1

Industrial Impacts on the Environment

1.1 Industrial Use of Natural Resources

1.1.1 Resource Availability and Use

The production of industrial materials and products begins with the extraction of natural resources from the environment. The availability of these resources is vital for the sustained functioning of both industrialised and developing societies. But increased resource use per capita in industrial countries and global population growth has led to increasing pressure on worldwide natural resources including air and water, arable land, and raw materials. Over the 20th century industrial production has thus increased by a factor of 40, energy use by a factor of 16, ocean fishing by a factor of 35, and global population from 1.5 to 6 billion people [McNeill, 2000]. Material flows in industrialised countries amount today to about 60 tonnes of material per capita and year. This corresponds to an ecological footprint of about 2.2 ha/capita, which is far above the productive area available on the planet, about 1.8 ha/cap [Loh, 2004]. It is obvious that resource use has to be reduced in the years to come.

Renewable resources have the capacity to be replenished, while non-renewable resources are only available in finite quantities. It is necessary to realise that, while as individuals we might not be able to think in longer terms than centuries, as a society we must. The half-life of plutonium is 24,000 years; the replacement of the water in the deep oceans takes 1,000 years. Non-renewable resources once removed from the geosphere will never be replenished. Renewable resources cannot be extracted at a rate higher than their rate of renewal, the so-called carrying capacity.

Even if the basic limitations for resource use have to do with their availability, the extraction of resources and their use in industry give rise to a series of environmental impacts. This

In this Chapter

chapter will give a general overview of these impacts and basic explanations on the mechanisms behind, as well as some information on how emissions from industry are controlled by legal and financial means.

1.1.2 Bulk Material, Minerals and Biotic Resources

There are different types of resources. All have their specific properties from the point of view of the environment. *Bulk material* is material extracted from the uppermost layer of the ground. This corresponds to the largest material flows. Bulk material is used e.g. in building and construction industry. The problem connected with its use is disturbed or destroyed areas of extraction, transportation costs etc.

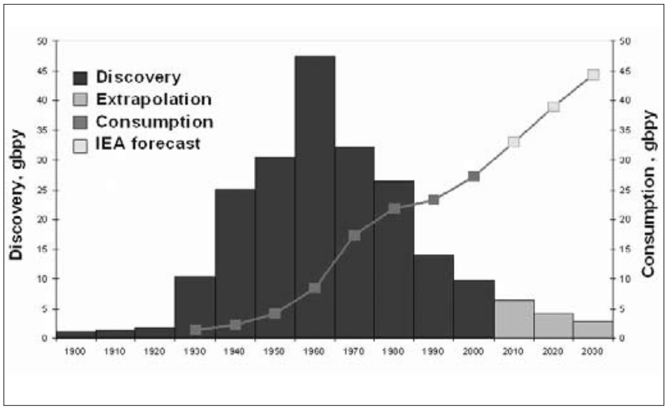

Figure 1.1 Oil rate of production versus rate of extraction. *Global oil discoveries peaked in the 1960s and are rapidly declining as oil becomes harder to find. Today there is a growing gap between new oil discoveries and production [ASPO Ireland, https://aspo-ireland.org/ see also Aleklett, 2006].*

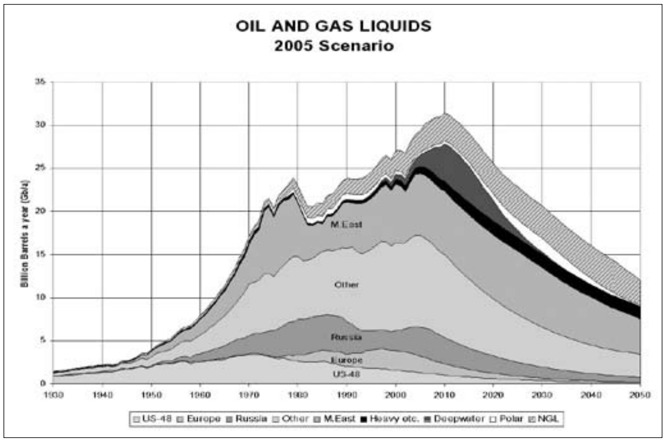

Figure 1.2 The oil depletion curve. *Oil availability over time is shown for a number of regions in the world. It is seen that e.g. the American oil is practically used up and the North Sea resources is declining. Oil is a finite resource. Peak oil refers to the time when global oil production is at its maximum. It is presently expected to occur 2008-2010. The production is then predicted to come to a very low level at about 2040. Natural gas production and consumption is seen to follow a similar pattern, with some ten years delay [ASPO Ireland, https://aspo-ireland.org/newsletter/Newsletter71.pdf]*

Macronutrients, nitrogen, phosphorus and calcium, are used in large quantities in agriculture but also in a long series of chemical compounds, such as phosphorus in detergents, and nitrogen in various plastics, that is, in chemical industry. Nitrogen compounds are mostly produced by reduction of atmospheric nitrogen into ammonia, a process that requires large amounts of energy, for which fossil fuels are used. Phosphorus is mined and as such is a non-renewable resource. The present layers are large, however, and will last more than 200 years, at the present rate of extraction.

Minerals are compounds mined from the bedrock used to produce metals. Metals are very varied. Iron, the most heavily used metal, is in a class by itself. Metals used mainly as alloys with iron, called ferro-alloy metals, include chromium, nickel, titanium, vanadium and magnesium. The traditional non-ferrous metals are aluminium, copper, lead, zinc, tin and mercury. Metals are of course by definition non-renewable. Iron and aluminium, however, which are very abundant in the surface of the planet, will not be depleted by present levels of use. All other metals are being mined at a rate of about one order of magnitude larger than the natural weathering. Some rare earth metals are already almost depleted.

Environmental problems, connected with the mining of ore and production of metals, are numerous. Mining often causes large-scale water pollution; especially strip mining is very destructive to large areas of the landscape, and it is resource consuming. The production of metal from the ore is usually dependent on reduction with oxygen in a smelter or furnace. It produces large amounts of solid waste, slag, and air pollutants, such as SO_x and NO_x and uses huge amounts of energy. Several of the metals are toxic and as such pollute the environment when they are emitted to air and water.

Biotic resources are biomass to provide food and fibre for our livelihood, and a long series of other products, such as pharmaceutical substances, as well as the landscape. These resources are *renewable*, but, of course, limited. The production rate of the biotic resources is referred to as the *carrying capacity* of the area considered. Biotic resources are used in several industrial sectors, such as the food processing industry, timber in e.g. the building industry, and wood in paper and pulp production. Agriculture and forestry is today conducted in an industrial fashion and several environmental concerns are shared with the manufacturing industry. This sector is also connected to a series of environmental impacts.

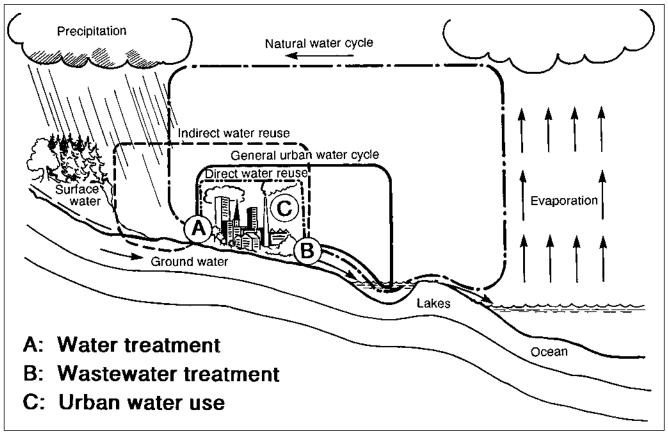

Figure 1.3 Water cycled. *The natural water cycle refers to the way water takes from precipitation, surface water runoff to the oceans and evaporation. A society may short cut this cycle by setting up so-called consumption cycles. These may be using surface water to which wastewater was discharged, as if often the case in urban water cycles, or even direct reuse of wastewater after treatment [Hultman et al., 2003].*

1.1.3 Energy

The availability of adequate energy resources is necessary for most economic activity and makes possible the high standard of living that developed societies enjoy. Although energy resources are widely available, some, such as oil and coal, are non-renewable; others, such as solar, although inexhaustible, are not currently cost effective for most applications. An understanding of global energy-usage patterns, energy conservation, and the environmental impacts associated with the production and use of energy is therefore very important.

Fossil energy resources include lignite, black coal, oil and gas. Coal, oil and gas, which were formed hundreds of millions of years ago, are fossil. The fossil fuels are *non-renewable*. They are presently used at a rate that is millions of times higher than their eventual renewal. Peat is formed on a time scale of thousands of years. Some consider peat fossil since it does not at all reform at the rate we might use it, while others do not include peat in the group of fossil fuels. Fossil fuel extraction and use constitute today the second largest resource flow on the planet.

Fossil fuel is limited, and the point in time at which oil will be depleted is today estimated as 2040. So-called peak oil, the year when half of the existing resources has been used up, is estimated to be about 2008-2010. Increased demand and increased scarcity of oil will lead to dramatic price increases. The spectacular development of Asia, with accelerated demand for energy, is presently pushing this scenario even closer in time.

Many environmental effects are associated with fossil energy consumption. Fossil fuel combustion releases large quantities of carbon dioxide into the atmosphere. During its long residence time in the atmosphere, CO_2 readily absorbs infrared radiation, contributing to global warming. Further, combustion processes release oxides of sulphur and nitrogen into the atmosphere where photochemical and/or chemical reactions can convert them into ground level ozone and acid rain. This will be further discussed below.

Flowing energy resources refer to resources which depend on the sun. They include solar heat, solar electricity and photosynthesis. *Streaming* energy resources includes waves, wind or flowing water. These are used in wave energy (which is technically difficult), wind energy and hydro power. These too have their environmental dilemmas. Hydro power requires large scale water reservoirs and changes natural water streams, while wind power influences the landscape in ways that are not always acceptable, a kind of visual pollution.

