Chapter 2
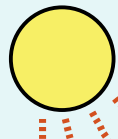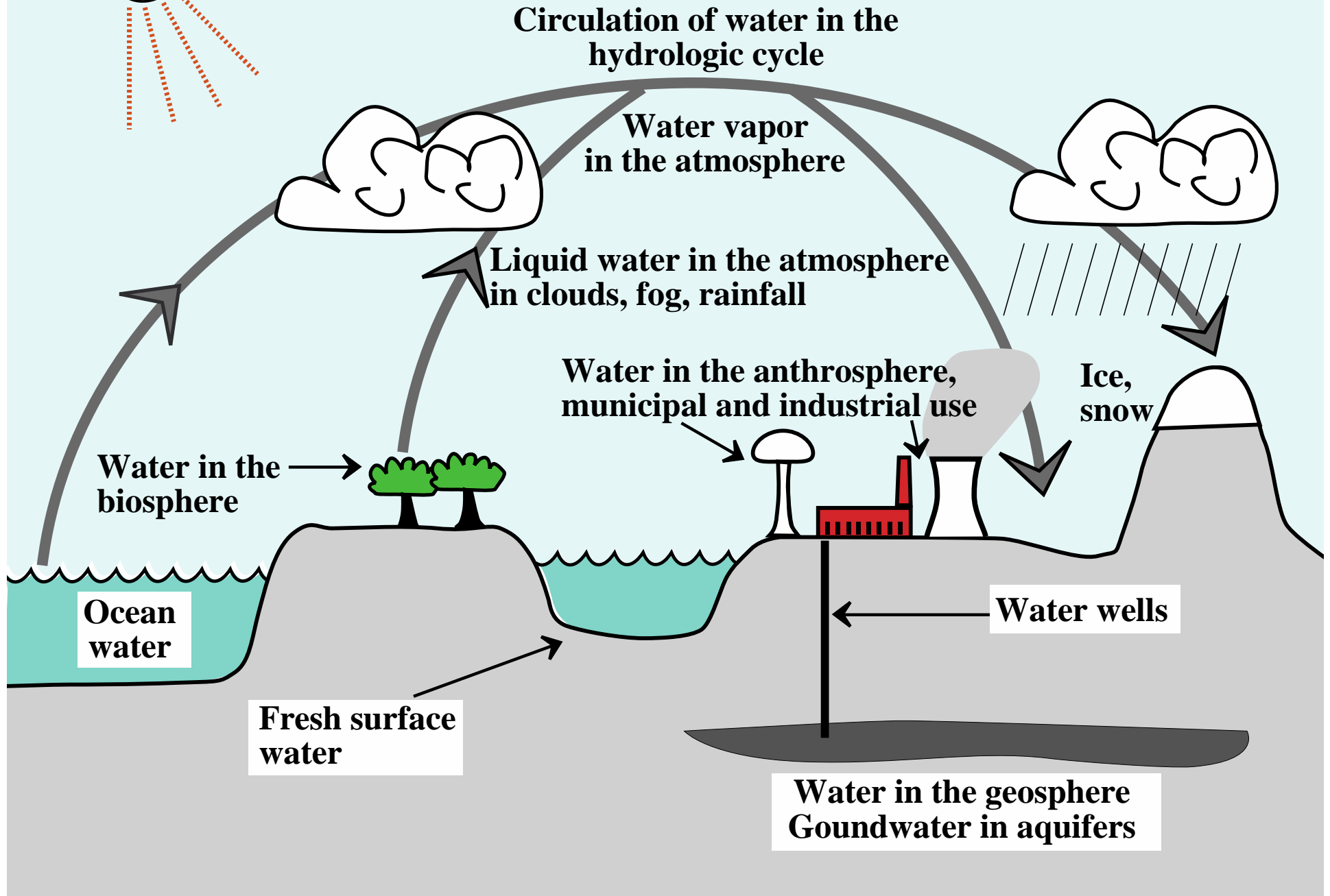# THE HYDROSPHERE AND WATER CHEMISTRY

Environmental Chemistry, 10th Edition
Stanley E. Manahan
Taylor and Francis/CRC Press
2017

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2.1 Water: An Essential Part of Earth's Natural Capital

Circulation of water in the hydrologic cycle

Water vapor in the atmosphere

Liquid water in the atmosphere in clouds, fog, rainfall

Water in the anthrosphere, municipal and industrial use

Ice, snow

Water in the biosphere

Ocean water

Water wells

Fresh surface water

Water in the geosphere Goundwater in aquifers

Science of Water

Hydrology: Study of water

Limnology: Science of fresh water

Oceanography: Science of oceans

Environmental and resource problems with water

• Too little water: Drought, global warming

• Too much water: Floods

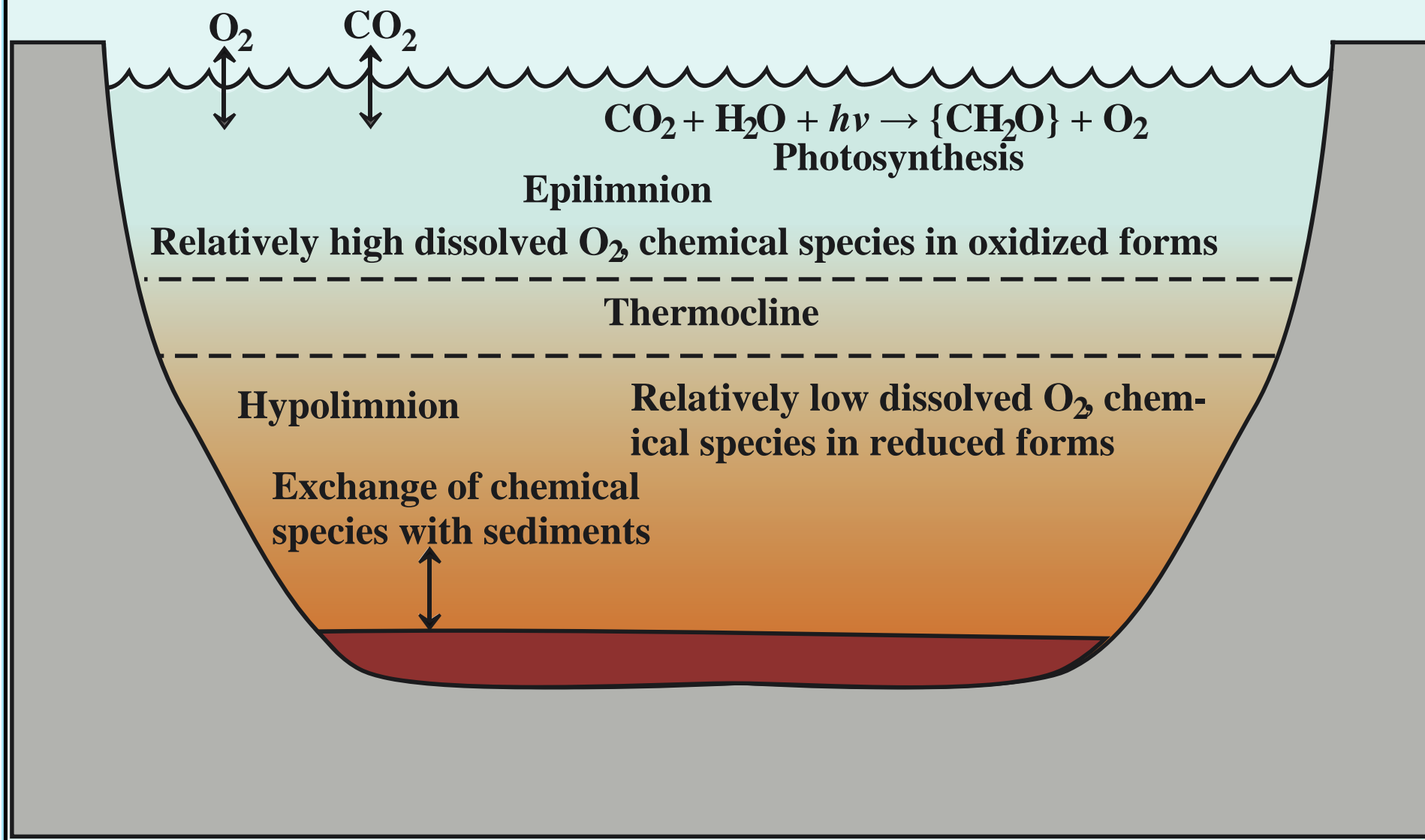• Waterborne diseases

• Contaminated water, water pollutants

Water chemistry must consider many factors

• Where water is found

• Interactions with geosphere (especially groundwater)

