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For BS Chemistry (4-Years)

An introduction to
Environmental Chemistry

By

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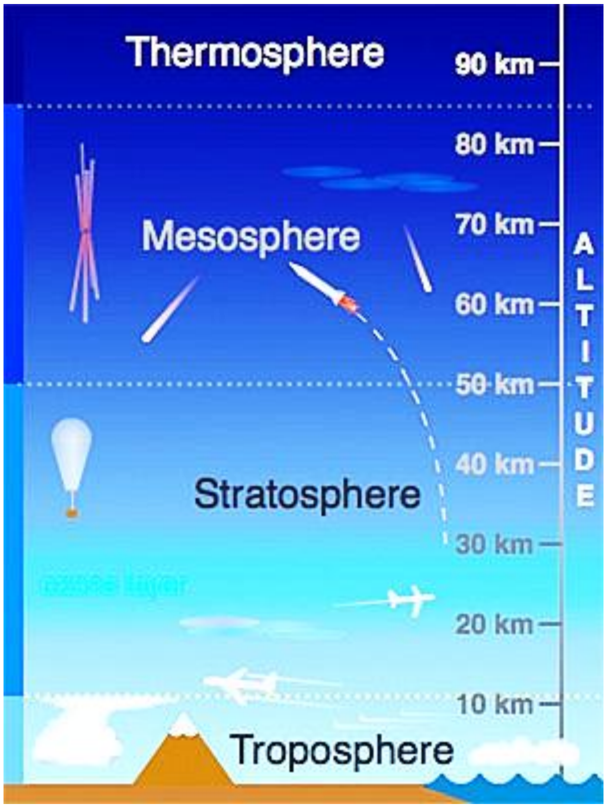
Contents

Structure & Composition of Atmosphere



Without our atmosphere, there would be no life on earth. Two gases make up the bulk of the earth's atmosphere: nitrogen (78%), and oxygen (21%). Argon, carbon dioxide and various trace gases make up the remainder.

Scientists divided the atmosphere into four layers according to temperature: troposphere, stratosphere, mesosphere, and thermosphere. The temperature drops as we go up through the troposphere, but it rises as we move through the next layer, the stratosphere. The farther away from earth, the thinner the atmosphere gets.

TROPOSPHERE

This is the layer of the atmosphere closest to the Earth's surface, extending up to about 10-15 km above the Earth's surface. It contains 75% of the atmosphere's mass. The troposphere is wider at the equator than at the poles. Temperature and pressure drops as you go higher up the troposphere.

The Tropopause: At the very top of the troposphere is the tropopause where the temperature reaches a (stable) minimum. Some scientists call the tropopause a "thermal layer" or "cold trap" because this is a point where rising water vapour cannot go higher because it changes into ice and is trapped. If there is no cold trap, Earth would loose all its water!

Most of what we call weather occurs in the troposphere. The uneven heating of the regions of the troposphere by the Sun causes convection currents and winds. Warm air from Earth's surface rises and cold air above it rushes in to replace it. When warm air reaches the tropopause, it cannot go higher as the air above it (in the stratosphere) is warmer and lighter ... preventing much air convection beyond the tropopause. The tropopause acts like an invisible barrier and is the reason why most clouds form and weather phenomena occur within the troposphere.

STRATOSPHERE

This layer lies directly above the troposphere and is about 35 km deep. It extends from about 15 to 50 km above the Earth's surface. The stratosphere is warmer at the top than the bottom. The lower portion has a nearly constant temperature with height but in the upper portion the temperature increases with altitude because of absorption of sunlight by ozone. This temperature increase with altitude is the opposite of the situation in the troposphere.

The Ozone Layer: The stratosphere contains a thin layer of ozone molecules (with three oxygen atoms) which forms a protective layer shielding life on Earth from the Sun’s harmful ultraviolet radiation. But this ozone layer is being depleted, and is getting thinner over Europe, Asia, North American and Antarctica. "Holes" are appearing in the ozone layer.

MESOSPHERE

Directly above the stratosphere, extending from 50 to 80 km above the Earth's surface, the mesosphere is a cold layer where the temperature generally decreases with increasing altitude. Here in the mesosphere, the atmosphere is very rarefied nevertheless thick enough to slow down meteors hurtling into the atmosphere, where they burn up, leaving fiery trails in the night sky.

THERMOSPHERE

The thermosphere extends from 80 km above the Earth's surface to outer space. The temperature is hot and may be as high as thousands of degrees as the few molecules that are present in the thermosphere receive extraordinary large amounts of energy from the Sun. However, the thermosphere would actually feel very cold to us because of the probability that these few molecules will hit our skin and transfer enough energy to cause appreciable heat is extremely low.

The thermosphere corresponds to the heterosphere, a zone where there is no uniform distribution of gases. In other words, the gases are not well-mixed; instead they are stratified that is layered, in accordance to their molecular masses. In contrast, the gases in the homosphere (consisting of the troposphere, stratosphere and mesosphere) are uniformly distributed.

The early Greeks considered "air" to be one of four elementary substances; along with earth, fire, and water, air was viewed as a fundamental component of the universe. By the early 1800s, however, scientists such as John Dalton recognized that the atmosphere was in fact composed of several chemically distinct gases, which he was able to separate and determine the relative amounts of within the lower atmosphere. He was easily able to discern the major components of the atmosphere: nitrogen, oxygen, and a small amount of something incombustible, later shown to be argon.

The development of the spectrometer in the 1920s allowed scientists to find gases that existed in much smaller concentrations in the atmosphere, such as ozone and carbon dioxide. The concentrations of these gases, while small, varied widely from place to place. In fact, atmospheric gases are often divided up into the major, constant components and the highly variable components, as shown in Table 1 and Table 2.

Nitrogen (N_2)	78.08%
Oxygen (O_2)	20.95%
Argon (Ar)	0.93%
Neon, Helium, Krypton	0.0001%

Table : Constant Components. Proportions remain the same over time and location.

Carbon dioxide (CO_2)	0.038%
Water vapor (H_2O)	0-4%
Methane (CH_4)	*trace*
Sulfur dioxide (SO_2)	*trace*
Ozone (O_3)	*trace*
Nitrogen oxides (NO, NO_2, N_20)	*trace*

Although both nitrogen and oxygen are essential to human life on the planet, they have little effect on weather and other atmospheric processes. The variable components, which make up far less than 1 percent of the atmosphere, have a much greater influence on both short-term weather and long-term climate. For example, variations in water vapor in the atmosphere are familiar to us as relative humidity. Water vapor, CO_2, CH_4, N_2O, and SO_2 all have an important property: They absorb heat emitted by Earth and thus warm the atmosphere, creating what we call the "greenhouse effect." Without these so-called greenhouse gases, the Earth's surface would be about 30 degrees Celsius cooler – too cold for life to exist as we know it.

Though the greenhouse effect is sometimes portrayed as a bad thing, trace amounts of gases like CO_2 warm our planet's atmosphere enough to sustain life. Global warming, on the other hand, is a separate process that can be caused by increased amounts of greenhouse gases in the atmosphere.

In addition to gases, the atmosphere also contains particulate matter such as dust, volcanic ash, rain, and snow. These are, of course, highly variable and are generally less persistent than gas concentrations, but they can sometimes remain in the atmosphere for relatively long periods of time. Volcanic ash from the 1991 eruption of Mt. Pinatubo in the Philippines, for example, darkened skies around the globe for over a year.

Though the major components of the atmosphere vary little today, they have changed dramatically over Earth's history, about 4.6 billion years. The early atmosphere was hardly the life-sustaining blanket of air that it is today; most geologists believe that the main constituents then were nitrogen gas and carbon dioxide, but no free oxygen.

In fact, there is no evidence for free oxygen in the atmosphere until about 2 billion years ago, when photosynthesizing bacteria evolved and began taking in atmospheric carbon dioxide and releasing oxygen. The amount of oxygen in the atmosphere has risen steadily from 0 percent 2 billion years ago to about 21.

Measuring the atmosphere

We now have continuous satellite monitoring of the atmosphere and Doppler radar to tell us whether or not we will experience rain anytime soon; however, atmospheric measurements used to be few and far between. Today, measurements such as temperature and pressure not only help us predict the weather, but also help us look at long-term changes in global climate (see our Temperature module). The first atmospheric scientists were less concerned with weather prediction, however, and more interested in the composition and structure of the atmosphere.

The two most important instruments for taking measurements in Earth's atmosphere were developed hundreds of years ago: Galileo is credited with inventing the thermometer in 1593, and Evangelista Torricelli invented the barometer in 1643. With these two instruments, temperature and pressure could be recorded at any time and at any place. Of course, the earliest pressure and temperature measurements were taken at Earth's surface. It was a hundred years before the thermometer and barometer went aloft.

While many people are familiar with Ben Franklin's kite and key experiment that tested lightning for the presence of electricity, few realize that kites were the main vehicle for obtaining atmospheric measurements above Earth's surface. Throughout the 18th and 19th centuries, kite-mounted instruments collected pressure, temperature, and humidity readings; unfortunately, scientists could only reach up to an altitude of about 3 km with this technique.

In Figure, Scientist launches a radiosonde. Instruments for collecting data are in the white and orange box. image © NASA Jet Propulsion Laboratory

Unmanned balloons were able to take measurements at higher altitudes than kites, but because they were simply released with no passengers and no strings attached, they had to be retrieved in order to obtain the data that had been collected. This changed with the development of the *radiosonde*, an unmanned balloon capable of achieving high altitudes, in the early 1930s. The radiosonde included a radio transmitter among its many instruments, allowing data to be transmitted as it was being collected so that the balloons no longer needed to be retrieved. A radiosonde network was developed in the United States in 1937, and continues to this day under the auspices of the National Weather Service.

Temperature in the atmosphere

Through examination of measurements collected by radiosonde and aircraft (and later by rockets), scientists became aware that the atmosphere is not uniform. Many people had long recognized that temperature decreased with altitude – if you've ever hiked up a tall mountain, you might learn to bring a jacket to wear at the top even when it is warm at the base – but it wasn't until the early 1900s that radiosondes revealed a layer, about 18 km above the surface, where temperature abruptly changed and began to increase with altitude. The discovery of this reversal led to division of the atmosphere into layers based on their thermal properties.

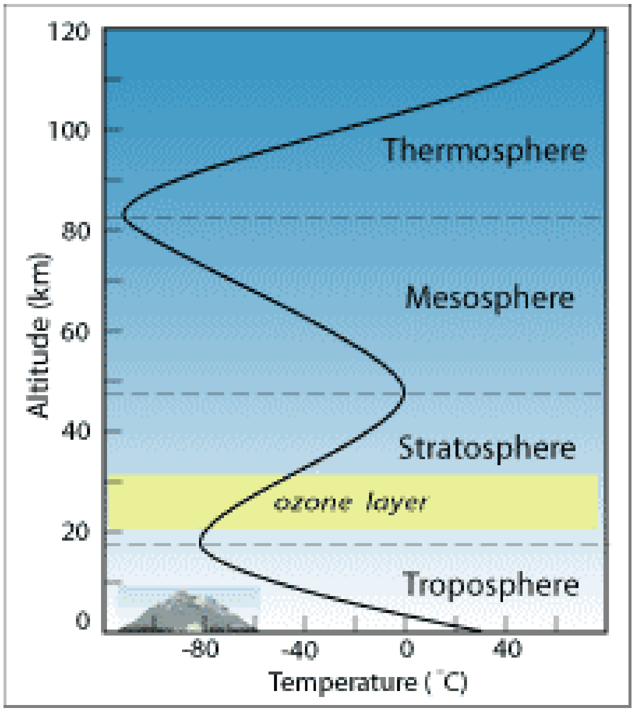


Figure : This graph shows how temperature varies with altitude in Earth's atmosphere.

The lowermost 12 to 18 km of the atmosphere, called the *troposphere*, is where all weather occurs – clouds form and precipitation falls, wind blows, humidity varies from place to place, and the atmosphere interacts with the surface below. Within the troposphere, temperature decreases with altitude at a rate of about 6.5° C per kilometer. At 8,856 m high, Mt. Everest still reaches less than halfway through the troposphere. Assuming a sea level temperature of 26° C (80° F), that means the temperature on the summit of Everest would be around -31° C (-24° F)! In fact, temperature at Everest's summit averages -36° C, whereas temperatures in New Delhi (in nearby India), at an elevation of 233 m, average about 28° C (82.4° F).

At the uppermost boundary of the troposphere, air temperature reaches about -100° C and then begins to increase with altitude. This layer of increasing temperature is called the *stratosphere*. The cause of the temperature reversal is a layer of concentrated ozone. Ozone's ability to absorb incoming ultraviolet (UV) radiation from the sun had been recognized in 1881, but the existence of the ozone layer at an altitude of 20 to 50 km was not postulated until the 1920s. By absorbing UV rays, the ozone layer both warms the air around it and protects us on the surface from the harmful short-wavelength radiation that can cause skin cancer.

It is important to recognize the difference between the ozone layer in the stratosphere and ozone present in trace amounts in the troposphere. Stratospheric ozone is produced when energy from the sun breaks apart O_2 gas molecules into O atoms; these O atoms then bond with other O_2 molecules to form O_3, ozone. This process was first described in 1930 by Sydney Chapman, a geophysicist who synthesized many of the known facts about the ozone layer. Tropospheric ozone, on the other hand, is a pollutant produced when emissions from fossil-fuel burning interact with sunlight.

Above the stratosphere, temperature begins to drop again in the next layer of the atmosphere called the *mesosphere*, as seen in the previous figure. This temperature decrease results from the rapidly decreasing density of the air at this altitude. Finally, at the outer reaches of Earth's atmosphere, the intense, unfiltered radiation from the sun causes molecules like O_2 and N_2 to break apart into ions. The release of energy from these reactions actually causes the temperature to rise again in the *thermosphere*, the outermost layer.

The thermosphere extends to about 500 km above Earth's surface, still a few hundred kilometers below the altitude of most orbiting satellites.

Pressure in the atmosphere

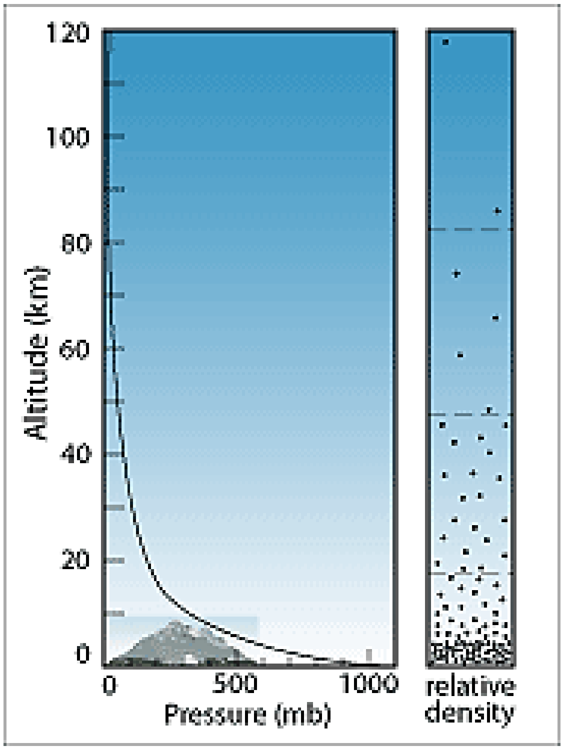


Figure : Pressure and density decrease rapidly with altitude.

Atmospheric pressure can be imagined as the weight of the overlying column of air. Unlike temperature, pressure decreases exponentially with altitude. Traces of the atmosphere can be detected as far as 500 km above Earth's surface, but 80 percent of the atmosphere's mass is contained within the 18 km closest to the surface.

Atmospheric pressure is generally measured in millibars (mb); this unit of measurement is equivalent to 1 gram per centimeter squared (1 g/cm^2). Other units are occasionally used, such as bars, atmospheres, or millimeters of mercury. The correspondence between these units is shown in the table below.

bars	**millibars**	**atmospheres**	**millimeters of mercury**
1.013 bar =	1013 mb =	1 atm =	760 mm Hg

At sea level, pressure ranges from about 960 to 1,050 mb, with an average of 1,013 mb. At the top of Mt. Everest, pressure is as low as 300 mb. Because gas pressure is related to density, this low pressure means that there are approximately one-third as many gas molecules inhaled per breath on top of Mt. Everest as at sea level – which is why climbers experience ever more severe shortness of breath the higher they go, as less oxygen is inhaled with every breath.

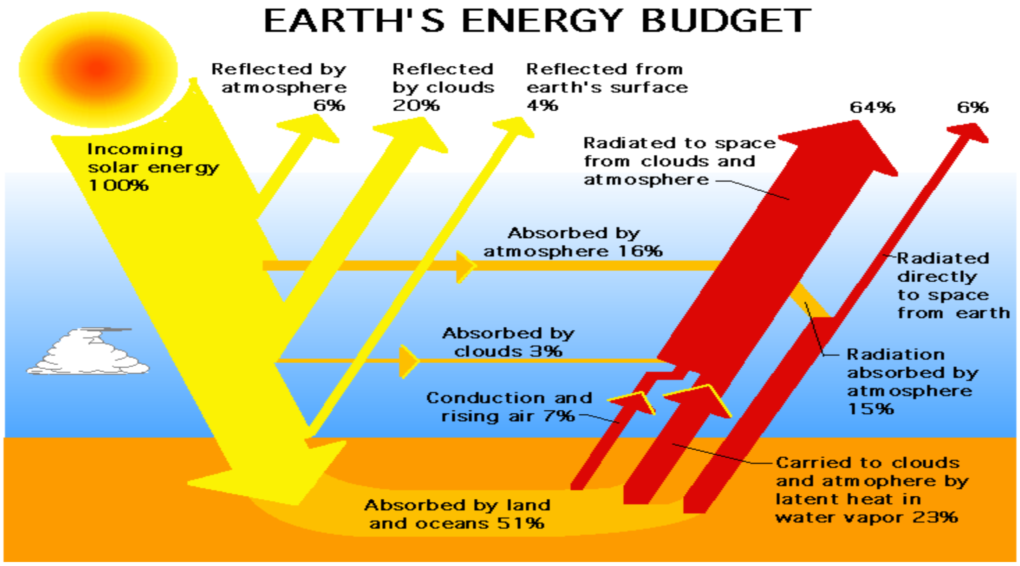
Though other planets host atmospheres, the presence of free oxygen and water vapor makes our atmosphere unique as far as we know. These components both encouraged and protected life on Earth as it developed, not only by providing oxygen for respiration, but by shielding organisms from harmful UV rays and by incinerating small meteors before they hit the surface. Additionally, the composition and structure of this unique resource are important keys to understanding circulation in the atmosphere, biogeochemical cycling of nutrients, short-term local weather patterns, and long-term global climate changes.

Gas	Concentration
Nitrogen, N_2	78.1% by volume
Oxygen, O_2	20.9% by volume
Argon, A	0.9% by volume
Carbon dioxide, CO_2	350 ppm
Water vapor, H_2O	0–4%, variable
Ozone, O_3	4–65 ppb
Methane, CH_4	1,750 ppb
Carbon monoxide,	CO 150 ppb
Nitrous oxide, N_2O	280 ppb

Temperature-Inversion

Why is the Earth's Surface Warm?

- Some of the sun's energy is converted to heat as it penetrates the earth's atmosphere
- The radiant heat of the sun also warms the surface of the earth

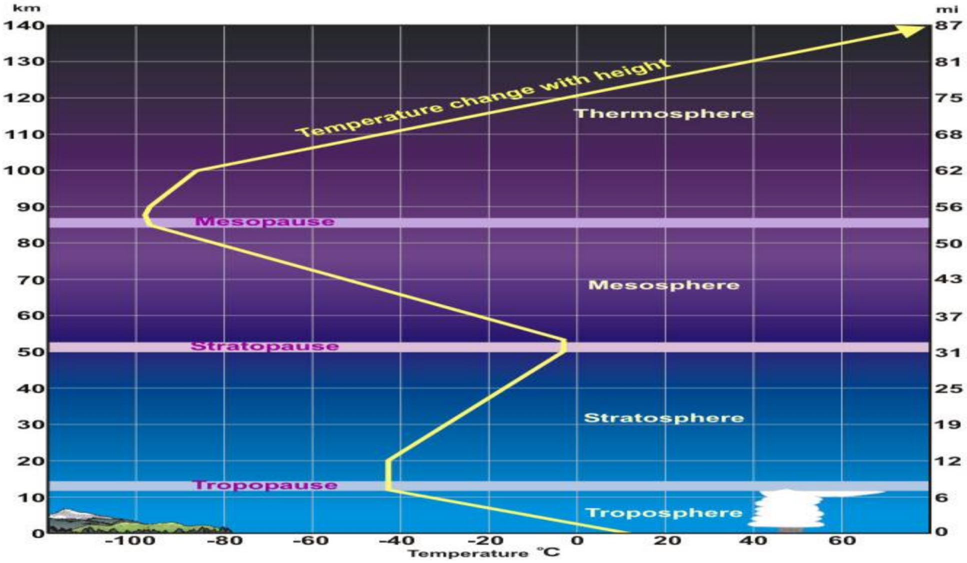


Heating of Air

- The warmed surface of the earth heats the air just above it in the troposphere by convection
    - **Troposphere = the lower atmosphere that we live in**
- Some of the sun's energy also heats the air through conduction and the rising of warmed air (convection)

Atmospheric Layers and Temperature

- As it rises, this warmed air in the troposphere expands and cools
- Density of the air decreases with the expansion of air, making it 'lighter' in weight

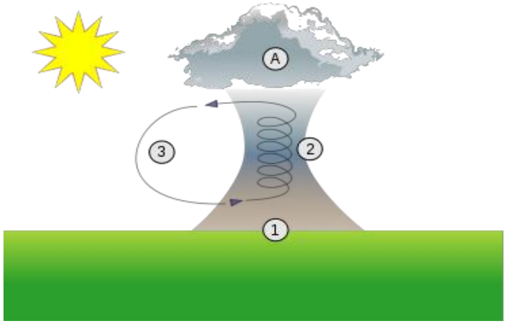


Air Temperature in the Lower Atmosphere

- Air temperature in the troposphere therefore gets cooler as altitude increases
    - Temperature at earth's surface= about 62°F/17°C

- Temperature at about 12 miles altitude = about 60°F/-51°C
- Height of troposphere is approx. 12 mi. at equator

Air Movement

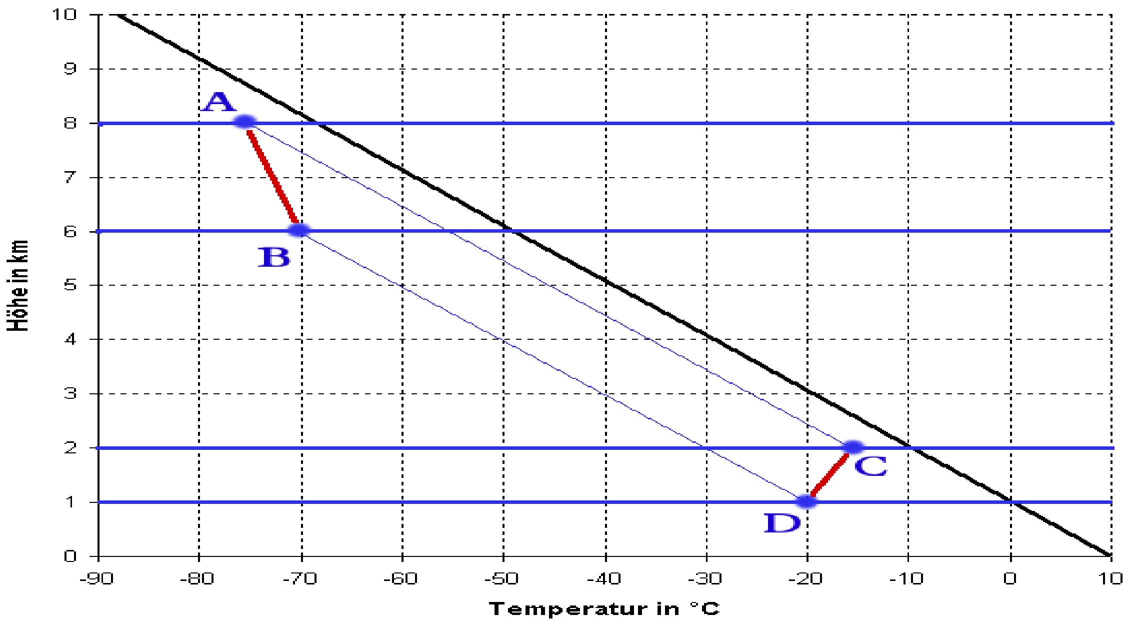


- As the warm air rises, cooler air (more dense, therefore heavier), rushes in to take its place
- This 'vertical mixing' is what causes wind

Thermal column. The cloud (A) is above the ground. The sun increases the temperature of the ground which will then warm the air above it (1). The bubble of hot air starts to rise (2) and begins to cool as it expands and moves **upward into cooler air. Due to its lower temperature, the air becomes cold enough to contract and then move downward (3) to repeat** the cycle.

What is a Temperature Inversion?

- A 'Temperature Inversion' occurs when the normal profile of warm at the surface and cooler as altitude increases is 'inverted' or turned upside down
- Cool air will be found at lower altitudes, with warmer air above during an inversion



Height (y-axis) versus Temperature (x-axis) under normal atmospheric conditions (black line). The path D-C illustrates an inversion aloft.

Temperature Inversions and Pollution

- The normal movement and mixing of cold and warm air in our atmosphere creates turbulence, which helps to lift and disperse pollutants
- Temperature inversions, however, keep cool, dense air near the surface, reducing the vertical movement

- Pollutants stay near the surface
- Pollutants become concentrated as more are added by everyday activities
- Pollutant concentrations may become hazardous

Favorable Conditions to Form a Temperature Inversion

- Calm winds ⇨ reduce vertical mixing
- Clear skies ⇨ increase rate of surface cooling
  - Less ‘greenhouse effect’

Rising smoke in Lochcarron, Scotland forms a ceiling over the valley due to a temperature inversion. The picture was taken on an afternoon
in January after a cold night.

Other Favorable Conditions for Forming a Temperature Inversion

- Long nights ⇨ greater duration of cooling
  - Inversions more common in winter due to longer nights
  - Inversions are stronger in winter because of the greater difference in temperature between the cool surface air and the warmer air aloft
- A very low angle of the sun in the sky (as in winter) ⇨ less daytime heating of air close to the ground and surface

Types of Temperature Inversions

- Radiation Temperature Inversion
- Subsidence Temperature Inversion

What Causes a Radiation Temperature Inversion?

