

ENVIRONMENTAL CHEMISTRY

- E1 Air pollution
- E2 Acid deposition
- E3 Greenhouse effect
- E4 Ozone depletion
- E5 Dissolved oxygen in water
- E6 Water treatment
- E7 Soil
- E8 Waste
- E9 Ozone depletion (HL)
- E10 Smog (HL)
- E11 Acid Deposition (HL)
- E12 Water and soil (HL)

16



Human activities involve intensive use of limited resources found in air, water and soil. Many of these activities produce waste products that build up in the environment to produce pollution with increasingly local and global effects. An understanding of this impact is essential with and beyond the study of chemistry. This option has many opportunities for discussing aim 8 issues and the international dimension.

© IBO 2007

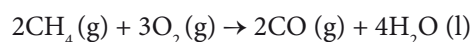
A primary air pollutant is one which is added directly to the air from a given source, such as carbon dioxide from the burning of fossil fuels. A secondary air pollutant, on the other hand, is formed in the atmosphere through chemical reaction(s), such as the formation of ozone in photochemical smog. The five major primary pollutants in the atmosphere are: carbon monoxide (CO), oxides of nitrogen (NO_x), oxides of sulfur (SO_x), particulates and volatile organic compounds (VOCs).

CARBON DIOXIDE

:C≡O: (CO) is a polar molecule with covalent bonding between the atoms. It is a colorless, odorless, tasteless, toxic compound which is not very soluble in water. It is formed due to the incomplete oxidation of carbon and carbon-containing compounds such as fossil fuels.

Main sources of carbon monoxide

Almost 90% of all CO production comes from natural sources – most of it from the atmospheric oxidation of methane gas, CH₄.



Methane is produced from the decomposition of organic matter in swamps and tropical regions (for example rice fields, rivers and lakes) under anaerobic (lack of oxygen) conditions, as well as from algae and other organic matter in oceans.

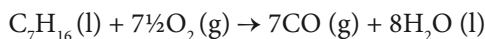
E1 AIR POLLUTION

- E.1.1 Describe the main sources of carbon monoxide (CO), oxides of nitrogen (NO_x), oxides of sulfur (SO_x), particulates and volatile organic compounds (VOCs) the atmosphere.

© IBO 2007

Dry air that is not polluted contains about 78% nitrogen gas, N₂, 21% oxygen gas, O₂, 1% argon, Ar, 0.03% carbon dioxide, CO₂ together with trace amounts of other gases. An air pollutant is a substance present in sufficient concentration in the air to produce a harmful effect on humans or other animals, vegetation or materials. It can be produced, naturally by processes such as volcanic activity and bacterial action, or produced by human activity ('man made') due to increased urbanization, industrialization (such as electrical power plants), transportation, forest fires, incineration of solid wastes amongst others.

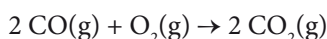
The other 10% CO comes from man-made sources, such as the combustion of fossil fuels used in industry, in particular gasoline (petrol) used in the internal combustion engine for transportation, and from forest fires. Carbon monoxide is a product if there is insufficient oxygen present such as in forest fires, or in automobiles when poor mixing of fuel and air takes place, or if there is insufficient oxygen present in an internal combustion engine. One example of incomplete combustion is:



Whereas the natural sources of CO tend to be widely distributed, two major problems with CO from human activity include:

- (1) localization, that is, it is produced in compact areas such as down-town core areas and on highways and major thoroughfares
- (2) high emission rates at rush hours.

Fungi in soil act as 'soil sinks' converting CO to CO_2 :



However, localization and high emission rates of CO occur in urbanized areas with less soil than rural areas and therefore fewer microorganisms to reduce CO concentrations. Refer to Figure 1601.

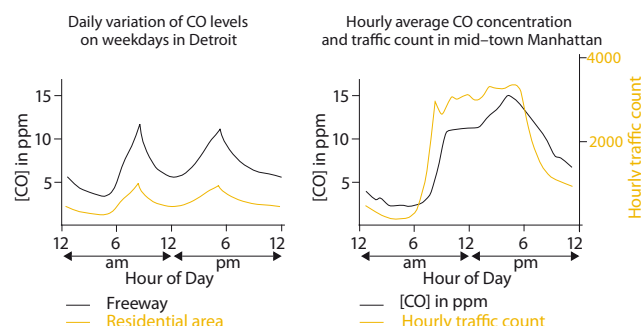


Figure 1601 The variation in CO levels in two large cities

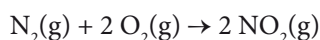
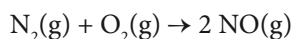
OXIDES OF NITROGEN (NO_x)

There are several (8) known oxides of nitrogen of which nitrous oxide (N_2O ; systematic name: dinitrogen monoxide) is found naturally and nitric oxide or nitrogen monoxide (NO) and nitrogen dioxide (NO_2) are found to be important components of polluted air.

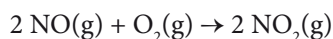
There is no reaction between nitrogen gas (N_2 , $:\text{N}\equiv\text{N}:$) and oxygen gas at room or moderately high temperatures due to the very high stability of the nitrogen–nitrogen triple bond. Any reaction between nitrogen and oxygen gas is highly endothermic. Under conditions of high temperatures (around 1500 °C found in automobile engines) a reaction between the two gases can take place, producing nitrogen oxides, NO_x .

Principal Sources of (NO_x)

Human activity produces about 10% of NO_x . Most human sources of NO_x are emitted as NO and a small amount as NO_2 gas during the high temperature combustion that takes place in an automobile engine, airplanes and rail engines; stationary sources such as furnaces fuelled by natural gas, coal, fuel oil and wood; industrial processes such as nitric acid manufacture as well as agricultural burning and forest fires.



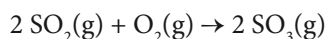
In the atmosphere the NO gas present (a primary pollutant) is rapidly converted to NO_2 , a secondary pollutant according to this equation.



Thus, most of the man-made NO_x pollution enters the environment as NO gas. The natural decomposition of nitrogen-containing compounds by bacterial action is, however, responsible for most of the N_2O and NO found in the environment. The high energy in lightning also results in some formation of N_2O and NO; natural NO is rapidly oxidised to NO_2 , a secondary pollutant. As with carbon monoxide, natural sources of NO_x are widely distributed, however, man made sources of NO_x are localized and can be present in high concentrations due to the use of automobiles.

OXIDES OF SULFUR, SO_x

Sulfur dioxide, SO_2 , is produced by far in the largest amount and sulfur trioxide, SO_3 , is produced in very small amounts. Once SO_2 is in the atmosphere, it is slowly oxidised to SO_3 . The presence of heavy metal pollutants and finely divided particulates such as ash can speed up the reaction, as can the presence of O_3 , hydroxyl free radical, $\cdot\text{OH}$ and sunlight as follows.

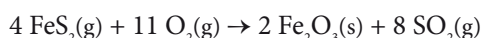
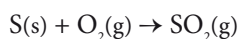


| | N_2O nitrous oxide | NO nitric oxide | NO_2 nitrogen dioxide |
|-------------------------------|---|--|--|
| Oxidation number of nitrogen: | + 1 | + 2 | + 4 |
| Lewis Structure | $\text{:}\ddot{\text{N}}=\text{N}=\ddot{\text{O}}\text{:}$ | $\text{:}\dot{\text{N}}=\ddot{\text{O}}\text{:}$ odd # electrons | $\begin{array}{c} \cdot \\ \text{N} \\ \diagup \quad \diagdown \\ \text{:O:} \quad \text{:O:} \end{array}$ odd # of electrons |
| Sources | All produced by natural sources from decomposition of nitrogen containing compounds by bacterial action in soil and from lightning. | 80% from natural sources (bacterial action); 20% from human sources from high temperature oxidation of N_2 in air in automobile and aircraft engines. | Nearly all made as secondary pollutant from NO . |

Figure 1602 The oxides of nitrogen

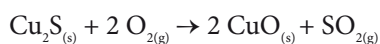
Principal sources

- (a) From sulfur containing fossil fuels such as coal: Low grade coal can contain up to 7% sulfur impurity (although the common percentage of sulfur in coal is between 1 and 5%). Coal contains sulfur as elemental sulfur, as iron pyrite FeS_2 and as organic sulfur compounds, since it was present in the proteins of the trees from which it was derived. The combustion process converts any sulfur to sulfur dioxide:



Coal combustion is the major contributor to sulfur oxide pollution. Petroleum and natural gas contribute little to this as most of the sulfur is removed, by reacting with hydrogen gas in the presence of a catalyst, during petroleum refining and natural gas processing. Some heavy fuels (used by ships and power stations) can however have a high sulfur content, contributing to SO_2 pollution.

- (b) From smelting plants which oxidise sulfide ores to the metal oxides:



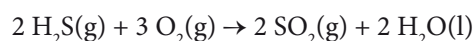
- (c) Sulfuric acid factories also release some sulfur dioxide. Sulfuric acid, H_2SO_4 is produced by the oxidation of sulfur dioxide, SO_2 gas by oxygen

in the presence of vanadium (V) oxide, V_2O_5 as a catalyst to form sulfur trioxide, SO_3 gas which reacts with water to produce the acid.



Natural sources

No major natural primary sources of sulfur dioxide are known although probably very small amounts are produced through volcanic and bacterial activity. However, sulfur dioxide is formed as a secondary pollutant in the atmosphere as a result of the atmospheric oxidation of hydrogen sulfide gas, H_2S :



Hydrogen sulfide gas is produced most importantly by the anaerobic decay of organic matter (in swamps, oceans, etc.) and also some by volcanic activity.

PARTICULATES

These are solid particles suspended or carried in the air and are generally large enough to be seen. Natural sources of particulates include sandstorms, volcanoes and forest fires started by lightning. Typical particulates from man-made sources include:

- (a) Smoke and soot produced by the combustion of coal, petroleum, wood etc.

- (b) Dust from mechanical break-up of solid matter.
- (c) Asbestos from industrial plants: asbestos is a fibrous material composed of silicate crystals. Having used asbestos in the past in the insulation of buildings, demolition of such buildings releases asbestos particles. Many countries now ban the use of asbestos as it causes scarring of lung tissue.
- (d) Metallic particles such as beryllium, mercury and arsenic from industrial plants and lead compounds in places where leaded gasoline is still in use. Beryllium oxide is used in spark plugs and as lining in high temperature furnaces (because of its very high melting point and high electrical resistivity). Mercury is present in fly ash and is also used in the manufacture of fungicides, pulp and paper.
- (e) When coal is burnt, most of the ash is carried away in the exhaust gases as finely divided powder called fly ash which consists of unburnt carbon and oxides of many metals including iron, magnesium and calcium, as well as sulfates. A typical coal burning power plant produces 1000 tons of fly ash a day.

VOLATILE ORGANIC COMPOUNDS

Volatile Organic Compounds (VOCs) are primary pollutants introduced directly into the environment. These include hydrocarbon gases or volatile organic liquids that are easily converted into gases which escape into the air. Recall that C_1 to C_4 hydrocarbons are gases and C_5 to C_{12} hydrocarbons are liquids due to the weak van der Waals' forces between these generally non-polar molecules which increase as their size increases.

Similarly to CO and NO_x , most hydrocarbons enter the environment from natural sources involving biological processes including a little from geothermal activity. Methane, the simplest alkane, and the largest natural source of hydrocarbons, is produced by the anaerobic bacterial decomposition of organic matter in bodies of water including swamps and oceans. Methane is also produced as a digestive gas in many animals. Trees and plants produce most of the rest of the natural volatile organic compounds called terpenes.

Petroleum, a complex mixture of very useful organic compounds, is the key source of VOC pollution produced by human activities. These include extracting, refining, transporting and using petroleum products, air pollution resulting at each stage. The fraction from petroleum that is used as vehicle fuel contains volatile hydrocarbons with

C_5 to C_{16} carbons. These evaporate easily in the internal combustion engine and produce vapor during storage and the filling of fuel tanks. Incomplete combustion of fuel, especially in gasoline and diesel engines, also produces VOCs that are released into the atmosphere through exhausts. Photochemical smog, which is secondary pollution from automobile exhausts, contains large amounts of methyl benzene, $C_6H_5CH_3$, as well as reactive benzene derivatives. Solvents used in paints and other similar products are also human sources of volatile hydrocarbons.

E.1.2 Evaluate current methods for the reduction of air pollution.

© IBO 2007

CURRENT METHODS FOR THE REDUCTION OF AIR POLLUTANTS

Several methods are being used including implementing policies to encourage the use of mass transportation. Others being tested include the use of alternate fuels such as solar and battery operated cars, 'hybrid' cars, fuel cells, hydrogen as a fuel and changes to engine design. Most solutions are directed towards the automobile as it is the largest man made source of primary pollutants.

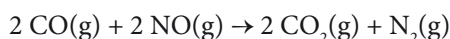
The combustion of hydrocarbon fuel and air mixture produces very high temperatures. The consequence of this sudden and rapid chemical process is that some VOCs remain unreacted, some undergo partial oxidation to carbon monoxide, and the high temperatures make a reaction between oxygen and highly stable nitrogen gas possible. By far the most common method for the reduction of these air pollutants includes exhaust systems that make it possible for the oxidation of carbon monoxide to carbon dioxide (which although it is a greenhouse gas is not a metabolic poison). However, the problem is complicated by the presence of other pollutants, namely oxides of nitrogen, particulates and VOCs also produced by the automobile.

| | Human source | Natural Source | Effect on Health | Methods of Control |
|--|--|--|---|--|
| Carbon monoxide (CO) | Incomplete combustion of fossil fuels used for transportation and industry; forest fires. Localized, high emissions produced. $C_7H_{16} + 7\frac{1}{2}O_2 \rightarrow 7CO + 8H_2O$ | From atmospheric oxidation of CH_4 (from anaerobic decomposition of organic matter). $2CH_4 + 3O_3 \rightarrow 2CO + 4H_2O$ | Metabolic poison. Interferes with O_2 transport; prevents haemoglobin from carrying O_2 ; deprives body cells of O_2 leading to asphyxiation. Heart has to pump faster. | 1. Catalytic converter 2. Lean burn engine (less fuel present with higher air/fuel ratio) 3. Thermal exhaust reactor |
| Oxides of Nitrogen (NO_x): N_2O, NO and NO_2 | High temperature combustion in automobiles produces mostly NO, nitric oxide. This is oxidised to NO_2 in the atmosphere. | Decomposition of N-containing compounds by bacterial action produces N_2O , and NO. (Nearly all NO_2 is man made). | NO_2 causes breathing problems, respiratory distress and pulmonary edema. HNO_3 (from NO_2) irritates the respiratory tract | 1. Catalytic converter. 2. Lean burning engines. 3. Recirculation of exhaust gases. |
| Oxides of sulfur (SO_x): SO_2 and SO_3 | Combustion of sulfur containing coal, smelting plants, sulfuric acid plants: $S + O_2 \rightarrow SO_2$ | No major direct sources of SO_x in nature, but oxidation of H_2S gas from decay of organic matter and volcanic activity. | Acid rain formed from SO_x pollution irritates the respiratory tract and adversely affects the elderly, the young and asthma sufferers. | 1. Alkaline scrubbing. 2. Limestone-based fluidized beds 3. Sulfur removed from fossil fuels before burning |
| Particulates | Combustion of fossil fuel use by industry, transportation, breakup of solid matter, industrial plants which produce smoke, soot, ash, dust | Blowing dust, volcanic activity, forest fires, biological sources such as pollen. | Irritation of the mucous membranes and lungs causing emphysema. Asbestosis and berylliosis cause scarring of lung tissue. | 1. Electrostatic precipitators. 2. Gravity settling chambers. 3. Cyclone separators. |
| Volatile organic compounds (VOCs) | Petroleum extracting, refining, transporting and use; solvents, incomplete combustion of gasoline, coal and wood. | CH_4 from biological anaerobic bacterial decomposition of organic matter; trees and plants produce terpenes. | Aromatic compounds cause irritation of mucous membrane; some, such as benzene and benzo(α)pyrene are carcinogenic. | 1. Catalytic converters. |

Figure 1603 Summary of air pollutant sources, health effects and methods of control

Reduction of CO , NO_x and VOCs using catalytic converter

Catalytic converters are quite remarkable in their ability not only to oxidize carbon monoxide to carbon dioxide, but also to convert NO (nitrogen monoxide) to nitrogen gas as follows.

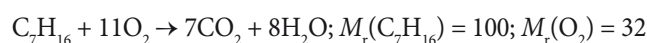


In the presence of small amounts of platinum-based catalysts, the pollutants CO and NO are converted to CO_2 and harmless nitrogen gas. The principal source of VOCs is from automobile exhausts. The catalytic converter effectively removes these as it can also oxidize volatile organic compounds (hydrocarbons) to carbon dioxide and water.

The average cost of an automobile is increased by about US \$600 – 800 and it also requires the use of high octane, non-leaded fuel since the catalyst in the converter is inactivated by the lead in leaded gasoline. Similarly, sulfur impurities in gasoline also poison the catalyst and have to be removed before the gasoline can be used as fuel.

