EWC 105
Environmental Chemistry

Lecture 12

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Lecture Outlines

Topics	Sub-Topics	References
Soil Chemistry	• Formation and composition of soil • Acid-Base and Ion exchange equilibria in soil • Nutrients and pollutants in soil • Soil-water partitioning, partitioning coefficients (K_d, K_{oc})	**1.** Environmental Chemistry Author – Stanley E. Manahan 8th ed., CRC Press **2.** Environmental Engineering Authors: Howard S. Peavy, Donald R. Rowe and George Tchobanoglous McGraw Hill International Edition **3.** Water Pollution – Causes, Effects and Control Author: P. K. Goel New Age International publishers

Composition of Soil

1. Inorganic Components

- **Sources** – weathering of parent rocks and minerals to form inorganic soil components results ultimately in the formation of inorganic colloids.
- **Role** –

  ✓inorganic soil colloids absorb toxic substances and hence enhances detoxification of substances which otherwise would harm plants

  ✓ increase soil productivity
- **Components** –

  ✓O_2, Si, Al, Fe, Ca, Na, K, Mg etc

Composition of Soil

1. Organic Components

- **Sources** –decay of vegetation/ plants

- **Role** –

  ✓Serves as food for microorganisms

  ✓ undergoes chemical reactions, such as ion exchange and influence the physical properties of soil

  ✓ some organics contribute to weathering of mineral matters during the process of soil formation

- **Components** –

  ✓Humus, fats, resins, waxes, N-containing compounds, P compounds,

Acid-Base Reactions in Soil

Soil acidity

- Oxidation of pyrite (FeS_2) in soil causes formation of acid-sulfate soils, often called cat-clays.

$$FeS_2 + 7/2\ O_2 + H_2O \longrightarrow Fe^{2+} + 2H^+ + 2SO_4^{2-}$$

- Cat clay soils may have pH values as low as 3.0.

- These soils are formed when neutral or basic marine sediments containing FeS_2 become acidic upon its oxidation when exposed to air.

Acid-Base Reactions in Soil

Adjustment of Soil Acidity

- Most plants grow best in soil with neutral pH.

- Addition of $CaCO_3$ in too acidic soil can restore the productivity of soil, required for optimum plant growth.

$$\{Soil\}\ (H^+)_2 + CaCO_3 \longrightarrow \{Soil\}\ Ca^{2+} + CO_2 + H_2O$$

Acid-Base Reactions in Soil

Adjustment of Soil Alkalinity

- In case of low rainfall, soil may become too basic/ alkaline due to the presence of basic salts, such as Na_2CO_3.

- Alkaline soils may be treated with aluminum or iron sulfate, which release acid on hydrolysis.

$$2Fe^{3+} + 3SO_4^{2-} + 6H_2O \longrightarrow 2Fe(OH)_3\,(s) + 6H^+ + 3SO_4^{2-}$$

Ion Exchange Equilibria in Soil

- The capacity of a sediment or soil to exchange cations is expressed as Cation Exchange Capacity (CEC)
- CEC - the number of miliequivalents (meq) of monovalent cations that can be exchanged per 100 gm soil (on a dry-weight basis)
- Both the minerals and organic portion of soil exchange cations.
- Cation exchange in soil make k, Ca, Mg and essential trace metals available to plants.

Ion Exchange Equilibria in Soil

- Competition of different cations for cation exchange sites on soil cation exchangers may be described semi-quantitatively by exchange constants.

- For example, soil reclaimed from an area flooded with seawater will have most of its cation exchanger sites occupied by Na^+, and restoration of fertility requires binding of nutrients cations, such as K^+.

$$\{Soil\}\ Na^+ + K^+ \rightleftharpoons \{Soil\}\ K^+ + Na^+$$

The exchange constant, $K_e = \dfrac{N_K \left[Na^+\right]}{N_{Na} \left[K^+\right]}$

Here, K_e expresses the relative tendency of soil to retain K^+ and Na^+.

Ion Exchange Equilibria in Soil

$$\{Soil\}\ Na^+ + K^+ \rightleftharpoons \{Soil\}\ K^+ + Na^+$$

The exchange constant, $K_e = \dfrac{N_K \left[Na^+\right]}{N_{Na} \left[K^+\right]}$

Here, N_K and N_{Na} are the equivalent ionic fractions of K and Na respectively bound to soil.

$[Na^+]$ and $[K^+]$ are the concentrations of thee ions in the surrounding soil water.

- For example, a soil with all cation exchange sites occupied by Na^+ would have a value of 1.00 for N_{Na}, whereas for half of cation exchange sites occupied by Na^+, N_{Na} is 0.50.

Nutrients in Soil

1. Nitrogen -

- In most soils, over 90% of the N is organic.

- Source – biodegradation of dead plants and animals, eventually hydrolyzed to NH_4^+, which can be oxidized to NO_3^- by the action of bacteria in the soil.

- Significance – for maintaining soil fertility

- Adverse effects –
  - ✓ Plants absorbing excessive nitrate nitrogen from heavily fertilized fields can poison animals as well as endanger public health.
  - ✓ Nitrate pollution of surface and groundwater has become a major problem in some agricultural area.

Nutrients in Soil

2. Phosphorus -

- % of P in plant material is relatively lower.

- In the existing pH range in most soils, the dominating utilizable species of orthophosphate ions are $H_2SO_4^-$ and HPO_4^{2-}.

- Significance – essential components for plant growth

- Adverse effect –

  ✓ P, applied as fertilizer leaches from the soil and hence causes water pollution in nearby water bodies.

Pollutants in Soil

Pesticides-

- Major concerns –

  ✓ Carryover of pesticides and biodegraded products to crops grown in later seasons

  ✓ Biological effects on organisms in terrestrial and aquatic ecosystems, including bioaccumulation and transfer through food chains

  ✓ Ground water contamination

  ✓ Effects on soil fertility

Pollutants in Soil

Pollutants from Livestock -

- Major concerns –

✓ Livestock manure having very high BOD, can rapidly deplete DO when it gets into waterways.

✓ Decomposition of animal waste produces inorganic N, which can pollute water with toxic nitrate.

✓ Inorganic N and P released to water from decomposition of livestock wastes can cause eutrophication.

✓ Nitrous oxide (N_2O) released to atmosphere can be an air pollutant.

✓ CH_4 produced from anaerobic decomposition is a potent greenhouse gas.

Fate of Pollutants in Soil-Water Interface

- The tendency of a solute in water to be retained by soil, sediment or aquifer mineral is expressed by parameter K_d, commonly known as soil-water partition coefficient.

$$K_d = C_s / C_w$$

where,

C_s = equilibrium concentration of the pollutant in solid

C_w = equilibrium concentration of the pollutant in water

- The organic fraction of the solid material in soil, sediments and minerals is often the material with the predominant affinity for organic pollutants/ contaminants.

Fate of Pollutants in Soil-Water Interface

- Designating the organic fraction as f_{OC} and the partition coefficient of the organic pollutant for the pure organic solid as K_{OC}, the following holds:

$$K_d = f_{OC} / K_{OC}$$

- This relationship represents that as the fraction of organic sorbent in the solid increases, the effective value of K_d increases as well.