

**The Islamic University of Gaza- Environmental Engineering Department
Environmental Chemistry I (EENV 2301)**

CHAPTER 4: ENVIRONMENTAL CHEMISTRY OF WATER

Aquatic Chemistry

Metal Ions and Calcium in Water

**Oxidation-Reduction - Complexation and Chelation and Water
Interactions with Other Phases**

Prepared by

Husam Al-Najar

Important Properties of Water

Property	Effects and Significance
Excellent solvent	Transport of nutrients and waste products, making biological processes possible in an aqueous medium
Highest dielectric constant of any common liquid	High solubility of ionic substances and their ionization in solution
Higher surface tension than any other liquid	Controlling factor in physiology; governs drop and surface phenomena
Transparent to visible and longer-wavelength fraction of ultraviolet light	Colorless, allowing light required for photosynthesis to reach considerable depths in bodies of water
Maximum density as a liquid at 4°C	Ice floats; vertical circulation restricted in stratified bodies of water
Higher heat of evaporation than any other material	Determines transfer of heat and water molecules between the atmosphere and bodies of water
Higher latent heat of fusion than any other liquid except ammonia	Temperature stabilized at the freezing point of water
Higher heat capacity than any other liquid except ammonia	Stabilization of temperatures of organisms and geographical regions

THE PROPERTIES OF WATER, A UNIQUE SUBSTANCE

Water has a number of unique properties that are essential to life and that determine its environmental chemical behavior.

Many of these properties are due to water's polar molecular structure and its ability to form hydrogen bonds.

SOURCES AND USES OF WATER: THE HYDROLOGIC CYCLE

The world's water supply is found in the five parts of the **hydrologic cycle**.

About 97% of Earth's water is found in the oceans.

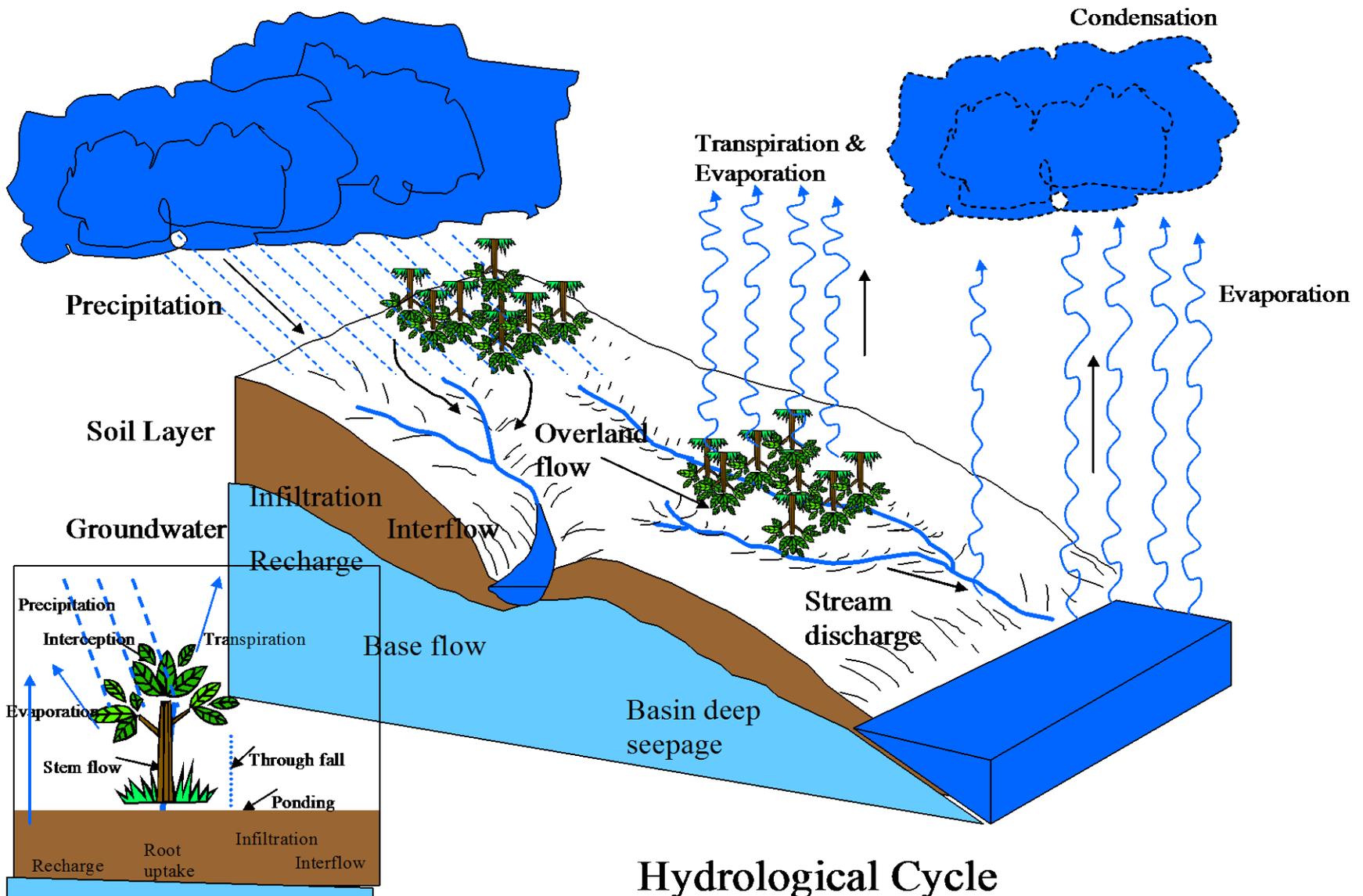
Another fraction is present as water vapor in the atmosphere (clouds).

Some water is contained in the solid state as ice and snow in snowpacks, glaciers, and the polar ice caps.

Surface water is found in lakes, streams, and reservoirs. Groundwater is located in aquifers underground.

There is a strong connection between the *hydrosphere, where water is found*, and the *lithosphere, or land; human activities affect both*.

The water that humans use is primarily fresh surface water and groundwater, the sources of which may differ from each other significantly.



THE CHARACTERISTICS OF BODIES OF WATER

The physical condition of a body of water strongly influences the chemical and biological processes that occur in water.

