

Water: Sources, Pollution, and Purification

Chapter 13

Introduction

- Water Usage in the United States
 - 300 L/day per person
 - 100,000 L/year per person
 - Only 2% is used for drinking and cooking
- Industrial Use is much larger than personal use
 - Thousands of L/pound of food
 - Thousands of L/pound of building material
- We will explore sources of water, how it is purified for humans, and its pollution problems

Drinking/cooking

Miscellaneous

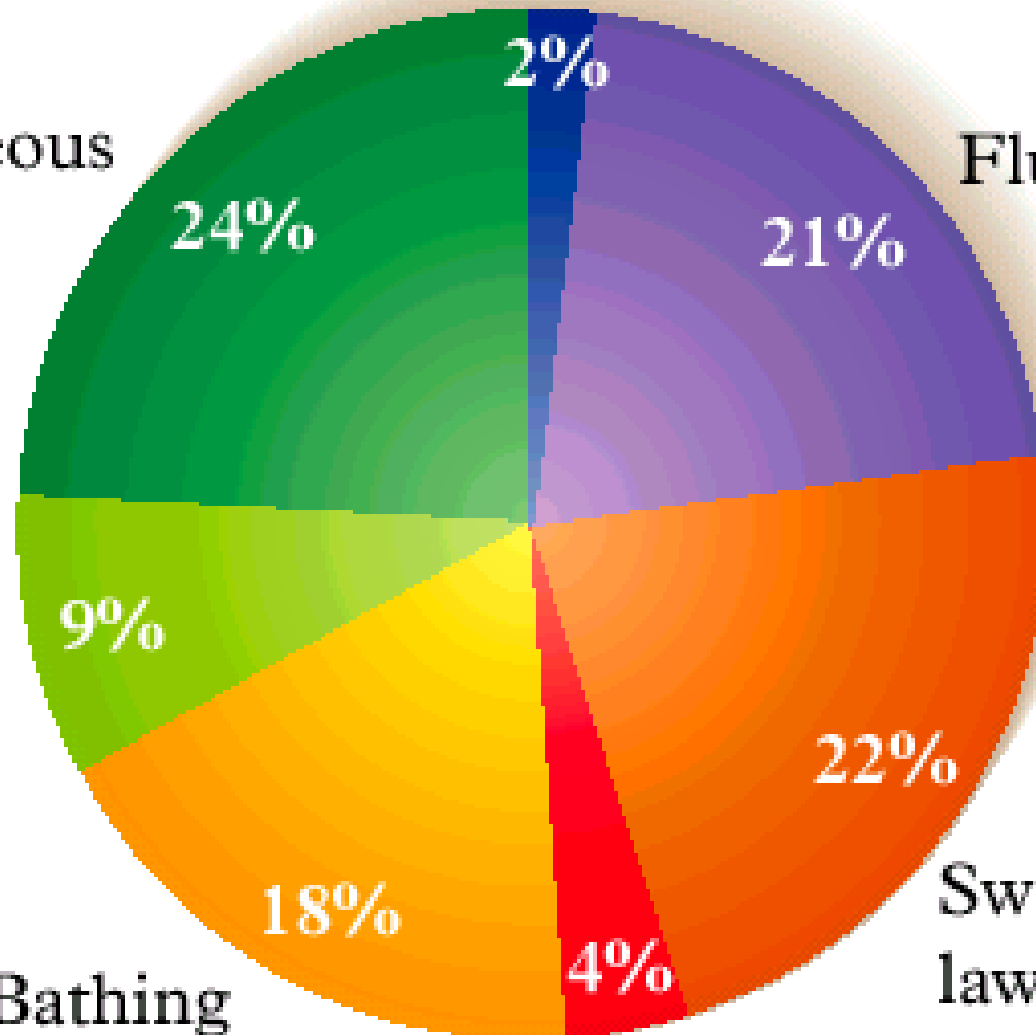
Flushing toilets

Laundry

Swimming pools/
lawns

Bathing

Dishwashing



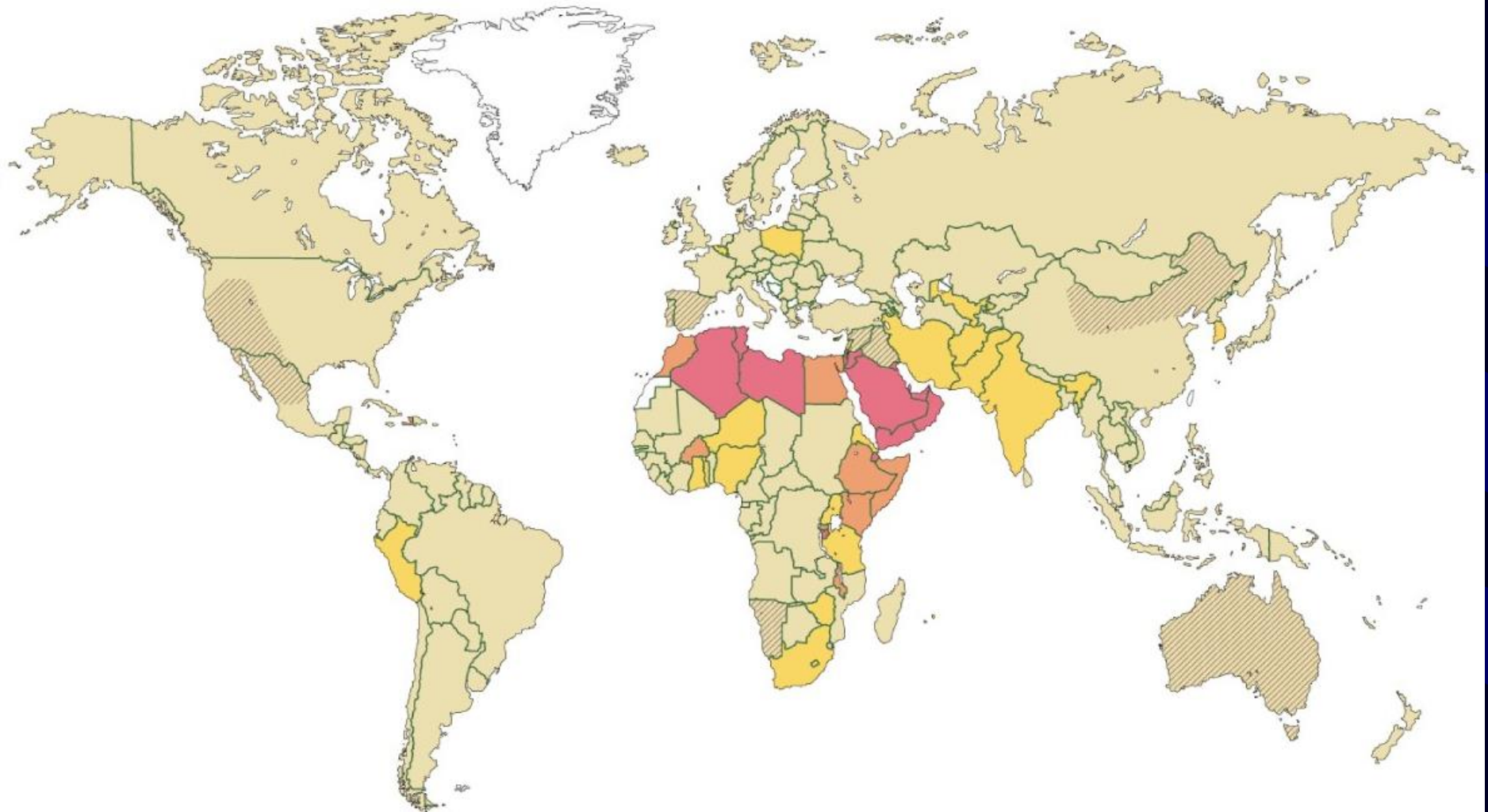
Sources of Drinking Water

- Inaccessibility of Drinking Water
 - 98% of Earth's water is Salty (Oceans)
 - 2% of Earth's water is fresh
 - Much of this is trapped as ice and snow in glaciers
 - 0.01% of Earth's water is fresh surface water: lakes and rivers
- Groundwater
 - 0.3% of Earth's water is < 1 km underground freshwater
 - Aquifer = permanent underground lake
 - Usually sand/gravel layer over rock/clay layer
 - Extract with a well: 39% of US public water + much irrigation

Source	cubic kilometers)	Percent of total
Total	1,403,477	100
Ocean	1,370,000	97.6
Ice and snow	29,000	2.07
Groundwater to 1 km	4,000	0.28
Lakes, reservoirs (fresh water)	125	0.009
Atmosphere	113	0.008
Saline lakes	104	0.007
Soil moisture	65	0.005
Plants	65	0.005
Swamps, marshes	3.6	0.003
Rivers, streams	1.7	0.0001

Adapted from W. P. Cunningham and B. W. Saigo, "Environmental Science—A Global Concern," Wm. C. Brown Publishers, Dubuque, Iowa, 1990, page 292.

