

# Disinfectants and Disinfection By-Products

## Session Objectives

---

- To describe the importance of disinfection in providing safe drinking water.
- To describe the key disinfectants evaluated in the *Guidelines* and describe their principal characteristics and effectiveness.
- To describe the key by-products formed by the principal disinfectants and describe the likely health risk from their presence in water.
- To describe the balance between microbiological and chemical health risks and emphasise the need to prioritise microbiological quality.

## Disinfectants and Disinfection By-Products

### **Introduction**

Disinfection of drinking-water is essential if we are to protect the public from outbreaks of waterborne infectious and parasitic diseases. The main disinfectants evaluated in the *Guidelines* are free chlorine, chloramines, chlorine dioxide and ozone.

As much as the perfect indicator organism does not exist, each of the commonly used disinfectants has its advantages and disadvantages in terms of cost, efficacy, stability, ease of application and formation of by-products.

Table 1 summarizes the Ct values for the four main disinfectant,

where C = disinfectant concentration in mg/litre, and  
t = the contact time in minutes required to inactivate a specified percentage of microorganisms.

**Table 1. Summary of C.t values (mg/L. min)for 99% inactivation at 5°C (Clark et al, 1993)**

Organism	Disinfectant			
	Free chlorine, pH 6 to 7	Pre-formed chloramine, pH 8 to 9	Chlorine dioxide, pH 6 to 7	Ozone pH 6 to 7
<i>E. coli</i>	0.034-0.05	95-180	0.4-0.75	0.02
Polio virus 1	1.1-2.5	768-3740	0.2-6.7	0.1-0.2
Rotavirus	0.01-0.05	3806-6476	0.2-2.1	0.006-0.06
Bacteriophage f <sub>2</sub>	0.08-0.18	-	-	-
<i>G. lamblia</i> cysts	47->150	-	-	0.5-0.6
<i>G. muris</i> cysts	30-630	-	7.2-18.5	1.8-2.0 <sup>a</sup>
<i>C. parvum</i>	7200 <sup>b</sup>	7200 <sup>c</sup>	78 <sup>b</sup>	5-10 <sup>c</sup>

a Values for 99.9% inactivation at pH 6-9.

b 99% inactivation at pH 7 and 25°C.

c 90% inactivation at pH 7 and 25°C.

From the Ct values, ozone is the most efficient and chloramine the least efficient, particularly for viral agents. Free chlorine is more effective than chlorine dioxide with regard to *E. coli* and rotavirus. Chlorine dioxide is more effective than free chlorine with regard to the protozoa *Giardia lamblia* and *muris*. Ozone is the most efficient disinfectant for *cryptosporidium parvum*. As the temperature increases, the Ct values decrease for all disinfectants. The effect of pH varies with the nature of the disinfectant and is most pronounced for chlorine.

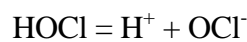
### **Chlorine and its by-products**

Chlorine is the most widely used drinking-water disinfectant. When added to water the following reaction occurs within a second or less:



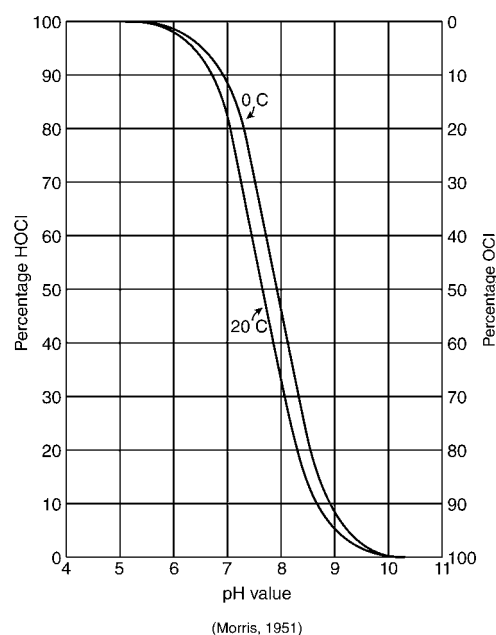
The magnitude of the equilibrium hydrolysis constant is such that hydrolysis to hypochlorous acid, HOCl, is virtually complete in fresh water at pH > 4 and at chlorine doses up to 100 mg/litre (Morris, 1982).

Hypochlorous acid is a weak acid that dissociates partially in water as follows:



The value of the acid ionization constant is about  $3 \times 10^{-8}$ . As shown in Figure 1, at 20°C and pH 7.5, there is an equal distribution of HOCl and OCl<sup>-</sup>. At pH 8, about 30% of the free chlorine is present as HOCl, and at pH 6.5, 90% is present as HOCl (Morris, 1982). The term free chlorine refers to the sum of hypochlorous acid and hypochlorite ion. Since HOCl is a considerably more efficient disinfectant than OCl<sup>-</sup>, and free chlorine, even as hypochlorite, is more effective than combined chlorine (e.g. chloramines), the *Guidelines* recommend that disinfection be carried out at pH less than 8 and at a free chlorine concentration  $\geq 0.5$  mg/litre.

Of all the disinfectants, the chemistry and toxicity of the reaction by-products of chlorine have been the most extensively studied.



**Figure 1: Distribution of hypochlorous acid and hypochlorite ion in water at different pH values and temperatures (Morris,1951)**

Since Rook's discovery of the formation of haloforms during chlorination of Rotterdam water supply (Rook, 1974), numerous halogenated compounds have been identified in chlorinated drinking-water and their toxicity assessed. Precursors of these halogenated compounds include natural humic and fulvic compounds and algal material. The most commonly found chlorine disinfection by-products are the trihalomethanes (THM), halogenated acetic acids, halogenated acetonitriles, chloral hydrate and the chlorinated phenols. Others include chlorinated furanone MX, halopicrins, cyanogen halides, haloketones and haloaldehydes. The halogenated disinfection by-products identified account for only about half of the total formed.

