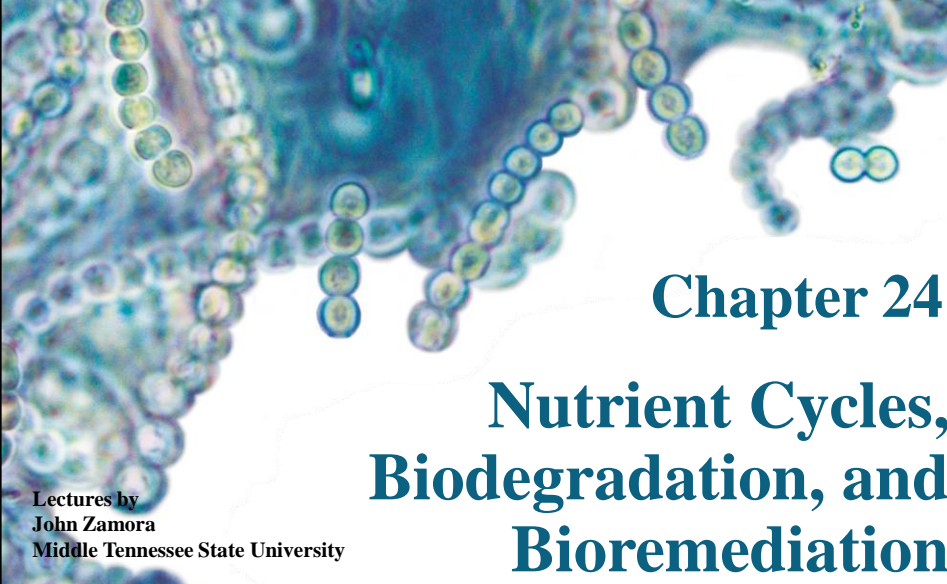


LECTURE PRESENTATIONS
For BROCK BIOLOGY OF MICROORGANISMS, THIRTEENTH EDITION
Michael T. Madigan, John M. Martinko, David A. Stahl, David P. Clark



Chapter 24
**Nutrient Cycles,
Biodegradation, and
Bioremediation**

Lectures by
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I. Nutrient Cycles

- 24.1 The Carbon Cycle
- 24.2 Syntrophy and Methanogenesis
- 24.3 The Nitrogen Cycle
- 24.4 The Sulfur Cycle
- 24.5 The Iron Cycle
- 24.6 The Phosphorus, Calcium and Silica Cycles

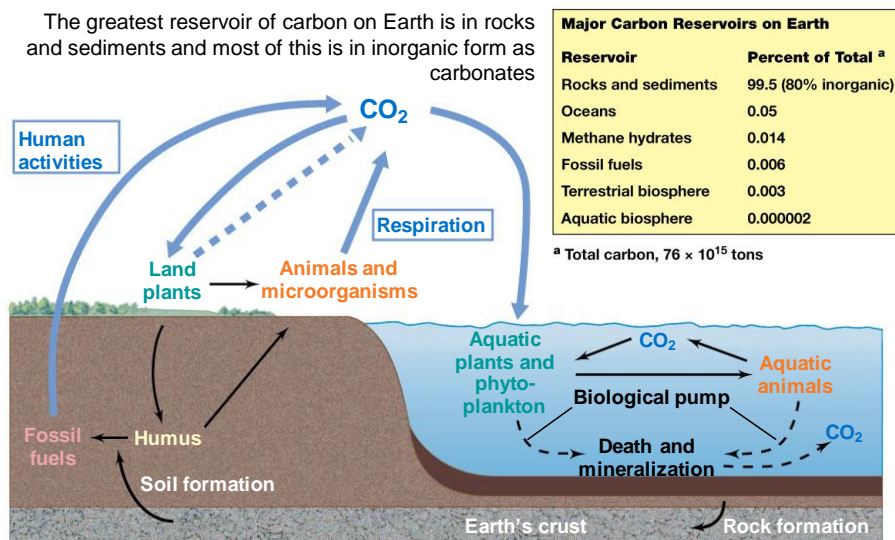
24.1 The Carbon Cycle

- Carbon is cycled through all of Earth's major carbon reservoirs (Figure 24.1)
 - Includes atmosphere, land, oceans, sediments, rocks and biomass
- Reservoir size and turnover time are important parameters in understanding the cycling of elements