1.1.4 Water

The availability of freshwater in sufficient quantity and purity is vitally important in meeting human domestic and industrial needs. Though 70% of the earth's surface is covered with water, the largest share exists in oceans and is too saline to meet the needs of domestic, agricultural, or other users. Of the total 1.36 billion cubic kilometres of water on earth, 97% is ocean water, 2% is locked in glaciers, 0.31% is stored in deep ground water reserves, and 0.32% is readily accessible freshwater (4.2 million cubic kilometres). Freshwater is continually replenished by the action of the hydrologic cycle.

The earth's water supply remains constant, but man is capable of altering the cycle of that fixed supply. Population increases, rising standards of living, and industrial and economic growth have placed greater demands on our natural environment. Our activities can create an imbalance in the hydrologic equation and can affect the quantity and quality of natural water resources available to current and future generations.

In many countries water use by households, industries, and farms has increased. People demand clean water at reasonable costs, yet the amount of fresh water is limited and the easily accessible sources have been developed. In developing countries availability of clean water remains one of the main concerns.

In the Baltic Sea region, in contrast to the global pattern, water use has effectively diminished over several years both in industry and households. Thus in many areas the per capita water use amounts to about 100 – 200 litres/day. Some 10 – 20 years ago this figure was closer to 400 litres/day. More efficient appliances in the households, water saving due to the increased price of water, and better water infrastructure are some of the explanations. Industrial water use has decreased as a result of better efficiency. Irrigation in agriculture does not constitute a large share of water use in the Baltic Sea region.

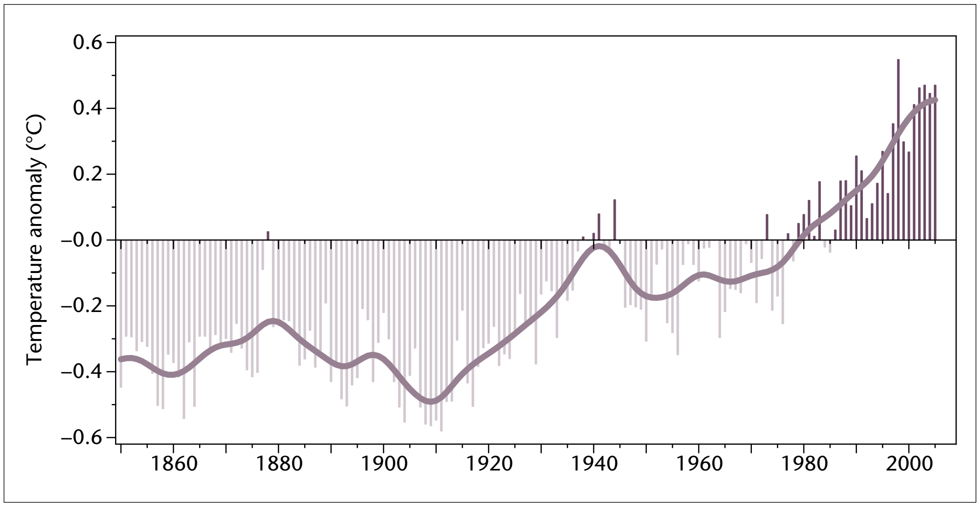

Figure 1.4 Average global temperature 1850-2005. *The temperature increase over the last 100 years is 0.6°C. The increase is however different for different regions. It was most dramatic during the 1990s [Brohan et al., 2006]. http://www.cru.uea.ac.uk/cru/info/warming/*

The withdrawal of water in the region varies from about 4% of the annual run off in Scandinavia to close to 18% in Poland. With the higher figure the water reuse in society becomes a reality, that is, wastewater discharged at some point will be used at another point.

The problem connected with water use in the Baltic Sea region is rather one of discharges of wastewater and runoff to recipients that are not able to handle the stream of pollutants. Fertilisers and other pollutants often overload water supplies with hazardous chemicals. Eutrophied and polluted surface water is a serious problem in most Baltic Sea countries.

1.2 Environmental Impacts – The Atmosphere

1.2.1 Global Warming

The atmosphere allows solar radiation from the sun to pass through without significant absorption of energy. Some of the solar radiation that reaches the surface of the earth, is absorbed, heating the land and water. Infrared radiation is emitted from the earth's surface, but certain gases in the atmosphere, so-called greenhouse gases (GHG), absorb this infrared radiation and re-direct a portion of it back to the surface, thus warming the planet and making life, as we know it, possible. This process is often referred to as the *greenhouse effect*. The surface temperature of the earth will rise until a radiative equilibrium is achieved between the rate of solar radiation absorption and the rate of infrared radiation emission.

The greenhouse effect contributes to a temperature increase on Earth of about 35°C. Water vapour is the most important greenhouse gas. Other greenhouse gases include carbon dioxide and methane.

Fossil fuel combustion, traffic, deforestation, agriculture and large-scale chemical production, have measurably altered the composition of gases in the atmosphere, and in particular increased the concentrations of carbon dioxide from the beginning of industrialisation and dramatically so the last several decades. This has resulted in an *enhancement* of the greenhouse effect. Table 1.1 is a list of the most important greenhouse gases along with their anthropogenic sources, emission rates, concentrations, residence times in the atmosphere, relative radiative forcing efficiencies, and estimated contribution to global warming [IPPC, 2001]. Since the 1990s a dramatic increase in global average temperature is ongoing. The observed temperature increase is in fair agreement with the calculated consequences of actual accumulation of anthropogenic carbon dioxide in global climate models. The possibility that the observed accelerated increase in global temperature is due to other, so called natural, causes is today not likely and a large majority of scientists agree that increased atmospheric concentration of GHG, the enhanced greenhouse effect, is a major cause of climate change.

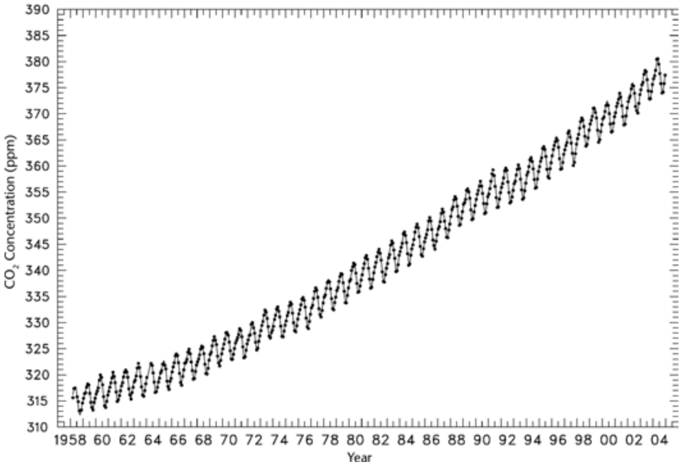

Figure 1.5 CO_2 concentrations in the atmosphere 1956-2004. *Data from Manua Loa mountain observatory on Hawaii where carbon dioxide concentrations in the atmosphere have been carefully monitored since 1956. The variation in the curve corresponds to the yearly breathing of the entire Earth ecosystem [Keeling and Whorf, 2005]. http://cdiac.esd.ornl.gov/trends/co2/graphics/mlo145e_thrudc04.pdf*

Climate change is today seen as the perhaps most serious threat to our environment and societal infrastructure worldwide. Climate change will affect the water cycle and water availability, the conditions for agriculture and forestry, lead to habitat change and biodiversity reduction. It will lead to an increase in sea water level, and therefore extinction of extensive low-lying land areas, especially in the Pacific area. It may at some point stop the so-called thermo-haline water circulation, and thereby the Gulf Stream, and thus make parts of Northern Europe and the Baltic Sea Region, dramatically colder.

1.2.2 Policies to Reduce Emissions of Greenhouse Gases

Fossil fuels are today dominating the world's energy flows and are a base for much industrial production. At the same time as the reduction of fossil fuel use seems remote, the environmental consequences of it are serious. The world leaders have reacted by efforts to reduce the emission of carbon dioxide. This is for all practical purposes identical to reduction of fossil fuel use. A major step was the elaboration of the Kyoto Protocol of the Climate Convention in 1997. This requires an average reduction of CO_2 emissions by 8% by 2008-2012 using 1990 as a base year. The Kyoto protocol finally went into force in February 2005 after the Russian Federation had signed and ratified as the latest of some 120 states. The largest fossil fuel dependent nation, United States, has, however, not yet done so.

Policy tools to achieve reduction of carbon dioxide emissions include taxes on emitted CO_2, already quite high in some countries, as well as subsidies for changes to other sources of energy. Substantial reductions of fossil fuel use is seen e.g. in Denmark (coal substituted mainly by wind power) Sweden (oil substituted mainly by nuclear power and biomass) and Germany (coal substituted in several ways, wind power and improved efficiency included). In addition for many years a large scale exchange of coal to gas has been on-going, which will reduce carbon dioxide emissions per energy unit. Finally, increased efficiency of energy use is a main strategy where much remains to be done, a strategy which is becoming increasingly interesting to industry as energy prices increase.

