Factors affecting non-point source loads
1. Source level
2. Partitioning in the soil
3. Degradation: microbial, photodecay
4. Leaching – Subsurface Transport
5. Runoff and sediment movement – surface transport
6. Volatilization
7. Plant uptake/Bioconcentration (animal uptake)
8. Chemical oxidation
9. Photo-transformation
10. Hydrolysis

Phase Relationships

<table>
<thead>
<tr>
<th>Mass</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_A = 0$</td>
<td>$V_A$</td>
</tr>
<tr>
<td>$M_w = \rho_s V_s$</td>
<td>$V_s$</td>
</tr>
<tr>
<td>$M_w = \rho_s V_w$</td>
<td>$V_W$</td>
</tr>
</tbody>
</table>

$M_{tot} = M_w + M_s$
$V_{tot} = V_A + V_w + V_s$

Bulk Density = $\rho_b = \frac{M_s}{V_{tot}}$

Water Content
Gravimetric $w = \frac{M_w}{M_s}$
Volumetric $\theta = \frac{V_w}{V_{tot}}$

Chemical transport by surface water
1. Particulate Phase
   - Adsorption to sediment
   - Chemical Solids (crystals or pellets)
2. Dissolved phase
Loading of chemical, $A \Rightarrow Y_A\left(\frac{g}{\text{runoff event}}\right)$

$Y_A = Y_S S_A + \forall C_A$

where

$Y_S = \text{Sediment Yield (Mg (metric tons)/event)}$

$S_A = \text{Adsorbed Chemical Conc. g/Mg = } \mu g/g$

$\forall = \text{Volume Runoff m}^3$

$C_A = \text{Dissolved concentration IN RUNOFF g/m}^3$

**Adsorption Isotherms**

**Adsorption Models ⇒ Isotherms**

1. **Freundlich**: Empirical Relationship

   $S_A = K C_A^{b}$

   where

   $S_A = \text{adsorbed concentration } \mu g/g$

   $C_A = \text{solute concentration } \mu g/cm^3 = g/m^3$

   $K = \text{adsorption coefficient } \left(\frac{cm^3}{g}\right)^{1/3}$

   $b = \text{empirical coefficient}$

2. **Langmuir**: Based on monolayer of chemical at saturation

   $S_A = \frac{ab C_A}{1 + b C_A}$

   $a = \text{empirical value of max possible adsorption (saturation) for the soil (mg/g)}$

   $b = \text{saturation coefficient (empirical) } \left(\frac{m^3}{g}\right)$

**Example** Phosphorus Adsorption

$S_A = \frac{ab C_p}{1 + b C_p}$

$a = \text{function (clay, oc)}$

$a \approx -3.5 + 10.7[\% \text{ clay}] + 49.5[\% \text{ oc}] \quad \text{ (for acid soils)}$

$b = \text{function (clay, oc, pH)}$

$b \approx 0.061 + \left[169,832 \times 10^{-\nu PH}\right] + 0.027[\% \text{ clay}] + 0.76[\% \text{ o.c.}]$

**Fertilizer Application Rate** 90 kg/ha P

Mixed by Tillage to 30 cm

Initial $P = 3.3 \mu g/cm^3$

$P_{added} = \frac{\left(90kg/ha\right)\left(10^5 \mu g/kg\right)10^{-8} (ha/cm^2)}{30cm} = 30 \mu g/cm^3 \quad \text{mass } P\text{ soil volume}$
\[ P_{\text{tot}} = S_p \rho_b + C_p \theta = 33.3 \frac{\mu g}{cm^3} \]

for our soil:
- clay = 20%
- silt = 55%
- sand = 25%
- pH = 6
- \( \rho_b = 1.5 \text{ g/cm}^3 \)
- \( \theta = 0.4 \text{ cm}^3/\text{cm}^3 \)
- oc = 1%
- a = 260 mg/g
- b = 1.53 cm\(^3\)/mg

1) \[ S_p = \frac{abC_p}{1 + bC_p} \]

2) \[ S_p = \frac{(P_{\text{tot}} - C_p \theta)}{\rho_b} \]

Substitute and solve

\[ abC_p \rho_b = (P - C_p \theta)(1 + bC_p) \]

\[ (b\theta)C_p^2 + (ab \rho_b + \theta - bP)C_p - P = 0 \]

\[ (0.612)C_p^2 + (546.15)C_p - 33.3 = 0 \]

\[ C_p = \frac{-546.15 \pm \sqrt{298.280.9 + 81.52}}{1.224} \]

\[ C_p = 0.0618 \frac{\mu g}{cm^3} \]

\[ S_p = 22.2 \frac{\mu g}{g} \]

\[ P_{\text{tot}} = 33.3 \frac{\mu g}{cm^3} \text{ soil} \]

\[ C_p \theta = 0.025 \frac{\mu g}{cm^3} \text{ soil} \]

\[ S_p \rho_b = 33.3 \frac{\mu g}{cm^3} \text{ soil} \]

For practical purposes:
A) \( P_{\text{total}} = S_p \rho_b \)
B) \( C_p \) is very small!

