Environmental Chemistry

Pollutant is a substance that has a harmful effect on the environment and is present in higher concentrations that it is at natural levels.

Effect depends on **concentration**, **relative toxicity**, and the **length of time** that it remains in the environment before becoming harmless due to natural processes.

Primary Air Pollutant - A pollutant released directly into the environment (Carbon dioxide, Carbon monoxide, Sulfur dioxide, Nitrogen Monoxide, Hydrocarbons/VOC's).

Secondary Air Pollutant – A pollutant that is created after it undergoes chemical change in the atmosphere.

Carbon Monoxide:

CO is toxic to humans at is hinders oxygen uptake in the blood. CO binds to the hemoglobin more favorably than does Oxygen according to the equation:

$$Hb + CO \leftrightarrows COHb$$

This binding can cause dizziness at low concentrations and can be fatal at high concentrations.

It is **colorless** and **odorless** therefore can pervade the blood at high levels without being easily detected.

Source:

Anthropogenic (human-made): incomplete combustion of fossil fuels and forest fires (incomplete combustion refers to the fact that the reaction is taking place with insufficient oxygen).

$$2C_{(s)} + O_{2\,(g)} \rightarrow 2CO_{(g)}$$

Natural source is the atmospheric oxidation of methane gas (Methane is formed by the decomposition of organic matter).

$$2CH_{4(g)} + 3O_{2(g)} \rightarrow 2CO + 4H_2O_{(l)}$$

Control Methods:

Reduce CO levels by:

- Controlling the air/fuel ratio and ensure that air is in excess.
- Using catalytic converter to oxidize CO to $CO_2$.
- Use thermal exhaust reactor

Lean Burn Engines:

Equation for the complete combustion of octane:

$$2C_8H_{18(g)} + 25O_{2(g)} \rightarrow 16CO_{2(g)} + 18H_2O_{(l)}$$

Complete combustion of octane requires air/fuel ratio 14-15.

Maximum power is attained by a 12.5-air/fuel ratio (more fuel) but this produces more CO.

Lean burn engines work effectively at an air/fuel ratio of 18 (more air, less CO).

Catalytic Converters:

Hot gas exhaust emissions are mixed with the air and passed over a platinum-based catalyst of two forms:

- Oxidation catalysts: used to convert CO to $CO_2$.

$$2CO + O_2 \rightarrow 2CO_2$$

- Three-way Catalysts: oxidize CO to $CO_2$ and Hydrocarbons to Water and $CO_2$ but also reduce NO to nitrogen gas.

$$2CO + 2NO \rightarrow \ 2CO_2 + \ N_2 \quad (requires\ catalyst\ and\ moderate\ temp)$$

Thermal Converters:

Thermal exhaust reactors use the heat of the exhaust gases to make more CO react with air to form $CO_2$. Unburned VOC's are also oxidized to water and carbon dioxide.

$$2CO + O_2 \rightarrow 2CO_2$$

$$C_xH_y + \_O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

$$(this\ equation\ can\ be\ used\ to\ balance\ the\ oxidation\ of\ most\ oranic\ compounds)$$

Nitrogen Oxides:

There is no reaction between nitrogen and oxygen at room temperature due to the stability of the triple covalent bond in the nitrogen gas molecule.

Main nitrogen based pollutants are $NO_2$ and $N_2O$. Both of these pollutants react with hydrocarbons to form **photochemical smog** and **nitric acid**. The produced nitric acid contributes to acid rain.

$NO_2$ is the more toxic and causes irritation of the eyes, nose, and breathing and respiratory problems.

All dinitrogen oxides and 80 percent of nitrogen monoxide is formed naturally from the decomposition of nitrogen-containing compounds via lighting or bacterial action in soil.

$N_2 + O_2 \rightarrow 2NO\ (lightning\ or\ bacteria\ act\ as\ catalysts)$.

Anthropogenic sources of nitrogen oxides include:

-Motor vehicles
-Coal and Oil-fired power stations
-Industrial burning of fossil fuels

In motor vehicles under high temperatures (1500 centigrade), the $N_2 + O_2 \rightarrow 2NO$ occurs anyway.

The brown color of the photochemical smog is due to the $NO_2$. Nitrogen dioxide is produced from the oxidation of NO.

$2NO + O_2 \rightarrow 2NO_2$

Methods of Control

Lean Burn Engines:

The problem in producing cleaner engines is that the conditions needed to oxidize CO are the same conditions, which produce Nitrogen Oxides.

High fuel content (low air/fuel ratio) mixture produces low nitrogen oxides and high carbon oxide emissions.

Air/fuel ratio 18:1 can lower emissions of both nitrogen oxides and carbon oxides. This can be done using the similar three-way catalytic converter that is used for the oxidation of carbon monoxide:

$2CO + 2NO \rightarrow\ 2CO_2 +\ N_2$

Exhaust gas recirculation: The EGR process recirculates exhaust gases back into the engine. This lowers to the operating temperature and reduces Nitrogen oxide emissions.

The lower the operating temperature of an engine, the lower the nitrogen oxide emission.

Sulfur Oxides:

Two types: $SO_2$ and $SO_3$

Sulfur dioxide is a primary pollutant that is produced naturally by volcanoes and rotting vegetables.

When sulfur dioxide is produced by the oxidation of Hydrogen Sulfide, it is considered a secondary pollutant:

$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$

Anthropogenic Sources:

Burning sulfur-containing fossil fuels. Coal contains sulfur as an element, iron pyrite, and organic sulfides.

$$S + O_2 \rightarrow SO_2$$

Smelting plants which oxidize sulfide ores to the metal oxides:

$$Cu_2O + 2O_2 \rightarrow 2CuO + SO_2$$

From sulfuric plants.

