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DISINFECTION BY-PRODUCTS

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INTRODUCTION

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This seminar was first proposed in 1991 to consider the results of research funded over several years by the Department of the Environment into the occurrence and significance of chlorination by-products. During 1992, the World Health Organisation's review of its guideline values for drinking water quality raised questions about the by-products of ozone and chlorine dioxide as well as those of chlorine. The scope of the seminar was then expanded to include these disinfectants.

Because of the wide interest in disinfection by-products, it was decided to invite representatives from research organisations, the water industry, regulators, the medical profession and the press to consider the process of disinfection and the significance of the by-products formed. The speakers, all experts in their fields, were invited from Europe and the United States, as well as the United Kingdom.

This publication includes the papers presented at the seminar and an account of the discussions, including the conclusions reached.

The seminar restated the need for adequate disinfection in order to protect consumers from water-borne microbial disease. Risks and benefits had to be assessed when considering the health implications of disinfection by-products. Consumers have to be informed, by rational debate, of the many inter-related issues, including the implications for water charges.

DISINFECTION BY-PRODUCTS - CURRENT STANDARDS AND REGULATIONS

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Chlorine has been used successfully for many years as a highly effective disinfectant for public supplies of drinking water. However, since chlorine is a reactive chemical and water contains traces of natural and sometimes man-made chemicals, both inorganic and organic, it would not be surprising if traces of unwanted by-products were formed. In the early 1970's Rook (1974) discovered chloroform in the chlorinated drinking water of Amsterdam and this observation was rapidly confirmed by other workers in many countries.

This in itself was not of particular note but coincidental studies of chloroform in laboratory rodents had shown that it was capable of causing an increase in tumours of the liver and kidney, albeit at extremely high doses. Concern over cancer as a major cause of death in western societies was becoming a public issue with the possibility that pollution by man-made chemicals was a significant contributor to cancer. This concern was particularly acute in the USA and was the driving force behind a number of epidemiological studies which found a positive association between cancer of the colon and rectum and the consumption of chlorinated surface water as compared to unchlorinated groundwater. The associations were weak and the studies had many flaws but they gave significant impetus to major research programmes looking at chlorinated drinking water.

In 1979 the USEPA promulgated a drinking water standard for total trihalomethanes (THM's) of 100 µg/l under the safe drinking water act. In 1984 the World Health Organisation published a tentative guideline value for chloroform of 30 µg/l in its Guidelines for Drinking Water Quality. The guideline value was based on an acceptable risk of increased cancer in consumers calculated using a mathematical model to extrapolate from the risk of an increase in liver tumours in mice given high doses of chloroform. The guideline was designated as tentative to reflect the uncertainties inherent in this process.

In the meantime the Directive relating to the Quality of Water Intended for Human Consumption, the basis of drinking water standards in the European Community, mentioned THM's but gave no specific maximum acceptable concentration. A non-statutory value for organochlorine compounds other than pesticides, PCB's and PCT's of 1.0 µg/l was given with the phrase that THM's should be as low as possible. This approach gave considerable flexibility to member states in the face of rapidly advancing research and was interpreted in a variety of ways to suit the particular circumstances of the individual states. The UK, for example, set a standard of 100 µg/l for total THM's measured as a three month rolling average.

A number of epidemiological studies have been carried out since the USEPA and UK standards for THM's were introduced. A number of these showed a weak positive association between cancer of the stomach, colon, rectum, bladder, or more recently pancreas, and the consumption of chlorinated water (Morris *et al* 1992, IJsselmuiden *et al* 1992). The most convincing of these is the association with bladder cancer in the large case control study carried out by Cantor *et al* (1987). However there are considerable difficulties in carrying out such studies, they are difficult to control adequately, exposure is uncertain and variable, exposure has changed with time and they are attempting to examine an increase in 'common' cancers. The results of such studies must therefore be interpreted with caution and they are the subject of much scientific debate. The International Agency of Research and Cancer evaluated the studies available in 1990 and concluded that the degree of evidence for the association between chlorinated drinking water consumption and cancer is inadequate.

Since the identification of chloroform and the other THM's there have been many other chlorination by-products identified including some such as the chlorinated acetic acids which can be present at similar concentrations to the THM's. Others such as MX (3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone) are present at a few tens of ng/l. The data on the toxicology of these substances is very variable in quantity and quality.

Attention has also turned to other oxidative disinfectants such as ozone and unwanted by-products of their use in the disinfection of drinking water are also being identified. Bromate is one such and this may well be of as great a significance for ozone as THM's were for chlorination.

The questions then arise about which disinfection by-products require regulation and how standards should be determined.

For some years dose response models which attempt to model the carcinogenesis process mathematically have been used to extrapolate the risk of cancer in animal studies to the risks of low environmental levels of exposure. These models are potentially very useful but they must be used with great care in setting standards because they usually err on the side of caution and the great uncertainties associated with them mean that the real risk could even be zero.

However there are substances which cause cancer in laboratory animals indirectly by a mechanism which will have a demonstrable threshold. In these cases the application of the models will be inappropriate and the more traditional approach of applying an uncertainty or safety factor to a no effect level in suitable animal studies will be the method of choice.

These questions have been recently addressed by WHO in revising the Guidelines for Drinking Water Quality. They have provided guidelines or provisional guidelines for 15 inorganic and organic disinfection by-products including individual THM's, chlorinated acetic acids and bromate (Table 1). Provisional values reflect either practical problems with analysis, as with bromate or uncertainties with the toxicology such as with di and trichloroacetic acid. No guidelines could be proposed for a further 8 substances, primarily due to a lack of toxicological data.

WHO have made a number of points pertaining to the development of standards for DBP's from their guidelines. First they emphasise that microbiological quality should never be compromised in attempting to control DBP's. Second they urge great care in selecting individual DBP's for inclusion in national regulations. There is no need to regulate all of the DBP's for which there are guidelines and WHO suggest that for chlorination DBP's, THM's and chlorinated acetic acids would probably be sufficient.

The lack of a guideline value for chlorate and the provisional guideline for chlorite are significant in highlighting the deficiencies in the toxicological data on these substances. There is a clear need to resolve the problems in the risk assessment since both substances, but particularly chlorate, are important by-products of chlorine dioxide, chlorination by hypochlorite and on site electrolytic generation of chlorine. This does not mean that they constitute an unacceptable risk but the uncertainties prevent absolute reassurance that there is an appropriate margin of safety associated with their presence in some drinking waters.

The current interest in regulating DBP's follows 20 years of research and investigation. WHO have examined the data and proposed guidelines for a number of DBP's. The thinking behind these guidelines is detailed in the supporting summaries and documentation. These will provide a good starting point in considering regulations for DBP's.

The questions facing regulators, water suppliers and researchers are as follows:

- Which DBP's occur, how often, and in what quantities?
- How well characterised are DBP's from disinfectants other than chlorine?
- What is the risk to consumers and how certain are we of these estimates?
- What are the implications for microbiological safety?
- What can be done to reduce DBP's and at what cost?
- How do the risks, benefits and costs relate?

The succeeding papers and the associated discussion in this volume address these questions and go a long way to providing many of the answers.

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Table 1. WHO Guidelines for by-products of disinfection.

Trihalomethanes	Standard should not be sum of individual guide values.
Bromoform	0.1 mg/l
Dibromochloromethane	0.1 mg/l
Bromodichloromethane	0.06 mg/l
Chloroform	0.2 mg/l
Monochloroacetic acid	No GV
Dichloroacetic acid	0.05 mg/l (P)
Trichloroacetic acid	0.1 mg/l (P)
Dichloroacetonitrile	0.09 mg/l (P)
Dibromoacetonitrile	0.1 mg/l (P)
Bromochloroacetonitrile	No GV
Trichloroacetonitrile	0.001 mg/l CF)
Trichloroacetaldehyde	0.01 mg/l (P)
Cyanogen chloride	0.07 mg/l (as CN-)
Chloropropanones	No GV
Chloropicrin	No GV
MX	No GV
Bromate	0.025 mg/l (P)
Formaldehyde	0.9 mg/l
Monochloramine	3.0 mg/l
Ditrichloramines	No GV
Chlorine	5.0 mg/l
Chlorite	0.2 mg/l (P)
Chlorate	No GV

No GV indicates inadequate information to set a guideline.

OCCURRENCE AND FORMATION OF CHLORINATION BY-PRODUCTS - A SUMMARY

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Occurrence and formation

This presentation deals with chlorination by-products (CBPs) and much of the work covered was carried out for the Department of the Environment over the last decade or so. Before discussing CBPs specifically it is useful to make some general comments.

CBPs are by-products of disinfection and associated processes. Disinfection refers to the use of chemical oxidants, such as chlorine, ozone and chlorine dioxide, in the treatment of drinking water to control pathogenic micro-organisms. However, these oxidants are also used for more general purposes, such as oxidation of iron, manganese and hydrogen sulphide, and the destruction of specific contaminants such as pesticides and chemicals responsible for odours and tastes. Chlorine is almost universally used and it has made a substantial contribution to public health.

By-products refer to low concentrations of chemicals produced in side-reactions, involving organic and inorganic constituents of raw water. Such by-products can be organic or inorganic in nature. The amount of chlorine used in water treatment is between 1 to 15 mg/l but up to 5 mg/l is typical. The organic matter in water is usually in the range 0.5 to 25 mg/l.

The main problem with CBPs and disinfection by-products (DBPs) in general is concern about possible adverse health effects, particularly cancer, caused by long-term consumption of drinking water. Acute effects are not a problem.

Prior to 1974 there was little real concern over CBPs and possible effects on health. However, during 1974 is was reported that chlorination commonly generated low levels of haloforms or trihalomethanes (THMs). Of particular concern was chloroform which was suspected of being a carcinogen. A variety of naturally occurring substances have been shown to react with chlorine to produce haloforms but humic substances seem to be the most important.

The EC Directive on the quality of water intended for human consumption (EC DWD) does not include THMs as a specific parameter but a comment added to parameter 32 "Organochlorine compounds other than pesticides" requires haloforms to be kept as low as possible. It was left to the competent national authority (DOE in the UK) to interpret "as low as possible". In the UK a standard of 100 µg/l for total haloforms, as a 3-month average, was established in the late 70's early 80's and this was built into the Water Regulations in 1989. In 1984 the World Health Organisation (WHO) set a tentative Guideline Value (GV) for chloroform at 30 µg/l.

In some European countries considerable concern over the chlorination process has developed and alternatives to the use of chlorine have been sought.

Research has shown that chlorination leads to low levels of many other CBPs. Table 1 shows some of the more important chlorination by-products. The chlorinated acetic acids, for example, were difficult to measure but now the availability of methods has revealed that these are very common CBPs and as prominent as THMs.

Laboratory experiments have shown that chlorination of humic substances produces additional by-products, such as chlorinated saturated and unsaturated carboxylic acids (Table 2). However, few of these have been monitored for in drinking water. Such experiments have also shown that unsaturated chemicals in water sources can form chlorohydrins but these also have not been monitored.

Studies on the reactivity of a range of industrial chemicals with aqueous chlorine (based on measuring consumption of chlorine in the laboratory) suggests that many chemicals, including some water treatment chemicals such as polyelectrolytes, can react (Table 3) but the by-products are unknown.

Brominated by-products are formed via the reaction of chlorine with bromide in water sources to produce hypobromous acid which then reacts, for example, with humic substances, to generate brominated by-products.

Some of the chlorination by-products are also bacterial mutagens, i.e. potential carcinogens (see below).

Evaluating the risks to health

The possible risks to health that CBPs may pose have been evaluated in four basic ways.

Identification of CBPs and evaluation of corresponding toxicity data

The main approach has been to identify the CBPs as comprehensively as possible and then to assess the available toxicity data. Where the data is insufficient then since the pure substances can be made available conventional toxicity testing can be carried out. This process has led to the existing standards on CBPs.

At present the existing drinking water standards tend to deal with a few CBPs, usually THMs. However, new WHO GVs have been agreed and these when published officially in 1993 will reflect the increase in information on DBPs generally where sufficient toxicological data are available. Table 4 gives a list of the GVs that relate to CBPs. These GVs, which are not meant to be taken as rigid values or used without consulting the background information which will be published with these, would not appear to pose a great problem for chlorination although the amount of data on the occurrence of trichloroacetonitrile (GV = 1 μg/l) is meagre.

For some CBPs insufficient toxicity data exists at present, e.g. chlorate and MX, and so additional standards may appear as information becomes available. Chlorate is of potential concern since it is present in commercial sodium hypochlorite solutions (NaOCl) and in NaOCl solutions generated by on-site electrolysis of brine. Ageing of stored NaOCl is a major factor and chlorate levels of up to 0.66 mg/l have been reported. Electrolytic generation can produce levels up to around 0.25 mg/l. Further study of these sources is under way.

Screening bioassays to detect the presence in drinking water of potentially hazardous CBPs

Many of the CBPs in water are difficult to identify and an assessment of their toxicity cannot be carried out. To combat this bioassays have been undertaken, to detect the presence of potentially important CBPs. In particular, bacterial mutagenicity assays have been used to detect the presence of bacterial mutagens. If a chemical is a bacterial mutagen then it is likely to be an animal carcinogen and, consequently, a possible human carcinogen. Such tests on concentrates of drinking water have shown that chlorination usually generates bacterial mutagens.

Attempts to identify the CBPs responsible have led to the identification of many chlorination-derived mutagens. Some of the more important are shown in Table 5 but of these only MX and related chemicals appear to have sufficient potency to account for much of the mutagenicity generated during chlorination. The significance of MX and related compounds awaits the outcome of toxicity testing.

Bioassays have also been used to see whether the bacterial mutagenicity formed during chlorination is of relevance to man. This has involved tests based on 'higher' cell systems. Thus tests for chromosome damage using extracts (and MX) have given positive findings as have point mutation tests in mammalian cells. However, tests using Drosophila proved negative. *In vivo* tests have given negative or inconclusive results on extracts and MX. There is considerable evidence that chlorination-derived mutagens (and MX) rapidly become bound to proteinaceous material.

Studies on animals (carcinogenicity studies on extracts)

The classical method of testing for carcinogenicity involving feeding studies over periods of time is very difficult to carry out with chlorinated drinking water since the levels of CBPs are too low. Tests using concentrated extracts are also difficult because

of the problems of producing enough extract in a consistent manner over a period of time and the feeding of complex mixtures in which the chemicals of real concern may be a minor components. What testing has been carried out has been inconclusive.

Epidemiological investigations

Studies on a possible association between the incidence of cancer in the population and consumption of DBPs or chlorinated water is difficult for the following reasons:

- any effect is almost certainly very small and therefore very difficult to detect;
- an effect may not be specific to drinking water;
- actual exposure to CBPs is difficult to estimate.

In 1991 the International Agency for Research on Cancer (IARC) issued a detailed review of such investigations in relation to the possible carcinogenicity of chlorinated water. It concluded that while some studies appeared to provide support for an elevated risk due to consumption of chlorinated water and the evidence was strongest for the urinary bladder, overall the sum of evidence was inadequate for the carcinogenicity of chlorinated water in humans. Subsequent studies do not appear to have altered the situation.

Potential solutions

Disinfection of water supplies forms one of several important barriers against microbiological risks to health and any solution to the problem of CBPs must not compromise this.

Water treatment

Since this is the subject of other presentations it will not be discussed. However, it is worth mentioning that caution is needed when trying to justify substituting one chemical disinfection regime for a chemically different regime solely on the basis of potential chemical risks to health. At present insufficient is known about the DBPs of any chemical oxidant as is demonstrated in the unexpected emergence of bromate as a potential problem.

Abandon chemical disinfection/oxidation

In the case of developed countries one could argue that since the major killer diseases have been eradicated chemical disinfection is not really necessary. However, the loss of an effective final barrier to infection if other barriers are breached seems unwise. In some European countries the degree of treatment has been increased such that for most of the time final disinfection is not used. For a surface-derived water the cost implications can be significant.

Tolerate chemical risks in light of benefits of disinfection

In developing countries this should go without saying but in developed countries the balancing of chemical risks, often based on inaccurate and unproven models, against microbiological risks is additionally complicated by political pressures and public perceptions. However, the ability to evaluate the overall risks involved with reasonable accuracy must be a worthy goal.

Summary

In terms of existing standards and the forthcoming WHO GVs the problem of CBPs appears manageable with available treatment technology. However, for some CBPs toxicological data are insufficient to allow the setting of a standard at present. The results of bioassays and epidemiological studies are suggestive but overall inconclusive.

There is an increasing need to be able to estimate and balance any chemical risks to health due to DBPs, which are likely to be very small, with corresponding microbiological risks which may be more substantial.

Table 1. Chlorination by-products.

Trichloromethane	Bromochloroacetonitrile	MX
Bromodichloromethane	Dibromoacetonitrile	EMX
Chlorodibromomethane	Trichloroacetonitrile	BMX
Tribromomethane	Trichloroethanal (chloral)	Chlorate
Chloroacetic acid	1,1-dichloropropanone	Chloramines
Dichloroacetic acid	1,1,1-trichloropropanone	Cyanogen chloride
Trichloroacetic acid	1, 1-dichloro-2-butanone	
Dibromoacetic acid	1,1,1-trichloro-2-butanone	
Chloroacetonitrile	Chloropicrin	
Dichloroacetonitrile	Chlorophenols	

Table 2. Chlorination of humic acid.

$CCl_2 = CHCOOH$	$HOOCCH_2CHClCOOH$
$CCl_2 = CClCOOH$	$HOOCCCl_2CH_2COOH$
$HOOCCCl_2COOH$	$HOOCCH = CClCOOH$
$HOOC(CH_2)_2COOH$	$HOOCCCl = CClCOOH$

Table 3. General reactivity of chemicals with chlorine.

Compound (10 mg/l)	% initial chlorine (1 mg/l) after 24 hours
Phenol	3.12
Creosote	3.82
EDTA Tetra sodium salt	7.08
Aniline	8.18
Urea	9.48
LT31 liquid cationic PE	12.00
Nitrilotriacetic acid	14.30
Malachite green	15.30
N50 non-ionic PE	18.20
A378 cationic PE	24.10
A3721 anionic PE	38.60
Toluene	50.40
Synperonic NP10	73.90
Atrazine	77.70
Isoproturon	82.10
MCPA	83.70
Polyethylene glycol	84.90
2,4,D	85.00
m-Xylene	89.70
Sodium dodecylbenzenesulphate	90.90
Formaldehyde	91.30
Methanol	94.70
Ethanediol	98.60

Table 4. Proposed new WHO GVs (µg/l).

			UK Water Regulations
Chlorite	200		500[c]
Bromate*	25[a]	(3[b])	
2,4,6-trichlorophenol*	200		
Formaldehyde	900		
Trichloromethane*	200		
Bromodichloromethane*	60		100[d]
Dibromochloromethane	100		
Bromoform	100		
Dichloroacetic acid	50		
Trichloroacetic acid	100		
Trichloroacetaldehyde	10		
Dichloroacetonitrile	90		
Dibromoacetonitrile	100		
Trichloroacetonitrile	1		
Cyanogen chloride	70 (as CN)		

* GV based on risk calculation.

[a] Level includes allowance for analytical difficulties.

[b] Level is value based on 10^{-5} risk factor.

[c] Total of chlorine dioxide, chlorite and chlorate.

[d] Total of THMs

Table 5. Chlorination-derived bacterial mutagens.

Bromoform
Bromodichloromethane
Dibromochloromethane
Chloral
1,1-dichloropropanone
1,1,1-trichloropropanone
1,1,3,3-tetrachloropropanone
Bromochloroacetonitrile
Dichloroacetonitrile
Chloropicrin
E-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid (EMX)
3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX)
3-chloro-4-(bromochloromethyl)-5-hydroxy-2(5H)-furanone (BMX-1)
3-chloro-4-(dibromomethyl)-5-hydroxy-2(5H)-furanone (BMX-2)
3-bromo-4-(dibromomethyl)-5-hydroxy-2(5H)-furanone (BMX-3)

OCCURRENCE AND FORMATION OF OZONATION BY-PRODUCTS

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Background

Interest in the use of ozone in drinking water treatment plants continues to grow with the imminent prospect of new regulations revising maximum contaminant levels for chlorine disinfection by-products, and because ozone offers several advantages over alternatives[2]. Many utilities employing chlorine as their only oxidant and disinfectant have discovered disturbing quantities of by-products in their finished water. These can only be removed by pretreatment of the water to remove the by-product precursors, before the application of chlorine, or by the use of alternative oxidant combinations such as ozone and chloramines. Many studies have investigated the use of ozone for this purpose and cite excellent microbial destruction, diminution of taste and odors, the reduction in chlorine demand, and enhancement of overall total organic carbon (TOC) removal among its many useful properties. In addition, ozone often effects a contrasting reduction in chlorinated by-products formation when ozone is used as a pre-treatment prior to final disinfection, especially if used as a preoxidant in conjunction with chloramines (as the final disinfectant).

Ozone chemistry in the aqueous phase

Appendix 1 is a summary of some of the important aspects of ozone chemistry as it relates to water treatment. Much of this has been developed as a result of fundamental studies in several laboratories, most significantly those of Jurg Hoigné and coworkers at EAWAG in Switzerland[3]. The essential points for this subject are:

- ozone is a powerful oxidant that is bound to form by-products with the natural organics in water supplies and some of the inorganics (i.e. bromide ion) and

- the by-products are likely to be more polar (organics) and in higher oxidation states (organics and inorganics) than their precursors. The truth is that relatively little is known of the identity of by-products formed by the interaction of ozone with natural water components, and even less has been studied of their occurrence in treatment plants employing ozone. This is a result, in part, of the limited analytical capability for extracting and determining the polar organic fraction from the aqueous matrix, some components of which are expected to be very polar and/or unstable and, therefore, not suited to standard preconcentration techniques. Clearly, a chemical methodology is needed to target ozonation by-products of health concern, and for application in field studies to determine their occurrence in actual drinking waters.

Purpose of the AWWARF project on ozone by-products

To address these issues, our group combined with others in the water treatment industry to form a consortium project ultimately supported by the American Water Works Association Research Foundation, with majority contributions from six utilities[4]. The project consisted of two, interconnected components: a laboratory phase in which analytical methods for targeted ozonation by-products were developed and/or optimized, and a survey phase in which ozone by-products were analyzed in water samples taken from selected treatment plants that utilized ozonation. The final report of the project will be published by AWWARF in the summer of 1993.

Summary of project results

Laboratory studies

In the laboratory-scale research, studies were carried out to determine what factors affected the levels of specific classes of ozone by-products that were identified in advance as important ones for study. These studies used primarily a local water source (University Lake, Orange County, NC) and, in some cases waters from supplies in other parts of North America. The specific classes of by-products that were targeted were as follows:

- aldehydes, ketones, carboxylic acids, and mixed aldo- or keto-acids; organic and inorganic brominated by-products; hydrogen peroxide and organic peroxides, and epoxides.

Most of the laboratory studies were carried out by ozonating the water in a 5-litre glass reactor but in a few cases a 70 litre stainless steel reactor was used. Ozone, generated from an air supply, was added to the water at chosen doses so as to achieve various ozone: TOC ratios. In some studies, the effect of the variation of other water quality parameters such as pH and alkalinity, was studied.

Carbonyl compounds

Several groups[5]have examined methods for the analysis of aldehydes, ketones, and mixed aldo- and keto-acids and have settled on aqueous phase derivatization with the reagent PFBHA: O-(2,3,4,5,6-Pentafluorobenzyl)-hydroxylamine hydrochloride (identical to PFBOA) originally used for drinking water analysis by Yamada and Somiya. This is the method eventually used in the survey phase as modified by Sclimenti *et al.*[6] Also, in this work we adapted the PFBHA method using Solid Phase Extraction (SPE) techniques to isolate the formed oximes. In the final version of the method, carbonyl compounds were first derivatized in the water sample with PFBHA, then passed through the SPE cartridge at low pH(4) where they were adsorbed. The PFBHA-derivatized oximes were then eluted from the cartridge with a minimum volume of methyl t-butyl ether (MTBE) so as to give an extraction ratio (water:MTBE) of approximately 100-250, thus enhancing the sensitivity of the analytical method. Laboratory studies examined the recovery of these compounds from different matrix waters and sought to establish sound quantification criteria for the aldehydes and mixed functional carbonyl compounds. The method promises to be of use in field studies where the extraction cartridge could be shipped to a remote laboratory for extraction and analysis; however, the method was used for only a few of the surveys conducted in this study. The most important result of the SPE work came about accidentally, as a result of some preliminary field studies using the PFBHA method. It was found that a commercial sample of methyl glyoxal being used as a standard in the field work (and by other laboratories) was not pure, as presumed. This led to erroneously high levels of methyl glyoxal in some of the early reports from this project, as well as other studies of aldehyde formation after ozonation. As a result of this discovery, it became clear that primary standards of the oximes are needed for optimization of the PFBHA method (see Cancilla *et al.*, 5c).

