

Chapter 15: Treatment processes, disinfection

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15.1 Introduction

To comply with the bacterial criteria of the *Drinking-water Standards for New Zealand 2005 revised 2008* (DWSNZ), all water supplies must be disinfected (section 4 of DWSNZ), except for bore waters that are shown to be secure (section 4.5 of DWSNZ). Refer to Chapter 3: Source Waters, section 3.2 for a discussion on demonstrating security of bore water. Some disinfection processes can also be used to achieve protozoal compliance.

The microbiological quality of drinking-water is the factor of most universal concern regarding the acceptability of a water for human consumption. The impact of poor microbiological quality on public health usually becomes evident to consumers much more rapidly than do the consequences of elevated levels of chemical contaminants of health significance. Consuming a glass of drinking-water containing disease-causing micro-organisms may affect one's health within a short time, whereas the chemical MAVs are based on the possible effects of an individual drinking two litres a day for 70 years.

Good microbiological quality of water at the consumer's tap is most reliably achieved by ensuring that the water entering the distribution system is microbiologically safe, and that there is a residual disinfectant in the distribution system to minimise the impact of any regrowth or contamination that enters the distribution system.

The ideal disinfectant should:

- effectively inactivate pathogens over a range of physical and chemical conditions
- produce a disinfectant residual which is stable and easily measured
- produce no undesirable by-products
- be easily generated, safe to handle, and suitable for widespread use
- be cost-effective
- be aesthetically acceptable.

No disinfectant presently in use meets all these requirements. Some compromises have to be made, and the characteristics of the particular supply and its water quality will govern the relative importance of these factors. Although secure bore waters do not need to be disinfected to ensure that safe water is entering the distribution system, without a disinfecting residual, the risk from subsequent contamination in the distribution system is increased. This increased risk is reflected in the criteria used for the allocation of grades during the water supply grading programme.

Where a water is treated by a disinfectant alone, total reliance is being placed on the disinfecting ability of that disinfectant to achieve safe drinking-water. More complete treatment takes advantage of other processes to aid in removing micro-organisms from the water, thereby increasing the number of barriers to infection and reducing the demands made on the microbial inactivation rates of the disinfectant. The benefit of multiple barriers is applied when allowing protozoal credits for some treatment processes to be added.

The most commonly used disinfectant, both in New Zealand and overseas, is chlorine, and the term chlorination is often used interchangeably with disinfection. The use of alternative disinfectants such as ozone, chlorine dioxide, and ultraviolet light has increased in recent years, mainly because they can also inactivate *Cryptosporidium* oocysts. These disinfectants will probably not displace chlorine because of the advantage in maintaining a FAC residual through the distribution system. They may also reduce the formation of the health-significant disinfection by-products associated with the use of chlorine in waters containing significant levels of natural organic matter. It is possible to maintain a chlorine dioxide residual throughout the distribution system, but often the dose required to do this results in the chlorite by-product exceeding its MAV of 0.8 mg/L, see section 15.5.3. WHO (2004b) discusses treatment processes suitable for pathogen control.

The EPA in Ireland (2011) produced their Water Treatment Manual: Disinfection. Water UK (2010) has summarised some check points for disinfection processes. DWI (2011) has prepared a list of disinfectants approved for use in water supplies in the UK.

The formation of disinfection by-products linked to chlorine can be reduced by improved chlorination practices, selection of different raw water sources, reduction in the levels of organic matter in the water prior to chlorination, or the use of alternative disinfectants. All disinfectants, except ultraviolet light, for which research has still to be undertaken, produce their own by-products of health significance. It is important, therefore, that the consequences of the use of an alternative disinfectant, especially with regard to its effect on the quality of the water to be treated, are investigated before resources are invested in its use.

In Peru (Anderson 1991) concerns about chlorine disinfection by-products led to the authorities discontinuing chlorination, which resulted in a major cholera epidemic spreading via the water supply. Regli et al (1993) concluded:

“the risk of death from known pathogens in untreated water is 100 to 1000 times greater than risk of cancer from known disinfection by-products in chlorinated drinking water, and the risk of illness from pathogens in untreated surface water is 10 000 to 1 000 000 times greater than risk of cancer from disinfection by-products in chlorinated drinking water”.

Note also that a microbiological problem can be caused in a matter of hours, whereas chemical MAVs are based on drinking 2 litres of water a day for a lifetime. Note further that turning a chlorinator off because of perceived issues related to oxidation of iron and manganese (for example), or the public's dislike of the taste/odour, is inviting microbiological problems.

Some process variation is normal and expected; however, too much variability can result in disinfection failures, leading to waterborne disease outbreaks. An objective of the DWSNZ, therefore, is to keep process variability within acceptable limits. Understanding the causes of process variations should prevent recurrences.

The following sections provide background information about disinfection and disinfectants that will act as a basic guide to their selection and use.

Risk management issues related to the disinfection processes covered in this chapter are discussed in the:

- MoH Public Health Risk Management Plan Guide PHRMP Ref: P7.1: Treatment Processes – Chlorine Disinfection
- MoH Public Health Risk Management Plan Guide PHRMP Ref: P7.2: Treatment Processes – Chlorine Dioxide Disinfection
- MoH Public Health Risk Management Plan Guide PHRMP Ref: P7.3: Treatment Processes – Ozone Disinfection
- MoH Public Health Risk Management Plan Guide PHRMP Ref: P7.4: Treatment Processes – Ultraviolet Irradiation Disinfection
- MoH Public Health Risk Management Plan Guide PHRMP Ref: P8.1: Treatment Processes – pH Adjustment
- MoH Public Health Risk Management Plan Guide PHRMP Ref: P11: Treatment Processes – Plant Construction and Operation.

Refer to Chapter 13: Treatment Processes: Coagulation and Filtration, section 13.1: Introduction, for a discussion on keeping records of all chemicals used in water treatment.

The 2008 DWSNZ include a new section, section 5.17: Alternative processes: treatment compliance criteria, whereby water suppliers may apply to the Ministry of Health to have other treatment processes assessed for a log credit rating. This approach, which is explained more fully in section 8.4.5 of the Guidelines, allows water suppliers to apply for a log credit rating (or a variation to the prescribed log credits) for a treatment plant or process:

- a) not covered in sections 5.1–5.16 of the DWSNZ
- b) that performs demonstrably better than its compliance criteria
- c) that performs to a lesser, but reliable, level than specified in its compliance criteria.

See <http://www.awwa.org/files/Resources/Standards/StandardsSpreadsheet.xls> for a list of AWWA Standards and Manuals covering disinfection, and the chemicals used for disinfection.

15.2 Disinfection effectiveness

A number of factors influence the effectiveness of disinfection. Some are applicable to all disinfectants, while others are more specific.

Bacteria

Reliable testing of pathogenic bacteria is a slow and expensive process for monitoring the microbiological quality of a water on a frequent basis. Therefore an indicator bacterium is used to assess bacterial quality, see Chapter 5: Microbiological Quality: section 5.3 for information about indicator organisms. The maximum acceptable value (MAV) for bacteria is less than 1 *E. coli* per 100 mL.

Testing for *E. coli* performs checks on the effectiveness of bacterial disinfection. Although the presence of a disinfectant residual does not guarantee that the water is microbiologically safe, it does greatly improve the likelihood that the water will be satisfactory. Frequent monitoring of the disinfectant dosage and its residual is therefore important as it provides a rapid and cheap means of supplementing the results of the less frequent microbiological sampling. Accurate methods of measuring the disinfectant residual are therefore important, and these are discussed in each of the sections dedicated to the individual disinfectants.

Measurement of the chlorine (or chlorine dioxide) residual only where it leaves the treatment plant is insufficient. In most instances the residual continues to decay as the water passes through the distribution system. This is in part due to both on-going reactions with impurities in the water and with substances adhering to, or growing on, the distribution system pipes.

Chlorine (or chlorine dioxide) residual measurements therefore need to be made occasionally at the most distant point in the distribution system. This will allow residuals at the extremes of the distribution system to be estimated from residual measurements at the plant. Changes in the disinfectant demand of the raw water will upset this relationship, and free available chlorine (FAC) measurements at the distribution system extremities should be made more frequently when significant changes in water quality occur. Some allowance for water quality changes can be made by operating with an FAC near the top end of the acceptable range.

Viruses

The DWSNZ do not have a MAV for viruses. However, it is considered that drinking-water with less than 1 *E. coli* per 100 mL and with a residual of at least 0.2 mg/L of free available chlorine (FAC) should be effective in inactivating viruses, see Chapter 7: Virological Compliance, section 7.6 for a limited discussion on C.t values.

Protozoa

The drinking-water MAV for total pathogenic protozoa is less than 1 infective (oo)cyst per 100 litres. Checks on the effectiveness of protozoal disinfection cannot be performed routinely by testing for *Giardia* or *Cryptosporidium*. Therefore the DWSNZ have defined a set of criteria for each treatment process that is known to remove or inactivate protozoa, refer to Chapter 8: Protozoa Compliance. These include chemical coagulation with filtration, some filtration processes, and some disinfection processes. The coagulation/filtration and filtration processes are discussed in their relevant treatment chapters, Chapters 13 and 14. Disinfection processes used to inactivate protozoa are discussed in this chapter.

15.2.1 C.t values

In a good quality water (if the pH and temperature are fairly consistent, and if the disinfectant mixes with the water efficiently), the extent to which a microbial population is inactivated depends on the concentration of the disinfectant and the time the micro-organisms are exposed to it. After the water has been dosed with disinfectant the number of viable organisms remaining is expected to decrease exponentially with time. In practice, these ideal conditions are not maintained, and there are deviations from theoretical behaviour.

It has been found experimentally that the contact time, t , required to achieve a 99.6 to 100 percent inactivation of micro-organisms is related to the concentration, C , of disinfectant used, by the equation:

$$t = \text{constant} \times C^n$$

Reported values for n range from 0.5 to 1.8 for most aqueous disinfectants. Generally, however, n approximates 1, and the equation is simplified to:

$$C \times t = \text{constant.}$$

Although this relationship is an approximation, and there are deviations from it, an estimate of the constant, or C.t value, is useful:

- C.t values provide an indication of the strength of the disinfectant; for the same micro-organism, strong disinfectants possess low C.t values and poor disinfectants require high C.t values
- for the same disinfectant and different organisms, C.t values give a measure of the resistance of different organisms to that disinfectant
- required contact times to achieve the required percentage inactivation at a particular disinfectant concentration can be calculated from C.t values. Viewed differently, the concentration required to achieve inactivation within a target contact time can be calculated.

The C.t values for inactivation of *Cryptosporidium* by chlorine dioxide and ozone appear in Tables 5.5 and 5.6 respectively in DWSNZ 2005. C.t tables for chlorine and *Giardia* were in the DWSNZ 1995.

As an example of how to use C.t tables, consider the calculation for inactivating pathogenic protozoa using ozone. Table 5.6 in the DWSNZ shows that to earn 3 log credits using ozone at 15°C, the C.t value is 19 min.mg/L. That means if the retention time in the ozone reactor is 19 minutes, the residual at the point of measurement must be at least 1 mg/L ozone. Or for a retention time of 9.5 minutes, the residual must be 2 mg/L.

15.2.2 Disinfectant concentration

The higher the concentration of the disinfectant residual in the water the more rapidly inactivation is achieved. Using Table 5.5 in the DWSNZ for 3 logs inactivation of *Cryptosporidium* oocysts by chlorine dioxide, we see that the C.t value at 15°C is 536 min.mg/L. So if the residual leaving the treatment plant is 0.3 mg/L the contact time needs to have been about 30 hours (ie, 536/0.3 minutes), but this reduces to nine hours if the residual is 1.0 mg/L. Note that C is the residual, not the dose. Table 5.5 covers temperatures 1 to 25°C; USEPA (2009) includes <1 and 30°.

For disinfection efficiency, high disinfectant concentrations are desirable because they will ensure rapid microbial inactivation. However, the possible toxicity of the disinfectant, its impact on the taste and smell of the water, and any production of health significant by-products from its chemical reactions, need to be taken into consideration. Often, relatively long contact times are available that allow the use of low disinfectant concentrations and a reduction in the adverse effects of the disinfectant.

15.2.3 Nature of the disinfectant

The disinfecting power of a disinfectant varies with the disinfectant. Using C.t values for a qualitative estimation of disinfecting ability, the following order of disinfecting strength, from strongest to weakest, is generally true for most micro-organisms:

- 1 ozone
- 2 chlorine dioxide
- 3 chlorine
- 4 chloramines.

For UV disinfection, a parameter similar to C.t value provides an indication of disinfecting ability of the unit, but in this instance C is the UV dose (see section 15.5.5).

Table 15.1 (Hoff 1986, in WHO 2004), which summarises C.t values that have been determined for a number of micro-organisms and a series of disinfectants, demonstrates this approximate ranking. What is evident from the table is that the ranking is only approximate and that it may change with the organism concerned, and with temperature and pH.

Table 15.1: C.t value ranges for 99 percent (2 log) inactivation of various micro-organisms by disinfectants at 5°C

| Micro-organism | Free chlorine pH 6–7 | Pre-formed chloramine pH 8–9 | Chlorine dioxide pH 6–7 | Ozone pH 6–7 |
|------------------------------|-------------------------|---------------------------------|----------------------------|-----------------|
| <i>E. coli</i> | 0.034–0.05 | 95–180 | 0.4–0.75 | 0.02 |
| poliovirus 1 | 1.1–2.5 | 768–3740 | 0.2–6.7 | 0.1–0.2 |
| rotavirus | 0.01–0.05 | 3806–6470 | 0.2–2.2 | 0.006–0.6 |
| phage f ₂ | 0.08–0.18 | – | – | – |
| <i>G. intestinalis</i> cysts | 47–> 150 | – | – | 0.5–0.6 |
| <i>G. muris</i> cysts | 30–630 | – | 7.2–18.5 | 1.8–2.0 |

Later data have become available. Some C.t values are similar, others quite different. The values depend on the contact time, pH, temperature, turbidity, the age or condition of the organisms, the ammonia and natural organic matter concentrations in the water, and basic test methodology. A safety factor has been incorporated in some C.t values, being the difference between experimental data and compliance values. Some test results refer to bacteria or viruses without stating which species were tested; in these situations it is often data from the more resistant members of the group that are quoted. To update Table 15.1, some later data from WHO (2004) have been included in the relevant disinfectant sections. WHO states that their data apply to micro-organisms in suspension, not embedded in particles or in biofilm.

15.2.4 Type of micro-organisms present

There are three main groups of pathogenic (disease-causing) micro-organisms that are of importance in potable waters in New Zealand. These are bacteria, viruses, and protozoal cysts or oocysts. Generally speaking, the resistance of these organisms to disinfectants decreases in the order: (oo)cysts are more resistant than viruses, which are more resistant than bacteria. Resistance to disinfectants also varies from species to species in each group.

Certain bacteria show a high level of resistance to disinfection processes. Spore forming bacteria such as *Bacillus* or *Clostridium* are highly resistant when disseminated as spores. Acid-fast and partially acid-fast bacteria such as *Mycobacterium* and *Nocardia* can also be highly resistant to chlorine disinfection. One study showed that nearly all of the bacteria surviving chlorine disinfection were Gram positive or acid fast, possibly because Gram-positive bacteria have thicker walls than Gram-negative ones (WHO 2004b).

The disease caused by the micro-organisms is as a result of ingestion. Diseases caused by inhalation of water while showering or due to faulty maintenance in some air conditioning systems, can be caused by *Legionella*, but are not covered in the DWSNZ; these are covered by other legislation such as the Building Act. However, a datasheet has been prepared for *Legionella*.

Cyanobacteria can also cause illness due to ingestion of their toxins. It is generally inadvisable to employ disinfectants to control cyanobacteria as their cells break up on death resulting in the release of the toxins. Oxidising disinfectants can, however, be used to destroy toxins present in the water, after any cells have been removed, see Chapter 9: Cyanobacteria Compliance.

15.2.5 pH

The impact of pH on disinfection depends on the disinfectant. For some disinfectants, such as chlorine, disinfecting efficiency is strongly pH dependent because the form of the disinfectant in the water changes with pH, see section 15.5.1. This is why the DWSNZ refer to FACE (free available chlorine equivalent) when discussing inactivation of bacteria by chlorination in water leaving the treatment plant.

Tables 12.1–12.6 in *Drinking-water Standards for New Zealand 1995* took this into account by providing C.t values for a number of pH ranges, and it can be seen that much longer contact times are required for the same degree of inactivation of *Giardia* at high pH compared with low pH.

Slight pH effects are noted for other disinfectants, despite there being no chemical change in the disinfectant. In these cases, the pH level may affect the susceptibility of the organism to the disinfectant.

15.2.6 Temperature

Disinfection processes (chemical and UV light) behave in many respects as chemical reactions. Higher temperatures therefore bring about an increase in the effectiveness of disinfection, in the absence of complicating factors. Conversely, the high doses or contact times needed to inactivate protozoa in very cold water may render the process uneconomic. For example, to gain 3 log credits using ozone, the C.t at 5°C is four times that required at 20°C.

15.2.7 Water quality

Water quality can have a major impact on the disinfection process in a number of ways.

Micro-organisms are able to adsorb on to or become occluded in suspended particulate matter, which affords them protection from disinfecting agents. Treatment processes should therefore reduce turbidity to as low a level as possible before the disinfectant is added. That is why turbidity requirements are specified as part of the bacterial and protozoal compliance criteria for disinfectants in the DWSNZ.

Dissolved and particulate constituents in the water may consume the disinfectant. These constituents make up the chemical disinfectant demand. The disinfectant demand is important because it is the disinfectant residual in the water, eg, the concentration of free available chlorine, not the disinfectant dose that determines the efficacy of a disinfectant. Sufficient disinfectant must therefore be added to the water to allow for the disinfectant demand reactions to occur, and still ensure that an adequate disinfecting residual is present.

For chemical disinfectants that are not intended to operate with a residual entering the distribution system, ie, ozone, this increased demand still requires a high dose in order to satisfy the C.t.

Some dissolved and particulate constituents in the water may absorb or scatter UV light so that less UV reaches the intensity meter. This too requires an increased dose to compensate. Some substances eg, lime or iron and manganese, can plate out on the UV appliance, thereby reducing the amount of UV light that enters the water flowing through.

Disinfectant demand reactions may produce substances that are undesirable for health reasons but this should not be a reason for stopping disinfection (section 15.1 and 15.4), or they may adversely affect the power of the disinfectant by destroying it, or by converting it to a less biocidal compound, eg, the formation of chloramines (see sections 15.5.1 and 15.5.2).

Because of the bearing that the water quality has on the disinfection process, the point at which the disinfectant is added in the treatment process is important. As a general rule, the later in the process the disinfectant is added, the higher the quality of the water it will be treating and the fewer the accompanying problems. Disinfectant consumption is lower, and hence so are treatment costs. Further, disinfection by-products are minimised and tastes and odours should be reduced.

Algae may plague some treatment plants at certain times of the year, or there may be problems with the development of other microbiological growths in the plant. Under these circumstances pre-oxidation/disinfection may need to be used, but other ways of eliminating biological problems should be sought before turning to pretreatment with disinfectants, because of the possible release of toxins or taste and odour compounds from algae killed by the disinfectant.

15.2.8 Regrowth

Regrowth of micro-organisms in a distribution system may occur, even after disinfection. This is encouraged by nutrients in the water, elevated temperatures and long retention times. Some disinfectants, in their role as oxidants (eg, ozone), may exacerbate the problem of regrowth by converting complex natural organic matter in the raw water to smaller organic molecules that are more readily assimilated by micro-organisms.

The presence of a disinfecting residual is sometimes insufficient to control regrowth, see Chapter 16: The Distribution System. Micro-organisms adsorbed to the walls of distribution system pipes can be protected from disinfectant residuals in much the same way as organisms absorbed into or adsorbed on to turbidity particles. Adequate disinfectant residuals may be present in distribution systems, and bacterial counts in the bulk water generally low. However, occasionally, clumps of bacteria that are growing on the pipe walls may slough off into the bulk water and produce high, intermittent bacterial counts. See also Chapter 5: Microbiological Quality, section 5.5.

15.2.9 Disinfectant mixing and retention time

The effectiveness of the disinfection process is reduced if the hydraulics of the treatment plant do not allow adequate mixing of the disinfectant with the water, and hence with the micro-organisms. Poor mixing may result in the micro-organisms not being exposed to the disinfectant concentration, or for the required time, intended in the system design. Both will result in the inactivation rate being less than expected.

The disinfectant contact time (t), also referred to as T_{10} in the *Guidance Manual for Compliance with the Filtration and Disinfection Requirements for Public Water Systems Using Surface Water* (USEPA 1991),¹ is an estimate of the detention time within a basin or treatment unit at which 90 percent of the water passing through the unit is retained within the basin or treatment unit. T_{10} can be determined through a tracer study (using dye, salt or lithium dilution testing) or estimated based on the theoretical detention time and baffling factor.

The theoretical detention time is the time that the water is in a basin, pipe, or unit process assuming perfect plug flow. Perfect plug flow assumes no short-circuiting within the basin, pipe, or unit process. The theoretical detention time is calculated by dividing the volume of the contact system based by the flow.

The volume of each contact basin, pipe, or unit process is used to calculate t . Some water treatment plants use the final water storage for some or all of the contact time. These can have fluctuating water levels that affect the volume. Allowance must be made for this. There are three options:

- 1 volumes can be based on the minimum volume that can occur in the treatment unit. This approach is the most conservative
- 2 volumes can be based on the actual volume realised in the treatment unit during peak hourly flow if adequate information is available to identify the actual volume
- 3 volumes can be based on the lowest volume realised in the treatment unit for that day.

¹ This reference was taken from the text of USEPA 2003d; another part of USEPA (2003) attributes it to AWWA 1991.

Tracer studies can be expensive so baffle factors have been developed that allow the detention time of a basin, pipe, or unit process to be estimated. Baffle factors were developed based on numerous tracer studies of basins with different sizes and configurations. Appendix C of the SWTR Guidance Manual covers this in detail. This was a 1991 publication; a lot of the same material was republished in the LT1ESWTR Disinfection Profiling and Benchmarking Technical Guidance Manual, which is available on the internet (USEPA 2003d); Chapter 4 and Appendix G are particularly useful.

Table 15.2: Baffle factors for use in measuring detention time

| Baffle condition | Baffle factor | Baffle description |
|------------------------|---------------|---|
| Unbaffled (mixed flow) | 0.1 | None, agitated basin, very low length to width ratio, high inlet and outlet flow velocities. |
| Poor | 0.3 | Single or multiple unbaffled inlets and outlets, no intra-basin baffles. |
| Average | 0.5 | Baffled inlet or outlet with some intra-basin baffles. |
| Superior | 0.7 | Perforated inlet baffle, serpentine or perforated intrabasin baffles, outlet weir or perforated launders. |
| Perfect (plug flow) | 1.0 | Very high length to width ratio (pipeline flow), perforated inlet, outlet, and intra-basin baffles. |

From USEPA 2003d, see Figure 15.1 for pictorial examples.