Use of Air to Fuel Ratio to reduce automobile pollution

Gasoline mixture consists of VOCs containing C_5 to C_8 hydrocarbons. Consider the complete combustion of C_7H_{16} represented by the equation:



1 mol C_7H_{16} (= 100g) requires 11 mol O_2 (= 352g) for complete combustion. Thus, 1.0 g C_7H_{16} requires 3.52 g oxygen. By mass, air contains about 22% oxygen and 78% nitrogen. Thus the mass of air required for 1.0 g C_7H_{16} is: $(100/22) \times 3.52 = 16g$, that is a theoretical air to fuel ratio by mass of 16:1. A similar calculation with C_8H_{18} gives a ratio of 14 to 1. Since gasoline is a mixture of hydrocarbons, an average value of air to fuel ratio of about 15 to 1 should give rise to complete combustion. However, the control of pollutants from automobiles is complicated because of the presence of other primary pollutants.

- (a) **Lower air to fuel ratio:** If there is more fuel present (a richer fuel mixture, that is a lower air to fuel ratio), then complete combustion does not take place. some unreacted VOCs remain and more carbon monoxide is produced but the lack of air reduces the amount of nitrogen oxides produced. Air can then be injected into the exhaust gases containing CO and unburnt HCs to oxidize these to carbon dioxide and water. This Thermal Exhaust Reactor method however requires expensive engine design.

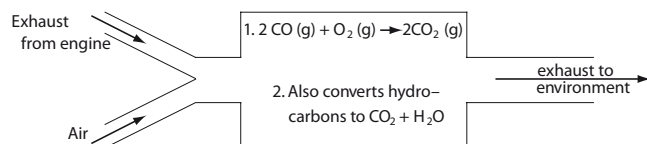


Figure 1604 A Thermal exhaust reactor

- (b) **Lean Burn Engines:** If there is excess air and less fuel present, this represents a lean mixture with higher air to fuel ratio. In this case, less carbon monoxide and volatile organic compounds will be present in the exhaust, but nitrogen oxides levels will increase. The graph shows the variation in concentration of exhaust emission gases with the composition of the air to fuel mixture. 'Lean burn' engines with modification use an air:fuel ratio of approximately 18:1 by volume to minimise the production of pollutants.

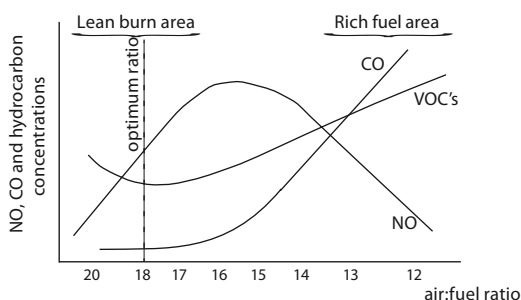


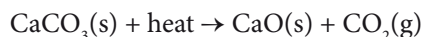
Figure 1605 Lean burn engines are better for the environment

The graph shows that CO% and VOCs% decrease as air to fuel ratio increases, NO_x increases up to about 16:1 air to fuel ratio. Thus, changing the air to fuel ratio changes the amount of these three pollutants, but does not reduce all three without affecting performance.

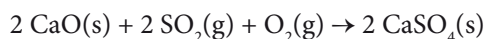
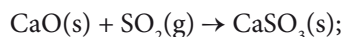
Reduction of oxides of sulfur by post-combustion methods

Post combustion methods, involve the removal of sulfur dioxide from exhaust gases after burning the coal but before releasing to the atmosphere:

- (1) Limestone fluidized beds involve adding powdered limestone, $CaCO_3$, with the coal in the combustion process. The heat from the combustion decomposes the limestone to calcium oxide:

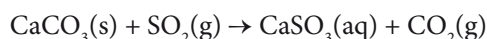
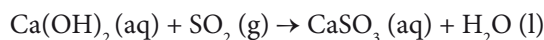
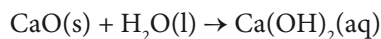


The calcium oxide reacts with the SO_2 produced to form $CaSO_3$, calcium sulfate(IV), and in the presence of oxygen $CaSO_4$, calcium sulfate(VI) forms:



The calcium sulfate, any unreacted calcium oxide and sulfur dioxide together with fly ash (particulates) are then absorbed into water in a wet-scrubber.

- (2) A wet alkaline scrubber is a cleaning device that uses a liquid, usually water based, to remove contaminants. This uses a counterflow method in which the alkaline liquid is sprayed downward while the gas stream moves upwards. The effectiveness depends on the contact between the alkaline liquid and the acidic sulfur dioxide:



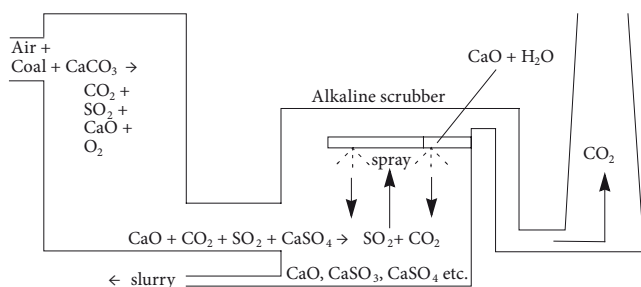
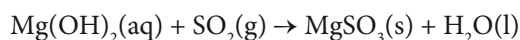


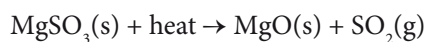
Figure 1606 The principle of a 'wet scrubber'

The waste slurry is transferred to settling ponds. Problems include the tendency of CaSO_3 to deposit on scrubber surfaces and the need for extremely large amounts of limestone, CaCO_3 which is converted to CaO by heating. Note that, by this method, the sulfur dioxide is being replaced by carbon dioxide, a greenhouse gas.

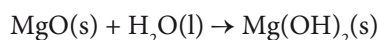
Other wet alkaline scrubbers use magnesium hydroxide as the alkaline material:



Magnesium sulfate(IV) formed in the slurry can be heated to convert it to MgO :



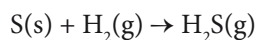
SO_2 formed can be used for the manufacture of sulfuric acid and the magnesium oxide treated with water to form magnesium hydroxide and recycled:



However, the heating requires large amounts of energy and is therefore very expensive.

Other methods of reducing oxides of sulfur in the atmosphere

- (1) Converting high sulfur coal to synthetic natural gas, SNG, CH_4 and the removal of most of the sulfur in the process of coal gasification. In this method, any sulfur is converted to hydrogen sulfide gas which is acidic and easily removed:



One major disadvantage is that it requires about 30% of the energy for the conversion of coal to SNG.

- (2) Using low sulfur, cleaner burning coal such as anthracite (hard coal) that has a high heat content. This type of coal is however much scarcer and more expensive.
- (3) During petroleum refining and natural gas processing, sulfur is removed by reaction with hydrogen gas, in the presence of a catalyst. Any sulfur present is reduced to hydrogen sulfide gas which is an acidic gas and easily removed (considered a pre-combustion method).
- (4) To desulfurize (remove sulfur from) high sulfur coal, the method of coal washing is used. Coal is finely ground and washed with water. Iron pyrites, FeS_2 , has high density, settles rapidly and is removed. However, even in finely ground coal, a lot of sulfur is trapped below the surfaces of the particles and is therefore not removed. Organic sulfur, chemically bonded to carbon atoms in coal cannot be removed by this physical process (also considered a pre-combustion method).

Reduction of Particulates

Electrostatic precipitation is the most important and effective method for the removal of very tiny particles suspended in the air.

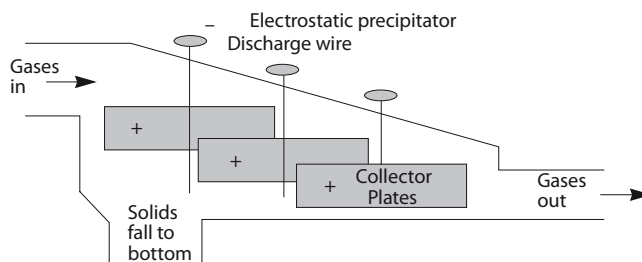


Figure 1607 The principle of electrostatic precipitation

In an electrostatic precipitator, a very high voltage is applied between the discharge wires and the collector plates which ionizes the gas molecules present:



The electrons produced collect on the particulates and the negatively charged particles are attracted to the positively charged collector plates. The collector plates have to be periodically shaken to remove the collected solid particles. This method can remove more than 98% of all particulate matter.

Summary of Automobile

Pollution

The sheer number of automobiles around the world makes this mode of transportation the major source of air pollution. These include unburnt VOC fuels that escape from the fuel tank, the engine and exhaust as well as carbon dioxide, carbon monoxide, particulates (soot) and oxides of nitrogen produced after combustion as well as lead (released as lead(II) bromide) if leaded gasoline is used. Methods of control of pollution from the automobile include:

- use of non-leaded gasoline to eliminate lead pollution.
- valves on gas tanks so gasoline can be pumped into the tank, but gasoline vapor cannot escape.
- different air to fuel ratios produce different amounts of pollutants. Lower air to fuel ratios produce less NO_x but more CO and VOCs due to incomplete combustion. Higher air to fuel ratios produce more complete combustion, thus less CO and VOCs but more NO_x as the more complete combustion produces higher temperatures and the presence of more oxygen favors NO_x production.
- thermal exhaust reactor, where the exhaust gases are mixed with air to oxidize carbon monoxide to carbon dioxide and any unburnt VOCs to CO_2 and H_2O .
- catalytic converters seem by far the most effective way of reducing pollution from the automobile. They use platinum-based catalysts through which

the exhaust gases pass and they convert unburnt VOCs to CO_2 and H_2O , CO to CO_2 and NO to N_2 . Because lead poisons the catalyst, an added advantage is that catalytic converters require the use of non-leaded gasoline thus eliminating lead pollution from automobiles.

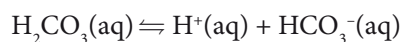
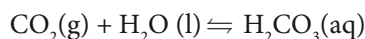
E2 ACID DEPOSITION

E.2.1 State what is meant by the term acid deposition and outline its origins.

© IBO 2007

The term **acid deposition** refers to acidic particles and gases that deposit or fall to the Earth. It includes both wet deposition of acidic gases such as oxides of sulfur and nitrogen and acidic particles brought down as precipitation by rain, fog and snow and dry deposition of acidic gases and particles in the absence of rain or precipitation.

Pure rain water is naturally acidic, $\text{pH} \approx 5.6$ ($[\text{H}^+] \approx 2.5 \times 10^{-6} \text{ mol dm}^{-3}$) due to dissolved carbon dioxide reacting to form carbonic acid, a very weak acid:



The environmental pollution called acid rain is any rain with pH less than 5.6. Recall that pH is a logarithmic scale with one pH unit corresponding to a difference in



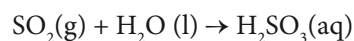
hydrogen ion concentration of a factor of 10. Thus acid rain of pH 4.2 has hydrogen ion concentration 25 times greater than pure rain water. Although extreme acid rain (pH of 1.7 recorded in Los Angeles in December 1982) is rare, the average rainfall in industrialized areas of the world has $[H^+]$ about 4 to 40 times greater than pure rain water (that is, pH 4 to 5 is common compared to a pH of 5.6). A pH of 4.0 in lakes is sufficient to kill fish life and such dead lakes do exist in North America, China and Russia among other places. Note that the pH of any water sample can be measured using pH paper showing colors of various pH values, or using a universal indicator, or a calibrated pH meter.

Research shows that acid deposition is associated with parts of a country where heavy industries are situated and also down-wind from such sites. Analysis of acid deposition indicates that oxides of sulfur, SO_x , and oxides of nitrogen, NO_x , are mostly responsible for the rain acidity (recall that many non-metallic oxides are acidic). Snow, fog, sleet, hail and drizzle all become contaminated with acids when SO_x and NO_x are present as pollutants.

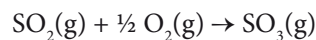
FORMATION OF ACID DEPOSITION:

From oxides of sulfur

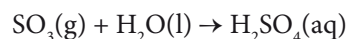
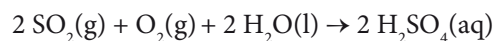
In the presence of moisture, sulfur dioxide produces sulfurous acid, a weak acid, but significantly stronger than carbonic acid:



Sulfur dioxide can be oxidized in the presence of O_3 , $\cdot OH$ (hydroxyl free radical) and sunlight to sulfur trioxide:



In the presence of moisture, sulfur oxides can be converted to sulfuric acid, a strong acid:

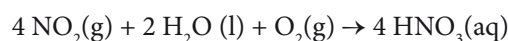


From oxides of nitrogen

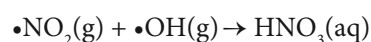
In the absence of oxygen, nitrogen dioxide can dissolve in water to produce a mixture of nitrous acid (HNO_2), a weak acid, and nitric acid (HNO_3), a strong acid:



Nitrogen dioxide gas can be converted to nitric acid, HNO_3 , a strong acid, in the presence of oxygen gas and moisture through a series of complicated reactions which can be summarized as:



The conversion of nitrogen dioxide to nitric acid can be accelerated by the presence of other pollutants present in the air, such as the hydroxyl free radical, $\cdot OH$, which is formed during photochemical smog can react with nitrogen dioxide, itself a free radical (with a lone electron):



E.2.2 Discuss the environmental effects of acid deposition and possible methods to counteract them.

© IBO 2007

Acid deposition affects humans, aquatic life, materials, soil, vegetation and visibility as follows

EFFECTS OF ACID RAIN ON HUMANS

Breathing air containing fine droplets of acid irritates the whole respiratory tract from mucous membranes in the nose and throat to the lung tissues. Also, it can cause severe eye irritation. Sulfate aerosols are also powerful irritants. The small sulfate particles penetrate the lungs where they become embedded and have adverse effects on asthmatics, the elderly and the young. Increased concentrations of $Al^{3+}(aq)$ in water due to acidic conditions may lead to Alzheimer's disease.

EFFECT ON AQUATIC LIFE

Salmon cannot survive if pH is as low as 5.5. If acidification of lakes and rivers takes place, it affects aquatic life. One major effect on fish is the increased concentration of Al^{3+} resulting from the leaching of soil by acid rain. Al^{3+} affects the function of the gills. **Eutrophication** results from nitrates in acid deposition.

EFFECT ON MATERIALS

Corrosion of basic materials such as marble or limestone (CaCO_3) and dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) takes place. The insoluble carbonates are converted to more soluble sulfates:



The sulfates can dissolve in water leading to considerable damage to structural and artists' stone. This is called 'stone leprosy' and has caused damage to cultural monuments in places like Egypt, Greece, Mexico and Turkey. The Egyptian sphinx (see Figure 1608) has suffered from both acid rain and being used for artillery target practice.

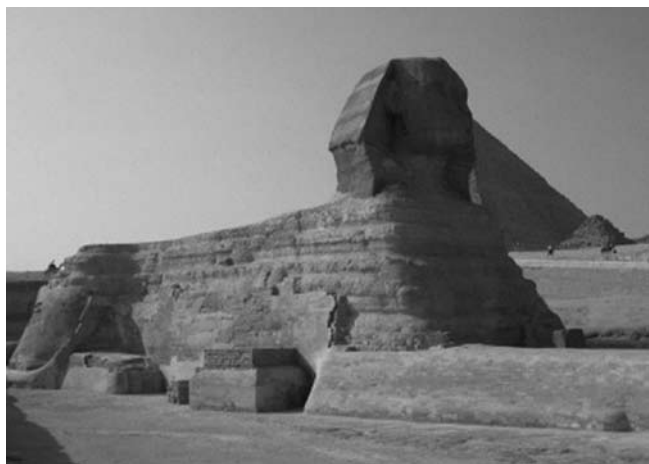


Figure 1608 The Egyptian sphinx

Corrosion of iron and steel is promoted by acid rain, a problem which is increased by high humidity, high temperatures and the presence of particulates. The overall reaction is:



Similarly deterioration of electrical equipment takes place as a result of corrosion. Acid rain pollution causes bleaching and weakening of fabrics and leather and

discoloration and embrittlement of paper. Acid rain can also leach heavy toxic metals such as lead, cadmium and mercury into the water system.

EFFECT ON SOIL AND VEGETATION

The extent to which plants can be damaged depends upon acid concentration and length of exposure. Acute injury due to short term exposure to high acid concentrations leads to attacks on cells producing dead areas of leaves which dry out and usually become bleached. Chronic injury due to long term exposure to even low acid concentrations disrupts chlorophyll synthesis, characterized by yellowing of leaves (as a result of acid entering the stomata of the leaves). Effects include bleached spots, yellowing of leaves, suppression of plant growth and reduction in yield. Acid rain also leaches or removes important nutrients such as Mg^{2+} from soil.

EFFECT ON VISIBILITY

The mist of sulfuric acid and sulfate aerosols in the atmosphere can cause great loss of visibility and can curtail air flights.

