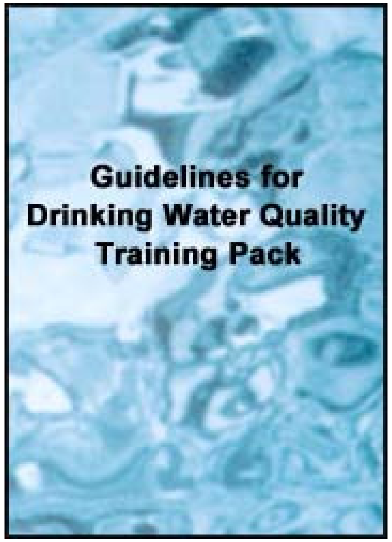

Guidelines for Drinking Water Quality - Training Pack (WHO)

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.**

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**
E. coli	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_2	0.08-0.18	-	-	-

G. lamblia cysts	47->150	-	-	0.5-0.6
G. muris cysts	30-630	-	7.2-18.5	1.8-2.0[a]
C. parvum	7200[b]	7200[c]	78[b]	5-10[c]

[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:

$$Cl_2 + H_2O = HOCl + H^+ + Cl^-$$

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:

$$HOCl = H^{+} + OCl^{-}$$

The value of the acid ionization constant is about 3×10^{-8}. As shown in Figure 1, at 20°C and pH 7.5, there is an equal distribution of HOCl and OCl^{-}. 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^{-}, 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.

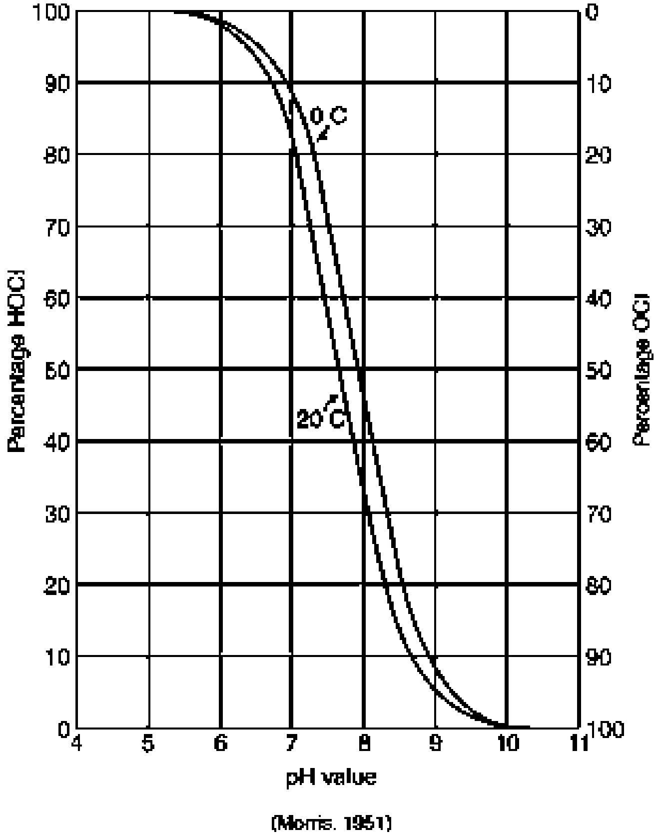

Figure 1: Distribution of hypochlorous acid and hypochlorite ion in water at different pH values and temperatures (Morris, 1951)

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:

$$HOCl + Br^- = HOBr + Cl^-$$

HOBr reacts with natural organic compounds to form brominated halomethanes.

Similarly, the presence of iodide may lead to the formation of mixed chlorobromoiodo-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:

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

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 <u>inadequate evidence</u> 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 byproducts.

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. 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.

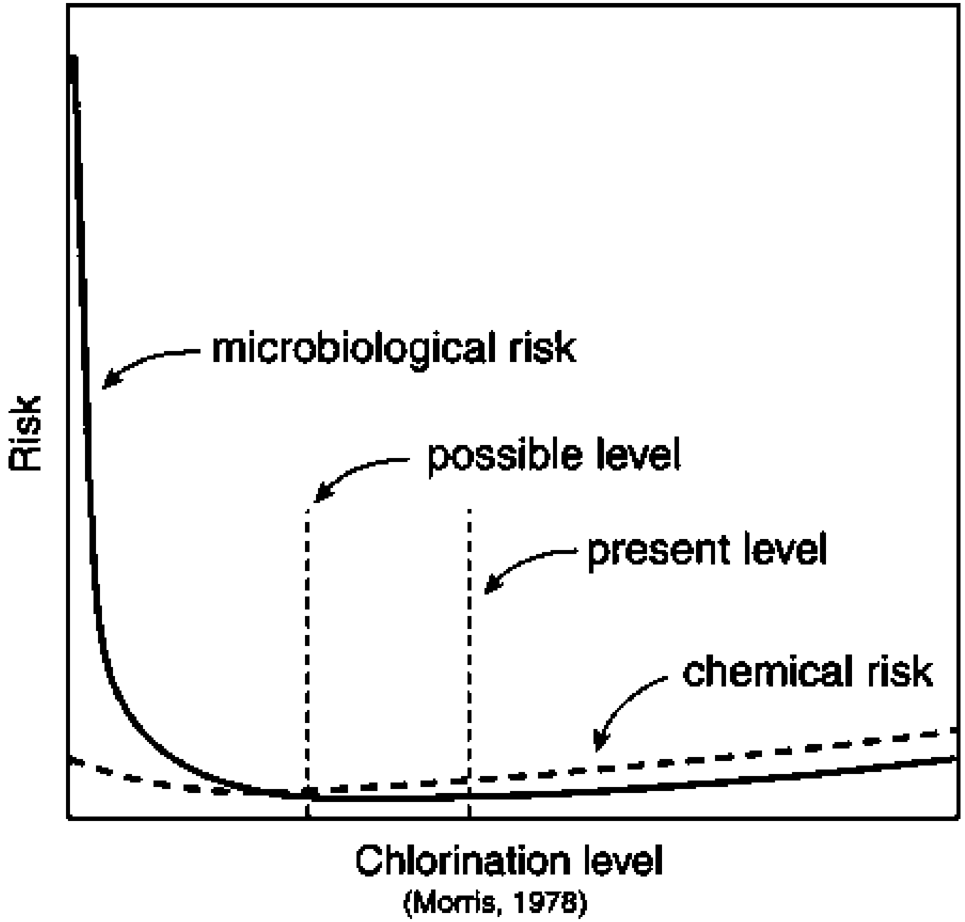

Figure 2: Risks and benefits of water chlorination (Morris, 1978)

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.

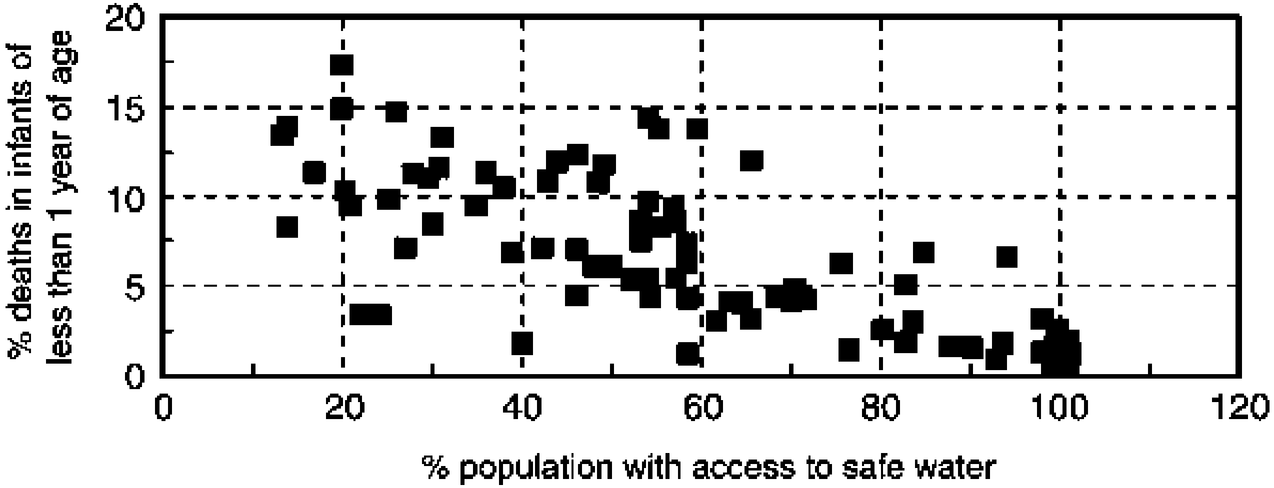

Figure 3: Infant mortality versus access to safe water (Regli et. al., 1993)

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 <u>never</u> be compromised." (1993 *Guidelines*)

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Annex 1
BACTERIOLOGICAL QUALITY OF DRINKING-WATER

Organisms	Guideline value
All water intended for drinking	
E. coli or thermotolerant coliform bacteria	Must not be detectable in any 100-ml sample
Treated water entering the distribution system	

E. coli 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
Treated water in the distribution system	
E. Coli 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.