Control Methods

Removing sulfur either before or after combustion can reduce sulfur dioxide emissions.

Pre-combustion:

Sulfur present in coal as a metal sulfide can be removed by crushing and washing with water because the high density of the metal sulfide sinks to the bottom and separates from the coal.

In crude oil, sulfur can be removed by mixing with potassium carbonate.

$$H_2S + CO_3^{2-} \leftrightarrows HS^- + HCO_3^-$$

Since the reaction is reversible the hydrogen sulfide can always be recovered.

Post-combustion:

Alkaline Scrubbing:

An Alkaline mixture is sprayed downwards into exhaust gases. The possible mixtures include Calcium Oxide (CaO) and Calcium Carbonate. Both of these react to form Calcium Sulfate.

Calcium Oxide:

$$CaO + SO_2 \rightarrow CaSO_3$$

$$CaSO_3 + O_2 \rightarrow CaSO_4$$

Calcium Carbonate:

$$CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$$

$$CaSO_3 + O_2 \rightarrow CaSO_4$$

Note that in both cases the end second reaction is the same. The assumption is that both reactions are occurring in an oxygen filled environment. The calcium sulfate can be deposited into a landfill or used to make plasterboard

Magnesium Oxide (MgO)

$$MgO + SO_2 \rightarrow MgSO_3$$

Note that with the application of heat, MgO can be regenerated:

$$MgSO_3 \rightarrow MgO + SO_2$$

Resulting Sulfur Dioxide can be used to make sulfuric acid.

Fluidized-bed Combustion:

In this method, coal is mixed with limestone on a metal plate. A strong airflow passes through the mixture. This strong airflow makes the mixture float above the plate making it behave as a fluid.

The heat produced from the combustion of coal makes calcium break up into Carbon Dioxide and Calcium Oxide:

$$CaCO_3 \rightarrow CaO + CO_2$$

In this method:

Sulfur Dioxide is formed by the combustion of Coal.

The same Sulfur Dioxide is then removed as Calcium oxide (which is formed as a result of the decomposition of Calcium Carbonate), reacts with Sulfur Dioxide to form Calcium Sulfate:

$$2CaO + 2SO_2 + O_2 \rightarrow 2CaSO_4$$

**Particulates** are solid particles of carbon and dust or liquid droplets of mist or fog which are carried in the air. Most particulates have a diameter of .001 to 10 micrometers.

Most particulates are polar and thus are attracted to water droplets to form aerosols.

Aerosols are gaseous suspensions of very small particles of a liquid.

Examples:

1.) Soot from the incomplete combustion of hydrocarbons and coal
2.) Dust from the mechanical decomposition of solid matter
3.) Sulfur from Organic Eruptions

Particulates can enter the body and cause emphysema, bronchitis, or cancer.

Particulates are usually inert solids, they are dangerous because they can act as catalysts for the production of secondary pollutants such as Sulfur dioxide and can increase the harmful effects of those gaseous pollutants.

Particulates can also absorb other pollutants and carry them into the lungs. For this reason, small particulates are more harmful than large ones because they have a larger surface area.

Sources:

Natural:
1.) Dust from mechanical decomposition of solid matter
2.) Sulfur from volcanic eruptions
3.) Pollen as well as bacterial and fungal spores.

Anthropogenic:
1.) Soot from incomplete combustion of hydrocarbons and coal in power stations.
2.) Arsenic from insecticides.

3.) Asbestos from the construction industry (release particles when buildings are demolished)
4.) Combustion of fossil fuels in furnaces.

Control Methods:

They can be controlled by the gravitational settling by rain and snow. They can be prevented from entering atmosphere by treating industrial emissions with filtration, centrifugal separation, settling tanks, scrubbing, and electrostatic precipitation.

Gravity settling tanks are used to filter out large particulates.

For a particulate contained gas X and suspended solid P, passing the particulate through a strong electric field yields two reactions:

$$X_{(g)} \rightarrow X^{+}_{(g)} + e^{-}$$

$$P_{(s)} + e^{-} \rightarrow P^{-}_{(s)}$$

The now charged particulates are attracted to collector plates and the air passing through has had 98 percent of particulate matter removed.

Wet Scrubbers: In this method water is passed through the particulate which is cleaned because the particulate is polar.

Cyclone Separators: Particulates are thrown outwards and collected there.

Volatile Organic Compounds

Extended exposure to aromatic hydrocarbons such as benzene of exposure to chloroethene can lead to cancer. Hydrocarbons can form secondary pollutants and photochemical smog.

Sources:

Natural:

1.) Methane is released by natural sources for example bacterial decomposition of organic matter in water and soil.

2.) Unsaturated hydrocarbons called terpenes are given out by plants.

Anthropogenic:

1.) Unburned petroleum products like gasoline being released from a car and other exhausts of things that process petrol.

Methods of Control: Catalytic Converter or thermal exhaust reactor.

## Acid Deposition

All rain water is naturally acidic because of dissolved carbon dioxide that produces carbonic acid.

$$CO_2 + H_2O \leftrightarrows H_2CO_3$$

The minimum pH of acid rain is attained with carbonic acid. Other forms of acid rain are sulfuric and nitric, which form pH's < 5.6.

Acid Deposition is the process by which acidic particles, gases, and precipitation leave the atmosphere.

