Extension 24: Bioconcentration, Energy Generation and Waste Disposal

1. Prerequisites

The key ideas required to understand this section are:

Topic	Book page
Importance of dissolved oxygen in water	435
Distribution ratio	184
Redox equations	106

2. Bioconcentration and biomagnification of species

### The bioconcentration of pesticides in fish

Pesticides are often washed from land into river or lake water. The concentrations of pesticide in the water is usually tiny, but pesticides are found at much higher concentrations in the oily tissue of the fish present. The concentration of chemicals in living things in this way is called **bioconcentration**.

Bioconcentration occurs when the polluted water passes through the gills of fish. The gills allow oxygen from the water to enter the bloodstream of the fish, but they also allow organochlorine compounds to enter the fatty tissue. The organochlorine compounds are distributed between the fatty (oily) tissue and water. As we would expect, organochlorine compounds are more soluble in oily tissue than in water (like dissolves like).

One way of assessing whether or not an organic compound is likely to bio-concentrate in fish is to determine its distribution ratio between a suitable oil and water. A convenient oil is octan-1-ol (usually known simply as octanol), $CH_3(CH_2)_6CH_2OH$. The distribution ratio is symbolised K_{ow} (o for octanol and w for water):

$$K_{ow} = \frac{\text{concentration of compound in octanol}}{\text{concentration of compound in water}}$$

The higher K_{ow} is, the more likely it is that the compound will build up in the fish. For example, K_{ow} of DDT at 20°C is about 100 000. This is an enormous ratio, and confirms that DDT has a tremendous potential for bioconcentration in fish. Because the K_{ow} values for many compounds are so large, it is usually more convenient to express the ratio as a logarithm, $\log K_{ow}$. For example, $\log K_{ow}$ (DDT) = log (1 × 10^5) = 5.0.

Crocodile [34.2]

Tiger fish [5.00]

Kapenta [0.16]

Water [<0.000 02]
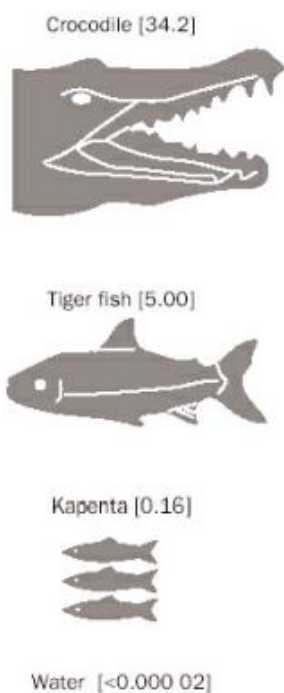
EXERCISE 24A

(i) The log Kow (25°C) values for Lindane, Dieldrin and Vinyl chloride are approximately 4, 3.5 and 0.6 respectively. Which substance is least likely to be absorbed into fatty tissue?

(ii) The concentration of DDT in a badly polluted lake was estimated to be 3×10^{-6} mg dm^{-3} (ppm). Assuming that the fatty tissue of fish is in equilibrium with the DDT concentration in the lake, estimate the concentration of DDT in the fish. Compare your answer with the measured concentrations which were in the range $0.5 - 2$ mg dm^{-3} (ppm).

Fig. 24.1 Biomagnification in Lake Kariba. DDT levels are given in units of micrograms of DDT per gram of animal fat. (Adapted from H. Berg, M. Kiibue and N. Kautsky, Ambio, 1992, vo.. 21, p. 444.)

Biomagnification

The concentration of pesticides at the top of the food chain is magnified because they consume large quantities of smaller animals. This effect is called biomagnification.

