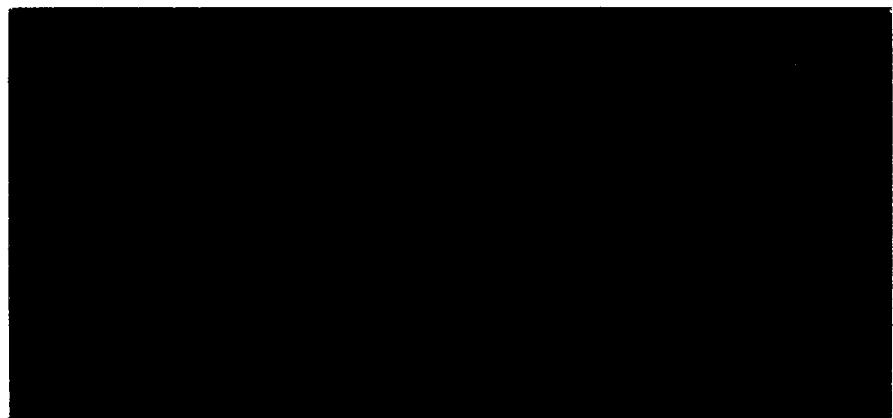
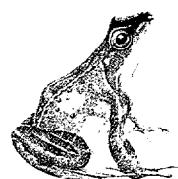


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**OZONE FOR CRYPTOSPORIDIA ELIMINATION - A REVIEW OF
OZONATION BY-PRODUCTS AND OZONE APPLICATION**

Final report to the Department of the Environment

DoE 2568-M(P)

APRIL 1991

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AND OZONE APPLICATION**

Final report to the Department of the Environment

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SUMMARY

I OBJECTIVE

To review information on by-products resulting from the application of ozone for drinking water disinfection; to consider and identify the best point in the treatment process to apply ozone; and to review recent practice in the design and installation of ozone facilities.

II REASONS

Cryptosporidium has been recognised as an important microbial contaminant of water. The oocysts of the parasite are resistant to most disinfectants, including chlorine, but may be effectively inactivated using ozone. Ozone is little used in the UK and there is little experience in the design, construction and operation of ozonation facilities. If ozone were to be used as a disinfectant to control Cryptosporidia, knowledge of the disinfection by-products resulting from its use, the best point to apply ozone, and how to engineer ozone plants into existing treatment plants would be required.

III CONCLUSIONS

Ozone reacts with a broad range of organic compounds in water to produce a variety of by-products. Most published information relates to laboratory tests which may not be directly relevant to drinking water ozonation. Increased concentrations of bromate, formaldehyde and other aldehydes, and organobromine compounds, including bromoform, have been reported in water as a result of the use of ozone, whereas concentrations of certain raw water contaminants and by-products of final chlorination may be reduced. There is little information on the potential health risk to the consumer from ozonation by-products in drinking water but it is likely to be small compared with the benefits.

Ozone should be applied as late as possible in the treatment process to avoid unwanted side reactions. With surface waters, biological filtration after ozonation will be required. Terminal disinfection with

chlorine or chloramine will be required to protect the distribution system. Installing ozone in an existing plant may involve significant engineering complexities.

IV RECOMMENDATIONS

Further studies should be undertaken to identify and quantify ozonation by-products in drinking water using pilot or full scale plant. The significance to health of ozonation by-products should be evaluated. However, any health risks posed by ozonation by-products in drinking water are probably low, and, consequently, there is no reason why ozone should not be used to eliminate Cryptosporidium.

With good quality (ie low content of organic matter and low bromide concentration) groundwaters, there should be no problems with unwanted side-effects and ozone can be applied ahead of terminal chlorination. With surface waters, where coagulation is used, ideally ozone should be provided after the existing filters, and an additional, biological, filtration stage should be installed following ozonation. If it is not possible to install additional filtration plant, ozone should be dosed after sedimentation but before sand filtration. Ozone should be applied before slow sand filters. Terminal chlorination or chloramination should always be provided.