Wet Deposition: Acid rain, fog, snow.
Dry Deposition: Acid gases and particles.

Acid rain is secondary pollutant:

$$H_2O + SO_2 \rightarrow H_2SO_3$$

$$2SO_2 + O_2 \rightarrow 2SO_3$$

$$H_2O + SO_3 \rightarrow H_2SO_4$$

The oxidation of sulfur dioxide is catalyzed by sunlight or aerosols.

In an internal combustion engine such as that of a car, the following reaction takes places:

$$N_2 + O_2 \rightarrow 2NO$$

Then, the produce nitrogen monoxide is oxidized to form nitrogen dioxide.

$$2NO + O_2 \rightarrow 2NO_2$$

When the produced nitrogen dioxide dissolves in water, either a mixture of nitric and nitrous acid is formed:

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

Alternatively, nitrogen dioxide reacts to form nitric acid rain:

$$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$$

## Effects of Acid Deposition:

In both dry and wet deposition of sulfur oxides, limestone (calcium carbonate) reacts with the sulfur oxide to produce Calcium sulfate:

$$2CaCO_3 + 2SO_2 + O_2 \rightarrow 2CaSO_4 + 2CO_2 \ (dry\ deposition)$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2 \ (wet\ deposition)$$

Calcium sulfate is more soluble so it washes out of the limestone. Calcium sulfate also has a greater molar volume so it causes stress in the structure.

Sulfur dioxide in dry deposition increases the rate of corrosion of metals:

$$Fe + SO_2 + O_2 \rightarrow FeSO_4\ (wet\ deposition)$$

Acid rain also corrodes metals via a simple displacement reaction:

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2\ (wet\ deposition)$$

The formation of the Fe(II) ion increase ionic conductivity as well as the rate of electrochemical corrosion reactions such as rusting.

In Aluminum (III) Oxide, the protective oxide layer is removed from aluminum yielding harmful Al(III) ions:

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O\ (wet\ deposition)$$

Effects on Plant Life:

-Acid rain (wet deposition) washes out the important nutrients $K^+, Mg^{2+}, and\ Ca^{2+}$ from the soil and increases $Al^{3+}$ concentrations.

-A reduction of $Mg^{2+}$ causes a reduction in chlorophyll levels of plants which hinders photosynthesis.

-$Al^{3+}$ ions are released from rocks under acidic conditions and clog roots preventing trees from taking up other vital nutrients.

-Sulfur dioxide in dry deposition blocks the stomata of plant leaves and prevents photosynthesis.

Effects on Water:

-Rivers are dead at a pH of 4.0 because at these acidic conditions Al(III) ions are released from rocks under the lake according to this equation:

$$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$$

- Nitric acid in acid rain causes eutrophication (excess nutrients). Nitrates cause excess plant growth causing plants to need more oxygen than normal and available in the water supply. This leads to plant death.

Effects on Humans:

- Breathing air containing acid gases irritates the respiratory tract from mucous membranes in the nose and throat to the lung tissue (leads to emphysema, asthma, bronchitis, and irritation of the eyes).

-Acid rain leads to a greater risk of poisonous Pb(II) and Cu(II) ions as well as Al(III) ions being released (Presence of aluminum(III) is linked to Alzheimer's and senile dementia).

Control Methods:

- Reduce sulfur and nitrogen oxide emissions.
- Switch to cleaner alternative energies.
- Use CaO (lime) or calcium hydroxide ($Ca(OH)_2$) to neutralize acid rain in lakes and rivers:

$$CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O$$

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$$

Greenhouse Effect:

The temperature of the Earth depends on the balance between incoming solar radiation (visible and ultraviolet region) and the energy leaving the Earth.

-Some of the solar radiation is reflected back into space.

-Some is absorbed by gases in the atmosphere.

Most solar radiation passes through the atmosphere and warms the Earth's surface.

- The Earth's warm surface will then radiate the energy in the form of **longer wavelength infrared radiation** which is absorbed by **carbon dioxide** and **water vapor** in the atmosphere.

When a given amount of radiation has the **same frequency** as that of the vibrations of a molecules covalent bond, the molecule will absorb the radiation and **increase its bond vibration frequency.**

This whole process warms the air and makes it return radiation to the Earths surface (again some of the air's radiation is sent back to space while some is returned to the earth).

This whole process of clustered radiation is called the greenhouse effect because the suns energy is trapped in an atmosphere that nevertheless continues to accept energy.

Greenhouse Gases and Effects:

Greenhouse effect occurs naturally.

Water is the main greenhouse gas due to its abundance but is usually not considered because it is formed from natural processes.

Carbon dioxide is a greenhouse gas whose concentration has been increasing since 1957. It is estimated that carbon dioxide contributes to 50 percent of global warming.

The ability of a gas to absorb infrared radiation depends on the change in dipole moment that occurs as the molecule vibrates.

Symmetrical non-polar molecules such as nitrogen and oxygen are not greenhouse gases.

Greenhouse factor: a gases ability to absorb infrared relative to carbon dioxide.

- One molecule of methane has the absorption capacity of 30 molecules of carbon dioxide.
-Chlorofluorocarbons have very high greenhouse factors but are present in low amounts.