- Cooling of the air at night near the ground

- Mechanism

1. Ground loses heat quickly after sunset
2. Air in contact with ground then cools quickly
3. Air above surface stays warm since air is a poor conductor of heat

Radiation Temperature Inversions

- Morning warming by the sun will often reverse a temperature inversion by afternoon
- Pollutants built up during the night also disperse

Radiation Temperature Inversions and Topography

- Areas in a mountain basin may experience prolonged radiation temperature inversions
- Cooler, denser air cannot rise up over mountains to laterally disperse pollutants
- Mountains also block the low angle of the winter sun, reducing warming of the air
- Cloudy weather will block the sun, further decreasing warming

What Causes a Subsidence Temperature Inversion?

- A high altitude mass of warm air moves into an area over cooler air near the surface
- High pressure pushes the warm air mass down, effectively capping the cooler air below

Fog may be seen under the inversion cap

Subsidence temperature inversions are usually short-lived

Subsidence Temperature Inversions and Topography

- Areas with mountains on three sides and the ocean on the fourth may experience frequent and prolonged subsidence temperature inversions
- Mechanism

  1. Ocean breezes cool the surface air

  2. Mountains surrounding prevent the cooler, heavier air from dispersing over the mountains and removing pollutants

Subsidence Temperature Inversions and Smog

- These conditions are especially problematic in areas like Los Angeles, CA
- Warm, sunny climate and high level of pollutants (vehicle, shipping, port) causes a photochemical smog
- Smog persists due to frequent subsidence temperature inversions for at least half the year (summer and fall)
- Low rainfall (15” per year) limits clearance of smog

How to Help Limit Temperature Inversions and Protect Yourself

- When the conditions are conducive to forming an inversion, reduce activities that might contribute, such as extra driving, burning wood, leaves, or refuse, etc.
    - Wood smoke contains much more particulate pollution than oil- or gas-fired furnaces
- Follow the Air Quality Index reports online, in the newspaper, or on radio and follow recommendations for any change in activity
- If you have respiratory problems, make a plan with your care-givers as to what you need to do if there is a thermal inversion with a lot of pollution close to the ground

Photochemical Smog

Introduction

The industrial revolution has been the central cause for the increase in pollutants in the atmosphere over the last three centuries. Before 1950, the majority of this pollution was created from the burning of coal for energy generation, space heating, cooking, and transportation. Under the right conditions, the smoke and sulfur dioxide produced from the burning of coal can combine with fog to create industrial smog. In high concentrations, industrial smog can be extremely toxic to humans and other living organisms. London is world famous for its episodes of industrial smog. The most famous London smog event occurred in December, 1952 when five days of calm foggy weather created a toxic atmosphere that claimed about 4000 human lives. Today, the use of other fossil fuels, nuclear power, and hydroelectricity instead of coal has greatly reduced the occurrence of industrial smog. However, the burning of fossil fuels like gasoline can create another atmospheric pollution problem known as photochemical smog. Photochemical smog is a condition that develops when primary pollutants (oxides of nitrogen and volatile organic compounds created from fossil fuel combustion) interact under the influence of sunlight to produce a mixture of hundreds of different and hazardous chemicals known as secondary pollutants. The Table below describes the major toxic constituents of photochemical smog and their effects on the environment.

Development of photochemical smog is typically associated with specific climatic conditions and centers of high population density. Cities like Los Angeles, New York, Sydney, and Vancouverfrequently suffer episodes of photochemical smog. In recent years, scientists have also noticed that smaller communities, like Kelowna and Kamloops, can develop similar pollution problems if conditions are right.

Major Chemical Pollutants in Photochemical Smog: Sources and Environmental Effects

Toxic Chemical	Sources	Environmental Effects	Additional Notes
Nitrogen Oxides (NO and NO2)	- combustion of oil, coal, gas in both automobiles and industry - bacterial action in soil - forest fires - volcanic action - lightning	- decreased visibility due to yellowish color of NO2 - NO2 contributes to heart and lung problems - NO2 can suppress plantgrowth - decreased resistance to	- all combustion processes account for only 5 % of NO2 in the atmosphere, most is formed from reactions involving NO -concentrations likely to rise in the future

		infection - may encourage the spread of cancer	
Volatile Organic Compounds (VOCs)	- evaporation of solvents - evaporation of fuels - incomplete combustion of fossil fuels - naturally occurring compounds like terpenes from trees	- eye irritation - respiratory irritation - some are carcinogenic - decreased visibility due to blue-brown haze	- the effects of VOCs are dependent on the type of chemical - samples show over 600 different VOCs in atmosphere - concentrations likely to continue to rise in future
Ozone (O3)	- formed from photolysis of NO2 - sometimes results from stratospheric ozone intrusions	- bronchial constriction - coughing, wheezing - respiratory irritation - eye irritation - decreased crop yields - retards plant growth - damages plastics - breaks down rubber - harsh odor	- concentrations of 0.1 parts per million can reduce photosynthesis by 50 % - people with asthma and respiratory problems are influenced the most - can only be formed during daylight hours
Peroxyacetyl Nitrates (PAN)	- formed by the reaction of NO2 with VOCs (can be formed naturally in some environments)	- eye irritation - high toxicity to plants - respiratory	- was not detected until recognized in smog - higher toxicity to plants than ozone

		irritation - damaging to proteins	

Development of Photochemical Smog

Certain conditions are required for the formation of photochemical smog. These conditions include:

1. A source of nitrogen oxides and volatile organic compounds. High concentrations of these two substances are associated with industrialization and transportation. Industrialization and transportation create these pollutants through fossil fuel combustion.

2. The time of day is a very important factor in the amount of photochemical smog present:

- Early morning traffic increases the emissions of both nitrogen oxides and VOCs as people drive to work.
- Later in the morning, traffic dies down and the nitrogen oxides and volatile organic compounds begin to be react forming nitrogen dioxide, increasing its concentration.
- As the sunlight becomes more intense later in the day, nitrogen dioxide is broken down and its by-products form increasing concentrations of ozone.
- At the same time, some of the nitrogen dioxide can react with the volatile organic compounds to produce toxic chemicals such as PAN.
- As the sun goes down, the production of ozone is halted. The ozone that remains in the atmosphere is then consumed by several different reactions.

3. Several meteorological factors can influence the formation of photochemical smog. These conditions include:

- Precipitation can alleviate photochemical smog as the pollutants are washed out of the atmosphere with the rainfall.
- Winds can blow photochemical smog away replacing it with fresh air. However, problems may arise in distant areas that receive the pollution.

- Temperature inversions can enhance the severity of a photochemical smog episode. Normally, during the day the air near the surface is heated and as it warms it rises, carrying the pollutants with it to higher elevations. However, if a temperature inversion develops pollutants can be trapped near the Earth's surface. Temperature inversions cause the reduction of atmospheric mixing and therefore reduce the vertical dispersion of pollutants. Inversions can last from a few days to several weeks.

4. Topography is another important factor influencing how severe a smog event can become. Communities situated in valleys are more susceptible to photochemical smog because hills and mountains surrounding them tend to reduce the air flow, allowing for pollutant concentrations to rise. In addition, valleys are sensitive to photochemical smog because relatively strong temperature inversions can frequently develop in these areas.

(c). Chemistry of Photochemical Smog

The previous section suggested that the development of photochemical smog is primarily determined by an abundance of nitrogen oxides and volatile organic compounds in the atmosphere and the presence of particular environmental conditions. To begin the chemical process of photochemical smog development the following conditions must occur:

- Sunlight.
- The production of **oxides of nitrogen** (**NOx**).
- The production of **volatile organic compounds** (**VOCs**).
- Temperatures greater than 18 degrees Celsius.

If the above criteria are met, several reactions will occur producing the toxic chemical constituents of photochemical smog. The following discussion outlines the processes required for the formation of two most dominant toxic components: ozone (O_3) and peroxyacetyl nitrate (PAN).

Note the symbol R represents a hydrocarbon (a molecule composed of carbon, hydrogen and other atoms) which is primarily created from volatile organic compounds.

Nitrogen dioxide can be formed by one of the following reactions. Notice that the nitrogen oxide (NO) acts to remove ozone (O_3) from the atmosphere and this mechanism occurs naturally in an unpolluted atmosphere.

$$O_3 + NO \text{ »»» } NO_2 + O_2$$

$$NO + RO_2 \text{ »»» } NO_2 + \text{other products}$$

Sunlight can break down nitrogen dioxide (NO_2) back into nitrogen oxide (NO).

$$NO_2 + \text{sunlight »»» } NO + O$$

The atomic oxygen (O) formed in the above reaction then reacts with one of the abundant oxygen molecules (which makes up 20.94 % of the atmosphere) producing ozone (O_3).

$$O + O_2 \text{ »»» } O_3$$

Nitrogen dioxide (NO_2) can also react with radicals produced from volatile organic compounds in a series of reactions to form toxic products such as peroxyacetyl nitrates (PAN).

$$NO_2 + R \text{ »»» products such as PAN}$$

It should be noted that ozone can be produced naturally in an unpolluted atmosphere. However, it is consumed by nitrogen oxide as illustrated in the first reaction. The introduction of volatile organic compounds results in an alternative pathway for the nitrogen oxide, still forming nitrogen dioxide but not consuming the ozone, and therefore ozone concentrations can be elevated to toxic levels.

Atmospheric Aerosols

Atmospheric aerosols (or particulate matter) are solid or liquid particles or both suspended in air with diameters between about 0.002 μm to about 100 μm.

Aerosol particles vary greatly in size, source, chemical composition, amount and distribution in space and time, and how long they survive in the atmosphere.

Three types of atmospheric aerosol have a significant effect on Earth's climate: **volcanic; desert dust; and human-made.**

Volcanic aerosol forms in the stratosphere after an eruption as droplets of sulfuric acid that can last up to two years, and reflect sunlight, lowering temperature.

Desert dust, mineral particles blown to high altitudes, absorb heat and may be responsible for inhibiting storm cloud formation.

Human-made sulfate aerosols, primarily from burning oil and coal, affect the behavior of clouds.

Although all hydrometeors, solid and liquid, can be described as aerosols, a distinction is commonly made between such dispersions (i.e. clouds) containing activated drops and crystals, and aerosol particles.

Atmosphere of Earth contains aerosols of various types and concentrations, including quantities of:

- natural inorganic materials: fine dust, sea salt, water droplets.
- natural organic materials: smoke, pollen, spores, bacteria
- anthropogenic products of combustion such as: smoke, ashes or dusts

Aerosols can be found in urban Ecosystems in various forms, for example:

- Dust,
- Cigarette smoke,
- Mist from aerosol spray cans,
- Soot or fumes in car exhaust.

The presence of aerosols in earth's atmosphere can influence Earth's climate, as well as human health.

Effects of Aerosols

- Volcanic eruptions release large amounts of sulphuric acid, hydrogen sulphide and hydrochloric acid into the atmosphere. These gases represent aerosols and eventually return to earth as acid rain, having a number of adverse effects on the environment and human life.

- Aerosols interact with the Earth's energy budget in two ways, directly and indirectly.

  E.g., a direct effect is that aerosols scatter sunlight directly back into space. This can lead to a significant decrease in the temperature, being an additional element to the greenhouse effect and therefore contributing to the global climate change.

  The indirect effects refer to the aerosols interfering with formations that interact directly with radiation. For example, they are able to modify the size of the cloud particles in the lower atmosphere, thereby changing the way clouds reflect and absorb light and therefore modifying the Earth's energy budget.

  - When aerosols absorb or adsorb pollutants, it facilitates the deposition of pollutants to the surface of the earth as well as to bodies of water. This has the potential to be damaging to both the environment and human health.
  - Aerosol particles with an effective diameter smaller than 10 μm can enter the bronchi, while the ones with an effective diameter smaller than 2.5 μm can enter as far as the gas exchange region in the lungs, which can be hazardous to human health.

Acid-Rain

What is Acid Rain?

Acid rain is a result of air pollution. When any type of fuel is burnt, lots of different chemicals are produced. The smoke that comes from a fire or the fumes that come out of a car exhaust don't just contain the sooty grey particles that you can see - they also contains lots of invisible gases that can be even more harmful to our environment.

Power stations, factories and cars all burn fuels and therefore they all produce polluting gases. Some of these gases (especially nitrogen oxides and sulphur dioxide) react with the tiny droplets of water in clouds to form sulphuric and nitric acids. The rain from these clouds then falls as very weak acid - which is why it is known as "acid rain".

How acidic is acid rain?

Acidity is measured using a scale called the pH scale. This scale goes from 0 to 14. 0 is the most acidic and 14 is the most alkaline (opposite of acidic). Something with a pH value of 7, we call neutral, this means that it is neither acidic nor alkaline.

Very strong acids will burn if they touch your skin and can even destroy metals. Acid rain is much, much weaker than this, never acidic enough to burn your skin.

Rain is always slightly acidic because it mixes with naturally occurring oxides in the air. Unpolluted rain would have a pH value of between 5 and 6. When the air becomes more polluted with nitrogen oxides and sulphur dioxide the acidity can increase to a pH value of 4. Some rain has even been recorded as being pH2.

Vinegar has a pH value of 2.2 and lemon juice has a value of pH2.3. Even the strongest recorded acid rain is only about as acidic as lemon juice or vinegar and we know that these don't harm us - so why do we worry about acid rain?

The Effects of Acid Rain

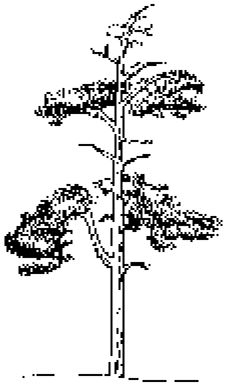
Acid rain can be carried great distances in the atmosphere, not just between countries but also from continent to continent. The acid can also take the form of snow, mists and dry dusts. The rain sometimes falls many miles from the source of pollution but wherever it falls it can have a serious effect on soil, trees, buildings and water.

Forests all over the world are dying, fish are dying. In Scandinavia there are dead lakes, which are crystal clear and contain no living creatures or plant life. Many of Britain's freshwater fish are threatened, there have been reports of deformed fish being hatched. This leads to fish-eating birds and animals being affected also. Is acid rain responsible for all this? Scientists have been doing a lot of research into how acid rain affects the environment.

Forests

It is thought that acid rain can cause trees to grow more slowly or even to die but scientists have found that it is not the only cause. The same amount of acid rain seems to have more effect in some areas than it does in others.

As acid rain falls on a forest it trickles through the leaves of the trees and runs down into the soil below. Some of it finds its way into streams and then on into rivers and lakes. Some types of soil can help to neutralise the acid - they have what is called a "buffering capacity".



Other soils are already slightly acidic and these are particularly susceptible to the effects of acid rain.

Acid rain can effect trees in several different ways, it may:

• dissolve and wash away the nutrients and minerals in the soil which help the trees to grow.

- cause the release of harmful substances such as aluminium into the soil.

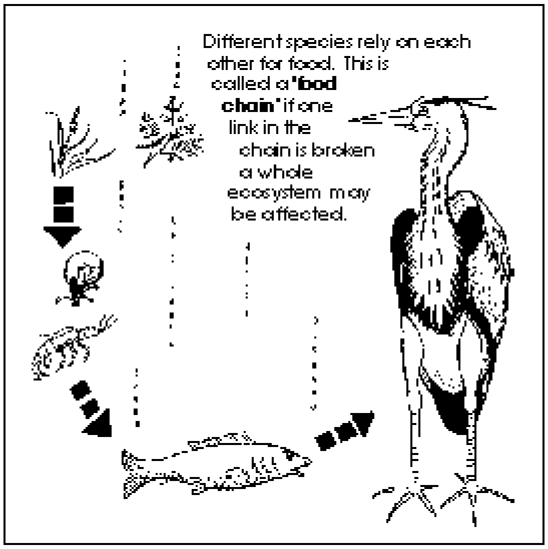
- wear away the waxy protective coating of leaves, damaging them and preventing them from being able to photosynthesise properly.

A combination of these effects weakens the trees which means that they can be more easily attacked by diseases and insects or injured by bad weather. It is not just trees that are affected by acid rain, other plants may also suffer.

Lakes and Rivers

It is in aquatic habitats that the effects of acid rain are most obvious. Acid rain runs off the land and ends up in streams, lakes and marshes - the rain also falls directly on these areas.

As the acidity of a lake increases, the water becomes clearer and the numbers of fish and other water animals decline. Some species of plant and animal are better able to survive in acidic water than others. Freshwater shrimps, snails, mussels are the most quickly affected by acidification followed by fish such as minnows, salmon and roach. The roe and fry (eggs and young) of the fish are the worst affected, the acidity of the water can cause deformity in young fish and can prevent eggs from hatching properly.



The acidity of the water does not just affect species directly, it also causes toxic substances like aluminium to be released into the water from the soil, harming fish and other aquatic animals.

Lakes, rivers and marshes each have their own fragile ecosystem with many different species of plants and animals all depending on one another to survive. If a species of fish disappears, the animals which feed on it will gradually disappear too. If the extinct fish used to feed on a particular species of large insect, that insect population will start to grow, this in turn will affect the smaller insects or plankton on which the larger insect feeds.

Buildings

Every type of material will become eroded sooner or later by the effects of the climate. Water, wind, ice and snow all help in the erosion process but unfortunately, acid rain can help to make this natural process even quicker. Statues, buildings, vehicles, pipes and cables can all suffer. The worst affected are things made from limestone or sandstone as these types of rock are particularly susceptible and can be affected by air pollution in gaseous form as well as by acid rain.

Where is it coming from?

Until relatively recently air pollution has been seen as a local issue. It was in southern Scandinavia in the late 1950's that the problems of acid rain were first observed and it was then that people began to realise that the origins of this pollution were far away in Britain and Northern Europe. One early answer to industrial air pollution was to build very tall chimneys. Unfortunately all this does is push the polluting gases up into the clouds allowing emissions to float away on the wind. The wind carries the pollution many hundreds of miles away where it eventually falls as acid rain. In this way Britain has contributed at least 16% of the acid deposition in Norway. Over ninety percent of Norway's acid pollution comes from other countries. The worst European polluters are Germany, UK, Poland and Spain, each of them producing over a million tons of sulphur emissions in 1994. Governments are now beginning to admit that acid rain is a serious environmental problem and many countries are now taking steps to reduce the amount of sulphur and nitrogen emissions.

What can be done?

Reduce emissions:

- Burning fossil fuels is still one of the cheapest ways to produce electricity so people are now researching new ways to burn fuel which don't produce so much pollution.

- Governments need to spend more money on pollution control even if it does mean an increase in the price of electricity.

- Sulphur can also be 'washed' out of smoke by spraying a mixture of water and powdered limestone into the smokestack.

- Cars are now fitted with catalytic converters which remove three dangerous chemicals from exhaust gases.

Find alternative sources of energy

- Governments need to invest in researching different ways to produce energy.

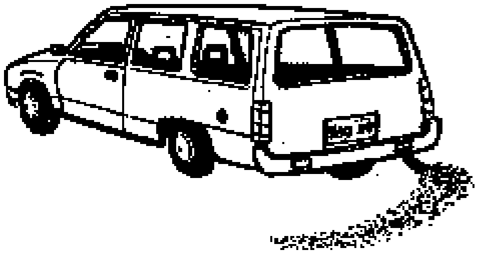
- Two other sources that are currently used are hydroelectric and nuclear power. These are 'clean' as far as acid rain goes but what other impact do they have on our environment?

- Other sources could be solar energy or windmills but how reliable would these be in places where it is not very windy or sunny?

- All energy sources have different benefits and costs and all theses have to be weighed up before any government decides which of them it is going to use.

Conserving Resources

- Greater subsidies of public transport by the government to encourage people to use public transport rather than always travelling by car.



- Every individual can make an effort to save energy by switching off lights when they are not being used and using energy-saving appliances - when less electricity is being used, pollution from power plants decreases.

- Walking, cycling and sharing cars all reduce the pollution from vehicles.

Restoring the Damage done by Acid Rain

Lakes and rivers can have powdered limestone added to them to neutralise the water - this is called "liming". Liming, however, is expensive and its effects are only temporary - it needs to be continued until the acid rain stops. The people of Norway and Sweden have successfully used liming to help restore lakes and streams in their countries. A major liming programme is currently taking place in Wales.

Green-House Gases

Water vapour: The main greenhouse gas is water vapour (H2O), which is responsible for about two-thirds of the natural greenhouse effect. In the atmosphere, water molecules capture the heat that the earth radiates and then re-radiate into all directions, warming earth's surface, before it is eventually radiated back to space.

Water vapour in the atmosphere is part of the hydrological cycle, a closed system circulating water – of which there is a finite amount on earth - from the oceans and land to the atmosphere and back again through evaporation and transpiration, condensation and precipitation. Human activities do not add water vapour to the atmosphere. However, warmer air can hold much more moisture, so increasing temperatures further intensify climate change.

Carbon dioxide: The main contributor to the enhanced (manmade) greenhouse effect is carbon dioxide (CO_2). Globally, it accounts for over 60% of the enhanced greenhouse gas effect. In industrialised countries, CO_2 makes up more than 80% of greenhouse gas emissions. There is a finite amount of carbon on earth, which, like water, is part of a cycle – the carbon cycle. This is a very complex system in which carbon moves through the atmosphere, the terrestrial biosphere and oceans. Plants absorb CO_2 from the atmosphere during photosynthesis. They use the carbon to build their tissue, and they release it back to the atmosphere when they die and decompose. The bodies of animals (and humans) also contain carbon since they are built from carbon taken in from eaten plants - or animals that eat plants. This carbon is released as CO_2 when they breathe (respiration) and when they die and decompose. Fossil fuels are the fossilised remains of dead plants and animals formed over millions of years under certain conditions, and that's why they contain a lot of carbon. Broadly speaking, coal is the remnant of buried forests while oil is converted oceanic plant life. (Oceans absorb CO_2 which, in dissolved form, is used by marine life in photosynthesis.) Many billions of tonnes of carbon are exchanged naturally each year between the atmosphere, the oceans and land vegetation. Carbon dioxide levels in the atmosphere appear to have varied less than 10% during the 10,000 years before the Industrial Revolution. Since 1800, however, concentrations have risen by about 30% as massive amounts of fossil fuels are burned to produce energy – mostly in developed countries. Currently we are emitting more than 25 billion tonnes of CO_2 into the atmosphere each year.

CO_2 can stay in the atmosphere for 50-200 years depending on how it is recycled back in to the land or the oceans.

Methane: The second-most important greenhouse gas for the enhanced greenhouse effect is methane (CH_4). Since the beginning of the Industrial Revolution, atmospheric methane concentrations have doubled and contributed some 20% to the enhancement of the greenhouse gas effect. In industrialised countries, methane accounts typically for 15% of greenhouse gas emissions.

Methane is created predominantly by bacteria that feed on organic material where there is a lack of oxygen. It is therefore emitted from a variety of natural and human-influenced sources, with manmade emissions accounting for the majority. Natural sources include wetlands, termites, and oceans. Human-influenced sources include the mining and burning of fossil fuels, livestock husbandry (cattle eat plants that ferment in their stomachs, so they exhale methane and their manure contains it), rice cultivation (flooded paddy fields produce methane since organic matter in the soil decomposes without sufficient oxygen) and landfills (again, organic waste decomposes without sufficient oxygen).

In the atmosphere, methane traps heat and is 23 times more effective at that than CO_2. Its lifetime is however shorter, between 10 and 15 years.

Nitrous oxide: Nitrous oxide (N_2O) is released naturally from oceans and rainforests and by bacteria in soils. Human-influenced sources include nitrogen-based fertilisers, fossil fuel combustion and industrial chemical production using nitrogen, such as sewage treatment. In industrialised countries, N_2O accounts for around 6% of greenhouse gas emissions. Like CO_2 and

methane, nitrous oxide is a greenhouse gas whose molecules absorb heat trying to escape to space. N_2O is 310 times more effective than CO_2 absorbing heat. Since the beginning of the Industrial Revolution, nitrous oxide concentrations in the atmosphere have increased by about 16% and contributed 4 to 6% to the enhancement of the greenhouse effect.

Fluorinated greenhouse gases: These are the only greenhouse gases that do not occur naturally, but have been developed by man for industrial purposes. Their share of greenhouse gas emissions from industrialised countries is around 1.5%. But they are extremely powerful – they can trap heat up to 22,000 times more effectively than CO2 - and they can stay in the atmosphere for thousands of years. Fluorinated greenhouse gases include hydrofluorocarbons (HFCs) which are used in cooling and refrigeration, including air conditioning; sulphur hexafluoride (SF6), which is used, for example, in the electronics industry; and perfluorocarbons (PFCs), which are emitted during the manufacture of aluminium and also used in the electronics industry. Arguably the best known of these gases are chlorofluorocarbons (CFCs), which are not only fluorinated greenhouse gases, but also deplete the ozone layer. They are being phased out under the 1987 Montreal Protocol on Ozone-Depleting Substances.

Global Warming and Greenhouse Effect

About 75 % of the solar energy reaching the earth is absorbed by the earth's surface, which increases its temperature. The rest of the heat radiates back to the atmosphere. Some of the heat is trapped by gases such as carbon dioxide, methane, ozone, chlorofluorocarbon compounds (CFCs) and water vapour in the atmosphere.

Thus, they add to the heating of the atmosphere. This causes global warming.

We all know that in cold places flowers ,vegetables and fruits are grown in glass covered areas called greenhouse. Do you know that we humans also live in a greenhouse? Of course, we are not surrounded by glass but a blanket of air called the atmosphere, which has kept the temperature on earth constant for centuries. But it is now undergoing change, though slowly. Just as the glass in a greenhouse holds the sun's warmth inside, atmosphere traps the sun's heat near the earth's surface and keeps it warm. This is called natural greenhouse effect because it maintains the temperature and makes the earth perfect for life.

In a greenhouse, solar radiations pass through the transparent glass and heat up the soil and the plants. The warm soil and plants emit infrared radiations. Since glass is opaque to infrared radiations (thermal region), it partly reflects and partly absorbs these radiations. This mechanism keeps the energy of the sun trapped in the greenhouse.

Similarly, carbon dioxide molecules also trap heat as they are transparent to sunlight but not to the heat radiation. If the amount of carbon dioxide crosses the delicate proportion of 0.03 per cent, the natural greenhouse balance may get disturbed. Carbon dioxide is the major contributor to global warming. Besides carbon dioxide, other greenhouse gases are methane, water vapour, nitrous oxide, CFCs and ozone.

Methane is produced naturally when vegetation is burnt, digested or rotted in the absence of oxygen. Large amounts of methane are released in paddy fields, coal mines, from rotting garbage dumps and by fossil fuels. Chlorofluorocarbons (CFCs) are man-made industrial chemicals used in air conditioning etc. CFCs are also damaging the ozone layer (Section 14.2.2).

Nitrous oxide occurs naturally in the environment. In recent years, their quantities have increased significantly due to the use of chemical fertilizers and the burning of fossil fuels. If these trends continue, the average global temperature will increase to a level which may lead to melting of polar ice caps and flooding of low lying areas all over the earth. Increase in the global temperature increases the incidence of infectious diseases like dengue, malaria, yellow fever, sleeping sickness etc.