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Figure 24.1 The carbon cycle



The carbon and oxygen cycles are closely connected, as oxygenic photosynthesis both removes CO₂ and produces O₂ and respiratory processes both produce CO₂ and remove O₂

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24.1 The Carbon Cycle

- CO₂ in the atmosphere is the most rapidly transferred carbon reservoir
- CO₂ is fixed by photosynthetic land plants and marine microbes
- CO₂ is returned to the atmosphere by respiration as well as anthropogenic activities
 - Microbial decomposition is the largest source of CO₂ released to the atmosphere

24.1 The Carbon Cycle

- Carbon and oxygen cycles are linked
- Phototrophic organisms are the foundation of the carbon cycle
 - Oxygenic phototrophic organisms can be divided into two groups: plants and microorganisms
 - Plants dominant organisms of terrestrial environments
 - Microorganisms dominate aquatic environments

24.1 The Carbon Cycle

- Photosynthesis and respiration are part of redox cycle (Figure 24.2)
- Photosynthesis

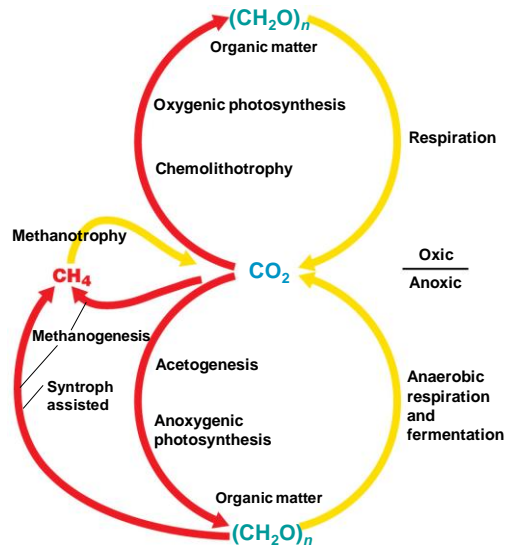
$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O}) + \text{O}_2$$
- Respiration

$$(\text{CH}_2\text{O}) + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$$
- The two major end products of decomposition are CH_4 and CO_2

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Figure 24.2 Redox cycle for carbon



The diagram contrasts autotrophic processes ($\text{CO}_2 \rightarrow$ organic compounds) and heterotrophic processes (organic compounds $\rightarrow \text{CO}_2$).

Yellow arrows indicate oxidations; red arrows indicate reductions.

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24.2 Syntrophy and Methanogenesis

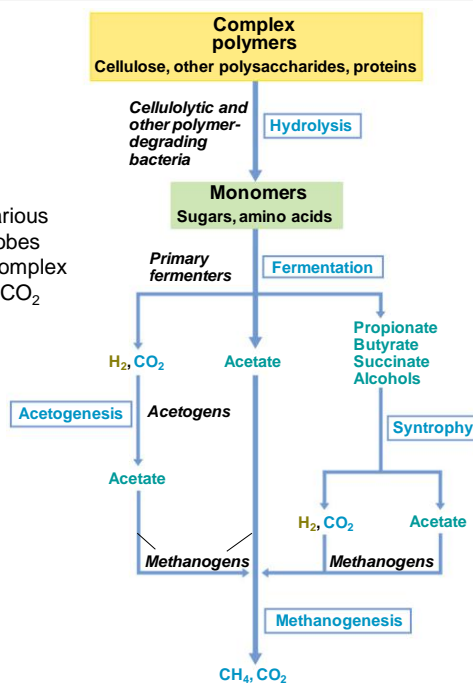
- Methanogenesis is central to carbon cycling in anoxic environments
- Most methanogens reduce CO_2 to CH_4 with H_2 as an electron donor; some can reduce other substrates to CH_4 (e.g., acetate)
- Methanogens team up with partners (syntrophs) that supply them with necessary substrates