• Organisms (especially microorganisms) in water

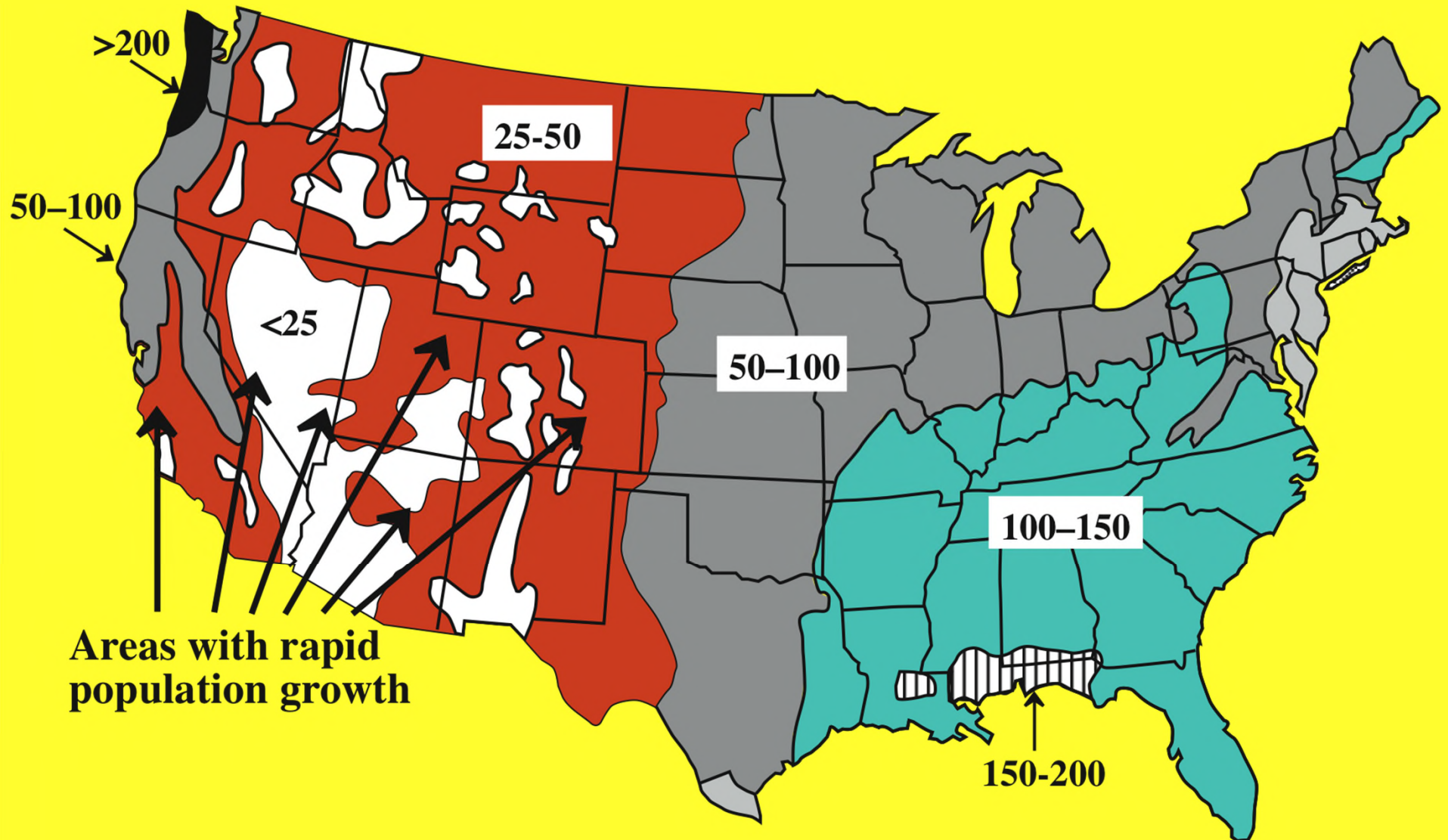• Human influences (interaction with anthrosphere)

Water very much involved with chemical fate and transport in the Earth System

Figure 2.2. The physical behavior of water has much to do with its chemical and environmental behavior and with aquatic life
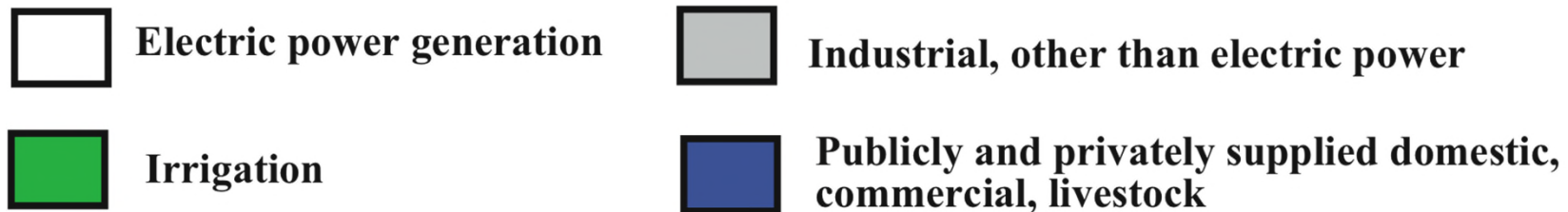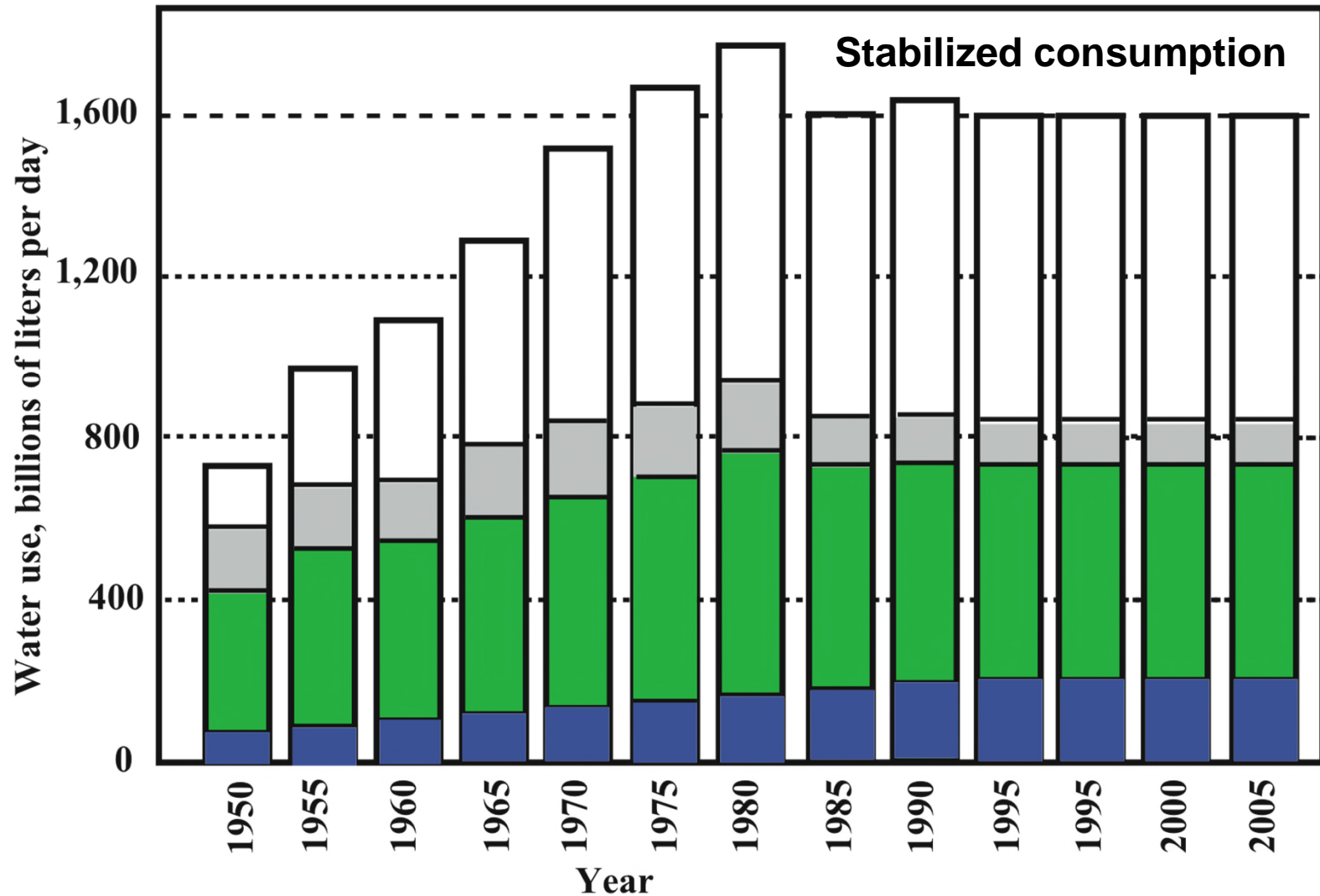

O_2 CO_2

$$CO_2 + H_2O + hv \rightarrow \{CH_2O\} + O_2$$
Photosynthesis

Epilimnion

Relatively high dissolved O_2, chemical species in oxidized forms

Thermocline

Hypolimnion   Relatively low dissolved O_2, chemical species in reduced forms

Exchange of chemical species with sediments

2.2 Sources and Uses of Water

>200

50–100

25-50

<25

50–100

100–150

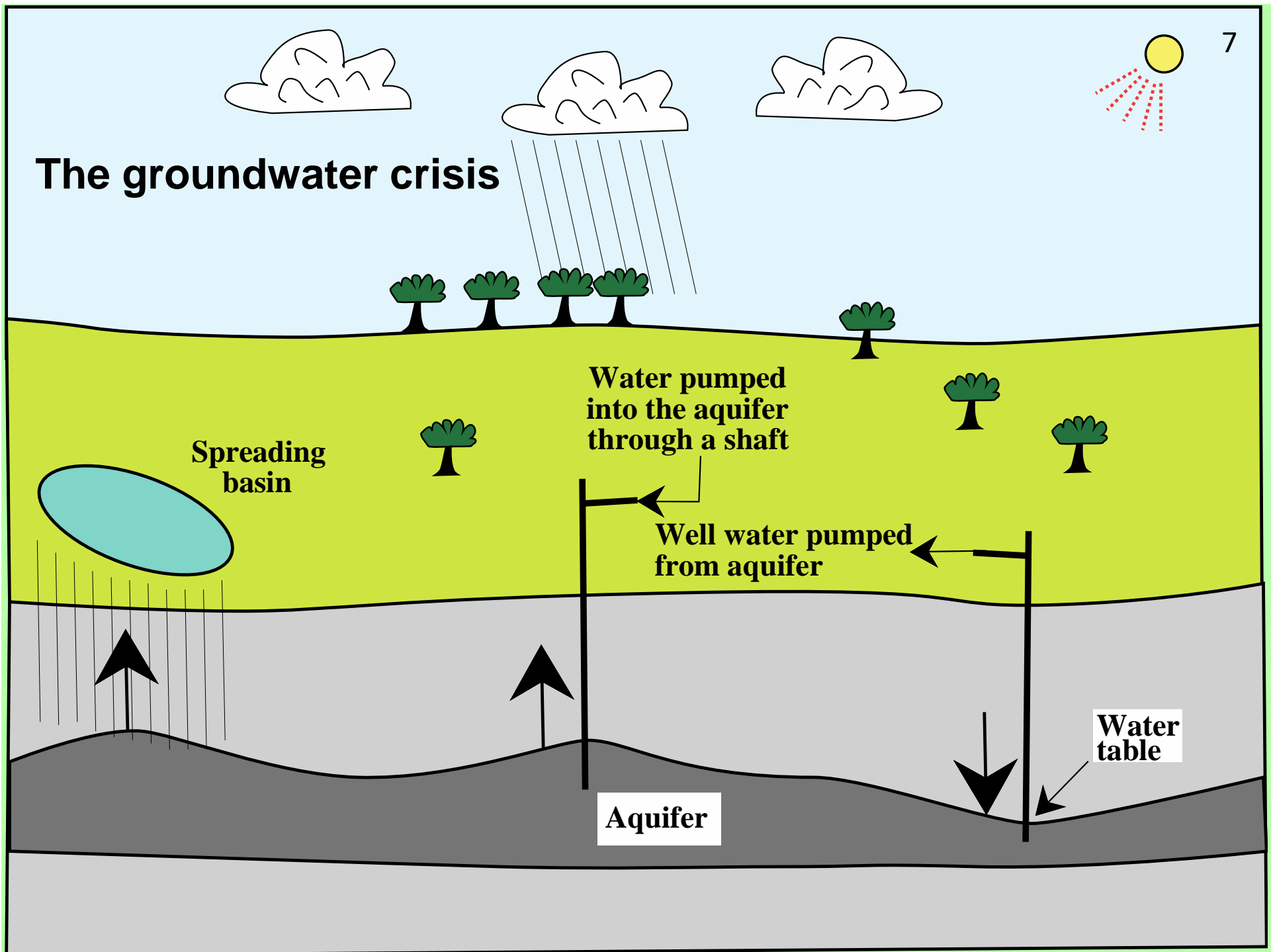150-200

Areas with rapid population growth

A major consideration regarding water sources is uneven distribution of water as shown by rainfall distribution in continental U.S., cm/year (Fig 2.3 showing average annual rainfall, cm/year)