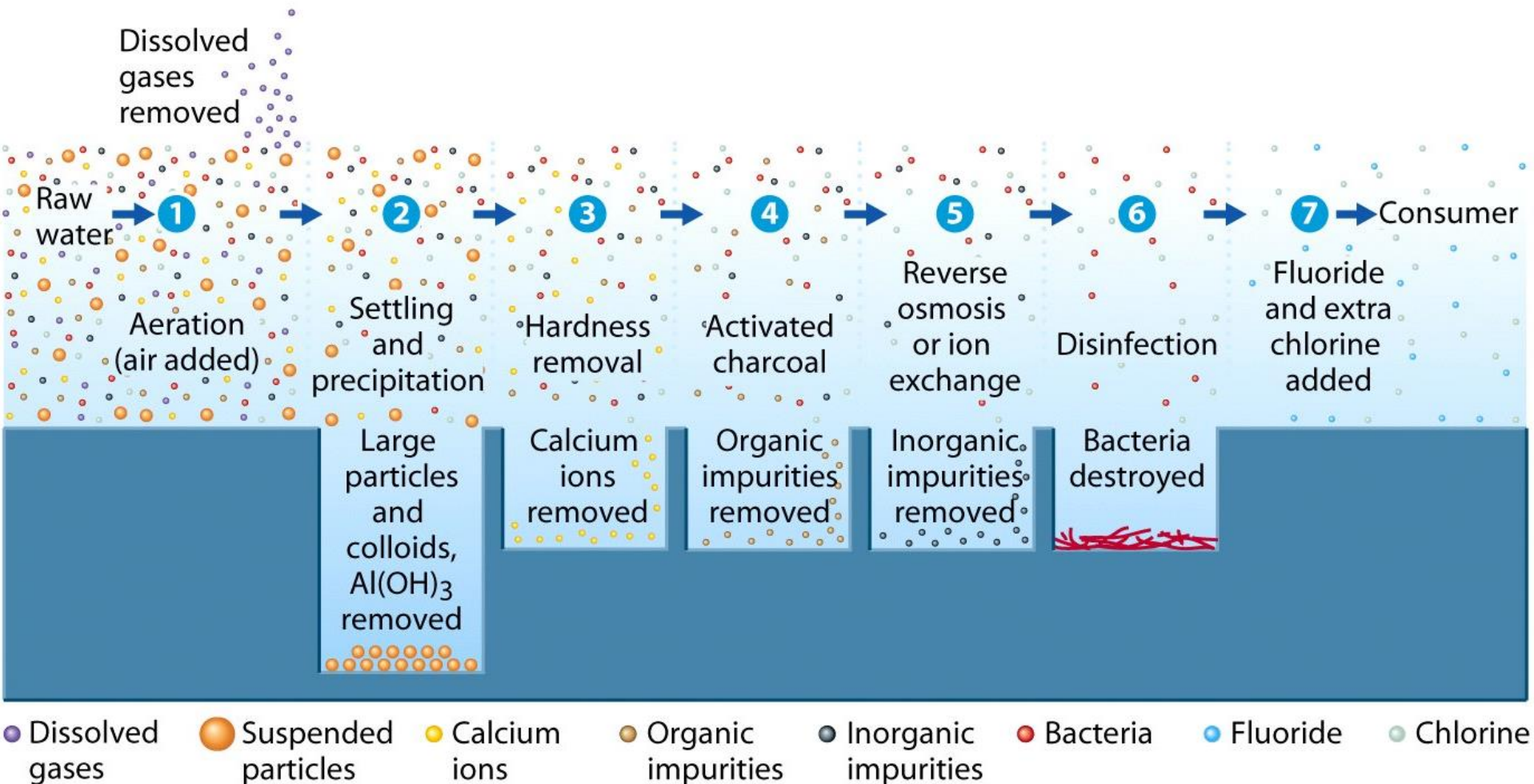
One-third of the Earth's people live in areas that experience at least seasonal water shortages. It is estimated this fraction will be two-thirds by 2025.



Water Purification

- Quality of Fresh Water is variable
 - Purification steps vary with the source of the water
 - Purification may be for purposes other than drinking
 - Wash water performs better when $\text{Ca}^{2+}/\text{Mg}^{2+}$ are removed
 - These ions have no ill effect in drinking water
- Aeration = removal of dissolved gases
 - Water from aquifers often has dissolved gases that may add an odor or flavor to the water
 - H_2S = Hydrogen Sulfide
 - CH_3SH = methanethiol (and other sulfur compounds)
 - Volatile organic compounds = carbon compounds that evaporate easily (acetone, ether, benzene)

Water Purification Steps



Aeration

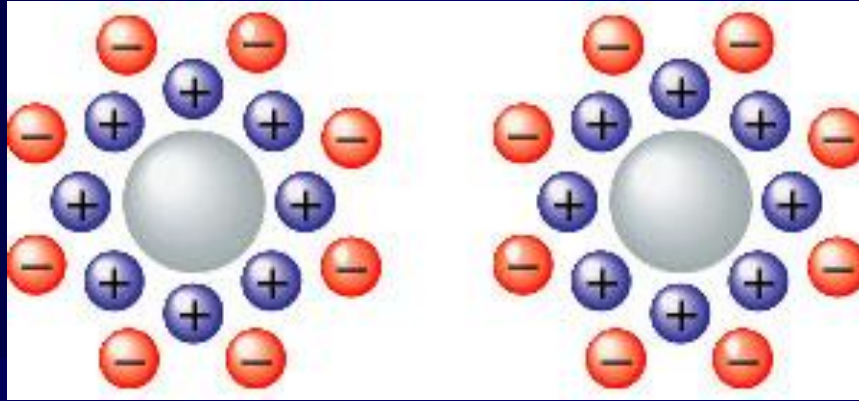
- Aeration = bubbling air through the water
 - Air bubbles absorb the other gases and remove them
 - O₂ in the air can oxidize some organics to CO₂ gas



- Cheap and widely used purification step
- Settling
 - Surface water often contains suspended particles from soil (clay = SiO₂ makes colloids) and animal/plant matter
 - Settling pond: larger (> 1 μm) particles settle to bottom