What can we do to reduce the rate of global warming?

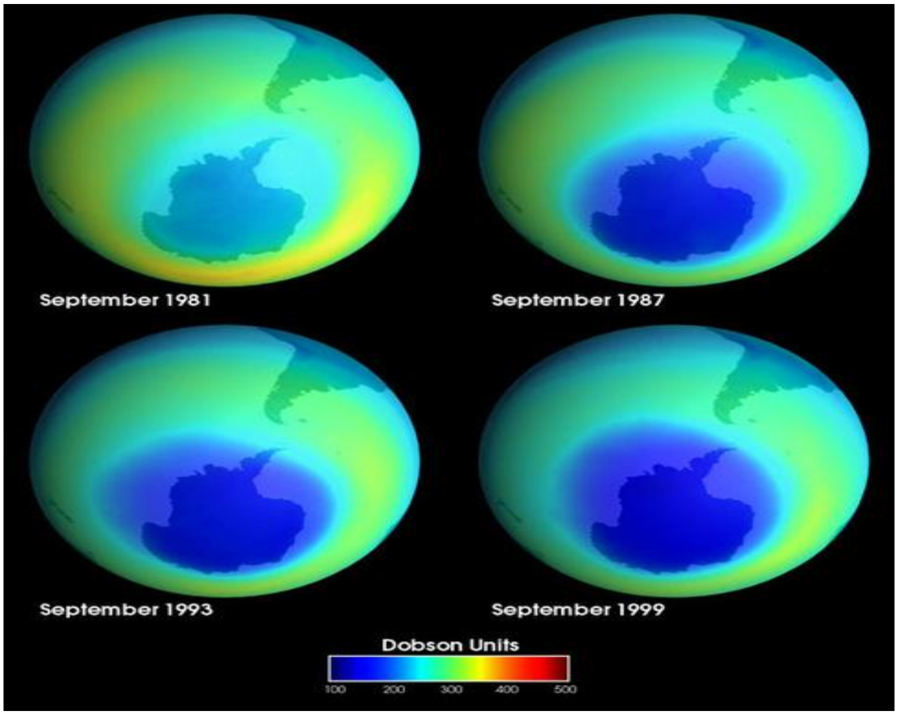
If burning of fossil fuels, cutting down forests and trees add to greenhouse gases in the atmosphere, we must find ways to use these just efficiently and judiciously. One of the simple things which we can do to reduce global warming is to minimise the use of automobiles. Depending upon the situation, one can use bicycle, public transport system, or go for carpool. We should plant more trees to increase the green cover. Avoid burning of dry leaves, wood etc. It is illegal to smoke in public places and work places, because it is harmful not only for the one who is smoking but also for others, and therefore, we should avoid it. Many people do not understand the greenhouse effect and the global warming. We can help them by sharing the information that we have.

Depletion of the Ozone Layer

The earth's stratospheric ozone layer plays a critical role in absorbing ultraviolet radiation emitted by the sun. In the last thirty years, it has been discovered that stratospheric ozone is depleting as a result of anthropogenic pollutants. There are a number of chemical reactions that can deplete stratospheric ozone; however, some of the most significant of these involves the catalytic destruction of ozone by halogen radicals such as chlorine and bromine.

Introduction

The atmosphere of the Earth is divided into five layers. In order of closest and thickest to farthest and thinnest the layers are listed as follows: troposphere, stratosphere, mesosphere, thermosphere and exosphere. The majority of the ozone in the atmosphere resides in the stratosphere, which



extends from six miles above the Earth's surface to 31 miles. Humans rely heavily on the absorption of ultraviolet B rays by the ozone layer because UV-B radiation causes skin cancer and can lead to genetic damage. The ozone layer has historically protected the Earth from the harmful UV rays, although in recent decades this protection has diminished due to stratospheric ozone depletion.

Figure 1. These images from the Total Ozone Mapping Spectrometer (TOMS) show the progressive depletion of ozone over Antarctica from 1979 to 1999. This "ozone hole" has extended to cover an area as large as 10.5 million square miles in September 1998. The previous record of 10.0 million square miles was set in 1996. Figure courtesy of NASA.

History of Ozone Depletion

Ozone depletion is largely a result of man-made substances. Humans have introduced gases and chemicals into the atmosphere that have rapidly depleted the ozone layer in the last century. This depletion makes humans more vulnerable to the UV-B rays which are known to cause skin cancer as well as other genetic deformities. The possibility of ozone depletion was first introduced by scientists in the late 1960's as dreams of super sonic transport began to become a reality. Scientists had long been aware that nitric oxide (NO) can catalytically react with ozone (O_3) to produce O_2 molecules; however, NO molecules produced at ground level have a half life far too short to make it into the stratosphere. It was not until the advent of commercial super sonic jets (which fly in the stratosphere and at an altitude much higher then conventional jets) that the potential for NO to react with stratospheric ozone became a possibility. The threat of ozone depletion from commercial super sonic transport was so great that it is often cited as the main reason why the US federal government pulled support for its development in 1971. Fear of ozone depletion was abated until 1974 when Sherwood Rowland and Mario Molina discovered that chlorofluorocarbons could be photolyzed by high energy photons in the stratosphere. They discovered that this process could releasing chlorine radicals that would catalytically react with O_3 and destroy the molecule. This process is called the Rowland-Molina theory of O_3 depletion.

The Chapman Cycle

The stratosphere is in a constant cycle with oxygen molecules and their interaction with ultraviolet rays. This process is considered a cycle because of its constant conversion between different molecules of oxygen. The ozone layer is created when ultraviolet rays react with oxygen molecules (O_2) to create ozone (O_3) and atomic oxygen (O). This process is called the **Chapman cycle**.

An oxygen molecules is photolyzed by solar radiation, creating two oxygen radicals:

$$h\nu + O_2 \rightarrow 2O^{\bullet}$$

Oxygen radicals then react with molecular oxygen to produce ozone:

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

Ozone then reacts with an additional oxygen radical to form molecular oxygen:

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

Ozone can also be recycled into molecular oxygen by reacting with a photon:

$$O_3 + h\nu \rightarrow O_2 + O^{\bullet}$$

It is important to keep in mind that ozone is constantly being created and destroyed by the Chapman cycle and that these reactions are natural processes, which have been taking place for millions of years. Because of this, the thickness the ozone layer at any particular time can vary greatly. It is also important to know that O_2 is constantly being introduced into the atmosphere through photosynthesis, so the ozone layer has the capability of regenerating itself.

Chemistry of Ozone Depletion

CFC molecules are made up of chlorine, fluorine and carbon atoms and are extremely stable. This extreme stability allows CFC's to slowly make their way into the stratosphere (most molecules decompose before they can cross into the stratosphere from the troposphere). This prolonged life in the atmosphere allows them to reach great altitudes where photons are more energetic. When the CFC's come into contact with these high energy photons, their individual components are freed from the whole. The following reaction displays how Cl atoms have an ozone destroying cycle:

$$Cl + O_3 \rightarrow ClO + O_2 \qquad \text{(step 1)}$$

$$ClO + O^{\bullet} \rightarrow Cl + O_2 \qquad \text{(step 2)}$$

$$O_3 + O^{\bullet} \rightarrow 2O_2 \qquad \text{(Overall reaction)}$$

Chlorine is able to destroy so much of the ozone because it acts as a catalyst. Chlorine initiates the breakdown of ozone and combines with a freed oxygen to create two oxygen molecules. After each reaction, chlorine begins the destructive cycle again with another ozone molecule. One chlorine atom can thereby destroy thousands of ozone molecules. Because ozone molecules are being broken down they are unable to absorb any ultraviolet light so we experience more intense UV radiation at the earths surface.

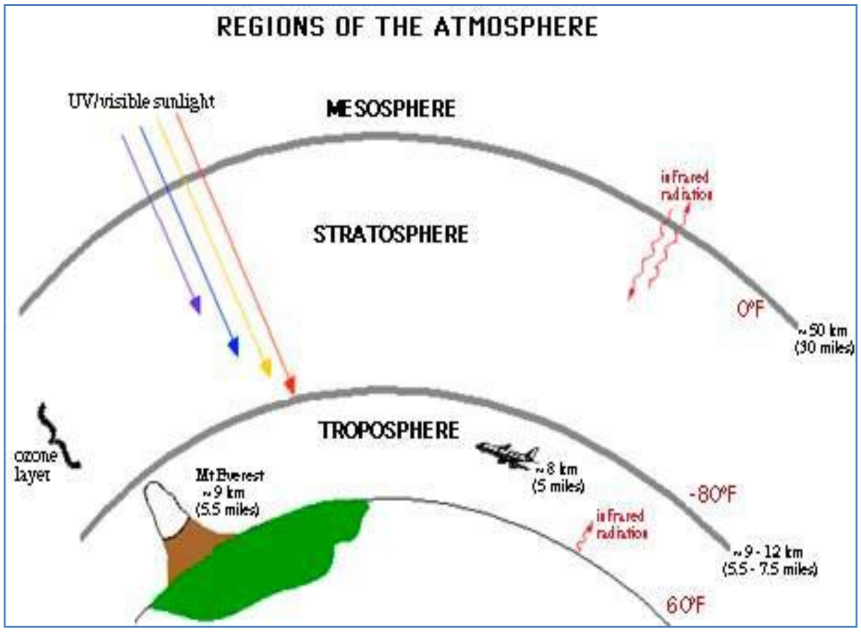


Figure. Much like sunscreen for the Earth, the ozone layer shields the Earth from the sun’s damaging UV-B radiation, which can adversely affect human health and ecosystems. Figure courtesy of NOAA.

The Ozone Hole

From 1985 to 1988, researchers studying atmospheric properties over the south pole continually noticed significantly reduced concentrations of ozone directly over the continent of Antarctica. For three years it was assumed that the ozone data was incorrect and was due to some type of instrument malfunction. In 1988, researchers finally realized their error and concluded that an enormous hole in the ozone layer had indeed developed over Antarctica. Examination of NASA satellite data later showed that the hole had begun to develop in the mid 1970's.

The ozone hole over Antarctica is formed by a slew of unique atmospheric conditions over the continent that combine to create an ideal environment for ozone destruction.

- Because Antarctica is surrounded by water, winds over the continent blow in a unique clockwise direction creating a so called "polar vortex" that effectively contains a single static air mass over the continent. As a result, air over Antarctica does not mix with air in the rest of the earth's atmosphere.
- Antarctica has the coldest winter temperatures on earth, often reaching -110 F. These chilling temperatures result in the formation of polar stratospheric clouds (PSC's) which are a conglomeration of frozen H_2O and HNO_3. Due to their extremely cold temperatures, PSC's form an electrostatic attraction with CFC molecules as well as other halogenated compounds
- As spring comes to Antarctica, the PSC's melt in the stratosphere and release all of the halogenated compounds that were previously absorbed to the cloud. In the antarctic summer, high energy photons are able to photolyze the halogenated compounds, freeing halogen radicals that then catalytically destroy O_3. Because Antarctica is constantly surrounded by a polar vortex, radical halogens are not able to be diluted over the entire globe. The ozone hole develops as result of this process.

Resent research suggests that the strength of the polar vortex from any given year is directly correlated to the size of the ozone hole. In years with a strong polar vortex, the ozone hole is seen to expand in diameter, whereas in years with a weaker polar vortex, the ozone hole is noted to shrink

Water Pollution

There are several **definitions** of water pollution given as follows.

“The presence of deleterious matter in such quantities to make the water unsuitable for its designated use.”

In Scientific sense, “water pollution is a distortion of the aquatic ecosystem,
Hence water pollution is such a change which ‘adversely affect the aquatic ecosystem in terms of the living organism, Oxygen content, the presence of toxins and so on.

pollution of water means “a departure from normal state (rather than a pure water ,for ideally unpolluted water is misconception) of water by human activities in such a manner to prevent it from being used for the purposes thought as normal”.

Normal areas of use include domestic, agricultural, Industrial, Fish, and other aquatic life and wild life including recreation and aesthetics.

The water (Prevention and control of pollution) act 1974 makes a legal definition of water pollution as

“Such contamination of water or such alteration of the physical, chemical, or Biological properties of water or such discharge of any sewage or trade effluent or any other liquid ,gaseous or solid substance into water as may ,or is likely to create a nuisance or render such water harmful or injurious to public health or safety or to domestic ,commercial ,industrial ,agricultural or other legitimate uses or to the life and health of animals or aquatic organism.”

There is a difference in contamination and pollution.

Pollution agents or activities producing damage in the environment damage the entire ecosystem.

While

Contamination supported by the environment without stopping the general chemical cycles and life cycles.

So, **Contaminated water** is defined as **" Water that is rendered un-useable for drinking."**

While

Potable water is safe and better for drinking.

Sources of water pollution

Generally,there are many sources of water pollution listed as follows.

1. Sewage leakages
2. High population density
3. oil spillage
4. Menace of Nipa palm and water hyacinth
5. Industrial waste dumped into our waters
6. Pollution of ground water through drilling activities
7. Flooding during rainy season which carries waste deposits into our waters.
8. Building lavatories and visionaries over running water or even the sea as it the practice in some riverine areas.

9. Radioisotopes
10. Heavy metal
11. Combustion
12. Toxic waste disposal at sea
13. Mineral processing plant (e.g. coal production)
14. Eroded sediments
15. Deforestation
16. Mining
17. Littering
18. Pesticides

19. herbicides and fertilizers
20. Failing septic system
21. House hold chemicals
22. Animal wastes.

But these are categorized in two terms.

1. Point sources
2. Non-point sources

Point sources are the **easiest to identify and control** as, These are direct sources of water pollution and can be reduced and monitored.

- Factories
- Sewage system
- Power plants
- Underground coalmines
- Oil wells

Non-point sources are ambiguously defined and harder to control.

The term non-point source encompasses a large range of sources such as:

- when rain or snow moves through the ground and picks up pollutants as it moves towards a major body of water.
- the runoff of fertilizers from farm animals and crop land.
- air pollutants getting washed or deposited to earth.
- storm water drainage from lawns, parking lots, and streets.

Kinds of water pollutants

- Inorganic Pollutants
- Organic Pollutants
- Biological Pollutants

1.Inorganic Pollutants

•Led (Pb) in gasoline

•Radionuclides

•Phosphorus, nitrogen (Great Lakes)

Inorganic Trace Contaminants

-Mercury—methyl Hg and dimethyl Hg in fish—Minamata Bay, Japan, 1950’s

-Lead—toxicity has been known for a long time

–Tetraethyl lead—anti-knock additive for gas, 1930-1966

Phosphates and Nitrates

•**Phosphates**—mostly a result of sewage outflow and phosphate detergents

–Additional phosphate grows excess algae…oxygen depletion

•**Nitrates**—sewage and fertilizers

2.Organic Pollutants

•Three classes of compounds

1. **–Pesticides and Herbicides**
2. **–Materials for common household and industrial use**
3. **–Materials for industrial use**

3.Pesticides

•Chlorinated hydrocarbons

- –DDT, heptachlor, etc—2-15 years

•Organophosphates

- –Malathion, methyl parathion—1-2 weeks

•Carbamates

- –Carbaryl, maneb, aldicarb—days to weeks

•Pyrethroids

- –Pemethrin, decamethrin—days to weeks

4.Herbicides

•Triazines—e.g. atrazine, paraquat

(interfere with photosynthesis)

•Systemic—phenoxy compounds, N compounds, Alar, glyphosate

(create excess growth hormones)

•Soil sterilants

trifluralin, dalapon

(kill soil microorganisms)

Where is all of this pollution coming from?

Bio-degradable waste

Biodegradable waste consists mainly of human and animal waste. When biodegradable waste enters a water supply, the waste provides an energy source (organic carbon) for bacteria. Organic carbon is converted to carbon dioxide and water, which can cause atmospheric pollution and acid rain; this form of pollution is far more widespread and problematic than other forms of pollutants, such as radioactive waste. If there is a large supply of organic matter in the water, oxygen-consuming (aerobic) bacteria multiply quickly, consume all available oxygen, and kill all aquatic life.

Plant nutrients

Plant nutrients, such as phosphates and nitrates, enter the water through sewage, and livestock and fertilizer runoff. Phosphates and nitrates are also found in industrial wastes. Though these chemicals are natural, 80 percent of nitrates and 75 percent of phosphates in water are human-added. When there is too much nitrogen or phosphorus in a water supply (0.3 parts per million for nitrogen and 0.01 parts per million for phosphorus), algae begin to develop. When algae blooms, the water can turn green and cloudy, feel slimy, and smell bad. Weeds start to grow and bacteria spread. Decomposing plants use up the oxygen in the water, disrupting the aquatic life, reducing biodiversity, and even killing aquatic life. This process, called eutrophication, is a natural process, but generally occurs over thousands of years. Eutrophication allows a lake to age and become more nutrient-rich; without nutrient pollution, this may take 10,000 years, but pollution can make the process occur 100 to 1,000 times faster.

Heat

Heat can be a source of pollution in water. As the water temperature increases, the amount of dissolved oxygen decreases. Thermal pollution can be natural, in the case of hot springs and shallow ponds in the summertime, or human-made, through the discharge of water that has been used to cool power plants or other industrial equipment. Fish and plants require certain temperatures and oxygen levels to survive, so thermal pollution often reduces the aquatic life diversity in the water.

Sediment

Sediment is one of the most common sources of water pollution. Sediment consists of mineral or organic solid matter that is washed or blown from land into water sources. Sediment pollution is difficult to identify, because it comes from non-point sources, such as construction, agricultural and livestock operations, logging, flooding, and city runoff. Each year, water sources in the United States are polluted by over one billion tonnes of sediment! Sediment can cause large problems, as it can clog municipal water systems, smother aquatic life, and cause water to become increasingly turbid. And, turbid water can cause thermal pollution, because cloudy water absorbs more solar radiation.

Hazardous and toxic chemicals

Hazardous and toxic chemicals are usually human-made materials that are not used or disposed of properly. Point sources of chemical pollution include industrial discharges and oil spills. The Oil Pollution fact sheet includes more detailed information about oil spills, as well as other sources of oil pollution. Non-point sources of chemical pollution include runoff from paved roads and pesticide runoff. Many people think industries produce the greatest amount of chemical pollution. But domestic and personal use of chemicals can significantly contribute to chemical pollution. Household cleaners, dyes, paints and solvents are also toxic, and can accumulate when poured down drains or flushed down the toilet. In fact, one drop of used motor oil can pollute 25 litres of water! And, people who use pesticides on their gardens and lawns tend to use ten times more pesticide per acre than a farmer would!

Radioactivity

Radioactive pollutants include wastewater discharges from factories, hospitals and uranium mines. These pollutants can also come from natural isotopes, such as radon. Radioactive pollutants can be dangerous, and it takes many years until radioactive substances are no longer considered dangerous. **Nuclear waste** can have detrimental effects on marine habitats. Mining and refining of uranium and thorium are also causes of marine nuclear waste.

Synthetic Organic Chemicals

These are some organic chemicals which cause water pollution.

i. Household cleaners
ii. Paints
iii. Pesticides and herbicides
iv. Plastics
v. Solvents
vi. Detergents

- These chemicals Reduce populations of desirable organisms
- These chemicals have Tendency to persist and bioaccumulate in the food chain
- They causes Behavioral and structural changes
- They Destroy food sources for higher-order organisms
- They fall Acute or chronic effects in aquatic organisms

Heavy or Trace Metals (e.g. Mercury, Copper, Nickel, Zinc, Selenium)

Heavy metals comes from;

i. Motor fuel and exhaust
ii. Auto brake linings
iii. Leachate from landfills
iv. Illegal hazardous waste disposal/spills

v. Consumer products
vi. Construction materials
vii. Naturally in soil

These metals causes

- These metals causes Bioaccumulation in fish tissues and can
- These metals Disrupt fish reproduction
- These metals can be passed up the food chain
- Human health concerns: eating contaminated
- fish can cause brain damage,
- birth defects and miscarriages

Bacteria & Pathogens

These organisms comes from ;

i. Improperly sited/maintained septic tanks
ii. Leachate from landfills
iii. Untreated municipal sewage
iv. Pet excrement

These organisms create

- Contaminate drinking water supplies
- shellfish beds, recreation areas
- Hepatitis or other infections
- Beach closures, limit recreational activities such as swimming, boating,surfing or diving, prohibitions on shellfish harvesting

Pollutants from industrial sources

Asbestos, Lead, Mercury are main major industrial pollutants which causes water pollution.

Asbestos causes

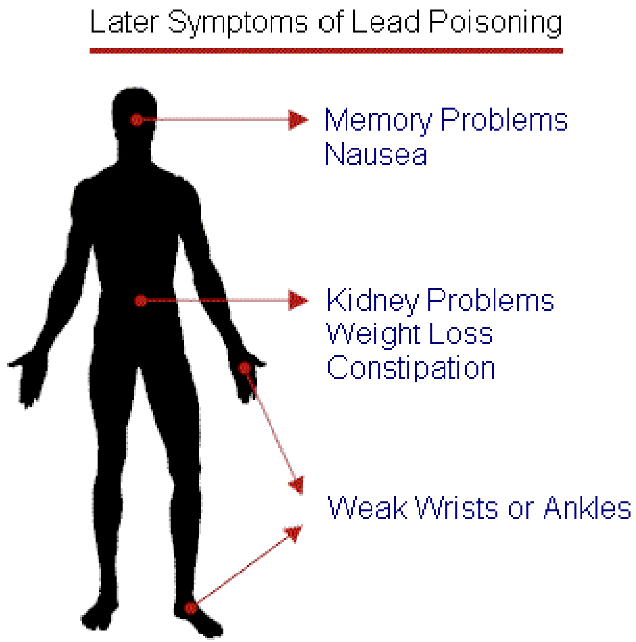
- Asbestosis
- Mesothelioma
- lung cancer
- Intestinal cancer
- liver cancer

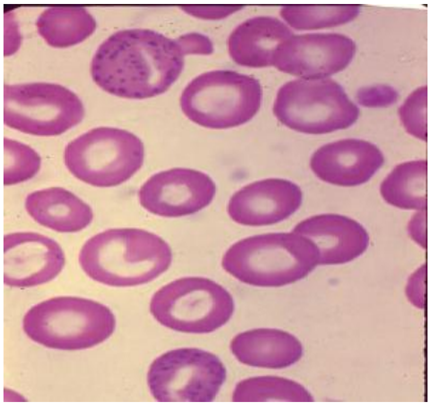
Lead is harmful to the health of many animals, including humans, as it can inhibit the action of bodily enzymes.

Mercury - is harmful to animal health as it can cause illness through mercury poisoning.

Petrochemicals – This is formed from gas or petrol and can be toxic to marine life.

Sulphur – This is a non-metallic substance that is harmful for marine life.





What impact does domestic waste have on water pollution?

The categories of water pollution that domestic waste fits into are biodegradable waste, hazardous and toxic chemical pollutants and PPCPs. Generally, wastewater treatment facilities are equipped to effectively remove harmful substances generated from biodegradable waste. The hazardous and toxic chemicals that individuals release into the environment are more dangerous (and more preventable). Chemicals, such as cleaners, dyes, paints, pesticides and solvents, which are poured down drains, are a substantial and dangerous form of pollution. Wastewater treatment facilities are generally unequipped to remove PPCPs from wastewater; water pollution from PPCPs is a growing concern. For more information about dangerous pollutants that are found in domestic products, see the Emerging Contaminants fact sheet.

What impact does industrial activity have on water pollution?

Industrial pollution comes in a variety of forms. There are many federal regulations regarding types and amounts of pollutants that can be emitted from industries, though in some countries, companies who are over their limit can buy "pollution credit" from companies who are under the targeted amount. Heat pollution is commonly caused by industries, but many regions have passed legislation requiring that power plants and industries cool water before they release it. Construction, mining and logging operations can cause great amounts of sediment to pollute lakes and streams. While agricultural practices are responsible for the most sediment pollution, construction and mining can lose up to 70 tonnes of sediment per acre per year, which is 15 times higher than the normal cropland rate.

What impact does agriculture have on water pollution? The greatest agricultural contributions to water pollution are through nutrient and sediment pollution. Livestock waste and fertilizers contain nitrogen and phosphorus, which, if carried to lakes and streams through runoff, can cause significant problems resulting in excess algae growth.

In the last ten years, the number of livestock in Manitoba has increased by about 65 percent, mostly in the form of pigs and cows. The livestock produce a large amount of waste, which many farmers use as fertilizer on their fields. In the Winnipeg area, thousands of hectares of farmland have been designed for efficient runoff, which minimizes flooding. However, when the water runs off, it carries organic matter from the fertilizers straight into the creeks that feed Lake Winnipeg. Agricultural practices in Manitoba are estimated to be responsible for about 17 percent of the phosphorus problem in Lake Winnipeg. There are several best management practices that can reduce the amount of agricultural water pollution, such as collecting animal wastes in a lagoon, or spraying pesticides in small amounts and at minimal runoff times.

Agricultural practices are the leading cause of sediment pollution, because bare lands are susceptible to large amounts of erosion. Erosion causes problems both for the water source and the farmland, which loses significant amounts of topsoil each year.

Natural Purification of Water

The water cycle driven by sun light ,purifies the water in many ways.Rain,lakes, and ground water therefore tend to be relatively clean of dissolved matter and are usually drinkable in natural state.

Water is purified in nature by a number of processes.But for ease,these are categorized in two terms.

1. **Physical Processes**
2. **Chemical Processes**

Physical processes: There are four physical processes ,involving forces as such gravity. Four are given as ;

1. **Dilution**
2. **Sedimentation**
3. **Filtration**
4. **Aeration**

1. **Dilution:** it is a reduction in concentration of a pollutant when it is discharged into water.It increases as one moves away from the point of pollutant discharge.Faster water increases the rate of dilution.Fast moving streams have ability to remove the waste upto five times more than slow moving streams.
2. **Sedimentation:** Settle down of suspended objects or particles in water is sedimentation.It changes as the size of objects and speed of water vary,Occuring most readily with larger objects and slow moving water. Small sized particles may suspended for a long period in water and covers a long distance.

3. **Filtration:** Filtering of water through sand and other settled sediments to remove the suspended objects in water.Very fine objects or particles can be filtered or removed if water percolates through fine sediments.
4. **Aeration:** It is the release of gaseous impurities into air or atmosphere.Water contains a no.of disloved matters.Aeration is mostly accelerated when more water is exposed to air.It is also effective in hot and faster waters.

Waste Water Treatment Methods

Water can be contaminated by the following agents:

- **Pathogens** – disease-causing organisms that include bacteria, amoebas and viruses, as well as the eggs and larvae of parasitic worms.
- **Harmful chemicals -** from human activities (industrial wastes, pesticides, fertilizers).
- **Chemicals and minerals -** from the natural environment, such as arsenic, common salt and fluorides.

Some **non-harmful contaminants** may influence the taste, smell, colour or temperature of water, and make it unacceptable to the community.