Surface water is found primarily in streams, lakes, and reservoirs.

Wetlands are productive flooded areas in which the water is shallow enough to enable growth of bottom-rooted plants.

Estuaries constitute another type of body of water, consisting of arms of the ocean into which streams flow. The mixing of fresh and salt water gives estuaries unique chemical and biological properties.

Estuaries are the breeding grounds of much marine life, which makes their preservation very important.

Water's temperature-density relationship results in the formation of distinct layers within nonflowing bodies of water. During the **summer** a surface layer (**epilimnion**) is heated by solar radiation and, because of its lower density, floats upon the bottom layer, or **hypolimnion**.

This phenomenon is called **thermal stratification**. When an appreciable temperature difference exists between the two layers, they do not mix, but behave independently and have very different chemical and biological properties.

The epilimnion, which is exposed to light, may have a heavy growth of algae.

As a result of exposure to the atmosphere and (during daylight hours) because of the photosynthetic activity of algae, the epilimnion contains relatively higher levels of dissolved oxygen and generally is aerobic.

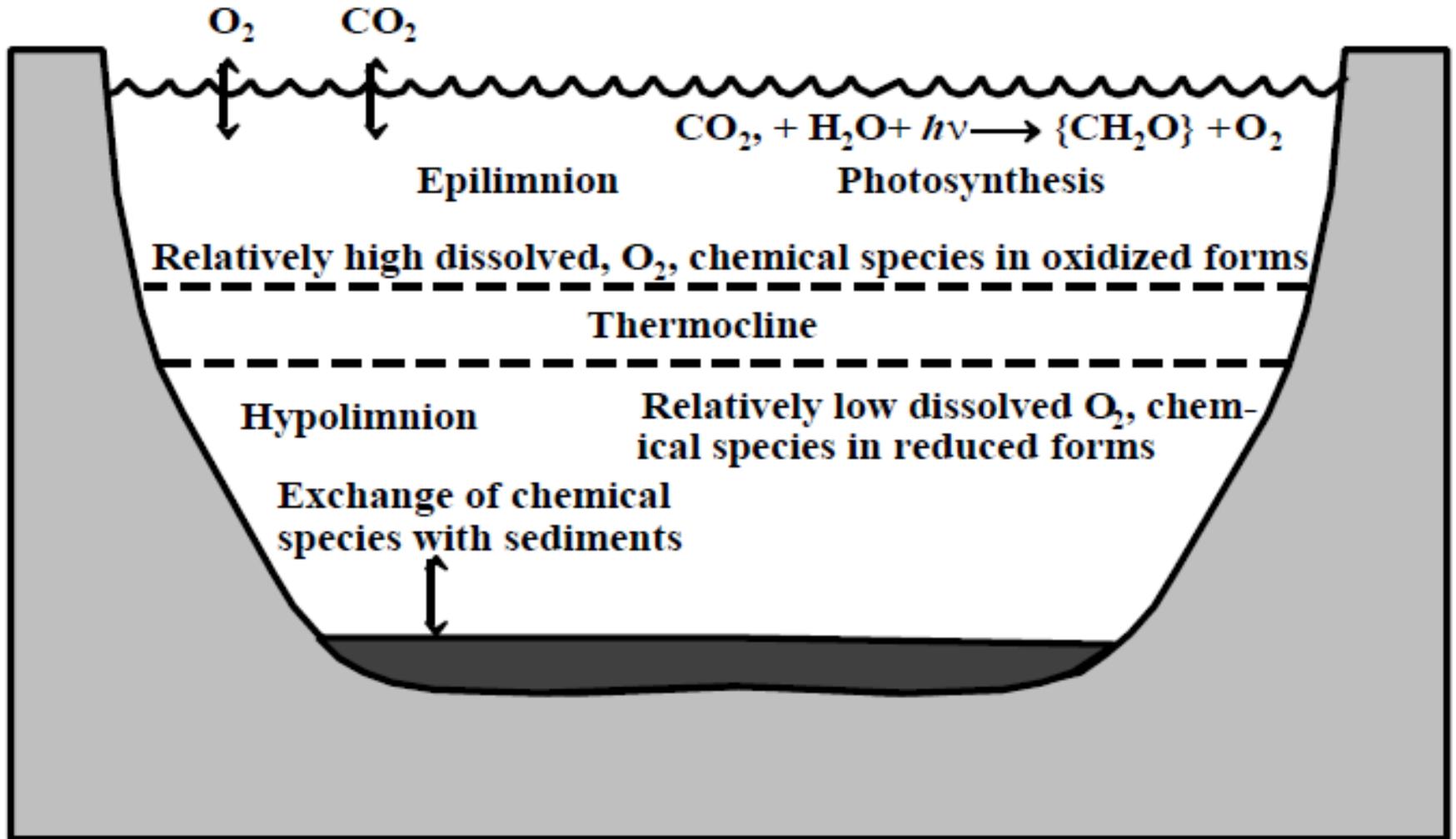
Because of the presence of O_2 , oxidized species predominate in the epilimnion.

In the hypolimnion, consumption of O_2 by bacterial action on biodegradable organic material may cause the water to become anaerobic. As a consequence, chemical species in a relatively reduced form tend to predominate in the hypolimnion.