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Figure 24.5 Anaerobic decomposition

In anaerobic decomposition various groups of fermentative anaerobes cooperate in the conversion of complex organic materials to CH_4 and CO_2



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24.2 Syntrophy and Methanogenesis

- Methanogens can be found in some protists (e.g. within the cells of protists inhabiting the termite hindgut)
- Possible that endosymbiotic methanogens benefit protists by consuming H_2 generated from glucose fermentation
- On a global basis, biotic processes release more CH_4 than abiotic processes



Termite

24.2 Syntrophy and Methanogenesis

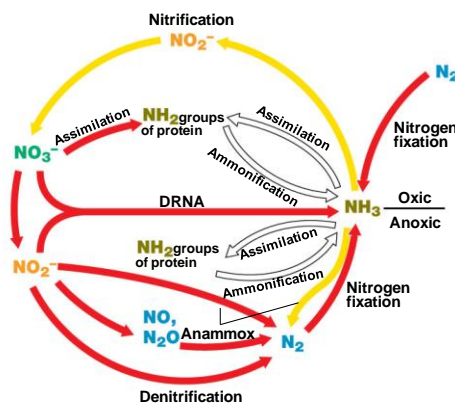
- Acetogenesis is another H_2 -consuming process competing with methanogenesis in some environments
 - Occurs in termite hindgut, permafrost soils
- Methanogenesis is energetically more favorable than acetogenesis
- Acetogens can ferment glucose and methoxylated aromatic compounds, whereas methanogens cannot
- Sulfate-reducing bacteria outcompete methanogens and acetogens in marine environments

24.3 The Nitrogen Cycle

- Nitrogen
 - A key constituent of cells
 - Exists in a number of oxidation states

Figure 24.7 Redox cycle for nitrogen

Key Processes and Prokaryotes in the Nitrogen Cycle	
Processes	Example organisms
Nitrification ($\text{NH}_4^+ \rightarrow \text{NO}_3^-$) $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ $\text{NO}_2^- \rightarrow \text{NO}_3^-$	<i>Nitrosomonas</i> <i>Nitrobacter</i>
Denitrification ($\text{NO}_3^- \rightarrow \text{N}_2$)	<i>Bacillus</i> , <i>Paracoccus</i> , <i>Pseudomonas</i>
N₂ Fixation ($\text{N}_2 + 8 \text{H} \rightarrow \text{NH}_3 + \text{H}_2$)	
Free-living	
Aerobic	<i>Azotobacter</i> Cyanobacteria
Anaerobic	<i>Clostridium</i> , purple and green phototrophic bacteria <i>Methanobacterium</i> (Archaea)
Symbiotic	<i>Rhizobium</i> <i>Bradyrhizobium</i> <i>Frankia</i>
Ammonification (organic-N \rightarrow NH_4^+)	Many organisms can do this
Anammox ($\text{NO}_2^- + \text{NH}_3 \rightarrow 2 \text{N}_2$)	<i>Brocadia</i>



Oxidation reactions are shown by yellow arrows and reductions by red arrows. Reactions without redox change are in white. DRNA, dissimilative reduction of nitrate to ammonia

The anammox reaction is $\text{NH}_3 + \text{NO}_2^- + \text{H}^+ \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$

24.3 The Nitrogen Cycle

- N₂ is the most stable form of nitrogen and is a major reservoir
 - Only a few prokaryotes have the ability to use N₂ as a cellular nitrogen source (*nitrogen fixation*)
 - *Denitrification* is the reduction of nitrate to gaseous nitrogen products and is the primary mechanism by which N₂ is produced biologically
- Ammonia produced by *nitrogen fixation* or *ammonification* can be assimilated into organic matter or oxidized to nitrate

