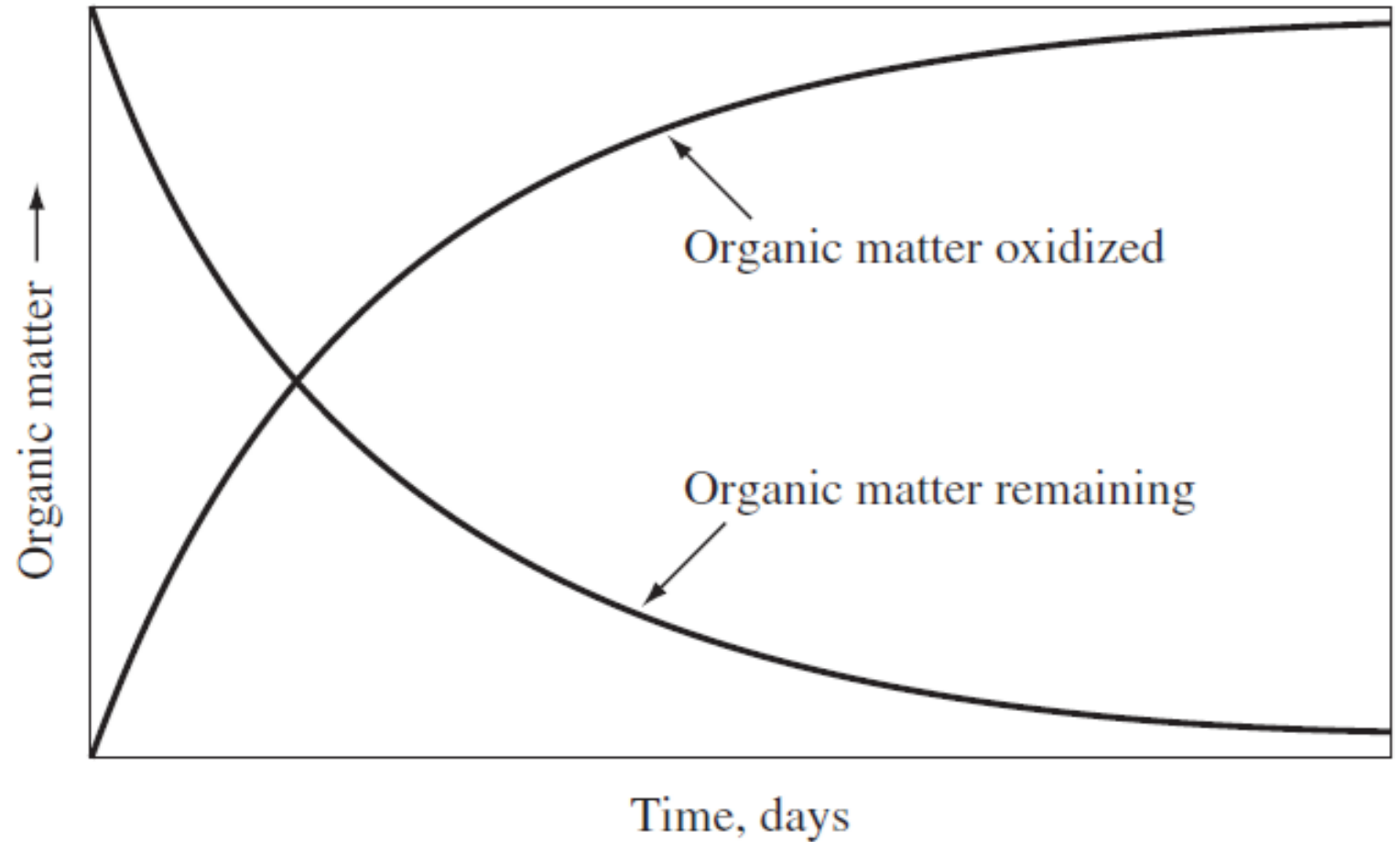


Water Pollution

Reference: Introduction to Environmental Engineering and Science,
Gilbert M. Masters Wendell P. Ela

Modeling BOD as a First-Order Reaction

The demand for oxygen to decompose the wastes decreases with time until there is no more demand.