Figure 2.4. Trends in U.S. Water Use, which has stabilized

Figure 2.4. Trends in U.S. Water Use, which has stabilized

Stabilized consumption

Legend:
- Electric power generation
- Industrial, other than electric power
- Irrigation
- Publicly and privately supplied domestic, commercial, livestock

The groundwater crisis

Water pumped
into the aquifer
through a shaft

Spreading
basin

Well water pumped
from aquifer

Water
table

Aquifer

Groundwater is a major source of municipal water

- Only source in some areas
- About 190 billion liters per day for irrigation in the U.S.

Rapid depletion of groundwater in some areas

- Especially problematic in California's Central Valley–the vegetable garden of the U.S.
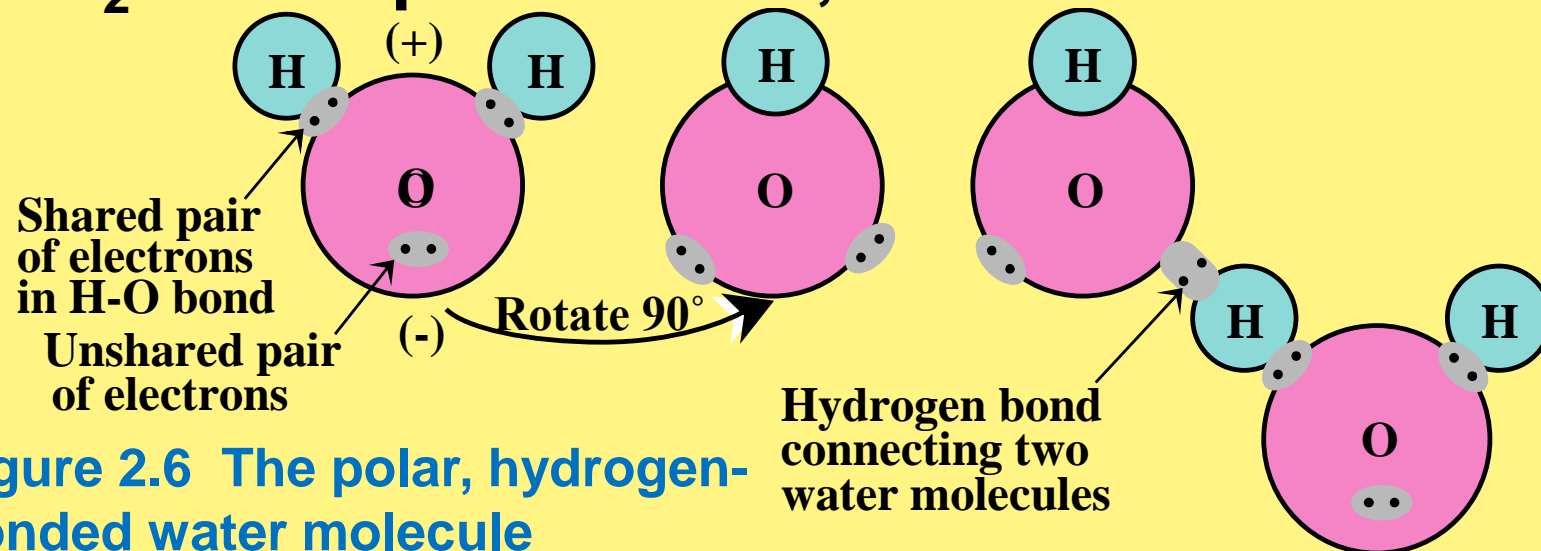- Severe in many areas of Africa and Asia

Measures to alleviate groundwater shortages, especially deeper wells

- Lowered water table, no more water can be pumped
- Intrusions of saline water, especially in coastal areas
- Irreversible damage to aquifer compaction, cannot be recharged
- Surface subsidence, even structural damage
- Depletion of surface water in lakes and rivers
- Contributes to desertification–productive land becomes desert

2.3 H$_2$O: Simple Formula, Remarkable Molecule

Figure 2.6 The polar, hydrogen-bonded water molecule

(labels in figure:) Shared pair of electrons in H-O bond; Unshared pair of electrons; (+); (-); Rotate 90°; Hydrogen bond connecting two water molecules; H; O

Characteristics of H$_2$O molecule

• **Electron pairs as far apart as possible → angular configuration**

• **Non-bonded pairs of electrons form hydrogen bonds**

Polarity and H-bonding give H$_2$O special properties

• **Good solvent for polar and ionic species**

• **Unique heat/temperature/density behavior**

• **High dielectric constant • High surface tension   • High heat capacity**
• **High heat of fusion   • High heat of evaporation**

• **Stratification of bodies of water**

Transparency allows photosynthesis by algae, photosynthetic bacteria, plants in water

# Hydrogen bonding with solute molecules and between water molecules
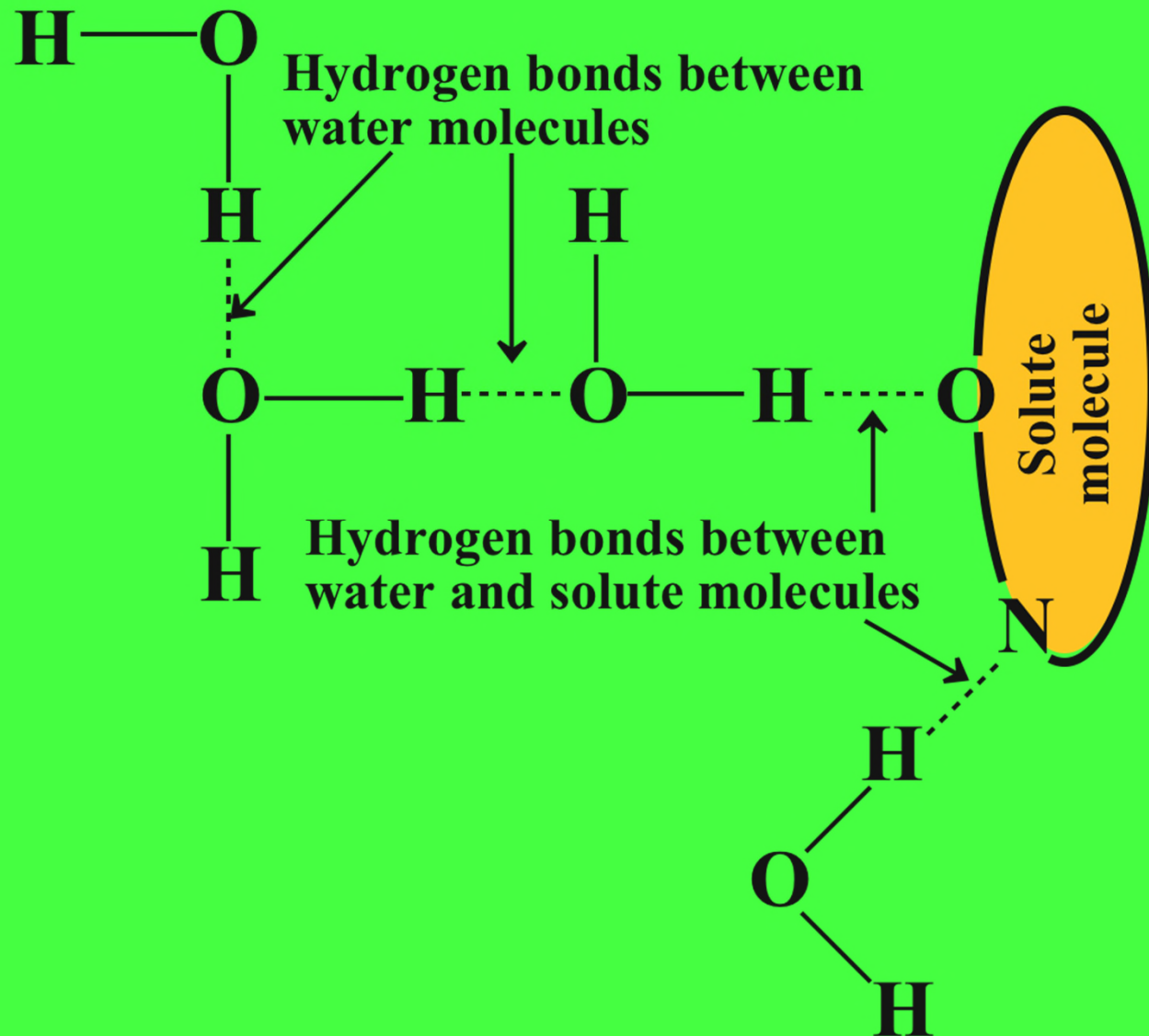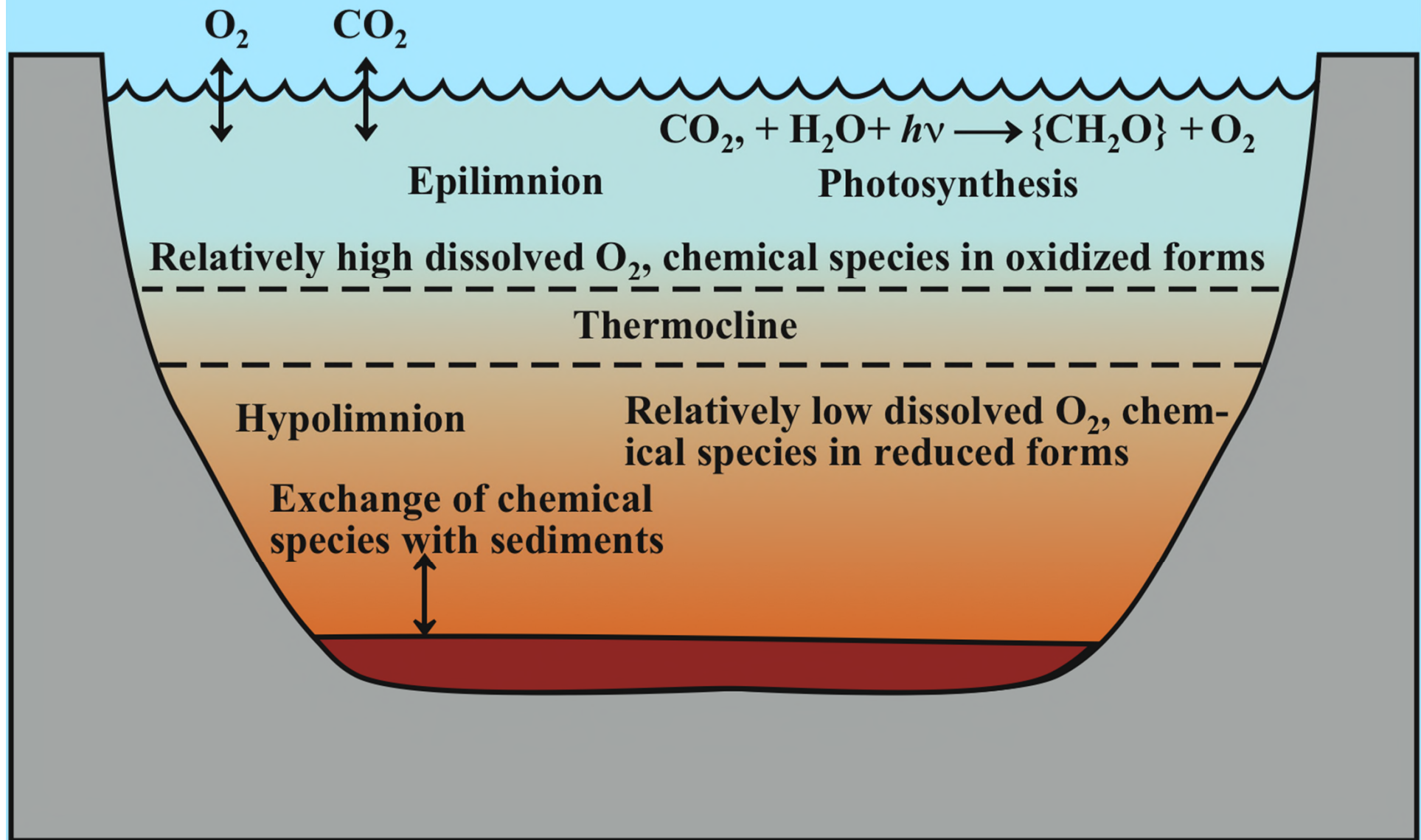
Table 2.1 Important Properties of Water