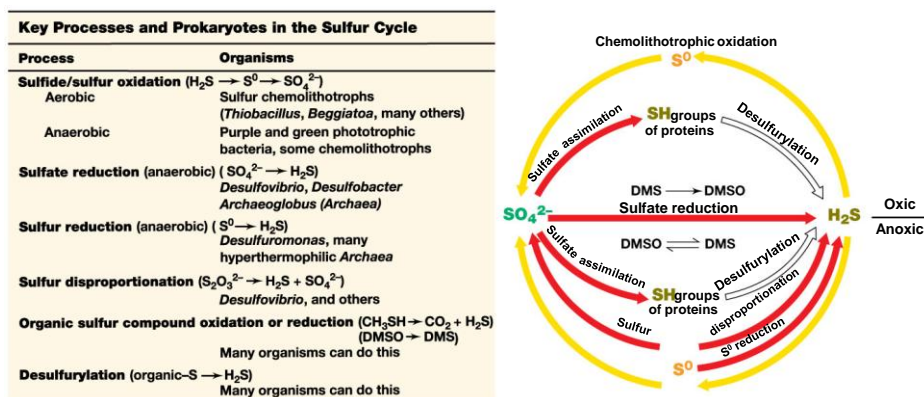
24.3 The Nitrogen Cycle

- *Anammox* is the anaerobic oxidation of ammonia to N₂ gas
 - $\text{NH}_3 + \text{NO}_2^- + \text{H}^+ \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$
- Denitrification and anammox result in losses of nitrogen from the biosphere

24.4 The Sulfur Cycle

- Sulfur transformations by microorganisms are complex (Figure 24.8)
- The bulk of sulfur on Earth is in sediments and rocks as sulfate and sulfide minerals (e.g., gypsum, pyrite)
- The oceans represent the most significant reservoir of sulfur (as sulfate) in the biosphere

Figure 24.8 Redox cycle for sulfur



Oxidations are indicated by yellow arrows and reductions by red arrows. Reactions without redox changes are in white. DMS, dimethyl sulfide; DMSO, dimethyl sulfoxide

24.4 The Sulfur Cycle

- Hydrogen sulfide (H_2S) is a major volatile sulfur gas that is produced by bacteria via sulfate reduction or emitted from geochemical sources
- Sulfide (S^{2-}) is toxic to many plants and animals and reacts with numerous metals
- Sulfur-oxidizing chemolithotrophs can oxidize sulfide (S^{2-}) and elemental sulfur (S^0) at oxic/anoxic interfaces

24.4 The Sulfur Cycle

- Organic sulfur compounds can also be metabolized by microorganisms
- The most abundant organic sulfur compound in nature is dimethyl sulfide (DMS)
 - Produced primarily in marine environments as a degradation product of dimethylsulfoniopropionate (an algal osmolyte)
- DMS can be transformed via a number of microbial processes

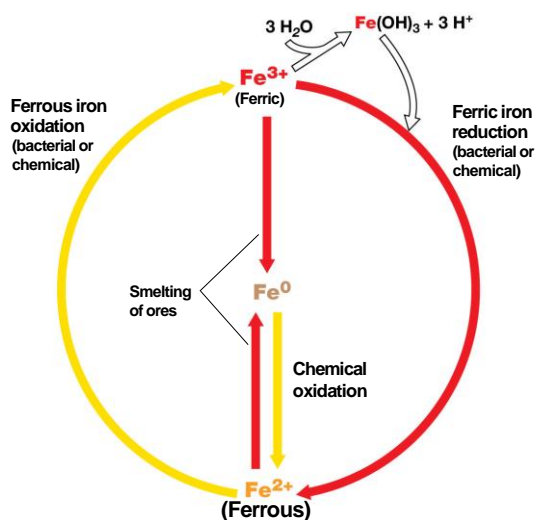
24.5 The Iron Cycle

- Iron is one of the most abundant elements in Earth's crust
- On Earth's surface, iron exists naturally in two oxidation states:
 - Ferrous (Fe^{2+})
 - Ferric (Fe^{3+})
 - The redox reactions in the iron cycle include both oxidations and reductions (Figure 24.9)

