8
Chemical aspects

Most chemicals arising in drinking-water are of health concern only after extended exposure of years, rather than months. The principal exception is nitrate. Typically, changes in water quality occur progressively, except for those substances that are discharged or leach intermittently to flowing surface waters or groundwater supplies from, for example, contaminated landfill sites.

In some cases, there are groups of chemicals that arise from related sources – for example, the DBPs – and it may not be necessary to set standards for all of the substances for which there are guideline values. If chlorination is practised, the THMs, of which chloroform is the major component, are likely to be the main DBPs, together with the chlorinated acetic acids in some instances. In some cases, control of chloroform levels and, where appropriate, trichloroacetic acid levels will also provide an adequate measure of control over other chlorination by-products.

Several of the inorganic elements for which guideline values have been recommended are recognized to be essential elements in human nutrition. No attempt has been made here at this time to define a minimum desirable concentration of such substances in drinking-water.

Fact sheets for individual chemical contaminants are provided in chapter 12. For those contaminants for which a guideline value has been established, the fact sheets include a brief toxicological overview of the chemical, the basis for guideline derivation, treatment achievability and analytical limit of detection. More detailed chemical reviews are available (http://www.who.int/water_sanitation_health/dwq/guidelines/en/).

8.1 Chemical hazards in drinking-water

A number of chemical contaminants have been shown to cause adverse health effects in humans as a consequence of prolonged exposure through drinking-water. However, this is only a very small proportion of the chemicals that may reach drinking-water from various sources.

The substances considered here have been assessed for possible health effects, and guideline values have been proposed only on the basis of health concerns. Additional

The lists of chemicals addressed in these Guidelines do not imply that all of these chemicals will always be present or that other chemicals not addressed will be absent.

consideration of the potential effects of chemical contaminants on the acceptability of drinking-water to consumers is included in chapter 10. Some substances of health concern have effects on the acceptability of drinking-water that would normally lead to rejection of the water at concentrations significantly lower than those of health concern. For such substances, health-based guideline values are needed, for instance, for use in interpreting data collected in response to consumer complaints.

In section 2.3.2, it is indicated that "In developing national drinking-water standards based on these Guidelines, it will be necessary to take account of a variety of environmental, social, cultural, economic, dietary and other conditions affecting potential exposure. This may lead to national standards that differ appreciably from these Guidelines." This is particularly applicable to chemical contaminants, for which there is a long list, and setting standards for, or including, all of them in monitoring programmes is neither feasible nor desirable.

It is important that chemical contaminants be prioritized so that the most important are considered for inclusion in national standards and monitoring programmes.

The probability that any particular chemical may occur in significant concentrations in any particular setting must be assessed on a case-by-case basis. The presence of certain chemicals may already be known within a particular country, but others may be more difficult to assess.

In most countries, whether developing or industrialized, water sector professionals are likely to be aware of a number of chemicals that are present in significant concentrations in drinking-water supplies. A body of local knowledge that has been built up by practical experience over a period of time is invaluable. Hence, the presence of a limited number of chemical contaminants in drinking-water is usually already known in many countries and in many local systems. Significant problems, even crises, can occur, however, when chemicals posing high health risk are widespread but their presence is unknown because their long-term health effect is caused by chronic exposure as opposed to acute exposure. Such has been the case of arsenic in groundwater in Bangladesh and West Bengal, for example.

For some contaminants, there will be exposure from sources other than drinking-water, and this may need to be taken into account when setting standards and considering the need for standards. It may also be important when considering the need for monitoring. In some cases, drinking-water will be a minor source of exposure, and controlling levels in water will have little impact on overall exposure. In other cases, controlling a contaminant in water may be the most cost-effective way of reducing exposure. Drinking-water monitoring strategies, therefore, should not be considered in isolation from other potential routes of exposure to chemicals in the environment.

Table 8.1 Categorization of source of chemical constituents

Source of chemical constituents	Examples of sources
Naturally occurring	Rocks, soils and the effects of the geological setting and climate
Industrial sources and human dwellings	Mining (extractive industries) and manufacturing and processing industries, sewage, solid wastes, urban runoff, fuel leakages
Agricultural activities	Manures, fertilizers, intensive animal practices and pesticides
Water treatment or materials in contact with drinking-water	Coagulants, DBPs, piping materials
Pesticides used in water for public health	Larvicides used in the control of insect vectors of disease
Cyanobacteria	Eutrophic lakes

The scientific basis for each of the guideline values is summarized in chapter 12. This information is important in helping to modify guideline values to suit national requirements or in assessing the significance for health of concentrations of a contaminant that are greater than the guideline value.

Chemical contaminants in drinking-water may be categorized in various ways; however, the most appropriate is to consider the primary source of the contaminant – i.e., to group chemicals according to where control may be effectively exercised. This aids in the development of approaches that are designed to prevent or minimize contamination, rather than those that rely primarily on the measurement of contaminant levels in final waters.

In general, approaches to the management of chemical hazards in drinking-water vary between those where the source water is a significant contributor (with control effected, for example, through source water selection, pollution control, treatment or blending) and those from materials and chemicals used in the production and distribution of drinking-water (controlled by process optimization or product specification). In these Guidelines, chemicals are therefore divided into six major source groups, as shown in Table 8.1.

Categories may not always be clear-cut. The group of naturally occurring contaminants, for example, includes many inorganic chemicals that are found in drinking-water as a consequence of release from rocks and soils by rainfall, some of which may become problematical where there is environmental disturbance, such as in mining areas.

8.2 Derivation of chemical guideline values

The criteria used to decide whether a guideline value is established for a particular chemical constituent are as follows:

— there is credible evidence of occurrence of the chemical in drinking-water, combined with evidence of actual or potential toxicity; or

— the chemical is of significant international concern; or
— the chemical is being considered for inclusion or is included in the WHO Pesticide Evaluation Scheme (WHOPES) programme (approval programme for direct application of pesticides to drinking-water for control of insect vectors of disease).

Guideline values are derived for many chemical constituents of drinking-water. A guideline value normally represents the concentration of a constituent that does not result in any significant risk to health over a lifetime of consumption. A number of provisional guideline values have been established at concentrations that are reasonably achievable through practical treatment approaches or in analytical laboratories; in these cases, the guideline value is above the concentration that would normally represent the calculated health-based value. Guideline values are also designated as provisional when there is a high degree of uncertainty in the toxicology and health data (see also section 8.2.6).

There are two principal sources of information on health effects resulting from exposure to chemicals that can be used in deriving guideline values. The first and preferred source is studies on human populations. However, the value of such studies for many substances is limited, owing to lack of quantitative information on the concentration to which people have been exposed or on simultaneous exposure to other agents. However, for some substances, such studies are the primary basis on which guideline values are developed. The second and most frequently used source of information is toxicity studies using laboratory animals. The limitations of toxicology studies include the relatively small number of animals used and the relatively high doses administered, which create uncertainty as to the relevance of particular findings to human health. This is because there is a need to extrapolate the results from animals to humans and to the low doses to which human populations are usually exposed. In most cases, the study used to derive the guideline value is supported by a range of other studies, including human data, and these are also considered in carrying out a health risk assessment.

In order to derive a guideline value to protect human health, it is necessary to select the most suitable study or studies. Data from well conducted studies, where a clear dose–response relationship has been demonstrated, are preferred. Expert judgement was exercised in the selection of the most appropriate study from the range of information available.

8.2.1 Approaches taken

Two approaches to the derivation of guideline values are used: one for "threshold chemicals" and the other for "non-threshold chemicals" (mostly genotoxic carcinogens).

It is generally considered that the initiating event in the process of genotoxic chemical carcinogenesis is the induction of a mutation in the genetic material (DNA) of somatic cells (i.e., cells other than ova or sperm) and that there is a theoretical risk at any level of exposure (i.e., no threshold). On the other hand, there are carcinogens that are capable of producing tumours in animals or humans without exerting a genotoxic activity, but acting through an indirect mechanism. It is generally believed that a demonstrable threshold dose exists for non-genotoxic carcinogens.

In deriving guideline values for carcinogens, consideration was given to the potential mechanism(s) by which the substance may cause cancer, in order to decide whether a threshold or non-threshold approach should be used (see sections 8.2.2 and 8.2.4).

The evaluation of the potential carcinogenicity of chemical substances is usually based on long-term animal studies. Sometimes data are available on carcinogenicity in humans, mostly from occupational exposure.

On the basis of the available evidence, the International Agency for Research on Cancer (IARC) categorizes chemical substances with respect to their potential carcinogenic risk into the following groups:

Group 1:	the agent is carcinogenic to humans
Group 2A:	the agent is probably carcinogenic to humans
Group 2B:	the agent is possibly carcinogenic to humans
Group 3:	the agent is not classifiable as to its carcinogenicity to humans
Group 4:	the agent is probably not carcinogenic to humans

According to IARC, these classifications represent a first step in carcinogenic risk assessment, which leads to a second step of quantitative risk assessment where possible. In establishing guideline values for drinking-water, the IARC evaluation of carcinogenic compounds, where available, is taken into consideration.

8.2.2 Threshold chemicals

For most kinds of toxicity, it is believed that there is a dose below which no adverse effect will occur. For chemicals that give rise to such toxic effects, a tolerable daily intake (TDI) should be derived as follows, using the most sensitive end-point in the most relevant study, preferably involving administration in drinking-water:

$$\mathrm{TDI} = (\mathrm{NOAEL\ or\ LOAEL})/\mathrm{UF}$$

where:

- NOAEL = no-observed-adverse-effect level
- LOAEL = lowest-observed-adverse-effect level
- UF = uncertainty factor

The guideline value (GV) is then derived from the TDI as follows:

$$\mathrm{GV} = (\mathrm{TDI} \times \mathrm{bw} \times \mathrm{P})/\mathrm{C}$$

where:

- bw = body weight (see Annex 3)
- P = fraction of the TDI allocated to drinking-water
- C = daily drinking-water consumption (see Annex 3)

Tolerable daily intake

The TDI is an estimate of the amount of a substance in food and drinking-water, expressed on a body weight basis (mg/kg or μg/kg of body weight), that can be ingested over a lifetime without appreciable health risk.

Acceptable daily intakes (ADIs) are established for food additives and pesticide residues that occur in food for necessary technological purposes or plant protection reasons. For chemical contaminants, which usually have no intended function in drinking-water, the term "tolerable daily intake" is more appropriate than "acceptable daily intake," as it signifies permissibility rather than acceptability.

Over many years, JECFA and JMPR have developed certain principles in the derivation of ADIs. These principles have been adopted where appropriate in the derivation of TDIs used in developing guideline values for drinking-water quality.

As TDIs are regarded as representing a tolerable intake for a lifetime, they are not so precise that they cannot be exceeded for short periods of time. Short-term exposure to levels exceeding the TDI is not a cause for concern, provided the individual's intake averaged over longer periods of time does not appreciably exceed the level set. The large uncertainty factors generally involved in establishing a TDI (see below) serve to provide assurance that exposure exceeding the TDI for short periods is unlikely to have any deleterious effects upon health. However, consideration should be given to any potential acute effects that may occur if the TDI is substantially exceeded for short periods of time.

No-observed-adverse-effect level and lowest-observed-adverse-effect level

The NOAEL is defined as the highest dose or concentration of a chemical in a single study, found by experiment or observation, that causes no detectable adverse health effect. Wherever possible, the NOAEL is based on long-term studies, preferably of ingestion in drinking-water. However, NOAELs obtained from short-term studies and studies using other sources of exposure (e.g., food, air) may also be used.

If a NOAEL is not available, a LOAEL may be used, which is the lowest observed dose or concentration of a substance at which there is a detectable adverse health effect. When a LOAEL is used instead of a NOAEL, an additional uncertainty factor is normally applied (see below).

Uncertainty factors

The application of uncertainty (or safety) factors has been widely used in the derivation of ADIs and TDIs for food additives, pesticides and environmental contaminants. The derivation of these factors requires expert judgement and careful consideration of the available scientific evidence.

Table 8.2 Source of uncertainty in derivation of guideline values

Source of uncertainty	Factor
Interspecies variation (animals to humans)	1–10
Intraspecies variation (individual variations within species)	1–10
Adequacy of studies or database	1–10
Nature and severity of effect	1–10

In the derivation of guideline values, uncertainty factors are applied to the NOAEL or LOAEL for the response considered to be the most biologically significant.

In relation to exposure of the general population, the NOAEL for the critical effect in animals is normally divided by an uncertainty factor of 100. This comprises two 10-fold factors, one for interspecies differences and one for interindividual variability in humans (see Table 8.2). Extra uncertainty factors may be incorporated to allow for database deficiencies and for the severity and irreversibility of effects.

Factors lower than 10 were used, for example, for interspecies variation when humans are known to be less sensitive than the animal species studied. Inadequate studies or databases include those where a LOAEL was used instead of a NOAEL and studies considered to be shorter in duration than desirable. Situations in which the nature or severity of effect might warrant an additional uncertainty factor include studies in which the end-point was malformation of a fetus or in which the end-point determining the NOAEL was directly related to possible carcinogenicity. In the latter case, an additional uncertainty factor was usually applied for carcinogenic compounds for which the guideline value was derived using a TDI approach rather than a theoretical risk extrapolation approach.

For substances for which the uncertainty factors were greater than 1000, guideline values are designated as provisional in order to emphasize the higher level of uncertainty inherent in these values. A high uncertainty factor indicates that the guideline value may be considerably lower than the concentration at which health effects would actually occur in a real human population. Guideline values with high uncertainty are more likely to be modified as new information becomes available.

The selection and application of uncertainty factors are important in the derivation of guideline values for chemicals, as they can make a considerable difference in the values set. For contaminants for which there is sufficient confidence in the database, the guideline value was derived using a smaller uncertainty factor. For most contaminants, however, there is greater scientific uncertainty, and a relatively large uncertainty factor was used. The use of uncertainty factors enables the particular attributes of the chemical and the data available to be considered in the derivation of guideline values.