**List of Greenhouse Gases and properties**:

Water:
Main Source: evaporation of oceans and lakes.
Greenhouse factor: 0.1
Relative Abundance: 0.10 percent
Contribution to increase Global warming: -

Carbon Dioxide:
Main Source: Combustion of fossil fuels and biomass.
Greenhouse factor: 1
Relative Abundance: 0.036 percent
Contribution to Global Warming: 50 percent

Methane:
Main Source: anaerobic decay of organic matter, intensive farming
Greenhouse factor: 30
Relative Abundance: 0.0017 percent.
Contribution to Global warming: 18 percent

Chlorofluorocarbons:
Main Source: refrigerants, pollutants, foaming agents, solvents
Greenhouse Factor: 20000
Relative Abundance: 0.00001
Contribution to Global Warming: 14 percent

Ozone:
Main Source: Secondary Pollutants and photochemical smog.
Greenhouse Factor: 2000
Relative Abundance: .000004
Contribution to Global Warming: 12

Dinitrogen Oxide:
Main Source: Artificial Fertilizer, combustion of biomass
Greenhouse Factor: 160
Relative Abundance: .0003
Contribution to Global Warming: 6 percent

Sulfur Hexaflouride:
Main Source: Used as an insulator in electrical industry
Greenhouse Factor: 22000
Relative Abundance: very low
Contribution to Global Warming: 0.05

Conclusions:
-Sulfur Hexafluoride has the largest greenhouse factor but lowest abundance and contribution.
-Carbon dioxide has the largest contribution to global warming.
-Water has the lowest greenhouse factor and highest relative abundance.

Effects for rise in Earth's Temperature (Predicted 2 degrees Celsius within 50 years):

- Changes in agriculture and biodistribution.

- Rising sea levels owing to the thermal expansion and the melting of polar ice caps and glaciers.

Particulates can lower the temperature of the Earth's surface by scattering light and preventing more radiation from reaching the surface.

**Ozone Depletion**

The earth has a layer of gas composed of oxygen and ozone that protects the surface from ultraviolet radiation from the sun.

Ozone has resonance and its oxygen-oxygen bonds are weaker than that of oxygen.

The part of the atmosphere at which ultraviolet radiation is absorbed by photochemical reactions is called the **stratosphere**. The stratosphere is 12 km above the earth's surface.

In the stratosphere, the UV light breaks the oxygen-oxygen covalent bond leading to the production of **two oxygen atoms that have unpaired electrons**. These atomic oxygen species are very reactive and are called free radicals.

$O_2 \rightarrow O^{\cdot} + O^{\cdot}$ (high energy UV light is catalyst)

Each gaseous oxygen free radical will react with another oxygen molecule to form ozone:

$O^{\cdot} + O_2 \rightarrow O_3$

Because this reaction is exothermic, the stratosphere becomes warm due to the increase in energy.

Next, UV light breaks apart the formed ozone molecule into another free radical and an oxygen molecule:

$O_3 \rightarrow O^{\cdot} + O_2$

Because the covalent bonds in ozone are weaker, a lower magnitude of UV light is needed to break apart the ozone molecule.

Finally the remaining free radical reacts with another ozone molecule to form two oxygen molecules:

$O^{\cdot} + O_3 \rightarrow 2O_2$

(This is another exothermic reaction which maintains the high temperature of the stratosphere. This is also the slowest of all reaction is the Chapman Cycle)

The level of ozone in the atmosphere (<10ppm) stays constant if the rate of formation of ozone = rate of removal (this is called the steady state).

Some pollutants namely chlorofluorocarbons and nitrogen oxides serve as catalyst for the decomposition of ozone.

Nitrogen Oxide:

$$NO^{\cdot} + O_3 \rightarrow NO_2^{\cdot} + O_2$$

$$NO_2^{\cdot} + O \rightarrow NO^{\cdot} + O_2$$

In this series of equations Nitrogen Monoxide serves as a catalyst because it is regenerated in the nitrogen dioxide free radical's reaction with elemental oxygen.

Chlorofluorocarbons have been used in aerosol's, refrigerants, solvents, foaming agents and plastics due to their low flammability and low toxicity.

CFC's remain inert in the troposphere but undergo photochemical decomposition in the stratosphere when exposed to high energy UV radiation.

These photochemical reactions produce highly reactive chlorine atoms such as in the case of Freon:

$$CCl_2F_2 \rightarrow CClF_2^{\cdot} + Cl^{\cdot}$$

C-Cl bonds break because they are weaker than the C-F bonds.

The reactive chlorine atoms then catalyze the decomposition of ozone in a similar way:

$$Cl^{\cdot} + O_3 \rightarrow ClO^{\cdot} + O_2$$

$$ClO^{\cdot} + O \rightarrow O_2 + Cl^{\cdot}$$

The net effect of this reaction is that an ozone molecule reacts with one oxygen free radical and produces two oxygen molecules:

$$O_3 + O^{\cdot} \rightarrow 2O_2$$

Because the chlorine free radicals are not used up, a single atom can lead to the decomposition of a large amount of the ozone layer.

Environmental Impact: Ozone layer protects surface of the Earth from high-energy UV rays that can break the bonds of biologically important molecules like DNA.

UV Radiation can cause:
- Skin Cancer
- Cataracts/Blindness
- Damage to plant cells
- Can affect all parts of marine ecosystem including zooplankton and phytoplankton, which reduce carbon dioxide levels and produce oxygen via photosynthesis.

Alternative to CFC's:

CFC's are expected to remain in the atmosphere for the next century because of their low reactivity.

The main problem with CFC's is the weak C-Cl bond. Therefore, possible replacement for CFC's would have to be unreactive but lack this bond.

-$C_3H_8$ and 2-methylpropane can be used as refrigerant coolants. C-H bond is stronger but both are flammable.