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Figure 24.9 Redox cycle for iron



The major forms of iron in nature are Fe^{2+} and Fe^{3+} ; Fe^0 is primarily a product of smelting of iron ores. Oxidations are shown by yellow arrows and reductions by red arrows. Fe^{3+} forms various minerals such as ferric hydroxide, $\text{Fe}(\text{OH})_3$

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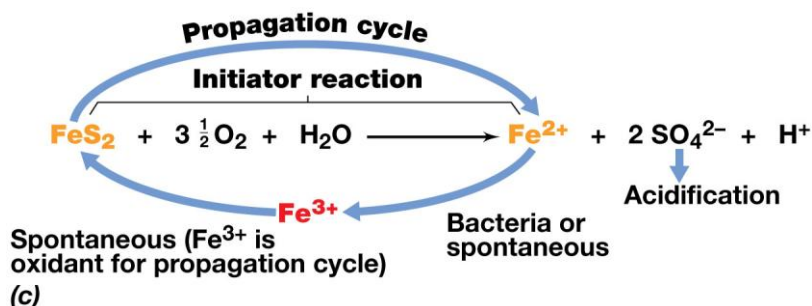
24.5 The Iron Cycle

- Fe^{3+} can be used by some microorganisms as electron acceptors in anaerobic respiration
- In aerobic acidic pH environments, acidophilic chemolithotrophs can oxidize Fe^{2+} (e.g., *Acidithiobacillus*)

24.5 The Iron Cycle

- Pyrite (FeS_2)
 - One of the most common forms of iron in nature
 - Its oxidation by bacteria can result in acidic conditions in coal-mining operations (Figure 24.11c)

Figure 24.11c Reactions in pyrite degradation



The primarily abiotic initiator reaction sets the stage for the primarily bacterial oxidation of Fe²⁺ to Fe³⁺. The Fe³⁺ attacks and oxidizes FeS₂ abiotically in the propagation cycle.

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24.5 The Iron Cycle

- Acid Mine Drainage
 - An environmental problem in coal-mining regions
 - Occurs when acidic mine waters are mixed with natural waters in rivers and lakes (Figure 24.12)
 - Bacterial oxidation of sulfide minerals is a major factor in its formation

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Figure 24.12 Acid mine drainage from a surface coal-mining operation



T. D. Brock

The yellowish-red color is due to the precipitated iron oxides in the drainage

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24.6 The Phosphorous, Calcium, and Silica Cycles

- Phosphorous Cycle
 - Organic and inorganic phosphates
 - Cycles through living organisms, water and soil
- Calcium Cycle
 - Reservoirs are rocks and oceans
 - Marine phototrophic microorganisms use Ca^{2+} to form exoskeleton (Figure 24.13)

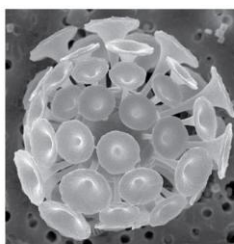
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Figure 24.13 The marine calcium (Ca) cycle



Jörg Bollman

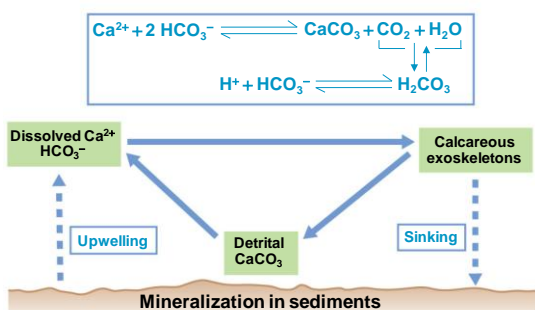


L. Cros and J.M. Fortino

Scanning electron micrographs of cells of the calcareous phytoplankton (a) *Emiliana huxleyi* and (b) *Discophaera tubifera*. The exoskeletons of these phytoplanktons are made of CaCO_3 .

