FATE OF SOIL POLLUTANTS-II

AAUE1003 SOIL POLLUTION
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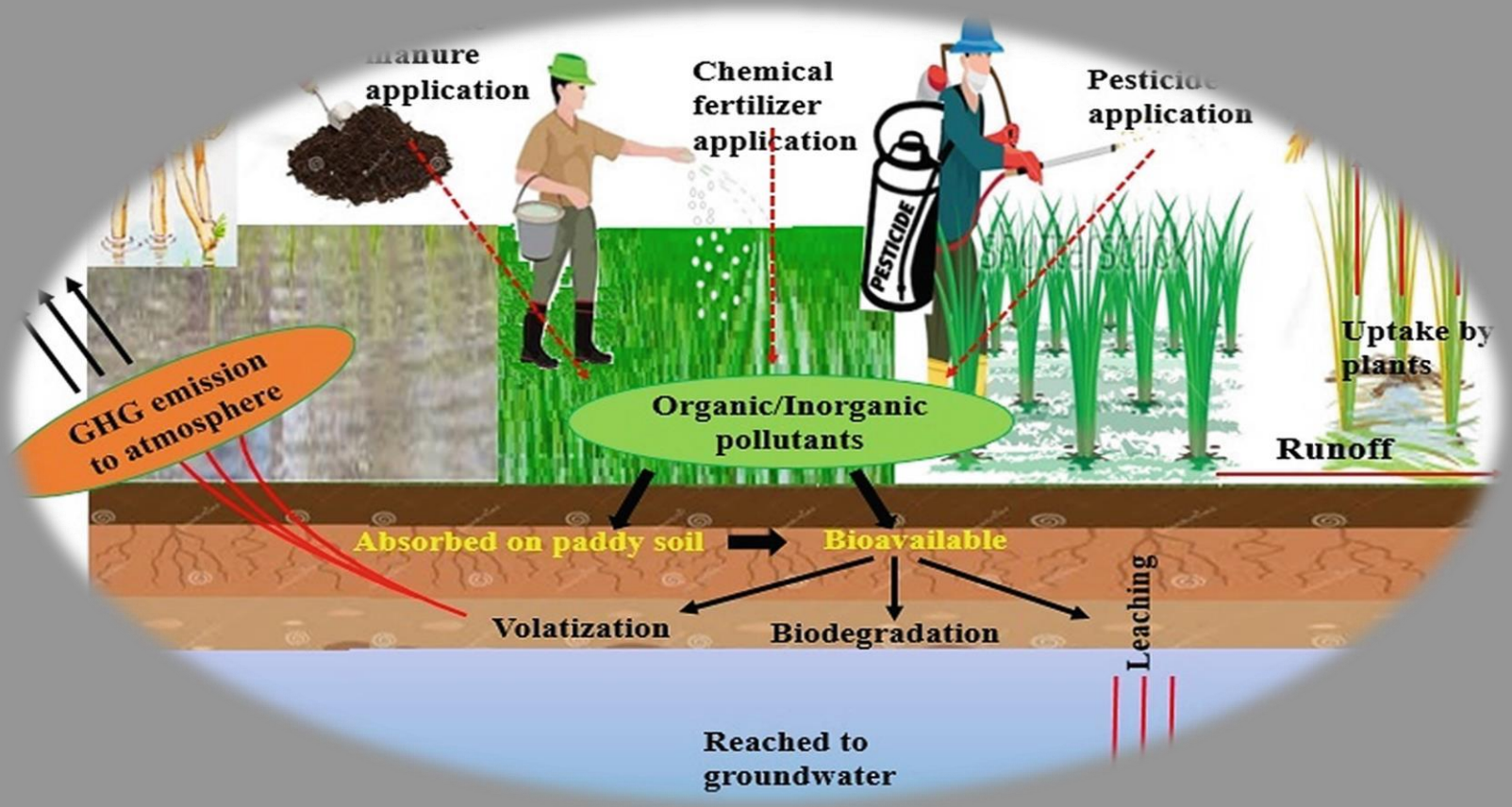
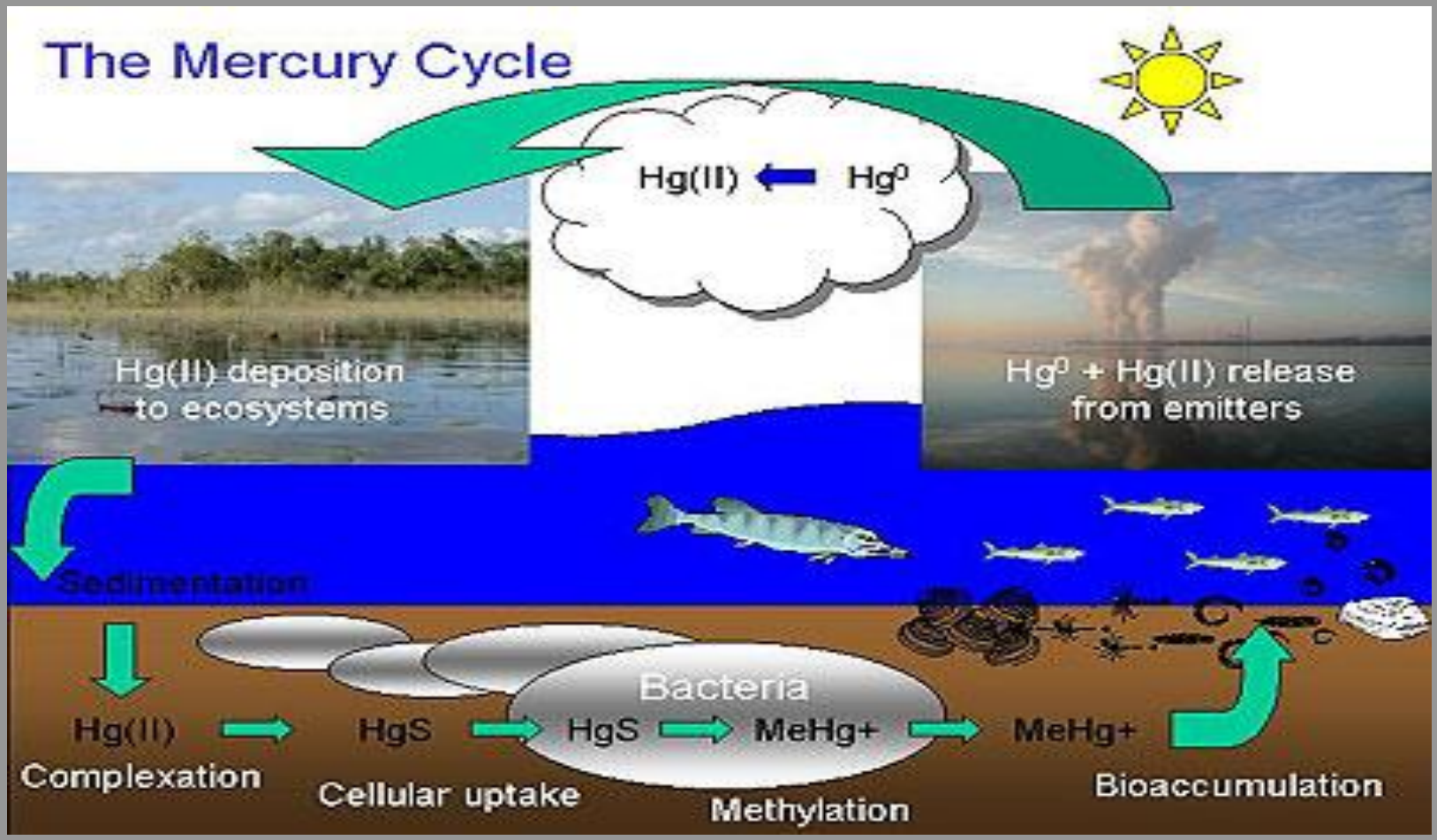