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**
E. coli	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	0.08-0.18			

Bacteriophage f2	0.08-0.18	-	-	-
G. lamblia cysts	47->150	-	-	0.5-0.6
G. muris cysts	30-630	-	7.2-18.5	1.8-2.0[a]
C. parvum	7200[b]	7200[c]	78[b]	5-10[c]

[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.

Presentation Plan

Section	**Key points**	**OHP**
Introduction	• disinfection of all waters supplied for drinking is recommended by WHO to protect public health	**1,2 Table 1**
	• main disinfectants evaluated in the *Guidelines* are: free chlorine, chloramines, chlorine dioxide and ozone	
	• overall ozone is the most effective disinfectant, although chlorine is also effective and efficient	
	• all disinfectants have advantages and disadvantages and all produce by-products	
	• a number of disinfection by-products were evaluated in the GDWQ	

	• a number of disinfection by-products were evaluated in the GDWQ	
Chlorine and its by-products	• chlorine is most common disinfectant	**3,4,5**
	• when chlorine is added to water it forms hypochlorous acid, hydrogen ion and a chlorine ion	
	• because of greater efficiency, the *Guidelines* recommend disinfection with chlorine is done at pH less than 8 and a free chlorine concentration of greater than 0.5 mg/l	
	• the use of chlorine leads to the formation of halogenated by-products, including the THMs	
	• precursors to THMs are natural humic and fulvic acids and algal material	
	• numerous other by-products may be formed (see paper or *Guidelines* for examples)	
	• impurities in gaseous and liquid chlorine of relevance to the nature of by-products are carbon tetrachloride and bromide	
	• GVs set for a number of chlorination by-products	
	• very difficult to estimate exposure to halogenated organic compounds in drinking-water	
	• may not need to set standards for all by-products included in *Guidelines*, it is better to concentrate on the major groups(e.g. THMs)	
	• microbiological quality of water should never be compromised by	

	concerns about disinfection by-products	
Chlorine	• free chlorine in drinking-water is not particularly toxic and health-based GV is 5 mg/l	
	• very unlikely consumers would accept such levels of chlorine as taste is noted as low as 0.3 mg/l	
	• do not use GV as desirable level of chlorination	
Tri-halomethanes	• these are principal by-products of chlorination, but only form 10 per cent of total organic compounds in drinking-water	**6**
	• THMs more likely to occur in chlorinated surface water than groundwater	
	• THM concentrations vary widely; increasing with increasing temperature, pH, chlorine dosage and on storage after exhaustion of free chlorine or dechlorination	
	• chloroform is most common THM (usually >90% of total THMs)	
	• when bromine present, brominated THMs likely to be dominant	
	• THM formation can be minimised by avoiding prechlorination and by optimising treatment	
	• THM removal is expensive and difficult	
Chloramine and by-products	• chloramines formed by reaction of chlorine and ammonia or organic amines	**7**
	• can get mono-, di- and trichloramines depending on pH and temperature	
	• chloramine by-products similar to free chlorine, with exception of	

	• chloramine by-products similar to free chlorine, with exception of cyanogen chloride	
	• monochloramine about 2000 to 100, 000 times less effective than free chlorine for inactivation of *E.coli* and rotaviruses	
Chlorine dioxide and by-products	• chlorine dioxide made at point of use because of its explosive hazard	**8**
	• chlorine dioxide does not form THMs or chloramines	
	• main by-products are chlorite, chlorate and chloride	
	• chlorine dioxide 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 rapidly disassociates	
	• GVs set for chlorite but not for chlorate	
Ozone and by-products	• ozone decomposes rapidly following application and thus no GV has been proposed	**9**
	• by-products include formaldehyde, other aldehydes, hydrogen peroxide and bromomethanes (see paper/*Guidelines* for further examples)	
	• ozone is the most efficient disinfectant with regard to microorganisms	
	• disadvantages include: lack of residual, biological regrowth problems in distribution systems, high cost and limited information on nature and toxicity of by-products	
	• when ozonation followed by chlorination, concentrations of brominated THMs may increase	

Balancing chemical and microbial risks	• currently a scarcity of quantitative assessment done of relative risks of microbial and chemical contamination of drinking-water	**10**
	• 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	
	• at very high chlorine concentrations, microbial risk increases as taste and odour cause the use of unsafe supplies	
	• chemical risks do not start at zero as always some hazard from organic matter prior to chlorination	
	• chemical risks are low initially but increase with increasing chlorine dosages	
	• 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	
	• 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	
Conclusions	• disinfection is important to assure a safe drinking-water supply	
	• limited information is available concerning health risk from disinfection by-products	
	• disinfection by-product formation may be reduced if treatment	

	process are optimised and prechlorination is avoided	
	• inadequate evidence exists concerning the carcinogenicity of chlorinated drinking-water	
	• more information is available concerning chlorine because it has been studied in more detail and this should not penalise the use of chlorine	
	• as microbiological quality is of paramount importance, disinfection should not be compromised	

Disinfectants Evaluated

- **Chlorine**
- **Chloramine**
- **Chlorine dioxide**
- **Ozone**
- **Iodine**

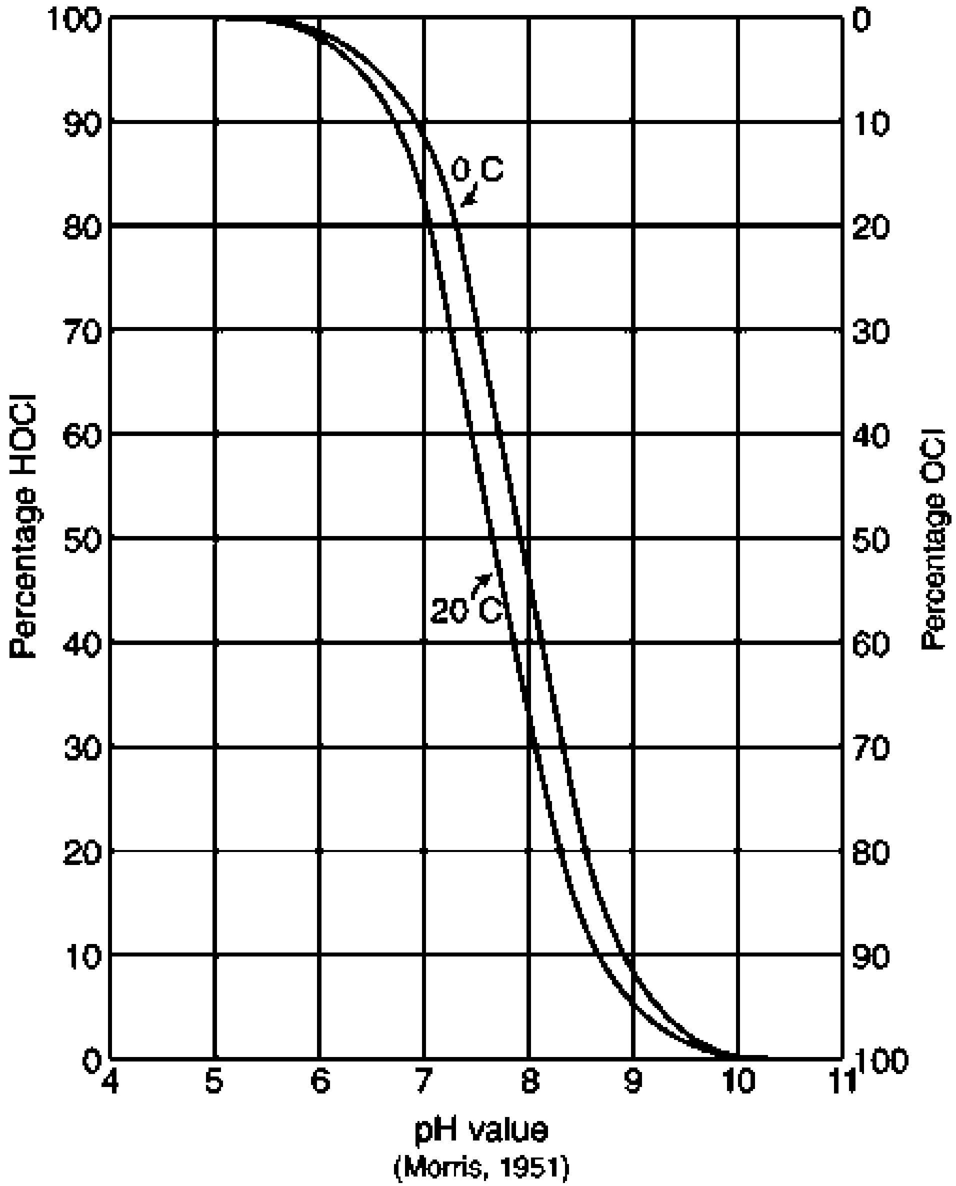
Disinfectants and Disinfectant by-products

