Pesticide Fate and Transport
(a.k.a. Where do pesticides go in the environment?)

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ECS 3119 - Pesticides and Fish and Wildlife Resources
Stevenson, WA
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Fate and Transport

• Where and how does a pesticide move in the environment?
  • Major routes of transport
  • Major environmental compartments in which the pesticide resides
Pesticides in the Environment

- Housed in one of 4 major environmental compartments.
Fate and Transport Processes

• Abiotic and biotic processes within a system
• Pesticides move and reside in a predictable manner based on their physical and chemical properties
Pesticide fate processes

- Wind erosion
- Volatilization
- Plant uptake
- Sorption to soil particles
- Microbial or chemical degradation
- Leach toward groundwater
- Runoff
- Photodegradation
Major Determinants of Pesticide Transport

- **Pesticide Application Methods**
  - **Form**: End-use product; major formulations; adjuvants; tank mix
  - **Application**: Maximum proposed rate; frequency; and timing; method
AERIAL DRIFT

APPLICATION FACTORS/ CONDITIONS INFLUENCING DRIFT

• high application height
• droplet sizes <200 µm
• high winds
• lack of thatch or vegetative cover
• high wind shear or pressure &/or small droplet size
Wind

low temperature
high relative
humidity

high temperature
low relative
humidity
Drift from Broadcast Methods: Fixed Wing > Helicopter > Air blast > Chemigation > Ground Spray

Drift is typically 15x greater at 25 ft from treatment site by fixed wing vs. ground boom
Major Determinants of Pesticide Transport (cont.)

- **Site Characteristics**
  - **Site description**: geographic/physical location, landscape/watershed location, slope/gradient, overall topography and hydrology
  - **Soil characteristics**: physical/chemical properties, description, classification
  - **Weather**: temperature, precipitation and irrigation (historical, actual), overall climate
  - **Management**: crops grown, pesticide usage (especially similar pesticides), crop/agronomic management history
  - **Catastrophic events**: prone to flooding or fire
Major Properties that Determine Fate

- **Physicochemical Properties**
  - Solubility (Water)
  - Volatility (Air)
  - Adsorption/Leachability (Water/Soil/Sediment)
  - Partitioning/Bioaccumulation (Biota & Soil)
  - Persistence/Degradation/Dissipation (All)
Connectivity of Aquatic Landscapes

Persistence/Degradation/Dissipation

Volutility

Solutebility

Adsorption/Leachability

Partitioning/Bioaccumulation

Figure 1 Movement of pesticides into and through aquatic ecosystems.
**Solubility**: a pesticide’s ability to dissolve in water

<table>
<thead>
<tr>
<th>Mobility Class</th>
<th>Water Solubility (ppm)</th>
<th>Examples (ppm, mg/ L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very High</td>
<td>3,000 – 1,000,000</td>
<td>Diquat 700,000</td>
</tr>
<tr>
<td>High</td>
<td>300 – 3,000</td>
<td>2,4-D 890</td>
</tr>
<tr>
<td>Medium</td>
<td>30 - 300</td>
<td>Carbaryl 40</td>
</tr>
<tr>
<td>Low</td>
<td>2 - 30</td>
<td>Parathion 24</td>
</tr>
<tr>
<td>Slight</td>
<td>0.5 - 2</td>
<td>Ethion 1</td>
</tr>
<tr>
<td>Immobile</td>
<td>&lt;0.5</td>
<td>DDT 0.0012</td>
</tr>
</tbody>
</table>
Solubility - Mobility Relationship

Low solubility ~ immobility ~ hydrophobic

High solubility ~ mobility ~ hydrophilic

Insoluble: < 0.1 ppm
Moderately soluble: 100 to 1,000 ppm
Very soluble: > 10,000 ppm
Factors that Affect Runoff to Surface Waters of Soluble Pesticides

- high rainfall or storm events
- no/sparse vegetation
- heavy irrigation
- saturated soil
- non-pervious soils
- sloped topography
- soil disturbances
- vegetated buffer (grass>shrubs>trees)
- moist soil
- pervious soils
- no or low slope
- no soil disturbances
- no or low rainfall
Pesticide movement in the hydrological system (Barbash and Resek 1996).
Temperatures Influence on Solubility

- Effects on chemical behavior:
  No single pattern, change T in a given direction may $\uparrow$, $\downarrow$, or not change toxicity, but...

