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

- Wind erosion
- Volatilization
- Sorption to soil particles
- Microbial or chemical degradation
- Runoff
- Plant uptake
- Leach toward groundwater
- Photodegradation
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

**Volutility**

- 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 > $1x10^{-3}$

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

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

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
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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
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Sorption

binding to soil or sediment particles
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](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 ($K_{OC}$)\textsuperscript{a}
• Organic matter is only a fraction of soil- more OC makes soil retain pesticides
• Organic matter content decreases with depth
• pH 5 to 9 common in Oregon
• Soil/sediment density & porosity
• Preferential flow paths & depth to water table

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

Volatilization

volatile loss from plant, water, or soil surfaces
Transport in Air

- Pesticide volatility indicated by vapor pressure$^a$
  - Low volatility $\sim 1 \times 10^{-8}$
  - Intermediate volatility $1 \times 10^{-8}$ to $1 \times 10^{-3}$
  - Highly volatile $\sim 1 \times 10^{-3}$

- 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

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$^a$ 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

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

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

• 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

Hazards of Surface Inversions

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**

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Degradation Pathways

- Photodegradation
- Chemical degradation: $H_2O, O_2, e^-$
- Microbial degradation
Photodegradation

breakdown by sunlight at the plant, soil, or water surface
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
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Chemical degradation

breakdown by processes not involving living organisms (abiotic)
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**Reactions with Water**

- Breakdown due to reaction with 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

```
O
O
Cl
O
Cl
Cl
O
Cl
H2O
```

chlorpyrifos

3,5,6 Trichloro-2-pyridinol

2,4-D reaction with water

```
Cl
O
Cl
O
Cl
Cl
H2O
```

2,4 D butyl ester

2,4 dichlorophenol
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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
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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
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Half-lives of Common Pesticides

2,4 D ester (Grass)  
- pH 6, $t_{1/2} = 4 \text{ yrs}$
- pH 9, $t_{1/2} = 37 \text{ hrs}$

Cythion  
- pH 9, $t_{1/2} = 12 \text{ hrs}$

Imidan  
- pH 7, $t_{1/2} = 9.4 \text{ hrs}$
- pH 9, $t_{1/2} = 5.5 \text{ min}$

Fusilade  
- pH 9, $t_{1/2} = 9 \text{ hrs}$

Captan  
- pH 7, $t_{1/2} = 8 \text{ hrs}$
- pH 9, $t_{1/2} = 4 \text{ min}$

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 °F = 231 days

77 °F = 69 days

99 °F = 17 days

122 °F = 4 days
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Microbial degradation

breakdown by microorganisms
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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 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.

Pesticide Fate Processes

- Volatile loss
- Photo-degradation
- Plant uptake – Metabolism
- Chemical degradation
- Microbial degradation
- Leaching/runoff

- Wind erosion
- Drift
- Volatilization
- Sorption to soil particles
- Microbial or chemical degradation
- Leach toward groundwater

Amount

Time
Forage and Manure

Pesticide application → Pesticide residues

Bedding, hay, manure → Pesticide residues

Rangeland, pasture, wheat

Compost

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

Half-life \( (DT_{50})_{\text{soil}} \) = 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

\(^1\text{Pesticide Properties Database: http://sitem.herts.ac.uk/aeru/footprint/index2.htm}\)
# Pesticides Used in Oregon

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

**Half-life (DT50)soil** = time for pesticide concentration to decrease 50%

- <30 = non persistent
- 30-100 = intermediate persistence
- 100-355 = persistent

**Koc** = 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** = log10 (Half-life) x [(4 - log10 (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** > 1x10^-3 indicates volatility and potential for drift
How Do We Assess Risk?

- What are the toxicological effects (endpoints)?
- At what dose level do the effects occur?
- How much chemical is a person being exposed to?

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