CONVERSION OF SOIL POLLUTANTS



The fates of pollutants in the soil are affected by multiple soil events occuring at the same or different times;

1) Physical processes
2) Chemical processes
3) Biological processes

1) Physical processes (effecting chemical mobility of pollutants)

- **The processes involves the physical conditions of pollutant distributionbut no chemical change occurrs**
- **Soil dispersion and distribution of the pollutants are usually related with "advection", "dispersion", and "volatilization" (evaporation).**
- **Three other important phenomena affecting pollutant mobility in top soil conditions;**

1.1) non-aqueous phase liquid (NAPL) pollution

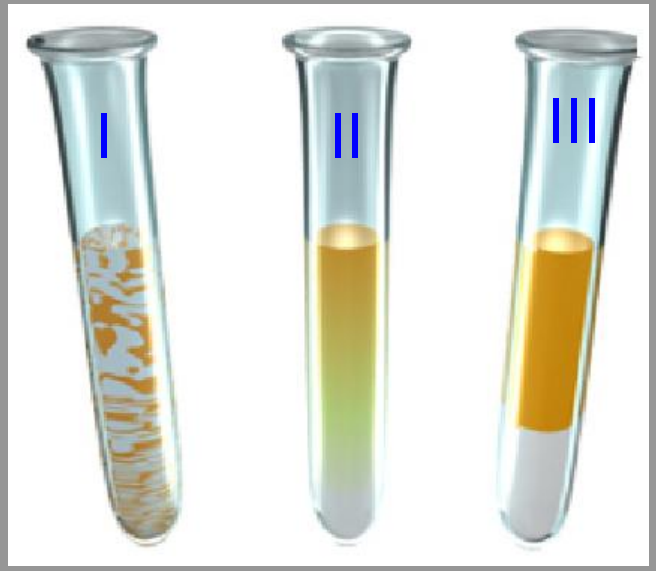
1.2) Acid-base balance

1.3) Precipitation-dissolution reactions

1.1) non-aqueous phase liquid (NAPL) Pollution

- Different insolubility characterisics of NAPL pollutants.