Based on animal toxicological studies, Guideline Values (GVs) have been recommended for a number of these compounds. Undoubtedly, the third edition of the *Guidelines*, planned for the year 2002, will include additional chlorination by-products.

The following chemicals resulting from chlorination of water supplies have been evaluated in the *Guidelines*:

- free chlorine (HOCl + OCl)
- trihalomethanes
- chlorinated acetic acids
- halogenated acetonitriles
- chloral hydrate (trichloroacetaldehyde)
- chlorophenols
- MX (3-chloro-4-dichloromethyl-5-hydroxy-2(5H)-furanone)

For countries wishing to control DBP, it may not be necessary to set standards for all of the DBP for which guideline values have been proposed. The trihalomethanes, of which chloroform is the major component, are likely to be the main DBP, together with the chlorinated acetic acids in some instances. In many cases, control of chloroform levels and, where appropriate, trichloroacetic acid will also provide an adequate measure of control over other chlorination by-products.

#### **(a) Chlorine**

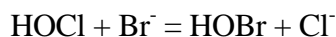
Free chlorine in drinking-water is not particularly toxic to humans. The major source of exposure to chlorine is drinking-water. Therefore, 100% of the TDI was allocated to drinking-water giving a health-based GV of 5 mg/litre for the sum of hypochlorous acid and hypochlorite ion. Based on the taste and odour threshold of free chlorine, it is doubtful however that consumers would tolerate such a high level of chlorine. Most individuals are able to taste chlorine at concentrations below 5mg/litre, and some at levels as low as 0.3 mg/litre. The health-based GV for chlorine should not be interpreted as a desirable level of chlorination.

#### **(b) Trihalomethanes**

The predominant chlorine disinfection by-products are the THMs. Nevertheless, they account for only about 10% of the total organic halogen compounds formed by water chlorination.

THMs are formed by the aqueous chlorination of humic substances, of soluble compounds secreted from algae and of naturally occurring nitrogenous compounds (Morris, 1982). THMs consist primarily of chloroform, bromodichloromethane, dibromochloromethane and bromoform.

When bromide is present in drinking-water, it is oxidized to hypobromous acid by chlorine:



HOBr reacts with natural organic compounds to form brominated halomethanes. Similarly, the presence of iodide may lead to the formation of mixed chlorobromiodo-methanes.

Some generalized statements can be made with regard to THMs in chlorinated drinking-water (IARC, 1991; Morris, 1982; Canada, 1993):

- Concentration of THMs in drinking-water varies widely and ranges from not detectable to 1 mg/litre or more;
- THM levels are higher in chlorinated surface water than in chlorinated groundwater;
- Concentrations of THMs tend to increase with increasing temperature, pH and chlorine dosage;
- Concentrations of THMs increase upon storage even after exhaustion of residual chlorine or after dechlorination. This indicates the formation of intermediates products leading to the slow production of THMs;
- Chloroform is usually the most abundant THM often accounting for greater than 90% of the total THM concentration;
- If there is a significant amount of bromide in the raw water, the brominated THMs, including bromoform, may be dominant;
- Formation of THMs can be minimized by avoiding pre-chlorination and by effective coagulation, sedimentation and filtration to remove organic precursors prior to final disinfection;
- Removal of THMs after their formation is difficult and involves resource-intensive processes such as activated carbon adsorption or air stripping.

Because trihalomethanes usually occur together, it has been the practice to consider total trihalomethanes as a group, and a number of countries have set guidelines or standards on this basis, ranging from 0.025 to 0.25 mg/litre.

In the 1993 WHO *Guidelines*, individual GV have been recommended for the four trihalomethanes. With an underlying assumption that the THMs may exert potential toxic effects through similar biological mechanisms, authorities may want to establish standards for total THMs that would account for possible additive effects and not simply add up the guideline values for the individual compounds in order to arrive at a standard. Instead, the following approach is recommended:

$$\frac{C_{\text{bromoform}}}{GV_{\text{bromoform}}} + \frac{C_{\text{DBCM}}}{GV_{\text{DBCM}}} + \frac{C_{\text{BDCM}}}{GV_{\text{BDCM}}} + \frac{C_{\text{chloroform}}}{GV_{\text{chloroform}}} \leq 1$$

where C = concentration, and  
GV = guideline value

### ***Epidemiological studies of carcinogenicity of chlorine and DBP***

In 1991, WHO International Agency for Research on Cancer (IARC) published an evaluation of the carcinogenic risks to humans of chlorinated drinking-water based on a number of animal toxicological and epidemiological studies. IARC concluded that because of one or more methodological weaknesses, the epidemiological studies reviewed cannot constitute the basis of valid risk assessment.

The epidemiological investigation of the relation between exposure to chlorinated drinking-water and cancer occurrence was considered problematic because any increase in relative risk over that in people drinking unchlorinated water is likely to be small and therefore difficult to detect in epidemiological studies. In all of the studies evaluated, estimates of exposure were imprecise and surrogates (e.g surface versus groundwater) do not reflect exposure during the relevant time periods for the etiology of the cancers in question. Many variables, such as smoking habits, dietary practices, use of alcohol, socio-economic status, and ethnicity are known to affect cancer incidence and were not taken into account in most of the studies (IARC, 1991).

In its overall evaluation, IARC concluded that there is inadequate evidence for the carcinogenicity of chlorinated drinking-water in humans as well as in experimental animals (IARC, 1991).

### ***Chloramine and its by-products***

Chloramine generally produces by-products similar to those observed with chlorine but at much lower concentrations. An exception to this is the formation of cyanogen chloride, CNCl (Bull and Kopfler, 1991). The use of chloramine as a disinfectant has increased in recent years because of limited formation of THMs, however, little is known about the nature of other by-products.