Possible methods to counteract acid deposition

Most efforts at reducing acid deposition are directed at the important sources of the pollutants, namely from coal and automobile engines and are discussed in detail in section E.1.2 above. These include the use of catalytic converters to reduce CO and NO_x , control of air to fuel ratio to reduce NO_x , coal pre-combustion methods to desulfurize high sulfur coal or convert it to SNG and post-combustion methods to remove oxides of sulfur by alkaline scrubbing and using limestone fluidized beds.

Other methods include promoting alternative energy sources such as solar and wind power and fuel cells, hybrid automobiles, increased public transportation, etc. Also, lime ($\text{CaO}/\text{Ca}(\text{OH})_2$) can be added to soil and lakes to neutralize excess acidity.

E3 GREENHOUSE EFFECT

E.3.1 Describe the greenhouse effect.

© IBO 2007

The temperature of the Earth depends on the amount of sunlight received, the proportions absorbed by the earth or reflected back into space, and the extent to which the atmosphere retains the heat. There is a natural steady state 'greenhouse effect' which keeps the Earth's average temperature warm enough (about 16 °C or 60°F) to be habitable. This effect is due to the presence of water vapor and carbon dioxide as 'greenhouse gases' found naturally in the atmosphere.

The **Greenhouse Effect** is the trapping of heat in the atmosphere. Short wavelength sunlight penetrates the atmosphere to warm the Earth's surface which absorbs some of the energy. The temperature of the surface of the Earth is much less than that of the surface of the sun, hence the outgoing radiation is of longer wavelength. This infrared radiation from the Earth is absorbed by the greenhouse gases, water vapor and carbon dioxide and reradiated back to Earth. Thus, greenhouse gases allow incoming solar radiation to reach the Earth, but absorb some of the heat radiated from the Earth, thus maintaining the global temperature. Without the greenhouse effect the Earth would be much colder than it is. Greenhouse gases in the atmosphere act similarly to glass or plastic on a greenhouse, that is, they act as a one way filter.

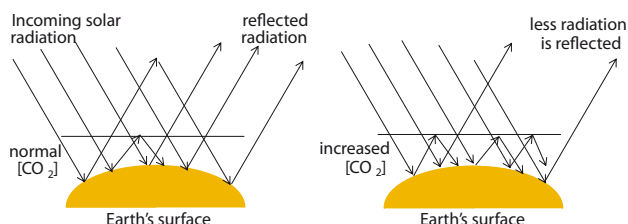


Figure 1609 The 'enhanced' greenhouse effect

In other words, the greenhouse effect allows visible and uv light of short wavelength to pass through the atmosphere to heat the air and the Earth but it traps the longer wavelength infrared heat rays emitted from the warm soil and air, thus raising the temperature of the atmosphere.

Global warming is the gradual increase in planet-wide temperatures. There is evidence to conclude that global warming is taking place. Surface land and ocean temperature records exist for more than a century and

indicate that, over that time period, average global temperatures have risen by about half a degree centigrade and the rate of temperature change is significantly faster than any observed changes in the last 10,000 years.

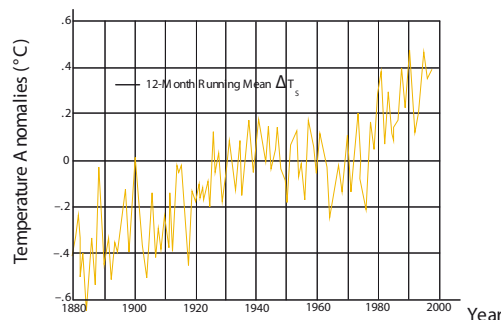


Figure 1610 Global surface air temperature

TOK Is climate change real or is there 'reasonable doubt'?

"There are lies, damned lies and statistics" (variously attributed to Benjamin Disraeli and Mark Twain) - probably nowadays that is starting to apply just as much to some fields of science as it is to the social sciences for which it was originally coined. How much evidence is required to prove something beyond reasonable doubt? The old question of inductive logic, though slightly tainted by hints that the person who is paying the piper might just influence the 'reasonable doubt' judgement. There were many studies on the effects of tobacco funded by cigarette manufacturers and on acid-rain funded by power generating companies, whose conclusions differed from more independent researchers.

With regard to climate change, there is little doubt that there have previously been tremendous differences in climate and not just on a geological timeframe. In the 18th century there were regular winter fairs held on the frozen River Thames, whereas even 50 years ago, before the current global warming scare really began, just a frost in London was unusual, let alone the whole river freezing. Another factor is the fact that the connection between mean global temperature and industrial pollution is a complex one for which we do not have models accepted by all scientists. When people differ it is human nature to speculate on the reasons underlying the fact that people do not agree with you, and then probably use these to impugn their scientific impartiality. It is not only in science that 'reasonable doubt' is a factor - it is interesting to speculate on what kind of world we might now be living in if different recent political leaders had been elected.

E.3.2 List the main greenhouse gases and their sources, and discuss their relative effects.

© IBO 2007

The major greenhouse gases introduced into the environment include methane CH_4 , water vapour, H_2O (g), carbon dioxide, CO_2 , dinitrogen monoxide, N_2O , ozone, O_3 and chlorfluorocarbons, CFCs. Their effects depend on their abundance and their ability to absorb heat radiation.

The increase in concentrations of greenhouse gases from human activity provide a circumstantial link to global warming. Atmospheric concentrations of greenhouse gases have increased significantly since the industrial revolution: CO_2 is up 25%, CH_4 is up over 145% and N_2O around 15%. The atmospheric concentration of methane is low, but it is about 30 times more effective than carbon dioxide in its ability to trap infrared radiation. However, methane has a relatively short average atmospheric lifetime compared with carbon dioxide. Compared to carbon dioxide, nitrous oxide is about 160 times more effective, whereas water is only a tenth as effective as carbon dioxide in its ability to trap infrared radiation. The concentrations of these gases in the atmosphere also vary, with water vapour being the most, and CFCs the least abundant. Also, the rate of increase of CFCs has been decreasing as their use has been controlled by legislation.

E.3.3 Discuss the influence of increasing amounts of greenhouse gases on the atmosphere.

© IBO 2007

The effects of Global Warming over the last century have resulted in

- an increase in temperature by about half a degree centigrade,
- a one percent increase in precipitation and
- about 15–20 cm worldwide rise in sea levels resulting from the partial melting of glaciers and polar ice-caps and the physical expansion of ocean water caused by warmer temperatures.

The change in the climate in most regions of the world will grow as the concentration of greenhouse gases continues to increase. The climate change will impact on health, agriculture, forests, water resources, coastal areas, species diversity, species numbers and natural areas.

| Gas | H_2O | CO_2 | CH_4 | N_2O | O_3 | CFCs |
|---------------------------------------|---|---|---|---|---------------------|---|
| Main Sources | Evaporation from bodies of water; product of hydrocarbon combustion | Combustion of fossil fuels, forest fires, decay of plants and animals | Anaerobic decomposition of organic matter; from ruminant animals (cows and sheep by bacterial breakdown of cellulose), rice paddies, oil and gas fields | Bacterial action, use of nitrogen-based fertilizers | Photo-chemical smog | In spray can propellants, old refrigerators and air conditioners, as solvents, production of plastic foams (no natural sources of CFCs) |
| % Vol. | 0 – 4% | 3.7×10^{-2} | 1.7×10^{-4} | 3×10^{-5} | 4×10^{-6} | 2×10^{-8} |
| Relative effectiveness* | 0.1 | 1 | 30 | 160 | 2000 | 10 000 – 25 000 |
| Contribution to global warming | | 50 – 60% | 15 – 18% | 6% | 12% | 8 – 14% |
| Atmospheric life / years | | 200 – 500 | 7 – 10 | 120 – 150 | | 80 |

* In comparison to arbitrary assigned value of 1 for CO_2

Figure 1611 Greenhouse gases, sources and effectiveness

E4 OZONE DEPLETION

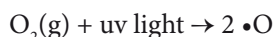
- E.4.1 Describe the formation and depletion of ozone in the stratosphere by natural processes.
- E.4.2 List the ozone-depleting pollutants, and their sources.
- E.4.3 Discuss alternatives to CFCs in terms of their properties.

© IBO 2007

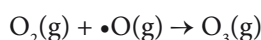
Ozone, O_3 , is a naturally occurring component of the stratosphere. It is a very pale bluish gas with an acrid (pungent-smelling) odor. Chemically it is very reactive (a powerful oxidizing agent) and hence it has harmful effects on living matter. Inhaling a small amount of ozone can be harmful, yet it is essential to life and health by its presence in the ozone layer, where it plays a vital role. The ozone layer is about 15 to 45 km above the Earth's surface and holds much of the air's ozone.

FORMATION OF OZONE

The photo-dissociation of molecular oxygen by ultraviolet (uv) light represents the principle mechanism of ozone's formation in the upper atmosphere. High energy, very short wavelength uv light from the sun splits the strong double bond in O_2 molecules into oxygen atoms which are extremely reactive free radicals containing unpaired electrons (represented by \bullet):



These oxygen atoms react with other oxygen molecules, O_2 to form O_3 :



DEPLETION OF OZONE

Unlike O_2 that contains a $O=O$ double bond, the resonance structures of ozone suggest that two (π) bonding electrons are spread over the entire structure of the molecule with a bond order of $1\frac{1}{2}$ in ozone (between a single and a double bond), and it is thus a weaker bond than in O_2 . This means that the bonds in ozone can be broken by light of a longer wavelength, and hence less energy, than that required to dissociate O_2 molecules.

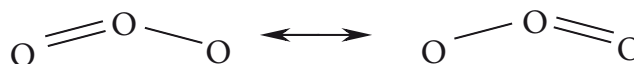
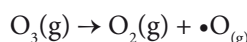
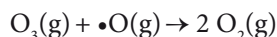


Figure 1613 The resonance structure of ozone

The reverse reaction takes place when O_3 absorbs rather longer wavelength uv light of less energy to form O_2 molecule and oxygen free radical:



The oxygen free radicals react with ozone to form O_2 gas:



Thus O_3 is constantly being formed and broken down. The ozone layer acts as a shield by absorbing 99% of the sun's harmful uv light of longer wavelength than that absorbed by O_2 and N_2 .

Ozone-depleting pollutants and their sources

Satellite data shows a clear decline over the last 30 years in ozone concentration in the latitudes 60° south to 60° north. Similarly satellite measurements show the greatest

| Health | Agriculture | Forests | Water Resources | Coastal Areas | Species and Natural Areas |
|--|--|--|---|---|--|
| Life cycles of pathogens and insects such as mosquitoes are affected by climate; greater chance of malaria, etc. | Effect on crop yields and geographic distribution of crops; some crops will thrive, others will not. | Insects and diseases may increase; increase in summer droughts would produce more forest fires. Higher temperatures and more rain should help forests grow more rapidly. | Decreased water quality due to flooding; floods more likely due to more intense rainfall; droughts more severe due to increased evaporation and drier soil. | Raise the level of seas eroding beaches, inundating low lands, increasing coastal flooding. | Loss of cold water fish habitat, shift in ecological areas, loss of habitats and species; desertification. |

Figure 1612 Effects of Global Warming

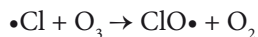
destruction of the ozone layer at the South Pole, covering an area almost equal in size to the North American continent. Satellite data over the North and South Poles clearly indicate that the ozone holes, where depletion of ozone has taken place, are seasonal with the lowest levels being found in the antarctic region during the antarctic spring.

Ozone in the ozone layer is being depleted by:

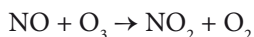
- (1) CFCs, chlorofluorocarbons (freons) are used in spray cans as a propellant and in old refrigerators and air conditioners, in fire extinguishers and as solvents. When released, the CFCs, because they are chemically very inert, do not decompose but float slowly through the atmosphere into the stratosphere. When they reach the unfiltered ultraviolet rays of the sun, they are turned into extremely reactive chlorine atoms with an unpaired electron, called chlorine free radicals. These react readily with the ozone as follows



Note that the average bond enthalpy of C–F bond is 484 kJ mol^{-1} and only 338 kJ mol^{-1} for the C–Cl bond; the C–Cl bond is weaker and breaks. The Cl atom, also a free radical, is very reactive and readily reacts with O_3 to produce O_2 :



- (2) Nitric oxide, formed from the high temperature reaction of N_2 and O_2 in aircraft engines, reacts with ozone reducing its concentration:



A decrease in O_3 concentration in the stratosphere means more uv light reaches the Earth, thus increasing cases of skin cancer and eye cataracts, more sunburn and damage to animals and plants including suppression of plant growth, genetic mutations and changes in the world's climate.

Alternatives to CFCs

CFCs are used because of their lack of reactivity, low toxicity and low flammability. Alternatives to CFCs must possess similar properties, but with no C–Cl bonds and it is preferable if they show little absorption of infrared radiation in order not to behave as greenhouse gases:

1. Hydrocarbons, such as propane, C_3H_8 and 2-methylpropane, $\text{CH}_3\text{CH}(\text{CH}_3)_2$, are used as refrigerant coolants. Although these do not lead to ozone depletion, they are flammable as well as being greenhouse gases (able to absorb infrared radiation) and would lead to global warming.
2. Hydrochlorofluorocarbons, HCFCs contain hydrogen, chlorine, fluorine and carbon atoms in their molecules, for example: CHF_2Cl , Chlorodifluoromethane. The presence of a hydrogen atom makes the compound decompose less easily since the C–H bond is stronger (412 kJ mol^{-1}) than the C–Cl bond. Nonetheless, these do reduce the ozone layer because of the presence of a C–Cl bond in the molecule and can only be considered a temporary solution.
3. Fluorocarbons: For example, CF_4 , tetrafluoromethane; C_2F_6 , hexafluoroethane. These have low reactivity, are neither toxic nor flammable and the very strong C–F bond makes them stable to uv radiation so they cannot catalyze ozone depletion. However, these are greenhouse gases, absorb infrared radiation and would eventually lead to an increase in the global temperature.
4. HFCs hydrofluorocarbons: For example, $\text{CF}_3\text{CH}_2\text{F}$, 1,1,1,2-tetrafluoroethane, without any chlorine atoms, are considered good alternatives to CFCs as no chlorine atoms, which are primarily responsible for ozone depletion, are involved. These also have low reactivity, low toxicity and low flammability, but do contribute to global warming.

E5 DISSOLVED OXYGEN IN WATER

The importance of dissolved oxygen

Human beings and land animals obtain oxygen for respiration from the air. For animals to survive in aquatic systems, water must contain a minimum concentration of dissolved oxygen. The dissolved-oxygen (DO) content of a body of water is one of the most important indicators of its quality. Recall that whereas water is a highly polar, bent molecule, diatomic oxygen is a non-polar molecule and hence its solubility in water is very low. At 20°C, it is about $2.8 \times 10^{-4} \text{ mol dm}^{-3}$. This is equivalent to 9 mg of oxygen per dm^{-3} of water (or 1000g water or a million mg of water) and is best expressed as 9 ppm (parts per million). As the temperature rises, the solubility of any gas decreases, in contrast to that of most solids.

The quality of water, at any temperature, can be determined by the amount of oxygen present. At 20°C, DO content of 8 to 9 ppm O_2 at sea level is considered to be water of good quality. As the DO level reaches 4.5 ppm oxygen, it is considered moderately polluted and below that concentration, highly polluted. The quality of water depends on several factors including oxygen demanding wastes and disease causing pathogens or microorganisms that can affect health. Organic substances such as plants, animal and human waste, waste from industrial processes such as meat packing and food processing plants and paper mills, are the main oxygen demanding wastes.

E.5.1 Outline biochemical oxygen demand (BOD) as a measure of oxygen-demanding wastes in water.

© IBO 2007

BOD, the **Biochemical Oxygen Demand** (some refer to it as the Biological Oxygen Demand), is a measure of the amount of oxygen consumed by the biodegradable organic wastes and ammonia in a given amount of water over a time period, normally 5 days, at 20°C. The effluent sample is diluted in oxygen saturated water and enclosed without an air space in a BOD sample bottle. After the 5 day incubation period, the decrease in dissolved oxygen is measured using an oxygen electrode. The greater the amount of oxygen-demanding wastes, the higher is the BOD:

| ppm BOD | Quality of Water |
|---------|---------------------|
| < 1 | Almost pure water |
| 5 | Doubtful purity |
| 20 | Unacceptable purity |

Figure 1614 BOD Values for Water

Untreated municipal sewage can be in the 100 to 400 ppm BOD range, whereas food processing plants can be up to 10 000 ppm, indicating very high oxygen demanding wastes present in the effluent of such plants.

E.5.2 Distinguish between aerobic and anaerobic decomposition of organic material in water.

© IBO 2007

Aerobic decomposition of organic matter in water in the presence of oxygen is a natural biological process in which bacteria that thrive in oxygen-rich environments break down and digest the organic matter. This is an oxidation process where the complex organic matter is broken down into simple organic material, carbon dioxide and water. Any organic nitrogen is converted into nitrates, NO_3^- , organic sulfur to sulfates, SO_4^{2-} and organic phosphorus to phosphates, PO_4^{3-} . Aerobic decomposition removes oxygen from the water, thus causing a decrease in dissolved oxygen (DO). The DO may decrease to zero if too much organic matter is present, killing aquatic life that depends on oxygen.