  As T $\uparrow$, biodegradation usually $\uparrow$

  As T $\uparrow$, solubility of organics $\uparrow$

  T $\uparrow$ generally $\uparrow$ toxicity if there is an effect
Volatility

The ability to transform into a gaseous state, become a vapor/gas or fume, generally from an aqueous phase.

Fugacity: A measure of the tendency of a substance, often a fluid, to move from one phase to another or from one site to another.
Wind Erosion

Vaporization

Photolysis

Vaporization, Advection

Redeposition

Plant & Plant Part Removal

Metabolism

Degradation

Leaching

Runoff

Vaporization, Redeposition

Wind Erosion

Photolysis

Vaporization, Advection

Redeposition

Plant & Plant Part Removal

Metabolism

Degradation

Leaching

Runoff
**FACTORS FAVORING VOLATILIZATION OR AEROSOL FORMATION OF COMPOUNDS**

**Highly Volatile:**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Volatilization Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trifluralin</td>
<td>high H, VP</td>
</tr>
<tr>
<td>Atrazine</td>
<td>low solubility</td>
</tr>
<tr>
<td>Butylate</td>
<td>low specific gravity</td>
</tr>
<tr>
<td>Quinclorac</td>
<td>low boiling point</td>
</tr>
<tr>
<td>Esters of 2,4-D, MCPA &amp; Triclopyr</td>
<td>high air/soil temperature</td>
</tr>
<tr>
<td>Bensulide</td>
<td>low humidity</td>
</tr>
<tr>
<td>1,3 Dichloropropane</td>
<td>fine, powdery soils</td>
</tr>
<tr>
<td></td>
<td>high winds</td>
</tr>
<tr>
<td></td>
<td>lack of thatch or vegetative cover</td>
</tr>
<tr>
<td></td>
<td>high application height</td>
</tr>
<tr>
<td></td>
<td>droplet sizes &lt;200 µm</td>
</tr>
<tr>
<td></td>
<td>high wind shear or pressure &amp;/or small droplet size</td>
</tr>
</tbody>
</table>
Tendency to Vaporize based on Vapor Pressure Index (=VP*10^7)

- <10 = low
- 10-1000 = moderate
- >1000 = high

Henry’s Law Constant (H or HLC) = VP/ S
Global Long-Range Transport and Deposition

Global Distillation Depends On:

- Volatility (Vapor Pressure, Henry’s Law Constant)
- Hydrophobicity ($K_{ow}$)
- Persistence in the Atmosphere (half-life > 2 days)

Global Importance of Semi-Volatile Organic Compounds

• Wide range of phys-chem properties (VP, $K_{ow}$, HLC) and biodegradability. Vapor pressure less than 10 Pa.

• Potential to partition to/from all environmental compartments (including biota and humans)

• Products of incomplete combustion (PAHs, PCDD/F) and industrial activities (PCBs), *pesticides (DDT, Lindane)*, and commercial products (fragrance materials)

• Historical *(OC pesticides like DDT)* and current use (Polybrominated diphenyl ethers and perfluorinated chemistries) compounds

➢ New focus on volatilization to the atmosphere, atmospheric fate and transport, and deposition from atmosphere to aquatic and terrestrial ecosystems worldwide.
Global Distribution of Pesticides in Tree Bark
Regional Deposition: Canadian Rockies

Growing Evidence: Long Range Transport of Current Use Pesticides

- Less persistent, less volatile, less hydrophobic than traditional organochlorine pesticides
- Important to also look for atmospheric degradation products
- Atmospheric transport during use periods (April – September)
- Markers for North American (regional) sources
Adsorption

- Process by which a pesticide is bound/adhered to a surface via chemical or physical attraction

- **Kd = DISTRIBUTION COEFFICIENT:**
  concentration of chemical sorbed to soil/concentration in aqueous solution
  High Kd = pesticide more strongly sorbed to soil
  Low Kd = pesticide more in solution