The retention time (t, in minutes) can be calculated once the theoretical detention time (in minutes) and baffle factor are known:

$$\text{retention time (t)} = \text{theoretical detention time} \times \text{baffle factor}$$

Long lengths of pipe (plug flow) before the first consumer offer excellent conditions for an effective contact time, because the chance of short-circuiting is almost nil. Once the pipe widens to the dimensions of a tank, areas of low flow and dead space develop see Figure 15.1. This means that some existing tanks with a low length/width ratio need to have appropriately designed baffles fitted to attain the optimum effectiveness achievable with the available volume, also see Stevenson (1995).

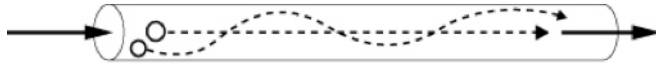
Full, rapid mixing is especially important for short contact disinfectants such as ozone and UV light where there is no opportunity for prolonged contact to overcome poor initial mixing, as there is with disinfectants that provide a disinfecting residual.

There is the potential with an inadequately mixed chloramination process for taste and odour products to be formed, particularly dichloramine, see section 15.5.2.

An alternative approach to using lithium, salt or dye is to take advantage of chemicals already being used, such as fluoride or chlorine, either after the fluoride or chlorine had been turned off, or by monitoring a stepped change in dosage. The flow rate should be kept constant for the duration of the test. Ideally, tracer tests should be performed for a range of flow rates, and the duration of a tracer test is three times the theoretical hydraulic detention time. See USEPA (1999a) and EPA (2011) for further information. Appendix D in USEPA (1999a) includes a worked example of measuring contact time using fluoride dosage.

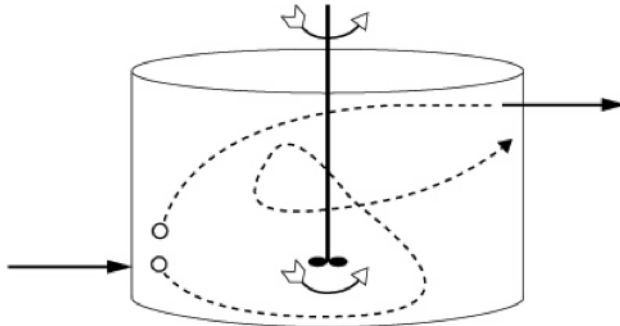
Figure 15.1: Baffle characteristics of a pipe and tank

(a) Plug flow in a pipe – baffling factor = 1.0



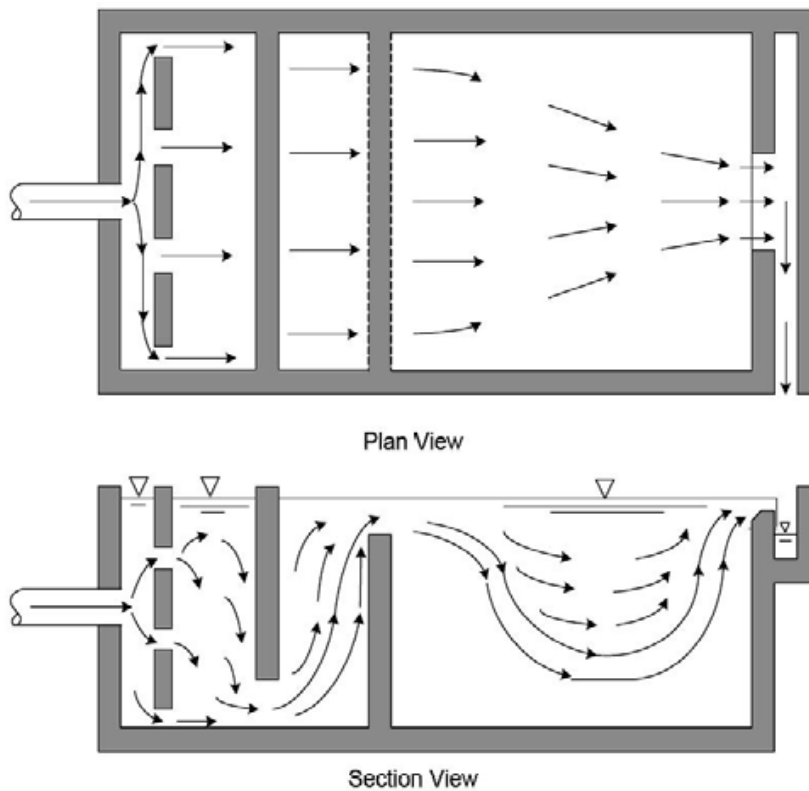
This pipe demonstrates a plug flow condition in which all of the material sent through the pipe discharges at the theoretical hydraulic detention time of the pipe.

(b) A tank with no baffling – baffling factor = 0.1



This unbaffled basin demonstrates short-circuiting in which some of the material entering the basin would come out almost immediately, while other material that enters at the same time will be detained for a longer period of time. Short-circuiting occurs in basins with poor baffling.

(c) An average mixing tank



Average baffling conditions. A good contact tank will prevent jetting at the inlet, will distribute flow across the full width and depth, and prevent streaming at the outlet. From USEPA (1999a), which includes drawings and assessments of various designs of mixing tanks.

15.3 Choice of disinfectant

The choice of disinfectant depends on the source and quality of the raw water, any other water treatment processes installed, and the types of organisms that need to be inactivated. Some towns allow the public to influence the choice, usually on subjective issues.

The main disinfection process used in New Zealand is chlorination, for reasons of cost, reliability in inactivating bacteria (and most probably viruses), and its ability to provide a disinfectant residual throughout the distribution system. Other methods that are available include chloramine, chlorine dioxide, ultraviolet light, hydrogen peroxide, and ozone. Although not widely used in New Zealand, these alternative disinfectants have been used for one or more of the following reasons:

- improved disinfection efficacy
- reduction in the formation of disinfection by-products
- inactivation of protozoa
- other benefits to the treatment process (eg, reduction in taste and odours).

However, the choice of alternative disinfectants needs to be considered carefully as they all have advantages and disadvantages. For example ultraviolet light, hydrogen peroxide and ozone do not provide a residual disinfection effect, with the result that numbers of heterotrophic bacteria may actually increase after treatment. Heterotrophic bacteria are described in Chapter 5: Microbiological Quality, section 5.3.6: Indicators of general quality.

An understanding of the effects that the expected variations in water quality, such as temperature, pH, and the organic matter content, will have on the effectiveness of the disinfectant is imperative when planning and designing a disinfection system. All of these factors will affect system operations, such as disinfectant concentration/contact time and the mixing regime. Variations should be accounted for during design in order to maximise disinfection efficiency and to improve the aesthetic qualities of the water after disinfection.

Generally there is no disinfection system available that meets all of the ideal operational needs, so a compromise between certain features is required. Many supplies use two disinfectants: UV light for protozoa and chlorine for bacteria/viruses.

The most appropriate disinfectant for a water supply, and the accompanying treatment processes that are required, eventually have to be judged on a case-by-case basis. As a general guide, consideration should be given to the following:

- the need to augment the disinfection process with physical treatment or chemical coagulation to aid the removal of disinfectant-resistant organisms, and to reduce the levels of suspended particulate matter which may shield micro-organisms from disinfecting agents
- failing that, the ability of the disinfectant to satisfactorily inactivate pathogens known (or likely) to be present in the source water within the restrictions of acceptable disinfectant residual and available contact time

- the need to treat the water with chemical coagulation and subsequent filtration to reduce the levels of colloidal and dissolved matter that absorb or consume the disinfectant
- the need to treat the water to remove precursors from which disinfection by-products might be formed
- the impact of the disinfectant on the concentration of organic nutrients in the water, that might encourage regrowth in the distribution system
- the use of two oxidants: one to improve disinfection, or minimise disinfection by-product formation, and the second to provide the disinfecting residual
- the susceptibility of the distribution system to external contamination, and its impact on the importance of a disinfectant residual
- the availability of reliable supplies of electricity and any chemicals or other consumables required
- the ease and accuracy with which disinfectant residuals can be measured
- the use of the oxidising power of the disinfectant for the control of iron, manganese, and tastes and odours
- the operational and capital costs of the planned disinfection system
- whether the technology is appropriate for the water supply concerned
- the needs, wants and concerns of the community.

A summary of the characteristics of the predominant disinfection techniques is provided in Table 15.3.

Table 15.3: Characteristics of different disinfectants

| | Chlorine | Chloramination | Ozone | Chlorine dioxide | UV light |
|--|--------------------|----------------|--------------|------------------|------------------------------|
| Size of plant | All sizes | All sizes | All sizes | All sizes | All sizes |
| Equipment reliability | Good | Good | Fair to good | Fair to good | Fair to good |
| Relative complexity of technology | Simple to moderate | Moderate | Moderate | Moderate | Simple to moderate |
| Safety concerns | Yes | Yes | Moderate | Yes | Minimal |
| Bactericidal | Good | Good | Good | Good | Good |
| Virucidal * | Moderate | Poor | Good | Good | Slight/moderate |
| <i>Giardia</i> | Moderate | Poor | Good | Good | Good |
| <i>Cryptosporidium</i> | Nil | Nil | Good | Moderate | Good |
| By-products of possible health concern | Yes | A few | Yes | Yes | Nil? Significance unresolved |
| Persistent residual | Moderate | Long | None | Long | None |
| Contact time needed | Moderate | Long | Short | Moderate | Short |
| pH dependent | Yes | Moderate | Slight | Slight | No |
| Process control | Well developed | Well developed | Developing | Developing | Developing |
| Capital costs | Low | Moderate | High | Moderate | Moderate |
| Operating costs | Low | Moderate | High | High | Moderate |
| Used in New Zealand | Extensively | No | Some | No | Quite common |

* See Chapter 7 for further discussion about viruses. Some types of virus, mainly the adenoviruses, are more resistant to disinfection processes, particularly UV.

15.4 Disinfection by-product formation

15.4.1 Introduction

Trihalomethanes were first discovered in chlorinated drinking waters in the mid-1970s (Rook 1974, Bellar et al 1974). Since then, the practice of prechlorination (dosing chlorine into the raw water) has largely been replaced with post-treatment chlorination which has greatly reduced the production of disinfection by-products (DBPs). Also, alternative disinfectants have been used to reduce the concentrations of DBPs in treated waters.

Two things have become apparent since the first discoveries. Firstly, closer examination of chlorinated waters has shown that trihalomethanes are only one of a large number of types of disinfection by-products that can be formed. Secondly, the use of an alternative disinfectant may relieve the problem of trihalomethane formation, but for all disinfectants, except ultraviolet irradiation (research on this is yet to be completed), other undesirable disinfection by-products can be produced.

New Zealand's foremost concern, like other countries, is to provide microbiologically safe water. **The microbiological quality of the water must never be sacrificed just to minimise disinfection by-product formation.** This is not to say that efforts should not be made to keep disinfection by-product concentrations to a minimum.

Chemical and compliance issues are discussed in Chapter 10: Chemical Compliance, sections 10.2, 10.6 and 10.7. DBPs with MAVs include the trihalomethanes (THMs), haloacetic acids (HAAs) and haloacetonitriles (HANs).

15.4.2 Formation

This section provides a brief overview of the factors affecting disinfection by-product formation, and consequently what steps a water supplier might take to reduce the formation of disinfection by-products in their supply. Factors affecting the formation of the less significant (in terms of their concentration) disinfection by-products have yet to be fully studied. Section 15.4.5 lists the DBPs found to date.

Disinfection processes using chlorine and ozone tend to produce the most DBPs due to their high reactivity. Chloramines and chlorine dioxide produce fewer THMs so have had less reason for study. Chlorinated species usually dominate over brominated species, except in (rare) waters with a high bromide concentration.

The order of dominance is generally THMs>HAAs>HANs. Organic chloramines (N-chloramines) are formed when chlorine reacts with amines, amino acids, proteinaceous material and other forms of organic nitrogen involving amino groups or linkages. The general reaction of amino acids with chlorine in aqueous solution has been known for many years, and reviews have been published (for example, Glaze et al 1982). Amino acids of the type $R-CH_2-CH(COOH)NH_2$ react readily with chlorine and initially form monochloramines ($R-CH_2-CH(COOH)NHCl$) and, depending on the conditions, dichloramines ($R-CH_2-CH(COOH)NCl_2$). Further reaction leads to nitriles ($R-CH_2CN$) and/or aldehydes ($R-CH_2CHO$). Organic chloramines are usually formed at slower rates than inorganic chloramines and are not considered to be effective disinfectants. While some organic chloramines are stable, others are not and degrade to many other by-products. Typically, high quality groundwater contains up to 1 mg/L (as organic carbon), river water contains 1 to 10 mg/L, while upland water may contain up to 20 mg/L (as organic carbon) which is almost entirely of natural origin (from humic substances) (IARC Monograph 52).

Factors affecting disinfection by-product formation include:

- the disinfectant, its dose, mixing efficacy and residual concentration
- impurities in the disinfectant
- natural organic matter (NOM) in the water being dosed (ie, precursors)
- other organic matter components (ie, precursors)
- pH of the water
- time that the disinfectant is in contact with the organic matter
- water temperature

- bromide ion concentration in the water, and to a lesser extent, iodide
- quality of the salt used for making chlorine, especially its bromide content
- age of hypochlorite solutions: see chlorate and perchlorate datasheets
- nitrite, or organic nitrogen concentration (applicable to chloropicrin formation)
- cleanliness of the distribution system.

These factors depend on both the water quality and the treatment process, hence variation in either water quality or treatment will create changes in disinfection by-product levels; these can vary seasonally as well. Health Canada (1995) found total trihalomethanes (TTHMs) and haloacetic acids (HAAs) were the major DBPs found in all facilities for all treatment processes and HAA levels often equalled or exceeded TTHM concentrations. Mean and median TTHM levels were higher in the summer than the winter and increased in the distribution system except for chlorine-chloramine treatment.

Generally, chloroform and bromodichloromethane are the most common THMs. There are up to nine chlorinated/brominated haloacetic acids, the main two being dichloroacetic acid and trichloroacetic acid; see datasheets.

An indication of the natural organic matter content can be gained by measuring the absorbance of the water at 254 nm in a silica cell. NOM matter contains compounds which disinfectants are able to react with to form disinfection by-products; the higher the organic matter concentration the greater the potential for disinfection by-product production. The major components of organic matter in water are humic and fulvic acids produced from the decay of vegetation. The concentration of organic matter in water may change markedly, and very rapidly, as the result of a rain event and even to the intensity of the rain, or more slowly on a seasonal basis. Most of the humic and fulvic acids that react with disinfectants to form disinfection by-products are small molecules, often with a molecular weight of less than 1,000. A lot of these are dissolved rather than colloidal, so are not removed to any significant degree by chemical coagulation. Despite this, chemical coagulation can achieve reductions in the formation of by-products well in excess of 50 percent (Reckhow and Singer 1990). The level of reduction depends on the chemical composition of the organic matter. Activated carbon should be more effective in removing low molecular weight humic substances.

Disinfectants can also react with chemicals not removed from the raw water, eg, with phenols, and with chemicals leached from plumbing and associated fittings, usually when made from plastics.

Unless groundwaters are in contact with buried organic matter, they generally contain low levels of organic matter due to the microbiological degradation and adsorption of organics, as the water percolates through subsurface strata.

Seasonal changes in water temperature can also cause changes in the concentrations of disinfection by-products formed. Chemical reaction rates increase with increasing temperature, hence, all other reaction conditions being the same, more disinfection by-products will be produced in warm water than cold water.

Disinfection by-product concentrations increase with increasing disinfectant concentration. The best-characterised relationship is between THM production and chlorine dose. There is a moderately steep increase in THM production as the chlorine dose is increased, until sufficient chlorine has been added to meet the full chlorine demand of the water. At doses beyond this value there is little increase in THM concentration as the chlorine concentration is increased.

The influence of pH on the concentration of disinfection by-products depends upon the category of disinfection by-product in question. Within the pH range of typical drinking-water, increasing the pH (up to pH 9.5) increases the concentrations of THMs, whereas the concentrations of trihaloacetic acids increase as the pH is decreased (maximum dichloroacetic acid production occurs at pH 7.0–7.5).

The production of disinfection by-products from organic matter is not instantaneous. The production of THMs, for example, may continue for weeks, although, at typical pH and temperature values, greater than 80 percent of the final concentration may be formed within 48 hours. Concentrations of trihalomethanes in a distribution system are therefore expected to be greater than the concentrations in the water leaving the treatment plant. The holding times in service reservoirs before the drinking-water enters the distribution system will have an influence on the disinfection by-product concentrations in the reticulated water; the longer the holding time in the reservoir, the higher the disinfection by-product concentrations entering the distribution system. However, it has been observed that haloacetic acids tend to exhibit higher concentrations near the treatment plant.

In light of the above discussion, it is not surprising that the concentrations of DBPs can vary considerably, even over a short time; Rizak in CRC (2002) noted one study that showed THM concentrations in samples collected every four hours from a continually running tap fluctuated as much as 44 percent.

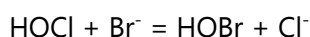
Because there is no online monitoring tool that can be used to monitor for DBP formation potential reliably WRF (2016a) evaluated the effectiveness of new on-line monitoring tools and response systems that can be used to detect subtle changes in the character and amount of NOM and its effect on disinfection by-product (DBP) formation potential. They evaluated:

- advanced online instrumentation technology (eg, scan units) based on UV spectral derivatives
- specific excitation/emission matrix (EEM) pairings from the 3-D fluorescence monitoring
- the output of the online units with NOM properties discerned from characterisation methods including fractionation techniques based on NOM polarity, as well as examination of spectral properties, including generating 3-D fluorescence spectra and analysing absorbance spectral slopes.

Some techniques correlated moderately well for both THMs and HAAs.

Brominated disinfection by-products

Brominated species form when using ozone due to free radical reactions; ozone's very high reactivity can rupture organic molecules, forming aldehydes, organic acids and ketones, not necessarily halogenated. Chlorine oxidises bromide to hypobromous acid (as below) which, like hypochlorous acid, is reactive:



The presence of bromide in water can affect the concentrations of disinfection by-products and the types of disinfection by-products formed. A lot of the bromide in New Zealand waters is from aerosols blown inland from the sea; it also occurs in geothermal and hydrothermal waters. Chlorine and ozone are both able to oxidise bromide to bromine (or hypobromous acid or hypobromite ion depending on the pH of the water), and ozone can further oxidise the hypobromite ion to bromate. About half the bromide is oxidised to bromate by ozone. When bromine or its compounds are present in the water, bromination reactions similar to the chlorination reactions that produce the chlorinated organic disinfection by-products may occur. These reactions produce disinfection by-products containing bromine at the expense of those disinfection by-products containing only chlorine. The reactions resulting in the incorporation of bromine into organic matter are faster than those incorporating chlorine. As a result, quite low bromide levels in the raw water can lead to a significant fraction of the total disinfection by-products formed containing bromine. The presence of bromide therefore changes the relative concentrations of the different by-products. Without high bromide levels, chlorinated species dominate (eg, chloroform, trichloroacetaldehyde, tetrachloropropanone, dichloroacetonitrile, trichloronitromethane); with elevated bromide levels (eg, 1 mg/L), these shift to brominated species (eg, bromoform, tribromoacetaldehyde, tetrabromopropanone, dibromoacetonitrile, tribromonitromethane). Bromide concentrations are generally low in New Zealand.

Iodinated disinfection by-products

The occasional detection of iodinated halomethanes is probably due to a similar mechanism involving iodides, which usually appear in drinking-water at even lower concentrations than bromide. DWI (2016) reports that during a US occurrence study the most iodine-containing THMs were found at a plant that treated a water source high in bromide (iodide was not measured) that used chloramines only or, on one occasion, used chlorine dioxide as a pre-oxidant. Plants that used chlorine only or ozone and chlorine typically produced some of the lowest levels of iodine-containing THMs.

DWI (2016) identified high risk sites for iodinated DBP formation in England and Wales. Iodide levels in boreholes in England and Wales from 2008 showed median values ranging from 1.0–15.1 µg/L. There was no single factor identified that contributes to high iodinated DBP formation but rather a combination of factors. These are listed below. Factors that contribute to higher iodinated DBP formation:

- high iodide concentration in raw water
- a shorter free chlorine contact time
- gentle pre-oxidation step in the water treatment process (eg, permanganate)
- lack of strong oxidation step in the water treatment process (eg, ozone)
- low bromide levels relative to iodide (low bromide:iodide ratio).

15.4.3 Toxicity

The UK Water Research Foundation (2009) analysed 66 USEPA priority drinking water disinfection by-products (DBPs) for their chronic cytotoxicity and acute genotoxicity in mammalian cells, and ranked the cytotoxicity and genotoxicity of the DBPs. They noted that the majority of DBPs have yet to be chemically characterised, and only a small fraction of DBPs have been evaluated for their biological and toxicological effects.

Some of their findings were:

- diiodoacetamide was the most cytotoxic agent and bromodichloromethane was the least cytotoxic
- the rank order from most cytotoxic to least cytotoxic for the DBP classes was haloacetaldehydes > haloacetamides > halonitromethanes > haloacetonitriles > > 2C-haloacids > haloacetic acids > halomethanes
- a majority (75.8 percent) induced significant levels of genomic DNA damage. In this group, iodoacetic acid was the most genotoxic. The least genotoxic was chlorodibromoacetic acid
- for induced genomic DNA damage, the rank order from the most genotoxic to the least genotoxic of the DBP classes was haloacetonitriles > haloacetamides > halonitromethanes > haloacetaldehydes > haloacetic acids > >2C-haloacids > halomethanes
- iodinated DBPs were more cytotoxic and genotoxic than their brominated and chlorinated analogues; note that iodinated DBPs are also usually the most rare
- in general, nitrogen-containing DBPs were more toxic than DBPs that did not contain nitrogen.