Allocation of intake

Drinking-water is not usually the sole source of human exposure to the substances for which guideline values have been set. In many cases, the intake of chemical contaminants from drinking-water is small in comparison with that from other sources, such as food and air. Guideline values derived using the TDI approach take into account exposures from all sources by apportioning a percentage of the TDI to drinking-water. This approach ensures that total daily intake from all sources (including drinking-water containing concentrations of the substance at or near the guideline value) does not exceed the TDI.

Wherever possible, data concerning the proportion of total intake normally ingested in drinking-water (based on mean levels in food, air and drinking-water) or intakes estimated on the basis of consideration of physical and chemical properties were used in the derivation of the guideline values. Where such information was not available, an arbitrary (default) value of 10% for drinking-water was used. This default value is, in most cases, sufficient to account for additional routes of intake (i.e., inhalation and dermal absorption) of contaminants in water. In some cases, a specific discussion is made of the potential for exposure from intake through inhalation and dermal uptake in bathing and showering where there is evidence that this is likely to be significant, usually in circumstances where the allocation of the TDI to drinking-water is greater than 10%.

It is recognized that exposure from various media may vary with local circumstances. It should be emphasized, therefore, that the derived guideline values apply to a typical exposure scenario or are based on default values that may or may not be applicable for all areas. In those areas where relevant exposure data are available, authorities are encouraged to develop context-specific guideline values that are tailored to local circumstances and conditions. For example, in areas where the intake of a particular contaminant in drinking-water is known to be much greater than that from other sources (i.e., air and food), it may be appropriate to allocate a greater proportion of the TDI to drinking-water to derive a guideline value more suited to the local conditions. In addition, in cases in which guideline values are exceeded, efforts should be made to assess the contribution of other sources to total intake in order to interpret the health significance of the exceedance and to orient remedial measures to sources of exposure that are most relevant.

Significant figures

The calculated TDI is used to derive the guideline value, which is then rounded to one significant figure. In some instances, ADI values with only one significant figure set by JECFA or JMPR were used to calculate the guideline value. The guideline value was generally rounded to one significant figure to reflect the uncertainty in animal toxicity data and exposure assumptions made.

8.2.3 *Alternative approaches*

Alternative approaches being considered in the derivation of TDIs for threshold effects include the benchmark dose (BMD) (IPCS, 1994), categorical regression (IPCS, 1994) and chemical-specific adjustment factors (CSAF) (IPCS, 2001).

Benchmark dose[1]

The benchmark dose (BMD) is the lower confidence limit of the dose that produces a small increase in the level of adverse effects (e.g., 5% or 10%; Crump, 1984) to which uncertainty factors can be applied to develop a tolerable intake.

The BMD has a number of advantages over the NOAEL:

- It is derived on the basis of data from the entire dose–response curve for the critical effect rather than from the single dose group at the NOAEL (i.e., one of the few preselected dose levels).
- Use of the BMD facilitates the use and comparison of studies on the same agent or the potencies of different agents.
- The BMD can be calculated from data sets in which a NOAEL was not determined, eliminating the need for an additional uncertainty factor to be applied to the LOAEL.
- Definition of the BMD as a lower confidence limit accounts for the statistical power and quality of the data. That is, the confidence intervals around the dose–response curve for studies with small numbers of animals and, therefore, lower statistical power would be wide; similarly, confidence intervals in studies of poor quality with highly variable responses would also be wide. In either case, the wider confidence interval would lead to a lower BMD, reflecting the greater uncertainty of the database. On the other hand, narrow confidence limits (reflecting better studies) would result in higher BMDs.

Categorical regression[2]

The theory and application of categorical regression have been addressed by Hertzberg & Miller (1985), Hertzberg (1989), Guth et al. (1991) (inhalation exposure to methylisocyanate) and Farland & Dourson (1992) (oral exposure to arsenic). Data on toxicity are classified into one of several categories, such as no-observed-effect level (NOEL) or NOAEL, or others, as appropriate. These categories are then regressed on the basis of dose and, if required, duration of exposure. The result is a graph of probability of a given category of effect with dose or concentration, which is useful in the analysis of potential risks above the tolerable intake, especially for comparisons among chemicals.

Depending on the extent of the available data on toxicity, additional estimations regarding the percentage of individuals with specific adverse effects are possible. Such estimations require, however, an understanding of the mechanisms of toxicity of the critical effect, knowledge of the extrapolation between the experimental animal and humans and/or knowledge of the incidence of specific effects in humans.

Similar to the BMD, categorical regression utilizes information from the entire dose–response curve, resulting in more precise estimates of risk when compared with the current approach (NOAEL-based tolerable intakes). However, categorical

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[1] This section has been taken from IPCS (1994).

[2] This section has been taken from IPCS (1994).

regression requires more information than the current tolerable intake method, and the interpretation of the probability scale can be problematic.

Chemical-specific adjustment factors

Approaches to the derivation of TDIs are increasingly being based on understanding of a chemical's mode of action in order to reduce reliance on empirical mathematical modelling and to eliminate the need to determine whether a threshold or non-threshold approach is more appropriate. This approach provides a departure from the use of default uncertainty factors and relies on the use of quantitative toxicokinetic and toxicodynamic data and "chemical-specific adjustment factors" (CSAFs) (IPCS, 2001) to assess interspecies and interindividual extrapolations in dose/concentration–response assessment. Previously, CSAFs were called "data-derived uncertainty factors" (Renwick, 1993; IPCS, 1994). The part of the CSAF approach that is at present best developed is the use of physiologically based pharmacokinetic models to replace the default values for extrapolation between species and between routes of exposure.

8.2.4 Non-threshold chemicals

In the case of compounds considered to be genotoxic carcinogens, guideline values were normally determined using a mathematical model. Although several models exist, the linearized multistage model was generally adopted. Other models were considered more appropriate in a few cases. Guideline values presented are the concentrations in drinking-water associated with an estimated upper-bound excess lifetime cancer risk of 10^{-5} (or one additional cancer per 100 000 of the population ingesting drinking-water containing the substance at the guideline value for 70 years).

The guideline values for carcinogenic substances have been computed from hypothetical mathematical models that cannot be verified experimentally. These models do not usually take into account a number of biologically important considerations, such as pharmacokinetics, DNA repair or protection by the immune system. They also assume the validity of a linear extrapolation of very high dose exposures in test animals to very low dose exposures in humans. As a consequence, the models used are conservative (i.e., err on the side of caution). The guideline values derived using these models should be interpreted differently from TDI-based values because of the lack of precision of the models. At best, these values must be regarded as rough estimates of cancer risk. Moderate short-term exposure to levels exceeding the guideline value for carcinogens does not significantly affect the risk.

8.2.5 Data quality

The following factors were taken into account in assessing the quality and reliability of available information:

- Oral studies are preferred (in particular, drinking-water studies), using the pure substance with appropriate dosing regime and a good-quality pathology.
- The database should be sufficiently broad that all potential toxicological end-points of concern have been identified.
- The quality of the studies is such that they are considered reliable; for example, there has been adequate consideration of confounding factors in epidemiological studies.
- There is reasonable consistency between studies; the end-point and study used to derive a guideline value do not contradict the overall weight of evidence.
- For inorganic substances, there is some consideration of speciation in drinking-water.
- There is appropriate consideration of multimedia exposure in the case of epidemiological studies.

In the development of guideline values, existing international approaches were carefully considered. In particular, previous risk assessments developed by the International Programme on Chemical Safety (IPCS) in EHC monographs and CICADs, IARC, JMPR and JECFA were reviewed. These assessments were relied upon except where new information justified a reassessment, but the quality of new data was critically evaluated before it was used in any risk assessment. Where international reviews were not available, other sources of data were used in the derivation of guideline values, including published reports from peer-reviewed open literature, national reviews recognized to be of high quality, information submitted by governments and other interested parties and, to a limited extent, unpublished proprietary data (primarily for the evaluation of pesticides). Future revisions and assessments of pesticides will take place primarily through WHO/IPCS/JMPR/JECFA processes.

8.2.6 Provisional guideline values

The use and designation of provisional guideline values are outlined in Table 8.3.

For non-threshold substances, in cases in which the concentration associated with an upper-bound excess lifetime cancer risk of 10^{-5} is not feasible as a result of inade-

Table 8.3 Use and designation of provisional guideline values

Situations where a provisional guideline applies	Designation	
Significant scientific uncertainties regarding derivation of health-based guideline value	P	
Calculated guideline value is below the practical quantification level	A	*(Guideline value is set at the achievable quantification level)*
Calculated guideline value is below the level that can be achieved through practical treatment methods	T	*(Guideline value is set at the practical treatment limit)*
Calculated guideline value is likely to be exceeded as a result of disinfection procedures	D	*(Guideline value is set on the basis of health, but disinfection of drinking-water remains paramount)*

quate analytical or treatment technology, a provisional guideline value (designated A or T, respectively) is recommended at a practicable level.

8.2.7 Chemicals with effects on acceptability

Some substances of health concern have effects on the taste, odour or appearance of drinking-water that would normally lead to rejection of water at concentrations significantly lower than those of concern for health. Such substances are not normally appropriate for routine monitoring. Nevertheless, health-based guideline values may be needed – for instance, for use in interpreting data collected in response to consumer complaints. In these circumstances, a health-based summary statement and guideline value are presented in the usual way. In the summary statement, the relationship between concentrations relevant to health and those relevant to the acceptability of the drinking-water is explained. In tables of guideline values, the health-based guideline values are designated with a "C."

8.2.8 Non-guideline chemicals

Additional information on many chemicals not included in these Guidelines is available from several credible sources, including WHO EHCs and CICADs (www.who.int/pcs/index), chemical risk assessment reports from JMPR, JECFA and IARC, and published documents from a number of national sources, such as the US EPA. Although these information sources may not have been reviewed for these Guidelines, they have been peer reviewed and provide readily accessible information on the toxicology of many additional chemicals. They can help drinking-water suppliers and health officials decide upon the significance (if any) of a detected chemical and on the response that might be appropriate.

8.2.9 Mixtures

Chemical contaminants of drinking-water supplies are present with numerous other inorganic and/or organic constituents. The guideline values are calculated separately for individual substances, without specific consideration of the potential for interaction of each substance with other compounds present. The large margin of uncertainty incorporated in the majority of the guideline values is considered to be sufficient to account for potential interactions. In addition, the majority of contaminants will not be continuously present at concentrations at or near their guideline value.

For many chemical contaminants, mechanisms of toxicity are different; consequently, there is no reason to assume that there are interactions. There may, however, be occasions when a number of contaminants with similar toxicological mechanisms are present at levels near their respective guideline values. In such cases, decisions concerning appropriate action should be made, taking into consideration local circumstances. Unless there is evidence to the contrary, it is appropriate to assume that the toxic effects of these compounds are additive.

8.3 Analytical aspects

As noted above, guideline values are not set at concentrations of substances that cannot reasonably be measured. In such circumstances, provisional guideline values are set at the reasonable analytical limits.

Guidance provided in this section is intended to assist readers to select appropriate analytical methods for specific circumstances.

8.3.1 Analytical achievability

Various collections of "standard" or "recommended" methods for water analysis are published by a number of national and international agencies. It is often thought that adequate analytical accuracy can be achieved provided that all laboratories use the same standard method. Experience shows that this is not always the case, as a variety of factors may affect the accuracy of the results. Examples include reagent purity, apparatus type and performance, degree of modification of the method in a particular laboratory and the skill and care of the analyst. These factors are likely to vary both between the laboratories and over time in an individual laboratory. Moreover, the precision and accuracy that can be achieved with a particular method frequently depend upon the adequacy of sampling and nature of the sample ("matrix"). While it is not essential to use standard methods, it is important that the methods used are properly validated and precision and accuracy determined before significant decisions are made based on the results. In the case of "non-specific" variables such as taste and odour, colour and turbidity, the result is method specific, and this needs to be considered when using the data to make comparisons.

A number of considerations are important in selecting methods:

- The overriding consideration is that the method chosen is demonstrated to have the required accuracy. Other factors, such as speed and convenience, should be considered only in selecting among methods that meet this primary criterion.
- There are a number of markedly different procedures for measuring and reporting the errors to which all methods are subject. This complicates and prejudices the effectiveness of method selection, and suggestions for standardizing such procedures have been made. It is therefore desirable that details of all analytical methods are published together with performance characteristics that can be interpreted unambiguously.
- If the analytical results from one laboratory are to be compared with those from others and/or with a numerical standard, it is obviously preferable for them not to have any associated systematic error. In practice, this is not possible, but each laboratory should select methods whose systematic errors have been thoroughly evaluated and shown to be acceptably small.

A qualitative ranking of analytical methods based on their degree of technical complexity is given in Table 8.4 for inorganic chemicals and in Table 8.5 for organic chemicals. These groups of chemicals are separated, as the analytical methods used differ

Table 8.4 Ranking of complexity of analytical methods for inorganic chemicals

Ranking	Example of analytical methods
1	Volumetric method, colorimetric method
2	Electrode method
3	Ion chromatography
4	High-performance liquid chromatography (HPLC)
5	Flame atomic absorption spectrometry (FAAS)
6	Electrothermal atomic absorption spectrometry (EAAS)
7	Inductively coupled plasma (ICP)/atomic emission spectrometry (AES)
8	ICP/mass spectrometry (MS)

greatly. The higher the ranking, the more complex the process in terms of equipment and/or operation. In general, higher rankings are also associated with higher total costs. Analytical achievabilities of the chemical guideline values based on detection limits are given in Tables 8.6–8.10.

There are many kinds of field test kits that are used for compliance examinations as well as operational monitoring of drinking-water quality. Although the field test kits are generally available at relatively low prices, their analytical accuracy is generally less than that of the methods shown in Tables 8.4 and 8.5. It is therefore necessary to check the validity of the field test kit before applying it.