Two equivalent ways to describe the time dependence of organic matter in a flask

- It is assumed that the rate of decomposition of organic wastes is proportional to the amount of waste that is left in the flask.
- If we let L_t represent the amount of waste demand left after time t , then, assuming a first-order reaction, we can write:

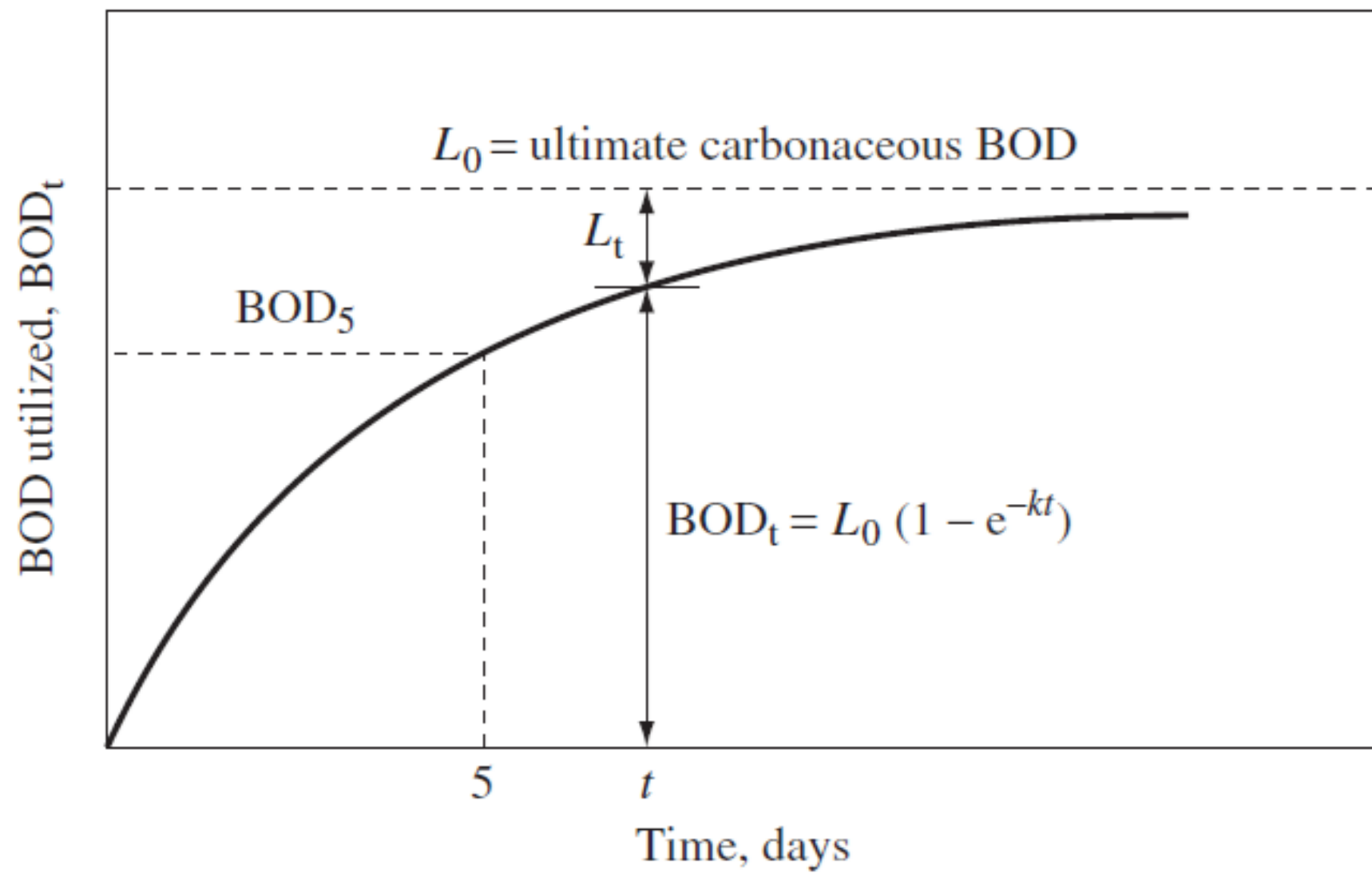
$$\frac{dL_t}{dt} = -kL_t \quad \text{where } k = \text{the BOD reaction constant (time}^{-1}\text{)}.$$

$$L_t = L_0 e^{-kt} \quad \text{where } L_0 \text{ is the } \textit{ultimate carbonaceous oxygen demand}.$$

- Ultimate carbonaceous oxygen demand is the total amount of oxygen required by microorganisms to oxidize the carbonaceous portion of the waste to carbon dioxide and water.
- L_0 is the sum of the amount of oxygen already consumed by the waste in the first t days, plus the amount of oxygen remaining to be consumed after time t .

$$L_0 = \text{BOD}_t + L_t$$

$$\text{BOD}_t = L_0(1 - e^{-kt})$$



$$\text{BOD}_t = L_0(1 - e^{-kt})$$

Sometimes the analysis is made using logarithms to the base 10 rather than the base e ,

$$\text{BOD}_t = L_0(1 - 10^{-Kt})$$
 where K is the reaction rate coefficient to the base 10

$$k = K \ln 10 = 2.303K$$

- The BOD reaction rate constant k is a factor that indicates the **rate of biodegradation** of wastes.
- As k increases, the rate at which dissolved oxygen is used increases, although the ultimate amount required, L_0 , does not change.
- The reaction rate will depend on a number of factors:
 - nature of the waste itself (for example, simple sugars and starches degrade easily while cellulose does not),
 - ability of the available microorganisms to degrade the wastes in question
 - temperature (as temperatures increase, so does the rate of biodegradation).

