Non-Crop Vegetation Management Course

Environmental Fate of Pesticides

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Key Points

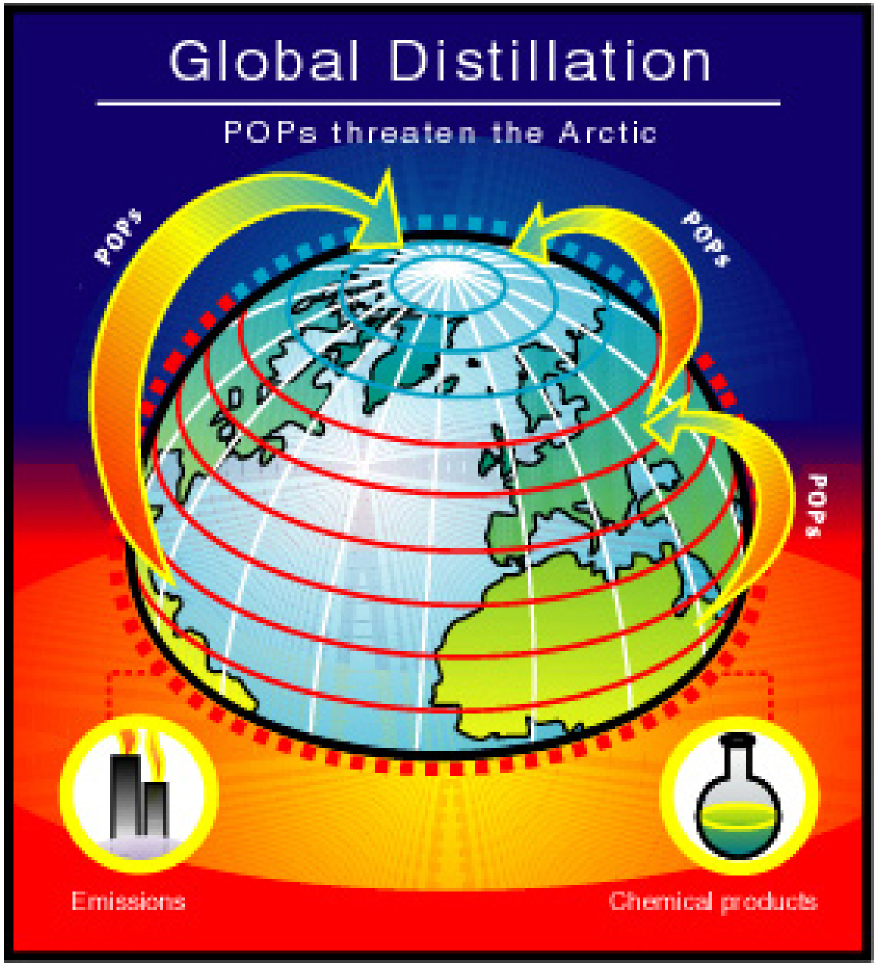
- Characterizing pesticide fate is important to understanding human exposure and the environment
- Pesticide fate is determined by chemical properties and environmental conditions
- Estimating exposure to pesticides relies on existing data, measurements, or models

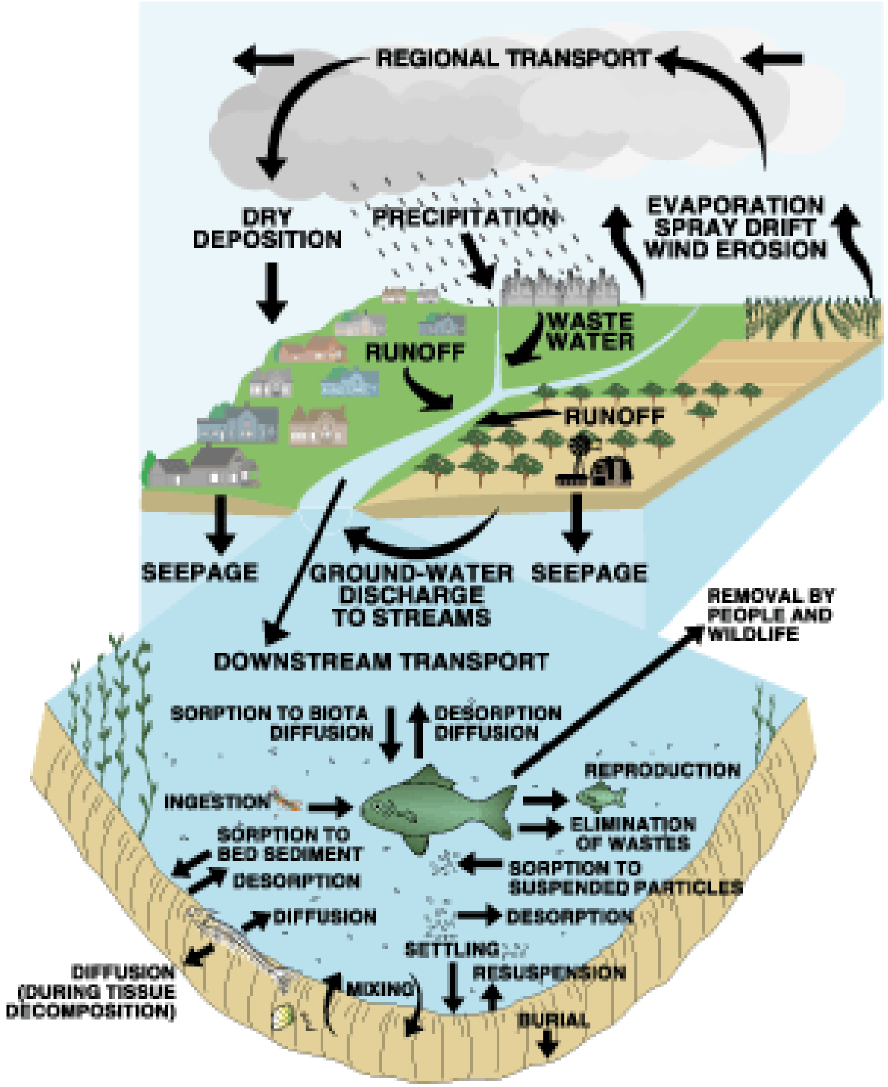
Objectives

- Identify key chemical properties of pesticides and environmental conditions that impact pesticide degradation and transport from the site of application

- Identify resources (**websites**) that identify chemical properties and opportunities to incorporate this information into decision-making processes for pest management