Table 8.5 Ranking of complexity of analytical methods for organic chemicals

Ranking	Example of analytical methods
1	HPLC
2	Gas chromatography (GC)
3	GC/MS
4	Headspace GC/MS
5	Purge-and-trap GC Purge-and-trap GC/MS

8.3.2 Analytical methods

In *volumetric titration*, chemicals are analysed by titration with a standardized titrant. The titration end-point is identified by the development of colour resulting from the reaction with an indicator, by the change of electrical potential or by the change of pH value.

Colorimetric methods are based on measuring the intensity of colour of a coloured target chemical or reaction product. The optical absorbance is measured using light of a suitable wavelength. The concentration is determined by means of a calibration curve obtained using known concentrations of the determinant. The UV method is similar to this method except that UV light is used.

For ionic materials, the ion concentration can be measured using an *ion-selective electrode*. The measured potential is proportional to the logarithm of the ion concentration.

Table 8.6 Analytical achievability for inorganic chemicals for which guideline values have been established, by source category[a]

	Field methods		Laboratory methods				
	Col	**Absor**	**IC**	**FAAS**	**EAAS**	**ICP**	**ICP/MS**
Naturally occurring chemicals							
Arsenic		#		+(H)	++□+++(H)	++(H)	+++
Barium				+	+++	+++	+++
Boron		++				++	+++
Chromium		#		+	+++	+++	+++
Fluoride	#	+	++				
Manganese	+	++		++	+++	+++	+++
Molybdenum					+	+++	+++
Selenium		#		#	+++(H)	++(H)	+
Uranium						+	+++
Chemicals from industrial sources and human dwellings							
Cadmium		#			++	++	+++
Cyanide	#	+	+				
Mercury					+		
Chemicals from agricultural activities							
Nitrate/nitrite	+++	+++	#				
Chemicals used in water treatment or materials in contact with drinking-water							
Antimony				#	++(H)	++(H)	+++
Copper	#	+++		+++	+++	+++	+++
Lead		#			+	+	++
Nickel		+		#	+	+++	++

[a] For definitions and notes to Table 8.6, see below Table 8.10.

Some organic compounds absorb UV light (wavelength 190–380 nm) in proportion to their concentration. *UV absorption* is useful for qualitative estimation of organic substances, because a strong correlation may exist between UV absorption and organic carbon content.

Atomic absorption spectrometry (AAS) is used for determination of metals. It is based on the phenomenon that the atom in the ground state absorbs the light of wavelengths that are characteristic to each element when light is passed through the atoms in the vapour state. Because this absorption of light depends on the concentration of atoms in the vapour, the concentration of the target element in the water sample is determined from the measured absorbance. The Beer-Lambert law describes the relationship between concentration and absorbance.

In *flame atomic absorption spectrometry (FAAS)*, a sample is aspirated into a flame and atomized. A light beam from a hollow cathode lamp of the same element as the target metal is radiated through the flame, and the amount of absorbed light is measured by the detector. This method is much more sensitive than other methods and free from spectral or radiation interference by co-existing elements. Pretreatment is either unnecessary or straightforward. However, it is not suitable for simultaneous analysis of many elements, because the light source is different for each target element.

Table 8.7 Analytical achievability for organic chemicals from industrial sources and human dwellings for which guideline values have been established[a]

	Col	GC	GC/PD	GC/EC	GC/ FID	GC/ FPD	GC/ TID	GC/ MS	PT- GC/MS	HPLC	HPLC/FD	HPLC/ UVPAD	EAAS	IC/FD
Benzene				++	+				+++					
Carbon tetrachloride				+					+					
Di(2-ethylhexyl)phthalate								++						
1,2-Dichlorobenzene			+++	+++					+++					
1,4-Dichlorobenzene			+++	+++					+++					
1,2-Dichloroethane				+++					++					
1,1-Dichloroethene				+++	+				+++					
1,2-Dichloroethene				++	++				+++					
Dichloromethane				#	+				+++					
Edetic acid (EDTA)								+++						
Ethylbenzene				+++	+++				+++					
Hexachlorobutadiene									+					
Nitrilotriacetic acid (NTA)		+++												
Pentachlorophenol				++					+++	+++				
Styrene				++	+				+++					
Tetrachloroethene				+++	+				+++					
Toluene					+++				+++					
Trichloroethene				+++	+				+++					+
Xylenes					+++				+++					

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[a] For definitions and notes to Table 8.7, see below Table 8.10.

Table 8.8 Analytical achievability for organic chemicals from agricultural activities for which guideline values have been established[a]

	Col	GC	GC/PD	GC/EC	GC/ FID	GC/ FPD	GC/ TID	GC/ MS	PT- GC/MS	HPLC	HPLC/FD	HPLC/ UVPAD	EAAS	IC/FD
Alachlor				□				+++						
Aldicarb												+		
Aldrin and dieldrin				+										
Atrazine								+++□						
Carbofuran							++				++			
Chlordane				+										
Chlorotoluron				□										
Cyanazine								++				+		
2,4-D				++				+++						
2,4-DB				++				++						
1,2-Dibromo-3-chloropropane				□				+++	++					
1,2-Dibromoethane								+	+					
1,2-Dichloropropane				+++					+++					
1,3-Dichloropropene				+++					+++					
Dichlorprop (2,4-DP)								+++						
Dimethoate								+++						
Endrin				+				#						
Fenoprop				+										
Isoproturon				+								+++		
Lindane				+										
MCPA				+++				+++				+++		
Mecoprop				++				++						
Methoxychlor		+++												
Metolachlor				+++										
Molinate								+++						
Pendimethalin				+++			++	+++						
Simazine					+		+	+++						
2,4,5-T			+	+++										
Terbuthylazine (TBA)								+++				++		
Trifluralin		+++						+++				+		

[a] For definitions and notes to Table 8.8, see below Table 8.10.

Table 8.9 Analytical achievability for chemicals used in water treatment or from materials in contact with water for which guideline values have been established[a]

	Col	GC	GC/PD	GC/EC	GC/ FID	GC/ FPD	GC/ TID	GC/MS	PT- GC/MS	HPLC	HPLC/FD	HPLC/ UVPAD	EAAS	IC
Disinfectants														
Monochloramine	+++													
Chlorine	+++									+++				+++
Disinfection by-products														
Bromate														+
Bromodichloromethane				+++					+++					
Bromoform				+++					+++					
Chloral hydrate				+				+						
(trichloroacetaldehyde)														
Chlorate														☐
Chlorite	☐													☐
Chloroform				+++					+++					
Cyanogen chloride														☐
Dibromoacetonitrile				☐				☐						
Dibromochloromethane				+++					+++					
Dichloroacetate				☐				☐						
Dichloroacetonitrile				+++				+						
Formaldehyde				☐				☐						
Monochloroacetate		++						++						
Trichloroacetate				☐				☐						
2,4,6-Trichlorophenol				+++				+++						
Trihalomethanes[b]				+++					+++					
Organic contaminants from treatment chemicals														
Acrylamide		+					+				+			
Epichlorohydrin				+	+				+					
Organic contaminants from pipes and fittings														
Benzo[*a*]pyrene								++			++			
Vinyl chloride				+					+					

[a] For definitions and notes to Table 8.9, see below Table 8.10.

[b] See also individual THMs.

Table 8.10 Analytical achievability for pesticides used in water for public health purposes for which guideline values have been established[a]

	Col	GC	GC/PD	GC/EC	GC/ FID	GC/ FPD	GC/ TID	GC/MS	PT- GC/MS	HPLC	HPLC/FD	HPLC/ UVPAD	EAAS	IC/FD
Chlorpyrifos				+++	+++	+	+++	+++						
DDT (and metabolites)				+++				+						
Pyriproxyfen								+++						

[a] For definitions and notes to Table 8.10, see below.

Definitions to Tables 8.6–8.10

Col	Colorimetry
Absor	Absorptiometry
GC	Gas chromatography
GC/PD	Gas chromatography photoionization detector
GC/EC	Gas chromatography electron capture
GC/FID	Gas chromatography flame ionization detector
GC/FPD	Gas chromatography flame photodiode detector
GC/TID	Gas chromatography thermal ionization detector
GC/MS	Gas chromatography mass spectrometry
PT-GC/MS	Purge-and-trap gas chromatography mass spectrometry
HPLC	High-performance liquid chromatography
HPLC/FD	High-performance liquid chromatography fluorescence detector
HPLC/ UVPAD	High-performance liquid chromatography ultraviolet photodiode array detector
EAAS	Electrothermal atomic absorption spectrometry
IC	Ion chromatography
ICP	Inductively coupled plasma
ICP/MS	Inductively coupled plasma mass spectrometry
FAAS	Flame atomic absorption spectrometry
IC/FAAS	Ion chromatography flame atomic absorption spectrometry
IC/FD	Ion chromatography fluorescence detector

Notes to Tables 8.6–8.10

+	The detection limit is between the guideline value and 1/10 of its value.
++	The detection limit is between 1/10 and 1/50 of the guideline value.
+++	The detection limit is under 1/100 of the guideline value.
#	The analytical method is available for detection of the concentration of the guideline value, but it is difficult to detect the concentration of 1/10 of the guideline value.
□	The detection method(s) is/are available for the item.
(H)	This method is applicable to the determination by conversion to their hydrides by hydride generator.

Electrothermal atomic absorption spectrometry (EAAS) is based on the same principle as FAAS, but an electrically heated atomizer or graphite furnace replaces the standard burner head for determination of metals. In comparison with FAAS, EAAS gives higher sensitivities and lower detection limits, and a smaller sample volume is required. EAAS suffers from more interference through light scattering by co-existing elements and requires a longer analysis time than FAAS.

The principle of *inductively coupled plasma/atomic emission spectrometry (ICP/AES)* for determination of metals is as follows. An ICP source consists of a flowing stream of argon gas ionized by an applied radio frequency. A sample aerosol is generated in a nebulizer and spray chamber and then carried into the plasma through an injector tube. A sample is heated and excited in the high-temperature plasma. The high temperature of the plasma causes the atoms to become excited. On returning to the ground state, the excited atoms produce ionic emission spectra. A monochromator is used to separate specific wavelengths corresponding to different elements, and a detector measures the intensity of radiation of each wavelength. A significant reduction in chemical interference is achieved. In the case of water with low pollution, simultaneous or sequential analysis is possible without special pretreatment to achieve low detection limits for many elements. This, coupled with the extended dynamic range from three digits to five digits, means that multi-element determination of metals can be achieved. ICP/AES has similar sensitivity to FAAS or EAAS.

In *inductively coupled plasma/mass spectrometry (ICP/MS)*, elements are atomized and excited as in ICP/AES, then passed to a mass spectrometer. Once inside the mass spectrometer, the ions are accelerated by high voltage and passed through a series of ion optics, an electrostatic analyser and, finally, a magnet. By varying the strength of the magnet, ions are separated according to mass/charge ratio and passed through a slit into the detector, which records only a very small atomic mass range at a given time. By varying the magnet and electrostatic analyser settings, the entire mass range can be scanned within a relatively short period of time. In the case of water with low pollution, simultaneous or sequential analysis is possible without special pretreatment to achieve low detection limits for many elements. This, coupled with the extended dynamic range from three digits to five digits, means that multi-element determination of metals can be achieved.

Chromatography is a separation method based on the affinity difference between two phases, the stationary and mobile phases. A sample is injected into a column, either packed or coated with the stationary phase, and separated by the mobile phase based on the difference in interaction (distribution or adsorption) between compounds and the stationary phase. Compounds with a low affinity for the stationary phase move more quickly through the column and elute earlier. The compounds that elute from the end of the column are determined by a suitable detector.

In *ion chromatography*, an ion exchanger is used as the stationary phase, and the eluant for determination of anions is typically a dilute solution of sodium hydrogen carbonate and sodium carbonate. Colorimetric, electrometric or titrimetric detectors can be used for determining individual anions. In suppressed ion chromatography, anions are converted to their highly conductive acid forms; in the carbonate–bicarbonate eluant, anions are converted to weakly conductive carbonic acid. The separated acid forms are measured by conductivity and identified on the basis of retention time as compared with their standards.

High-performance liquid chromatography (HPLC) is an analytical technique using a liquid mobile phase and a column containing a liquid stationary phase. Detection of the separated compounds is achieved through the use of absorbance detectors for organic compounds and through conductivity or electrochemical detectors for metallic and inorganic compounds.

Gas chromatography (GC) permits the identification and quantification of trace organic compounds. In GC, gas is used as the mobile phase, and the stationary phase is a liquid that is coated either on an inert granular solid or on the walls of a capillary column. When the sample is injected into the column, the organic compounds are vaporized and moved through the column by the carrier gas at different rates depending on differences in partition coefficients between the mobile and stationary phases. The gas exiting the column is passed to a suitable detector. A variety of detectors can be used, including flame ionization (FID), electron capture (ECD) and nitrogen–phosphorus. Since separation ability is good in this method, mixtures of substances with similar structure are systematically separated, identified and determined quantitatively in a single operation.

The *gas chromatography/mass spectrometry (GC/MS)* method is based on the same principle as the GC method, using a mass spectrometer as the detector. As the gas emerges from the end of the GC column opening, it flows through a capillary column interface into the MS. The sample then enters the ionization chamber, where a collimated beam of electrons impacts the sample molecules, causing ionization and fragmentation. The next component is a mass analyser, which uses a magnetic field to separate the positively charged particles according to their mass. Several types of separating techniques exist; the most common are quadrupoles and ion traps. After the ions are separated according to their masses, they enter a detector.

The *purge-and-trap packed-column GC/MS method* or *purge-and-trap packed-column GC* method is applicable to the determination of various purgeable organic compounds that are transferred from the aqueous to the vapour phase by bubbling purge gas through a water sample at ambient temperature. The vapour is trapped with a cooled trap. The trap is heated and backflushed with the same purge gas to desorb the compounds onto a GC column. The principles of GC or GC/MS are as referred to above.