Some examples are:

1. Birds of prey (such as falcons and eagles) have also shown high concentrations of DDT in their bodies. High concentrations of DDT can cause bird eggs to have very thin shells and fewer eggs then survive to hatch. This has caused a dramatic fall in the population of some birds. Tighter controls on the use of DDT have resulted in a slow recovery in these populations.
2. Studies in Lake Kariba in Africa, as illustrated in Fig. 24.1 By eating large numbers of smaller fish, tigerfish build up concentrations of DDT in their tissue. By eating tiger fish (and other prey) the crocodile accumulates even larger levels of DDT.

3. Energy and the environment

The generation of most of the energy necessary to support our increasing energy needs contributes to the reduction of natural resources and the pollution of the environment. Many attempts to solve one of these problems has resulted in creating another – for example, catalytic converters were introduced to destroy pollutants (NO, hydrocarbons and CO) emitted from car exhausts. The catalysts present oxidise carbon-containing pollutants to CO_2 and reduce NO to harmless N_2. Continued use of these catalysts, however, uses up rare-metal resources (such as platinum) and increases petrol consumption.

Current energy options

At present, most of our energy comes from fossil fuels. It has been estimated that, in the future, more coal reserves will be available than those for petroleum and natural gas. The burning of coal with a high sulfur content, however, can contribute to environmental problems.

EXERCISE 24B

Coal typically contains 2.5% sulfur by mass. What volume of sulfur dioxide is released into the atmosphere, measured at 20°C and 1 atm, when 1 tonne of coal is burned? (1 tonne = 1000 kg)

Nuclear emissions

The disposal of radioactive waste in most Western countries is strictly regulated. Compared with the volume of waste produced by conventional industry and by oil, gas and coal powered powered stations, the volume of highly radioactive waste generated by the nuclear power industry is tiny. Of all the radioactive waste, the disposal of highly radioactive waste from used nuclear reactor fuel (high level waste) is the most controversial. The waste is first allowed to cool, and during this period some of the short-lived isotopes completely decay away. Most of the waste contains uranium which is eventually extracted to make new fuel, and about 1% of it is plutonium. The remainder is stored in special containers. It is planned to turn this radioactive waste into a tough glass-like material (vitrification) for long-term storage. The long half-lives of some of the radionuclides in the waste mean that the storage areas will always need to be monitored and protected. Affluent countries (such as the USA, Canada and the European states) have, in recent times, produced a nuclear industry which (on average) produces less pollution and harm than many conventional industries (such as the coal, oil and chemical industries). However, poorer countries have a less satisfactory record. In addition to the Chernobyl accident (see information box 1), there have been a series of disturbing incidents in the former USSR in which relatively large amounts of radionuclides have been disposed of recklessly. The dumping of old submarine nuclear reactors at sea is one example.

BOX 1: Chernobyl

At 1.23 am on April 26th, 1986, one of the nuclear reactors at Chernobyl, Ukraine, went into an uncontrolled chain reaction which produced a massive pressure of steam. Two seconds later, the enormous steam pressure created an explosion which blew the thousand tonne safety cover off the top of the reactor. Huge amounts of radioactive material were blown into the air and the graphite moderator caught fire. Local fireman showed immense bravery in tackling the fire and equally brave helicopter pilots dropped dolomite (a form of calcium carbonate containing magnesium) on to the flames. Under the intense heat, the calcium carbonate decomposed into carbon dioxide (and calcium oxide), with the CO_2 produced helping to extinquish the flames. Many of the firemen and pilots died within a few weeks of being exposed to such high levels of radiation.

Away from the immediate area surrounding Chernobyl, the most damaging radionuclides were strontium-90 ($t_{1/2}$ = 28 yr), caesium-137 ($t_{1/2}$ = 30 yr), and iodine-131 ($t_{1/2}$ = 8 days). These radionuclides produced a 'fallout' which caused extensive contamination over much of Europe, particularly on high grounds where the rainfall is greater such as Scotland, North Wales and Cumbria.

Strontium is in the same group as calcium in the Periodic Table, and both metals have similar chemical reactions. It is not surprising therefore, to find radioactive strontium taking the place of calcium during pregnancy and infant growth.