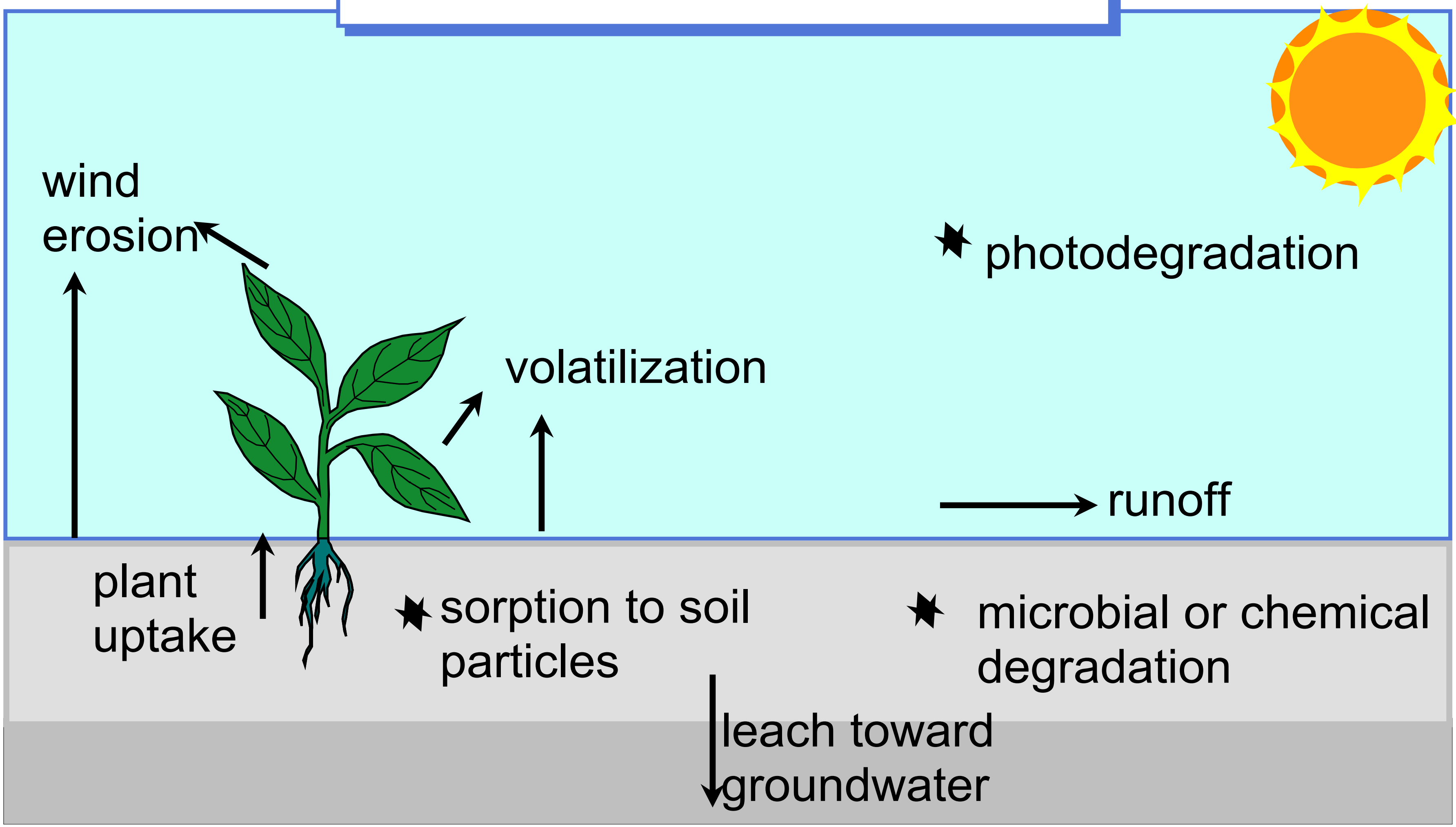
Chemicals in the environment





Source: U.S. Geological Survey

Chemical fate processes



Pesticide fate in the environment

Interactions between pesticides and other molecules
(clues from chemical properties & knowledge of reactions)

↓

Environmental factors
(Temperature, pH, light intensity, water chemistry, microbial activity, natural organic matter, etc.)

↓

Environmental processes
(e.g. air/water exchange, sorption/desorption, chemical, photochemical and biological transformation)

Pesticide fate in the environment

Reactions & Why they are Important?

- Reactions with water, sun (UV), and air
- Biotransformation in soil in the presence and absence of air (oxygen)
- Reactions in soils and water limit the lifetime (and biological effects) of pesticides

Pesticide fate in the environment

Water Solubility

- Ability to dissolve in water -usually expressed in mg/L (parts per million)[a]
  - Low solubility < 50
  - Intermediate solubility 50 - 500
  - Highly solubility > 500
- Determines the tendency for pesticides to move or transfer from water to air, soil, and organisms

[a] See http://sitem.herts.ac.uk/aeru/footprint/en/index.htm for the Henry's Law constants of pesticides

Pesticide fate in the environment

Volatility

- Tendency to go into air phase
- Volatility is a measure of a chemical's tendency to interact with itself (e.g., pesticide formulation) and other molecules like those that make up water and soil organic matter
- Volatility is critical for predicting the tendency of pesticides to move from the site of application to air, water, soil, and plants/organisms
  - Low volatility < $1x\ 10^{-8}$
  - Intermediate volatility $1x10^{-8}$ to $1x10^{-3}$
  - Highly volatility > $1x10^{-3}$

[a] See http://sitem.herts.ac.uk/aeru/footprint/en/index.htm for the Henry's Law constants of pesticides

Pesticide fate in the environment

Movement from Water to Air

- The tendency to move from water to air is estimated using tools based on chemical properties including solubility and volatility

  The Henry's Law constant is the relation between volatility and solubility, the bigger the value the more likely to move to air[a]

- Simple estimations indicate if movement or loss into air will be important (e.g., methyl bromide)

[a] See http://sitem.herts.ac.uk/aeru/footprint/en/index.htm for the Henry's Law constants of pesticides

Pesticide fate in the environment

Tendency to Move into Organic Phases

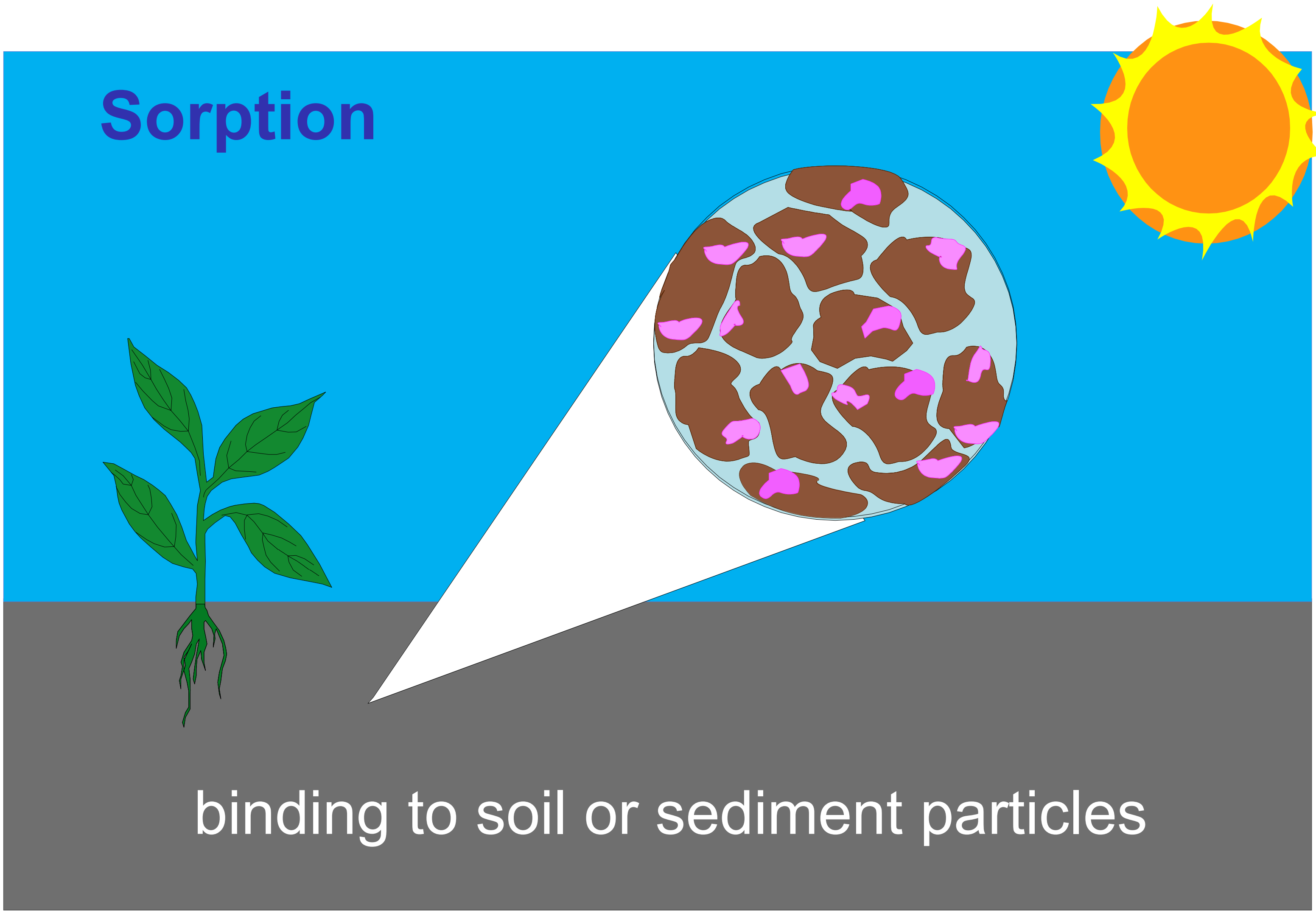
- We have created tools based on ideas borrowed from pharmaceutical science that estimate drug uptake into humans for predicting the movement of pesticides
- Application for estimating bioconcentration by organisms and uptake onto soil and sediment organic matter