Settling

- Colloids will never settle out



- 0.001—1 μm diameter particles with charge

- Alum = $\text{Al}_2(\text{SO}_4)_3$ is added to settle the colloids



Alum

Lime

Aluminium Hydroxide

- $\text{Al}(\text{OH})_3$ forms gel that traps colloids and settles out

Softening

- Softening
 - Hard Water = water with dissolved Ca^{2+} and/or Mg^{2+}

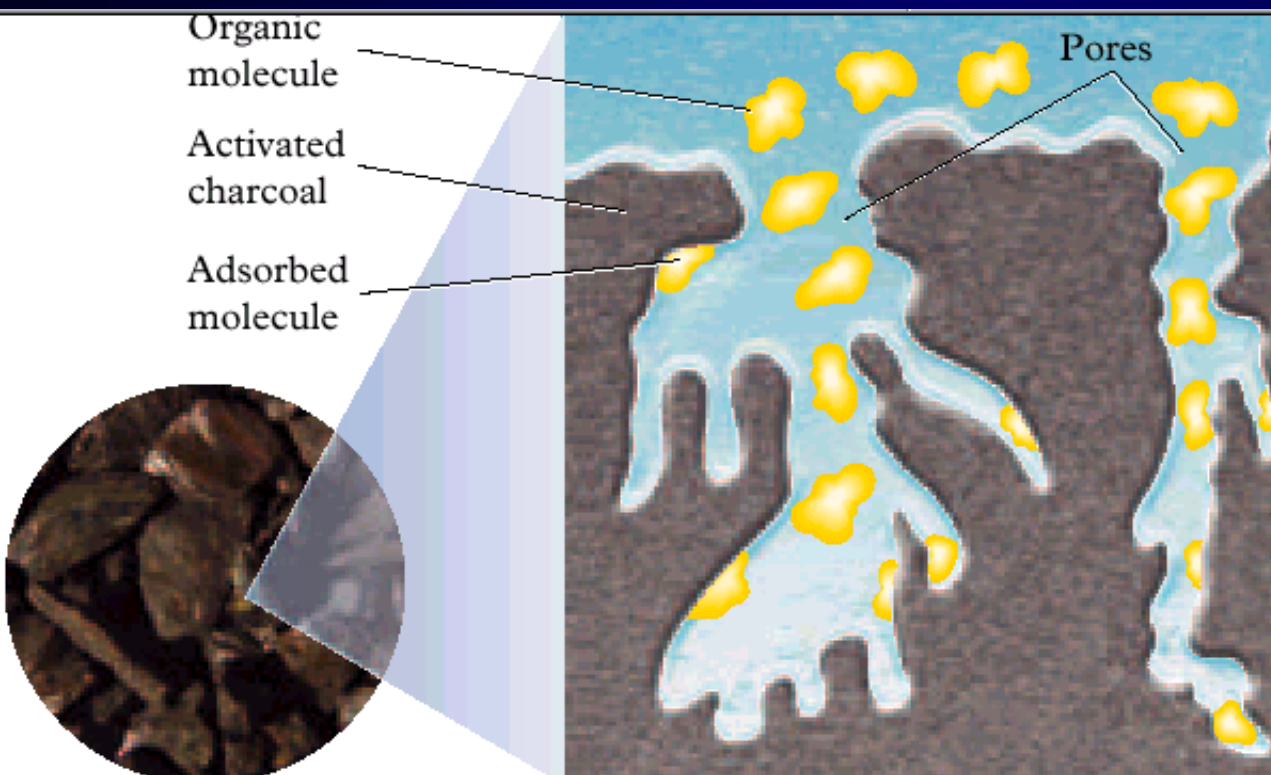
$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3$ solid is filtered out

$\text{Mg}^{2+} + 2 \text{OH}^- \rightarrow \text{Mg}(\text{OH})_2$ solid is filtered out

- The result is called soft water
- Hard Water Problems (McPherson)
 - Ca^{2+} and Mg^{2+} form precipitates with soap = scum
 - Ca^{2+} and/or Mg^{2+} form precipitates with CO_3^{2-} = scale

Charcoal Purification

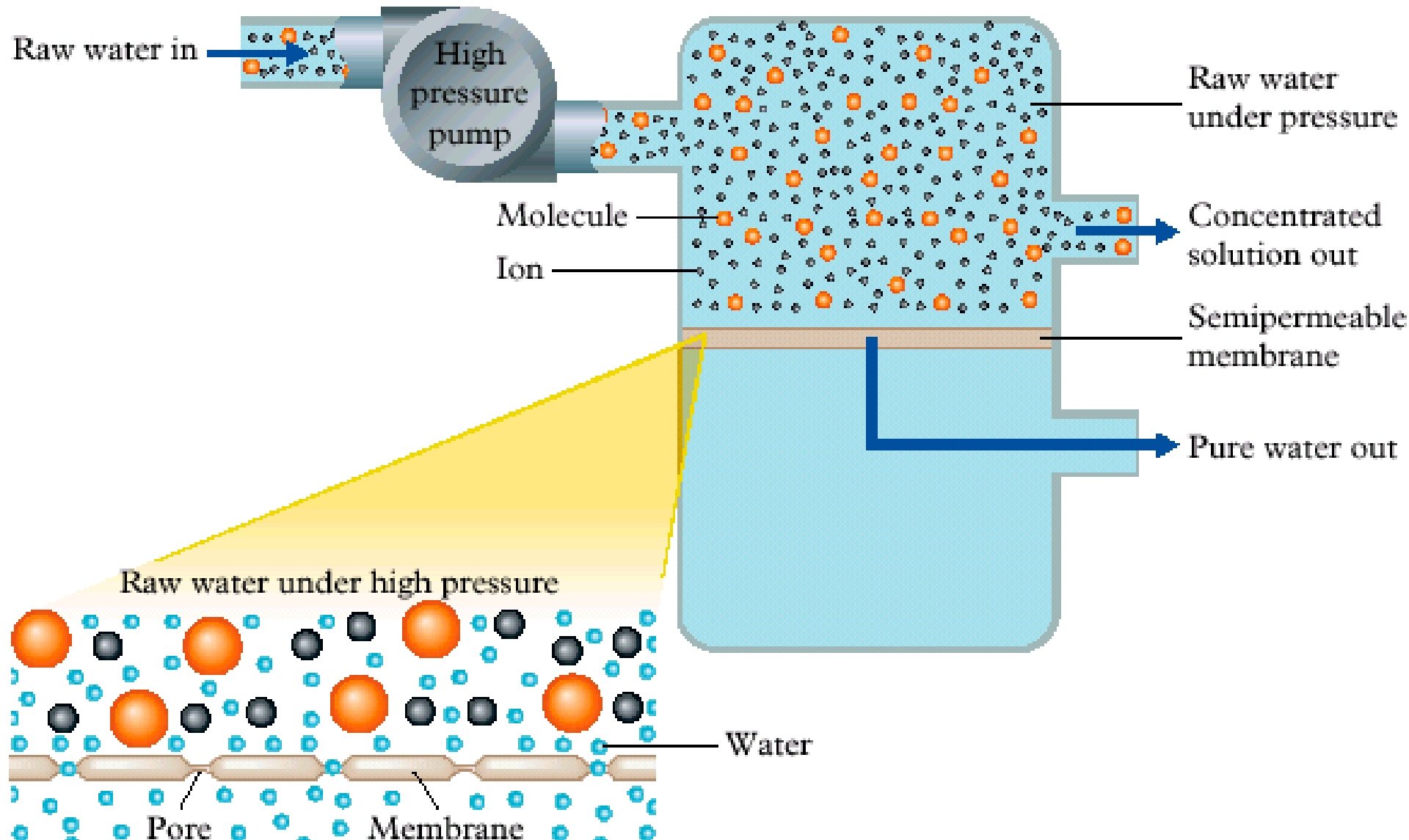
- Charcoal Purification
 - Nonionic (neutral compounds like most organics) will adsorb to the surface of charcoal (like dissolves like)
 - Activated carbon = finely divided charcoal with large surface area
 - Pesticides, chlorinated solvents, and other organics not previously removed are trapped by the carbon
 - Expensive, not done widely
 - Many individuals buy charcoal filters for tap water
 - After the charcoal is saturated, you must discard and get a new filter



Reverse Osmosis

- Reverse Osmosis
 - Osmosis = natural movement of water from high concentration to low concentration through a membrane
 - Reverse osmosis = purification of water using high pressure to force water from low to high concentration
 - Membrane only allows water, not ions, to pass due to size
 - Cellulose acetate is often the membrane compound
 - Ions removed: Na^+ , K^+ , Pb^{2+} , Hg^{2+} , NO_3^- , PO_3^{2-}
 - Problems: expensive, wasteful (discard more H_2O than keep)
 - Desalination = fresh water from salt water
 - Expensive, less than 0.1% of fresh water used is desalinated