Anaerobic decomposition of organic matter in water takes place in the absence of oxygen by microorganisms that do not require oxygen. Typical anaerobic decomposition reaction products due to the reduction of organic matter in the presence of water include:

- ammonia and amines (with a strong fishy smell) from nitrogen and hydrogen
- methane (biogas or marsh gas), from the carbon and hydrogen
- hydrogen sulfide, H_2S (foul rotten egg smell) from organic sulfur
- phosphine, PH_3 from phosphorus.

E.5.3 Describe the process of eutrophication and its effects.

© IBO 2007

Plant nutrients such as nitrates from nitrogen-containing animal and human waste and fertilizers, and phosphates from detergents and fertilizers lead to excessive growth of aquatic plant life, often in the form of algal blooms. This can make water taste and smell bad and can kill shell fish, as in the case of 'red tides.' Red tides are caused by several species of marine plankton (microscopic plant-like cells) that can produce chemical toxins. Dead plants fall to the bottom of bodies of water where, in the presence of oxygen, they are broken down or decay due to bacterial activity, thus depleting the concentration of oxygen. Consequently, fish die of asphyxiation (lack of oxygen); anaerobic processes produce toxic substances such as hydrogen sulfide and phosphine and that part of the water becomes lifeless. This process is known as **eutrophication**.

E.5.4 Discuss the source and effects of thermal pollution in water.

© IBO 2007

Power plants and many industrial processes use huge quantities of fresh water to cool and condense steam. The cooling water subsequently becomes warm (or hot) and if this is dumped into streams, rivers or lakes, it leads to **thermal pollution**. Two major effects of thermal pollution on bodies of water include that on dissolved oxygen and that on the metabolic rates of aquatic life.

The concentration of any gas such as oxygen dissolved in a liquid decreases as temperature is increased (that is, more of the gas bubbles out). This is complicated by the fact that if the less dense warm water is not rapidly mixed with a body of deep, cooler, more dense water, it can stay on the top, is unable to absorb as much oxygen from the atmosphere and leads to overall reduced levels of dissolved oxygen.

| Temperature /°C | 0 | 20 | 40 |
|-----------------|----|----|-----|
| Solubility /ppm | 15 | 9 | 6.5 |

Figure 1615 The Effect of Temperature on the Solubility of Oxygen Gas in Water

A moderate increase in temperature generally speeds up the rate at which biochemical reactions occur, thus, not only is the DO (dissolved oxygen) level decreased as temperature increases, but the metabolic rates of aquatic

animals increase and require more oxygen. As a result, thermal pollution has adverse effects on both dissolved oxygen and the rate of consumption of oxygen in bodies of water.

E6 WATER TREATMENT

Approximately three quarters of the Earth's surface is covered by water with the world's oceans containing most of it, as shown in the table below:

| | oceans | glaciers, ice caps | ground water | lakes, rivers | atmosphere |
|---|--------|-----------------------|-----------------|------------------|------------|
| % | 97.3 | 2.1 | 0.6 | 0.015 | 0.001 |

Figure 1616 The distribution of Water on Earth

E.6.1 List the primary pollutants found in waste water and identify their sources.

© IBO 2007

Water is a unique, highly polar substance capable of hydrogen bonding and this property allows it to dissolve many chemicals. Thus some toxic substances as well as bacteria and viruses can be carried by water. Water used by humans, whether for personal use or by industry, becomes impure and is returned to the environment into lakes, rivers, oceans, reservoirs or aquifers (natural underground reservoirs). Water that is unsuitable for drinking, irrigation, industrial use or washing is considered **polluted water**.

E.6.2 Outline the primary, secondary and tertiary stages of waste water treatment, and state the substance that is removed during each stage.

© IBO 2007

Sewage is the water-carried wastes (that is used water) that flows away from any community. It can contain domestic, sanitary, commercial and industrial wastes. Such sewage may contain disease causing microorganisms, organic materials as well as other toxic substances such as heavy metal ions. The purpose of sewage treatment is to remove hazardous materials, reduce the BOD (Biological Oxygen Demand) of the sewage and kill microorganisms prior to discharge.

| Pollutants | Sources |
|--|---|
| Heavy metals (for example, Cadmium, Copper, Mercury, Lead, Zinc) | Cd: Rechargeable batteries, metal plating and pigments Cu: household plumbing, copper mining and smelting Hg: Batteries, mercury salts as fungicides, mercury cells in chlor-alkali industry, discharge from pulp and paper mills |
| Pesticides (include DDT, fungicides and herbicides) | Agricultural practices. |
| Dioxins | From by-products of industrial processes such as waste incineration, forest fires and burning fuels, manufacture of chlorinated pesticides; used in Agent Orange as a defoliant in Vietnam war. |
| PCBs | Very stable compounds that were used widely as coolants and lubricants in capacitors, transformers, and other electrical equipment. |
| Organic matter | Waste treatment plants, decomposition of plants and animals, oil spills, industrial waste |
| Nitrates (present as highly soluble salts) | Agriculture: Chemical nitrate fertilizers for farming; from acid rain. |
| Phosphates | Detergents and chemical phosphate fertilizers. |

Figure 1617 Sources of primary pollutants in waste water

Different types of sewage treatment with different levels of effectiveness are carried out in the world depending on the availability of resources since the cost increases with more advanced treatment. These are classified as primary, secondary and tertiary stages of sewage treatment. Each level of treatment reduces the level of the pollutants in the sewage and thus the original BOD, with the tertiary treatment being the most effective but by far the most expensive to build and operate.

PRIMARY SEWAGE TREATMENT

The effluent is first passed through screens and traps which filter out large objects such as trash and debris and, from the surface, remove floating objects including grease (which has a high BOD). It then passes through settling tanks where smaller heavier objects such as rocks and stones settle and can be transferred to land fills. Next, the sewage passes through holding or sedimentation tanks or ponds where it is allowed to settle and sludge is removed from the bottom. The mechanical process of **sedimentation** can be speeded up by adding chemicals which allow suspended particles to join together to form large clumps. This process is called **flocculation** (the large clumps formed are called flocs) and can be achieved by the addition of aluminium sulfate, $Al_2(SO_4)_3$, the aluminium ions cause particles to clump together and precipitate out. The flocs formed settle to the bottom.

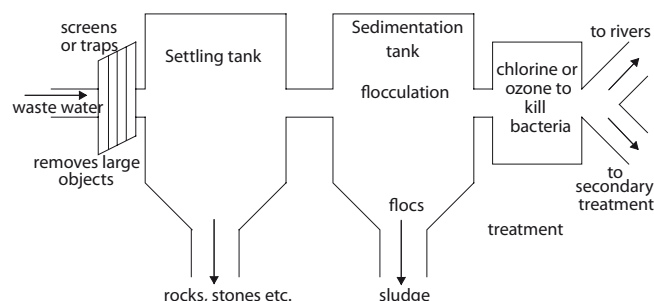


Figure 1618 Primary sewage treatment

Depending on the amount of BOD wastes, primary treatment is generally not sufficient to improve the quality of water to safe levels, even if it is treated with chlorine or ozone to kill pathogens. A typical primary treatment domestic sewage plant can remove about 30 – 40% of the BOD waste and secondary treatment is essential to further reduce BOD levels.

SECONDARY SEWAGE TREATMENT

This involves microbial activity and requires aeration in which air, or air enriched with oxygen, is bubbled, using large blowers, through sewage mixed with bacteria-laden sludge. This allows aerobic bacteria to thoroughly mix with the sewage in order to oxidize and break down most of the organic matter. The process is thus biological in nature and is called an **activated sludge process**.

Then the water, containing decomposed suspended particles, is passed through a sedimentation tank where

large quantities of biologically active sludge collect. Part of this is recycled and the rest has to be disposed off. Secondary sewage treatment can remove most (about 90%) organic oxygen-demanding wastes and suspended particles. Primary and secondary treatments cannot remove dissolved inorganic substances such as nitrates, phosphates and heavy metal ions, which require further treatment. The effluent from secondary treatment may then be sent to a tertiary plant for further treatment or released into lakes, rivers etc. before which it may be treated with chlorine or ozone gas to kill pathogenic bacteria.

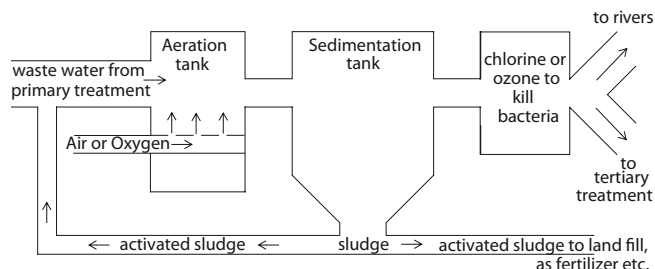


Figure 1619 Secondary sewage treatment

TERTIARY SEWAGE TREATMENT

These processes involve specialized chemical, biological and or physical treatment that further purify the water after it has undergone primary and secondary treatments. It can remove the remaining organic materials, nutrients and substances not taken out by the biological processes in secondary treatment, such as toxic metal ions as well as nitrate and phosphate ions. Examples of tertiary treatment include carbon bed, chemical precipitation and biological processes.

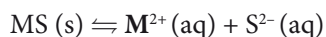
Carbon bed method

This uses activated carbon black. It consists of tiny carbon granules with large surface areas which have been treated and activated by high temperatures. This then has the ability to readily adsorb organic chemicals from the waste waters. Adsorption is the attraction of a substance to the surface of a solid substance. Carbon beds are effective against many toxic organic materials and charcoal filters are often used to further purify tap water for drinking purposes.

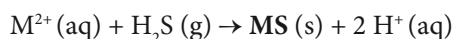
Chemical Precipitation

Certain toxic heavy metal ions such as cadmium, lead and mercury can easily be precipitated as their sulfide salts

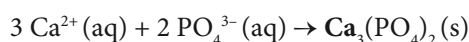
whose solubilities in water are incredibly small. For the reaction:



the K_c value (also called K_{sp} , the solubility product constant) at 25°C is of the order of 10^{-28} for CdS and PbS, and for HgS it is of the order of 10^{-52} . Thus if carefully controlled amounts of hydrogen sulfide gas are bubbled through a solution containing heavy metal ions, these can be precipitated as the corresponding sulfides which can then be filtered out. Excess hydrogen sulfide (being acidic) can then be easily removed:

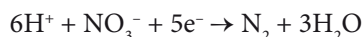


Similarly, the presence of phosphate ions, PO_4^{3-} , can be reduced to very low levels by the addition of calcium ions, Ca^{2+} , since the solubility product constant K_{sp} of calcium phosphate is very small (1.2×10^{-26}).



Anaerobic biological process

This is **denitrification** which turns the nitrogen in nitrates back to atmospheric nitrogen, N_2 . This is achieved by anaerobic organisms (denitrifying bacteria). This is a reduction process in which the oxidation number of nitrogen is reduced from +5 in the nitrate ion, NO_3^- to zero in N_2 . At the same time, carbon in the organic matter is oxidized to CO_2 . The net ionic half-equation for the reduction reaction can be summarized as:



Denitrification therefore reduces nitrate contamination in ground water.

E.6.3 Evaluate the process to obtain fresh water from sea water using multi-stage distillation and reverse osmosis.

© IBO 2007

DISTILLATION

Sea water, containing on average about 3.5% dissolved salts by mass, is not fit for human consumption. It is equally unfit for agricultural and industrial uses where the high salt content would cause dehydration of plants (water loss by the process of osmosis) and lead to corrosion of

equipment. **Desalination** processes remove salts from sea water and brackish water to produce fresh water. Two methods in common use to desalinate sea water are multi-stage distillation and reverse osmosis.

Distillation is the process that allows the separation of a volatile liquid from non-volatile materials. Heating the solution allows for the volatile water to be converted to water vapor that can be separated and collected as fresh water leaving behind the non-volatile salts in solution. Large scale desalination by distillation is made more efficient by using a multistage process to maximize the use of heat so that when condensation of vapor produces heat in one stage, it is used to heat water in the second stage and so on.

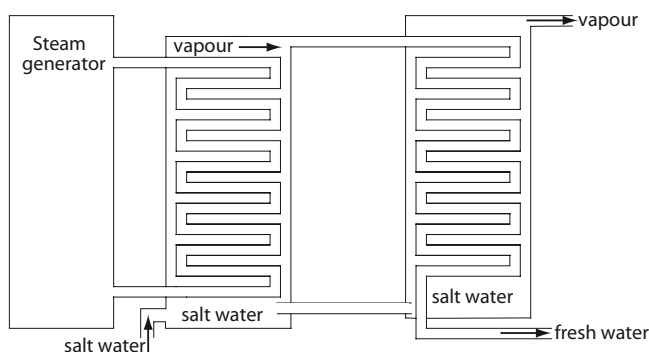


Figure 1621 The Distillation process

REVERSE OSMOSIS

Osmosis is the natural tendency of a solvent such as water to move from a region of high solvent concentration (purer water) to one of lower solvent concentration (less pure water) through a **semi-permeable membrane**. Thus, it is a tendency to equalize concentrations across the membrane. A semi-permeable membrane allows water, but not ions or large molecules, to pass through. If pure water and salt water are separated by a semipermeable membrane then, due to osmosis, pure water (of higher solvent concentration) will move into the salt water thus diluting it. This flow of water can in fact be stopped if a pressure equal to the osmotic pressure of the solution is applied. Indeed, if the pressure applied is greater, then the flow of the solvent takes place in the opposite direction and the process is called **reverse osmosis**.

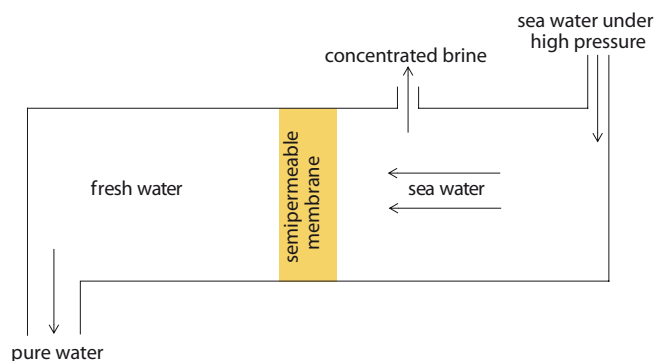
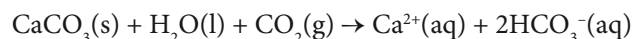


Figure 1622 Reverse Osmosis

Because reverse osmosis does not require a phase change as does distillation, it requires less energy. Energy is still however required to produce the pressure necessary for reverse osmosis, hence this process is still too expensive for many nations to use. The world's largest desalination reverse osmosis plant is in Saudi Arabia, producing about 50% of that nation's drinking water.

E7 SOIL

Over 80% of the Earth's crust is made of the elements oxygen, silicon and aluminium with smaller amounts (between 1 – 5% each) of calcium, iron, potassium, magnesium and sodium. Lesser amounts of other elements such as phosphorus and sulfur are also present. Soil, a vital part of the Earth, is a complex, heterogeneous mixture of interacting materials. It results from the weathering of rocks due to its breakdown by biological decay of organic matter by microbial action due to bacteria and fungi in the soil and by physical and chemical means. For example, chemical weathering of limestone, calcium carbonate, produces dissolved ions and the rate of reaction of weathering depends on the temperature and the surface area:



Soil consists of four components: inorganic matter (the largest component in soil due to weathering of rocks), water, air and smaller amounts of organic matter. The amount of air and water in the soil affects how life forms survive and decay after death. Bacteria and fungi convert the organic matter into a typically water insoluble mixture called humus containing about half its mass as carbon and about 5% nitrogen. As a result, soil composition varies tremendously depending on how and where it is formed and what life forms live in it. Inorganic matter contains mostly silica, silicates and aluminosilicates.

The structure of silica, silicon(IV) oxide, SiO_2 , is a tetrahedron with silicon covalently bonded to four oxygen atoms (Figure 1623 (a)) in which each oxygen atom is shared between two Si atoms to form a giant covalent structure. Figure 1623 (b) shows one example of silicate chain structure in which two of the four oxygen atoms are bonded to other tetrahedra. Since Al^{3+} has a similar size to Si^{4+} , Al can replace Si to form aluminosilicate structure (Figure 1623 (c)).