$$k_T = k_{20}\theta^{(T-20)}$$

θ is 1.047

The dilution factor P for an unseeded mixture of waste and water is 0.030. The DO of the mixture is initially 9.0 mg/L, and after five days, it has dropped to 3.0 mg/L. The reaction rate constant k has been found to be 0.22 day^{-1} .

- a. What is the five-day BOD of the waste?
- b. What would be the ultimate carbonaceous BOD?
- c. What would be the remaining oxygen demand after five days?
- d. What would the five-day BOD of this waste be at 25°C ?

Solution

- a. From (2), the oxygen consumed in the first five days is

$$\text{BOD}_5 = \frac{\text{DO}_i - \text{DO}_f}{P} = \frac{9.0 - 3.0}{0.030} = 200 \text{ mg/L}$$

b. The total amount of oxygen needed to decompose the carbonaceous portion of the waste can be found by rearranging (11):

$$L_0 = \frac{\text{BOD}_5}{(1 - e^{-kt})} = \frac{200}{(1 - e^{-0.22 \times 5})} = 300 \text{ mg/L}$$

c. After five days, 200 mg/L of oxygen demand out of the total 300 mg/L would have already been used. The remaining oxygen demand would therefore be $(300 - 200) \text{ mg/L} = 100 \text{ mg/L}$.

d. First we will adjust the reaction rate constant with (14) using a value of θ equal to 1.047:

$$k_{25} = k_{20}\theta^{(T-20)} = 0.22 \times (1.047)^{(25-20)} = 0.277/\text{day}$$

So, from (12),

$$\text{BOD}_5 = L_0(1 - e^{-k_5}) = 300(1 - e^{-0.277 \times 5}) = 225 \text{ mg/L}$$

III. NUTRIENTS

- Nutrients are chemicals, such as nitrogen, phosphorus, carbon, sulfur, calcium, potassium, iron, manganese, boron, and cobalt, that are essential to the growth of living things.
- In terms of water quality, nutrients can be considered as pollutants when their concentrations are sufficient to allow excessive growth of aquatic plants, particularly algae (lead to **blooms of algae**, which eventually die and decompose).
- Their decomposition removes oxygen from the water (**exerts oxygen demand**), potentially leading to levels of DO that are insufficient to sustain normal life forms.
- Algae and decaying organic matter add color, turbidity, odors, and objectionable tastes to water that are difficult to remove and that may greatly reduce its acceptability as a domestic water source.
- The process of **nutrient enrichment (eutrophication)**, is especially important in lakes.



- Not only is nitrogen capable of contributing to eutrophication problems, but when found in drinking water in a particular form, **nitrate**, it can pose a serious public health threat.
- Certain bacteria **converting nitrate to nitrite** are found in the alkaline digestive tract of infants, but not later in adults as the digestive system becomes more acidic.
- Hemoglobin in the bloodstream is oxidized by nitrite to **methemoglobin**, which cannot carry oxygen. The oxygen starvation characteristic of *methemoglobinemia* causes a bluish discoloration of the infant; hence, it is commonly referred to as the **blue baby syndrome**.
- In extreme cases, the victim may die from suffocation. Usually after the age of about six months, the digestive system of a child is sufficiently developed and this syndrome does not occur.

- Major sources of nitrogen include municipal wastewater discharges, runoff from animal feedlots, chemical fertilizers, and nitrogen-deposition from the atmosphere, especially in the vicinity of coal-fired power plants.
- Aquatic species require a long list of nutrients for growth and reproduction, but from a water-quality perspective, the three most important ones are **carbon, nitrogen, and phosphorus**.
- Human activities provide enough phosphorus to allow excessive growth of aquatic weeds and algae. Human sources of phosphorus include agricultural runoff in fertilized areas, discharges from animal feedlots, and domestic sewage. In sewage, part of the phosphorus is from human feces and part is from detergents.
- The nutrient that is least available relative to the plant's needs is called the **limiting nutrient**.
- Carbon is usually available from a number of natural sources, including alkalinity, dissolved carbon dioxide from the atmosphere, and decaying organic matter, so it is not often the limiting nutrient.
- It is usually either nitrogen or phosphorus that controls algal growth rates.
- In general, **seawater is most often limited by nitrogen**, whereas **freshwater lakes are most often limited by phosphorus**.