Peroxides and epoxides

Other ozone by-products investigated in the laboratory phase are the peroxides and epoxides. The chemistry of ozone interactions in natural waters is responsible for short-lived peroxygenated intermediates as well as hydrogen peroxide. The peroxides were analyzed by a modified method in which a peroxidase enzyme reacts with the peroxide in the presence of a hydrogen donor (p-hydroxyphenylacetic acid, POHPA), resulting in the formation of a fluorescence dimer of the POHPA.[7] This method also detects certain organic hydroperoxides which were quantified as a group and monitored in ozonated water, including through treatment plants. Some initial work was also undertaken to establish an analytical procedure for stabilizing epoxides and making them amenable to chromatographic separation. The method involved the isolation and derivatization of the epoxides with anhydrous HCl to form chlorohydrins. These could be detected by GC/ECD but the method was not developed fully enough to be used in field studies.

Brominated by-products

The laboratory study also included a detailed investigation of brominated by-products formed by the ozonation of waters containing bromide ion. This is of concern since some American water supplies have rather high natural bromide levels, and previous studies have shown that bromide may either be oxidized to bromate ion or to hypobromous acid, which may then react with natural organic matter (NOM) to form brominated organics such as bromoform, brominated acids, bromoacetonitriles, etc. (Figure 1). Bromination of NOM is thought to occur primarily by HOBr whereas oxidation to bromate involves primarily the conjugate base, hypobromite[9]. A systematic study was carried out of the by-products obtained when University Lake water, to which various amounts of bromide had been added, was oxidized with ozone (ozone:TOC ~ 1)[9]. In addition to the brominated organics listed above, the samples after ozonation were analyzed for dissolved, adsorbable (on GAC) organic bromide (DOBr) and bromate (by ion chromatography). Also, in the course of this study of ozonation with enhanced levels of bromide ion, there was found a group of previously unidentified, labile compounds identified as bromohydrins[10]. Subsequently, we have shown that these bromohydrins are due in part to bromination of impurities in the two solvents (pentane and MTBE) used for extraction. However, they may also be legitimate disinfection by-products. In general, the accurate recovery and quantification of these compounds is very dependent on their preservation in transit to the analytical laboratory. Ammonium sulphate was the most effective quenching agent for hypobromous acid, the active brominated species resulting from the interaction of inorganic bromide with ozone. Also, it was found that bromate does appear to form at significant levels with elevated bromide levels and its concentration is enhanced at high pH. The presence of ammonia, on the other hand, tends to tie-up the hypobromous acid and reduce the formation of these brominated by-products. These compounds also are formed by reaction of the natural water with aqueous bromine, irrespective of prior ozonation, and, since HOBr is formed in the process, by chlorination in the presence of high bromide levels. However, the nature of their precursors is unknown.

The survey phase

The analytical methods developed in this study together with existing methods for disinfection by-products were then applied in a survey of selected treatment plants in the US and Canada which use ozone. The selection of the plants was based partially on the variety of the treatment trains and raw water qualities providing a wide input into the by-product data base of formation and fate of ozonation by-products. In addition, pilot studies at some locations were performed with a focus on varying bromide concentrations in order to determine the likelihood that the identified brominated organic by-products do occur in plant waters.

The most significant aldehydes formed are formaldehyde, acetaldehyde, and the dialdehydes glyoxal and methyl glyoxal. The plant surveys indicate that these compounds are removed by filters which possess an active biomass (the dialdehydes more slowly than the monoaldehydes), but that subsequent oxidation with a post-disinfectant can reform them to some extent[11].

The survey phase also demonstrated for the first time, the formation of organic peroxides and hydrogen peroxide in ozonation plants. Organic peroxides appear to accompany hydrogen peroxide formation but it was found that both groups of by-products are apparently removed during filtration, and can be reformed at sub-ppb levels by post-disinfectants at the plant.

Table 1 shows a summary of the by-products found at several of the plants studied in the survey phase. It should be noted that these studies were only "snapshots" and should not be interpreted in a very detailed manner. They show, however, that ozonation does produce by-products when used in drinking water treatment and that many of these, with the exception of bromate, are removed by biological filtration. The oxidation by-products of ozone identified in this study can be considered as surrogates for remaining unidentified components which can, therefore, be controlled to some extent by the application of appropriate physical and biological treatment.

Finally, this study was also able to monitor the effect of plant treatment with and without ozone on the formation of chlorination by-products currently regulated or discussed for regulation. In all cases, the use of ozone reduces the levels of halogenated by-products formed by subsequent chlorination or chloramination and consequently, the disinfectant demand.

Summary

The practical conclusions reached in the laboratory and survey phases are as follows:

- aldehydes and aldo-acids, especially formaldehyde, glyoxal and methyl glyoxal are ubiquitous ozone DBPs, formed in all of the treatment plants studied. Dimethyl glyoxal and glyoxylic acid were found in those cases when the methods for these analytes were employed;

- these compounds are removed by filters which possess an active biomass, but subsequent oxidation with a post-disinfectant (chlorine or chlorine dioxide) can reform them to some extent;

- both organic peroxides and hydrogen peroxide are found in water after ozonation, are largely removed during filtration, but may be reformed at sub-ppb levels by post-disinfectants;

- organic bromides as measured by DOBr are formed in larger amounts at low pH (Figure 2) whereas bromate is formed at higher pH values. This illustrates the trade-off associated with lowering of pH for control of bromate in that the toxicological hazards of brominated organics that might formed thereby are not well understood.

Subsequently, our group in conjunction with Krasner, Daniel and Najm have examined bromate production in more detail[12]. Some of the conclusions of that study are:

- ozone dose and pH play critical roles in the formation of bromate. Bromide levels of >0.18 mg/l yielded measurable bromate when a target ozone residual for disinfection was met. When bromide was <0.06 mg/l bromate was typically not detected (MDL 5-10 µg/l). Ammonia may or may not be an option to control bromate,[13] but lowering pH is an effective control option;

- in a pilot study with ozone added in one, two or three stages to water containing 0.32 mg Br/l, CT values >0.48 min
- mg/l could be achieved with bromate formation less than or equal to 11 µg/l. The target CT value could not be reached with addition of hydrogen peroxide.

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Appendix 1. Properties of ozone as an oxidant

Ozone is a powerful chemical oxidant acting through O_3 and OH radical chemistry

O_3 is a selective oxidant reacting with bromide (not chloride), reduced metals (Mn-II), some amino acids, activated aromatics (e.g. phenols), compounds with Π-bonds (e.g. olefins, nitriles, etc.)

OH is less selective, reacting rapidly with essentially all C-H bonds, aromatics, Π-bonds, bromide and reduced metals

OH is formed from decomposition of ozone stimulated by contaminants in natural water and hydrogen peroxide

By-products arise from a mix of O_3 and OH chemistry and are generally in a more polar or oxidized state than their precursors.

Table 1. Formation of ozonation by-products in US municipal water treatment plants[1].

WATER QUALITY (mg/L)				(/cm)	O_3	BY-PRODUCTS (ug/L)			
Br^-	pH	TOC	NH_3	UV_{254}	TOC	BrO_3^-	ΣVOBr*	CYANBr*	Σ ALD*
0.O2	7.4	2.4	<0.01	0.043	1.3	5	<0.2	7.8	49
0.19	7.2	8.1	1.6	0.219	1.1	10	<0.2	NA	147
0.06	7.6	3.5	0.03	0.056	0.5	<5	<0.2	NA	35
<0.01	7.1	2.9	0.06	0.062	0.6	<5	<0.2	NA	21
<0.01	6.9	0.88	<0.01	0.056	0.9	<5	NA	NA	30
0.05	7.6	2.9	<0.2	0.158	0.7,0.3	<5, 8	<0.2	1.9	14, 5
0.28	8.0	2.6	<0.01	0.092	0.4	<5	0.3	NA	39
0.22	7.9	3.2	NA	0.071	0.4	18	NA	14	30
0.24	7.8	25.9, 16.7	0.82, 0.29	0.82, 0.29	0.12, 0.18	<5	NA	<0.2	40

* ΣVOBr = sum of bromoform, dibromoacetonitrile, brominated acids
* CYANBr = cyanogen bromide; ΣALD = formaldehyde, acetaldehyde, glyoxal, methyl glyoxal

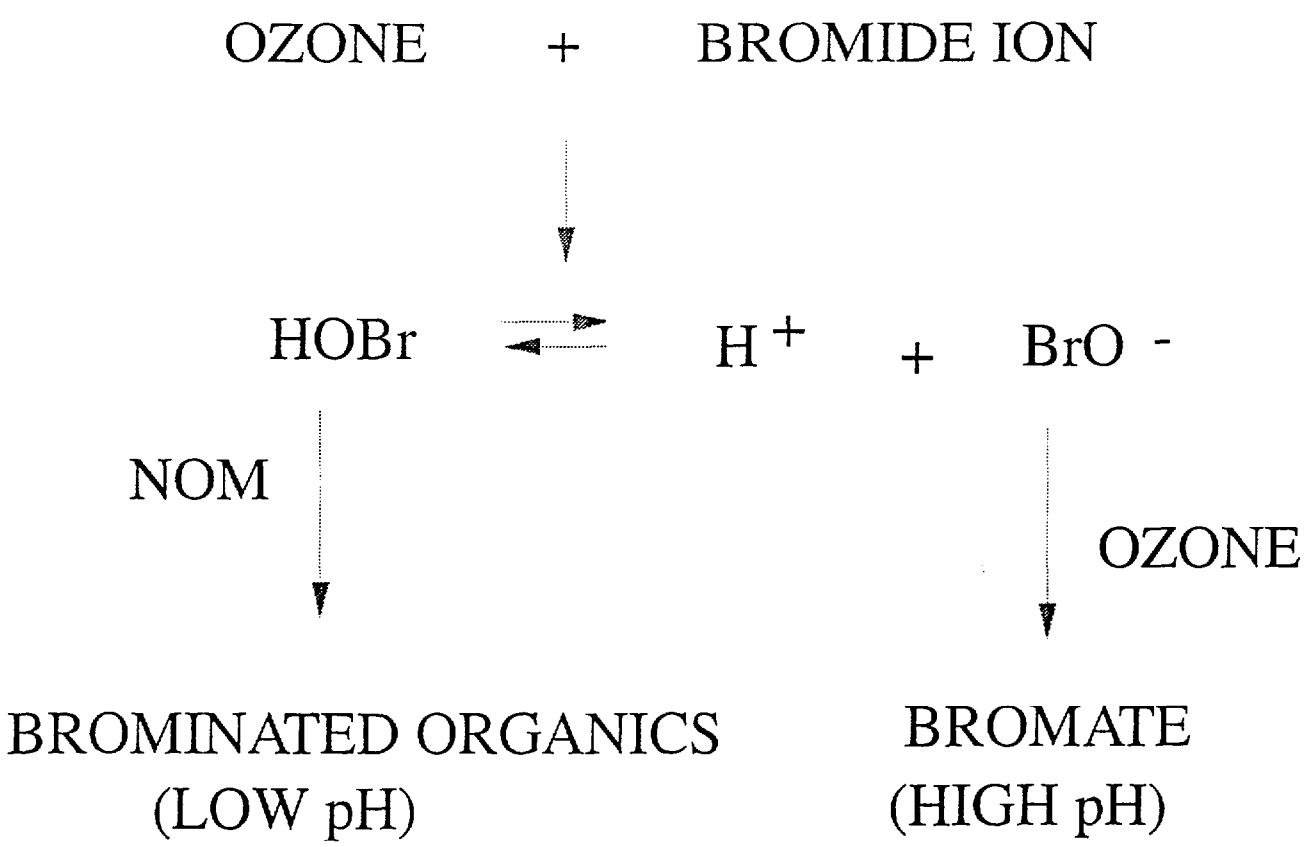
OZONE + BROMIDE ION
HOBr
H +
+
BrO -
NOM
OZONE
BROMINATED ORGANICS
(LOW pH)
BROMATE
(HIGH pH)

Figure 1.

- DOBr is formed upon ozonation of water with added bromide and is higher at low pH values

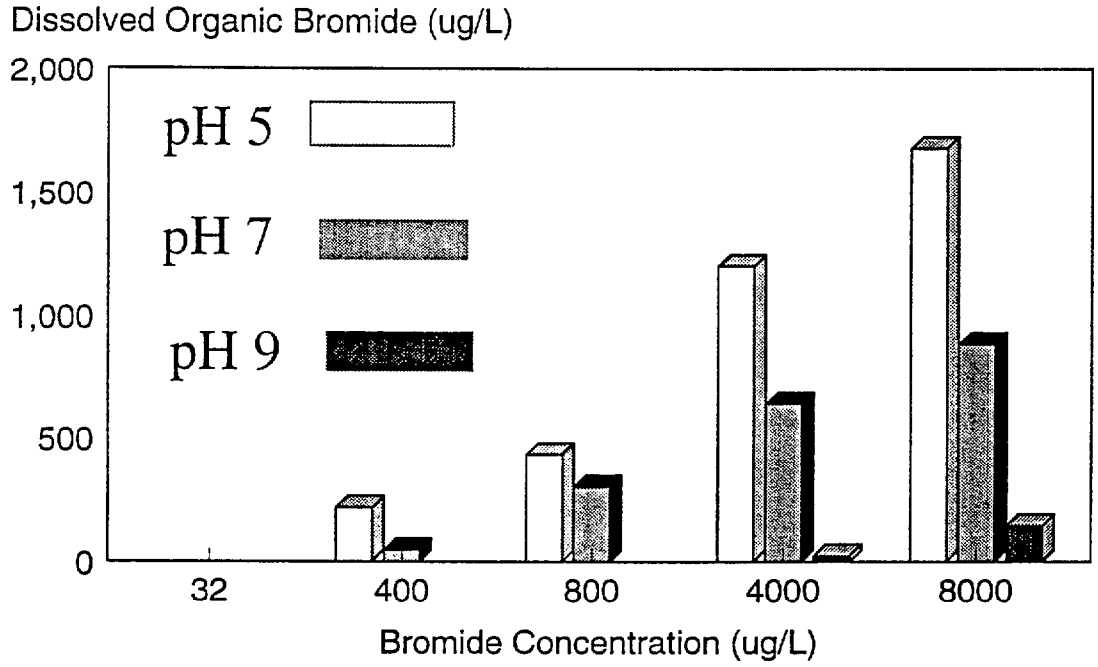

Figure 2. Conclusions of the lab study.

TOXICOLOGICAL RISK ASSESSMENTS OF CHLORINATION AND OZONATION BY-PRODUCTS†

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Introduction

The first indication that disinfection of drinking water leads to the formation of by-products came from the observation that trihalomethanes were formed following chlorination (Rook, 1974, Bellar *et al.*, 1974). This coincided in time with the completion of the National Cancer Institute's carcinogenesis bioassay of chloroform NCI, 1976). The positive results of this bioassay quickly lead to the development of the maximum contaminant limit (MCL) of 100 µg/l for total trihalomethanes in drinking water. Quantitative risk assessment had little to do with the selection of this value, rather it was established as a practical limit that most utilities could attain. Since that time it has become clear that the trihalomethanes are simply one of many by-products of chlorination. Moreover, by-products are now being associated with other disinfectants (Bull and Kopfler, 1991).

Relatively little is really known about the potential human health effects of the myriad of chemicals that are produced at low levels in drinking water with disinfection. Epidemiological data suggest, but do not prove, that chlorine or chlorination by-products may be increasing the incidence of certain cancers in the human population (IARC, 1991). There are data in experimental animals indicating that individual by-products of chlorine and other disinfectants are carcinogenic in experimental animals at doses which are several orders of magnitude greater than those which occur in drinking water. Other toxicological effects (e.g. developmental defects, neurotoxicity) of concern have also been associated with high doses of various by-products in experimental animals and in with a limited number in humans (Bull, 1992). Despite these data there is no direct and conclusive evidence that the by-products of disinfection affect human health at the concentrations found in drinking water.

As data accumulates on specific by-products, the US Environmental Protection Agency is forced to consider regulation of these compounds under the Safe Drinking Water Act. The Agency attempts to estimate the magnitude of the health risks that are associated with the concentrations that are found in drinking water. If the risk that is estimated by extrapolation using fairly rigid guidelines reaches unacceptable levels, the Agency will then develop regulations.

In the case of disinfectants and their by-products, however, some consideration must also be given to the beneficial effects of drinking water disinfection. In particular, the impact that suspending or modifying disinfection practice might have on waterborne infectious disease must be considered. What magnitude of cancer risk can he accepted to insure that waterborne infectious disease does not run rampant in communities served by public water supplies? How clearly must these risks be demonstrated? If high risks are acceptable from disinfectant by-products, how should the generally much smaller calculated risks associated with other carcinogens that occur in drinking water be considered? Regulation of trichloroethylene at concentrations posing a calculated extra risk of 1 case in a population of one million makes little sense if the risks from disinfection by-products typically run 100 to 1000 times this risk (Bull *et al.*, 1990b).

The intent of this paper focuses more specifically on by-products that have not been previously regulated. Essentially, it attempts to identify compounds that might limit the use of a particular disinfectant based on current data of on the specific compound or related chemicals. It should be recognized that part of the priority given to these chemicals is a function of methods that are currently used in risk assessment. In several cases the clear course of action is not to regulate, but to study these chemicals further to be certain that the risks are real before discarding a clearly beneficial public health measure.

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Sources of uncertainty in assessing risks from disinfectants

As regulations are developed for specific disinfectant by-products, it must be kept in mind that there are many uncertainties associated with the estimates of risks associated with the use of individual disinfectants that are frequently not acknowledged. Much of the uncertainty arises from simply not knowing what the by-products are. In the case of chlorine, several hundred compounds have been found or can be predicted to occur. For most of these by-products, there is very little known about their toxicology. On the other hand, most of these by-products occur at submicrogram concentrations and some are of little concern because they are essentially normal food stuffs (e.g. fatty acids). Once the toxic effects of a compound have been established, however, there is a question of how the results obtained from a test system relate to human risk at the submilligram/l concentrations found in drinking water. Without some knowledge of the mechanism of action it is very difficult to predict with confidence whether an effect seen at much higher doses in experimental animals will be seen in humans. It is extremely important to keep these facts in mind when establishing a guideline or a standard for a by-product that is specific to one disinfectant. When such guidelines are established they inevitably push the industry towards alternatives for which little data is available. Consequently, a standard that is intended to protect the public health has some probability of actually increasing hazards to the consuming public.

The uncertainties with alternate disinfectants are not uniform. Based on the types of uncertainties outlined in Table 1, there are certainly fewer uncertainties with chlorine than with the alternatives. With chlorine a very large number of by-products have been identified and belong to the chemical classes indicated in Table 2. Within those classes that occur in the highest concentration (trihalomethanes, haloacetates and haloacetonitriles) are chemicals for which substantial toxicological data bases exist. For members of these groups of halogenated by-products for which no data exist, there are sufficient data on at least one or two congeners that suggest toxicological properties that might be of concern. Because they have been of toxicological concern for some period of time, the concentrations at which the trihalomethanes occur in drinking water are known and there is fragmentary data on the haloacetates (except for bromodichloroacetate and dibromochloroacetate). If it is accepted that the upper 95% confidence limit of the linearized multistage model projects realistic risks, then the concentrations of these by-products are sufficiently high in the average water supply to preclude the use of chlorine as a disinfectant. Thus, the major question is whether the methodology properly estimates the risks from these by-products. Consequently, research efforts that will be most useful are those that are directed at determining whether the underlying assumptions of the linearized multistage model can be appropriately applied to each of the major by-products of chlorination. If the assumptions prove to be warranted the risks associated with these by-products are of a sufficient magnitude that there is little practical reason to be overly concerned about by-products that occur at lower concentrations.

In general, the by-products of chloramines are probably fairly similar to those of chlorine. However, this has not been systematically investigated beyond the relative efficacy of chloramine and chlorine for producing trihalomethanes and requires more study. Cyanogen chloride is a by-product that requires the presence of a source of ammonia to be formed. Consequently, it is formed at higher concentrations with chloramine than with chlorine (Bull and Kopfler, 1991).

On the other hand, the major sources of uncertainty with chlorine dioxide and ozone are that their by-products have not been identified. Those by-products of ozone that have been recently recognized as problems are found in water supplies containing bromide in the source water. Under these conditions ozone generates brominated analogs of most chlorination by-products. In addition, it will produce bromate, a compound that has been recognized as a carcinogen for some time (IARC, 1987).

The importance of mechanism of action in estimating risks at low doses

Within the community of toxicologists, the dangers of extrapolating data from experimental animals to humans and from high doses to the low concentrations found in the environment have always been recognized. However, the development of a number of statistical models for low dose extrapolation in the middle to late 70s has dominated regulatory policy in the US for more than 15 years. The model most frequently used is the linearized multistage model developed by Crump *et al.* (1976). It was an attractive model because it took into account some well recognized characteristics of carcinogenesis induced by tumour initiators, which have been largely found to be mutagenic. However, when the data base is limited to 2 doses of a chemical at or near the maximally tolerated doses and the 95% upper confidence limit is utilized for the estimate, this model approximates a one-hit model. Essentially the estimate can he made by drawing a line from the observed data to a 0,0 intercept when dose is plotted against extra cancer risk.

This type of model essentially makes the assumption that the carcinogen is inducing cancer by producing a mutation. The mutations produced are considered essentially irreversible which results in a cumulative probability of cancer that is linear with dose. However, as data has been collected by the National Toxicology Program's bioassay program, it has become increasingly apparent that many of the chemicals producing carcinogenic responses at maximally tolerated doses are not inherently mutagenic (Ashby and Tennant, 1991; Bull and Kopfler, 1991). To the extent to which these compounds act by activating reversible mechanisms, it is probable that their effects are not appropriately modelled by the linearized multistage model.

Cohen and Ellwein (1991) and Ellwein and Cohen (1992) have described the impact of chemicals acting by different types of mechanisms on cancer rates over a lifetime. For example, chemicals that enhance the rate of cell division in an organ can have a major impact on cancer incidence if they are administered at effect doses because they drastically reduce the latency for tumour development. However, the effects of such chemicals drop off very quickly as doses are decreased.

Statistical models have been developed for obtaining estimates of cancer risk at low doses that separately utilize data on a chemical's effect on mutation rate and cell division. The most commonly employed model of this type is the Moolgavkar, Venson and Knudson model (Moolgavkar and Knudson, 1981) which models these effects in two populations of cells, the normal cells in a tissue and those which have been initiated for cancer (referred to as intermediate cells). When such a model is applied to estimating the risks for a compound that contributes most of its activity by increasing rates of cell division, estimates of the risk in the range of one in a million and one in ten thousand extra lifetime risk for cancer can differ from those obtained by the linearized multistage model by orders of magnitude (Pastenbauch *et al.*, 1991).

As a consequence of these considerations, it is important to recognize that most of the disinfectant by-products that will be discussed are non-mutagenic or weakly mutagenic. Therefore, when estimates are provided in this manuscript utilizing the linearized multistage model, it may be concluded that many, if not all, of these estimates exaggerate the true risk actually associated with each by-product. However, it also needs to be recognized that the data required for alternate models to the linearized multistage model go beyond the information obtained in the usual two-year study. Either some measure of the change of tumour size and numbers with time or measures of cell proliferation rates in normal and intermediate cell populations within the target organ are needed. In general such data is not available for the disinfection by-products. However, it is being developed in various laboratories for selected trihalomethanes and haloacetates.

Hazards directly associated with disinfectants

The toxicological data that is available for chlorine and chloramine suggests that there is little cause for concern with these disinfectants at the concentrations that would normally be seen at the tap. No specific toxicological effects have been observed at the maximum concentrations that animals would drink in water. At high doses animals do not gain weight because of depressed water consumption. Consequently, the MCL recommended by EPA (Table 3) would appear to be conservative.

Chlorine dioxide does appear to produce some specific effects related to blood thyroxine concentrations (Berez *et al.*, 1982, Orme *et al.*, 1985). At similar doses, delays in brain development have been noted (Taylor and Pfohl, 1985; Toth *et al.*, 1990). More recently, it appears that these two effects may be independent (Toth *et al.*, 1990). These data have led EPA to propose an MCL of 1 mg/l.

Ozone is not stable in water and is virtually dissipated before it reaches the tap. Therefore, direct toxic effects of ozone experienced via other routes of exposure are not relevant to the use of ozone in drinking water.

Based on available data, it appears that there is little to fear from residuals of proposed alternate disinfectants at the minimum concentrations required to effectively disinfect drinking water. Therefore, questions about the relative safety of chemical disinfectants must primarily address the toxicology of by-products.

Hazards associated with by-products

Chlorination

By-products of the disinfectants fall into two classes, inorganic vs. organic (Table 2). The organic by-products can be further divided into halogenated and non-halogenated compounds.

The focus of research on chlorination by-products has been very heavily on the halogenated organic by-products. This is primarily because the presence of halogen on a compound served as a clear marker of reaction with chlorine, not because halogenated organic compounds are the more important from a toxicological point of view. The relative ease of detecting halogenated compounds also accounts for the much greater knowledge about chlorination by-products than for the alternatives.

The by-products of chlorine that have received the most study are those in the trihalomethane, haloacetic acid and haloacetonitrile classes. This is because these compounds account for a sizable fraction of the total organic halogen (TOX) produced in the chlorination of drinking water.

