Chemical Properties and Effects on Pollutant Fate

Properties of Matter

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical conductivity</td>
<td>Ability to carry electricity</td>
<td>Copper is a good electrical conductor, so it is used in wiring.</td>
</tr>
<tr>
<td>Heat conductivity</td>
<td>Ability to transfer energy as heat</td>
<td>Aluminum is a good heat conductor, so it is used to make pots and pans.</td>
</tr>
<tr>
<td>Density</td>
<td>Mass-to-volume ratio of a substance; measure of how tightly matter is &quot;packed&quot;</td>
<td>Lead is a very dense material, so it is used to make sinkers for fishing lines.</td>
</tr>
<tr>
<td>Melting point</td>
<td>Temperature at which a solid changes state to become a liquid</td>
<td>Ice melts to liquid water at the melting point of water.</td>
</tr>
<tr>
<td>Boiling point</td>
<td>Temperature at which a liquid boils and changes state to become a gas at a given pressure</td>
<td>Liquid water becomes water vapor at the boiling point of water.</td>
</tr>
<tr>
<td>Index of refraction</td>
<td>Extent to which a given material bends light passing through it</td>
<td>The index of refraction of water tells you how much light slows and bends as it passes through water.</td>
</tr>
<tr>
<td>Malleability</td>
<td>Ability to be hammered or beaten into thin sheets</td>
<td>Silver is quite malleable, so it is used to make jewelry.</td>
</tr>
<tr>
<td>Ductility</td>
<td>Ability to be drawn into a thin wire</td>
<td>Tantalum is a ductile metal, so it is used to make fine dental tools.</td>
</tr>
</tbody>
</table>

Physical Characteristics

- Melting point
- Boiling point
- Vapor pressure
- Color
- State (solid, liquid, gas, plasma)
- Density
- Electrical conductivity
- Solubility
- Adsorption to a surface
- Hardness

Characteristics of Chemical Changes

- Reaction with acids
- Reaction with bases (alkalis)
- Reaction with oxygen (combustion)
- Ability to act as oxidizing agent
- Ability to act as reducing agent
- Reaction with other elements
- Decomposition into simpler substances
- Corrosion
Chemical Fate Processes

- TRANSPORT
- TRANSFORMATION/ DEGRADATION
- SORPTION
- VOLATILIZATION
- BIOLOGICAL PROCESSES

Example: PESTICIDE FATES

Chemical Transport Processes

- RUNOFF
- EROSION
- WIND
- LEACHING
- MOVEMENT IN STREAMS OR GROUNDWATER

Transformation and Degradation Processes

- Biological Transformations due to microorganisms
  - aerobic
  - anaerobic
  - facultative
- Most Important reaction for many chemicals
Transformation and Degradation Processes

- Chemical Transformations
  - Hydrolysis
  - Oxidation-Reduction

- Photochemical Processes
  - Only in the presence of light
  - Only on or near the surface

### Transformation and Degradation Processes

- Usually assumed to follow a first-order linear function
  \[ \frac{dC}{dt} = KC \]
- This leads to an exponential decay function for the concentration
  \[ C = C_0 e^{Kt} \]

### EXAMPLE

- Metolachlor: $T_H = 90$ days
- Initial Agricultural Application Concentration = 1.5 kg/ha
- Estimate the concentration at 120 days.

\[
K = \frac{-0.6931}{90} = -0.0077 / \text{day}
\]
\[
C = 1.5 e^{-0.0077(120)} = 0.595 \text{ kg/ha}
\]
Concentration in Water \( C_w \)

Concentration in Soil \( C_s \)

\[ C_s = K_d C_w \]

Linear, Instantaneous, Reversible Adsorption Model

**Properties Influencing Adsorption**

- Organic Matter Content
- Clay Content
- Soil Water Content
- Soil Bulk Density
- Soil Temperature