Reverse Osmosis



Ion Exchange

- Ion Exchange
 - Often used as an alternative softening step
 - Resin = organic polymer beads with cation binding sites

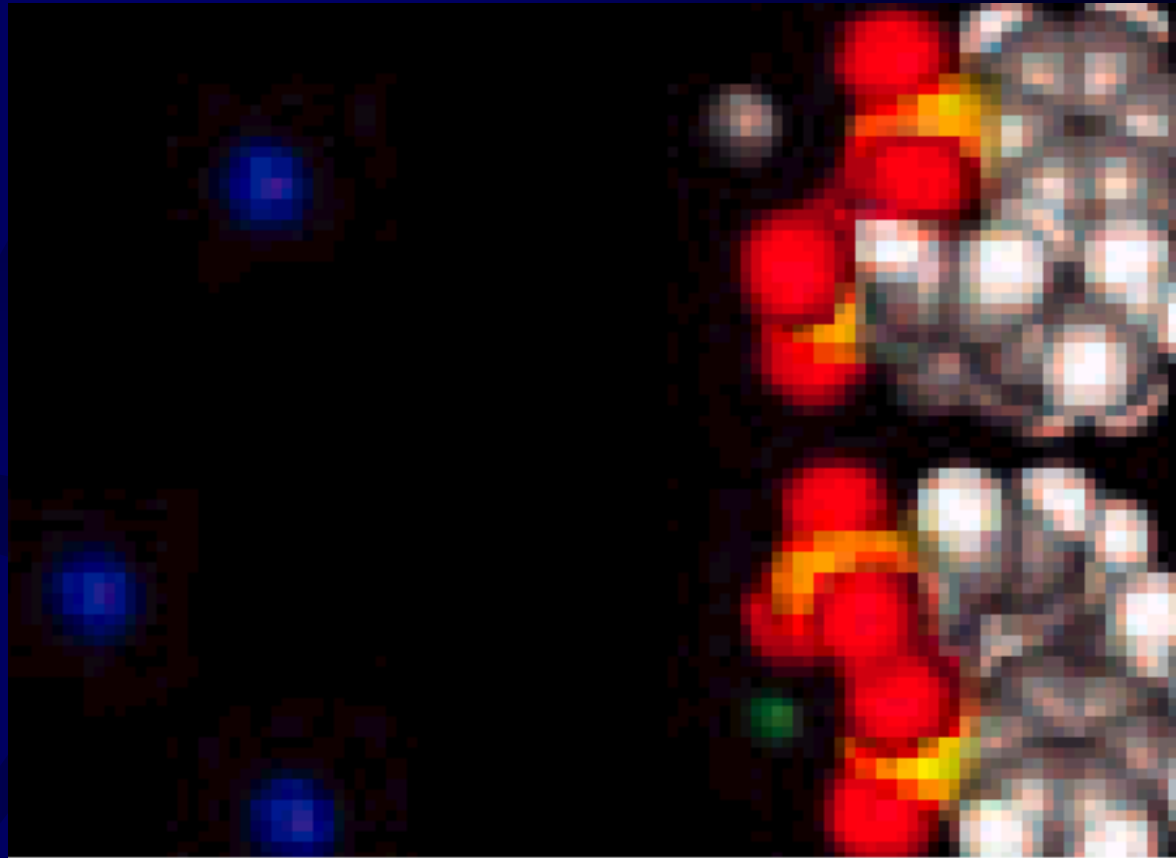
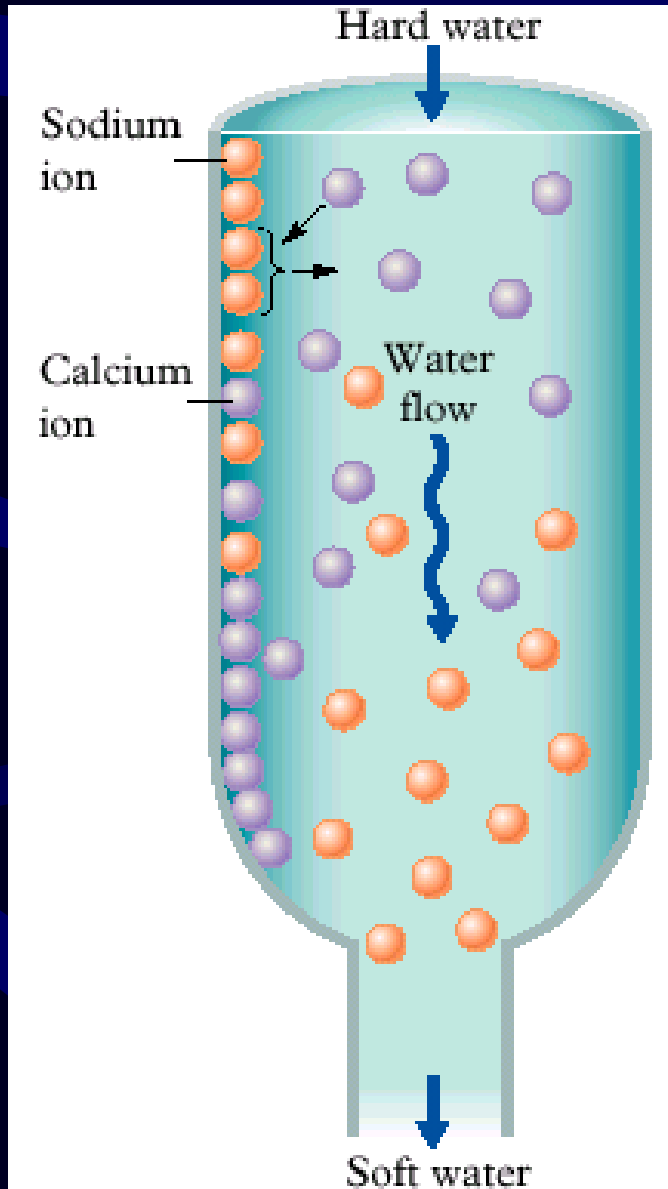