Although these compounds have a variety of toxicological effects, it is their ability to induce cancer in experimental animals that drives the risk assessments. In Table 5, by-products of disinfection that have been shown to produce cancer are identified. Some indication of the concentrations that occur is provided by listing of a expected median and highest concentrations reported. Since survey data that is available is quite limited for some of these compounds, the figures should be taken simply as a measure of the relative importance of the by-product. The extent to which the compound becomes a critical by-product depends upon how closely the concentration approaches one which will give rise to a risk estimate of 1 extra cancer case per 10,000 population in a lifetime using the upper 95% confidence limit of the linearized multistage model (10^{-4} lifetime risk). This is the concentration that corresponds to the highest risk at which the Office of Drinking Water has declared it will set an MCL.

With the exception of bromate and hydrogen peroxide, all of these by-products in Table 5 can be produced by chlorination. However, only bromodichloromethane (BDCM), dichloroacetate (DCA) and trichloroacetate (TCA) are found at median concentrations that approach those calculated to increase cancer risk to 10^{-4} in a lifetime. Obviously, this means that many systems may significantly exceed these concentrations with a corresponding greater risk.

Based on our current knowledge, the cancer risks attributed to chlorination are going to be dominated by the haloacetates. Therefore, it is very important to determine whether the crude estimates of risk made for these compounds using the linearized multistage model are dependable.

The basic problem with the linearized multistage model can be illustrated in Figure 1. The curves are drawn to indicate the quantitative relationship between actual experimental data (from DeAngelo *et al.*, 1991) that demonstrates that DCA was carcinogenic in mice and the extrapolation to a selected risk level in drinking water. Clearly positive results were obtained at concentrations of 3.5 and 5 g/l. No significant effects was observed at 0.5 g/l (although a recent report [Daniel *et al.*, 1992] utilizing longer exposure times does demonstrate a carcinogenic response at this dose) and an apparently anomalous response was observed at a dose of 0.05 g/l. When EPA utilizes the upper 95% confidence limit of risk from application of the linearized multistage model to these data, it can be roughly modelled by simply drawing a straight line through a hypothetical 0,0 intercept. In the case of DCA there is a factor of 166,000 between the concentration estimated to give rise to an extra cancer case per million population in a lifetime and the lowest dose giving a positive response. This factor is actually smaller for DCA than for many other compounds because testing extended significantly below the maximally tolerated doses. The problem is that there is no practical means of actually confirming the validity of these estimates either in epidemiological studies of human populations or in controlled studies in experimental animals.

Since the risks at low doses cannot be confirmed empirically, an alternate approach must be taken to determine if these risks are real. Three basic questions must be answered:

- How likely is the carcinogenic response observed in experimental animals to be produced in exposed humans?
- Is the mechanism by which the chemical produces cancer consistent with the default assumptions embodied in current applications of the linearized multistage model?

- Do the brominated analogs of DCA and TCA possess the same types of toxicological properties?

While answers to these questions are not in, it is interesting to note that the answers appear quite different for the members of this class for which we have appropriate data.

With these principles in mind, TCA should not be treated as a human carcinogen for at least two reasons:

- it has only been shown to produce cancer in a single species to date:

- it has been shown to be a peroxisome proliferator (DeAngelo *et al.*, 1989).

Chemicals that are peroxisome proliferators in rodents do not elicit this same response in humans, apparently because humans lack a functional peroxisome proliferator activated receptor (PPAR), a protein that has been identified in rodents (Isseman and Green, 1990). As a consequence, peroxisome proliferators are not thought to present a carcinogenic hazard to humans. This conclusion is supported by a variety of experiments showing that primary hepatocytes of rodents respond to these compounds with a proliferation of peroxisomes, but human cells do not respond. The major concern about this hypothesis is that the causal link between proliferation of peroxisomes and the induction of cancer has not been established. It is of concern because the ability to induce peroxisomes frequently does not parallel the carcinogenic potency of these compounds in rodents (Keith *et al.*, 1992).

DCA is also a weak peroxisome proliferator (DeAngelo *et al.*, 1989). With further study, it has become clear that the carcinogenic doses of DCA are significantly below those which induce peroxisome synthesis (Bull *et al.*, 1990a; DeAngelo *et al.*, 1991). Moreover, DCA produces liver tumours in rats as well as mice (DeAngelo, personal communication). Therefore, the causes of cancer produced by DCA are probably very different from those of TCA and cannot be so easily dismissed.

A question requiring immediate attention with chlorination is whether the brominated analogs in the haloacetate and other groups (Table 4) are more or less carcinogenic than their chlorinated analogs. In waters containing trace amounts of bromide a variety of mixed bromochloro and bromo organic compounds are produced with chlorination. Preliminary experiments in our laboratory with bromochloroacetate (BCA) indicate that it produces non-cancer effects that are very similar to those produced with DCA (i.e. large accumulations of glycogen in hepatocytes which we believe is indirectly associated with the carcinogenic effects of this chemical), but clearly produces no increase in the numbers of peroxisomes. Conversely, dibromoacetate (DBA) produces little evidence of glycogen accumulation in hepatocytes, but does induce the synthesis of peroxisomes. Bromodichloroacetate (BDCA), however, behaves very differently than either DCA or TCA, producing neither accumulations of glycogen nor peroxisome proliferation. However, it does cause rather large increases in the rate at which normal hepatocytes divide. If these three analogs are all shown to be carcinogenic, it is probable that three distinctly different mechanisms are involved. These mechanisms will each have their own implications on the methodology that should be used to estimate risks at low doses.

A recently recognized problem with chlorination is the fact that hypochlorite solutions generate considerable quantities of chlorate on standing. There are no specific data to indicate that the levels of chlorate that would end up in drinking water would be hazardous to human health. However, the data available in the open scientific literature on chlorate is very sparse and inadequate to project a safe level. For this reason, the Science Advisory Board of the US EPA argued against establishing an MCL for chlorate until better data could be generated. In the interim period a health advisory (HA) of 400 µg/l (Table 4) has been suggested. Since this by-product has not been adequately tested, this limit could change dramatically as soon as adequate toxicological data becomes available. This is of some concern since the brominated analog of chlorate, bromate, is clearly a carcinogen (IARC, 1987).

Chloramination

The by-products of chloramination are thought to be largely similar to those that are produced by chlorination, but at generally lower concentrations. The one exception to this is cyanogen chloride, whose formation depends upon there being a source of ammonia in the water (Ohya and Kanno, 1985). It is formed at significantly higher concentrations than in systems utilizing only chlorine. The concentrations observed are still rather modest, usually in the low µg/l range. There is little data on this compound relevant to the development of a drinking water standard (Bull and Kopfler, 1991).

Chlorine dioxide

The only by-products of chlorine dioxide that are known to present some difficulties to its use are chlorate and chlorite. Avoiding production of these compounds in drinking water disinfected with chlorine dioxide is virtually impossible. Some recently initiated research is examining the possibility that chlorite might be rather straight-forwardly removed from the drinking water. This does not appear to be feasible with chlorate.

There is a reasonably good data base to show that chlorite induces hemolytic anaemia in a variety of animal species. The proposed MCL was developed based on a very subtle effect (i.e. depressed red cell glutathione concentrations) observed at doses below those producing measurable decreases in hematocrit or red blood cell concentrations (Heffernan *et al.*, 1979). Therefore, even though a smaller margin of safety was utilized in calculating the MCL, it should be adequately protective.

The situation with chlorate from chlorine dioxide is essentially the same as identified in discussing hypochlorite solutions above. Rather sizable concentrations might be encountered in drinking water treated with chlorine dioxide under certain circumstances. Therefore, it is very important that the toxicological hazards associated with this compound be established.

Ozone

The by-products of ozonation have been poorly characterized and quantified. There are data to indicate that the nature of the by-products produced with ozone vary considerably with the concentration added. For example, low doses of ozone have been shown to produce by-products which induce mutations in *Salmonella* tester strains whereas higher concentrations do not (Cognet *et al.*, 1987).

Ozone produces brominated by-products in drinking waters that contain small amounts of bromide (Krasner *et al.*, 1989). These are generally brominated analogs within the same classes of chemicals produced by chlorination. Except for bromoform, however, the toxicology of these compounds has not be characterized. Without whole animal carcinogenesis bioassays, it is impossible to determine if these chemicals are more or less hazardous than their chlorinated analogs. Of particular concern, are the bromine containing acetic acids discussed earlier.

Bromate is an inorganic by-product that has only been associated with ozone to date (Bull and Kopfler, 1991). This compound has been shown carcinogenic in rats and hamsters (IARC, 1987). Applying the linearized multistage model to estimate the probability of induction of cancer at low doses, bromate is almost an order of magnitude more potent as a carcinogen than the next most potent by-product (Bull and Kopfler, 1991).

The mechanism by which bromate induces cancer has not yet been established. A number of studies have demonstrated that it does possess genotoxic activity. It has been shown to be mutagenic in the *Salmonella* tester strain, TA100, in the presence of a metabolic activating system and to produce chromosomal aberrations in a Chinese hamster fibroblast cell line (Ishidate *et al.*, 1984). It also produces micronuclei in polychromatic erythrocytes of mice *in vivo* by both intraperitoneal and oral methods of dosing (Hayashi *et al.*, 1988; Hayashi *et al.*, 1989). Consequently, bromate does have genotoxic properties. However, it is not clear how this activity is related to the induction of renal tumours.

Studies reporting carcinogenic responses did not indicate the extent to which non-tumour pathology was associated with doses that induced tumours (Kurokawa *et al.*, 1983; Takamura *et al.*, 1985; Kurokawa *et al.*, 1986a), although renal tubular damage was an acknowledged finding in these studies (Kurokawa *et al.*, 1986b). The results of human poisoning cases also indicate that bromate has a high potential for producing renal tubular cell necrosis (Kuwahara *et al.*, 1984; Warshaw *et al.*, 1985; Lichtenberg *et al.*, 1989).

Fujii *et al.* (1984) reported that unchanged bromate could be found in the urine of rats administered oral doses of bromate in doses of 5 mg/kg and above. Thus, bromate appears to have sufficient stability to be absorbed and induce oxidative stress in the kidney at high doses. Some support for this hypothesis was recently obtained by Kasai *et al.* (1987) who detected oxidative damage in renal DNA isolated from rats treated with high oral doses of bromate. Single intraperitoneal doses of 40 mg/kg and above produce significant increases in the levels of 8-hydroxydeoxyguanosine in renal DNA (Sai *et al.*, 1991) and was closely associated with increased lipid peroxidation.

It is of interest to note that the dose-response relationship between renal tumour induction and bromate dose is suggestive of a threshold response. As the daily dose increases from 2.4 to 5.3 mg/kg, there is a large increase in tumour incidence (Kurokawa *et al.*, 1986). While the numbers of animals per group were limited in this study (i.e. effective numbers per group ranged from 19 to 24 animals), the overall shape of the curve suggests that something important occurs at approximately 5 mg/kg. This is remarkably close to the doses at which unchanged bromate is detectable in urine. Such behaviour would be expected at a point where antioxidant defences become overwhelmed.

Mixed disinfectants

Utilization of mixed disinfectants is just now being investigated. Most frequently, this involves the use of ozone followed by addition of either chlorine or chloramine. Chlorine dioxide might also be followed with these two disinfectants. It is not yet clear whether altogether new by-products might arise from this practice. However, some normal by-products of chlorination have been reported to be decreased, while others have increased (Bull and Kopfler, 1991). Until there are more thorough evaluations of these processes, it will not be possible to determine whether they increase or decrease risks associated with disinfection.

Identification of critical by-products

Based on current information, DCA and TCA are the chlorination by-products of most concern. It may be predicted that the calculated hazards with chlorination will be significantly increased when bioassays of the brominated acetic acids have been completed. Consequently, it is likely that this class of by-products will increase the median calculated risks of chlorination of drinking water significantly above 1 additional cancer case in a population of 10,000 in a lifetime. This may force suspension of chlorine as a disinfectant. However, it must be said that the risks due to this compound at low doses are not sufficiently well characterized to suspend the usage of this very important disinfectant.

Bromate is clearly the critical by-product with ozonation. The concentrations present are dependent on the bromide concentration, but there is also a complex relationship with the availability of substrate for organic substitution of bromine. There is unpublished evidence that removal of natural organic material in water to reduce formation of brominated organics enhances the formation of bromate. If monitoring data indicate that bromate routinely occurs at concentrations above 5 µg/l in waters that have relatively modest concentrations of bromide, ozone may not be usable in such supplies. Again, it is extremely important to understand how bromate induces cancer and determine whether the linearized multistage model is the appropriate methodology for estimating cancer risks from this compound to low doses.

There must also be some concern about the potency of brominated analogs of the haloacetates when ozonation is employed. However, dibromoacetate appears to be the major by-product since ozone does not appear capable of activating chloride.

Discussion

A certain level of frustration crops into analysis of important problems in environmental health. The urgency of finding the appropriate answers inevitably seems to become confounded in a problem that is much more complex than originally thought. This is certainly the case with disinfection by-products. Based on current data, it is already clear that this process introduces significantly greater risk of cancer from drinking water when considered on a national basis than any other source of contamination of the aquatic environment. However, the true estimates of how great this risk is remains illusive.

The history of disinfection by-products is a lesson on how the regulatory process tends to interfere with the solution of an environmental problem. The naiveté with which regulatory agencies, such as the USEPA, initially approached this problem is partially responsible for the dilemma that the industry now finds itself. Rather than initiating a broadly based program to investigate this problem, the first efforts were simply directed at determining whether disinfectants could be identified that did not produce trihalomethanes. This resulted in some rather dramatic changes in disinfection practice, but not necessarily all of the changes were in desirable directions. In particular, many utilities switched to the use of chloramines as their disinfection to reduce disinfection by-products, but probably to the detriment of the microbial quality of their product water. It took considerable time to recognize the simple fact that all commonly used disinfectants are reactive and will inevitably produce reaction products. Given this situation, it should not have been surprising that some of the by-products of alternate disinfectants

would have toxic effects as well. This partially accounts for the fact that the dimensions of the problem and the challenge that it presents to the risk assessment community are only now receiving the attention they need. 18 years later. There is now a large body of research information that has been developed in laboratories around the world by a relatively small group of scientists and engineers. Despite a respectable mound of data, however, there is considerable work that is needed before this problem can be resolved. This is in part because so much of the research has focused on the effects that are produced with individual disinfectant by-products with too little attention paid to integrating the many different types of hazards that are really involved in choosing between different disinfection processes. Moreover, these effects must placed into the larger context of delivering potable water in systems of varying size and with source waters of different quality.

It is essential that work goes on to define the toxicological properties of the individual by-products. This work, however, needs to be fit into a framework that provides for efficient investigation of the hazards associated with each disinfectant strategy, including the microbial hazards. From a by-product standpoint, this starts with an efficient screening program to identify those compounds that are of greatest importance. Compounds identified as important based on their concentration in finished water or from the screening of their toxicological properties should tested in systems that provide the appropriate dose-response information for estimating their contribution to adverse health effects. Those chemicals that appear at concentrations that would limit the utilization of a particular disinfectant should be studied to determine their mechanism of action and comparative metabolism. Then risk assessment models appropriate to the extrapolation of these data to the levels found in drinking water should be developed and applied. Finally, however, regulatory agencies should regulate this area sparingly until there is either evidence of imminent hazard or until the issue is resolved.

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Table 1. Sources of uncertainty in assessing risks from disinfectant by-products.

1. The chemical nature of by-products and their concentrations in drinking water are unknown.
2. Absence of toxicological data on established by-products.
3. Inadequate understanding of the mechanisms of toxicity:

   Does effect in the test system occur in humans?
   Can the effect occur at doses that would be encountered in drinking water?
   What is the basis for determining variability in sensitivity?
4. Poor definition of effective dose.
5. Interactions between contaminants.

Table 2. Classes of disinfectant by-products.

		Organic	
Disinfectant	Inorganic	Halogenated	Non-halogenated
Chlorine	Chlorate	Trihalomethanes Haloacetates Haloacetonitriles Haloaldehydes Haloketones Halofuranones Chloropicrin	Aldehydes Carboxylic Acids
Chloramine		Cyanogen chloride Others generally thought to be the same as chlorine, but lower conc.	
Chlorine Dioxide	Chlorite Chlorate	Not well characterized	
Ozone	Bromate Hydrogen Peroxide	Bromomethanes Bromoacetates Bromoaldehydes Bromoketones Iodinated analogs	Aldehydes Carboxylic Acids

Table 3. Potential health effects of disinfectants.

Disinfectant	Health effect	NOAEL/LOAEL[a]	Proposed MCL[b] (mg/l)
Chlorine	Non-specific effects	NOAEL 16.7 mg/kg[c]	6
Chloramine	Non-specific effects	NOAEL 9.6 mg/kg[d]	4
Chlorine	Depressed thyroxine levels	LOAEL 14 mg/kg	1.0
Dioxide	Delayed brain development	LOAEL 14 mg/kg	
	Hemolytic Anemia	Inconsistent results	

a NOAEL/LOAEL = No observed adverse effect level/Lowest observed adverse effect level.

b MCL = Maximum contaminant level.

c Daniel *et al.* (1991).

d NTP (1990).

Table 4. **Potentially[a] carcinogenic by-products of drinking water disinfectants.**

By-product	Disinfectant	Probable regulatory range µg/l[b]	Expected median conc.[c]	Highest reported conc.[d]
Trihalomethanes				
Trichloro-	HOCl, $ClNH_2$	9 - 900	26	470
Bromodichloro -	HOCl, $ClNH_2$	0.5 - 50	9.1	180
Dibromochloro -	HOCl, $ClNH_2$	Considered NC[e]	5.7	280
Tribromo-	O_3, HOCl, $ClNH_2$	5 - 500	4.4	280
Haloacetates				
Dichloro-	HOCl, $ClNH_2$	0.3 - 30	23[f]	79
Trichloro-	HOCl, $ClNH_2$	Considered NC[e]	20[f]	103
Aldehydes				
Trichloroacetaldehyde	HOCl, $ClNH_2$	0.6 - 60	6	19
Formaldehyde	O_3, HOCl, $ClNH_2$	NC oral route[g]	8	30
Acetaldehyde	O_3, HOCl, $ClNH_2$	NC oral route[g]	2	10
Miscellaneous				
Bromate	O_3	0.05 - 5[h]	5	33[i]
Hydrogen Peroxide	O_3	Considered NC[e]		
2,4,6-Trichloro-phenol	HOCl	38 - 3800	<1	2
Chloropicrin	HOCl	Considered NC[e]	0.8	1.5

a Potentially carcinogenic means that the chemical has been shown to be carcinogenic in at least one species of experimental animal.

b Where carcinogenicity data is judged to be a probable carcinogen for man by EPA criteria, a regulatory range has been calculated that approximates the concentrations calculated to give rise to one additional cancer death per 10,000 to 1,000,000 population in a lifetime.

c Expected mean concentration equal to that found as a mean in national surveys. See Bull and Kopfler (1991) for sources of the data.

d Highest concentration reported in a drinking water. See Bull and Kopfler (1991) for source of data unless otherwise noted.

e Considered NC = considered non-carcinogenic on lack of evidence. Usually because it produces tumours in only one species.

f Technical Support Division, Office of Drinking Water, US EPA Cincinnati, OH. Data supplied to the EPA SAB in April of 1992.

g NC oral route means that these compounds have tested negative in well designed carcinogenesis bioassays utilizing the oral route of exposure.

h EPA draft criteria document for bromate, 1992.

i Krasner *et al.* (1992).

Table 5. Potential health effects for inorganic by-products of disinfectants.

Disinfectant	Health effect	NOAEL/LOAEL	MCL(HA)[a] µg/l
Chlorite	Oxidant damage to RBC	NOAEL = 1 mg/kg	400
Chlorate	Poorly studied	NOAEL = 0.04 mg/kg[b]	400
Bromate	Renal cancer	See Table 4	See Table 4
Hydrogen Peroxide	GI tumours	See Table 4	See Table 4

a MCL = maximum contaminant limit, (HA) = health advisory suggested by EPA's Drinking Water Committee of the SAB as interim measure to the Office of Drinking Water.

b Results from study in humans where no higher doses were utilized. Therefore, an effect level has not been determined. However, higher doses do produce lethal effects in animals.

Table 6. By-products that have been detected in drinking water that are structurally related to carcinogens or which are mutagenic, but have not been appropriately tested.

By-product	Disinfectant	Expected mean conc. µg/l	Reported conc. µg/l
Haloacetates			
Bromo-	HOCl, $ClNH_2$, O_3	<0.5[b]	1.6[b]
Bromochloro-	HOCl, $ClNH_2$	3.2[b]	17
Bromodichloro-	HOCl, $ClNH_2$	Not reported	
Dibromochloro-	HOCl, $ClNH_2$	Not reported	
Dibromo-	HOCl, $ClNH_2$, O_3	<0.4[b]	6.9[b]
Tribromo-	HOCl, $ClNH_2$	Not reported	
Haloacetonitriles			
Dichloro-	HOCl, $ClNH_2$	2.0	24
Trichloro-	HOCl, $ClNH_2$	Detected	
Bromochloro-	HOCl, $ClNH_2$	0.5	10
Dibromo-	HOCl, $ClNH_2$, O_3	0.5	2.5
Miscellaneous			
Chlorate	HOCl, ClO_2	100 - 1000	Unknown
1,1-dichloropropanone	HOCl	0.5	1.4
1,1,1-trichloropropanone	HOCl	0.6	2.2
3-Chloro-4-(dichloro-methyl)-5-hydroxy-2(5H) furanone	HOCl	0.005	0.067

a Studies from which figures were derived are identified in Bull and Kopfler (1991), unless otherwise noted.

b Technical Support Division, Office of Drinking Water, US EPA Cincinnati, OH. Data provided to the EPA SAB in April, 1992.

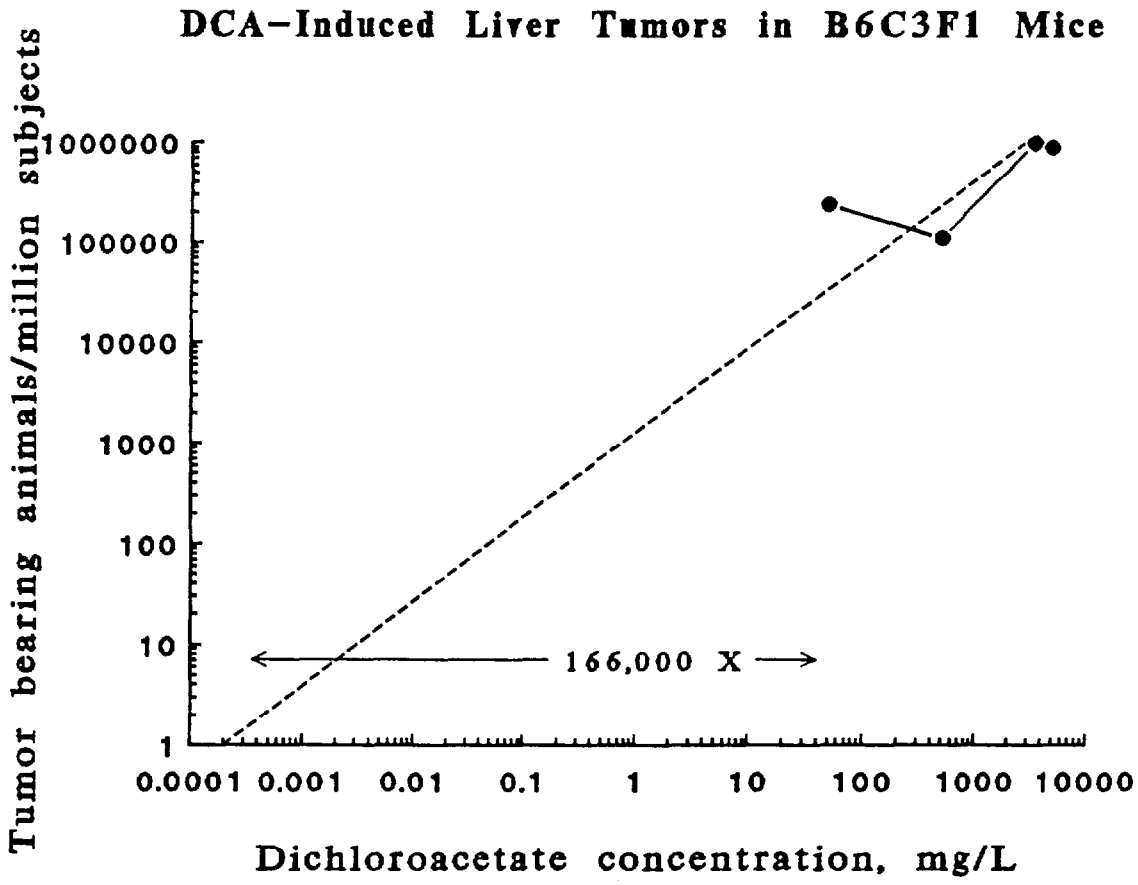

Figure 1. Relationship between experimental data demonstrating a carcinogenic response to dichloroacetate in B6C3F1 mice and concentration in drinking water calculated to produce one additional cancer case per million population per lifetime (Taken from data of DeAngelo *et al.*, 1991).