- An indication/measure of a pesticide’s leachability

- **Leachable** – the ability of a pesticide to dissolve & move through soils generally via the process of percolation by water.
Conceptual Model

- Applied Pesticide
  - Volatilization
  - Transformations: microbial chemical
  - Leaching
  - Plant Uptake
  - Lateral Flow
  - Sorption / Retention
  - Transformation
  - Spray Drift
  - Surface Runoff
Leachability of Various Soil Types

Gravel > Sand > Sandy Loam > Loam > Silty Loam
> Silt > Clay > Peat

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Grain Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>&lt;2 µm</td>
</tr>
<tr>
<td>Silt</td>
<td>2 to 50 µm</td>
</tr>
<tr>
<td>Sand</td>
<td>50 – 2000 µm</td>
</tr>
<tr>
<td>Gravel</td>
<td>&gt;2000 µm</td>
</tr>
</tbody>
</table>
Partitioning

- $K_{oc}$ - Organic carbon-normalized partitioning coefficient: a measure of a pesticide's differential solubility between the sediment and interstitial (pore) water. [adsorption to organic matter]

- $K_{ow}$ - Octanol/water partitioning coefficient: a measure of the pesticide's differential solubility in organic (octanol) and aqueous (water) solutions. [absorption in lipid]
Pesticide movement to, from and within sediment and aquatic biota in surface waters (Nowell et al. 1999)
Qualitative Mobility Assessment Based on $K_{oc}$

ASTM recommendations (ASTM, 1996)

<table>
<thead>
<tr>
<th>$K_{oc}$</th>
<th>Mobility Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 50</td>
<td>very high</td>
</tr>
<tr>
<td>50 - 150</td>
<td>high</td>
</tr>
<tr>
<td>150 - 500</td>
<td>medium</td>
</tr>
<tr>
<td>500 - 2000</td>
<td>low</td>
</tr>
<tr>
<td>2000 - 5000</td>
<td>slight</td>
</tr>
<tr>
<td>5000 +</td>
<td>immobile</td>
</tr>
</tbody>
</table>

Log $K_{oc}$ is used as an indication of a chemical’s tendency to leach.
### Classification of Chemical Mobility in Soil

<table>
<thead>
<tr>
<th>Mobility Class</th>
<th>Example</th>
<th>$K_{oc}$ in Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very High</td>
<td>Ethylene dibromide</td>
<td>32</td>
</tr>
<tr>
<td>High</td>
<td>Monuron</td>
<td>83</td>
</tr>
<tr>
<td>Medium</td>
<td>Atrazine</td>
<td>170</td>
</tr>
<tr>
<td>Low</td>
<td>Lindane</td>
<td>1,300</td>
</tr>
<tr>
<td>Slight</td>
<td>Trifluralin</td>
<td>3,900</td>
</tr>
<tr>
<td>Immobile</td>
<td>Parathion</td>
<td>10,000</td>
</tr>
<tr>
<td></td>
<td>Chlorpyrifos</td>
<td>14,000</td>
</tr>
<tr>
<td></td>
<td>DDT</td>
<td>240,000</td>
</tr>
</tbody>
</table>

High $K_{oc}$ ~ immobile in soil ~ low leachability

Low $K_{oc}$ ~ mobile in soil ~ high leachability
Octanol-Water Partition Coefficient

\[ K_{ow} \] – ratio of a compound’s solubility in n-octanol and water at equilibrium (on a log scale)

The log Kow is used as an indicator of a chemical's tendency to bioaccumulate

.. so if DDT was dissolved in a beaker of equal volumes octanol and water and you measure:

  3 micrograms / liter in the water phase and
  3 grams / liter in the octanol phase...
$K_{ow} - \text{ratio of solubility in n-octanol and water at equilibrium (on a log scale)}$

**DDT:**

3 micrograms / liter in the water phase and 3 grams / liter in the octanol phase...

$$= 3,000,000 \text{ micrograms / liter}$$

$$K_{ow} = \log \left( \frac{\text{[DDT in octanol]}}{\text{[DDT in water]}} \right)$$

$$= \log \left( \frac{3,000,000}{3} \right)$$

$$= \log (1,000,000)$$

$$= 6$$

$K_{ow}$ for DDT = 6.19
**Application:**

So if DDT is highly lipophilic ($K_{ow} = 6.19$), which of the following would likely be the best to measure to document avian exposure to DDT?