15.4.4 Occurrence

The USEPA has regulated two groups of organic DBPs, the trihalomethanes (THMs) and the haloacetic acids (HAAs). These two groups only represent a fraction of the DBPs formed in municipal drinking water systems, so there is interest in identifying and controlling exposure to non-regulated DBPs that may be deemed to be hazardous. To gather data a project in the US involved 13 sampling campaigns from 11 WTPs between January 2011 and June 2012. Samples were collected from about a dozen sites representing finished water; water with low, medium, and high water ages; and water from sites typically associated with nitrification or low chlorine residuals. Results indicated that concentrations of most unregulated DBPs were highly variable between different utilities and even across some service areas within a single system. There were no reliable or universal relationships between the regulated THMs and HAAs and the

non-regulated compounds. However, there were patterns that could be identified based on residual disinfectant type, pH, and treatment, especially the use of strong oxidants and long free chlorine contact times for systems using chloramines. Most water systems have bacteria with dehalogenase genes that are capable of biodegrading a wide range of DBPs. Proliferation of these organisms to the point that they actually depress DBP levels in the system is less common and seems to be related to areas prone to nitrification. Many non-regulated DBPs are subject to alkaline hydrolysis and abiotic degradation. Stability of these compounds in actual distribution systems is often greater than expected from simple laboratory experiments, suggesting protective mechanisms may be at play (WRF 2016c).

15.4.5 Booster chlorination

Typically, chemical disinfectants are added to treated drinking water at the treatment plant and is sufficient to maintain a residual up to the consumers' taps. However, where the distribution system is lengthy, it may be necessary to add or boost the disinfectant concentration in the network to maintain a residual throughout. DEFRA (2017) commissioned a study on the formation of DBPs during booster chlorination in the UK. The literature review found:

- THM concentration increases when more chlorine is added during booster chlorination
- the rate of chlorine decay and corresponding THM formation can be modelled using a second order decay model
- the concentration of free chlorine residual present in the water is not related to the level of THMs formed when free chlorine levels are less than 1 mg/L
- HAA concentration can increase or decrease or stay the same after booster chlorination
- HAA behaviour depends on the concentration of free chlorine residual in the water
- HAAs can be degraded if the chlorine residual is low and the correct type of bacteria are present in the water.

When considering all of the data collected over the study period, the increase in THMs after booster chlorination was statistically significant at the 95 percent confidence level when comparing the means; the increase was just over 10 percent. The change in HAAs after booster chlorination was not significant at the 95 percent confidence level.

15.4.6 DBPs found to date

Because chlorine is used extensively around the world, most studies have been directed towards chlorinated by-products.

UV light can convert nitrate to nitrite but this is only significant if both the UV dose and the nitrate content are high; also it has also been reported that aldehydes may be able to form. Reckhow et al (2010) report results of a study where chlorination followed UV disinfection. UV treatment of two sets of waters did not substantially change the tendency to form trihalomethanes, haloacetic acids, or total organic halogen under the conditions of these tests. Evidence was found of small reductions in the formation of these DBPs, but the decreases did not exceed 10%. Formation of chloropicrin and 1,1,1-trichloropropanone increased as a result of medium-pressure UV treatment but remained at levels well below those of the regulated DBPs. Low-pressure UV did not cause any detectable increase in chloropicrin formation.

Ozone can directly or indirectly react with bromide to form brominated ozone DBPs, including bromate ion (BrO_3^-). In the presence of NOM, non-halogenated organic DBPs, such as aldehydes, ketoacids and carboxylic acids, are formed during ozonation, with aldehydes (eg, formaldehyde) being dominant. If both NOM and bromide are present, ozonation forms hypobromous acid, which, in turn, leads to the formation of brominated organohalogen compounds (eg, bromoform).

The major chlorine dioxide DBPs include chlorite (ClO_2^-) and chlorate ions (ClO_3^-), with no direct formation of organohalogen DBPs. Unlike the other disinfectants, the major chlorine dioxide DBPs are derived from decomposition of the disinfectant as opposed to reaction with precursors.

Use of chloramine as a secondary disinfectant generally leads to the formation of cyanogen chloride (CNCl), a nitrogenous compound, and significantly reduced levels of chlorine DBPs.

Table 15.4 summarises some individuals and groups of DBPs or impurities that have been observed; the degree of significance often depends on the composition of the raw water and treatment conditions – see individual datasheets.

Modern analytical instrumentation allows researchers to detect extremely low levels of an enormous range of chemicals, and when the concentration is higher in the treated water than in the raw water, these chemicals are often called disinfection by-products. It has almost become a competition to see who can 'discover' new DBPs; some of the newer DBPs have been called 'emerging DBPs'. Following Table 15.4 is an extensive listing; some of these chemicals have a datasheet. Concentrations are frequently no more than a few nanograms/L, and the effects at these levels are usually unknown or surmised.

Table 15.4: Disinfection by-products often present in disinfected waters

| Disinfectant | Significant organohalogen products | Significant inorganic products | Significant non-organohalogen products |
|---------------------------------|---|---|--|
| Chlorine, and hypochlorous acid | chloral hydrate chloroacetones chlorophenols chloropicrin haloacetic acids (HAAs) haloacetonitriles (HANs) halofuranones (includingMX) halogenated aromatics halogenated hydrocarbons halohydrins N-chloramines trihalomethanes (THMs) | chlorate (mostly from hypochlorite use) dichloramine monochloramine perchlorate trichloramine | aldehydes cyanoalkanoic acids nitrosamines |
| chlorine dioxide | | chlorite chlorate | unknown |
| chloramine | chloral hydrate chloramino acids chloroacetones cyanogen chloride haloacetonitriles N-chloramines | chlorate dichloramine hydrazine nitrite, nitrate trichloramine | aldehydes ketones nitrosamines |
| ozone | bromoform cyanogen bromide dibromoacetonitrile dibromoacetone haloacetic acids halohydrins | bromate chlorate epoxides hydrogen peroxide hypobromous acid iodate ozonates | aldehydes carboxylic acids glyoxalic acid ketones pyruvic acid |

The following is a list of DBPs and CAS numbers that are not routinely monitored (Simmons et al 2002):

- 3,3-dichloropropenoic acid (3,3-dichloroacrylic acid)
- bromoacetonitrile [590-17-0]
- chloroacetonitrile [107-14-2]
- tribromoacetonitrile [75519-19-6]
- bromodichloroacetonitrile [60523-73-1]
- dibromochloroacetonitrile [144772-39-4]
- chloropropanone (chloroacetone) [78-95-5]
- 1,3-dichloropropanone (1,3-dichloroacetone) [534-07-6]
- 1,1- dibromopropanone (1,1-dibromoacetone)
- 1,1,3-trichloropropanone (1,1,3-trichloroacetone) [921-03-9]
- 1-bromo-1,1-dichloropropanone (1-bromo-1,1-dichloroacetone)
- 1,1,1,3-tetrachloropropanone (1,1,1,3-tetrachloroacetone) [16995-35-0]
- 1,1,3,3-tetrachloropropanone (1,1,3,3-tetrachloroacetone) [632-21-3]
- 1,1,3,3-tetrabromopropanone (1,1,3,3-tetrabromoacetone)

- 1,1,1,3,3-pentachloropropanone (pentachloroacetone)
- hexachloropropanone (hexachloroacetone) [116-16-5]
- dimethylglyoxal (2,3-butanedione)
- chloroacetaldehyde [107-20-0]
- dichloroacetaldehyde [70-02-7]
- bromochloroacetaldehyde
- tribromoacetaldehyde [115-17-3]
- 3-chloro-4-(bromochloromethyl)-5-hydroxy-2(5H)-furanone (BMX-1)
- 3-chloro-4-(dibromomethyl)-5-hydroxy-2(5H)-furanone (BMX-2)
- 3-bromo-4-(dibromomethyl)-5-hydroxy-2(5H)-furanone (BMX-3)
- (E)-2-chloro-3-(bromochloromethyl)-4-oxobutenoic acid (BEMX-1)
- (E)-2-chloro-3-(dibromomethyl)-4-oxobutenoic acid (BEMX-2)
- (E)-2-bromo-3-(dibromomethyl)-4-oxobutenoic acid (BEMX-3)
- 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX)
- 3-chloro-4-(dichloromethyl)-2-(5H)-furanone (red-MX)
- (E)-2-chloro-3-(dichloromethyl)-butendioic acid (ox-MX)
- (E)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid (EMX)
- 2,3-dichloro-4-oxobutenoic acid (mucochloric acid) [87-56-9]
- chloromethane (methyl chloride) [74-87-3]
- bromomethane (methyl bromide) [74-83-9]^b
- dibromomethane [74-95-3]
- bromochloromethane [74-97-5]
- bromochloroiodomethane
- dichloroiodomethane
- dibromoiodomethane
- chlorodiiodomethane
- bromodiiodomethane
- iodoform [75-47-8]
- chlorotribromomethane
- carbon tetrachloride [56-23-5]
- 1,1,1,2-tetrabromo-2-chloroethane
- bromochloromethyl acetate
- chloroacetamide [79-07-2]
- bromoacetamide [683-57-8]
- dichloroacetamide [683-72-7]
- dibromoacetamide
- trichloroacetamide [594-65-0]
- bromonitromethane [563-70-2]
- chloronitromethane
- dibromonitromethane
- bromochloronitromethane
- dichloronitromethane

- bromodichloronitromethane
- dibromochloronitromethane
- tribromonitromethane (bromopicrin)
- 2-hexenal [505-57-7]; [6728-26-3]
- 5-keto-1-hexanal
- methylethyl ketone (2-butanone) [78-93-3]
- cyanoformaldehyde
- 6-hydroxy-2-hexanone
- benzyl chloride.

Chemical Abstracts Service (CAS) numbers listed when available.

Others referred to by Hrudey in CRC (2002) include:

- 1,1-dichloropropanone
- 1,1,1-trichloropropanone
- glyoxal
- 2-hexanal
- acetaldehyde
- formaldehyde
- isobutyraldehyde
- isovaleraldehyde
- 2-methylbutyraldehyde
- phenylacetaldehyde
- glyoxylic acid
- pyruvic acid
- ketomalonic acid
- 2-tert-butylmaleic acid
- acetate
- formate
- oxalate
- trichloroanisole
- nitrosodimethylamine (NDMA).

Note: halohydrin is a traditional term for alcohols substituted by a halogen atom at a saturated carbon atom otherwise bearing only hydrogen or hydrocarbyl groups (usually used to mean β -halo alcohols). Example: $\text{BrCH}_2\text{CH}_2\text{OH}$ (ethylene bromohydrin or 2-bromoethanol), $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{OH}$ trimethylene chlorohydrin or 3-chloropropan-1-ol), and $\text{PhCH}(\text{OH})\text{CH}_2\text{Cl}$ (styrene chlorohydrin or 2-chloro-1-phenylethanol); see IUPAC (1997).

As analytical techniques improve and detection limits lower, researchers record increasing numbers of chemical determinands in water, and in disinfected water. Simmons et al (2002) stated that more than 500 DBPs had been identified. See Goslan et al (2010) and Richardson (2005) for further developments. Kimura et al (2019) developed an enhanced technique for simultaneously measuring 39 currently unregulated compounds comprising four HALs, nine HKs, 10 HAMs, six HANs, four HNMs, and six I-THMs.

15.4.7 Further reading

The AWWA book entitled *Formation and Control of Disinfection By-Products in Drinking Water* contains a detailed compilation of the chemistry of DBP formation in Chapter 3 (Krasner 1999).

Disinfectants and Disinfectant By-Products, Environmental Health Criteria 216, was published under the joint sponsorship of the United Nations Environment Programme, the International Labour Organisation and the World Health Organization, and produced within the framework of the Inter-Organization Programme for the Sound Management of Chemicals (IPCS 2000).

The USEPA (2001) produced a guidance document on the control of disinfection by-products and microbial contaminants in drinking water.

Myllycangas (2004) studied several aspects of DBP production.

Then the USEPA (2006b) produced a series of manuals aimed to help water suppliers to identify distribution system locations with high concentrations of trihalomethanes (THMs) and haloacetic acids (HAAs).

USEPA (2007a) is a guide designed for small community water systems serving fewer than 10,000 people that are required to comply with the Stage 2 Disinfectants and Disinfection Byproducts Rule (Stage 2 DBPR); it has a large section on monitoring.

Chlorination Disinfection By-products and Risk of Congenital Anomalies in England and Wales. DWI (2007). This large national study found little evidence for a relationship between THM concentrations in drinking water and risk of congenital anomalies.

USEPA (2010) offers guidance in controlling disinfection by-products to water suppliers that receive their water from another authority, ie, from a bulk supplier.

DEFRA (2017) includes an excellent summary of current thinking about the production, occurrence and decay of THMs and HAAs in drinking water.

15.5 Disinfection processes

The Hazardous Substances and New Organisms (HSNO) Act 1996 now controls some aspects relating to the use of some chemicals used in water treatment, see Chapter 2: Management of Community Supplies, section 2.4.2 for further discussion.

15.5.1 Chlorine

The first recorded continuous use of chlorine as a disinfectant for a water was in Belgium just after the beginning of the 20th century. It is now the most widely used disinfectant throughout the world, including New Zealand, and this widespread use has been a major factor in reducing illness and deaths due to waterborne diseases.

Chlorine is really only used to inactivate bacteria, viruses and, if the dose/time is high/long enough, *Giardia*. *Cryptosporidium* requires a stronger disinfectant. Table 15.5 includes data from WHO (2004). See Table 15.1 for some earlier data. Table 15.5 presents conservative estimates of microbial reductions based on the more resistant or persistent pathogenic members of the group.

Table 15.5: Chlorine C.t values for 99 percent inactivation (2 logs)

| Micro-organism | C.t values | Conditions |
|------------------------|-----------------|-----------------|
| Bacteria | 0.08 mg.min/L | 1–2°C; pH 7 |
| | 3.3 mg.min/L | 1–2°C; pH 8.5 |
| Viruses | 12 mg.min/L | 0–5°C; pH 7–7.5 |
| | 8 mg.min/L | 10°C; pH 7–7.5 |
| <i>Giardia</i> | 230 mg.min/L | 0.5°C; pH 7–7.5 |
| | 100 mg.min/L | 10°C; pH 7–7.5 |
| <i>Cryptosporidium</i> | Not inactivated | |

Ex WHO 2004.

Chlorine has a drinking-water MAV of 5 mg/L. It is highly improbable that any water supply in New Zealand will contain anything like this concentration. See the datasheets for further information.

Figure 11.3 in WHO (2004a) was taken from Jacangelo (2002). It shows a comparison of the C.t values for 2-log inactivation of a range of micro-organisms by free chlorine. *Cryptosporidium* spp are by far the most resistant. Some other fairly resistant organisms are the mycobacteria and legionellae bacteria.

15.5.1.1 Chlorine chemistry

Water supplies are chlorinated using chlorine gas (Cl₂) liquefied under pressure in cylinders or drums, solid commercial calcium hypochlorite ('CaOCl₂' or sometimes referred to by various trade names such as HTH), or a solution of sodium hypochlorite

(NaOCl). Sodium hypochlorite can be purchased, or made onsite, electrolytically, from salt. ANSI/AWWA Standard B200-12 covers sodium chloride.

Cyanuric acid, usually added to water as sodium dichloroisocyanurate, is commonly used in swimming pools, and is also used to disinfect drinking-water, primarily in emergencies. See datasheets.

Most chlorine products are derived from salt so the main impurity will usually be bromide which is oxidised to bromine, thence bromate; sodium hypochlorite used for water treatment should be checked for bromate (AWWA Standard B300). Low grade salt tends to foul the chlorine production process, so these days, impurity levels are quite low. Mercury and carbon tetrachloride used to be impurities in liquid chlorine but these are maintained at very low levels now.

Chlorine reacts with water to form hypochlorous acid (HOCl) and hydrochloric acid, reaction (i). In the pH range typical of drinking water, the hypochlorous acid molecule (disinfecting) dissociates, reaction (ii), to form the very weak disinfectant, hypochlorite ion (OCl⁻).



The relative concentrations of hypochlorous acid and hypochlorite ion are controlled predominantly by the pH (and to some extent by temperature). At low pH values, almost all of the chlorine exists as hypochlorous acid, while at high pH values, only the hypochlorite ion is present. Table 15.6 provides an indication of how the hypochlorous acid molecule and hypochlorite ion concentrations change with pH.

Table 15.6: Variation of hypochlorous acid and hypochlorite ion with pH

| pH | Percentage of total chlorine | |
|-----|---------------------------------|--------------------------------|
| | Percentage of hypochlorous acid | Percentage of hypochlorite ion |
| 6.0 | 96 | 4 |
| 7.0 | 79 | 21 |
| 7.5 | 55 | 45 |
| 8.0 | 28 | 72 |
| 8.5 | 11 | 89 |
| 9.0 | 4 | 96 |

Table 15.6 shows that the relative concentrations of hypochlorous acid and hypochlorite ion change rapidly over the pH range usual for treated waters. This is also plotted in Figure 17.6 in Chapter 17: Monitoring, section 17.4.1. From these it is theoretically possible to calculate FACE, the free available chlorine equivalent, which is the FAC concentration that would have the same disinfecting power as the chlorine solution would have at pH 8. An easier approach is given in Chapter 6: Bacterial Compliance, section 6.3.7, Table 6.1.

The change in the form of the chlorine is important, because the hypochlorous acid molecule is a much more potent disinfectant than the hypochlorite ion. It is therefore necessary to measure both the chlorine concentration in the water and the pH, to

determine whether the water is being disinfected properly. For water leaving the treatment plant, FACE levels are measured after a contact of at least 30 minutes (see sections 4.3, 4.3.2.1 and Figure A1.1 of DWSNZ). Because water in the distribution system has had a much longer contact time, much of it at a pH less than 8.0, FAC measurements are considered to be a satisfactory indicator of disinfecting efficacy in the distribution system.

Chlorine is chemically very reactive and is consumed by reaction with inorganic and organic contaminants in water. The amount of chlorine destroyed by these substances is known as the chlorine demand. It is also destroyed by UV light, eg, sunlight.

For chlorine to be used most effectively as a disinfectant, the water must be dosed with enough chlorine to meet the demand, and still produce a residual. This is break-point chlorination. The residual of hypochlorous acid and hypochlorite ion is termed the free available chlorine (FAC), and it is the hypochlorous acid within the FAC that provides the disinfecting power.

The absence of a FAC residual indicates the absence of a satisfactory disinfectant. It is the responsibility of the water supplier to ensure that the treatment plant is suitably equipped to maintain an adequately disinfected water. It is the operator's responsibility to ensure that the equipment is properly maintained, and a supply of chlorine is always available. Standing the gas cylinder on scales will enable the operator to assess when the cylinder is likely to run out. Some water supplies have a 'change-over' panel which automatically switches from the cylinder in use when it empties to the reserve cylinder.

The characteristics of the source water of the supply need to be taken into account when the method of chlorine dose control is being selected. Waters in which the chlorine demand and the flow through the plant are almost constant can be chlorinated adequately by manual control. Where the water quality is fairly constant, but the flow rates change, a flow proportional controller is necessary.

Waters in which both the chlorine demand and the flow rate change require an automated system, with the dosing controlled by measurement of the FAC residual in the water. If unattended, neither manual nor flow proportional controls can alter their dose rates to match changes in raw water quality.

Chlorine's reactivity should be borne in mind when a disinfectant is being selected. It is a strong oxidant, and the majority of its reactions result in the oxidation of other substances in the water. In this role it aids in the removal of iron and manganese, and the reduction of some tastes and odours by destruction of the organic compounds from which they arise.

Chlorine reacts with any ammonia in the water to form chloramines, see next section. This reaction is often a major contributor to the initial or instantaneous chlorine demand. Normally the ammonia concentration is low enough and the chlorine dose high enough for break-point chlorination to occur, ie, all the ammonia is oxidised to nitrogen. If the FACE of the water entering the distribution system is more than 0.2 mg/L, bacterial compliance has been achieved, even if there is still a trace of monochloramine present, and compliance in the distribution system can be achieved by *E. coli* monitoring. In these situations, any ammonia present should not cause any problems. Chlorine can also react with amino compounds.

Higher concentrations of ammonia are often found in groundwaters. If a bore water is secure, no disinfection is needed. If the water supplier chooses to add chlorine (or chloramines) in order to maintain a residual in the distribution system, compliance can be measured by *E. coli* monitoring and FAC monitoring (see DSWNZ section 4.4).

If the bore water is not secure, some form of disinfection 'at the treatment plant' will be needed. Bacterial compliance of water leaving the treatment plant can be achieved by any of bacterial compliance criteria 1 to 5. If compliance criterion 2 is employed (chlorination) and the groundwater contains ammonia, at least some of the FAC will be converted to chloramines. Water suppliers will need to ensure that the combined residual disinfectants remain at an effective concentration throughout the distribution system.

Ammonia removal is expensive. If a groundwater contains a high concentration of ammonia, there may be an advantage in gaining bacterial compliance using criterion 1 (*E. coli* monitoring) or criterion 5 (UV disinfection). If maintaining a disinfecting residual in the distribution system is desired, chlorinating to form monochloramine should be satisfactory, but *E. coli* will need to be monitored.

Fairly large natural organic molecules, such as humic and fulvic acids, are usually present in surface waters, and may contribute to the chlorine demand. The oxidation of these compounds by chlorine (often slowly and therefore in the distribution system) can lead to their partial disintegration and the production of compounds which micro-organisms are able to use as a food source. The presence or production of these compounds in water entering distribution systems can enhance the regrowth of micro-organisms, particularly if there is little or no FAC.

Reactions that result in chlorine being incorporated into other compounds can also occur during chlorine's reactions, and these products may be undesirable. They can lead to chlorinated organic compounds that may be carcinogenic, and substances that can cause tastes and odours. Chlorine is also able to oxidise bromide to hypobromous acid and hypobromite, which, like their chlorine counterparts, hypochlorous acid and hypochlorite, will incorporate bromine into organic substances. The presence of bromide in waters undergoing chlorination is the source of disinfection by-products containing bromine and mixtures of chlorine and bromine.

The storage of high concentration hypochlorite solutions (sodium and calcium hypochlorite solutions) for extended periods of time should be avoided. At high concentrations, these chlorine solutions decompose with the production of chlorate and perchlorate. Sufficient chlorate can be produced for it to be detectable in the treated water.

Dry calcium hypochlorite is a powerful oxidant and is dangerous if mishandled. It should not be allowed to come into contact with heat, combustible materials, or reducing agents, and spillages should be washed away with large amounts of water. Follow the instructions on the containers.

15.5.1.2 Disinfection using chlorine

The difference in the disinfecting powers of hypochlorous acid and the hypochlorite ion make accurate pH measurement and its control during chlorination very important, refer Table 15.6. Hypochlorous acid is a strong disinfectant with excellent bactericidal properties. As with other disinfectants, it is not quite so effective against viruses and considerably less so against protozoa (particularly *Cryptosporidium*), and for these reasons, a multiple barrier approach to water treatment, using physical processes, produces a much more effective means of producing a safe water than disinfection alone.