SOME RECENT UK OBSERVATIONS ON BROMATE FORMATION IN NATURAL WATERS

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Introduction

Bromate is a suspected carcinogen and is included in the World Health Organisation Guidelines for drinking water due to be published in May 1993. The WHO has set a provisional guide value of 25 µg/l taking account of some of the analytical problems associated with the determination of bromate at low levels in drinking water. Based on the use of low dose extrapolation models, an upper 95% confidence limit risk of 1 in 10^5 of the population gives rise to a value of 3 µg/l.

Oxidants used in water treatment such as ozone can react with bromide in natural waters to produce bromate.

Although the increase in the use of ozone has highlighted the problem with bromate production it is possible that the use of chlorine could also give rise to significant levels of bromate in drinking water. Chlorine will oxidise bromide to hypobromous acid but further oxidation of the hypobromous acid to bromate is not thought to occur. However, bromate has been detected in hypochlorite solutions. It is not clear whether the bromate found was the product of the manufacture of the hypochlorite or resulted from storage of the solutions.

The use of one site electrolytic chlorine generation is another potential source of bromate. The brine used in the generator cells will inevitably contain bromide which can undergo electrolysis to form bromate.

However, it remains likely that it will be through the use of ozone that the highest concentrations of bromate will occur. There is little information available concerning the occurrence of bromate in ozonated waters or on the factors which control its formation.

In the UK a number of utilities have supported a WRc Common Interest Research Programme (CIRP), project number U-0415 "By-Products of Ozonation" which includes bromate formation as a key study area. In addition, Thames Water Utilities Ltd (TWUL) has commenced work on bromate analysis and occurrence within its in-house research programme.

Some observations arising from this work are shown in Tables 1 and 2.

Analysis of bromate

WRc have evaluated and developed EPA method 300 for the analysis of bromate. Thames Water laboratories implemented this method at the end of 1992. The limit of detection is currently found to be 1-2 µg/l by both laboratories with 1.6 µg/l being quoted by WRc.

Summary of analytical method for bromate

The conditions used for the analysis of bromate were as follows:

Instrument	Dionex DX300
Column	AS9SC column and AG9SC guard column
Concentrator	TAC-2
Eluant	8 mM sodium bicarbonate
Flow rate	1 ml/min
Injection volume	500 µl
Temperature	Ambient
Detector	Conductivity
Suppressor	Anion micro membrane
Suppressor regenerant	50 mN sulphuric acid
Suppressor flow	5 ml/min
Detection limit	1.6 µg/l
Purge eluant	4 mM sodium carbonate and 1.5 mM sodium bicarbonate
Purge programme	100% 8 mM sodium bicarbonate for 6 mins, purge with purge eluant for 5 mins then re-equilibrate with sodium bicarbonate for 20 mins.
Sample preparation	Filter 10 ml deionised-distilled water through a GF/F filter paper and discard. Filter 10 ml sample and discard. Filter a further 10 ml of sample and collect. Filter 8 ml of sample through a prewashed Maxi-Clean IC-Ba cartridge (30 ml distilled-deionised water). Discard the first ml, collect the remainder. Filter the sample from IC-Ba cartridge through a prewashed Dionex On-Guard Ag cartridge (5 ml distilled-deionised water). Discard the first 2 ml and collect the remainder for IC analysis.

Results and discussion

A number of pilot plants using combinations of ozone, hydrogen peroxide, granular activated carbon and conventional treatment have been surveyed by WRc using the above analytical techniques for bromate. A few full scale plants using conventional gas chlorination or on-site electrochemically generated sodium hypochlorite have also been surveyed either by WRc or Thames Water. The Kempton Advanced Water Treatment Plant (AWT) has also been subjected to intensive bromate formation studies over the 6 month period August 1992 to January 1993.

Some of the findings are summarised in Table 1 and expanded in detail for some ozonation sites in Table 2. Most of this data was obtained between August and October 1992. Winter data from the Kempton AWT plant has shown a marked reduction in bromate formation under similar bromide and ozonation conditions (Figure 1). This is so far unexplained. It is noted that in the summer high bromate formation did not correspond with expected bromide reductions at some lowland sites. A "bound" bromide precursor not detectable by the ion-chromatography method has been hypothesised as an explanation.

The combination of ozone and peroxide added together at Kempton AWT has so far produced consistently low (<6 µg/l) bromate when ozone alone exceeded 20 µg/l bromate (Figure 2). Conflicting results are reported by other UK and US researchers.

In all cases where ozone has been added with no observable residual within the reactor then bromate has been less than or equal to 3 µg/l. This mainly applies to pre-ozonation conditions.

Reducing agents such as sulphur dioxide and sodium metabisulphite have had little effect on reducing preformed bromate.

Granular activated carbon (GAC) in virgin condition has been found to reduce bromate for a short (uneconomic?) period so far undefined. GAC operated for any significant period of weeks or months loses this capability even with 30 minutes contact.

Conclusions

1. A method for the analysis of low levels of bromate in drinking water has been developed. The detection limit of the method is 2 µg/l although it is possible to detect the presence of bromate down to about 1 µg/l.

2. A survey of bromate concentrations in water taken from ozonation pilot plants indicated that bromate could be produced under typical ozonation condition. The levels found varied between <1 and 98 µg/l.

3. Ozone dose, contact time and the presence of an ozone residual all appear to affect the level of bromate produced.

4. Lowering the pH at which ozonation takes place reduces the concentration of bromate produced.

5. The effect of using hydrogen peroxide in conjunction with ozone is unclear. Results from one pilot plant indicate that a reduction in bromate production can be achieved using an excess of peroxide. Other results indicate that the use of peroxide can cause an increase in bromate formation.

6. No threshold level of bromide in the source water appears to be required before bromate production can occur. In waters with a low organic content and ozone demand, the presence of a relatively large ozone residual could result in the production of bromate despite the presence of very low levels of bromide in the raw water.

7. Once formed, bromate is not removed by currently available treatment such as sulphur dioxide or granular activated carbon.

8. Bromate formation has not been observed at the current limit of detection from the use of gas chlorine.

9. Bromate formation has been observed during on-site generation of sodium hypochlorite. The levels are of the order of 1-2 µg/l of bromate per mg/l of chlorine applied.

10. Current methods of bromide analysis by ion chromatography may not identify all potential bromine containing precursors to bromate formation in natural waters.

Acknowledgments

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Table 1. Oxidation of UK natural waters - observed bromate levels.

Oxidation process	Bromate µg/l
Gas chlorination	<1
Electrochlorination	<1 to 10 (Approx 2 µg/l bromate per 1 mg/l chlorine)
Commercial hypochlorite	No data from UK yet
Ozonation	< 1 to 98
Ozone + hydrogen peroxide	2 to 12 (inconsistent between sites)

Table 2. Bromide and bromate (µg/l) survey; UK trial sites.

Sample point	Site A BrO_3	Site A Br	Site B BrO_3	Site B Br	Site C BrO_3	Site C Br	Site C BrO_3	Site C Br	Site D BrO_3	Site D Br	Site D BrO_3	Site D Br	Site E BrO_3	Site E Br	Site E BrO_3	Site E Br
Date sampled			19/8/92		2/10/92		16/10/92		7/9/92		19/10/92		12/10/92		29/10/92	
Raw water	<1	82	<1	77	<1	176	<1	185	<1	104	<1		<1	46	<1	46
			<1	81	<1	188	<1	181	<1		<1		<1	45	<1	50
Pre-ozone	<1	101	2	77	<1	177	<1	200	<1	104	<1		<1	<20	<1	22
			3	77	<1	182	<1	206	<1		<1		<1	35	<1	24
Main ozone	4	84			20	178	29	155	60	94	20		1	24	1	41
					19	169	28	168	59	94			<1	34	<1	25
SO_2/bisulphite	7	81							60	91	22					
									59		22					
GAC filters	6	82	3	79	23	189	42	178	45	101			2	26	6	34
			2	84	21	177	41	167	46				2	50	6	1
													SSFs		SSFs	
					22	178	27	176					No GAC		No GAC	
					27	181	27	181								
Chlorination	5	33			18	30	35	35			Tertiary					
					19	30	33	35			Ozone					
											94					
Distribution 1	5	<20									98					
Distribution 2	6	<20														

Operating conditions

Raw water		River	River	River	River	River		
pH	7.8	7.5			8.6	9.0		
Hardness		Hard	Hard	Hard	Hard	Hard	Soft	Soft
Alkalinity								
TOC mg/l		Low			~5	~5	High	High
Ammonia µg/l					<50	<50		
Temperature					16.3	11.8		
Pre-ozone								
Dose mg/l	1.2	3.0	1.0	1.0	1.8	1.3	2.0	2.0
Residual mg/l	0.0				0.0	0.0		
Contact mins		5-10	8.0	8.0	6.0	4.0		
Main-ozone								
Dose mg/l	8.4		2.5	2.5	2.9	2.4	2.0	4.0
Residual mg/l	0.5		0.5	0.5	0.5	0.6		
Contact mins			9.0	9.0	13.0	10.0		
GAC filters								
Contact mins					30.0	20.0		

SUMMARY OF DISCUSSION - DAY 1

The discussion on the first day largely centred around public perception of drinking water quality and the issues involved in this subject. A summary is provided below under four main subject areas:

- Public education
- Bottled water
- Risk assessment
- Cost

Public education

The issue of how the public become involved in the debate on drinking water quality was discussed in detail. It was noted that the public are generally not aware of the background to most of the issues, but that the subject is of great interest, simply because all of us are 'consumers'. Given that the public are involved, the onus was felt to be on the water supplier to provide more (and better) information on the range of issues covered by the general phrase "drinking water quality". Too often the only sources of information have been pressure groups and a press inevitably looking for 'problems'. It was pointed out that customer queries and complaints that are met on an individual basis, often result in a satisfied customer who, for example, would then understand the need for disinfection. In the US, the law requires public notification of any changes in water treatment and standards. The question clearly remains, however, whether the public take any notice or indeed understand the reasons for the changes. Political action groups are powerful in the US and put pressure on Congress. The action groups do not necessarily look in depth at the issues or consider what the public think, but assume that the public have an intrinsic right to 'pure' drinking water. The concept that there is no such thing as 'pure' water and that the aim is to provide safe water needs to be emphasised. No specific conclusions were reached during the discussion, but it was generally agreed that there is an urgent need to educate consumers and that water suppliers have a prime role in this context.

Bottled water

The reasons for the recent popularity of bottled water were discussed. People often assume that bottled water is safer than tap water, with many in some countries (ca 30%) only drinking bottled water. There is some doubt whether a persons preference for bottled water arises from health concerns or simply that they like the taste. If the latter is the case, then the water suppliers have to improve the taste of their product in order to compete. However, it was also recognised that tap water and bottled water were different products and should not really be in competition. It was suggested that the use of ozone might improve taste and odour of drinking water, making it more acceptable to the consumer. Chlorinous taste problems remain one of the major areas of public complaints, although it was recognised that some people feel that a chlorine taste provides reassurance that the water is safe to drink. Risk assessments have not been carried out on bottled water - possible concerns include leaching from the plastic bottles, high mineral concentrations and microbial content. It was pointed out that further legislation for bottled water was being considered.

Risk assessment

The concept of risk assessment (in this context the relative risks from the presence of disinfection by-products (DBPs) in water relative to microbiological safety) needs to be explained to the public - however, it is a complicated area. Risk assessments should also be carried out for other water uses (e.g. showers, cooking). The perceived risk of cancer is very much greater than that of water-borne microbial disease. This is partly because people probably have faith in medical science being able to fight water-borne microbial diseases, but also because there is a much greater fear factor with cancer; everyone probably knows of someone who has died from cancer, but typhoid and cholera etc. have been virtually eradicated in the West. It is important that the public are made aware of the very real risks posed by ineffective disinfection, and how they compare to the theoretical health risks from DBPs in drinking water. The high impact of cancer on public perception must not be underestimated (contrasted with e.g. the impact of lead). The media play a critical role in influencing the public and it is possibly through the media that the balance will have to be redressed. It was suggested that there were clearly much greater risks in life than drinking tap water. However, people have to drink water and therefore feel that it should not pose any risks, whereas other risks can be minimised through choice.

Costs

Any costs involved in imposing tighter standards for DBPs in drinking water will ultimately be met by the consumer. Will the consumer choose to pay for higher standards or prefer cheaper water with less stringent standards? Again, any useful consumer input has to be obtained from informed sources and this reinforces the need for education. The public should be told of the cost of improving standards, but in a way that they will understand. In order to do this, the water suppliers need to produce costs related to tangible, and recognisable, benefits to the consumer. A reduction in overall risk may not mean much to the average consumer, who is probably far more interested in improvements in palatability. The main concern of consumers will be the taste, odour and appearance of their drinking water. These features could well be relatively unaffected by the extensive investment in methods for reducing levels of DBPs.

In the US, statutes govern any change to water treatment practice. The main goal is that an acceptable risk should be 'zero', and hence regulations are introduced that are aimed at achieving this. The public are not involved directly in this decision making process, although they are consulted.

STRATEGIES FOR DISINFECTION BY-PRODUCT REMOVAL AND METHODS FOR MINIMISING THEIR FORMATION

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New regulations are being considered by the US Environmental Protection Agency and the World Health Organisation concerning a variety of disinfection by-products (DBPs) formed during chlorination as well as oxidation processes: haloacetonitriles, haloketones, haloacids, chloropicrin, low molecular weight aldehydes and so on. Many surveys to assess the presence of such products in drinking waters are underway. This renewed interest for DBPs stems from their suspected carcinogenic or mutagenic properties. In addition to possible long term health effects, specific DBPs may also induce immediate water quality deterioration due to their objectionable organoleptic properties or cause bacterial regrowth problems in networks due to their ability to be used as a substrate by micro-organisms.

This paper will discuss the possible strategies for minimising the presence of DBPs in drinking waters. In fact, it is difficult, if not impossible to single out any one type of strategy that is generally applicable to all situations. Existing treatment lines have very different natures according to:

- the condition and type of resource (Fig. 1);
- priorities established between quality objectives which may be different from one country to another;
- the plant treatment capacity (small plant in a rural area as opposed to large plant in an urban environment).

The different strategies developed as examples in this article correspond to the most complex case of surface water treatment.

What is the most suitable treatment line for minimising the formation of chlorinated DBPs through chlorination?

It is currently accepted that the amount of chlorinated DBPs is closely related to the simultaneous occurrence of free chlorine and organic precursors in the water. In the most classic situation of a treatment line including a preoxidation step using chlorine, followed by a clarification step, either direct filtration or coagulation-settling-filtration and final disinfection, several solutions are possible to limit the formation of DBPs:

Since coagulation removes some organic carbon and therefore certain organic compound precursors, it is possible to perform first chlorination treatment on settled water (1). However, this scheme is viable only for waters with small amounts of organic matter. Furthermore, it does not make it possible to benefit from the effects of chlorine during settling.

If the main objective of pre-chlorination corresponds to ammonium removal, it is possible to make use of the differences between the rapid reaction rates of chlorine with ammonium on one hand and the slower reaction rates of chlorine with precursors. Powdered Activated Carbon addition used shortly after chlorine application can make it possible to limit DBP formation.

By making further use of these differences between reaction rates in the case of surface waters that contain ammonium, it is possible to considerably decrease the quantity of DBPs by remaining immediately below the break point chlorine dosage, or even better at the monochloramine occurrence threshold. This is a viable solution if the raw water quality is not too critical and, above all, if the resource is not subject to abrupt variations.

When the raw water does not contain ammonium in noticeable amounts, ammonium can be added to the water so as to treat with chloramines. This is a practice described in the American literature (2), but that has been hardly used in France where ammonium removal is one of the priority objectives of water treatment. Because of the different reaction kinetics, the order of reagent addition is very important: ammonium addition prior to chlorine addition makes it possible to considerably limit by-product formation. Unfortunately, in the case of traces of iodide, ammonium addition must be performed after chlorination if iodinated

by-product formation is to be avoided. At very low concentrations, these products can give intense pharmaceutical flavours to the water (3).

As a conclusion, it is possible to partially limit the formation of halogenated by-products at the water pretreatment level through the control of such parameters as pH and ammonium concentration, but in most cases the raw surface water variability makes automation of these solutions very difficult, hence making these solutions temporary.

What are the available processes for the removal of halogenated DBPs?

If one accepts the necessity of pretreatment using chlorine so as to remove ammonium or to avoid any settling tank misfunction for instance, it becomes necessary to consider DBP removal. Since a certain number of surface water plants use granulated activated carbon (GAC) filtration or a combination of ozonisation and GAC filtration for removing trace organics such as pesticides, algae metabolites, etc., numerous works have been undertaken to evaluate the efficiency of such treatment lines. Since currently identified halogenated DBPs occurring in chlorinated waters belong to a wide range of chemical families (Fig. 2) (4), only a few general conclusions will be mentioned in this paper.

If oxidation by molecular ozone is hardly efficient, the combination ozone-hydrogen peroxide, which leads to the formation of hydroxy radicals turns out to be a very efficient treatment for MX removal, MX being the most mutagenic by-product currently identified (Fig. 3).

GAC filtration is not a cost effective option for TTHM (Total trihalomethanes) and trichloroacetic acid removal. Its efficiency amounts to 30 to 60% for the removal of haloketones and constitutes a satisfactory treatment for the removal of trihaloacetonitriles, chloropicrine and monochloro- and monobromo-acetic acids, provided that the empty bed contact time is long enough (5).

Other solutions can equally be considered. Neutralisation of residual chlorine by a reducing agent such as sodium disulfite leads to the destruction of some DBPs but not THMs. Stripping seems to be an efficient process for the most volatile compounds such as chloroform, but not for the most polar products (6).

In summary, since the combination ozone-GAC filtration does not turn out to be an efficient process except for the removal of some halogenated DBPs or certain other nuisances induced by pre-chlorination (Fig. 4) (7)) it is preferable to consider another strategy for perfect DBP control.

What are the alternative preoxidants?

Several preoxidants can be considered as a function of the treatment objective: disinfection, good clarifier operation, ammonium removal, algae removal, etc. The use of chloramines has already been discussed above. Potassium permanganate is sometimes used for manganese removal. Chlorine dioxide is hardly used, as it is often considered as unacceptable because of the potential toxicity of its inorganic by-products. The solutions currently adopted, at least in European countries, are mainly:

- the abandon of any oxidation prior to clarification treatment, with the possibility of temporary chlorination to solve transient situations such as unusual algae blooms;

- the use of preozonation that may have several advantages as a function of applied treatment rates. In the USA, a true oxidation treatment is applied with treatment rates at 1 mg/l and with relatively large contact times. The objective is then to perform a disinfection as well as complete as possible an oxidation of the organic matter, within a single step, i.e. without a post ozonisation step after the clarification step. In Europe and more specifically in France, preozonation is performed at much lower rates (0.2 mg/l ozone with relatively low contact times). The objective is then to increase the coagulation-flocculation efficiency with respect to organic matter and algae removal. Treatment lines generally include a post ozonisation followed by GAC filtration (8) (9).

Whichever solution is adopted, two problems remain:

- removal of the ammonium that may occur in raw water. This removal can be performed through biological nitrification that may occur within the settler or in the filters, provided that the water temperature is not too low and that the contact time in the filters is sufficient;

- the necessity of post-disinfection and, in many countries, the desire to maintain a disinfectant residual concentration in the distribution network right up to the consumers tap, which leads to the necessity to optimize organic compound precursor removal.

DBP precursor removal: myth or reality?

DBP precursor removal must be close to removal of the totality of organic matter in the water, whose concentration is evaluated by measuring the Total Organic Carbon (TOC) or Dissolved Organic Carbon (DOC). It is often forgotten that the least expensive method for reducing these parameters is still coagulation-flocculation-settling that it is possible to optimize to that end:

- coagulant rate adapted to organic matter removal instead of only particle removal;

- control of reagent addition rate through the use of transducers such as the streaming current detector (10);

- use of adapted coagulants such as poly aluminium chlorides (11).

Combinations of ozone- or ozone/hydrogen peroxide-GAC have been widely used and described in the literature since the beginning of the 80s, thus they will not be described here. The conclusions are very positive in general, but often give rise to contradictory conclusions from one water to another, for example in the case of determination of optimal ozonisation conditions. This comes most notably from the fact that experiments are only decided and evaluated as a function of surrogate parameters such as TOC, DOC, UV absorption, which leaves too large a part to empiricism. Optimization of DBP precursor removal necessitates a better knowledge of the organic matrix of waters.

Analytical techniques such as Pyrolysis-GC/MS make it possible to quantify relative concentrations of four large families of natural polymers that represent the essential organic matrix of surface waters: carbohydrates or polysaccharides, polyhydroxyaromatics, proteins or peptides and aminosugars (12). These four families have very different behaviour with respect to different oxidation or disinfection agents used in water potabilisation as shown in Table 1. This is why polyhydroxyaromatics and proteins correspond with a strong potential for halogenated by-product formation whereas carbohydrates do not react with chlorine. The example in Figure 5 illustrates this point. Applied to two fulvic acid samples available on the market, Pyrolysis-GC/MS gives a perfect explanation of the difference obtained by determining their THM formation potentials. The relative ratios between these chemical families vary, not only according to the geographical site (Fig. 6), but also for the same site as a function of time: for example, as a function of seasons (Fig. 7).

Different treatment processes adapted to removal of these families of natural polymers are indicated in Table 2. This is the way optimal operating conditions of the oxidation-adsorption combination, which is still the most efficient treatment, correspond to total removal of polyhydroxyaromatic and protein families.

Ozone- or ozone/hydrogen peroxide-GAC combinations offer multiple other advantages such as taste and odour removal (7), pesticide removal as well as inactivation of bacteria, viruses and parasites (8) (13).

What about ozonisation by-products?

Many research teams are studying the identification of ozonisation by-products (8) (14). Some of these by-products, notably aldehydes, will probably be the object of future recommendations by the WHO. Even if there are still a large number of unknowns to be solved, many results show that installation of GAC filtration downstream from ozonisation leads to resulting by-product removal provided, of course, that the plant operating conditions are appropriate. Figures 8 and 9 are good examples of this strategy. Formed aliphatic aldehydes are responsible for fruity flavours, which are quite well removed by GAC

filtration (Fig. 8). Ozonisation leads to a significant increase of biodegradable organic carbon, a large part of which is removed by biodegradation with GAC filters (Fig. 9) (7) (8).

If the raw water contains bromide, the use of oxidants such as ozone, ozone/hydrogen peroxide and chlorine can lead to the formation of bromate. The guide level for bromate as proposed by the WHO may be very low (25 µg/l?). Theoretically formation of bromate can be limited through a decrease in pH or the addition of ammonia but this needs to be confirmed (15).

What is the most suitable strategy for post-disinfection?

In some cases, the treated water is distributed without maintaining a disinfection residual concentration in the distribution network, even though this is not a viable hypothesis in the case of most surface waters. The disinfection agents generally used are chlorine, chloramines and chlorine dioxide because they are the only ones that have a lasting effect.

Whatever its nature, the disinfectant must be applied under optimal conditions and notably avoiding overdosages. The contact tank must be designed in such a way to have hydraulic behaviour making it possible to avoid any "stagnant region" (16). In the case of chlorine, treatment control may be realised by a chlorine demand transducer.

Finally, the distribution network must be considered as a reactor in which physical, chemical and biological reactions occur that are liable to generate modifications in the distributed water. For example, thanks to hydraulic modelling coupled with models of chlorine depletion in the network, it is possible, by using mapping systems and chlorine measurement microcaptors, to manage network operation as one would manage a reactor (17) (18). This approach also has the advantage of making it easier to implement network rechlorination. In fact, to maintain a predetermined residual right up to the consumer's tap, it is preferable to chlorinate in several steps rather than have high residual concentrations at the plant outlet (7).

A step toward treatment lines without reagents?

Awareness of the potential risks associated with the addition of chemical reagents to the water is contributing to the development of physical processes whose efficiency is not dependent on the addition of a chemical product. Two methods should be cited: radiation techniques such as UV radiation and separation techniques using membranes.

Disinfection using ultraviolet radiation is much more prevalent in Europe than in North America. This radiation reacts with the nucleic acids of the exposed cells and causes their inactivation. The UV dosage necessary to kill micro-organisms depends on two factors: intensity and exposure time. Unfortunately, this technology presents several disadvantages:

- it is only marginally effective for inactivating protozoan cysts;
- it leaves no lasting effect on treated water so an additional disinfectant should be necessary;
- its efficiency may be considerably affected in the presence of suspended particles or high concentrations of organic matter that absorb UV radiation (fulvic acids, colour, etc.). *A priori*, this process is more adapted to the treatment of well protected underground waters (19).

Micro-, ultra- and nanofiltration membranes constitute absolute physical barriers that reject and thus remove all particles, micro-organisms or dissolved compounds whose size is superior to the diameter of the pores of the considered membrane and, in theory, without the addition of chemical reagents. Anselme *et al.* (20) have recently published a comparative study of these different techniques; the main conclusions are as follows:

- As far as treatment of ground and surface waters with low concentrations of organic matter is concerned, hollow fibre cellulosic ultrafiltration appears to be the best and most reliable technology for the production of clarified and disinfected (including virus removal) waters (Fig. 10). Nanofiltration can remove hardness and organic matter as a single unit operation and low molecular weight cut-off ultrafiltration (500 to 1,000 Daltons) is the best compromise between economic consideration and water quality. However, these two processes necessitate a clarification pretreatment step if the fouling index of the water is higher than 5 (Fig. 10).