Water from surface sources is often contaminated by microbes, whereas groundwater is normally safer, but even groundwater can be contaminated by harmful chemicals from human activities or from the natural environment. Rainwater captured by a rooftop harvesting system or with small catchment dams is relatively safe, provided that the first water is allowed to flow to waste when the rainy season starts. The amount of water to be treated should also be assessed. This can be estimated by assuming that each person will need a minimum of 20–50 litres of water a day for drinking, cooking, laundry and personal hygiene.

A community should be consulted when choosing a water-treatment system and should be made aware of the costs associated with the technology. In particular, community members should be made aware of the behavioural and/or cultural changes needed to make the system effective over the long-term and thus be acceptable to them.

Communities may also need to be educated about protecting water sources from animal or human contamination, and mobilized. It should be emphasized that all the positive effects of a water-treatment system could be jeopardized if the water is not drawn, stored and transported carefully and hygienically.

Following household and community water-treatment technologies are described in greater detail:

Household water-treatment systems

- boiling
- household slow sand filter
- domestic chlorination

Community water-treatment systems

- storage and sedimentation
- up-flow roughing filter
- slow sand filtration
- chlorination in piped water-supply systems

Straining through fine cloth

Consists in pouring raw waterthrough a piece of fine, clean, cotton cloth to remove some of the suspended solids.

Aeration

Oxidizes iron (Fe) and manganes (Mn). Good aeration of the water is also important for slow, sand filtration to be effective, especially if there is not enough oxygen in the surface water. Water can easily be aerated by shaking it in a vessel, or by allowing it to trickle through perforated trays containing small stones.

Storage/pre-settlement

Storing water for only one day can eliminate some bacteria, but it should be stored for 48 hours to eliminate cercaria (snail larvae). The longer the water is stored, the more the suspended solids and pathogens will settle to the bottom of the container. The top water can then be used after sedimentation.

Coagulation, flocculation and settlement

In coagulation, a liquid coagulant, such as aluminium sulfate, is added to the water to attract suspended particles. The water is then gently stirred to allow the particles to come together and form larger particles (flocculation), which can then be removed by sedimentation, settlement or filtration. The amount of coagulant needed will depend on the nature of the contaminating chemical compounds and solids.

Slow sand filtration

Water passes slowly downwards through a bed of fine sand at a steady rate. The water should not be too turbid, otherwise the filter will get clogged. Pathogens are naturally removed in the top layer where a biological film builds up. A potential problem is that some households do not use this technology effectively and the water can remain contaminated.

Rapid sand filtration

The sand used is coarser than in slow sand filtration and the flow rate is higher. The method is used to remove suspended solids and is effective after the water has been cleared with coagulation/flocculation. There is no build-up of biological film, hence the water will still need to be disinfected. It is easier to remove trapped debris from up flow sand filters, compared to filters in which the water flows downwards.

Charcoal filter

Granular charcoal (or granulated activated carbon) can be used in filtration and is effective in improving the taste, odour and colour of the water. However, it should be replaced regularly, because bacteria can breed in it.

Ceramic filter

The filter is a porous, unglazed ceramic cylinder and impurities are deposited on its surface. Filters with very small pores can remove most pathogens. Open, porous ceramic jars can also be used. The ceramic filter method can only be used with fairly clear water.

Solar disinfection

Ultraviolet radiation from the sun will destroy most pathogens, and increasing the temperature of the water enhances the effectiveness of the radiation. In tropical areas, most pathogens can be killed by exposing the contaminated water to sun for five hours, centred around midday. An easy way to do this, is to expose (half-blackened) clear glass/plastic bottles of water to the sun. Shaking the bottle before irradiation increases the effectiveness of the treatment. The water must be clear for this treatment to be effective.

Chemical disinfection

Chlorination is the most widely used method of disinfecting drinking-water. Liquids (such as bleach), powders (such as bleaching powder), and purpose-made tablets can be used. Iodine can also be used as a chemical disinfectant. Deciding on the right amount of chlorine to use can be difficult, because the effectiveness of chlorination depends on the quality of the untreated water, which may vary according to the season.

Boiling

Bringing the water to a rolling boil will kill most pathogens, and many are killed at lower temperatures (e.g. 70 °C). This approach can be expensive, however, because fuel/charcoal is needed to boil the water.

Desalination/evaporation

Desalination by distillation produces water without chemical salts and the method can be used at household level. The method can be expensive because of the capital investment needed and because fuel/charcoal is used to heat the water. The volume of water produced is also low.

Should water be chlorinated?

The water-treatment methods described above can reduce the number of pathogens in water, but do not always eliminate them completely. And although boiling and solar disinfection are effective, the methods are impractical with large volumes of water. In contrast, chemical disinfection inactivates pathogenic organisms and the method can be used with large volumes of water.

Chlorine compounds usually destroy pathogens after30 minutes of contact time, and free residual chlorine (0.2–0.5 mg per litre of treated water) can be maintained in the water supply to provide ongoing disinfection.

Several chlorine compounds, such as sodium hypochlorite and calcium hypochlorite, can be used domestically, but the active chlorine concentrations of such sources can be different and this should be taken into account when calculating the amount of chlorine to add to the water.

The amount of chlorine that will be needed to kill the pathogens will be affected by the quality of the untreated water and by the strength of the chlorine compound used. If the water is excessively turbid, it should be filtered or allowed to settle before chlorinating it.

Reducing the concentration of chemicals in water

Iron and manganese Water collected from boreholes can have a high concentration of iron (greater than 0.3 mg/l, the WHO guideline value). This can be the result of a naturally high iron content in the soil, or the result of corrosion (from iron pipes, borehole casings and screens).

The iron gives the water an unpleasant metallic taste and odour, stains laundry and white enamel on sinks and bowls, and discolours food. Although such levels of iron are not known to be harmful, the undesirable properties can cause communities to accept contaminated water that has no taste, instead of safe water that has a metallic taste.

Most of the iron can be removed simply, by aerating the water and filtering it through sand and gravel. The sand and gravel used in the filters will need to be cleaned periodically. Similar problems arise when water has excessive manganese concentrations (above0.1 mg/l, the WHO guideline value), but again the water can be treated by aeration, followed by filtration and settlement.

Fluoride

High concentrations of fluoride (above 1.5 mg/l, the WHO guideline value) can damage bones and teeth. Low-cost treatment methods include the Nalgonda system (which uses lime to soften the water), and using alum as a coagulant. With either treatment, the water is then left to settle at the same time it is being chlorinated.

Arsenic

Arsenic is widely distributed throughout the Earth's crust and enters water as dissolved minerals. It can also enter water bodies in industrial effluents, or by deposition from the atmosphere. Arsenic concentrations greater than the WHO guideline value of 0.01 mg/l are toxic. Simple treatment methods include adding lime to soften the water, or adding alum as a coagulant, followed by settlement. When arsenic (or fluoride) is to be removed at household level, the implementation should always be carefully planned and supported by the community.

Solar disinfection

The principle underlying solar disinfection is that microorganisms are vulnerable to light and heat. One easy and simple way to treat water is to use the SODIS system (Solar Disinfection), which has been tested both in the laboratory and in the field. A transparent container is filled with water and exposed to full sunlight for several hours.

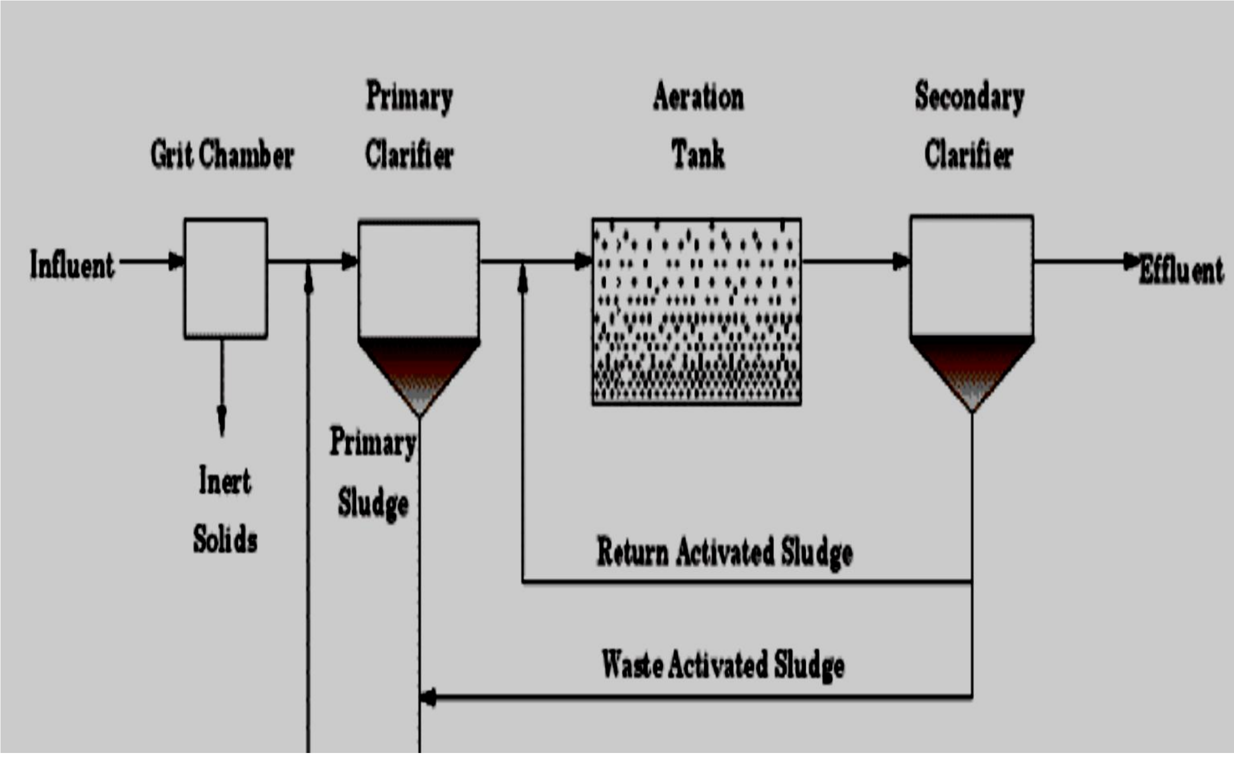
As soon as the water temperature reaches 50 °C, the inactivation process is accelerated and usually leads to complete bacteriological disinfection. More information on this method can be obtained from the Swiss Federal Institute for Environmental Science and Technology (EAWAG).

Secondary (Biological) Treatment:

The activated sludge process:

- **Is a form of aerobic biological treatment for reducing soluble BOD (dissolved organic matter.**
- **Involves the suspension of microorganisms within the wastewater in a reactor (aeration tank or basin) -- A suspended growth process.**

Recycles a portion of the microorganisms back into the reactor, which decouples micro-organism retention time ("solids retention time") from hydraulic residence time [microorganism concentration is independent of hydraulic residence time]



TERTIARY TREATMENT

Tertiary or advanced wastewater treatment is usually considered to be any treatment beyond conventional secondary treatment to remove suspended or dissolved substances. Tertiary wastewater treatment can have one or several objectives. One common objective is further reduction in suspended solids concentration after secondary clarification. Nitrogen and phosphorus removal also are common tertiary wastewaters treatment objectives. Existing wastewater treatment plants can be retrofit without the addition of new tanks or lagoons to incorporate biological nutrient removal (Randall et al., 1999). In addition, tertiary wastewater treatment can be used to remove soluble refractory, toxic, and dissolved inorganic substances. In the treatment of MPP wastewaters, tertiary wastewater treatment is most commonly used for further reductions in nutrients and suspended solids.

Water Quality Criteria

Idaho's water quality standards prescribe certain criteria that must be met to ensure the beneficial uses of the state's surface waters are supported. These criteria can be numeric or narrative. Numeric criteria are use-specific, while narrative criteria are general, applying to all waters regardless of use. Federal water quality standard regulations require that together, the numeric and narrative criteria must contain sufficient parameters or constituents to protect the beneficial use.

Common Water Quality Measures

Some of the more common measures of water quality are temperature, turbidity, bacteria, dissolved oxygen, and pH. Less common are measurements of sediment and nutrients. Rarely, or in limited locations, measurements of toxic substances such as metals, pesticides, and ammonia are available. All are important in influencing the health or utility of a water body.

Numeric Water Quality Criteria

Individual numeric criteria are based on specific data and scientific assessment of adverse effects. Numeric guidelines assign numbers that represent limits and/or ranges of chemical concentrations, like dissolved oxygen, or physical conditions, like water temperature.

Narrative Water Quality Criteria

To supplement numeric criteria, Idaho has adopted narrative criteria, which are statements that describe the desired water quality goal, such as Idaho's waters being "free from" pollutants. These "fuzzy" criteria require much case-by-case interpretation but are important in bridging gaps in knowledge.

Site-Specific Water Quality Criteria

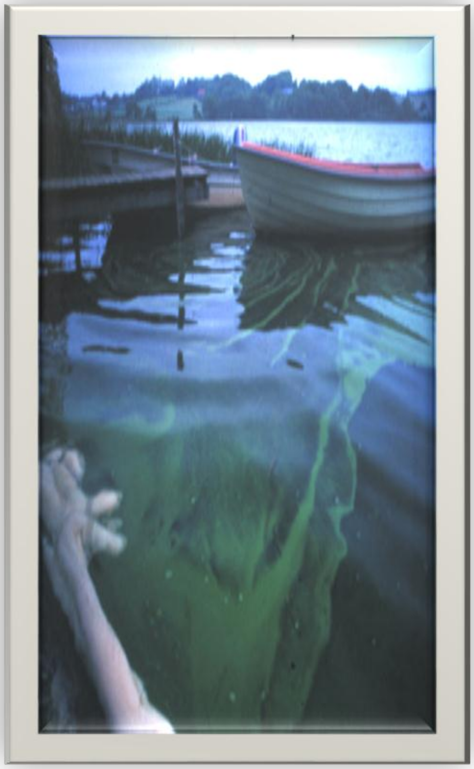
IAfter site-specific analyses in some water bodies, it may be prudent to develop alternative criteria. Site-specific criteria may be developed to more appropriately regulate sources of pollution while still protecting designated and existing beneficial uses. These new criteria would then be applicable only to the segment for which they were developed.

Toxic Substance Criteria

A toxic substance is any substance, material, or disease-causing agent that, upon exposure, ingestion, inhalation, or assimilation into an organism will cause death, disease, malignancy, physical deformations, or other abnormalities in affected organisms or their offspring. Toxic criteria exist to protect both aquatic life and human health. Because aquatic life and human health differ in sensitivity to various toxins, the parameters for which criteria are set, as well as their levels, usually differ as well.

Eutrophication

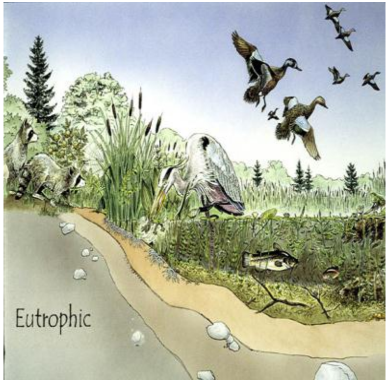
The process by which a body of water progresses from its origin to its extinction. This process happens in stages.

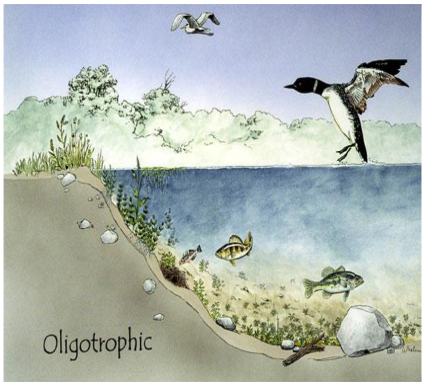


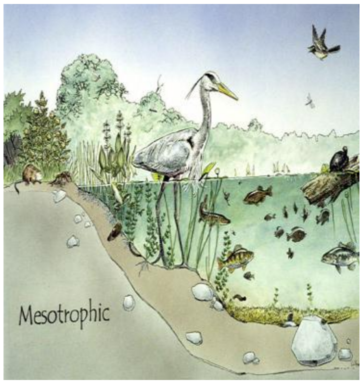
- Eutrophication is the accumulation of nutrients in aquatic ecosystems. OR
- Eutrophication are Harmful changes in water caused by too much fertilizer or nutrients getting into the water. OR
  - The increase in organic matter leading to the over enrichment of a system.

- It alters the dynamics of a number of plant, animal and bacterial populations; thus, bringing about changes in community structure.
- It is a form of water pollution and like all other forms of pollution is the result of human activities influencing ecological cycles.

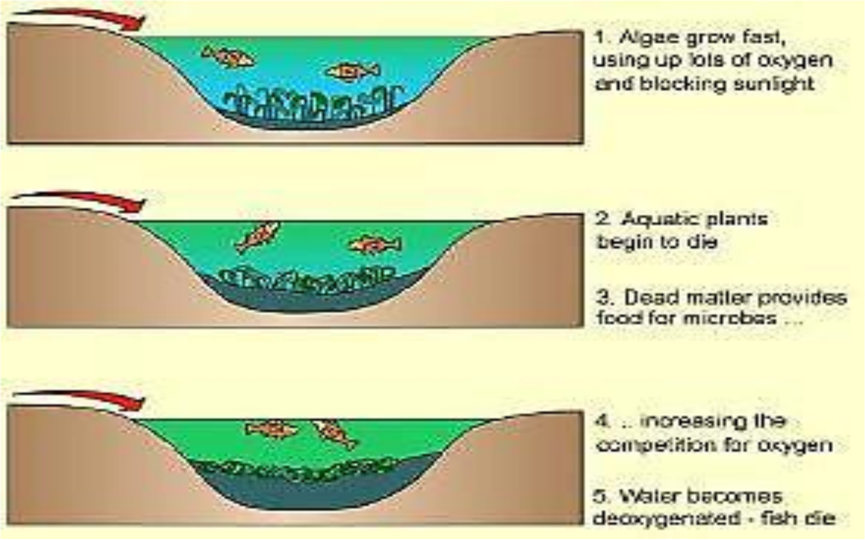
Natural Eutrophication : a process that occurs as a lake or river ages over a period of hundreds or thousands of years.







Cultural Eutrophication : a process that occurs when humans release excessive amounts of nutrients; it shortens the rate of aging to decades.



Organic Matter created by primary producers

Phytoplankton or Algae

- Feed on CO2, Sunlight, and
- Nutrients, the limiting factor

Primary Nutrients

Nitrogen and Phosphorus

- Major Sources vary by Location

Long Island Sound

- 60% of nitrogen load from wastewater of NYC

Chesapeake Bay

- 25% of N and P loads from point sources

Mississippi River

- 10% of N and 40% P form point sources

Non Point Sources

- Erosion of soil
  - Major phosphorus additions
- Agricultural Runoff
  - Manures and fertilizers
- Atmospheric Deposition
  - Fossil Fuel Combustion

Aquatic Interaction

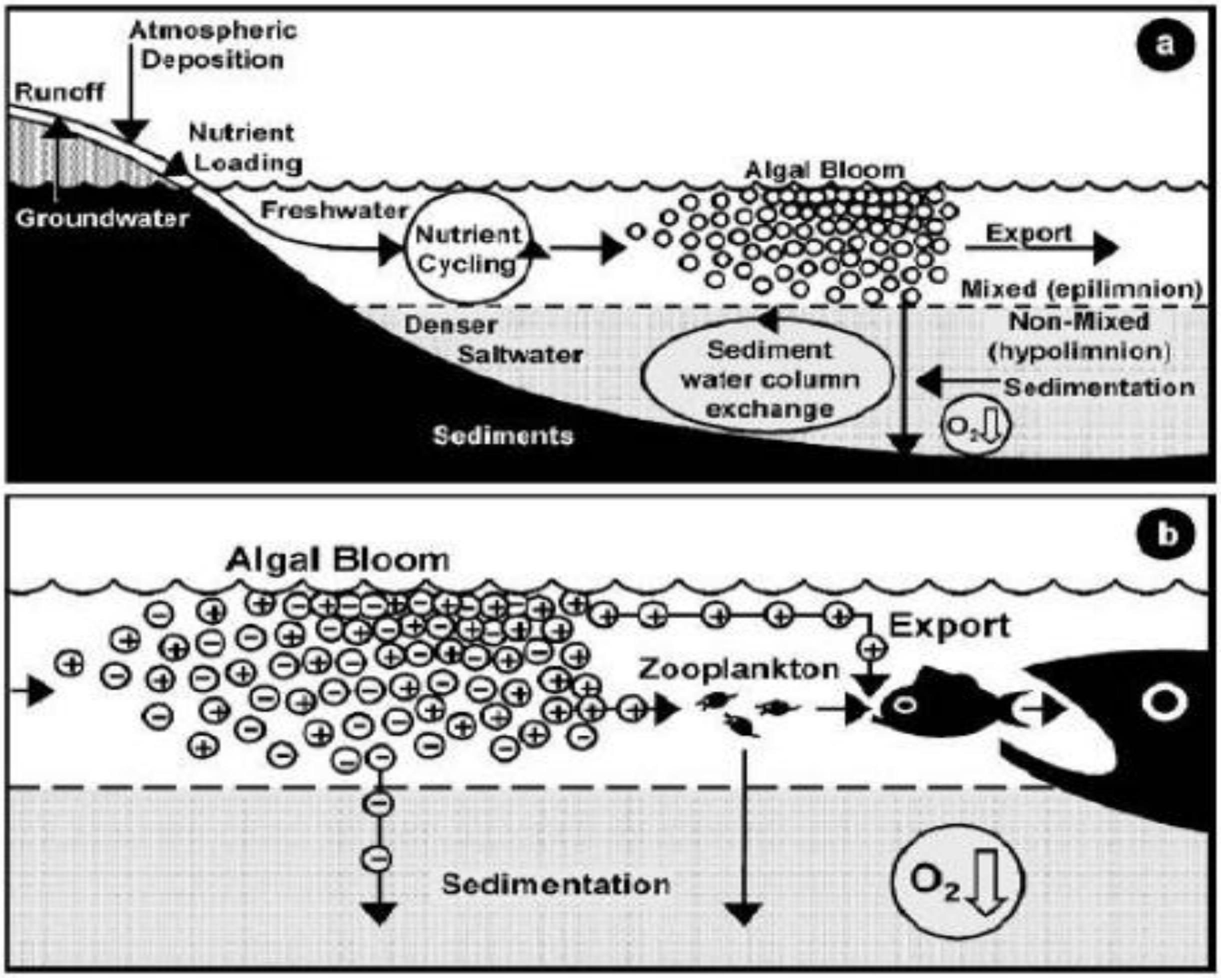
- Phytoplankton Nutrient Consumption
- Phytoplankton Community Change
    - Dinofagellate
    - Cyanobacteria
- Unconsumed Phytoplankton
    - Fall to Bottom Waters

- Microbes Breakdown

Phytoplankton

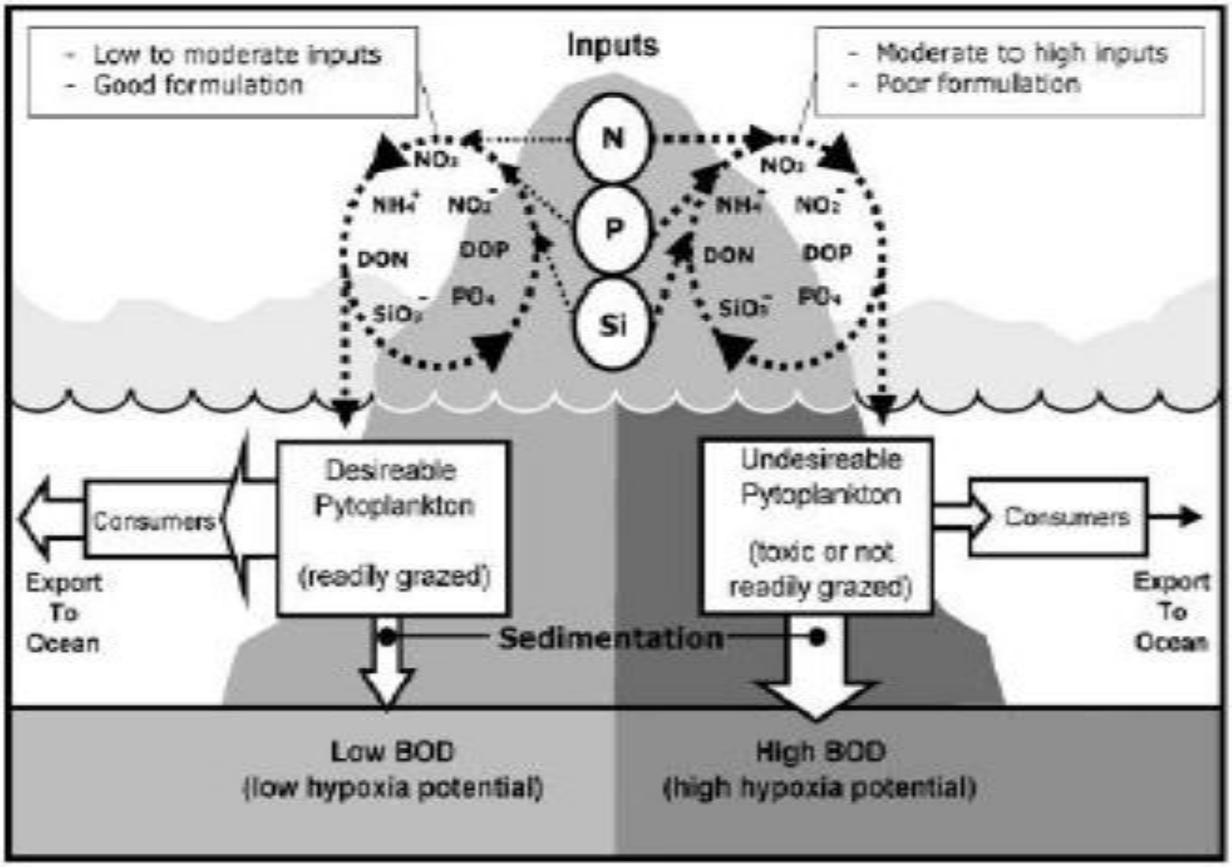
- Use Oxygen during Process

Aquatic Interactions



Massive Algae Blooms

- Block Light to Plants Below Habitat for Smaller Species is Destroyed



Major Physical Parameter

- Discharge Rate
    - Residence Time
    - Oxygen Replenishment
    - Break Stratification

Interactions Result

- Oxygen Depletion by Microbes
- Blooms Blocking Light
    - No Food or Oxygen
        - Mobile Organisms Move
        - Stationary Organisms Die

Harmful Algae Blooms

- Unconsumed Blooms
- Toxic Blooms
    - Can Cause Death to
        - Fish
        - Sea Birds
        - Aquatic Mammals
        - Also Death or Illness to humans

Detergents

Detergents are organic compounds, which have both polar and non-polar characteristics. They tend to exist at phase boundaries, where they are associated with both polar and non-polar media. Detergents are of three types: **anionic, cationic,** and **non-ionic**. **Anionic** and **cationic** have permanent negative or positive charges, attached to non-polar (hydrophobic) C-C chains. **Non-ionic detergents** have no such permanent charge; instead, they have a number of atoms which are weakly electropositive and electronegative. This is due to the electron-attracting power of oxygen atoms.

kinds of Detergents

There are two kinds of detergents with different characteristics:

- **phosphate detergents**
- **surfactant detergents.**

Detergents that contain phosphates are highly **caustic,** and surfactant detergents are **very toxic**.