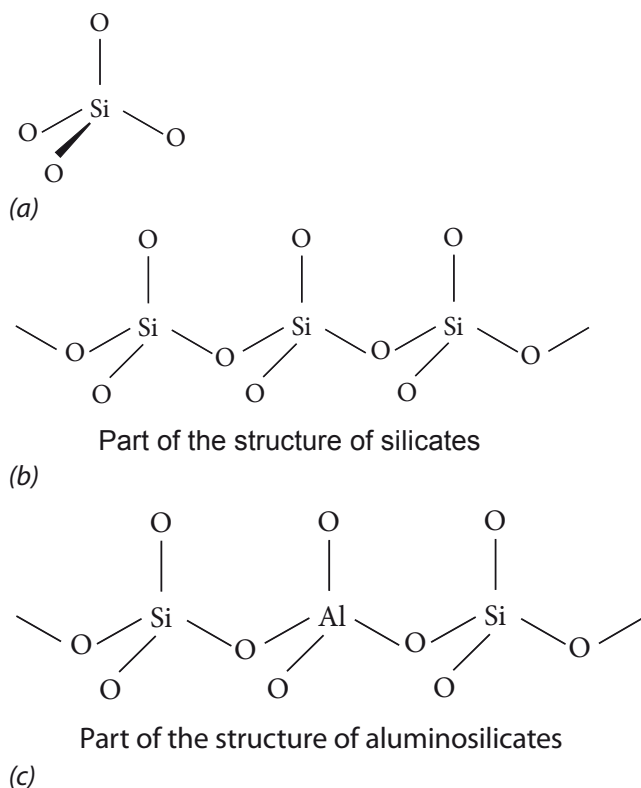


Figure 1623 (a), (b) and (c)

In the silica structure, SiO_2 , if one in every four tetrahedrons contain Al^{3+} instead of Si^{4+} , then the structure will be short one electron, making it an anion with a one negative charge and an empirical formula $\text{AlSi}_3\text{O}_8^-$ instead of SiO_2 . Similarly, if two in every four tetrahedrons contain Al^{3+} instead of Si^{4+} , then the structure will be short two electrons, making it an anion with two negative charges and an empirical formula $\text{Al}_2\text{Si}_2\text{O}_8^{2-}$ instead of SiO_2 . The existence of these ions in inorganic matter and the presence of the highly electronegative oxygen explains its ability to hold on to plant nutrient cations such as K^+ , NH_4^+ , Ca^{2+} , Mg^{2+} and to form salts such as $\text{NaAlSi}_3\text{O}_8$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$.

The soil food web is incredibly complex and is made of a great diversity of organisms from the simplest bacteria and algae to earthworms and plants. Some, like plants and algae, use the sun's energy to convert carbon dioxide to

sugar. Others use the energy and nutrients. Soil sustains life. Nutrients found in soil that occur as dissolved ions, such as Ca^{2+} , K^+ , NH_4^+ and Mg^{2+} , are absorbed through the roots and are essential for plant growth. Calcium is used in plant cell wall synthesis. Potassium controls the amount of water that enters via osmosis. Nitrogen is used in the synthesis of amino acids and thus proteins, and iron, nitrogen and magnesium are used in the synthesis of chlorophyll. Decaying plants replace nutrients. However, several factors such as acid deposition, water runoff from soil, pollution, pesticides and harvesting of crops change and deplete the amounts of essential soil nutrients. Soil management includes crop rotation and the addition of fertilizers to replenish plant nutrients.

E.7.1 Discuss salinization, nutrient depletion and soil pollution as causes of soil degradation.

© IBO 2007

SALINIZATION

Salinization is the accumulation of water soluble ions or salts in the soil due to continual irrigation to grow crops. Water for irrigation contains small amounts of dissolved salts such as calcium chloride (CaCl_2), magnesium sulfate (MgSO_4) and sodium chloride (NaCl). As the water is used by plants or evaporates due to high atmospheric temperature, and where salts are not washed away due to poor drainage or low rainfall, the salts accumulate over time, leading to salinization of the soil. Another major cause of salinization in some parts of the world (for example Australia) is the rise of the water table. This is caused in part by the removal of large native plants and a consequent reduction in evapo-transpiration. This in turn allows the soil water to get close enough to the surface to evaporate and in doing so increase the salt concentration on or near the surface.

Salinization reduces plant growth as the increased concentrations of ions reduce the ability of the roots to take up water. For example, the effect of sodium chloride on seed germination and plant growth can be easily studied in the laboratory by keeping all variables such as time, temperature, size of seeds, amount and type of soil, amount of water etc. constant and varying only the concentration of ions. This is due to the phenomenon of osmosis which is the movement of water from a region of low ion concentration in the roots to high ion concentration in the soil (to eventually reach infinite dilution). According to UN Food and Agricultural Organization article, *The salt of the earth: hazardous for food production*, "Irrigation

produces much of the world's food, but about a tenth of the world's irrigated land has been damaged by salt. This has become a profound threat to food security."

NUTRIENT DEPLETION OR LOSS

This is the removal of essential nutrients and minerals from the soil food web by crops that grow and are continually harvested due to agricultural practices, and leads to soil degradation. **Nutrient depletion** or loss results in decreased soil quality and can lead to a serious decline in the yield of crops, thus affecting food supply. Replenishing the mineral nutrients and carrying out crop rotation so that the same nutrients are not used each time is important to improve soil quality. However, overuse of nitrate and phosphate fertilizers can lead to environmental pollution as the chemicals can end up in ground and surface water. This can lead to eutrophication, which is the excess growth of aquatic life such as algal blooms.

SOIL POLLUTION OR CONTAMINATION

This arises from the presence of man-made chemicals such as **pesticides** and **herbicides**. Pesticides provide better harvests by killing insect pests. Herbicides kill unwanted plants or weeds and fungi are controlled using **fungicides**. Pesticides can lead to lower crop yields by destroying very small flora and fauna, and similarly to fertilizers, they leach into ground water polluting it. Soil pollution also arises from the addition of nitrate and phosphate fertilizers to replenish the soil with nitrogen and phosphorus. Soil contamination is also caused by domestic and industrial waste added directly to soil or by wastes leached from land fill sites. These may contain heavy metals such as arsenic, chromium, copper, mercury, lead and zinc and organic contaminants such as polychlorobiphenyls (PCBs,) and polyaromatic hydrocarbons (PAHs). Similar to leaching of fertilizers, these poisonous chemicals can pollute ground water, affect water supplies and create health risks.

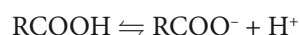
E.7.2 Describe the relevance of the soil organic matter (SOM) in preventing soil degradation and outline its physical and biological functions.

© IBO 2007

The term **soil organic matter** (SOM) refers to the mixture of non-living organic components present in the soil in various stages of decomposition arising from the chemical and biological action on plant matter and organisms. The amount of carbon in the organic constituents in the soil

is a measure of the organic matter present; the organic carbon can be determined experimentally by titration with a dichromate(VI) solution. Soil organic matter includes humic substances, the organic matter converted into a mixture by bacteria and fungi, smaller molecules such as sugars and amino acids and high molecular mass polysaccharides and proteins.

Humic acids of different composition and molar masses containing the phenolic acid (ArOH) and carboxylic acid functional groups (RCOOH) are present in the soil organic matter. These are weak acids and dissociate partially:



The anion RCOO^- is able to chelate or bind to plant nutrients containing multivalent cations such as Ca^{2+} , Fe^{2+} , Mg^{2+} , as well as trace metal ions: Zn^{2+} , Mn^{2+} , Co^{3+} . The strength of the bond depends on the charge to size (charge density) of the hydrated ion: the higher the charge density, the stronger the binding, for example: $\text{Al}^{3+}(\text{aq}) > \text{Mg}^{2+}(\text{aq}) > \text{K}^+(\text{aq})$.

RELEVANCE OF SOIL ORGANIC MATTER IN PREVENTING SOIL DEGRADATION

SOM plays an important role in soil quality, and thus in producing high crop yields, in a variety of ways. In deserts, for example, organic matter (called 'sweet soil' which stinks of organic fertilizer) added to sand can greatly improve plant growth. Soil organic matter contains a pool of mineral nutrients it can exchange with plant roots, it holds on to water, improves soil structure and reduces soil erosion. The functions of SOM are biological, physical and chemical and interactions between all three (see Section E.12.4 for chemical function):

Biological

Organic soil matter binds to many nutrients and is a substantial reservoir of the mineral nutrients nitrogen, phosphorus and sulfur that are made available to microbes and plants for growth. Nitrogen is used in the synthesis of proteins and chlorophyll. Phosphorus is used in the synthesis of enzymes and the storage of energy. Sulfur is used in the synthesis of some amino acids, the building blocks of proteins. Typically soil organic matter contains about 5% nitrogen. Bacteria and fungi decompose the organic matter and release the nutrients to the plant roots in the soil.

Mineralization

This is the slow process by which organic matter containing nitrogen and phosphorus is broken down or mineralized to release nitrogen and phosphorus to roots. Thus a biological function of soil organic matter is to provide a source of mineral nutrients N, P and S. Soil/plant system resilience is maintained since plant residue contains nutrients that contribute to soil organic matter upon decomposition. Thus, SOM becomes a reservoir of nutrients that are stored in the soil and released to plants on an ongoing basis.

Physical

Soil clusters collect together in stable forms due to the presence of organic matter. This reduces soil erosion, and increases the ability of air and water to move through the soil. As a result, like a sponge, soil organic matter can absorb several times its mass of water and thus influences soil's water retention property. It also improves soil structure since the porous soil makes it possible for roots to spread through the soil.

Organic matter also affects soil thermal properties by influencing soil temperature. Thermal properties are related to soil temperature and the transfer of heat through the soil. Moist soil has higher heat capacity than dry soil due to the higher heat capacity of water. Thus, soil with higher water content (and thus higher thermal capacity) experiences smaller temperature changes. Recall:

Heat absorbed, $Q = mc\Delta T$

If c , the heat capacity is large then, for the amount of heat absorbed, the change in temperature, ΔT will be small. For dry soil, the heat capacity is smaller and for the same heat absorbed, the change in temperature will be larger.

E.7.3 List common soil pollutants and their sources.

© IBO 2007

We live in a world where the population and the demand for petroleum products continue to increase at an alarming rate and there is wide spread use of chemicals for

| Common Organic Soil Pollutants | Sources |
|---|---|
| Petroleum hydrocarbons | Discharges and accidents from petroleum industry from oil fields, tankers, pipelines, refining plants |
| Agrichemicals including fertilizers and pesticides containing organochlorine compounds | Agriculture: over-application of fertilizers, use of pesticides which leach into ground; chlorine-organic pesticides with long half lives remain in the soil for many years |
| Volatile organic compounds (VOCs): these include ethylene glycol (ethan-1,2-diol), methylbenzene, methanal | Household products, fuels from gasoline, cleaning and degreasing products, chemicals from copiers and printers, glues, markers, paints |
| Solvents such as hexane, methyl benzene, acetone, dimethyl sulfoxide (DMSO), ethanol, 2-propanol, 1-butanol | Dry cleaning, electronics industry, manufacture of paints |
| Polycyclic aromatic hydrocarbons (PAHs) such as benzo(a)pyrene (a carcinogen) | Tar, coal, crude oil spills, incomplete combustion of wood, vegetation, waste incineration, industrial emission and waste |
| Polychlorinated biphenyls (PCBs) | Incinerator stacks, leaks from enclosed electrical equipment (where PCBs were used as insulating fluids), leaks from hydraulic fluids |
| Organotin compounds, for example, triphenyl tin (TPhT) | PVCs (where alkyl tin compounds are used as stabilizers), ship paints which are used as biocidal agents as an antifoulant coating to hulls of ships below the water line, stopping plants and marine life forms attaching to the hull |
| Semi-volatile organic compounds (SVOCs), those with boiling points greater than 200°C such as PCBs, PAHs | From pesticides and fungicides in agriculture and chemicals used in preserving wood, propellants, fuels |

Figure 1624 Common organic soil pollutants and their sources

industry and agriculture. Waste in landfill sites and sludge from treatment plants continue to pollute the earth but often there is a lack of laws and regulations to minimize pollution and protect health.

E8 WASTE

According to the World Wildlife Fund's 2006 *Living Planet Report*, we are now turning resources into waste at a pace 25% faster than the Earth can turn waste back into resources, with first world countries having a considerably larger 'ecological footprint' than poor ones. A combination of population increase and rise in the standard of living has led to an increase in mining, biological waste containing high organic biodegradable waste, medical waste from hospitals and veterinary practices, nuclear waste, fly ash from power plants, industrial and municipal waste amongst others. Excessive use of plastics, packaging and non-recyclable materials adds to the problem. Recyclable materials such as paper, glass, and metals are dumped into garbage, further complicating the waste problem.

E.8.1 Outline and compare the various methods for waste disposal.

© IBO 2007

Methods of waste disposal include landfill sites, incineration, large scale composting, recycling and the burial of radioactive wastes.

E.8.2 Describe the recycling of metal, glass, plastic and paper products and outline its benefits.

© IBO 2007

Please see Figure 1626 on the next page.

E.8.3 Describe the characteristics and sources of different types of radioactive waste.

© IBO 2007

The French physicist Henri Becquerel (1896) accidentally discovered **radioactivity** which is the ability of some isotopes to undergo reactions involving nuclear change or transformation. There are three common types of radioactive emissions, as follows.

Alpha particles are positively charged helium nuclei, ${}^4_2\text{He}$, that have low penetrating power (a few centimeters of air) and can be stopped by clothing, paper or skin.

Beta particles or β -rays are a stream of electrons that are negatively charged that have moderate penetrating power (about a hundred times the penetrating power of alpha particles). They can penetrate a few meters of air and can be stopped by 1 mm thick aluminium foil.

Gamma rays are high energy electromagnetic radiation that have high penetrating power (about 100 times the penetrating power beta particles). They can penetrate a few kilometers of air and several centimeters of lead but can be stopped by about 10 cm of lead or several meters of concrete.

| | Landfill sites | Incineration |
|-----------|---|---|
| Waste | Waste volume is increasing whereas availability of landfill sites is decreasing and are often at capacity; takes up precious land space; leaves ugly, smelly sites. | On incineration, reduces volume; slag produced sent to landfill sites, but can also be used in building roads and in construction industry. |
| Costs | Involves transportation costs as landfill sites tend to be away from cities and towns (for years, Toronto waste was transported to Michigan for disposal). | Involves transportation costs as incinerator sites tend to be away from cities and towns. Uses energy in running incinerator plants; however, the energy produced from the combustion of the waste in a closed-loop process can be used to reduce energy costs. |
| Pollution | Source of underground water and soil pollution due to leaching which can be reduced by lining the landfill site. Anaerobic decomposition of organic waste releases methane, CH_4 , a greenhouse gas; also produces toxic substances such as ammonia, hydrogen sulfide, etc. Medical waste has to be sterilized before being disposed of in landfill sites. | Emission of pollutants on burning plastics release dioxins into the environment. Incineration destroys disease causing microorganisms. |

Figure 1625 Comparison of landfill sites and incineration

| | Recycling process | Benefits |
|----------------|--|--|
| Metals | <p>Involves collecting and separating these out into ferrous and non-ferrous metals (e.g., Al cans from steel and tin cans which are iron cans coated with tin; tin cans are de-tinned and the tin sold).</p> <p>The metal products are cut up and powerful magnets used to separate ferrous metals from the mixture. In the non-ferrous mixture, the lighter aluminium is separated from other high density metals by flotation.</p> | <p>Recycling metals conserves natural resources (the raw materials)</p> <p>Reduces energy, water and landfill usage: recycling Al uses about 95% less energy and steel uses about 50% less energy Less energy use means less greenhouse gases released</p> <p>Aluminium and steel are the most recycled metals, and can be recycled over and over again.</p> |
| Glass | <p>Glass is separated by colour, namely: colourless, amber and green (coloured glass maintains its colour permanently). However, glass mirrors, window panes, light bulbs are made of different compositions and often are not recyclable; glass containers for food and drinks are of similar composition and are recyclable.</p> <p>Crushed waste glass called 'cullet' is exposed to a magnet to remove any ferrous metals and to a vacuum to remove paper and plastic. It is then mixed with raw materials (sand, limestone and soda ash) and melted at 1200°C. The glass formed is moulded or blown into new products such as bottles, jars and tiles.</p> | <p>Saves raw materials and mining wastes</p> <p>Takes about one-third less energy compared to virgin glass from raw materials</p> <p>Uses about half the water compared to virgin glass</p> <p>Reduces use of landfill sites</p> <p>Glass cullet can be used in highway construction and landscaping</p> <p>Glass can be recycled over and over again.</p> |
| Plastics | <p>Plastics have different properties due to their different compositions (for example, polyethene versus polystyrene) and are thus difficult and expensive to separate and recycle. The numbering system used in some countries facilitates separation and recycling of similar plastics.</p> <p>Low density polyethylene (LDPE) or polypropylene (PP) plastics used for packaging bakery and food products and polystyrene (PS) plastics are typically not recyclable. However, plastics made of polyethylene terephthalate (PET) and high density polyethylene (HPE) include many dairy product containers, juice and household containers can be recycled by melting these and re-moulding into new shapes.</p> | <p>Recycling plastics saves landfill sites as it occupies a great deal of space and reduces the need for more incinerators</p> <p>Uses less petrochemical raw materials</p> <p>Uses less energy and water compared to virgin plastics</p> <p>Recycled PET has many uses including fibre for pillows, jackets, automobile seats and insulation material.</p> |
| Paper products | <p>Waste paper has to be separated as paper coated with wax or plastic cannot be recycled. Paper is chopped and mixed with water and chemicals such as clay as filler, calcium oxide (CaO, lime) and CaCO_3 and heated for alkaline pulping. This breaks the paper into fibres (small pieces of cellulose) and produces pulp (a soggy mixture).</p> <p>Spinning the pulp in cylinders removes heavy objects like paper clips and staples. Ink is removed from pulp by washing with water. Surfactant chemicals are added to remove ink and glue from the pulp. Other chemicals remove colours (dyes).</p> <p>Often fresh pulp is added and if it is not treated to remove lignin, the glue in wood that holds fiber together, the paper turns yellow with time when exposed to light as is the case with paper used to make newspapers. Hydrogen peroxide, H_2O_2 or chlorine dioxide, ClO_2 is typically used to bleach paper to produce white recycled paper.</p> | <p>Recycled paper uses about half the energy and water used to produce virgin paper</p> <p>Reduces the number of trees that have to be cut down and preserves forests</p> <p>Saving forests means less greenhouse gas, carbon dioxide is reduced and forests provide habitat for wildlife</p> <p>Extends the life of landfill sites</p> <p>However, paper cannot be recycled over and over again as the fibre loses strength on recycling</p> <p>Economic benefit: all recycling produces jobs</p> |

Figure 1626 Recycling processes and its benefits

Half-life, $t_{1/2}$ of a radioactive substance is the time required for one-half of the amount of radioactive material to decay; it is independent of the amount of the radioactive sample present and follows first order kinetics, namely an exponential decay. Each radioisotope has its own characteristic half-life which can range from 10^{-7} seconds ($^{212}_{84}\text{Po}$ has $t_{1/2} = 3 \times 10^{-7}$ s) to a few billion years ($^{238}_{92}\text{U}$ has $t_{1/2} = 4.5 \times 10^9$ years). Pu-239, a product of nuclear reactions and a highly toxic substance has $t_{1/2} = 24\,000$ years.