In the absence of any virological compliance criteria in DWSNZ, it is suggested that to produce a water with a negligible viral risk, a water should be chlorinated to give a FAC residual equal to or greater than 0.2 mg/L after at least 30 minutes contact time, see Chapter 7: Virological Compliance, section 7.6. The water being disinfected should have a pH equal to or less than 8, and a turbidity less than 1 NTU.

A number of factors need to be taken into account when establishing a chlorine dose rate at the treatment plant. Generally, the first and most basic requirement is to achieve a minimum of 0.2 mg/L FACE after 30 contact time. In many cases, the chlorinator is set to match this residual, and the mean dose rate can only be determined by dividing the chlorine consumed by the volume of water treated. Many water supplies will want to achieve a higher residual leaving the treatment plant than 0.2 mg/L allowing a residual to pass to the extremities of the distribution system. The desired residual leaving the plant can only be determined by trial and error, the result of many FAC tests at many parts of the distribution system.

The difference between the chlorine dose and the point where the chlorine residual is measured is called the chlorine demand (between those two points). The chlorine demand of treated water varies seasonally due to water temperature and quality, and with water demand (ie, retention time), so the set point at the treatment plant will need to be changed accordingly. An observant operator will be aware of the chlorine demand and how it varies; if it increases fairly quickly, it may be a warning of a big change in source water quality, or even a treatment problem.

Chlorination of water with sufficient contact time has been shown to be effective against *Giardia*, but at the concentrations acceptable in drinking-waters it is ineffective against *Cryptosporidium*.

Despite chlorination being a well-established practice around the world, water suppliers may still lose control of the process; for example, across England and Wales DWI recorded on average one chlorination failure per month, the majority of which lasted less than 24 hours (median six hours) (DWI 2015).

15.5.1.3 Chlorine measurement

Many methods for measuring chlorine have been reported, but only a few are used to any great extent on a routine basis. Iodine-based methods, amperometric methods, methods using N,N-diethyl-p-phenylenediamine (DPD) and the syringaldazine method (FACTS) are described in *Standard Methods for the Examination of Water and*

Wastewater (APHA 2005, 21st edition). In New Zealand, DPD-based manual methods are the most widely used, while online methods usually use amperometric methods. ANSI/AWWA C670-09 covers online chlorine analysers.

All methods suffer from drawbacks. Some of these are worsened by the chemistry of the water to be treated, hence the water chemistry, and its influence on potential difficulties with the methods should be considered when selecting a method. Typical interferences arise from methods not being specific to chlorine. As a result, erroneously high chlorine results can arise from the presence of other strong oxidising agents, and *combined available chlorine* (CAC), also known as *total chloramines*, which are the products of reactions between chlorine and organic and inorganic nitrogen compounds. The chloramines are discussed more fully in the following section. Metals, such as manganese, can also interfere with these methods.

Iodine-based methods measure all oxidising agents in the water. This, together with their relatively low sensitivity, makes them of little use in routine potable water analysis.

Amperometric methods, while being more accurate than the DPD methods, are not as simple and require greater skill to perform. Amperometric methods are, therefore, generally less suitable for manual use at treatment plants. The amperometric titration endpoint is indicated instrumentally, which is an advantage over visual endpoint determination if the analyst experiences colour blindness, or is conducting the titration in poor lighting conditions.

DPD reacts with oxidising agents to produce a pink colour. In New Zealand this colour-forming reagent is used as the basis to measure chlorine by hand-held comparator or Nessleriser (colour matching by eye), by spectrophotometer (instrumental colour measurement), or by titration with ferrous ammonium sulphate (FAS). Chloramines can increase the FAC reading if high combined chlorine concentrations are present. These methods, without modification, may therefore be unsuitable for source waters with high ammonia or organic nitrogen concentrations. Ensuring that the FAC reading is obtained rapidly after mixing the reagents will minimise the interference of combined chlorine. Alternatively, the FACTS method is tolerant of much higher concentrations of CAC; however reagent solubility can create problems with this method.

The maximum chlorine concentration that can be measured reliably by the DPD/FAS titration is 5 mg/L as Cl₂. Unreliable results will be obtained with chlorine concentrations higher than this, and at high enough concentrations chlorine will bleach the pink colour. Samples must be diluted with chlorine-demand free water if high chlorine concentrations need to be measured. To distinguish between an excess of chlorine and an absence of chlorine, first add a little of the water sample to the indicator, rather than adding the indicator to the sample. A high chlorine concentration will become apparent by the pink colour developing, then fading as it is bleached. The maximum concentration using colorimetric techniques depends on the method used.

Precautions, common to all methods, need to be taken to make the measurements as accurate as possible. These include immediate analysis on-site of the chlorine after sampling, performance of the measurements away from strong light, thorough rinsing of glassware after iodide has been used for combined chlorine measurements, and care that reagent solutions are changed regularly to avoid significant decomposition.

When field methods require colorimetric interpretation, all persons who have undertaken FAC tests must undertake the calibration exercise against the referee method. The identity of the person performing each field test must be recorded. The analyst making the measurement should be familiar with both the referee and field methods and possible causes of inaccuracy. Refer also to Chapter 6. DWI (2005) discusses a procedure for analytical quality control for chlorine field tests. A good feature of their Guidance is the use of stable iodate solutions in lieu of reactive chlorine solutions.

Because of chlorine's high reactivity and its destruction by UV light, ie, sunlight, care is required in selecting the sample site for checking online instruments. The sample taken for calibration should be collected immediately upstream of the point where the water flow enters the online instrument, and needs to be tested as soon as possible thereafter. As soon as the sample has been collected, the online instrument reading should be noted, this being as close as possible to the concentration of FAC that the online instrument is reporting to be in the sample.

It is normal to conduct titrations in triplicate, averaging the results. However, formal procedures are required (document in the WSP or other appropriate manual) for dealing with a result outside the expected range; see APHA (2005) and Chapter 17 of the *Guidelines*.

As noted above, the hypochlorous acid molecule and hypochlorite ion are the forms of chlorine present in drinking waters. Although Cl₂ does not exist in potable waters, for historical reasons FAC, CAC and total chlorine are still expressed as mg/L as Cl₂.

15.5.2 Chloramines

Monochloramine is really only used to inactivate bacteria. Viruses, *Giardia* and *Cryptosporidium* require a much stronger disinfectant. A C.t of 1000 mg.min/L means 1 mg/L residual after 1000 minutes (16.7 hours) of contact, or 4 mg/L after 250 minutes (note that the MAV is 3 mg/L). The lack of practical experience in NZ conditions and the relatively poor inactivation of viruses by monochloramine are the main reasons why it is not offered in the DWSNZ as a means of achieving bacterial compliance of water leaving the treatment plant, ie, there is no equivalent to bacterial compliance criterion 2. Any plants using chloramines need to satisfy bacterial compliance criterion 1. Overseas, water leaving the treatment plant that has bacterial compliance is sometimes dosed with monochloramine in order to maintain a residual in the (usually large, and sometimes dirty) distribution system. See USEPA (2007) for a list of publications on chloramine.

Table 15.7 includes data from WHO (2004). See Table 15.1 for some earlier data. The table presents conservative estimates of microbial reductions based on the more resistant or persistent pathogenic members of the group.

Table 15.7: Monochloramine C.t values for 99 percent inactivation (2 logs)

| Micro-organism | Contact time (C.t) | Conditions |
|----------------|--------------------|------------|
|----------------|--------------------|------------|

| | | |
|------------------------|-----------------|---------------|
| Bacteria | 94 mg.min/L | 1–2°C; pH 7 |
| | 278 mg.min/L | 1–2°C; pH 8.5 |
| Viruses | 1240 mg.min/L | 1°C; pH 6–9 |
| | 430 mg.min/L | 15°C; pH 6–9 |
| <i>Giardia</i> | 2550 mg.min/L | 1°C; pH 6–9 |
| | 1000 mg.min/L | 15°C; pH 6–9 |
| <i>Cryptosporidium</i> | Not inactivated | |

Ex WHO 2004.

The efficiency decreases under conditions of high pH and low temperature. For example, the inactivation of *E. coli* is approximately 60 times slower at pH 9.5 and temperatures of 2 and 6°C than at pH 7 and temperatures between 20 and 25°C (stated in USEPA 1999).

Figure 11.4 in WHO (2004a) was taken from Jacangelo (2002). It shows a comparison of the C.t values for 2-log inactivation of a range of micro-organisms by chloramine. *Cryptosporidium* spp are by far the most resistant. Some other fairly resistant organisms are the mycobacteria and legionellae bacteria, *Giardia* and poliovirus.

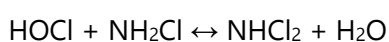
The monochloramine MAV of 3 mg/L can be expressed as 4.14 mg/L when measured as Cl₂. It is highly improbable that any water supply in New Zealand will contain anything like this concentration. See the datasheets for further information.

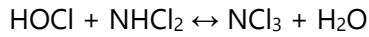
Chloramines are the products of reaction between nitrogen-containing compounds and chlorine. The full family of compounds includes both organic and inorganic chloramines, but members of the group of inorganic chloramines are those of greatest interest in water disinfection. At present, chloramines are not known to be used intentionally in any water supplies in New Zealand. They may have a role in the disinfection of some supplies through their inadvertent production from the reaction of chlorine with ammonia naturally present in the water.

Users of kidney dialysis equipment are the most critical group that can be impacted by the use of chloramines. Chloramines can cause methemoglobinemia and adversely affect the health of kidney dialysis patients if chloramines are not removed from the dialysate water. Chloramines can also be deadly to fish. The residuals can damage the gill tissues, enter the red blood cells, and cause an acute blood disorder. Chloramine residuals should be removed from the water prior to the water contacting any fish. As such, fish hobbyists should be notified, along with pet stores and aquarium supply establishments (USEPA 1999).

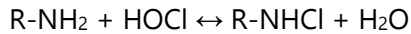
15.5.2.1 Chemistry

Chloramines used for disinfection are produced by the reaction of chlorine with ammonia (or ammonium ion). ANSI/AWWA B305-06 and B306-07 cover ammonia. Three chloramines can be formed from this reaction depending upon the pH of the water and the ratio of chlorine to ammonia. They are monochloramine (NH₂Cl), dichloramine (NHCl₂), and trichloramine or nitrogen trichloride (NCl₃).





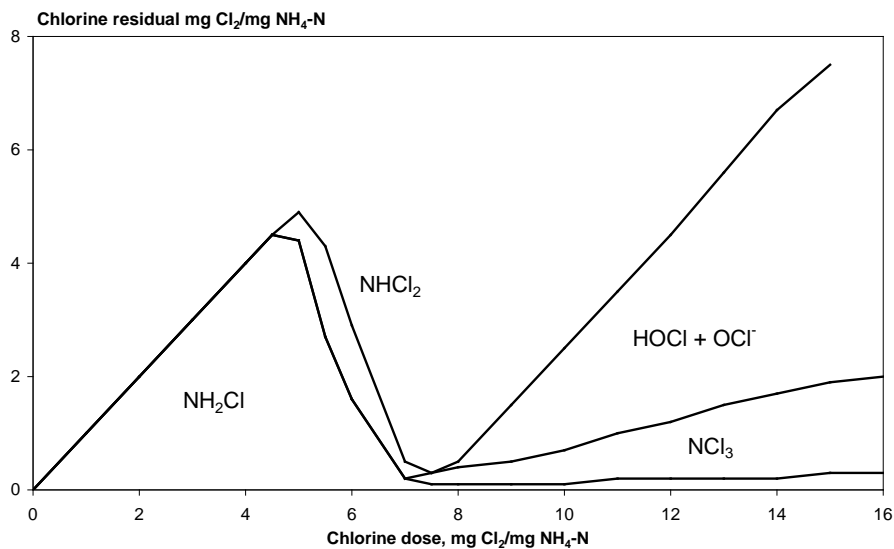
Chlorine also reacts with nitrogen containing organic compounds such as amino acids and proteinaceous matter to form organic chloramines (which have little biocidal activity), as in the following general expression:



Water treatment conditions are controlled to preferentially produce monochloramine. Formation of the other two chloramines, particularly trichloramine, is undesirable because of aesthetic problems. Dichloramine can cause tastes and odours, and irritation of eyes and breathing passages can result from contact with trichloramine.

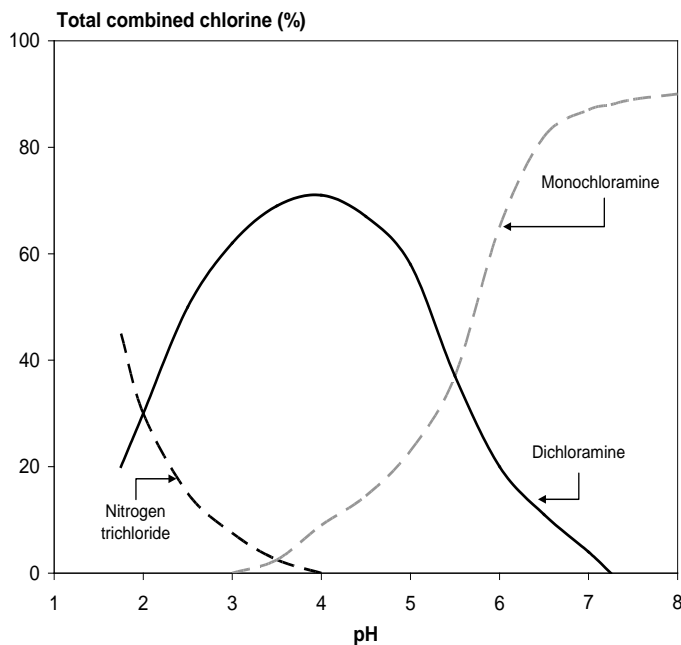
Increasing the chlorine to ammonia ratio favours the formation of the chloramines containing more chlorine, namely, dichloramine and trichloramine. Figure 15.2 (Figure 6-1 in USEPA 1999) shows why a ratio of around 4:1 is usually not exceeded in the production of monochloramine. The pH conditions that apply in Figure 15.2 are 6.5–8.5.

Figure 15.2: The effect of chlorine to nitrogen ratios in producing chloramines compounds



In practical disinfection conditions, it is generally considered that dosing at Cl₂:N = 4:1 in the pH range 7.0–8.5 will produce a monochloramine residual with traces of dichloramine and no free chlorine. Considerable dichloramine formation can occur in poorly mixed systems. Figure 15.3 (Figure 6-2 in USEPA 1999) shows the effect of pH on chloramines production and why a low pH should be avoided, either directly or as a result of poor mixing.

Figure 15.3: Distribution diagram for chloramine species with pH



In Australia most water suppliers producing chloramine use gaseous chlorine; smaller authorities use 25 percent aqua ammonia, and bigger authorities use anhydrous ammonia. A low chlorine to ammonia ratio appears to produce fewer taste and odour problems and greater efficiency of monochloramine formation but increases the risk of nitrification due to higher levels of excess ammonia in the distribution system, where they can be oxidised to nitrite, and ultimately to nitrate (AWWA 2004). Three Australian authorities use a ratio 2:1, eight use 3:1, one uses 3.5:1, and three use 4:1. Chlorine dose rates vary from 0.7–0.9 mg/L up to 9.5 mg/L. Most authorities aim to achieve a monochloramine residual of 0.2–0.5 mg/L (as chlorine) at the extremity of the system (UWRAA 1990). Nitrification can result in increased concentrations of nitrite and nitrate, and if the ammonia content is particularly high, the nitrite MAV could be exceeded. Treatment to produce a monochloramine residual poses the risk of nitrite formation in the distribution system, especially in low-flow stagnant areas, because bacteria on surfaces and in deposits may nitrify any slight excess of ammonia (WHO 2004b).

The method by which the chloramines are generated has a bearing on the disinfection of the water and on the formation of disinfection by-products. Chlorination of the water followed by addition of ammonia offers the advantage of the disinfecting power of chlorine before it is converted into chloramines, which are much less effective disinfectants. However, it does allow the formation of the disinfection by-products associated with chlorination, albeit at lower concentrations, because of the brief contact time before ammoniation.

Adding the ammonia before chlorine also leads to some disinfection by-product formation, possibly because of competition between the ammonia and natural organic chemicals for reaction with the chlorine. The formation of disinfection by-products can be minimised by pre-forming the monochloramine offline. The rapid deactivation rate of bacteria and viruses produced by FAC is not available using either of these two approaches. If traces of phenolic substances are present, adding the ammonia first will avoid the formation of chlorophenols.

Chloramines, both inorganic and organic, can be formed unintentionally during the chlorination of waters containing ammonia, or organic nitrogen compounds that are naturally present in the water. The presence of these compounds complicates the important measurement of FAC, and may also lead to unpleasant tastes and odours. Their concentration should therefore be minimised by treatment adjustment.

Chloramines, when present as nuisance compounds, can be oxidised to nitrogen gas by chlorine and, to a small extent, to nitrate. This is achieved by ensuring that sufficient chlorine is added to the water to obtain a FAC residual. Dosing with insufficient chlorine will result in unnecessary chloramine production.

There are two reasons for the present interest in the use of chloramines for disinfection.

Firstly, it is chemically less reactive, and consequently a chloramine residual will last longer, maybe up to 20 days in the distribution system. This is an advantage in distribution systems where the maintenance of a chlorine residual is difficult because of either the extent or the condition of the network. It has been used increasingly in Australia where FAC has been unsuccessful in very long pipelines with high water temperatures, and in water that has often not undergone full treatment. In some cases chloramines have been abandoned in Australia due to biofilm problems, and when taste and odour problems could not be resolved (UWRAA 1990).

Secondly, chloramines create lower concentrations of chlorinated disinfection by-products than chlorine (except for cyanogen chloride, which is produced in higher concentrations by the chloramine process), so long as the method of generation minimises the contact between free chlorine and the water being treated (as noted above). Note however that recent studies have suggested that iodinated DBPs may be more toxic than the equivalent chloro- or bromo-BPBs. DEFRA (2009) stated:

There is evidence that the formation of iodinated DBPs is increased by chloramination and reduced by ozonation and that iodinated-THMs may be removed by GAC to some extent. Chloramination is not common in the UK, while ozonation and GAC are widely used. Taking all this information, together with modelling which estimates the formation of iodinated DBPs and limited monitoring data, it appears likely that the levels of iodinated DBPs in England and Wales will be no higher and will probably be lower than the low concentrations detected in the USA. It should be noted that the introduction of a standard for haloacetic acids in England and Wales may lead to an increased use of chloramination and if this occurred, further consideration of the concentration of iodinated DBPs in drinking water would be advisable.

Disinfection by-products are also discussed in Chapter 10: Chemical Compliance, sections 10.2.1, 10.2.2, 10.2.3, 10.2.5.3, 10.3.2 and 10.4.1, and in the individual datasheets.

15.5.2.2 Disinfection using monochloramine

Monochloramine is a much weaker bactericide than chlorine (dichloramine is somewhat stronger than monochloramine, and there are no data on the disinfecting

powers of trichloramine). Although dichloramine is expected to be a stronger virucide than monochloramine, some studies have shown the opposite.

Limited studies have shown that the sensitivities of a number of enteric pathogenic bacteria and the indicator organism, *E. coli*, to chloramines, are similar. Other studies have shown that some viruses are inactivated more slowly than *E. coli*. The use of *E. coli* as an indicator organism for bacteria would therefore appear to be sound, but the organism is an unreliable guide on which to judge the overall microbiological safety of a water disinfected with chloramines.

The efficacy of all disinfectants is temperature dependent, but the biocidal properties of chloramines are severely affected by low temperatures.

Because of its poorer disinfecting power, monochloramine requires longer contact times to achieve the same percentage inactivation as the equivalent concentration of chlorine. This should be kept in mind if chloramination is being considered for small distribution systems where contact times may be short. Chloramine concentrations of less than 2 mg/L as Cl₂ have been shown to take several hours to inactivate 99 percent of some virus species. See Table 15.7.

Nitrite can occur in the distribution system at higher concentrations when chloramination is used, but the occurrence is almost invariably sporadic. Nitrification occurs when bacteria oxidise ammonia to nitrite. Ammonia can appear in the raw water, can be produced as an end-product of the degradation of chloramine, or as an excess from chloramine production. The risk of methaemoglobinaemia therefore may become an important consideration. All water systems that practise chloramination should monitor their systems closely and regularly to verify disinfectant levels, microbiological quality and nitrite levels. If nitrification is detected (eg, reduced disinfectant residuals and increased nitrite levels), steps should be taken to modify the treatment process or water chemistry in order to maintain a safe water quality. Some trials have shown that dosing sodium chlorite as low as 0.1 mg/L can arrest the nitrification process (McGuire et al 2004). Efficient disinfection must never be compromised.

Chloramines are more toxic than chlorine to most aquatic organisms. In general, they are extremely toxic at low levels to all fish. The introduction of chloramines for disinfection may therefore create difficulties for private consumers or businesses using the reticulated water supply for keeping aquatic animals and organisms.

Chloraminated water is also unsuitable for renal dialysis patients. Removal of the chloramines from the water using activated carbon is necessary.

15.5.2.3 Measurement of chloramines

Combined available chlorine, or combined chlorine, is the chlorine present in chloramines. Any system that measures total chlorine is measuring FAC plus chloramines, see section 15.5.1.3. DPD methods can be used to measure combined chlorine, because the chlorine incorporated in these compounds can be released to develop the pink colour in the same way as chlorine. The measurement of combined chlorine is therefore a measure of the chloramines present either as a disinfectant or as

by-products of chlorination. At low combined chlorine concentrations the reaction with DPD is slow, but the speed of the colour development is increased by the addition of iodide to the reaction.

Methods using DPD have been reported for distinguishing between mono-, di- and trichloramine. These methods are prone to interference in waters containing organic nitrogen compounds, and manganese. As a result, trying to distinguish between the different inorganic chloramines in natural waters is of little value, and only combined chlorine as a total value need be reported. The monochloramine result can be falsely high if the reagents are not fresh. Refer to APHA (2005) and the datasheet for further information.

Chloramine concentrations, like the concentration of chlorine, are usually expressed in units of mg/L (as Cl₂) where mg/L chloramine x 71/51.5 = mg/L as chlorine:

where:

- 71 is the molecular weight of chlorine (Cl₂)
- 51.5 is the molecular weight of monochloramine (NH₂Cl).

Because the success of chloramination depends on dosing two chemicals, both dosed at the correct rate and in the correct ratio, it is strongly recommended that the chloramine concentration be monitored continuously at the water treatment plant.

15.5.3 Chlorine dioxide

Chlorine dioxide (ClO₂) was first used as a water disinfectant in the early years of the 20th century. Chlorine dioxide was used for some years in New Plymouth.

