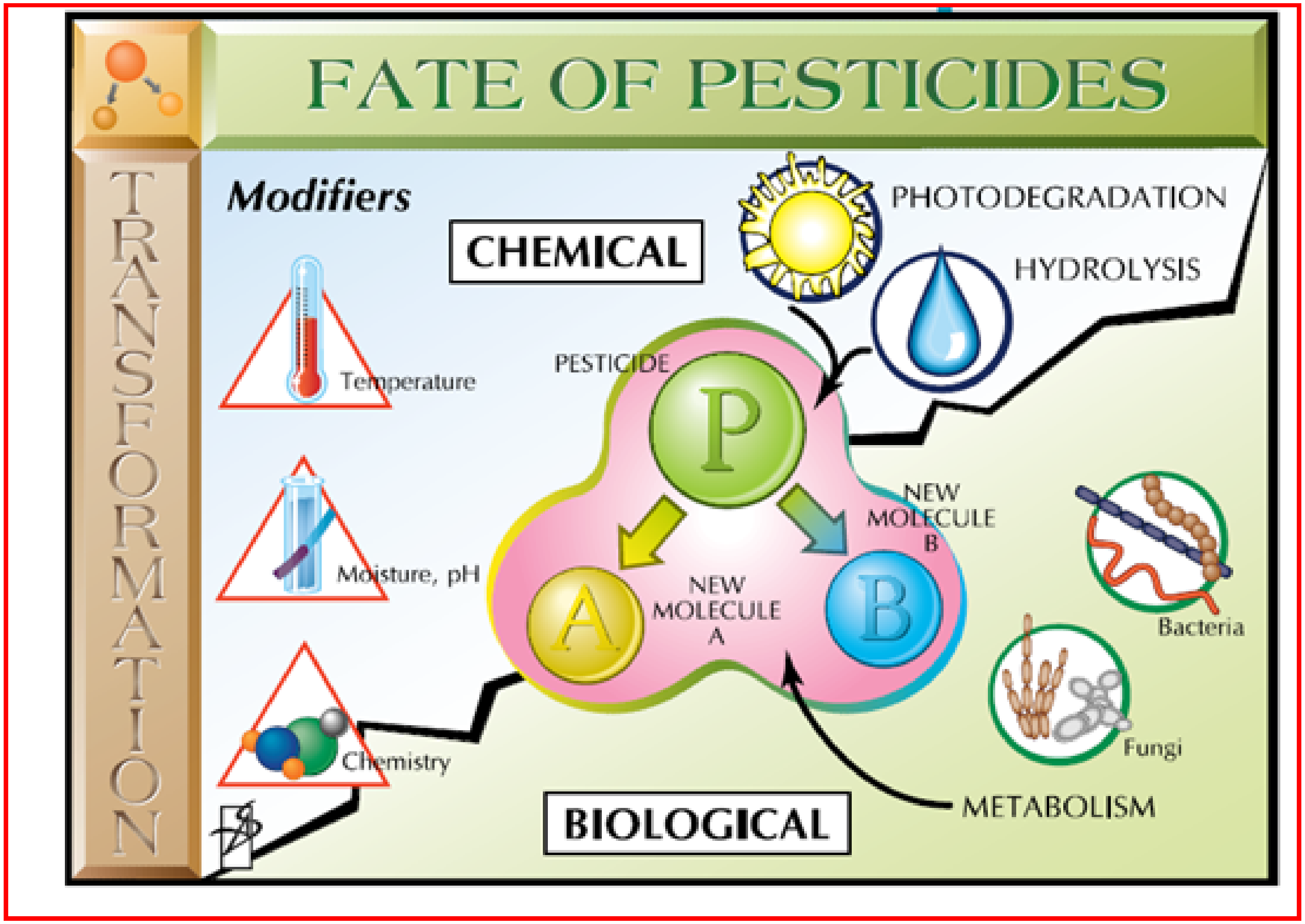
Cs = concentration of pesticide sorbed to soil