Property	Effects
Excellent solvent	Transport of nutrients and waste products enabling biological processes to occur 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 ultraviolet light	Colorless, allowing light required for photosynthesis to reach considerable depths in
Maximum density as a liquid at 4°C	Ice floats and vertical circulation is 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	The temperature of water in a body of water is stabilized at the freezing point of water
Higher heat capacity than any other liquid except ammonia	Stabilization of temperatures of organisms and geographical regions

Polar water molecule and solvent effects on ions
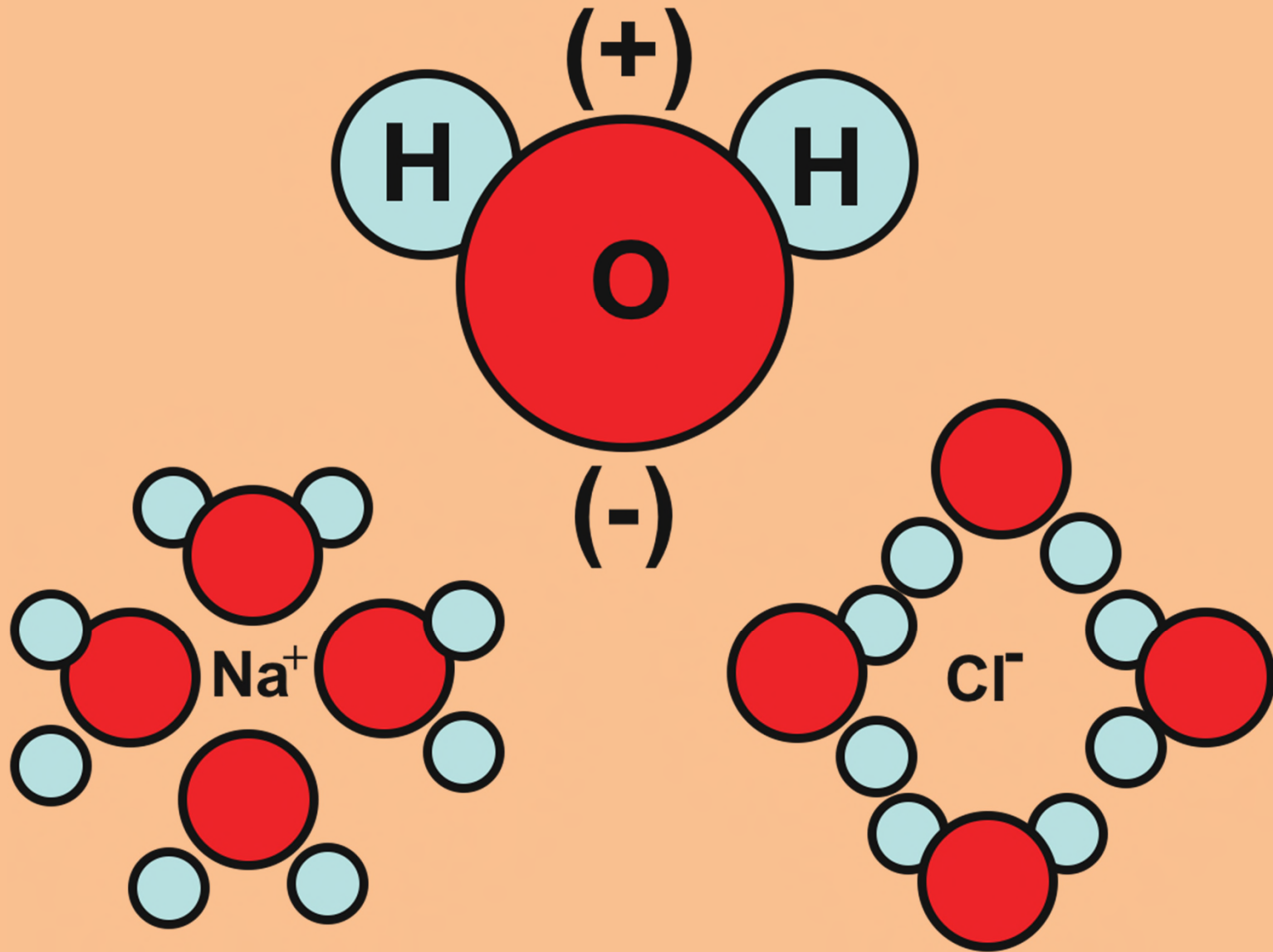
Figure 2.6. Thermal stratification of a lake

Overturn in fall tends to stir up bottom sediment

$$CO_2, + H_2O + h\nu \longrightarrow \{CH_2O\} + O_2$$

Photosynthesis

Epilimnion

Relatively high dissolved O_2, chemical species in oxidized forms

Thermocline

Hypolimnion

Relatively low dissolved O_2, chemical species in reduced forms

Exchange of chemical species with sediments

2.4 Life in Water (Biota)

Autotrophic organisms

- **Utilize solar or chemical energy**
- **Synthesize complex biochemicals from simple inorganic compounds**
- **Photosynthetic aquatic algae are producers that make biomass from CO_2 and other inorganic compounds**

Heterotrophic organisms metabolize organic materials

- **Decomposers (reducers) break down material of biological origin**

Productivity is the ability of organisms in a body of water to produce biomass that is the basis of the food chain

- **Eutrophication caused by excess productivity**

Decay of excess biomass

- **Consumption of oxygen**

Main physical factors affecting aquatic life

- **Temperature**
- **Transparency**
- **Turbulence**

Oxygen in water

- **Dissolved oxygen, DO**
- **Biochemical oxygen demand, BOD, from degradable substances**

2.5 Introduction to Aquatic Chemistry

Common chemical phenomena occur in water

- Acid-base • Solubility • Oxidation-reduction
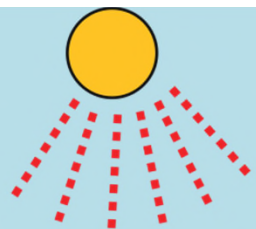- Complexation • Biochemical (oxidation-reduction)