-Fluorocarbons are not flammable and their strong C-F bond makes them stable to UV radiation so that they cannot catalyze ozone decomposition.

-Hydrochlorofluorocarbons (HCFC's) contain hydrogen, chlorine, and fluorine. Although they do contain the C-Cl bond, most molecules are destroyed in the lower atmosphere before reaching the stratosphere. They are approximately 20 times less destructive than CFC's.

-Hydrofluorocarbons are considered the best alternative.

| Species | Flammable | Toxicity |
|---|---|---|
| $CCl_2F_2$ | no | moderate |
| $CH_3CH(CH_3)CH_3$ | yes | high |
| $CF_4$ | no | no effects known |
| $CHClF_2$ | no | moderate |
| $CF_3CH_2F$ | no | low |

Dissolved Oxygen in Water

The dissolved oxygen content of water is one of the most important indicators of its quality. Aquatic plants and animals need it for respiration. Microorganisms consume oxygen when they decompose organic matter.

Lowest concentration of oxygen needed is 0.003 g $dm^{-3}$.
Maximum solubility is 0.009 g $dm^{-3}$.

Biological Oxygen Demand – the quantity of water needed to oxidize organic matter in a sample of water over a five day period at a specified temperature. The higher the BOD value the lower the quality of water.

Another definition is… the amount of water needed by bacteria to decompose the organic matter aerobically in a fixed volume of water over a set period of time.

Oxygen is needed by bacteria to metabolize their food (organic matter). They perform such operation as…

The oxidation of carbon into carbon dioxide.
The oxidation of organic hydrogen to water.
The oxidation of nitrogen to soluble nitrates.

Fish and other organisms cannot survive when the BOD is greater than the oxygen content. Fast flowing stream and rivers are less polluted because the moving water allows it to be re-oxygenated by the atmosphere. Static bodies do not have this opportunity.

The BOD is measured by leaving a 0.009 g $dm^{-3}$ sample of water at 25 degrees Celsius for 5 days. During this time, the bacteria aerobically decompose organic matter. The remaining oxygen is measured by redox titration called the Winkler Method.

**Aerobic and Anaerobic Decomposition**

When there is an excess of oxygen demanding waste, organic matter is reduced rather than oxidized.

| element | aerobic decay product | anaerobic decay product |
|---|---|---|
| carbon | $CO_2$ | $CH_4$ |
| hydrogen | $H_2O$ | $CH_4$,$NH_3$, $H_2S$,$H_2O$ |
| oxygen | $H_2O$ | $H_2O$ |
| nitrogen | $NO_3^-$ | $NH_3$ and amines |
| sulfur | $SO_4^{2-}$ | $H_2S$ |
| phosphorus | $PO_4^{3-}$ | $PH_3$ |

The addition of extra nutrients (eutrophication) also increases the BOD of water because the nutrients promote plant growth.

-Nitrate ion promotes plant growth through protein synthesis.
-Nitrogen is needed for amino acids and proteins.
-Phosphate ion is used for storage and energy transfer.

When the algae die due to insufficient oxygen the amount of nutrients further increase and lead to a further fall in oxygen concentration which makes aerobic decomposition futile. Anaerobic bacteria take over and produce gases such as ammonia and hydrogen sulfide creating unpleasant smells and poisons in the water. This will cause deaths until there is no life remaining.

Main contributors to eutrophication are artificial fertilizers containing nitrate and phosphate ions and detergents that contain phosphates. The nitrate ions can also enter the water body via acid rain.

Phosphates can be removed by reaction with Al(III) or Ca(II) to form insoluble compounds:

$$Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2$$

$$Al^{3+} + PO_4^{3-} \rightarrow AlPO_4$$

Because all nitrates are soluble they are more difficult to remove.

**Thermal Pollution**

-The higher the temperature of the water, the lower its oxygen concentration.
-Metabolic rate of organisms increases with temperature and this places additional demand for oxygen in the water.

Thermal pollution can be controlled by trickling water through a porous material and blowing air in the opposite direction so that the heat from the water is brought down and sent to the air where its effects are not as damaging.

**Primary Pollutants in Waster Water and their Sources**:

Excessive nitrate levels can interact with hemoglobin and effect oxygen transport in babies.

Low acidity of a baby's stomach allows bacteria that reduce the nitrate (V) ion ($NO_3^-$) to the nitrate (III) ion ($NO_2^-$). The nitrate (III) ion decrease the oxygen carrying capacity of hemoglobin by oxidizing the Fe(II) to Fe(III) ion which forms methaemoglobin, a substance that cannot transport oxygen.

Nitrates are also a possible cause of stomach cancer in adults because they can be converted to nitrites, which can then combine with amine to form nitrosoamines. Nitrosoamines are carcinogenic.

Heavy Metals

Many heavy metal ions such as those of mercury and cadmium can interfere with other necessary ions such as Zn(II), Mg(II) and Ca(II).

**Mercury**:

Main Sources: Paints, Batteries, and Agriculture

Health Hazard: Serious damage to nerves and brain, depression, irritability, blindness, insanity, Minatama disease.

Environmental Hazard: reproductive system failure in fish, kills and inhibits fish. Biological magnification in food chain.

**Lead**:

Main Sources: Lead Paints, pipes, lead glazes on glasses and pottery, tetraethyl lead in petrol.

Health Hazard: Burning mouth pains, constipation/diarrhea, kidney failure, brain damage, coma and death from liver/heart failure.