Fallout iodine is deposited on plants. Cows and sheep consume contaminated grass and some ends up in the animals' milk. This explains why milk from contaminated areas was banned during the Chernobyl crisis.

Caesium-137 has the longest half-life of the three contaminants and therefore remains present in the environment longest. It also ends up in animal milk. It was caesium-137 which caused milk and livestock restrictions to be kept in force long after the hazard from iodine-131 had receded.
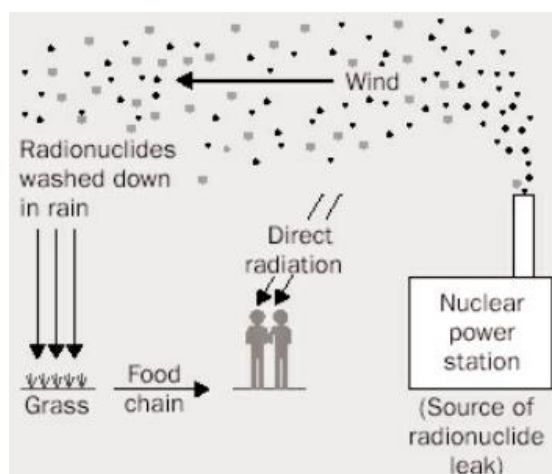
Fig. 24.2 Radioactive materials emitted from an accident at a nuclear power station can directly irradiate individuals, plants and animals. It can be washed down by rain.

Possible future sources of energy

Wind and tidal energy can be made use of by direct conversion of these energies to electricity. Hydroelectric and geothermal power, which use waterpower to generate electricity and underground heat to produce steam, respectively, are possible future energy sources. Although these are "clean" energy options, even large-scale usage of all of them could only supply a limited amount of our total energy requirement.

An ideal energy source is one that is widely available, cheap and does not add to the Earth's pollutants. Two possibilities for the future are solar energy and nuclear fusion.

Solar energy

Energy from the sun can be captured by using solar power cells that directly convert sunlight into electricity. These cells have already been used in space vehicles. On earth, solar energy is intermittent, but the energy could be stored. For example, hydrogen gas could be produced by the electrolysis of suitable salt solutions, using electricity produced by solar energy. Hydrogen can be stored, piped and burned without pollution or used in a **fuel cell**.

Green plants already utilise solar energy. They contain chlorophyll molecules that absorb some of the electromagnetic radiation emitted by the sun and this energy is used by the plant to convert carbon dioxide and water to carbohydrates.

$$6CO_2(g) + 6H_2O(l) \xrightarrow[\text{chlorophyll}]{\text{solar energy}} C_6H_{12}O_6(aq) + 6O_2(g)$$
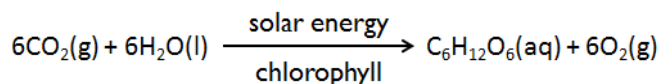
Oxygen is also released. This process of converting solar energy into stored chemical energy is known as **photosynthesis**. Chemists are interested in producing chemicals that might mimic this process and allow it to be controlled.

Nuclear fusion

The fusion of two light nuclei into a heavier nucleus, would release a great deal of energy (similar reactions produce the sun's energy release). Fusion reactors are generally recognised as posing fewer safety hazards than nuclear fission reactors. In 1989, "cold fusion" was announced by two scientists in the USA. They claimed that during the electrolysis of deuterium oxide, using palladium electrodes the deuterium became sufficiently concentrated in the palladium electrode to fuse and

unexpectedly large amounts of energy were generated. This report caused a great deal of excitement amongst many researchers but, to date, the claim has not been substantiated and many scientists remain sceptical of the idea.