- Dry cleaning cehmicals, oil and its derivates may exhibit different behaviors depending on their density and solubility characterisics in soil water



- Low density NAPLs forms floating layers in water (I and II)

- High density NAPLs may form impermeable layers (III)

1.2) Acid-base reactions (buffering) in soil

- Acids are substances that can take up protons (releasing H+ to the environment) in chemical reactions

  - Ionisation of hydrochloric acid:

    $$HCl^0\,(\text{neutral}) \rightleftarrows H^+ + Cl^-$$

  - Ionisation of sulphuric acid:

    $$H_2SO_4^0\,(\text{neutral}) \rightleftarrows 2H^+ + SO_4^{2-}$$

  - Ionisation of carbonic acid:

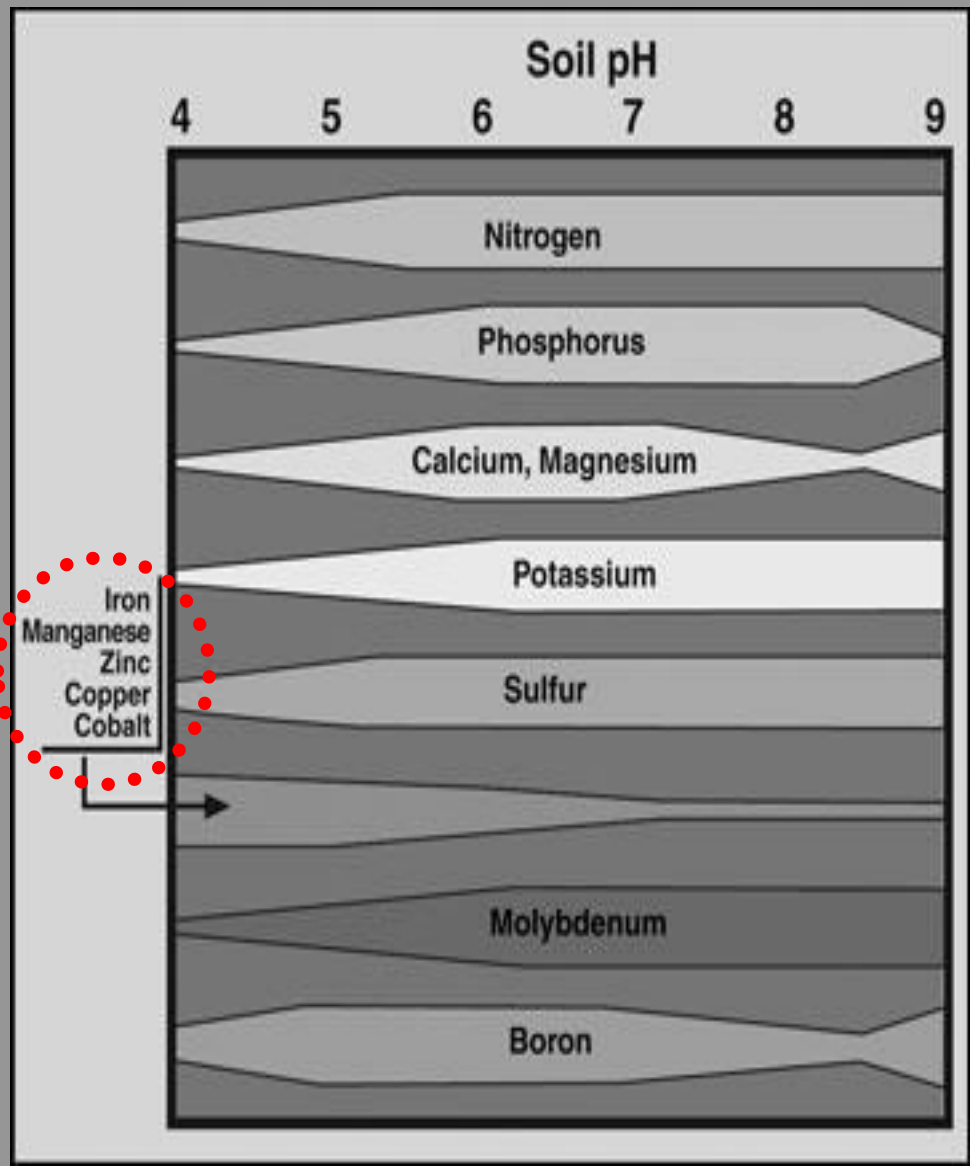
    $$H_2CO_3^0\,(\text{neutral}) \rightleftarrows H^+ + HCO_3^-$$