- **Overall ozone is the most effective disinfectant, although chlorine is effective and efficient**

- **All disinfectants have advantages and disadvantages and all produce by-products**

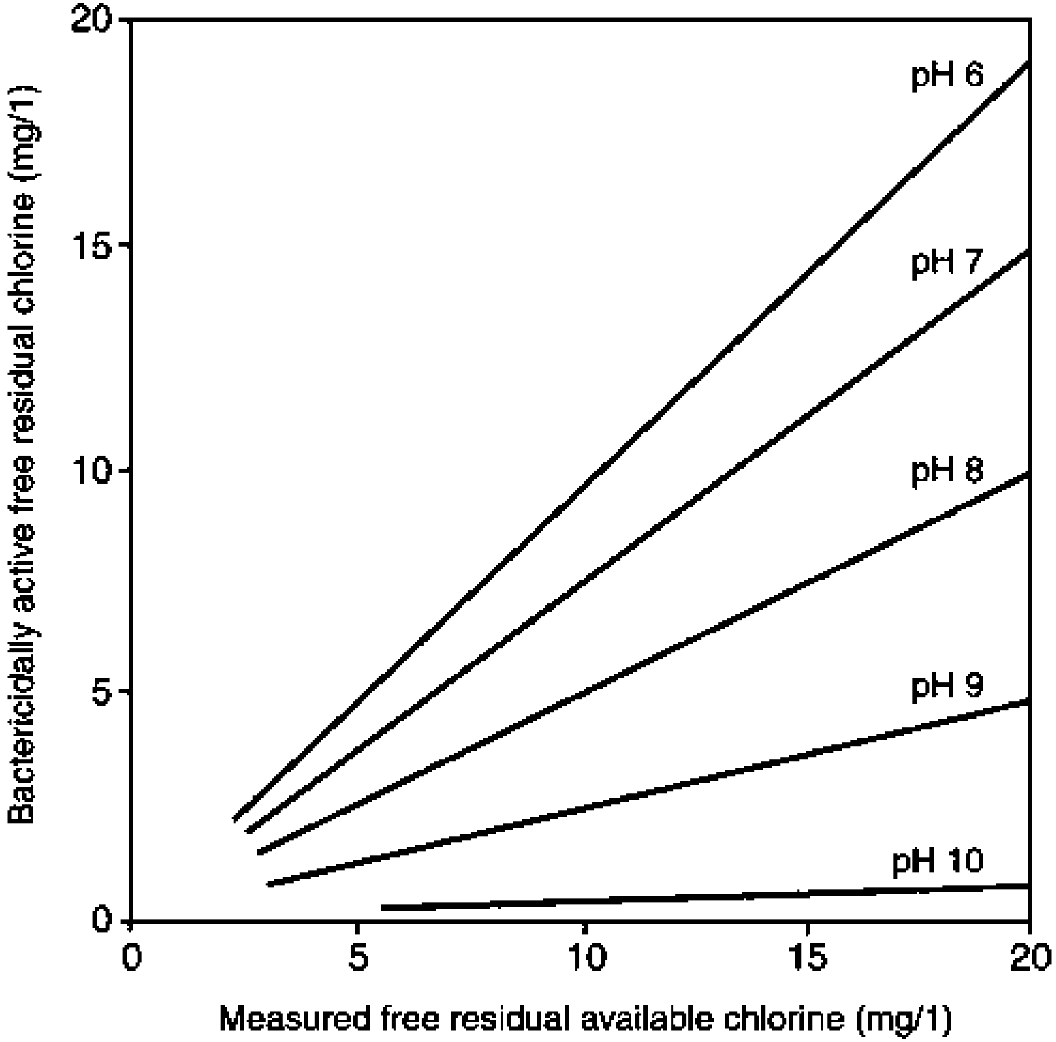
- **A number of disinfectant by-products were evaluated in the Guidelines**

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



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

Chlorine

- **Chlorine is the most common disinfectant**

- **Chlorine by-products**

  - **» Free chlorine**
  - **» Trihalomethanes (THMs)**
  - **» Chlorinated acetics acids**
  - **» Halogenated acetonitriles**
  - **» Chloral hydrate (trichloroacetaldehyde)**
  - **» Chlorophenols**
  - **» MX**

(3-chloro-dichlormethyl-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 increaseing temperature, pH and chlroine dosage**

- **THMs consist primarily of:**

  » **Chlroform**
  » **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-organisims**

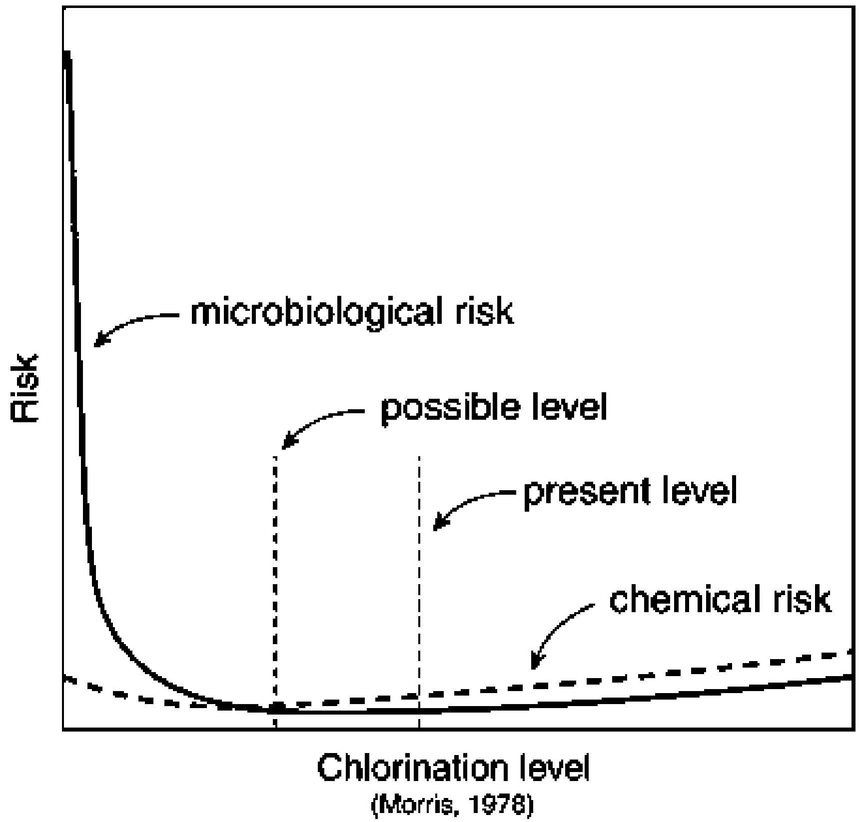
- **Decomposes rapidly following application thus no GV has been proposed for ozone**

- **By-products include:**

  - **» formaldehyde**
  - **» aldehydes**
  - **» hydrogen peroxide**
  - **» bromomethanes**