If one starts with 100 g of Pu-239 at time zero, then after one half-life (24 000 years), 50 g of the original isotope will remain as half will have been converted to decay products.

After two half-lives, the mass remaining will be $\frac{100}{2^2} = 25$ g.

After seven half-lives ($= 7 \times 24\,000 = 168\,000$ years), the amount remaining will be ≈ 0.8 g. Thus, the Pu-239 produced in nuclear power plants as a waste product will last for tens of thousands of years before it decays to less than 1% of its present amount.

E.8.4 Compare the storage and disposal methods for different types of radioactive waste.

© IBO 2007

Radioactive waste storage and disposal depends on the amount and type of activity it produces and the half-life of the radioisotopes involved.

Low level radioactive waste decreases to background radiation within 500 years with about 90% of it decreasing to general levels within 100 years. This waste can be compacted to reduce volume and buried in shallow lined, land-burial trenches. Together with intermediate level nuclear waste, they can also be stored in steel containers in concrete vaults below ground. Combustible dry low-level

waste can be incinerated with regulations on how much radiation can be released into the environment. Dumping into landfill sites or diluting by dumping into the sea are generally banned. Caesium and strontium, products of fission are low-level nuclear wastes; these can be removed by the use of ion-exchange resins.

High-level waste comprises a small volume of all nuclear waste but contains most of the radioactivity. Spent fuel is temporarily stored in pools of water to absorb the heat produced by high level radioactivity. Long term storage of high-level nuclear waste seems most problematic. One method used is to contain it securely by making liquid waste into glass (vitrifying it) followed by burial deep underground in geologically stable (earthquake free), non-leachable environments such as granite rock, or used salt mines. The containers are meant to be non-corrosive (to decrease the possibility of leaching by water) and kept intact for hundreds of thousands of years for the radioactivity to decrease to background levels.

HIGHER LEVEL

E9 OZONE DEPLETION (HL)

E.9.1 Explain the dependence of O_2 and O_3 dissociation on the wavelength of light.

© IBO 2007

Diatomic oxygen, O_2 , and ozone (triatomic oxygen), O_3 , are allotropes. An oxygen molecule has a double bond between the oxygen atoms (bond order of two).



| Type of radioactive waste | Characteristics of radioactive waste | Sources of radioactive waste |
|---|---|---|
| Low-level waste (> 90% of the volume of nuclear waste but contains only about 1% of the radioactivity). | Contain small amounts of radioisotopes producing low activity alpha and low-energy beta particles of short half-lives; thus radioactivity is low. | Include clothes, gloves, paper, plastic and glass products from nuclear fuel cycle, hospitals and nuclear research facilities; radioisotopes from industry monitoring thickness of paper, plastics. |
| Medium or intermediate-level waste. | Contain greater amounts of radioisotopes with intermediate activity and generally of intermediate half-lives. | Mostly from nuclear reactor parts and processing nuclear fuel. |
| High-level waste (occupies a small volume of nuclear waste but contains most of the radioactivity). | Contain large amounts of radioisotopes of high activity due to high energy beta and gamma rays with generally long half-lives that remain radioactive for long periods. | Mostly from spent fuel rods and processing of spent nuclear fuel. |

Figure 1627 Characteristics and sources of radioactive wastes

Ozone, on the other hand is triatomic and can be represented by two resonance structures (bond order of one and a half):

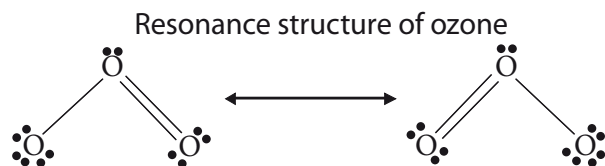


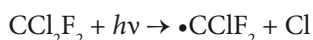
Figure 1628 The resonance structure of ozone

The double bond in the oxygen molecule, results in a stronger bond compared with ozone. To dissociate an oxygen molecule, therefore, requires greater energy than to dissociate an ozone molecule. Since the wavelength of light is inversely proportional to its energy, the stronger double bond in the oxygen molecule requires radiation of lower wavelength (242 nm or less) compared with the dissociation of ozone which requires higher wavelength (330 nm or less). Thus, ozone absorbs harmful uv rays in the range 240 to 330 nm that oxygen does not absorb.

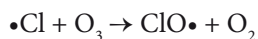
E.9.2 Describe the mechanism in the catalysis of O_3 depletion by CFCs and NO_x .

© IBO 2007

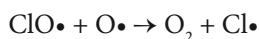
Chlorofluorocarbons (CFCs) are stable compounds with a variety of uses such as in refrigeration and as propellants in aerosol sprays. In the upper atmosphere, uv light is able to break the weaker C–Cl bonds by homolysis to produce chlorine free radicals.



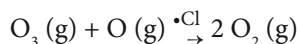
The chlorine free radicals can react with ozone to produce oxygen molecules and $\bullet ClO$ (this is the propagating step where one free radical is used up and another is formed in its place):



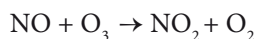
The newly formed free radical $\bullet ClO$ can also react with an oxygen free radical to form a diatomic oxygen molecule and regenerate the chlorine free radical:



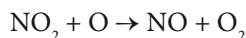
These two steps combined, remove both ozone and atomic oxygen in the upper atmosphere by converting them to diatomic oxygen. In the process a chlorine free radical is reformed, that is, it effectively catalyses the conversion of ozone and atomic oxygen to oxygen gas:



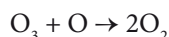
Similarly, nitrogen monoxide, NO, formed by the high temperature reaction between nitrogen and oxygen gases in supersonic aircraft engines, reacts with ozone, reducing its concentration:



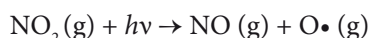
The nitrogen dioxide formed can react with an oxygen free radical:



The net result of the presence of nitrogen monoxide is the depletion of ozone:



Any NO_2 formed either by this reaction or by oxidation with O_2 also undergoes photo-dissociation in the presence of uv light to promote other photochemical reactions:

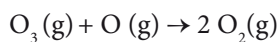
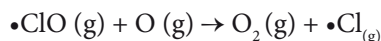


E.9.3 Outline the reasons for greater ozone depletion in polar regions.

© IBO 2007

Data shows a decrease in ozone concentrations in Antarctica in the 1980s and 1990s compared with earlier data. This was caused by increased ozone depleting pollutants. Data also indicates that the ozone concentrations over Antarctica show a seasonal variation with a greater depletion around October during the polar spring producing the ozone hole. A return to more normal concentrations occurs in November as the spring progresses.

The ozone hole can be explained by the fact that during the South Pole winter from June to September, the temperatures are frigid, trapping very cold air at the pole and immediately converting any water vapor present into ice crystals. These ice particles behave as surface catalysts and provide the surface area over which pollutants present in the polar atmosphere combine to produce reactive chemicals such as chlorine molecules. After the long, cold winter darkness, when the sun comes out in October, the photo-dissociation of chlorine molecules takes place in the presence of ultra violet light from the sun's rays. This produces chlorine free radicals which catalyze the destruction of ozone over Antarctica to produce the ozone hole.



As the spring progresses in Antarctica, the ice crystals in the stratosphere melt and are no longer available as surface catalysts for the production of chlorine molecules. This, combined with the flow of air containing ozone from the lower altitude warmer regions, replaces the destroyed ozone and by November the ozone concentration increases. Similar, but not as drastic ozone depletion, has also been observed over the North Pole during the Arctic spring. The temperatures around the North Pole do not go down to the same extremes as those at the South Pole (down to -90°C) and the air with the ozone from lower altitudes is better able to diffuse, reducing the overall effect on the ozone layer.

E10 SMOG (HL)

Smog, a term coined from the words ‘smoke’ and ‘fog’ arose from the conditions of coal smoke and fog experienced by the city of London in the early part of the 19th Century. The so-called ‘London smog’, also known as industrial or reducing smog is one of two types of smog. It is caused by the combustion of sulfur containing coal used for heating, manufacturing processes and the generation of electricity. It consists of water droplets, sulfur dioxide and trioxide, soot and ash (particulate matter) and sulfuric acid.

The reducing smog is found in coal burning cities such as Chicago and Beijing which can experience cool or cold, wet winters and where thermal inversion can trap cold, still air close to the Earth’s surface. As a result of increased pollution controls, bans on the use of coal as a domestic fuel, and measures such as the use of alkaline scrubbers which remove SO_x and particulates pollution, severe episodes of industrial smog are on the decline.

E.10.1 State the source of primary pollutants and the conditions necessary for the formation of photochemical smog.

© IBO 2007

The other type of smog, called **photochemical smog** is an oxidizing smog. This is a chemical soup containing hundreds of different substances formed in the atmosphere as a result of free radical reactions brought

about by ultraviolet radiation from the sun (thus called photochemical smog). It was first observed in Los Angeles in the 1940s. Automobile pollution is the main source of this type of smog and unlike industrial smog it is almost free of sulfur dioxide.

The main sources of primary pollutants for photochemical smog are volatile organic chemicals (VOCs) and nitrogen oxides (NO_x), especially nitrogen monoxide, NO from automobile exhaust and the furnaces of power plants. The main condition that promotes photochemical smog is the ultraviolet radiation from sunlight. Temperature or thermal inversion, windlessness and bowl-shaped cities such as Mexico City allow the collection of pollutants which are not dispersed and worsen the smog.

Under normal conditions, there is a gradual decrease in the temperature as the altitude increases. The warmer, less dense air near the Earth’s surface, warmed by the earth, rises. At the same time, pollutants produced near the surface of the Earth move with the warm air to the upper atmosphere. Cooler air takes the place of the rising warmer air near the Earth’s surface, warms up and rises, in turn creating air currents which allow the pollutants produced to be dispersed. **Thermal inversion** (also called temperature inversion) is the abnormal temperature arrangement of air masses where a layer of warmer air is trapped between two layers of colder air.

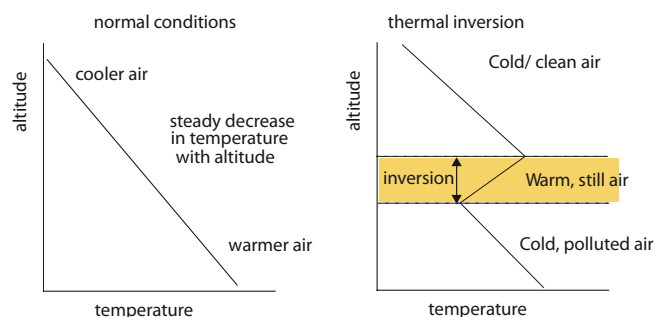


Figure 1629 Thermal inversion

Prevailing winds give rise to the horizontal movement of air. However, surrounding hills, mountains or valleys in places such as Mexico City and Los Angeles hinder the horizontal movement of air. The flow of cold air from the surrounding hills and mountains into these cities creates the cool lower layer. Under windless conditions, pollutants can collect over a city without being dispersed. This creates a situation where warm air on top stays over a polluted air mass and the cooler, more dense, air stays near the earth, stopping vertical movement. The warm air mass effectively acts as a lid, trapping polluted air close to the ground. The warm, dry, cloudless conditions of thermal inversion are ideal for the formation of photochemical

smog as any ultraviolet light from the sun's rays is easily able to reach the Earth.

E.10.2 Outline the formation of secondary pollutants in photochemical smog.

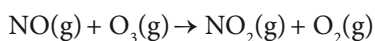
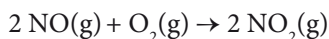
© IBO 2007

Research has clearly identified the role of sunlight in initiating photochemical smog in which particulates and unburnt volatile organic chemicals (VOCs) act as catalysts and reactants in the formation of secondary pollutants. It is found that photochemical smog follows a general, daily, cyclic pattern:

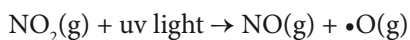
1. The release of VOCs, nitrogen oxides and particularly nitrogen monoxide, NO, as primary pollutants from the combustion of fossil fuels at high temperature in internal combustion engines and in the furnaces of power plants, cause smog. The automobile is the main source; nitrogen monoxide, along with volatile organic chemicals and particulates peaks during morning rush hours:



2. With the increase in the concentration of nitrogen monoxide, it is oxidized to brown nitrogen dioxide gas either by oxygen or primarily by ozone:

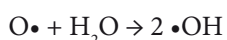
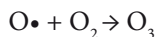


3. As soon as solar radiation is available in the morning, photo-dissociation of the nitrogen dioxide takes place to produce oxygen atoms:



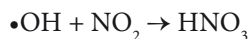
The atomic oxygen formed is a highly reactive species containing unpaired electrons and is called a free radical.

4. The oxygen free radicals initiate a series of important reactions to produce secondary pollutants such as ozone and hydroxyl free radicals, $\bullet\text{OH}$:



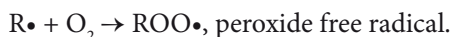
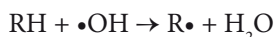
Ozone and hydroxyl free radical levels therefore peak later in the day. These are photochemical oxidants capable of oxidizing other substances not easily oxidized by diatomic oxygen under atmospheric conditions. For example:

The hydroxyl free radical reacts with nitrogen dioxide to produce nitric acid:

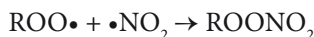


5. The photochemical oxidants carry out the oxidation of VOCs to produce a wide variety of secondary pollutants including aldehydes (RCHO) and toxic substances such as peroxyacyl nitrates, PANs, which are powerful lachrymators (cause eyes to water). These then disperse in the atmosphere reaching a maximum concentration in the afternoon. A sequence of reactions involving free radicals leading to the formation of PAN can be shown as follows:

Propagation of free radicals takes place where one radical is used up but another formed:



Termination of free radicals takes place when two free radicals combine:



A specific example is the formation of PAN:

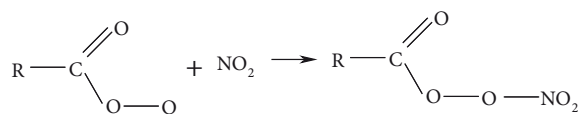


Figure 1630 The formation of peroxyacyl nitrates

E11 ACID DEPOSITION (HL)

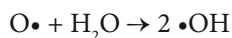
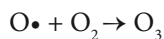
E11.1 Describe the mechanism of acid deposition caused by the oxides of nitrogen and oxides of sulfur.

© IBO 2007

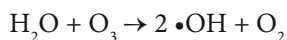
Oxides of nitrogen include nitrogen monoxide, NO and nitrogen dioxide, NO₂. Photo-dissociation of NO₂ in the presence of sunlight produces oxygen free radicals:



The oxygen free radicals initiate a series of important reactions to produce secondary pollutants such as ozone and hydroxyl free radicals, •OH, the later being a propagation step, where one free radical, O• is replaced by another, •OH:



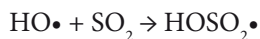
The ozone formed can also react with water to form the hydroxyl free radicals:



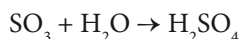
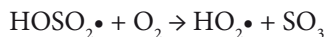
The hydroxyl free radicals react with nitrogen monoxide and nitrogen dioxide to produce nitrous acid and nitric acid respectively:



Sulfur dioxide is a primary pollutant produced from the combustion of sulfur containing coal. The hydroxyl free radicals react with sulfur dioxide to produce HSO₂• (HOSO₂•):



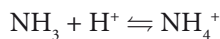
Another propagation step leads to the formation of sulfur trioxide, the anhydride of sulfuric acid. SO₃ reacts rapidly with moisture present in the air to produce sulfuric acid, a strong acid:



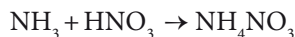
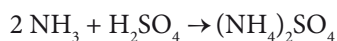
E11.2 Explain the role of ammonia in acid deposition.