- Resin prefers to bind cations of higher charge



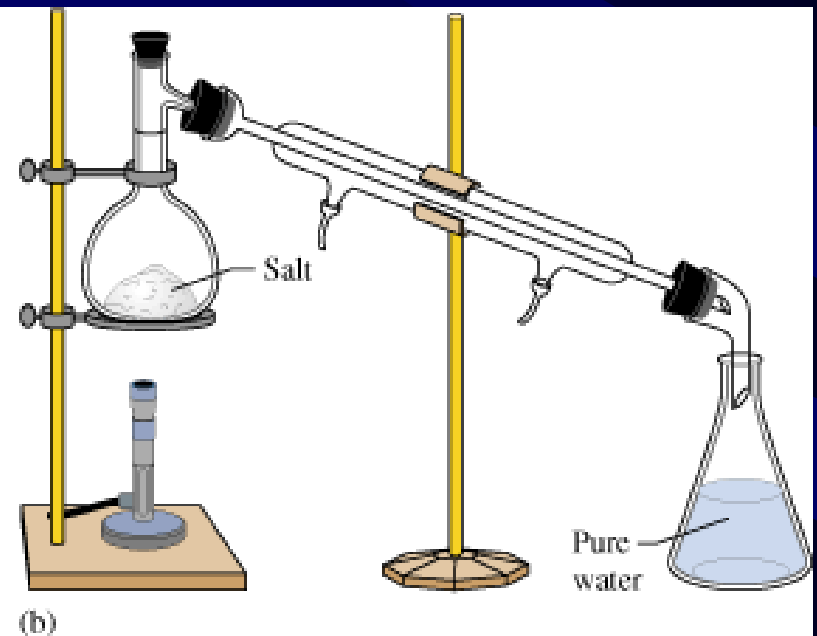
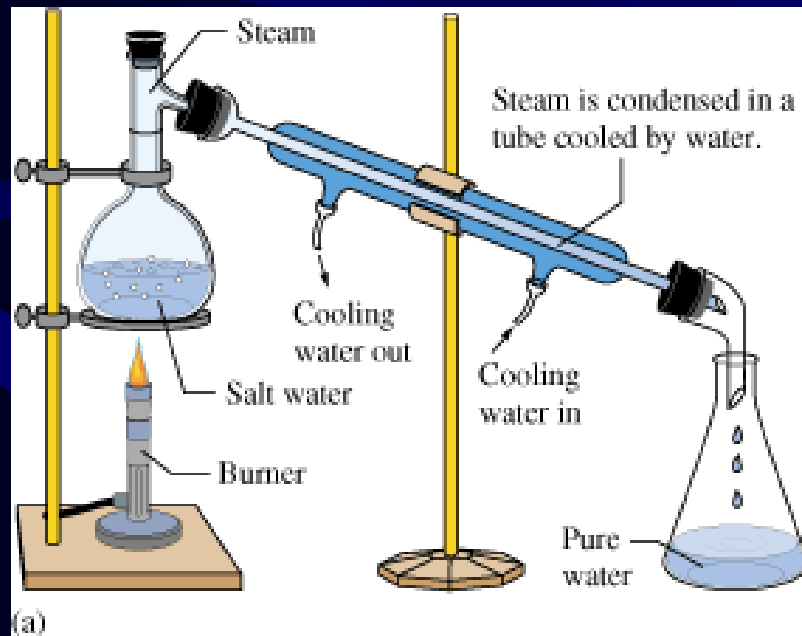
- Resin can be regenerated





Distillation

- Distillation = boil off pure water and leaving the undesired compounds behind
 - Expensive and energy inefficient
 - Used for desalination in a few places (solar stills)



Arsenic Removal Example

- Arsenic (As) is a toxic, cancer causing element
 - Groundwater often contains As as arsenate AsO_4^{3-}
 - Naturally occurring component of some minerals
 - Byproduct of smelting gold, silver, copper, nickel
 - World Health Organization (WHO) says 10 ppb is safe
 - 1% of US public water has As > 25 ppb
 - US law just been changed from 50 ppb to 10 ppb
 - Removal of As
 - Can't use ion exchange because arsenate is an anion
 - $\text{Fe}^{3+} + \text{AsO}_4^{3-} \rightarrow \text{FeAsO}_4$ solid which is then filtered off

Disinfection by Chlorination

- Bacteria/Viruses not all removed by purification
 - Disinfection = killing bacteria/viruses in water
 - HOCl = hypochlorous acid is the active compound
 - Passes through cell membrane to kill microorganisms
 - 75% of US population uses chlorinated water
 - Large scale chlorination:
$$\text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{HOCl} + \text{HCl}$$
 - Cl₂ gas is toxic and must be handled by experts

Small-scale Chlorination

- Swimming pools use chlorination, but not Cl_2



Calcium hypochlorite

Hypochlorous acid

- pH must be kept just above 7.0 by buffer
 - NaHSO_4 sodium bisulfate is most often used as buffer
 - If acidic pH: $\text{NH}_3 + 3 \text{HOCl} \text{ ----> } \text{NCl}_3 + 3 \text{H}_2\text{O}$
 - Nitrogen trichloride is a strong eye irritant
- Sunlight degrades HOCl, so it must be replenished
$$2 \text{OCl}^- + \text{UV light} \text{ ----> } 2 \text{Cl}^- + \text{O}_2$$

Drawbacks of Chlorination

- Chlorination of organics in the water
 - Phenols become toxic chlorophenols (bad taste, odor)
 - Can be overcome by using ClO_2 instead of HOCl
- Trihalomethanes = THM's (chloroform = CHCl_3)
 - Any organic molecule can end up as CHCl_3 with HOCl
 - WHO limit < 100 ppb; 1% US drinking water > 100ppb
 - Removal by activated charcoal is effective but expensive
 - CHCl_3 causes liver cancer, suspected in others
 - CHCl_3 gas in shower is just as dangerous as drinking
 - Chlorinated well water is safer; no organics

Residual Chlorine Protection

- Even if chlorine is not used as a disinfectant, it is usually added to prevent re-infection
 - Purified water is often stored/transported prior to use
 - Organic matter is already removed so no CHCl_3 formed
 - Combined Chlorine = NCl_3 , NHCl_2 , NH_2Cl usually used for protection purposes
 - Slower disinfecting agent, but lasts longer than HOCl
 - 1 ppm residual chlorine is considered safe from re-infection

Other Disinfection Methods

- Ozone = O_3 gas used in Europe
 - Can't be stored, so it must be made on site (expensive)
 - 10 minutes contact with water will disinfect it
 - No residual protection
 - Effective against viruses (HOCl is not)
 - May form toxic oxidized organics (formaldehyde H_2CO)
- Chlorine Dioxide = ClO_2 used in 300 N. Am. cities
 - Does not chlorinate organics, so no $CHCl_3$ formed
 - Must be made on site: $NaClO_2 \rightarrow ClO_2 + Na$
 - May leave some ClO_2^- , ClO_3^- in water--toxic

Other Disinfection Methods

- UV light alters DNA killing microorganisms
 - 10 s irradiation is effective
 - Same effect UV light has on skin—cancer
 - Dissolved substances and colloids block light
 - Small setups possible—Melhorn Deionized water
- Is it worth the risk to disinfect water?
 - Waterborne diseases kill 20 million people/year
 - 0.5 million killed in Peru in the 1990's by cholera
 - CHCl_3 appears much less fatal!

Groundwater Pollution by Organics

- Importance of groundwater pollution
 - Ignored until about 1980 (out of site, out of mind)
 - Has been used increasingly as drinking water
 - Can't be cleaned up easily like surface water can:
 - Pump-and-treat: continuous process, very expensive
- Organic Compounds in Groundwater
 - Leachate = liquid draining (leaching) from surface source
 - Landfills
 - Industrial Sites
 - Agricultural Land
- 1940—1980 was the age of groundwater pollution

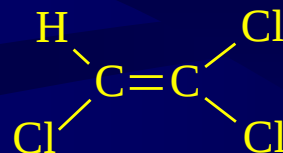
Organic Compounds in Groundwater

- Typical contaminants

- Most organic surface pollutants are broken down in the soil by bacteria, light, or oxidation. Only a few aren't.

- THM's like CHCl_3

- C_2HCl_3 = trichloroethene



- More dense than water, so collects at the bottom of aquifer



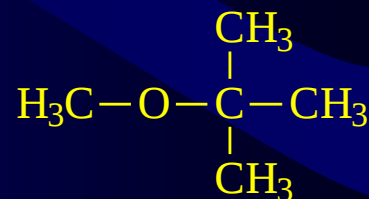
- BTX Hydrocarbons (benzene, toluene, xylene)

- Source is gasoline (steel tanks corrode and leak)