(a)

(b)



(c)

The marine calcium cycle; dynamic pools of Ca^{2+} are shaded in green. Detrital CaCO_3 is that in fecal pellets and other organic matter from dead organisms. Note how H_2CO_3 formation decreases ocean pH.

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24.6 The Phosphorous, Calcium, and Silica Cycles

- Silica Cycle
 - The marine silica cycle is controlled by unicellular eukaryotes that build cell skeletons called frustules (Figure 24.14)
 - Examples: diatoms, dinoflagellates, and radiolarians

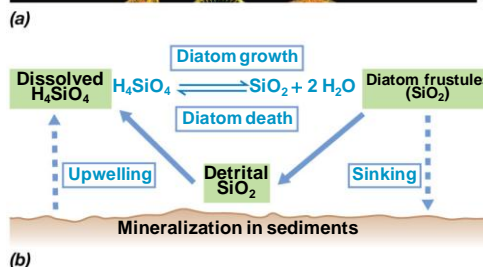
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Figure 24.14 The marine silica cycle



(a) Dark-field photomicrograph of a collection of diatom shells (frustules). The frustules are made of SiO_2 .



(b) The marine silica cycle dynamic pools of Si are shaded in green

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II. Biodegradation and Bioremediation

- 24.7 Microbial Leaching
- 24.8 Mercury Transformations
- 24.9 Petroleum Biodegradation and Bioremediation
- 24.10 Xenobiotics Biodegradation and Bioremediation

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24.7 Microbial Leaching

- Bioremediation
 - Refers to the cleanup of oil, toxic chemicals, or other pollutants from the environment by microorganisms
 - Often a cost-effective and practical method for pollutant cleanup

24.7 Microbial Leaching

- Microbial leaching
 - The removal of valuable metals, such as copper, from sulfide ores by microbial activities
 - Particularly useful for copper ores

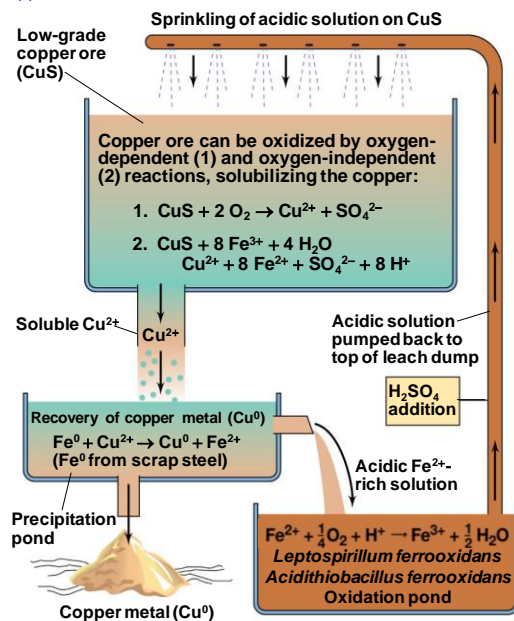
24.7 Microbial Leaching

- In microbial leaching, low-grade ore is dumped in a large pile (the leach dump) and sulfuric acid is added (Figure 24.16)
- The liquid emerging from the bottom of the pile is enriched in dissolved metals and is transported to a precipitation plant
- Bacterial oxidation of Fe^{2+} is critical in microbial leaching as Fe^{3+} itself can oxidize metals in the ores

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Figure 24.16 Arrangement of a leaching pile and reactions in the microbial leaching of copper sulfide minerals to yield metallic copper



- Reaction 1 occurs both biologically and chemically.
- Reaction 2 is strictly chemical and is the most important reaction in copper-leaching processes.
- For reaction 2 to proceed, it is essential that the Fe^{2+} produced from the oxidation of sulfide in CuS to sulfate be oxidized back to Fe^{3+} by iron chemolithotrophs.