© IBO 2007

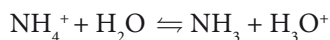
Ammonia, NH₃ contains a lone electron pair on the nitrogen, is able to accept a proton and is a weak base:



In the atmosphere, sulfuric acid and nitric acid formed as acid deposition pollutants can be neutralized by ammonia to form ammonium salts, ammonium sulfate, (NH₄)₂SO₄ and ammonium nitrate, NH₄NO₃:



Both (NH₄)₂SO₄ and NH₄NO₃ are salts of a weak base and a strong acid; the conjugate acid of the weak base, NH₄⁺ is therefore weakly acidic whereas both anions SO₄²⁻ and NO₃⁻ are neutral, making the salts weakly acidic in aqueous solution:



The weakly acidic salts formed in the atmosphere fall to the ground or are removed from the atmosphere by rain and enter the soil as NH₄⁺. Plants use nitrogen as nitrates, NO₃⁻ with its highest oxidation of +5. Thus, the ammonium ion with an oxidation number of -3 must be oxidized to +5. This process is called **nitrification** and is catalyzed by bacteria. The overall reaction is:



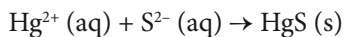
The process also makes the soil more acidic with the formation of H⁺.

E12 WATER AND SOIL (HL)

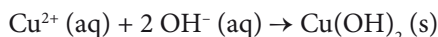
E.12.1 Solve problems relating to the removal of heavy-metal ions and phosphates by chemical precipitation.

© IBO 2007

Many metal ions form sparingly or slightly soluble salts. Chemical precipitation of such salts is a major method of removing heavy-metal ions and phosphates. For example, hydrogen sulfide, H_2S or soluble sulfides such as sodium sulfide, Na_2S , can be used to remove ions of heavy metals such as mercury, cadmium, lead and zinc by chemical precipitation:



Similarly, heavy metal ions such as copper, cobalt and iron can be removed as hydroxides from water sewage and soil by chemical precipitation:

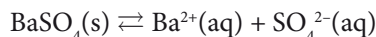


The following general solubility rules help explain the concept of using chemical precipitation for the removal of heavy-metal ions and phosphates from water and soil:

- 1 All carbonates, CO_3^{2-} and phosphates, PO_4^{3-} except those of Li^+ , Na^+ , K^+ and NH_4^+ are insoluble.
- 2 All sulfides, S^{2-} except those of Groups I, II and NH_4^+ are insoluble.
- 3 All hydroxides and oxides except alkali metals are insoluble (those of Sr^{2+} , Ca^{2+} and Ba^{2+} are sparingly soluble).
- 4 All Cl^- , Br^- and I^- salts are water soluble except those of Ag^+ , Hg_2^{2+} and Pb^{2+} .
- 5 All sulfates are water soluble except those of Ba^{2+} , Ca^{2+} , Pb^{2+} and Sr^{2+} .
- 6 Most nitrate (NO_3^-) salts are soluble.
- 7 Most salts of Na^+ , K^+ , and NH_4^+ are soluble

Quantitative aspects of solubility equilibria

Barium ions in water can be precipitated out by adding sulfate ions. The resulting barium sulfate is only slightly soluble in water and establishes the following equilibrium:



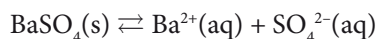
The equilibrium constant expression for such a precipitation reaction is given by:

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] (= 1.0 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6} \text{ at } 25^\circ\text{C})$$

K_{sp} is called the **solubility product constant** (note the concentration of solid does not appear because it is also a constant) and, because K_{sp} is temperature dependent, the particular temperature at which it is measured must be quoted. Thus, in a saturated solution of a slightly soluble ionic compound, the product of the concentrations of the individual ions raised to the powers indicated by the coefficients is a constant at a given temperature. Precipitation depends on K_{sp} ; a precipitate will form if the product of the ions in the mixture of solutions, when substituted into the K_{sp} expression, exceeds the numerical value of K_{sp} at that temperature.

The value of the solubility product is related to the solubility of the salt and the solubility can be calculated given the value of K_{sp} :

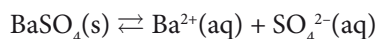
For example, if the solubility is $x \text{ mol dm}^{-3}$, in the case of, BaSO_4 , where one Ba^{2+} is produced for each SO_4^{2-} :



$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = x^2 = 1.0 \times 10^{-10} (\text{mol}^2 \text{ dm}^{-6})$$

$$x = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$$

Consider the solubility of BaSO_4 in a 0.10 mol dm^{-3} sodium sulfate, Na_2SO_4 , a strong electrolyte that is fully dissociated in solution. If the solubility of BaSO_4 in solution is now $y \text{ mol dm}^{-3}$, we can calculate this value as follows:



$$y + 0.01 \approx 0.01 \text{ (since } y \ll 0.10\text{)}$$

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 0.10y = 1.0 \times 10^{-10}$$

$$y = 1.0 \times 10^{-9} \text{ mol dm}^{-3} \text{ (and: } y + 0.10 \approx 0.10 \text{ is correct)}$$

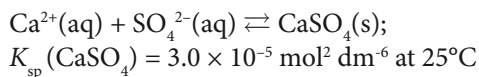
Thus, in pure water, BaSO_4 has a solubility of $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ whereas in the presence of a common ion, the solubility is reduced by 10^4 to $1.0 \times 10^{-9} \text{ mol dm}^{-3}$. This is called the common ion effect, a qualitative aspect of solubility equilibria. If a salt containing one of the ions is added, stress is placed on the system. The equilibrium is disturbed and the reverse reaction is favoured according to **Le Chatelier's principle**, to use up some of the ions added. More precipitate is formed and its solubility decreases in the presence of a common ion, as illustrated in the BaSO_4 example above. Thus, the solubility of a solid is always lower in a solution of a salt containing any common ions. Refer to Figure 1632 for some common K_{sp} values.

| | | |
|--|--|--------------------------------------|
| CaSO_4 : 3.2×10^{-4} | $\text{Mg}(\text{OH})_2$: 1.2×10^{-11} | FeS : 5.0×10^{-18} |
| CaCO_3 : 4.8×10^{-9} | $\text{Ca}(\text{OH})_2$: 2.5×10^{-16} | HgS : 1.0×10^{-26} |

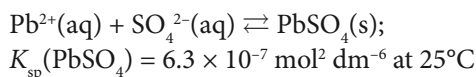
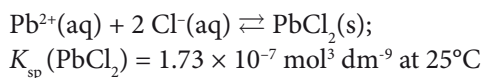
Figure 1632 Some K_{sp} values

Application of precipitation in water and soil chemistry

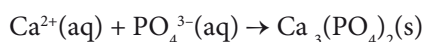
Sludge and hard water contain calcium ions, $\text{Ca}^{2+}(\text{aq})$, which can be precipitated out as calcium sulfate by adding sodium sulfate. The net ionic equation for the precipitation reaction is as follows:



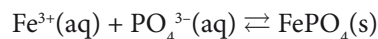
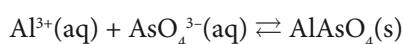
Lead ions, Pb^{2+} can be precipitated out as lead chloride by adding sodium chloride or as lead sulfate by adding sodium sulfate:



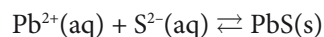
Phosphate ions form a precipitate with iron or aluminium oxide or with calcium ions:



Metal salts such as aluminium nitrate, iron(III) chloride or iron(III) sulfate can be used to remove arsenic (as arsenate) and phosphate from water by chemical precipitation:



The very low solubility of heavy metal sulfides can be used to remove Cd, Hg, Pb, Zn from water and soil:

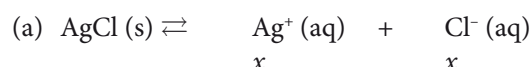


Example 1

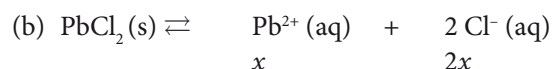
- Write the solubility product constant expression for the following compounds and indicate K_{sp} value in terms of x , if x is its molar solubility:

(a) AgCl (b) PbCl_2 (c) As_2S_3 (d) $\text{Ca}_3(\text{PO}_4)_2$ (e) $\text{Fe}(\text{OH})_3$

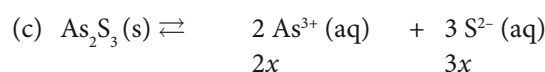
Solution



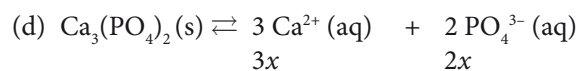
$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = x^2$$



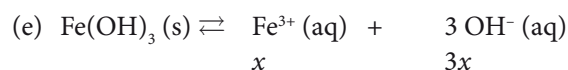
$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = x(2x)^2 = 4x^3 \text{ (note that } [\text{Cl}^-] = 2x)$$



$$K_{\text{sp}} = [\text{As}^{3+}]^2[\text{S}^{2-}]^3 = (2x)^2(3x)^3 = 108x^5$$



$$K_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2 = (3x)^3(2x)^2 = 108x^5$$



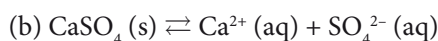
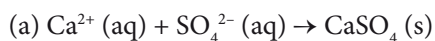
$$K_{\text{sp}} = [\text{Fe}^{3+}][\text{OH}^-]^3 = x(3x)^3 = 27x^4$$

Example 2

- (a) Calcium ions present in hard water are precipitated by adding sulfate ions. Write the net ionic equation for the reaction.

- (b) Given $K_{sp}(\text{CaSO}_4) = 3.0 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$ at 25°C , calculate its molar solubility in water at 25°C .
- (c) Determine if a precipitate will form when the ion concentrations are: $[\text{Ca}^{2+}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{SO}_4^{2-}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$.
- (d) Calculate the minimum concentration of sulfate ion required to precipitate the Ca^{2+} .

Solution



If the solubility is $x \text{ mol dm}^{-3}$, then:

$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = x^2 = 3.0 \times 10^{-5}$$

$$x = 5.5 \times 10^{-3} \text{ mol dm}^{-3}$$

(c) $[\text{Ca}^{2+}][\text{SO}_4^{2-}] = 1.0 \times 10^{-3} \times 1.0 \times 10^{-2} = 1.0 \times 10^{-5} < K_{sp}$. Thus there is no precipitate formed and no equilibrium present.

$$(d) K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = 0.001 x = 3.0 \times 10^{-5}$$

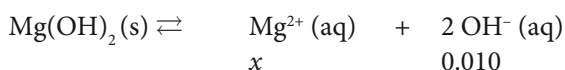
$$x = 3.0 \times 10^{-2} \text{ mol dm}^{-3}$$

Example 3

3. Water containing $0.010 \text{ mol dm}^{-3}$ magnesium ions precipitates magnesium hydroxide on the addition of sodium hydroxide.
Given $K_{sp}(\text{Mg}(\text{OH})_2) = 1.0 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$:

- (a) Calculate the concentration of Mg^{2+} left in solution if enough NaOH is added to produce a hydroxide concentration of $0.010 \text{ mol dm}^{-3}$.
- (b) Calculate the percentage of Mg^{2+} remaining in solution.

Solution



$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^{-}]^2 = x \times (0.010)^2 = 8.9 \times 10^{-12}$$

$$x = 8.9 \times 10^{-8} \text{ mol dm}^{-3}$$

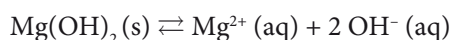
$$(b) \% \text{Mg left} = \frac{8.9 \times 10^{-8}}{1.0 \times 10^{-2}} \times 100 = 0.00089\% (8.9 \times 10^{-4} \%)$$

Example 4

4. Magnesium hydroxide has a K_{sp} value of $8.9 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$. Calculate the concentrations of the ions in a saturated solution of $\text{Mg}(\text{OH})_2$ and its pH.

Solution

If $[\text{Mg}^{2+}] = x$, then $[\text{OH}^{-}] = 2x$



$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^{-}]^2 = x(2x)^2 = 4x^3 = 8.9 \times 10^{-12}$$

$$x = [\text{Mg}^{2+}] = 1.3 \times 10^{-4} \text{ mol dm}^{-3} \text{ and}$$

$$[\text{OH}^{-}] = 2x = 2.6 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{pOH} = -\log_{10}[\text{OH}^{-}] = -\log_{10}[2.6 \times 10^{-4}] = 3.58$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.58 = 10.42$$

Example 5

5. From a consideration of the data below, determine the order of decreasing molar solubility (highest one first) of the salts AgCl , Ag_2CO_3 and Ag_3PO_4 .

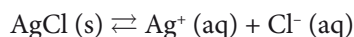
Solution

$$K_{sp}(\text{AgCl}) = 1.0 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6};$$

$$K_{sp}(\text{Ag}_2\text{CO}_3) = 6.3 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9};$$

$$K_{sp}(\text{Ag}_3\text{PO}_4) = 2.0 \times 10^{-21} \text{ mol}^4 \text{ dm}^{-12}$$

Note : The order cannot be deduced from the K_{sp} values as all these do not contain 1:1 ions.



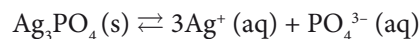
$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = x^2 = 1.0 \times 10^{-10};$$

$$x = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$$



$$K_{sp} = [\text{Ag}^+]^2[\text{CO}_3^{2-}] = (2x)^2 \cdot x = 4x^3 = 6.3 \times 10^{-12};$$

$$x = 1.16 \times 10^{-4} \text{ mol dm}^{-3}$$



$$K_{sp} = [\text{Ag}^+]^3[\text{PO}_4^{3-}] = (3x)^3 \cdot x = 27x^4 = 2.0 \times 10^{-21};$$

$$x = 2.9 \times 10^{-6} \text{ mol dm}^{-3}$$

Thus, order of decreasing solubility is: $\text{Ag}_2\text{CO}_3 > \text{AgCl} > \text{Ag}_3\text{PO}_4$

Selective Precipitation

Consider a solution containing $0.010 \text{ mol dm}^{-3}$ each of barium chloride and strontium chloride.

Given $K_{sp}(\text{BaSO}_4) = 1.5 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$ and $K_{sp}(\text{SrSO}_4) = 7.6 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$, and since both contain 1:1 ions, we can deduce that BaSO_4 will precipitate first if sulfate ions are added to the mixture. This is because the sulfate ion concentration required to precipitate Ba^{2+} ions will be less than that required to precipitate Sr^{2+} ions as shown by the calculation:

$K_{sp}(\text{BaSO}_4) = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$. For the precipitation of $[\text{Ba}^{2+}]$:

$$[\text{SO}_4^{2-}] = \frac{K_{sp}(\text{BaSO}_4)}{[\text{Ba}^{2+}]} = \frac{1.5 \times 10^{-9}}{0.010} = 1.5 \times 10^{-7} \text{ mol dm}^{-3}$$

$K_{sp}(\text{SrSO}_4) = [\text{Sr}^{2+}][\text{SO}_4^{2-}]$. For the precipitation of $[\text{Sr}^{2+}]$:

$$[\text{SO}_4^{2-}] = \frac{K_{sp}(\text{SrSO}_4)}{[\text{Ba}^{2+}]} = \frac{7.6 \times 10^{-7}}{0.010} = 7.6 \times 10^{-5} \text{ mol dm}^{-3}$$

Sr^{2+} ions will not begin to precipitate until the sulfate ion concentration reaches $7.6 \times 10^{-5} \text{ mol dm}^{-3}$. Until this concentration of $[\text{SO}_4^{2-}]$, the concentration of Ba^{2+} left in solution will be:

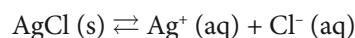
$$[\text{Ba}^{2+}] = \frac{K_{sp}(\text{BaSO}_4)}{[\text{SO}_4^{2-}]} = \frac{1.5 \times 10^{-9}}{7.6 \times 10^{-5}} = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$$

The original concentration of $[\text{Ba}^{2+}] = 0.010 \text{ mol dm}^{-3}$, and the concentration of $[\text{Ba}^{2+}]$ left $= 2.0 \times 10^{-5}$ after the addition of sufficient $[\text{SO}_4^{2-}]$ to begin Sr^{2+} precipitation. At this point, the percentage of $[\text{Ba}^{2+}]$ left in solution is:

$$\frac{2.0 \times 10^{-5}}{0.010} \times 100 = 0.20\%$$

Thus, 99.8% Ba^{2+} is selectively precipitated out of solution before Sr^{2+} precipitation begins.

Consider the equilibrium between the precipitate AgCl and its ions, Ag^+ and Cl^- :



$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$; thus, $[\text{Ag}^+] = \frac{K_{sp}}{[\text{Cl}^-]}$ where K_{sp} is a constant.