Cs = Cw * Kd

or

Cs = Cw * (% Organic Carbon * K_{OC}/100.0)

Pesticide Degradation



Pesticide Degradation

Pesticide degradation is usually simulated using First Order Degradation Equation

- Remember from calculus

$$C_0 = C_{1/2}\, e^{(-kt1/2)}$$

$\rightarrow$ $\ln(C_{0/}\, C_{1/2}) = \ln(e^{(-kt_{1/2})})$

$\rightarrow$ $\ln(0.5) = -k\ \ t_{1/2}$

$\rightarrow$ $-\ln(0.5)/t_{1/2} = k$

Where

C_0 = Initial Concentration

$C_{1/2}$ = ½ of Initial Concentration

$t_{1/2}$ = time needed to reach ½ of Initial Concentration

k = half-life degradation rate

Types of Degradation of Pesticides

In the core studies for pesticide regulation, several degradation processes are measured, including:

- Soil photolysis
- Aerobic soil metabolism
- Anaerobic soil metabolism
- Hydrolysis
- Aqueous photolysis
- Aerobic aqueous metabolism
- Volatility

Photolysis

- Chemical decomposition induced by light or other radiant energy
- Involves the breakdown of organic pesticides by direct or indirect energy from sunlight
- Light energy can be absorbed by the pesticide or by secondary materials (e.g., organic matter) which become ‘activated’ and, in turn, transfer energy to the pesticide
- In either case, pesticides absorb energy from sunlight, become unstable or reactive, and degrade

Photolysis (continued)

- Photolysis can occur in water, in air, or on surfaces such as soil or a plant leaf
- Photolytic reactions occur near the surface of the ground (in the top few hundredths of an inch) or near water surfaces, where light can penetrate
- Soil photolysis is a measure of the degradation rate of pesticides in surface soil due to light decomposition
- Water photolysis is a measure of the degradation of pesticides in surface water due to light decomposition
- Soil and water photolysis half-lifes are usually obtained from laboratory data

Microbial Degradation

The transformation process that results when soil microorganisms (bacteria and fungi) either partially or completely metabolize (break down) a pesticide.

- In the presence of oxygen it is termed aerobic metabolism
- In the absence of oxygen it is termed anaerobic metabolism

Aerobic Metabolism Degradation

- Normally transformed into carbon dioxide and water
- Process of microbial degradation that takes place in the root zone of soils and surface water

Anaerobic Metabolism Degradation

- Microorganism degradation may produce additional end products such as methane
- Microorganisms using anaerobic metabolism for breaking down pesticides are typical in:
  - waterlogged soils in terrestrial systems
  - bottom sediments of ponds, lakes, and rivers
  - groundwater
  - soil profile

Modeling Uses of Aerobic and Anaerobic Metabolism Values

- Laboratory studies are conducted separately for aerobic soil metabolism, aqueous aerobic metabolism, and anaerobic soil metabolism
- Typically:
  - aerobic soil metabolism half-life is used to simulate degradation of pesticide in the field
  - aqueous aerobic metabolism half-life is used to simulate pesticide degradation in the water column of a water body
  - anaerobic metabolism half-life is used to simulate pesticide degradation in the benthic sediment of a water body. May also be used to simulate degradation in the field soil horizons below the root zone

Lumped Parameters (Wikipedia.com)

- **Lumped parameters** are a simplification in a mathematical model of a physical system where variables that are spatially distributed fields are represented as single scalars instead
- A good example of a lumped parameter model is the representation of an electrical network, graphically represented by a circuit diagram in which voltages are assigned to the vertices and currents to the edges of the diagram. The mathematical analyses of such a circuit model is much simpler than solving the Maxwell equations for the actual physical system
- Another example of a temperature field is replaced by average temperatures. It can be a reasonable approach if the system is homogeneous enough

Lumped Parameters (continued)