Pesticide fate in the environment

Tendency to Move into Soil

- ‘Sorption’ (**stickiness**) is the term to describe the association of pesticides with soil & sediment
- Soil sorption is highly dependent of the soil type and particularly soil organic content
- Generally, soils higher in clay and organic matter have a higher ‘sorption capacity
- Actual measurement of pesticide movement through soil and into groundwater requires expensive field work so estimates of transport potential are often made

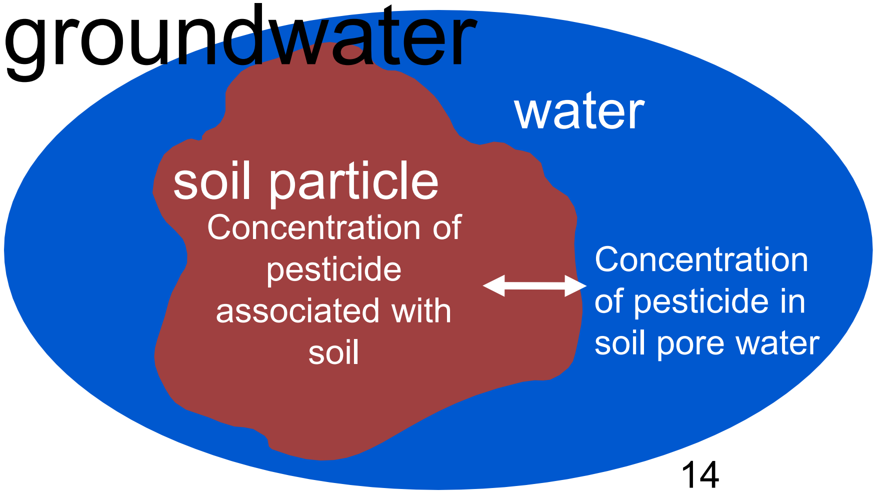
Pesticide fate in the environment



Oregon State University

Pesticides Transport to Groundwater

- Penetration through soil to groundwater occurs when pesticides associate with soil pore water, which is directly related to the chemical property of water solubility[a]
- Soil organic carbon directly impacts pesticides transport to groundwater



[a] See http://sitem.herts.ac.uk/aeru/footprint/en/index.htm for the water solubility of pesticides

Factors influencing pesticide transport

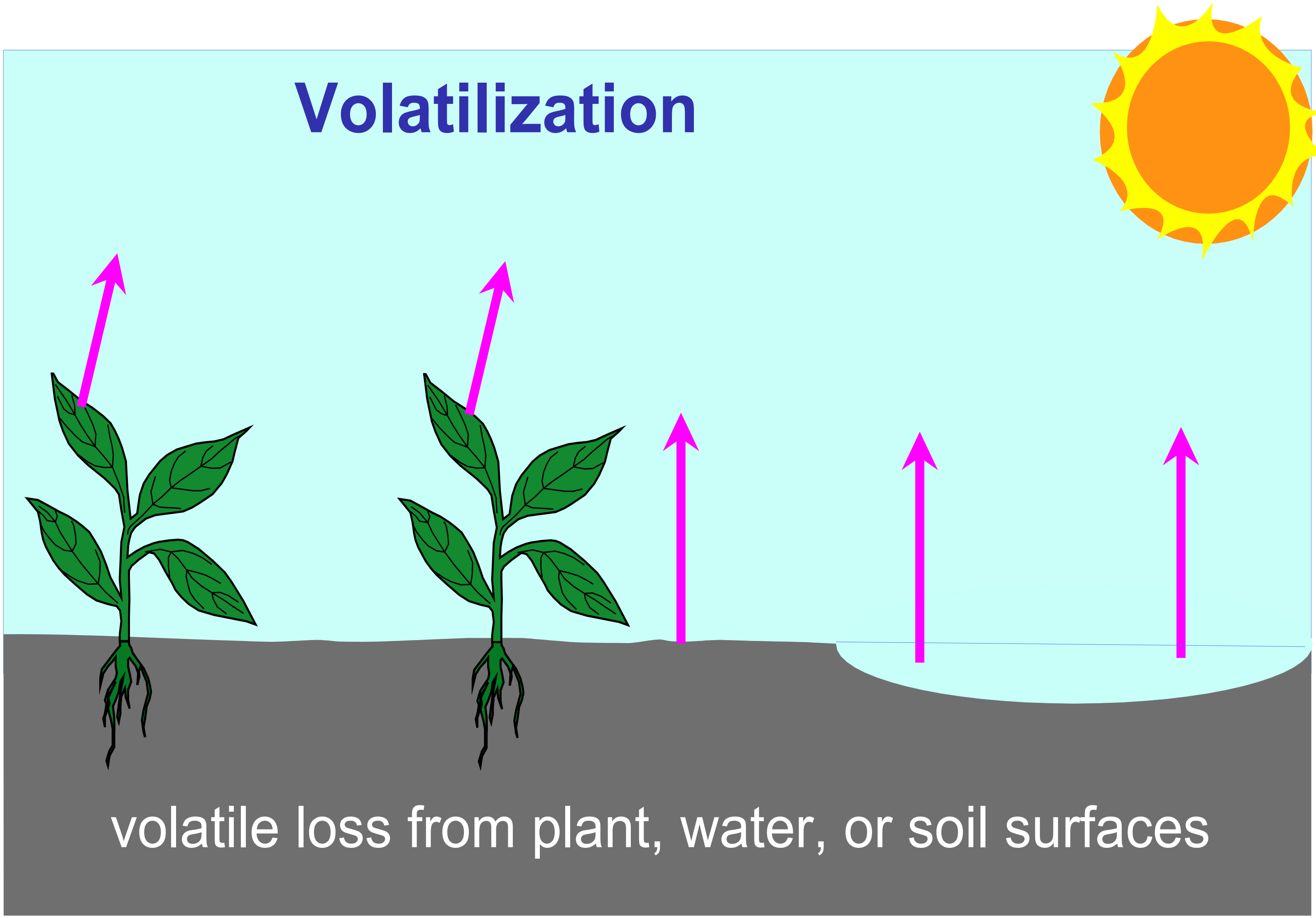
- Organic carbon: water partition coefficients (K_{OC})[a]-
- Organic matter is only a fraction of soil- more OC makes soil retain pesticide**s**
- Organic matter content decreases with depth
- pH 5 to 9 common in Oregon
- Soil/sediment density & porosity
- Preferential flow paths & depth to water table