BOX 2: Solar Cells

A solar battery, or solar cell, is a "sandwich" of silicon wafers. The silicon wafers have chemicals such as arsenic or boron added to them which make them either have a deficiency of electrons or an excess of electrons. (See Fig. 24.3.)
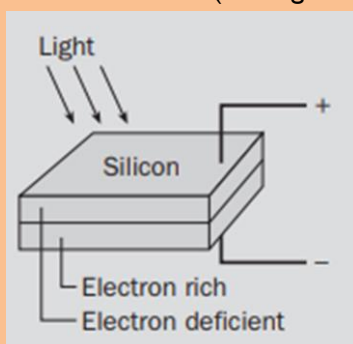

Fig. 24.3 A Solar Cell. When sunlight falls on the cell, energy is absorbed and electrons can move from one silicon layer to another. If the cell is part of a circuit, an electric current flows.

BOX 3: Fuel Cells

Many fuel cells use the reaction between hydrogen and oxygen to produce electricity. The gases are fed into the cell, where they react at the electrodes. The best electrodes are made of platinum.
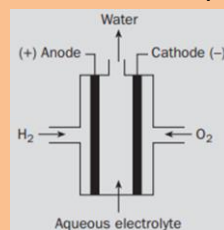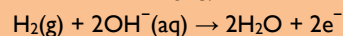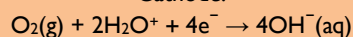

Fig. 24.4 A Fuel Cell. The reactions that take place are:
Anode:
$$H_2(g) + 2OH^-(aq) \rightarrow 2H_2O + 2e^-$$
Cathode:
$$O_2(g) + 2H_2O^+ + 4e^- \rightarrow 4OH^-(aq)$$
The product, water, proves useful in a space shuttle.

Energy conservation

Whilst it is desirable to exploit new, non-polluting sources of energy, energy conservation can significantly reduce both the rate of depletion of current resources and environmental pollution. Examples of how such energy savings might be made include: use of trains or buses instead of cars for transportation, (thus saving fuel) use of fossil fuels for heating rather than electricity (energy is wasted in the generation of electricity) and the improved insulation of buildings.

5. Managing waste

The production and disposal of waste is the cause of a great deal of environmental pollution. As well as household waste, which includes sewage and municipal garbage, many industrial wastes from manufacturing processes (some of which may be highly toxic) require treatment and/or safe disposal.

Recycling

When materials are recycled, there is often a twofold benefit – as well as saving on the cost of raw material, waste disposal costs may be reduced. Examples of recycling by industry are:

1. The collection and recycling of glass (in bottle banks);
2. The use of scrap metal in the manufacture of steel;
3. Recovery of energy from burning combustible waste.

Sewage treatment

The main stages in the treatment of sewage are as follows:

1. The removal of large solids that get into the system by filtering the wastewater through screens. The solids that are removed are disposed of in landfill sites.
2. Settlement in tanks to allow the removal of solids that settle out (called sludge). This process also allows removal of grease, which floats to the surface and can be skimmed off.
3. The organic content of wastewater will have a high biochemical oxygen demand. This is substantially reduced by degradation of the organic matter using microbial oxidation.

Various physical and chemical processes are applied in order to improve the quality of the wastewater. These include: chemical removal of the phosphate, coagulation, further filtration and disinfection. Disinfection may be carried out using chlorine; however, ozone is increasingly used because of concen over the possible production of organic chlorine compounds during water chlorination. The safe disposal of the sludge produced during water treatment is a problem. The sludge is dried and then may be incinerated, digested or dumped.

EXERCISE 24C

Phosphate

Phosphate (PO_4^{3-}) may be precipitated from wastewater as its calcium salt by treatment with limewater, [$Ca(OH)_2(aq)$].

(i) Write a balanced ionic equation for this reaction.

(ii) (ii) If 1 dm^3 of a solution of wastewater contains a concentration of 0.0003 mol dm^{-3} of phosphate, what mass of Ca^{2+} must be added before calcium phosphate is precipitated? Assume there is no increase in volume upon adding the solid calcium salt and that it is completely dissociated in water. Calcium phosphate has $K_s = 1 \times 10^{-24}$ (mol dm^{-3})^5 at room temperature.