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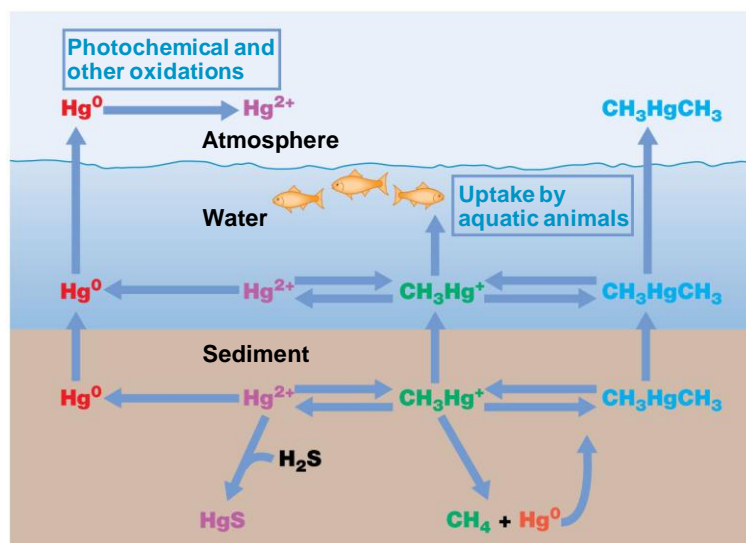
24.7 Microbial Leaching

- Microorganisms are also used in the leaching of uranium and gold ores.
- Some bacteria are able to reduce U^{6+} to U^{4+}
- U^{4+} forms an immobile uranium mineral, uraninite, thus limiting the movement of uranium into groundwater.

24.8 Mercury Transformations

- Mercury has tendency to concentrate in living tissues and it is highly toxic
- The major form of mercury in the atmosphere is elemental mercury (Hg^0), which is volatile and oxidized to mercuric ion (Hg^{2+}) photochemically (Figure 24.18)
- Most mercury enters aquatic environments as Hg^{2+}

Figure 24.18 Biogeochemical cycling of mercury



The major reservoirs of Hg are water and sediments. Hg in water can be concentrated in animal tissues; it can be precipitated as HgS from sediments. The forms of mercury commonly found in aquatic environments are each shown in a different color.

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24.8 Mercury Transformations

- Hg^{2+} readily absorbs to particulate matter where it can be metabolized by microorganisms
- Microorganisms form methylmercury (CH_3Hg^+), an extremely soluble and toxic compound
- Several bacteria can also transform toxic mercury to nontoxic forms

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24.8 Mercury Transformations

- Bacterial resistance to heavy metal toxicity is often linked to specific plasmids that encode enzymes capable of detoxifying or pumping out the metals

24.9 Petroleum Biodegradation and Bioremediation

- Prokaryotes have been used in bioremediation of several major crude oil spills (Figure 24.20)

Figure 24.20 Environmental consequences of large oil spills and the effect of bioremediation



US Environmental
Protection Agency

(a) A contaminated beach along the coast of Alaska in 1989.



US Environmental
Protection Agency

(b) The rectangular plot (arrow) was treated with inorganic nutrients to stimulate bioremediation of spilled oil by microorganisms, whereas areas above and to the left were untreated.