[a] See http://sitem.herts.ac.uk/aeru/footprint/en/index.htm for octanol water partition coefficients of pesticides and EPA EPIWIN suite for estimates of organic carbon: water partition coefficients (http://www.epa.gov/opptintr/exposure/pubs/episuite.htm)

Pesticides and Runoff

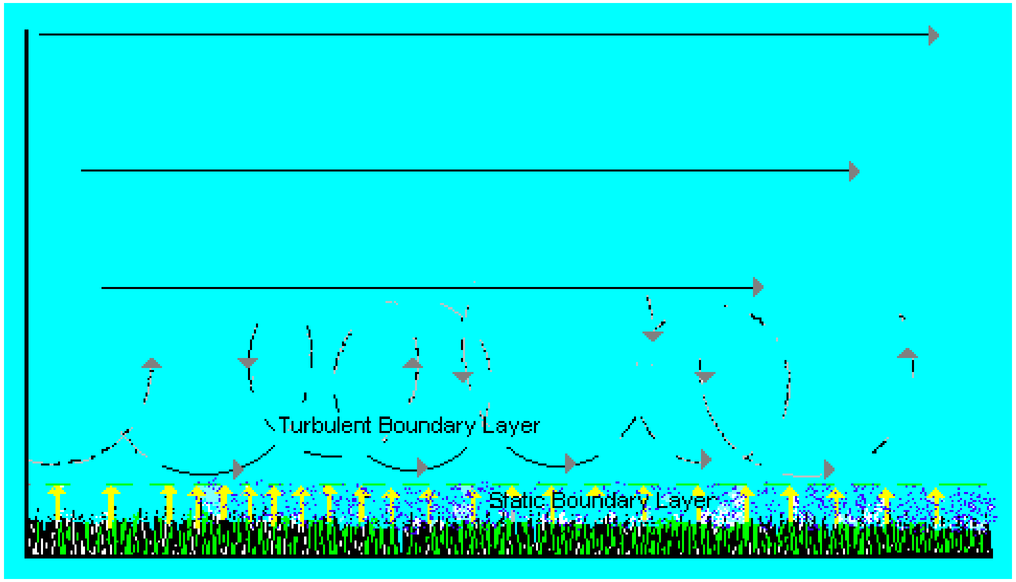
- More of an issue for western Oregon, less of an issue for eastern Oregon
- What does not run into the soil will runoff
- Depends on % field capacity, crop, soil permeability, water table, etc.
- Timing of runoff producing event relative to pesticide application

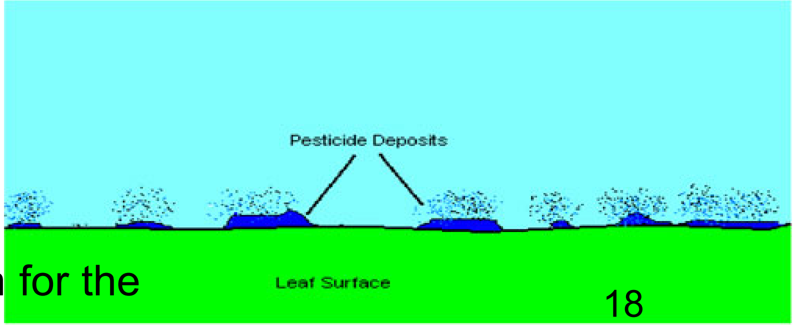
Pesticide fate in the environment



Transport in Air

- **Pesticide volatility indicated by vapor pressure[a]**
  - Low volatility ~ 1x 10^{-8}
  - Intermediate volatility $1x10^{-8}$ to $1x10^{-3}$
  - Highly volatile ~ $1x10^{-3}$
- **Concentrations highest at the ground surface and decrease with height**
- **Pesticides volatilize from leaf surfaces to air but can redeposit on leaf surfaces**
- **Inversion situations keep pesticides close to ground**





[a] See http://sitem.herts.ac.uk/aeru/footprint/en/index.htm for the vapor pressure (in units of mm Hg) for pesticides

Volatile loss from Turf as Percent Applied

Pesticide	Application Rate (kg a.i./Ha)	Volatility (relative scale)	24 hr Volatile loss as % Applied
Chlorpyrifos	1.9	3	17
Ethofumesate	2.5	0.6	6
Triclopyr (acid)	1.1	0.2	5
Triadimefon	3.1	0.06	2
Propiconazole	2.2	0.06	1
Cyfluthrin	0.2	0.004	ND

Results may vary for applications other than turf grass and by time of year

Inversions and Pesticides[a]

- Spraying pesticides during inversions causes damage to other crops and to the environment
- Surface inversions = **cool air near the** earth's surface and temperatures increase with height

[a] http://www.apvma.gov.au/use_safely/spray_drift/inversions.php

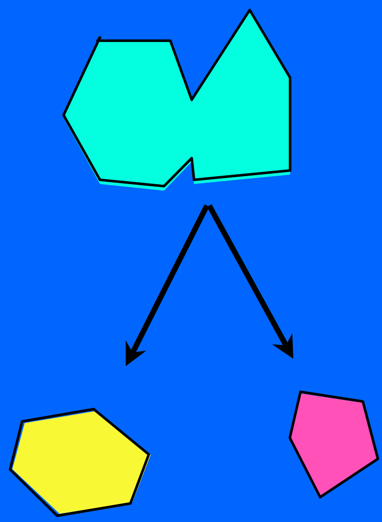
Hazards of Surface Inversions[a]

Surface inversions suppress the dispersion of airborne pesticides so that they:

- **remain at high concentrations** for long periods close to the target
- **travel close to the surface over great distance** (miles) in light breezes
- **move downslope and concentrate into low lying regions** (e.g., Hood River)
- transport in **unpredictable directions**