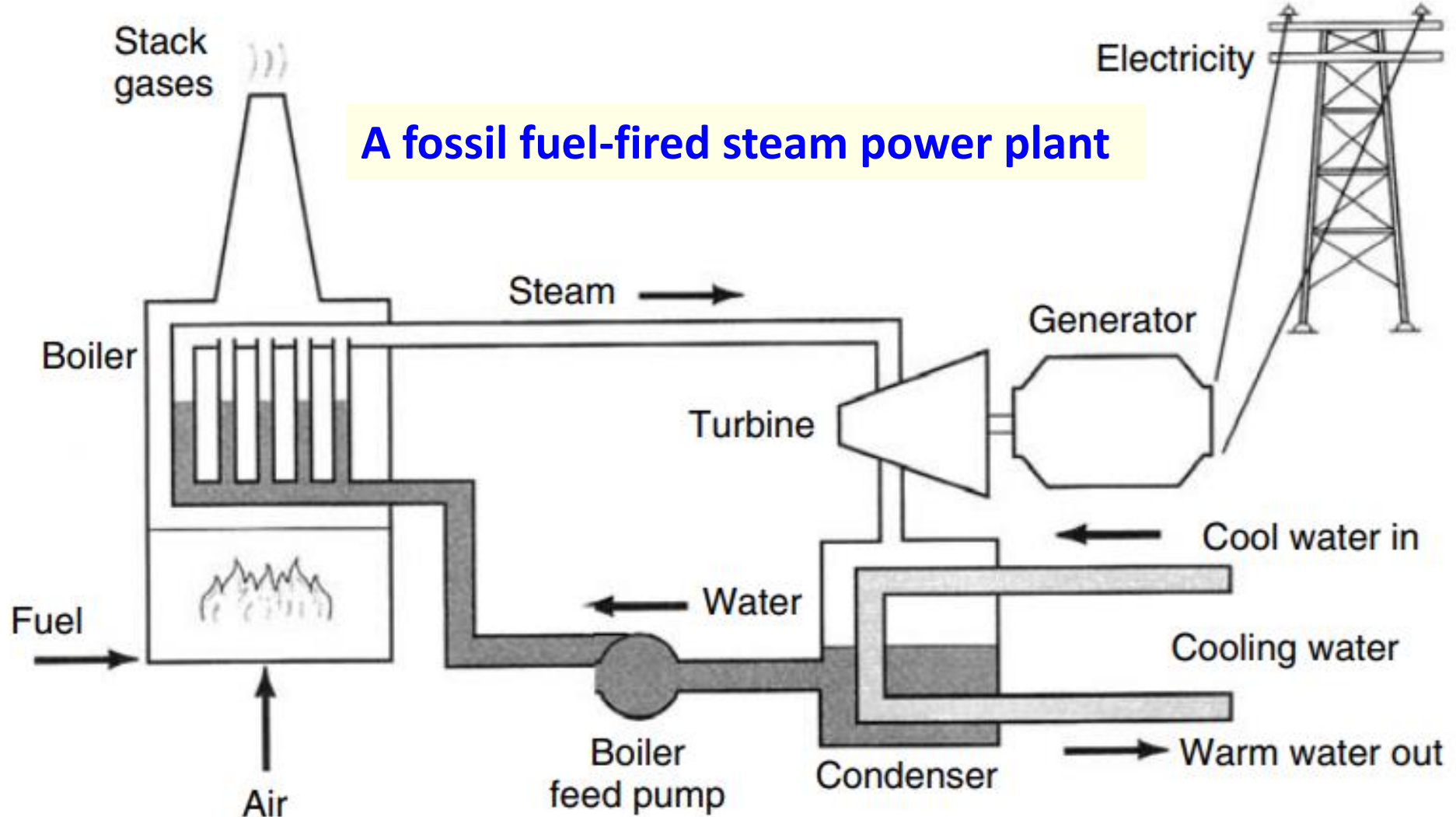
- Nutrients may come from either *point-sources* or *nonpoint-sources*.
- The most common **point-sources** are the discharge pipes from industries and wastewater treatment plants but may also include discharges from waste disposal sites, mines, animal feedlots, and large construction sites where the polluted water is collected in networks of pipes or channels and taken to a central point before discharge.
- **Nonpoint-sources** are usually more intermittent than point sources and are characterized by many points of entry to the receiving water. Runoff from agricultural lands, pastures and ranges, small construction sites, urban areas, abandoned mines, and logging sites are typical nonpoint-sources of pollution.
- Point sources, have been the focus of most remedial effort in the past 30 years, are easier to treat and monitor because they are more continuous and centralized.
- Nonpoint-sources are now the largest contributor to surface water pollution, and agriculture is the largest contributor to nonpoint source pollution.