The differences are that

- surfactant detergents are used to enhance the wetting, foaming, dispersing and emulsifying properties of detergents.
- Phosphate detergents are used in detergents to soften hard water and help suspend dirt in water.

What do we use them for?

Detergents are very widely used in both industrial and domestic premises like soaps and detergents to wash vehicles. The major entry point into water is via sewage works into surface water. They are also used in pesticide formulations and for dispersing oil spills at sea. The degradation of alkylphenol polyethoxylates (non-ionic) can lead to the formation of alkylphenols (particularly nonylphenols), which act as endocrine disruptors.

High phosphate detergents such as tri-sodium phosphate (TSP) can be purchased at some paint and hardware stores. Regular cleaning with high phosphate detergents has proven to be effective in reducing lead dust. Lead dust accumulates in window wells and around doors or any other high friction surfaces.

What occurs if detergents show up in freshwaters?

Detergents can have poisonous effects in all types of aquatic life if they are present in sufficient quantities, and this includes the biodegradable detergents. All detergents destroy the external mucus layers that protect the fish from bacteria and parasites; plus they can cause severe damage to the gills. Most fish will die when detergent concentrations approach 15 parts per million. Detergent concentrations as low as 5 ppm will kill fish eggs. Surfactant detergents are implicated in decreasing the breeding ability of aquatic organisms.

Detergents also add another problem for aquatic life by lowering the surface tension of the water. Organic chemicals such as pesticides and phenols are then much more easily absorbed by the fish. A detergent concentration of only 2 ppm can cause fish to absorb double the amount of chemicals they would normally absorb, although that concentration itself is not high enough to affect fish directly.

Phosphates in detergents can lead to freshwater algal blooms that releases toxins and deplete oxygen in waterways. When the algae decompose, they use up the oxygen available for aquatic life.

The main contributors to the toxicity of detergents were the sodium silicate solution and the surfactants-with the remainder of the components contributing very little to detergent toxicity. The potential for acute aquatic toxic effects due to the release of secondary or tertiary sewage effluents containing the breakdown products of laundry detergents may frequently be low. However, untreated or primary treated effluents containing detergents may pose a problem. Chronic and/or other sublethal effects that were not examined in this study may also pose a problem.

Phosphates in water and their removal

Phosphates are chemical compounds containing phosphorus. Phosphorus is a non-metallic element which is necessary for life and is found in rock as inorganic phosphates. As water runs over and through rocks it carries off small amounts of minerals such as calcium, magnesium, and phosphates. Inorganic phosphates are a plant nutrient and are taken in by plants with water and incorporated into organic phosphate compounds. Animals obtain their essential phosphorus from phosphates in water and plant material. Natural waters have a phosphorus concentration of approximately 0.02 parts per million (ppm) which is a limiting factor for plant growth. On the other hand, large concentrations of this nutrient can accelerate plant growth.

Phosphates enter waterways through man made sources also. Per capita we contribute approximately 3.5 pounds of phosphate yearly to our environment . The addition of large quantities of phosphates to waterways accelerates algae and plant growth in natural waters; enhancing eutrophication and depleting the water body of oxygen. This can lead to fish kills and the degradation of habitat with loss of species. Large mats of algae can form and in severe cases can completely cover small lakes. As a result, water can become putrid from decaying organic matter. When the concentration of phosphates rises above 100 mg/liter the coagulation processes in drinking water treatment plants may be adversely affected. Manmade sources of phosphate include human sewage, agricultural run-off from crops, sewage from animal feedlots, pulp and paper industry, vegetable and fruit processing, chemical and fertilizer manufacturing, and detergents.

Nitrogen removal

Nitrogen is removed through the biological oxidation of nitrogen from ammonia to nitrate (nitrification), followed by denitrification, the reduction of nitrate to nitrogen gas. Nitrogen gas is released to the atmosphere and thus removed from the water.

Nitrification itself is a two-step aerobic process, each step facilitated by a different type of bacteria. The oxidation of ammonia (NH_3) to nitrite (NO_2^-) is most often facilitated by Nitrosomonas spp. ("nitroso" referring to the formation of a nitroso functional group). Nitrite oxidation to nitrate (NO_3^-), though traditionally believed to be facilitated by Nitrobacter spp. (nitro referring the formation of a nitro functional group), is now known to be facilitated in the environment almost exclusively by Nitrospira spp.

Denitrification requires anoxic conditions to encourage the appropriate biological communities to form. It is facilitated by a wide diversity of bacteria. Sand filters, lagooning and reed beds can all be used to reduce nitrogen, but the activated sludge process (if designed well) can do the job the most easily. Since denitrification is the reduction of nitrate to dinitrogen (molecular nitrogen) gas, an electron donor is needed. This can be, depending on the wastewater, organic matter (from feces), sulfide, or an added donor like methanol. The sludge in the anoxic tanks (denitrification tanks) must be mixed well (mixture of recirculated mixed liquor, return activated sludge [RAS], and raw influent) e.g. by using submersible mixers in order to achieve the desired denitrification.

Sometimes the conversion of toxic ammonia to nitrate alone is referred to as tertiary treatment.

Many sewage treatment plants use centrifugal pumps to transfer the nitrified mixed liquor from the aeration zone to the anoxic zone for denitrification. These pumps are often referred to as Internal Mixed Liquor Recycle (IMLR) pumps.

The bacteria Brocadia anammoxidans, is being researched for its potential in sewage treatment. It can remove nitrogen from waste water.[12] In addition the bacteria can perform the anaerobic oxidation of ammonium and can produce the rocket fuel hydrazine from waste water.

Phosphorus removal

Every adult human excretes between 200 and 1000 grams of phosphorus annually. Studies of United States sewage in the late 1960s estimated mean per capita contributions of 500 grams in urine and feces, 1000 grams in synthetic detergents, and lesser variable amounts used as corrosion and scale control chemicals in water supplies.[15] Source control via alternative detergent formulations has subsequently reduced the largest contribution, but the content of urine and feces will remain unchanged. Phosphorus removal is important as it is a limiting nutrient for algae growth in many fresh water systems. (For a description of the negative effects of algae, see Nutrient removal). It is also particularly important for water reuse systems where high phosphorus concentrations may lead to fouling of downstream equipment such as reverse osmosis.

Phosphorus can be removed biologically in a process called enhanced biological phosphorus removal. In this process, specific bacteria, called polyphosphate-accumulating organisms (PAOs), are selectively enriched and accumulate large quantities of phosphorus within their cells (up to 20 percent of their mass). When the biomass enriched in these bacteria is separated from the treated water, these bio solids have a high fertilizer value.

Phosphorus removal can also be achieved by chemical precipitation, usually with salts of iron (e.g. ferric chloride), aluminum (e.g. alum), or lime.[7]:18 This may lead to excessive sludge production as hydroxides precipitates and the added chemicals can be expensive. Chemical phosphorus removal requires significantly smaller equipment footprint than biological removal, is easier to operate and is often more reliable than biological phosphorus removal.Another method for phosphorus removal is to use granular laterite.

Once removed, phosphorus, in the form of a phosphate-rich sewage sludge, may be dumped in a landfill or used as fertilizer. In the latter case, the treated sewage sludge is also sometimes referred to as biosolids

Detrimental effects

Toxic heavy metals "can bind to vital cellular components, such as structural proteins, enzymes, and nucleic acids, and interfere with their functioning. Symptoms and effects can vary according to the metal or metal compound, and the dose involved. Broadly, long-term exposure to toxic heavy metals can have carcinogenic, central and peripheral nervous system and circulatory effects. For humans, typical presentations associated with exposure to any of the "classical" toxic heavy metals, or chromium (another toxic heavy metal) or arsenic (a metalloid), are shown in the table.

Element	**Acute exposure** usually a day or less	**Chronic exposure** often months or years
Cadmium	Pneumonitis (lung inflammation)	Lung cancer Osteomalacia (softening of bones) Proteinuria (excess protein in urine; possible kidney damage)
Mercury	Diarrhea Fever Vomiting	Stomatitis (inflammation of gums and mouth) Nausea Nephrotic syndrome (nonspecific kidney disorder) Neurasthenia (neurotic disorder)

		Parageusia (metallic taste) Pink Disease (pain and pink discoloration of hands and feet) Tremor
Lead	Encephalopathy (brain dysfunction) Nausea Vomiting	Anemia Encephalopathy Foot drop/wrist drop (palsy) Nephropathy (kidney disease)
Chromium	Gastrointestinal hemorrhage (bleeding) Hemolysis (red blood cell destruction) Acute renal failure	Pulmonary fibrosis (lung scarring) Lung cancer
Arsenic	Nausea Vomiting Diarrhea Encephalopathy Multi-organ effects Arrhythmia Painful neuropathy	Diabetes Hypopigmentation/Hyperkeratosis Cancer

Phosphorus Removal

Advanced waste treatment normally requires removal of phosphorus to reduce algal growth. Algae may grow at PO_4^{3-} levels as low as 0.05 mg/L. Growth inhibition requires levels well below 0.5 mg/L. Since municipal wastes typically contain approximately 25 mg/L of phosphate (as orthophosphates, polyphosphates,

and insoluble phosphates), the efficiency of phosphate removal must be quite high to prevent algal growth. This removal may occur in the sewage treatment process (1) in the primary settler; (2) in the aeration chamber of the activated sludge unit; or (3) after secondary waste treatment. Activated sludge treatment removes about 20% of the phosphorus from sewage.
Thus, an appreciable fraction of largely biological phosphorus is removed with the sludge. Detergents and other sources contribute significant amounts of phosphorus to domestic sewage and considerable phosphate ion remains in the effluent. However, some wastes, such as carbohydrate wastes from sugar refineries, are so deficient in phosphorus that supplementation of the waste with inorganic phosphorus is required for proper growth of the microorganisms degrading the wastes.

Under some sewage plant operating conditions, much greater than normal phosphorus removal has been observed. In such plants, characterized by high dissolved oxygen and high pH levels in the aeration tank, removal of 60-90% of the phosphorus has been attained, yielding two or three times the normal level of phosphorus in the sludge. In a conventionally operated aeration tank of an activated sludge plant, the CO_2 level is relatively high because of release of the gas by the degradation of organic material. A high CO_2 level results in a relatively low pH, due to the presence of carbonic acid. The aeration rate is generally not maintained at a very high level because oxygen is transferred relatively more efficiently from air when the dissolved oxygen levels in water are relatively low. Therefore, the aeration rate normally is not high enough to sweep out sufficient dissolved carbon dioxide to bring its concentration down to low levels. Thus, the pH generally is low enough that phosphate is maintained primarily in the form of the $H_2PO_4^-$ ion. However, at a higher rate of aeration in a relatively hard water, the CO_2 is swept out, the pH rises, and reactions such as the following occur:

$$5Ca^{2+} + 3HPO_4^{2-} + H_2O \rightarrow Ca_5OH(PO_4)_3(s) + 4H^+$$

The precipitated hydroxyapatite or other form of calcium phosphate is incorporated in the sludge floc. Reaction 8.9.3 is strongly hydrogen ion-dependent, and an increase in the hydrogen ion concentration drives the equilibrium back to the left. Thus, under anaerobic conditions when the sludge medium becomes more acidic due to higher CO_2 levels, the calcium returns to solution.

Chemically, phosphate is most commonly removed by precipitation. Some common precipitants and their products are shown in Table .Precipitation processes are capable of at least 90-95% phosphorus removal at reasonable cost.

Table : **Chemical Precipitants for Phosphate and Their Products**

Precipitant(s)	Products
$Ca(OH)_2$	$Ca_5OH(PO_4)_3$ (hydroxyapatite)
$Ca(OH)_2$ + NaF	$Ca_5F(PO_4)_3$ (fluorapatite)
$Al_2(SO_4)_3$	$AlPO_4$
$FeCl_3$	$FePO_4$
$MgSO_4$	$MgNH_4PO_4$

Lime, $Ca(OH)_2$, is the chemical most commonly used for phosphorus removal:

$$5Ca(OH)_2 + 3HPO_4^{2-} \rightarrow Ca_5OH(PO_4)_3(s) + 3H_2O + 6OH^-$$

Lime has the advantages of low cost and ease of regeneration. The efficiency with which phosphorus is removed by lime is not as high as would be predicted by the low solubility of hydroxyapatite, $Ca_5OH(PO_4)_3$. Some of the possible reasons for this are slow precipitation of $Ca_5OH(PO_4)_3$, formation of nonsettling colloids; precipitation of calcium as $CaCO_3$ in certain pH ranges, and the fact that phosphate may be present as condensed phosphates (polyphosphates) which form soluble complexes with calcium ion.

Phosphate can be removed from solution by adsorption on some solids, particularly activated alumina, Al_2O_3. Removals of up to 99.9% of orthophosphate have been achieved with this method.

Nitrogen Removal

Next to phosphorus, nitrogen is the algal nutrient most commonly removed as part of advanced wastewater treatment. Nitrogen in municipal wastewater generally is present as organic nitrogen or ammonia. Ammonia is the primary nitrogen product produced by most biological waste treatment processes. This is because it is expensive to aerate sewage sufficiently to oxidize the ammonia to nitrate through the action of nitrifying bacteria. If the activated sludge process is operated under conditions such that the nitrogen is maintained in the form of ammonia, the latter may be stripped in the form of NH_3 gas from the water by air. For ammonia stripping to work, the ammoniacal nitrogen must be converted to volatile NH_3 gas, which requires a pH substantially higher than the pKa of the

NH_4^+ ion. In practice, the pH is raised to approximately 11.5 by the addition of lime (which also serves to remove phosphate). The ammonia is stripped from the water by air.

Nitrification followed by denitrification is arguably the most effective technique for the removal of nitrogen from wastewater. The first step is an essentially complete conversion of ammonia and organic nitrogen to nitrate under strongly aerobic conditions, achieved by more extensive than normal aeration of the sewage:

$$NH_4^+ + 2O_2 \text{ (Nitrifying bacteria) } \rightarrow NO_3 + 2H^+ + H_2O$$

Common Processes for the Removal of Nitrogen from Wastewater

Process

Air stripping ammonia

Principles and conditions

Ammonium ion is the initial product of biodegradation of nitrogen waste. It is removed by raising the pH to approximately 11 with lime, and stripping ammonia gas from the water by air in a stripping tower. Scaling,icing, and air pollution are the main disadvantages.

Process

Ammonium ion exchange

Principles and conditions

Clinoptilolite, a natural zeolite, selectively removes ammonium ion by ion exchange:

$$Na^{+}\{\text{-clinoptilolite}\} + NH_4^{+} \rightarrow NH_4^{+}\{\text{-clinoptilolite}\} + Na^{+}.$$

The ion exchanger is regenerated with sodium or calcium salts.

Process

Biosynthesis

Principles and conditions

The production of biomass in the sewage treatment system and its subsequent removal from the sewage effluent result in a net loss of nitrogen from the system.

Process

Nitrification-denitrification

Principles and conditions

This approach involves the conversion of ammoniacal nitrogen to nitrate by bacteria under aerobic conditions,

$$2NH_4^{+} + 3O_2 \text{ Nitrosomonas } 4H^{+} + 2NO_2^{-} + 2H_2O$$

$$2NO_2^{-} + O_2 \text{ Nitrobacter } 2NO_3^{-}$$

followed by production of elemental nitrogen (denitrification):

$$4NO_3^{-} + 5\{CH_2O\} + 4H^{+} \rightarrow 2N_2(g) + 5CO_2(g) + 7H_2O$$

Typically, denitrification is carried out in an anaerobic column with added methanol as a food source (microbial reducing agent).

Process

Chlorination

Principles and conditions

Reaction of ammonium ion and hypochlorite (from chlorine) results in denitrification by chemical reactions:

$$NH_4^{+} + HOCl \rightarrow NH_2Cl + H_2O + H^{+}$$

$$2NH_2Cl + HOCl \rightarrow N_2(g) + 3H^{+} + 3\,Cl^{-} + H_2O$$

The second step is the reduction of nitrate to nitrogen gas. This reaction is also bacterially catalyzed and requires a carbon source and a reducing agent such as methanol, CH_3OH.

$$6NO_3^- + 5CH_3OH + 6H^+ \text{ (Denitrifying bacteria)} \rightarrow 3N_2(g) + 5CO_2 + 13H_2O$$

The denitrification process may be carried out either in a tank or on a carbon column. In pilot plant operation, conversions of 95% of the ammonia to nitrate and 86% of the nitrate to nitrogen have been achieved.

Organic Matters in Water & Its Decomposition

What are Organic Matters?

OM is matter composed of organic compounds that has come from the remains of organisms such as plants and animals and their waste products in the environment. Organic Chemical is any compound that contains Carbon.Natural Organic Matter (NOM) is the organic material present in surface or ground water. Common NOM compounds include **proteins, polysaccharides**, and **humic substances.** Organic matter is connected to life. OM is also connected to energy. Organic molecules can also be made by chemical reactions that don't involve life.

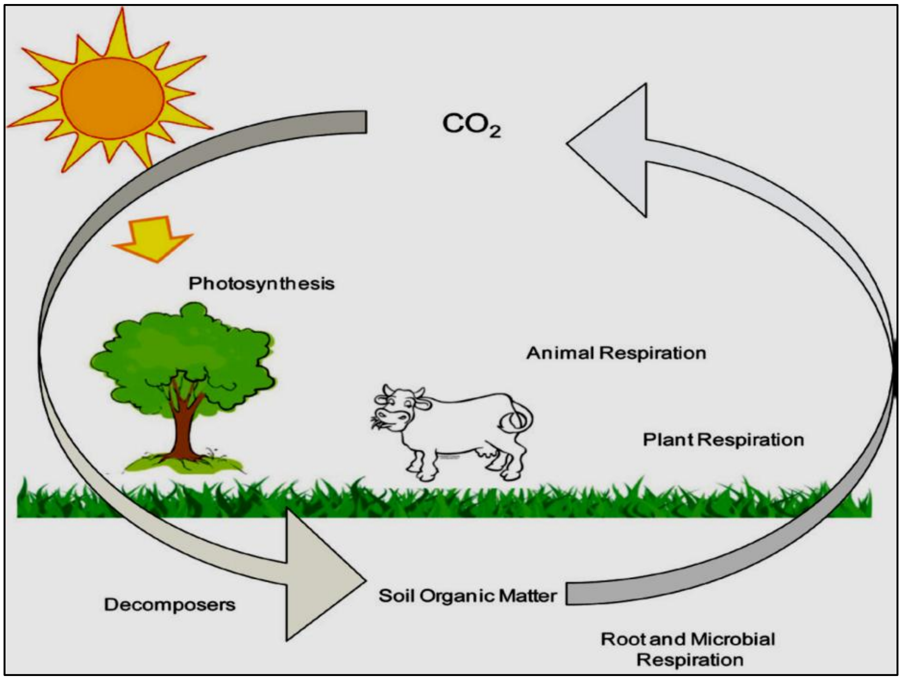
The Connection between Organic Matter and Energy

Simply, nature stores energy using carbon. Take crops growing in a field. Plants use energy from sunlight, carbon dioxide (CO_2) from the air, and moisture from the soil to create carbohydrates (CH_2O) through photosynthesis. Written as a simple chemical formula**, photosynthesis** is:

$$CO_2 + H_2O + \text{energy} \rightarrow CH_2O + O_2$$

Also, remember plants use photosynthesis to clean CO_2 and add oxygen (O_2) to the atmosphere.

We will come back to the O_2 a little later. For now, think of photosynthesis as storing a portion of the sun's energy as OM. If you don't believe OM is stored energy, stand in front of logs burning in a fireplace, or try to outrun a grass fire. The heat you feel was once sunlight before photosynthesis converted it to OM.



Fortunately for life on earth, other living creatures can unlock the energy stored in OM for their own use (Fig. 1). When a cow eats grass, she is harvesting the same energy that the prairie fire releases. Some types of OM contain more energy than others. It is easier to fatten a cow on grain than grass, because OM in the grain (starch) is more digestible than OM in grass (cellulose). The cow stores energy as fat – which is even more energy rich than cellulose or starch.

Oxygen is a key ingredient in unlocking the energy stored in OM. Whether chemical (combustion) or biological (metabolism), O_2 is consumed in aerobic conversion of OM to energy. A simplified chemical formula for the process is:

$$OM + O_2 \rightarrow CO_2 + H_2O + energy$$

In combustion, energy is released as heat. Living creatures use metabolic energy from OM to live, grow, and reproduce. They release some of the energy as heat. Warm blooded creatures use a portion of the metabolic heat to maintain an elevated body temperature.

Not all life on earth requires oxygen to live. Anaerobic organisms,organisms that live in the absence of O_2, also tap into the energy stored in OM. Anaerobic digestion is an industrial process that harnesses energy from OM conversion. A simplified chemical formula for anaerobic digestion is:

$$OM + heat \rightarrow CH_4 + CO_2 + H_2O + energy$$

Notice that energy in the form of heat appears on the left hand side of the formula. Anaerobic organisms need warm temperatures (20^o C and above) to make the process work efficiently.

Some of the energy released from OM is stored as CH_4 (Methane). Methane is a flammable gas, and we can release its stored energy through combustion:

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2O + heat$$

So, if a digester uses heat from burning methane, and we combine the metabolism and combustion parts of digestion, we end up with the same equation as aerobic conversion to energy:

$$OM + O_2 \rightarrow CO_2 + H_2O + energy$$

Oxygen Demand and Respiration

Organic Matter content of a pollutant is measured indirectly by observing the amount of oxygen needed to digest it. The two basic measurements of oxygen use are Oxygen Demand and Respiration Rate. Oxygen demand is the total amount of O2 required to aerobically degrade OM. Oxygen demand is further divided into Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD). Respiration rate is the rate at which O2 is removed from the atmosphere or water.

Classification of NOM

NOM is generally classified into two components.

1. Humic substances (HSs)
2. Non-humic substances (nHSs).

- Humic substances are usually the major components of NOM in water with humic acids (HAs) and fulvic acids (FAs) as the major fractions.
- The major fractions of Non-humic substances are proteins, polysaccharides, and carboxylic acids.

Both humic acids and fulvic acids(FAs) represent a broad class of heterogeneous organic materials. Because of their complexity and heterogeneity, they cannot be well characterized in terms of a specific chemical structure.

Properties of NOM

The most important properties of these substances are

- Molecular weight
- Functional groups
- Charge behavior

HAs and FAs are macro-molecules with molecular weights of several hundred or higher. Has and FAs carry weakly acidic functional groups such as carboxylic and phenolic groups. Dissociation of these functional groups induces negative charges of HAs.

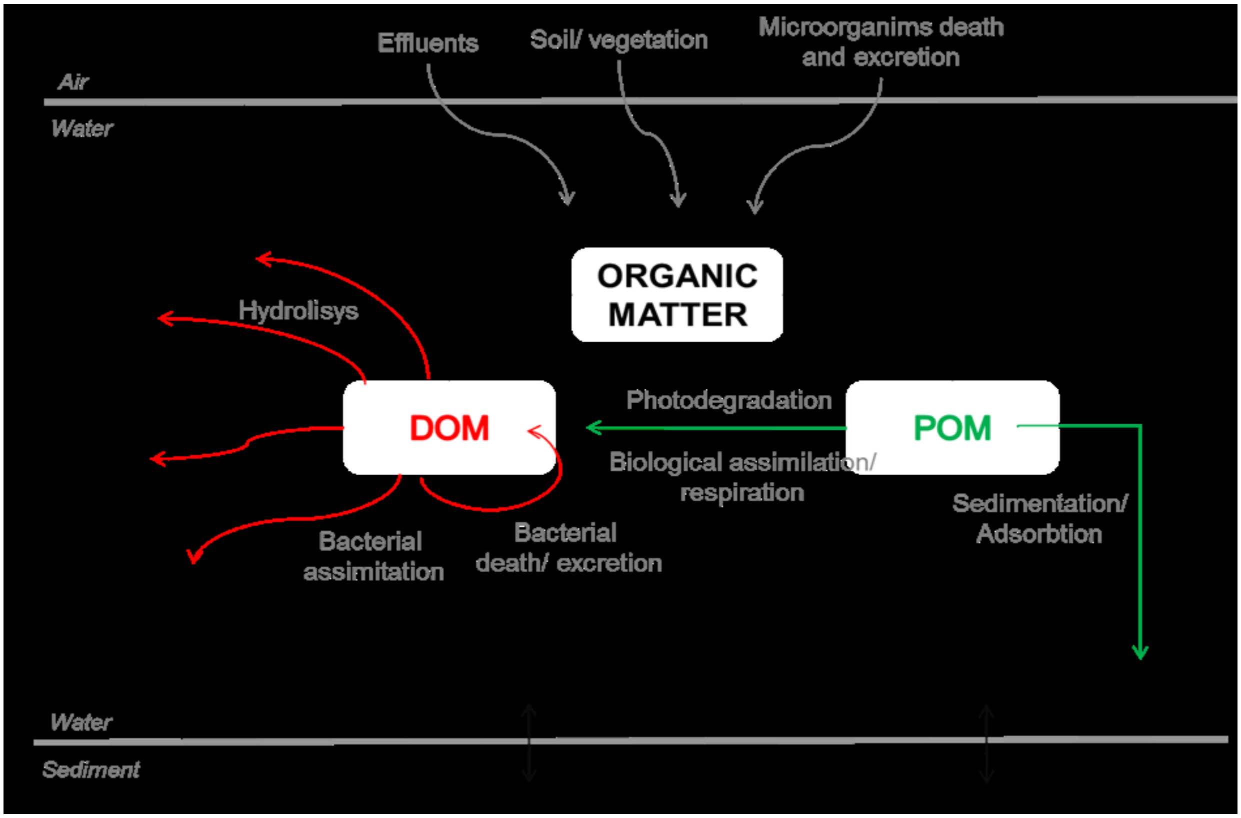
The macro-molecular nature and charge behavior of HAs and FAs play a significant role in increasing the colloidal stability of particles that bind with NOM and in the removal of NOM from water.

What are the origins of organic pollutants?

Organic pollutants originate from

1. Domestic Sewage
2. Urban run-off

3. Industrial effluents
4. Farm wastes
5. Surface water-derived from algal or phytoplankton
6. Synthetic organic substances of anthropogenic sources
7. Petroleum Refining
8. Terrestrial Sources involved the followings;
    i. Biomass leaching
    ii. Degradation
    iii. Microbial biomass formation
    iv. Release of recently formed carbon
    v. Soil/sediment leaching
    vi. Aquatic food web transformations



<u>Sewage effluents</u> is the greatest source of organic materials discharged to freshwaters.