The principle of *enzyme-linked immunosorbent assay (ELISA)* is as follows. The protein (antibody) against the chemical of interest (antigen) is coated onto the solid material. The target chemical in the water sample binds to the antibody, and a second antibody with an enzyme attached is also added that will attach to the chemical of interest. After washing to remove any of the free reagents, a chromogen is added that will give a colour reaction due to cleavage by the enzyme that is proportional to the quantity of the chemical of interest. The ELISA method can be used to determine microcystin and synthetic surfactants.

8.4 Treatment

As noted above, where a health-based guideline value cannot be achieved by reasonably practicable treatment, then the guideline value is designated as provisional and set at the concentration that can be reasonably achieved through treatment.

8.4.1 Treatment achievability

The ability to achieve a guideline value within a drinking-water supply depends on a number of factors, including:

- — the concentration of the chemical in the raw water;
- — control measures employed throughout the drinking-water system;
- — nature of the raw water (groundwater or surface water, presence of natural background and other components); and
- — treatment processes already installed.

If a guideline value cannot be met with the existing system, then additional treatment may need to be considered, or water should be obtained from alternative sources.

The cost of achieving a guideline value will depend on the complexity of any additional treatment or other control measures required. It is not possible to provide general quantitative information on the cost of achieving individual guideline values. Treatment costs (capital and operating) will depend not only on the factors identified above, but also on issues such as plant throughput; local costs for labour, civil and mechanical works, chemicals and electricity; life expectancy of the plant; and so on.

A qualitative ranking of treatment processes based on their degree of technical complexity is given in Table 8.11. The higher the ranking, the more complex the

Table 8.11 Ranking of technical complexity and cost of water treatment processes

Ranking	Examples of treatment processes
1	Simple chlorination Plain filtration (rapid sand, slow sand)
2	Pre-chlorination plus filtration Aeration
3	Chemical coagulation Process optimization for control of DBPs
4	Granular activated carbon (GAC) treatment Ion exchange
5	Ozonation
6	Advanced oxidation processes Membrane treatment

Table 8.12 Treatment achievability for naturally occurring chemicals for which guideline values have been established[a,b]

	Chlorination	Coagulation	Ion exchange	Precipitation softening	Activated alumina	Activated carbon	Ozonation	Membranes
Arsenic		+++ <0.005	+++ <0.005	+++ <0.005	+++ <0.005			+++ <0.005
Fluoride		++			+++ <1			+++ <1
Manganese	+++ <0.05	++					+++ <0.05	+++ <0.05
Selenium		++	+++ <0.01		+++ <0.01			+++ <0.01
Uranium		++	+++ <0.001	++	+++ <0.001			

[a] Symbols are as follows:
++ 50% or more removal
+++ 80% or more removal

[b] The table includes only those chemicals for which some treatment data are available. A blank entry in the table indicates either that the process is completely ineffective or that there are no data on the effectiveness of the process. For the most effective process(es), the table indicates the concentration of the chemical, in mg/litre, that should be achievable.

process in terms of plant and/or operation. In general, higher rankings are also associated with higher costs.

Tables 8.12–8.16 summarize the treatment processes that are capable of removing chemical contaminants of health significance. The tables include only those chemicals for which some treatment data are available.

These tables are provided to help inform decisions regarding the ability of existing treatment to meet guidelines and what additional treatment might need to be installed. They have been compiled on the basis of published literature, which includes mainly laboratory experiments, some pilot plant investigations and relatively few full-scale studies of water treatment processes. Consequently:

- Many of the treatments outlined are designed for larger treatment plants and may not necessarily be appropriate for smaller treatment plants or individual type treatment. In these cases, the choice of technology must be made on a case-by-case basis.
- The information is probably "best case," since the data would have been obtained under laboratory conditions or with a carefully controlled plant for the purposes of experimentation.
- Actual process performance will depend on the concentration of the chemical in the raw water and on general raw water quality. For example, chlorination and removal of organic chemicals and pesticides using activated carbon or ozonation will be impaired if there is a high concentration of natural organic matter.

Table 8.13 Treatment achievability for chemicals from industrial sources and human dwellings for which guideline values have been established[a,b]

	Air stripping	Coagulation	Ion exchange	Precipitation softening	Activated carbon	Ozonation	Advanced oxidation	Membranes
Cadmium		+++ <0.002	+++ <0.002	+++ <0.002				+++ <0.002
Mercury		+++ <0.0001		+++ <0.0001	+++ <0.0001			+++ <0.0001
Benzene	+++ <0.01				+++ <0.01	+++ <0.01		
Carbon tetrachloride	+++ <0.001	+			+++ <0.001			+++ <0.001
1,2-Dichlorobenzene	+++ <0.01				+++ <0.01	+++ <0.01		
1,4-Dichlorobenzene	+++ <0.01				+++ <0.01	+++ <0.01		
1,2-Dichloroethane	+				+++ <0.01	+	++	
1,2-Dichloroethene	+++ <0.01				+++ <0.01	+++ <0.01		
1,4-Dioxane						+++ no data		
Edetic acid (EDTA)					+++ <0.01			
Ethylbenzene	+++ <0.001	+			+++ <0.001	+++ <0.001		
Hexachlorobutadiene					+++ <0.001			
Nitrilotriacetic acid (NTA)					+++ no data			
Pentachlorophenol					+++ <0.0004			
Styrene	+++ <0.02				+++ <0.002			
Tetrachloroethene	+++ <0.001				+++ <0.001			
Toluene	+++ <0.001				+++ <0.001	+++ <0.001	+++ <0.001	
Trichloroethene	+++ <0.02				+++ <0.02	+++ <0.02	+++ <0.02	
Xylenes	+++ <0.005				+++ <0.005		+++ <0.005	

[a] Symbols are as follows:

+	Limited removal
++	50% or more removal
+++	80% or more removal

[b] The table includes only those chemicals for which some treatment data are available. A blank entry in the table indicates either that the process is completely ineffective or that there are no data on the effectiveness of the process. For the most effective process(es), the table indicates the concentration of the chemical, in mg/litre, that should be achievable.

Table 8.14 Treatment achievability for chemicals from agricultural activities for which guideline values have been established[a,b]

	Chlorination	Air stripping	Coagulation	Ion exchange	Activated carbon	Ozonation	Advanced oxidation	Membranes	Biological treatment
Nitrate				+++ <5				+++ <5	+++ <5
Nitrite	+++ <0.1					+++ <0.1	+++ <0.1		
Alachlor					+++ <0.001	++	+++ <0.001	+++ <0.001	
Aldicarb	+++ <0.001				+++ <0.001	+++ <0.001		+++ <0.001	
Aldrin/dieldrin			++		+++ <0.00002	+++ <0.00002		+++ <0.00002	
Atrazine			+		+++ <0.0001	++	+++ <0.0001	+++ <0.0001	
Carbofuran	+				+++ <0.001			+++ <0.001	
Chlordane					+++ <0.0001	+++ <0.0001			
Chlorotoluron					+++ <0.0001	+++ <0.0001			
Cyanazine					+++ <0.0001	+		+++ <0.0001	
2,4-Dichlorophenoxyacetic acid (2,4-D)			+		+++ <0.001	+++ <0.001			
1,2-Dibromo-3-chloropropane		++ <0.001			+++ <0.0001				
1,2-Dibromoethane		+++ <0.0001			+++ <0.0001				
1,2-Dichloropropane (1,2-DCP)					+++ <0.001	+		+++ <0.001	
Dimethoate	+++ <0.001				++	++			
Endrin			+		+++ <0.0002				
Isoproturon	++				+++ <0.0001	+++ <0.0001	+++ <0.0001	+++ <0.0001	
Lindane					+++ <0.0001	++			
MCPA					+++ <0.0001	+++ <0.0001			
Mecoprop					+++ <0.0001	+++ <0.0001			
Methoxychlor			++		+++ <0.0001	+++ <0.0001			
Metalochlor					+++ <0.0001	++			

continued

Table 8.14 ***Continued***

	Chlorination	Air stripping	Coagulation	Ion exchange	Activated carbon	Ozonation	Advanced oxidation	Membranes	Biological treatment
Simazine	+				+++ <0.0001	++	+++ <0.0001	+++ <0.0001	
2,4,5-T			++		+++ <0.001	+			
Terbuthylazine (TBA)			+		+++ <0.0001	++			
Trifluralin					+++ <0.0001			+++ <0.0001	

[a] Symbols are as follows:
+ Limited removal
++ 50% or more removal
+++ 80% or more removal

[b] The table includes only those chemicals for which some treatment data are available. A blank entry in the table indicates either that the process is completely ineffective or that there are no data on the effectiveness of the process. For the most effective process(es), the table indicates the concentration of the chemical, in mg/litre, that should be achievable.

- For many contaminants, potentially several different processes could be appropriate, and the choice between processes should be made on the basis of technical complexity and cost, taking into account local circumstances. For example, membrane processes can remove a broad spectrum of chemicals, but simpler and cheaper alternatives are effective for the removal of most chemicals.
- It is normal practice to use a series of unit processes to achieve desired water quality objectives (e.g., coagulation, sedimentation, filtration, GAC, chlorination). Each of these may contribute to the removal of chemicals. It may be technically and

Table 8.15 Treatment achievability for pesticides used in water for public health for which guideline values have been established[a,b]

	Chlorination	Coagulation	Activated carbon	Ozonation	Advanced oxidation	Membranes
DDT and metabolites	+	+++ <0.0001	+++ <0.0001	+	+++ <0.0001	+++ <0.0001
Pyriproxyfen			+++ <0.001			

[a] Symbols are as follows:
+ Limited removal
+++ 80% or more removal

[b] The table includes only those chemicals for which some treatment data are available. A blank entry in the table indicates either that the process is completely ineffective or that there are no data on the effectiveness of the process. For the most effective process(es), the table indicates the concentration of the chemical, in mg/litre, that should be achievable.

Table 8.16 Treatment achievability for cyanobacterial cells and cyanotoxins for which guideline values have been established[a,b,c]

H	Chlorination	Coagulation	Activated carbon	Ozonation	Advanced oxidation	Membranes
Cyanobacterial cells		+++				+++
Cyanotoxins	+++		+++	+++	+++	

[a] Chlorination or ozonation may release cyanotoxins.
[b] +++ = 80% or more removal.
[c] The table includes only those chemicals for which some treatment data are available. A blank entry in the table indicates either that the process is completely ineffective or that there are no data on the effectiveness of the process.

economically advantageous to use a combination of processes (e.g., ozonation plus GAC) to remove particular chemicals.

- The effectiveness of potential processes should be assessed using laboratory or pilot plant tests on the actual raw water concerned. These tests should be of sufficient duration to identify potential seasonal or other temporal variations in contaminant concentrations and process performance.

8.4.2 Chlorination

Chlorination can be achieved by using liquefied chlorine gas, sodium hypochlorite solution or calcium hypochlorite granules and on-site chlorine generators. Liquefied chlorine gas is supplied in pressurized containers. The gas is withdrawn from the cylinder and is dosed into water by a chlorinator, which both controls and measures the gas flow rate. Sodium hypochlorite solution is dosed using a positive-displacement electric dosing pump or gravity feed system. Calcium hypochlorite has to be dissolved in water, then mixed with the main supply. Chlorine, whether in the form of chlorine gas from a cylinder, sodium hypochlorite or calcium hypochlorite, dissolves in water to form hypochlorous acid ($HOCl$) and hypochlorite ion (OCl^-).

Different techniques of chlorination can be used, including breakpoint chlorination, marginal chlorination and superchlorination/dechlorination. Breakpoint chlorination is a method in which the chlorine dose is sufficient to rapidly oxidize all the ammonia nitrogen in the water and to leave a suitable free residual chlorine available to protect the water against reinfection from the point of chlorination to the point of use. Superchlorination/dechlorination is the addition of a large dose of chlorine to effect rapid disinfection and chemical reaction, followed by reduction of excess free chlorine residual. Removing excess chlorine is important to prevent taste problems. It is used mainly when the bacterial load is variable or the detention time in a tank is not enough. Marginal chlorination is used where water supplies are of high quality and is the simple dosing of chlorine to produce a desired level of free residual chlorine. The chlorine demand in these supplies is very low, and a breakpoint might not even occur.

Chlorination is employed primarily for microbial disinfection. However, chlorine also acts as an oxidant and can remove or assist in the removal of some chemicals – for example, decomposition of easily oxidized pesticides such as aldicarb; oxidation of dissolved species (e.g., manganese(II)) to form insoluble products that can be removed by subsequent filtration; and oxidation of dissolved species to more easily removable forms (e.g., arsenite to arsenate).

A disadvantage of chlorine is its ability to react with natural organic matter to produce THMs and other halogenated DBPs. However, by-product formation may be controlled by optimization of the treatment system.

8.4.3 Ozonation

Ozone is a powerful oxidant and has many uses in water treatment, including oxidation of organic chemicals. Ozone can be used as a primary disinfectant. Ozone gas (O_3) is formed by passing dry air or oxygen through a high-voltage electric field. The resultant ozone-enriched air is dosed directly into the water by means of porous diffusers at the base of baffled contactor tanks. The contactor tanks, typically about 5 m deep, provide 10–20 min of contact time. Dissolution of at least 80% of the applied ozone should be possible, with the remainder contained in the off-gas, which is passed through an ozone destructor and vented to the atmosphere.

The performance of ozonation relies on achieving the desired concentration after a given contact period. For oxidation of organic chemicals, such as a few oxidizable pesticides, a residual of about 0.5 mg/litre after a contact time of up to 20 min is typically used. The doses required to achieve this vary with the type of water but are typically in the range 2–5 mg/litre. Higher doses are needed for untreated waters, because of the ozone demand of the natural background organics.

Ozone reacts with natural organics to increase their biodegradability, measured as assimilable organic carbon. To avoid undesirable bacterial growth in distribution, ozonation is normally used with subsequent treatment, such as filtration or GAC, to remove biodegradable organics, followed by a chlorine residual, since it does not provide a disinfectant residual. Ozone is effective for the degradation of a wide range of pesticides and other organic chemicals.