- Aerobic and anaerobic metabolism half-lifes are examples of lumped parameters
- In the laboratory studies, total pesticide residues are obtained from combined soil and water. Loss of residues is counted as degraded residues. Degradation rates are based on the ratios of the remaining total residues to the initial total residues applied to the test system
- There is no way of knowing what the independent half-lives in water versus soil are from the laboratory studies. Thus, we usually assume that the half-life is the same in both media. In other words, the metabolism studies generate “lumped” half-life estimates for the water and soil

Hydrolysis

- A process by which a pesticide reacts with a water molecule
- Hydrolysis reactions generally substitute an hydroxyl (OH) group from water (HOH or H_20 is the chemical structure of water) into the structure of the pesticide, displacing another group
- Reaction with water breaks apart the molecule, and the extent of breakdown is pH dependent
- Hydrolysis studies are part of the core pesticide registration studies. Results are generally reported for pH5, pH7, and ph9. These are the values used in modeling

Volatilization

- A process whereby a solid or liquid evaporates into the atmosphere as a gas
- The process provides a significant pathway of transfer for a few pesticides. In principle, volatilization is an escape mechanism
- Compounds with high vapor pressure and low water solubility have a tendency to volatilize
- The tendency of a pesticide to volatilize from water is approximated by the ratio of its vapor pressure to its aqueous solubility
- The same is partially true for soils, but the tendency for a pesticide to volatilize from soil also can be inversely proportional to its potential to bind to soil

Volatilization (continued)

- Environmental factors that tend to increase volatilization include:
  - high temperature
  - low relative humidity
  - air movement
- A pesticide that is tightly sorbed to soil will have a lower solution concentration and be less likely to volatilize
- Volatile pesticides usually are incorporated (plowed into the soil) after application to reduce loss into the atmosphere

Volatilization (continued)

- Vapor pressure and Henry’s Law Constant are typically used to estimate volatility in the models
- Vapor pressure is part of the physical property studies submitted for registration of a pesticide

Henry's Law Constant

Definition of Henry's Law (Wikipedia):

- "The solubility of a gas in a liquid is proportional to the pressure *of that gas* above the liquid."
- For modeling, Henry's Law Constant can be estimated using the following:

Henry's Law Constant (atm-m^3/mole)=

$$\frac{\text{Vapor Pressure (Torr)}/760.0}{\text{Solubility (mg/L)}/\text{Molecular Weight (g/mole)}}$$

Toxicologically Significant Metabolites

- Pesticides can also degrade to “daughter” products that have pesticide activity or are “toxicologically significant”
- Toxicologically significant metabolites are metabolites that comprise >= 10% of the parent compound
- Unless toxicology tests are conducted separately for these metabolites, these are assumed to have the same levels of concern as the parent. When modeling, concentrations of these metabolites are usually added to the concentration of the parent on a parent equivalent basis

Modeling Metabolites

- Many of the models have the ability to simulate simultaneous formation and decay of parent compounds to metabolites
- Estimating the rate of transformation from parent to metabolite and degradation of the metabolite can be difficult and depends on amount of time-dependent data you have. Also requires non-linear regression and kinetic techniques to estimate transformation and decay rates
- Generally, toxicologically significant metabolites are simulated as independent chemicals. Rate of application is set to peak percent of parent compound times application rate of the parent compound

Pesticide Application Modeling Parameters

Generally are:

- Application date
- Application rate (lb ai/A or kg ai/ha)
- Percent off-field drift
- Percent application efficiency
- Pesticide application method