V RESUME OF CONTENTS

The reactions of ozone with organic compounds in water are reviewed, and published information from laboratory studies of by-products are summarised. Ozonation by-products in drinking water are reviewed. The applications of ozone for drinking water treatment are considered with a view to optimising the placement of ozone to minimise unwanted side reactions. Recommendations on the best place to install ozone are made and the practical aspects, including costs, of ozonation facilities are considered.

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SECTION 1 - INTRODUCTION

1.1 BACKGROUND

Cryptosporidium has recently been recognised as an important microbial contaminant of water (Rose 1988). Cryptosporidium is a protozoan parasite which infects the small intestine and is now accepted as a common cause of acute diarrhoeal disease in humans (Peeters *et al* 1989). Ingestion of contaminated water is one of the principal modes of transmission of the organism. Both surface and groundwaters may be contaminated by oocysts of Cryptosporidium.

Few commercial disinfectants have been found to penetrate the oocysts of the parasite, and normal chlorination of drinking water and filtration have both been found to be ineffective in removing the oocysts (Peeters *et al* 1989). Ozone, and to a lesser extent chlorine dioxide, have been reported to be more effective. The disinfection of water containing oocysts remains an area of continuing research but on the available evidence it appears likely that ozone will be the disinfectant of choice.

Ozonation of drinking water has been practised in France since 1906, and currently over 700 French waterworks have ozonation facilities (Bourbigot 1990). Ozone is also used in other European countries, especially Germany and Switzerland, and is being used increasingly in the United States (Tate 1990). One of the reasons for this is to avoid the formation of potentially harmful by-products resulting from the chlorination of water. Ozonation also produces organic by-products but less is known of their formation, identity and potential health effects.

Ozonation has been little used in the United Kingdom, largely because it acquired a tarnished reputation when used for colour removal after problems were encountered at the Loch Turret treatment plant (Hyde and Zabel 1986). Consequently, there is relatively little UK experience in the design, installation and operation of drinking water ozonation plants.

The present study was undertaken to summarise, by means of a literature review, available information on the by-products formed during ozonation and also to consider the most appropriate point in the water treatment process for application of ozone for disinfection.

1.2 OBJECTIVES

This study was undertaken under contract to the Department of the Environment with the following objectives:

- i) To collate and summarise published information on chemical by-products arising from the action of ozone, applied at doses used for disinfection, on the organic substances in water including aliphatic and aromatic substances, amino acids, heterocyclic compounds, humic and fulvic acids and selected pesticides.
- ii) To consider and identify the best point for application of ozone in the water treatment process to achieve adequate disinfection and to minimise unwanted side-reactions.
- iii) To review recent practice in the application of ozone in Europe and North America, and to consider practical aspects of installing ozonation facilities in existing drinking water treatment plants.

SECTION 2 - BY-PRODUCTS

2.1 OZONE REACTIONS

Natural waters contain organic material in the concentration range between 0.5 and 30 mg l⁻¹, much of this in the form of humic substances. These substances are ubiquitous in natural waters and consist of complex associations of high molecular weight compounds derived from chemical and biological action on plant degradation products (Aiken *et al* 1985).

In addition, a wide range of low molecular weight compounds are present at low concentrations ($\mu\text{g l}^{-1}$ range), eg amino acids, carbohydrates, fatty acids (Aiken *et al* 1985, Fielding *et al* 1981) and there may be man-made organic compounds such as pesticides and polynuclear aromatic hydrocarbons (PAHs). These compounds may react with ozone during water treatment ozonation and form a variety of by-products.

Some organic substrates can be oxidised completely by ozone to carbon dioxide and water. However, the conditions for such reactions are unlikely to be achieved during normal water treatment practice. Reactions are likely to be incomplete, resulting in the formation of intermediate and final products in various ratios depending on the conditions used.