Chlorine dioxide is a stronger disinfectant than chloramines, equal or superior to chlorine on a mass-dose basis, is effective over a wider pH range, and can be used to inactivate protozoa, as well as bacteria and viruses. Unlike chlorine, it does not react (hydrolyse) with water to form a disinfectant such as or equivalent to hypochlorous acid; the gas chlorine dioxide is reasonably soluble in water, about 1000–2000 mg/L. Also unlike chlorine, it does not react with ammonia to form chloramines.

Chlorine dioxide cannot be purchased; it is made at the water treatment plant. Chlorine dioxide packs are available for travellers and for emergency use and can be purchased, for example, at sports shops.

Table 15.8 includes data from WHO (2004). See Table 15.1 for some earlier data. The table presents conservative estimates of microbial reductions based on the more resistant or persistent pathogenic members of the group.

Table 15.8: Chlorine dioxide C.t values for 99 percent inactivation (2 logs)

| Micro-organism | Contact time (C.t) | Conditions |
|----------------|--------------------|---------------|
| Bacteria | 0.13 mg.min/L | 1–2°C; pH 7 |
| | 0.19 mg.min/L | 1–2°C; pH 8.5 |

| | | |
|------------------------|--------------|--------------|
| Viruses | 8.4 mg.min/L | 1°C; pH 6–9 |
| | 2.8 mg.min/L | 15°C; pH 6–9 |
| <i>Giardia</i> | 42 mg.min/L | 1°C; pH 6–9 |
| | 7.3 mg.min/L | 25°C; pH 6–9 |
| <i>Cryptosporidium</i> | 40 mg.min/L | 22°C; pH 8 |

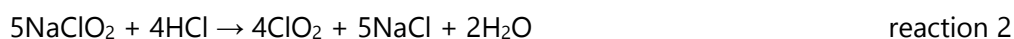
Ex WHO 2004.

Note that the USEPA (2003a) C.t values (and as adopted by DWSNZ) for *Cryptosporidium* are much higher. The WHO value is a summary of results from laboratory studies. The USEPA C.t values have been developed for the real situation of reliably achieving x logs inactivation, within defined confidence bounds, in all types of water treatment plants, receiving a variety of raw waters. The units of concentration are as ClO₂, not Cl₂, see section 15.5.3.3.

Figure 11.7 in WHO (2004a) was taken from Jacangelo (2002). It shows a comparison of the C.t values for 2-log inactivation of a range of micro-organisms by chlorine dioxide. The most resistant organisms are *Cryptosporidium*, legionellae bacteria, mycobacteria, *Giardia* and calcivirus.

15.5.3.1 Chemistry

Chlorine dioxide (ClO₂), a gas at normal temperatures, is unstable (air concentrations of 10 percent or greater are explosive) and cannot be compressed. It can be stored as a liquid for short periods below 4°C but it soon dissociates into chlorine and oxygen. For these reasons it has to be produced on-site, most frequently by the reaction of sodium chlorite and chlorine at low pH (reaction 1). The reaction of acid with sodium chlorite can be used to produce chlorine dioxide free of chlorine (reaction 2), therefore trihalomethanes will not form, but the process is less efficient for larger plants. Small plants may also add chlorite and persulphate (reaction 3). Equipment for generating chlorine dioxide is usually a proprietary product, which should be commissioned, operated, maintained and monitored according to the supplier's instructions.



Chlorine dioxide production is somewhat dependent on reaction pH and reactor design (USEPA 1999). An excess of chlorine results from reaction 1, albeit generally less than 2 percent. Because FAC can be present with the chlorine dioxide produced by this process, the DWSNZ allow the sum of the two disinfectants to be used in bacterial compliance monitoring. However, for protozoal compliance, only the chlorine dioxide component can be reported. This requires the use of analytical techniques that can measure each disinfectant (in plants using reaction 1).

Recently, production of chlorine dioxide from sodium chlorate (NaClO₃) has been introduced as a generation method where in NaClO₃ is reduced by a mixture of concentrated hydrogen peroxide (H₂O₂) and concentrated sulphuric acid. Only a few plants have been installed, all overseas.

Sodium chlorite is a powerful oxidant and, like solid hypochlorites, is dangerous if mishandled or stored incorrectly. It should not be allowed to come into contact with combustible materials, or reducing agents, and spillages should be washed away with large amounts of water. ANSI/AWWA Standard B303-10 covers sodium chlorite.

Unlike chlorine, which reacts with water, chlorine dioxide dissolves in water, but does not react with it. While it is readily soluble, it is extremely volatile and can be removed rapidly from solution by aeration. It is therefore important that systems handling chlorine dioxide are sealed to ensure that loss of the gas cannot occur throughout-gassing.

Chlorine dioxide is decomposed rapidly by sunlight and UV light, so a chlorine dioxide residual will quickly disappear from open reservoirs or sections of a treatment plant open to the sun.

Although chlorine dioxide is a compound of chlorine, it acts more as an oxidising agent than a chlorinating agent. It does not form trihalomethanes through reaction with natural organic matter, and this is one of the reasons why interest in its use has increased (apart from its ability to inactivate protozoa). However, chlorine is often used to generate chlorine dioxide, and small amounts of chlorine are usually present in the output from the generator. As a result, some formation of chlorinated organic by-products will still occur, although at much lower levels than if chlorine had been used as the disinfectant. Bromide is oxidised very slowly by chlorine dioxide, hence brominated disinfection by-products will not appear in significant concentrations when the chlorine dioxide used contains very little, or no, chlorine.

Changing to chlorine dioxide treatment to take advantage of its stronger oxidation potential can sometimes alleviate tastes that arise when chlorine is used. Oxidation by chlorine dioxide is also used to help in the oxidation of iron and manganese, although this is greatly hindered if the metals are complexed with organic matter.

The disinfection by-products of greatest concern resulting from the use of chlorine dioxide are the inorganic oxychlorine ions, chlorate and chlorite (both MAVs are 0.8 mg/L). Chlorate is an impurity formed during the generation of chlorine dioxide. Chlorite is formed from reactions with contaminants, such as natural organic matter; it may also appear as an excess of raw material. More toxicological information about chlorate and chlorite is contained in the datasheets for these compounds.

The chlorine dioxide dose is usually limited by the concentration of chlorite reaching its MAV of 0.8 mg/L. Chlorate production is less of a problem. Chlorine dioxide demand trials are needed to check the development of chlorite. USEPA (1999) reported the results of a trial dose of 1.4 mg/L chlorine dioxide. After three minutes the ClO_2 concentration was 0.47 mg/L and chlorite was 0.76 mg/L. After 1 hour these were 0.11 and 1.11 mg/L respectively. Chlorate concentrations were around 0.06 mg/L throughout the trial.

Chlorine dioxide is consumed rapidly by reaction with organic matter. The use of chlorine dioxide as close to the end of the treatment process as possible reduces reaction with organic matter, and thereby minimises chlorite formation and improves the economics of treatment. Where raw waters are low in organic matter (and chlorite

formation will therefore be lower), pre-treatment with chlorine dioxide may be advantageous in the control of biological growth.

Unpleasant odours associated with the use of chlorine dioxide can arise. These appear to result from reaction between chlorine dioxide volatilising from tap water, and organic compounds in the air. The most frequently reported odours are described as being like cat urine, kerosene or new carpets.

15.5.3.2 Disinfection using chlorine dioxide

Bacteria are inactivated rapidly by chlorine dioxide, and it has been reported to be even more effective in inactivating viruses, although the results of different studies are conflicting. The ability to inactivate viruses appears similar to chlorine in acid and neutral conditions, but is superior at higher pH values. The effectiveness of chlorine dioxide in inactivating bacteria and viruses is generally equal, or superior, to that of chlorine on a mass-dose basis (ie, 1 mg of ClO_2/L is equal to or superior to 1 mg of Cl_2/L). It is a poorer disinfectant than ozone.

Chlorine dioxide is thought to inactivate micro-organisms through direct oxidation of tyrosine, methionyl, or cysteine-containing proteins, which interferes with important structural regions of metabolic enzymes or membrane proteins (taken from WHO 2004b, Chapter 3.3.3).

Cysts of *Giardia* and oocysts of *Cryptosporidium* can be inactivated by chlorine dioxide. It may be difficult to reach the required dose without exceeding the MAVs for chlorite and chlorate. It may be possible to overcome this problem by using a very long contact time in order to satisfy the C.t values for the various log removals (Table 5.5 of DWSNZ). For example:

For 3 log credits at 15°C, C.t = 536, therefore $C = 536/t$ (in minutes), so:

for 4 hours' contact: $C = 536/240 = 2.23 \text{ mg/L}$

for 48 hours' contact: $C = 536/2880 = 0.19 \text{ mg/L}$.

Note that C is the residual, not the dose; see section 15.2.9 for methods for calculating t.

To achieve the required C.t value, reliably covering periods with variations in flow, temperature or disinfectant demand, it is recommended that water suppliers establish a control limit. This should be documented in the WSP, along with actions that will prevent the situation worsening to the extent of transgressing the protozoa compliance criteria. The control limit, or margin of safety, will depend on the nature of the source water, the treatment processes, short-term flow fluctuations, and whether the contact tank has a constant volume.

There are conflicting reports about the pH dependence of the bactericidal properties of chlorine dioxide, although at low bacterial levels in natural waters the dependence appears to be slight. Inactivation of protozoa is not pH dependant.

See USEPA (1999) for a full discussion on the use of chlorine dioxide. Refer also to Chapter 10 of the review draft LT2ESWTR Toolbox Guidance Manual (USEPA 2009) which discusses issues related to the use of chlorine dioxide.

15.5.3.3 Chlorine dioxide measurement

During its reactions with other substances, chlorine dioxide can be converted to chlorite or chloride, depending on the pH and the substances with which it reacts. In the pH range expected in drinking-water treatment the predominant end-product is chlorite. The oxidising potential of this reaction is less than that of the reaction that converts chlorine dioxide to chloride.

These two processes by which chlorine dioxide can oxidise other substances complicate the reporting of results, and can lead to misunderstanding about the disinfecting powers of chlorine dioxide residuals. Confusion can arise in the expression of the chlorine dioxide concentration because many texts provide calculations from the raw test readings that express chlorine dioxide in mg/L as Cl_2 , assuming that chlorine dioxide is fully reduced to chloride during its reactions. Expression of the concentration of chlorine dioxide in mg/L as Cl_2 , and on the basis that it is converted to chloride (which it isn't), can give a false impression of the disinfecting capabilities of the chlorine dioxide residual and of the oxidising capabilities of the chlorine dioxide present in the water unless the method of measurement is clearly stated and its chemistry understood. These problems can be overcome largely by expressing the results of chlorine dioxide measurements as mg/L ClO_2 . The chlorophenol red method referred to in the chlorine dioxide datasheet expresses its results directly as mg/L ClO_2 . If either the APHA amperometric or DPD method referenced in the datasheet is being used for chlorine dioxide measurement, the factors provided in the method can be used to express the results in mg/L ClO_2 .

The measurement of chlorine dioxide in water can be complicated, especially if chlorine and chloramines are also present, and if the concentrations of chlorite and chlorate are also required. Chloramines should not cause analytical problems if the ammonia content in the raw water is low. Iodometric, amperometric and DPD methods of measuring chlorine dioxide are documented.

The iodometric method given in *Standard Methods for the Examination of Water and Wastewater* (21st edition 2005, APHA, AWWA, WEF) can be used for measuring chlorine dioxide in pure solutions, ie, for temporary standards, but is of little value for field measurements.

The amperometric method is a modification of that used for chlorine measurement. The methods in APHA (2005) can produce results for FAC, chloramines, chlorite, chlorate and chlorine dioxide. These involve up to four separate measurements made under different test conditions, followed by a series of calculations. Requiring four measurements leads to a higher level of uncertainty.

If chlorine dioxide is produced by the acid/chlorite process, there should be no FAC or chloramines present, in which case the chlorine dioxide concentration can be measured directly; this allows continuous monitoring.

Being reactive, chlorine dioxide must be measured as soon as possible after collecting the sample. For bacterial and protozoal compliance testing, the DWSNZ require online measurement. To avoid the fairly high analytical uncertainty in the measurement of

chlorite and chlorate by the methods discussed above, they should be measured by ion chromatography for compliance purposes.

The DPD method is a modification of the chlorine method, in which any chlorine is neutralised by the addition of glycine. The chlorine dioxide measurement requires only one reading, but if chlorine is to be determined as well, the difference of two readings is required, and the determination of chlorite requires three readings.

The chlorophenol red method is reported to be a relatively simple, sensitive and specific method (no interference from chlorine, chlorite, chlorate or chloramines) for the measurement of chlorine dioxide. The chlorophenol indicator can be used as part of a colorimetric or titration method (Harp et al 1981).

A lissamine green/horseradish peroxidase spectrophotometric method was developed (USEPA 2005) for WTP monitoring.

15.5.4 Ozone

Note: The ozone section of the 1995 edition of the Guidelines contained only two pages, mainly because at that time, ozone was not used in New Zealand for disinfecting drinking-waters. By 2005, more detailed protozoa compliance criteria had been developed for the DWSNZ, based largely on treatment processes rather than monitoring protozoa in the water supply. The efficacy of ozone in inactivating protozoa suggests the process may be used more often in the future. Therefore this section has been expanded to 7–8 pages. Further information also appears in Chapter 8: Protozoa Compliance, section 8.4.4.2, which discusses compliance issues related to ozone, including a summary of how the USEPA derived the C.t values for 1, 2 and 3 log removals.

These Guidelines aim to provide the reader with a general understanding of the issues related to disinfection using ozone for disinfecting drinking-water in New Zealand. This section deals more with operational matters; Chapter 8 covers compliance issues. Because compliance is largely determined by assessing operational requirements (section 5.15 of the DWSNZ), inevitably there will be some overlap.

Although ozone was first used for water treatment near the turn of the century, its recent increased usage has stemmed from concerns over the disinfection by-products produced by chlorine, and due to its relative ease in inactivating protozoal (oo)cysts.

Ozone is a potent bactericide, a strong virucide and it can inactivate cysts/oocysts and spores. Cysts and spores are approximately ten times more resistant to ozone than viruses. Ozone is a more powerful disinfectant than chlorine for all classes of organism by factors ranging from 10 to 100. The germicidal efficiency changes only slightly over the pH 6.5 to 8, the range of interest in most potable waters. Table 15.9 includes data from WHO (2004). See Table 15.1 for some earlier data. The table presents conservative estimates of microbial reductions based on the more resistant or persistent pathogenic members of the group.

Table 15.9: Ozone C.t values for 99 percent inactivation (2 logs)

| Micro-organism | Contact time (C.t) | Conditions |
|------------------------|--------------------|--------------|
| Bacteria | 0.02 mg.min/L | 5°C; pH 6–7 |
| Viruses | 0.9 mg.min/L | 1°C |
| | 0.3 mg.min/L | 15°C |
| <i>Giardia</i> | 1.9 mg.min/L | 1°C; pH 6–9 |
| | 0.63 mg.min/L | 25°C; pH 6–9 |
| <i>Cryptosporidium</i> | 40 mg.min/L | 1°C |
| | 4.4 mg.min/L | 22°C |

Ex WHO 2004.

Figure 11.5 in WHO (2004a) was taken from Jacangelo (2002). It shows a comparison of the C.t values for 2-log inactivation of a range of micro-organisms by ozone. The most resistant organisms are *Cryptosporidium*, the mycobacteria and legionellae.

Table 7.7 in WHO (2017) shows the range of C.t values found for ozone for 2-log inactivation:

| | |
|----------|---|
| viruses | 0.006 to 0.2 min mg/L at 0-10°C, pH 7–9 |
| bacteria | 0.02 min mg/L at 15-25°C, pH 6.5–7 |
| protozoa | 0.5 to 40 min mg/L. |

Ozone is used in drinking-water treatment for a variety of purposes including:

- disinfection
- oxidising inorganic compounds, including iron, manganese, and sulphide (see Chapter 18)
- oxidation of organic compounds for colour removal, increasing the biodegradability of organic compounds, reduction of disinfection by-products (DBPs) and reduction of chlorine demand
- oxidation of trace organic compounds, such as those producing taste and odour, phenolic compounds, and some pesticides.

In the majority of applications it is added as a disinfectant. Ozone is not dosed to remove a measurable, specific contaminant in the water (at least, not measurable on-site). An ozone dosing installation is operated under similar principles to that of a chlorine installation, ie, it is dosed to achieve a desired C.t after a given contact time (note that C.t is absolute hydraulic residence time, not contact time). As with chlorine, the contact time in a contactor will vary with plant flow and, consequently the rate of dosing ozone (in g/h) will vary. As with chlorine, the ozone demand can change too. The ozone dose rate is also varied to meet any change in demand. This is achieved by continuously monitoring the ozone concentration and altering the ozone dose rate to achieve the desired outlet concentration. Thus an ozone dosing installation maintains the required C.t by ensuring a minimum ozone dose is maintained through changes in flow (contact time) and ozone demand.

15.5.4.1 Ozone chemistry and production

Ozone, O₃, is a toxic, unstable form of oxygen. It is a stronger oxidising agent than oxygen and one of the strongest of the oxidising agents used to treat water. As a result of its instability it has to be produced on-site. It is produced by the reaction between an oxygen atom and an oxygen molecule.

Ozone is produced by passing dry air, oxygen, or a mixture of the two, through two electrodes separated by a dielectric and a discharge gap. A high voltage is applied, resulting in a flow of electrons through the discharge gap. The electrons provide the energy required to dissociate the oxygen molecule, leading to the formation of ozone.

The four major components of an ozone treatment system are:

- gas feed
- ozone generator
- ozone contactor
- ozone off-gas destructor.

Gas feed

This is commonly high purity oxygen, air, or a mixture of the two. For a given ozone generator the rate of production is greater when oxygen is used as the feed gas.

Liquid oxygen feeds are relatively simple and consist of storage tanks, evaporators, filters and pressure regulators, required to limit the gas pressure for the ozone generators.

Air systems are reasonably complicated, as the air presented to the generator should be clean, free of contaminants and dry, with a maximum dew point of –60°C. An air preparation system consists of compressors, filters, desiccant dryers and pressure regulators. Filters are required to remove particles greater than 1 mm and oil droplets greater than 0.05 mm. Granular activated carbon filters are used to remove any hydrocarbons present in the feed gas. Moisture is removed to prevent arcing that can result in damage to the dielectrics.

Ozone generator

The most common ozone production method is by corona discharge. The yield of ozone varies according to voltage, the discharge gap width, frequency, and feed gas pressure. There are trade-offs in design and operating parameters. For example, as voltage is increased, the electrodes and dielectric material are more subject to failure.

The two configurations are parallel plates and concentric cylinders, with the parallel plate more commonly used in small systems. As most of the energy used in the generator is lost as heat, a cooling system is required to maintain generator efficiency. Whereas the parallel plate system can be cooled with air, the most common coolant used is water.

The most common ozone contactors are the bubble diffuser, injector and turbine mixer.

Bubble diffuser contactors

The depth of water in the contact tank is typically 5–7 metres to achieve 85–95 percent efficiency in ozone transfer. They can be constructed in counter-current (water and ozone flowing in opposite directions), co-current (same direction) and alternating co-current/counter-current configurations. Most treatment plants use two or three chambers for ozone contact and for reaction.

Not all of the ozone is transferred to the water. The contact chambers are covered to contain the ozone gas above the water, from where it is transferred to an ozone destructor. Some designs take the off-gas from the main contactors to a contact chamber upstream to provide another ozonation stage in the process and also provide a more efficient use of the ozone generated.

WRF (2016b) reports a case study which provided full-scale evidence regarding the difference between ozone dissolution using fine bubble diffusion (FBD) versus side stream injection (SSI) with degas. The results are intended to further the understanding of design and operation of the systems by design engineers and utilities.

Injectors

A venturi section is used to generate a negative pressure and ozone is injected under this partial vacuum. Additional contact time is required to meet the C.t requirements of the installation. This is normally provided in a plug flow reactor.

Turbine mixer

The ozone gas is fed into a contactor and the turbine mixer is used to mix the ozone with the water. The chamber water depth can vary from about 2–4.5 m. As with injector mixers, there may not be sufficient contact time to meet C.t requirements and additional contact volume may be required.

Off-gas destruction

As the ozone concentration in the off-gas will be much greater than the fatal concentration, the ozone has to be converted back to oxygen prior to release. These destructors can either be operated at high temperatures or use a catalyst to allow operation at lower temperatures. The off-gas is drawn through the contactor, creating a partial vacuum to reduce the risk of escape.

15.5.4.2 Disinfection using ozone

The rate at which organisms are inactivated by a disinfectant increases with increasing temperature, but this can adversely affect the overall efficiency of the ozonation process. This arises from a decrease in the efficiency of transfer of ozone into water as temperature increases.

Ozone is able to achieve disinfection with less contact time and at lower concentrations than chlorine, chlorine dioxide and monochloramine, but its instability and reactivity

means that it is unable to provide a disinfecting residual. Ozone is generally used as the primary disinfectant and oxidising agent, with a secondary disinfectant such as chlorine or monochloramine added downstream, to provide a residual.

Ozone in aqueous solution may react with microbes either by direct reaction with molecular ozone or by indirect reaction with the radical species formed when ozone decomposes. Ozone is known to attack unsaturated bonds, forming aldehydes, ketones or carbonyl compounds. Additionally, ozone can participate in electrophilic reactions, particularly with aromatic compounds, and in nucleophilic reactions with many of the components of the microbial cell. Carbohydrates and fatty acids react only slightly with ozone, but amino acids, proteins, protein functional groups (eg, disulphide bonds) and nucleic acids all react very quickly with it. It is likely, therefore, that microbes become inactivated through ozone acting on the cytoplasmic membrane (due to the large number of functional proteins), the protein structure of a virus capsid, or nucleic acids of micro-organisms. Free radicals formed by the decomposition of ozone are generally less effective for microbial inactivation than molecular ozone, because microbial cells contain a high concentration of bicarbonate ions that quench the free radical reaction, and many microbial cells also contain catalase, peroxidase, or superoxide dismutase to control the free radicals produced by aerobic respiration. Taken from WHO (2004b), Chapter 3.3.4.

When chlorine (or chloramine) is used as the secondary disinfectant, it should be added after the ozone residual has been reduced to zero. The reaction between ozone and chlorine/ chloramine would result in an increased chlorine/chloramine dose requirement. Further, the oxidation of chlorine can lead to the production of chlorates.

The stability of ozone decreases with increasing pH and temperature, so that at 15°C and a pH of 7.6 the lifetime of the residual is of the order of 40 minutes, but at higher temperatures it can be as low as 10–20 minutes.

The contactor should be designed to provide plug flow hydraulics. This will result in the minimum overall volume and maintain the required C.t value for the system. The volume is determined from the applied ozone dose, the disinfection C.t requirement and the estimated residual ozone concentration.

