

circumstances, heated effluents are discharged to rivers which are also polluted with toxic or organic matter, and the effects of elevated temperature may be difficult to distinguish from other pollution effects. Since *low* temperatures can also limit biological processes, in some circumstances artificially-elevated temperatures may actually be beneficial in terms of overall productivity. Also, local conditions undoubtedly influence the impact of heated effluents. In many countries, power generation reaches its maximum during the winter months when river temperatures are low and river discharges high. In others, depending upon climatic and economic factors, demands for electric power (for refrigeration or air-conditioning) in summer, when river discharges are lowest and temperatures naturally highest, may approach or exceed winter levels. The effects of heated effluents on the ecology of receiving waters may therefore be expected to vary from one region to another. Finally, the effects of elevated temperatures may be difficult to predict or detect without detailed knowledge of specific local circumstances. For example, increased temperature will accelerate microbial decomposition of organic matter. In sluggish, poorly-aerated waters this will accentuate the effects of organic pollution; but in turbulent waters which re-aerate rapidly from the atmosphere, the effect of elevated temperature would be to reduce the extent of the zone within which the adverse effects of organic inputs manifested themselves, and in a lightly-polluted water might lead to a beneficial increase in overall productivity. It is therefore unwise to attempt generalisations on the effects of thermal pollution; each case must be considered individually.

2.7 Toxic Pollution

There are about four million different chemical substances in existence, a number which increases by about 300000 every year. Of these, about 63000 are in common use (Maugh, 1978). Goodman (1974) estimated that about 10000 chemicals are produced in quantities exceeding 500 kg yr⁻¹. A large proportion of these thousands of chemicals are, presumably, only produced and/or used in only a small number of locations. Nevertheless the number of pollutants which can be considered as widespread is still formidably large. A realistic figure is indicated by the 1978 Great Lakes Water Quality Agreement between the US and Canadian governments (reprinted in Nriagu and Simmons, 1983). Appendix 1 of this agreement lists 271 different substances which, on the basis of toxicological and discharge data, are considered hazardous to the North American Great Lakes. Appendix 2 of the same agreement lists a further 106 'potentially hazardous polluting substances'.

The present discussion is confined, of necessity, to a general description of the sources and characteristics of some of the major categories of toxic pollutant. The categories chosen are for convenience, and are not necessarily mutually exclusive;

many pesticides, for example, contain heavy metals. It is not at all easy to give specific descriptions of the effects of a given pollutant, because of the diversity of the chemicals involved, the wide range of environmental conditions which prevail in different receiving waters, the fact that poisons frequently occur in complex mixtures, and the enormous differences in the physiology of the organisms which are exposed to them. The study of pollutant toxicity and toxic effects is described in some detail in Chapters 1 and 4. Specific information on the toxicity and toxic effects of pollutants is best sought in review articles and other data compilations, which are referred to where appropriate. A very comprehensive reference work is that of Hellowell (1986). It is important to note, however, that toxicity data obtained from such compilations can be extremely misleading, for reasons which are explained fully in Chapter 4. It is recommended that wherever possible the original sources are consulted, and the validity of the data assessed in relation to the methodological criteria described in Chapter 4.

2.7.1 Heavy Metals

'Heavy metals' is an imprecise term that is generally taken to include the metallic elements with an atomic weight greater than 40, but excluding the alkaline earth metals, alkali metals, lanthanides and actinides. The most important heavy metals from the point of view of water pollution are zinc, copper, lead, cadmium, mercury, nickel and chromium. Aluminium (see Section 2.9) may be important in acid waters. Some of these metals (e.g. copper, zinc) are essential trace elements to living organisms, but become toxic at higher concentrations. Others, such as lead and cadmium, have no known biological function. Industrial processes, particularly those concerned with the mining and processing of metal ores, the finishing and plating of metals and the manufacture of metal objects, are the main source of metal pollution. In addition, metallic compounds are widely used in other industries: as pigments in paint and dye manufacture; in the manufacture of leather, rubber, textiles and paper; and many others. Quite apart from industrial sources, domestic wastes contain substantial quantities of metals because the water has been in prolonged contact with copper, zinc or lead pipework or tanks. The prevalence of heavy metals in domestic formulations, such as cosmetic or cleansing agents, is frequently overlooked. Some forms of intensive agriculture give rise to severe metal pollution; copper, for example, is widely added to pig feed and is excreted in large quantities by the animals. Mance (1987) gives a detailed review of metal pollution.

