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

Volatilization
Leaching
Runoff

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

Transport Phenomena
• Diffusion
• Volatilization
• Runoff & Erosion
• Leaching

(Mass Transfer)

Proportional Disappearance of Pesticides from Soil by Different Pathways

Can We Generalize to Other Contaminants????

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

Volatilization

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

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

Sodergren & Larsson 1982

Jetdrop impacter (ng/cm²)

Surface microlayer (ng/L)

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

Jetdrop impactor (ng/cm²)

Collector

Sediment + PCBs

Sodergren & Larsson 1982

Effect of Sediment Perturbations on Volatilization of PCBs

Spencer 1990
Effect of Droplet Size on Drift Distance

<table>
<thead>
<tr>
<th>Droplet Diameter (microns)</th>
<th>Distance (ft.) in 10 ft fall with 3 mph wind</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

Bode & Butler '81

Effect of Spray Particle Sizes on Downwind Drift Deposition

Ground Sprayer, 45 ft swath
Low Boom Position (~2 ft off ground)

AgDRIFT Modeling

Effect of Wind Speed on Downwind Drift Deposition

Wind Speed
- 5 mph
- 10 mph

Helicopter (Bell)
0.075 lb Al/acre
VMD ~340 µm
5 ft boom ht

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

Runoff & Erosion

 Soil Models for Texture & Moisture Holding Capacity

<table>
<thead>
<tr>
<th>Texture</th>
<th>Coarse</th>
<th>Fine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>(large particles)</td>
<td></td>
</tr>
<tr>
<td>Silt Loam</td>
<td>(small particles)</td>
<td></td>
</tr>
<tr>
<td>Silt Loam</td>
<td>(with macropore)</td>
<td></td>
</tr>
</tbody>
</table>

Runoff

3-10 mm

Weakly Adsorbed
- \( K_w < 50 \)
- may leach or run off

Moderately Adsorbed
- \( 50 < K_w < 500 \)
- high potential for run off

Strongly Adsorbed
- \( K_w > 5000 \)
- runoff loss with saturation

URL: scarab.msu.montana.edu/extension/MT_PAT/Pesticides/environment.ppt
**Only Pesticide in Top Centimeter Is Susceptible To Runoff**

But Amount Moving Is Concentration Dependent

Herbicide in Runoff (water + sediment), mg/L

\[ y = 0.05x^{1.2} \]

\[ R = 0.93 \]

Herbicide in soil, 0 - 1 cm, mg/kg

(Leonard 1990)

**Effect of Rills On Pesticide Runoff**

**Factors Affecting Surface Transport**

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

**Combination of Pesticide Degradation & Aging Reduces Surface Runoff Over Time**

Pesticide in Runoff (µg/L, ppb)

(Leonard 1990)

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

% of Pesticide Lost

Appropriate BMP

- erosion & sediment control
- runoff control & chemical incorporation
- timing, rate formulation additives

**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 \( \approx 0.3 \) mm/sec -- 20 mm/sec

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

Pignatello et al. 1993
Operational Factors Affecting Leaching

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

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

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

- Overhead Sprinkler
- Furrow
- Microirrigation (Surface or Subsurface)