Table 1.1 Greenhouse gases and Global Warming contributions. *Data are based on IPCC, 2001, but updated for atmospheric concentrations and contribution to enhanced global warming for* CO_2 *and all other gases (2004) through the Carbon Dioxide Information Analysis Center (CDIAC) (see http://cdiac.ornl.gov/pns/current_ghg.html). The concentration given for* CO_2 *in January 2007 was not used in the calculations of the contribution to enhanced global warming.*

Gas	Source	Estimated Anthropogenic Emission Rate	Preindustrial Global Conc.	Approx. Current Conc.	Estimated Residence Time in the Atmosphere	Radiative Forcing Efficiency (CO_2=1)	Estimated Contribution to Enhanced Global Warming
Carbon Dioxide (CO_2)	Fossil fuel combustion deforestation	6 000 Mt/yr	280 ppm	377 ppm, 383 ppm (2007)	50-200 yrs	1	55%
Methane (CH_4)	Anaerobic decay, cattle, natural gas, coal mining, biomass burning	300-400 Mt/yr	0.7 ppm	1.85 ppm	10 yrs	58	17%
Nitrous oxide (N_2O)	Deforestation, agricultural practices, land clearing, low-temperature fuel combustion	4-6 Mt/yr	0.27 ppm	0.31 ppm	140-190 yrs	206	5%
CFC's	Refrigerants, air conditioners, foam-blowing agents, aerosol propellants, solvents	1 Mt/yr	0	0.0004-0.001 ppm	6-110 yrs	4 860	11%
Tropospheric ozone (O_3)	Photochemical reactions involving VOCs and NO_X	No direct emission	NA	0.022 ppm	Hours-days	2 000	12%

The Kyoto protocol includes trading of emission rights. This is now becoming an important economic incentive to reduce fossil fuel use in industry, as it was introduced in the European Union in 2004. Units such as power plants in less developed countries, for which it is less costly to reduce emissions, will sell emission rights to units where fossil fuel substitution or efficiency increase is already far advanced. This may accelerate the march away from fossil fuel dependency.

Some technical solutions to the problems, such as sequestration of carbon dioxide in the underground, e.g. in emptied oil wells, are at hand but these probably will play only a minor role in the near future. Thus we should expect that the efforts to implement strategies of substitution of fossil fuel with flowing energy resources will soon be intensive.

1.2.3 Stratospheric Ozone Depletion

The solar radiation reaching the earth's surface is sharply cut out at wavelengths below about 290 nm, although the radiation entering the top of the atmosphere includes considerable amounts of radiation at shorter wavelengths. The reason is that small quantities of ozone (O_3), chiefly in the layers between 15 and 40 km above ground level, effectively filter out the missing radiation and use it to produce the warm conditions of the upper stratosphere (Figure 1.6).

The energy-rich ultraviolet radiation with wavelengths shorter than 240 nm is absorbed in the stratosphere by oxygen molecules splitting them into two free oxygen radicals. The free oxygen radicals combine with other oxygen molecules (O_2) forming ozone (O_3). The creation of O_3 is continuous as long as the sun shines, yet the amount of O_3 remains small and is largely confined to the stratosphere. This is because ozone is attacked by other gases diffusing upward from the earth's surface. The most important of these in nature is nitrous oxide (N_2O), emanating from the soil and from certain industrial processes. In the stratosphere it is quickly oxidised to NO, and this attacks O_3:

$$N_2O + O_3 \longrightarrow 2NO + O_2$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

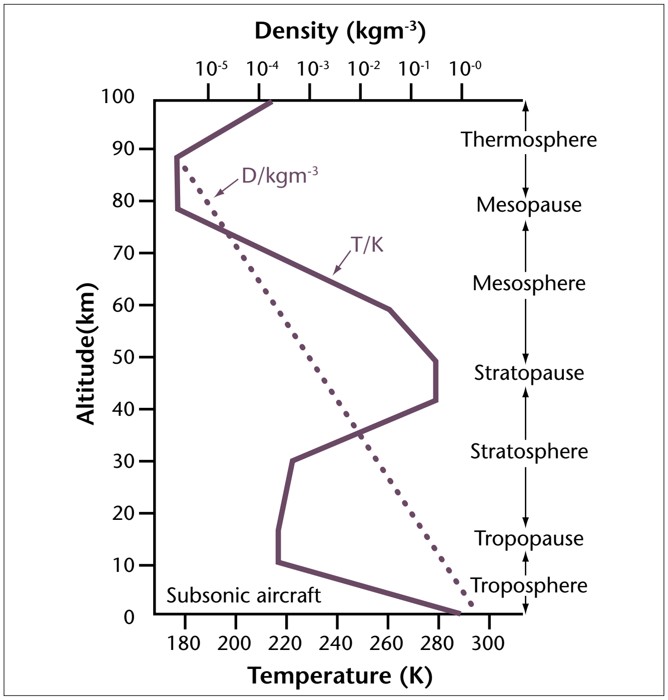

Figure 1.6 *Structure as density (dotted line) and temperature profile (solid line) of the atmosphere [IChemE, 1993].*

This and other processes create a natural equilibrium: ultraviolet radiation creates ozone, and other natural processes lead to its decay. The ozone is formed in the stratosphere. Of the total amount of ozone in the atmosphere, 90% is found in the stratosphere, where it constitutes the so-called *ozone layer*.

Ultraviolet radiation has shorter wavelengths than visible light and is commonly divided in three types:

UV-A 320-400 nm, passes the atmosphere and will in the main reach the Earth's surface.

UV-B 280-320 nm, is over 99% absorbed by the ozone layer in the stratosphere.

UV-C <280 nm, is completely absorbed by the atmosphere.

On penetrating the atmosphere and being absorbed by biological tissues, UV radiation damages protein and DNA molecules on the surfaces of all living things. If the full amount of ultraviolet radiation falling on the stratosphere reached Earth's surface, it is doubtful that any life could survive. We are spared more damaging effects from ultraviolet rays because most UV-B radiation (over 99%) is absorbed by ozone in the stratosphere. For that reason, stratospheric ozone is commonly referred to as the *ozone shield*.

In 1985 British scientists discovered that the ozone concentration over the Antarctic had decreased dramatically, about 50%, during the Antarctic spring in October-November. They later proved that this had been ongoing since the late 1970s. The uniquely large loss of stratospheric ozone over the South Pole was called the *Antarctic Ozone Hole*. This phenomenon has been growing since then, with about 5% yearly loss of ozone. Since the 1990s a reduction of ozone concentrations has also been recorded over the Arctic. Here it appears in the late Nordic winter and early spring. It so far amounts to about a 25% reduction.

The environmental consequences of the increased UV radiation caused by this loss of stratospheric ozone include reduced photosynthesis and increased cancer incidence.

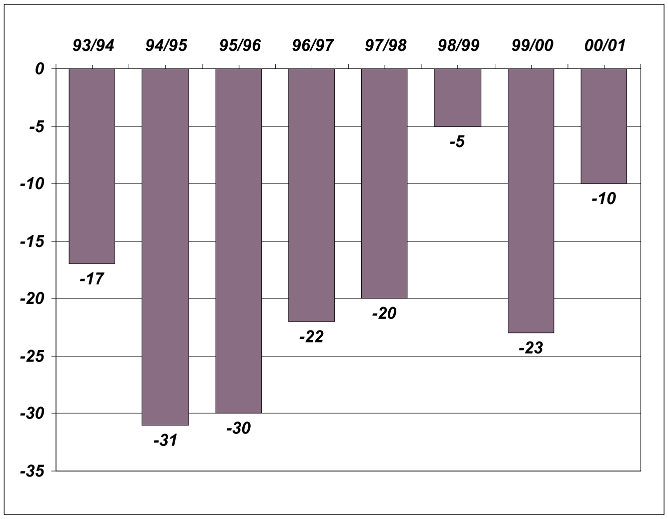

Figure 1.7 Ozone losses over the Arctic. *Figures show losses in % over winter months. The variation depends a lot on air currents. When a stable low pressure area over the Arctic isolates the cold air for longer periods the ozone content may sink by more than 30% [Murtagh, 2003].*

1.2.4 Ozone-destroying Substances

In 1974 two American researchers, Rowland and Molina, showed that atomic chlorine catalysed the breakdown of ozone. Some chlorine is present naturally in the atmosphere, mostly originating from salt in the sea, but they suspected that some halogenated substances emitted from society might be a threat to stratospheric ozone. Later *freons*, or CFCs, were identified as the major culprit behind the stratospheric ozone destruction.

Chlorofluorocarbons (CFCs) are a kind of halogenated hydrocarbons. They are non-reactive, non-flammable, non-toxic organic molecules in which both chlorine and fluorine atoms replace all or several of the hydrogen atoms. Their thermodynamic properties are the primary reason for their use as 1) heat-transfer fluids in refrigerators, air conditioners and heat pumps; 2) foaming agents in production of plastic foams; 3) solvents for use in the electronic industry for cleaning parts that must be meticulously purified; and 4) pressurising agents for aerosol cans.

All of these uses led to the release of CFCs into the atmosphere, where they mixed with the normal atmospheric gases and eventually, because of their stability and extremely long residence time in the atmosphere, reached the stratosphere. Here they are subjected to the intensive UV radiation, inducing photochemical reactions that break the molecules up.

There are a large number of different reactions involved in this reaction chain. The most important ones are:

$$CF_2Cl_2 + \text{UV–C} \longrightarrow CF_2Cl + Cl^{\bullet} \qquad (1)$$

The second chlorine atom is also freed in a similar reaction yielding one more chlorine radical. The chlorine radicals then act as catalysts as described by:

$$Cl^{\bullet} + O_3 \longrightarrow ClO + O_2 \qquad (2)$$

$$ClO + ClO \longrightarrow 2Cl^{\bullet} + O_2 \qquad (3)$$

Table 1.2 *Serious air pollution incidents [IChemE, 1993].*

Year	Incident	Pollutant	Number of excess fatalities	Number of cases of illness
852	London, England	Complaints of foul air due to burning of sea-coal		
1873	London	SO_2, particulates	"excess deaths"	
1880	London	SO_2, particulates	27% increase	
1892	London	SO_2, particulates	1484	
1930	Meuse Valley, Belgium	Fluorides, SO_2, particulates	63	6000
1948	Dondora, Penn., USA	SO_2, particulates	17	6000
1948	London	SO_2, particulates	700 – 800	
1953	London	SO_2, particulates	4000	
1956	London	SO_2, particulates	1000	
1960	Osaka, Japan	SO_2, particulates		
1962	London	SO_2, particulates	700	
1976	Seveso, Italy	Complex mixture + dioxins		28
1984	Bhopal, India	Methyl isocyanate gas	2000	
1986	Chernobyl, USSR	Radioactive gases		

Reactions 2 and 3 are called the *chlorine cycle*, because chlorine is continuously regenerated as it reacts with ozone. Thus each free chlorine radical released in the stratosphere will be able to catalyse the break-down of tens of thousands of ozone molecules before other reactions removes the chlorine from the chlorine cycle.