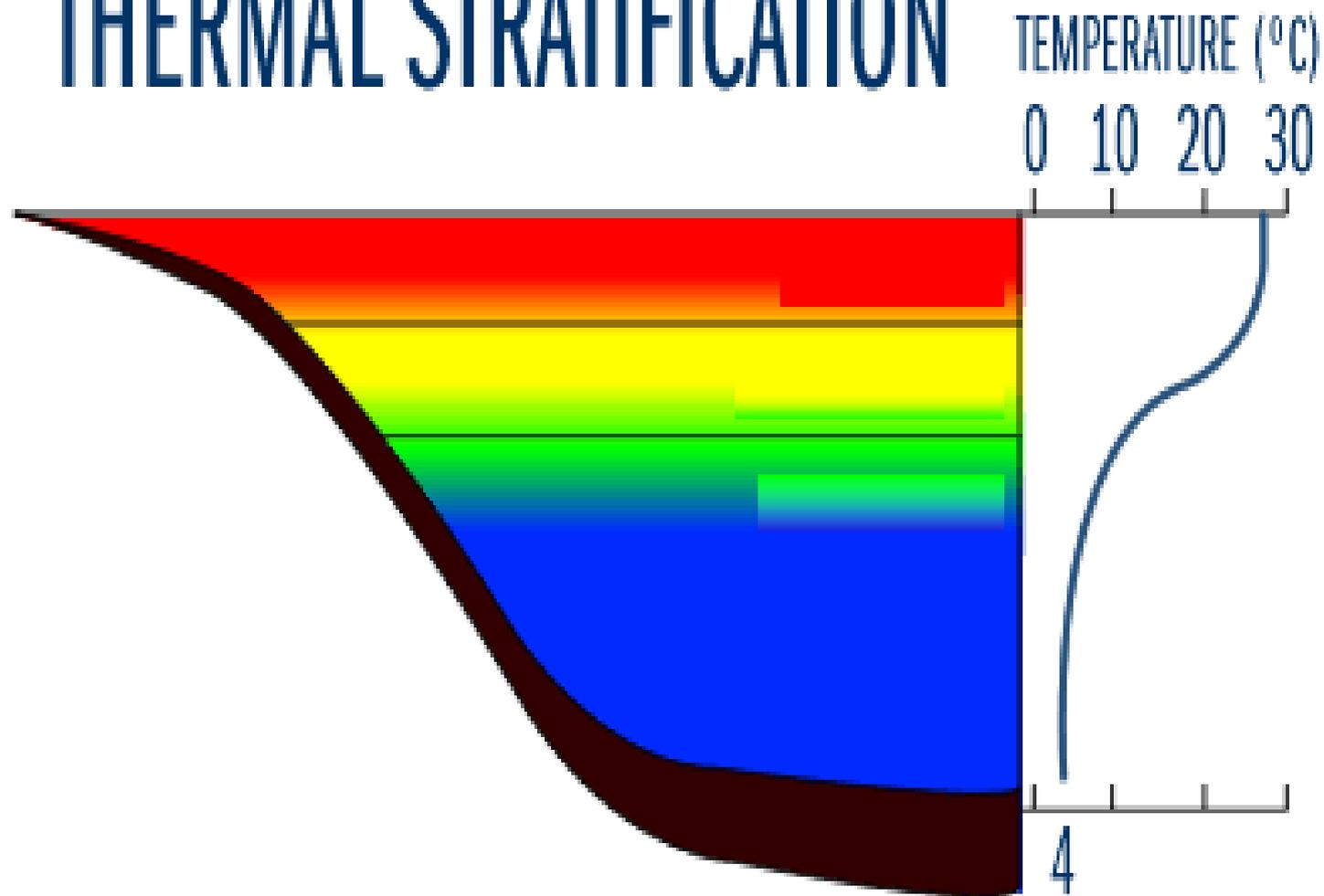
The chemistry and biology of the Earth's vast oceans are unique because of the ocean's high salt content, great depth, and other factors. Oceanographic chemistry is a discipline in its own right.

The environmental problems of the oceans have increased greatly in recent years because of ocean dumping of pollutants, oil spills, and increased utilization of natural resources from the oceans.

Stratification of a lake



THERMAL STRATIFICATION



Aquatic Chemistry:

Many aquatic chemical processes are influenced by the action of algae and bacteria in water.

Algal photosynthesis fixes inorganic carbon from HCO_3^- ion in the form of biomass (represented as $\{\text{CH}_2\text{O}\}$), in a process that also produces carbonate ion, CO_3^{2-} .

Carbonate undergoes an acid-base reaction to produce OH^- ion and raise the pH, or it reacts with Ca^{2+} ion to precipitate solid CaCO_3 .

Most of the many oxidation-reduction reactions that occur in water are mediated (catalyzed) by bacteria. For example, bacteria convert inorganic nitrogen largely to ammonium ion, NH_4^+ , in the oxygen-deficient (anaerobic) lower layers of a body of water.

Near the surface, where O_2 is available, bacteria convert inorganic nitrogen to nitrate ion, NO_3^- .

Metals in water may be bound to organic chelating agents, such as pollutant nitrilotriacetic acid (NTA) or naturally occurring fulvic acids.

Gases are exchanged with the atmosphere, and various solutes are exchanged between water and sediments in bodies of water.

Several important characteristics of unpolluted water should be noted.

One of these is gas solubility. Since it is required to support aquatic life and maintain water quality, oxygen is the most important dissolved gas in water.

Dissolved Oxygen (DO): Water in equilibrium with air at 25°C contains 8.3 milligrams per liter (mg/L) of dissolved O₂.

DO is the measurement of oxygen dissolved in water and available for fish and other aquatic life. Indicates health of an aquatic system.