- **Disdavantges include:**

  » **lack of residual**
  » **biological regrowth in distribution systems**
  » **high cost**
  » **limited information on toxicity of its by-products**



Balancing chemical and microbiological risks

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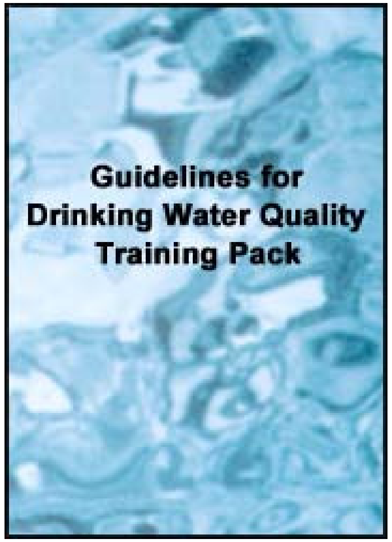


Guidelines for Drinking Water Quality - Training Pack (WHO)

Inorganic Constituents and Aesthetic Parameters

Session Objectives

- **To describe the process of setting Guideline Values for inorganic parameters and describe the narrow divide between toxic and essential elements.**

- **To describe some basic physico-chemical characteristics of water.**

- **To provide some examples of inorganic chemicals to illustrate the uses of GVs for inorganics and highlight priority substances.**

- **To describe the basis of monitoring of physical and chemical parameters.**

All substances are poisons; there is none which is not a poison. The right dose differentiates a poison and a remedy.

PARACELSUS (1493-1541)

Introduction

Many of the inorganic and aesthetic constituents evaluated in the *Guidelines* are known to be essential for life. Chromium, copper, fluoride, iodine, manganese, molybdenum, and selenium are essential elements in human nutrition; arsenic and nickel are considered by some researchers as essential elements. Of the aesthetic constituents, iron, chloride, calcium and magnesium (hardness), sodium and zinc are essential elements.

A classification into "essential" and "toxic" elements is fraught with difficulties since as science advances, there is a constant shift of the elements from one group to the other. Toxicity is inherent in all elements, and is a function of the concentration to which humans are exposed. Paracelsus' statement remains valid, "The right dose differentiates a poison and a remedy". Ordinary salt, calcium, magnesium and iron, are all toxic above certain doses. This is illustrated in Figure 1 below.

The plateau of "safe and adequate intake of essential elements" are mainly a matter for nutritionists to decide.

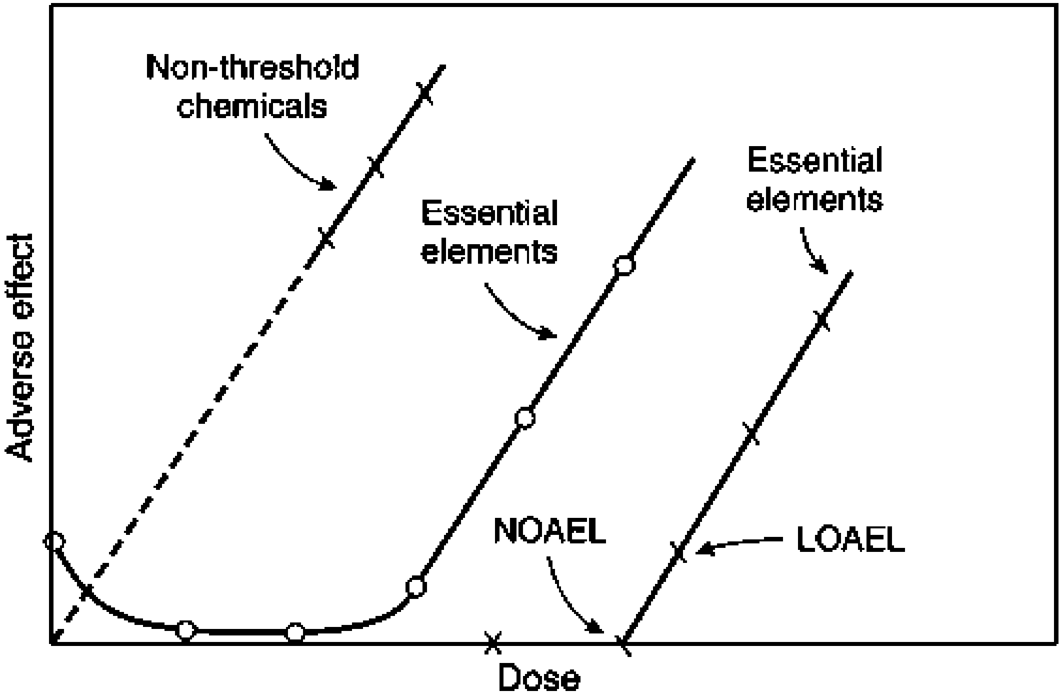


Figure 1. Dose-response curve (Source: Galal-Gorchev, 1995)

> ***Notes:*** **NOAEL: no observed adverse effect limit; LOAEL: lowest observed adverse effect limit; Threshold chemicals: only toxic above certain dose, therefore have a NOAEL; Non-threshold chemical: toxic at any dose, therefore do not have a NOAEL**

No attempt has been made in the *Guidelines* to define a minimum desirable concentration of essential elements in drinking-water. The *Guidelines* are concerned with the quantification of toxic effects.

A few of the inorganic chemicals and aesthetic constituents of common interest to many countries will be discussed here to illustrate the approach taken in deriving, or not deriving, guideline values (GV). A complete list of inorganic substances for

which GVs have been derived is given in Table A2.2 (A) in Annex 2 of Volume 1 of the Guidelines.

Inorganic Constituents

Asbestos in drinking-water: no health hazard

Because of numerous inquiries from governments, industry and academia on the potential adverse health effects from asbestos in drinking-water, WHO issued the attached Press Release.

Asbestos is used in a large number of applications, particularly construction materials, such as asbestos cement (A/C) sheet and pipe, electrical and thermal insulation, and friction products, such as brake linings.

Asbestos is introduced into water by the natural dissolution of asbestos-containing minerals as well as from industrial effluents, atmospheric pollution, and A/C pipes in water distribution systems. High levels of asbestos have been found in drinking-water from corrosion of A/C pipes.

The asbestos content of food has not been well studied because of the lack of a simple, reliable analytical method. Based on crude estimates, intake of asbestos in food may be significant compared with that in drinking-water. Concentrations of 7 million fibres per litre (MFL) in beer and 12 MFL in soft drinks have been reported.

Asbestos is a known human carcinogen by the inhalation route. Based on the inhalation route, IARC has assigned it to Group 1 (the agent is carcinogenic to humans), while recognising that asbestos behaved differently by the oral route.

Asbestos was not found to be carcinogenic in several animal feeding studies. Epidemiological studies of population exposed to high levels of asbestos in drinking-water (200 MFL) did not reveal any excess cancer risk. It was therefore concluded that ingested asbestos is not hazardous to health and there was no need to establish a GV for asbestos in drinking-water.

Another question that needs to be answered is: Can high concentration of asbestos fibres in drinking-water become airborne and create a health hazard?

In a study in New York State, asbestos contamination in excess of 10 billion fibres per litre was detected in a community's drinking-water. Mean airborne asbestos concentrations were significantly higher in a small number of homes with water containing this elevated concentration of asbestos than in three control homes; however, the difference in concentrations was primarily due to increased numbers of short (<1 µm) fibres, which are considered to contribute little to health risk. Moreover, all fibre concentrations determined in this limited study were within the range of those measured in indoor and outdoor air in other investigations.

In another study, using a conventional drum-type humidifier, testing showed that release of asbestos fibres to air from water containing 40 ± 10 MFL was negligible.

The final question - does corrosive water transported in A/C pipe pose any specific or unique health risk? Corrosive water does not create a specific health risk as it relates to A/C pipe since asbestos fibres in drinking-water do not pose a health risk and are not transferred into the air. However, corrosive water is an important problem that must be addressed by all water utilities no matter what type of water pipe material is used in the distribution system or homes. Proper

selection of the quality of A/C pipes is important and some national institutions have issued standards for A/C pipes suitable for water with different degrees of aggressiveness.

Fluoride and dental health

Fluoride levels between 0.5 and 1 mg/litre provide substantial protection against dental caries. However, for fluoride, the margin between beneficial and toxic effects is rather small (see Figure 1). Excessive exposure may lead to adverse health effects varying from mottling of teeth to crippling skeletal fluorosis.