EXERCISE 24D

Chlorination

These reactions occur when chlorine dissolves in water:

$$\underline{Cl_2} + H_2O \rightarrow H^+ + \underline{Cl^-} + \underline{HOCl}$$
$$\underline{HOCL} \rightleftharpoons H^+ + \underline{OCl^-}$$
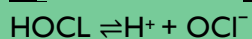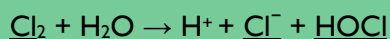
(i) Work out the oxidation number for chlorine in the underlined species.

(ii) "Active chlorine" kills bacteria. It is present in chlorine-containing species that can act as oxidising agents. Which species in (i) are oxidising agents? Which one is not and why?

BOX 3: Coagulation

Coagulation is used to aggregate fine suspended material, so that it may have sufficient size and density to settle out or **flocculate**. For example, $Al_2(SO_4)_3$ or $Fe_2(SO_4)_3$ are added to the water, whereupon the insoluble hydroxides are formed at pH values ≥7:

$$Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$$
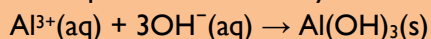
The **gelatinous** (jelly-like) precipitate of hydroxide formed carries suspended material with it as it settles. The suspended material consists of colloidal particles, that would not otherwise settle out. The precipitate that forms can filtered off and consumes hydroxide ions, neutralising alkaline waters and resulting in a decrease of pH.

Incineration

Incineration converts organic materials to CO_2 and H_2O. It may serve to destroy household waste, chemical waste and biological waste (e.g. from hospitals). A high temperature is required, usually in excess of 1000°C, and a plentiful supply of oxygen. Exhaust gases must be filtered. The process greatly reduces the volume of waste - an inorganic ash is left behind, which is disposed of by landfill. Incineration provides a means to dispose of the relatively inert PCBs and the high temperatures generated allow endothermic reactions, such as the destruction of C-Cl bonds in organochlorine compounds, to take place.

The chief disadvantage of incineration is that it might lead to air pollution. The ash from municipal incinerators is very finely divided and can be ingested into the lungs.

Incomplete combustion of PCBs can cause formation of the highly toxic chloro compounds such as polychlorodibenzodioxins (PCDDs) and polychlorodibenzofurans (PCDFs). This is most likely to happen in older municipal waste incinerators, when a combination of insufficient oxygen and too low a temperature for safe incineration might occur.

Digestion

Anaerobic digestion occurs when microorganisms degrade wastes in the absence of oxygen. It may be used to treat sewage sludge, but the process can also be used to degrade a variety of toxic organic wastes. Carbon dioxide and methane, which may be used as a fuel, are the products. The overall process is described by the equation:

$$2\{CH_2O\} \rightarrow CO_2 + CH_4$$
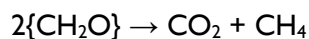
where "CH_2O" is a general formula for organic waste.

Dumping

Ocean dumping of sewage sludge has been widely practised in the seas around the UK. However, the practice of application of sludge to the land is increasing. The sludge contains nitrogen and phosphorus which make it useful as a fertilizer; however urban areas often produce sludge with a highly toxic metal content, so the amount of such sludge dumped in this way must be carefully controlled.

EXERCISE 24E

Sewage treatment

A sewage treatment plant processes 100 000 dm³ of wastewater per day. The waste contains 400 ppm (mg dm⁻³) of biodegradable $\{CH_2O\}$.

(i)   If all of the $\{CH_2O\}$ is converted to methane by anaerobic digestion, how many dm³ of methane (at 0°C and 1 atm) could be produced on a daily basis? (Assume the molar volume of any gas at 0°C and 1 atm to be 22.4 dm³)

(ii)   Write an equation for the burning of methane in oxygen.