**Chemical Properties Influencing Adsorption**

- Electronic Structure (ionic or non-ionic)
- Water Solubility
- Solution Composition
- Solution Concentration
- pH

**Organic Carbon Partitioning Coefficient**

\[ K_d = K_{oc} \left( \frac{\%OC}{100} \right) \]

\[ \%OC = \%OM / 1.724 \]

\[ K_d = K_{oc} \left( \frac{\%OM}{172.4} \right) \]
Chemical Transport Pathways

• $K_d > 250$: The chemical is so strongly adsorbed that very little will be transported except with eroded soil particles.
• $250 > K_d > 50$: Transport depends on the sediment concentration of the runoff.
• $50 > K_d > 1$: Enough will stay in solution that most will be transported with surface runoff water.

• $K_d < 0.1$: The chemical is so weakly adsorbed that the first rainfall will wash it into the soil profile before initiation of runoff.

VOLATILIZATION

• Of concern for surface-located chemicals
• Affected by
  – temperature and soil water content
  – adsorptivity and concentration
  – vapor pressure and solubility (Henry’s Constant)

Biological Processes affecting Chemicals

• Interception
• Washoff
• Uptake/Penetration
• Translocation
• Metabolism/Decay
Reaction Quotient and Chemical Equilibrium

\[ aA + bB \xrightarrow{k_c} cC + dD \]

\[ Q = \text{reaction quotient} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{\text{products}}{\text{reactants}} \]

\[ K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{k_1}{k_2} \]

At equilibrium, \( Q = K_{eq} \)

Brönsted-Lowry Model

- For an acid:
  \[ K_a = K_{eq} = \frac{[H^+][A^-]}{[HA]} \]

- For a base:
  \[ \text{B}^- + \text{H}_2\text{O} \leftrightarrow \text{HB} + \text{OH}^- \]
  where \( \text{B}^- \) = base
  \( \text{HB} \) = conjugate acid
  \[ K_{eq} = K_b = \frac{[\text{HB}][\text{OH}^-]}{[\text{B}^-]} \]

Acid-Base Equilibria: Brönsted-Lowry Model

- An acid donates a proton (H⁺)
- A base accepts a proton

- ‘HA’ is used to denote a generic acid
  \[ \text{HA} + \text{H}_2\text{O} \leftrightarrow \text{A}^- + \text{H}_3\text{O}^+ \]
  Where \( \text{H}_3\text{O}^+ \) = hydronium ion

- Or
  \[ \text{HA} \leftrightarrow \text{H}^+ + \text{A}^- \]
  Where \( \text{A}^- \) = conjugate base

Strong Acids

- Strong acids have relatively high \( K_a \)s.

Example:
- HClO₄ \( K_a = 10^7 \)
- HCl \( K_a = 10^3 \)
- H₂SO₄ \( K_a = 10^3 \)
- HNO₃ \( K_a = 10^1 \)
Introduction and Review of Solubility Equilibria

- When the ions of a sparingly soluble salt are brought together in solution, it is observed that if the concentration of these ions is sufficiently large, a solid is formed that will settle from the solution. For example, consider the reaction:

  \[ \text{Ca}^{2+} (aq) + \text{CO}_3^{2-} (aq) \rightleftharpoons \text{CaCO}_3 (s) \]

- If the concentration of the calcium and carbonate ions is not excessively high, the formation of calcium carbonate may be observed to be time-dependent. (It will take a period of time for visible \( \text{CaCO}_3 (s) \) to form).

- Precipitation has therefore been concluded to be a two-step process:
  1. Nucleation – condensation of ions to very small particles.
  2. Particle growth – agglomeration/growth of these ions as a result of diffusion of ions from solution.

- In order for nucleation to occur, solute ions attraction must be strong enough to displace solvent molecules separating the ions.