8.4.4 Other disinfection processes

Other disinfection methods include chloramination, the use of chlorine dioxide, UV radiation and advanced oxidation processes.

Chloramines (monochloramine, dichloramine and "trichloramine," or nitrogen trichloride) are produced by the reaction of aqueous chlorine with ammonia. Monochloramine is the only useful chloramine disinfectant, and conditions employed for chloramination are designed to produce only monochloramine. Monochloramine is a less effective disinfectant than free chlorine, but it is persistent, and it is therefore an attractive secondary disinfectant for the maintenance of a stable distribution system residual.

Although historically chlorine dioxide was not widely used for drinking-water disinfection, it has been used in recent years because of concerns about THM production associated with chlorine disinfection. Typically, chlorine dioxide is generated immediately prior to application by the addition of chlorine gas or an aqueous chlorine solution to aqueous sodium chlorite. Chlorine dioxide decomposes in water to form chlorite and chlorate. As chlorine dioxide does not oxidize bromide (in the absence of sunlight), water treatment with chlorine dioxide will not form bromoform or bromate.

Use of UV radiation in potable water treatment has typically been restricted to small facilities. UV radiation, emitted by a low-pressure mercury arc lamp, is biocidal between wavelengths of 180 and 320 nm. It can be used to inactivate protozoa, bacteria, bacteriophage, yeast, viruses, fungi and algae. Turbidity can inhibit UV disinfection. UV radiation can act as a strong catalyst in oxidation reactions when used in conjunction with ozone.

Processes aimed at generating hydroxyl radicals are known collectively as advanced oxidation processes and can be effective for the destruction of chemicals that are difficult to treat using other methods, such as ozone alone. Chemicals can react either directly with molecular ozone or with the hydroxyl radical ($HO\cdot$), which is a product of the decomposition of ozone in water and is an exceedingly powerful indiscriminate oxidant that reacts readily with a wide range of organic chemicals. The formation of hydroxyl radicals can be encouraged by using ozone at high pH. One advanced oxidation process using ozone plus hydrogen peroxide involves dosing hydrogen peroxide simultaneously with ozone at a rate of approximately 0.4 mg of hydrogen peroxide per litre per mg of ozone dosed per litre (the theoretical optimum ratio for hydroxyl radical production) and bicarbonate.

8.4.5 Filtration

Particulate matter can be removed from raw waters by rapid gravity, horizontal, pressure or slow sand filters. Slow sand filtration is essentially a biological process, whereas the others are physical treatment processes.

Rapid gravity, horizontal and pressure filters can be used for direct filtration of raw water, without pretreatment. Rapid gravity and pressure filters are commonly used to filter water that has been pretreated by coagulation and sedimentation. An alternative process is direct filtration, in which coagulation is added to the water, which then passes directly onto the filter where the precipitated floc (with contaminants) is removed; the application of direct filtration is limited by the available storage within the filter to accommodate solids.

Rapid gravity filters

Rapid gravity sand filters usually consist of open rectangular tanks (usually $<100\ m^2$) containing silica sand (size range 0.5–1.0 mm) to a depth of between 0.6 and 2.0 m. The water flows downwards, and solids become concentrated in the upper layers of the bed. The flow rate is generally in the range 4–20 $m^3/m^2 \cdot h$. Treated water is collected via nozzles in the floor of the filter. The accumulated solids are removed periodically by backwashing with treated water, sometimes preceded by scouring of the sand with air. A dilute sludge that requires disposal is produced.

In addition to single-medium sand filters, dual-media or multimedia filters are used. Such filters incorporate different materials, such that the structure is from coarse to fine as the water passes through the filter. Materials of suitable density are used in order to maintain the segregation of the different layers following backwashing. A common example of a dual-media filter is the anthracite–sand filter, which typically consists of a 0.2-m-deep layer of 1.5-mm anthracite over a 0.6-m-deep layer of silica sand. Anthracite, sand and garnet can be used in multimedia filters. The advantage of dual- and multimedia filters is that there is more efficient use of the whole bed depth for particle retention – the rate of headloss development can be half that of single-medium filters, which can allow higher flow rates without increasing headloss development.

Rapid gravity filters are most commonly used to remove floc from coagulated waters (see section 8.4.7). They may also be used to reduce turbidity (including adsorbed chemicals) and oxidized iron and manganese from raw waters.

Roughing filters

Roughing filters can be applied as pre-filters prior to other processes such as slow sand filters. Roughing filters with coarse gravel or crushed stones as the filter medium can successfully treat water of high turbidity (>50 NTU). The main advantage of roughing filtration is that as the water passes through the filter, particles are removed by both filtration and gravity settling. Horizontal filters can be up to 10 m long and are operated at filtration rates of 0.3–1.0 $m^3/m^2 \cdot h$.

Pressure filters

Pressure filters are sometimes used where it is necessary to maintain head in order to eliminate the need for pumping into supply. The filter bed is enclosed in a cylindrical shell. Small pressure filters, capable of treating up to about 15 m^3/h, can be manufactured in glass-reinforced plastics. Larger pressure filters, up to 4 m in diameter, are manufactured in specially coated steel. Operation and performance are generally as described for the rapid gravity filter, and similar facilities are required for backwashing and disposal of the dilute sludge.

Slow sand filters

Slow sand filters usually consist of tanks containing sand (effective size range 0.15–0.3 mm) to a depth of between 0.5 and 1.5 m. The raw water flows downwards, and turbidity and microorganisms are removed primarily in the top few centimetres of the sand. A biological layer, known as the "schmutzdecke," develops on the surface of the filter and can be effective in removing microorganisms. Treated water is collected in underdrains or pipework at the bottom of the filter. The top few centimetres of sand containing the accumulated solids are removed and replaced periodically. Slow sand filters are operated at a water flow rate of between 0.1 and 0.3 $m^3/m^2 \cdot h$.

Slow sand filters are suitable only for low-turbidity water or water that has been pre-filtered. They are used to remove algae and microorganisms, including protozoa, and, if preceded by microstraining or coarse filtration, to reduce turbidity (including adsorbed chemicals). Slow sand filtration is effective for the removal of organics, including certain pesticides and ammonia.

8.4.6 Aeration

Aeration processes are designed to achieve removal of gases and volatile compounds by air stripping. Oxygen transfer can usually be achieved using a simple cascade or diffusion of air into water, without the need for elaborate equipment. Stripping of gases or volatile compounds, however, may require a specialized plant that provides a high degree of mass transfer from the liquid phase to the gas phase.

For oxygen transfer, cascade or step aerators are designed so that water flows in a thin film to achieve efficient mass transfer. Cascade aeration may introduce a significant headloss; design requirements are between 1 and 3 m to provide a loading of 10–30 $m^3/m^2 \cdot h$. Alternatively, compressed air can be diffused through a system of submerged perforated pipes. These types of aerator are used for oxidation and precipitation of iron and manganese.

Air stripping can be used for removal of volatile organics (e.g., solvents), some taste- and odour-causing compounds and radon. Aeration processes to achieve air stripping need to be much more elaborate to provide the necessary contact between the air and water. The most common technique is cascade aeration, usually in packed towers in which water is allowed to flow in thin films over plastic media with air blown counter-current. The required tower height and diameter are functions of the volatility and concentration of the compounds to be removed and the flow rate.

8.4.7 Chemical coagulation

Chemical coagulation-based treatment is the most common approach for treatment of surface waters and is almost always based on the following unit processes.

Chemical coagulants, usually salts of aluminium or iron, are dosed to the raw water under controlled conditions to form a solid flocculent metal hydroxide. Typical coagulant doses are 2–5 mg/litre as aluminium or 4–10 mg/litre as iron. The precipitated floc removes suspended and dissolved contaminants by mechanisms of charge neutralization, adsorption and entrapment. The efficiency of the coagulation process depends on raw water quality, the coagulant or coagulant aids used and operational factors, including mixing conditions, coagulation dose and pH. The floc is removed from the treated water by subsequent solid–liquid separation processes such as sedimentation or flotation and/or rapid or pressure gravity filtration.

Effective operation of the coagulation process depends on selection of the optimum coagulant dose and also the pH value. The required dose and pH can be determined by using small-scale batch coagulation tests, often termed "jar tests." Increasing doses of coagulant are applied to raw water samples that are stirred, then allowed to settle. The optimum dose is selected as that which achieves adequate removal of colour and turbidity; the optimum pH can be selected in a similar manner. These tests have to be conducted at a sufficient frequency to keep pace with changes in raw water quality and hence coagulant demand.

Powdered activated carbon (PAC) may be dosed during coagulation to adsorb organic chemicals such as some hydrophobic pesticides. The PAC will be removed as an integral fraction of the floc and disposed of with the waterworks sludge.

The floc may be removed by sedimentation to reduce the solids loading to the subsequent rapid gravity filters. Sedimentation is most commonly achieved in horizontal flow or floc blanket clarifiers. Alternatively, floc may be removed by dissolved air flotation, in which solids are contacted with fine bubbles of air that attach to the floc, causing them to float to the surface of the tank, where they are removed periodically as a layer of sludge. The treated water from either process is passed to rapid gravity filters (see section 8.4.5), where remaining solids are removed. Filtered water may be passed to a further stage of treatment, such as additional oxidation and filtration (for removal of manganese), ozonation and/or GAC adsorption (for removal of pesticides and other trace organics), prior to final disinfection before the treated water enters supply.

Coagulation is suitable for removal of certain heavy metals and low-solubility organic chemicals, such as certain organochlorine pesticides. For other organic chemicals, coagulation is generally ineffective, except where the chemical is bound to humic material or adsorbed onto particulates.

8.4.8 Activated carbon adsorption

Activated carbon is produced by the controlled thermalization of carbonaceous material, normally wood, coal, coconut shells or peat. This activation produces a porous material with a large surface area (500–1500 m^2/g) and a high affinity for organic compounds. It is normally used either in powdered (PAC) or in granular (GAC) form. When the adsorption capacity of the carbon is exhausted, it can be reactivated by burning off the organics in a controlled manner. However, PAC (and some GAC) is normally used only once before disposal. Different types of activated carbon have different affinities for types of contaminants.

The choice between PAC and GAC will depend upon the frequency and dose required. PAC would generally be preferred in the case of seasonal or intermittent contamination or where low dosage rates are required.

PAC is dosed as a slurry into the water and is removed by subsequent treatment processes together with the waterworks sludge. Its use is therefore restricted to surface water treatment works with existing filters. GAC in fixed-bed adsorbers is used much more efficiently than PAC dosed into the water, and the effective carbon use per water volume treated would be much lower than the dose of PAC required to achieve the same removal.

GAC is used for taste and odour control. It is normally used in fixed beds, either in purpose-built adsorbers for chemicals or in existing filter shells by replacement of sand with GAC of a similar particle size. Although at most treatment works it would be cheaper to convert existing filters rather than build separate adsorbers, use of existing filters usually allows only short contact times. It is therefore common practice to install additional GAC adsorbers (in some cases preceded by ozonation) between the rapid gravity filters and final disinfection. Most groundwater sources do not have existing filters, and separate adsorbers would need to be installed.

The service life of a GAC bed is dependent on the capacity of the carbon used and the contact time between the water and the carbon, the empty bed contact time (EBCT), controlled by the flow rate of the water. EBCTs are usually in the range 5–30 min. GACs vary considerably in their capacity for specific organic compounds, which can have a considerable effect upon their service life. A guide to capacity can be obtained from published isotherm data. Carbon capacity is strongly dependent on the water source and is greatly reduced by the presence of background organic compounds. The properties of a chemical that influence its adsorption onto activated carbon include the water solubility and octanol/water partition coefficient ($\log K_{ow}$). As a general rule, chemicals with low solubility and high $\log K_{ow}$ are well adsorbed.

Activated carbon is used for the removal of pesticides and other organic chemicals, taste and odour compounds, cyanobacterial toxins and total organic carbon.

8.4.9 Ion exchange

Ion exchange is a process in which ions of like charge are exchanged between the water phase and the solid resin phase. Water softening is achieved by cation exchange. Water is passed through a bed of cationic resin, and the calcium ions and magnesium ions in the water are replaced by sodium ions. When the ion exchange resin is exhausted (i.e., the sodium ions are depleted), it is regenerated using a solution of sodium chloride. The process of "dealkalization" can also soften water. Water is passed through a bed of weakly acidic resin, and the calcium and magnesium ions are replaced by hydrogen ions. The hydrogen ions react with the carbonate and bicarbonate ions to produce carbon dioxide. The hardness of the water is thus reduced without any increase in sodium levels. Anion exchange can be used to remove contaminants such as nitrate, which is exchanged for chloride. Nitrate-specific resins are available for this purpose.

An ion exchange plant normally consists of two or more resin beds contained in pressure shells with appropriate pumps, pipework and ancillary equipment for regeneration. The pressure shells are typically up to 4 m in diameter, containing 0.6–1.5 m depth of resin.

Cation exchange can be used for removal of certain heavy metals. Potential applications of anionic resins, in addition to nitrate removal, are for removal of arsenic and selenium species.

8.4.10 Membrane processes

The membrane processes of most significance in water treatment are reverse osmosis, ultrafiltration, microfiltration and nanofiltration. These processes have traditionally been applied to the production of water for industrial or pharmaceutical applications but are now being applied to the treatment of drinking-water.

High-pressure processes

If two solutions are separated by a semi-permeable membrane (i.e., a membrane that allows the passage of the solvent but not of the solute), the solvent will naturally pass from the lower-concentration solution to the higher-concentration solution. This process is known as osmosis. It is possible, however, to force the flow of solvent in the opposite direction, from the higher to the lower concentration, by increasing the pressure on the higher-concentration solution. The required pressure differential is known as the osmotic pressure, and the process is known as reverse osmosis.

Reverse osmosis results in the production of a treated water stream and a relatively concentrated waste stream. Typical operating pressures are in the range 15–50 bar, depending on the application. Reverse osmosis rejects monovalent ions and organics of molecular weight greater than about 50 (membrane pore sizes are less than 0.002 μm). The most common application of reverse osmosis is desalination of brackish water and seawater.