A) feathers

B) adipose

C) excreta (uric acid)
**$K_{ow}$s for a Few Pesticides**

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>$K_{ow}$</th>
<th>Log $K_{ow}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>parathion</td>
<td>$\sim1,000:1$</td>
<td>3.8</td>
</tr>
<tr>
<td>chlorpyrifos</td>
<td>$\sim50,000:1$</td>
<td>4.7</td>
</tr>
<tr>
<td>DDT</td>
<td>$&gt;1,000,000:1$</td>
<td>6.2</td>
</tr>
</tbody>
</table>

High log $K_{ow}$ ~ more hydrophobic ~ more bioaccumulative
Low log $K_{ow}$ ~ more hydrophilic ~ less bioaccumulative
**“BIO” - TERMS**

- **Bioconcentration** - Uptake across the membranes (i.e. through non-dietary routes like the gills) and generally used in reference to waterborne exposures.

- **Bioaccumulation** - Accumulation through the food chain (i.e. consumption of food, water/sediment) or direct water and/or sediment exposure.

- **Biomagnification** - Transfer of chemicals via food chain through two or more trophic levels as a result of the former two processes.
  - Residue levels increase (usually an order of magnitude) from one trophic level to the next.
Organochlorines in the food chain

Organochlorines are transported from agricultural and urban sources through soil erosion, runoff, and precipitation.

Organochlorines accumulate in streambed sediments and in tissues of aquatic invertebrates and fish.
**Bioconcentration Factor (BCF)** - A ratio of the concentration of a chemical in an organism to the concentration in the surrounding medium.

- Most commonly used as a measure of direct partitioning from water to aquatic organisms.

\[
\text{BCF (unitless)} = \frac{[\text{chemical in the organism}]}{[\text{chemical in the water}]}
\]
Fig. 2.25 — Relationship between octanol/water partition (P oct) coefficient and bioaccumulation factor (BCF) in trout muscle. Water quality can be inferred by the accumulation of contaminants in fish tissue.
Persistence

Persistence or Longevity of a pesticide depends upon several factors:

- Degradation of parent compound (stability)
- Environmental conditions (temperature, pH, anaerobic/aerobic habitat, UV light)
  - As T ↑, biodegradation usually ↑
- Dissipation/Volatilization

<table>
<thead>
<tr>
<th>Classification</th>
<th>Half-Life Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-persistent</td>
<td>&lt; 30 days</td>
</tr>
<tr>
<td>Moderately Persistent</td>
<td>&gt; than 30 days, &lt; than 100 days</td>
</tr>
<tr>
<td>Persistent</td>
<td>&gt; 100 days</td>
</tr>
</tbody>
</table>
Dissipation is... simply lose

- Foliar Interception & Dissipation
- Wash off
- Surface Runoff
- Lateral Flow
- Tile Drainage
- Leaching
- Transformations microbial chemical
- Sorption / Retention
- Applied Pesticide
- Plant Uptake
- Volatilization
- Spray Drift
Expression of Persistence: Half-life

Example - Malathion

- Half-Life in Soil: 24 hrs to 6 days
- Half-Life in Water: 1.5 days to 21 wks
- Half-Life in Air: 1.5 days
- Log $K_{OW}$: 2.36 (moderately lipophilic)
- Boiling Point: 156-157 C
- Solubility in Water: 143 ppm at 20 C

Half-life ($t_{1/2}$) is the time required to reduce by half the amount of toxicant in an environmental compartment.
Stability/ Persistence