Aquatic systems are complicated, open, and dynamic

- Solid phases • Gas phases • Organisms

Simplified models based upon equilibrium conditions

- Rates of processes (kinetics) also important

Figure 2.7. Major aquatic chemical processes

Gas exchange with the atmosphere

O_2

CO_2

NO_3

Reduction Oxidation

NH_4^+

Chelation

Cd^{2+}

$$2HCO_3^- + h\nu \xrightarrow{\text{Photosynthesis}}$$

$$\{CH_2O\} + O_2(g) + CO_3^{2-}$$

$$CO_3^{2-} + H_2O \xrightarrow{\text{Acid-base}} HCO_3^- + OH^-$$

$$Ca^{2+} + CO_3^{2-} \xrightarrow{\text{Precipitation}} CaCO_3(s)$$

$$2\{CH_2O\} + SO_4^{2-} + 2H^+ \xrightarrow[\text{action}]{\text{Microbial}}$$

$$H_2S(g) + 2H_2O + 2CO_2(g)$$

Leaching   Uptake

Sediment

Ground-water
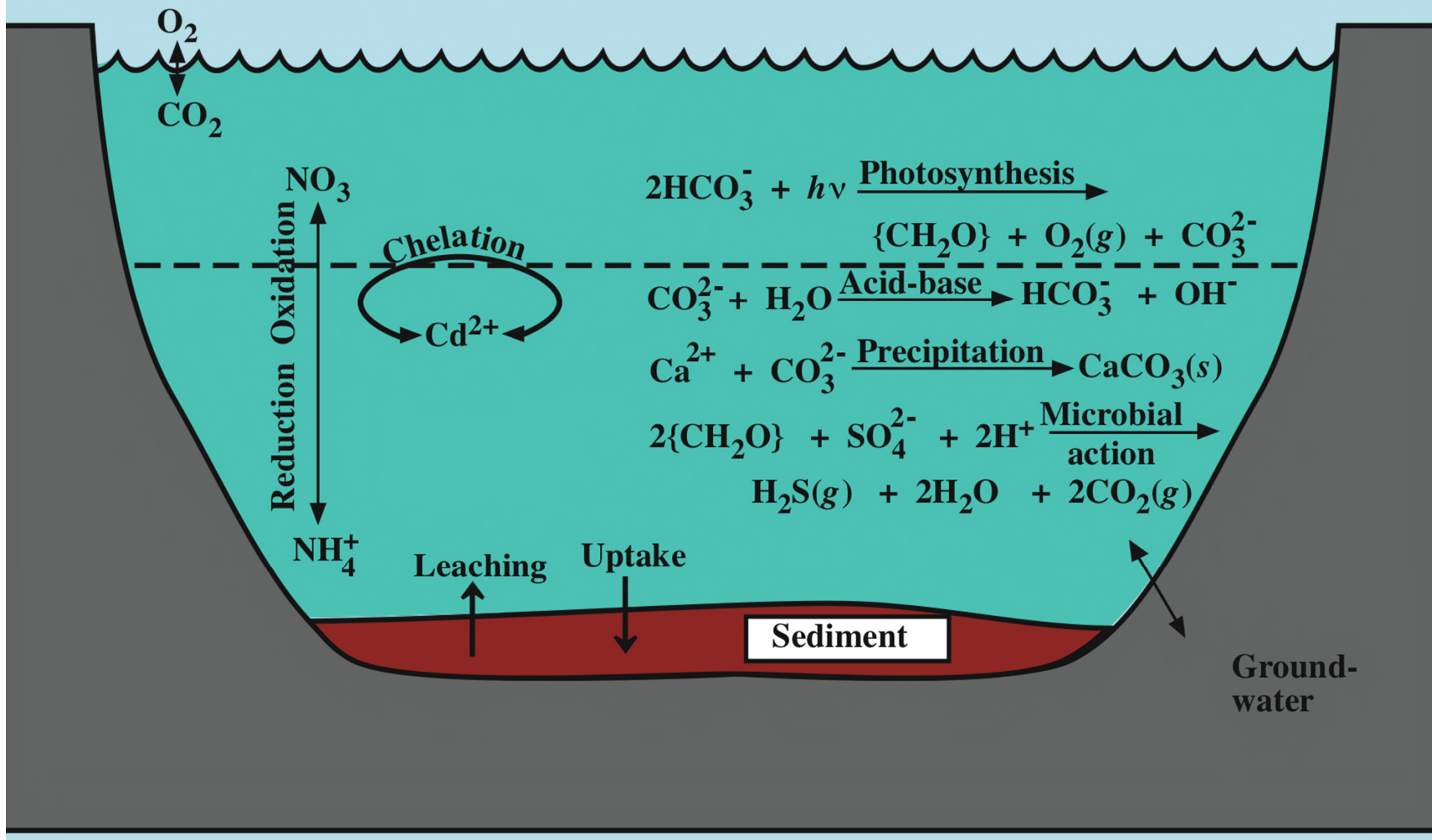
2.6 Gases in Water

- O_2 for fish

- CO_2 to support algal growth

Henry's law: *The solubility of a gas in a liquid is directly proportional to the partial pressure of the gas in contact with the liquid.*

Oxygen in water

- From air (20.95% O_2 on basis of dry air)
- 8.32 mg/L O_2 in water in equilibrium with air at 25˚C
- Decreases with increasing temperature

Oxygen consumed by biodegradation of biomass, $\{CH_2O\}$

- $\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O$
- 8.3 mg O_2 consumed by only 7.8 mg $\{CH_2O\}$

2.7 Water Acidity and Carbon Dioxide in Water

Acidity: **Capacity to neutralize OH^-**

Alkalinity: **Capacity to neutralize H^+**

HCO_3^- as acid releases H^+

• **$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$**
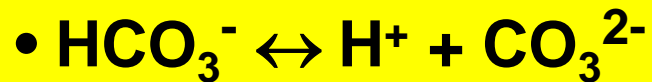
HCO_3^- as base accepts H^+

• **$HCO_3^- + H^+ \leftrightarrow H_2O + CO_2$**
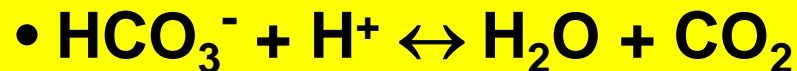
Strong acids such as HCl contribute to free mineral acid, a pollutant

• **Acid mine water from H_2SO_4**

Hydrated metal ions as acids

• **$Al(H_2O)_6^{3+} \leftrightarrow Al(H_2O)_5(OH)^{2+} + H^+$**

Carbon Dioxide in Water

From air and as product of organic matter decay

• **In water mainly as $CO_2(aq)$**

• **Relatively little as H_2CO_3**

Acid-base equilibria for carbon dioxide species

• **$CO_2(aq) + H_2O \leftrightarrow H^+ + HCO_3^-$**

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[CO_2]} = 4.45 \times 10^{-7} \quad pK_{a1} = 6.35$$

• **$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$**

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11} \quad pK_{a2} = 10.33$$

Slight acidity of unpolluted rainwater

Air is 406 parts per million CO_2 (in year 2017)

- **Water in equilibrium with this air has**

  $[CO_2(aq)] = 1.328 \times 10^{-5}$ mol/L

- **$CO_2(aq) + H_2O \leftrightarrow H^+ + HCO_3^-$**

- **$[H^+] = [HCO_3^-]$**

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[CO_2]} = 4.45 \times 10^{-7} \quad pK_{a1} = 6.35$$

Solving the above gives

- **$[H^+] = 2.48 \times 10^{-6}$ mol/L**

- **pH = 5.61**

Figure 2.8. Distribution of CO_2 and carbonate species in water as a function of pH
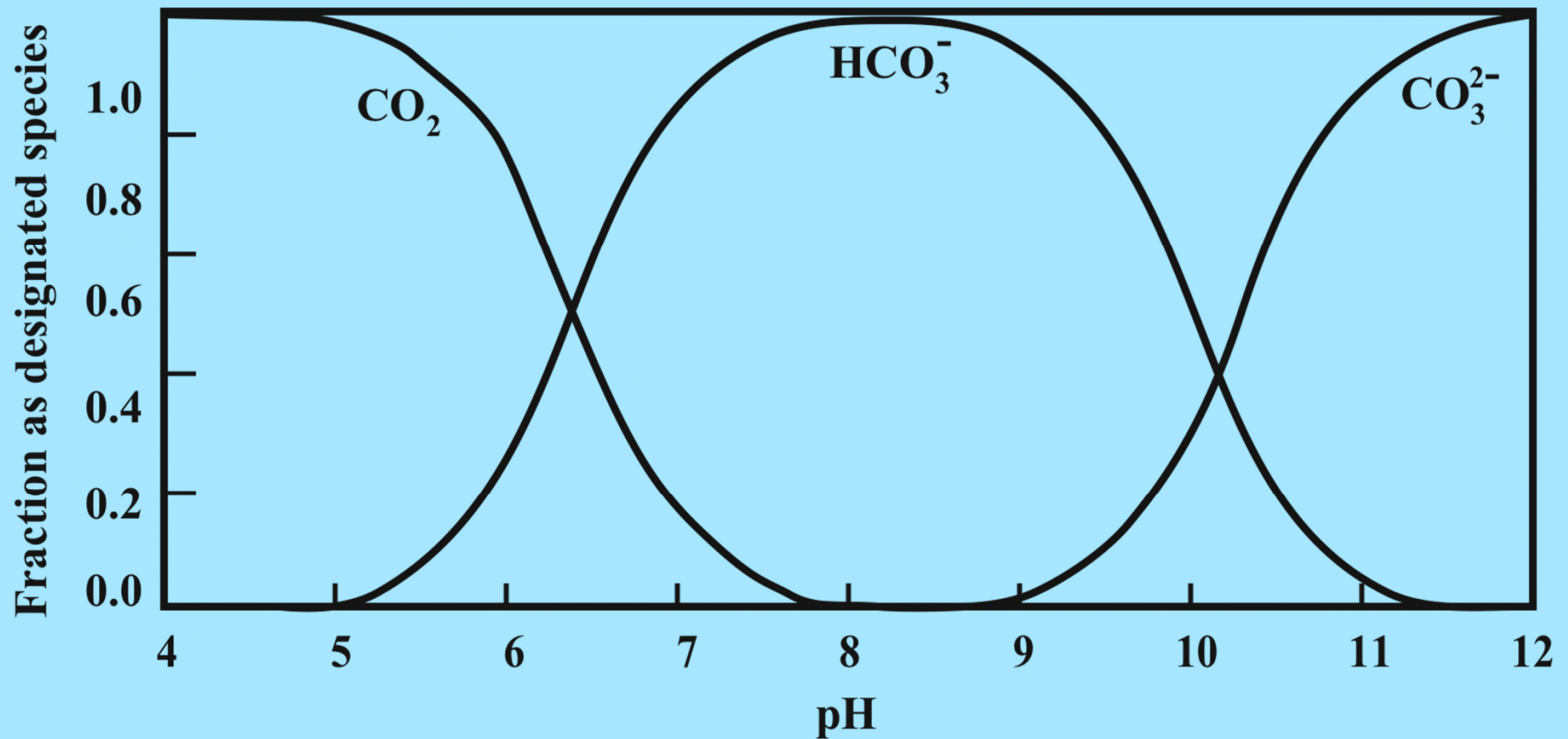
2.8 Alkalinity

Alkalinity is the capacity to accept H^+ ion

• Most commonly: $HCO_3^- + H^+ \leftrightarrow CO_2(aq) + H_2O$

• Other common contributors: OH^-, CO_3^{2-}

Alkalinity

• Buffers water pH

• Carbon source for algal growth

• Reacts with some water treatment chemicals

Complete formula for alkalinity applicable over wide pH range: $[alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$