Nanofiltration uses a membrane with properties between those of reverse osmosis and ultrafiltration membranes; pore sizes are typically 0.001–0.01 μm. Nanofiltration membranes allow monovalent ions such as sodium or potassium to pass but reject a high proportion of divalent ions such as calcium and magnesium and organic molecules of molecular weight greater than 200. Operating pressures are typically about 5 bar. Nanofiltration may be effective for the removal of colour and organic compounds.

Lower-pressure processes

Ultrafiltration is similar in principle to reverse osmosis, but the membranes have much larger pore sizes (typically 0.002–0.03 μm) and operate at lower pressures. Ultrafiltration membranes reject organic molecules of molecular weight above about 800 and usually operate at pressures less than 5 bar.

Microfiltration is a direct extension of conventional filtration into the submicrometre range. Microfiltration membranes have pore sizes typically in the range 0.01–12 μm and do not separate molecules but reject colloidal and suspended material at operating pressures of 1–2 bar. Microfiltration is capable of sieving out particles greater than 0.05 μm. It has been used for water treatment in combination with coagulation or PAC to remove dissolved organic carbon and to improve permeate flux.

8.4.11 Other treatment processes

Other treatment processes that can be used in certain applications include:

- precipitation softening (addition of lime, lime plus sodium carbonate or sodium hydroxide to precipitate hardness at high pH);
- biological denitrification for removal of nitrate from surface waters;
- biological nitrification for removal of ammonia from surface waters; and
- activated alumina (or other adsorbents) for specialized applications, such as removal of fluoride and arsenic.

8.4.12 Disinfection by-products – process control measures

In attempting to control DBP concentrations, it is of paramount importance that the efficiency of disinfection is not compromised and that a suitable residual level of disinfectant is maintained throughout the distribution system.

All chemical disinfectants produce inorganic and/or organic DBPs that may be of concern.

The principal DBPs formed during chlorination are THMs, chlorinated acetic acids, chlorinated ketones and haloacetonitriles, as a result of chlorination of naturally occurring organic precursors such as humic substances. Monochloramine produces lower THM concentrations than chlorine but produces other DBPs, including cyanogen chloride.

Ozone oxidizes bromide to produce hypohalous acids, which react with precursors to form brominated THMs. A range of other DBPs, including aldehydes and carboxylic acids, may also be formed. Of particular concern is bromate, formed by oxidation of bromide. Bromate may also be present in some sources of hypochlorite, but usually at concentrations that will give rise to levels in final water that are below the guideline value.

The main by-products from the use of chlorine dioxide are chlorite ion, which is an inevitable decomposition product, and chlorate ion. Chlorate is also produced in hypochlorate as it ages.

The basic strategies that can be adopted for reducing the concentrations of DBPs are:

- changing process conditions (including removal of precursor compounds prior to application);
- using a different chemical disinfectant with a lower propensity to produce by-products with the source water;
- using non-chemical disinfection; and/or
- removing DBPs prior to distribution.

Changes to process conditions

The formation of THMs during chlorination can be reduced by removing precursors prior to contact with chlorine – for example, by installing or enhancing coagulation (this may involve using higher coagulant doses and/or lower coagulation pH than are applied conventionally). DBP formation can also be reduced by lowering the applied chlorine dose; if this is done, it must be ensured that disinfection is still effective.

The pH value during chlorination affects the distribution of chlorinated by-products. Reducing the pH lowers the THM concentration, but at the expense of increased formation of haloacetic acids. Conversely, increasing the pH reduces haloacetic acid production but leads to increased THM formation.

The formation of bromate during ozonation depends on several factors, including concentrations of bromide and ozone and the pH. It is not practicable to remove bromide from raw water, and it is difficult to remove bromate once formed, although GAC filtration has been reported to be effective under certain circumstances. Bromate formation can be minimized by using lower ozone dose, shorter contact time and a lower residual ozone concentration. Operating at lower pH (e.g., pH 6.5) followed by raising the pH after ozonation also reduces bromate formation, and addition of ammonia can also be effective. Addition of hydrogen peroxide can increase or decrease bromate formation.

Changing disinfectants

It may be feasible to change disinfectant in order to achieve guideline values for DBPs. The extent to which this is possible will be dependent on raw water quality and installed treatment (e.g., for precursor removal).

It may be effective to change from chlorine to monochloramine, at least to provide a residual disinfectant within distribution, in order to reduce THM formation and subsequent development within the distribution system. While monochloramine provides a more stable residual within distribution, it is a less powerful disinfectant and should not be used as a primary disinfectant.

Chlorine dioxide can be considered as a potential alternative to both chlorine and ozone disinfection, although it does not provide a residual effect. The main concerns with chlorine dioxide are with the residual concentrations of chlorine dioxide and the by-products chlorite and chlorate. These can be addressed by controlling the dose of chlorine dioxide at the treatment plant.

Non-chemical disinfection

UV irradiation or membrane processes can be considered as alternatives to chemical disinfection. Neither of these provides any residual disinfection, and it may be considered appropriate to add a small dose of a persistent disinfectant such as chlorine or monochloramine to act as a preservative during distribution.

8.4.13 Treatment for corrosion control

General

Corrosion is the partial dissolution of the materials constituting the treatment and supply systems, tanks, pipes, valves and pumps. It may lead to structural failure, leaks, loss of capacity and deterioration of chemical and microbial water quality. The internal corrosion of pipes and fittings can have a direct impact on the concentration of some water constituents, including lead and copper. Corrosion control is therefore an important aspect of the management of a drinking-water system for safety.

Corrosion control involves many parameters, including the concentrations of calcium, bicarbonate, carbonate and dissolved oxygen, as well as pH. The detailed requirements differ depending on water quality and the materials used in the distribution system. The pH controls the solubility and rate of reaction of most of the metal species involved in corrosion reactions. It is particularly important in relation to the formation of a protective film at the metal surface. For some metals, alkalinity (carbonate and bicarbonate) and calcium (hardness) also affect corrosion rates.

Iron

Iron is frequently used in water distribution systems, and its corrosion is of concern. While structural failure as a result of iron corrosion is rare, water quality problems (e.g., "red water") can arise as a result of excessive corrosion of iron pipes. The corrosion of iron is a complex process that involves the oxidation of the metal, normally by dissolved oxygen, ultimately to form a precipitate of iron(III). This leads to the formation of tubercules on the pipe surface. The major water quality factors that determine whether the precipitate forms a protective scale are pH and alkalinity. The concentrations of calcium, chloride and sulfate also influence iron corrosion. Successful control of iron corrosion has been achieved by adjusting the pH to the range 6.8–7.3, hardness and alkalinity to at least 40 mg/litre (as calcium carbonate), oversaturation with calcium carbonate of 4–10 mg/litre and a ratio of alkalinity to $Cl^- + SO_4^{2-}$ of at least 5 (when both are expressed as calcium carbonate).

Silicates and polyphosphates are often described as "corrosion inhibitors," but there is no guarantee that they will inhibit corrosion in water distribution systems. However, they can complex dissolved iron (in the iron(II) state) and prevent its precipitation as visibly obvious red "rust." These compounds may act by masking the effects of corrosion rather than by preventing it. Orthophosphate is a possible corrosion inhibitor and, like polyphosphates, is used to prevent "red water."

Lead

Lead corrosion (plumbosolvency) is of particular concern. Lead piping is still common in old houses in some countries, and lead solders have been used widely for jointing copper tube. The solubility of lead is governed by the formation of lead carbonates as pipe deposits. Wherever practicable, lead pipework should be replaced.

The solubility of lead increases markedly as the pH is reduced below 8 because of the substantial decrease in the equilibrium carbonate concentration. Thus, plumbosolvency tends to be at a maximum in waters with a low pH and low alkalinity, and a useful interim control procedure pending pipe replacement is to increase the pH to 8.0–8.5 after chlorination, and possibly to dose orthophosphate.

Lead can corrode more rapidly when it is coupled to copper. The rate of such galvanic corrosion is faster than that of simple oxidative corrosion, and lead concentrations are not limited by the solubility of the corrosion products. The rate of galvanic corrosion is affected principally by chloride concentration. Galvanic corrosion is less easily controlled but can be reduced by dosing zinc in conjunction with orthophosphate and by adjustment of pH.

Treatment to reduce plumbosolvency usually involves pH adjustment. When the water is very soft (less than 50 mg of calcium carbonate per litre), the optimum pH is about 8.0–8.5. Alternatively, dosing with orthophosphoric acid or sodium orthophosphate might be more effective, particularly when plumbosolvency occurs in non-acidic waters.

Copper

The corrosion of copper pipework and hot water cylinders can cause blue water, blue or green staining of bathroom fittings and, occasionally, taste problems. Copper tubing may be subject to general corrosion, impingement attack and pitting corrosion.

General corrosion is most often associated with soft, acidic waters; waters with pH below 6.5 and hardness of less than 60 mg of calcium carbonate per litre are very aggressive to copper. Copper, like lead, can enter water by dissolution of the corrosion product, basic copper carbonate. The solubility is mainly a function of pH and total inorganic carbon. Solubility decreases with increase in pH, but increases with increase in concentrations of carbonate species. Raising the pH to between 8 and 8.5 is the usual procedure to overcome these difficulties.

Impingement attack is the result of excessive flow velocities and is aggravated in soft water at high temperature and low pH.

The pitting of copper is commonly associated with hard groundwaters having a carbon dioxide concentration above 5 mg/litre and high dissolved oxygen. Surface waters with organic colour may also be associated with pitting corrosion. Copper pipes can fail by pitting corrosion, which involves highly localized attacks leading to perforations with negligible loss of metal. Two main types of attack are recognized. Type I pitting affects cold water systems (below 40 °C) and is associated, particularly, with hard borehole waters and the presence of a carbon film in the bore of the pipe, derived from the manufacturing process. Tubes that have had the carbon removed by cleaning are immune from Type I pitting. Type II pitting occurs in hot water systems (above 60 °C) and is associated with soft waters. A high proportion of general and pitting corrosion problems are associated with new pipe in which a protective oxide layer has not yet formed.

Brass

The main corrosion problem with brasses is dezincification, which is the selective dissolution of zinc from duplex brass, leaving behind copper as a porous mass of low mechanical strength. Meringue dezincification, in which a voluminous corrosion product of basic zinc carbonate forms on the brass surface, largely depends on the ratio of chloride to alkalinity. Meringue dezincification can be controlled by maintaining a low zinc to copper ratio (1 : 3 or lower) and by keeping pH below 8.3.

General dissolution of brass can also occur, releasing metals, including lead, into the water. Impingement attack can occur under conditions of high water velocity with waters that form poorly protective corrosion product layers and that contain large amounts of dissolved or entrained air.

Zinc

The solubility of zinc in water is a function of pH and total inorganic carbon concentrations; the solubility of basic zinc carbonate decreases with increase in pH and concentrations of carbonate species. For low-alkalinity waters, an increase of pH to 8.5 should be sufficient to control the dissolution of zinc.

With galvanized iron, the zinc layer initially protects the steel by corroding preferentially. In the long term, a protective deposit of basic zinc carbonate forms. Protective deposits do not form in soft waters where the alkalinity is less than 50 mg/litre as calcium carbonate or waters containing high carbon dioxide concentrations (>25 mg/litre as carbon dioxide), and galvanized steel is unsuitable for these waters. The corrosion of galvanized steel increases when it is coupled with copper tubing.

Nickel

Nickel may arise due to the leaching of nickel from new nickel/chromium-plated taps. Low concentrations may also arise from stainless steel pipes and fittings. Nickel leaching falls off over time. An increase of pH to control corrosion of other materials should also reduce leaching of nickel.

Concrete and cement

Concrete is a composite material consisting of a cement binder in which an inert aggregate is embedded. Cement is primarily a mixture of calcium silicates and aluminates together with some free lime. Cement mortar, in which the aggregate is fine sand, is used as a protective lining in iron and steel water pipes. In asbestos–cement pipe, the aggregate is asbestos fibres. Cement is subject to deterioration on prolonged exposure to aggressive water, due either to the dissolution of lime and other soluble compounds or to chemical attack by aggressive ions such as chloride or sulfate, and this may result in structural failure. Cement contains a variety of metals that can be leached into the water. Aggressiveness to cement is related to the “aggressivity index,” which has been used specifically to assess the potential for the dissolution of concrete. A pH of 8.5 or higher may be necessary to control cement corrosion.

Characterizing corrosivity

Most of the indices that have been developed to characterize the corrosion potential of waters are based on the assumption that water with a tendency to deposit a calcium carbonate scale on metal surfaces will be less corrosive. The Langelier Index (LI) is the difference between the actual pH of a water and its "saturation pH," this being the pH at which a water of the same alkalinity and calcium hardness would be at equilibrium with solid calcium carbonate. Waters with positive LI are capable of depositing calcium carbonate scale from solution.

There is no corrosion index that applies to all materials, and corrosion indices, particularly those related to calcium carbonate saturation, have given mixed results. The parameters related to calcium carbonate saturation status are, strictly speaking, indicators of the tendency to deposit or dissolve calcium carbonate (calcite) scale, not indicators of the "corrosivity" of a water. For example, there are many waters with negative LI that are non-corrosive and many with positive LI that are corrosive. Nevertheless, there are many documented instances of the use of saturation indices for corrosion control based on the concept of laying down a protective "eggshell" scale of calcite in iron pipes. In general, waters with high pH, calcium and alkalinity are less corrosive, and this tends to be correlated with a positive LI.

The ratio of the chloride and sulfate concentrations to the bicarbonate concentration (Larson ratio) has been shown to be helpful in assessing the corrosiveness of water to cast iron and steel. A similar approach has been used in studying zinc dissolution from brass fittings – the Turner diagram.