Bioaccumulation

Lesser

Less

Carbamates and OPs
Malathion
Carbaryl

Greater

More

OCs
DDT
Endrin

<table>
<thead>
<tr>
<th>Persistence</th>
<th>Pesticide</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1 day</td>
<td>Malathion</td>
</tr>
<tr>
<td>&lt;2 days</td>
<td>Lindane</td>
</tr>
<tr>
<td>&lt;3 days</td>
<td>Simazine</td>
</tr>
<tr>
<td>&lt;1 week</td>
<td>Diazinon, Dursban, Azinphos-methyl, Parathion, 2,4-D, Methoxychlor</td>
</tr>
<tr>
<td>&lt;2 weeks</td>
<td>Dichlorobenil</td>
</tr>
<tr>
<td>&lt;3 weeks</td>
<td>Diquat, Endothal</td>
</tr>
<tr>
<td>1 month</td>
<td>Heptachlor, Dieldrin</td>
</tr>
<tr>
<td>4 months</td>
<td>Sodium arsenate</td>
</tr>
<tr>
<td>&gt;5 months</td>
<td>DDT</td>
</tr>
<tr>
<td>&gt;6 months</td>
<td>DDD, Camphechlor</td>
</tr>
</tbody>
</table>
Degradation

The process by which a chemical is reduced to a less complex compound via:

- Microorganisms/Biota (Metabolism)
- Water (Hydrolysis)
- Sunlight (Photolysis)
- Air or Other Agents (Degradates)
Processes of Degradation/Transformation

Structural changes to parent compounds "generally" result in lower toxicity and more hydrophilic secondary products.

- **Reduction**: adding H molecule to reactive group (gain electron).

\[ \text{CCl}_4 \rightarrow \text{CHCl}_3 \]
Chemical Degradation Processes (cont.)

- **Oxidation**: adding or replacing reactive portions of the compound with oxygen (lose electron)

![Chemical structures showing the oxidation process from Parathion to Paraoxon](image-url)
Chemical Degradation Processes (cont.)

- **Hydrolysis**: Adding an OH\(^-\) group to the reactive portion of a compound

![Chemical structure of carbaryl and 4-hydroxy carbaryl](attachment:image.png)
Hydrolysis is an important breakdown pathway for many pesticides, especially OPs, so pH of the water helps determine pesticide persistence.

Pesticide Half-Lives in Weeks at Different Water pHs

<table>
<thead>
<tr>
<th>Insecticide</th>
<th>pH 4.5</th>
<th>pH 6.0</th>
<th>pH 8.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorpyrifos</td>
<td>11</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>Diazinon</td>
<td>0.5</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>Malathion</td>
<td>18</td>
<td>6</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Summary

- Pesticide Water Biota
- Soil/Sediment
- Atmosphere

Solubility

- Vol./VP
- Adsorption/Kd

- Solubility

- Water

- BCF
- K_{ow}

- K_{oc}

- H
Distribution of pesticides among air, surface water, soils, and aqueous sediments based on fugacity calculations (Mackay et al. 1997).
Figure 1  Movement of pesticides into and through aquatic ecosystems.
Assessing Threats to Groundwater and Surface Waters

Detection More Likely:
- High pesticide use
- High recharge
- High soil permeability
- Unconsolidated or karst
- No confining layer(s)
- Dug or driven wells
- Shallow wells
- Wells with leaky seals

Detection Less Likely:
- Low pesticide use
- Low recharge
- Low soil permeability
- Bedrock
- Thick confining layer(s)
- Drilled wells
- Deep wells
- Wells with proper seals
Characteristics of Pesticides Likely to Contaminate Groundwater

**Pesticide Characteristics:**
- Water Solubility $> 30$ ppm (medium to high)
- $K_{oc} < 500$ (mobility medium to high)
- Hydrolysis Half-life $>25$ weeks
- Photolysis Half-life $>1$ week
- Soil Half-life $>2$ weeks

**Field Conditions:**
- Precipitation or irrigation $>25$cm/yr
- Porous/leachable soils that drain quickly (sand)
- Soil pH that promotes chemical stability
Miscellaneous Transport Mechanisms

- clopyralid in urine & manure, remains phytotoxic at 1 ppb
Miscellaneous Transport Mechanisms

Fire → Oust on rangeland → High Winds → Dust → >100,000 acres crop damage
100 farmers, $100,000,000 in claims
(Damage on crops from soil residues of 31 pptr - 11 ppb)
Questions?