1.2.5 Reduction of Ozone-depleting Substances and the Montreal Protocol

The global production of CFCs reached its peak in 1986 with about 1,300,000 tonnes yearly. In the EU countries alone production was 700,000 tonnes. Efforts to reduce production started in the 1970s with voluntary actions. In 1979 CFCs were outlawed as propellants in spray cans in many western countries. Production increased, however, as they found new uses. After the 1985 discovery of the ozone hole the pressure to reduce freon production and use increased. Finally a 1987 agreement in Montreal to totally eliminate the use of ozone-depleting substances was signed by many nations. The Montreal protocol has led to significant reductions in CFC production and use. In 1995 the production was 10-20% of the peak value, and in 2003 it was almost eliminated.

The ozone concentration in the stratosphere is predicted to have reached its lowest values at about 2003-4 and then increase. The inter-annual variations are, however, large and final confirmation will have to await a longer time series.

1.3 Industrial Air Pollution

1.3.1 Air Pollution

Air pollution is certainly not a new phenomenon. Indeed, early references to it date to the Middle Ages, when smoke from burning coal was already considered such a serious problem that in 1307, King Edward I banned its use in lime kilns in London. In more recent times, though still decades ago, several serious episodes focused attention on the need to control the quality of the air we breathe. The worst of these occurred in London, in 1952. A week of intense fog and smoke (smog) resulted in over 4,000 excess deaths that were directly attributed to the pollution. Table 1.2 shows a number of other serious air pollution incidents.

All these episodes have had significant health effects. In addition, there have been incidents of severe crop, forest, and materials damage, and the costs have been substantial.

The early air pollution episodes were clearly detectable by the senses without special aids or instrumentation. Particles in urban atmospheres reduced visibility and were aesthetically dirty. Sulphur dioxide smelled, caused silvered surfaces to turn black, caused plant damage, and in extreme situations, made breathing difficult. Ozone caused rubber and synthetic materials to deteriorate very quickly, and photochemical smog containing high concentrations of ozone caused eye irritation. Nitrogen oxides, NO and NO_2, and hydrocarbons, of which there are several thousand different species, were found to be precursors of photochemically formed ozone and Peroxy Acetyl Nitrate (PAN) in a shallow layer of the atmosphere at the earth's surface. It was also well recognised that carbon monoxide represented a severe health hazard at extremely low concentrations.

Figure 1.8. Forest dying after acid rain in Izierskie, the Sudety Mountains, in 1995. *The area, in the so-called black triangle bordering Poland, Czech Republic, and Eastern Germany, was especially badly hit by acid rain in the period up to the mid 1990s.* *(Photo: iStockphoto)*

1.3.2 Acidification

One of the most serious air pollution problems has been that of acid rain. The water of unpolluted rain, snow, hail, mist and fog is not pure H_2O. It contains small but significant concentrations of dust, dissolved solids and gases. Of particular importance is the presence of dissolved carbon dioxide as this maintains the pH of clean rainwater at about 5.6. This is due to its equilibrium with the 380 ppm of carbon dioxide in the atmosphere. The epithet acid rain is therefore reserved for precipitation (rain, snow, fog, etc.) that has a pH appreciably lower than expected in the absence of pollution. Usually all precipitation with a pH of 5 or lower is referred to as acid rain.

Acid rain is produced when sulphur dioxide (SO_2) and/or the oxides of nitrogen (NO_X) and their oxidation products are present in moisture in the atmosphere.

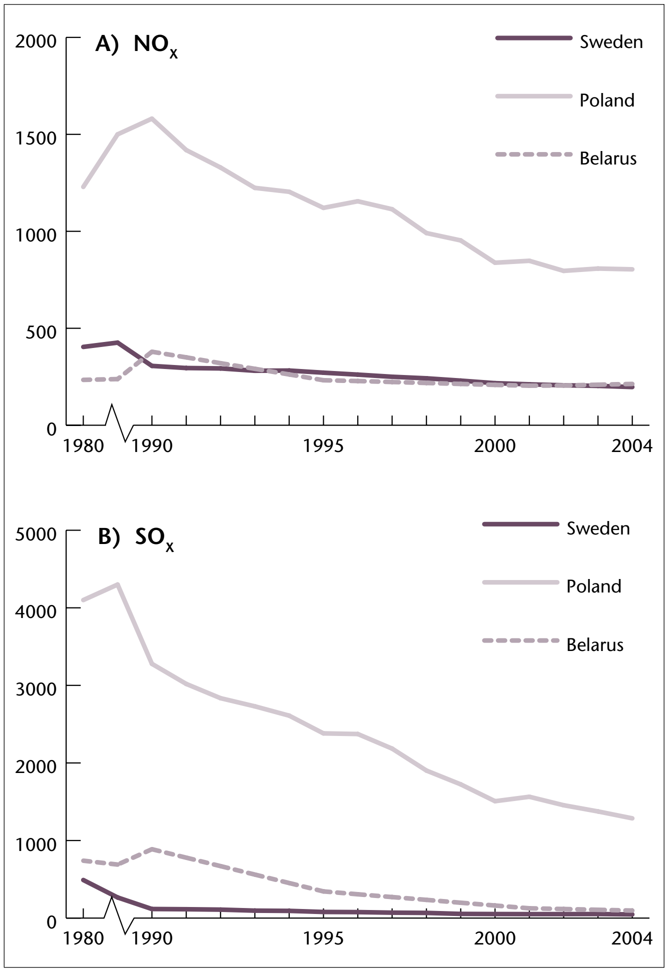

Figure 1.9 Changes in anthropogenic emissions of nitrogen oxides (A) and sulphur oxides (B) from 1980. *The* NO_2 *and* SO_2 *emissions (1,000 tonnes per year) in Belarus, Poland and Sweden are given as examples of the trends in Europe [EMEP, Expert Emissions. http://webdab.emep.int/]*

Both acid rain and acid mine drainage contribute significantly to the acidification of natural waters. The environmental consequences are serious and far reaching. Tens of thousands of lakes in Norway and Sweden, and to some extent Finland, where the buffering capacity of the soil is limited, have pH values low enough, below 4.5, to kill all higher life, caused by acid rain. This is due both to the pH itself and to the leaching of aluminium from sediment at lower pH. The aluminium thus brought into solution is toxic, especially to fish. Also other metals, e.g. mercury, become more mobile as a result of the lower pH. Acids and/or alkalis discharged by chemical and other industrial plants make a stream unsuitable not only for recreational use but also for propagation of fish and other aquatic life.

Other effects of acidifying substances in air include health effects, especially on children. It also leads to the destruction of materials, e.g. cultural monuments in limestone or sandstone, and it has corrosive effects on e.g. metals. It further has an effect on reducing harvest in agriculture and in forestry. Forests killed by acid rain in Central Europe were one of the first serious concerns caused by acid rain. The value of damage caused by acid rain in Europe was estimated in 1997 to about 91 billion euros yearly. It is much more than the costs of measures needed to stop this pollution.

1.3.3 Sulphur Oxides

The major cause of acid rain is the emission of *sulphur dioxide* (SO_2). SO_2 has an unpleasant odour that is detectable at concentrations greater than about 1 ppm. Its concentrations in the atmosphere range from less than 1 ppb in locations very remote from industrial activity to 2 ppm in highly polluted areas. However, concentrations of 0.1 to 0.5 ppm are more typical of urban locations in industrialised countries, while levels of around 30 ppb are normal for rural areas in the northern hemisphere. Sulphur dioxide is oxidised in the atmosphere to the highly damaging secondary pollutants sulphuric acid (H_2SO_4) and/or its acid anhydride, sulphur trioxide (SO_3). SO_X refers to both di- and trioxides of sulphur in any proportion.

Sulphur dioxide is produced mainly as the result of the burning of sulphur-containing fossil fuels, particularly coal and oil, during electricity generation. Other industrial processes, notably metal sulphide ore roasting, for example of nickel (NiS), lead (PbS) and copper (Cu_2S), in order to recover the metal, make a sizeable contribution. The principal natural sources of sulphur dioxide are volcanic and biological activity. The latter is mainly an indirect source, providing reduced sulphur compounds (particularly H_2S and $(CH_3)_2S$) which are rapidly oxidised in the air to sulphur dioxide.

There are two principal sink mechanisms for atmospheric sulphur dioxide. These are direct deposition from the gas phase onto wet or dry surfaces (a process known as *dry deposition*) and oxidation to sulphur trioxide and/or sulphuric acid, which subsequently are efficiently removed from the air during precipitation (*wet deposition*), contributing to the phenomenon of acid rain.

1.3.4 Nitrogen Oxides

Oxides of nitrogen usually originate from power stations and from vehicle emissions. As a rule, they contribute less than SO_x to the problem of acid rain. Three of the oxides of nitrogen are significant primary pollutants. These are nitrous oxide (dinitrogen oxide, N_2O), nitric oxide (NO) and nitrogen dioxide (NO_2).

Nitrous oxide (N_2O) is an un-reactive gas found at a level of about 0.3 ppm. Nitrous oxide is a greenhouse gas and therefore contributes to global warming. In addition, its unreactiveness and therefore very long residence time in the atmosphere (20-100 years) allows it to enter the stratosphere, where it by photochemical reactions produces nitric oxide (NO) and thus contributes to the depletion of stratospheric ozone. The main source of atmospheric nitrous oxide is probably microbial reduction (denitrification) of nitrate (NO_3-) that occurs in soils and waters with low oxygen contents. This is a natural process as well as a process used in the denitrification of wastewaters. The production of N_2O is a side reaction to the main reaction that converts nitrate to molecular nitrogen gas (N_2).