The *Guidelines* recommend a GV of 1.5 mg/litre on the assumption that the daily per capita consumption of drinking-water is about 2 litres. At this level, dental fluorosis may occur in a certain proportion of the population. In setting national standards for fluoride, it is particularly important to consider climatic conditions, volumes of water intake, and intake of fluoride from other sources (e.g. food, air).

Nitrate and nitrite

Nitrate and nitrite in drinking-water may be of natural origin, or can be leached from septic tanks, pig farms and feed lots. Use of fertilizers (too much and at the wrong time of the year) can also result in nitrate pollution.

High concentration of nitrate, and especially nitrite in drinking-water may cause methaemoglobinaemia. Groups especially susceptible to methaemoglobin formation are young infants, children and pregnant women.

Epidemiological studies indicate that at levels of nitrates less than 50 mg/litre (as

nitrate), there does not seem to be any problem with methaemoglobinaemia. There are considerable uncertainties as to the level of nitrite which may cause such clinical effects. On the assumption that nitrite was ten times more potent than nitrate (on a molar basis) with respect to methaemoglobin formation, the *Guidelines* recommend a provisional GV of 3 mg/litre (as nitrite). In addition, since nitrite and nitrate exert similar toxicological effect and may occur simultaneously, the following condition was also specified:

$$\frac{C_{nitrite}}{GV_{nitrite}} + \frac{C_{nitrate}}{GV_{nitrate}} \leq 1$$

where

C = concentration in drinking-water
GV = guideline value

Lead and IQ

In 1986 the Joint FAO/WHO Expert Committee on food Additives (JEFCA) established a provisional tolerable weekly intake (PTWI) of lead from all sources of 25 µg lead/kg body weight (equivalent to 3.5 µg/kg body weight per day) for infants and children on the basis that lead is a cumulative poison and that there should be no accumulation of body burden of lead. In 1993, the Committee reconfirmed this PTWI and extended it to all age groups.

Assuming a 50% allocation of the PTWI to drinking-water for a 5-kg bottle-fed infant consuming 0.75 litres of drinking-water per day, the health-based guideline value is 0.01 mg/litre (rounded figure).

The most significant health effect from lead is the association of lead exposure with reduced cognitive development and intellectual performance in children. Results of studies on children with blood lead concentrations below 25 μg/dl indicate that, on average, the intelligence quotient (IQ) is reduced by 1-3 points for each 10 μg/dl increment in the blood lead concentration. Existing epidemiological studies do not provide evidence of a threshold.

Steps are now being taken to reduce all sources of lead exposure of children with some apparent success in various countries. In countries where lead has been removed from petrol, and where there is no specific source of excess lead exposure, blood lead concentrations in children are decreasing and are now approximately 4-6 μg/dl. The almost complete elimination of lead-soldered side-seams in canned foods in a number of countries has also contributed to the reduction in lead exposure. Corrosion control measures are being implemented to reduce the lead content of drinking-water and new plumbing and fittings now seldom contain lead.

Aesthetic Aspects

Contrary to the 1984 *Guidelines*, the 1993 *Guidelines* do not propose guideline values for substances and parameters that affect the acceptability of drinking-water to consumers. The Review Groups were of the opinion that guideline values should be recommended only for those substances that are directly relevant to health. A list of substances which may give rise to consumer complaints is given in Table A2.5 in Volume 1 of the *Guidelines.*

In the case of characteristics based on human sensory evaluation, judgement is

often subjective. Aesthetic/organoleptic characteristics are very much subject to social, economic and cultural considerations, and the establishment of standards for the aesthetic quality of drinking-water should take into consideration implementation possibilities, and the existing socio-economic and environmental constraints. When resources are severely limited, establishment of priorities becomes even more important, and such priorities should be set in relation to their direct impact on health. Some countries have elected to set enforceable standards for constituents of health significance, whereas recommendations only are made for aesthetic and organoleptic characteristics.

Total dissolved solids

Total dissolved solids (TDS) in drinking-water consist mainly of chloride, sulphate, carbonates, sodium, magnesium and calcium. Excessive dissolved solids in drinking-water may lead to objectionable taste, and corrosion or encrustation in water distribution system. At concentrations greater than approximately 1000 mg/litre, the taste of water becomes increasingly unpalatable.

As far as health aspects are concerned, there is no evidence of adverse physiological reactions at TDS levels greater than 1000 mg/litre. On the contrary, there are vague indications from epidemiological studies that high levels of certain salts (calcium and magnesium) may have beneficial health effects.

It should be emphasized that the factor of acclimatization to TDS is particularly important. Many people enjoy highly mineralized waters containing more than 2000 mg/l of TDS.

Removal of TDS from drinking-water is an expensive proposition, and if a national standard for TDS is being considered, it should take into account the feasibility of implementation.

Turbidity

Particles in drinking-water are aesthetically objectionable, and can serve as shields for pathogenic microorganisms. Moreover, many toxic chemicals such as pesticides and heavy metals are selectively adsorbed on suspended particulate matter. The efficiency of disinfection may be reduced in the presence of turbidity: the disinfectant is unable to reach the target organism because of a physical barrier and/or chemical reactions with turbidity particles may occur thus decreasing the available disinfectant concentration. Where disinfection is practised, the turbidity should preferably be less than 1 Nephelometric Turbidity Unit and always below 5.

The effect of turbidity depends on its physico-chemical characteristics. Certain water supplies, such as groundwater, may contain non-organic turbidity, which may not affect disinfection. The complex factors involved in the potential health risk from the presence of turbidity precluded the derivation of a health-based GV.

References

WHO (1994) Fluorides and oral health. WHO Technical Report Series 846. Geneva.

WHO (1993) Evaluation of certain food additives and contaminants (lead). WHO Technical Report Series 837. Geneva.

Presentation Plan

Section	Key points	OHP
Introduction	• many of both the inorganic substances and aesthetic parameters evaluated in the *Guidelines* are known to be essential for life	**1,2**
	• classification of substances into 'toxic' and 'essential' is fraught with difficulties. With ongoing research there is a constant shift of substances between the two groups	
	• toxicity is inherent in all substances, the dose or concentration of a substance differentiates between a poison and a remedy	
	• safe and adequate intake and concentrations for essential substances is a matter for nutritionists	
	• *Guidelines* do not define a minimum desirable concentration of essential elements, they only define toxic levels	
Physico-chemical characteristics of water	• water has set of physico-chemical characteristics which affect quality in their own right and influences the ability of water to contain other substances	**3,4**
	• physical characteristics include: temperature, colour, turbidity, suspended solids and dissolved solids	
	• chemical characteristics include: pH, alkalinity, acidity, hardness, dissolved oxygen and oxygen demand	
Asbestos	• asbestos is widely used and may be a reinforcement in concrete	
	• asbestos in water has been shown to have no adverse health	