Monochloramine is about 2000 and 100 000 times less effective than free chlorine for the inactivation of *E. coli* and rotaviruses, respectively. Monochloramine cannot therefore be relied upon as primary disinfectant. It is useful for maintaining a residual disinfectant in distribution systems. The shift to monochloramine to control THM formation may thus compromise disinfection and the *Guidelines* caution against such procedure. Organic chloramines are even less effective disinfectants than monochloramine.

### ***Chlorine dioxide and its by-products***

Because of its explosive hazard, chlorine dioxide is manufactured at the point of use.  $\text{ClO}_2$  is generated through the reaction of sodium chlorite and chlorine. Chlorine dioxide reactions with humic substances do not form significant levels of THMs. In addition, it does not react with ammonia to form chloramines. The main disinfection by-products of chlorine dioxide are chloride, chlorate and chlorite.

Chlorine dioxide is more effective towards inactivation of *Giardia* cysts than free chlorine, but less effective towards rotavirus and *E. coli*. Unlike chlorine, the disinfection efficiency of chlorine dioxide is independent of pH and the presence of ammonia.

A provisional GV was recommended for chlorite while no adequate data were available to recommend a GV for chlorate. No GV has been recommended for chlorine dioxide *per se* because of its rapid breakdown in aqueous solutions and the chlorite GV is adequately protective for potential toxicity from chlorine dioxide. Furthermore, the taste and odour threshold for chlorine dioxide in water is 0.4 mg/litre which constitutes a limiting factor and a signal for its presence at higher concentrations in drinking-water.

Other reaction by-products of chlorine dioxide with organics in drinking-water have not been well characterized but include aldehydes, carboxylic acids, haloacids, chlorophenols, quinones and benzoquinone (Bull and Kopfler, 1991). In a recent article, more than 40 organic disinfection by-products were identified in a pilot plant in Indiana which uses chlorine dioxide as a primary disinfectant. The toxicity of these by-products is largely unknown (Richardson et al. 1994).

### ***Ozone and its by-products***

Ozone decomposes rapidly following application, and for this reason no GV has been proposed for ozone.

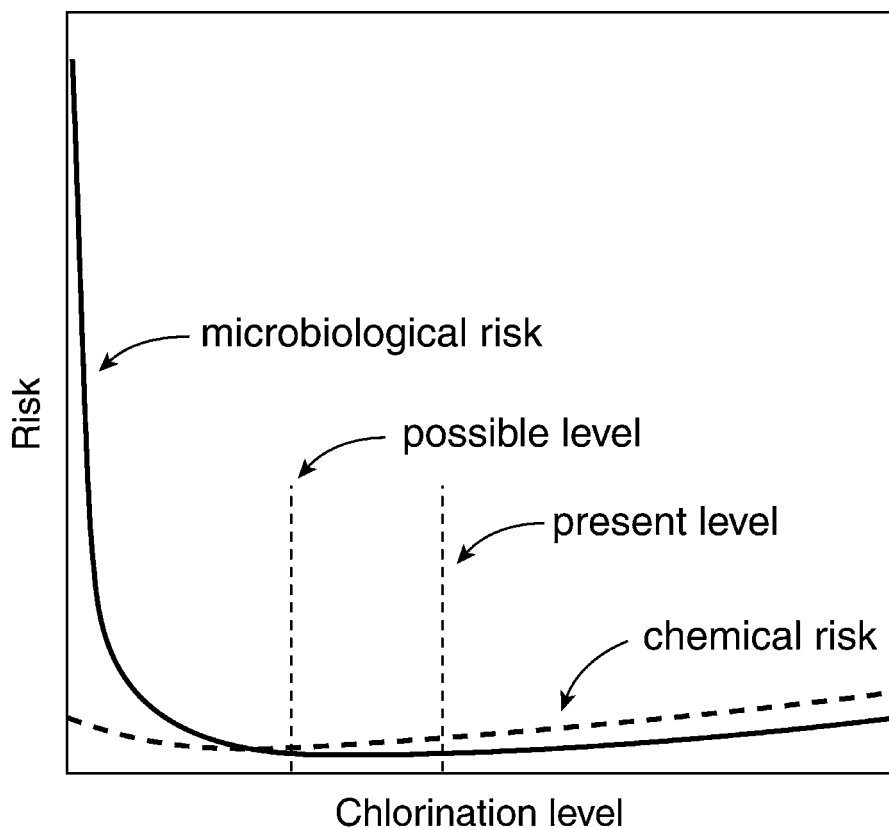
By products of ozonation that have been identified include formaldehyde and other aldehydes, carboxylic acids, hydrogen peroxide, bromate, bromomethanes, brominated acetic acids, brominated acetonitriles and ketones. Guideline values have been recommended for bromate and formaldehyde.

Ozone is the most efficient disinfectant for all types of microorganisms. Disadvantages include lack of disinfectant residual, biological regrowth problems in distribution systems, high cost, and limited information on the nature and toxicity of its by-products.

### ***Balancing Chemical and Microbial Risks***

Quantitative assessments of risks associated with the microbial contamination of drinking-water are scarce. Although there are gaps in our knowledge, we cannot afford to postpone action until rigorous quantitative assessment of chemical versus microbial risks are available and every answer is known.

A semi-quantitative presentation of risks associated with disinfection was first attempted by Morris (1978) and is given in Figure 2. The following is more or less a quote of his work: The risk of waterborne infectious disease is very high when no chlorination is used, and drops sharply to a low value when even minimal levels of chlorination are maintained. We know this on the basis of a century's experience, Morris stated. As the level of chlorination is increased the risk continues to drop slightly, but never quite reaches zero, for no system is perfect. At very high levels of chlorine the microbial risk increases as taste and odour may cause the use of unsafe supplies.