Nitric oxide (NO) and *nitrogen dioxide* (NO_2) are collectively referred to as NO_x. They are both highly reactive gases and therefore have extremely short residence times in the atmosphere. Levels of nitrogen dioxide vary from less than 1 ppb in remote areas to 0.5 ppm during severe periods of pollution in urban areas. While NO_x compounds are pollutants in their own right, contributing both to acidification and eutrophication, the main problems they cause are associated with the secondary pollutants that they produce (See 1.3.6 *Tropospheric Ozone*).

Almost all NO_x emissions are in the form of NO, which is a colourless gas that has no known adverse health effects at concentrations found in the atmosphere. However, NO is easily oxidised to NO_2, by oxygen, ozone or radicals. NO_2 can irritate the lungs, cause bronchitis and pneumonia, and lower resistance to respiratory infections. Nitrogen dioxide reacts with the hydroxyl radical ($OH^\bullet$) in the atmosphere to form nitric acid (HNO_3), which corrodes metal surfaces and contributes to the acid rain problem. It also can cause damage to terrestrial plants and is a significant contributor to eutrophication, especially in nitrogen-limited estuaries.

The main natural sources of NO_x are biomass burning (forest fires), electrical storms, in situ ammonia oxidation, and, in the case of nitric oxide, anaerobic soil processes. Estimates of the total flux generated vary, but are typically in the range 30 to 40 million tons NO_x/year globally. This is roughly comparable with the anthropogenic flux, which is estimated to be 60 to 70 million tons NO_x/year. The clearly dominating source is transportation, including work machines and shipping, burning of fossil fuels and biomass and industrial processes. Another substantial source for nitrogen emissions comes from agriculture in the form of diffuse ammonia emissions from animal farming and fluid fertilising.

There are two principal routes that NO_x is formed in combustion processes. *Thermal* NO_x is created when nitrogen and oxygen in the combustion air are heated to a high enough temperature (above 1000ºC) to oxidise the nitrogen. *Fuel* NO_x results from the oxidation of nitrogen compounds that are chemically bound in the fuel molecules themselves.

1.3.5 Convention on Reduction of Air Born Long-Range Transboundary Pollution, LRTP

Claims that acidification of lakes and rivers was caused by industrial emissions of SO_x and NO_x have been advanced by Sweden and Norway since the early 1970s. In 1979 thirty nations signed the Convention on reduction of air born Long-Range Transboundary Pollution (LRTP), a convention within the UN-ECE, the United Nations Economic Commission for Europe. The convention came into force in 1983. In 1985 the sulphur protocol with solid commitments of reduction of SO_x emissions was signed. As a result emissions were generally cut by 30% up to 1993, and in some cases by up to 80%. It has since continued to decrease. A protocol on nitrogen oxides was signed in 1988. However this has been less successful, as some of the signatory nations were not able to reduce emissions at all.

Reduction of sulphur emissions is technically fairly easy and cost-efficient. It has thus been rather successful. European emissions of sulphur dioxide were highest around 1980 when they amounted to about 56 million tonnes. By 2006 they had decreased to about 12 million tonnes.

European emissions of NO_x peaked around 1990, when they amounted to an estimated 28 million tonnes. By 2004 this figure had decreased to about 16 million tonnes.

1.3.6 Tropospheric Ozone

When oxides of nitrogen, volatile organic compounds (VOCs), and sunlight come together, they can initiate a complex set of reactions that produce a number of secondary pollutants known as *photochemical oxidants*.

Volatile Organic Compounds include un-burnt hydrocarbons emitted from exhaust pipes and smoke stacks when fossil fuels are not completely combusted along with gaseous hydrocarbons that enter the atmosphere when solvents, fuels, and other organic compounds evaporate. The transportation sector is responsible for about one-third of anthropogenic VOC emissions.

Photochemical oxidants are the most significant agents in formation of *photochemical smog*. Ozone (O_3) is the most abundant of the photochemical oxidants. Other components of photochemical smog are formaldehyde (HCHO), Peroxy Benzoyl Nitrate (PBzN), Peroxy Acetyl Nitrate (PAN), and acrolein (CH_2CHCOH).

Tropospheric ozone is formed when sunlight makes nitrogen dioxide split into NO and a free oxygen radical:

$$NO_2 + hv \longrightarrow NO + O^{\bullet}$$

$$NO + O_2 \longrightarrow NO_2 + O^{\bullet}$$

$$O^{\bullet} + O_2 + M \longrightarrow O_3 + M$$

M represents a molecule whose presence is necessary to absorb excess energy from the reaction. Without M, the ozone would have too much energy to be stable, and it would dissociate back to $O^{\bullet}$ and O_2. Atomic oxygen radicals in turn will react with water to form $OH^{\bullet}$, the *hydroxyl radical*, a key substance in atmospheric organic chemistry. The hydroxyl radical will initiate the reaction sequence involving VOCs such as ethane (C_2H_6), propane (C_3H_8) etc. to form aldehydes. The removal of NO by these reactions slows the rate at which O_3 is removed, while the addition of NO_2 increases the rate at which it is produced, which allows higher levels of O_3 to accumulate in the air.

The tropospheric ozone contributes to the global warming but has above all direct effects on vegetation and human health. Ozone will penetrate into the leaf tissues of plants and trees where it damages cell membranes and enzymes. It also disturbs the cell's ability to photosynthesise. Ozone leads to a less efficient water utilisation in the plants and makes them more sensitive to drought. Ozone has been shown to seriously reduce yields of major agricultural crops, such as corn, wheat, soy beans, and peanuts. Ozone alone is thought to be responsible for about 90% of all of the damage that air pollutants cause agriculture.

Ozone and other components of photochemical smog are known to cause many annoying respiratory effects, such as coughing, shortness of breath, airway constriction, headache, chest tightness, and eye, nose, and throat irritation. These symptoms can be especially severe for asthmatics and others with impaired respiration, but also healthy individuals who engage in strenuous activities for relatively modest periods of time, e.g. jogging, experience these symptoms at levels near the ambient air quality standard.

Figure 1.10 *Car exhaust is one of the worst environmental health problems. (Photo: Inga-May Lehman Nådin)*

1.3.7 Particulate Pollutants

Atmospheric particulate matter consists of any dispersed matter, solid or liquid, in which the individual aggregates range from molecular clusters of 0.005 µm diameter to coarse particles up to about 100 µm. As a category of pollutants, particulate matter is extremely diverse and complex. Size and chemical composition, as well as concentration, are important characteristics.

A number of terms are used to categorise particulates, depending on their size and phase (liquid or solid). The most general term is *aerosol*, which applies to any tiny particles, liquid or solid, dispersed in the atmosphere. Solid particles are called *dusts* (1 to 1000 µm) if they are caused by grinding or crushing operations and *fumes* (0.03 to 0.3 µm) if they are formed when vapours condense. Liquid particles may be called *mist* (0.07 to 10 µm). Mists are concentrated to *fog*. *Sprays* (10 to 1000 µm) are particles formed from the atomisation of liquids. *Smoke* (0.5 to 1 µm), and *soot* are terms used to describe particles composed primarily of carbon that result from incomplete combustion of carbon containing compounds. *Fly ash* (1 to 1000 µm) is non-combustible particles connected with combustion gases in the burning of coal.

Smog is a term that was derived from smoke and fog. There are two types of smog. *Gray or industrial smog* is an irritating, greyish mixture of soot, sulphurous compounds, and water vapour (a combination of smoke and fog). This kind of smog is mostly found in industrial areas and where coal is the primary energy source. *Brown or photochemical smog* is produced when several pollutants from automobile exhausts, nitrogen oxides and volatile organic hydrocarbons are undergoing photochemical reactions induced by sunlight. Typically this smog appears during the morning rush traffic and only begins to disappear by the end of the evening commuter traffic.

The particles of largest interest have aerodynamic diameters in the range 0.1 μm to 10 μm (roughly the size of bacteria). Large particles that enter the respiratory system can be trapped by the hairs and lining of the nose. Once captured, they can also be driven out by a cough or sneeze. Smaller particles, however, are often able to traverse the many turns and bends in the upper respiratory system, they tend to follow the air stream into the lungs, where they are adsorbed or go back out again.

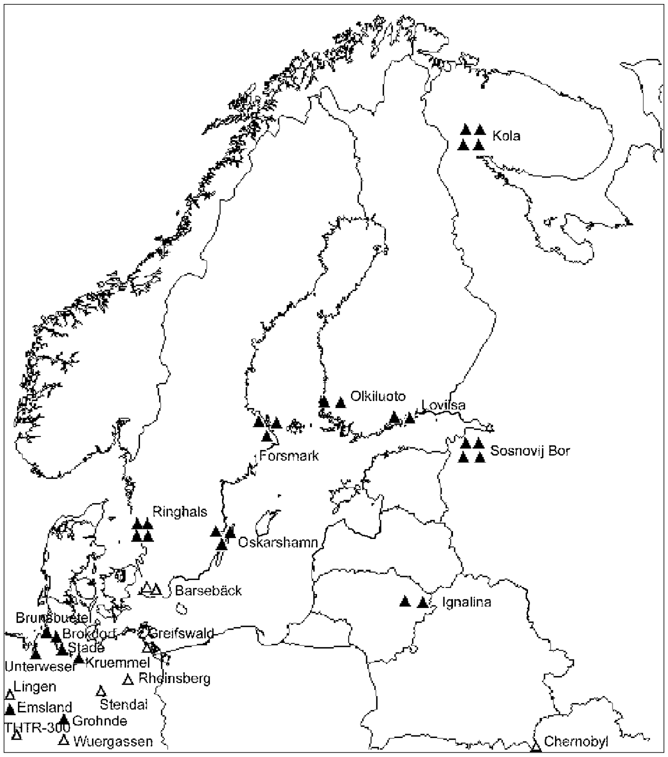

Figure 1.11 Nuclear power plants in the Baltic Sea region. *Each triangle is a reactor, and each group of reactors is a power plant. White triangles denote reactors that have been shutdown or cancelled. The two reactors at Greifswald were closed 1990, the Chernobyl ones 2001 and the two of Barsebäck at 2005. Ignalina will close at 2009 as part of the EU accession agreement. Several new reactors are planned notably in Finland, Russia and Ukraine. [Based on information from INSC at Argonne National Laboratory, http://www.insc.anl.gov/pwrmaps/]*