Anthropogenic sources of organic matter represent a great contribution for the increasing of organic matter levels in surface waters, especially in developing countries.

Effluents derived from **Agricultural, Domestic, and Industrial activities** can alter not only the quality or water, but may cause impacts in the natural ecological succession.

Agricultural practices can release significant amount of organic compounds derived from pesticides,herbicides and consequently, their degradation by-products.

Urban activities produce daily an elevated amount of sewage, with a variable composition that depends on levels and kinds of treatment applied.

Photosynthesis and Respiration are reactions that complement each other in the environment. Through photosynthesis, autotrophs organism produces organic matter and oxygen converting inorganic nutrients and CO_2 using solar energy.

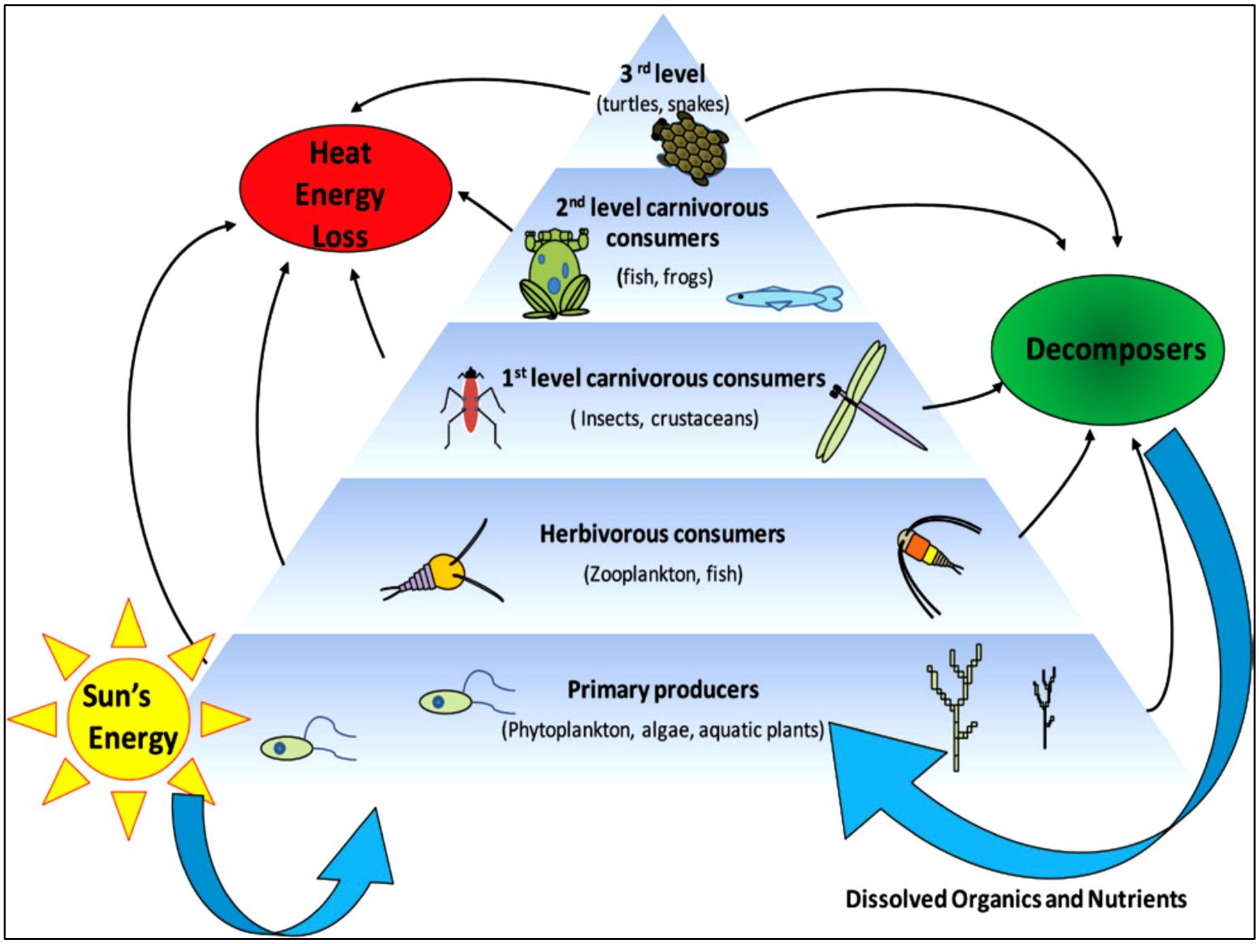
Additionally, through a set of **Metabolic Reactions**, living organisms convert organic matter into energy.

Petroleum Refining. Oil is mixed with water in the refining process to remove salts and other impurities.

Carbohydrates are the building blocks of life. In other words, they are the basic ingredients of OM.

Conversion of energy to organic matter, sometimes called **Primary Production**, also takes place in aquatic environments .

Aquatic plants, plankton, and some **microorganisms** use photosynthesis to create OM and pass it further up the food chain.



Impacts of OM

1. NOM does not affects the human's health directly but affects indirectly.
2. NOM has direct effects for aesthetic and operational reasons.
3. The Color,Taste,Odour of waste water caused by NOM make the water much less palatable for consumers.e.g. The appearance of water may be yellow or brown due to NOM.
4. NOM is known to be major precursor for Disinfection By-Products (DBPs).
5. OM Directly affects the aquatic life. For Example , Fishes lay eggs on the places in water where the temperature is low and CO_2 is normal or in excess amount.But when OM is added to water then the aquatic ecosystem or environment is disturbed. There is a suitable time period for hatching the fish eggs.But when the OM is added then due to disturbance in aquatic environment,the eggs hatch abnormally and off-springs

6. When the infected fishes are eaten by animal or humans, then OM present in fishes,creates the health problems.
7. DOM’s effect on water quality is multifaceted. It can detrimentally affect water quality through odour or colour, and it can also form toxic compounds in the process of water treatment. Conversely it can assist in the formation of singlet oxygen, which can then decompose pollutants, which in themselves are not photo-oxidisable One of the greatest ecological problems, if not the greatest, is the loss of agricultural
8. soil either through erosion or desertification. One means of combating this is by improving a soil’s hydrology through altering its physical structure..
9. DOM causes global warming.

Need to Remove OM

Although OM itself does not impose a direct health threat, removal of OM from
water is becoming more important for aesthetic, health, and operational reasons.
The initial driving force for removing OM was its adverse effect on aesthetic water quality because the color, taste, or odor caused by OM can make water much less palatable
for the consumer.
For example, the presence of OM molecules can make water appear
yellow or brown. More importantly, however, OM is now known to be the major precursor for many disinfection by-products (DBPs).

The chemical compounds known as DBPs are formed when an oxidant such as chlorine is added to water that contains organic matter. Removal of OM to reduce the formation of DBPs has become a major focus for water utilities in the past two decades.

A **coagulation** process that is optimized for both particle removal and OM reduction is known as enhanced coagulation (EC). OM also has adverse impacts on the operation of other treatment processes.

By reacting with chemical disinfectants to form DBPs, OM induces a disinfectant demand. Some OM molecules contain chemical functional groups that can absorb light in the ultraviolet (UV) range and thus reduce the efficiency of UV disinfection facilities. OM can foul membranes, reducing flux or increasing operating pressure.

Short-chain molecules of OM (e.g., as a result of oxidation) can serve as a food source for microbial growth in filter beds or the distribution system.

Current regulatory requirements for particle removal and OM reduction are based on a balance between adequate inactivation of microbial pathogens and minimizing the production of DBPs. These **requirements** are discussed below:

• OM is regulated under the Disinfectants and Disinfection By-products Rule(D/DBPR), with reduction related to requirements for minimum removal percentages of TOC between the source and finished water. These removal levels range from 15 pecent to 50 percent and are based on TOC levels in the source water and the source water alkalinity.

• Compliance with OM removal requirements typically indicates that a utility is effectively using its coagulation and filtration processes to significantly reduce the concentrations of DBP precursors and the formation of DBPs.

- Alternative compliance criteria for OM removal exist.

These criteria are designed to provide flexibility to water utilities that use source water either with a proven low potential to form DBPs (indicated by low concentrations of TOC, specific ultraviolet absorbance [SUVA],and DBPs) or that have source waters that are not amenable to significant TOC removal as indicated by site-specific bench-scale jar test results.

Optimizing treatment processes to remove OM and particles and also to control microbiological contaminants may involve setting coagulant doses to achieve OM removal, reducing coagulation pH, improving mixing conditions, and/or using alternative approaches for oxidation of OM and inactivation of microorganisms. Water treatment operators need effective tools for quick and accurate assessment of treatment performance and evaluations of alternatives.

Organic materials with fewer complex carbon compounds will decompose faster. Materials with more nitrogen also decompose faster because nitrogen is needed by decomposing organisms.

pH, temperature, moisture, and aeration also affect decomposition rate. Decomposition proceeds more quickly when pH is neutral, temperature is warm, and both oxygen and moisture are available.

Principles of Metal Extraction

The metals industry

Metals are one of the most commonly used resource in the world. Very few metals are found native, i.e. uncombined in nature, they must be mined, and extracted from their ores before use. Taken as a whole the most important driving force behind production methodology is price. The raw materials must be as cheap as possible, the processes must be cost efficient and the metal must be profitable to manufacture.

All phases of production are analysed with these considerations in mind.

What follows is a look at some of the most important metals and their manufacturing processes

The whole process depends very much on the type of metal being extracted, but can be broken down into roughly the same steps:

- Mining of ore containing rock
- Separation, purification or preparation of useful ore
- Extraction
- Purification of meta

1. Mining of ore containing rock

The composition of rock around the world varies greatly and locations with metal bearing ore have been sought ever since man was able to extract metals. Nowadays the search is still going on for important deposits of rock with high percentages of the mineral in question. This search is now taking place under the sea and in other inhospitable environments.

Recently, for example, rock containing an appreciable percentage of rare earth elements has been discovered under the pacific ocean. This is a particulaly important discovery as virtually 99% of known working deposits are in china and rare earths are essential in the manufacture of the strong neodymium magnets needed for the computer industry

2. Separation, purification or preparation of useful ore

Very few metal ores occur in a pure enough form to be used directly in the extraction process. The first stage is to separate the useful ore from the rock. This may not be necessary in some cases, for example, the extraction of iron, but essential in the extraction of aluminum.

This separation may be physical, such as floatation, or chemical such as digestion of the required compound in a strong base or acid followed by re-precipitation and filtration.

Most ores are either oxides or sulfides. The sulfides are usually converted to oxides by roasting in air. This tends to release sulfur in the form of sulfur (IV) oxide, a pollutant and acidic gas. However, it is also a useful gas in that it is used for the manufacture of sulfuric acid by the contact process.

3. Extraction of metal from ore

Metals are all electropositive and need to be reduced to become metallic elements. Hence, all extraction processes use reduction. For the less reactive metals chemical reduction suffices, but for the more reactive metals electrochemical reduction is needed.

4. Purification of metal

Metals that are extracted by reductive processes usually need to be further processed to make them industrially useful.

MACRO & MICRO NUTRIENTS

Primary (macro) nutrients are nitrogen, phosphorus, and potassium. They are the most frequently required in a crop fertilization program. Also, they are need in the greatest total quantity by plants as fertilizer.

NITROGEN

- Necessary for formation of amino acids, the building blocks of protein
- Essential for plant cell division, vital for plant growth
- Directly involved in photosynthesis
- Necessary component of vitamins
- Aids in production and use of carbohydrates
- Affects energy reactions in the plant

PHOSPHORUS

- Involved in photosynthesis, respiration, energy storage and transfer, cell division, and enlargement
- Promotes early root formation and growth
- Improves quality of fruits, vegetables, and grains
- Vital to seed formation
- Helps plants survive harsh winter conditions
- Increases water-use efficiency
- Hastens maturity

POTASSIUM

- Carbohydrate metabolism and the break down and translocation of starches
- Increases photosynthesis

- Increases water-use efficiency
- Essential to protein synthesis
- Important in fruit formation
- Activates enzymes and controls their reaction rates
- Improves quality of seeds and fruit
- Improves winter hardiness
- Increases disease resistance

SECONDARY NUTRIENTS

The secondary nutrients are calcium, magnesium, and sulphur. For most crops, these three are needed in lesser amounts that the primary nutrients. They are growing in importance in crop fertilization programs due to more stringent clean air standards and efforts to improve the environment.

CALCIUM

- Utilized for Continuous cell division and formation
- Involved in nitrogen metabolism
- Reduces plant respiration
- Aids translocation of photosynthesis from leaves to fruiting organs
- Increases fruit set
- Essential for nut development in peanuts
- Stimulates microbial activity

MAGNESIUM

- Key element of chlorophyll production
- Improves utilization and mobility of phosphorus
- Activator and component of many plant enzymes
- Directly related to grass tetany
- Increases iron utilization in plants
- Influences earliness and uniformity of maturity

SULPHUR

- Integral part of amino acids
- Helps develop enzymes and vitamins
- Promotes nodule formation on legumes
- Aids in seed production
- Necessary in chlorophyll formation (though it isn't one of the constituents)

MICRONUTRIENTS

The micronutrients are boron, chlorine, cooper, iron, manganese, molybdenum, and zinc. These plant food elements are used in very small amounts, but they are just as important to plant development and profitable crop production as the major nutrients. Especially, they work "behind the scene" as activators of many plant functions.

BORON

- Essential of germination of pollon grains and growth of pollen tubes
- Essential for seed and cell wall formation
- Promotes maturity
- Necessary for sugar translocation
- Affects nitrogen and carbohydrate

CHLORINE

- Not much information about its functions
- Interferes with P uptake
- Enhances maturity of small grains on some soils

COPPER

- Catalyzes several plant processes
- Major function in photosynthesis
- Major function in reproductive stages
- Indirect role in chlorophyll production
- Increases sugar content
- Intensifies color
- Improves flavor of fruits and vegetables

IRON

- Promotes formation of chlorophyll
- Acts as an oxygen carrier
- Reactions involving cell division and growth

MAGANESE

- Functions as a part of certain enzyme systems
- Aids in chlorophyll synthesis
- Increases the availability of P and CA

MOLYBDENUM

- Required to form the enzyme "nitrate reductas" which reduces nitrates to ammonium in plant
- Aids in the formation of legume nodules
- Needed to convert inorganic phosphates to organic forms in the plant

ZINC

- Aids plant growth hormones and enzyme system
- Necessary for chlorophyll production
- Necessary for carbohydrate formation
- Necessary for starch formation
- Aids in seed formation

Ion Exchange Mechanism

As soils are formed during the weathering processes, some minerals and organic matter are broken down to extremely small particles. Chemical changes further reduce these particles until they cannot be seen with the naked eye. The very smallest particles are called colloids.

The mineral clay colloids are plate like in structure and crystalline in nature. In most soils; clay colloids exceed organic colloids in amount.

Colloids are primarily responsible for the chemical reactivity in soils. The kind of parent material and the degree of weathering determine the kinds of clays present in the soil. Since soil colloids are derived from these clays, their reactivity is also influenced by parent material and weathering. Each colloid (inorganic and organic) has a net negative (-) charge developed during the formation process. This means it can attract and hold positively (+) charged particles. An element with an electrical charge is called an ion.

Potassium, sodium (Na), hydrogen (H), Ca and Mg all has positive charges. They are called cations and ions with negative charges, such as nitrate and sulfate, are called anions.

Negatively charged colloids attract cations and hold them like a magnet holds small pieces of metal. This characteristic explains; why nitrate-N is more easily leached from the soil than ammonium-N. Nitrate has a negative charge like soil colloids. So, NO^{3-} is not held by the soils, but remains as a free ion in soil water to be leached through the soil profile in some soils and under some rainfall conditions. The charges associated with soil particles attract simple and complex ions of opposite charge. Thus, a given colloidal mixture may exhibit not only a maze of positive and negative surface charges but also an equal complex complement of simple cations and anions such as Ca^{2+} and $S0^{4-}$ that are attracted by the particle charges.

The adsorbed anions are commonly present in smaller quantities than the cations because the negative charges generally predominate on the soil colloid.

Mechanism of Cation Exchange: The exchange of cations has been explained on the basis of the electro-kinetic theory of ion exchange. According to this theory, the adsorbed cations forming the outer shell of the ionic double layer are supposed to be in a state of oscillation when suspended in water, forming a diffuse double layer. Due to these oscillations, some of the cations move away from the surface of the clay micelle. In the presence of the solution of an electrolyte a cation of the added electrolyte slips in between the inner negative layer and the outer oscillating positive ion. The electrolyte cation is now adsorbed on the micelle and the surface cation remains in solution as an exchanged ion. Thus the exchange of cations takes place. Cations are positively charged nutrient ions and molecules. While, clay particles are negatively charged constituents of soils. These negatively charged particles (clay) attract, hold and release positively charged nutrient ions (cations). Organic matter particles also have a negative charge to attract cations. Sand particles carry little or no charge and do not react. Cations held by soils can be replaced by other cations. This means they are exchangeable. For example, Ca^{++} can be exchanged for H^+ and /or K^+ and vice versa.

Cation Exchange Capacity (CEC): The CEC is the capacity of soil to hold and exchange cations. The cation exchange capacity is defined simply as the sum total of the exchangeable cations that a soil can adsorb. The higher the CEC of soil the more cations it can retain. Soils differ in their capacities to hold exchangeable K^+ and other cations.

The CEC depends on amount and kinds of clay and organic matter present. A high-clay soil can hold more exchangeable cations than a low-clay soil. CEC also increases as organic matter increases. Clay minerals usually range from 10 to 150 meq/100 g in CEC values. Organic matter ranges from 200 to 400 meq/100 g. So, the kind and amount of clay and organic matter content greatly influence the CEC of soils. Clay soils with high CEC can retain large amounts of cations against potential loss by leaching. Sandy soils, with low CEC, retain smaller quantities.

This makes timing and application rates important in planning a fertilizer programme. For example, it may not be wise to apply K on very sandy soils in the middle of a monsoon, where rainfall can be high and intense. Fertilizer application should be split to prevent leaching and losses through erosion. Also, splitting N applications to meet peak crop demand are important to reduce the potential for nitrate leaching on sands as well as finer-textured soils.

Means of Expression: The cation exchange capacity is expressed in terms of equivalents or more specifically, as milli equivalents per 100 gram and is written as meq /100g. The term equivalent is defined as one gram of atomic weight of hydrogen (or the amount of any other ion) that will combine with or displace this amount of hydrogen for monovalent ions such as Na+, K+, NH4+ and Cl -, the equivalent weight and atomic weight are same, since they can replace one H ion. Divalent cations such as Ca++ and Mg++ can take the place of two H+ ions. The milliequivalent weight of a substance is one thousandth of its atomic weight. Since the atomic weight of hydrogen is about 1 gram. The term milliequivalent (meq.) may be defined as 1 milligram of hydrogen.

This unit of exchangeable cations i.e. milliequivalent per 100 g of soil (meq/100g) was used prior to 1982. In the newer metric system the term equivalent is not used, however, now moles are the accepted chemical unit. All the calculation and concepts of "equivalents" are still mentally used but the notation must be written differently. The old "equivalent" is represented by moles (+) or mole, which indicates a monovalent ion portion. For example, to write 12.5 meq/100 g in the newer metric system, it can be written as: 12.5 c mol (+) kg-1 of soil (centimoles) or 125 m mol (+) kg-1 of soil (millimoles).

Replacing power of cations: The replacing power of cations varies with the type of ion, its size and degree of hydration, valence and concentration and the kind of clay mineral involved, as it is controlled by number of factors no single order of replacement can be given. All other factors being equal the replacing power of monovalent cations increases in the following order: Li < Na < K < Rb < Cs < H and for divalent cations: Mg < Ca < Sr < Ba. In case of mixture of monovalent and divalent cations as they exist in normal soils the replacing power increases in the following order: Na < K < NH4 < Mg < Ca < H. This means Na is more easily replaced than K and K more easily than NH4 and so on.

Percent base saturation: The percent of total CEC occupied by the major cations has been used in the past to develop fertilizer programs. The idea is that certain nutrient ratios or 'balances' are needed to ensure proper uptake by the crop for optimum yields. Research has shown, however, that cation saturation ranges and ratios have little or no utility in a vast majority of agricultural soils. Under field conditions, ranges of nutrients can vary widely with no detrimental effects, so long as individual nutrients are present in sufficient levels in the soil to support optimum plant growth.

Importance of Cation Exchange: Cation exchange is an important reaction in soil fertility, in causing and correcting soil acidity and basicity, in changes altering soil physical properties, and as a mechanism in purifying or altering percolating waters. The plant nutrients like calcium, magnesium, and potassium are supplied to plants in large measure from exchangeable forms.

Soil pH and the Availability of Plant Nutrients

Soil pH is a characteristic that describes the relative acidity or alkalinity of the soil. Technically, pH is defined as the negative (-) log or base 10 value of the concentration of hydrogen ions (H+). Pure water will be close to a neutral pH, that is 10 to the minus 7 concentration of H+ ions (10-7 [H+]). This concentration is expressed as 7. Any value above 7 means the H+ ion concentration is lower than at a neutral pH and the solution is alkaline and there are more hydroxyl (OH-) ions present than H+ ions. Any value below 7 means the H+ ion concentration is greater than at neutral pH and the solution is acidic. Soils are considered acidic below a pH of 5, and very acidic below a pH of 4. Conversely, soils are considered alkaline above a pH of 7.5 and very alkaline above a pH of 8. Typically, soil pH values are measured when 10 g of air-dried soil is mixed with 20 ml of double-distilled water or 20 ml of 0.01 M $CaCl_2$ solution, and the pH is measured using an appropriate electrode connected to a pH meter. This soil analysis is a regular part of most if not all soil test protocols.

The availability of some plant nutrients is greatly affected by soil pH. The “ideal” soil pH is close to neutral, and neutral soils are considered to fall within a range from a slightly acidic pH of 6.5 to slightly alkaline pH of 7.5. It has been determined that most plant nutrients are optimally available to plants within this 6.5 to 7.5 pH range, plus this range of pH is generally very compatible to plant root growth.

Nitrogen (N), Potassium (K), and Sulfer (S) are major plant nutrients that appear to be less affected directly by soil pH than many others, but still are to some extent. Phosphorus (P), however, is directly affected. At alkaline pH values, greater than pH 7.5 for example, phosphate ions tend to react quickly with calcium (Ca) and magnesium (Mg) to form less soluble compounds. At acidic pH values, phosphate ions react with aluminum (Al) and iron (Fe) to again form less soluble compounds. Most of the other nutrients (micronutrients especially) tend to be less available when soil pH is above 7.5, and in fact are optimally available at a slightly acidic pH, e.g. 6.5 to 6.8. The exception is molybdenum (Mo), which appears to be less available under acidic pH and more available at moderately alkaline pH values.

In some situations, materials are added to the soil to adjust the pH. On a field scale, this is most commonly done for acidic soils to raise the pH from 4.5 to 5.5 up to 6.5 or approaching neutrality. This is done by applying and incorporating a liming material, often finely ground calcitic limestone or dolomitic limestone, that is spread using specialized lime spreaders, or spin-spreaders adapted with vibrating systems to prevent bridging of the material in the hoppers of the spreaders. It is possible to lower the pH of a soil using a liquid acid solution, or finely ground elemental S that oxidizes to sulfuric acid through the action of soil inhabiting S-oxidizing bacteria. However, this is rarely done on a field-scale basis because of the high cost. It is more commonly done in horticulture production applications where individual plant containers or limited areas (e.g. <10 to 20 acres) are managed to lower the pH for acidic soil adapted plants such as some flowers, trees, and/or small fruits (i.e. blueberry and cranberry). It is important to note that most on-going crop production will gradually lower the soil pH as the H+ ions are released and converted over to nitrate by soil microbes. This is especially true where N fertilizers such as anhydrous ammonia, ammonium sulfate, and urea are applied.

Whether or not you try to adjust pH, it is important to understand other methods to increase the availability and use of added nutrients. This can be done in a number of ways for the nutrients mentioned above that are adversely affected by extremes in soil pH, acidic or alkaline. For example, P-containing fertilizer can be applied in or close to the seed-row at planting to facilitate early season uptake of phosphate ions by crop roots before allowing it to react with soil cations that dominate under acidic or alkaline soil pH conditions. Under alkaline soil pH values, the phosphate fertilizer can be applied in bands with fertilizer which generates an ionized form of ammonia (NH_4). That will allow slight acidification of the soil adjacent to the fertilizer band. Another method is to manufacture compound nutrient fertilizer granules that contain the N, P, and even elemental S-containing fertilizers, for application to alkaline soils. The soil adjacent to the granule will also be acidified slightly and allow enhanced P uptake when the crop roots intercept the granules. Yet another example is the foliar application of soluble Fe fertilizer compounds to Fe-deficient crops grown in high pH soils where the fertilizer react so fast with soil that the nutrient is tied up and unavailable to plants. This is why soil applied Fe fertilizers often do not successfully correct Fe deficiencies. By avoiding the soil and applying the Fe to the leaves, the small amount of plant-required Fe is successfully introduced into the crop.

Next time you have soil samples taken on your fields, take time to note what the pH values are in your results. It is useful to compare these values to previous soil test pH values and determine if there is a trend of soil pH change. By monitoring the pH values regularly (every 2 to 3 years) in a field, you may consider action to raise the pH of the soil from acidic to near neutral pH values by liming. Increased nutrient availability and improved crop growth can be achieved when adding liming material to an excessively acidic soil. This can be especially important for crops requiring neutral pH, such as legume forages or pulses, as the Rhizobia species bacteria do not nodulate and fix N effectively under pH values less than 5.5.

Green Chemistry

Green chemistry is a pro-active approach to pollution prevention. It targets pollution at the design stage, before it even begins. If chemists are taught to develop products and materials in a manner that does not use hazardous substances, then much waste, hazards and cost can be avoided. Green Chemistry is designing chemical products and processes that reduce or eliminate the use and/or the generation of hazardous substances.

Think about the simple equation of risk: Risk = Hazard x Exposure. Traditional approaches to pollution prevention focus on mitigating the hazard or end-of-pipe pollution prevention controls. These traditional technologies focus on limiting the exposure of a hazardous material. Unfortunately, exposure precautions can and will fail (i.e., gloves can tear, goggles can break, chemical releases can occur). Green chemistry goes to the root of the problem and aims to eliminate the hazard itself.Green Chemistry is the ONLY science that focuses on the intrinsic hazard of a chemical or chemical process. It seeks to minimize or eliminate that hazard so that we do not have to worry about exposure.

What is the difference between Environmental Science and Green Chemistry?