(Morris, 1978)

**Figure 2: Risks and benefits of water chlorination (Morris, 1978)**



The chemical risk does not start at zero for there is some hazard connected with the organic matter before chlorination. The chemical risk decreases initially because destruction of chemicals by oxidation more than compensate for the formation of new chemicals at low levels of chlorination. Because of the formation of by-products, the chemical risk increases with increasing level of chlorination. Intuitively, he depicted the chemical risk from chlorination as being considerably lower than the microbial risk from a non-disinfected supply.

In developed countries, since filtration and chlorination became common for community water supplies, morbidity and mortality due to waterborne intestinal diseases, particularly typhoid fever and cholera, have declined to negligible levels. Almost all of the waterborne outbreaks that still occur are associated with the use of untreated water or water from systems in which chlorination was inadequate.

Other health impact studies concern the beneficial effects on health of safe and sufficient water supplies and adequate sanitation, three factors that are so intertwined that it is often not feasible to draw definite lines of demarcations between them. Together, they constitute the pillars of public health protection. Projected reduction in morbidity achievable through the provision of safe and sufficient water supplies and adequate sanitation are estimated to be (WHO, 1992):

#### **Projected reduction in morbidity (%)**

Cholera, typhoid	80
Diarrhoeal diseases	40
Dracunculiasis	100
Schistosomiasis	60

When applying these percentage reductions to the global morbidity and mortality rates for these diseases, the benefits of saving millions of lives through these interventions are immediately apparent.

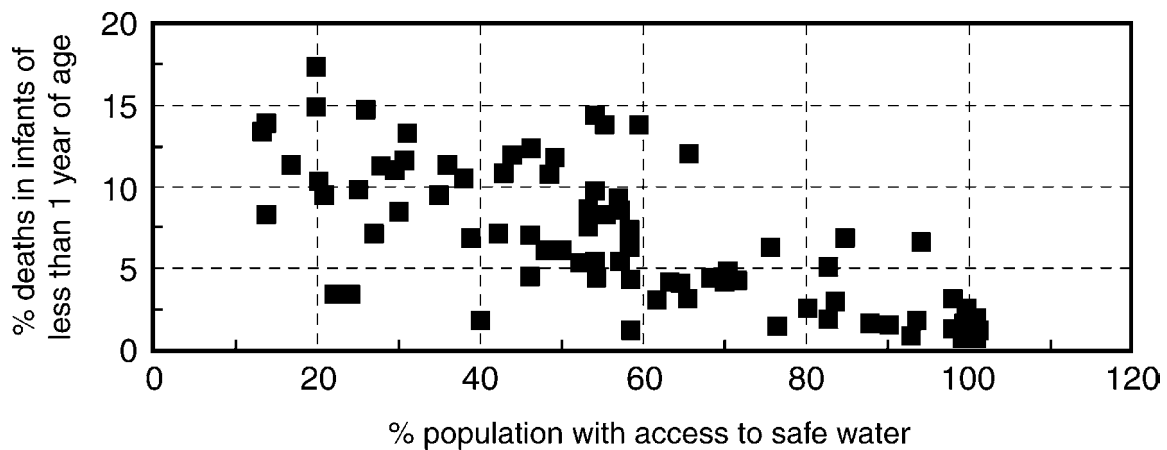
As shown in Figure 3 overleaf, provision of safe drinking-water can result in a 20% reduction in infant mortality (Regli et al., 1993).

In their pioneering work on comparison of estimated risk from known pathogens in untreated surface water and chlorination by products in drinking-water, Regli et al. (1993) concluded that:

- the risk of death from pathogens is at least 100 to 1000 times greater than the risk of cancer from disinfection by-products (DBPs);
- the risk of illness from pathogens is at least 10 000 to 1 million times greater than the risk of cancer from DBPs;
- morbidity and mortality rates from pathogens compared with those from DBPs, may be considerably higher in developing countries where the sanitary and health status is not as good;

- in societies where infant mortality and life expectancy is low, many people would not be expected to live long enough to incur cancer, which also causes much higher differences in risk resulting from exposure to pathogens versus DBPs cited above.

While this last statement seems cynical, it does reflect the true situation in many developing countries.



**Figure 3. Infant mortality versus access to safe water (Regli et. al., 1993)**

### **Conclusion**

Adequate disinfection of drinking-water is the most important priority to assure a safe water supply. Recent cholera outbreaks in Latin America and Rwanda provide dramatic evidence of the importance of adequate water disinfection. There is some limited evidence of possible health effects from disinfectant by-products, particularly possible cancer risks from chloroform and the other trihalomethanes and by-products. This evidence is based on high-dose animal studies.

Epidemiological studies conducted to date do not provide any evidence that disinfectants and their by-products affect human health at the concentrations found in drinking-water. The International Agency for Research on Cancer has concluded that there is inadequate evidence for the carcinogenicity of chlorinated drinking-water in humans and experimental animals.

Although stated in qualitative way, the message of the *Guidelines* is clear:

**The estimated risks to health from disinfectants and their by-products are extremely small in comparison to the real risks associated with inadequate disinfection, and it is important that disinfection should not be compromised in attempting to control such by-products. The destruction of microbial pathogens through the use of disinfectants is essential for the protection of public health.**

All disinfectants by necessity are reactive substances and produce by-products. Little is known about the nature and toxicity of the by-products of ozone, chlorine dioxide or chloramines. The

by-products of chlorination are the ones that have been most extensively identified and their toxicity assessed. Disinfection with chlorine should not be penalized for this reason. In addition, in many countries, if disinfection can be practised at all, it will be through the use of chlorine.