- Surface waters with high organic matter concentrations are quite difficult to treat using membrane processes. For small treatment plants with a production capacity lower that 200 m^3/h, treatment combining powdered activated carbon adsorption and cellulosic UF can be a viable technology, but for large treatment plants membrane processes should be implemented as a polishing treatment. In this case, nanofiltration and the combined PAC/cellulosic UF processes can be considered as viable technologies (Fig. 11).

Conclusions

The numerous tools described in this article for controlling DBP formation show that there is no treatment that can be considered a universal remedy and that consequently, it is nearly impossible to suggest a universal treatment line. The strategy to be adopted depends not only on the nature of the resource and its variability over time, but also on many other parameters, such as hierarchical organization of quality objectives recommended in each country. Thus, disinfection practices in France significantly differ from US practices in that the chlorine doses applied are usually much lower while on the other hand the use of ozone is much more frequent. Also, most major French treatment plants include an activated carbon filtration process which is likely to remove part of the DBPs as well as part of their precursors.

In the case of surface waters containing more than 3 mg/l of TOC, a treatment line including preozonation (with a variant without preoxidation), a clarification step, oxidation by ozone or the combination ozone-hydrogen peroxide, adsorption on GAC and finally post-disinfection with chlorine or chloramines is, without any doubt, the unanimous choice for large capacity plants. For smaller plants and waters presenting less potential risks, it would be necessary to weigh different solutions such as membranes.

The adoption of more and more stringent norms concerning DBPs by most large organizations may lead to the condemnation of a certain number of disinfection practices and possibly unbalance the necessary equilibrium between short and long term risks. Without a doubt, adequate solutions can be developed that take these two types of risk into account, but not without detrimental effects on potable water costs. Therefore, the real question is: what reasonable risk is acceptable?

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Table 1.

MACRO-MOLECULES	PROBLEMS DUE TO THE FORMATION OF OXIDATION BY-PRODUCTS	
	Chlorination	Ozonation
Proteins	○ Formation of THM + ○ Formation of TOX and organic chloramines +++ ○ Formation of aldehydes + → Problems of tastes and toxicity	○ Formation of aldehydes and acids + → Problems of fruity tastes and odors
Polyhydroxy-aromatics	○ Formation of THM and TOX +++ ○ Formations of aldehydes and acids + → Problems of tastes and toxicity	○ Formation of aldehydes and acids +++ → Problems of - fruity tastes and odors - bacteria regrowth - toxicity ?
Polysaccharides	0	0
Aminosugars	○ Formation of THM,TOX and organic chloramines → Problems of tastes and toxicity ?	0

Table 2. **Efficiency of different treatments for the removal of organic matter contained in water.**

	Coagulation *	Adsorption * (activated carbon)	Chlorination	Ozonation	Biodegradation
Proteins	+	+	++	+	+++
Polyhydroxy-aromatics	+++	+++	+++	++	+
Polysaccharides	0	0	0	0	+
Aminosugars	++	?	0 ?	0	?

(+++ good removal ; 0 no removal ,
* Dependent on molar weight)

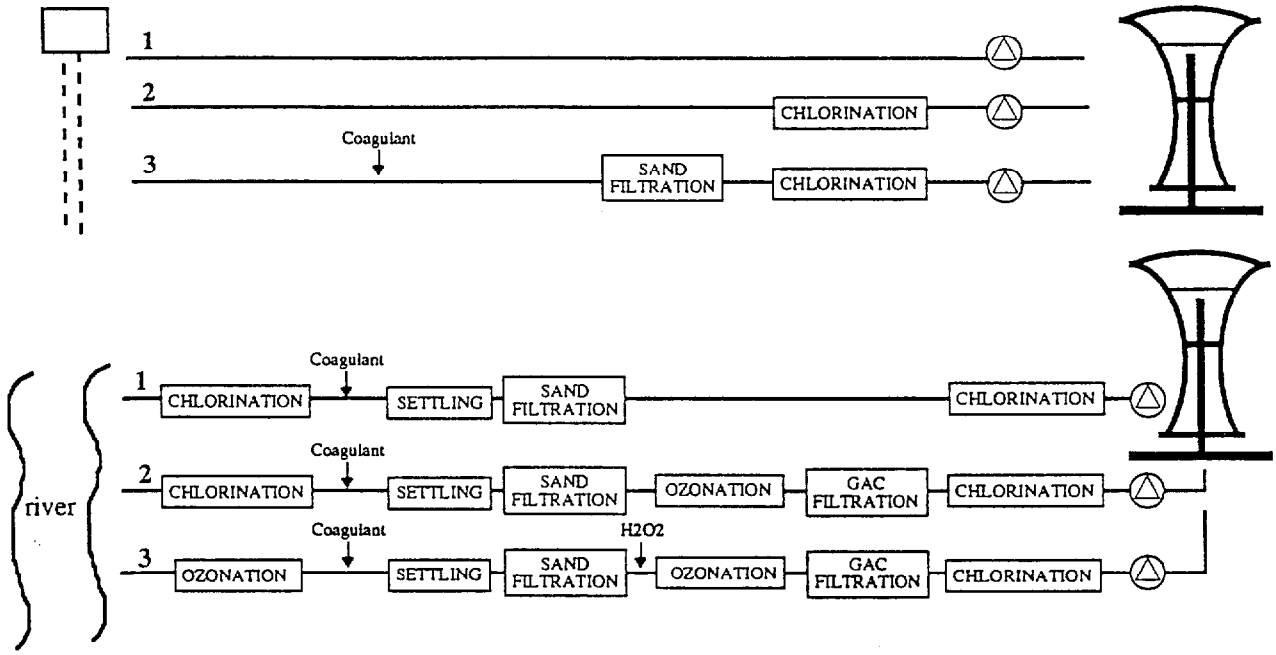

Figure 1. **Examples of treatment trains according to different types of raw water.**

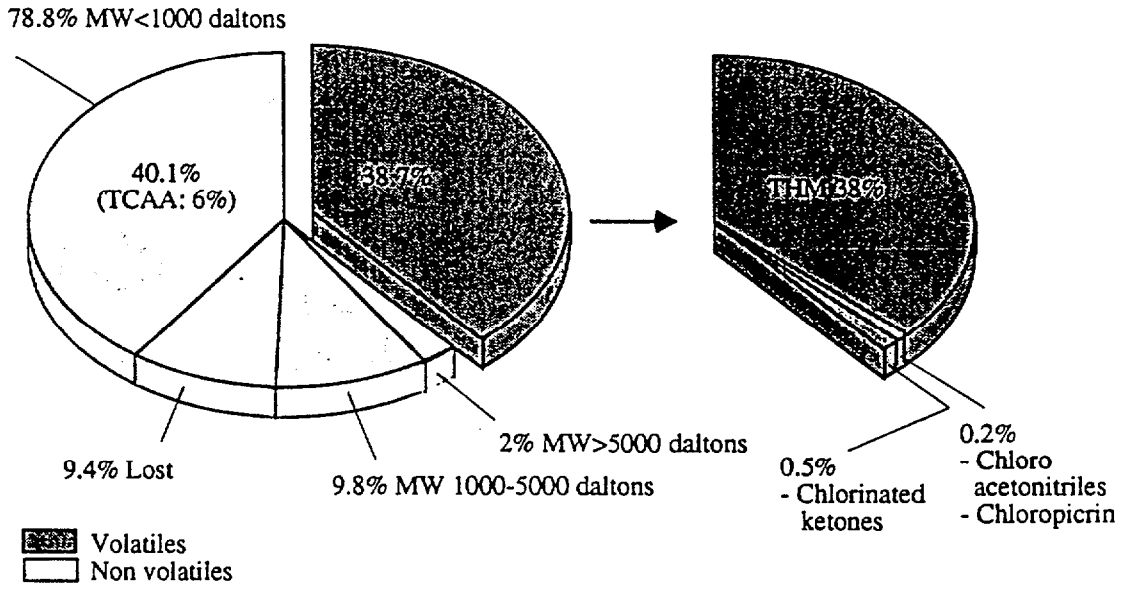

Figure 2. **Pie diagram for molecular weight of TOX distribution after pre-chlorination of a reservoir water (Cholet, France) and specification of the volatile fraction.**

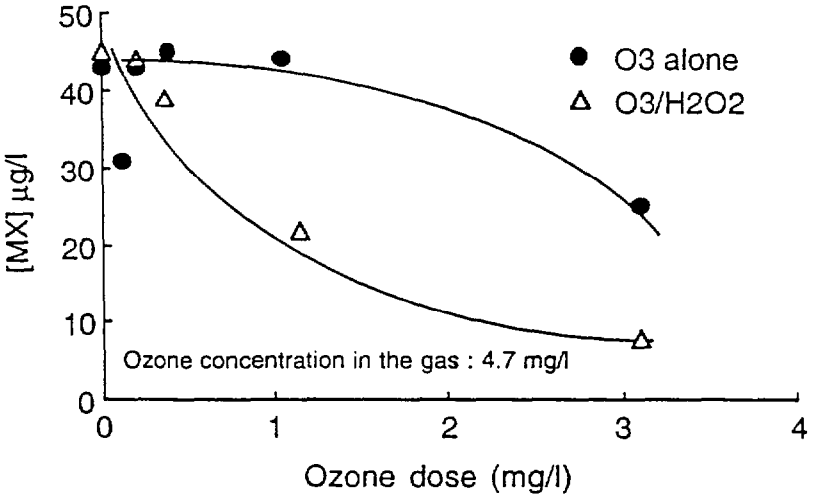

Figure 3. **Removal of MX by oxidation.**

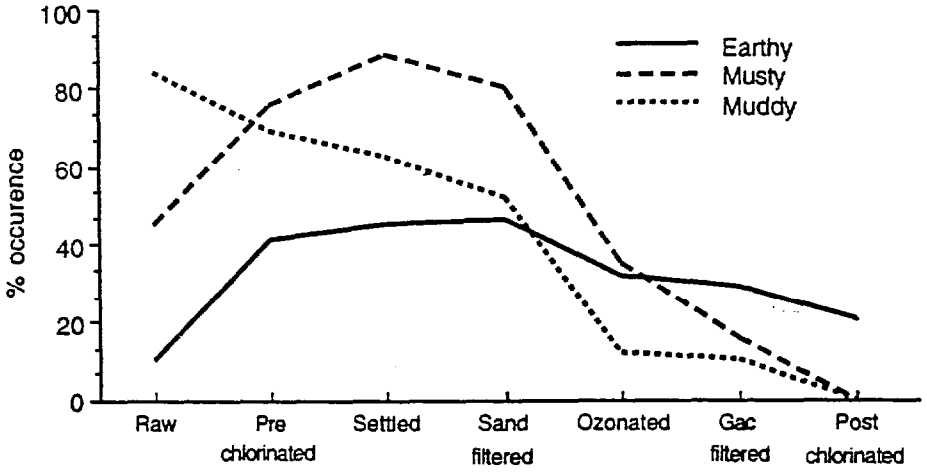

Figure 4. **Occurrence frequency of odours on Morsang treatment plant (Paris, France).**

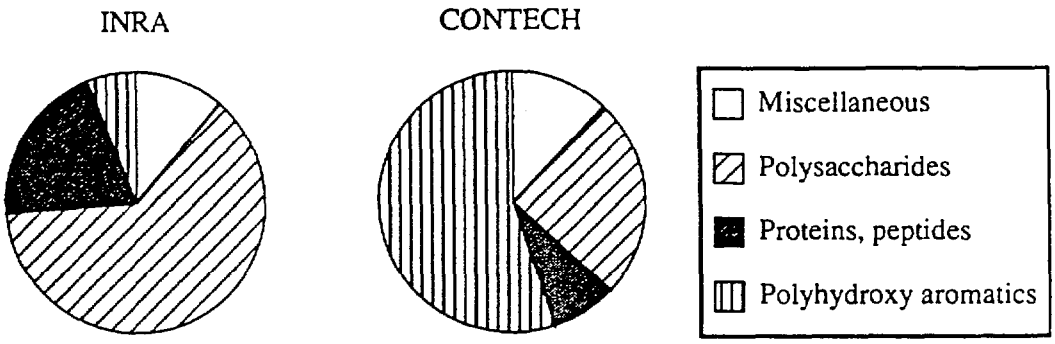

Figure 5. **Characterization of two fulvic acid samples (INRA and CONTECH) by pyrolysis-GC/MS. In the same chlorination conditions (1 mg of chlorine/mg of FA, 72h) they gave different THMFP values respectively 42 µg/l for INRA and 163 µg/l for CONTECH.**

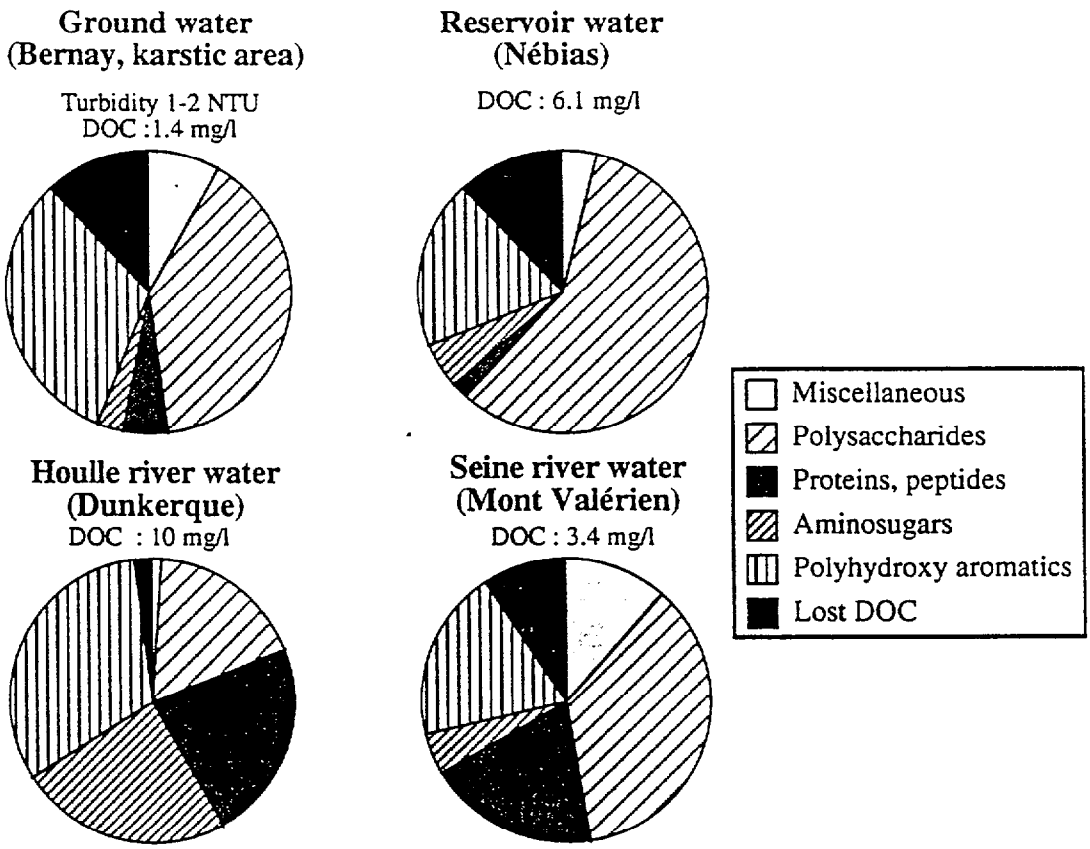

Figure 6. **Characterization of the organic matrix of different types of water.**

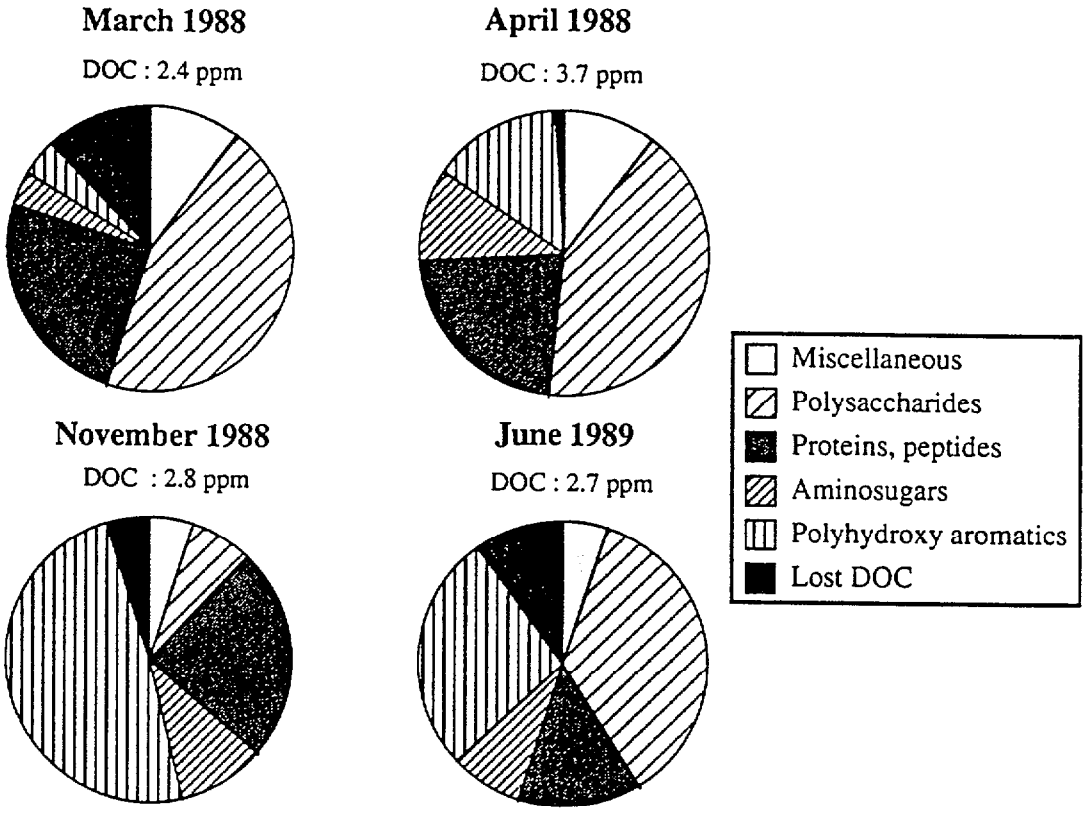

Figure 7. **Seasonal variations in the composition of the organic matrix of Seine river water (Suresnes downstream of Paris).**

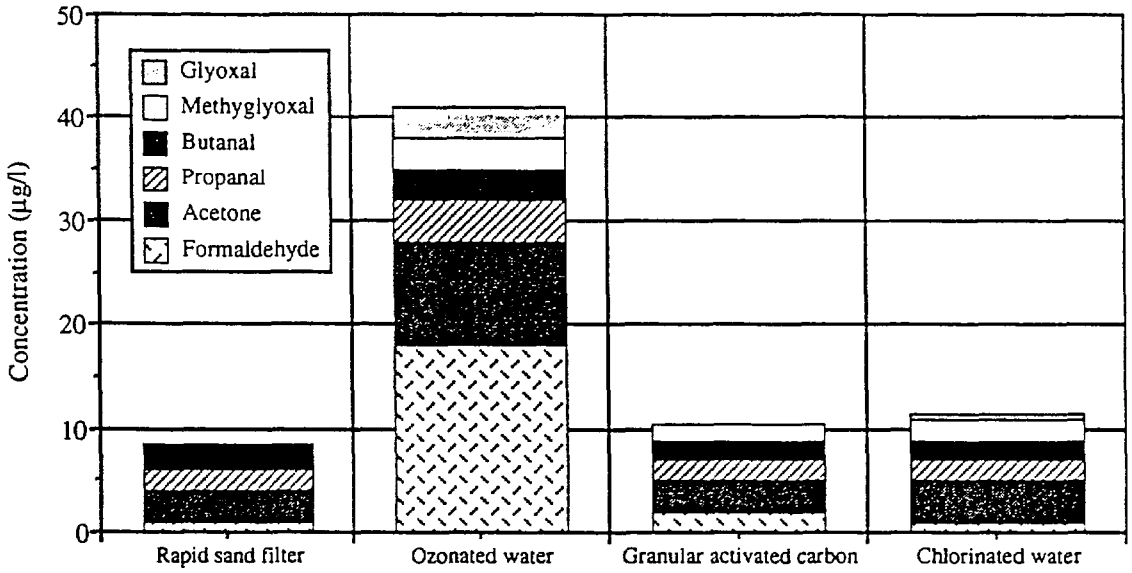

Figure 8.1. Fate of aldehydes in two different plants - Morsang/Seine upstream of Paris : DOC in the rapid sand filtered water : 2 ppm.

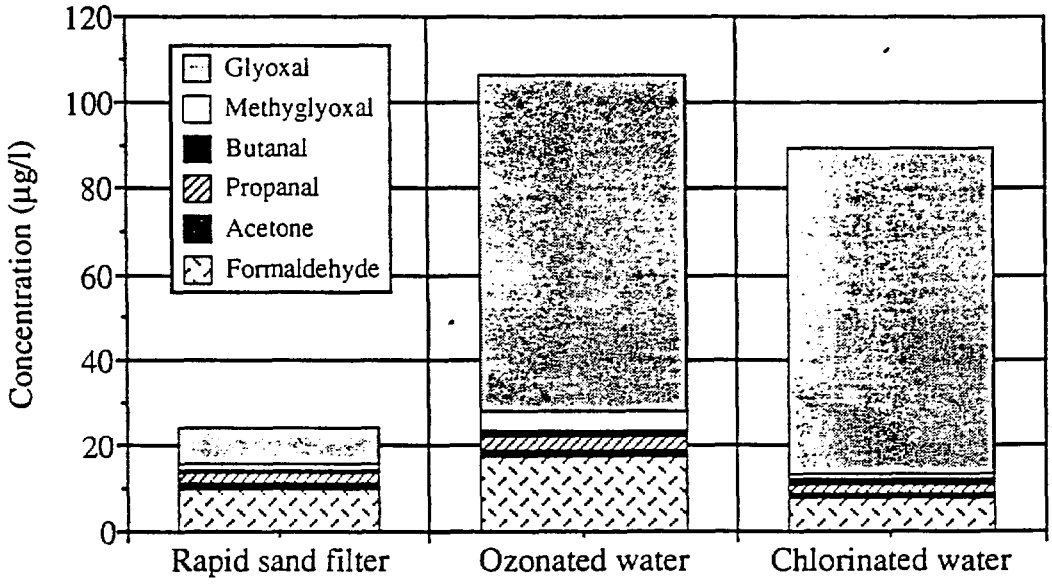

Figure 8.2. Fate of aldehydes in two different plants - Alençon : DOC in the rapid sand filtered water : 3.5 to 4 ppm.