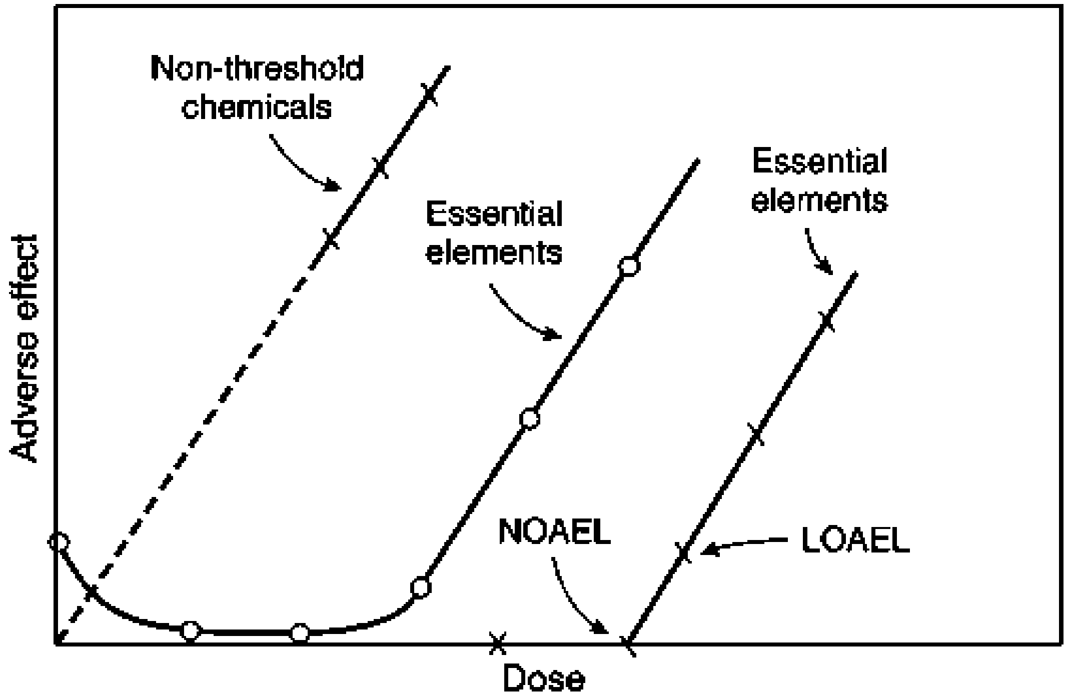
	• asbestos in water has been shown to have no adverse health effect	
	• asbestos pipes should be protected from 'aggressive' water	
Fluoride	• margin between toxic and essential levels is very narrow	**5**
	• fluoride levels between 0.5mg/l & 1mg/l protect against dental caries	
	• exposure to excess levels of fluoride may give rise to adverse health effects from mottling of teeth to crippling skeletal fluorosis	
	• GV set at 1.5 mg/l on basis of consumption of 2 litres per day, above this dental fluorosis expected in some of population	
Nitrate & nitrite	• may be of natural origin or leached from on-site sanitation, intensive animal husbandry, also from inappropriately applied fertiliser	**6**
	• high nitrate and nitrite concentrations may lead to methaemoglobinaemia in infants and pregnant women	
	• GV of 50mg/l nitrate set, as below this epidemiological studies indicate that there is no significant risk of methaemoglobinaemia	
	• uncertainty concerning concentration of nitrite that leads to clinical effects, assumed 10 times more potent than nitrate, GV of 3 mg/l given	
	• as both may occur together, important that the sum of the ratio of concentration of nitrite to the GV and concentration of nitrate to the GV is ≤ 1	
Lead	• exposure to excess lead may lead to intellectual impairment in	**7**

	children	
	• no threshold for health effects have been identified	
	• all exposure to lead is now being reduced and in the water supply this means removal of lead pipes and lead-containing fittings.	
Aesthetic aspects	• no GVs set for these in the 2nd edition as these are highly societal influenced	
	• turbidity should be kept to below 1TU as above this level disinfection may be compromised, although in some groundwaters have non-organic turbidity which does not affect disinfection	

Introduction

"All substances are poisons; there is none which is not a poison. The right dose differentiates a poison and a remedy".

Paracelsus (1493-1541)



Dose-response of Chemicals

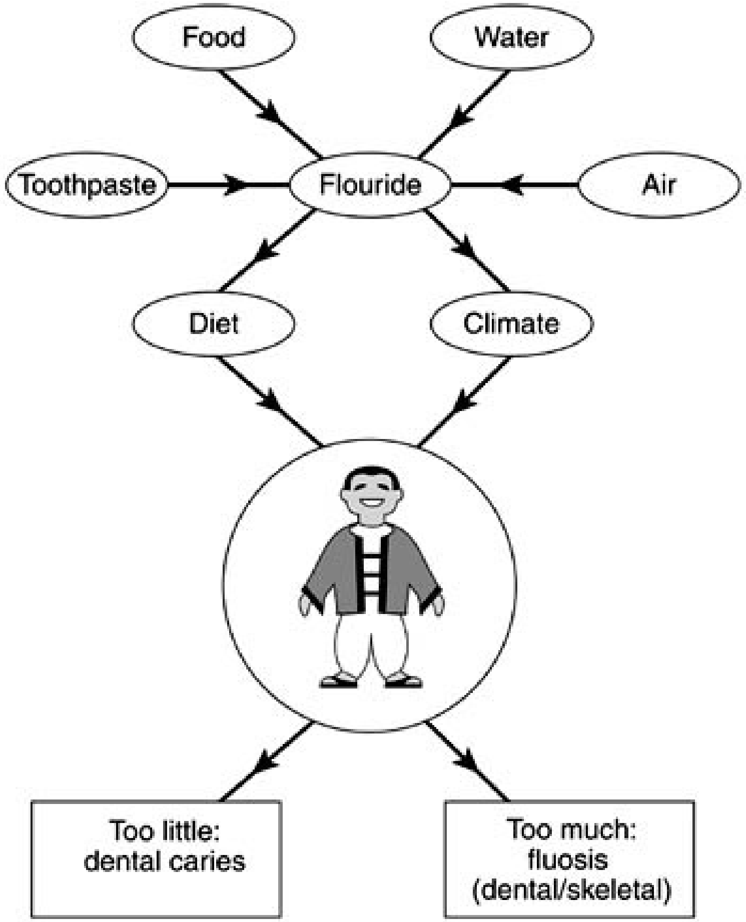
Source: Galal-Gorchev, 1995

Physical Characteristics of Water

- **Temperature**
- **Taste and odour**
- **Colour**
- **Turbidity**
- **Suspended solids**
- **Conductivity**
- **Total dissolved solids**

Chemical Characteristics of Water

- **pH**
- **Alkalinity**
- **Acidity**
- **Hardness**
- **Dissolved oxygen**
- **Oxygen demand**
- **Nitrogen**
- **Chloride**



Sources of Fluoride and Impact on Health

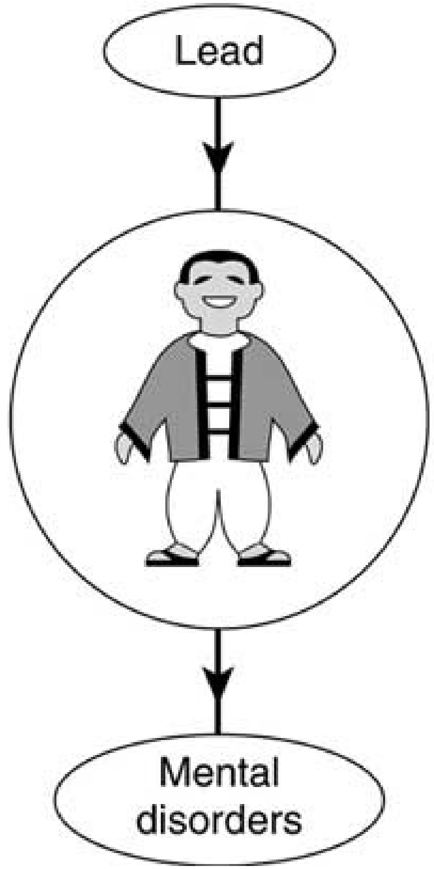
Guideline Value for Nitrate and Nitrite in Drinking-water

$$\frac{C_{nitrite}}{GV_{nitrite}} + \frac{C_{nitrate}}{GV_{nitrate}} \leq 1$$

where:

C = concentration

GV = Guideline Value



Lead and Health

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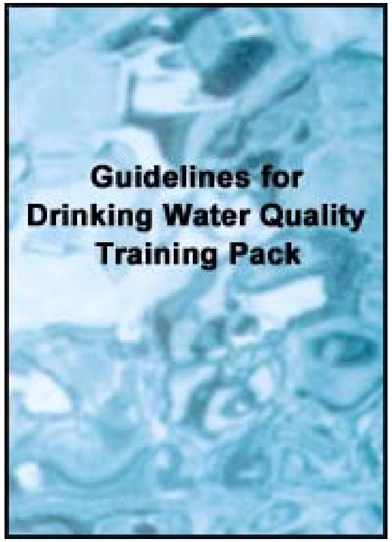
Guidelines for Drinking Water Quality - Training Pack (WHO)

(introduction...)


Guidelines for
Drinking Water Quality
Training Pack

Planning (Practical Exercise)

Organic Chemicals

Session Objectives

- **To demonstrate the range of organic chemicals that may be found in drinking-water and describe the sources of such chemicals.**

- **To describe the health risks associated with the consumption of drinking-water containing organic contaminants.**

- **To highlight the taste and odour problems associated with organic contamination.**

Introduction

Specific chlorinated alkanes, chlorinated ethylenes, aromatic hydrocarbons, chlorinated benzenes, and miscellaneous organic chemicals were evaluated in the 1993 WHO *Guidelines for Drinking-Water Quality*.