(iii)   The standard enthalpy of combustion of methane, ΔH^θ_c(298 K) = –890 kJ mol⁻¹. How much energy (at 298K and 1 atm) could be generated by the burning of one day's production of methane?

Revision questions

1. Chemical waste is often destroyed by incineration. Why isn't this possible with radioactive waste?

2. Background radioactivity in Europe showed a considerable rise in the early 1960's and 1986 before falling back to its current level. Suggest a reason for these peaks.

3. Estimate the time it takes for 99% of samples of $^{137}_{55}Cs$ and $^{131}_{53}I$ to decay away.

4. Study the following data for two toxic insecticides:

Insecticide	log K_{oct}	$t_{1/2}$ (soil)
Chlordane	5.5	3 yrs
Parathion	3.8	< 3 weeks

Comment upon the importance of these figures.

Answers

Exercises
Exercise 22A
   (i) Vinyl chloride
   (ii) K_{oct} = 100 000 so that $DDT_{(oct)}$ = 100 000 × 3 × 10^{-6} = 0.3 mg dm^{-3} (ppm)
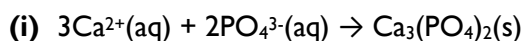**Exercise 22B**
$S(s) + O_2(g) \rightarrow SO_2(g)$
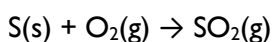
1 tonne coal = 1000 kg which contains $\frac{2.5 \times 1000 \times 1000}{100}$ g S or

$\frac{2.5 \times 1000 \times 1000}{100 \times 32}$ mol S

$= \frac{2.5 \times 1000 \times 1000 \times 24}{100}$ dm^3 SO_2

1.e. 1.9 × 10^4 dm^3 SO_2.
Exercise 22C
   (i) $3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s)$
   (ii) $Ks = [Ca^{2+}]^3[PO_4^3]^2$
      $[Ca^{2+}]^3 = Ks/[PO_4^3]^2$
      = 1 × $10^{-24}/[3 \times 10^{-4}]^2$ mol^3 dm^{-9}
      Solving for $[Ca^{2+}]$ and multiplying by 40 (atomic mass of calcium)
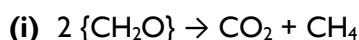   Gives mass of Ca^{2+} needed to be added = 9 × 10^{-5} g dm^{-3}
Exercise 22D
   (i) Cl_2O
      Cl^- –1
      HOCl, OCl^- + 1 (O is –2)
   (ii) All can act as oxidising agents except Cl-, because it cannot be reduced
Exercise 22E
   (i) $2\{CH_2O\} \rightarrow CO_2 + CH_4$
      400 mg in 1 dm^3 is 400 × 100 000 mg in the volume of waste, or
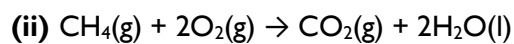 $\frac{400 \times 100\ 000}{1000 \times 30}$ mol of $\{CH_2O\}$
      From the equation, this is equivalent to
      $\frac{400 \times 100\ 000}{1000 \times 30 \times 2}$

Or

$$\frac{400 \times 100\,000 \times 22.4}{1000 \times 30} \text{ dm}^3 \text{ CH}_4$$

= 1.5 × 10^4 dm^3

(ii) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

(iii) 5.9 × 10^5 kJ

Revision questions

1. Radioactive particles would be released into the atmosphere, radioactivity is not destroyed by chemical reactions.

2. Nuclear testing during the 1950s. The accident at Chernobyl.

3. 1/100 of the sample would remain. In one half-life, ½ the sample would remain, in two half-lives ½ × ½ would remain and so on.

So, (½)^x must be 1/100

Therefore, x is just under 7 half-lives or 210 yr (Cs) and 56 days (I)

4. The high log K_{oct} values suggest that bioconcentration in fish is likely. The long residence time of chlordane indicates that it will persist for a much longer time in the environment with (other things being equal) a greater degree of environmental damage.