Water treatment for corrosion control

To control corrosion in water distribution networks, the methods most commonly applied are adjusting pH, increasing the alkalinity and/or hardness or adding corrosion inhibitors, such as polyphosphates, silicates and orthophosphates. The quality and maximum dose to be used should be in line with specifications for such water treatment chemicals. Although pH adjustment is an important approach, its possible impact on other aspects of water supply technology, including disinfection, must always be taken into account.

It is not always possible to achieve the desired values for all parameters. For example, the pH of hard waters cannot be increased too much, or softening will occur. The application of lime and carbon dioxide to soft waters can be used to increase both the calcium concentration and the alkalinity to at least 40 mg/litre as calcium carbonate.

8.5 Guideline values for individual chemicals, by source category

8.5.1 Naturally occurring chemicals

There are a number of sources of naturally occurring chemicals in drinking-water. All natural water contains a range of inorganic and organic chemicals. The former derive from the rocks and soil through which water percolates or over which it flows. The latter derive from the breakdown of plant material or from algae and other microorganisms that grow in the water or on sediments. Most of the naturally occurring chemicals for which guideline values have been derived or that have been considered for guideline value derivation are inorganic. Only one, microcystin-LR, a toxin produced by cyanobacteria or blue-green algae, is organic; it is discussed in section 8.5.6.

The approach to dealing with naturally occurring chemicals will vary according to the nature of the chemical and the source. For inorganic contaminants that arise from rocks and sediments, it is important to screen possible water sources to determine whether the source is suitable for use or whether it will be necessary to treat the water to remove the contaminants of concern along with microbial contaminants. In some cases, where a number of sources may be available, dilution or blending of the water containing high levels of a contaminant with a water containing much lower levels may achieve the desired result.

A number of the most important chemical contaminants (i.e., those that have been shown to cause adverse health effects as a consequence of exposure through drinking-water) fall into the category of naturally occurring chemicals. Some naturally occurring chemicals have other primary sources and are therefore discussed in other sections of this chapter.

Guideline values have not been established for the chemicals listed in Table 8.17 for the reasons indicated in the table. Summary statements are included in chapter 12.

Guideline values have been established for the chemicals listed in Table 8.18, which meet the criteria for inclusion. Summary statements are included for each in chapter 12.

8.5.2 Chemicals from industrial sources and human dwellings

Chemicals from industrial sources can reach drinking-water directly from discharges or indirectly from diffuse sources arising from the use and disposal of materials and products containing the chemical. In some cases, inappropriate handling and disposal may lead to contamination, e.g., degreasing agents that are allowed to reach ground-

Table 8.17 Naturally occurring chemicals for which guideline values have not been established

Chemical	Reason for not establishing a guideline value	Remarks
Chloride	Occurs in drinking-water at concentrations well below those at which toxic effects may occur	May affect acceptability of drinking-water (see chapter 10)
Hardness	Occurs in drinking-water at concentrations well below those at which toxic effects may occur	May affect acceptability of drinking-water (see chapter 10)
Hydrogen sulfide	Occurs in drinking-water at concentrations well belowthose at which toxic effects may occur	May affect acceptability of drinking-water (see chapter 10)
pH	Values in drinking-water are well below those at which toxic effects may occur	An important operational water quality parameter
Sodium	Occurs in drinking-water at concentrations well below those at which toxic effects may occur	May affect acceptability of drinking-water (see chapter 10)
Sulfate	Occurs in drinking-water at concentrations well below those at which toxic effects may occur	May affect acceptability of drinking-water (see chapter 10)
Total dissolved solids (TDS)	Occurs in drinking-water at concentrations well below those at which toxic effects may occur	May affect acceptability of drinking-water (see chapter 10)

Table 8.18 Guideline values for naturally occurring chemicals that are of health significance in drinking-water

Chemical	Guideline value[a] (mg/litre)	Remarks
Arsenic	0.01 (P)	
Barium	0.7	
Boron	0.5 (T)	
Chromium	0.05 (P)	For total chromium
Fluoride	1.5	Volume of water consumed and intake from other sources should be considered when setting national standards
Manganese	0.4 (C)	
Molybdenum	0.07	
Selenium	0.01	
Uranium	0.015 (P, T)	Only chemical aspects of uranium addressed

[a] P = provisional guideline value, as there is evidence of a hazard, but the available information on health effects is limited; T = provisional guideline value because calculated guideline value is below the level that can be achieved through practical treatment methods, source protection, etc.; C = concentrations of the substance at or below the health-based guideline value may affect the appearance, taste or odour of the water, resulting in consumer complaints.

water. Some of these chemicals, particularly inorganic substances, may also be encountered as a consequence of natural contamination, but this may also be a by-product of industrial activity, such as mining, that changes drainage patterns. Many of these chemicals are used in small industrial units within human settlements, and, particularly where such units are found in groups of similar enterprises, they may be a significant source of pollution. Petroleum oils are widely used in human settlements, and improper handling or disposal can lead to significant pollution of surface water and groundwater. Where plastic pipes are used, the smaller aromatic molecules in petroleum oils can sometimes penetrate the pipes where they are surrounded by earth soaked in the oil, with subsequent pollution of the local water supply.

A number of chemicals can reach water as a consequence of disposal of general household chemicals; in particular, a number of heavy metals may be found in domestic wastewater. Where wastewater is treated, these will usually partition out into the sludge. Some chemicals that are widely used both in industry and in materials used in a domestic setting are found widely in the environment, e.g., di(2-ethylhexyl)phthalate, and these may be found in water sources, although usually at low concentrations.

Some chemicals that reach drinking-water from industrial sources or human settlements have other primary sources and are therefore discussed in other sections of this chapter. Where latrines and septic tanks are poorly sited, these can lead to contamination of drinking-water sources with nitrate (see section 8.5.3).

Identification of the potential for contamination by chemicals from industrial activities and human dwellings requires assessment of activities in the catchment and of the risk that particular contaminants may reach water sources. The primary approach to addressing these contaminants is prevention of contamination by encouraging good practices. However, if contamination has occurred, then it may be necessary to consider the introduction of treatment.

Table 8.19 Chemicals from industrial sources and human dwellings excluded from guideline value derivation

Chemical	Reason for exclusion
Beryllium	Unlikely to occur in drinking-water

The chemical listed in Table 8.19 has been excluded from guideline value derivation, as a review of the literature on occurrence and/or credibility of occurrence in drinking-water has shown evidence that it does not occur in drinking-water.

Guideline values have not been established for the chemicals listed in Table 8.20 for the reasons indicated in the table. Summary statements for each are included in chapter 12.

Guideline values have been established for the chemicals listed in Table 8.21, which meet all of the criteria for inclusion. Summary statements are included in chapter 12.

8.5.3 Chemicals from agricultural activities

Chemicals are used in agriculture on crops and in animal husbandry. Nitrate may be present as a consequence of tillage when there is no growth to take up nitrate released from decomposing plants, from the application of excess inorganic or organic fertilizer and in slurry from animal production. Most chemicals that may arise from agriculture are pesticides, although their presence will depend on many factors, and not all pesticides are used in all circumstances or climates. Contamination can result from application and subsequent movement following rainfall or from inappropriate disposal methods.

Some pesticides are also used in non-agricultural circumstances, such as the control of weeds on roads and railway lines. These pesticides are also included in this section.

Table 8.20 Chemicals from industrial sources and human dwellings for which guideline values have not been established

Chemical	Reason for not establishing a guideline value
Dichlorobenzene, 1,3-	Toxicological data are insufficient to permit derivation of health-based guideline value
Dichloroethane, 1,1-	Very limited database on toxicity and carcinogenicity
Di(2-ethylhexyl)adipate	Occurs in drinking-water at concentrations well below those at which toxic effects may occur
Hexachlorobenzene	Occurs in drinking-water at concentrations well below those at which toxic effects may occur
Monochlorobenzene	Occurs in drinking-water at concentrations well below those at which toxic effects may occur, and health-based value would far exceed lowest reported taste and odour threshold
Trichlorobenzenes (total)	Occur in drinking-water at concentrations well below those at which toxic effects may occur, and health-based value would exceed lowest reported odour threshold
Trichloroethane, 1,1,1-	Occurs in drinking-water at concentrations well below those at which toxic effects may occur

Table 8.21 Guideline values for chemicals from industrial sources and human dwellings that are of health significance in drinking-water

Inorganics	**Guideline value (mg/litre)**	**Remarks**
Cadmium	0.003	
Cyanide	0.07	
Mercury	0.001	For total mercury (inorganic plus organic)
Organics	**Guideline value[a] (µg/litre)**	**Remarks**
Benzene	10[b]	
Carbon tetrachloride	4	
Di(2-ethylhexyl)phthalate	8	
Dichlorobenzene, 1,2-	1000 (C)	
Dichlorobenzene, 1,4-	300 (C)	
Dichloroethane, 1,2-	30[b]	
Dichloroethene, 1,1-	30	
Dichloroethene, 1,2-	50	
Dichloromethane	20	
Edetic acid (EDTA)	600	Applies to the free acid
Ethylbenzene	300 (C)	
Hexachlorobutadiene	0.6	
Nitrilotriacetic acid (NTA)	200	
Pentachlorophenol	9[b] (P)	
Styrene	20 (C)	
Tetrachloroethene	40	
Toluene	700 (C)	
Trichloroethene	70 (P)	
Xylenes	500 (C)	

[a] P = provisional guideline value, as there is evidence of a hazard, but the available information on health effects is limited; C = concentrations of the substance at or below the health-based guideline value may affect the appearance, taste or odour of the water, leading to consumer complaints.

[b] For non-threshold substances, the guideline value is the concentration in drinking-water associated with an upper-bound excess lifetime cancer risk of 10^{-5} (one additional cancer per 100 000 of the population ingesting drinking-water containing the substance at the guideline value for 70 years). Concentrations associated with estimated upper-bound excess lifetime cancer risks of 10^{-4} and 10^{-6} can be calculated by multiplying and dividing, respectively, the guideline value by 10.

Guideline values have not been established for the chemicals listed in Table 8.22, as a review of the literature on occurrence and/or credibility of occurrence in drinking-water has shown evidence that the chemicals do not occur in drinking-water.

Guideline values have not been established for the chemicals listed in Table 8.23 for the reasons indicated in the table. Summary statements are included in chapter 12.

Guideline values have been established for the chemicals listed in Table 8.24, which meet the criteria for inclusion. Summary statements are included in chapter 12.

8.5.4 Chemicals used in water treatment or from materials in contact with drinking-water

Chemicals are used in water treatment and may give rise to residuals in the final water. In some cases, such as monochloramine and chlorine, this is intentional, and their

Table 8.22 Chemicals from agricultural activities excluded from guideline value derivation

Chemical	Reason for exclusion
Amitraz	Degrades rapidly in the environment and is not expected to occur at measurable concentrations in drinking-water supplies
Chlorobenzilate	Unlikely to occur in drinking-water
Chlorothalonil	Unlikely to occur in drinking-water
Cypermethrin	Unlikely to occur in drinking-water
Diazinon	Unlikely to occur in drinking-water
Dinoseb	Unlikely to occur in drinking-water
Ethylene thiourea	Unlikely to occur in drinking-water
Fenamiphos	Unlikely to occur in drinking-water
Formothion	Unlikely to occur in drinking-water
Hexachlorocyclohexanes (mixed isomers)	Unlikely to occur in drinking-water
MCPB	Unlikely to occur in drinking-water
Methamidophos	Unlikely to occur in drinking-water
Methomyl	Unlikely to occur in drinking-water
Mirex	Unlikely to occur in drinking-water
Monocrotophos	Has been withdrawn from use in many countries and is unlikely to occur in drinking-water
Oxamyl	Unlikely to occur in drinking-water
Phorate	Unlikely to occur in drinking-water
Propoxur	Unlikely to occur in drinking-water
Pyridate	Not persistent and only rarely found in drinking-water
Quintozene	Unlikely to occur in drinking-water
Toxaphene	Unlikely to occur in drinking-water
Triazophos	Unlikely to occur in drinking-water
Tributyltin oxide	Unlikely to occur in drinking-water
Trichlorfon	Unlikely to occur in drinking-water

presence confers a direct benefit to the consumer. Some arise as unwanted by-products of the disinfection process (see Table 8.25) and some as residuals from other parts of the treatment process, such as coagulation. Some may arise as contaminants in treatment chemicals, and others may arise as contaminants in, or as corrosion products from, materials used as pipes or in other parts of the drinking-water system. Some chemicals used in water treatment (e.g., fluoride) or in materials in contact with drinking-water (e.g., styrene) have other primary sources and are therefore discussed in detail in other sections of this chapter.

The approach to monitoring and management is preferably through control of the material or chemical, and this is covered in more detail in section 4.2. It is also important to optimize treatment processes and to ensure that such processes remain optimized in order to control residuals of chemicals used in treatment and to control the formation of DBPs.

Guideline values have not been established for the chemicals listed in Table 8.26 for the reasons indicated in the table. Summary statements are included in chapter 12.

Table 8.23 Chemicals from agricultural activities for which guideline values have not been established

Chemical	Reason for not establishing a guideline value
Ammonia	Occurs in drinking-water at concentrations well below those at which toxic effects may occur
Bentazone	Occurs in drinking-water at concentrations well below those at which toxic effects may occur
Dichloropropane, 1,3-	Data insufficient to permit derivation of health-based guideline value
Diquat	Rarely found in drinking-water, but may be used as an aquatic herbicide for the control of free-floating and submerged aquatic weeds in ponds, lakes and irrigation ditches
Endosulfan	Occurs in drinking-water at concentrations well below those at which toxic effects may occur
Fenitrothion	Occurs in drinking-water at concentrations well below those at which toxic effects may occur
Glyphosate and AMPA	Occurs in drinking-water at concentrations well below those at which toxic effects may occur
Heptachlor and heptachlor epoxide	Occurs in drinking-water at concentrations well below those at which toxic effects may occur
Malathion	Occurs in drinking-water at concentrations well below those at which toxic effects may occur
Methyl parathion	Occurs in drinking-water at concentrations well below those at which toxic effects may occur
Parathion	Occurs in drinking-water at concentrations well below those at which toxic effects may occur
Permethrin	Occurs in drinking-water at concentrations well below those at which toxic effects may occur
Phenylphenol, 2- and its sodium salt	Occurs in drinking-water at concentrations well below those at which toxic effects may occur
Propanil	Readily transformed into metabolites that are more toxic; a guideline value for the parent compound is considered inappropriate, and there are inadequate data to enable the derivation of guideline values for the metabolites

Guideline values have been established for the chemicals listed in Table 8.27, which meet the criteria for inclusion. Summary statements are included in chapter 12.