Many of these organic chemicals are widely used as solvents, in chemical synthesis, in petroleum products, and in the production of plastics and resins. Some 30 organic chemicals were evaluated and guideline values (GV), or provisional guideline values, recommended for 27 of these.

Some organic substances do not have a 'no observed adverse effect limit' (NOAEL) - the highest concentration of a substance which causes no detectable adverse

health effect. Therefore for some substances, a provisional guideline has been set on the basis of the 'lowest adverse effect limit' (LOAEL) - the lowest concentration or dose of a substance where there is a detectable adverse effect. Where a LOAEL is used, an additional uncertainty factor (UF) - a measure of the uncertainty regarding the information about a substance - is used. For further information, please refer to the background paper for Session II of this teaching pack or to the *Guidelines Volume 1 and 2*.

Adequate toxicological data were not available to derive guideline values for a number of chemicals, including 1,1-dichloroethane, 1,3-dichlorobenzene, dialkyltins, and a number of polynuclear aromatic hydrocarbons, with the exception of benzo[a]pyrene.

For most of the aromatic hydrocarbons and chlorinated benzenes, the taste and/or odour thresholds of these chemicals are well below the health-based guideline values, thus constituting an assurance that the GVs would not be exceeded or even approached. Consumers complaints would constitute a safety net against such a situation.

A number of organic chemicals were considered to be genotoxic and carcinogenic and the linearized multistage extrapolation model was used to derive guideline values corresponding to an upper bound estimate of an excess cancer risk of 10^{-5}.

For most organic chemicals that show a threshold for toxic effects, little was known of the magnitude of exposure from drinking-water relative to other sources. Consequently, the default value of 10% of the TDI was allocated to drinking-water.

Nitrilotriacetic acid (NTA) is a compound used in detergents, and tributyltin oxide (TBTA) is used in boat paints. Substantial exposure may occur from drinking-water, and consequently 50% and 20% of the TDI was allocated to drinking-water for NTA and TBTA respectively.

Di(2-ethylhexyl)adipate and di(2-ethylhexyl)phtalate are used in food-contact materials and therefore exposure from food is expected to be high. Therefore, only 1% of their respective TDI was allocated to drinking-water.

Because of their general persistence in the environment and concern over their potential toxicity, a large number of the organic chemicals evaluated are chlorine-containing chemicals.

For further information please see the *Guidelines for Drinking Water Quality* Volumes 1 and 2.

Presentation Plan

Section	Key points	OHP
Introduction	• there are many organic chemicals that may be found in drinking water	**1,2,3**
	• these are very diverse in nature	
	• many organic chemicals found in water are derived from industry	
The *Guidelines*	• the *Guidelines* review some specific organic chemicals	**4**
	• a total of 30 organic substances reviewed and Guideline derived	

	for 27 of these (inadequate data on the others)	
Exposure from drinking-water	• for most organics, there is little information available on exposure from drinking-water relative to other sources, therefore have high uncertainty factors	
	• often use a LOAEL rather than a NOAEL as many non-threshold organic subsatnces	
Genotoxic & carcinogenic organics	• some organics are considered genotoxic and carcinogenic	
	• linerized multistage extrapolation model used to derive GVs corresponding to 10^{-5} excess risk	
	• most aromatic hydrocarbons and chlorinated benzenes have taste and odour thresholds well below health-based Guideline Values, a margin of safety therefore exists	

Example of Organic Pollutants by Class and Typical Use 1

- **Halogenated aliphatic (chain) hydrocarbons**

  » Trihalomethanes (THMs) may be formed during disinfection of drinking-water; other compounds used as solvents for decaffeinating coffee, general solvents and in products such as propellant, degreasers, spot removers and dyes

- **Aromatic (ring) hydrocarbons**

» Many products derived from fossil fuels, also as additives in petrol, moth balls, adhesives and cigarette smoke

- Chloro-and nitro-aromatic hydrocarbons

  » Fungicides and explosives

- Phthalates

  » Phthalates are added to plastic to make them flexible; found in rain wear, footwear, shower curtains, childrens toys

Example of Organic Pollutants by Class and Typical Use 2

- Halogenated ethers

  » Halogenated ethers are used in production of plastics and resins and in research laboratories

- Phenols

  » Fungicide; wood preservative; Chloro-dichloro-, trichloro-phenols are by-products in the production of pentachlorophenol

- Organochlorines

  » DDT, lindane, aldrin and chlorodane are examples of the extremely persistent organochlorine pesticides widely used in the 1950s and 1960s.

The Breakdown of Organic Compounds

- **Enter water from a variety of sources including:**

  » Human/animal wastes
  » Plants
  » Soil erosion
  » Industrial wastes

- **Generally unstable, may be oxidised to stable and relatively inert end products e.g. CO_2, NO_3, H_2O**

- **Oxidation: loss of electrons to an oxidising agent such as oxygen or chlorine which accepts electrons**

- **Oxidation of organic compounds occurs in aerobic or anaerobic conditions**

- **Quantity of organic material and the quantity of oxygen needed to oxidise it estimated by using:» Biochemical oxygen demand (BOD)**

  » Permanganate value (PV)
  » Chemical oxygen demand (COD)

Organics reviewed in the *Guidelines*

- **A total of 30 organic substances reviewed in the following groups:**

  » Chlorinated alkanes (5 substances)

- » **Chlorinated ethenes (5 substances)**
- » **Aromatic hydrocarbons (6 substances)**
- » **Chlorinated benzenes (5 substances)**
- » **Miscellaneous organic constituents (9 substances)**

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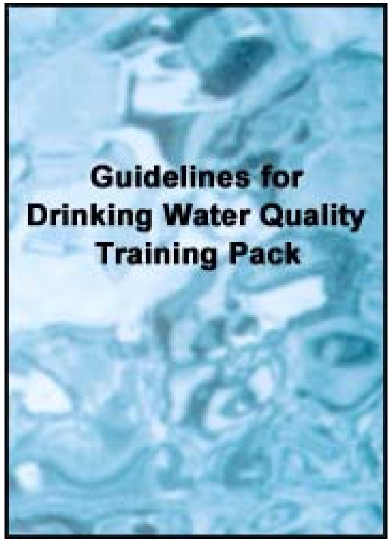

Guidelines for Drinking Water Quality - Training Pack (WHO)

Pesticides in Drinking-Water

Session Objectives

- To demonstrate the conflict in pesticide use between agricultural and public health needs.
- To describe the two principal methods of pesticide classification.
- To describe the GVs set for pesticides and their by-products.

Pesticides are used for agricultural as well as public health purposes. Often a choice has to be made between their detrimental effects on the environment and

their use for disease vector control, as for example, for malaria or schistosomiasis control. The adverse environmental effects of pesticides used in public health can often be mitigated through proper selection and application procedures. Equally, many pesticides have both beneficial and harmful health effects - their use may reduce the presence of particular vectors, although they may be toxic is consumed through water. In these circumstances, the relative benefits and dis-benefits should be evaluated.

With all pesticides, whether they have harmful health effects or not, the application should be well focused both in terms of application technique, quantity used and timing of application. As a general rule, the minimum of pesticide should be applied by the most efficient method at the most suitable time to achive the required goal. Over-application and/or application at times when the action is less likely to be effective should be avoided.

Pesticides can be classified according to chemical class (e.g. organochlorine, carbamate, organophosphorus, chlorophenoxy compounds) or according to their intended use (e.g. fungicide, herbicide, fumigant). It is important to know both since the chemical structure of the pesticide and its use often determine its behaviour in the environment, occurrence in drinking-water and toxicity to humans. Table 1 indicates the chemical class and use of the pesticides evaluated in the *Guidelines.*

Of the 36 pesticides evaluated, 28 contain chlorine. Organophosphorus pesticides were not evaluated although their use has increased as replacement for organochlorine pesticides. However, the organophosphorus pesticides are readily hydrolysed in water, adsorbed on sediments, or readily degraded in soil. As a

result, they are seldom if ever found in drinking-water.