IV. SALTS

- Water naturally accumulates a variety of dissolved solids, or *salts*, as it passes through soils and rocks on its way to the sea.
- These salts typically include such cations as **sodium**, **calcium**, **magnesium**, and **potassium**, and anions such as **chloride**, **sulfate**, and **bicarbonate**.
- Measure of salinity is the concentration of **total dissolved solids (TDS)**.
- **Fresh water** = less than **1,500 mg/L TDS**; **brackish waters** = up to **5,000 mg/L**; **saline waters** = above **5,000 mg/L**; **Seawater** = **30,000 to 34,000 mg/L TDS**.
- The concentration of dissolved solids is an important indicator of the usefulness of water for various applications. Drinking water = recommended maximum TDS= 500 mg/L. As the concentration of salts in irrigation water increases above 500 mg/L, the need for careful water management to maintain crop yields becomes increasingly important.
- Irrigated agriculture, especially in arid areas, is always vulnerable to an accumulation of salts due to this evapotranspiration on the cropland itself. In addition, irrigation drainage water may pick up additional salt as it passes over and through soils. As a result, irrigation drainage water is always higher in salinity than the supply water and, with every reuse, its salt concentration increases even more.

V. THERMAL POLLUTION

- A large steam-electric power plant requires an enormous amount of cooling water. A typical power plant, for example, warms about **150,000 m³/hr of cooling water by 10°C** as it passes through the plant's condenser.



- If that heat is released into a local river or lake, the resulting rise in temperature can adversely affect life in the vicinity of the thermal plume. For some species, such as trout and salmon, any increase in temperature is life threatening. Sudden changes in temperature caused by periodic plant outages, can make it difficult for the local ecology to acclimate.
- As water temperature increases, **two factors** combine to make it more difficult for aquatic life to get sufficient oxygen from the water. The first results from the fact that **metabolic rates tend to increase with temperature**, generally by a factor of 2 for each 10°C rise in temperature. This causes an increase in the amount of oxygen required by organisms.
- At the same time, the **available supplies of dissolved oxygen (DO) are reduced** because the amount of DO that the water can hold decreases with increase in temperature. Thus, as temperatures increase, the demand for oxygen goes up, and the amount of DO available goes down.

VI. HEAVY METALS

- Metals are characterized by high thermal and electrical conductivity, high reflectivity and metallic luster, strength, and ductility. From a chemical perspective, a metal is an element that will give up one or more electrons to form a cation in an aqueous solution.
- Including the metalloids, about 80 elements can be called metals.
- The term **heavy metal** is often used to refer to metals with specific gravity greater than about 4 or 5.
- Most metals are toxic, including aluminum, arsenic, beryllium, bismuth, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, selenium, strontium, thallium, tin, titanium, and zinc.
- In terms of their environmental impacts, the most important heavy metals are mercury (Hg), lead (Pb), cadmium (Cd), and arsenic (As).

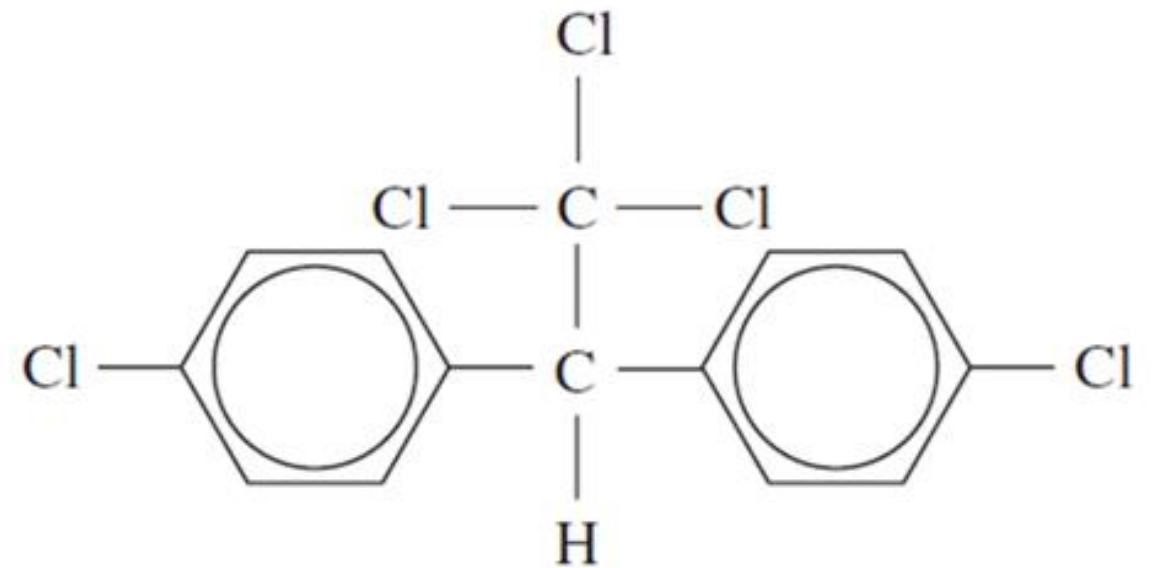
- Some of these metals, such as iron, are essential nutrients in our diets, but in higher doses, they can cause a range of adverse impacts on the body, including nervous system and kidney damage, creation of mutations, and induction of tumors.
- The most important route for the elimination of metals after they are inside a person is via the **kidneys**. Kidneys can be considered to be complex filters whose primary purpose is to eliminate toxic substances from the body. The kidneys contain millions of excretory units called **nephrons**, and chemicals that are toxic to the kidneys are called **nephrotoxins**.
- Cadmium, lead, and mercury are examples of nephrotoxic metals.
- Metals differ from other toxic substances in that they are **totally nondegradable** (virtually indestructible in the environment). Thus, the waste products be disposed of so as to minimize further environmental and human impacts.
- Ex. arsenic-bearing residuals from the water treatment will be sent to municipal solid waste landfills, where it may be mobilized into the **landfill leachate**—the liquids that drain out of the disposed solid waste.