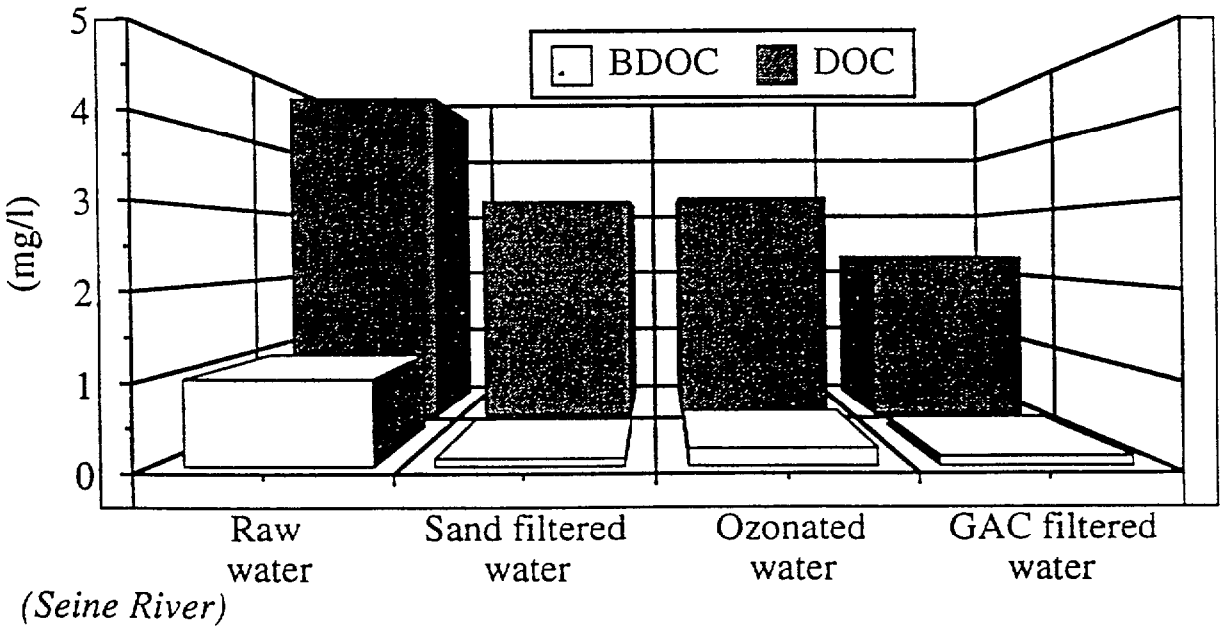

Figure 9. **Evolution of biodegradable (BDOC) and dissolved organic carbon (DOC) in a treatment plant (Seine river water, downstream of Paris).**

Treatment line Seine River Water		Presence of Giardia (N/m3)	Presence of Cryptosporidium (N/m3)
Upstream of Paris			
Cl2 + coagulation + settling + filtration	RW	1000 to 24.000 7⊕ / 7 samples	1000 to 40.000 7⊕ / 7 samples
	TW	0 to 200 2⊕ / 7 samples	0 to 140 2⊕ / 5 samples
Ultrafiltration	TW	0⊕ / 7 samples	0⊕ / 7 samples
Downstream of Paris			
O3 + coagulation + settling + filtration	RW	4000 to 47.000 7⊕ / 7 samples	600 to 9500 7⊕ / 7 samples
	TW	0 to 750 3⊕ / 7 samples	0 to 150 1⊕ / 3 samples
+ O3 + GAC	TW	0⊕ / 7 samples	0⊕ / 3 samples
Ultrafiltration	TW	0⊕ / 7 samples	0⊕ / 3 samples

Figure 10. **Removal efficiency of Giardia and Cryptosporidium by different processes : Comparison of data obtained by conventional treatment trains and UF filtration (n⊕ = number of positive responses, RW: raw water, TW: treated water).**

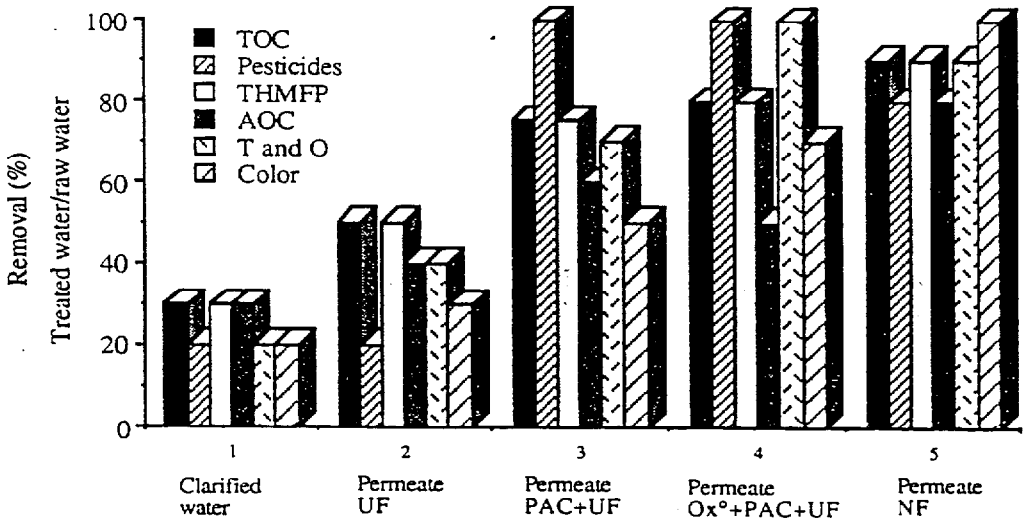

Figure 11. Treatment of a clarified surface water : removal of organic compounds by UF and NF processes (PAC : Powdered Acitvated Carbon, Ox° : Ozonation).

MICROBIOLOGICAL IMPLICATIONS OF MINIMISING DISINFECTION BY-PRODUCTS

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1. Introduction

The fundamental and primary purpose of water treatment is the protection of public health by providing an adequate supply of drinking water free from microbial agents which could cause disease.

The phrase "microbial agents which could cause disease" can have different interpretations depending on the type of population served. Traditionally the primary pathogenic agents have been considered in this context, but it is now realised that certain sectors of the population, notably the very young and the elderly, can be susceptible to micro-organisms hitherto considered as "opportunistic pathogens". This latter group of organisms also pose a special threat to the increasing number of immuno-compromised individuals in our communities.

1.1. Multiple barriers

Ensuring freedom from waterborne disease depends on creating barriers to the transmission of infection. In this context the sanitary reforms of the late 19th century which ensured an adequate supply of treated water from reliable sources and carriage of wastewater away from the source of supply were the single most effective measure to improve public health and limited the devastation previously caused by cholera and typhoid.

The principle of creating barriers to the transmission of infection has always been recognised for water supply. In water treatment, multiple barriers are used since no single barrier can be relied upon to provide absolute safety and there is no safe level for microbiological contamination. Examples of the multiple barriers used in water supply can be illustrated by reference to groundwater and surface waters.

In groundwaters the following barriers are important to the maintenance of good microbiological quality:

- percolation through soil, recharge and infiltration;
- zones of exclusion and protection;
- integrity of the well lining and cap;
- disinfection;
- piped distribution.

In surface water treatment the following barriers are used to achieve good microbiological quality:

- impoundment with restricted access to man and animals;
- pre-chlorination or ozonation;
- coagulation, sedimentation;
- filtration;
- terminal disinfection;
- piped distribution with disinfectant residual.

Disinfection, usually by chlorine, has been and still is an important component of the multiple barrier approach. How important is difficult to quantify, but the literature suggests that, in the UK between 1937 and 1987, the major outbreaks linked to public and private water supplies were associated with failures of or deficiencies in chlorination. Additionally the multitude of barriers used in the Netherlands indicates the extent of treatment required before disinfection can be abandoned. More recently in the UK outbreaks of Cryptosporidiosis have demonstrated the need for multiple, microbiologically-efficient barriers in addition to chlorination.

Final disinfection of drinking water must therefore be considered as only part of the system of multiple barriers providing, in most instances, the final safeguard to public health protection. The microbiological implications of minimising disinfection by-products by reduced chlorination need careful consideration if the margin of safety provided by current disinfection strategies is to be maintained.

1.2. Alternative strategies

Treatment strategies must be designed to ensure that final waters contain a minimal microbial challenge to disinfection. Additionally, if the use of disinfectant residuals in distribution is to be abandoned or minimised, the biostability of the water will have to be enhanced so that deterioration in quality through the growth or "regrowth" of micro-organisms does not occur.

The following strategies can be considered as means of reducing the need for disinfection:

- improve the microbiological quality of source waters to reduce the challenge to water treatment;
- greater use of biological treatment processes which are efficient at removing micro-organisms (slow sand filtration, activated carbon filters);
- try to achieve biostable waters.

2. Improved source water quality

2.1. Impoundment

Logarithmic frequency distributions for *E coli* concentrations in some rivers, lakes and reservoirs used for abstraction are shown in Figs 1 and 2. Clearly, the lakes and reservoirs are of much better microbiological quality with 50 percentiles of around 20 *E coli* per 100ml. In contrast the 50 percentile values for the rivers are between 1 and 2 orders of magnitude greater. Water abstracted from the lakes and reservoirs would therefore present a significantly smaller microbiological challenge to water treatment processes and indicate the value of the natural purification processes which occur in impounded waters.

2.2. Pre-chlorination

Pre-chlorination or ozonation of abstracted waters is often used as one of the preliminary stages of water treatment since it assists in controlling biofouling of the plant and aids subsequent coagulation. Microbiologically it achieves the same degree of microbiological removal as impoundment. Table 2.1 shows the percentage removal figures observed for a range of micro-organisms during pre-chlorination of an abstracted river water.

Table 2.1. Microbiological efficiency of pre-chlorination.

Observed percentage removal efficiencies for a range of micro-organisms:

Escherichia coli	99%
Faecal streptococci	98%
Clostridium perfringens	90%
Enteric viruses	90%
Heterotrophic bacteria	80%

The impact of pre-chlorination on the microbiological removal which occurs during subsequent treatment stages is demonstrated by the figures shown in Table 2.2. In this table the results of analysis for *E coli* monitoring are shown from two different water treatment plants. In Plant A, pre-chlorination is followed by rapid sand filtration and final disinfection. In Plant B, there is no pre-chlorination stage, but a two-stage filtration process (rapid sand followed by slow sand filtration) is employed before final disinfection. At the plant without pre-chlorination it is clear that the rapid sand filter has little impact on the *E coli* content of the water and if slow sand filtration had not been employed a high microbial challenge would have been present at the final disinfection stage.

Table 2.2. Comparison of *E coli* removal with and without pre-chlorination.

Treatment	*E coli* count/100ml	
	Plant A	Plant B
Raw water	2130	982
Pre-chlorination	11	
Rapid sand filtration	>1	226
Slow sand filtration	-	2
Final disinfection	<1	<1

At the plant using pre-chlorination the *E coli* content of the water is significantly reduced before rapid sand filtration. Although rapid sand filtration has a low microbial removal efficiency, at this plant it reduced the *E coli* concentration to below the limits of detection of the analysis technique (1/100ml), perhaps due to the continuing residual from the pre-chlorination, before the water was given final disinfection.

Although discontinuing the use of pre-chlorination would have benefits in terms of reducing by-product formation, the figure given in Tables 2.1 and 2.2 demonstrate the microbiological advantages of this process. Certainly in the situation shown in Table 2.2 the figures suggest that an additional biological process, such as slow sand filtration, would be essential if discontinuing pre-chlorination was not to jeopardise the safety margin provided by terminal disinfection.

3. Microbial efficiency of filtration

3.1. Rapid and slow sand filtration

The figures in Table 2.1 for the treatment works not employing pre-chlorination demonstrate the relative microbial removal efficiencies of slow and rapid sand filtration. Rapid sand filtration is a physical process and as such removes less than 90% of the bacteria in the water. Slow sand filtration is a biological process in which predation, adsorption and competitive forces within the upper biologically active layers give better than 99% removal of indicator bacteria such as *E coli*. Again, this supports the view expressed in Section 2.2 that where pre-chlorination is to be discontinued, a biological process will be required to reduce the microbial population of a water. If this additional biological treatment is not introduced increased levels of final disinfection would be necessary to ensure adequate protection of public health.

3.2 Filter backwashing

During the period between routine backwashing of rapid sand filters micro-organisms accumulate within the depth of the filter. During backwash these bacteria are flushed out by the backwash water, which is treated before disposal or return to the influent of the plant. In Table 3.1 are shown the counts of thermotolerant coliform organisms (presumptive *E coli*) observed in the effluent of a rapid sand filter immediately before and upto 60 minutes after backwashing. Also shown are two results for the analysis of the backwash waters at the start and after 5 minutes of the backwash cycle.

Table 3.1. Increase in the microbial challenge to final disinfection presented by filter backwashing.

Status (minutes)	Thermotolerant coliforms per litre
Before backwash	1
During backwash	
0	100
5	9
Back in service	
0	3
5	22
10	77
20	31
30	22
45	7
60	6

In general returning filter backwash waters to the head of the works would appear not to represent an extraordinary challenge to the preliminary stages of treatment. The initial concentration of 100 thermotolerant coliforms/100ml will generally be less than that found in the source water. However, it should be pointed out that recent experience with the parasite *Cryptosporidium* suggests that returning backwash waters to the head of the works is undesirable. In this case the number of cryptosporidia in backwash waters can represent a significant increase over the concentrations found in the abstracted water. Returning the backwash waters to the head of the works can therefore create a considerable challenge to treatment and so increase the chance of breakthrough by this organism or indeed by an other resistant pathogen present in the particulate matter.

After backwash, the filter effluent is run to waste or returned to the head of the works until a prescribed turbidity is reached. Once this level of turbidity is achieved the filter is brought back into service. In general the time taken to achieve the prescribed turbidity is less than 10 min. The results shown in Table 3.1 indicate that the concentration of thermotolerant coliform organisms in the filter effluent does not correlate with this return to acceptable turbidity. In the situation shown the thermotolerant coliform count reached a maximum 20 minutes after the filter was brought back in to service. Although not extremely high this maximum count represents an increased microbial challenge to the next stage of treatment, which at this works was final disinfection.

The introduction of an increased microbial load at this stage of treatment circumvents the protection afforded by the use of multiple barriers, and places undue reliance on terminal disinfection.

3.3. Granular activated carbon

The use of granular activated carbon as a replacement for sand in rapid filters and as a biological process has found support as a treatment strategy which, when combined with ozonation, can minimise by-product formation. However, micro-organisms colonise activated carbon beds and proliferate using the organic carbon adsorbed by the carbon. This occurs regardless of whether pre-oxidation is used. The accumulated biofilm in the beds is continually being sloughed and this produces filter effluents which contain significantly more micro-organisms than sand filters. In effect, this is a similar situation to that described in Section 3.2, in that the treatment process is contributing to an increased microbial load at an advanced stage in the treatment process.

Table 3.2 shows typical microbiological results from the monitoring of a treatment plant using granular activated carbon (GAC) as a replacement, for sand in rapid gravity filter. An existing rapid sand filter is operated in parallel with the GAC filter, both being supplied from the same coagulation process A direct comparison of the two filter effluents can therefore be made.

Table 3.2. Comparison of the microbial content of a sand and a GAC filter effluent.

	E coli /100ml	FS /100ml	CL p /100ml	HPC/ml 37°C	HPC/ml 22°C
Raw water	2130	630	2320	280	19818
pre-chlorination	23	10	150	55	2609
Coagulation and sedimentation	0	37	0	7	233
Sand filtration	0*	0*	0	5	293
GAC filtration	4*	1*	0	772	264

FS = faecal streptococci, Cl.p = *Clostridium perfringens*
HPC = Heterotrophic plate count organisms at 22°C or 37°C
* = per litre

The most significant feature of the results is the apparent increase in numbers of certain bacteria in the GAC filter effluent when compared with either the influent to the bed (the effluent from coagulation) or the sand filter effluent. The greatest increase is seen in the 22°C heterotrophic plant count, although these organisms are regarded of no sanitary or public health significance. However, the observed increase in the 37°C heterotrophic plate count is of greater concern, since some of these organisms could be of public health significance. The apparent presence of *E coli* in the GAC effluent, albeit at a low concentration of 4/litre, is of particular concern since this organism is the primary indicator of sanitary quality. The significance of *E coli* at this stage of the treatment process could represents a serious erosion of the safety margins provided by the multiple barriers since, if it is assumed that it could multiply in the GAC bed, then it must be assumed that waterborne bacterial pathogens might also. In any case this finding places a greater demand on terminal disinfection.

There are other doubts about the microbiological aspects of the use of GAC. It is suggested that filter fines may be carried through the disinfection stage and into distribution. Bacteria attached to these fines will be protected from disinfection and may act as an inoculum for regrowth within the distribution system. There are therefore several microbiological aspects to the use of GAC which require study before this form of treatment can be used beneficially in the minimisation of disinfectant by-product formation.

4. Biostability

The biostability of a water is a measure of its ability to support microbial growth and is dependent mainly on the amount of organic carbon it contains which can be utilised by micro-organisms. Not all the total organic carbon in a water can be utilised by micro-organisms. The part which can be used by micro-organisms is termed the Assimilable Organic Carbon (AOC) or the Biological Dissolved Organic Carbon (BDOC). In the UK, groundwaters contain significantly less AOC than treated waters from lowland surface sources. Although groundwaters are relatively biostable as compared to these surface derived sources, they still contain more AOC than workers in the Netherlands recommend for waters not requiring a residual chlorine to prevent microbial growth in distribution. These workers recommend that AOC concentrations below 20 µg/l are required for biostability and this has been achieved in the Netherlands by the use of biological processes such as dune filtration. This figure is well below the content of any of the groundwater sources in the UK.

Biological treatment processes remove AOC, but oxidation processes such as chlorination or ozonation convert TOC to AOC. Thus even though a treatment works may employ a biological process the AOC entering distribution will still be relatively high due to the oxidation which occurs during terminal disinfection.

Treatments suggested for the removal of the precursors of by-products of disinfection have some concordance with those being studied for minimising AOC. To these ends pre-oxidation (usually ozone) followed by GAC filtration is being investigated.

However for best possible AOC removal the GAC filters must be operated with extended empty bed contact times to allow biological treatment to take place. As discussed in Section 3.3 the effluents from these filters may not be microbiologically desirable and, as such, final disinfection will need to be applied which will again lead to the generation of AOC and biological instability. At the present time, pre-oxidation by ozone is under suspicion of producing undesirable, possibly carcinogenic by-products such as formaldehyde from organic carbon. It is one of the benefits of GAC filtration that the biological activity will remove these by-products.

4.1. Granular activated carbon and AOC

Table 4.1 shows the results of monitoring the AOC concentration in parallel treatments, one employing sand filtration the other GAC.

Table 4.1. Impact of GAC treatment on AOC (µg/l).

Treatment A		Treatment B	
raw water	99	raw water	95
pre-chlorination		pre-chlorination	
coag/sed	122	coag/sed	136*
GAC filtration	77**	Sand filtration	139**
Final water	132	Final water	123

* = No biological activity due to chlorine residual
** = GAC removes chlorine residual, some biological activity

Pre-chlorination leads to an overall gain in AOC in both streams. The GAC removes the chlorine residual which allows biological activity to reduce the AOC concentration from 122 µg/l to 77 µg/l. There is no equivalent reduction by the sand filter, due to the chlorine residual persisting throughout this treatment. Although the GAC filter reduces the AOC concentration final disinfection leads to an increase of 55 µg/l. The end result of the treatment is therefore some removal of TOC as AOC, but a final water which contains a higher concentration of AOC than the raw water and which is less biostable.

4.2. Ozonation and AOC

Table 4.2 shows the impact of ozonation on the AOC content of water. A pre-ozonation dose of about l mg/l increases the AOC content of the raw water from 231 µg/l to 321 µg/l. This is reduced by coagulation and sedimentation to 191 µg/l. A further ozonation step with a dose of 3-8 mg/l increases the AOC concentration to 441 µg/l. Rapid gravity filtration using GAC reduces this to 199 µg/l presumably due to biological activity in the bed. The impact of final disinfection is not large presumable because of the previous effects of the more powerful oxidant ozone. The final water has a AOC content very similar to the raw water and so cannot be viewed as being of greater biostability. Had the GAC filter been operated as BAC (Biological Activated Carbon) with a greater empty bed contact time it can be suggested that the AOC content of the effluent would have been reduced.

Table 4.2. The impact of ozonation on AOC.

Treatment	AOC (µg/l)
raw water	231
pre-ozonation	321
coagulation/ sedimentation	191**
further ozonation	441
GAC filtration	199**
Final water	203

** = biological activity

4.3. Coagulation, sedimentation and AOC

Because of the microbiological shortcomings of GAC discussed in Section 3.3 microbiologists are looking to see if other treatment processes can be optimised for AOC removal. In this context the coagulation and sedimentation process has potential in terms of its retention time. In Table 4.2 coagulation and sedimentation reduced AOC significantly and it is being postulated that this removal is attributable to biological activity in this process. The use of pre-chlorination before coagulation and sedimentation would inhibit this biological activity due to the presence of a chlorine residual. The results shown in Table 4.1 would support this view, since at this works pre-chlorination followed by coagulation and sedimentation resulted in an increase in AOC. Ozonation on the other hand does not have an inhibitory effect on biological activity, due to the lack of residual effect.

4.4. Discussion

If the use of disinfectant residuals in distribution is to be abandoned or minimised, the biostability of waters entering distribution must be improved. To this end oxidation processes, followed by biological treatment, can reduce AOC, but these process need to be optimised both in terms of their ability to remove AOC and their position in the overall treatment process.

5. Conclusions

- the microbiological security of the water treatment process is essential to the protection of public health and the microbiological implications of any proposed changes in treatment strategies must be thoroughly evaluated to ensure they do not erode current margins of safety;

- the multiple barrier approach to water treatment must be retained. If minimising disinfectant by-product formation requires a reduction in the effectiveness of disinfection then alternative barriers to micro-organisms must be included in the treatment strategy;

- although pre-chlorination has considerable disadvantages in the context of minimising chlorination by-products it performs a useful if not essential role in reducing the microbial challenge to subsequent water treatment processes;

- pre-ozonation may be more desirable than pre-chlorination since it is a more powerful disinfectant, and does not leave a disinfectant residual which can inhibit subsequent biological treatment processes;

- greater use of biological treatment processes would give improved removal of AOC and micro-organisms and so allow the level of terminal disinfection to be reduced;

- GAC treatment appears to have some microbiological shortcomings which must be thoroughly elucidated. However, GAC appears to be so valuable for removing by-product precursors that every effort should be made to optimise the microbiological performance of this form of treatment;

- the optimisation of water treatment to minimise by-product formation, produce water with greater biostability and preserve or enhance public health protection are complementary goals which must be achieved through the close co-operation of chemists, microbiologists and water treatment engineers. If research efforts are not integrated it seems likely that particular goals may be achieved without adequate consideration of the consequences to the other aims of water treatment.

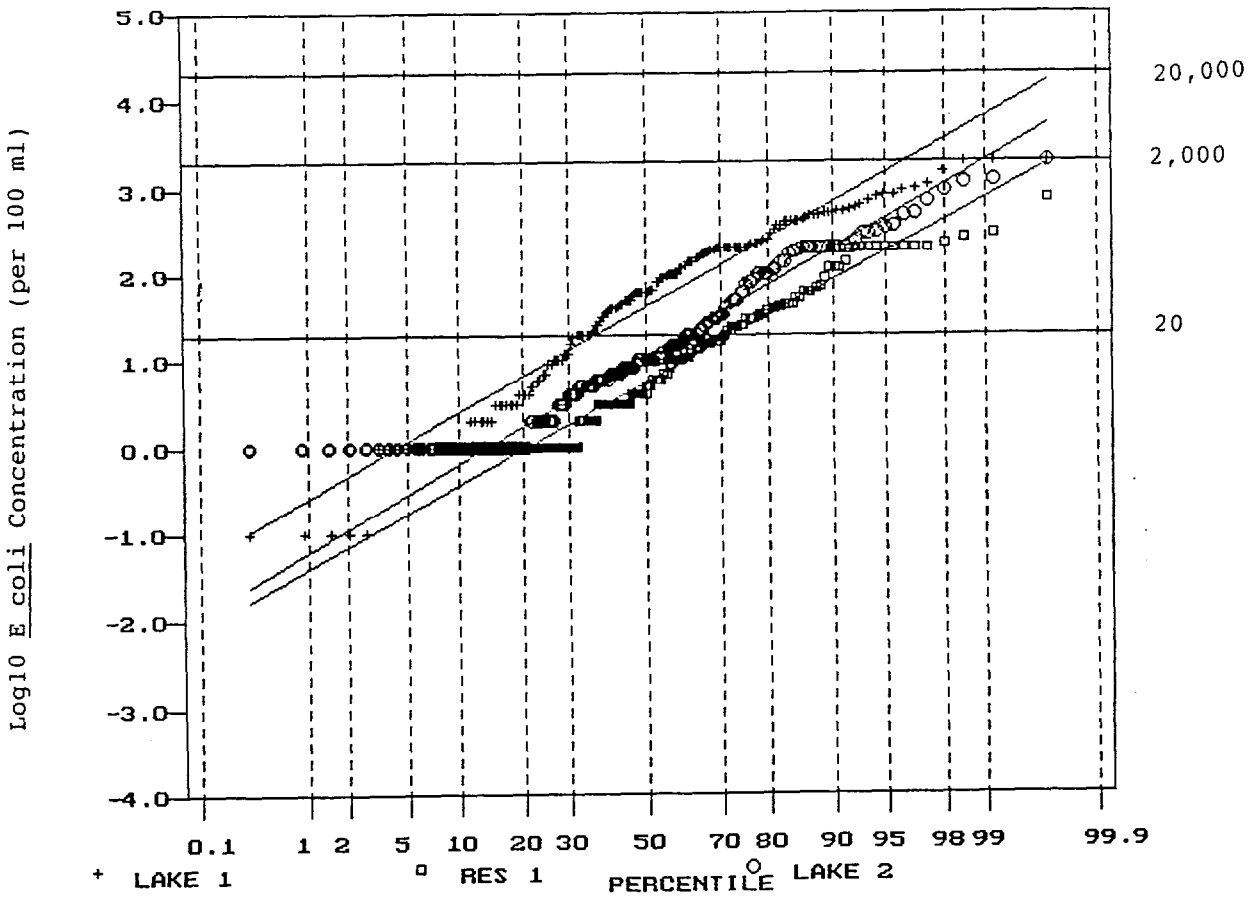

Figure 1. Logarithmic frequency distributions for *E coli* concentrations from two lakes and a reservoir used for abstraction.