Pesticide Application Methods

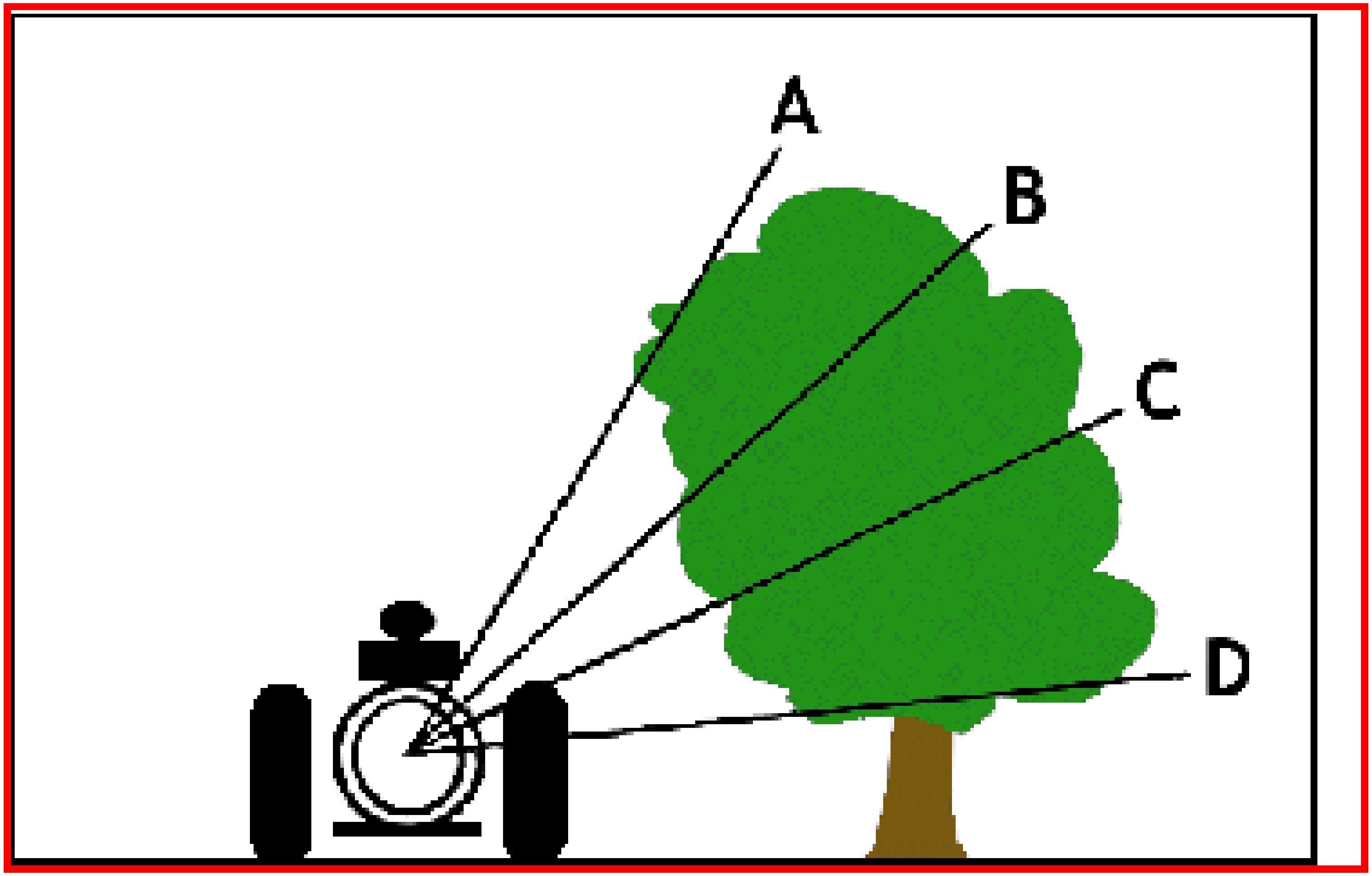
For modeling purposes, these are categorized as:

- Aerial
- Orchard airblast
- Ground – foliar or surface applied
- Soil incorporated – plowed into the soil

Aerial Application Illustration

A crop duster applies a low-insecticide bait on a soybean field.