Ozone may react with organic compounds in aqueous solution in the following ways (Doré 1985):

- i) dipolar cycloaddition }
- ii) electrophilic attack } direct reactions
- iii) nucleophilic attack }
- iv) radical reactions indirect reactions

Examples of such reactions include, respectively:

- i) formation of aldehydes, ketones or acids from unsaturated aliphatic compounds;
- ii) formation of substituted phenols from substituted benzenes;
- iii) formation of aromatic aldehydes from aromatic imines;
- iv) formation of hydroxyphenol from phenol.

The direct reactions (i-iii) tend to be specific and occur at relatively slow reaction rates. The radical reactions (iv) occur as a result of

the decomposition of ozone in water, predominantly to produce hydroxyl radicals. Reactions of hydroxyl and other radicals occur at relatively fast rates and are less specific than the direct reactions.

The nature and amount of organic by-products resulting from aqueous ozonation depend on various factors, mainly the chemical nature of the substrate, substrate and ozone concentrations, ozone-to-substrate ratio, water pH and the presence of other organic and inorganic compounds in the water. The latter can affect by-product formation by:

- i) competition for the oxidant (ie oxidation of iron or manganese ions from Fe^{2+} or Mn^{2+} to Fe^{3+} or Mn^{4+} respectively);
- ii) reaction with inorganic compounds, eg bromide, to produce bromate, bromine and hypobromous acid; the latter two will react with organic substances to form organobromine compounds;
- iii) inhibition of radical reactions by radical scavengers (eg bicarbonate or phosphate anions).

2.2 REACTIONS OF OZONE WITH ORGANIC SUBSTANCES IN AQUEOUS SOLUTION

Ozone can react with naturally occurring and man-made organic substances in water to form a variety of by-products. Ozone is generally more reactive than chlorine towards raw water contaminants such as PAHs and pesticides. Thus its application in drinking water treatment may be beneficial by destroying such compounds. However, the products of such reactions are often unknown, and consequently it is not possible to assess whether they are more or less desirable than the original contaminants in terms of any possible health effects on consumers.

The following sections and Table 1 summarise the available information on the reactivity and by-products of organic substances. The studies were carried out in the laboratory, often under conditions which are atypical of normal water treatment practice. In particular, substrate concentrations were often higher than might be encountered in raw waters

Table 1 - Reactivity of organic substances with ozone and products of their reactions

Compound	Reactivity	Products	Reference
Humic and Fulvic Acids	+	alkanes, aldehydes, aliphatic keto compounds, hydroxyacids and diacids, benzoic acids, phthalates, furans	Legube <u>et al</u> 1989
Protein and amino acids			
protein	+	?	Nebel 1981
amino acids	+	?	Nebel 1981
glycine	+	formaldehyde, glyoxylic acid	Yamada and Somiya 1980
leucine	+	formaldehyde, pyruvic acid	Yamada and Somiya 1980
Carbohydrates			
glucose	(+)	arabinose, gluconic acid	Legube <u>et al</u> 1989
xylose	(+)	xylonic acid	Legube <u>et al</u> 1989
cellobiose	(+)	glucose, arabinose, gluconic acid	Legube <u>et al</u> 1989
lactose	(+)	glucose, galactose	Legube <u>et al</u> 1989
maltose	(+)	?	Legube <u>et al</u> 1989
galactose	(+)	?	Legube <u>et al</u> 1989
saccharose	(+)	?	Legube <u>et al</u> 1989
Aliphatic Compounds			
alkanes	-	-	Fielding <u>et al</u> 1989
alkenes	++	aldehydes	Fielding <u>et al</u> 1989
saturated acids			
saturated fatty acids (C _{8,10,12,14,16-18})	-	-	Fielding <u>et al</u> 1989 Reynolds <u>et al</u> 1989a
acetic acid	-	-	Al-Hayek <u>et al</u> 1989
formic acid	(+)	?	Al-Hayek <u>et al</u> 1989
oxalic acid	-	-	Al-Hayek <u>et al</u> 1989