- Metals may be inhaled, as is often the case with lead, for example, and they may be ingested. How well they are absorbed in the body depends somewhat on the particular metal in question and the particular form that it exists in.
- For example, liquid **mercury** is not very toxic and most of what is ingested is excreted from the body. Mercury vapor, on the other hand, is highly toxic. As a vapor, it enters the lungs where it diffuses into the bloodstream. When blood containing mercury reaches the brain, the mercury can pass into the brain, where it causes serious damage to the central nervous system.
- By contrast, **lead** does not pose much of a threat as a vapor since it has such a low vapor pressure, and is most dangerous when it is dissolved into its ionic form. Lead dissolved in blood is transferred to vital organs, including the kidneys and brain, and it readily passes from a pregnant woman to her fetus.
- Children and fetuses are the most at risk since their brains are growing rapidly, and exposure to lead can cause severe and permanent brain damage.

VII. PESTICIDES

- Pesticide is a term used to cover a range of chemicals that kill organisms that humans consider undesirable.
- Pesticides can be delineated as **insecticides, herbicides, rodenticides, and fungicides**.
- **INSECTICIDES:**
 - There are three main groups of synthetic organic insecticides: **organochlorines (also known as chlorinated hydrocarbons), organophosphates, and carbamates**.
 - The most widely known **organochlorine pesticide** is **DDT** (dichlorodiphenyltrichloroethane), which has been widely used to control insects that carry diseases such as malaria (mosquitoes), typhus (body lice), and plague (fleas). Organochlorine insecticides in general are highly toxic to insects, but their acute human toxicity is relatively low.
 - It was DDT's impact on food chains, rather than its toxicity to humans, that led to its ban in the developed countries of the world (it is still used in developing countries).
 - DDT enters the food chain and becomes increasingly concentrated at each successive trophic level, a phenomenon known as **biomagnification**.
 - **DDT** are **very persistent**, which means they last a long time in the environment before being broken down into other substances, and they are **soluble in hydrocarbon solvents**, which means they easily accumulate in fatty tissue.

- The accumulation of organochlorine pesticides in fatty tissue means that organisms at successively higher trophic levels in a food chain are consuming food that has successively higher concentrations of pesticide.
- At the top of the food chain, body concentrations of these pesticides are the highest, and it is there that organochlorine toxicity has been most recognizable.
- Birds, for example, are high on the food chain, and it was the adverse effect of DDT on their reproductive success that focused attention on this particular pesticide.



DDT: *p,p'*-dichlorodiphenyltrichloroethane

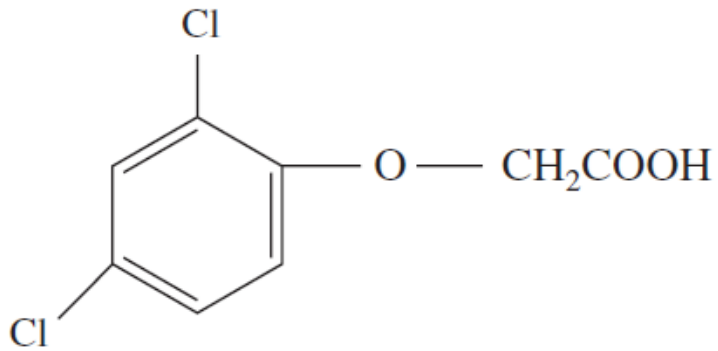
- Other widely used organochlorines included methoxychlor, chlordane, heptachlor, aldrin, dieldrin, endrin, endosulfan, and Kepone.
- Animal studies have shown that dieldrin, heptachlor, and chlordane produce **liver cancers**, and aldrin, dieldrin, and endrin cause **birth defects** in mice and hamsters.
- Given the ecosystem disruption, their potential long-term health effects in humans (e.g., cancer), and the biological resistance to these pesticides that many insect species have developed, organochlorines have largely been replaced with organophosphates and carbamates.