There are now more and more indication that the estimated risks to health from disinfectants and their by-products are several order of magnitude lower than the real risks associated with inadequate disinfection. So while there is great scientific certainty that inadequately disinfected water results in devastating microbial disease epidemics, there is relatively great uncertainty regarding the possible health risks from DDBPs. In establishing standards for disinfectants by products, it is emphasized that **"Where local circumstances require that a choice must be made between meeting either microbiological guidelines or guidelines for disinfectants or disinfectant by-products, the microbiological quality must always take precedence, and where necessary, a chemical guideline value can be adopted at a higher level of risk. Efficient disinfection must never be compromised."** (1993 *Guidelines*)

## **References**

Bull R.J., Kopfler F.C. (1991). Health Effects of Disinfectants and Disinfection By-products, American Water Works Association, Denver.

Canada Health and Welfare (1993). Water treatment principles and applications. Canadian water and wastewater association, Ottawa.

Clark RM, Hurst CJ, Regli S (1993). Costs and benefits of pathogen control in drinking-water. In: Safety of water disinfection: balancing chemical and microbial risks. Craun G.F. ed. ILSI Press, Washington, D.C.

International Agency for Research on Cancer (1991). IARC monographs on the evaluation of carcinogenic risks to humans, Volume 52 Chlorinated drinking-water; chlorination by-products; some other halogenated compounds; cobalt and cobalt compounds, Lyon.

Morris J.C. (1951), unpublished research, Harvard University, 1951

Morris J.C. (1978). Conference summary. In: Water chlorination environmental impact and health effects. Volume 2. Jolley RL, Gorchev H., Hamilton D.H. eds., Ann Arbor Science, Ann Arbor, Michigan.

Morris J.C. (1982). Health perspective in the oxidative treatment of water for potable supply. Part 2 Health assessment of current oxidant-disinfectants. National Institute for Water Supply. Leidschendam, Netherlands.

Regli S., Berger P., Macler B., Haas C. (1993). Proposed decision tree for management of risks in drinking-water: consideration for health and socioeconomic factors. In: Safety of water disinfection: balancing chemical and microbial risks. Craun G.F. ed. ILSI Press, Washington, D.C.

Richardson S.D., Thruston A.D., Collette T.W. (1994). Multispectral identification of chlorine dioxide disinfection byproducts in drinking-water. Environ. Sci. Technol., 28: 592-599.

Rook J.J. (1974). Formation of haloforms during chlorination of natural waters. J. Soc. for water treatment and examination 23: 234-243.

World Health Organization (1992). Our planet, our health. Report of the WHO Commission on health and environment. Geneva.

**Annex 1**  
**BACTERIOLOGICAL QUALITY OF DRINKING-WATER**

<b>Organisms</b>	<b>Guideline value</b>
<b>All water intended for drinking</b>	
<i>E. coli</i> or thermotolerant coliform bacteria	Must not be detectable in any 100-ml sample
<b>Treated water entering the distribution system</b>	
<i>E. coli</i> or thermotolerant coliform bacteria	Must not be detectable in any 100-ml sample
Total coliform bacteria	Must not be detectable in any 100-ml sample
<b>Treated water in the distribution system</b>	
<i>E. Coli</i> or thermotolerant coliform bacteria	Must not be detectable in any 100-ml sample
Total coliform bacteria	Must not be detectable in any 100-ml sample. In the case of large supplies, where sufficient sample are examined, must not be present in 95% of samples taken throughout any 12-month period.

## Disinfectants and Disinfectant By-Products

Table 1: Summary of C.t values (mg/L. min) for 99% inactivation at 5° C (Clark et al, 1993)

Organism	Disinfectant			
	Free chlorine, pH 6 to 7	Pre-formed chloramine, pH 8 to 9	Chlorine dioxide, pH 6 to 7	Ozone pH 6 to 7
<i>E. coli</i>	0.034-0.05	95-180	0.4-0.75	0.02
Polio virus 1	1.1-2.5	768-3740	0.2-6.7	0.1-0.2
Rotavirus	0.01-0.05	3806-6476	0.2-2.1	0.006-0.06
Bacteriophage f <sub>2</sub>	0.08-0.18	-	-	-
<i>G. lamblia</i> cysts	47->150	-	-	0.5-0.6
<i>G. muris</i> cysts	30-630	-	7.2-18.5	1.8-2.0 <sup>a</sup>
<i>C. parvum</i>	7200 <sup>b</sup>	7200 <sup>c</sup>	78 <sup>b</sup>	5-10 <sup>c</sup>

a Values for 99.9% inactivation at pH 6-9.

b 99% inactivation at pH 7 and 25°C.

c 90% inactivation at pH 7 and 25°C.

# Disinfectants and Disinfectant By-Products

## Presentation Plan

Section	Key points	OHP
<b>Introduction</b>	<ul style="list-style-type: none"> <li>• disinfection of all waters supplied for drinking is recommended by WHO to protect public health</li> <li>• main disinfectants evaluated in the <i>Guidelines</i> are: free chlorine, chloramines, chlorine dioxide and ozone</li> <li>• overall ozone is the most effective disinfectant, although chlorine is also effective and efficient</li> <li>• all disinfectants have advantages and disadvantages and all produce by-products</li> <li>• a number of disinfection by-products were evaluated in the GDWQ</li> </ul>	<p><b>1,2</b></p> <p><b>Table 1</b></p>
<b>Chlorine and its by-products</b>	<ul style="list-style-type: none"> <li>• chlorine is most common disinfectant</li> <li>• when chlorine is added to water it forms hypochlorous acid, hydrogen ion and a chlorine ion</li> <li>• because of greater efficiency, the <i>Guidelines</i> recommend disinfection with chlorine is done at pH less than 8 and a free chlorine concentration of greater than 0.5 mg/l</li> <li>• the use of chlorine leads to the formation of halogenated by-products, including the THMs</li> <li>• precursors to THMs are natural humic and fulvic acids and algal material</li> <li>• numerous other by-products may be formed (see paper or <i>Guidelines</i> for examples)</li> <li>• impurities in gaseous and liquid chlorine of relevance to the nature of by-products are carbon tetrachloride and bromide</li> <li>• GVs set for a number of chlorination by-products</li> <li>• very difficult to estimate exposure to halogenated organic compounds in drinking-water</li> <li>• may not need to set standards for all by-products included in <i>Guidelines</i>, it is better to concentrate on the major groups (e.g. THMs)</li> <li>• microbiological quality of water should never be compromised by concerns about disinfection by-products</li> </ul>	<p><b>3,4,5</b></p>