Table 1 - Continued

Compound	Reactivity	Products	Reference
unsaturated acids			
hexadec-9-enoic	++	heptanal, heptanoic acid, 9-oxononanoic acid, nonanedioic acid	Fielding <u>et al</u> 1989 Reynolds <u>et al</u> 1989a
octadec-9,12-dienoic	++	hexanal, hexanoic acid, 9-oxononanoic acid, nonanedioic acid	Fielding <u>et al</u> 1989
maleic acid	(+)	?	Al-Hayek <u>et al</u> 1989
citraconic acid	+	glyoxalic, pyruvic, hydroxypyruvic, acetic, formic, oxalic acid	Gauduchea <u>et al</u> 1987
alcohols			
ethyl alcohol	+	acetaldehyde, acetic acid	Laplanche and Martin 1984
propan-2-ol	+	acetone, acetic acid	Laplanche and Martin 1984
aldehydes			
glyoxal	+	glyoxylic acid, oxalic acid, carbon dioxide	Caprio <u>et al</u> 1989
glyoxylic acid	+	oxalic acid	Glaze 1986
Aromatic Hydrocarbons and PAHs			
toluene	-	-	Fielding <u>et al</u> 1989
xylene (o,m,p)	-	-	Fielding <u>et al</u> 1989
ethylbenzene	-	-	Legube <u>et al</u> 1983
diethylbenzene	-	-	Legube <u>et al</u> 1983
styrene	+	benzaldehyde, benzoic acid, ring fragmentation products, hydrogen peroxide	Glaze 1986
naphthalene	++	phthalic acid, o-carboxybenzaldehyde, oxalic acid, formic acid, hydrogen peroxide	Fielding <u>et al</u> 1989 Glaze 1986 Legube <u>et al</u> 1983
fluorene	(+)	fluorene-9-one, hydroxylated fluorene, homophthalic acid, phthalic acid, oxalic acid	Fielding <u>et al</u> 1989 Helleur <u>et al</u> 1979 Dreher and Klamberg 1988
phenanthrene	++	?	Fielding <u>et al</u> 1989

Table 1 - Continued

Compound	Reactivity	Products	Reference
fluoranthene	+	fluorene-9-one-1-carboxylic acid, phthalic acid, fluorene-1,9-dicarboxylic acid, oxalic acid	Dreher and Klamberg 1988
acenaphthene acid,	+	1-indanone-7-carboxylic acid, indan-1,7-dicarboxylic acid, oxalic acid	Dreher and Klamberg 1988
pyrene	++	?	Fielding <i>et al</i> 1989
benzo(a)pyrene	++	?	Butkovic <i>et al</i> 1983
Aromatic Compounds (excluding hydrocarbons)			
phenol	++	hydroxylated benzenes, catechol, quinones, hydroquinone, p-benzoquinone, cis-cis-muconic acid, cis-butenedioic (maleic) acid, glyoxal, glyoxylic acid, mesoxylic acid, oxalic acid, formic acid, carbon dioxide, polymerised products	Rice <i>et al</i> 1980 Sokratova <i>et al</i> 1982 Al-Hayek <i>et al</i> 1989 Chrostowski <i>et al</i> 1983 Duguet <i>et al</i> 1985
phthalic acid	+	monohydroxyphthalic acid, salicylic acid, dihydroxybenzoic acid, muconic acid, other short-chain oxidation products	El Dine <i>et al</i> 1984
4-phenylazo-1-naphthol	+	1,4-naphthoquinone, phenol, nitrogen	Matsui <i>et al</i> 1981
aniline	+	2,3-dioxopropanoic acid, 2-oxopropanedioic acid, oxalic acid, glyoxal	Gilbert 1983
nitrobenzene	++	oxalic acid, carbon dioxide	Caprio <i>et al</i> 1984