Phosphorus Yield

\[ Y_p = AW(SDR)(ER)S_p \]

A = soil loss (tons/ha)
W = watershed area (ha)
SDR = sediment delivery ratio (unitless)
ER = sediment enrichment ratio (unitless)
\( S_p = \) adsorbed P concentration (g/ton) = (\( \mu g/g \))

\( Y_p = \) P yield (g)
For prior example, if:
\[ A = 10 \text{ tons/ha} \]
\[ W = 50 \text{ ha} \]
\[ SDR = 0.2 \]
\[ ER = 1.3 \]
\[ SP = 22.2 \text{ g/ton} \]
\[ Y_P = (10)(50)(0.5)(1.3)(22.2) = 2900g = 2.9kg \]

Suppose watershed empties into a 3 ha lake of depth \( H=5m \). What is the loading to the lake?
\[ P = \frac{2.886g}{3ha} \times \frac{ha}{10,000m^2} = 0.10g/m^2 \]

**Pesticides**

Amount of pesticides reaching waterways are function of:
1. Rate of application
2. Persistence [conservation or nonconservation]
3. Mobility

3 classes of pesticides:
1. Insecticides
   a. Organochlorine – very conservative  \( \text{DDT} \Rightarrow 10 \text{ yrs} \)
   b. Organophosphorus
   c. Carbamate
2. Herbicides
   a. Generally non-conservative
   b. Some may persist up to a year
3. Fungicides
   a. Typically in orchards and on vegetable farms

**Pesticide Adsorption**

Pesticide Mobility
Sorption of pesticides
Most are non-ionic=adsorption is to organic matter less to clay
Some are organic cations – diquet and paraquat – adsorb strongly to clays

\[ S=KC \] Special case Freundlich
\[ S = \text{adsorbed concentration } \mu g/g \]
\[ C = \text{solute concentration } \mu g/cm^3 \]

\[ K = \text{adsorption coefficient } cm^3/g \]
$$K = \text{fnc}(\text{o.c.}, \text{pesticide type})$$

$$K = K^1 \times \left[\%\text{o.c./100}\right]$$

<table>
<thead>
<tr>
<th>Mobility class</th>
<th>$$K^1$$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>&lt;15</td>
</tr>
</tbody>
</table>

$$K^1 = K_{oc}$$

**Pesticides Example:**

**Lindane:** class 1 pesticide ⇒ $$K_{oc} = 2000 \left(\frac{cm^3}{g}\right)$$

- Application rate 11.4 kg/ha
- o.c. soil = 3%
- $$\rho_b = 1.2 \frac{g}{cm^3}$$
- $$\theta = 0.3$$
- $$K = 2000(0.6) = 60 \frac{cm^3}{g}$$
- incorporated depth = 7.6 cm
- Total Pesticide, $$T$$

$$T = \frac{11.4 \text{ kg}}{\text{ha}} \frac{10^9 \mu g}{\text{kg}} \frac{1}{7.5 \text{ cm}} = 15.2 \frac{\mu g}{cm^3}$$

1) $$S_L = KC_L$$

2) $$T = S_L \rho_b + C_L \theta$$

$$T = (K_p + \theta) C$$

$$C = 15.2 \frac{\mu g}{cm^3}$$

$$S = 60 \left(\frac{cm^3}{g}\right) 0.21 \frac{\mu g}{cm^3} = 12.6 \frac{\mu g}{g}$$

$$T = 15.14 + 0.06$$

**Microbial Degradation**

**Pesticide Relationships**

EPA/600/3-87/015

Processes, Coefficients, and Models for Simulating Toxic Organics and Heavy Metals in Surface Waters

- Biological Transformation
- Michaelis-Menton kinetics
\[
\frac{dT}{dt} = -k_b T
\]

where \( k_b = \frac{\hat{\mu} X}{Y(K_m + T)} \)

\( \hat{\mu} \) = max specific growth rate of culture (1/doubling time)

\( X \) = biomass concentration (cells/cm\(^3\))

\( Y \) = yield coefficient (cells produced/toxicant removed)