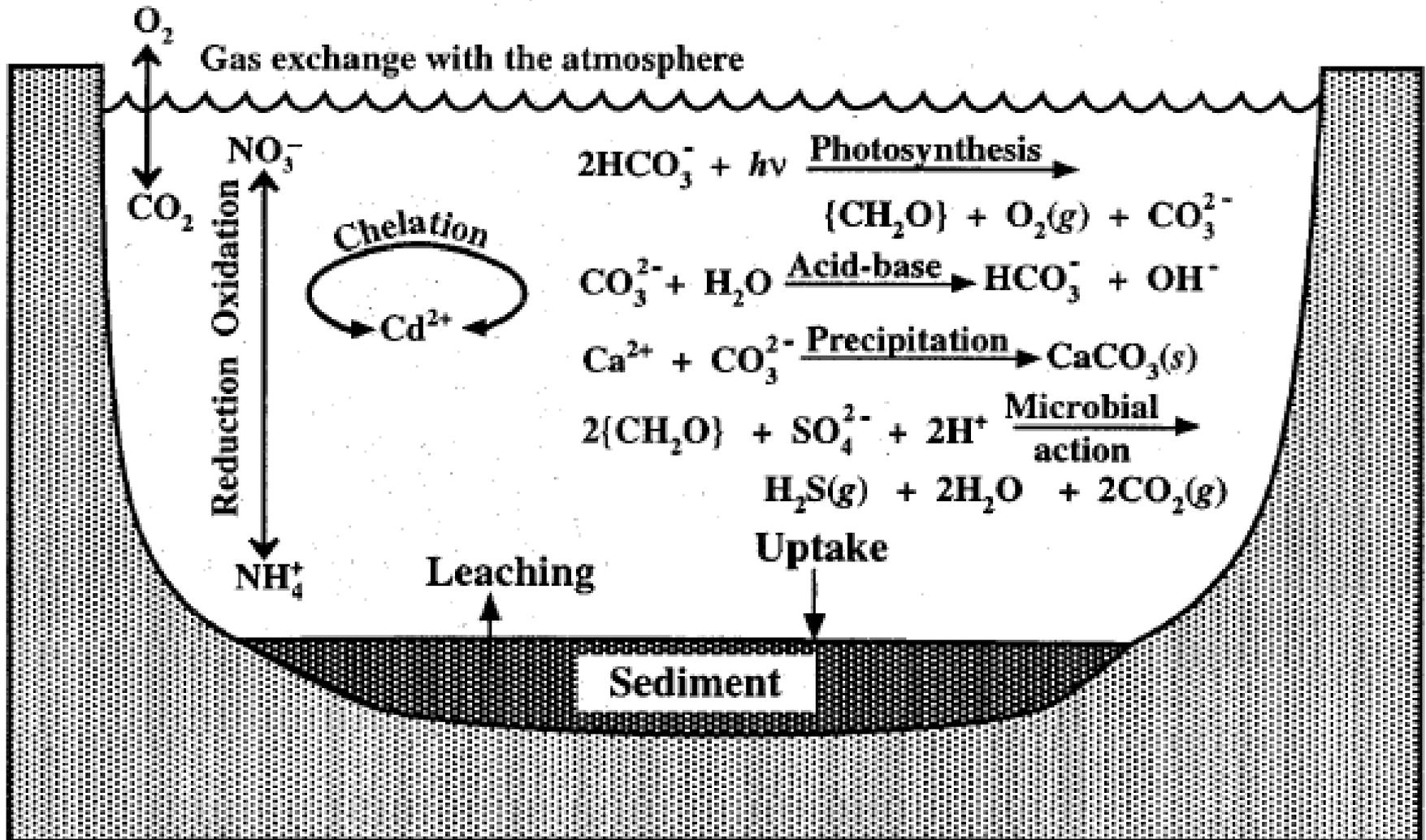
Can range from 0-18 ppm.

Most natural water systems require 5-6 ppm to support a diverse population.

Varies with time of day, weather, temperature.

This Figure summarizes important aspects of aquatic chemistry applied to environmental chemistry.

As shown in this figure, a number of chemical phenomena occur in water. Many aquatic chemical processes are influenced by the action of **algae and bacteria** in water.



Alkalinity: Alkalinity refers to the capability of water to neutralize acid.

Buffering capacity – resistance to pH changes.

Common natural buffer: CO_3 (carbonates – like limestone).

Protects aquatic life.

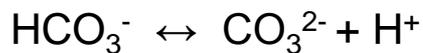
Commonly linked to water hardness.

In natural systems: 50 – 150 mg/L as CaCO_3 .

Effects of pH on Various Buffers

Mixture of an acid (or base) and its conjugate base (or acid)

chemical equilibrium:



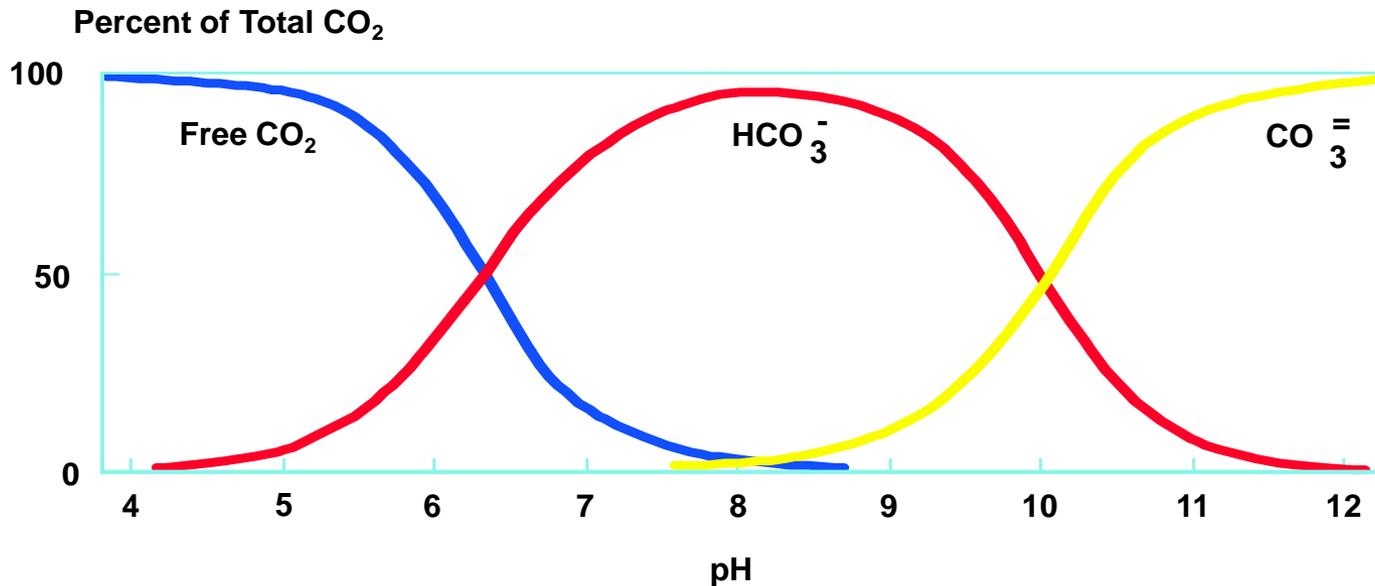
OH^- is a strong base.

HCO_3^- is a weak acid

more OH^- than HCO_3^- , it completely neutralizes it and just have OH^-

more HCO_3^- than OH^- , then it partially neutralizes it and detect only HCO_3^-

- Water with low alkalinity are very susceptible to changes in pH.
- Water with high alkalinity are able to resist major shifts in pH.
- As increasing amounts of acid are added to a water body, the pH of the water decreases, and the buffering capacity of the water is consumed.