- Similarly, bases release OH- ions to the reaction environment

$$NaOH^0\,(\text{neutral}) \rightleftarrows Na^+ + OH^-$$

- When a strongly acidic or basic substance is released into the soil solution, the pH of the environment can be balanced without no big change depending on the release or retention of H+ ions in the soil solution. This ion balance is managed by the colloidal surfaces of the soil and determines the **"buffering ability of the soil".**

- However, this potential of the soil may lose its effectiveness if it is exposed to a continuous or high level of material input (contamination).
- In suc cases, big changes occur in soil reaction affecting the behaviors and movements (solubility-precipitation and transfer-distribution) of many useful-harmful elements and compounds in the soil.



1.3) Çözünme ve çökelme reaksiyonları

- The most important phase distribution processes occurring in the soil environment are "dissolution" (transition from gas-solid phase to liquid state) and "precipitation" (transition from liquid state to solid state)

- Dissolution is the initial stage of the pollutant mobilization process. On the other hand, precipitation acts as an "inhibitor" (inhibitor) in terms of pollutant mobility.

- The solubility of a substance in the soil environment depends on the nature of the substance as well as physical-chemical conditions such as temperature, pressure, pH, and Eh (redox potential).

- A general assessment in terms of pollutants is that the solubility of organic toxic substances is lower compared to inorganic salts, which is related to the hydrophobic (water-repellent) nature of organic pollutants.

- Another factor affecting pollutant solubility is the amount (concentration) of the substance in question already present in the soil solution and the distance-proximity to the point "solubility balance''* at ambient temperature conditions

*The highest soluble value of a substance under certain temperature and pressure conditions

2) Chemical processes (that change the chemical composition of the pollutant)

2.1 Redox mechanism

2.2 Complex formation-chelation

2.3 Hydrolysis

2.1. Redox

- The most effective soil mechanism changing chemical characteristics of heavy metals (over oxidation-reduction processes)
- Usually catalyzed by microorganisms

(Substance A releases an electron, reducer)

(Substance B receives an elektron, oxidizer)

(Redox: substance A donates electrons to B)

Electron loss means "**oxidation**" and electron acquisition means "**reduction**." In a certain chemical reaction, the electrons lost by the reactant necessarily gain another reactant. Therefore, oxidation and reduction events happen **continuously and simultaneously**, gaining soil **a redox potential**

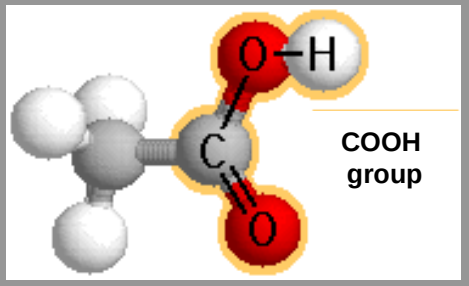
Factors effecting heavy metal transport in soil

- soil pH,
- metal concentration,
- redox potential,
- soil surface chemistry (type and content of clay minerals),
- the concentration of inorganic (eg H3PO4) and organic matter that can compound with the metal

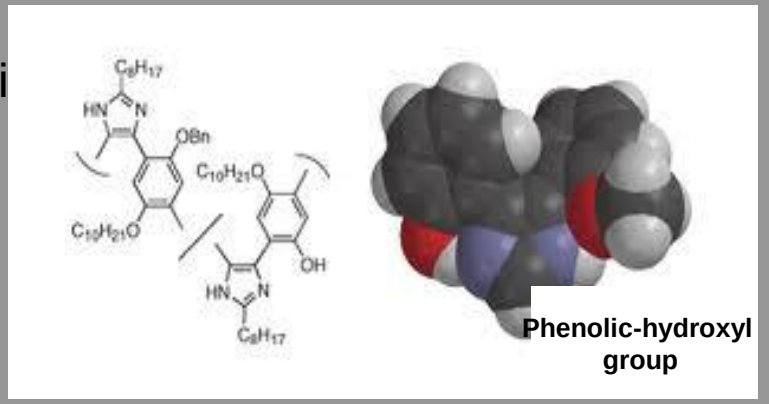
2.2. Complexation and Chelation

Humic substances in soil

- The most important component of soil organic matter (humus) consists of “C-H-N-O” groups.