Section	Key points	OHP
<b>Chlorine</b>	<ul style="list-style-type: none"> <li>• free chlorine in drinking-water is not particularly toxic and health-based GV is 5 mg/l</li> <li>• very unlikely consumers would accept such levels of chlorine as taste is noted as low as 0.3 mg/l</li> <li>• do not use GV as desirable level of chlorination</li> </ul>	
<b>Tri-halomethanes</b>	<ul style="list-style-type: none"> <li>• these are principal by-products of chlorination, but only form 10 per cent of total organic compounds in drinking-water</li> <li>• THMs more likely to occur in chlorinated surface water than groundwater</li> <li>• THM concentrations vary widely; increasing with increasing temperature, pH, chlorine dosage and on storage after exhaustion of free chlorine or dechlorination</li> <li>• chloroform is most common THM (usually &gt;90% of total THMs)</li> <li>• when bromine present, brominated THMs likely to be dominant</li> <li>• THM formation can be minimised by avoiding prechlorination and by optimising treatment</li> <li>• THM removal is expensive and difficult</li> </ul>	<b>6</b>
<b>Chloramine and by-products</b>	<ul style="list-style-type: none"> <li>• chloramines formed by reaction of chlorine and ammonia or organic amines</li> <li>• can get mono-, di- and trichloramines depending on pH and temperature</li> <li>• chloramine by-products similar to free chlorine, with exception of cyanogen chloride</li> <li>• monochloramine about 2000 to 100, 000 times less effective than free chlorine for inactivation of <i>E.coli</i> and rotaviruses</li> </ul>	<b>7</b>
<b>Chlorine dioxide and by-products</b>	<ul style="list-style-type: none"> <li>• chlorine dioxide made at point of use because of its explosive hazard</li> <li>• chlorine dioxide does not form THMs or chloramines</li> <li>• main by-products are chlorite, chlorate and chloride</li> <li>• chlorine dioxide more effective than free chlorine in inactivation of <i>Giardia</i> cysts but less effective against <i>E.coli</i> and rotaviruses</li> <li>• no GV for chlorine dioxide in water as it rapidly disassociates</li> <li>• GVs set for chlorite but not for chlorate</li> </ul>	<b>8</b>
<b>Ozone and by-products</b>	<ul style="list-style-type: none"> <li>• ozone decomposes rapidly following application and thus no GV has been proposed</li> <li>• by-products include formaldehyde, other aldehydes, hydrogen peroxide and bromomethanes (see paper/<i>Guidelines</i> for further examples)</li> </ul>	<b>9</b>



Section	Key points	OHP
<b>Ozone and by-products</b> <i>(continued)</i>	<ul style="list-style-type: none"> <li>• ozone is the most efficient disinfectant with regard to microorganisms</li> <li>• disadvantages include: lack of residual, biological regrowth problems in distribution systems, high cost and limited information on nature and toxicity of by-products</li> <li>• when ozonation followed by chlorination, concentrations of brominated THMs may increase</li> </ul>	
<b>Balancing chemical and microbial risks</b>	<ul style="list-style-type: none"> <li>• currently a scarcity of quantitative assessment done of relative risks of microbial and chemical contamination of drinking-water</li> <li>• semi-quantitative presentation has been done by Morris: this showed that risk of infectious water-borne disease is high where chlorination not practised and this decreases sharply with even minimal levels of chlorination, though can never reach zero risk</li> <li>• at very high chlorine concentrations, microbial risk increases as taste and odour cause the use of unsafe supplies</li> <li>• chemical risks do not start at zero as always some hazard from organic matter prior to chlorination</li> <li>• chemical risks are low initially but increase with increasing chlorine dosages</li> <li>• risk of death from pathogens is at least 100 to 1000 times greater than risk of cancer from disinfected by-products and risk of illness from pathogens at least 10,000 to 1 million times greater</li> <li>• morbidity and mortality rates from pathogens compared to cancer risk from by-products may be much higher in developing countries where sanitary and health status poor</li> </ul>	<b>10</b>
<b>Conclusions</b>	<ul style="list-style-type: none"> <li>• disinfection is important to assure a safe drinking-water supply</li> <li>• limited information is available concerning health risk from disinfection by-products</li> <li>• disinfection by-product formation may be reduced if treatment process are optimised and prechlorination is avoided</li> <li>• inadequate evidence exists concerning the carcinogenicity of chlorinated drinking-water</li> <li>• more information is available concerning chlorine because it has been studied in more detail and this should not penalise the use of chlorine</li> <li>• as microbiological quality is of paramount importance, disinfection should not be compromised</li> </ul>	