A common value to assume for alkalinity is

$1.00 \rightarrow 10^{-3}$ mol/L

At pH 7, essentially all alkalinity is from HCO_3^-

At pH 10 significant contributions from CO_3^{2-}, OH^-

• About half the carbon at pH 10 as at pH 7

2.9 Calcium and Other Metal Ions in Water

• **Exist as hydrated metal ions such as $Al(H_2O)_6^{3+}$**

• **The +3 hydrated metal ions lose H^+ so are acidic**

Dissolved Carbon Dioxide and Calcium Carbonate Minerals

For water in equilibrium with air (400 ppm CO_2) and $CaCO_3$ (*s*) (see illustration on next slide):

$[CO_2] = 1.309 \times 10^{-5}$ mol/L $[Ca^{2+}] = 5.18 \times 10^{-4}$ mol/L

$[HCO_3^-] = 1.04 \times 10^{-3}$ mol/L $[H^+] = 5.63 \times 10^{-9}$ mol/L

$[CO_3^{2-}] = 8.63 \times 10^{-6}$ mol/L   pH = 8.25

Figure 2.9 Carbon dioxide-calcium carbonate equilibria

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca^{2+} + 2HCO_3^-$$

2.10 Complexation and Chelation

$Fe(H_2O)_6^{2+} + CN^- \leftrightarrow Fe(H_2O)_5CN^+ + H_2O$

$Fe(H_2O)_5CN^- + CN^- \leftrightarrow Fe(H_2O)_4(CN)_2 + H_2O$
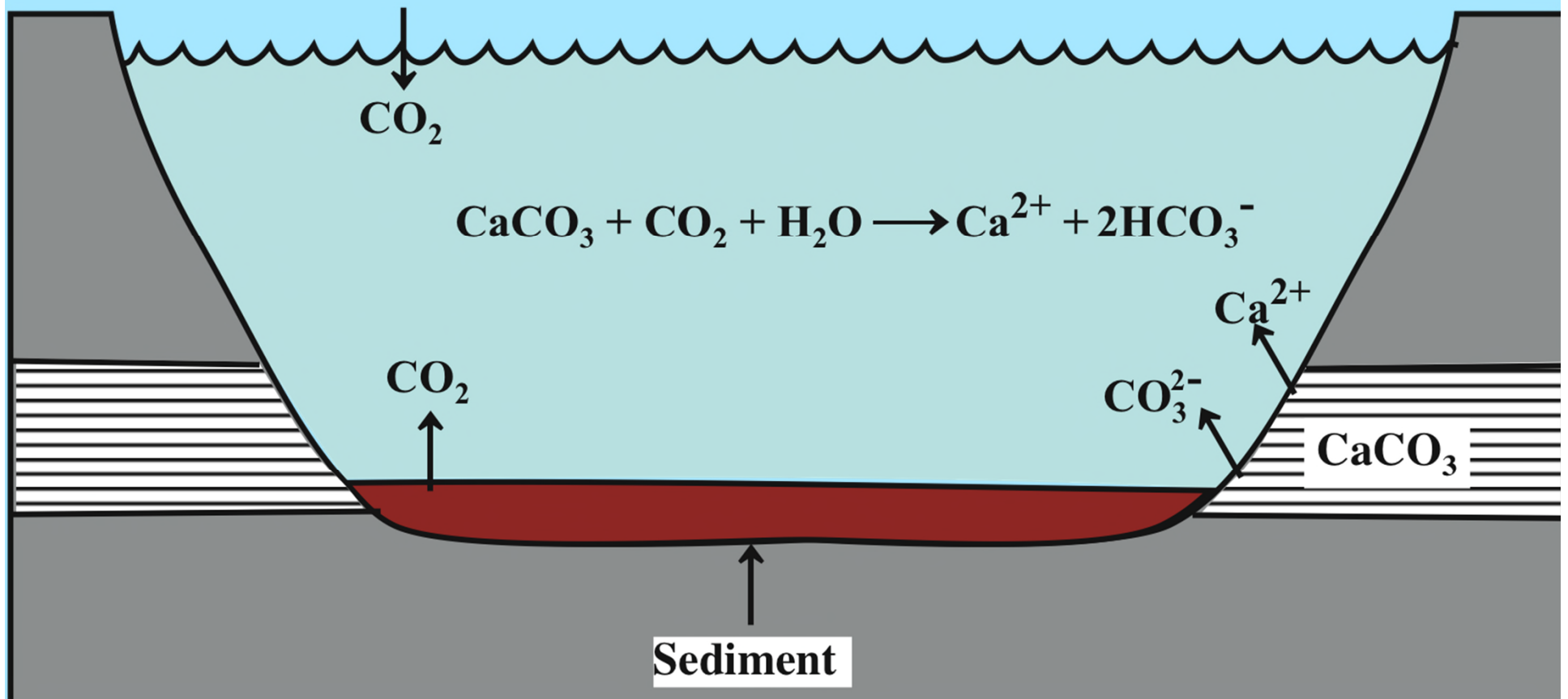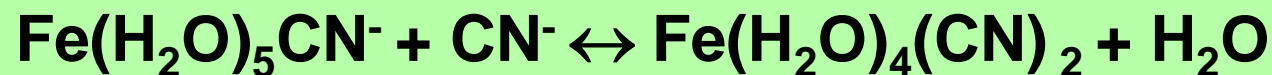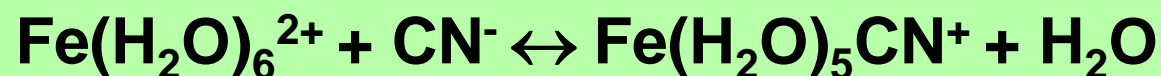
The reactions above show

- **Complexation**

- **A ligand (CN⁻) binding to a metal ion, a reversible process**

- **Formation of a complex (ion), or coordination compound**

- **CN⁻ ion in the above example is a unidentate ligand**

Chelation occurs with chelating agents that can bind in more than one place

Organometallic compounds are formed by irreversible binding of organic groups to metal atoms

Complexation and chelation affect ligands and metals

- Oxidation-reduction, decarboxylation, hydrolysis, and biodegradation of ligands
- Solubilization, precipitation, adsorption, distribution, transport, and effects of metal ions
- Biochemical effects of metals including bioavailability, toxicity, uptake by organisms

Occurrence of chelating agents

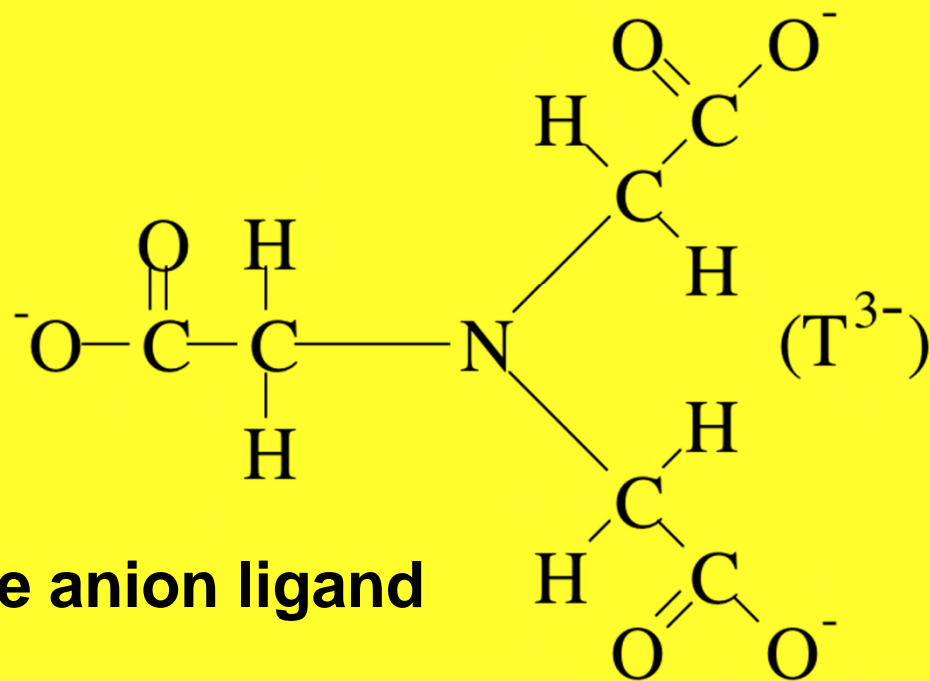- Biocompounds such as hemoglobin
- Metabolic products of organisms
- Pollutants such as from metal plating wastes

Chelating agents in water may facilitate algal growth by making soluble nutrient iron available

2.10 Bonding and Structure of Metal Complexes
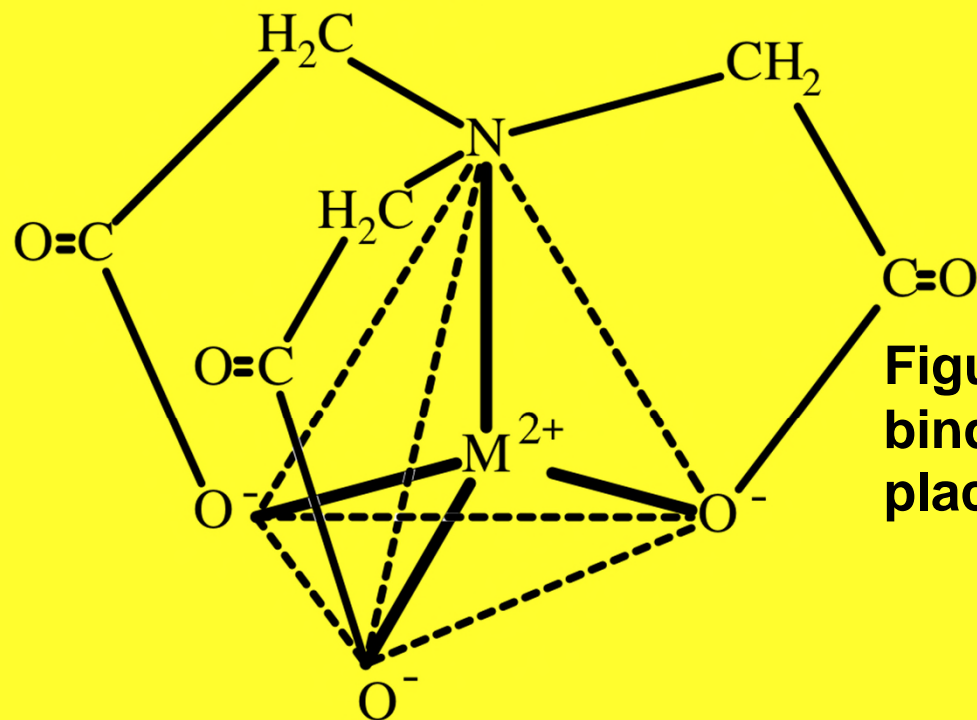
Figure 2.10 Nitrilotriacetate chelate binding a metal ion in four different places