- The **ORGANOPHOSPHATES**, such as parathion, malathion, diazinon, TEPP (tetraethyl prophosphate), and dimethoate, are effective against a wide range of insects, and **they are not persistent**.
- However, they are **much more acutely toxic to humans** than the organochlorines that they have replaced. They are rapidly absorbed through the skin, lungs, and gastrointestinal tract, so unless proper precautions are taken, they are very hazardous to those who use them.
- Humans exposed to excessive amounts have shown a range of symptoms, including tremor, confusion, slurred speech, muscle twitching, and convulsions.

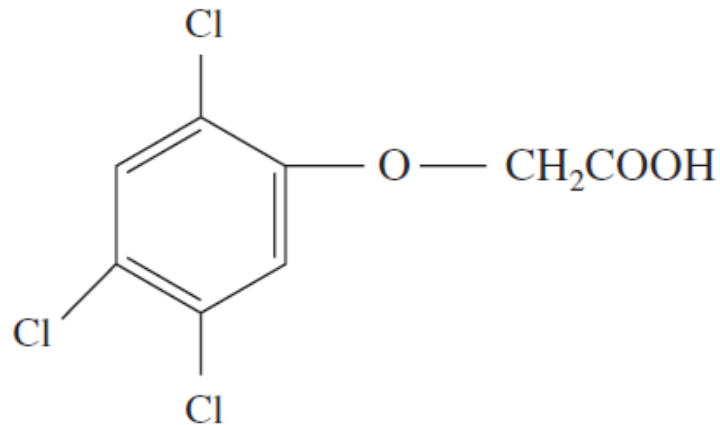
- The third category of insecticides, **CARBAMATES**, is derived from carbamic acid.
- They are similar to organophosphates in that they are **short-lived** in the environment (not being around long enough to bioaccumulate in food chains).
- These have **high human toxicity**.
- Popular carbamate pesticides include propoxur, carbaryl, and aldicarb.
- Acute human exposure to carbamates has led to a range of symptoms such as nausea, vomiting, blurred vision, and, in extreme cases, convulsions and death.

HERBICIDES:

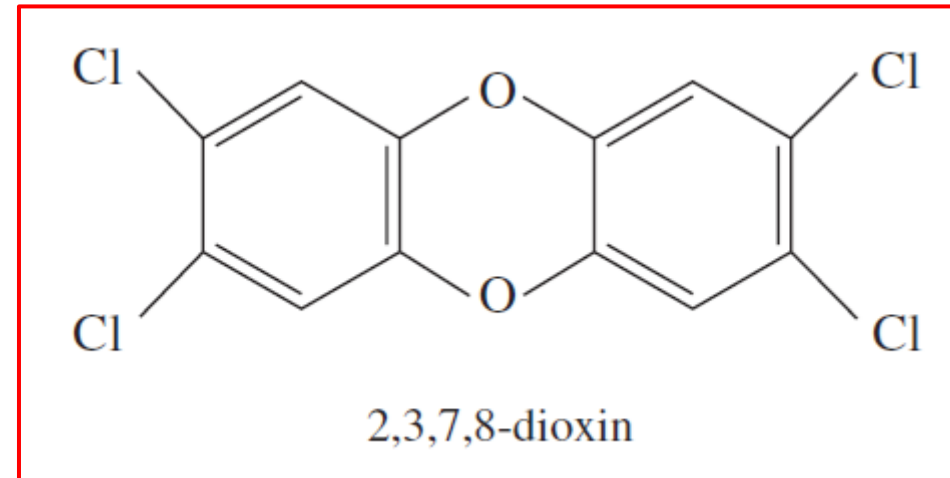
- **Chlorinated hydrocarbons** are often used as herbicides.
- The chlorophenoxy compounds 2,4,5-T and 2,4-D are among the most well known. The herbicide 2,4,5-T has been banned in part because the manufacturing process produces a highly toxic side-product, **dioxin**. Dioxins also enter the environment as products of combustion from incinerators.