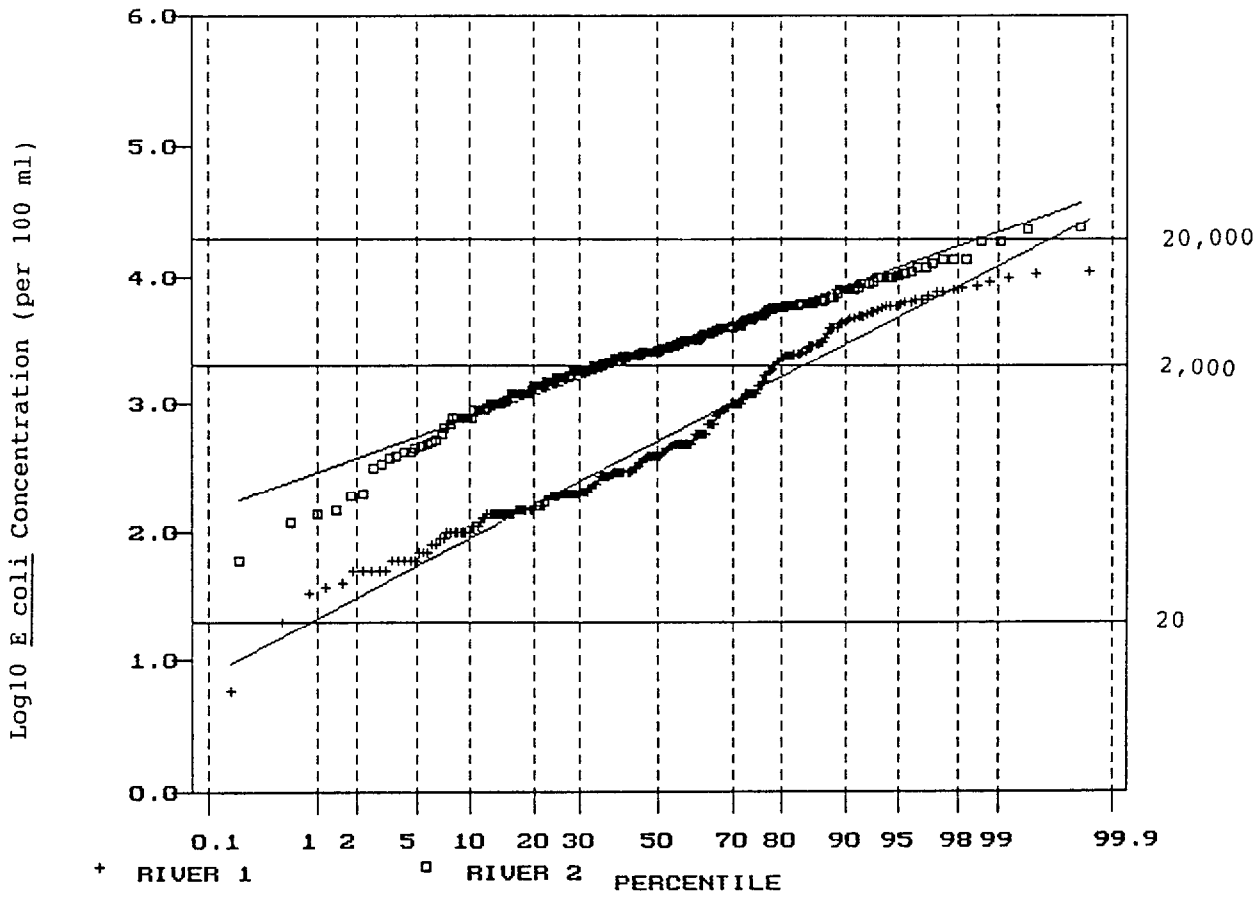

Figure 2. **Logarithmic frequency distributions for *E coli* concentrations from two river abstraction sites.**

RISKS OF DISINFECTION BY-PRODUCTS IN RELATION TO THE BENEFITS OF DISINFECTION: DEVELOPMENT OF US DRINKING WATER REGULATIONS FOR DISINFECTION BY-PRODUCTS

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The US Environmental Protection Agency (EPA) is in the process of developing National Primary Drinking Water Regulations (NPDWRs) for chemical water disinfectants and their associated by-products ("Disinfection By-product (DBP) Rule"). This effort has pointed out complexities and conflicts in the consideration of the public health hazards involved, in establishing public health goals for drinking water, in determining feasible technical solutions and in crafting appropriate regulations.

Public health interests require that drinking water be microbiologically safe. The US Safe Drinking Water Act (SDWA: US Public Law 99-339) and its amendments mandate treatment of source waters to ensure microbially safe drinking water. However, the disinfection process itself may lead to contamination of drinking water with disinfectants and by-products that pose human health threats. The SDWA also requires that EPA regulate these contaminants in drinking water to protect human health. Therefore, the goals of the DBP Rule must be to ensure that (1) drinking water remains microbiologically safe at any limits set for disinfectants and their by-products and that (2) the disinfectants and by-products do not pose an unacceptable health risk at these limits.

Several difficulties have been encountered in the development of this regulation. One difficultly is that major concerns remain as to the health risks posed by waterborne micro-organisms and by both known and unknown by-products under the wide range of water qualities observed. A second problem arises in the discussion of suitable technologies to minimize these risks. Some approaches to minimising a particular contaminant may in fact increase risks from other contaminants or introduce new contaminants. Other problems include practical considerations of implementation for the oversite agencies involved, particular and conflicting points of view of the various "publics" affected by these regulations, and cost considerations to all concerned.

Health risks and goals associated with microbial contamination and disinfection

In EPA's regulatory development, human health risks arising from drinking water contaminants are evaluated based on available toxicity and exposure information. From these risks, Maximum Contaminant Level Goals (MCLGs) are established for contaminants determined to pose health threats to the public. The MCLG is set at a level where no known or anticipated adverse health outcome is expected from a lifetime exposure. For contaminants that are known or probable human carcinogens, the MCLG is set at zero, representing the assumption that no exposure threshold exists for carcinogens, thus no exposure is considered to be without risk. For non-carcinogens, the MCLG is based on experimentally-determined levels where no adverse effects are observed. MCLGs are not enforceable, but aspirational. The corresponding enforceable Maximum Contaminant Levels (MCLs) are set as close to the MCLGs as is feasible. The determination of feasibility includes assessment of practical analytical methods, treatment technologies, and to some extent, costs. In the situation where it is not feasible to monitor a contaminant, a treatment technique can be mandated in lieu of a MCL. All NPDWRs that require compliance with a MCL or treatment technique must also specify a Best Available Technology (BAT) that can be used to achieve the standard, although the specified technology need not be used if the utility can comply using another technology.

For previous EPA NPDWRs, MCLGs, MCLs and treatment techniques for individual contaminants have been set independently without respect to their impact on regulations for other contaminants. The development of the DBP Rule has pointed out the impossibility of independently establishing MCLs and treatment techniques for microbes and DBPs, since their occurrences are so closely interrelated and possible BATs may conflict.

Microbial health risks and goals

A growing body of evidence indicates that the incidences of waterborne illness and death in the US are substantial (Tables 1, 2)[1]. In EPA's previous drinking water regulations involving micro-organisms (Surface Water Treatment Rule (SWTR)[2]; Total Coliform Rule)[3], the concern was to minimize all microbial illnesses resulting from all waterborne microbial pathogens, without specific regard to the relative risk of an infection from a given organism or for the severity of an illness arising from the infection. The Total Coliform Rule uses coliform bacteria, fecal coliforms and *E. coli* as surrogates for microbial contaminants in general and specifies a MCL for total coliforms. The SWTR specifies filtration and disinfection to achieve at least a 99.9% removal/inactivation of *Giardia* and 99.99% removal/inactivation of viruses. *Giardia* was selected as the organism of concern due to its resistance to disinfection compared to viruses and bacteria, even though the associated illness (giardiasis) is not considered either life-threatening or severe. The assumption was made that if *Giardia* infections were limited by treatment to a given level, that treatment would also minimize infections from the other pathogens of health concern.

We have been increasingly concerned that other organisms, particularly viruses, may be both more infective than *Giardia* and produce illnesses more severe than giardiasis, including death (Tables 1-3)[1-4]. If occurrence levels for these organisms were substantially higher than those estimated for the SWTR, significant waterborne microbial illness could exist in the population. While outbreaks of waterborne illness are generally infrequent[8] it is understood that such outbreaks are typically under-reported and that a relatively high level of illness (0.5-1%) is required in a community before an outbreak is recognised [4]. An endemic level of waterborne microbial illness is thus possible and is supported both by data from the Centers for Disease Control[1] and from the studies of Payment, *et al* [9].

A major goal of the SWTR is to achieve a risk of *Giardia* infection less than 1/10,000 per year. This value is being considered as an acceptable risk level for waterborne microbial illness[5,6]. Lifetime premature mortality estimates derived from this risk level have been calculated to be from about 4/10,000 to 4/1,000,000[5,6].

Disinfectant health risks and goals

Chlorine, chloramine and chlorine dioxide are the three disinfectants being considered for regulation under the DBP Rule. Their toxicities have been considered as resulting solely from non-cancer endpoints. Possible MCLGs have been calculated (Table 4). We would like to set MCLs for these chemicals as close to the MCLGs as possible while still allowing their use as primary disinfectants and the use of chlorine and chloramine as distribution system ("residual") disinfectants. We continue to believe that chlorine and chloramine are safe and effective disinfectants for waterborne pathogens. It is unclear at this time if chlorine dioxide will thus remain available.

By-product health risks

Of the large number of disinfection by-products resulting from chlorination, ozonation and other oxidation practices, EPA has focused attention on 10 specific halogen compounds. Four halomethanes (chloroform, bromodichloromethane, chlorodibromomethane, bromoform), two haloacetic acids (dichloroacetic acid, trichloroacetic acid), chloral hydrate, bromate, chlorate and chlorite comprise this group of contaminants. As with the disinfectants, possible MCLGs have been calculated by EPA for these contaminants based on evaluations of their toxicities (Table 4).

Regulatory focus has been on bromodichloromethane, dichloroacetic acid and bromate, due to their relatively higher cancer risks (Table 5). EPA has typically regulated individual carcinogens at a lifetime upperbound 95th percentile risk level of 2/10,000 to 2/10,000,000. We are concerned that MCLs for these contaminants in this range could be difficult to achieve using accepted treatment technologies.

Chloral hydrate, trichloroacetic acid, chlorate and chlorite are not classed by EPA as known or probable human carcinogens at this time. Reported levels in drinking water are generally below the corresponding MCLGs for these contaminants.

Interrelatedness of microbial, disinfectant and by-product risks

Since it is understood that the use of disinfectants to minimise waterborne microbial risks results in some risks from the disinfectants and their by-products, EPA has taken some effort to characterise the nature and magnitude of this relationship under typical water treatment scenarios. Models predicting post-treatment contamination levels and health risks from various influent source water qualities and treatment trains have been developed and, to some extent, validated [5-7]. These models have been used to characterise the current, baseline situation and to consider possible BATs to achieve specific DBP and microbial target levels.

For example, we considered the effect on drinking water-derived health risks from utilities simultaneously complying with existing NPDWRs and possible DBP MCLs. Figures 1 and 2 show resulting risks for a system using surface water and conventional treatment of coagulation, sedimentation, filtration and chlorine disinfection, given an average surface water source quality. These risks were estimated based on compliance with the SWTR and a range of possible total trihalomethane (TTHM) and total haloacetic acid (THAA) MCLs. Note that as more stringent MCLs are met and cancer risks diminish, microbial illness (as *Giardia* infections) increases substantially. We estimate deaths from waterborne microbial illness at about one per 1000, thus these data indicate an inverse relationship where, for each DBP-related cancer prevented, perhaps five microbially-related deaths occur.

The increase in microbial illness with stricter DBP MCLs is based on our considerations of approaches likely to be taken by utilities to comply with these MCLs. Figure 3 shows typical levels of surface water treatment prior to the imposition of the SWTR. While many systems did not achieve the 3-log removal/inactivation of *Giardia*, many achieved far greater levels. Figure 4 estimates the current situation resulting from the SWTR and the current TTHM standard of 100 µg/l. While all systems are expected to achieve 3-log removal/inactivation, many will have reduced chlorine disinfection to meet the TTHM standard, thus reducing their inactivation of microbials. With the imposition of a stringent TTHM MCL of 25 µg/l (Figure 5), few if any utilities could be expected to maintain removal/inactivation levels above the required 3-logs for *Giardia*.

Possible regulatory approaches

Over the course of the last several years, regulatory discussion for the DBP Rule has evolved from a strict concern for health risks from carcinogenic disinfection by-products to efforts to ensure a diminuation of total waterborne health risk, including a balancing of microbial and chemical risks. Currently, three key health issues are driving this activity: (1) these regulations should at a minimum not result in increased microbial risks and ideally reduce existing risks; (2) they should control for known contaminants with associated known health risks; (3) they should, as far as is possible, control for unknown contaminants with unknown health risks. Microbial and chemical health risks must first be adequately estimated and then regulations crafted to bring these risks into parity and to the desired acceptable total health risk level.

Based on the results of the modelling efforts, we are concerned that stringent standards for disinfection by-products could lead to utilities reducing water treatment to achieve only the minimum required disinfection, which would increase the risk of microbial illness. To prevent this, a regulatory element being considered would enhance existing standards to require higher levels of disinfection treatment for poorer quality surface water sources. Utilities would be required to monitor microbial pathogens such as *Giardia*, coliform bacteria and/or viruses in their surface source waters. Treatment would be specific to contamination levels. This has been termed the "Enhanced Surface Water Treatment Rule (ESWTR)".

EPA does not currently require groundwater sources to be disinfected, although many do disinfect. To prevent groundwater-based systems from eliminating disinfection to meet by-product standards and to address microbial risks from contaminated groundwater, a Groundwater Disinfection Rule (GWDR) is in development that will mandate disinfection of these sources, unless they can be shown to be neither contaminated nor vulnerable to contamination by micro-organisms.

A regulatory approach being considered for control of both the known and unknown by-product health risks is to mandate that a utility achieve limits on by-product precursor materials, such as dissolved organic material or bromide. Numerical standards for certain individual by-products could then be then promulgated based on average water quality characteristics following precursor treatment. This approach would allow a utility more flexibility to select feasible treatment technologies appropriate to its source water. By maximising control of precursors, disinfection treatment would not necessarily need to be altered.

"Best Available Technologies" and other possible technical solutions to the above regulatory approaches remain to be determined. The SDWA strictly specifies that a BAT be established for each standard that is economically feasible for large water systems. However, for many smaller water systems, the specified technologies may be prohibitively expensive, with the result that such systems may not be able to comply with a given standard or achieve its health goals. Additional concerns about setting numerical standards and specifying treatment techniques arise from needs that these regulations be administratively implementable.

Regulatory options resulting from negotiation

After several years of preliminary efforts, EPA has adopted an approach to developing the DBP Rule that brings together representatives of affected groups to negotiate an acceptable approach to this rule. These groups include state and federal regulators, utilities, public interest groups and health organizations. This process began in November 1992 and will likely conclude in March 1993.

The general approach that has evolved has separated out the formal development of the ESWTR and GWDR from the DBP Rule, although all rules will be linked sequentially. The DBP Rule will be promulgated in two phases. It is intended to promulgate a Phase I DBP Rule to become effective about 1997. This will be followed by the ESWTR and GWDR about the year 2000. The Phase II DBP Rule would occur about 2002.

The Phase I DBP Rule is likely to specify that all drinking water systems achieve MCLs for TTHMs = 80 µg/l and for THAAs = 60 µg/l, with dates of compliance based on system size and source water type. Surface water systems with greater than 10,000 service connections are currently required to comply with a TTHM MCL and would be the first to comply with this rule. Smaller surface water systems would be next, followed by groundwater systems.

For conventional surface water systems, "enhanced coagulation" will be generally required if total organic carbon levels are greater than 2 mg/l. The definition of enhanced coagulation has yet to be determined.

Regulatory limits would be set for distribution system residual disinfectants of perhaps a maximum of 4 mg/l for chlorine and 4-6 mg/l for chloramine. Systems using ozone would have to meet an MCL for bromate; those systems using chlorine dioxide would have to meet an MCL for chlorite. The MCL values are yet to be determined.

Larger surface water systems would be required to immediately begin a two-year routine monitoring program for microbial pathogens, including *Giardia*, *Cryptosporidium*, viruses and coliforms. Data from this effort would be used to develop the ESWTR.

The water and chemical industries would contribute substantial monies ($30 million over five years) for research to determine the most cost-effective means for reducing total DBP and microbial risk. This would include, but not be limited to, consideration of membrane and ozone technologies.

Conclusion

While the results of the negotiated rulemaking are promising, EPA has a legal deadline of April 1993 to determine if this process will produce a proposal to which all parties will agree. If this process fails, EPA must develop a proposal on its own, although it would likely be very similar to that discussed above. EPA is under a court order to propose the DBP Rule by June 1993.

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Table 1. Waterborne domestic microbial infection, 1985*.

Disease or agent	Incidence	Fatality/case (%)
Total Water-borne	940,000	0.1
Campylobacteriosis	320,000	0.1
E. coli	150,000	0.2
Misc. enteric	10,000	1.0
Salmonella, nontyphi.	60,000	0.1
Shigella	30,000	0.2
Typhoid	60	6.0
Vibrio (excl. Cholera)	1,000	4.0
Yersiniosis (excl. plague)	1,800	0.05
Norwalk	300,000	0.0001
Giardia	70,000	0.0001

*Data calculated from BENNETT, J.V. *et al.*[1].

Table 2. Suspected waterborne diseases and organisms*.

Disease or agent	Fatality/case (%)
Cholera	1.0
Legioneliosis	15
Enteroviral disease (excl. polio)	0.001
Hepatitis A	0.3
Poliomyelitis	10
Rotavirus	0.01
Coxsackieviruses	-
Echovirus	-
Reovirus	-

*Data from BENNETT, J.V. *et al.*[1].

Table 3. Concentrations of organisms resulting in a 1/10,000 annual risk of infection*.

Organism	number/liter
Rotavirus	2.2×10^{-7}
Polio III	2.6×10^{-7}
Endamoeba coli	6.2×10^{-7}
Giardia	6.8×10^{-6}
Polio I	1.5×10^{-5}
Echovirus 12	6.8×10^{-5}
Polio I	1.9×10^{-3}

*Data from REGLI, S. *et al.*[3].

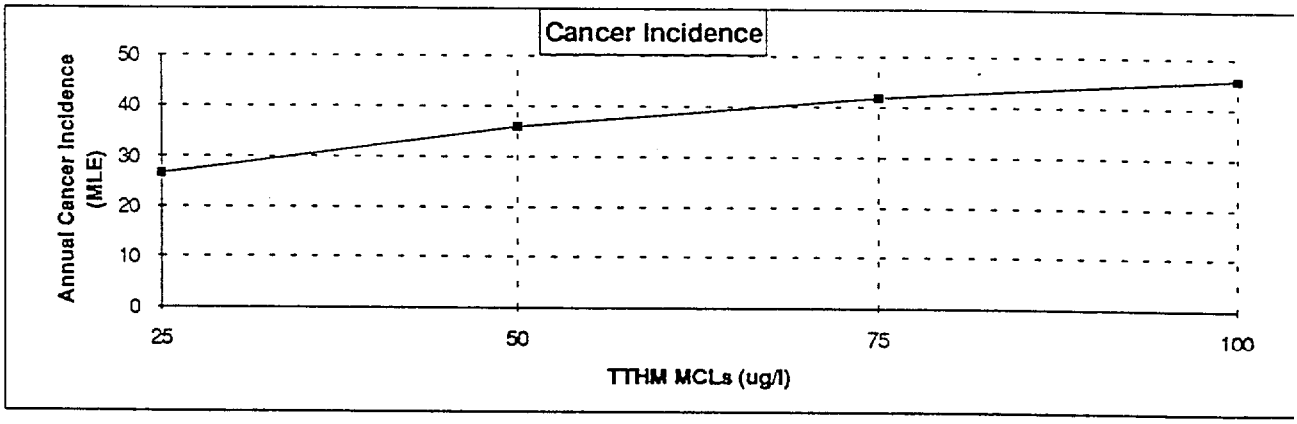
Table 4. Candidate compounds for regulation.

Trihalomethanes	dDaft MCLG	Health effect and cancer status (tentative)
chloroform (CM)	0	cancer, B2
bromodichloromethane (BDCM)	0	cancer, B2
dibromochloromethane (DBCM)	60 µg/l	liver, C
bromoform (BM)	0	cancer, B2
total THMs	0	cancer, B2
haloacetic acids (HAs)		
trichloroacetic acid (TCA)	100 µg/l	liver, C
dichloroacetic acid (DCA)	0	cancer, B2
total HAs monochloroacetic acid (MCA) trichloroacetic acid (TCA) dichloroacetic acid (DCA) monobromoacetic acid (MBAA) dibromoacetic acid (DBAA)	0	cancer, B2
Other		
chloral hydrate (CH)	5 µg/l	liver, C
bromate	0	cancer, B2
chlorine	4 mg/l	blood, D
chloramines	3 mg/l	blood, C
chlorine dioxide	0.8 mg/l	blood, neurological, D
chlorite	0.3 mg/l	blood, D
chlorate	health advisory	

Table 5. Drinking water concentrations for lifetime cancer risks (upper 95th percentile confidence interval) (µg/l).

By-product	10^{-4}	10^{-5}	Occurrence range
Bromodichloromethane	60	6	0-100
Bromoform	400	40	0-50
Chloroform	600	60	0-340
Dichloroacetic acid*	10	1	0-80
Bromate*	5	0.5	unk

*tentative risk estimate (11/92)



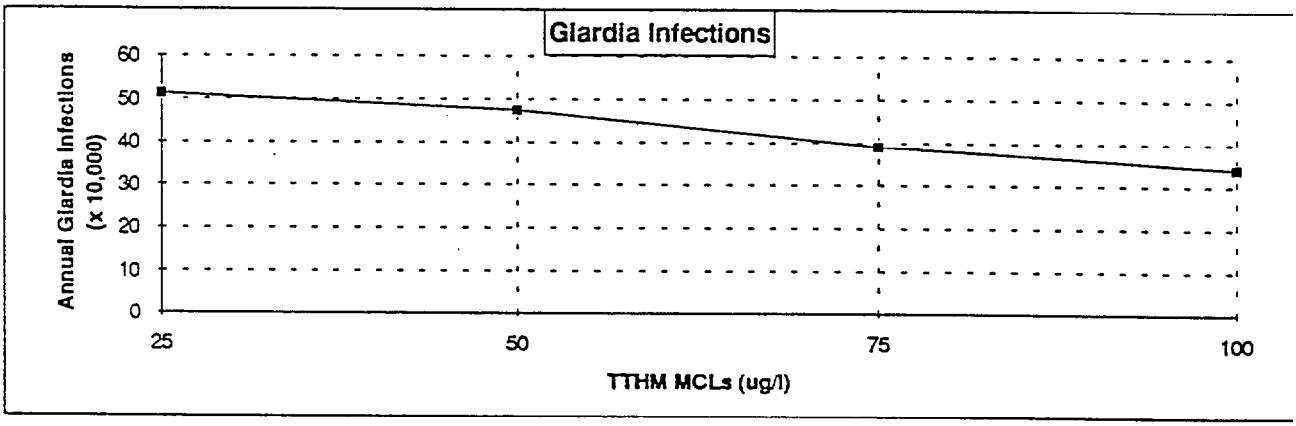
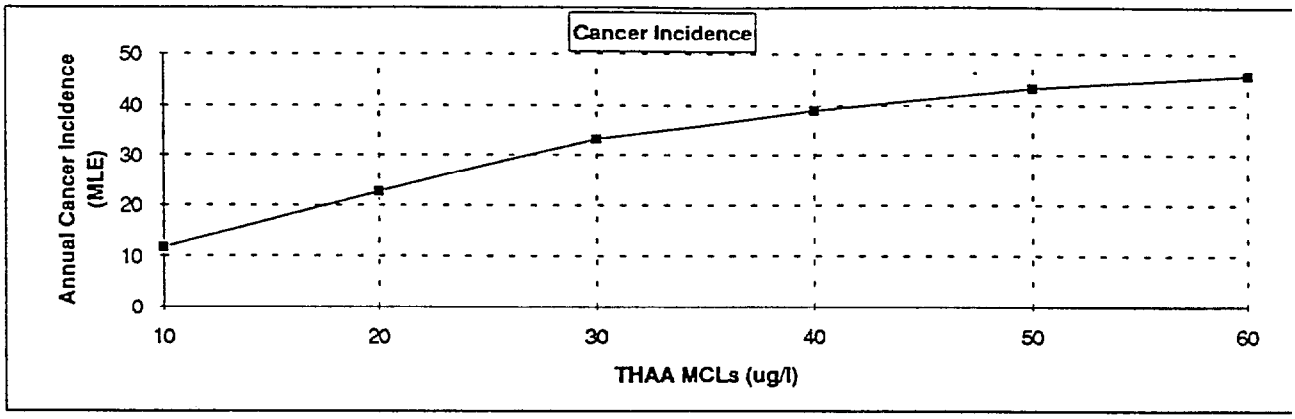


Figure 1. Annual health risks.



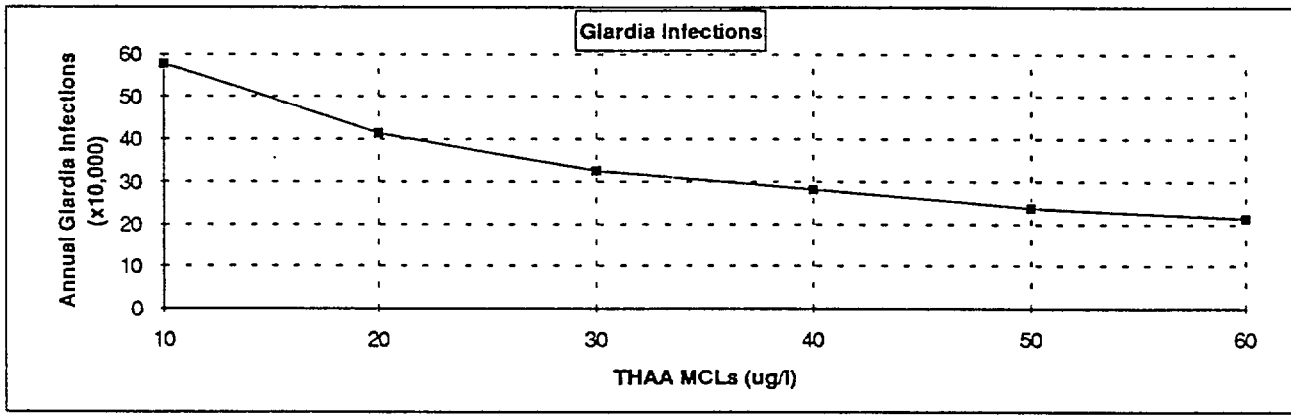


Figure 2. Annual health risks.