Orchard Airblast Illustration



Ground Application Illustrations

A Manual Backpack-type Sprayer

Large Self-Propelled agricultural 'Floater' Sprayer, engaged in pre-emergent pesticide application

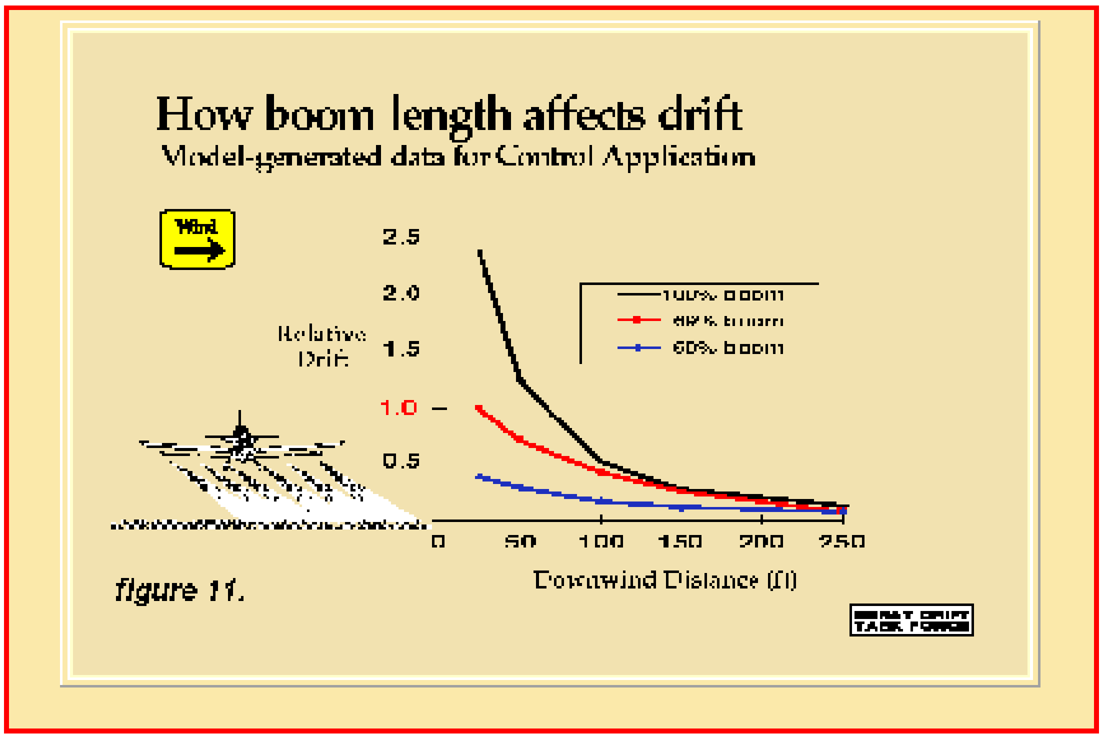
Pesticide Application and Drift

- Drift from application is the major source of surface water contamination resulting from pesticide application
- Highest contamination from aerial application
- Followed by orchard airblast
- Low amount of drift ground application
- Soil incorporated – really no drift, pesticide is buried. Usually simulated as 0% drift
- Off-field drift is a function of release height, nozzle size (which controls droplet size), carrier (water vs. oil), temperature, and humidity

AGDRIFT Model

Drift modeling, i.e., % drift as a function of distance and equipment type, can be performed using the AGDRIFT Model

http://www.agdrift.com/AgDRIFT2/Download.htm



Sources of Environmental Fate Data for Pesticides

- For registered chemicals, if possible, confirm e-fate parameters from EPA RED Documents, FACT sheets, or New Active Ingredient documents. Available at http://www.epa.gov/pesticides/
- Directly from core physical/chemical and environmental fate study reports for pesticide registrations
- Additional sources:
  - USDA-ARS Pesticide Properties Database http://www.ars.usda.gov/Services/docs.htm?docid=14199
  - UC Davis EXTOXNET http://extoxnet.orst.edu/
  - US EPA Pesticide Properties Database http://cfpub.epa.gov/pfate/home.cfm