Environmental Hazard: toxic to plants and animals. Biological magnification in food chain.

**Cadmium**:

Main sources: metal plating, rechargeable batteries, pigments, by-product of Zinc refining.

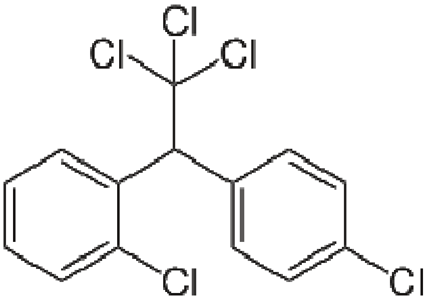
Health Hazard: Cd is in the same group as zinc and can therefore replace it in reaction in enzyme system making them ineffective. Itai-Itai disease makes bones brittle. Kidney and lung cancer in humans.

Environmental Hazard: toxic to fish and produces birth defects in mice.

## Pesticides:

Insecticides: Kill insects
Fungicides: Kill Fungi
Herbicides: Kill Weeds

DDT is one example of a pesticide. It is dichloro-diphenyl-trichloroethane.



Know how to draw this. Remember phenyl rings can be hexagons with rings in the middle.

DDT is very stable and fat soluble. These two properties allow phenyl to build up over time in animals at the top of the food chain. This accumulation mechanism is called biological magnification and occurs with the introduction of lead and mercury as well.

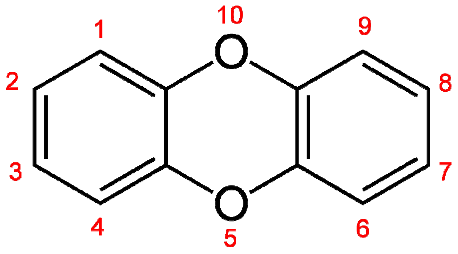
Keep in mind that DDT is usually released at low concentrations (which are harmless) but eventually build up as described above.

### Dioxins

-Dioxins are compounds that contain two benzene rings connected by oxygen atoms.

-Each benzene ring can have up to four chlorines attached as well.

-Dioxins are10,000 times more poisonous than cyanide ions.



Sources:

-Dioxins are added when organochloro compounds are incinerated.

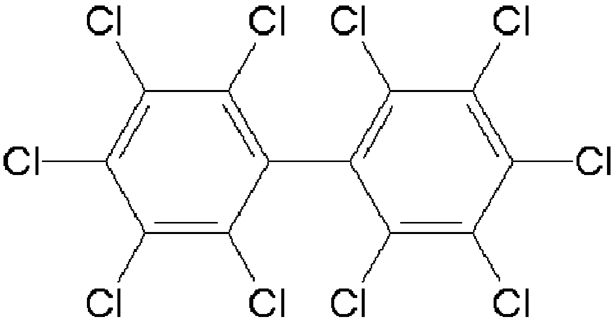
- There are also trace amounts of dioxins in herbicides.

Effects:

- Dioxins thrive in fat and liver cells.
- Symptoms:
  - Damage to liver and heart
  - Loss of memory
  - Concentration problems
  - Depression
- Chloracne is a skin disease that occurs when the body attempts to remove dioxins through the skin.
- Dioxin’s causes malfunction in fetuses.

## Polychlorinated biphenyls

- Have **high electrical resistance** and so are used in electrical transformers and capacitors.



Basic structure is two connected phenyl rings with chlorines bonded to each. **Note that the number of chlorines does not have to be the same.**

- Thrive in fatty tissue much like DDT and Dioxin’s.

Effects:

- Reduce reproductive efficiency.
- Impair learning in children.
- Carcinogenic

## Waste-water Treatment

Purpose:

- Remove hazardous materials from water.
- Kill microorganisms prior to discharge.
- Reduce BOD.

Methods:

- Untreated water released into the environment where it is broken down by microorganisms. **Septic tanks** or **cess pits** are used.

-Waste water is broken down by bacteria and passed into the ground.

**Primary Methods**

-Waste water is first based through screens and grids to remove large insoluble solud objects such as grease.

-The water is then allowed to settle in a sedimentation tank.

-Sludge forms and is removed from the bottom of the tank (the process of **flocculation**, or the addition of chemical catalysts to allow suspended particles to form large clumps is implemented to speed up this process)

The large clumps (flocs) are produced by the addition of **aluminum sulfate** and **calcium hydroxide**:

$$Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_3 + 3CaSO_4$$

Typical primary treatment reduces 30-40 percent of most waste.

**Secondary Methods**

-Large blowers used to bubble air enriched with oxygen through waste water which is mixed with bacteria inhabited sludge.

-Additional oxygen allows microorganisms to oxidize organic matter.

-The water, now containing suspended decomposed organic matter is passed into a sedimentation tank where large clumps of it are collected and disposed of.

Steps one and two comprise the <u>activated sludge method</u>.

Secondary methods remove 90 percent of oxygen-demanding wastes.

**Tertiary Methods**

-Purpose is to remove remaining organic and inorganic substances such as nitrates, phosphates, and heavy metal ions.

- Heavy metals including cadmium can be removed by precipitation wherein hydrogen sulfide is bubbled through the sample. (sulfide salts are preferred because they are not very soluble in water.)

-In the case of cadmium, hydrogen sulfide is bubbled through cadmium containing water sample:

$$Cd^{2+} + H_2S \rightarrow CdS + 2H^+$$

Insoluble sulfide salts are then filtered out of the solution.