The mathematical relation between the concentrations of the ions can be represented neatly in a graphical form, as shown in Figure 1632.

A: The curve represents concentrations at precipitation. This suggests an infinite concentration of ions that can lead to equilibrium.

B: Where a solution contains a lower concentration of ions, no precipitate forms and no equilibrium is present.

C: A solution contains a higher concentration of ions than it can precipitate at equilibrium, a precipitate forms and an equilibrium is established between the solid precipitate and ions in solution.

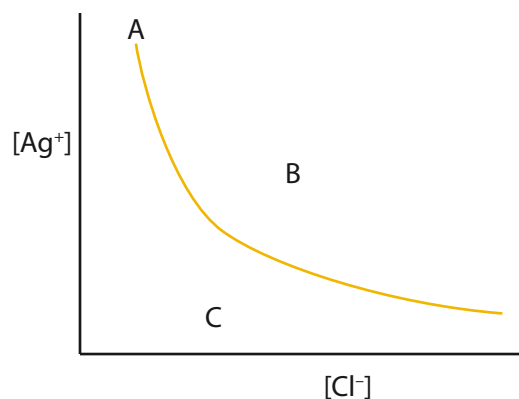


Figure 1633 Relation between $[\text{Ag}^+]$ and $[\text{Cl}^-]$ ions

Applications of K_{sp} :

1. Calculate the water solubility of a solid given its K_{sp} value.
2. Determine the effect of adding a common ion on the solubility.
3. Calculate the concentration of one ion in equilibrium with the solid when the concentration of the other ion is given.

- When two ionic solutions are added, determine whether a precipitate will form or not.
- In a mixture of two slightly soluble ionic compounds, can selectively precipitate one.

E.12.2 State what is meant by the term cation-exchange capacity (CEC) and outline its importance.

© IBO 2007

Cation-exchange capacity (CEC) is the extent to which the negative charges on clay and/or humus in the soil can exchange nutrient cations at the roots of plants. CEC is an indicator of soil fertility. Some cations such as K^+ , Ca^{2+} and Mg^{2+} are important plant nutrients, but others for example Na^+ and Al^{3+} are not.

CEC values depend on the type of soil and how much organic matter is present. Soil organic matter contains humic acid anions that are able to bind to nutrient cations. Thus, sand with little organic matter has low CEC value. Soil with clay and organic matter has high CEC value; the larger the CEC value, the more cations the soil can absorb and make available to plants. The importance of CEC is the availability of the key mineral nutrients to plants and reflects the soil's ability to exchange and adsorb cation nutrients.

Adsorption occurs due to electrical attraction in which the positively charged cations are held by particles containing negative charges in the soil organic matter and in clay. Clay in which Si(IV) and Al(III) have been replaced, for example, by Fe(II) result in a net negative charge on the surface. These negative charges attract cations. The higher the number of negative charges, the higher its CEC.

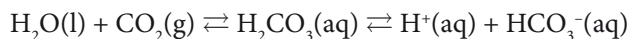
Humus in soil organic matter occupies a large surface area and contains many anionic sites due to the partial dissociation of the presence of phenolic and carboxylic acid groups. Thus it can adsorb large amounts of nutrient cations and humus is a very good storehouse for plant nutrients. Thus, adding SOM increases CEC. As plants take up nutrients from the soil, cation exchange takes place and these cations are replaced by hydrogen ions.

E.12.3 Discuss the effects of soil pH on cation-exchange capacity and availability of nutrients.

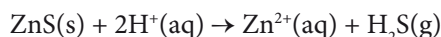
© IBO 2007

Water in the soil plays several key roles. For example, Group 1 metal ions such as Na^+ and K^+ are water soluble and are removed on regular irrigation of soil. Potassium ions control the amount of water that enters via osmosis; thus removal of potassium ions affects its ability to control water by osmosis.

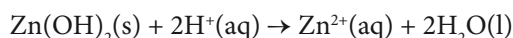
Carbon dioxide in the air reacts with water to form H_2CO_3 , a weak acid:



Natural rain water therefore is acidic and has a pH ~ 5.6 . This makes the soil acidic (lowers its pH) making it possible for more metal ions to dissolve. For example, zinc sulfide is insoluble in water, but dissolves in an acid by reacting with H^+ ions by forming H_2S :

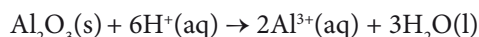


Similarly, zinc hydroxide, a base, is insoluble in water but reacts with H^+ ions:

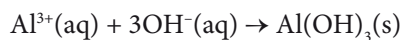
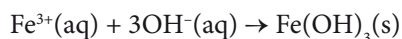


H^+ from acid deposition can replace nutrient cations in the soil such as Zn^{2+} and Mg^{2+} .

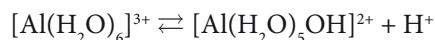
Alumina, Al_2O_3 is insoluble in water and is amphoteric: it reacts as a base with H^+ ions to form soluble Al^{3+} (aq) ions:



In basic conditions, Fe^{3+} and Al^{3+} react with OH^- to form insoluble hydroxides:

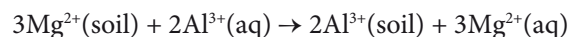


Hydrated ions such as $[Al(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{3+}$ with the high charge densities (charge to size ratio of the metal ion) attract the negative part of the water dipole to produce weakly acidic solutions:



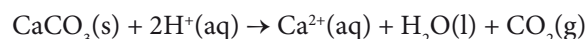
Ions such as Al^{3+} , Fe^{3+} and Mn^{2+} are soluble in acidic solutions, but Al^{3+} and Mn^{2+} are toxic to plants. Al^{3+} is not a plant nutrient. However, its presence in soil below pH 5 is problematic. Due to its high charge density (charge

to size ratio) and thus high chelating effect of binding onto the negative surfaces in clay and humus, it is able to displace important plant nutrient cations such as Ca^{2+} and Mg^{2+} from the soil:



These can then be lost, for example, due to irrigation. The soil pH needs to stay above pH 5 in order to avoid losing plant nutrients by the presence of Al^{3+} ions by the above process.

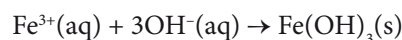
In acidic soil, insoluble calcium carbonate and magnesium carbonate are converted to soluble Ca^{2+} and Mg^{2+} ions respectively and can be lost to water drainage:



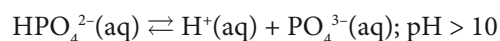
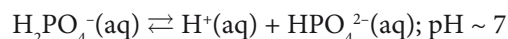
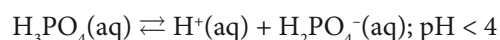
In such cases, CaCO_3 or MgCO_3 can be added to the acidic soil to replenish the nutrients:



Acidic soil below pH 5.5 affects microbes' ability to fix NH_4^+ to N_2 . Thus below about pH 5.5, NH_4^+ ions, which are weakly acidic, accumulate in the soil. Soil below pH 4 is too acidic and leads to poor plant growth. Lime can be added judiciously to reduce soil acidity and increase its pH to a more acceptable level (about pH 6 to 6.5). If soil pH increases too much, ions such as Fe^{3+} precipitate out as insoluble hydroxides leading to deficiency of important nutrients:



Soil pH affects the amount of phosphate ion present in solution. Phosphoric(V) acid, H_3PO_4 is a weak, triprotic acid. Its first dissociation is at low pH whereas the third dissociation is at high pH, both typically out of soil pH range:

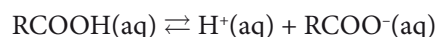


Thus, as plants absorb inorganic phosphorus from the soil as H_2PO_4^- and HPO_4^{2-} , its supply depends on having a soil pH between about 6 and 7.5. In acidic soil below pH 5, the presence of Al^{3+} and Fe^{3+} produce insoluble phosphate compounds thus decreasing the availability of phosphorus to plants. Above pH 7, phosphates of Ca^{2+} and Mg^{2+} precipitate out.

Micro-nutrients such as iron, manganese and zinc are available in acidic soil. As soil pH approaches 7, their availability decreases as they precipitate out as hydroxides and may have to be supplemented. If soil is too basic, soil organic matter containing humic acids or acidic ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$ can be added. Ammonium sulfate is a salt of a weak base, NH_3 and a strong acid, H_2SO_4 . It therefore consists of the cation, NH_4^+ that is weakly acidic (and anions, SO_4^{2-} , that are neutral):



CEC depends on soil pH. SOM contains humic acids which exhibit buffering capacity over the pH 6.5 to 7.5 range. For example, the weakly acidic carboxylic acid group dissociates as follows:



Increased soil pH reduces H^+ in the above equation. This pushes the equilibrium to the right (Le Chatelier's principle) and produces more anions in the organic soil matter. This is able to bind to more cation nutrients and thus increase the soil's CEC. Increasing soil pH to 7 increases soil CEC; thus checking and maintaining soil pH is essential.

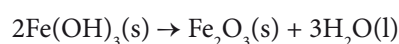
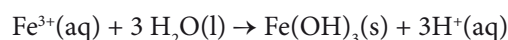
E.12.4 Describe the chemical functions of soil organic matter (SOM).

© IBO 2007

The major chemical functions of soil organic matter (SOM) are that it :

- has the ability to increase CEC of the soil
- behaves as a buffer and hence controls soil pH
- removes heavy metals and pesticides through its chelating ability.

Soil organic matter can greatly increase the cation exchange capacity (CEC, the extent to which it can exchange nutrient cations at the roots) of soil due to the presence in humic acid anions from carboxylic acid and phenolic functional groups (RCOO^- and ArO^-). This makes it possible to chelate to nutrient cations, hence SOM prevents these from precipitating out as insoluble compounds. If cations such as Fe^{3+} are not able to bind to anions in SOM, these ions form insoluble oxides, hydroxides or carbonates and thus become unavailable to plants through the roots:



SOM thus acts as a nutrient reservoir for plants. It is not able to bind to anions such as a nitrate, NO_3^- , phosphates (H_2PO_4^- and HPO_4^{2-}) and sulfate, SO_4^{2-} . However, N, P and S are bonded in the organic matter and made available to plants due to microbial activity in the soil organic matter. These effects are further enhanced by the large surface area of SOM.

A buffer system is able to minimize the effect on pH (that is, its pH changes only slightly) when small amounts of an acid or a base are added to it. Soil organic matter is an important buffer system that maintains soil pH due to changes in the hydrogen ion concentration. Consider the dissociation of the weak carboxylic acid groups present in humus:



If H^+ is added to the system, the equilibrium is disturbed; the reverse reaction is favoured using up some of the acid added, a new equilibrium is established and the change in pH of the soil is minimised. Similarly, if $\text{OH}^-(\text{aq})$ is added, it reacts with the H^+ present; the equilibrium is disturbed, the forward reaction is favoured to replace some of the acid used up, a new equilibrium is established and again the change in pH of the soil is minimised.

Plants require phosphorus for early root development and growth; phosphorus deficiency may lead to fewer flowers, yellowing of leaves and stunted growth. Calcium phosphate is the main inorganic phosphorus source but it is not always available. Organic phosphorus, which comes from the phosphate used by living organisms, is relatively immobile in the soil. Organic phosphate is converted slowly into inorganic ions; the process is called mineralization and organic soil matter is an important source of phosphorus to the plants. The ability of humic acid anions from the carboxylic acid and phenolic group to chelate or bind plant nutrient cations is very important in soil chemistry. For example, soil organic matter enhances phosphorus availability through its chelating ability.

Soil organic matter is able to chelate and hold on to toxic cations such as Al^{3+} , heavy metals ions such as Hg^{2+} . It can also deactivate pesticides as they can be broken down by soil organisms. This decreases the amount of pollution that reaches and affects the water supply. Soil organic matter is able to bind to soil mineral nutrients such as iron cations which can otherwise precipitate out as insoluble salts and make them available to plants.

OPTION E: ENVIRONMENTAL CHEMISTRY QUESTIONS

E1 Air pollution

- List the five major primary pollutants in the atmosphere and describe their main natural and anthropogenic sources. Illustrate your answer with appropriate equations. State methods that can be used to reduce each of the pollutants.
- (a) Describe the electrostatic precipitation method of reducing the release of particulate matter into the atmosphere.
(b) Describe the method for reducing the release of sulfur dioxide into the atmosphere.

E2 & E11 Acid deposition

- (a) Define acid deposition and explain why natural rain water is acidic.
(b) State the pH of pure rain water and, with the aid of an equation, explain why rain is naturally acidic.
(c) Determine how many times more concentrated is rain of pH 4 acidic compared to that of pH 6.
- (a) List two major pollutants responsible for acid deposition and give one man-made and one natural source of each. Write equations for the formation of acids from the pollutants.
(b) Outline the effect of acid deposition on marble objects and on plant growth.
(c) Describe two methods each for the reduction of each of the two pollutants.

E3 Greenhouse effect

5. (i) Describe and explain the 'greenhouse effect'.
- (ii) List five greenhouse gases other than CFCs and list the main source for each.
- (iii) CFCs are produced in much less amount compared to the other greenhouse gases. State one reason why CFC is considered an important greenhouse gas.
- (iv) Discuss the effects of global warming.

E4 & E 9 Ozone depletion

6. (a) Without external influence, explain how the environment is able to maintain more or less constant ozone concentration in the upper atmosphere. Illustrate your answer with appropriate equations.
- (b) Explain why the allotropes of oxygen require energies of different wavelengths to undergo dissociation.
- (c) (i) State two sources of chlorofluorocarbons in the atmosphere.
- (ii) Explain how the presence of CFCs may lead to ozone depletion. Use dichlorodifluoromethane as an example to illustrate your answer with appropriate equations.
- (iii) Explain why the ozone layer depletion in the polar regions seems the greatest in the winter months.
- (iv) List three harmful effects on the human health of the decrease of ozone in the upper atmosphere.
- (v) Suggest four possible alternatives to CFCs and list their advantages and disadvantages.

E5 Dissolved oxygen in water

7. (a)
- (i) Explain the importance of dissolved oxygen in water.
- (ii) List three factors that affect the concentration of dissolved oxygen in water, and explain the effect of increasing each one on dissolved oxygen content and on the quality of the water.
- (b) Define the term *Biological oxygen demand*.
- (c) Define the term *eutrophication* and explain how nitrates are involved in the process.
- (d) Distinguish between aerobic and anaerobic decomposition of organic material in water and list products of C, N, S and P in each process.

E6 Water treatment

8. Explain why many substances dissolve in water.
9. (i) State the purpose of sewage treatment.
- (ii) List the main materials removed during various methods of sewage treatment.
- (iii) Explain the purpose of adding aluminium sulphate in primary sewage treatment.
- (iv) Describe how waste in sewage is removed in secondary treatment
10. (a) State the names of two methods used for obtaining pure water from sea water. Explain the principle behind each method.
- (b) Explain why nitrates and phosphates are not removed during primary and secondary treatment. Explain how ions such as Cd and phosphate can be removed. Illustrate your answer with appropriate equations.

E7 & 12 Soil

11 (a)

- (i) List three major and three minor elements present in the Earth's crust.
- (ii) List the four components of soil and identify the one in the largest amount and its source.
- (iii) Define the term *humus* and list its carbon and nitrogen content.
- (iv) Describe the structure of silica, SiO_2 and explain the consequence of replacing one in every four tetrahedrons contain Al^{3+} instead of Si^{4+} in the silica structure.

12. Define the terms *salinization*, *nutrient depletion* and *soil pollution*, describe how each arises and discuss their impact on the quality of soil.

13.(i) Define the term *soil organic matter (SOM)*.

(ii) List the composition of SOM and state how its carbon content can be measured experimentally.

(iii) Describe the relevance of SOM.

14. Define the process of *mineralization* and describe the relevance of SOM in terms of biological, physical and chemical functions.

15.(a) Calcium ions present in hard water are precipitated by adding sulfate ions. Write the net ionic equation for the reaction.

(b) Given $K_{\text{sp}}(\text{CaSO}_4) = 3.0 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$ at 25°C , calculate its molar solubility in water at 25°C .

(c) Determine if a precipitate will form when the ion concentrations are: $[\text{Ca}^{2+}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{SO}_4^{2-}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$.

(d) Calculate the minimum concentration of sulfate ion required to precipitate the Ca^{2+} .

16. State the meaning of the term cation-exchange capacity (EC) and outline its importance.

17.(a) Use relevant equations to discuss the effects of soil pH on cation-exchange capacity and availability of:

(i) Zn (ii) Al

(b) Explain how soil pH affects the amount of phosphate ions present in solution.

E8 Waste

18. Outline and compare the two main methods of disposing of waste.

19. List five commonly recycled materials and identify the appropriate benefits for each type of recycled material.

20. Describe the characteristics, sources and storage methods of different types of radioactive waste.

E10 Smog

21.(i) List the primary pollutants produced in photochemical smog and state its main cause.

(ii) Explain why the concentration of the primary pollutants increases in the mornings and the role of sunlight in the formation of chemical smog. Use appropriate equations to illustrate your answer.

(iii) State two health problems caused by chemicals in photochemical smog.

(iv) Outline three methods of reducing photochemical smog.