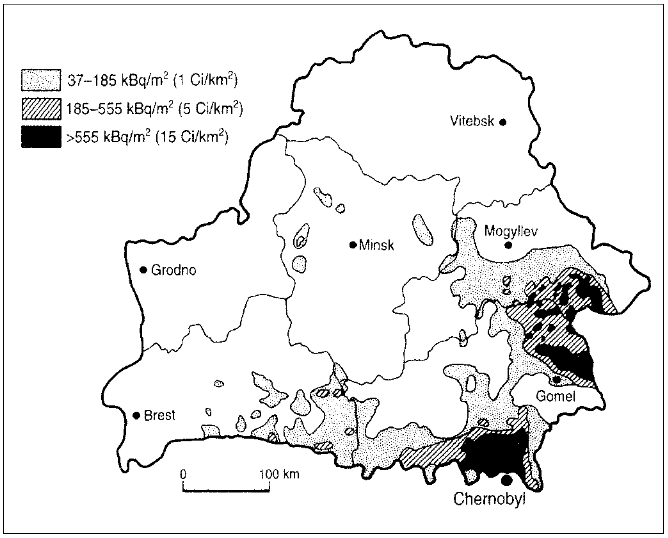

Figure 1.12 *Radiation fallout in Belarus after the Chernobyl accident [Redrawn from Walker et. al., 2001].*

The chemical and physical nature of particles is extremely important when assessing the effects of the emissions. Metallic oxides from spray painting and the coating industries; catalyst dusts from refineries; asbestos fibres from the insulation, cloth, and pipe industries; and special chemical releases such as barium, beryllium, boron, and arsenic from the metals processing or manufacturing industries and cadmium, lead, and mercury from batteries are designated as hazardous particles because they are highly toxic or carcinogenic and are in the respirable size range (< 2.5 μm). The largest industrial particle emissions are ash from combustion of coal, oil and solid wastes; carbon particles from the combustion and processing of fossil fuels; and particles from quarrying and mining and their associated industries.

Iron and steel plants emit large quantities of small particles to the atmosphere. Most of the particles are oxides of iron, carbonate fluxing materials, or oxides of metals used to produce special alloys. Most of these are smaller than 2.5 μm. The shift to basic oxygen furnaces has resulted in a shift of particle emissions to even smaller sizes and in greater quantities.

Coarse particle inhalation frequently causes or exacerbates upper respiratory diseases, including asthma. Fine particle inhalation can decrease lung functions and cause chronic bronchitis. Inhalation of specific toxic substances such as asbestos, coal mine dust, or textile fibres are now known to cause specific associated cancers (asbestosis, black lung cancer, and brown lung cancer, respectively). Asbestos is especially hazardous in this respect since asbestos fibres effectively adsorb other carcinogenic substances, such as benzo(a)pyrene, and are suspected to subsequently act as transport media for these substances into the cells of the lung tissue.

1.3.8 Radioactivity

Severe environmental contamination by radioactive pollution emitted into the air, has occurred on a number of occasions. These include the aftermath of the dropping of nuclear bombs on Hiroshima and Nagasaki in Japan at the end of the Second World War, but also fall-out from the atmospheric testing of nuclear weapons before 1962. Fall-out from tests in the North by the Soviet army is still serious in the Northern Baltic Sea region.

Perhaps the most pressing public concern with regard to nuclear energy production is the possibility of a serious accident and the following radioactive pollution. Such accidents have occurred, notably at Three Mile Island in Pennsylvania in 1979, and at Chernobyl in Ukraine in 1986, one of the most severe environmental disasters in the Baltic Sea region. The emissions from a melt-down in a nuclear power plant has a mixture of radioactive nuclides, most of them very short lived but some staying radioactive for many years. In practice the first days and weeks of a nuclear fall-out is dominated by iodine nuclides, and later by radioactive caesium 137. The latter isotope with a half-life of 27 years is what today and for many years to come will be the main concern after the Chernobyl disaster.

Figure 1.13 Excessive amounts of nutrients, entrophication, leeds to growth of algae. *In small bays, algal growth may cause both a terrible sight and smell. (Photo: www.nps.gov)*

Table 1.3 *Total dissolved solids levels for different types of waters [Tchobanoelous and Schroeder, 1985].*

Water type	TDS value
Freshwater	< 1 500 mg/L
Brackish water	1 500 – 5 000 mg/L
Saline water	> 5 000 mg/L
Sea water	30 000 – 34 000 mg/L

The so-called nuclear fuel cycle consists of mining of uranium, enrichment processing, its fission in the nuclear reactor, and finally disposal and storage of nuclear waste. All of these stages give rise to risk of radioactive pollution and exposure to humans. Mining and mineral processing of uranium ore may lead to high exposure for miners. Also, mine tailings may contain residual radioactivity, and in some cases these tailings have not been disposed of in the proper manner.

Radioactive, also called nuclear, waste is generated by a number of different industries and services, from both the civilian and military sectors. Sources include nuclear power generation and nuclear weapons production. To a lesser extent medical and scientific research applications involve radio nuclides. The main public attention is focused on the major producer of non-military radioactive waste, the nuclear power industry, and, in particular, the nature and safe disposal of the wastes generated by the final stages of the nuclear fuel cycle.

1.4 Industrial Water Pollution

1.4.1 Organic Pollution

Water pollution occurs when the discharge of wastes impairs water quality or disturbs the natural ecological balance. By far the greatest volume of pollution is caused by the discharges of organic material into freshwater systems. Municipal sewage, industrial wastewater and agricultural wastewaters are waste streams rich in organic matter.

The organic waste provides a rich substrate for bacteria. As the organic pollutants are decomposed by biological activity in the water, oxygen dissolved in the water is consumed, thereby lowering the oxygen levels in the water. The decomposition processes also liberate nutrient components such as nitrates and phosphates. The concentration of organic pollutants in water is measured in terms of its *biological oxygen demand* (BOD), which is the amount of oxygen required by microorganisms to degrade the wastes biologically. Another way of determining the level of organic contamination is the *chemical oxygen demand*, or COD, the amount of oxygen needed to oxidise the wastes chemically. While BOD gives a measure of the concentration of easily biological degradable components, COD measures the total content of biologically degradable organic matter as well as the content of oxidisable inorganic components.

Case Study 1.1
Mercury Pollution: The Minamata Disaster

In the early 1950s, the Minamata disaster in Japan sparked off widespread public concern about the pollution of the environment by mercury and other toxic metals. A local factory used mercuric oxide as a catalyst in the production of acetaldehyde and vinyl chloride. Effluent contaminated with mercury was discharged from the factory into Minamata Bay, where it by bacterial action was converted to the highly toxic methyl form:

$$Hg^{2+} \longrightarrow CH_3Hg^+ \longrightarrow (CH_3)_2Hg$$

The first indication of mercury poisoning was the development of nervous disease in many local cats and dogs, with a number of fatalities. Later, local residents started to show a variety of symptoms including numbness of limbs, deafness and mental derangement. By 1958 there were over 50 reported cases of “Minamata disease”, 21 of which proved fatal. The consumption of seafood contaminated with mercury was pinpointed as the cause and the sale of fish from Minamata Bay was banned. It was found that nearly all of the victims ate fish from the bay three times a day.

However the connection between the high levels of mercury in local fish and shellfish and the effluent from the local factory was not apparently made. The factory continued to discharge mercury for another decade until economic pressure forced its closure. By 1975 the disease had claimed over 100 lives, out of a 800 confirmed cases of Minamate disease.

Source: Kutsuna, 1968 (see also Hylander & Meili, 2005 and Hylander & Goodsite, 2006).

Figure 1.14 A hospital in Minamata Japan in 2001. *The 40-year old man in the wheelchair was born paralysed. He is one of the victims from the 1962 mercury poisoning disasters that killed over 100 in the village and harmed many more. The Minamata disaster was a turning point in the history of concern for the environment. (Photo: Lars Hylander)*

Wastewater with a high content of organics is generated in e.g. the food processing industry, and the pulp and paper industry.

1.4.2 Nutrients

Eutrophication is the enrichment of waters by inorganic plant nutrients. Nutrients are chemicals, such as nitrogen, phosphorus, carbon, sulphur, calcium, potassium, iron, manganese, boron, and cobalt that are essential to the growth of living organisms.

In terms of water quality, nutrients can be considered as pollutants when their concentrations are sufficient to allow excessive growth of aquatic plants, particularly algae. These form algal blooms, usually dominated by blue-green algae, also called cyanobacteria. Sunlight is prevented from reaching the aquatic plants underneath and these will eventually die. Large quantities of dead organic matter from the submerged vegetation and the algal blooms themselves become available for decomposition, stimulating the growth of bacteria, and causes problems of oxygen depletion. It finally leads to levels of dissolved oxygen insufficient to sustain higher life forms. Algae and decaying organic matter cause discolouring, turbidity, odours, and objectionable tastes of water that is difficult to remove and greatly reduce its usefulness as a domestic water source. In oxygen depleted environments anaerobic decomposition of organic matter will lead to the formation of methane and hydrogen sulphide gas.

Aquatic species require a long list of nutrients for growth and reproduction, but from a water quality perspective, the three most important ones are carbon, nitrogen, and phosphorus. Plants require relatively large amounts of each of these three nutrients, and unless all three are available, growth will be limited. The nutrient that is least available relative to the plants’ needs is called the *limiting nutrient*. In general, sea water is most often limited by nitrogen, while freshwater lakes are most often limited by phosphorus. The eutrophication of the Baltic Sea is dependent on either phosphorus or nitrogen, depending on the situation and the place.