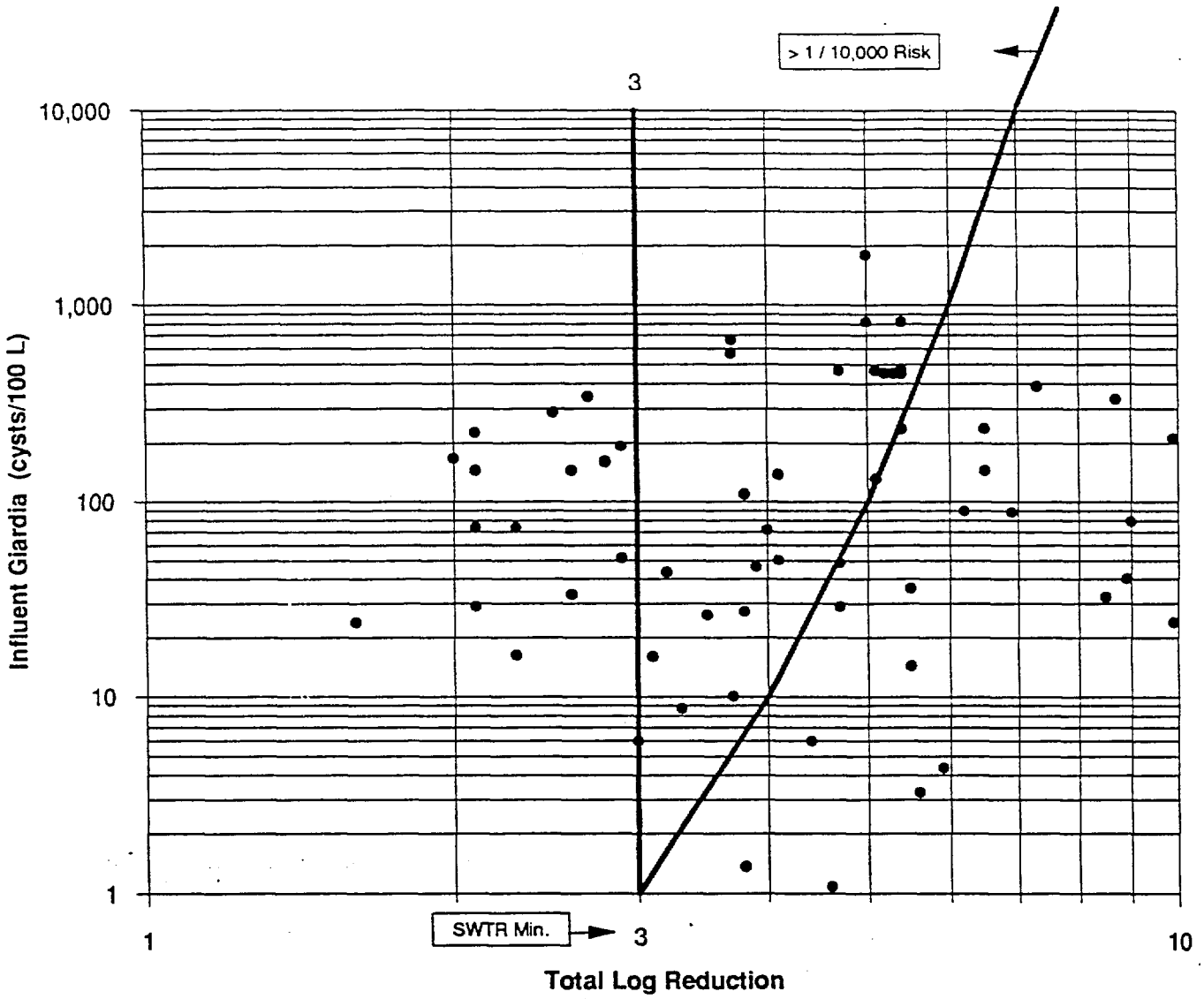


Figure 3. Influent *Giardia* vs. Total Log Reduction (Winter) from LeChevallier.

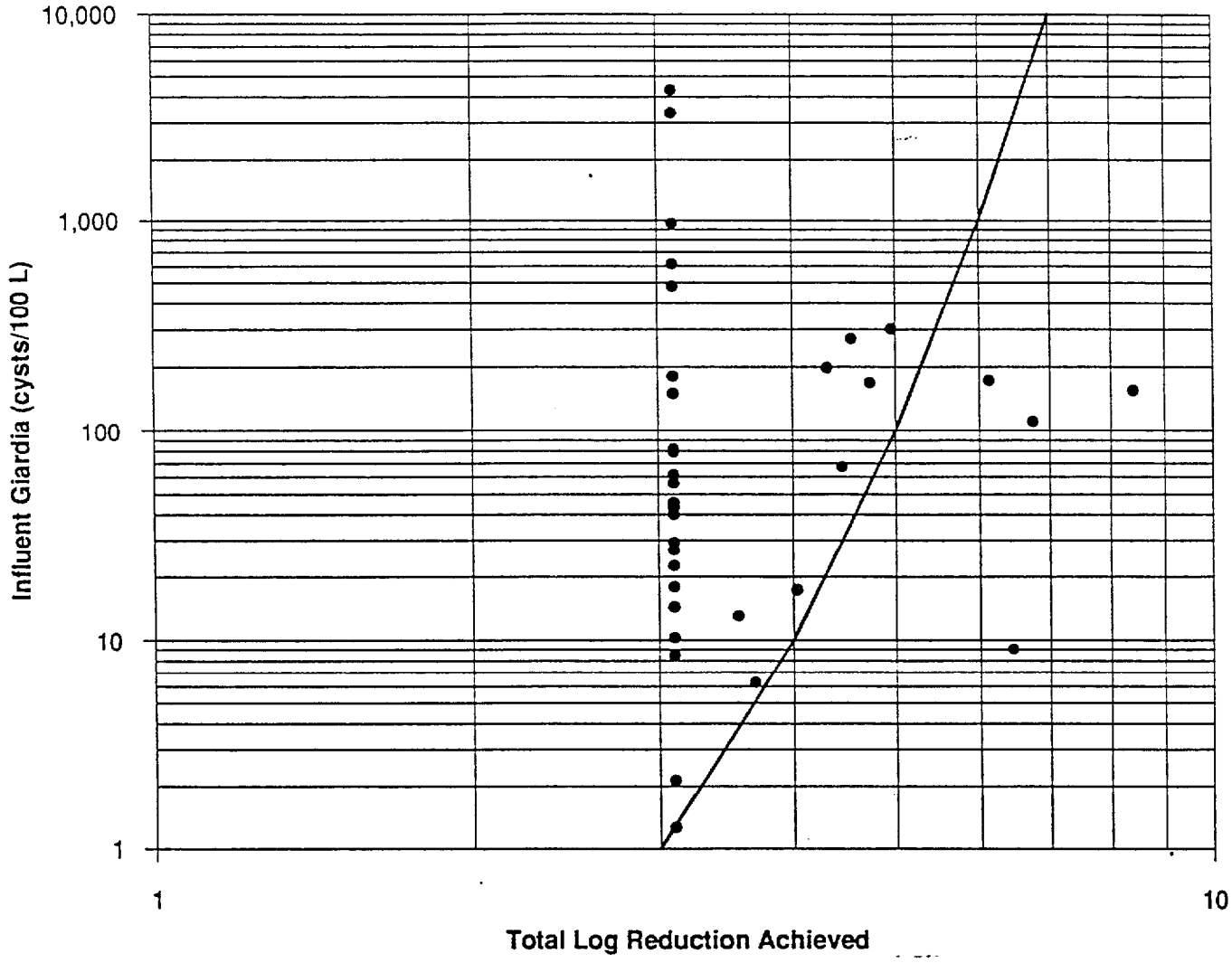


Figure 4. SWTR scenario : with alternative disinfectants TTHM MCL = 100 (µg/l) Number of plants = 39.

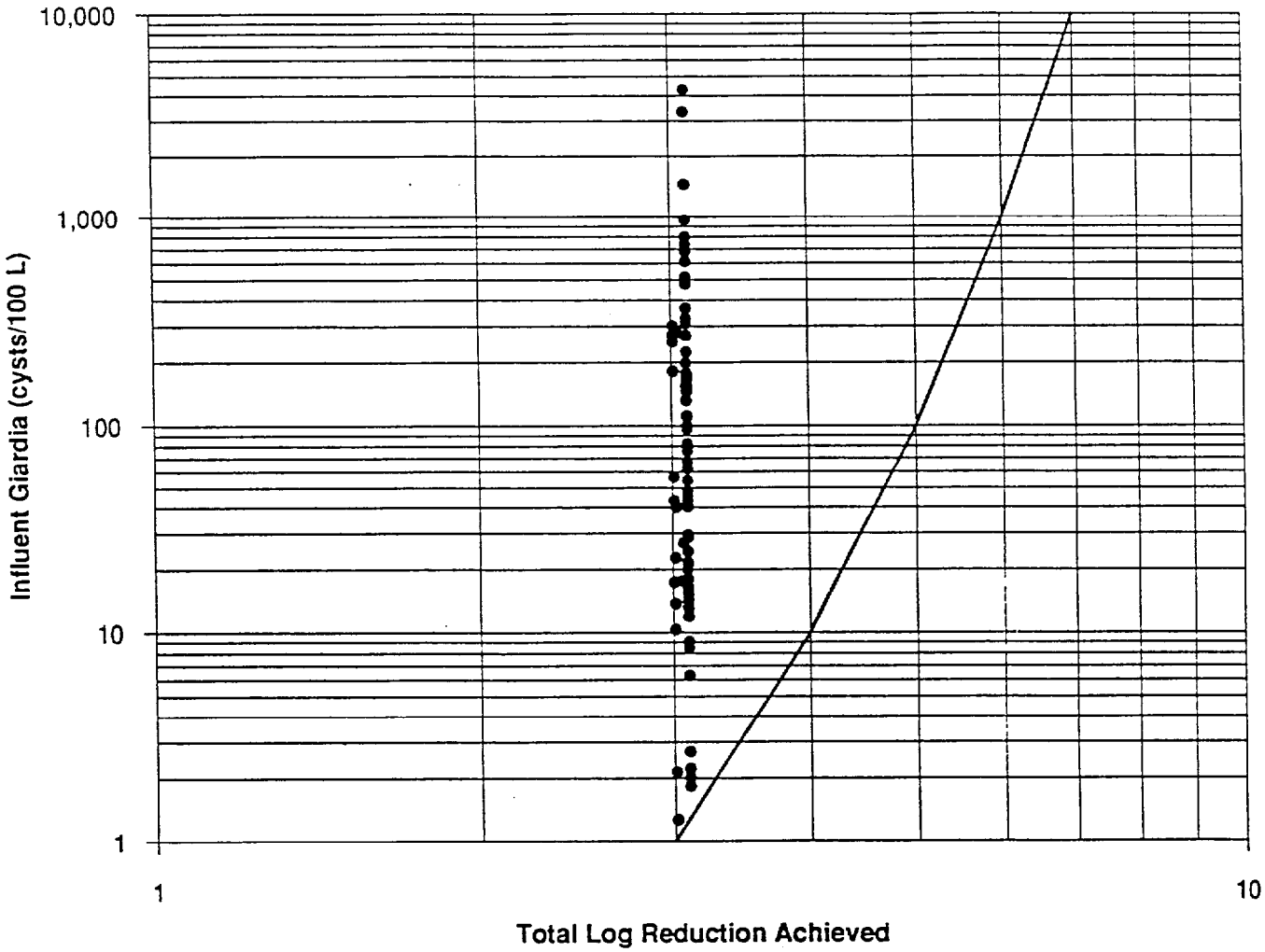


Figure 5. SWTR scenario : with alternative disinfectants TTHM MCL = 25 (µg/l Number of plants treating = 83.

FUTURE DEVELOPMENTS IN WATER TREATMENT

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The significance and control of disinfection by-products has been the subject of intense research and discussion in the water industry over the last 15-20 years.

There is universal consensus that reduction of by-products should not compromise disinfection effectiveness, and thus solutions to the problem depend on a very careful and planned balancing of relative risks. Interestingly, growing customer pressures from chlorine taste complaints provide a further incentive to get this balance right.

With the growing knowledge of the wide range of microbial species that may be found in water, and their health significance, the objectives of disinfection are becoming harder to define with any degree of precision. When there was less concern about the adverse effects of chlorine, it was easy to err on the side of caution and use oxidative disinfectants to excess. With the need to develop more sophisticated approaches to disinfection in order to control by-products it therefore becomes increasingly important to be clear about the objectives of disinfection.

The prime objective must be to remove or inactivate harmful organisms. However, as our knowledge of pathogenity increases it becomes more and more difficult to define 'harmful'. It is, for example, impossible to achieve sterility in distributed water, but should we be concerned about the potential slight risks from opportunist pathogens that may be present in some waters, especially for immunocompromised individuals, or should we only be concerned with providing water that can safely be used by the vast majority of normal healthy consumers?

In general it is suggested that there should be three separate, but interlinked, disinfection objectives. The first and one of the most important is to control bacterial faecal pathogens for which the best indicator is still *E. coli*. The second and probably equally important is to control non-bacterial faecal pathogens such as protozoal parasites, primarily through provision of a multibarrier approach including both catchment protection and treatment. Finally it is necessary to control opportunistic pathogens by careful management of biofilms that will inevitably colonise the inside of all distribution system pipework.

In practice, control of microbial quality at the customer tap is a complex water management task that relies on more than just good treatment at the waterworks. Achieving this goal, without generating unacceptable disinfection by-product levels, or taste complaints, thus requires control of the raw water catchment, introduction of multistage and more tightly controlled water treatment, sophisticated control and management of the water distribution system, and high standards of repair, maintenance and refurbishment of the associated water infrastructure.

These management tasks can be broadly grouped into three main target areas:

1. Improved control of source works disinfection

   This includes better catchment protection, reducing disinfection by-product precursors without the use of oxidants, improving the design and operation of disinfection contactors, use of newer physico-chemical processes such as UV and membranes, and much more careful monitoring and control of the whole treatment process.

2. Preventing ingress of contaminated water

   This relates primarily to maintaining the integrity of the distribution system, as well as good hygienic practice for repairs.

3. Biofilm management

   This is an area of growing importance and relies on increasingly sophisticated management procedures, including reduced particulate breakthrough from the treatment plant, reducing the nutrient content of water, optimising control of the distribution system to increase water turnover and use of good quality pipes and fittings, including those in domestic properties.

Future developments in this area are most likely to come from refinement of existing techniques, processes and systems rather than any radical and major new technology. In particular, introduction of new and/or improved monitoring and control systems will be of particular significance to utility managers in this regard.

The extent to which these increasingly sophisticated techniques can be introduced depends on a range of factors including the quality of the raw water, the precise disinfection objectives, the level of by-products that can be tolerated, the condition of the water infrastructure, the amount of finance that is available and the ability to master the high level of technology that is required.

At no time should adequate disinfection be compromised but the ultimate goal must be to deliver safe and taste free high quality water at the tap from whatever raw water source, without the use of oxidative disinfectants at all. The holy grail for water professionals is to achieve this task without dramatically increasing the cost of water.

SUMMARY OF DISCUSSION - DAY 2

The bulk of the discussion on the second day of the seminar was related to the US EPA approach to disinfection by-products (DBPs) and risk assessment. A summary of the main points of this discussion is given below. Topics arising from other presentations are also summarised.

EPA risk assessment policy

The EPA is currently considering regulation of a wide range of DBPs in addition to those already regulated. The need to balance mandatory requirements for disinfection, via compliance with the surface water treatment rule (SWTR) and the coliform rule, with future legislation on DBPs is critical in setting standards. The EPA is proposing to regulate 83 chemicals initially, with a further 25 additional compounds every 3 years. The US Safe Drinking Water Act specifies that a best available technology (BAT) for each standard is established that is economically feasible for large water systems. The BAT will have to include disinfection options and will be based on large treatment works with the possibility of application to smaller works. The BAT does not include the use of new technologies, and therefore there seems to be no pressure or incentive for utilities to develop new processes. Why the EPA needed to provide details of the BAT was queried - would it not be simpler to specify the limit and leave it to the individual utilities to employ processes to meet the limit? In reply, it was pointed out that the statute requires the EPA to specify the BAT in order to give utilities a chance of meeting the limits. The possibility was raised of providing a number of different options rather than a single BAT, mainly to avoid the possibility of a particular BAT failing to achieve the necessary standards in all cases (because of differences in water types etc). It was stated that other treatment options can be used as long as the end result is at least as effective as the BAT specified.

The approach adopted by the EPA to risk assessment was raised. It was noted that in 1985, an estimated 1000 deaths in the US were caused by water-borne diseases. Other data suggest that up to 25% of the population can suffer illness due to microbial contamination of the water, but it is seldom reported or diagnosed as such. In 1985, 80% of breaches of maximum contaminant levels (MCLs) related to microbiological limits, and of these over 90% occurred in small systems. Data were available for Giardia, and therefore this was included in the surface water treatment rule (SWTR). One of the major goals of the SWTR is to achieve a risk of Giardia infection of less than 1 case in 10000 per year. Since Giardia is hard to inactivate, it is thought that if this can be achieved then levels of other microbes will be even lower. It was pointed out, however, that Giardia is not a problem in groundwater, so other measurements are required to show satisfactory inactivation (e.g. for viruses).

An example of the type of model used to evaluate the relative risks of microbial activity versus DBPs was outlined. By lowering the MCL for trihalomethanes (THMs), a lower cancer risk should be attained. This decrease in risk, however, is small. If the reduction in THM levels is achieved through the use of a lower disinfection dose, then the microbiological infection risk increases significantly. Models estimate that 200 extra deaths from water-borne microbial diseases could arise for a reduction of 15 cancer deaths. The proposed rule has to be devised so that there is no increase in the risk of microbial infection, and ideally that there is a net decrease. It was suggested that there were some weaknesses in the microbial model due to lack of quantitative data. It was emphasised that DBPs with known risks must be controlled, as must those with unknown risks. The possibility was discussed of monitoring certain compounds as representatives of certain groups of DBPs (e.g. bromodichloromethane for THMs) to avoid extensive monitoring. The difficulty of trying to improve disinfection while minimising DBP formation was again emphasised.

The EPA has adopted an approach to developing the DBP rule that brings together representatives of the affected groups to negotiate an acceptable approach to the rule (the negotiated regulations approach). In this way state and federal regulators, utilities, public interest groups and health organisations are all involved in decision making, although it is not known how successful this approach will be.

Other areas of discussion

The possibility of minimising the need for disinfection through better control of source waters was raised. One option would be better protection of catchments. It was felt that this was one way forward, but in practice would be extremely difficult to achieve. Another possible solution would be to increase impoundment. Again, this would be desirable, but the costs would be high since long storage times would be required to achieve significant degradation of contaminants/bacteria.

It was emphasised that it is important to strike a balance between producing 'sterile' water (which is not healthy for consumers, since they need to build up some immunity) and 'safe' water. Another issue raised was whether it was possible to reduce the 'age' of water, i.e. the time spent in the pipe. Computer models help, enabling better management of water in the distribution system. It was suggested that the pipe has to be considered as a 'chemical reactor' and its management should be addressed accordingly.

The use of UV irradiation as a disinfectant could be one option for minimising by-product formation. It was thought likely, however, that the public may be suspicious of this technique, although it is already used extensively in small water supplies. In addition, there is little information on possible by-product formation from UV disinfection.

SUMMARY OF KEY POINTS FROM SEMINAR

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The seminar dealt with five key areas:

- Formation of by-products
- Health risks
- Remedial measures
- Standards and legislation
- Costs

Formation of by-products

1. The principal problems with disinfection by-product (DBP) formation occur with surface waters, although occasionally treatment of groundwaters can cause problems. The UK's high proportion of supplies from surface water rank it among the top four in the EC.

2. Data on occurrence of DBPs comes from laboratory and field investigations. In the laboratory, the state of development of analytical techniques determines the number of compounds found. Field data are still limited.

3. The DBPs found depend on a combination of raw water quality and disinfectants/oxidants used. With chlorine alone, reaction with organic substances leads to the formation of the well known THMs. In addition upwards of 20 other chlorinated compounds have been detected. When bromide is present, an additional 8-10 brominated species have been detected, resulting in 10 groups of compounds in all.

4. The use of ozone results in the formation of aldehydes, keto-acid, peroxides and epoxides. These may be removed by filtration and biological treatment, but can reform on final chlorination.

5. When bromide is present in the raw water, the use of ozone can result in the formation of bromate, which is of concern because of its classification by WHO as a genotoxic carcinogen with potentially low limits in drinking water.

6. WHO have set guideline values for 15 by-products, with a further 8 requiring more data prior to any guidelines being proposed. There is some possibility of narrowing this down to a few key parameters for monitoring purposes, but there is not uniform scientific agreement on this approach.

Health risks

7. The essential task is to consider both the microbiological and the chemical risks. Microbiological risks affect all ages and have an instant effect but, in developed countries, medication is available. Chemical risks inspire more fear, affect later life, are additional to a high existing background, but have limited medical remedies.

8. UK figures on water-borne disease show a good track record, with around 200 cases per annum, but no deaths in 50 years. Figures for the USA are different, with a higher incidence of illness and a positive death rate.

9. For chemicals there are considerable uncertainties in estimating risks. For all but genotoxic carcinogens, there is a considerable margin of safety even when limits are exceeded. For genotoxic carcinogens there is a theoretical risk at all concentrations, but this is probably considerably overstated.

10. Even accepting the risk model estimates, perspective is needed in assessing the possibility of additional cancers against the existing background. The epidemiological studies of Morris *et al* applied to the UK suggest an addition of 1.4% to cancer cases from water. However, estimates using the risk model with 8 genotoxic substances at the 10^{-5} risk level for a lifetime give an addition of 0 to 0.02%.

11. There is some uncertainty about whether a real balance exists between microbiological and chemical risks, because this suggests that measures to reduce chemical risks automatically increase microbiological risks. This seems doubtful.

12. An all important question is public perception. Scientific justification without change of public perception is not enough. The zero risk in drinking water perception will require careful adjustment.

Remedial measures

13. Avoidance of by-product formation is possible if raw water sources are used which are pathogen-free, and hence do not require disinfection, or are low in organics and disinfectants do not produce by-products.

14. By-product formation can be limited where disinfection is necessary by modifying the use of chlorine or using alternative disinfectants. However, the latter approach has now been shown to produce other by-products in some circumstances.

15. An alternative approach is to enhance conventional treatment to reduce disinfection requirements by reducing pathogen penetration. There are still mixed feelings about substantial reductions in, or abandonment of, a residual in distribution.

16. Advanced treatment can be used to reduce precursors thus minimising by-products. There is some evidence, however, that despite a reduction in potential precursors at the treatment stage, by-products can still increase in distribution.

17. Removal of DBPs once formed is not an easy treatment option. Both bromate and halogenated organic compounds are difficult to remove. Some DBPs, such as aldehydes, can be removed or reduced by GAC filtration.

Standards and legislation

18. Currently UK Regulations require disinfection of all supplies plus compliance with limits for trihalomethanes and total coliforms. In 1992 the Chief Inspector's report shows non-compliance in supply zones of 1.2% of determinations for total coliforms (3.2% of zones) and 0.2% of determinations for faecal coliforms (9.9% of zones). For trihalomethanes the figures were 4.6% of determinations (5.2% of zones). This indicates that a balance problem already potentially exists.

19. Advanced treatment, especially activated carbon, is being installed on many surface water supplies to meet other limits such as pesticides, and to improve taste and odour. This will help the by-product problem unless ozone is required for waters containing bromide.

20. Revision of the Regulations will follow from action at EC level to revise the directive or at national level following publication of the revised WHO Guidelines. Both exercises will need to take account of the list of 15 by-products given guideline values by the WHO. Consideration will need to be given to the values and compliance rules, as well as the impact on monitoring load. The possibility of using a few screening parameters will need to be explored.

21. An alternative approach is to define a treatment solution to reduce risks but not work to a series of limits. This is a philosophy developed for some substances in the USA, but would be a novel approach for European legislation.

Costs

22. There is a clear relationship between risk reduction and cost, which becomes asymptotic towards zero risk. The question is who decides on acceptable risks/costs. The customer is not in a position to and experience shows that decisions are often driven by pressures from environmental campaigns. Public perception is again a critical factor. Water suppliers, however, need sufficient notice of change to allow for stable longer term investment plans.