8.5.5 Pesticides used in water for public health purposes

Some pesticides are used for public health purposes, including the addition to water to control the aquatic larval stages of insects of public health significance (e.g., mosquitos for the control of malaria and typhus). There are currently four insecticide compounds and a bacterial larvicide recommended by WHO (under WHOPES) for addition to drinking-water as larvicides: temephos, methoprene, pyriproxyfen, permethrin and *Bacillus thuringiensis israelensis.* Of these, only pyriproxyfen has been reviewed to date. Other insecticides that are not recommended for addition to water for public health purposes by WHOPES but may be used in some countries as aquatic larvicides, or have been used as such in the past, include chlorpyrifos and DDT.

Table 8.24 Guideline values for chemicals from agricultural activities that are of health significance in drinking-water

Non-pesticides	Guideline value[a] (mg/litre)	Remarks
Nitrate (as NO_3^-)	50	Short-term exposure
Nitrite (as NO_2^-)	3	Short-term exposure
	0.2 (P)	Long-term exposure

Pesticides used in agriculture	Guideline value[a] (μg/litre)	Remarks
Alachlor	20[b]	
Aldicarb	10	Applies to aldicarb sulfoxide and aldicarb sulfone
Aldrin and dieldrin	0.03	For combined aldrin plus dieldrin
Atrazine	2	
Carbofuran	7	
Chlordane	0.2	
Chlorotoluron	30	
Cyanazine	0.6	
2,4-D (2,4-dichlorophenoxyacetic acid)	30	Applies to free acid
2,4-DB	90	
1,2-Dibromo-3-chloropropane	1[b]	
1,2-Dibromoethane	0.4[b] (P)	
1,2-Dichloropropane (1,2-DCP)	40 (P)	
1,3-Dichloropropene	20[b]	
Dichlorprop	100	
Dimethoate	6	
Endrin	0.6	
Fenoprop	9	
Isoproturon	9	
Lindane	2	
MCPA	2	
Mecoprop	10	
Methoxychlor	20	
Metolachlor	10	
Molinate	6	
Pendimethalin	20	
Simazine	2	
2,4,5-T	9	
Terbuthylazine	7	
Trifluralin	20	

[a] P = provisional guideline value, as there is evidence of a hazard, but the available information on health effects is limited.

[b] For substances that are considered to be carcinogenic, the guideline value is the concentration in drinking-water associated with an upper-bound excess lifetime cancer risk of 10^{-5} (one additional cancer per 100 000 of the population ingesting drinking-water containing the substance at the guideline value for 70 years). Concentrations associated with estimated upper-bound excess lifetime cancer risks of 10^{-4} and 10^{-6} can be calculated by multiplying and dividing, respectively, the guideline value by 10.

In considering those pesticides that may be added to water used for drinking-water for purposes of protection of public health, every effort should be made not to develop guidelines that are unnecessarily stringent as to impede their use. This approach enables a suitable balance to be achieved between the protection of drinking-water

Table 8.25 Disinfection by-products present in disinfected waters (from IPCS, 2000)

Disinfectant	Significant organohalogen products	Significant inorganic products	Significant non-halogenated products
Chlorine/ hypochlorous acid	THMs, haloacetic acids, haloacetonitriles, chloral hydrate, chloropicrin, chlorophenols, *N*-chloramines, halofuranones, bromohydrins	chlorate (mostly from hypochlorite use)	aldehydes, cyanoalkanoic acids, alkanoic acids, benzene, carboxylic acids
Chlorine dioxide		chlorite, chlorate	unknown
Chloramine	haloacetonitriles, cyanogen chloride, organic chloramines, chloramino acids, chloral hydrate, haloketones	nitrate, nitrite, chlorate, hydrazine	aldehydes, ketones
Ozone	bromoform, monobromoacetic acid, dibromoacetic acid, dibromoacetone, cyanogen bromide	chlorate, iodate, bromate, hydrogen peroxide, hypobromous acid, epoxides, ozonates	aldehydes, ketoacids, ketones, carboxylic acids

quality and the control of insects of public health significance. However, it is stressed that every effort should be made to keep overall exposure and the concentration of any larvicide as low as possible.

As for the other groups of chemicals discussed in this chapter, this category is not clear-cut. It includes pesticides that are extensively used for purposes other than public health protection – for example, agricultural purposes, in the case of chlorpyrifos.

Guideline values that have been derived for these larvicides are provided in Table 8.28. Summary statements are included in chapter 12.

8.5.6 Cyanobacterial toxins

Cyanobacteria (see also section 11.5) occur widely in lakes, reservoirs, ponds and slow-flowing rivers. Many species are known to produce toxins, i.e., "cyanotoxins," a number of which are of concern for health. Cyanotoxins vary in structure and may be found within cells or released into water. There is wide variation in the toxicity of recognized cyanotoxins (including different structural variants within a group, e.g., microcystins), and it is likely that further toxins remain unrecognized.

The toxins are classified, according to their mode of action, as hepatotoxins (microcystins and cylindrospermopsins), neurotoxins (anatoxin-a, saxitoxins and anatoxin-a(S)) and irritants or inflammatory agents (lipopolysaccharides). The hepatotoxins are produced by various species within the genera *Microcystis*, *Planktothrix*, *Anabaena*, *Aphanizomenon*, *Nodularia*, *Nostoc*, *Cylindrospermopsis* and *Umezakia*. The cyanotoxins occurring most frequently in elevated concentrations (i.e., >1 μg/litre) seem to be microcystins (oligopeptides) and cylindrospermopsin (an alkaloid), whereas the cyanobacterial neurotoxins appear to occur in high concentrations only occasionally.

Table 8.26 Chemicals used in water treatment or materials in contact with drinking-water for which guideline values have not been established

Chemical	Reason for not establishing a guideline value
Disinfectants	
Chlorine dioxide	Rapid breakdown of chlorine dioxide; also, the chlorite provisional guideline value is protective for potential toxicity from chlorine dioxide
Dichloramine	Available data inadequate to permit derivation of health-based guideline value
Iodine	Available data inadequate to permit derivation of health-based guideline value, and lifetime exposure to iodine through water disinfection is unlikely
Silver	Available data inadequate to permit derivation of health-based guideline value
Trichloramine	Available data inadequate to permit derivation of health-based guideline value
Disinfection by-products	
Bromochloroacetate	Available data inadequate to permit derivation of health-based guideline value
Bromochloroacetonitrile	Available data inadequate to permit derivation of health-based guideline value
Chloroacetones	Available data inadequate to permit derivation of health-based guideline values for any of the chloroacetones
Chlorophenol, 2-	Available data inadequate to permit derivation of health-based guideline value
Chloropicrin	Available data inadequate to permit derivation of health-based guideline value
Dibromoacetate	Available data inadequate to permit derivation of health-based guideline value
Dichlorophenol, 2,4-	Available data inadequate to permit derivation of health-based guideline value
Monobromoacetate	Available data inadequate to permit derivation of health-based guideline value
MX	Occurs in drinking-water at concentrations well below those at which toxic effects may occur
Trichloroacetonitrile	Available data inadequate to permit derivation of health-based guideline value
Contaminants from treatment chemicals	
Aluminium	Owing to limitations in the animal data as a model for humans and the uncertainty surrounding the human data, a health-based guideline value cannot be derived; however, practicable levels based on optimization of the coagulation process in drinking-water plants using aluminium-based coagulants are derived: 0.1 mg/litre or less in large water treatment facilities, and 0.2 mg/litre or less in small facilities
Iron	Not of health concern at concentrations normally observed in drinking-water, and taste and appearance of water are affected at concentrations below the health-based value
Contaminants from pipes and fittings	
Asbestos	No consistent evidence that ingested asbestos is hazardous to health
Dialkyltins	Available data inadequate to permit derivation of health-based guideline values for any of the dialkyltins
Fluoranthene	Occurs in drinking-water at concentrations well below those at which toxic effects may occur
Inorganic tin	Occurs in drinking-water at concentrations well below those at which toxic effects may occur
Zinc	Not of health concern at concentrations normally observed in drinking-water, but may affect the acceptability of water

Table 8.27 Guideline values for chemicals used in water treatment or materials in contact with drinking-water that are of health significance in drinking-water

Disinfectants	Guideline value[a] (mg/litre)	Remarks
Chlorine	5 (C)	For effective disinfection, there should be a residual concentration of free chlorine of ≥0.5 mg/litre after at least 30 min contact time at pH <8.0
Monochloramine	3	

Disinfection by-products	Guideline value[a] (μg/litre)	Remarks
Bromate	10[b] (A, T)	
Bromodichloromethane	60[b]	
Bromoform	100	
Chloral hydrate (trichloroacetaldehyde)	10 (P)	
Chlorate	700 (D)	
Chlorite	700 (D)	
Chloroform	200	
Cyanogen chloride	70	For cyanide as total cyanogenic compounds
Dibromoacetonitrile	70	
Dibromochloromethane	100	
Dichloroacetate	50 (T, D)	
Dichloroacetonitrile	20 (P)	
Formaldehyde	900	
Monochloroacetate	20	
Trichloroacetate	200	
Trichlorophenol, 2,4,6-	200[b] (C)	
Trihalomethanes		The sum of the ratio of the concentration of each to its respective guideline value should not exceed 1

Contaminants from treatment chemicals	Guideline value[a] (μg/litre)	Remarks
Acrylamide	0.5[b]	
Epichlorohydrin	0.4 (P)	

Contaminants from pipes and fittings	Guideline value[a] (μg/litre)	Remarks
Antimony	20	
Benzo[*a*]pyrene	0.7[b]	
Copper	2000	Staining of laundry and sanitary ware may occur below guideline value
Lead	10	
Nickel	20 (P)	
Vinyl chloride	0.3[b]	

[a] P = provisional guideline value, as there is evidence of a hazard, but the available information on health effects is limited; A = provisional guideline value because calculated guideline value is below the practical quantification level; T = provisional guideline value because calculated guideline value is below the level that can be achieved through practical treatment methods, source control, etc.; D = provisional guideline value because disinfection is likely to result in the guideline value being exceeded; C = concentrations of the substance at or below the health-based guideline value may affect the appearance, taste or odour of the water, causing consumer complaints.

[b] For substances that are considered to be carcinogenic, the guideline value is the concentration in drinking-water associated with an upper-bound excess lifetime cancer risk of 10^{-5} (one additional cancer per 100 000 of the population ingesting drinking-water containing the substance at the guideline value for 70 years). Concentrations associated with estimated upper-bound excess lifetime cancer risks of 10^{-4} and 10^{-6} can be calculated by multiplying and dividing, respectively, the guideline value by 10.

Table 8.28 Guideline values for pesticides used in water for public health purposes that are of health significance in drinking-water

Pesticides used in water for public health purposes[a]	Guideline value (μg/litre)
Chlorpyrifos	30
DDT and metabolites	1
Pyriproxyfen	300

[a] Only pyriproxyfen is recommended by WHOPES for addition to water for public health purposes.

Table 8.29. Guideline values for cyanotoxins that are of health significance in drinking-water

	Guideline value[a] (μg/litre)	Remarks
Microcystin-LR	1 (P)	For total microcystin-LR (free plus cell-bound)

[a] P = provisional guideline value, as there is evidence of a hazard, but the available information on health effects is limited.

Cyanotoxins can reach concentrations potentially hazardous to human health primarily in situations of high cell density through excessive growth, sometimes termed “bloom” events. These occur in response to elevated concentrations of nutrients (phosphorus and sometimes nitrogen) and may be triggered by conditions such as water body stratification and sufficiently high temperature. Blooms tend to recur in the same water bodies. Cells of some cyanobacterial species may accumulate at the surface as scums or at the theromocline of thermally stratified reservoirs. Such accumulations may develop rapidly, and they may be of short duration. In many circumstances, blooms and accumulations are seasonal.

A variety of resource protection and source management actions are available to decrease the probability of bloom occurrence, and some treatment methods, including filtration and chlorination, are available for removal of cyanobacteria and cyanotoxins. Filtration can effectively remove cyanobacterial cells and, with that, often a high share of the toxins. Oxidation through ozone or chlorine at sufficient concentrations and contact times can effectively remove most cyanotoxins dissolved in water.

Chemical analysis of cyanotoxins is not the preferred focus of routine monitoring. The preferred approach is monitoring of source water for evidence of blooms, or bloom-forming potential, and increased vigilance where such events occur. Analysis of cyanotoxins requires time, equipment and expertise, and quantitative analysis of some cyanotoxins is hampered by the lack of analytical standards. However, rapid methods, such as ELISA and enzyme assays, are becoming available for a small number, e.g., microcystins.

Chemical analysis of cyanotoxins is useful for assessing the efficacy of treatment and preventive strategies, i.e., as validation of control measures in a WSP (see chapter 4). While guideline values are derived where sufficient data exist, they are primarily intended to inform setting targets for control measures.

A provisional guideline value has been established for microcystin-LR, which meets the criteria for inclusion (see Table 8.29). Microcystin-LR is one of the most toxic of more than 70 structural variants of microcystin. Although, on a global scale, it appears to be one of the most widespread microcystins, in many regions it is not the most commonly occurring variant, and others may well be less toxic. If the provisional guideline value for microcystin-LR is used as a surrogate for their assessment and for setting targets, this serves as a worst-case estimate. A more detailed discussion of using "concentration equivalents" or "toxicity equivalents" for relating microcystins to microcystin-LR is given in Chorus & Bartram (1999).