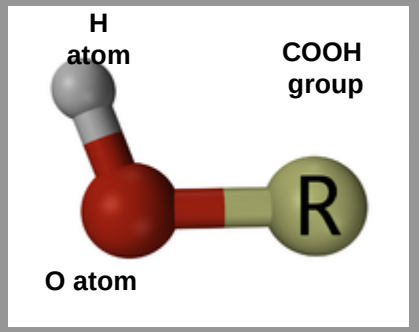
- These functional groups are carboxyl, hydroxyl, methoxyl and phenolic hydroxyl.
- These groups react with a large number of organi and inorganic substances in the soil over many different chemical reactions, thus gaining humic substances "colloidal" property.



- In agricultural sense, the colloidal surfaces (i.e. humic acids) retain nutrients for changing period of times and serve them back to plant growth

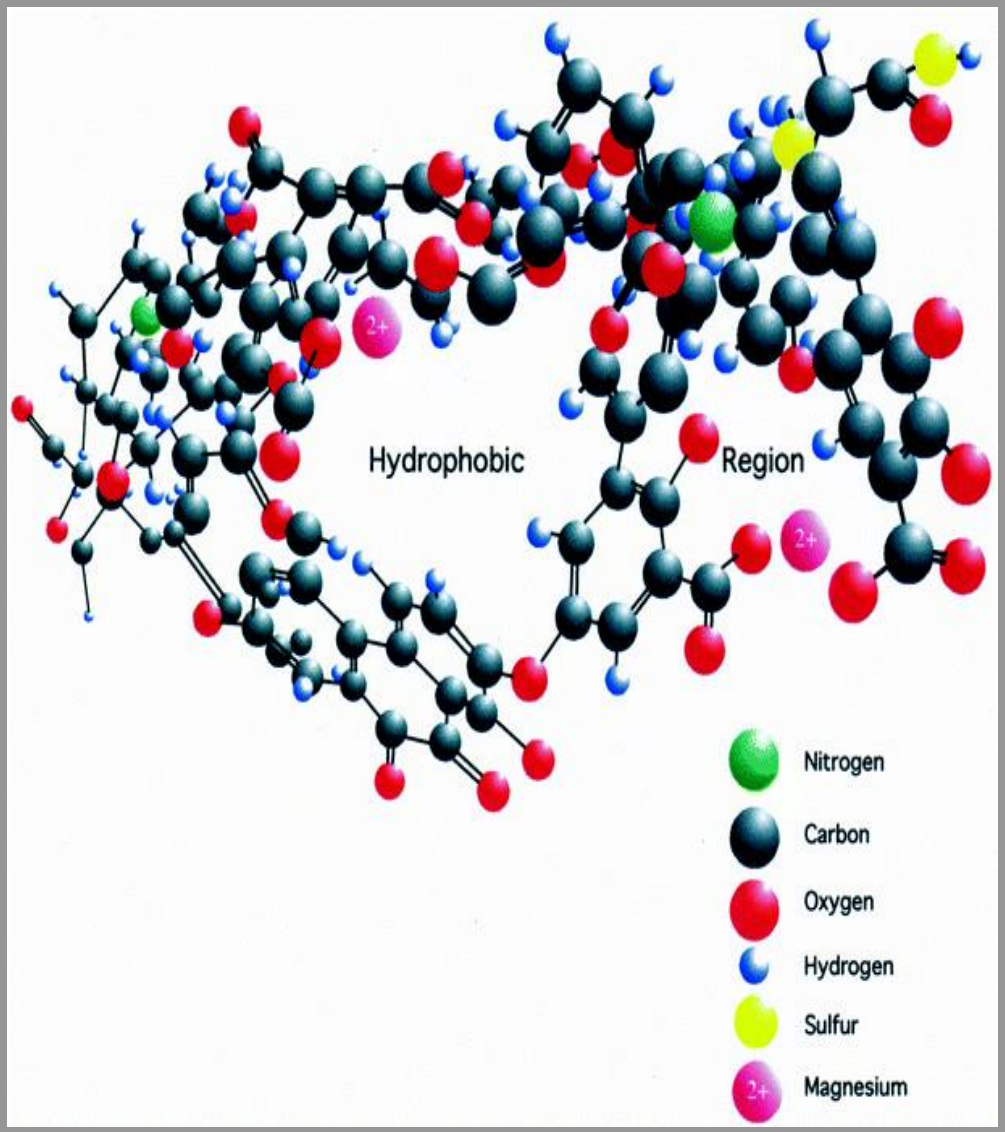
- This feature also fulfills the function of ‘’trapping unwanted organic and inorganic substances” so plants and soil organisms can not have access with such toxic substances