Acidity as applied to natural water systems is the capacity of the water to neutralize OH⁻

Acidity generally results from the presence of weak acids such as H₂PO₄⁻, O₂, H₂S, proteins, fatty acids, and acidic metal ions, particularly Fe³⁺.



Total Hardness = Ca^{2+} hardness + Mg^{2+} hardness + other divalent cations

Carbonate Hardness:

- Ca^{2+} , Mg^{2+} associated with HCO_3^- , CO_3^{2-}
- Often called "temporary hardness" because heating the water will remove it.
- When the water is heated, the insoluble carbonates will precipitate and tend to form bottom deposits in water heaters.
- The amount of hardness in excess of this is called noncarbonate hardness.

Non-Carbonate Hardness:

- Ca^{2+} , Mg^{2+} associated with other ions, Cl^- , NO_3^- , SO_4^{2-}

Example 1: From water analysis:

	mg/l	meq/l
Ca ²⁺	140	140/20= 7
Mg ²⁺	24	24/12.15= 2
HCO ₃ ⁻	305	305/61= 5
CO ₂		
Total hardness = Ca ²⁺ + Mg ²⁺ = 7+2 = 9 meq/l		
Carbonate hardness = 5 meq/l		
Non- Carbonate hardness = 4 meq/l		

Note: total hardness more than carbonate hardness

Solution 1:

	mg/l	meq/l
Ca ²⁺	80	80/20= 4
Mg ²⁺	12	12/12.15= 1
HCO ₃ ⁻	305	305/61= 5
CO ₂		
Total hardness = Ca ²⁺ + Mg ²⁺ = 4+1 = 5 meq/l		
Carbonate hardness = 5 meq/l		
Non- Carbonate hardness = 0 meq/l		

Note: total hardness equals carbonate hardness

Continue example 1.:

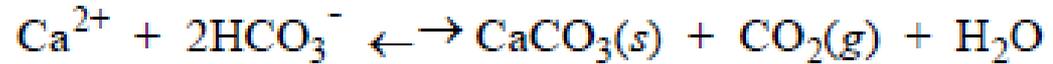
	mg/l	meq/l
Ca ²⁺	70	70/20= 3.5
Mg ²⁺	6	6/12.15= 0.5
HCO ₃ ⁻	305	305/61= 5*
CO ₂		
Total hardness = Ca ²⁺ + Mg ²⁺ = 3.5 + 0.5 = 4 meq/l		
Carbonate hardness = 5 meq/l		
Non- Carbonate hardness = 0 meq/l		

Note: total hardness less than carbonate hardness

*** 1 eq HCO₃⁻ / l is related to Na⁺, K⁺ etc**

Temporary hardness is due to the presence of calcium and bicarbonate ions in water and may be eliminated by boiling the water.

Increased temperature may force this reaction to the right by evolving CO₂ gas, and a white precipitate of calcium carbonate may form in boiling water having temporary hardness.



Substances present in natural water

Water is H₂O when it is absolutely pure

Absolutely pure water does not exist in nature

The substance present in water are either in a solid, liquid or gas form.

- Particles of molecular size or dissolved particles $d < 1\text{nm} = 10^{-9}\text{ m}$
- Particles of colloidal size $1\text{ nm} < d < 1\text{ }\mu\text{ m}$
- Suspended particles $d > 1\text{ }\mu\text{ m}$

Dissolved substance

a) Inorganic dissolved substance like cations and anions:

Cations	Monovalent	Na^+ , K^+ , NH_4^+
	divalent	Ca^{2+} , Mg^{2+} , Fe^{2+} , Mn^{2+}
	trivalent	Fe^{3+} , Al^{3+}
anions	Monovalent	Cl^- , HCO_3^- , NO_2^- , NO_3^- , H_2PO_4^- (dihydrogen phosphate)
	divalent	SO_4^{2-} , CO_3^{2-} , HPO_4^{2-}
	trivalent	PO_4^{3-}

And molecules like CO_2 (H_2CO_3), N_2 , O_2 , H_2S

The concentration in water expressed in mg/l or g/m³

Another unit is meq/l.

In this case the atomic weight of the element or compound divided by the valency.

So Na⁺ atomic weight 23 1 meq/l = 23/1 mg/l

 Ca²⁺ atomic weight 40 1 meq/l = 40/2 mg/l

For neutrality the total amount of cations expressed in meq/l must be equal to the total amount of anions expressed in meq/l.

Example 2:

We got the following laboratory analysis of a groundwater:

Cations	mg/l	Anions	mg/l
Na ⁺	46	Cl ⁻	106.5
K ⁺	4	HCO ₃ ⁻	152
Ca ²⁺	60	SO ₄ ²⁻	24
Mg ²⁺	12.1	NO ₃ ⁻	3

Cations	Molecular weight	Anions	Molecular weight
Na ⁺	23	Cl ⁻	35.5
K ⁺	39.1	HCO ₃ ⁻	61
Ca ²⁺	40	SO ₄ ²⁻	96
Mg ²⁺	24.1	NO ₃ ⁻	62

Cations	mg/l	meq/l	Anions	mg/l	meq/l
Na ⁺	46	$46 / (23/1) = 2$	Cl ⁻	106.5	$105.5 / (35.5/1) = 3$
K ⁺	4	$4 / (39.1/1) = 0.1$	HCO ₃ ⁻	152	$152 / (61/1) = 2.5$
Ca ²⁺	60	$60 / (40/2) = 3$	SO ₄ ²⁻	24	$24 / (96/2) = 0.5$
Mg ²⁺	12.1	$12.1 / (24.1/2) = 1$	NO ₃ ⁻	3	$3 / (62/1) = 0.05$
Total cations		6.1	Total anions		6.05

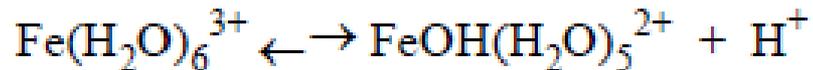
METAL IONS IN WATER

Metal ions in water, commonly denoted M^{n+} , exist in numerous forms.

metal ion, Mg^{2+} for example, cannot exist as a separate entity in water.