Nitrilotriacetate anion ligand

(T^{3-})

2.12 Calculations of Species Concentrations

Stepwise formation constants when multiple ligands may bond to metal ions

Overall formation constants for two or more ligands bonding

2.13 Complexation by Deprotonated Ligands
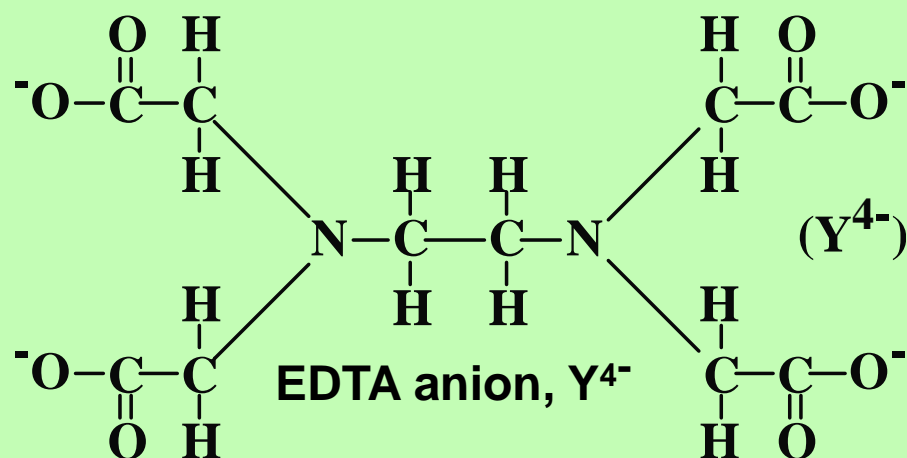
Textbook example of copper chelation by completely ionized EDTA

At pH 11 at excess EDTA at 200 mg/L the concentration of unchelated EDTA is only

EDTA anion, Y^{4-}

$[Cu^{2+}] = 2.3 \times 10^{-20}$ mol/L

$[CuY^{2-}] = 7.9 \times 10^{-5}$ mol/L

$[Cu^{2+}]/[CuY^{2-}] = 3.0 \times 10^{-14}$

- Vastly reduced free copper ion concentration in excess EDTA
- Influence chemical effects of Cu^{2+}
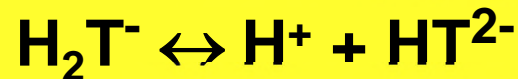- Influence biochemical effects of Cu^{2+}

2.14 Complexation by Protonated Ligands

Examples shown with NTA, a triprotic acid chelating agent (structural formula of anion of NTA on an earlier slide)

$H_3T \leftrightarrow H^+ + H_2T^-$
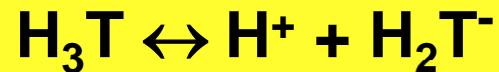
$$K_{a1} = \frac{[H^+][H_2T^-]}{[H_3T]} = 2.18 \times 10^{-2} \quad \textbf{pK}_{a1} = \textbf{1.66}$$

$H_2T^- \leftrightarrow H^+ + HT^{2-}$

$$K_{a2} = \frac{[H^+][HT^{2-}]}{[H_2T^-]} = 1.12 \times 10^{-3} \quad \textbf{pK}_{a2} = \textbf{2.95}$$

$HT^- \leftrightarrow H^+ + T^{3-}$

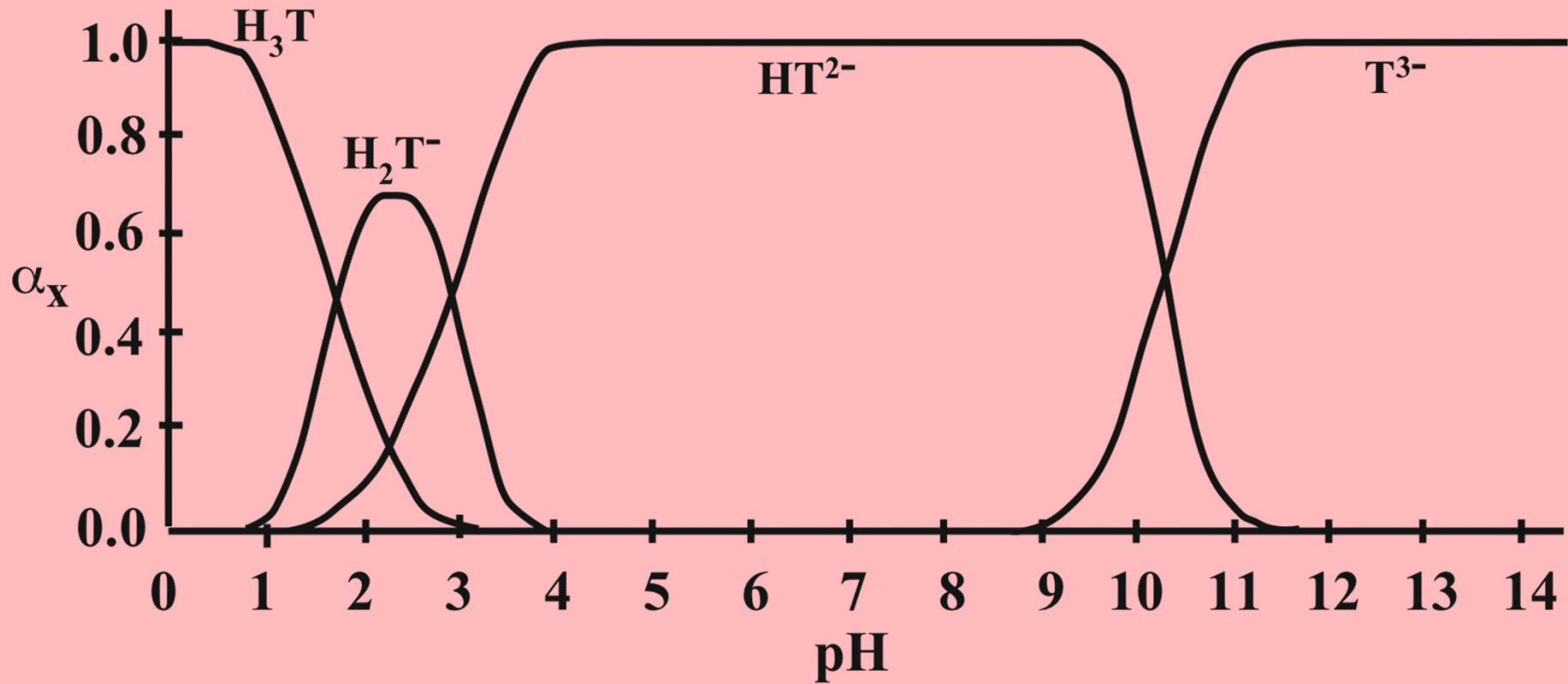$$K_{a3} = \frac{[H^+][T^{3-}]}{[HT^{2-}]} = 5.25 \times 10^{-11} \quad \textbf{pK}_{a3} = \textbf{10.28}$$

Throughout the normal range of pH in natural waters the predominant unchelated NTA species is HT^-

• See distribution of species diagram on the next slide

Figure 2.11 Distribution of species as a function of pH for unchelated nitrilotriacetic acid (NTA)

2.15 Solubilization of Lead Ion from Solids by NTA

A major concern with the introduction of pollutant chelating agents into water is their ability to dissolve and transport heavy metals. Several examples are presented for the chelating agent NTA reacting with lead-containing solids under various conditions. The first example is shown here and the results are given for the other examples, which are presented in the textbook. An approach is shown in which the overall reaction is broken down into its constituent reactions. These are then added together to get the overall reaction, then their equilibrium constant expressions are multiplied to give the expression for the overall reaction.

Assume a water sample contains 25 mg/L of the trisodium NTA salt, $N(CH_2CO_2Na)_3$ formula mass 257 in equilibrium with solid $Pb(OH)_2$. Under these conditions
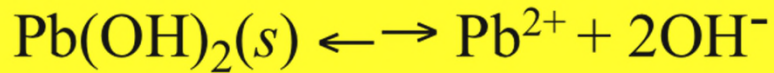
- **Unchelated NTA is present as HT^{2-} (see diagram of distribution of NTA species as a function of pH)**

- **The other possible soluble form of NTA is the lead chelate, PbT^-**

- **At pH 8.00, $[OH^-] = 1.00 \times 10^{-6}$ mol/L**

- **The solubilization reaction is**

  $Pb(OH)_2(s) + HT^{2-} \leftrightarrow PbT^- + OH^- + H_2O$

- **The degree of solubilization of lead is given by the ratio $[PbT^-]/[HT^{2-}]$**

The calculation of this ratio is shown on the following slide

- **$[PbT^-]/[HT^{2-}] = 20.7$ under the conditions given showing that essentially all the NTA is bound to lead as soluble PbT^-**

$$Pb(OH)_2(s) \longleftrightarrow Pb^{2+} + 2OH^-$$

$$K_{sp} = [Pb^{2+}][OH^-]^2 = 1.61 \times 10^{-20}$$

$$HT^{2-} \longleftrightarrow H^+ + T^{3-}$$

$$K_{a3} = \frac{[H^+][T^{3-}]}{[HT^{2-}]} = 5.25 \times 10^{-11}$$

$$Pb^{2+} + T^{3-} \longleftrightarrow PbT^-$$

$$K_f = \frac{[PbT^-]}{[Pb^{2+}][T^{3-}]} = 2.45 \times 10^{11}$$

$$H^+ + OH^- \longleftrightarrow H_2O$$

$$\frac{1}{K_w} = \frac{1}{[H^+][OH^-]} = \frac{1}{1.00 \times 10^{-14}}$$

$$Pb(OH)_2(s) + HT^{2-} \longleftrightarrow PbT^- + OH^- + H_2O$$
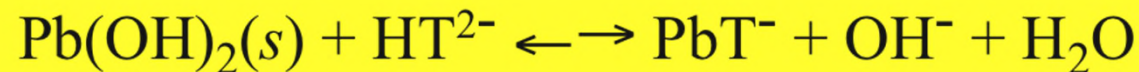
$$K = \frac{[PbT^-][OH^-]}{[HT^{2-}]} = \frac{K_{sp}K_{a3}K_f}{K_w} = 2.07 \times 10^{-5}$$

$$\frac{[PbT^-]}{[HT^{2-}]} = \frac{K}{[OH^-]} = \frac{2.07 \times 10^{-5}}{1.00 \times 10^{-6}} = 20.7$$