Both areas of study seek to make the world a better place. The two are complimentary to each other. Environmental Science identifies sources, elucidates mechanisms and quantifies problems in the earth's environment. Green Chemist seeks to solve these problems by creating alternative, safe technologies. Green ry Chemistry is not Environmental Chemistry. Green Chemistry targets pollution prevention at the source, during the design stage of a chemical product or process, and thus prevents pollution before it begins.

Is Green Chemistry more expensive that traditional Chemistry?

No. A simplified analysis of the cost structure associated with any chemical process takes into account the cost of materials, equipment and the human resources necessary. But, in reality, disposal, treatment and regulatory costs associated with the buying, using and generating hazardous materials involves numerous hidden costs. When you buy and use a hazardous material you are paying for it twice, once when you use it and once when you get rid of it. It makes sense that if you use materials that are non-hazardous and thus have minimal regulatory or disposal costs associated with them, the benefit to the economic bottom line is obvious. The Presidential Green Chemistry Challenge Award has provided illustrations of several examples where industry has not only accomplished goals of pollution prevention,but has achieved significant economic benefits simultaneously.

How are Chemists taught Green Chemistry?

One way that chemists are learning how to do Green Chemistry is by following the 12 principles of Green Chemistry. They are a set of guidelines that chemists use in order to perform chemistry in a better way. As you take a closer look at them, you will find they are very intuitive and simply good practice. The powerpoint presentation that goes along with this module will help to explain the 12 principles. Each is briefly described below.

The 12 Principles of Green Chemistry:

1.Prevention

This principle is the most obvious and over-arches the other principles. It goes back to the old adage "an ounce of prevention is worth a pound of cure". It is better to prevent waste than clean environmental disasters that history there have been many cases of up to after-the-fact. Through out demonstrated this (Bopal, India; Love Canal; Times Beach; Cuyahoga River).

2.Atom Economy

This principle gets into the actual chemistry of how products are made. As chemists, atoms are assembled to make molecules. The molecules are assembled together to make materials. This principle states that it is best to use all the atoms in a process. And, those atoms that are not used end up as waste. The atom economy is a simple calculation that can be used when teaching stoichiometry and chemical reactions. The calculation is: A.E. = Formula Weight (FW) of Product divided by the FW of all of the reactants. It is a simple measure of the amount of waste in a process.

3.Less Hazardous Chemical Synthesis

This principle is focused on how we make molecules and materials. The goal is to reduce the hazard of the chemicals that are used to make a product (the reagents). Throughout the history of how we have invented products and developed the process for making them, chemists have traditionally not thought about what reagents they are using and the hazards that are associated with them. Chemists have traditionally used whatever means necessary. Today we are finding that less hazardous reagents and chemicals can be used in a process to make products… and, many times they are made in a more efficient manner!

4.Designing Safer Chemicals

The previous principle was focused on the process. This principle focuses on the product that is made. Everyone wants safe products. Everyone also wants products that do what they are supposed to do (they have to work!). This principle is aimed at designing products that are safe, non-toxic and efficacious. A good example of this is pesticides; which are products that are designed to be toxic. Many researchers are focused on created pesticides that are highly specific to the pest organism, but non-toxic to the surrounding wildlife and ecosystems.

5.Safer Solvents and Auxiliaries

Many chemical reactions are done in a solvent. And, traditionally organic solvents have been used that pose hazards and many are highly toxic. They also create volatile organic compounds (VOC's) which add to pollution and can be highly hazardous to humans. This principle focuses on creating products in such a way so that they use less hazardous solvents (such as water). We use solvents regularly in our daily lives (cleaning products, nail polish, cosmetics, etc.) and in the chemistry laboratory. An example that many can relate to is that of nail polish products. Have you walked by a nail salon and caught a smell of the solvents that are used? The solvents traditionally used have potential toxicity and are certainly not pleasant to smell. A water-based alternative polish would avoid the exposure that goes along with the nail products and reduce the hazards associated with traditional products.

6.Design for Energy Efficiency

Today there is a focus on renewable energy and energy conservation. We use energy for transportation purposes and to provide electricity to our homes and businesses. Traditional methods for generating energy have been found to contribute to global environmental problems such as Global Warming and the energy used can also be a significant cost. This principle focuses on creating products and materials in a highly efficient manner and reducing the energy associated with creating the products, therefore reducing associated pollution and cost.

7.Use of Renewable Feed stocks

90-95% of the products we use in our everyday lives are made from petroleum. Our society not only depends on petroleum for transportation and energy, but also for making products. This principle seeks to shift our dependence on petroleum and to make products from renewable materials that can be gathered or harvested locally. Biodiesel is one example of this where researchers are trying to find alternative fuels that can be used for transportation. Another example is alternative, bio-based plastics. PLA(polylactic acid) is one plastic that is being made from renewable feed stocks such as corn and potato waste.

8.Reduce Derivatives

This principle is perhaps the most abstract principle for a non-chemist. The methods that chemists use to make products are sometimes highly sophisticated. And, many involve the manipulation of molecules in order to shape the molecules into what we want them to look like. This principle aims to simplify that process and to look at natural systems in order to design products in a simplified manner.

9.Catalysis

In a chemical process catalysts are used in order to reduce energy requirements and to make reactions happen more efficiently (and many times quicker). Another benefit of using a catalyst is that generally small amounts (catalytic amount versus a stoichiometric amount) are required to have an effect. And, if the catalyst is truly a “green” catalyst it will have little to no toxicity and it will be able to be used over-and-over again in the process. Enzymes are wonderful examples of catalysts that have been proven to perform amazing chemistry – our bodies are wonderful examples! Green chemists are investigating using enzymes to perform chemistry in the laboratory in order to obtain the desired product. Many times enzymes will have reduced toxicity, increased specificity and efficiency.

10. Design for Degradation

Not only do we want materials and products to come from renewable resources, but we would also like them to not persist in the environment.There is no question that many products we use in our daily lives are far to opersistent. Plastics do not degrade in our landfills and pharmaceutical drugs such as antibiotics build up in our water streams. This principle seeks to design products in such a way so that they perform their intended function and then, when appropriate, will degrade into safe, innocuous by-products when they are disposed of.

11. Real-time Analysis for Pollution Prevention

Imagine if you have never baked a cake before in your life and you did not have a cookbook to refer to. You mix the ingredients that you believe you need and you place the cake in the oven. But, for how long do you cook it and at what temperature? How will you know when the cake is done? What happens if you cook it too long or for not enough time? This process is similar to what chemists have to do when they make products. How long do they allow the reaction to run for? When do they know it will be "done"? If there was a way to see inside the reaction and to know exactly when it would be done, then this would reduce waste in the process and ensure that your product is "done" and is the right product that you intended to make.

12. Inherently Safer Chemistry for Accident Prevention

This principle focuses on safety for the worker and the surrounding community where an industry resides. It is better to use materials and chemicals that will not explode, light on fire, ignite in air, etc. when making a product. There are many examples where safe chemicals were not used and the result was disaster. The most widely known and perhaps one of the most devastating disaster was that of Bhopal, India in 1984 where a chemical plant had an accidental release that resulted in thousands of lives lost and many more injuries. The chemical reaction that occurred was an exothermic reaction that went astray and toxic fumes were released to the surrounding community. When creating products, it is best to avoid highly reactive chemicals that have potential to result in accidents. When explosions and fires happen in industry, the result is often devastating.

Atom Economy

Like most other people, chemists are concerned with environmental pollution. This concern has given rise to a field called green chemistry, which involves the design of chemical products and processes that minimize environmental problems.

P. T. Anastas and J. C. Warner describe 12 principles of green chemistry in their book Green Chemistry: Theory and Practice (Oxford University Press: New York, 1998). One of the principles, called **atom economy**, involves—among other things—designing reactions in such a way that the quantity of reactants that end up in the desired final product is the maximum possible.

We can define the percent atom economy (% AE) of a reaction by the formula

$$\% \text{ AE} = \frac{\text{formula mass of desired final product}}{\text{sum of formula masses of all the reactants}} * 100\%$$

Atom economy also must consider substances such as solvents, separation agents, and drying agents that are used in the process but are not directly part of the chemical reaction. Using a green chemistry approach, chemists attempt to either reduce the amount of or eliminate completely as many of these substances as possible. Those that cannot be eliminated are reused or recycled when possible.

As an example, consider two ways to make ethylene oxide, which is used to sterilize medical devices and as an intermediate in the synthesis of ethylene glycol and other chemicals. The old way, called the chlorohydrin route, starts with the hydrocarbon ethylene, chlorine, and calcium hydroxide, and involves several steps. (The process is named for one of the intermediates $HOCH_2CH_2Cl$, called chlorohydrin.) The overall reaction produces the desired ethylene oxide but has calcium chloride and water as by-products:

,

$$C_2H_4 + Cl_2 + Ca(OH)_2 \rightarrow C_2H_4O + CaCl_2 + H_2O$$

Assuming 100% yield for all the reactions involved, the atom economy for the overall reaction is

$$\% \text{ AE} = \frac{\text{formula mass of } C_2H_4O}{\text{sum of formula masses of } C_2H_4 + Cl_2 + Ca(OH)_2} * 100\%$$

$$\% \text{ AE} = \frac{44.05 \text{ u}}{} * 100\% = 25.46\%$$

28.05 u + 70.91 u + 74.09 u

The newer process uses a catalyst (a substance that speeds up a reaction without itself being used up). Ethylene and oxygen react to give ethylene oxide as the sole product: Assuming a 100% yield in this reaction, the atom economy is also 100%: Manufacturing processes can be highly complex. At times, by-products can either be used directly or serve as starting materials for other processes. Such factors should be considered in the overall atom economy. In the case of calcium chloride, however, the current need is not great, and so it is not a valuable by-product. Clearly, the catalytic route to ethylene oxide, with no by-products to worry about, is “greener” than the Chlorohydrin path.

$$C_2H_4 + 1/2\ O_2 \rightarrow C_2H_4O$$

$$\%\ AE = \frac{\text{formula mass of } C2H4O}{\text{sum of formula masses of } C2H4 + 1/2O_2} * 100\%$$

$$\%\ AE = \frac{44.05\ u}{28.05\ u + 16.00\ u} * 100\% = 100\%$$

SUPERCRITICAL FLUID EXTRACTION

Supercritical fluid extraction is the most effective and efficient way to extract valuable constituent botanicals. Supercritical Fluid Extraction (SFE) is the process of separating one component (the extractant) from another (the matrix) using supercritical fluids that is CO2 as the extracting solvent. CO2 is the king of extraction solvents for botanicals. Extraction conditions for supercritical CO2 are above the critical temperature of 31°C and critical pressure of 74 bar. Supercritical fluids are highly compressed gases, which have combined properties of gases and liquids in an intriguing manner. Supercritical fluids can lead to reactions, which are difficult or even impossible to achieve in conventional solvents. It is a fast process completed in 10 to 60 minutes. A supercritical fluid can be separated from analyte by simply releasing pressure, leaving almost no trace and yields a pure residue.

Key words: Supercritical fluid extraction, Applications.

Extraction can be defined as the removal of soluble material from an insoluble residue, either liquid or solid, by treatment with a liquid solvent. It is therefore, a solution process and depends on the mass transfer phenomena. The controlling factor in the rate of extraction is normally the rate of diffusion of the solute through the liquid boundary layer at the interface.

Extraction involves the separation of medicinally active portions of plant or animal tissue from the inactive or inert components using selective solvents in standard extraction procedures. The products so obtained from plants are relatively impure liquids, semisolids or powders intended only for oral or external use. So extraction continues to be of considerable interest in order to obtain improved yields of drug derived from plant and animal sources. Techniques of extraction methods continue to be investigated and applied to obtain higher yields of the active substances from natural sources. The principle methods of extraction are -

- Maceration
- Percolation
- Digestion
- Infusion
- Decoction

Solvent extraction

Solvent extraction also known as liquid-liquid extraction and partitioning, is a method to separate compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent. It is an extraction of a substance from one liquid phase into another liquid phase. It is a basic technique in chemical laboratories, where it is performed using a separatory funnel. In other words, this is the separation of a substance from a mixture by preferentially dissolving that substance in a suitable solvent. Solvent extraction may be made use analytically for concentrating or rejecting a particular substance, or for the separation of mixtures. This process usually separates a soluble compound from an insoluble compound. Solvent extraction is used in nuclear processing, ore processing, production of fine organic compounds, processing of perfumes and other industries. Thus, although the method can be used for extraction and preconcentration of a wide range of non volatile or semi volatile species from water using only routine laboratory equipments, its use is decreasing in most situations because solvents of the required purity tend to be expensive, and can also cause problems with proper disposal after use.

Supercritical fluid extraction

Often the analysis of complex materials requires, as a preliminary step that is,
separation of the analyte or analytes from a sample matrix. Ideally, an analytical separation
method should be rapid, simple and inexpensive; should give quantitative recovery of analytes without loss or degradation; should yield a solution of the analyte that is sufficiently concentrated to permit the final measurement to be made without the need for concentration;
should generate little or no laboratory wastes that have to be disposed off.

For many years, one of the most common methods for performing analytical separations on complex environmental, pharmaceutical, food and petroleum samples was based upon extraction of bulk samples with hydrocarbon or chlorinated organic solvents using a Soxhlet extractor. Unfortunately, liquid extraction frequently fails to meet several of the ideal criteria. They usually require several hours or more to achieve satisfactory recoveries of analytes and even sometimes fails to do. The solvent costs are often high. The solutions of the recovered analytes are often so dilute so that a concentration step must follow the extraction. Analyte degradation or loss as well as atmospheric pollution may accompany this concentration step.

Beginning in the mid-1980, chemists began to explore the use of supercritical fluids for the separation of analytes from the matrix of many samples of interest to industry and governmental agencies because use of reagents of this type avoids many of the problems for organic liquid extractants.

What is Supercritical Fluid Extraction ?

Supercritical fluids have been investigated since last century, with the strongest
commercial interest initially focusing on the use of supercritical toluene in petroleum and shale oil refining during the 1970s. Supercritical water is also being investigated as a means of destroying toxic wastes, and as an unusual synthesis medium. The biggest interest for the last decade has been the applications of supercritical carbon dioxide, because it has a nearambient critical temperature (310C), thus biological materials can be processed at temperatures around 350C. The density of the supercritical CO_2 at around 200 bar pressure is close to that of hexane, and the solvation characteristics are also similar to hexane; thus, it acts as a non-polar solvent. Around the supercritical region, CO2 can dissolve triglycerides at concentrations up to 1% mass. The major advantage is that a small reduction in temperature, or a slightly larger reduction in pressure, will result in almost the entire solute precipitating out as the supercritical conditions are changed or made sub critical. Supercritical fluids can produce a product with no solvent residues. Examples of pilot and production scale products include decaffeinated coffee, cholesterol-free butter, low-fat meat, evening primrose oil, squalene from shark liver oil, etc. The solvation characteristics of supercritical CO_2 can be modified by the addition of an entrainer, such as

ethanol, however some entrainer remains as a solvent residue in the product, negating some of the advantages of the "residue-free" extraction.

Supercritical fluid extraction (SFE) is the process of separating one component (the extractant) from another (the matrix) using supercritical fluids as the extracting solvent. Extraction is usually from a solid matrix, but it can also be from liquids. SFE can be used as a sample preparation step for analytical purposes, or on a larger scale to either strip unwanted material from a product (e.g. decaffeination) or collect a desired product (e.g. essential oils). Carbon dioxide (CO_2) is the most used supercritical fluid, sometimes modified by co-solvents such as ethanol or methanol. Extraction conditions for supercritical CO_2 are above the critical temperature of 31°C and critical pressure of 74 bar. Addition of modifiers may slightly alter this. Supercritical extraction mostly uses carbon dioxide at high pressure to extract the high value products from natural materials. Unlike other processes, the extraction process leaves no solvent residue behind. Moreover the CO2 is non-toxic, nonflammable, odorless, tasteless, inert, and inexpensive. Due to its low critical temperature 31°C, carbon dioxide is known to be perfectly adapted in food, aromas, essential oils and nutraceutical industries.

Supercritical fluid

A supercritical fluid is any substance at a temperature and pressure above its critical point. It can diffuse through solids like a gas, and dissolve materials like a liquid. Additionally, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties of a supercritical fluid to be "fine-tuned". Supercritical fluids are suitable as a substitute for organic solvents in a range of industrial and laboratory processes. Carbon dioxide and water are the most commonly used supercritical fluids, being used for decaffeination and power generation, respectively.

CO_2 is the kind of extraction solvents for botanicals. It leaves no toxic residue behind. Its extraction properties can be widely and precisely manipulated with subtle changes in pressure and temperature.

There are two types of CO_2 extraction

Low pressure cold extraction

Ii involves chilling CO_2 at 35-550F and pumping it through the plant material at between 800-1500 psi.

Supercritical extraction

It involves heating the CO2 to above 870F and pumping it above 1100 psi. Usually, this is between 6000-10000 psi. Supercritical fluid CO2 can best be described as a dense fog when CO2 is used in a dense liquid state. Low-pressure CO2 is often the best method for producing high quality botanical extracts. CO2 loading rate in this state means that you have to pump many volumes of CO_2 through botanical. The loading rate is typically 10-40 volumes. For this reason, it is important to have pumped CO_2, which has a much faster loading rate 2-10 volumes and a wide range of uses.

Properties of supercritical fluid

- Supercritical fluids have highly compressed gases, which combine properties of gases and liquids in an intriguing manner.
- Supercritical fluids can lead to reactions, which are difficult or even impossible to achieve in conventional solvents.
- Supercritical fluids have solvent power similar to light hydrocarbons for most of the solutes. However, fluorinated compounds are often more soluble in supercritical CO_2 than in hydrocarbons; this increased solubility is important for polymerization.
- Solubility increases with increasing density (that is with increasing pressure).

Rapid expansion of supercritical solutions leads to precipitation of a finely divided solid. This is a key feature of flow reactors.

- The fluids are commonly miscible with permanent gases (e.g. N_2 or H_2) and this leads to much higher concentrations of dissolved gases than can be achieved in conventional solvents.

In general terms, supercritical fluids have properties between those of a gas and a liquid.

Table 1: Critical properties for some components commonly used as supercritical Fluids

Critical properties of various solvents (Reid et al., 1987)

Solvent	Molecular weight (g/mol)	Critical temperature (K)	Critical pressure MPa (atm)	Critical density (g/cm3)
Carbon dioxide (CO_2)	44.01	304.1	7.38 (72.8)	0.469
Water (H_2O) (acc. IAPWS)	18.015	647.096	22.064 (217.755)	0.322
Methane (CH_4)	16.04	190.4	4.60 (45.4)	0.162
Ethane (C_2H_6)	30.07	305.3	4.87 (48.1)	0.203
Propane (C_3H_8)	44.09	369.8	4.25 (41.9)	0.217

Ethylene (C2H4)	28.05	282.4	5.04 (49.7)	0.215
Propylene(C3H6)	42.08	364.9	4.60 (45.4)	0.232
Methanol(CH3OH)	32.04	512.6	8.09 (79.8)	0.272
Ethanol(C2H5OH)	46.07	513.9	6.14 (60.6)	0.276
Acetone (C3H6O)	58.08	508.1	4.70 (46.4)	0.278

Table 2: Density, diffusivity and viscosity for typical liquids, gases and supercritical fluids

Comparison of gases, supercritical fluids and liquids

	Density (kg/m3)	Viscosity (@Pa·s)	Diffusivity (mm^2/s)
Gases	1	10	1-10
Supercritical fluids	100-1000	50-100	0.01-0.1
Liquids	1000	500- 1000	0.001

All supercritical fluids are completely miscible with each other so for a mixture, a single phase can be guaranteed, if the critical point of the mixture is exceeded. The critical point of a binary mixture can be estimated as the arithmetic mean of the critical temperatures and pressures of the two components,

Tc (mix) = (Mole fraction A) x TcA + (Mole fraction B) x TcB. …(1)

For greater accuracy, the critical point can be calculated using equations of state, such as the Peng Robinson, or group contribution methods. Other properties, such as density, can also be calculated using equations of state.

Supercritical fluid extraction process

The system must contain a pump for the CO2, a pressure cell to contain the sample, a means of maintaining pressure in the system and a collecting vessel. The liquid is pumped to a heating zone, where it is heated to supercritical conditions. It then passes into the extraction vessel, where it rapidly diffuses into the solid matrix and dissolves the material to be extracted. The dissolved material is swept from the extraction cell into a separator at lower pressure, and the extracted material settles out. The CO2 can then be cooled, recompressed and recycled, or discharged to atmosphere.

Pumps

Carbon dioxide is usually pumped as a liquid, usually below 5°C and a pressure of about 50 bars. The solvent is pumped as a liquid as it is then almost incompressible. As a supercritical fluid, much of the pump stroke will be "used up" in compressing the fluid, rather than pumping it. For small-scale extractions (up to a few grams/minute), reciprocating CO2 pumps or syringe pumps are often used. For larger scale extractions, diaphragm pumps are most common. The pump heads will usually require cooling, and the CO2 will also be cooled before entering the pump.

Pressure vessels

Pressure vessels can range from simple tubing to more sophisticated purpose built vessels with quick release fittings. The pressure requirement is at least 74 bars, and most extractions are conducted at less than 350 bar. However, sometimes, higher pressures will be needed, such as extraction of vegetable oils, where pressures of 800 bars are sometimes required for complete miscibility of the two phases.

The vessel must be equipped with a means of heating. It can be placed inside an oven for small vessels, or oil or electrically heated jacket for larger vessels. Care must be taken if rubber seals are used on the vessel, as the CO2 may dissolve in the rubber, causing swelling, and the rubber will rupture on depressurization.

Pressure maintenance

The pressure in the system must be maintained from the pump right through the pressure vessel. In smaller systems (up to about 10 mL/min), a simple restrictor can be used. This can be either a capillary tube cut to length, or a needle valve, which can be adjusted to maintain pressure at different flow rates. In larger systems a backpressure regulator will be used, which maintains pressure upstream of the regulator by means of a spring, compressed air, or electronically driven valve. Whichever is used, heating must be supplied, as the adiabatic expansion of the CO2 results in significant cooling. This is problematic, if water or other extracted material is present in the sample, as this may freeze in the restrictor or valve and cause blockages.

Collection

The supercritical solvent is passed into a vessel at lower pressure than the extraction vessel. The density, and thus, dissolving power, of supercritical fluids varies sharply with pressure, and hence, the solubility in the lower density CO2 is much lower, and the material precipitates for collection. It is possible to fractionate the dissolved material using a series of vessels at reducing pressure. The CO2 can be recycled or depressurized to atmospheric pressure and vented. For analytical SFE, the pressure is usually dropped to atmospheric, and now the gaseous carbon dioxide is bubbled through the solvent to trap the precipitated components.

Heating and cooling

This is an important aspect. The fluid is cooled before pumping to maintain liquid conditions, and then heated after pressurization. As the fluid is expanded into the separator, heat must be provided to prevent excessive cooling. For small-scale extractions, such as for analytical purposes, it is usually sufficient to pre-heat the fluid in a length of tubing inside the oven containing the extraction cell. The restrictor can be electrically heated, or even heated with a hair dryer. For larger systems, the energy required during each stage of the process can be calculated using the thermodynamic properties of the supercritical fluid.

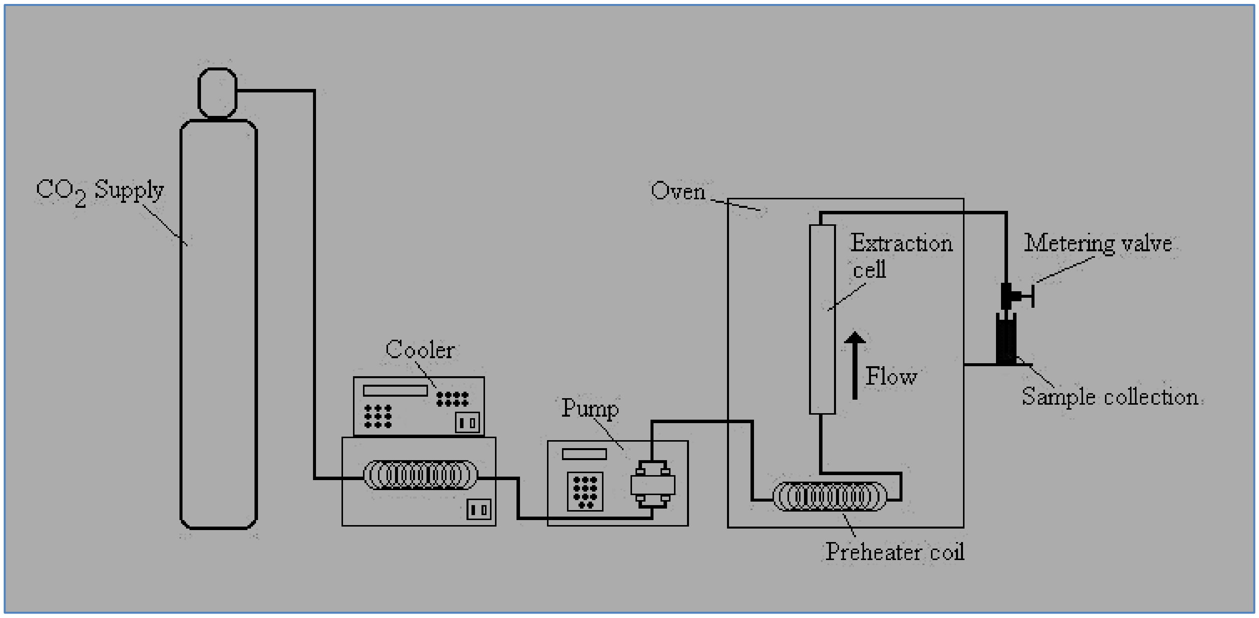


Fig. 3: Schematic diagram of SFE apparatus

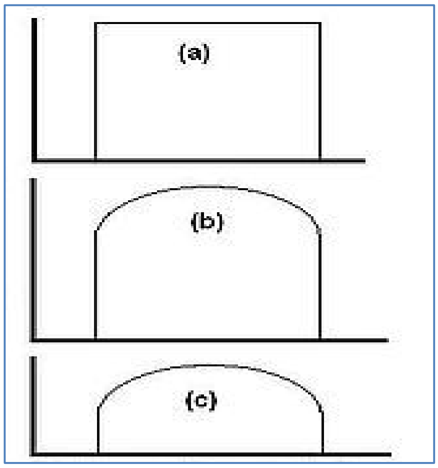


Fig. 4: Concentration profiles during a typical SFE extraction

There are two essential steps to SFE, transport (by diffusion or otherwise) from with the solid particles to the surface, and dissolution in the supercritical fluid. Other factors, such as diffusion into the particle by the SF and reversible release such as desorption from an active site are sometimes significant, but not dealt in detail here. Fig. 4 shows the stages during extraction from a spherical particle where at the start of the extraction, the level of extractant is equal across the whole sphere Fig. 4(a). As extraction commences, material is initially extracted from the edge of the sphere, and the concentration in the center is unchanged Fig 4(b). As the extraction progresses, the concentration in the center of the sphere drops as the extractant diffuses towards the edge of the sphere Fig. 4(c).