To secure the highest stability of their outer electron shells, metal ions in water are bonded, or *coordinated, to water molecules in forms such as the hydrated metal cation $M(H_2O)_x^{n+}$*

Metal ions in aqueous solution seek to reach a state of maximum stability through chemical reactions including acid-base,



precipitation,



and oxidation-reduction reactions:



Metals may exist in water reversibly bound to inorganic anions or to organic compounds as metal complexes, or they may be present as organometallic compounds containing carbon-to-metal bonds.

OXIDATION-REDUCTION

Oxidation-reduction (redox) reactions in water involve the transfer of electrons between chemical species.

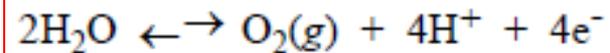
In natural water, wastewater, and soil, most significant oxidation-reduction reactions are carried out by bacteria.

The relative oxidation-reduction tendencies of a chemical system depend upon the activity of the electron, e^- .

When the electron activity is **relatively high**, chemical species (even including water) tend to accept electrons and are **reduced**.



When the electron activity is **relatively low**, the medium is **oxidizing**, and chemical species such as H_2O may be oxidized, losing electrons



The relative tendency toward oxidation or reduction is based upon the electrode potential, E

E is defined as exactly zero when the activity of H^+ is exactly 1 (concentration approximately 1 mole per liter) and the pressure of H_2 gas is exactly 1 atmosphere.

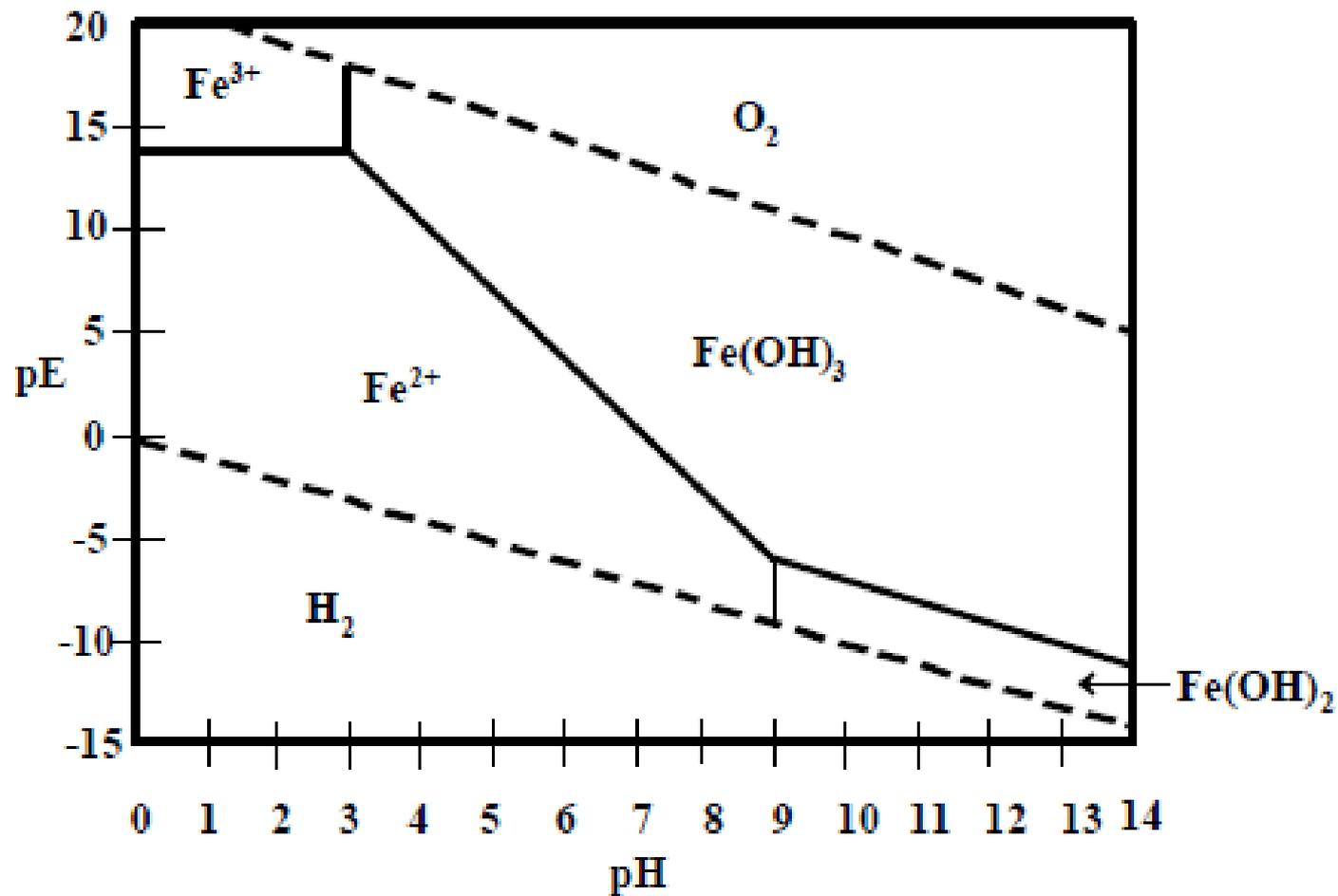
$$pE = -\log a_e$$

The value of pE is calculated from E by the relationship,

$$pE = \frac{E}{\frac{2.303RT}{F}}$$

where R is the gas constant, T is the absolute temperature, and F is the Faraday (the amount of electric charge per mole of electrons). At 25°C for E in volts, $pE = E/0.0591$.

A simplified pE-pH diagram for iron in water (maximum total soluble iron concentration 1.0×10^{-5} M).



Oxidation-reduction reactions in water: Most of the many oxidation-reduction reactions that occur in water are mediated (catalyzed) by bacteria.

For example: In the **oxygen-deficient (anaerobic)** lower layers of a body of water bacteria convert inorganic nitrogen largely to ammonium ion, NH_4^+ .

Near the surface: where O_2 is available bacteria convert inorganic nitrogen to nitrate ion, NO_3^- .

Metals in water may be bound to organic chelating agents, such as pollutant nitrilotriacetic acid (NTA) or naturally occurring fulvic acids.

b) The organic dissolved substance:

Organic matter ($C_a H_b O_c$): Are not specified generally in water analysis except in case they are toxic. Generally some parameters are used based upon the oxygen consumption of the organic compound involved.