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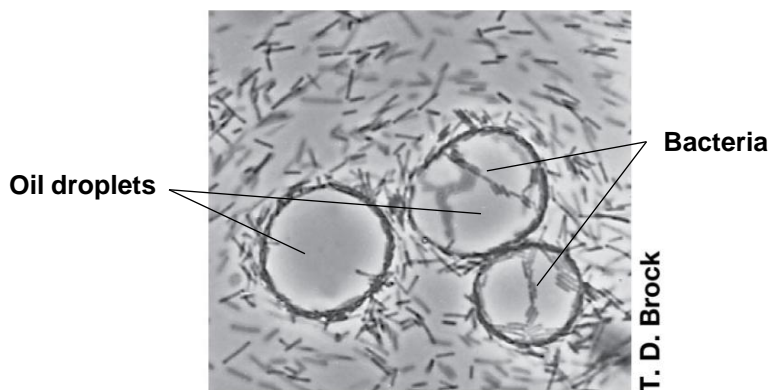
24.9 Petroleum Biodegradation and Bioremediation

- Diverse bacteria, fungi and some cyanobacteria and green algae can oxidize petroleum products aerobically
- Oil-oxidizing activity is best if temperature and inorganic nutrient concentrations are optimal
- Hydrocarbon-degrading bacteria attach to oil droplets and decompose the oil and disperse the slick (Figure 24.21)

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Figure 24.21 Hydrocarbon-oxidizing bacteria in association with oil droplets



The bacteria are concentrated in large numbers at the oil-water interface, but are actually not within the droplet itself

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24.9 Petroleum Biodegradation and Bioremediation

- Gasoline and crude oil storage tanks are potential habitats for hydrocarbon-oxidizing microbes
- If sufficient sulfate is present, sulfate-reducing bacteria can grow and consume hydrocarbons

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24.10 Xenobiotics Biodegradation and Bioremediation

- Xenobiotic compound
 - Synthetic chemicals that are not naturally occurring
 - Examples: pesticides, polychlorinated biphenyls, munitions, dyes, and chlorinated solvents (Figure 24.23)
 - Many degrade extremely slowly

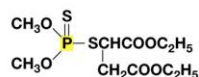
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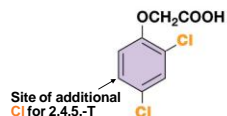
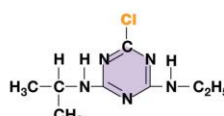
Figure 24.23 Examples of xenobiotic compounds



DDT, dichlorodiphenyltrichloroethane (an organochlorine)

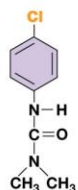


Malathion, mercaptosuccinic acid diethyl ester (an organophosphate)

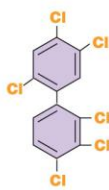
2,4-D, 2,4-dichlorophenoxyacetic acid
Site of additional Cl for 2,4,5-T

Atrazine, 2-chloro-4-ethylamino-6-isopropylaminotriazine

Although none of these compounds exist naturally, microorganisms exist that can break them down.



Monuron, 3-(4-chlorophenyl)-1,1-dimethylurea (a substituted urea)



Chlorinated biphenyl (PCB), Trichloroethylene shown is 2,3,4,2',4',5'-hexachlorobiphenyl



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24.10 Xenobiotics Biodegradation and Bioremediation

- Pesticides
 - Common components of toxic wastes
 - Include *herbicides*, *insecticides*, and *fungicides*
 - Represent a wide variety of chemicals
 - Some can be used as carbon sources by microorganisms
 - Some can be used as electron donors

24.9 Xenobiotics Biodegradation and Bioremediation

- Some xenobiotics can be degraded partially or completely if another organic material is present as a primary energy source (*cometabolism*)

24.10 Xenobiotics Biodegradation and Bioremediation

- Chlorinated xenobiotics can be degraded anaerobically (*reductive dechlorination*) or aerobically (*aerobic dechlorination*)
- Reductive dechlorination is usually a more important process as anoxic conditions develop quickly in polluted environments

24.10 Xenobiotics Biodegradation and Bioremediation

- Plastics of various types are xenobiotics that are not readily degraded by microorganisms
The recalcitrance of plastics has fueled research efforts into a biodegradable alternative (*biopolymers*)