Generators should be checked daily when in operation and their maintenance requires skilled technicians. If trained maintenance staff is not available at the plant, the equipment manufacturer should do this work.

After a shutdown, dry air or oxygen should be passed through the generator to remove any moisture prior to energising the electrodes. At initial start-up and after long downtimes, this process may take up to 12 hours and usually longer when air is the feed gas. A small flow of dry air can be passed through the generator continuously when it is in standby mode to maintain the dry condition.

Filters and desiccant dryers in air preparation systems should be changed periodically, with the frequency depending on the quality of the inlet air and the number of hours in operation. Compressors require periodic service, depending on the type and operating time. Liquid oxygen tanks should be periodically pressure tested. Piping and contact chambers should be inspected periodically to check for leaks and corrosion.

Disinfection by-product (DBP) control

The key variables that determine ozone's effect in the oxidation of DBP precursors, prior to chlorination, are dose, pH, alkalinity, and the nature of the organic material. At low pH levels, precursor destruction is quite effective; above some critical pH, ozone is less effective, and sometimes increases the amount of chlorination by-product precursors. For most humic substances the critical pH is 7.5, which is about the level at which decomposition of ozone to hydroxyl free radicals increases rapidly, thus increasing organic oxidation rates.

Higher alkalinities help reduce THM formation potential (THMFP). This is because alkalinity scavenges any hydroxyl free radicals formed during ozonation, leaving molecular ozone as the sole oxidant, which has a lower oxidation potential than the hydroxyl free radical. Given neutral pH and moderate levels of bicarbonate alkalinity, THMFP level reductions of 3–20 percent have been shown at ozone doses ranging from 0.2 to 1.6 mg ozone per mg carbon.

The formation of bromate (BrO_3^-) as a disinfection by-product of ozone is of greater health significance than the formation of organic disinfection by-products. Bromate is formed by the oxidation of bromide in the water. Factors that lead to reduced bromate formation are: low bromide concentration, low pH, high NOM concentration, and a high ammonia concentration. This is because:

- 1 a low bromide concentration limits the amount of bromate that can form
- 2 low pH favours the formation of molecular O_3 and reduces the formation of free radicals from ozone. It is the free radicals that are the primary route to bromate
- 3 high NOM acts as a sink for bromide. Bromide is initially oxidised to BrO^-/BrOH , which will react with NOM if it gets the opportunity. The higher the NOM concentration the greater the likelihood of this reaction taking place, and the less bromine there is available to go on to form bromate
- 4 ammonia provides another sink for bromide. Again, after the initial oxidation of bromide, the BrO^-/BrOH reacts rapidly with ammonia if it gets the opportunity, thereby stopping bromate formation.

Both 3 and 4 work by increasing the rate at which a process that competes with bromate formation occurs.

By-products

Ozone can produce undesirable by-products. It can break down organic matter such as humic substances to small organic compounds that are assimilated more readily by micro-organisms. This can promote microbial regrowth in distribution systems. The increased assimilable organic carbon concentration can be reduced by filtration and by adsorption using granular activated carbon beds. This should be considered to minimise any regrowth problems that may be associated with ozone.

Ozone can oxidise any bromide present in the water to bromate. The oxidation reaction with bromide leads to the production of hypobromous acid and hypobromite. Hypobromite can be oxidised to bromate, a possible carcinogen. The hypobromous acid and hypobromite can react with organic matter present to form brominated organic compounds, similar to those formed by chlorine.

Ozone treatment is inadvisable for waters containing bromide, such as bore waters prone to seawater intrusion. One of the products of the reaction with chloride is chlorate, which has a MAV of 0.8 mg/L.

See section 15.4 and Chapter 10: Chemical Compliance, section 10.2, which also discuss DBPs. Some ozone disinfection by-products are listed in the Datasheets Index, section 3.2(a). Refer also to Chapter 11 of the review draft LT2ESWTR Toolbox Guidance Manual (USEPA 2009) which discusses issues related to the use of ozone.

15.5.4.3 Ozone measurement

The ozone process can be monitored, with manual control often used for small systems. Flow and ozone monitors can be used together, to match dose to water flow and ozone demand. Ozone generation can be controlled to meet these process demands.

The process is very reliable and can be highly automated, requiring only a modest degree of operator skill and time to operate an ozone system.

Instrumentation can play an important role in the safe and efficient operation of an ozone system. To maintain a safe working environment, gas phase ozone concentrations should also be measured:

- in workspaces where personnel routinely visit, such as ozone generator rooms
- on the outlet from the off-gas destructor, to ensure the destructor is achieving the correct ozone concentration in air being discharged to the environment.

These monitors should be linked to the ozone generator, shutting down in the event of raised ozone levels detected.

Ozone residual measurement: sampling

As the half-life of ozone in water is very short, from 1 to 40 minutes, the ozone concentration has to be measured very soon after the sample is taken. Online sampling should be designed to minimise the detention time. Separate sample ports should be provided at the outlet of each contact chamber to provide the maximum flexibility in measuring ozone in water residuals through the ozonation process. The sample pipe inlets need to be located in the main stream and be extended into the contactor chamber to ensure a representative sample is obtained. The inlet pipe requires to be designed to minimise the potential for picking up gas bubbles and also to prevent clogging, should there be solids present in the feed water. See Appendix C in the review draft LT2ESWTR Toolbox Guidance Manual (USEPA 2009).

Standardisation of online ozone residual monitors

Online analysers can be used to monitor continuously the ozone residual in water and provide C.t information for earning protozoa log credits, automatically. These analysers need to be standardised against grab samples on a regular basis, at least weekly. The water temperature is needed too.

USEPA (2009) states in section 11.4.1:

The concentration of ozone must be measured with the indigo colorimetric method, APHA Standard Method 4500-O₃ B

USEPA (2009) describes ozone residual measurement in Appendix C.

Checking by a Ministry of Health recognised laboratory is preferred, but if the analyser is checked using a field test method, the field test method should be calibrated against the referee method (Indigo Colorimetric Method, Standard Methods 4500-O₃, APHA 2005, 21st edition) at least once every six months (DWSNZ section 5.15.3: Ozone analyser calibration) by a Ministry of Health recognised laboratory.

Ozone residual measurement: testing (manual)

Because ozone is so reactive it is necessary to cross-check multiple samples, preferably five, using the following procedure:

- 1 Obtain an analyser reading while the grab sample is being collected, with an appropriate time delay to allow for flow time in the sample line.
- 2 Promptly measure the ozone residual concentration in the grab sample, using the indigo method.
- 3 Calculate the average grab sample ozone residual value and the average analyser ozone residual value.
- 4 Compare the average of the online and grab-sample results. The average of the online analyser should not deviate more than 10 percent or 0.05 mg/L (whichever is larger) from the grab sample average. If it is more than this, adjust the meter reading as per the manufacturer's instructions. It is important that the online analyser not record more than 10 percent or 0.05 mg/L greater than the grab samples. A negative deviation bias, while not affecting public health, may also be useful as an indication of a malfunctioning unit.
- 5 Allow the analyser to stabilise for a period of 30 minutes after adjusting the meter reading and repeat steps 1 to 4 until the difference calculated in step 4 is less than 10 percent of the grab sample average or less than 0.05 mg/L.

The indigo method assumes that high-purity reagents are used. Several reports have been published discussing a potential biasing where reported results could be significantly low. The potential biasing involves the value of the sensitivity factor used in the calculation. Water suppliers using this method should keep up-to-date with any developments.

Process control: automatic

For automatic systems, the dose rate of ozone (usually in g/h) will be adjusted according to flow and ozone residual, possibly through computed C.t. Where ozone is dosed as a disinfectant downstream of other treatment processes, such as coagulation/clarification/filtration, the ozone demand is likely to be reasonably stable. Where there is no pre-treatment, the potential for a varying ozone demand is greater, for example, when specifying ozone on water subject to algae growth.

The process control should reflect the potential in not achieving the required C.t and, consequently, the desired log removal. This will mean operating at a slightly raised C.t to ensure that the conditions to meet the log credit undertaking are always being achieved. The operating design margin of safety is likely to vary according to the expected variations in ozone demand of the feed water, water temperature, efficacy of any upstream treatment process, short term variations in ozone generation and fluctuations in flow. This margin of safety is in effect a control limit, as required in the DWSNZ, and as such, the principles and potential follow-up actions must be documented in the WSP.

Process control: manual

While systems under automatic control have the potential of not achieving the target C.t in a very small proportion of the daily throughput, manually controlled systems, by their nature, present a risk to a larger proportion of the daily throughput. The margin of safety allowed for in the design of ozone disinfection systems should reflect this potential risk. It may be cost-effective to install automatic control. Note that section 5.15 of the DWSNZ requires online measurement for bacterial and protozoal compliance.

15.5.5 Ultraviolet disinfection

Note: The UV section of the 1995 edition of the Guidelines contained only 2.5 pages, because at that time, UV was used mainly in a few small water supplies to inactivate bacteria. By 2005, more detailed protozoal compliance criteria had been developed for the DWSNZ, based largely on treatment processes rather than monitoring protozoa in the water supply. The recent acknowledgement of the efficacy of UV in inactivating protozoa suggests the process may be used more often in the future. Therefore this section has been expanded to over 10 pages. Further information also appears in Chapter 8: Protozoa Compliance, section 8.4.4.3, which discusses compliance issues related to UV, including a summary of how the USEPA derived the C.t values and operational criteria for 1, 2 and 3 log removals.

These Guidelines aim to provide the reader with a general understanding of the issues related to disinfection using ultraviolet light (UV) for disinfecting drinking-water in New Zealand. This section deals more with operational matters; Chapter 8 covers compliance issues. Because compliance is largely determined by assessing operational requirements (section 5.16 of the DWSNZ), inevitably there will be some overlap. A lot of excellent material appears in the *Ultraviolet Disinfection Guidance Manual for the Final Long Term 2 Enhanced Surface Water Treatment Rule* (USEPA 2006a). Note that in the UK, water suppliers are also recommended to use this USEPA publication (DWI 2010, 2016b). Refer also to Chapter 13 of the review draft LT2ESWTR Toolbox Guidance Manual (USEPA 2009) which discusses issues related to UV disinfection. ANSI/AWWA F110-12 is a Standard for Ultraviolet Disinfection Systems for Drinking Water. WRF (2015) reports on MP UV research since the 2006 UVDGM. The findings are likely to be incorporated into validation procedures. WRF (2016) reports possible improvements in the validation process by using Lagrangian actinometry using dyed microspheres.

UV light has been used for disinfection of drinking-water for many decades and large installations now exist or are underway in Europe and the United States. In New Zealand several of the largest water suppliers have committed to the installation of UV disinfection equipment in their water treatment plants (WTP).

Over the years the terminology and units have changed, not always similarly in Europe and the US. The International Ultraviolet Association has attempted to standardise these (Bolton 2000 and 2004).

There has been a recent growth in interest in UV disinfection. This interest has been driven by concerns related to disinfection by-products of chlorination processes, the resistance of certain protozoa such as *Cryptosporidium* to chlorine, and the identification that relatively low doses of UV can stop *Cryptosporidium* from being infective; at much lower doses than those required to kill the organisms.

While it is true that none of the disinfection by-products discussed in section 15.4 appear during ultraviolet disinfection, sunlight is known to degrade large humic molecules. Work has still to be done to characterise the effect of ultraviolet treatment on natural organic matter in water, and its health implications. DWI (2015a) reviewed the literature on the effects of UV disinfection on the chemical composition of water. They concluded that the potential formation of DBPs as a result of treatment by appropriately designed and maintained UV systems is low. The most significant DBPs are nitrite, and bromate formed from prechlorinated supplies containing bromide; the formation of both can be minimised by appropriate water treatment and UV system design. Nitrite is formed by reduction of nitrate at a wavelength of less than 230 nm. The formation of nitrite by MP lamps is minimised by the incorporation of quartz sleeves to remove the lower wavelength UV. Similarly, absorption of UV by natural organic compounds in water may also occur at lower wavelength, and any changes to water chemistry from this mechanism may influence DBP formation. No significant cytotoxicity or genotoxicity was observed with samples of raw reservoir surface water treated with UV at doses of 23 to 138 J/cm². When UV at doses typically used for disinfection is followed by chlorination, the formation of:

- THMs and HAAs is unlikely to be affected but potentially may increase by c. 10 percent (LP or MP)
- aldehydes, carboxylic acids, TCP or HANs is unlikely to be affected
- chloropicrin and bromopicrin is likely to increase. The formation of both is promoted by higher concentration of nitrate, while the formation of bromopicrin is promoted by higher concentration of bromide
- cyanogen chloride is likely to increase
- chloral hydrate and halonitromethanes is likely to increase, at the single µg/L level (LP UV) or µg/L level (MP UV)
- nitrosamines is likely to be reduced.

When chlorination is followed by UV at doses typically used for disinfection:

- there is potential for bromate formation if bromide is present
- the chlorine decay rate may increase but this effect is unlikely to be of practical significance.

The use of UV for inactivation of protozoa has been recognised in the DWSNZ, where up to 3.0 log inactivation credits (99.9 percent reduction in infectivity) are allowed for protozoal compliance by using UV technology. This is consistent with the approach of the LT2ESWTR (USEPA 2003a and 2006).

The Ultraviolet Disinfection Guidance Manual for the Final Long Term 2 Enhanced Surface Water Treatment Rule, USEPA (2006) states:

Many microorganisms have enzyme systems that repair damage caused by UV light. Repair mechanisms are classified as either photo repair or dark repair. Microbial repair can increase the UV dose needed to achieve a given degree of inactivation of a pathogen, but the process does not prevent inactivation.

Even though microbial repair can occur, neither photo repair nor dark repair is anticipated to affect the performance of drinking-water UV disinfection, as described below:

- photo repair of UV irradiated bacteria can be prevented by keeping the UV disinfected water in the dark for at least two hours before exposure to room light or sunlight. Treated water typically remains in the dark in the piping, reservoirs, and distribution system after UV disinfection. Most water supplies also use chemical disinfection to provide further inactivation of bacteria and viruses and protection of the distribution system. Both of these common practices make photo repair unlikely to be an issue. One study showed that *Cryptosporidium* can undergo some DNA photo repair. Even though the DNA is repaired, infectivity is not restored
- dark repair is also not a concern because the required UV doses are derived from data that are assumed to account for dark repair.

Table 15.10 includes data from Table 7.6 in WHO (2004). See Table 15.1 for some earlier data. The table presents conservative estimates of microbial reductions based on the more resistant or persistent pathogenic members of the group. See next section why various standards require much more than 10 mJ/cm² for inactivation of *Cryptosporidium*.

Table 15.10: UV irradiation doses required for 99 percent inactivation (2 logs)

| Micro-organism | Dose |
|------------------------|-----------------------|
| Bacteria | 7 mJ/cm ² |
| Viruses | 59 mJ/cm ² |
| <i>Giardia</i> | 5 mJ/cm ² |
| <i>Cryptosporidium</i> | 10 mJ/cm ² |

A more complete table was compiled in DWI (2016a, Table C.1), and copied here as Table 15.11. Table C.2 in DWI (2016a) covers inactivation of many bacteria and their spores.

Table 15.11: UV dose (mJ/cm²) for inactivation of protozoa and viruses

| Target | Log ₁₀ inactivation | | | | | | | |
|---------------------------------|--------------------------------|-----|-----|------|-----|-------|-----|------|
| | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 |
| Protozoa | | | | | | | | |
| <i>Giardia</i> | 1.5 | 2.1 | 3.0 | 5.2 | 7.7 | 11 | 15 | 22 |
| <i>Cryptosporidium</i> | 1.6 | 2.5 | 3.9 | 5.8 | 8.5 | 12 | 15 | 22 |
| Viruses | | | | | | | | |
| "Viruses" | 39 | 58 | 79 | 100 | 121 | 143 | 163 | 186 |
| Adenovirus type 40 ² | | 56 | | 111 | | 167 | | |
| Poliovirus ² | | 7 | | 15 | | 22 | | 30 |
| Adenovirus type 41 ³ | | | | | | | | 112 |
| Hepatitis A ³ | | | | | | | | 21 |
| Coxsackie virus B5 ³ | | | | | | | | 36 |
| Poliovirus type 1 ³ | | | | | | | | 27 |
| Rotavirus SA11 ³ | | | | | | | | 36 |
| Murine norovirus ⁴ | | 7.3 | | 14.6 | | 21.9 | | 29.2 |
| Feline calicivirus ⁴ | | 6.3 | | 12.5 | | 18.8 | | 25 |
| Echovirus 12 ⁴ | | 7.4 | | 14.8 | | 22.23 | | 29.6 |

1 USEPA (2006)

2 Hijnen WAM, Beerendonk EF and Medema GJ (2006)

3 Bolton JR and Cotton CA (2008)

4 Park GW, Linden KG and Sobsey MD (2011)

15.5.5.1 The UV disinfection process

Germicidal effects of UV light

UV light can be categorised as UV-A, UV-B, UV-C or vacuum-UV, with wavelengths ranging from about 40 to 400 nm. The UV light effective for inactivating micro-organisms (the germicidal range) is in the UV-B and UV-C ranges of the spectrum (200–310 nm), with maximum effectiveness around 265 nm. Thymine bases on DNA and ribonucleic acid (RNA) are particularly reactive to UV light and form dimers (thymine–thymine double bonds) that inhibit transcription and replication of nucleic acids, thus rendering the organism sterile, ie, a micro-organism cannot infect a host because it cannot replicate. Thymine dimers can be repaired in a process termed photo reactivation in the presence of light, or dark repair in the absence of light. As a result, the strategy in UV disinfection is to provide a sufficiently high dosage to ensure that nucleic acid is damaged beyond repair. Taken from WHO (2004b), Chapter 3.3.5.

All the light produced by low pressure UV lamps is within the germicidal range. Medium pressure lamps produce some light outside the germicidal range so require more electricity for a given duty compared with low pressure lamps. Three types of lamps are used:

- **Low-pressure (LP) lamp:** a mercury-vapour lamp that operates at an internal pressure of 0.13 to 1.3 Pa and electrical input of 0.5 watts per centimetre (W/cm). This results in essentially monochromatic light output at 254 nm. These are commonly used on smaller supplies. They have the highest energy efficiency of the three types of mercury vapour lamp, but another important characteristic, given the discontinuous usage pattern of the typical domestic water supply, is their relatively low operating temperature; lamps which run hotter are more dependent on continuous water flow to dissipate the heat generated; DWI (2016a).
- **Low-pressure high-output (LPHO) lamp:** low-pressure mercury-vapour lamps with heavy duty electrodes that operate under increased electrical input (1.5 to 10 W/cm), resulting in a higher UV intensity than low-pressure lamps. They also have essentially monochromatic light output at 254 nm. They run hotter than LP lamps. They are being used increasingly by the larger water suppliers.
- **Medium-pressure (MP) lamp:** a mercury vapour lamp that operates at an internal pressure of 1.3 to 13,000 Pa and electrical input of 50 to 150 W/cm. This results in a polychromatic (or broad spectrum <200 nm to >400 nm) output of UV and visible light at multiple wavelengths, including wavelengths in the germicidal range. MP lamps have a much higher output than LP lamps but are less efficient in converting electricity into germicidal UV. Fewer MP lamps are required for a given duty than LP or LPHO lamps because of the higher output. They are used by the bigger supplies when the higher electricity cost can be offset against lower capital cost (smaller plant, smaller building to house the plant) and lower maintenance cost (because of the lower number of lamps); DWI (2016a).

LED (light emitting diode) technology represents the most likely alternative to the mercury vapour lamp in the future. LEDs are configurable, switchable and don't require the warming up period of mercury vapour lamps. They are safer to handle (no glass or mercury). However, efficiencies are <10%, lifetimes limited to about 1,000 hours and production costs are high. Very small-scale LED UV devices (eg, for laboratory use) are available, but further development will be necessary for larger-scale devices to be both technically and economically viable (DWI 2016a).

Dose (fluence)

The amount of inactivation that is achieved is a function of the amount of UV light that the micro-organisms receive. This is called the UV dose, or more correctly, the fluence. The SI units of UV dose are J/m². The units of mJ/cm² are also used. One mJ/cm² is equal to 10 J/m².

The dose is the product of the intensity of UV light and the time that the micro-organisms are exposed to it. The unit of intensity is watts (W). The unit of time is seconds (s). Consequently the dose is sometimes referred to as mW.s/cm² or W.s/m². One mJ/cm² is equal to 1 mWs/cm².

It has been shown (Buhkari et al 1999) in ideal laboratory collimated beam studies that UV light can provide a 4-log inactivation of *Cryptosporidium* at received UV doses less than 20 mJ/cm². It is generally considered that a received UV dose of 12 mJ/cm² can produce a 3-log inactivation of *Cryptosporidium* (USEPA 2003a and 2006).

It is normally very difficult to assess the UV dose that is being provided by a UV reactor because there are many uncertainties. The uncertainties include hydraulic flow paths, the response of the sensor to different angles of light, different water qualities and variation in lamp output. Reactors are typically validated (or certified) to provide a reduction equivalent dose (RED). (The RED is a calculated dose for a flow-through UV reactor that is based on biosimetry). The dose required for a given log inactivation in the commonly used LT2ESWTR tier 1 approach, the German DVGW Technical Standard W294 approach and the Austrian ÖNORM M5873-1 approach, is at least three times greater than the received UV dose that is found in collimated beam studies (compare with data in Table 15.10). The much higher dose accounts for the uncertainty in the reactor and ensures that the required level of inactivation is achieved.

The dose required to inactivate adenoviruses in laboratory tests has been found to be an order of magnitude higher than the dose required for *Cryptosporidium*. For this reason UV disinfection is not currently considered to be effective for inactivation of all viruses. Table 1.4 in USEPA (2006) states that a dose of 39 mJ/cm² will only achieve 0.5 log inactivation of virus and that 3 logs require a dose of 143 mJ/cm². Note however that the USEPA Table is based on adenovirus, the most resistant type. Figure 2.8 (Shapes of UV Dose-Response Curves), in the same manual shows a curve for rotavirus that implies that a dose of 40 mJ/cm² may achieve about 4 log inactivation of rotavirus. Figure 2.8 is followed by this paragraph:

Microbial response to UV light can vary significantly among micro-organisms. The UV sensitivity of viruses and bacteriophage can vary by more than two orders of magnitude (Rauth 1965). With bacteria, spore-forming and gram-positive bacteria are more resistant to UV light than gram-negative bacteria (Jagger 1967). Among the pathogens of interest in drinking-water, viruses are most resistant to UV disinfection followed by bacteria, *Giardia* cysts, and *Cryptosporidium* oocysts.