# Disinfectants Evaluated

---

---

- Chlorine
- Chloramine
- Chlorine dioxide
- Ozone
- Iodine



# Disinfectants and Disinfectant by-products

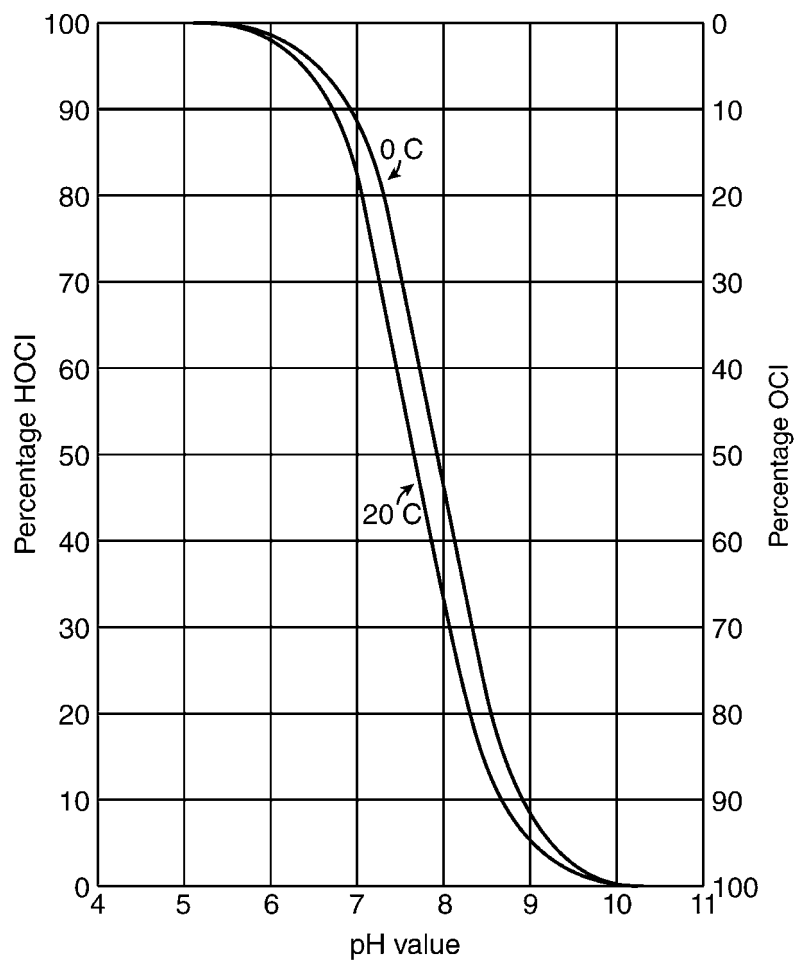
---

- Overall ozone is the most effective disinfectant, although chlorine is effective and efficient
- All disinfectants have advantages and disadvantages and all produce by-products
- A number of disinfectant by-products were evaluated in the Guidelines

*Microbiological quality of water should never be compromised by concerns about disinfection by-products*



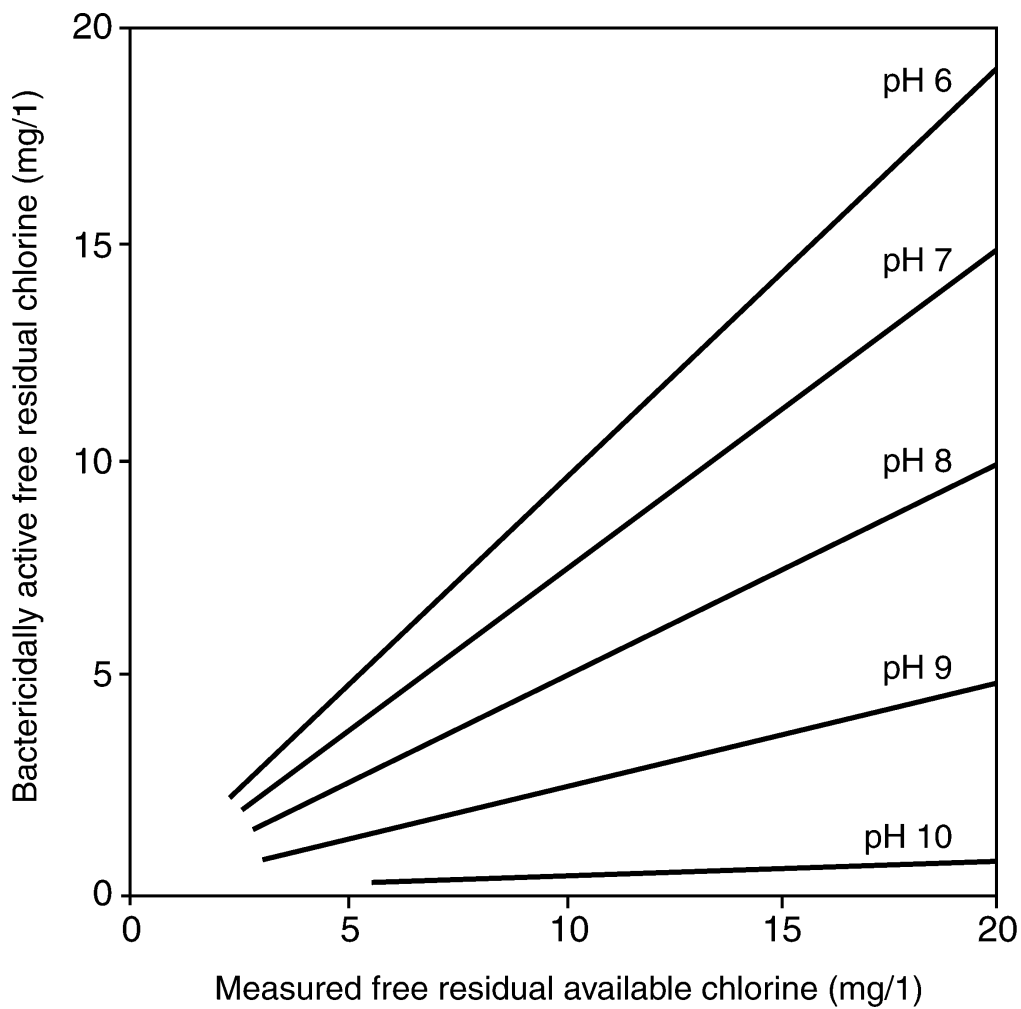
# Distribution of Hypochlorous Acid and Hypochlorite Ion in Water at Different pH Values and Temperatures



(Morris, 1951)



# Relationship between Measured Free Residual Available Chlorine ( $\text{HOCl}^+$ , $\text{OCl}^-$ ) and Bactericidally Active ( $\text{HOCl}$ )