Measurements of organic matter:-

Many parameters have been used to measure the concentration of organic matter in water. The following are the most common used methods:

Biochemical oxygen demand (BOD).

BOD₅ is the oxygen equivalent of organic matter. It is determined by measuring the dissolved oxygen used by microorganisms during the biochemical oxidation of organic matter in 5 days at 20°C

Chemical oxygen demand (COD)

It is the amount of oxygen necessary to oxidize all the organic carbon completely to CO₂ and H₂O.

Is measured by oxidation with potassium dichromate (K₂Cr₂O₇) in the presence of sulfuric acid and silver and expressed in milligram per liter.

COMPLEXATION AND CHELATION

a metal ion in water may combine with an ion or compound that contributes electron pairs to the metal ion. Such a substance is an electron donor

cadmium ion in water combines with a cyanide ion ligand to form a complex ion

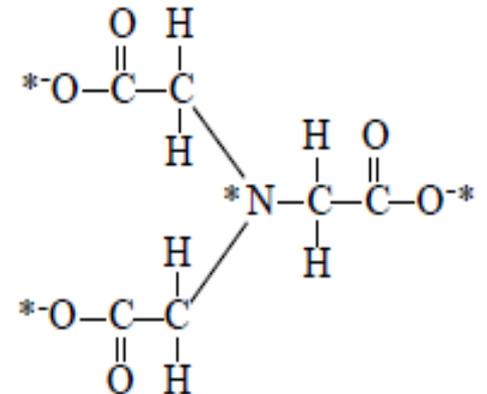


Additional cyanide ligands can be added to form the progressively weaker (more easily dissociated) complexes with the chemical formulas $\text{Cd}(\text{CN})_2$, $\text{Cd}(\text{CN})_3^{-}$, and $\text{Cd}(\text{CN})_4^{2-}$.

a unidentate ligand, only one site that bonds to the cadmium metal ion

A chelating agent has more than one atom that can be bonded to a central metal ion at one time to form a ring structure. One such chelating agent is the nitrilotriacetate (NTA) ligand, which has the following formula

This ion has four binding sites, each marked with an asterisk (*) which can simultaneously bond to a metal ion.

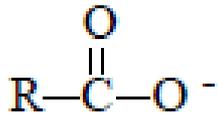


Generally, since a chelating agent may bond to a metal ion in more than one place simultaneously, chelates are more stable than complexes involving unidentate ligands.

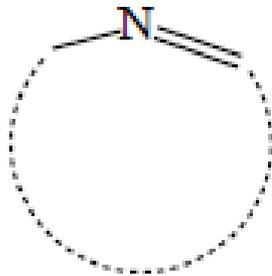
Stability tends to increase with the number of chelating sites available on the ligand.

Structures of metal chelates take a number of different forms, all characterized by rings in various configurations.

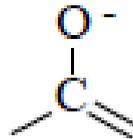
The ligands found in natural waters and wastewaters contain a variety of functional groups which can donate the electrons required to bond the ligand to a metal ion. Among the most common of these groups are:



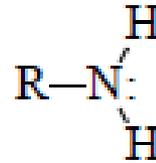
Carboxylate



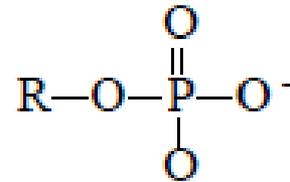
Heterocyclic nitrogen



Phenoxide



Aliphatic and aromatic amino



Phosphate

Complexation may cause changes in oxidation state of the metal and may result in a metal becoming solubilized from an insoluble compound. The formation of insoluble complex compounds removes metal ions from solution.

These ligands complex most metal ions found in unpolluted waters and biological systems (Mg^{2+} , Ca^{2+} , Mn^{2+} , Fe^{2+} , Cu^{2+} , Zn^{2+} , VO^{2+}).

They also bind to contaminant metal ions such as Co^{2+} , Ni^{2+} , Sr^{2+} , Cd^{2+} , and Ba^{2+} .

Occurrence and Importance of Chelating Agents in Water

Chelating agents are common potential water pollutants.

These substances can occur in sewage effluent and industrial wastewater such as metal plating wastewater.

Chelates formed by the strong chelating agent ethylenediaminetetraacetate (EDTA) have been shown to greatly increase the migration rates of radioactive ^{60}Co from pits and trenches used for disposal of intermediate-level radioactive waste.

EDTA was used as a cleaning and solubilizing agent for the decontamination of hot cells, equipment, and reactor components.

Such chelates with negative charges are much less strongly sorbed by mineral matter and are vastly more mobile than the unchelated metal ions.

Complexation by Humic substances

The most important class of complexing agents that occur naturally are the humic substances.

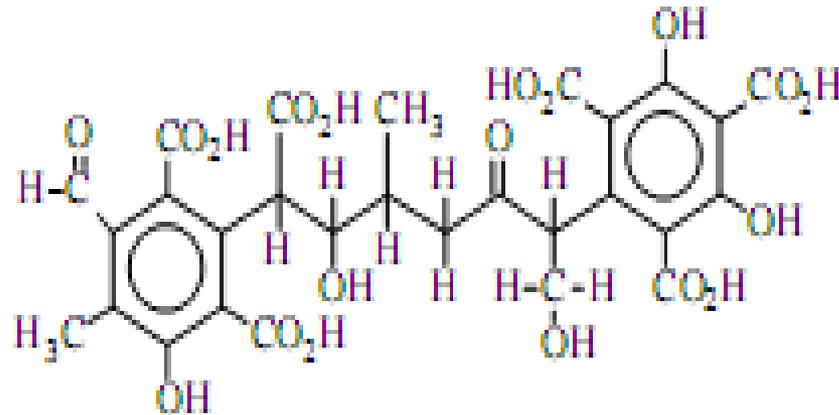
These are *degradation-resistant materials*, formed during the decomposition of vegetation, that occur as deposits in soil, marsh sediments, peat, coal, lignite, or in almost any location where large quantities of vegetation have decayed.