-Phosphate ions can be removed by the addition of Ca(II) and Al(III) ions:

$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_2(PO_4)_3$

$Al^{3+} + PO_4^{3-} \rightarrow AlPO_4$

### Ion Exchange

Soluble nitrate ions can be exchanged for hydroxide ions via resins and zeolites:

$Y - OH + NO_3^- \rightarrow Y - NO_3^- + OH^-$

$X - H^+ + M^+ \rightarrow X - M^+ + H^+$

So both positive ions and negative ions can be replaced by the addition of resins and zeolites. The remaining hydrogen and hydroxide ions then combine to form water

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

The ion exchange resin can also be used to remove salt from sea water.

The method is very expensive because resins and zeolites have to be regenerated many times for large volumes of water.

## Biological Methods

Anaerobic bacteria can turn nitrates back into nitrogen gas.
Algae can remove nitrates by treating them as nutrients.

## Activated Carbon Bed Method

Activated carbon is comprised of tiny carbon granules activated by high temperatures.
Granules are able to absorb organic chemicals readily.
-Activated carbon is often used on toxic organic materials and charcoal filters and therefore can purify tap water.
Carbon can be reactivated after organic matter is oxidized to carbon dioxide and water by heating to high temperature again.

## Reverse Osmosis

Osmosis- The process by which water passes from dilute to concentrated solution through a semi-permeable membrane.

The semi-permeable membrane allows the solvent but not solute to pass through.

If 70 ATM's are applied to the concentrated solution, the water solvent will pass through the membrane leaving solutes behind.

Membrane must withstand pressure.

## Chlorine and Ozone Treatment

Number of deaths caused by bacteria is reduced with treatment by ozone and chlorine.

Advantages of Chlorine:
-Chlorine prevents spread of waterborne infections such as typhoid fever.
-Chlorine remains in water longer than ozone and provides residual protection against pathogenic bacteria.
-Cheaper to produce.
-Can be easily liquefied and shipped.

Disadvantages of Chlorine:
-Ineffective against viruses.
-Can chlorinate dissolved organic solvents to produce carcinogenic compounds.
-Leaves no chemical taste.

Advantages of Ozone:
-Ozone kills viruses and bacteria.
-Leaves no chemical taste.
-Oxidized products are less toxic.

Disadvantages of Ozone:
-No residual protection against microorganisms.
-More expensive.
-Must be produced on site because highly reactive.
-Shorter retention time.

Both chlorine and ozone function as strong oxidizing agents.

## Soil

Soil is formed by the biological, chemical and physical weathering of rock.
- Soil is a mixture of inorganic and organic matter including air and water.

Layers of soil are called horizons.
-The upper most layer of soil contains the most living material from the decomposition of dead organisms.
-The subsoil levels contain inorganic material from the parent rock.

Order of soil component in decreasing size:

Gravel (2.000-60.000 mm), Sand (0.060 -2.000 mm), Silt (0.006-0.060 mm), Clay (0.002-0.006mm)

Soil provides plants with nitrogen, phosphorus, potassium, magnesium, and sulfur.
Carbon, hydrogen, and oxygen come from the air.

The dark color of the soil is due to **humus** (decomposed organic matter).

## Soil Degradation:

Soil degradation occurs when human activity hinders the soils' ability to support life.

Causes:

- -Intensive farming
- -Desertification
- -Erosion
- -Pollution

Acidification, salinity, nutrient depletion, and chemical contamination are all forms of soil degradation.

## Salinization

Salinization occurs when soils are irrigated continually. (Irrigation waters contain dissolved salts).

Soils remain after irrigation water evaporates and the salts begin to accumulate in the top level of the soil (whitish crust on soil surface).

- Plants die in soil that is too salty
  - When salt levels become toxic
  - Dehydration (roots cannot take in water if salt concentration is too high).

Control Method:

Flushing the soil with water (this can cause salinization in nearby lakes and rivers.

## Nutrient Depletion:

Nutrients that plants consume are returned after the plant dies and decomposes.

Farmers who harvest plants remove nutrients that would have otherwise returned to the soil.

Methods of Nutrient Replacement:

Adding legumes in crop rotation
Adding manure or compost
Plowing land to aerate the soil

Legumes are host to nitrogen-fixing bacteria which use the enzyme nitrogenase to convert atmospheric nitrogen to ammonia.

Intensive farming rapidly depletes nutrients and excessive use of artificial fertilizer is harmful for the environment.

## Soil Pollution

Sources: Mining, excessive use of agricultural chemicals, improper disposal of toxic waste.

Polluted soil contaminates plants which contaminate animals.

Herbicides, insecticides, and fungicides disrupt food chain (biological magnification).

## Soil Organic Matter

SOM – organic constituents of the soil (plant and animal tissues and their partial decomposition products.

SOM's are only about 5 percent of the soil mass.

SOM's are a source of food and is made up of high molecular mass organic materials such as polysaccharides and proteins, sugars and amino acids, etc.

Humus- the residue left after the decomposition of organic matter by bacteria.

It takes 400 years to make 1 cm of soil.

SOM's loosen the soil which increases its pore space:

- Density of the soil is reduced.
- Soil particles stick together forming aggregates or crumbs.
- More pores allow more intakes of oxygen, water, and nutrients.
- Increase in pore space makes plant root development easier.

Lone pairs of electrons on nitrogen atoms and the oxygen atoms on carboxyl and hydroxyl groups allow humus to bind to positive ions. These humic substance can then serve as positive ion exchangers:

$$RCOOH(humus) + K^+ \leftrightarrows RCOOK(humus) + H^+$$

The reaction is reversible and depends on the relative concentrations of the ions.