Major sources of nitrogen include municipal wastewater discharges, run-off from animal husbandry, chemical fertilisers, and nitrogen deposition from the atmosphere, mostly originating from combustion processes. In addition, certain bacteria and blue-green algae can obtain their up-take of nitrogen directly from the atmosphere. While there are usually enough natural sources of nitrogen to allow algae and aquatic weeds to grow, there is not much phosphorus available from nature, so it tends to become the controlling nutrient in rivers and lakes.

Human activities, however, often provide enough phosphorus to allow excessive growth of aquatic weeds and algae. Major anthropogenic sources of phosphorus are agricultural run-off from heavily fertilised areas and domestic wastewaters.

1.4.3 Salts

Water naturally accumulates a variety of dissolved solids as it passes through soils and rocks on its way to the sea. These salts typically include such cations as sodium, calcium, magnesium, and potassium, and anions such as chloride, sulphate, and bicarbonate. The commonly used measure of salinity is the concentration of *total dissolved solids* (TDS). Table 1.3 shows the approximate values of TDS for different types of waters.

The concentration of dissolved solids is an important indicator of the usefulness of water for various applications. Drinking water, for example, has a recommended maximum TDS concentration of 500 mg/L. Animals can tolerate higher concentrations. Of greater importance, however, is the salt tolerance of crops. At concentrations above 2100 mg/L, water is generally unsuitable for irrigation except for the most salt tolerant of crops, but already with salt concentrations within the range of freshwater (500-1500) it becomes increasingly important with careful water management to maintain crop yields.

Large amounts of salts are discharged from mining activities.

1.5 Pollution by Toxic Substances

1.5.1 Pollution by Heavy Metals

Most metals are toxic. *Heavy metals* is often used as a term to refer to some toxic metals with high specific gravity. In terms of their environmental impacts, the most important heavy metals are mercury (Hg), lead (Pb), and cadmium (Cd). Also arsenic (As), although not a metal, is often included in the group. Here we will also include asbestos, being an inorganic mineral.

Metals differ from other toxic substances in that they are totally non-degradable in the environment. Most heavy metals are distributed in the environment dissolved in water. Several of them may however also be emitted as air pollutants. This is in particular the case for arsenic, asbestos, cadmium, lead and mercury.

Metals may be inhaled, and they may be ingested. How well they are absorbed in the body depends somewhat on the particular metal in question and the particular form that it exists in. Metals bound to organic compounds are most easily taken up in the body and accumulated. The heavy metals are neurotoxic, carcinogenic or toxic to the kidneys.

Metals are produced in many different industries and also typically released in the flue gases during incineration of fossil fuels. Metallurgic industries are obviously important but also e.g. tanning of leather that usually uses chromium, some compounds of which are very toxic. Another source are the dental services which until recently discharged considerable amounts of toxic mercury.

Figure 1.15 Pike in blacklisted lakes. *Pike is one of the fish which accumulates mercury in blacklisted lakes, to the despair of the young fisherman in the photo. In Sweden in the 1960s, large pikes had 5-8 mg Hg/kg w.w. (a few even more than 10 mg/kg in the 1950s). (Photo: www.duiops.net/seresvivos/)*

1.5.2 The Heavy Metals

Inorganic liquid *mercury* is not very toxic, while mercury vapour is highly toxic, as are mercury compounds, such as methyl mercury. As such it enters the lungs, where it diffuses into the bloodstream. Mercury causes serious damage to the central nervous system, and is associated with a series of symptoms.

Most often mercury is released to the environment in its metallic, liquid or vapour, forms. As vapour it is emitted to the atmosphere from industrial or combustion sources. Historically pulp and paper industry released large amounts of mercury to water. Mercury is also emitted as an air pollutant, from the chlor-alkali industry for production of chlorine and sodium hydroxide, waste incineration and coal fired power plants. A large portion of the mercury emitted to the environment over the years can be found deposited in the ground and in the sediment in rivers and lakes, from where it is slowly leaking as methyl mercury into the water bodies. There it is transported through the food chains to the top consumers such as pike and perch, and then to humans and predatory birds and animals living on the fish. This bioaccumulation and biomagnification of mercury puts the top consumers at risk.

In contrast to mercury, *lead* does not pose much of a threat as a vapour. It is most dangerous when it is dissolved into its ionic form, Pb^{2+}. Lead dissolved in blood is transferred to vital organs, including the kidneys and brain. Children and foetuses are most at risk since their brains are growing rapidly and exposure to lead may lead to severe and permanent brain damage. Lead may be present in the food and water we consume and in the air we breathe. Until the introduction of unleaded fuel the combustion of leaded gasoline, containing organically bound lead, was the largest source of lead pollution in the atmosphere. Lead accumulates slowly in the body. Initial symptoms of lead poisoning include decreased haemoglobin synthesis, while later on, the central nervous system is damaged.

Cadmium, a metal toxic to most species, is released into the environment from industries (electroplaters, battery producers, etc.) in sufficient quantities to warrant its classification as a pollutant. Though mostly considered a water borne toxic it also is emitted as cadmium fumes, and as such suspected to be carcinogenic. Cadmium, together with lead and mercury, accumulates in the kidneys, where it is also toxic.

Arsenic is a by-product of copper and lead smelting and the roasting of gold, silver, and cobalt ores. It is primarily an airborne pollutant, but it can contaminate bodies of water and accumulate in fish. It is also a component of some agricultural insecticides and fungicides. Arsenic is also a serious natural contaminant of ground waters in particular in India and Bangladesh. Arsenic is a carcinogen contributing to occupationally related lung cancer.

In the form of fibres, *asbestos* is an airborne pollutant, and inhalation of these fibres over an extended period can result in asbestos pneumoconiosis, or asbestosis. Asbestos is a carcinogen. Lung cancer among people exposed to asbestos "dust" occurs with a frequency more than twice that of the general population. Asbestos has been used for the production of asbestos-cement floor tiles, brake linings, and gaskets and the manufacture of fireproof linings and textile, but has in many countries been phased out and replaced with other materials.

Figure 1.17 White-tailed eagle (Haliaeëtus albicilla). *This magnificent bird of prey, the largest in the Baltic Sea region, was until recently threatened by extinction due to the contamination of DDT and PCB. The white-tailed eagle was saved by a long-term programme where non-polluted carcasses were made available as food. From 1999 the white-tailed eagle population has been increasing in the Baltic Sea region. (Photo: Hannu Ekblom, Finland)*

1.5.3 Persistent Organic Pollutants

Persistent organic pollutants (POPs) include an array of chemicals from mainly three sources: Pesticides based on organochlorine or organo-phosphorus compounds; various compounds used in industry, such as PCB, flame retardants, plastic components etc, and several by-products from chemical processes, such as dioxins. Persistent organic pollutants are characterised by their extremely slow decomposition. Many of them also directly affect an organism's health, and these are called *toxic pollutants*.

Toxic organic substances mostly act on the cellular level. The biological activity in a cell depends critically on the function of the cell membranes. Different substances are passively or actively transported across the membranes. Water soluble substances are separated outside the cells and excreted via the kidneys. A toxic substance which is soluble in fat, on the other hand, can pass through the cell membranes into the cells, where the substances can be accumulated and eventually disturb the function of the cell and cause damage.

Figure 1.16 Pesticides. *Spraying with pesticides. (Photo: iStockphoto)*

Most persistent organic pollutants are hydrocarbons containing chlorine or other halogen atoms, especially bromine. These organo-halogen compounds are very stable – persistent – and are readily soluble in fats and oils. They therefore easily penetrate cell membranes, and finally are accumulated in fatty tissue. This fact, called *bioaccumulation*, means that the substance eventually reaches concentrations where it becomes toxic. The toxins are also typically accumulated in the food chains, a phenomenon called *biomagnification*. Animals at successively higher trophic levels in a food chain are consuming food that has successively higher concentrations. At the top of the food chain body concentrations of these pollutants are the highest, and it is here that organo-chlorine toxicity has been most recognisable.

The main sources of emissions of toxic organic pollutants are: use of pesticides, industrial processes, incineration plants,

Case Study 1.2 The Bhopal Disaster

The world's worst industrial disaster, in terms of fatalities, occurred in Bhopal, India, in 1984. In the early hours of the morning of 3rd of December, an extremely toxic gas, methylisocyanate (MIC), escaped from a local pesticide plant. Denser than air, it lingered in the vicinity of the factory, a densely populated shanty-town area. People were killed as they slept or fled from the choking gas. Within two hours, the highly poisonous gas had spread to cover an area of 60 km^2. The initial death toll exceeded 2500, with hundreds of thousands injured.

The pesticide plant at Bhopal was owned by Union Carbide, India Ltd (UCIL), a subsidiary of the multinational chemical company Union Carbide Corporation (UCC). UCC owns 50.9% of the stock of UCIL.

The Bhopal plant was used for the production of carbamate pesticides, mainly carbaryl (brand name Sevin), together with small amounts of butylphenyl methylcarbamate and aldicarb (brand name Temik), all destined for the Indian market. The first two of these pesticides are classed as 'moderately hazardous' by the World Health Organisation whilst aldicarb is classed as 'extremely hazardous'. The extremely toxic substance methylisocyanate (MIC) is used as an intermediary in the production of these pesticides.

Methylisocyanate has the chemical formula $CH_3–N=C=O$. It is a highly volatile liquid, with a boiling point of 39°C. It is very unstable and in the presence of certain external substances, including water, polymerises rapidly. This exothermic reaction releases large quantities of heat which in turn accelerates the polymerisation reaction. At UCIL in Bhopal, large quantities of MIC were stored underground in three stainless steel tanks. At the time of the accident 62 tons of MIC were stored at the plant, although only 5 tonnes were needed each day. Refrigeration was installed to keep the stored MIC in liquid form and help prevent a runaway polymerisation reaction from occurring.

Just after midnight on 2 December 1984, the pressure inside one of the three methylisocyanate storage tanks was observed to rise rapidly. The tank was equipped with a safety valve designed to rupture at 40 psi and release gas into a vent. When this burst, the safety valve within the vent itself popped, allowing methylisocyanate to escape into the atmosphere through the 33 m high vent tube.