# Chlorine

---

- Chlorine is the most common disinfectant
- Chlorine by-products
  - » Free chlorine
  - » Trihalomethanes (THMs)
  - » Chlorinated acetic acids
  - » Halogenated acetonitriles
  - » Chloral hydrate (trichloroacetaldehyde)
  - » Chlorophenols
  - » MX  
(3-chloro-dichloromethyl-5-hydroxy-2(5H)-furanone)

May not need to set standards for all by-products included in the Guidelines, it is better to concentrate on the major groups (e.g. THMs)



# Trihalomethanes

---

- The principal by-product of chlorination
- Formed by the aqueous chlorination of humic substances
- More likely to occur in chlorinated surface water than groundwater
- Concentrations of THMs tend to increase with increasing temperature, pH and chlorine dosage
- THMs consist primarily of:
  - » Chloroform
  - » Bromodichloromethane
  - » Dibromochloromethane
  - » Bromoform
- Formation of THMs can be minimised by avoiding prechlorination and optimising treatment



# Chloramine and its By-products

---

- Chloramines formed by reaction of chlorine and ammonia or organic amines
- Mono-, di- and trichloramines may be formed depending upon pH and temperature
- Chloramine by-products similar to free chlorine with the exception of cyanogen chloride
- Mono-chloramine is a less effective disinfectant than free chlorine and cannot be relied upon as a primary disinfectant; though useful for maintaining a residual.





## Chlorine dioxide and its By-products

---

- Chlorine dioxide made at point of use because of its explosive hazard
- Reactions with humic substances do not form significant levels of THMs or chloramines
- Main by-products are:
  - » chlorite
  - » chlorate
  - » chloride
- More effective than free chlorine in inactivation of *Giardia* cysts but less effective against *E.coli* and rotaviruses
- No GV for chlorine dioxide in water as it dissociates rapidly. GVs set for chlorite but not chlorate



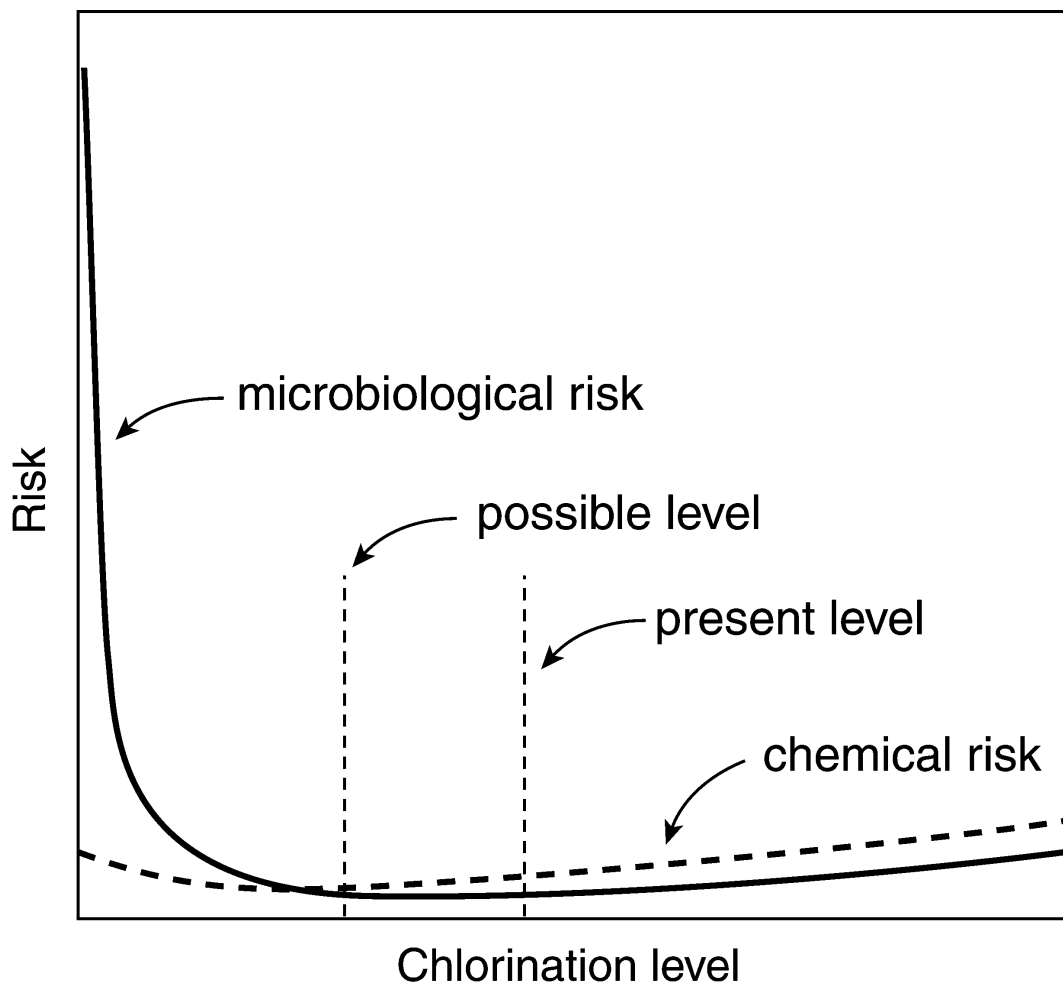
# Ozone and its By-products

---

- Most efficient disinfectant for all types of micro-organisms
- Decomposes rapidly following application thus no GV has been proposed for ozone
- By-products include:
  - » formaldehyde
  - » aldehydes
  - » hydrogen peroxide
  - » bromomethanes
- Disadvantages include:
  - » lack of residual
  - » biological regrowth in distribution systems
  - » high cost
  - » limited information on toxicity of its by-products



# Balancing chemical and microbiological risks



(Morris, 1978)