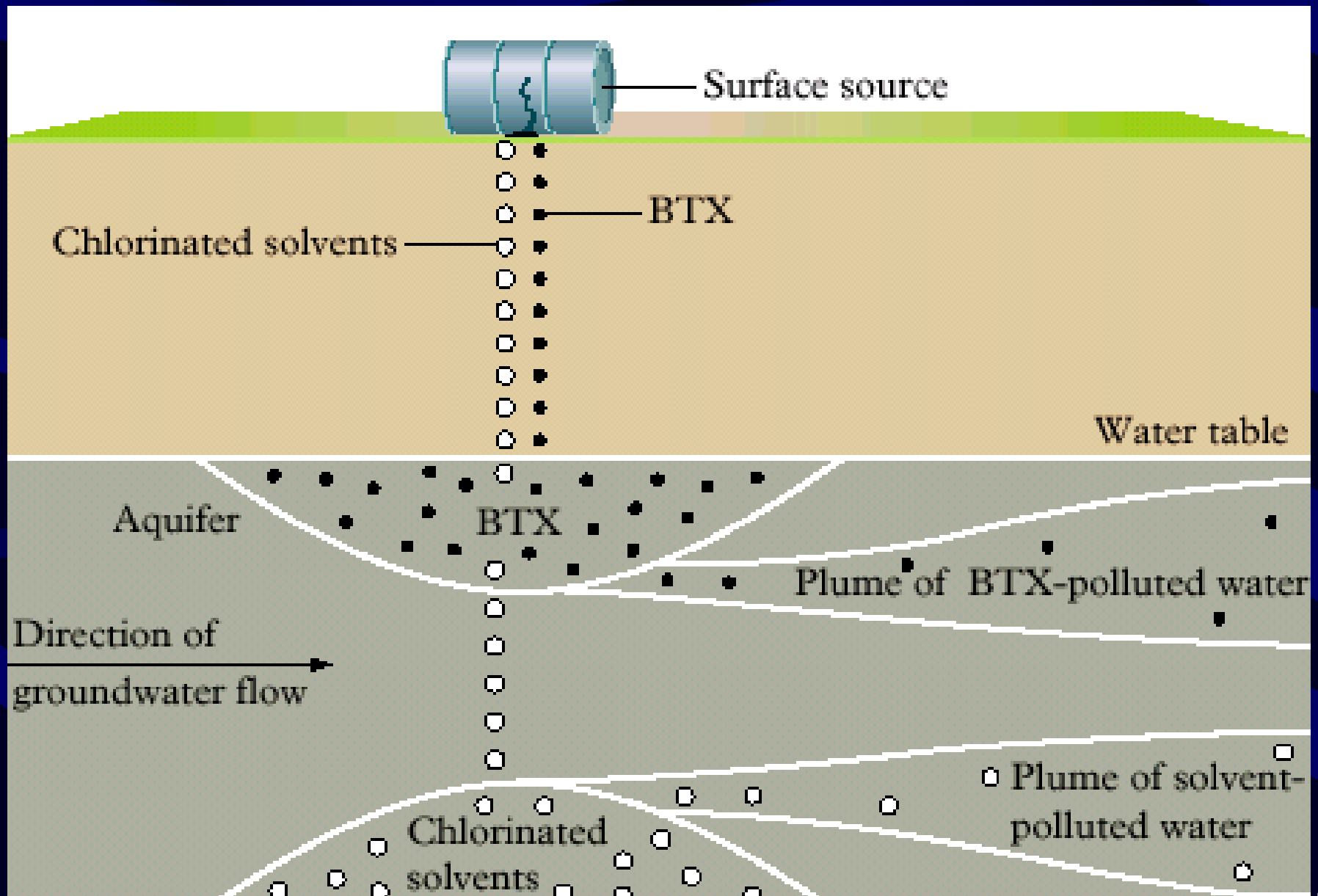
- Fairly soluble in water, rest of gasoline is not

- Less dense than water, so floats on top of aquifer

- MTBE = methyl t-butyl ether gas additive also in this layer



Groundwater Pollution by Organics



Water Pollution by Nitrogen Compounds

- Nitrogen is used by plants: NO_3^- (nitrate), NH_4^+ (ammonium cation) used as fertilizers
 - Environmental Protection Agency (EPA) limit for nitrate in drinking water is 10 ppm
 - Uncontaminated groundwater = 2 ppm nitrate
 - 9% of shallow aquifers have > 10 ppm nitrate
 - Cities usually use deep aquifers which are less contaminated
 - Rural wells in shallow aquifers often face nitrate problem
 - Sources of nitrate
 - Fertilized farmland
 - Unfertilized farmland still produces nitrate due to high plant and microorganism activity

Nitrate Health Risks

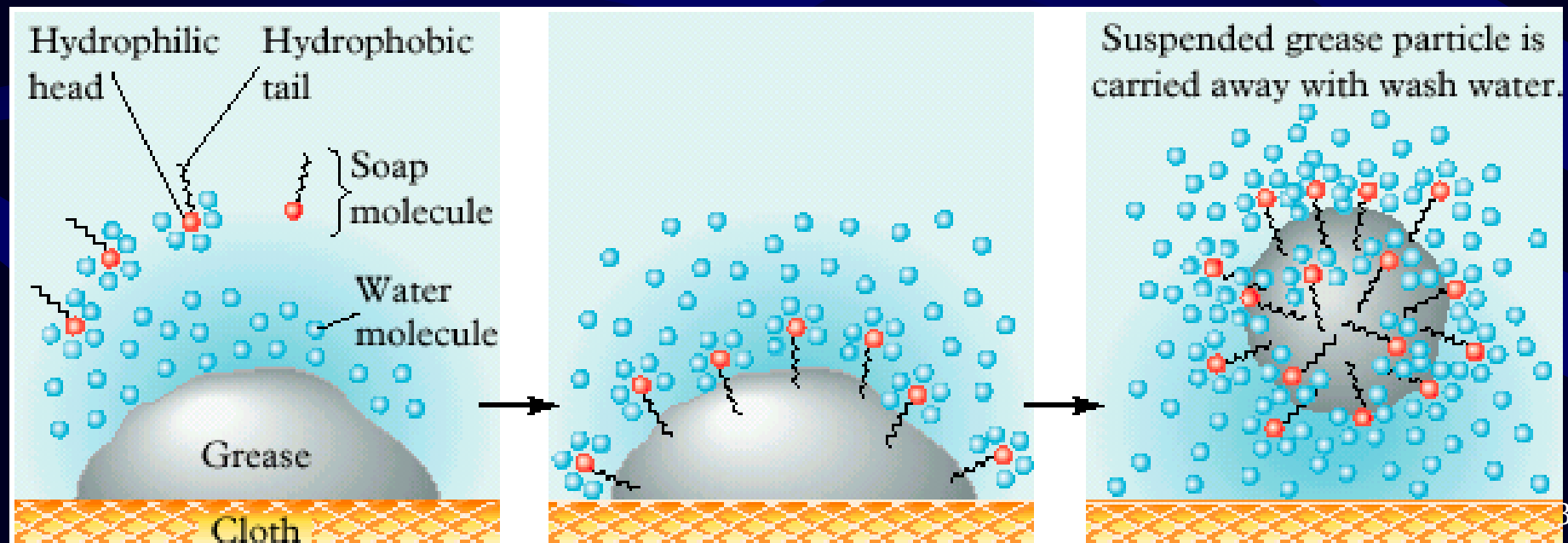
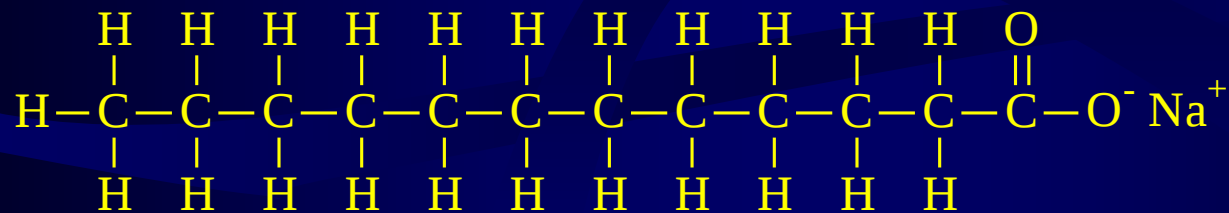
- Methemoglobinemia = “blue baby syndrome”
 - NO_3^- + bacteria $\rightarrow$ NO_2^- (nitrite anion)
 - NO_2^- combines with Hemoglobin, blocking oxygen transport (thus the blue color)
 - Most adults have enzymes that return the Hemoglobin to a useful state
 - Most infants don't yet have the mechanism to do this
 - Largely a rural problem, as is nitrate pollution