The plant was fitted with two safety devices designed to deal with a gas escape. One of these, the vent gas scrubber, was turned on. This device consists of a packed tower through which a solution of caustic soda is poured in order to destroy the escaping gas. Although there is evidence to show that this system worked, it was not adequate to deal effectively with the escaping gas. The vent gas scrubber was designed to destroy only 88 kg/h of MIC, whilst the gas escape was in the region of 20,000 kg/h. A second safety device, a flare tower designed to burn off escaping gas, was shut for maintenance at the time of the accident. As a result, 40-45 tonnes of highly toxic methylisocyanate gas poured into the air during the next 40 minutes before the safety valve was re-sealed.

Investigations into the accident at Bhopal revealed that, as suspected, a runaway polymerisation reaction had occurred in one of the methylisocyanate storage tanks. This was evident from damage in the tank that the internal temperature had exceeded 300°C. The runaway reaction had been initiated by the accidental introduction of water during the cleaning of the MIC pipes, a task undertaken without proper precautions.

An estimated 200,000 people were affected by the gas, many thousands of whom descended on the local hospital. Tragically, there was very little knowledge of how to treat the gas victims and many more subsequently died. Those who did survive suffered from a variety of ailments including blindness, blackouts and nausea. Little was known at the time about the long-term effects of exposure to methylisocyanate. This made effective treatment of the survivors problematic.

The Bhopal disaster is described in several places, see e.g.:
http://www.bhopal.org/whathappened.html
http://en.wikipedia.org/wiki/Bhopal_Disaster

wastewater treatment plants, combustion processes and power plants.

1.5.4 Pesticides

Many toxic compounds are used as *pesticides*. The term pesticide is used to cover a range of chemicals that kill organisms that society considers undesirable. Pesticides can be delineated as insecticides, herbicides, rodenticides, and fungicides. There are three main groups of synthetic organic insecticides: chlorinated hydrocarbons, organo-phosphates, and carbamates.

The most widely known organo-chlorine pesticide is DichloroDiphenylTrichloroethane (DDT) which has been widely used to control insects that carry diseases such as malaria, typhus, and plague over many years. Predatory birds, for example, are at the top of the food chain, and it was the adverse effect of DDT on their reproductive success that focused attention on this particular pesticide. DDT, and its metabolite, DDE interferes with the enzyme that regulates the distribution of calcium in birds, resulting in eggs with shells that are too thin to support the weight of the nesting parent. DDT is since the 1970s forbidden to use in the countries in the Baltic Sea region, but it is still used in e.g. Africa, from where it may travel as air pollutant and be deposited in the colder climate further north.

Other widely used organo-chlorines included methoxychlor, chlordane, heptachlor, aldrin, dieldrin, endrin, endosulfan, and Kepone®. Animal studies have shown that dieldrin, heptachlor, and chlordane produce liver cancers, and aldrin, dieldrin, and endrin have been shown to cause birth defects in mice and hamsters.

Organo-phosphorus biocides include parathion, malathion, diazinon, TEPP (tetraethyl pyrophosphate), dimethoate, Parathion and Dipterex. Like DDT, they are nerve poisons used to control insect pests on crops. They are much more acutely toxic to humans than the organo-chlorines that they have replaced. Insecticides, carbamates, are derived from carbamic acid, H_2NCOOH, are short-lived in the environment and do not bioaccumulate in food chains, but they also share the disadvantage of high human toxicity.

1.5.5 Industrial Chemicals and By-products

Polychlorinated biphenyls (PCBs) belong to the same family of substances as DDT, the *chlorinated hydrocarbons*. Unlike DDT, which is a single compound, PCBs are a chemical family of 209 congeners. PCBs lack flammability, which makes them very suitable for use as dielectric fluids in power transformers and capacitors. PCBs were also used as plasticizers and as de-inking fluids in the recycling of newspapers. PCBs are very persistent and lipophilic (fat-soluble) and therefore subject to the processes of bioaccumulation and biomagnification. PCBs are volatile and can escape into the atmosphere, although the main escape route is as water pollutants from sewage water, toxic dumps and landfills, but they are also suspected of playing a significant role in the formation of dioxins in waste incineration and landfill fires. PCB is outlawed as of the 1970s in most countries in the Baltic Sea region, but it is still leaking from technical infrastructure, buildings etc.

More recently organic compounds containing bromine atoms have been used as flame retardants in everything from textiles to computers. Some of these substances have been observed to bioaccumulate and are found in the Baltic Sea fauna.

Chlorinated hydrocarbons are also used as herbicides. The chlorophenoxy compounds, 2,4,5-T and 2,4-D, are among the best known.

Figure 1.18 Landfill fire. *PCBs are suspected of playing a significant role in the formation of dioxins in waste incineration and landfill fires. (Photo: http://www.btfire.org/)*

2,4,5-T has been banned in part because the manufacturing process also produces a highly toxic side-product, dioxin. Dioxin is also formed in combustion processes from e.g. polyaromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB).

Dioxins represent a family of chemicals referred to as polychlorinated dibenzo-para-dioxins (PCDD) or polychlorinated dibenzofurans (PCDF). The most toxic of these compounds is 2,3,7,8-tetrachlor-dibenzo-p-dioxin (TCDD). This chemical occurs as an impurity in the manufacture of many chemicals and pesticides having a trichlorophenol base. When plastics or PCBs are burned, small amounts are released to the atmosphere, as from pulp and paper mills, pesticide plants, vehicles, forest and landfill fires and cigarette smoke. Dioxins are formed optimally in the temperature range 180 to 400ºC in low temperature fires. Dioxins, especially TCDD, are extremely toxic in concentrated form, causing damage to the kidney, liver and the nervous system. They are powerful teratogens (damaging to the growing foetus) and also possibly carcinogenic.

More recently many of the persistent pollutants have been shown to act as hormones, causing e.g. a different sex differentiation in fish and amphibians. There are some indications that they may cause reduced fertility in men and breast cancer in women.

1.5.6 Measures to Control the Use of Chemicals

A number of legal actions have been taken to reduce and control the use of toxic chemicals in society. The first steps to ban the use of some of the worst pollutants were taken as early as the 1970s when e.g. DDT and PCB were outlawed in Western Europe. Several EU directives control the use of chemicals and pesticides and prescribe how risk assessment and registration of such chemicals should be done.

In 2001 the signing of the so-called Stockholm Convention resulted in a black list of the worst pollutants with the aim to ban them entirely and globally. In 2006 the European Council agreed on the implementation of the REACH Directive, accepted as a proposal to the Commission in October 2003. REACH – Registration, Evaluation and Authorisation of CHemicals – will make industry responsible for management of all chemicals and implement a proper system for registration, risk evaluation and use. It is a long-term programme which aims to achieve full control of the close to 100,000 chemicals presently used in the European Union, most of them with poorly or not-at-all evaluated environmental and medical effects.

Study Questions

1. List the five important categories of environmental impacts of industry.
2. Which categories of resources are used for industrial production? List these according to amounts, and make some estimate of the amounts.
3. Discuss the concepts of non-renewable and renewable resources and the carrying capacity.
4. Climate change is today a major environmental threat. Describe how and the main causes.
5. List the main sources of air pollution. What global environmental problems have been caused by air pollution? Name international agreements on reduction of emissions into the atmosphere, and mark the main directions of the policy in this sphere.
6. Describe some historic disastrous events caused by air pollution. List where and when they occurred, the approximate number of individuals affected, and the causes.
7. Discuss the history of stratospheric ozone depletion, and which measures were made to stop it, and if these were successful.
8. List the main sources of air pollution. What global environmental problems have been caused by air pollution? Name international agreements on reduction of emissions into the atmosphere, and mark the main directions of the policy in this sphere.
9. Eutrophication is one of the most difficult problems in the Baltic Sea. Explain what it is, its causes, and how one may deal with it.
10. Both mercury and lead pollution is more severe when these metals are present in organic compounds. Describe when this happens and give examples of serious pollution events caused by such compounds.
11. PCB is one of the worst organic pollutants, previously a much used industrial chemical, now outlawed. Describe what PCB is, how it was used, and if it is still a problem.
12. Use the Internet to find out more about the REACH Directive, and how it will be implemented in your country.
13. List the main sources and components of discharges into water, and the impacts these pollutions may lead to.

Abbreviations

DDT	DichloroDiphenylTrichloroethane.
PAH	PolyAromatic Hydrocarbons.
PAN	Peroxy Acetyl Nitrate.
PCB	PolyChlorinated Biphenyls.
ppb	parts per billion.
ppm	parts per million.
TDS	Total Dissolved Solids.
VOC	Volatile Organic Compounds.

Internet Resources

CRU, Climatic Research Unit
– Information sheet no. 1: Global Temperature Record
http://www.cru.uea.ac.uk/cru/info/warming/

CDIAC, Carbon Dioxide Information Analysis Center
– Atmospheric carbon dioxide record from Mauna Loa
http://cdiac.esd.ornl.gov/trends/co2/sio-mlo.htm

EMEP, Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe
http://www.emep.int/

WebDab 2006, EMEP activity data and emission database
– Expert Emissions used in EMEP models
http://webdab.emep.int/

INSC, International Nuclear Safety Centre
– Maps of Nuclear Power Reactors
http://www.insc.anl.gov/pwrmaps/

ASPO Ireland,
Association for the Study of Peak Oil & gas, Ireland
https://aspo-ireland.org/

The Bhopal Disaster
http://www.bhopal.org/whathappened.html

Environmental Science of Baltic University
http://www.balticuniv.uu.se/environmentalscience/

IPCC – Climate Change 2001: Synthesis Report
http://www.ipcc.ch/pub/syreng.htm

IPCC – Graph on Global Temperatue Change
http://www.ipcc.ch/present/graphics/2001syr/large/05.16.jpg