A UV disinfection system

A typical system for drinking water disinfection will consist of the following elements:

- the shell of the pressurised UV reactor
- UV lamps
- quartz sleeves
- UV ballasts
- UV intensity sensors mounted inside the UV reactor
- a control panel
- a cleaning device.

UV disinfection of drinking-water is typically achieved in an enclosed, pressurised reactor (or appliance). While it is possible to use open channel UV disinfection, this approach is rare in drinking-water applications and is not discussed further.

The enclosed reactor contains UV lamps that produce photons of UV energy by applying a voltage across a mercury gas mixture. Low mercury vapour pressures of 0.001 to 0.01 torr (SI units: 0.13 to 1.3 Pa) and a temperature of 50–100°C will produce essentially monochromatic UV light at around 253.7 nm. At higher vapour pressures from 100–10,000 torr (SI units 13 – 1.3 x 10³ kPa) and temperatures of 600–900°C the lamps will produce UV light over a broad spectrum and are commonly called medium pressure lamps. Low pressure lamps are further divided into historic low output lamps and the new high output (or intensity) lamp (LPHO). Most low pressure UV systems now use LPHO lamps and low intensity lamps are not discussed further.

UV lamps will degrade with time, producing less UV light per unit of electricity used. A lamp is usually considered to have reached the end of its life when the UV output has dropped to 70–80 percent of its output following burn-in. The elevated operating temperature of the lamp when it is running, and also the number of starts that the lamp has been through, cause the degradation. Manufacturers will provide a guarantee on the number of hours that a lamp will run before its output is reduced to 70 or 80 percent of the output achieved after around 100 hours of operation. The guarantee will normally specify a maximum number of starts per day for the lamp.

LPHO lamps are more efficient at turning electricity into germicidal light, so they have lower electricity costs. They operate at a lower temperature, so their expected lifetime is significantly longer and also they are not affected by fouling as much as medium pressure lamps.

The advantages of medium pressure lamps include higher UV output per lamp than lower pressure lamps, so fewer lamps, ballasts, and sensors need to be installed. It also means that the reactor will require less space. Fewer lamps can also mean there is less water pressure loss.

The choice between LPHO and medium pressure lamps is site-specific. Once manufacturers have guaranteed prices and lifetimes for all the items of equipment, a financial comparison between the two is possible. The site-specific issues that affect the decision include the temperature of the raw water, the chemicals that cause fouling in the water, and whether there is a certified/validated reactor that matches the required duty. Other site-specific issues such as the available space or water pressure may also influence this decision.

Quartz sleeves surround the lamps and separate them from the water. O-rings are used to seal the end of the quartz sleeves. The surface of the quartz sleeve that is exposed to water can become fouled. This is discussed below. Generally fouling occurs more rapidly on sleeves surrounding medium pressure lamps because they operate at a higher temperature, and solubility of CaCO₃ decreases with increasing temperature.

The ballasts regulate the power supply at the appropriate level needed for energising and driving the UV lamps. UV reactors may use electronic ballasts, electromagnetic ballasts or transformers. The benefits of different types of ballasts can be explored with the manufacturer.

The control panel may consist of a programmable logic controller (PLC) or a simpler device for recording and displaying the intensity and lamp status. Some control systems are capable of varying the output of the UV lamps to reduce the amount of electricity that is used. Large reactors that have more than one group of lamps may use the control system to turn off banks of lamps when low flows or high quality water mean that they are not all required.

The cleaning system needs to clean the outside of the quartz lamps and the window over the UV intensity sensor. There are two common types of cleaning devices. One uses mechanical cleaning by a rubber wiper that is automatically moved up and down inside the reactor. Some mechanical systems also have an acid in the wipers to assist the cleaning process. The second method is to isolate the reactor and then circulate an acid solution through the inside of the reactor. The acid cleans the internal surfaces, then drained from the reactor that is flushed and put back into service. The chemical method of cleaning requires the reactor to be taken out of service.

15.5.5.2 Water quality

A number of water quality factors can affect the performance of the UV disinfection process.

UV transmittance

Light emitted from a UV lamp that is absorbed by substances in the water flowing through the reactor is not available to inactivate micro-organisms. This loss of UV light is the most important water quality parameter for the design of UV disinfection systems. The quality of the water is defined by the amount of UV light at a wavelength of 254 nm that passes through a certain path length of water compared with the amount that passes through the same path length of distilled water. This is typically called the transmittance (T) of the water. The path length that is most commonly used is 10 mm and this is often shown with a subscript ie, T_{10} . For example if the water allows 94 percent of light at a wavelength of 254 nm to pass through a 10 mm path length then the UV transmittance is called 94 percent or $T_{10} = 94$ percent, or $UVT = 94$ percent in a 10 mm cell.

While transmittance is generally related to a 10 mm path length there are other ways of defining it. For example, it may be referred to as the spectral absorption coefficient (SAC) at a wavelength of 254 nm. This represents the absorbance over a one metre path length. The SAC can be converted to a transmittance over a 10 mm path length by the equation $T_{10} = 10^{-(SAC/100)}$. See Chapter 8, section 8.4.4.3, sub-heading UV transmittance for an example of converting from the European SSK unit; SAC is the English translation of SSK.

Another common source of confusion in New Zealand has been referring to the transmittance over a longer path length. The conversion from a transmittance over a path length of x (T_x) to T_{10} can be achieved using the equation $T_{10} = T_x^{(10/x)}$. For example, a transmittance of 90 percent over a path length of 100 mm ($T_{100} = 90\%$) is equal to $T_{10} = 90\%^{(10/100)} = 98.95\%$. For reasons of consistency, transmittance should really be reported for a path length of 10 mm.

The UV transmittance has a large effect on the size of the UV reactor required. A decrease of the UV transmittance from 92 percent cm^{-1} to 90 percent cm^{-1} will change the size of the required reactor by more than 25 percent. The large effect of UV transmittance on the size of the equipment required means that detailed knowledge of the water quality is required before purchasing a UV system. Ideally continuous UVT data of the water to be treated should be obtained over a 12-month period. If this is not possible then regular sampling must be carried out at different times of the day during different seasons and raw water conditions.

Transmission is sometimes measured as absorbance. Appendix A1.5.9 of the DWSNZ shows the conversion; the basic equation is $\text{UV abs} = -\log_{10}T$.

An indication of the UV absorbance or UVT likely to be found in different waters follows (all based on measurements at 254 nm with a 10 mm path length):

| UVT | UV abs | Typical raw water |
|------|--------|---|
| 1.00 | 0 | Distilled water; maybe rainwater |
| 0.98 | 0.009 | Lake Taupo; clean bore water |
| 0.94 | 0.027 | Clean stream water; water after alum coagulation and filtration |
| 0.90 | 0.046 | River water when not in flood |
| 0.85 | 0.071 | Lake water when catchment not heavily bushed |
| 0.80 | 0.097 | Lake water from bush catchment |
| 0.75 | 0.125 | Lake water from heavily bushed catchment; streams from beech forest |

Section 5.16.1 of the DWSNZ specifies the UVT requirements. Chapter 8, section 8.4.4.3 of the Guidelines discusses compliance requirements in more detail.

Water treatment chemicals that lower the UV transmittance (ie, raise the absorbance)

Most water treatment chemicals do not significantly impact UV transmittance. Those that may, include hypochlorite ions, ferric ions, permanganate and ozone. The effect of hypochlorite ions is minimal and a free available chlorine concentration of 3.5 mg/L will only reduce the T_{10} by around 1 percent (Cushing et al 2001). Care should be taken to ensure that permanganate and ozone are not present at the point where UV disinfection is going to be installed. A concentration of 0.057 mg/L ferric iron will reduce the UVT by 1 percent, ie, raise the UV absorbance from 0.041 to 0.046 in a 1 cm cell (USEPA 2006a).

The lime dosing point should not be immediately upstream of the UV reactors as it may raise the turbidity.

Turbidity

Turbidity is the most common indicator of water quality used in New Zealand. The effect of turbidity on UV disinfection is related to the shielding and shading effects that limit potential inactivation of micro-organisms. The DWSNZ require that water being

disinfected with UV light has a turbidity of less than 1.0 NTU for 95 percent of the time and never has a turbidity of more than 2.0 NTU.

Temperature

Low temperatures affect the output of UV lamps. This effect is greater for LPHO lamps than for medium pressure lamps. In most applications the temperature of the water will be warm enough that there is no noticeable effect on the output of the lamps. The effect of water temperatures less than 10°C should be discussed with UV lamp manufacturers. Many New Zealand water supplies are less than 10°C for a lot of the year.

Chemicals that cause fouling of quartz sleeves

Many substances cause coatings or deposits to form on surfaces when water containing them flows past. The deposition can occur more rapidly if the surface has a higher temperature. The surface of the quartz sleeve is submerged in water and is at an elevated temperature due to the operating temperature of the lamps. The deposition of solids on the outside of the quartz sleeve can absorb or reflect UV light, thereby reducing the effectiveness of disinfection. Once the absorption of light reaches a level where the intensity measured by the UV intensity sensor is too low, the sleeves must be cleaned using a cleaning system such as those described above.

Water quality parameters that can increase the rate of build-up on quartz sleeves include high levels of:

- calcium
- alkalinity
- hardness
- iron
- pH (an indirect effect)
- natural organic matter.

Information to UV manufacturers

Information on the above parameters should be provided to manufacturers when specifying the requirements for a UV system. The end-user should specify the design water quality parameters. This should include an absolute statement of the design UV transmittance but percentile values should be provided for other parameters. The end-user must define the design UV transmittance based on operational requirements and the acceptable risk of off-specification water.

Raw water quality information should cover all possible conditions, preferably spanning at least one year for surface water supplies. Any other available water quality data should also be supplied. The additional data may not be used, but provision of information to all parties can only benefit the final installation.

Performance validation/certification

Refer to Chapter 8: Protozoa Compliance, section 8.4.4.3.

15.5.5.3 Design, installation and commissioning issues

The installation of a UV reactor must comply with its own technical requirements, interact correctly with the other aspects of the treatment process and comply with the conditions for which the reactor was validated. The following are some guidelines for the design of installation of UV reactors.

Redundancy

Good engineering practice should be followed with redundancy for UV reactors. Redundancy should consider the effect of shut-down of the reactor system for routine cleaning (if required) and for changing of lamps. Redundancy also needs to consider the failure of the equipment and the time required for operators to attend to repair the equipment. Spares should be carried onsite. UV systems are relatively easy to service.

Hydraulics

It is very important that the upstream, and to a lesser degree, downstream hydraulic flow conditions are at least as good as those under which the reactor was validated. Better hydraulic flow conditions provide a more even cross-sectional velocity distribution and provide more efficient and reliable disinfection. The hydraulic conditions that were used in the validation procedure need to be identified so that the installation can be designed appropriately.

If there is to be more than one duty UV reactor to treat a given flow of water then the splitting of the flow between the reactors must be considered to lower the maximum instantaneous flow rate that will go through one reactor. Flow splitting can be achieved passively by providing equal restriction to flow in parallel routes between two points of equal pressure or can be achieved using flow meters and control valves. If a control valve is being used for flow modulation it should be installed downstream of the UV reactor.

The pressure drop across the UV reactor will normally be 150–1000 mm of water head. The exact drop needs to be incorporated into the hydraulic profile of the WTP. The headloss associated with valves, pipe-work bends, expansions, contractions etc also needs to be considered.

UV reactors must be completely full. If not, overheating of the casing and lamps may occur, one possible outcome being release of mercury. This can be achieved by ensuring that the downstream discharge is higher than the highest point on the UV reactor. Low level switches and temperature sensors on the top of the UV reactor can also be installed to safeguard the reactor against operation without full flow. When appropriate, air valves should be installed on the high point of UV reactors to release entrained gases.

Most UV reactors, especially medium pressure reactors, require flow at all times to ensure that sufficient cooling is supplied to the lamps. The designer should consult with the manufacturer to determine the length of time that flow can be stopped without overheating the system.

The system can be designed with a means to stop off-specification water from reaching the reticulation. Different ways to achieve this can include starting a standby reactor, or bank within a reactor, upon failure of a UV reactor and diverting water to waste if it is detected as off specification. The implication of any reduction in water supply needs to be considered.

UV reactors will only be rated for operation with a certain pressure of water. The allowable operating pressure should be checked with the manufacturer.

Isolation valves are required for UV reactors. Automatic isolation can be included to minimise the production of off-specification water. The implications of automatic flow isolation and flow restriction on the hydraulic grade and operation of the WTP must be considered.

Start-up and cool-down

All UV reactors require time for lamps to heat up before they can produce their rated UV light output. Generally this is about five minutes. Some lamps need to cool before they can restart. Both conditions should be confirmed with the manufacturer. The implications of the delay for start-up and cool down need to be incorporated into the UV system design, particularly in terms of continuity of power supply and reaction to off-specification water.

Electrical design

If there are voltage variations in the power supply, lamps may lose their arc and need to restart. This can take 10–20 minutes. The quality of the power supply must be checked to ensure that this will not happen. Outages of power will stop the UV system and require the cool down and start-up process. The likelihood and effect of a power loss should be considered, and if required an un-interruptible power supply may need to be installed.

The end-user must determine the requirements of the control system to operate the UV reactors. The control system may conduct such functions as controlling the output of UV lamps, changing the number of banks that are in operation, monitoring of instrument readings, sending alarms to operators, recording lamp run hours, monitoring lamp status.

Alarms

Section 4.3.3 of the USEPA UV Guidance Manual breaks alarms into three classes:

- A minor alarm generally indicates that a UV reactor requires maintenance but that the UV reactor is operating in compliance. Minor alarms also can be set for conditions just short of failure conditions so that major alarm conditions are not reached. For example, a minor alarm would occur when the UVT is within 1 percent UVT of the minimum allowed UVT or when the end-of-lamp-life based on hours of operation is reached, indicating the possible need for lamp replacement.
- A major alarm indicates that the UV reactor requires immediate maintenance (eg, the UV sensor value has dropped below the validated setpoint) and that the unit

may be operating off-specification. Based on the water supply's disinfection objectives, this condition may also be handled as a critical alarm.

- A critical alarm typically shuts the unit down until the cause of the alarm condition is remedied. An example of a critical alarm is the UV reactor's temperature exceeding a pre-determined maximum value, resulting in automatic shut-down to prevent overheating and equipment damage.

To maintain reactor integrity and compliance with the DWSNZ, the designer needs to decide which conditions require a visual or audible type of alarm, or set off a pager, or shut the system down. Alarm conditions should be recorded, and their causes reported.

15.5.5.4 Operational activities

Operational staff should carry out daily checks of the UV system. These checks should be fully described in the operation manuals. These checks should include a visual inspection of the reactors and piping and a check of the status of the system and lamps. The operator should also manually purge from the top of the UV reactors at regular intervals to determine if there is any air build-up.

The commonest causes for poor disinfection include using lamps beyond their prescribed life, poor upstream treatment, and build-up of film or sediment in the appliance, often caused by clay, iron, manganese or lime. Inadequate attention to these matters readily causes the system to fail. *E. coli* were often found in small water supplies using UV disinfection during the 1990s, giving the process an undeserved bad reputation.

The operator should regularly review operational data such as the UV intensity, the flow rate, the UV transmittance and the electricity usage. If variable output lamps are installed the operator should also review the lamp output that is being selected by the control system. Operational staff should aim to detect any anomalies in the data and investigate them. This may lead to early detection of a problem.

Chemical cleaning of the reactors should be conducted initially three-monthly. The operational staff should record the intensity immediately before and after a cleaning event in order to evaluate the magnitude of fouling that is removed and to determine how frequently cleaning is required. This information should be recorded in the operation and maintenance manuals. If there is little build-up on the sleeve surfaces then the cleaning frequency could be reduced.

Operational staff could track the degradation of lamp output by observing the intensity that is recorded after cleaning events. When doing so the effect of UV transmittance will need to be taken into account. In addition the operator should frequently review the lamp run time and compare the hours run with the hours expected to the end of lamp life output.

The ballast cooling fans should be inspected at regular intervals to check their operation and ensure there is no build-up of dust.

The operational staff should check to ensure that algae are not growing in the light provided by the UV. This will not be a problem if a chlorine residual is carried through the UV reactors; however, this is not normal practice.

The standardisation of any online UV transmittance monitors should be checked using grab samples of the water on a weekly basis.

Other operational activities will include replacement of lamps and calibration of the UV intensity sensors. These activities should be conducted following the requirements of the validation, the DWSNZ, and the manufacturer's instructions.

Control limits

The process control limits (or parameters that must be monitored to ensure that the dose is being delivered) are the UV intensity or dose, the flow through each reactor, and the UV transmittance. The UV intensity and the flow are limits because they are directly related to the dose delivered. The UV transmittance is a limit because it can affect the sensitivity of the UV intensity sensor. The values for these control limits are defined in the certification procedure. Operational staff should monitor these process control limits and record any transgressions.

Staff should also establish operational control limits that act as an early warning that disinfection conditions are approaching the stage where some adjustment may be needed, thereby avoiding transgressions, and to ensure that these do not become a non-compliance. Measures that can be taken, and recommended actions, should be itemised in the WSP.

Safety

UV light is dangerous. The manufacturer's instructions must be followed.

Lamp breakages in reactors may result in a risk to human health through exposure to mercury in the water supplied. Lamps and sleeves may both be liable to break as a result of:

- the impact of debris in the water
- excessive water hammer
- differential or over-heating
- mechanical forces such as wiper jams.

Correctly applied operating procedures should be in place to minimise the risk of breakages and appropriate monitoring should be in place to detect breakages. Water suppliers are expected to have documented action plans for identifying and responding to on-line lamp breakages. DWI (2016b).

15.5.6 Bromine

The decision on whether bromine can serve as a disinfectant for drinking-water and wastewater treatment is likely to be a balance between the dose required to achieve efficacy, its advantages over other disinfectants, particularly chlorine, aesthetic impacts, preventing potential adverse health effects from chronic exposure, and cost. Any potential risk of adverse effects should be considered in context of the benefit of water

disinfection which should always take precedence. Bromine disinfection is superior to chlorine for microbiological inactivation when applied to low quality water containing ammonia and other nitrogenous components. This may give support for the use of bromine as a potential alternative to chlorine in disaster relief scenarios, however, further investigations would be required. Also, these potential benefits should be balanced with the significant issues surrounding the ease and safety of bromine generation and its subsequent use for water purification purposes. Practical handling of free bromine is a safety issue; it is usually combined with dimethylhydantoin (DMH), an organic carrier (WHO 2018).

Bromine is a good germicidal agent with disinfecting powers similar to chlorine at the same pH. In a similar way to chlorine, bromine reacts with ammonia to form bromamines. Unlike the chloramines, which are much poorer disinfectants than chlorine, monobromamine and bromine have similar germicidal properties. Ammonia in the water, therefore, does not have the adverse impact it does for chlorine.

Bromine appears to be effective against cysts of the protozoan parasite *Entamoeba histolytica*, and there is some evidence of limited effectiveness against oocysts of *Cryptosporidium parvum*; studies on the efficacy of bromine against *Giardia* cysts were not available (WHO 2018).

Elemental bromine was evaluated in a series of batch tests where it was found that a dose of at least 1 mg/L and a contact time of 1 hour was required to achieve 5 log reductions of *E. coli* (Patil et al 2013).

The datasheet for bromine covers health issues. Toxicity studies in humans or animals for bromine per se via ingestion are very limited; this is mostly due to the corrosiveness and high reactivity of bromine; it quickly forms bromide in living tissues. The greatest potential concern to humans from using bromine as a drinking-water disinfectant may stem from the generation of brominated DBPs. The formation of brominated DBPs during water disinfection with chlorine has been well studied. There are toxicity data in some of these studies that indicate that brominated DBPs may be more toxic in some respects than their chlorinated analogs. Currently the potential for formation of brominated DBPs from the use of bromine as an alternative drinking-water disinfectant in POU devices has not been comprehensively addressed, although some devices have been shown to produce minimal amounts of brominated products (WHO 2018).

Bromine is rarely used to disinfect potable waters because of its cost and the difficulties in handling the very corrosive bromine liquid. Compounds containing active bromine, such as the dibromo- and bromochloro-methylhydantoins (eg, N-bromo-N-chloro-5,5-dimethylhydantoin) or dibromocyanuric acid are used to treat swimming pools. See datasheets.

15.5.7 Iodine

Iodine-based disinfection of water has a long history: iodine in concentrations between 2.5 to 7 mg/L have been used for potable water treatment since the early 1900s, especially for military operations. Also, in more recent times, iodine (and bromine) has become attractive for particular applications. Elemental iodine is used, for example, as

a drinking-water disinfectant aboard space vessels at a residual concentration of approximately 2 ppm. The more general use of iodine is impeded, however, by the potential for excess iodine intake, cost and the possibility of the formation of toxic DBPs. Iodine may provide superior disinfection to chlorine for water of poor quality. The reduced overall reactivity of iodine prompts slower reactions with organic material and thus a lower disinfectant demand. The low reactivity with organic nitrogenous contaminants results in improved maintenance of residual iodine concentrations (WHO 2018).

Iodine, like two other halogens, chlorine and bromine, is a good disinfectant, but is rarely used in potable water treatment, except in some instances for the treatment of very small supplies. The main drawbacks to its use are its cost, the iodine taste it imparts, and the possible health effects associated with its long-term use. See datasheets. It can be used for emergency disinfection. Its disinfecting power is pH sensitive. Iodine is not effective against *Cryptosporidium*, and needs a longer contact time to inactivate *Giardia* than when used to inactivate bacteria. It has some effectiveness against viruses. A fairly common form of commercially available iodine is tetraglycine hydroperiodide.

Iodine, as a 2 percent tincture, was evaluated in a series of batch tests where it was found that a dose of at least 0.5 mg/L and a contact time of 30 minutes was required to achieve 5 log reductions of *E. coli* (Patil et al 2013).

The Utah State Government has deemed that iodine disinfection is no longer allowed in public water supplies because of adverse health implications for the public.

The World Health Organization (WHO 2005) states that iodine use (to disinfect water) over a long period of time is not recommended for infants or pregnant women, those with a history of thyroid disease, and those with known hypersensitivity to iodine. Excess iodine can interfere with the functioning of the thyroid gland. Travellers intending to use iodine daily for all water consumed for more than 3–4 weeks should consult their physician beforehand, and not use it in excessive amounts when treating drinking-water. Remove excess iodine by carbon filtration. It may be possible to purchase iodine taste and odour neutralising tablets (usually ascorbic acid) – follow the instructions.

Health Canada states that iodine disinfection of drinking water should be reserved for emergency and occasional use (eg, at a weekend cottage or in recreational vehicles). Iodine should not be used for long-term continuous disinfection because it is physiologically active, and ingestion in excessive amounts may be harmful.