[a] http://www.apvma.gov.au/use_safely/spray_drift/inversions.php

Degradation Pathways



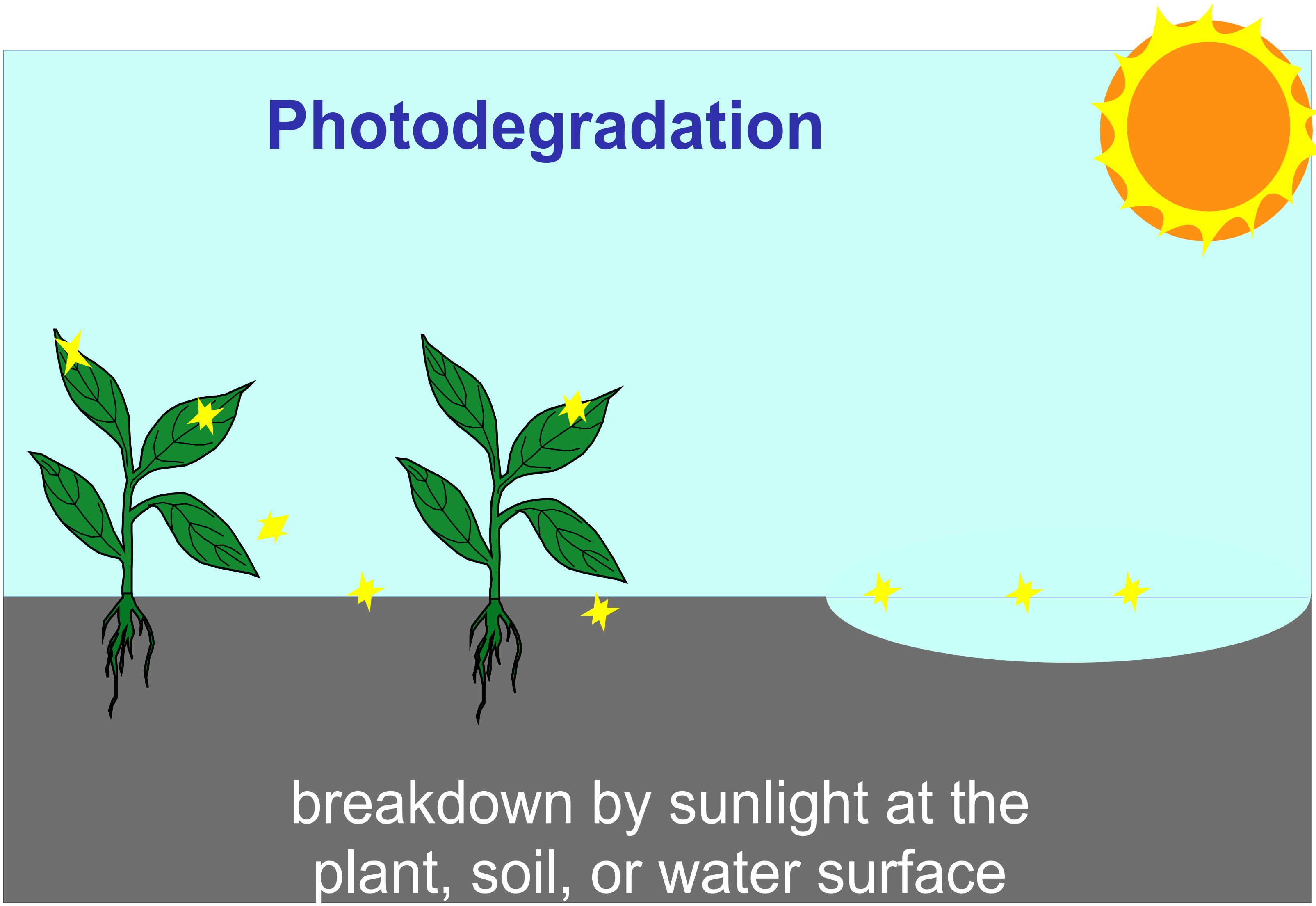
Photodegradation

Chemical degradation

H_2O, O_2, e-

Microbial degradation

Pesticide fate in the environment



Pesticide fate in the environment

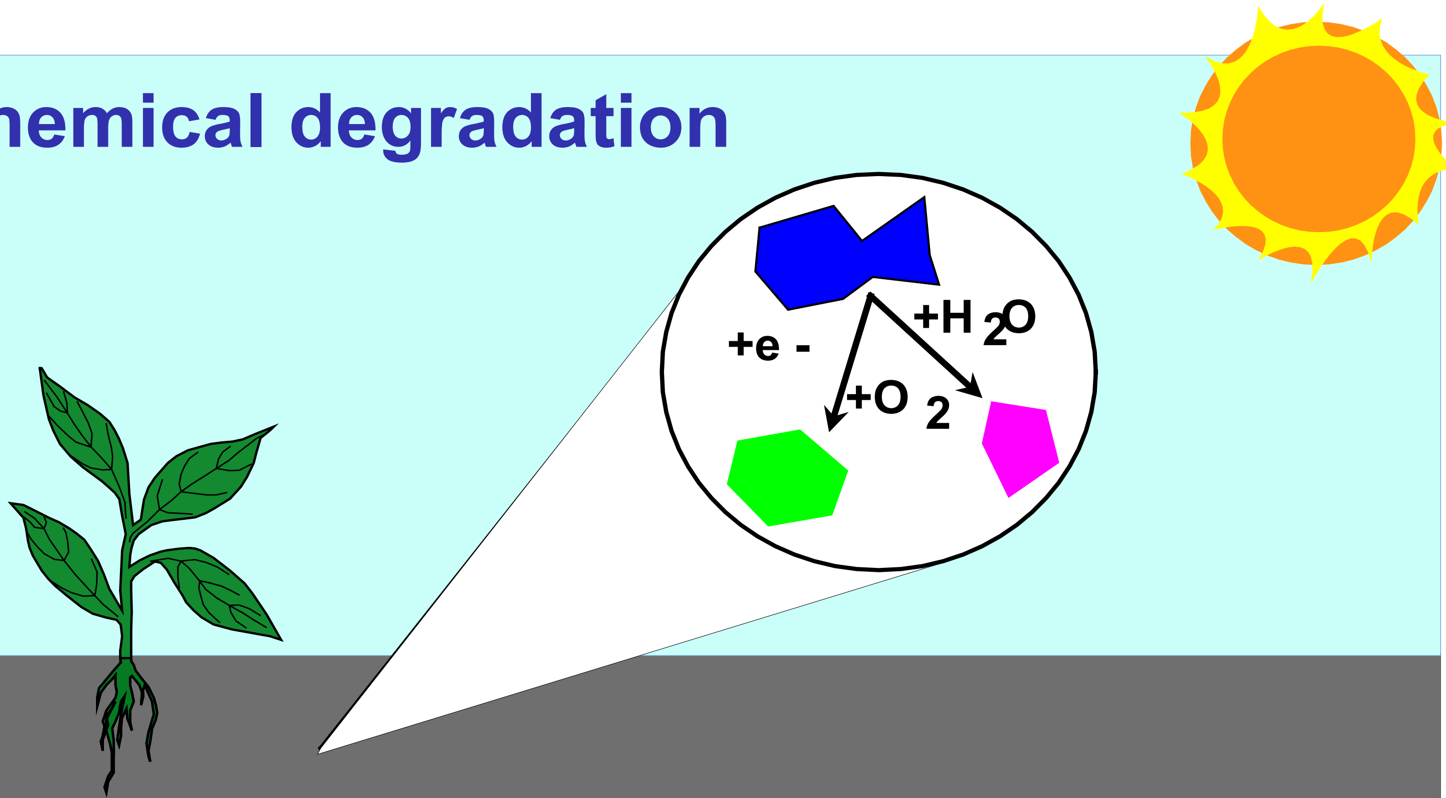
Reactions in Sunlight

- Pesticides absorb light and are directly transformed by the energy from the sun that breaks the pesticide’s chemical bonds

- Many pesticides do not directly absorb sunlight, but are transformed by ‘oxidizers formed by sunlight