Heavy metals may be classed (see Table 2.4) generally as toxic or very toxic to aquatic animals and to many plant species, though large interspecific differences in susceptibility occur even within closely-related groups of

Table 2.4 Degrees of pollutant toxicity, classified according to the scheme proposed by the Joint IMCO/FAO/UNESCO/WHO Group of Experts on the Scientific Aspects of Marine Pollution (1969)

Degree of toxicity	Acute toxicity threshold, (mg l ⁻¹)
Practically non-toxic	Above 10 000
Slightly toxic	1000–10 000
Moderately toxic	100–1000
Toxic	1–100
Very toxic	Below 1

organisms. Relatively little is known about the interaction of heavy metals with the aquatic microbial flora. Algae, macroinvertebrates and fishes have, however, been widely studied. In general, the heavy metals may be listed in approximate order of decreasing toxicity as follows: Hg, Cd, Cu, Zn, Ni, Pb, Cr, Al, Co. However, this sequence is very tentative and the position of each element in the series will vary with the species tested and the conditions of the experiment. Apart from some remarkable interspecific variations in susceptibility to metals, the toxicity of most metals varies enormously with the environmental conditions, mainly because of the effect of environmental conditions on the chemical speciation of the metal (see Section 4.2). Study of the ecological effects of heavy metals as water pollutants is often hampered by the fact that other pollutants are normally additionally present. However, there is an enormous literature on heavy metal toxicity (see, for example, Alabaster and Lloyd, 1980; Hellawell, 1986; Mance, 1987; Whitton and Say, 1975) and some important aspects of the impact of heavy metals as water pollutants have already been discussed in Chapter 1.

Two features of heavy metal toxicity which should not be overlooked are their ability to form organometal complexes and their potential for bioaccumulation. There is some evidence (see Section 4.2) that the presence of organic substances can reduce heavy metal toxicity considerably, at least as measured in conventional toxicity tests. However, a number of organometal compounds are known to be particularly hazardous to aquatic life. Tributyltin, for example, a constituent of antifouling paints, is implicated in severe environmental damage in harbours, boatyards and inland waters, and appears in the 'Black Lists' of substances compiled by international organisations such as the European Union and United Nations Environment Programme. Similarly, the dangers associated with methylated forms of mercury are well known. Many metals, whether organically-complexed or not, are known to accumulate in plant and animal tissues to very high levels, posing a potential toxic hazard to the organisms themselves, or organisms higher in the food chain including humans, which may consume them.

2.7.2 Ammonia, Cyanides and Phenols

Ammonia, cyanides and phenols are considered together because, with copper and zinc, they are the most widespread and serious toxic water pollutants in industrialised countries. Ammonia and its compounds are ubiquitous constituents of industrial effluents because ammonia is a staple raw material in many branches of the chemical industry; it is, therefore, a common end-product of industrial processes as well as an important by-product of others, notably the production of coke and gas from coal, from power generation and from most processes involving the heating or combustion of fuel. It is also a natural product of the metabolism of organic wastes in treatment plants and receiving waters. The toxicity of ammonia to fish is well documented, and although less is known of its effect on invertebrates it appears that levels of ammonia which are tolerable to fish present little danger to most invertebrates (Alabaster and Lloyd, 1980). In aqueous solution, ammonia forms an equilibrium between unionised ammonia, ammonium ion and hydroxide ions:



Unionised ammonia is very toxic to most organisms, but ammonium ion is only moderately toxic. The toxicity of the solution therefore depends on the quantity of unionised ammonia. This in turn depends upon the pH and temperature of the water; as pH and temperature rise, the proportion of unionised ammonia also rises. The effect of pH and temperature on ammonia toxicity is therefore considerable. In order to know whether a given level of total ammonia is likely to be toxic, it is necessary to use the pH and temperature values to calculate the corresponding level of free ammonia. (Some authors, such as Alabaster and Lloyd (1980) and Hellawell (1986), have published tables or nomographs to facilitate the calculation.) As an example, the European Inland Fisheries Advisory Commission (EIFAC) recommends that unionised ammonia concentrations should not exceed 0.025 mg l^{-1} . In a water of pH 8.5 at a temperature of 20°C , this corresponds to a *total* ammonia concentration of 0.22 mg l^{-1} . In a cooler, acid water, however (pH 6.5, 5°C), a concentration of *total* ammonia of 63.3 mg l^{-1} would be acceptable, whereas at pH 6.5 and 20°C , the maximum acceptable concentration of *total* ammonia would be 20 mg l^{-1} .

Cyanide is also a very common constituent of industrial effluents, being produced from processes involving coking and/or combustion such as steelworks, gas production and power generation. Cyanides are also used in the hardening, plating and cleaning of metals. Cyanides dissociate in aqueous solution:



The dissociation, and consequently the toxicity of cyanide, is pH-dependent, low pH favouring the formation of undissociated HCN which is highly toxic. Cyanide ions readily form complexes with heavy metal ions. The stability and toxicity of