Removal of Nitrogen

- Ammonium ion removal
 - Ammonium cation is converted to ammonia gas and removed by aeration
$$\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$$
 - Ion exchange works because ammonium is a cation
- Nitrate removal
 - Denitrification = bacteria can turn NO_3^- into N_2 gas

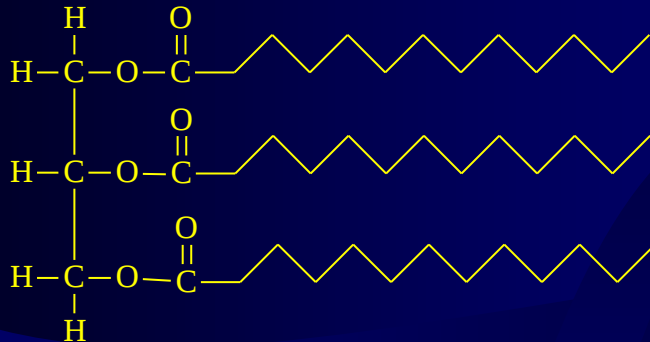
Surface Water Phosphate Pollution

- Soap = sodium or potassium salt of a fatty acid
 - Water soluble end due to the anion
 - Grease soluble end due to the hydrocarbon



Traditional Soaps

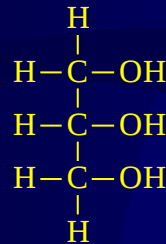
- Soaps from animal fats



Heat

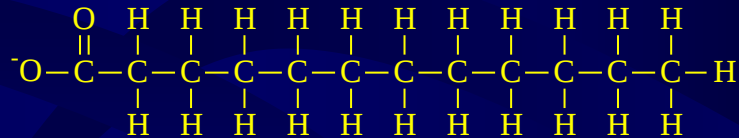


Triglyceride = Animal Fat



+

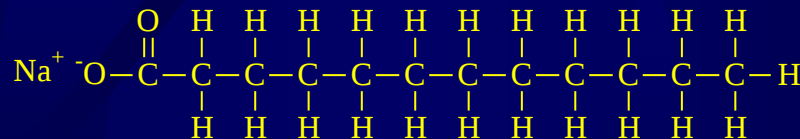
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Glycerine

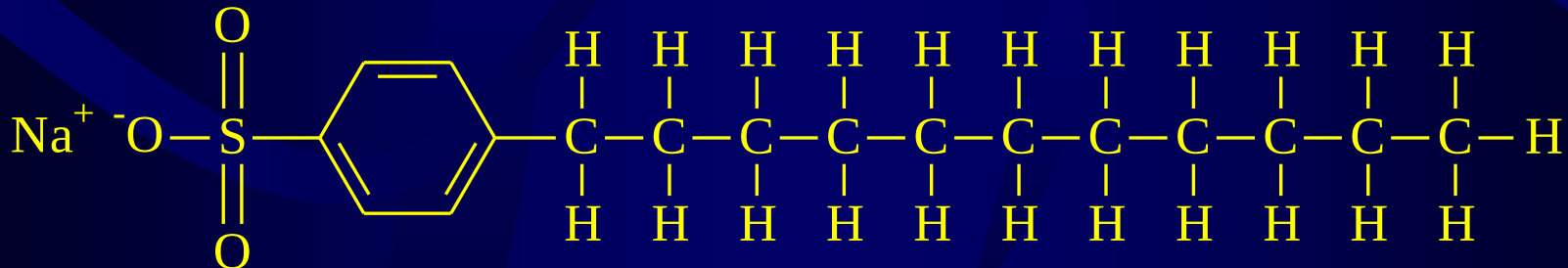
Fatty Acid

$\xrightarrow{\text{Na}_2\text{CO}_3}$



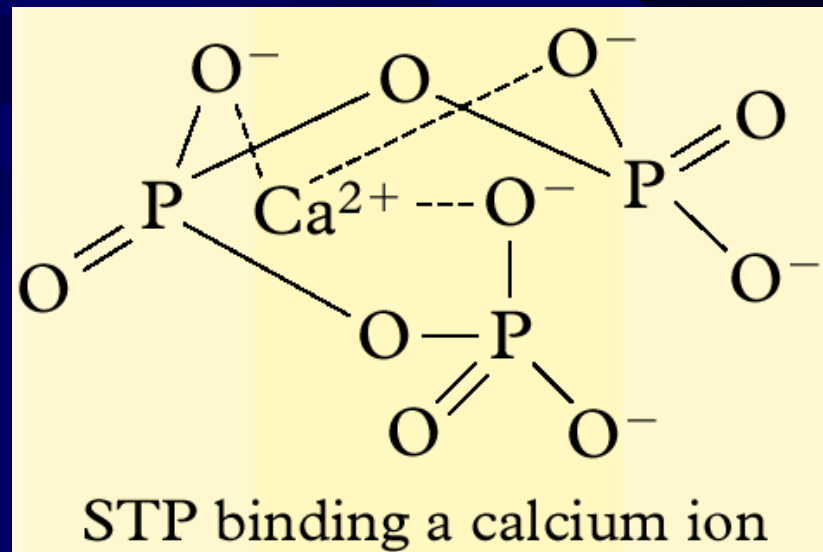
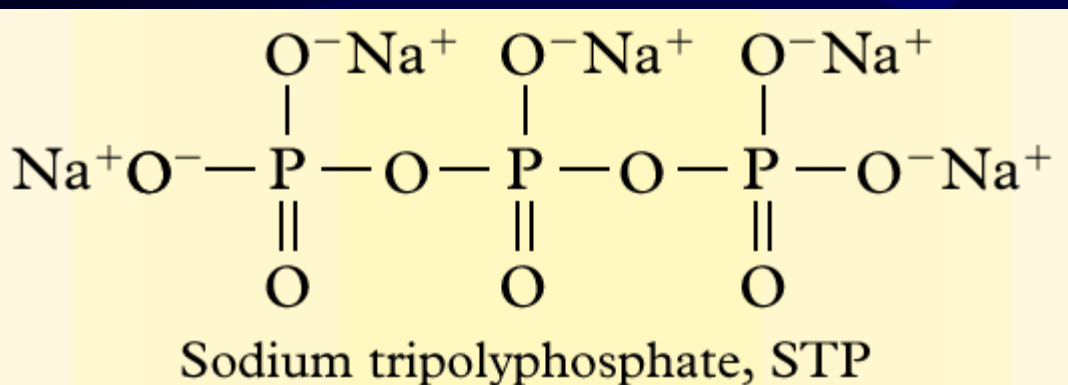
Detergents

- Problems with soap
 - Ca^{2+} and Mg^{2+} form precipitates (scum) with soap
 - Deposits on the item you are cleaning
 - Removes usefulness of the soap
 - Soft water solves this problem
- Detergents = synthetic molecules work like soap
 - Sulfonate anion instead of carbonate makes no scum
 - Biodegradable