This cation exchange capacity (CEC) allows humus to provide certain nutrients as they are needed. If potassium ions were taken out of solution by plants, the equilibrium while shift to the left and more potassium ions will be release to compensate for that loss.

-Micronutrients are prevented from being washed away by acid rain or irrigation.

-The cation exchange capacity also allows humus to bind to toxic heavy metals and remove them from the ecosystem.

The equilibrium below shows us that because humus has weak organic acids, it can act as a natural buffer.

(A buffer resists changes in pH when small amount of acid or alkali's are added).

$$RCOOH(humus) + H_2O \leftrightarrows RCOO^-(humus) + H_3O^+$$

When the pH is low, the hydronium ion concentration is high, the equilibrium shifts to the left, resisting pH change (and vice versa)

$$RCOOH(humus) + OH^- \leftrightharpoons RCOO^-(humus) + H_2O$$

Humus provides nitrogen, phosphorus, and sulfur.

The dark color absorbs heat and warms the soil.

Farming practices determine the soil organic matter content. **Tillage** reduces SOM's because as oxygen is stirred in aerobic bacteria oxidize and consume organic matter.

Crops that return little organic residue to the soil lead to lower levels of organic material.

Composts, manure, and sewage sludge lead to high levels of SOM's. Manure and sludge break down quickly and release nutrients for plant growth.

Organic Soil Pollutants

Humus has a strong affinity for organic compounds. OC's have low solubility in water and because they are absorbed by humus they tend to stay in the top level of the soil.

Examples of Soil Pollutants:

- Petroleum Hydrocarbons
- Agrichemicals
- VOC's
- Polyaromatic Hydrocarbons
- Polychlorinated Biphenyls.

Waste:

Open Dumping: Inexpensive and Convenient. Causes air and ground pollution. Makes rodents and insects a health hazard.

Landfill

Purpose: Isolate waster from ground water as well as air.

Material must be controlled to prevent toxins from reaching ground water.

Leaching is prevented by lining landfills with synthetic materials or impermeable clay.

Organic material in landfills is decomposed by anaerobic bacteria to produce **methane**. (other products include hydrogen sulfide and organic acids).

Closed landfills must be monitored to ensure that organic acids will not leach out and transport heavy metals to groundwater.

- Non-biodegradable substance cannot be broken down by bacteria. Some plastic bags can be combined with natural polymers such as **starch**, **cellulose**, and **proteins**, to become biodegradable.
  - The bacteria will decompose the polymer and break the bag into smaller pieces, increasing the surface area.

## Incineration

Incineration produces waste of a more uniform composition and reduces bulk because organic matter is converted to gas.

Heat produced maintains the necessary temperature 800-1000 centigrade.

Carbon dioxide produced is a greenhouse gas.

Incomplete combustion of plastics leads to poisonous carbon monoxide.

Combustion of PVC results in hydrogen chloride which causes acid rain.

Temperature control reduces production of dioxins.

## Recycling

Reduces:

- use of raw materials
- energy costs
- level of pollutants
- need of land for waste disposal

### Metals:

Aluminum recycling is viable because of its resistance to corrosion and high cost of extraction. Recycled metals are used as alloys which reduces need for complete purification.

### Glass:

Glass is fragile and can be broken into many pieces.

Different color glasses have different chemical compositions so they must be separated.

Glass is then crushed and melted.

- Can reduce energy costs
- Can reduce need for sandstone and limestone.
- Is not degraded in recycling process so can be reused many times.

### Plastics

Purpose: to preserve crude oil.

Plastics are heated up and split in the absence of air into their monomers. This is called **pyrolysis**.

Monomers are then separated by **fractional distillation**. They are then used as chemical feedstock by industries to produce other plastics.

Thermoplastics can be melted down and remolded.

The cost of recycling must be less than that needed to produce new materials.

The mixture of plastics is often weaker than individual plastics and therefore has a limited range of uses.

Paper:

Paper does not decompose in landfill sites.

- Paper must first have the ink additives removed.
- It is then added to water to form a slurry.
- **Repulping** process: cellulose fibers are separated mechanically.
- If white paper is needed, it is bleached using peroxides.
- Recycled paper has reduced strength because cellulose fibers are weakened during the repulping process.

Nuclear Waste:

**Low Level Waste**: Radioisotopes use in research laboratories and patient treatment in hospitals.
Have low levels of radioactivity and short half-lives.
High volumes.
Sources: hospitals: clothing, paper towels, fuel containers.

**High Level Waste**: Spent fuel rods from nuclear power stations.
High levels of radioactivity and long half-lives.
Low Volumes.
Sources: nuclear industry, spent fuel rods, military.

**Half-life**: The time taken for radioactivity to fall down to half its initial value.

Disposal Methods:

<u>Low level wastes</u>:

Decay process produces energy therefore low level wastes are stored in cooling ponds until reactivity reaches safe levels.

Water is then passed through ion exchange resin that removes isotopes responsible for activity. Other disposal method is keeping substances locked in steel barrels in concrete vaults.

<u>High level wastes</u>:

Products from nuclear industry maintain reactivity for long periods of time. There is no way to speed the decay process.

Disposal is a problem because products of decay form other **daughter products** that can produce other nuclear reactions. High level wastes are stored in deep pools containing a **neutron absorber**. Fuel rods are then cased in glass or ceramic and stored in geologically stable and remote areas (granite rock caverns) to prevent leaching to water.