Pesticide fate in the environment

Chemical degradation



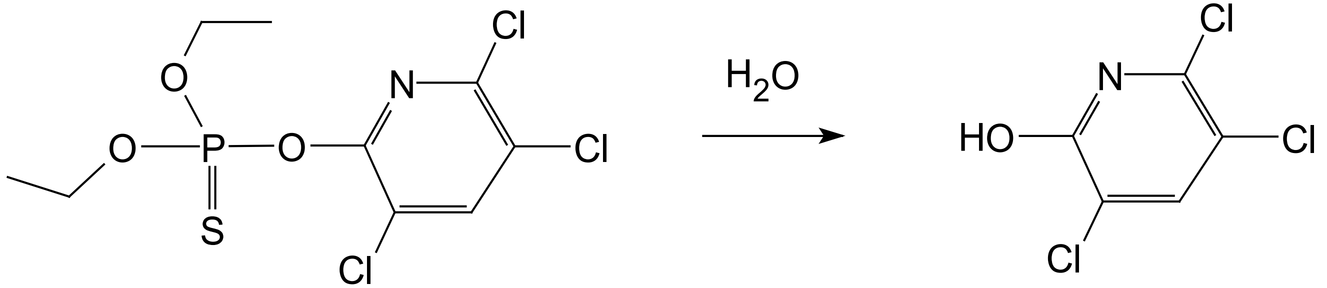
breakdown by processes not involving living organisms (abiotic)

Pesticide fate in the Environment

Reactions with Water

- Breakdown due to reaction water is important for many pesticides
- Changes in chemical structure impact the environmental behavior of pesticide degradation products
  - Degradation products are often more soluble in water, which translates to mobility in soil and sediment (runoff or leaching to groundwater)

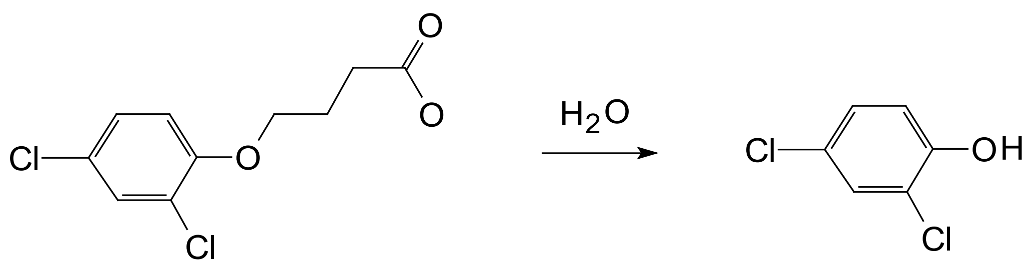
Chlorpyrifos (Dursban) reaction with water



chlorpyrifos

3,5,6 Trichloro-2-pyridinol

2,4-D reaction with water



2,4 D butyl ester

2,4 dichlorophenol

Pesticide fate in the Environment

Factors Impacting Rates of Pesticide Breakdown

- Soil pH influence the rate of pesticide breakdown due to reaction with water
  - pH of soils east of the Cascades ranges from about 5.4 (Union county) to 9.6 (neutral to basic)
- Dissolved organic matter and metal ions
- Temperature
- Tough to generalize- all chemicals are different, like people

Pesticide fate in the Environment

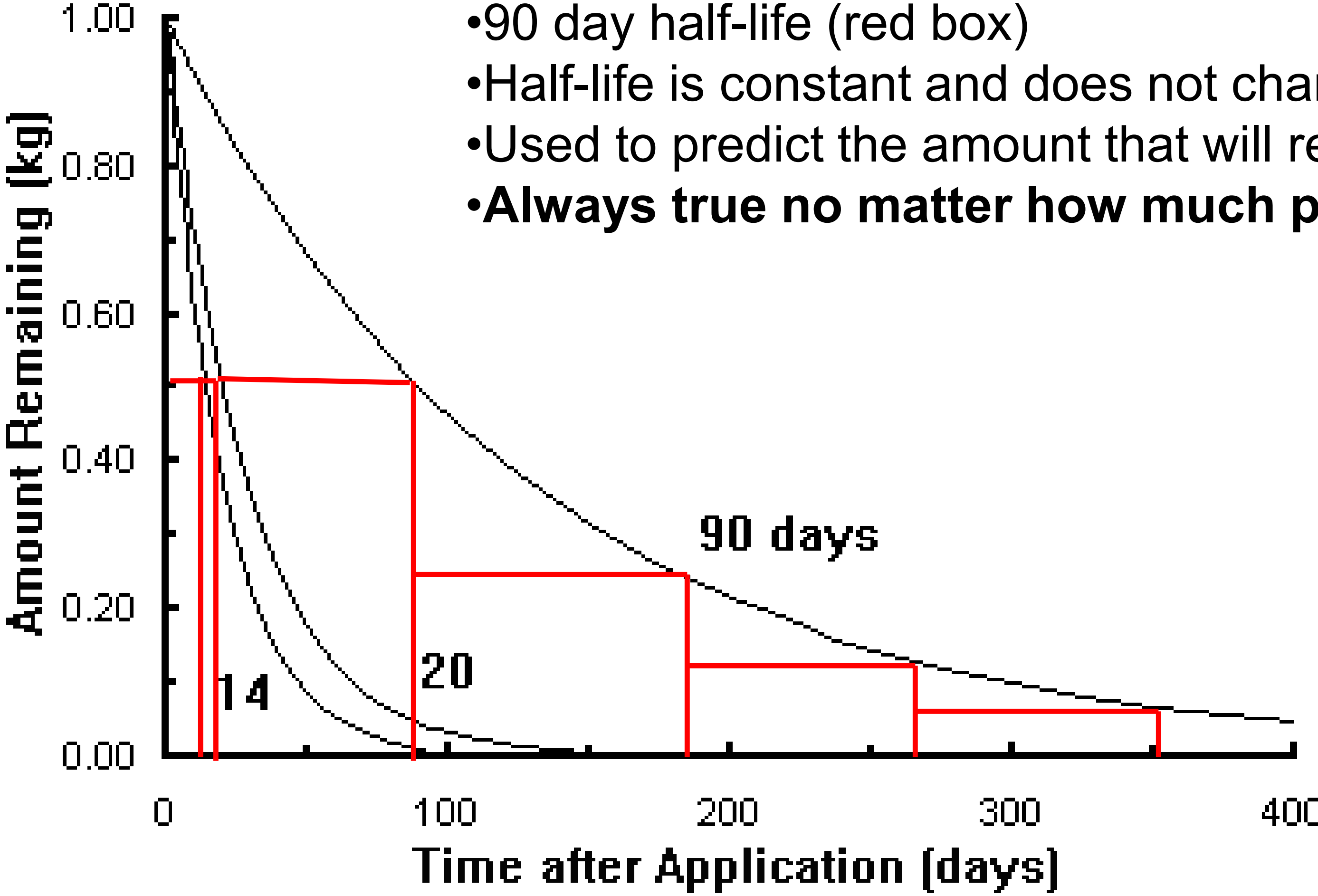
Describing Rates of Pesticide Breakdown

- Half-life is used to describe the time it takes for pesticide breakdown to occur
- Definition of half-life = the amount of time it takes the pesticide to decay to half its original concentration
- Database[a] indicates if half-life values $(DT_{50})_{soil}$ are determined from lab or field studies (aerobic)

[a] http://sitem.herts.ac.uk/aeru/footprint/en/index.htm

Pesticide dissipation half-life

- 90 day half-life (red box)
- Half-life is constant and does not change
- Used to predict the amount that will remain
- **Always true no matter how much present**



Pesticide fate in the Environment

Half-lives of Common Pesticides

2,4 D ester (Grass)	pH 6, $t_{1/2}$ = 4 **yrs** pH 9, $t_{1/2}$ = 37 hrs
Cythion	pH 9, $t_{1/2}$ = 12 hrs
Imidan	pH 7, $t_{1/2}$ = 9.4 hrs pH 9, $t_{1/2}$ = 5.5 min
Fusilade	pH 9, $t_{1/2}$ = 9 hrs
Captan	pH 7, $t_{1/2}$ = 8 hrs pH 9, $t_{1/2}$ = 4 min