Reaction of NTA with Lead Carbonate

Lead carbonate, $PbCO_3$, is the predominant lead species in water under many conditions. The example shown in the text is for water containing 25 mg Na_3T in equilibrium with $PbCO_3$ at pH 7.00. The following apply (see equilibrium constant expressions in text):

• **Reaction:** $PbCO_3(s) + HT^{2-} \longleftrightarrow PbT^- + HCO_3^-$

$$K = \frac{[PbT^-][HCO_3^-]}{[HT^{2-}]} = \frac{K_{sp}K_{a3}K_f}{K'_{a2}} = 4.06 \times 10^{-2}$$

• **Assume a reasonable value of $[HCO_3^-] = 1.00 \times 10^{-3}$ mol/L**
• **Ratio of chelated to unchelated NTA:**

$$\frac{[PbT^-]}{[HT^{2-}]} = \frac{K}{[HCO_3^-]} = \frac{4.06 \times 10^{-2}}{1.00 \times 10^{-3}} = 40.6$$

This ratio shows that under typical conditions NTA would dissolve lead from solid $PbCO_3$

Reaction of NTA with PbCO$_3$(s) in the presence of 1.00 × 10^{-3} mol/L Ca^{2+} at pH 7.00 and [HCO$_3^-$] = 1.00 × 10^{-3} mol/L

- **The reaction and its equilibrium constant are**

$$PbCO_3(s) + CaT^- + H^+ \longleftrightarrow Ca^{2+} + HCO_3^- + PbT^-$$

$$K'' = \frac{[Ca^{2+}][HCO_3^-][PbT^-]}{[CaT^-][H^+]} = 5.24$$

**Putting the known concentrations into this expression and solving**

- **[PbT$^-$]/[HCO$_3^-$] = 0.524**
- **About 1/3 of the NTA is bound with Pb^{2+} and 2/3 with Ca^{2+}**
- **Therefore, the presence of excess Ca^{2+} significantly inhibits NTA from dissolving lead from lead carbonate**

2.16 Polyphosphates and Phosphonates in Water

Figure 2.12. The first two members of the family of polyphosphoric acids which, in the partially ionized form chelate metals
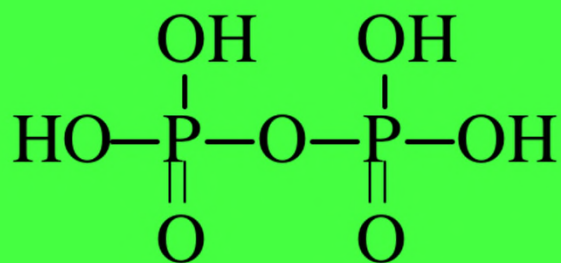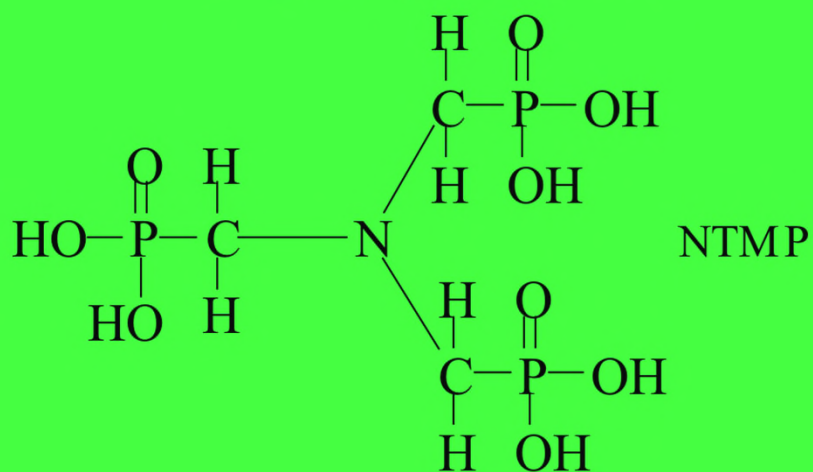

Pyrophosphoric
(diphosphoric) acid
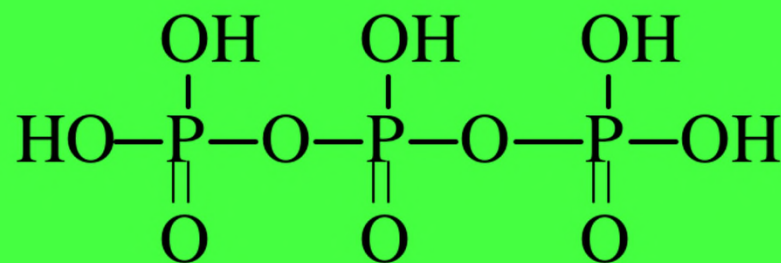
Triphosphoric acid

A phosphonate with chelating capabilities

NTMP

# 2.17 Complexation by Humic Substances

Humic substances are biodegradation-resistant residues remaining from the biodegradation of plant biomass

• High-molecular mass polyelectrolytic macromolecules
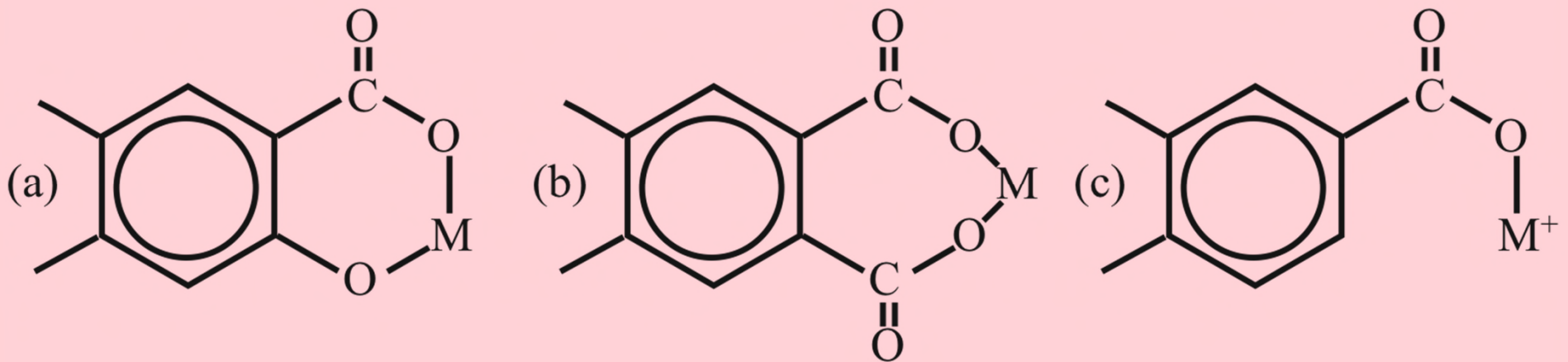
When a sediment or soil is treated with base solution

• Humin material is humic substance not extracted

• Humic acid precipitates from acidified extract

• Fulvic acid remains in acidified solution
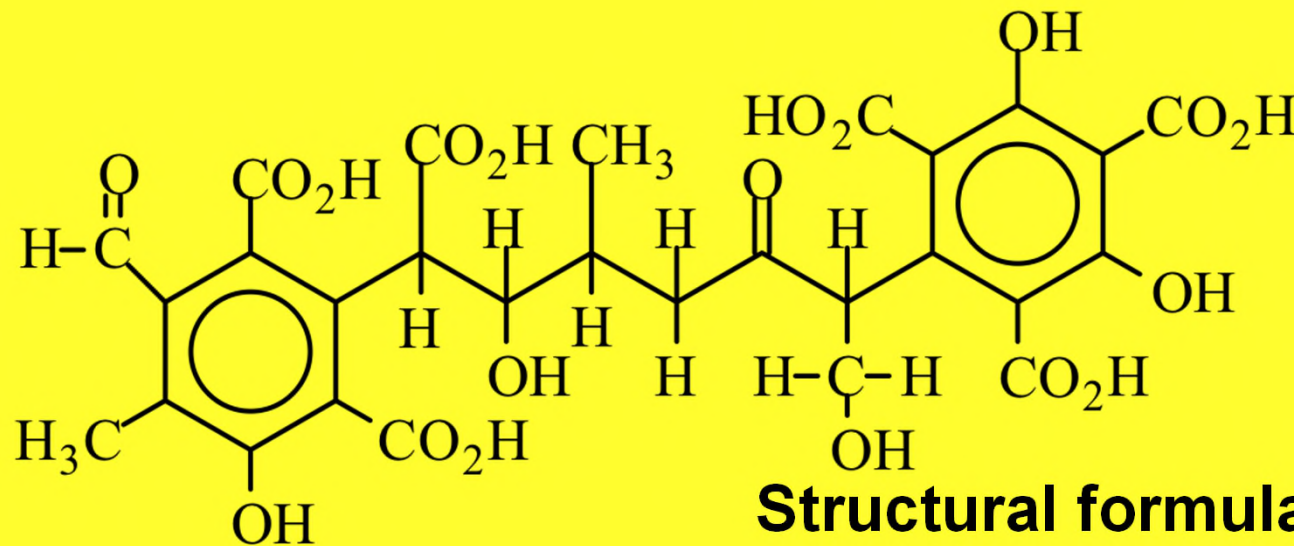
Structural formula of a hypothetical fulvic acid molecule

Figure 2.13. Binding and chelation of a metal ion, M^{2+}, by humic substance

Humic substances are important in some natural waters
• Chelate metals
• Cause problems with metals (iron) removal from water
• Water color, especially when bound to iron (gelbstoffe)
• Insoluble humin and humic acid remove metals from
  solution
• Precursors to trihalomethane ($CHCl_3$) production in water
  chlorination

2.18 Complexation and Redox Processes

Complexation and chelation shift oxidation-reduction equilibria

• **Usually by stabilization of oxidized form of metal**

• **Dissolve protective oxide coatings**