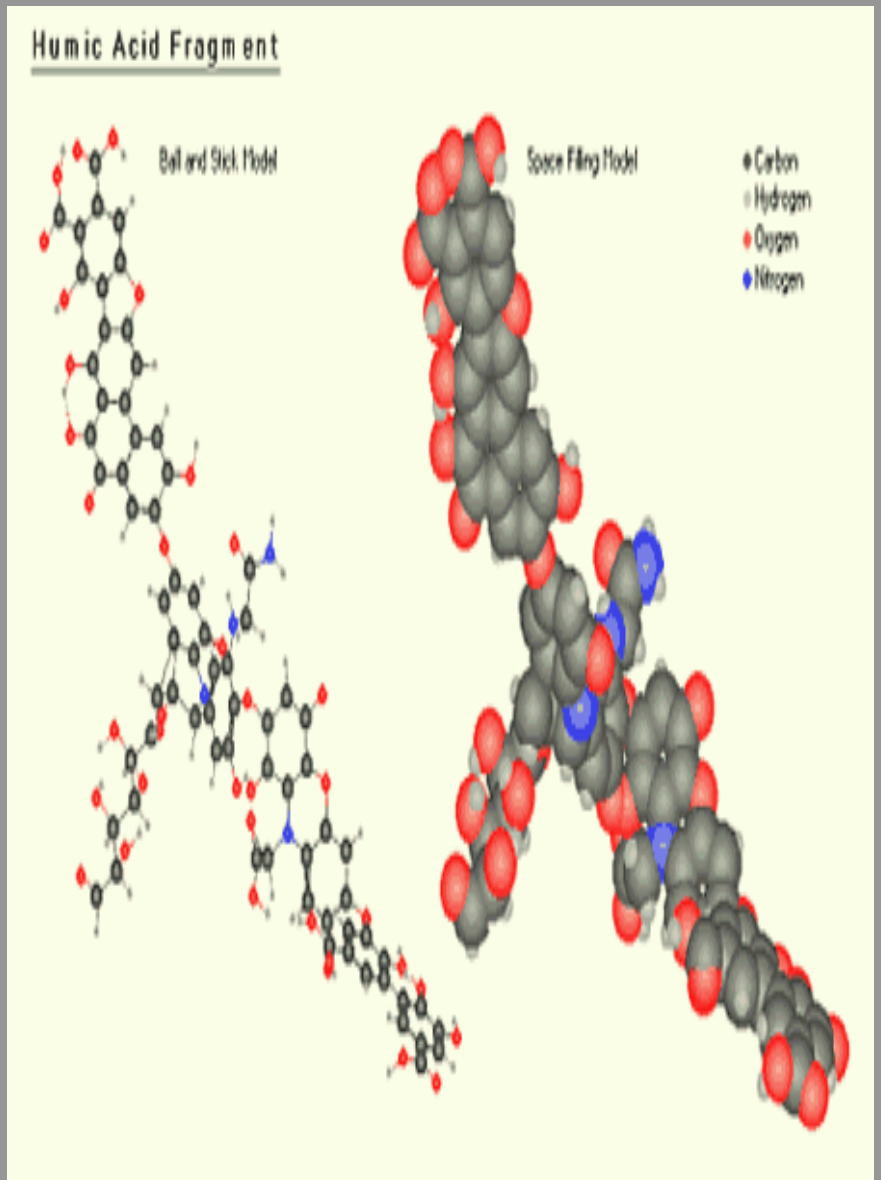
(controlling bioavailability of pollutants)