The point is that each pesticide is different, some fast others quite slow and depends on pH

Pesticide fate in the Environment

Guthion breakdown (pH 7) with temperature

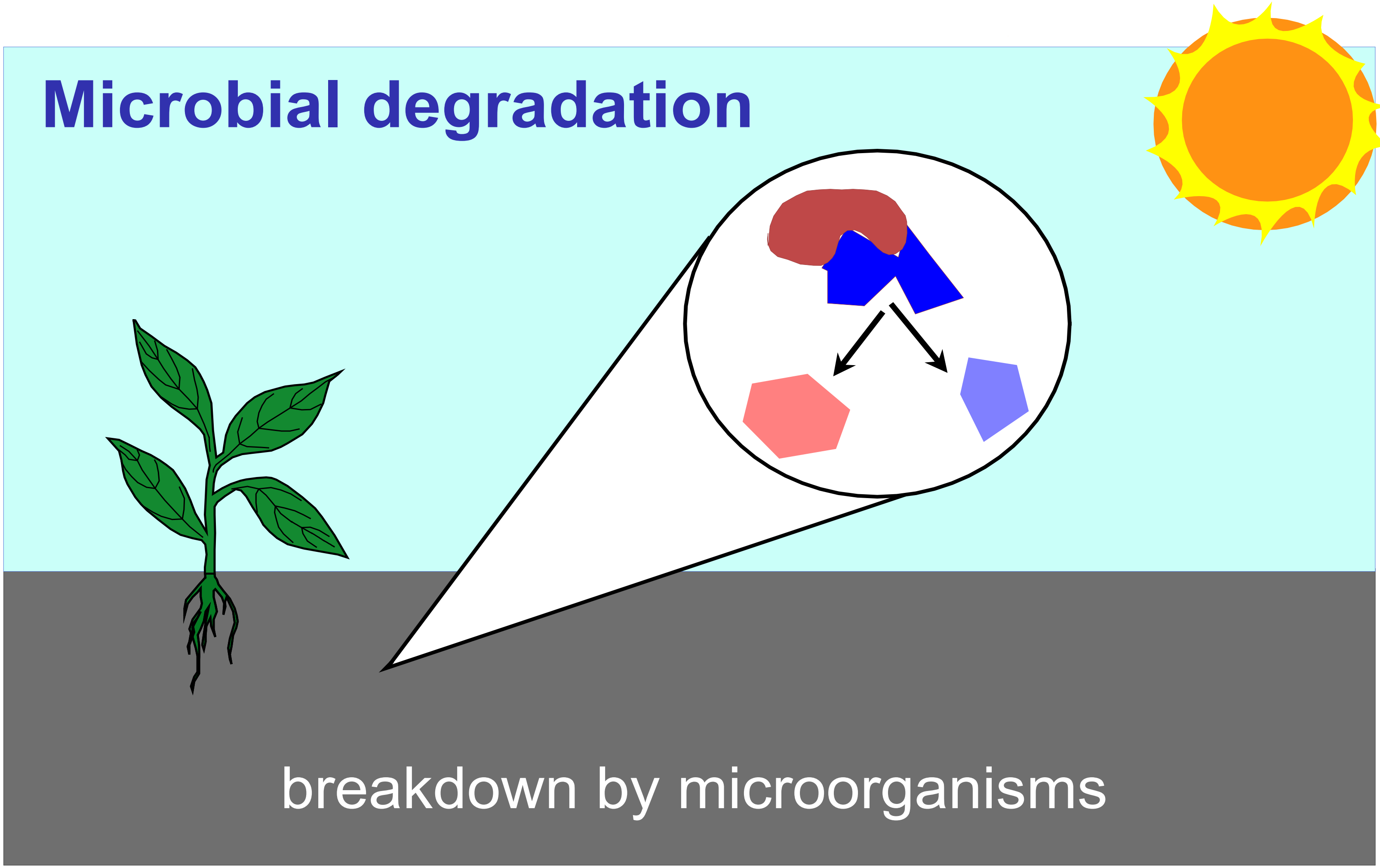
43 ^{o}F = **231** days

77 ^{o}F = **69** days

99 ^{o}F = **17** days

122 ^{o}F = **4** days

Pesticide fate in the environment



Pesticide fate in the environment

Microbial degradation

- Microorganisms (bacteria and fungi) use the pesticide as an energy source for growth
- Pesticides are degraded ‘accidentally’ by organisms – not used for energy- tends to happen when other ‘food’ sources are available (carbon, nitrogen)
- Pesticides molecules link with themselves or with soil components
- Pesticides get incorporated into microorganisms
- Pesticides are degraded due to changes cause by microbial activity