The US Army (USAPHC) issued iodine-based tablets to American Soldiers in 1952 and continues to provide the tablets in addition to other emergency field drinking water products. Iodine-based products can be divided into two categories; iodine solutions and iodine resins.

Iodine solutions are made by adding iodine (eg, tincture of iodine, a 2 percent iodine solution), or by adding a tablet containing iodine along with carrier and stabilising agents to enhance dissolvability. Iodine resins are solid-phase iodine disinfectants. Iodine resins are used by passing water through the resin where disinfection occurs through direct contact of the microorganism and the iodine sorbed on to the resin.

Iodine resins are generally considered demand-release disinfectants; they generally produce a dilute iodine residual.

When iodine is added to water, it may remain unchanged or it may hydrolyse into five different species depending on pH and the initial iodine concentration. The main reaction is:



At pH levels above 8, biocidal capability may drop sharply because HOI becomes unstable and decomposes to iodate and iodide, which are not effective biocides. In addition to the formation of hypiodous acid (HOI) and iodide ion (I^-), hypiodite ion (OI^-), triiodide ion (I_3^-), and iodate (HIO_3) may be formed. Under typical concentrations used in drinking water disinfection, and at typical pH ranges for natural water sources, hypiodite ion, triiodide ion, and iodate are not considered to be formed at any appreciable concentrations. Only iodine and hypiodous acid are capable of biocidal activity. Iodine is up to three times more cysticidal and six times more sporocidal than hypiodous acid. Hypiodous acid, on the other hand, is 40 times more virucidal and up to four times more bactericidal than iodine.

Preparation of iodine resins involves binding polyiodide ions to a strong-base anion resin, creating a positively charged resin. Most microorganisms are negatively charged at typical pH levels encountered in natural waters. These opposite charges produce an electrostatic attraction that helps bring the microorganism into direct contact with the iodine resin. There are generally two types of iodine resins produced for drinking water treatment, a triiodide (I_3^-) and a pentaiodide (I_5^-) resin; pentaiodide resin has been shown to have better biocidal capabilities than triiodide resin. Resins do not appear to be as affected by pH or low temperature.

Most manufacturers of iodine solution systems recommend dosages between 4 and 16 mg/L with contact times ranging from 20–35 minutes, resulting in C.t.s of 80–560 mg-min/L. The use of POU devices using iodine should be appropriately approved or certified to ensure efficacy and safety.

See Chapters 7 and 8 for the effect of iodine on viruses and protozoa.

15.5.8 Potassium permanganate

Potassium permanganate is a moderately strong oxidant sometimes used as a pre-oxidant to aid in the removal of iron and manganese, and tastes and odours. It may oxidise some organic substances that would otherwise react with chlorine to form disinfection by-products. Its disinfecting ability however is poor, and is strongly influenced by the pH. High pH levels severely reduce its germicidal properties. High pH enhances the oxidation of organic matter. Potassium permanganate might be used in emergencies, but even then only in small supplies.

Potassium permanganate is used as a pretreatment before physical treatment processes, because the insoluble brown, or brown-black manganese oxides produced from it have to be removed before the water passes into the distribution system. Care

must be taken not to overdose permanganate, as it imparts a pink colour to the water, hence it is impracticable to maintain a disinfecting residual.

Refer to the Alternative Disinfectants and Oxidants Guidance Manual USEPA (1999) for further information.

15.5.9 Hydrogen peroxide

Hydrogen peroxide has been used as a general disinfecting agent for more than a century, but its use in the treatment of potable water has been very limited. This is in part due to its instability in storage and the difficulty in preparing concentrated solutions. It is a strong oxidising agent, but a poor disinfectant achieving little or questionable inactivation of bacteria, protozoa and viruses. It might be used in emergencies, but even then only in small supplies.

Hydrogen peroxide, as a 30 percent solution, was evaluated in a series of batch tests where it was found that a dose of at least 1000 mg/L and a contact time between 0.5 to 1 hour was required to achieve 5 log reductions of *E. coli* (Patil et al 2013). At this dose it would be very expensive.

Although of little value itself, hydrogen peroxide has been used in conjunction with other disinfectants to achieve improved oxidation of organic matter. Its use with ozone and ultraviolet light (see section 15.5.11) produces increased concentrations of hydroxyl radicals. These are short-lived, very strongly oxidising chemical species, which react with the organic matter.

15.5.10 Silver and other metal ions

Metal ions exhibit low biocidal activity, and are poor oxidising agents, unlike the more commonly used water disinfectants. However, silver has been known to have antibacterial properties since Roman times. The increased use of nanosilver in a range of (as yet largely) experimental drinking-water treatment systems, its use in conjunction with ceramic filters, and its perceived potential to be a water disinfectant that does not result in disinfection by-products in the treated water, have raised the profile of this chemical (WHO 2018). See also datasheet for nanoparticles.

The slow rate of inactivation of micro-organisms by silver requires long contact times to achieve adequate disinfection. Synergistic effects that improve the efficacy of metal ions as disinfectants have been reported in mixes of metal ions (eg, silver and copper, Pyle et al 1992) or mixes of peroxy-compounds and metal ion (eg, silver and hydrogen peroxide, Armon et al 2000). Although the rates of disinfection achieved by these mixtures are still low compared with those of the halogens and their compounds, and ozone, they produce long-lasting residuals that provide some control of biofilms.

Silver, as a solution of silver nitrate, was evaluated in a series of batch tests where it was found that a dose of at least 20 mg/L and a contact time of two hours was

required to achieve 5 log reductions of *E. coli* (Patil et al 2013). A dose of 10 mg/L was possible when using nano-silver.

The World Health Organization (WHO 2005) states that, contrary to widespread perception, silver is not an effective disinfectant (particularly so regarding *Cryptosporidium*) and is thus not recommended for water disinfection. Its presence in some filters is intended only to extend the life of the filter by retarding growth of non-disease causing bacteria that may plug filter pores.

The biocidal efficacy of silver is decreased by low pH and high dissolved solids concentrations, particularly the presence of phosphate. It is not satisfactory for disinfecting drinking-waters because of its slow action, and although it is effective against some bacteria, it is ineffective against others and against viruses. WHO (2018) notes that in the one study on protozoan parasite reduction by silver, there was only limited effectiveness on *Cryptosporidium* infectivity and a log₁₀ reduction was not documented. For silver ions and nanoparticles, only one study on bacteriophage reduction in water has been reported, with effective log₁₀ reduction (ie, 3–4 log₁₀ reductions) by ions and 'biogenic' silver (zerovalent silver nanoparticles on a bacterial carrier matrix) but not by chemically-produced nanoparticles.

It is difficult to draw any strong conclusions about the efficacy of silver (ionic silver and silver nanoparticles) in drinking-water treatment because of the wide range of approaches used in the various studies reviewed. The studies have used different types of silver (silver salts versus silver nanoparticles; capped silver nanoparticles versus bare silver nanoparticles; differently sized silver nanoparticles; silver nanoparticles created using different synthesis methods), different methodologies, different cells and microorganisms, different concentrations of test organisms and exposure for different time periods. Based on the current available evidence, which is particularly limited for viruses and protozoa, silver does not appear to meet the WHO minimum performance recommendations for POU treatment products, which require effectiveness for two of the three pathogen classes (WHO 2018).

A combination of copper and silver ions can inactivate bacteria and viruses, although contact times may be long (hours to days). Low levels of chlorine (0.1 mg/L) combined with silver (0.038 mg/L) and copper (0.38 mg/L) resulted in more than 5-log inactivation of *E. coli* in tap water within 120 seconds.

Silver (0.03 mg/L) and hydrogen peroxide (0.03 mg/L) together provided a long-lasting residual effect capable of more than 5-log inactivation of *E. coli* in phosphate buffer (pH 6.8) after one hour exposure (taken from WHO 2004b, Chapter 3.4.3). Trade literature implies that a dose of 30 mg/L hydrogen peroxide (as H₂O₂) plus 0.03 mg/L silver is effective for biofilm control; that sounds rather expensive. One worker considered that the combination was no more effective than hydrogen peroxide on its own, but that maybe the silver stabilised the solution.

A fairly new range of biocides, eg, bismuth-2,3-dimercaptopropanol, are in production, primary for use in water supplies in buildings to control biofilms and slime build up in hot water systems.

Copper has been used in conjunction with SODIS: see section 15.5.6.9.

15.5.11 Advanced oxidation processes

Advanced oxidation processes (AOP) generate highly reactive hydroxyl free radicals to oxidise various compounds in the water. Hydroxyl radicals are produced during the spontaneous decomposition of ozone. By accelerating the ozone decomposition rate, the highly reactive hydroxyl radical concentration is elevated, which increases the oxidation rate. This procedure increases the contribution of indirect oxidation over direct ozone oxidation.

Several methods have been used to increase ozone decomposition to produce higher concentrations of hydroxyl radicals. One of the most common of these involves adding hydrogen peroxide to ozonated water, a process commonly referred to as peroxone. Similar results are expected from other advanced oxidation processes such as ozone plus UV, ozone at high pH, hydrogen peroxide plus UV, UV in combination with titanium dioxide (TiO₂) and other combinations. A wide range of organic and potentially inorganic disinfection by-products are formed.

The UK WRc for DWI (2018) identified 14 AOPs with actual or potential application for drinking water treatment, the main eight being:

| | | | |
|----------------------------------|---|---------------------|--|
| UV/H ₂ O ₂ | O ₃ /H ₂ O ₂ | O ₃ /UV | O ₃ /UV/H ₂ O ₂ |
| UV/Cl ₂ | UV/S ₂ O ₈ | UV/TiO ₂ | UV/TiO ₂ /H ₂ O ₂ |

Their literature review of the above AOPs identified a total of 78 DBPs, nine of which were prioritised for high level risk assessment. Those where adverse health effects cannot be excluded were (datasheets prepared):

| | |
|-------------------------------|-----------------------------|
| 2-hydroxy-5-nitrobenzoic acid | 2-methoxy-4,6-dinitrophenol |
| 4-hydroxy-3-nitrobenzoic acid | 4-nitrocatechol |

The others were (no datasheets):

| | |
|------------------------------|---------------------------|
| 2-nitrohydroquinone | 3,5-dinitrosalicylic acid |
| 4-nitrobenzene-sulfonic acid | 4-nitrophthalic acid |
| 5-nitrovanillin | |

At the time of the study, the only WTPs in the UK using AOP were also using GAC which is likely to have reduced the concentrations of these DBPs.

a) Peroxone (ozone + hydrogen peroxide)

Research has been carried out into the use of peroxone to control organics and to oxidise taste and odour compounds (eg, geosmin and 2-methylisoborneol [MIB]) while providing sufficient levels of molecular ozone to guarantee C.t values and primary disinfection.

A key issue with the use of peroxone as a disinfection process is that the process does not provide a measurable disinfectant residual. Whereas ozone residuals may persist for 5–10 minutes, hydroxyl radicals are very short-lived. It is therefore not possible to calculate C.t values similar to the use of other disinfectants. While no credit can be given for hydroxyl free radicals because they cannot be measured directly, some credit may be considered for any detected ozone in peroxone systems. Peroxone does provide

pathogen inactivation, but equivalent C.t values or methods of calculating equipment C.t credits have not been established at the date of publication of the guidance document, *Alternative Disinfectants and Oxidants Guidance Manual* (USEPA 1999).

The key difference between ozone and peroxone is in the primary oxidation mode; that is, direct oxidation or hydroxyl radical oxidation. The reactivities of these compounds create a different effect in the reactions with water constituents and, thus, disinfection effectiveness. The peroxone process is a good disinfection process, not as effective as ozone on its own, and can only receive C.t credit if it has a measurable ozone residual.

b) Ozone + UV light

The USEPA (2003) evaluated a combined UV/O₃ system for disinfecting small supplies. They concluded that the combined system by far achieved the highest removal rates for bacterial contamination, presumably in comparison with chlorine, UV and ozone. A table in their handbook shows that the UV/O₃ system achieved an extra log removal of *Cryptosporidium* too. This may be due to the ozone component increasing the UVT (ie, reducing the UV absorbance).

The combined system is also more effective in removing organic contaminants such as MTBE than using ozone on its own. The handbook did not discuss the effect of varying the relative doses of the UV light and ozone.

DWI (2015a) stated that disinfection doses for UV are typically about 40 mJ/cm², whereas AOP doses are at least an order of magnitude higher.

c) UV peroxide

A UV peroxide plant was installed at Invercargill's Branxholme WTP for T&O control, followed by a GAC contactor for residual peroxide quenching. The UV peroxide system was able to achieve up to 1.7 log removal of 2-MIB during a peak taste and odour event. The hydrogen peroxide (as a 50 percent solution) dose was about 4 mg/L and the UV dose up to 800 mJ/cm². Plants at Paeroa and Waihi have been in operation over the 2017/18 summer (Stevenson and Zipfel 2018).

15.5.12 Mixed oxidants (chlorine-based)

The use of mixtures of oxidants for microbial inactivation has gained attention as a way to maximise the efficiency of current disinfectants, or as some may say, making use of the impurities in the raw ingredients. The chemistry of mixed oxidant production is complex, resulting in a solution of free chlorine, chlorine dioxide, ozone and various oxidation states of chlorine. Using lower grades of salt is likely to generate a range of bromine by-products too. The oxidants can be produced from a sodium chloride brine in an electrolytically generated cell.

Venczel et al (1997) examined the inactivation of *Cryptosporidium* oocysts and *Clostridium perfringens* spores in oxidant demand-free water at pH 7 and 25°C using a disinfectant dose of 5 mg/L and contact times up to 24 hours. Free chlorine produced no measurable inactivation of *Cryptosporidium parvum* oocysts after exposure for

4–24 hours, although *Clostridium perfringens* spores were reduced by 1.4 logs after four hours. In contrast, a mixed oxidant solution resulted in more than 3-log inactivation of both oocysts and spores with four hours' exposure. Other researchers, however, have found the mixed oxidant process equivalent to free chlorine for inactivation of biofilm samples (Crayton, Camper and Warwood 1997).

Additional research is needed to improve the understanding of the chemistry of seemingly incompatible oxidants within the mixed oxidant reaction (taken from WHO 2004b, Chapter 3.3.6). Proponents of mixed oxidant disinfection rarely seem to define the product in detail. One such product occasionally marketed in New Zealand is called MIOX.

15.5.13 Membrane technologies

Membrane technology (also see Chapter 14: Treatment Processes, Filtration and Chapter 19, section 19.3: Individual supplies) includes processes such as nanofiltration, reverse osmosis and ultrafiltration. These technologies are receiving increased attention for the treatment of water. They do not achieve disinfection by chemical inactivation of the micro-organisms, but by physically removing them from the water. The efficiency with which smaller micro-organisms are removed depends on the characteristics of the membrane and the size and filterability of the cells or (oo)cysts. If membrane technologies were to be used as the sole disinfecting process, a membrane process ideally must be selected that would ensure virus removal. RO is claimed to be able to do that.

Microfiltration also removes micro-organisms, but being coarser, cannot be relied upon to remove a high proportion of micro-organisms smaller than the protozoa, ie, the bacteria and viruses.

When microbial growth that will foul the membrane is not a problem, chemical disinfectants are not required and the formation of disinfection by-products is not a concern. However, many waters may require the use of chemical disinfectants to control biofouling of the membranes. Disinfection by-products may be formed in these cases.

Like UV treatment, this physical means of disinfection does not provide a disinfecting residual. Depending on the technology used, and the pore size of the membrane, very high percentages of rejection of the natural organic matter from which disinfection by-products are formed, can be achieved. Post-disinfection to maintain a residual in these instances will not lead to significant disinfection by-product formation.

15.5.14 Sunlight (solar disinfection or SODIS)

Section 3.4 of WHO (2009) states:

Laboratory tests showed that at a water temperature of 50°C, only a quarter of the ultraviolet light required at 30°C is necessary to kill the same level of faecal coliforms. Householders should fill 1 to 2 litre clear, plastic polyethylene

terephthalate (PET) bottles with water, place them on their roofs for at least 6 h during the daytime and store the water in the bottles until it is actually consumed. Under cloudy conditions, the length of exposure must be increased; for simplicity, solar disinfection users are told to keep bottles on the roof for 1 sunny day or 2 days if cloudy. As suspended solids may block the ultraviolet radiation, water with high levels of turbidity (> 100 NTU) must undergo some process (filtration, flocculation or simple sedimentation) to reduce particulate prior to use.

Solar disinfection has been subject to rigorous testing, both in the laboratory and under field conditions, and evaluated for effectiveness and cost-effectiveness in preventing diarrhoeal disease. While such testing has included permanently mounted panels and other configurations (Kang, Roy and Balraj 2006), the solar disinfection bottle system has been particularly well documented. Testing in both the laboratory and the field has shown the approach to be effective against a variety of faecal pathogens (Wegelin et al 1994; Heaselgrave et al 2006) and in reducing diarrhoeal disease (Conroy et al 1996, 1999, 2001; Lijima et al 2001; Rose et al 2006). *Giardia* and *Cryptosporidium* have both shown susceptibility to sunlight (McGuigan et al 2006). A cost-effectiveness analysis reported that the mean cost of implementing the intervention in 13 countries, including hardware (new bottles) and programme costs, was US\$0.63 per person per year, just below the US\$0.66 cost attributed to the SWS and far less than the US\$3.03 for ceramic filters and US\$ 4.95 for flocculant-disinfectant sachets (Clasen et al 2007a).

The summary of the same WHO publication states:

Solar disinfection, which synergistically applies the biocidal action of heat and ultraviolet radiation, has also been shown to be effective, both microbiologically and in reducing diarrhoeal disease and cholera. Although continuous commercial systems are used in some settings, the approach that has gained the largest traction among low-income populations consists simply of filling clear plastic bottles with water and placing them on the roof to expose the water to sunlight for at least six hours. Like boiling, this method is fundamentally a behaviour change strategy more than a product and thus has little commercial potential. Accordingly, it is promoted exclusively by governments and NGOs. Despite these limitations, solar disinfection reported more than 2.1 million users as of the end of 2007. While the delivery strategy and low cost may overcome some of the disparities in uptake that are more likely to impact market-driven HWTS products, scaling up solar disinfection widely has thus far met challenges in acceptability and longer-term use, partly due to some resistance in gaining credibility among potential users, some inconvenience, its inability to deliver improvements in water aesthetics and its lack of aspirational appeal. These are, however, many of the same challenges that boiling has had to overcome.

Due to concerns of chemicals leaching from plastic bottles, a study by Asiimwe et al (2013) found that glass bottles are as effective as PET bottles for inactivating *E. coli*.

See also WHO (2011a). The efficacy of the process is dependent on oxygenation, sunlight intensity, exposure time, temperature, turbidity and size of water vessel (depth of water).

Because the pasteurising effect of elevated temperature is an important component of the disinfection process, it is suggested that the bottles be placed on a dark surface. See www.sodis.ch for an extensive bibliography.

The WHO Guidelines (2004) state:

Where there is a concern about the quality of drinking-water in an emergency situation that cannot be addressed through central services, then the appropriateness of household-level treatment should be evaluated, including, for example:

- bringing water to a rolling boil and cooling before consumption
- adding sodium or calcium hypochlorite solution, such as household bleach, to a bucket of water, mixing thoroughly and allowing to stand for about 30 minutes prior to consumption; turbid water should be clarified by settling and/or filtration before disinfection
- vigorously shaking small volumes of water in a clean, transparent container, such as a soft drink bottle, for 20 seconds and exposing the container to sunlight for at least six hours
- applying products such as tablets or other dosing techniques to disinfect the water, with or without clarification by flocculation or filtration
- end-use units and devices for field treatment of drinking-water.

The inactivation of four *Salmonella* serovars was examined in sunlit and dark microcosms. First order decay was observed in sunlit microcosms; the time until 90 percent inactivation was of the order of 10 minutes. A significant shoulder, of the order of one hour in length, was observed in the freshwater microcosms during which concentrations were stable. Serovar Mdandaka decayed more slowly than other serovars in both seawater and freshwater. The serovars were extremely stable in the dark microcosms showing little to no decay over 53 days (Boehm et al 2012).

The effect of sunlight on viruses in water PET bottles was reported by Carratalà et al (2016). Good inactivation of MS2 virus was achieved with >6 log units for a fluence of 1.34 kJ/cm² (corresponding to the recommended six hours of sunlight) in Swiss tap water at 22°C. In the dark controls for only 2-log inactivation was observed after an equivalent exposure time. In contrast, no inactivation of the ϕ X174 virus was observed after exposure to a fluence of 1.34 kJ/cm². The inactivation rate constant did not vary statistically from zero and was the same as the inactivation rate constant in the dark experiments. For HAdVs about 3 log inactivation occurred at a fluence of 1.34 kJ/cm². The inactivation rate constant for HAdV dark controls was similar to that observed under simulated sunlight and therefore exposure to light seems not to contribute significantly to the inactivation of HAdV during SODIS. For EV about 1.5 log inactivation was achieved after exposure to a fluence of 1.34 kJ/cm². There was no significant inactivation observed for the dark controls. The authors conclude that SODIS application procedures recommended for bacterial inactivation do not apply to enteric viruses. However, removal of viruses during SODIS may still be substantial for reactive (oxygen) species-susceptible viruses (such as enteroviruses), especially if the water temperature is high and the organic matter content of the source water is low.

The potentially wide application of SODIS has led to studies which may enhance the process. McLaughlin et al (2016) found that adding copper wire to the PET bottle was

effective in inactivating *E. coli*, while earlier studies had shown that storing water overnight in copper pots eliminated a range of pathogenic bacteria (Sudha et al 2012). Sudha had also shown that copper pots were effective in eliminating rotavirus.

15.5.15 Heat

It is generally accepted that water that has been brought to a 'rolling' boil should be safe to drink, from a bacteriological, virological and protozoal point of view.

What is less well known is the effect of sub-boiling water. WHO (2015) is a Technical Brief "Boil Water" which includes a table summarising studies that have examined thermal inactivation in liquids at temperatures approaching 100°C. Bacteria are particularly sensitive to heat, and rapid kills – less than one minute per log (90 percent) reduction – are achieved at temperatures above 65°C. Viruses are inactivated at temperatures between 60°C and 65°C, but more slowly than bacteria. However, as shown for poliovirus and hepatitis A, as temperatures increase above 70°C, a greater than 5 log inactivation (99.999 percent reduction) is achieved in less than one minute. *Cryptosporidium parvum* oocysts are inactivated in less than one minute once temperatures exceed 70°C. The data for *Giardia* cysts are more limited, but inactivation at temperatures ranging from 50°C to 70°C has been reported.

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