R: covalent chemical bond with a hydrocarbon or organic substance

3D view of humic substances in soil





- Chelation" is the formation of a "chain" or "cage" structure between the metal and the functional organic groups. The organic structure linking with metal is called "chelator" agent and the final chemical structure formed is called "chelate".
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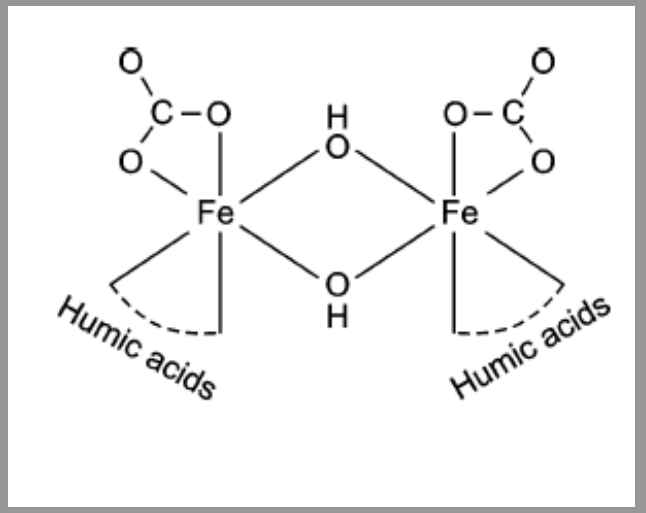
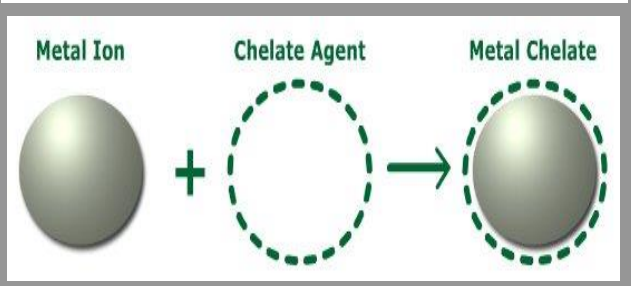
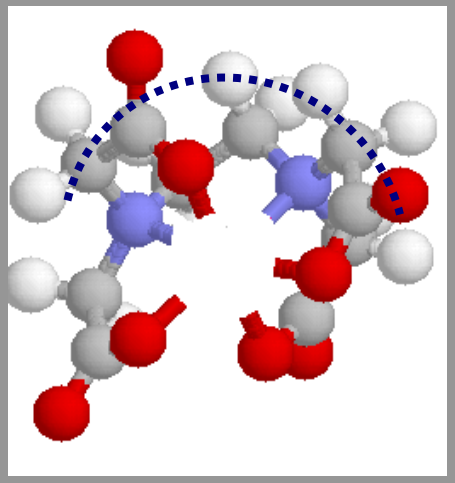
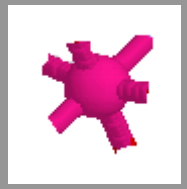
- Chelate is derived from the Greek word "Chela", meaning ‘’crab claw’’
- Chelate formation makes metals less accessible (bioavailable) in nature (especially in aquatic systems
- Chelation also affects the adsorption of metals to clay-colloid surfaces.



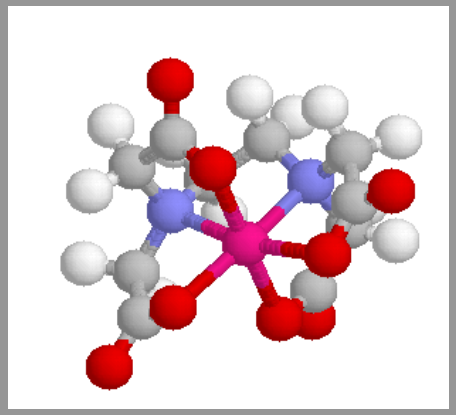




Chelating organic complex

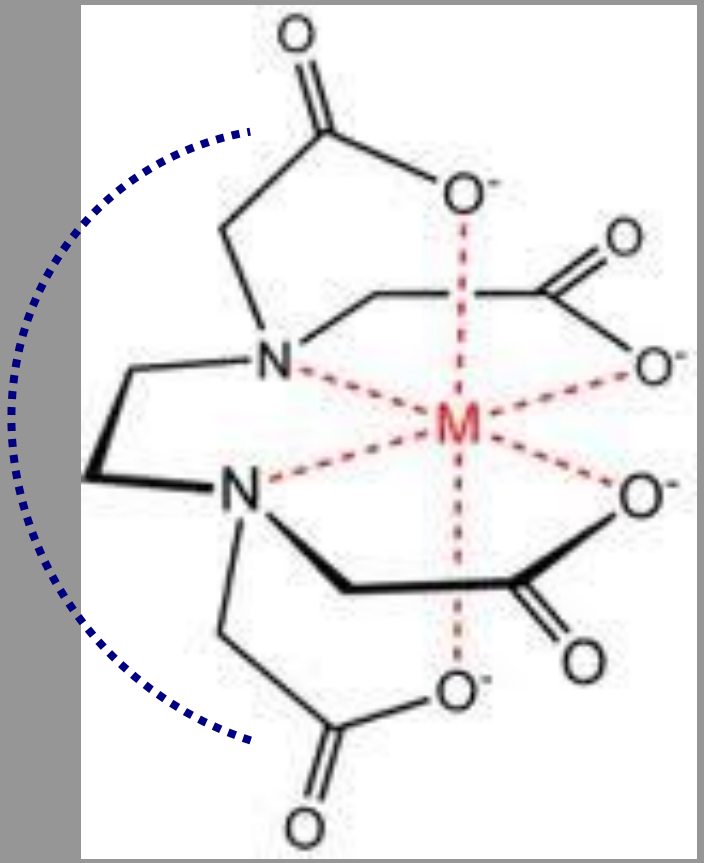


Chelated substance
(Metal)