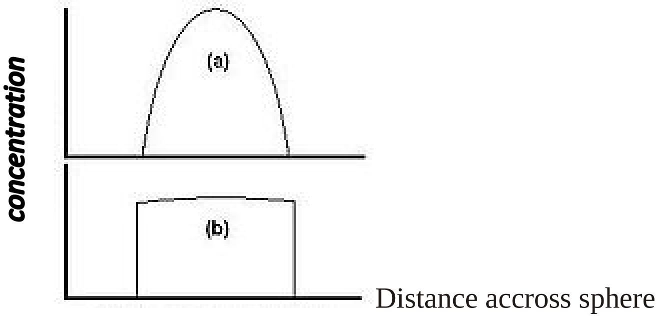


Fig. 5: Concentration profiles for (a) diffusion limited and (b) solubility limited extraction

The relative rates of diffusion and dissolution are illustrated by two extreme cases in Fig. 5. Fig. 5(a) shows a case where dissolution is fast relative to diffusion. The material is carried away from the edge faster than it can diffuse from the center, so the concentration at the edge drops to zero. The material is carried away as fast as it arrives at the surface, and the extraction is completely diffusion limited. Here, the rate of extraction can be increased by increasing diffusion rate, for example raising the temperature, but not by increasing the flow rate of the solvent. Fig. 5(b) shows a case where solubility is low relative to diffusion. The extractant is able to diffuse to the edge faster than the solvent can carry it away, and the concentration profile is flat. In this case, the extraction rate can be increased by increasing the rate of dissolution, for example by increasing flow rate of the solvent.

The extraction curve of % recovery against time can be used to elucidate the type of extraction occurring. Fig. 6(a) shows a typical diffusion controlled curve. The extraction is initially rapid, until the concentration at the surface drops to zero, and the rate then becomes much slower. The % extracted eventually approaches 100%. Fig. 6(b) shows a curve for solubility limited extraction. The extraction rate is almost constant, and only flattens off towards the end of the extraction. Fig. 6(c) shows a curve where there are significant matrix effects, where there is some sort of reversible interaction with the matrix, such as desorption from an active site. The recovery flattens off, and if the 100% value is not known, then it is hard to tell that extraction is less than complete.

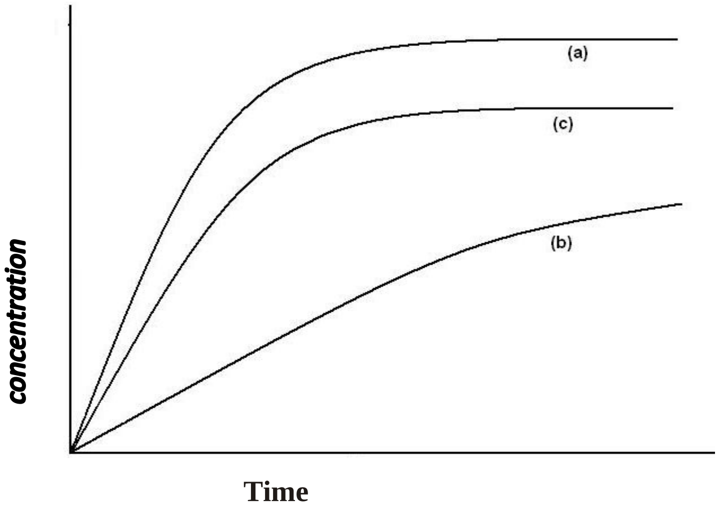


Fig. 6: Extraction profile for different types of extraction

Optimization

The optimum will depend on the purpose of the extraction. For an analytical extraction is to determine, say, antioxidant content of a polymer, then the essential factors are complete extraction in the shortest time. However, for production of an essential oil extract from a plant, then quantity of $CO2$ used will be a significant cost, and "complete" extraction is not required; a yield of 70 - 80% perhaps being sufficient to provide economic returns. In another case, the selectivity may be more important, and a reduced rate of extraction will be preferable if it provides greater discrimination. Therefore, few comments can be made, which are universally applicable. However, some general principles are outlined below.

Maximizing diffusion

This can be achieved by increasing the temperature, swelling the matrix, or reducing the particle size. Matrix swelling can sometimes be increased by increasing the pressure of the solvent, and by adding modifiers to the solvent. Some polymers and elastomers in particular are swelled dramatically by CO2, with diffusion being increased by several orders of magnitude in some cases.

Maximizing solubility

Generally, higher pressure will increase solubility. The effect of temperature is less certain, as close to the critical point, increase in the temperature causes a decrease in density, and hence, dissolving power. At pressures well above the critical pressure, solubility is likely to increase with temperature. Addition of low levels of modifiers (sometimes called entrainers), such as methanol and ethanol, can also significantly increase solubility, particularly of more polar compounds.

Optimizing flow rate

The flow rate of CO2 should be measured in terms of mass flow rather than by volume because the density of the CO2 changes according to the temperature both; before entering the pump heads and during compression. Coriolis flow meters are best used to achieve such flow confirmation. To maximize the rate of extraction, the flow rate should be high enough for the extraction to be completely diffusion limited (but this will be very wasteful of solvent). However, to minimize the amount of solvent used, the extraction should be completely solubility limited (which will take a very long time). Flow rate must therefore be determined depending on the competing factors of time and solvent costs, and also capital costs of pumps, heaters and heat exchangers. The optimum flow rate will probably be somewhere in the region where both solubility and diffusion are significant factors.

Advantages

Environmental improvement and reduced product contamination

SFE is an alternative to liquid extraction using solvents such as hexane or dichloromethane. There will always be some residual solvent left in the extract and matrix, and there is always some level of environmental contamination from their use. In contrast, carbon dioxide is easy to remove simply by reducing the pressure, leaving almost no trace, and it is also environmentally benign. The use of SFE with CO2 is approved by the Soil Association for organic products. The CO2 used is largely a by-product of industrial processes or brewing, and its use in SFE does not cause any extra emissions.

Selectivity

The solvent strength of a supercritical fluid can be varied by change in the pressure and a lesser extent in the temperature.

For example, volatile oils can be extracted from a plant with low pressures (100 bar), whereas liquid extraction would also remove lipids. Lipids can be removed using pure CO2 at higher pressures, and then phospholipids can be removed by adding ethanol to the solvent.

Speed

It is a fast process and completed in 10 to 60 minutes. It is a diffusion-based process, with the solvent required to diffuse into the matrix, and the extracted material to diffuse out of the matrix into the solvent. Diffusivities are much faster in supercritical fluids than in liquids, and therefore extraction can occur faster. Also, there is no surface tension and viscosities are much lower than in liquids, so the solvent can penetrate into small pores within the matrix inaccessible to liquids.

Purity

A supercritical fluid can be separated from analyte by simply releasing pressure. Supercritical fluids are cheap, inert and nontoxic. Thus, they are readily disposed off after an extraction is completed by allowing them to evaporate into the atmosphere.

Recovery

Recovery of analytes becomes simple.

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Integrated Pest Management

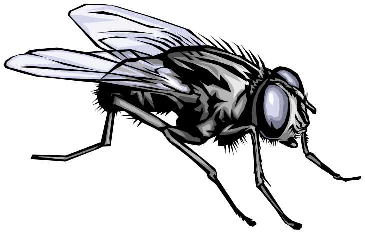
Reducing Pesticide Use

- an effective & environmentally sensitive approach to pest management
- relies on a combination of commonsense practices
- may include the judicious use of pesticides.

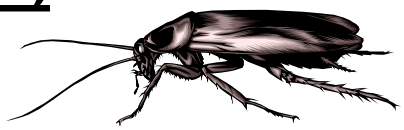
History of IPM

- Humans formed villages & started planting food crops.
- Pests became a problem - attacked them & their crops.
- Humans learned pest control - physical & cultural practices
  - tillage to expose & eliminate soil insects
  - timing of planting, crop rotation
  - pruning, dusting with sulfur
- Physical & cultural methods refined & used into the late 1800's
- Improved crop protection methods = increased acreage
- Equipment became larger & faster = larger acreage
- Monoculture replaced diversification
- pest problems
- Search for more effective pest control measures
- The age of chemical research started:
  - Late 1900's to 1940's
- Use of physical & cultural controls

- Use of pesticides
- Pest resistance
- pest problems
- In the mid 1940's: DDT, organochlorines OP's & carbamates,
- Led to almost total dependence on chemicals
- 1962: "Silent Spring" by Rachel Carson
- Pointed out adverse effects:
    - health, environment
- Late 1960's to 1970's:
    - Develop more benign crop protection
- 1980's - IPM principles applied to urban sites



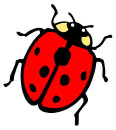
Integrated Pest Management (IPM)

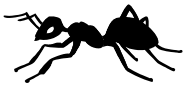


- **Goal of IPM:** control pests,

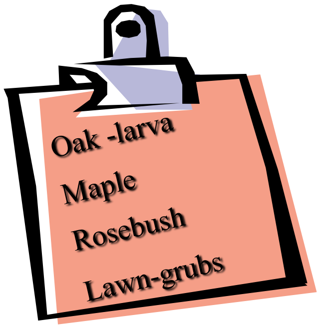
not eradicate entire population

- Treatments are **not** made acc. to a predetermined schedule
- Based on results of monitoring
- Treatments are chosen & timed to be most effective & least disruptive to natural pest controls

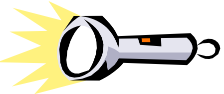




IPM Strategies



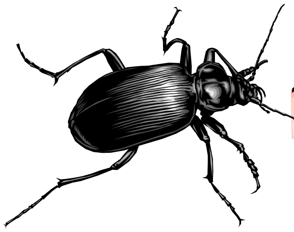
- Monitoring & identification



- ## Physical controls

- ❖ Habitat modification
- ❖ Exclusion
- ❖ caulking, sealing
- ❖ putting up screens
- ❖ air doors

Mechanical controls



Sanitation

Cultural controls

for example- To maintain a healthy lawn:

- Develop healthy soil.
- Choose the right grass type.
- Mow high, often.
- Water deeply.
- Reduce thatch build-up.
- Set realistic goals.
- Biological controls - Bt, nematodes, parasitic wasps, beneficial insects
- Least hazardous pesticides used only when absolutely necessary.

For example:

- Baits - gel, tamper-proof containers

Recycling

Wherever possible, recycling and reuse should be accomplished on-site because it avoids having to move wastes, and because a process that produces recyclable materials is often the most likely to have use for them. The four broad areas in which something of value may be obtained from wastes are the following:

- Direct recycle as raw material to the generator, as with the return to feedstock of raw materials not completely consumed in a synthesis process

- Transfer as a raw material to another process; a substance that is a waste product from one process may serve as a raw material for another, sometimes in an entirely different industry

- Utilization for pollution control or waste treatment, such as use of waste alkali to neutralize waste acid

- Recovery of energy, for example, from the incineration of combustible hazardous wastes.

Examples of Recycling

Recycling of scrap industrial impurities and products occurs on a large scale with a number of different materials. Most of these materials are not hazardous but, as with most large-scale industrial operations, their recycling may involve the use or production of hazardous substances. Some of the more important examples are the following:

- **Ferrous metals** composed primarily of iron and used largely as feedstock for electric-arc furnaces
- **Nonferrous metals**, including aluminum (which ranks next to iron in terms of quantities recycled), copper and copper alloys, zinc, lead, cadmium, tin, silver, and mercury
- **Metal compounds**, such as metal salts
- **Inorganic substances** including alkaline compounds (such as sodium hydroxide used to remove sulfur compounds from petroleum products), acids (steel pickling liquor where impurities permit reuse), and salts (for example, ammonium sulfate from coal coking used as fertilizer)
- **Glass**, which makes up about 10 percent of municipal refuse
- **Paper**, commonly recycled from municipal refuse
- **Plastic**, consisting of a variety of moldable polymeric materials and composing a major constituent of municipal wastes
- **Rubber**
- **Organic substances**, especially solvents and oils, such as hydraulic and lubricating oils
- **Catalysts** from chemical synthesis or petroleum processing
- Materials with **agricultural uses**, such as waste lime or phosphate containing sludges used to treat and fertilize acidic soils

Waste Oil Utilization and Recovery

Waste oil generated from lubricants and hydraulic fluids is one of the more commonly recycled materials. Annual production of waste oil in the U.S. is of the order of 4 billion liters. Around half of this amount is burned as fuel and lesser quantities are recycled or disposed as waste. The collection, recycling, treatment, and disposal of waste oil are all complicated by the fact that it comes from diverse, widely dispersed sources and contains several classes of potentially hazardous contaminants. These are divided between organic constituents (polycyclic aromatic hydrocarbons, chlorinated hydrocarbons) and inorganic constituents (aluminum, chromium, and iron from wear of metal parts; barium and zinc from oil additives; lead from leaded gasoline).

The first of these uses distillation to remove water and light ends that have come from condensation and contaminant fuel. The second, or processing, step may be a vacuum distillation in which the three products are oil for further processing, a fuel oil cut, and a heavy residue. The processing step may also employ treatment with a mixture of solvents including isopropyl and butyl alcohols and methyl ethyl ketone to dissolve the oil and leave contaminants as a sludge; or contact with sulfuric acid to remove inorganic contaminants followed by treatment with clay to take out acid and contaminants that cause odor and color. The third step employs vacuum distillation to separate lubricating oil stocks from a fuel fraction and heavy residue. This phase of treatment may also involve hydrofinishing, treatment with clay, and filtration.

Waste Oil Fuel

For economic reasons, waste oil that is to be used for fuel is given minimal treatment of a physical nature, including settling, removal of water, and filtration. Metals in waste fuel oil become highly concentrated in its fly ash, which may be hazardous.

Waste Solvent Recovery and Recycle

The recovery and recycling of waste solvents has some similarities to the recycling of waste oil and is also an important enterprise. Among the many solvents listed as hazardous wastes and recoverable from wastes are dichloromethane, tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane, benzene, liquid alkanes, 2- nitropropane, methylisobutyl ketone, and cyclohexanone. For reasons of both economics and pollution control, many industrial processes that use solvents are equipped for solvent recycle.

A number of operations are used in solvent purification. Entrained solids are removed by settling, filtration, or centrifugation. Drying agents may be used to remove water from solvents, and various adsorption techniques and chemical treatment may be required to free the solvent from specific impurities. Fractional distillation, often requiring several distillation steps, is the most important operation in solvent purification and recycling. It is used to separate solvents from impurities, water, and other solvents.

Recovery of Water from Wastewater

It is often desirable to reclaim water from wastewater. This is especially true in regions where water is in short supply. Even where water is abundant, water recycling is desirable to minimize the amount of water that is discharged. A little more than half of the water used in the U.S. is consumed by agriculture, primarily for irrigation. Steam-generating power plants consume about one-fourth of the water, and other uses, including manufacturing and domestic uses, account for the remainder.

The three major manufacturing consumers of water are chemicals and allied products, paper and allied products, and primary metals. These industries use water for cooling, processing, and boilers. Their potential for water reuse is high and their total consumption of water is projected to drop in future years as recycling becomes more common.

The degree of treatment required for reuse of wastewater depends upon its application. Water used for industrial quenching and washing usually requires the least treatment, and wastewater from some other processes may be suitable for these purposes without additional treatment. At the other end of the scale, boiler makeup water, potable (drinking) water, water used to directly recharge aquifers, and water that people will directly contact (in boating, water skiing, and similar activities) must be of very high quality. The treatment processes applied to wastewater for reuse and recycle depend upon both the characteristics of the wastewater and its intended uses. Solids can be removed by sedimentation and filtration.

Biochemical oxygen demand is reduced by biological treatment, including trickling filters and activated sludge treatment. For uses conducive to the growth of nuisance algae, nutrients may have to be removed. The easiest of these to handle is nutrient phosphate, which can be precipitated with lime. Nitrogen can be removed by denitrification processes.

Two of the major problems with industrial water recycling are heavy metals and dissolved toxic organic species. Heavy metals may be removed by ion exchange or precipitation by base or sulfide. The organic species are usually removed with activated carbon filtration. Some organic species are biologically degraded by bacteria in biological wastewater treatment. One of the greater sources of potentially hazardous wastewater arises from oil/water separators at wash racks where manufactured parts and materials are washed. Because of the use of surfactants and solvents in the washwater, the separated water tends to contain emulsified oil that is incompletely separated in an oil/water separator. In addition, the sludge that accumulates at the bottom of the separator may contain hazardous constituents, including heavy metals and some hazardous organic constituents. Several measures that include the incorporation of good industrial ecology practice may be taken to eliminate these problems. One such measure is to eliminate the use of surfactants and solvents that tend to contaminate the water, and to use surfactants and solvents that are more amenable to separation and treatment.

Another useful measure is to treat the water to remove harmful constituents and recycle it. This not only conserves water and reduces disposal costs, but also enables recycling of surfactants and other additives.

The ultimate water quality is achieved by processes that remove solutes from water, leaving pure H2O. A combination of activated carbon treatment to remove organics, cation exchange to remove dissolved cations, and anion exchange for dissolved anions can provide very high quality water from wastewater. Reverse osmosis can accomplish the same objective.

However, these processes generate spent activated carbon, ion exchange resins that require regeneration, and concentrated brines (from reverse osmosis) that require disposal, all of which have the potential to end up as hazardous wastes

CO_2-Sequestration

Carbon sequestration means capturing carbon dioxide (CO_2) from the atmosphere or capturing anthropogenic (human) CO_2 from large-scale stationary sources like power plants before it is released to the atmosphere. Once captured, the CO_2 gas (or the carbon portion of the CO_2) is put into long-term storage.

CO_2 sequestration has the potential to significantly reduce the level of carbon that occurs in the atmosphere as CO_2 and to reduce the release of CO_2 to the atmosphere from major stationary human sources, including power plants and refineries.[1]

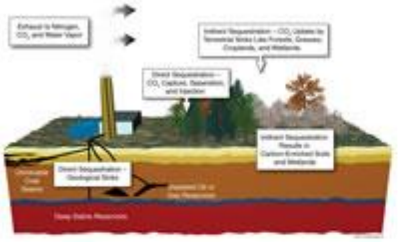
There are two major types of CO_2 sequestration: terrestrial and geologic.

Terrestrial Sequestration

Terrestrial (or biologic) sequestration means using plants to capture CO_2 from the atmosphere and then storing it as carbon in the stems and roots of the plants as well as in the soil. In photosynthesis, plants take in CO_2 and give off the oxygen (O_2) to the atmosphere as a waste gas. The plants retain and use the carbon to live and grow. When the plant winters or dies, part of the carbon from the plant is preserved (stored) in the soil. Terrestrial sequestration is a set of land management practices that maximizes the amount of carbon that remains stored in the soil and plant material for the long term. No-till farming, wetland management, rangeland management, and reforestation are examples of terrestrial sequestration practices that are already in use. It is important to remember that terrestrial sequestration does not store CO_2 as a gas but stores the carbon portion of the CO_2 (the C in the CO_2). If the soil is disturbed and the soil carbon comes in contact with oxygen in the air, the exposed soil carbon can combine with O_2 to form CO_2 gas and reenter the atmosphere, reducing the amount of carbon in storage.

Learn more about the considerations for terrestrial sequestration in the region.

Learn about terrestrial sequestration field projects in the PCOR



Partnership region.

Geologic Sequestration

Geologic sequestration is putting CO_2 into long-term storage in geologic zones deep underground.

Geologic sequestration is the method of storage that is generally considered for carbon capture and storage (CCS) projects. CCS is the practice of capturing CO_2 at anthropogenic sources before it is released to the atmosphere and then transporting the CO_2 gas to a site where it can be put into long-term storage.

Before geologic sequestration can be widely used, two issues need to be addressed:

1. Only a handful of specialized facilities like natural gas-processing plants, coal gasification plants, and ethanol plants currently have processes that separate CO_2 and make it available for geologic sequestration. Actions are under way now to develop economical methods of separating and capturing CO_2 at other large-scale systems like power plants that produce relatively large quantities of anthropogenic CO_2.
2. Although pure CO_2 has been stored as a gas in natural underground deposits for millions of years and oil field operators have safely pumped millions of tons of CO_2 underground into oil-producing formations to increase production (CO_2 flooding), we need validation demonstrations in geologic environments to ensure that we understand the best ways to site the systems as well as monitor the CO_2 in storage over the long term.

Why is it important?

Carbon dioxide (CO_2) capture and sequestration (CCS) could play an important role in reducing greenhouse gas emissions, while enabling low-carbon electricity generation from power plants.

As estimated in the U.S. Inventory of Greenhouse Gas Emissions and Sinks , more than 40% of CO_2 emissions in the United States are from electric power generation. CCS technologies are currently available and can dramatically reduce (by 80-90%) CO_2 emissions from power plants that burn fossil fuels. Applied to a 500 MW coal-fired power plant, which emits roughly 3 million tons of CO_2 per year, [1] the amount of GHG emissions avoided (with a 90% reduction efficiency) would be equivalent to:

- Planting more than 62 million trees, and waiting at least 10 years for them to grow.
- Avoiding annual electricity-related emissions from more than 300,000 homes.

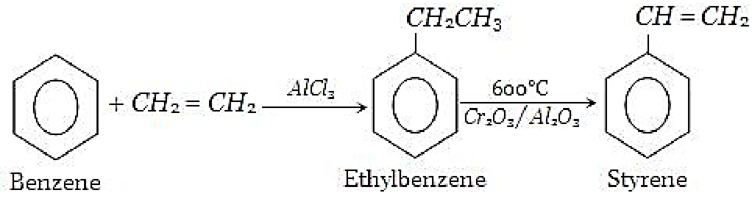
Green synthesis (Less Hazardous Chemical Synthesis)

In today's society, contributions from the field of chemistry are evident all around us. Advancements in chemistry have led to the production of medicines to alleviate our pain, polyester to keep us warm, fertilizers to provide our crops with nutrients, cooking oil to add flavor to our food, and many other things. These same advancements have also generated numerous toxic chemicals, from the insecticides sprayed on our crops to the compounds found in water-based paints. Not only are these toxins harmful to our health, they are also damaging to the environment. For example, the release of chlorofluorocarbons (CFCs) and related compounds generated during chemical processes contributes to the depletion of the ozone layer, which in turn increases the amount of harmful solar radiation that makes it to the Earth's surface. In the year 2000, 7 billion pounds of toxic materials were released by the U.S. alone.

Green chemistry is an approach that aims to eliminate the usage and generation of hazardous substances by designing better manufacturing processes for chemical products. Specifically, the goal of making the finished product and by-products less toxic directs the decisions made during chemical production. Aspects of the manufacturing process considered include the initial selection of chemicals, the mechanism of chemical synthesis, the end products of the process, and the management of toxic products generated during production. By limiting the hazard intrinsic to the chemical products, the risk introduced by the product is consequently reduced. In addition to protecting the environment, green chemistry has the potential to benefit the large and diverse group of people whose job or residence places them at risk for exposure to toxic chemicals produced by manufacturing.

Production of styrene (=benzene ring with CH=CH₂ tail)

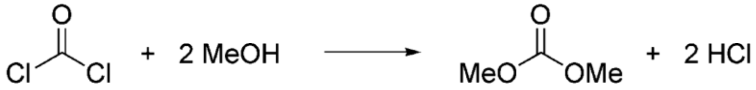
- **Traditional route:** Two-step method starting with benzene, which is carcinogenic) and ethylene to form ethylbenzene, followed by dehydrogenation to obtain styrene



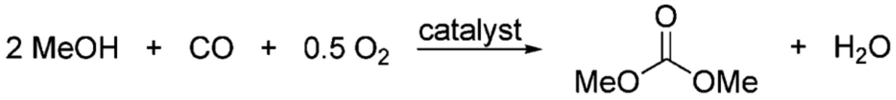
Greener route: To avoid benzene, start with xylene (cheapest source of aromatics and environmentally safer than benzene)

syntheses of dimethyl carbonate -which is greener?

Traditional synthesis: from phosgene and methanol



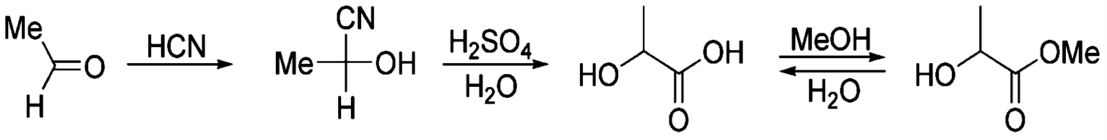
Modern synthesis -methanol carbonylation



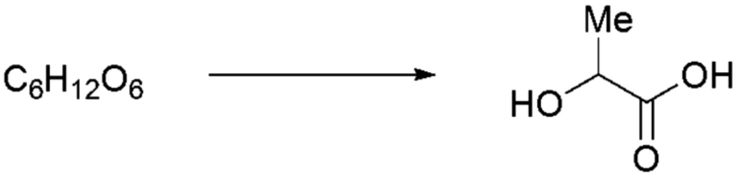
Route 2 is preferred since it avoids the use of phosgene and it gives less harmful side-products (route 2 also produces purer product, so energy intensive purification steps are eliminated).

Syntheses of lactic acid (HOCHMeCO2H) -which is greener?

Chemical –hydrocyanation of acetaldehyde



Biochemical –fermentation of sugars or starch



Synthesis of Maleic anhydrite

The "old" Method used as a starting material **benzene** (C_6H_6) and a catalyst which was composed of oxides of Vanadium and Molybdenum , V_2O_5 and MoO_3

$$2\ C_6H_6 + 9O_2\ (\text{air}) \rightarrow \text{catalysts} \rightarrow 2\ C_4H_2O_3 + H_2O + 4\ CO_2$$

The "new greener" Method with starting material **n-butane** and catalyst $(VO)_2P_2O_5$

$$\mathbf{C_4H_{10} + 3.5\ O_2\ (air) \rightarrow catalyst \rightarrow C_4H_2O + 4H_2O}$$

The Efficiency of the "Green" Method of Adipic Acid

The "old", traditional method for the adipic acid with cyclohexanone/cyclohexanol oxidation by Nitric acid.

In the presence of catalyst copper/vanadium [Cu(0.1-05% & V (0.02-0.1%)] The reaction is:

$$C_6H_{12}O + 2\ HNO_3 + H_2O \rightarrow C_6H_{10}O_4 + NO_x\ (NO, NO_2, N_2O, N_2)$$

In this method the negative aspect is the release of nitrogen oxides

The new "greener" method. The preparation from cyclohexene oxidized by H_2O_2 in the presence of the catalyst $N\alpha_2WO4.2H_2O$ (1%)

$$C_6H_{10} + 4\ H_2O_2 \rightarrow \text{catalysts} \rightarrow C_6H_{10}O_4 + 4\ H_2O$$

Good Luck

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