- Also the collision frequency between the ions must be sufficiently high to promote nucleation.

\[ \Rightarrow \text{Supersaturated solutions do exist. Precipitation does not occur instantaneously.} \]
Solubility Equilibrium: Slightly Soluble Salts

- In general, for a slightly soluble compound $C_A$, the dissolution equation is:

$$C_A(s) \rightleftharpoons aC(aq) + bA(aq)$$

- And the solubility equilibrium expression for an ideal solution:

$$K_{sp} = [C]^a[A]^b$$

Where:
- $K_{sp}$ = solubility product (equilibrium constant)
- $[C]$ = cation concentration
- $[A]$ = anion concentration

- Remember that the concentration of the solid is not included and is assumed to be 1. $K_{sp}$ ALWAYS refers to the dissolution reaction and determines the components of a saturated solution.
- If $[C][A]^b$ is less than $K_{sp}$, no precipitate forms. If $[C][A]^b$ is greater than $K_{sp}$, precipitate forms in proportion to the reverse of the dissolution reaction until $[C][A]^b$ equals $K_{sp}$.

### Concept and Importance of Bioaccumulation

- It is a process by which persistent environmental pollution leads to the uptake and accumulation of one or more contaminants, by organisms in an ecosystem.
- The amount of a pollutant available for exposure depends on its persistence and the potential for its bioaccumulation.
Basic Factors Affecting Bioaccumulation
- Water, soil, air, plants, and any of their combinations can be an ecosystem for chemical bioaccumulation.
- Bioaccumulants tend to be persistent, stable, and lipophilic environmental pollutants.
- Chemicals tending to move freely within an organism’s body are less likely to be accumulated by organisms.

Uptake of Bioaccumulants
- The uptake of many bioaccumulants by organisms is typically initiated by passive transport, as chemical molecules tend to move from high to low concentration.
- This first step is affected by the bioaccumulant’s lipophilicity and water solubility.
- Some chemicals also have a high affinity for binding with proteins or the ability to dissolve in fats, thus prolonging the storage of these substances inside an organism.

Breakdown of Pollutants
- The biological breakdown of chemicals is called metabolism; this ability varies among individual species.
- Some chemicals are highly fat-soluble but are easily metabolized; these chemicals do not accumulate in organisms.
- Thus, biological breakdown is one of the factors leading to one of the two specific consequences of chemical bioaccumulation: bioconcentration or biomagnification.

BAF, BCF, BMF
- Bioaccumulation Factor (BAF) is the ratio of a test chemical’s concentration in a test organism’s tissues to that in the surrounding medium, when all potential uptake mechanisms are included.
- Bioconcentration Factor (BCF) is a specific case of BAF, when the uptake is only from the surrounding medium.
- Biomagnification Factor (BMF) is the ratio of a test chemical’s concentration in the tissues of an organism, to that in the organism’s prey.
**Numerical Criteria for Bioaccumulation Potential**
- In the USA, chemicals are considered bioaccumulative if they have a degradation half-life > 30 days; or
- If they have a bioconcentration factor greater than 1,000; or
- If their log $K_{ow}$ is greater than 4.2.
- These values are lower (i.e., more health conservative) than those set forth by Canada and many other Western countries.

**Bioconcentration Factor (I)**
- Many bioconcentration factor (BCF) assessments are based on aquatic measurements because fish provides a rich lipophilic microenvironment for bioaccumulation.
- BCF is typically measured as the ratio of the concentration of a chemical in a test organism to the chemical’s concentration in the surrounding medium.
- For many lipophilic chemicals, BCFs can be calculated using the regression equation: $\log BCF = -2.3 + 0.76 \times (\log K_{ow})$.

**Bioconcentration Factor (III)**
- For a bioconcentration factor (BCF) to be estimated from a site-specific study, three (3) conditions should be met.
- For a BCF to be estimated from a laboratory study, five (5) conditions should be met.
- These conditions include: sufficient duration for observation; a subthreshold test levels; and the use of test guidelines acceptable to the regulatory authorities.