\( K_m = 1/2 \) saturation constant (value of T where \( k_b = \frac{1}{2} \hat{\mu} \))

\[
k_b = \frac{\left( \frac{1}{I} \right) \left( \frac{\# \text{ cells}}{\text{vol}} \right)}{\left( \frac{\# \text{ cells}}{M_p} \right) \left( \frac{M_p}{\text{vol}} \right)} = \left( \frac{1}{I} \right)
\]

Table A.1. (EPA Handbook)

\[
T = T_o e^{-k_b t}
\]

Factors affecting biodegradation rates:
1. Temperature
   \( k = k_{20} \theta^{(T-20)} \)
   \( \theta \Rightarrow 1.04 - 1.13 \)
2. Nutrients – necessary for growth
3. Acclimation – shock load toxicant \( \Rightarrow \) may kill portion of organisms
4. Population Density – (a lag occurs if # of organisms too few)

Oxidation
\( 2^{\text{nd}} \) order
\[
\frac{dT}{dt} = -KO_x T
\]

\( O_x \) = conc. of oxidant
Under natural waters $O_s$ is constant source

$\Rightarrow 1^{\text{st}}$ order

$$\frac{dT}{dt} = -KT$$

**Photolysis**

![Diagram of photolysis process]

- Energy increase
- Molecule $\rightarrow$ Excited electron state
- Back to original molecule $\rightarrow$ Loses energy $\rightarrow$ Converted to new molecule

$$\frac{dT}{dt} = -k_a \phi T$$

$k_a$ is rate constant for adsorption of light by the toxicant

$$\phi = \frac{\text{number moles toxicant released}}{\text{number einsteins adsorbed}}$$

(unit of light – molar basis of photons)

$\phi$ = efficiency of transformation

$k_a$ = intensity $\times$ adsorption
Indirect Photolysis

\[
\frac{dT}{dt} = -k_2 \times T = -k_p T
\]

2nd order psuedo 1st order

k2 is indirect photolysis rate constant
x is conc. of non-target intermediary

Volatilization
Movement from liquid to gaseous phase.

\( f_{inc} \) (molecular wt.)

Two-Film Theory

Mass moves from areas of high to low conc.

\( H = \frac{p}{c} \) Henry’s Law

\( H = \) Henry’s law constant

\( p = \) partial pressure of chemical in gas film

\( c = \) solubility of chemical in the fluid film

Liquid/gas film resistance
Liquid Film Controls

\[ H > 0.1 \]

\[
\left( 2.2 \times 10^{-3} \, \text{atm} \cdot \text{m}^3 \text{mole}^{-1} \right)
\]

Gas Film Controls

\[ H < 0.1 \]

Rate Transfer Eq. – Liquid to Gas

\[
\frac{dc}{dt} = K_L \left( c_s - c \right)
\]

\( c_s \) = saturated chemical conc.

\( K_L \) = rate transfer coefficient

\( d \) = avg. fluid depth

\( K_L \) is computed as geometric mean resistance in series

\[
\frac{1}{K_L} = \frac{1}{K_{li}} + \frac{1}{K_{gi}}
\]

\( K_{li} \) & \( K_{gi} \) can be computed from diffusivities of the chemical in liquid and air, respectively.

Liquid Film Transfer

\( K_{li} \) from comparing to oxygen transfer as standard

\[
K_{li} = K_a \left( \frac{D_l}{D_{02}} \right)^{\frac{1}{2}} \left\langle \text{Rivers & Lakes} \right. \]

\( K_a \) = oxygen re-aeration coef.

\( D_{02} \) = diffusivity \( O_2 \) in water = \( 2.4 \times 10^{-5} \, \text{cm}^2 \text{s}^{-1} \) at \( 20^\circ \text{C} \)

\( D_l \) = diffusivity chemical in water

\[
D_l = \left( 22 \times 10^5 \right) \left( \frac{M_w^{2/3}}{c^2} \right) \left( \text{cm}^2 \text{s}^{-1} \right)
\]

Gas Film Transfer

\[
K_{gi} = \frac{0.001}{h} \left( \frac{D_g}{v_g} \right)^{\frac{3}{2}} \left\langle \text{Lakes} \right. \]

\( h \) = water depth (m)

\( v_g \) = kinematic viscosity air \( \left( 0.12 \sim 0.17 \, \text{cm}^2 \text{s}^{-1} \right) \)

\( w \) = wind speed (m/s)
$D_g = \text{diff. chemical in air}$

$D_g = 1.9 M_w^{2/3} \left( \frac{cm^2}{s} \right)$

**Fig. 6-8.** Persistence of pesticides for soils. (Redrawn from Kearney et al.)