Pollution

There have always been problems with pollution on the local scale (and even regulations against it). To give one local example, during the reign of Edward III (1327-1377) there were complaints from visitors to London about the 'danger of contagion from the stench of burning sea-coal'. The problem was not seriously tackled for another six centuries until after the 'Great Smog' of December 1952. Increasingly, there is concern about the effects of pollutants on the environment.

The *bubble of influence* for a given environmental impact may be on a number of scales. The problem briefly mentioned above is essentially a local problem. Other problems of this class include pollution from transport (lead NO_2 and NO). A good example of a regional problem is that of *acid rain.* We will discuss this in more detail below. An example of a global problem is the large-scale emissions of carbon dioxide giving rise to the excessive 'greenhouse effect' and global climate change. Some problems may occur on more than one scale. The specific issue, say, of the air quality down the Euston Road is a local problem. However, the carbon dioxide emitted by the cars is part also of a global problem.

Although we shall consider air pollution, we should not forget pollution problems elsewhere in the environment. These may affect

- Water supply (nitrates from farming, lead in pipes)
  waste into the sea (sewer pipes, discharges from ships)
- Ground (burial of toxic wastes)

It is also worth noting that some natural events cause pollution on a massive scale; volcano emissions are perhaps the most obvious example.

Acid rain; an example of air pollution on a regional scale.

Combustion converts coal and oil into heat but also releases a variety of air pollutants (including suspended particulates) ; sulphur dioxide, nitrogen oxides, carbon monoxide [in addition to carbon dioxide]. SO_2 is the major pollutant from coal combustion. Another significant pollutant is the various oxides of nitrogen. In Europe the emissions are divided as follows

- 61% from power stations
- 28% from refineries and industry
- 5% from domestic use
- 4% from commercial and public use
- 2% from transport

Different coals have different sulphur content – mainly in the form of FeS_2 (iron pyrites). SO_2 dissolves in water to give sulphuric acid (H_2SO_4) – acid rain. The nitrogen oxides also contribute to acid rain since they can produce nitric acid (HNO_3) through oxidation and dissolution in water. This thus becomes part of the hydrologic cycle and can be carried great distances. The effect of acid rain depends on the eco-system (in particular the geology) of the region where the rain falls. Limestone neutralises acid rain; granite, gneiss, quartz, sandstone have little effect on the acidity.

The definition of pH.

The pH (potential of hydrogen) scale is a measure of hydrogen ion concentration in aqueous solution. It is defined as

$$pH = -\log_{10} ([H^+ (aq)])$$

Since the *ionic product* of water $K_W = [H^+(aq)][OH^- (aq)] = 10^{-14}$ mol^2dm^{-6} (usually referred to a mol^2l^{-2}) and when the solution is neutral, $[H^+ (aq)] = [OH^- (aq)]$, then for a neutral solution, $[H^+ (aq)] = 10^{-7}$ mol dm^{-3} (mol/litre) and pH = 7. If the pH of a solution is less than seven it is acid (excess $[H^+ (aq)]$); if the pH is greater than seven it is alkaline (excess $[OH^- (aq]$).

All rainwater is acidic. Natural rainwater has a pH of about 5.6 (due to dissolved CO_2 in the water; formally this gives carbonic acid, H_2CO_3 although the pure compound is unstable and cannot be isolated). SO_2 (having first oxidised to SO_3) and NO_2 dissolve in water to give acid rain (H_2SO_4 and HNO_3) with typical pH values of 4.0 – 4.5 (about the acidity of vinegar). If the pH of water falls below five it affects fish. Below pH=4.5 newly-hatched fish die or are deformed by calcium deficiency. If pH < 4.5 and aluminium is in the soil, it is released from the rocks and attacks fish gills leading to suffocation. Since the 1970's the effects of SO_2 emissions on the ecological cycle have been investigated in detail. This followed the recording of the death of fish in Scandinavian lakes.

Formation of acid rain

The process of formation can be summarised as follows (see also the diagram)

1. Release of sulphur and nitrogen oxides from natural and human sources. In Europe 90% of SO_2 release and 50% or more of NO_x release is due to human activities.
2. There is some dry deposition of SO_2, but most of the emission remains airborne for hundreds of kilometres (particularly in dry weather if the emission is from tall stacks). While airborne, it is oxidised to SO_3. This process is much faster once SO_2 is incorporated into water droplets. The oxide dissolves to give sulphuric acid
3. For this oxidation to happen, there must be a more effective oxidant that O_2. Usually this is H_2O_2 (hydrogen peroxide) or ozone. These are produced in the atmosphere by photochemical reactions (in particular the presence of NO_x at low altitudes)
4. An important further factor is natural ammonia rising from the land. The oxidation of SO_2 is inhibited by the presence of acid. The ammonia can enhance the conversion rate by neutralising the acid.
5. Primary NO_x emissions are oxidised (NO to NO_2) as a gas. There can be dry decomposition of nitrate particles which are then incorporated into water droplets in clouds to give HNO_3 – nitric acid
6. Acid rain therefore contains sulphate, nitrate, ammonium and hydrogen ions (in addition to the bicarbonate found naturally).

The figure shows the distribution of acid rain (given as pH) over Western Europe. Note the 'holes' where the pH falls below 4.1 Quantifying the damage caused is complicated by the fact that the damage depends not only on the acidity of the rain, but also the geology of the region the rain falls in. Rocks such as limestone are naturally alkaline and can neutralise acid rain. Granite, quartz and sandstone are poor neutralisers. Although major ecological problems have been attributed to acid rain (fish kills in Sweden, forest die-back in Germany), final proof is lacking . A summary of the position in 1986 is given in a European Commission report (quoted from Blunden and Reddish)

‘It has not been unequivocally established that environmental impacts are caused by acid pollutant emissions .... nevertheless circumstantial evidence would suggest that acid emissions and their subsequent chemical transformation and precipitation are at least a partial contributory cause to the observed effects and may be giving rise to as yet unidentified impacts, some of which could be irreversible’

On this basis an EC directive was issued in 1988 setting targets of reducing the SO_2 levels from the 1980 figures by 23% (by 1993), 42% (by 1997) and 57% (by 2003) for all plants over 50MW. Simultaneously, reductions of NO_x by 10% (by 1993) and 305 (by 1998) were agreed. This has required installation of flue-gas desulphurisation equipment in large coal-burning power stations in the UK. In fact, the targets are being met by two other developments (i) importing low-sulphur coal (ii) the ‘dash to gas’. It is also worth noting that desulphurisation requires large quantities of limestone (where is it to be mined?) and the resulting calcium sulphate must be disposed of. The other product of the reaction is CO_2 i.e. we dispose of acid rain by adding to the greenhouse effect! (although to be fair, this contribution is very small).