CHELATE

crab claw ☺



2.3 Hydrolysis

A chemical reaction taking place between water and any substance to produce protons (H +) or electrons (OH-)

$$AB + HOH \rightleftharpoons AH + BOH$$

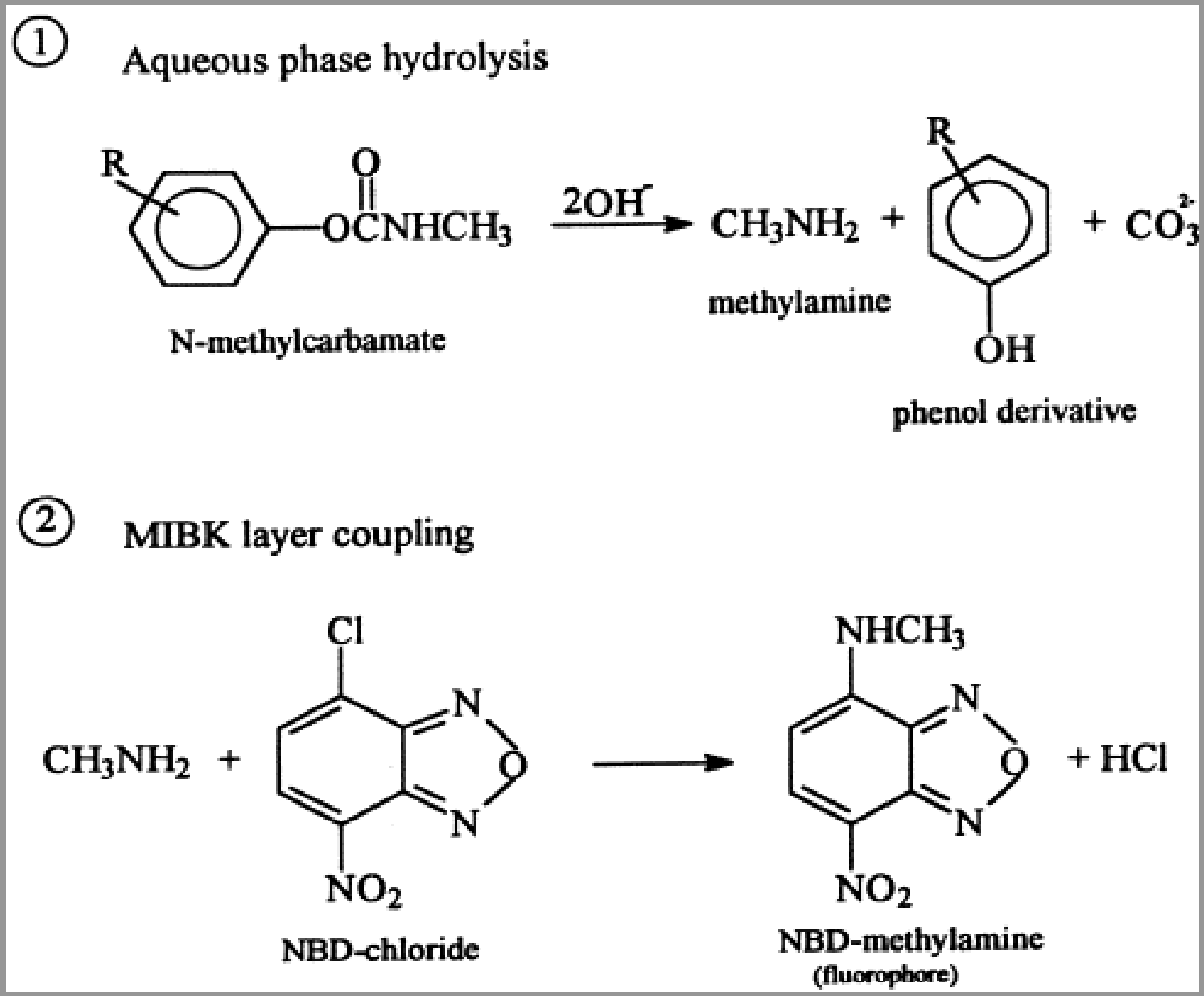
Most hydrolysis involves organic compounds, or ionic molecules, (hydrolyses of salts, acids, and bases.

Organic pollutants moving through the soil profile can be hydrolyzed (by binding water to their molecules or displacing their functional groups with water) into other substances (e.g. exchange of halides in alkyl halides to form alcohol)

$$RX + H_2O \rightleftharpoons R\text{-}OH + HX$$

R: alkil group
X: halid

Hydrolysis of methylcarbamate (common active substance of many different pesticides



3) Biological Processes (biodegradation and biotransformation)

- degradation and transformation of organic compounds due to intracellular and extracellular enzyme activities.
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- This process is known as "biodegradation" in the case of complete break down and disappearance of the substance;
- If a substance is released to the external environment after a change in its chemical structure by the cell, the process is referred as ‘’biological transformation" (biotransformation ".