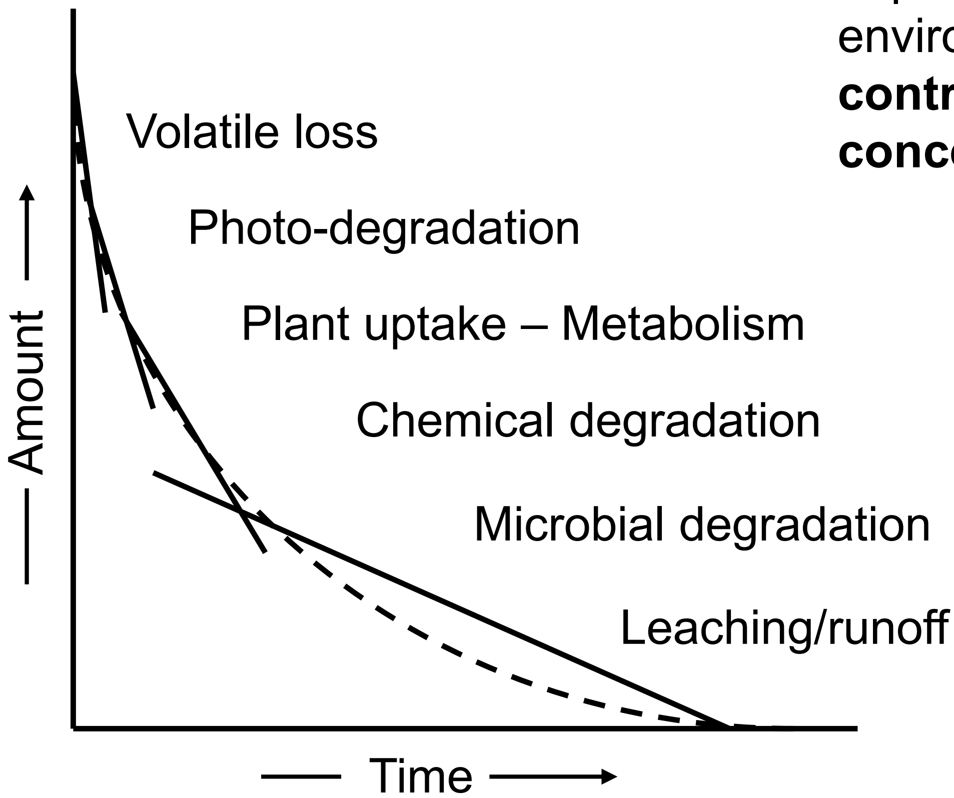
Pesticide fate in the environment

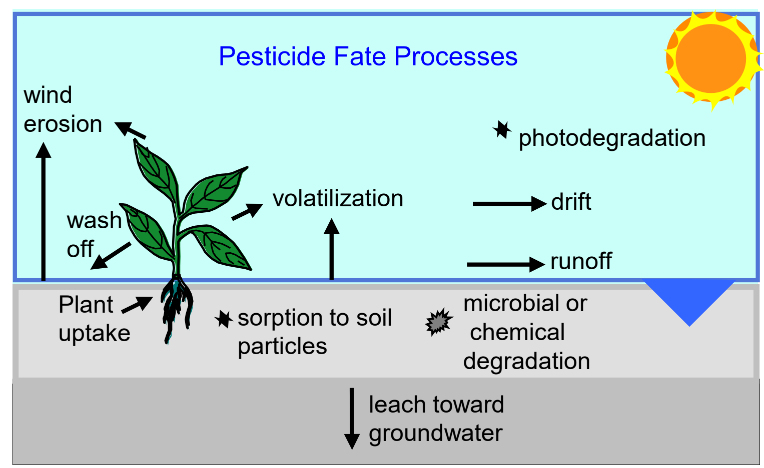
Microbial degradation

- Ideally pesticides are broken down to nontoxic products such as carbon dioxide, water, and minerals (**ideal but not often**)
- Partial breakdown may result in intermediate products that may be toxic – often happens when pesticides are accidentally transformed by microorganisms and not used as a food/energy source (**residues may have biological activity**)
- Rates of microbial degradation are influenced by environmental conditions that that impact microbial growth
  - temperature, pH, oxygen content, moisture, organic matter and nutrients
  - **anything that makes microbial activity greater has the potential to make pesticide degradation faster**

Pesticide Dissipation in the Environment

How fast and which pathway predominates depends on chemical properties and environmental conditions= **all possible contributions help decrease pesticide concentrations**





Forage and Manure

Pesticide application

Pesticide residues

Pesticide residues

Pesticide residues

Bedding, hay, **manure**

Rangeland, pasture, wheat

X Compost

X Crops for human consumption

Oregon Issues

- Picloram damage to trees due to drift; contaminated groundwater in Klamath basin (volatile; GUS=6)
- Oxyfluorfen in fish after truck spill in Gorge (high K_{OC})
- Pendimethalin in groundwater (low GUS!?)
- Terbacil and potential for groundwater contamination (GUS=4.7)
- Diuron in surface water (intermediate GUS=1.8)

Key Properties[1]

Half-life $(DT_{50})_{soil}$=time for pesticide concentration to decrease 50%

<30 = non persistent

30-100 = intermediate persistence

100-355 = persistent

K_{OC} = organic carbon:water partition coefficient (tendency for pesticide to associate with organic matter in soil and plants)

<15 = very mobile

15-500 = mobile to moderately mobile

500 = slightly to non-mobile

GUS- tendency to leach to groundwater

$$GUS = \log_{10}(\text{Half-life}) \times [(4 - \log_{10}(Koc)]$$

> 2.8 = likely to leach

1.8-2.8 = intermediate leachability

< 1.8 = unlikely to leach

[1]Pesticide Properties Database: http://sitem.herts.ac.uk/aeru/footprint/index2.htm

Pesticides Used in Oregon

Crop	Trade name	Common name	Half-life (days)	Koc	GUS	Vapor pressure (mPa)
Right of Way	Tordon	**Picloram-drift**	20-49	20-40	6.0	1.2x10-3
Right of Way	Spike	tebuthiuron	360-1300	40-80	5.5	2.7x10-1
Right of Way	Milestone	**Aminopyralid**	8-35	8	4.8	2.6x10-9
Right of Way	Roundup	glyphosate	12	800-60000	-0.49	1.2x10-3
Grass	Karmex	**Diuron-surf/gw**	20-231	110-810	1.8	1.2x10-3
Grass	Stinger	clopyralid	2-24	5	5.1	1.4
Sugar Beet	Outlook	dimethenamid	3 - 35	140	2.4	3.7x10-1
Sugar Beet	Roneet	cycloate	9-133	130-270	2.8	8.2x10+2

Half-life $(DT_{50})_{soil}$=time for pesticide concentration to decrease 50%

<30 = non persistent

30-100 = intermediate persistence

100-355 = persistent

K_{OC} = organic carbon:water partition coefficient (tendency for pesticide to associate with organic matter in soil and plants)

500 = slightly to non-mobile ('sticky')

15-500 = mobile to moderately mobile

<15 = very mobile

GUS- tendency to leach to groundwater GUS = $\log_{10}$(Half-life) x [(4 - $\log_{10}$(Koc)] the larger Koc (stickier to organic carbon) the more GUS increases

< 1.8 = unlikely to leach

1.8-2.8 = intermediate leachability

> 2.8 = likely to leach

Vapor pressure > 1 x10^{-3} indicates volatility and potential for drift

How Do We Assess Risk?

Hazard Identification

- What are the toxicological effects (endpoints)?
-

Dose-Response Assessment

- At what dose level do the effects occur?

Exposure Assessment

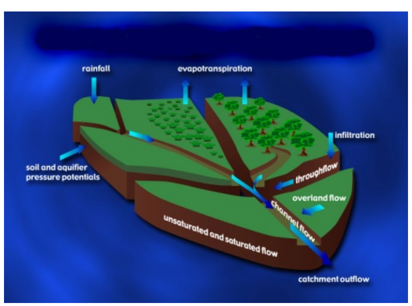
- How much chemical is a person being exposed to?

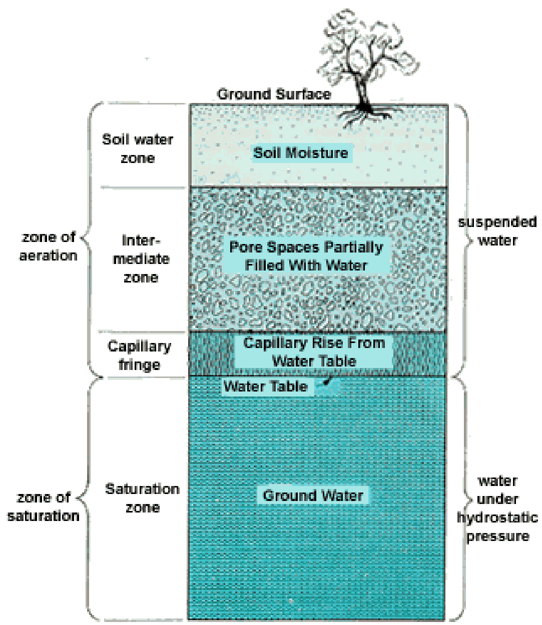
Risk Characterization

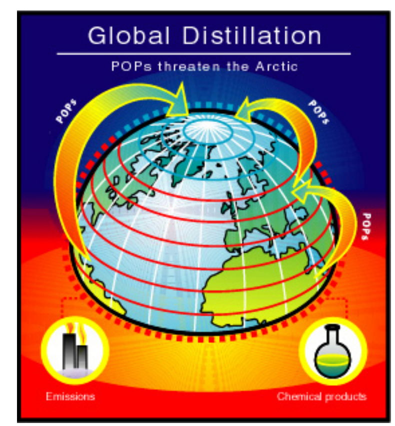
- Combine the hazard, dose-response, and exposure information to describe the overall magnitude of the risk

Environmental Fate Models

- We have models for large and small scales
- Models have large uncertainties
- “All models are wrong, but some are useful.”
- “Useful models are generally right but precisely wrong.”







Summary

- Characterizing pesticide fate is important to understanding human exposure
- Pesticide fate is determined by chemical properties and environmental conditions
- Estimating exposure to pesticides relies on existing data, measurements, or models