2,4-Dichlorophenoxyacetic acid
(2,4-D)



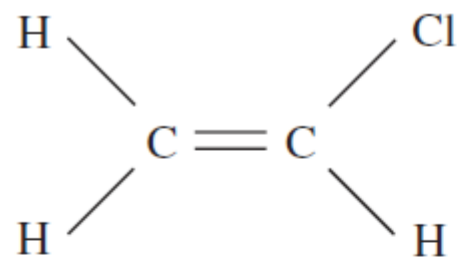
2,4,5-Trichlorophenoxyacetic acid
(2,4,5-T)



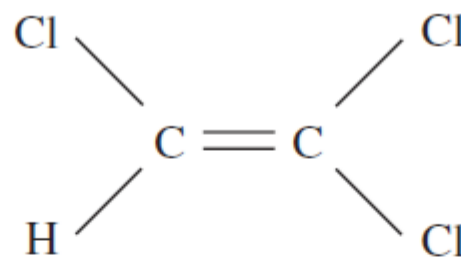
VIII. Volatile Organic Chemicals

- They are often used as **solvents** in industrial processes and a number of them are either known or suspected **carcinogens or mutagens**.
- Five VOCs are especially toxic, and their presence in drinking water is cause for special concern: vinyl chloride, tetrachloroethylene, trichloroethylene, 1,2-dichloroethane, and carbon tetrachloride.
- They are not often found in concentrations above a few $\mu\text{g/L}$ in surface waters, but in **groundwater**, their concentrations can be hundreds or thousands of times higher.
- Their volatility also suggests the most common method of treatment, which is to **aerate** the water to encourage them to vaporize and disperse in the atmosphere. Since volatilization does not destroy the VOC but simply transfers it to the air, it is important that the resulting atmospheric concentration does not reach a level of concern.

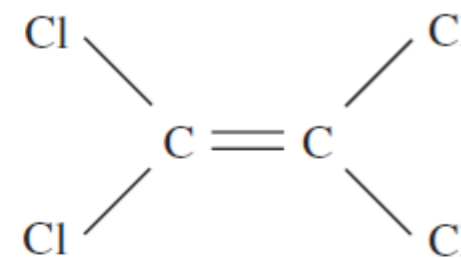
The most toxic of the five is *vinyl chloride* (chloroethylene). It is a known human carcinogen used primarily in the production of polyvinyl chloride resins.



Vinyl chloride

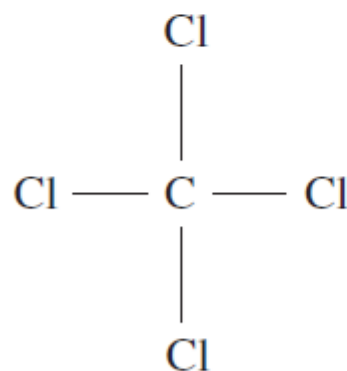


Trichloroethylene

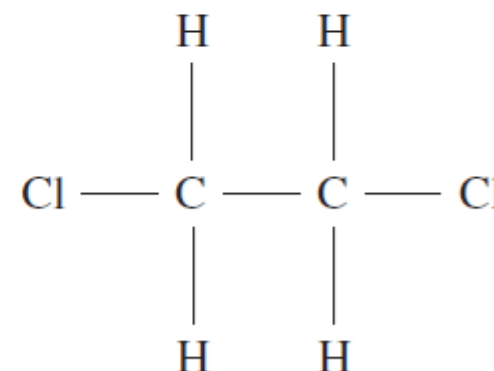


Tetrachloroethylene

Carbon tetrachloride was a common household cleaning agent that is now more often used in grain fumigants, fire extinguishers, and solvents. It is very toxic if ingested (only a few milliliters can cause death). It is relatively insoluble in water, and therefore only occasionally found in contaminated groundwater



Carbon tetrachloride



1,2-Dichloroethane

Tetrachloroethylene is used as a solvent, as a heat transfer medium, and in the manufacture of CFCs. Most commonly found in groundwater. It causes tumors in animals.

IX. Emerging Contaminants

- Since the 1990s, many previously little-recognized pollutants have become classified as *emerging contaminants*—contaminants that by meeting some combination of the foregoing attributes warrant particular interest and concern.
- Much of this identification and characterization of emerging contaminants impacts depends on improvements in instrumentation, sampling, and analytic techniques.
- Foremost among the emerging contaminants are ***endocrine disrupting chemicals (EDCs)***.
- EDCs (Numerous chemicals) interfere with the natural functioning of the endocrine system either by being or acting like a natural hormone, blocking or counteracting the action of a natural hormone, or increasing or reducing the production of natural hormones.

- Hundreds of chemicals, including flame retardants, metals (e.g., arsenic, cadmium), pesticides, natural plant material, detergents, combustion byproducts, and pharmaceuticals are considered to be possible EDCs.
- At present, there is no firm evidence that the environmentally measured concentrations of EDCs are causing human health effects, although it has been suggested that EDCs are a factor in increased incidences of reproductive organ cancers.