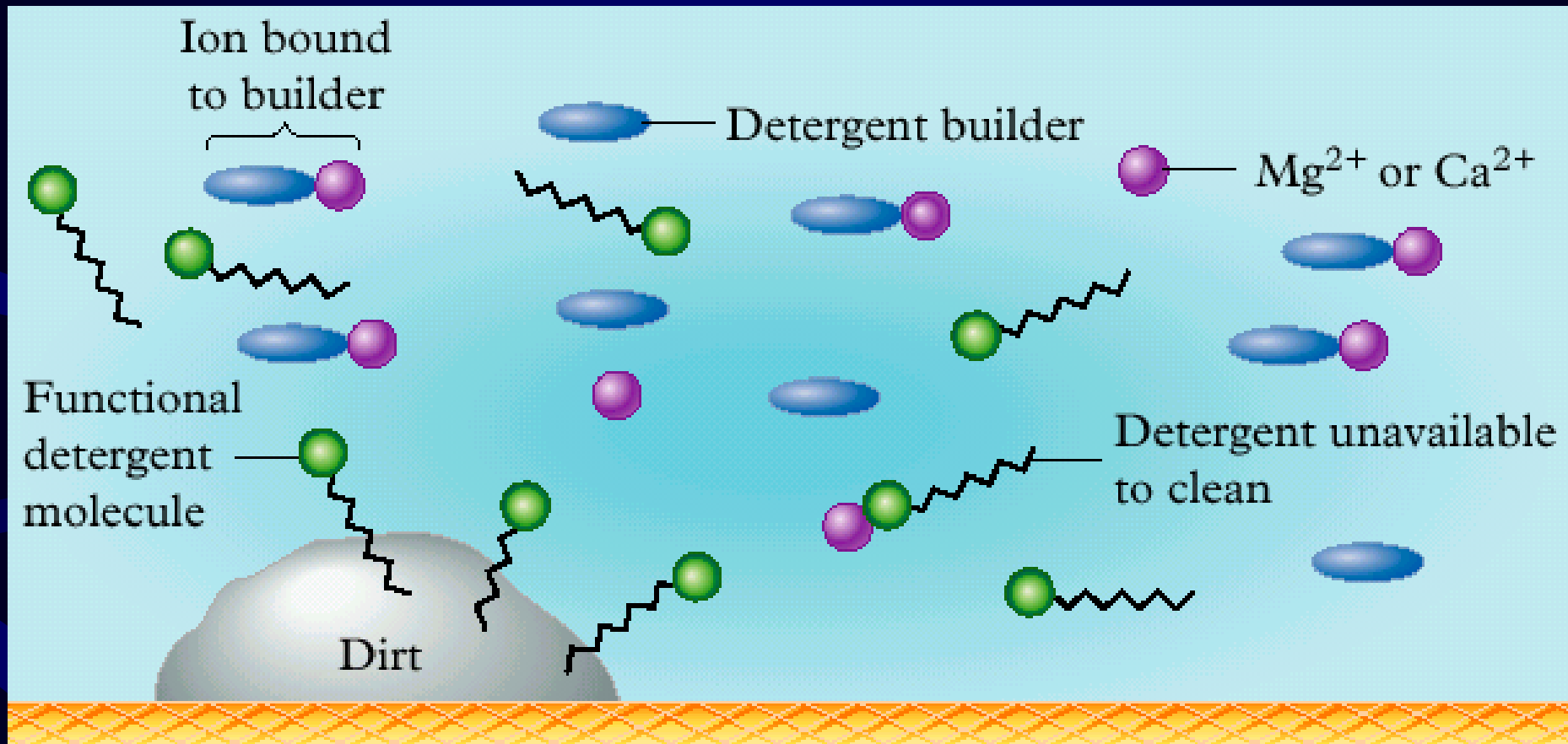


Builders

- Ca^{2+} and Mg^{2+} still tie up detergents, but no scum
 - Builder = simple molecules that bind Ca^{2+} and Mg^{2+}
 - Keeps these ions from using up the detergents
 - Chelating agents = bind the cation in more than one place
 - Phosphates are excellent builders



Detergent assisted by Builders cleaning a stain



Problems with Phosphates

- Polyphosphate Builders are converted to phosphate



- Contaminates water when wash water is discarded
- Can use citrate or zeolite builders to avoid phosphate

- Phosphate Pollution

- Point Source = specific site such as a city or factory
- Nonpoint Source = numerous small sources like farms
 - Phosphate is often contained in fertilizers as well as Nitrogen
 - Many small sources can add up to much pollution

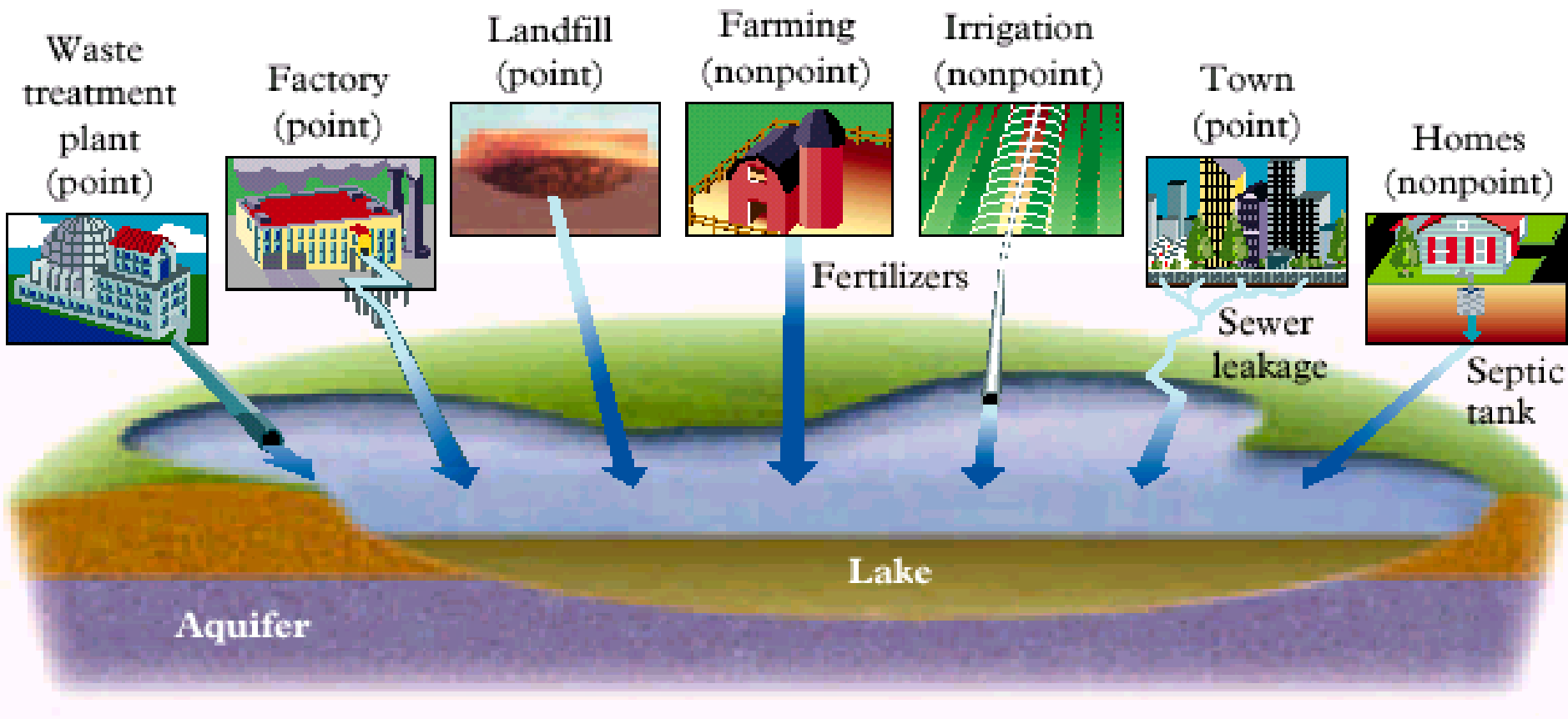


Figure 13.15 Point and nonpoint sources of pollution.

Algal Bloom

- Algal Bloom occurs with too much phosphate
 - P is often the limiting nutrient for plant growth
 - Phosphate pollution adds more phosphate to the system and allows algae to grow very rapidly
 - When they die, their decomposition uses up all O₂
 - Fish and other animals and plants die

- Removal of Phosphate:



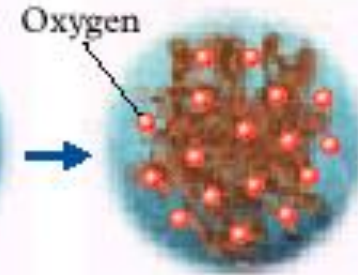
Algal Bloom



Excess
phosphate



Increased
algal growth



Oxygen
Decomposing
algae use oxygen
dissolved in water.



Fish die due to
lack of oxygen.