Many of the pesticides evaluated are herbicides. Because of their frequent use near waterbodies they have often been found in surface water. Furthermore many of these herbicides are fairly mobile in soil and readily migrate into groundwater.

While the use of organochlorine pesticides has declined in industrialized countries, their use continues in developing countries for public health as well as for agricultural purposes. For this reason, several organochlorine pesticides were evaluated in the *Guidelines*.

The toxicological basis of the guideline values and exposure assumptions made, as reflected in the percentage allocation of the TDI to drinking-water, are summarized in Tables 2 and 3.

For organochlorine pesticides such as aldrin/dieldrin, chlordane, DDT, heptachlor, and hexachlorobenzene only 1% of the TDI was allocated to drinking-water since it is known that these pesticides are highly persistent, have a high bioaccumulation potential, and are often found in food (Table 2).

In the majority of cases limited information was available on the contribution of drinking-water to the total exposure. Therefore a default value of 10% of the TDI was used (Table 3).

While considerable information is available on the toxicity of metabolites of pesticides formed in mammalian systems, the nature and toxicity of the environmental degradation products of pesticides are largely unknown and have not been taken into consideration in the *Guidelines*.

Alachlor, 1,2-dibromo-3-chloropropane, 1,3-dichloropropene and hexachlorobenzene were considered to be carcinogenic. The linearized multistage extrapolation model was therefore used to derive guideline values corresponding to an upper-bound estimate of an excess lifetime cancer risk of 1 per 100,000 of the population exposed.

Because limited information was available on the toxicity of 1,3-dichloropropane, ethylene dibromide and MCPB, no guideline values were derived for these pesticides.

Not all pesticides that have been found in water have been evaluated in the *Guidelines*. However, over 240 pesticides have been evaluated by the Joint FAO/WHO Meeting on Pesticide Residues (JMPR). Such evaluations could be used by countries wishing to establish standards or guidelines for pesticides of national concern.

In many circumatances, it may not be the principla component of the pesticide which is of concern, but impurities and by-products. It may be more effective to control the release of toxic substances into the aqautic environment through proper product quality control that by establishing standards for drinking-water. It may be more appropriate therefore, to ensure that product quality standards and their enforcement are in place than drinking-water quality standards.

References

International Programme on Chemical Safety (IPCS). Summary of Toxicological Evaluations Performed by the Joint FAO/WHO Meeting on Pesticide Residues,

1996.

Table 1: Chemical family and use of pesticides evaluated in the Guidelines

PESTICIDE	CHEMICAL FAMILY	USE
alachlor	CA	HB
aldicarb	CB	AC IN NE
aldrin/dieldrin	OC	IN TE
atrazine	TR	HB
bentazone	BT	HB
carbofuran	CB	AC IN NE
chlordane	OC	IN TE
chlorotoluron	UR	HB
DDT	OC	IN
1,2-dibromo-3-chloropropane	HH	FM NE
2,4-D	PO	HB
2,4-DB	PO	HB
1,2-dichloropropane	HH	FM
1,3-dichloropropane	HH	--
1,3-dichloropropene	HH	FM FU IN NE
dichlorprop	PO	HB IG
ethylene dibromide	BR	IN FU
fenoprop	PO	HB

fenoprop	PO	HB
heptachlor and heptachlor epoxide	OC	IN TE
hexachlorobenzene	OC	FU
isoproturon	UR	HB
lindane	OC	IN
MCPA	PO	HB
MCPB	PO	HB
mecoprop	PO	HB
methoxychlor	OC	IN
metolachlor	AM	HB
molinate	TC	HB
pendimethaline	DA	HB
pentachlorophenol	OC	FU HB IN
permethrin	PY	IN
propanil	AN	HB
pyridate	PA	HB
simazine	TR	HB
2,4,5-T	PO	HB
trifluralin	DA	HB

Key for Table 1:

Codes for chemical use

AM acetamide
AN anilide
BR bromide
BT benzothiadiazole
CA chloroacetanilide
CB carbamate
DA dinitroaniline
HH halogenated hydrocarbon
OC organochlorine
PA pyridazine
PO phenoxy
PY pyrethroid
TC thiocarbamate
TR triazine
UR urea

Codes for use

AC acaricide
FM fumigant
FU fungicide
HB herbicide
IG growth regulator
IN insecticide

NE nematicide

TE termiticide

Table 2: Risk assessment of pesticides where substantial exposure from food is expected

PESTICIDE	NOAEL mg/kg bw/d	UF	% TDI	GV, µg/l (IARC Group)
aldrin/dieldrin	0.025	250	1	0.03 (3)
bentazone	10	100	1	30
chlordane	0.05	100	1	0.2 (2B)
DDT	0.25	10	1	2 (2B)
heptachlor + epoxide	0.025	200	1	0.03 (2B)
lindane	0.5	100	1	2 (2B)
permethrin	5	100	1	20 (3)

Key:

GV guideline value

LOAEL lowest-observed-adverse-effect level

NOAEL no-observed-adverse-effect level

P provisional

% TDI percent of tolerable daily intake allocated to drinking-water

UF uncertainty factor

Table 3: Risk assessment of pesticides where knowledge of exposure from different media is limited

PESTICIDE	NOAEL mg/kg bw/d	UF	% TDI	GV, µg/l (IARC Group)
aldicarb	0.4	100	10	10 (3)
atrazine	0.5	1000	10	2 (2B)
carbofuran	0.05	30	10	5
chlorotoluron	11.3	1000	10	30
2,4-D	1	100	10	30 (2B)
2,4-DB	3	100	10	90 (2B)
1,2-dichloropropane	100 (LOAEL)	10000	10	20 P (3)
dichlorpop	3.64	100	10	100 (2B)
fenoprop	0.9	300	10	9 (2B)
isoproturon	3	1000	10	9
MCPA	0.15	300	10	2 (2B)
mecoprop	1	300	10	10 (2B)
methoxychlor	5	1000	10	20 (3)
metolachlor	3.5	1000	10	10
molinate	0.2	100	10	6
pendimethalin	5 (LOAEL)	1000	10	20
pentachlorophenol	3	1000	10	9 P (2B)

propanil	5	1000	10	20
pyridate	3.5	100	10	100
simazine	0.52	1000	10	2 (3)
2,4,5-T	3	1000	10	9 (2B)
trifluraline	0.75	100	10	20 (3)

Key:

GV	guideline value
LOAEL	lowest-observed-adverse-effect level
NOAEL	no-observed-adverse-effect level
P	provisional
% TDI	percent of tolerable daily intake allocated to drinking-water
UF	uncertainty factor

Presentation Plan

Section	**Key points**	**OHP**
Introduction	• there are conflicting uses of pesticides - agricultural and public health uses	
	• adverse environmental effect of pesicides can often be mitigated through proper selection and application procedures	
Classification	• there are two methods of classifying pesticides a) according to chemical class	**Table 1**

	b) according to their intended use	
	• it is important to know both these to determine its behaviour in the environment, occurrence in drinking water and toxicity to humans	
The *Guidelines*	• of the 35 pesticides evaluated, 28 contain chlorine	**Tables 2,3 OHP 1**
	• many of the evaluated pesticides are herbicides and readily migrate into groundwater	
	• in developing countries organochlorine pesticides have particular use in public health as well as agricultural practices and have thus been evaluated in the *Guidelines*	
	• setting GVs for pesticides is often difficult because of uncertaintity about health impacts	
	• the percentage allocation of the TDI to drinking water, reflects the toxicological basis of the Guideline levels and exposure assumptions made	
	• the nature and toxicity of the environmental degradation products of pesicides are largely unknown and are therefore not taken into account in the *Guidelines*	
	• the linearized multistage extrapolation model was used to derive guideline values based on an upper-bound estimate of an excess lifetime cancer risk of 1 per 100,000 of the population exposed	
	• standards and guidelines for pesicides can be established using	

the evaluations made by the Joint FAO/WHO Meeting on Pesticide Residues

Pesticides in the *Guidelines*

- **Of the 35 pesticides evaluated, 28 contain chlorine**
- **Many of the pesticides evaluated are herbicides and readily migrate into groundwater**
- **Organochlorine pesticides have been included since they still have public health uses in developing countries**
- **Setting GVs is difficult due to uncertainty of health impacts**
- **10% of the TDI allocated to drinking-water**
- **Nature and toxicity of the environmental degration products of pesticides are largely unknown**