They are commonly classified on the basis of **solubility**. If a material containing humic substances is extracted with strong base, and the resulting solution is acidified, the products are:

- (a) a nonextractable plant residue called **humin**;
- (b) a material that precipitates from the acidified extract, called **humic acid**;
- (c) an organic material that remains in the acidified solution, called **fulvic acid**. Because of their acid-base, sorptive, and complexing properties, both the soluble and insoluble humic substances have a strong effect upon the properties of water. In general, fulvic acid dissolves in water and exerts its effects as the soluble species. Humic acid remains insoluble and affects water quality through exchange of species, such as cations or organic materials, with water.

Humic substances are high-molecular-mass, polyelectrolytic macromolecules. Molecular masses range from a few hundred for fulvic acid to tens of thousands for the humic acid and humin fractions.

Some feeling for the nature of humic substances can be obtained by considering the following structure of a hypothetical molecule of fulvic acid:



The binding of metal ions by humic substances is one of the most important environmental qualities of humic substances.

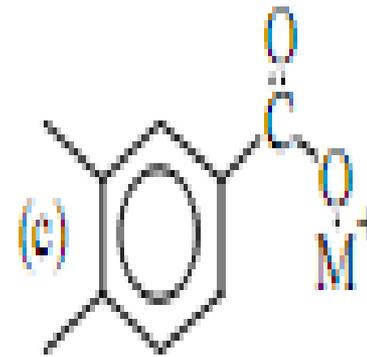
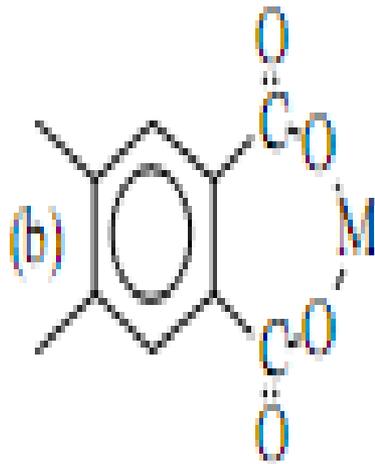
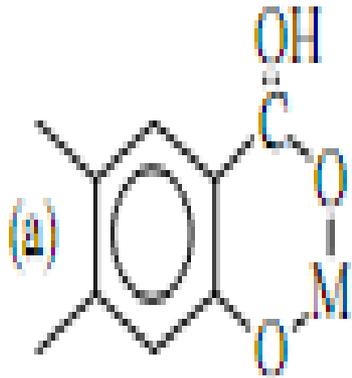
The binding of metal ions by humic substances is one of the most important environmental qualities of humic substances.

This binding can occur as chelation between a **carboxyl group** and a **phenolic hydroxyl group**, as chelation between two carboxyl groups, or as complexation with a carboxyl group.

Binding of a metal ion, M^{2+} , by humic substances by chelation between

(a) carboxyl and phenolic hydroxyl,

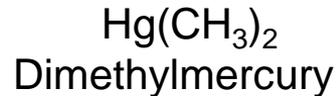
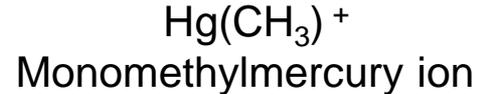
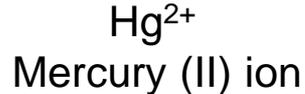
(b) two carboxyl groups, and (c) by complexation with a carboxyl group.



Metals Bound as Organometallic Compounds

Another major type of metal species important in hazardous wastes consists of organometallic compounds, which differ from complexes and chelates in that they are bonded to the metal by a **carbon-metal bond** and the organic ligand is frequently not capable of existing as a stable separate species.

Typical examples of organometallic compound species are:



Organometallic compounds may enter the environment directly as pollutant industrial chemicals and some, including organometallic mercury, tin, selenium, and arsenic compounds, are synthesized biologically by bacteria.

Some of these compounds are particularly toxic because of their mobilities in living systems and abilities to cross cell membranes

WATER INTERACTIONS WITH OTHER PHASES

Most of the important chemical phenomena associated with water do not occur in solution, but rather through interaction of solutes in water with other phases.

For example, the oxidation-reduction reactions catalyzed by bacteria occur in bacterial cells. Many organic hazardous wastes are carried through water as emulsions of very small particles suspended in water.

Some hazardous wastes are deposited in sediments in bodies of water, from which they may later enter the water through chemical or physical processes and cause severe pollution effects.

Films of organic compounds, such as hydrocarbon liquids, may be present on the surface of water. Exposed to sunlight, these compounds are subject to photochemical reactions. Gases such as O_2 , CO_2 , CH_4 , and H_2S are exchanged with the atmosphere.

Photosynthesis occurs in suspended cells of algae, and other biological processes, such as biodegradation of organic wastes, occur in bacterial cells. Particles contributing to the turbidity of water may be introduced by physical processes, including the erosion of streams or sloughing of water impoundment banks.

Chemical processes, such as the formation of solid $CaCO_3$ may also form particles in water.

Sediments

Sediments bind a wide variety of chemical species and are sites of many chemical and biochemical processes.

Anaerobic fermentation of organic matter by bacteria produces methane gas evolved from sediments, along with CO₂ and, frequently, H₂S.

Similar bacteria produce mobile HgCH₃ and Hg(CH₃)₂ from insoluble, relatively harmless inorganic mercury compounds.

Sediments are sinks for many hazardous organic compounds and heavy metal salts that have gotten into water.

Colloids

The most important interactions between species dissolved in aqueous solution and species in other phases occur with **colloidal particles** ranging from *(0.001 to 1 μm) in diameter* and suspended in water, enabling maximum exposure to the water and solutes dissolved in it.

Colloids have a strong influence on aquatic chemistry. Because of their extremely small size, these particles **have a very high surface-to-volume ratio**. Toxic substances in colloidal form are much more available to organisms in water than they are in bulk form. To remove colloidal particles from water, chemical treatment measures are applied to cause colloidal particles to **aggregate** together (processes called **coagulation or flocculation**), and the solids are removed by filtration.

As an example of a water-treatment process in which water alkalinity is important, consider the use of filter alum, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ **as a coagulant**. The hydrated aluminum ion is acidic, and, when it is added to water, it reacts with base to form gelatinous aluminum hydroxide,



which settles and carries suspended matter with it. This reaction removes alkalinity from the water. Sometimes, the addition of more alkalinity is required to prevent the water from becoming too acidic.