Table 1 - Continued

Compound	Reactivity	Products	Reference
Heterocyclic compounds			
indole	+	N-formylanthranilic acid, oxalic acid	Dreher and Klamberg 1988
carbazole	+	N-formylanthranilic acid, oxalic acid	Dreher and Klamberg 1988
isobarbituric acid	+	formyloxaluric, oxaluric, and formic acid	Gauduchea <u>et al</u> 1987
benzo(b)thiophene	+	o-sulfobenzoic acid, o-sulfophenol, oxalic acid	Dreher and Klamberg 1988
dibenzothiophene	(+)	dibenzothiophene sulfone	Dreher and Klamberg 1988
quinazoline	(+)	pyridine-4,5-dicarboxylic acid	Dreher and Klamberg 1988
purines and pyrimidines	+	?	Doré <u>et al</u> 1989
Surfactants			
para-toluenesulfonic acid	+	acetic, formic, pyruvic, oxalic and sulphuric acid	Rice <u>et al</u> 1980
nonylphenyl heptakis ethoxylate	++	?	Fielding <u>et al</u> 1989
prapagen WKT unsat. components	++	aldehydes, carboxylic acids, quaternary carboxylic acids	Fielding <u>et al</u> 1989 Corless <u>et al</u> 1989
saturated components	-	-	Fielding <u>et al</u> 1989
Chlorinated Compounds			
o-chlorophenol	+	?	Gauduchea <u>et al</u> 1987
chlorobenzene	-	-	Legube <u>et al</u> 1983
1,2,4-trichlorobenzene	-	-	Legube <u>et al</u> 1983
chloronitrobenzene	(+)	?	Duguet <u>et al</u> 1989
trichloroethylene	(+)	?	Duguet <u>et al</u> 1989
tetrachloroethylene	(+)	?	Duguet <u>et al</u> 1989

Table 1 - Continued

Compound	Reactivity	Products	Reference
Miscellaneous			
geosmin	+	?	Duguet <u>et al</u> 1989
2-methylisoborneol	+	?	Duguet <u>et al</u> 1989
mercaptans	+	disulfides, alkylsulfonic acids	Faujour <u>et al</u> 1980

- no reaction, no products
- + reaction with ozone (compound consumption not reported)
- (+) reaction with ozone (partial consumption of compound reported)
- ++ reaction with ozone (complete consumption of compound reported)
- ? products not identified

and sometimes the ozone doses were higher than those normally applied in drinking water treatment. The pH conditions and the expression of the ozone dose were also variable. Where substrate concentrations and ozone doses used in laboratory experiments reflected those likely to be encountered in water treatment processes, the ozone-to-substrate ratio would have been very high because there would have been no competition for the ozone from other compounds. It is difficult, therefore, to extrapolate the results to water treatment practice.

Nevertheless, broadly similar results were frequently reported from a variety of such laboratory studies and they undoubtedly provide a useful guide to the likely destruction of organic substances by ozone and the possible by-products to be expected. However, results of laboratory experiments need to be verified either in pilot plant studies or at treatment works.

2.2.1 Humic substances (humic and fulvic acids)

In contrast to the large number of publications concerning products of the chlorination of aqueous solutions of humic substances (humic and fulvic acids), there is little information on products of ozonation. Reported products include alkanes, aliphatic diacids, aldehydes, aliphatic keto compounds, benzoic acids, phthalates and furans (Lawrence et al 1980, Watts 1985, Killops et al 1985, Legube et al 1989). Watts (1985) noted that much of the ozonated humic material was non-volatile and not amenable to identification by gas chromatography-mass spectrometry.

Legube et al (1989) reported that ozonation of an aqueous solution of fulvic acids lowered their potential during subsequent chlorination to produce chloroform, dichloroacetic acid and trichloroacetic acid. Production of the latter was reduced further when bicarbonate ions were present during ozonation. However, ozonation of an aqueous solution of fulvic acids in the presence of bromide ions resulted in the production of brominated organics, including bromoform, bromoacetic acid and

dibromoacetic acid (due to the reaction of ozone with bromide to produce hypobromous acid which in turn reacts with organic substances to produce organobromine compounds, see Section 2.1).

2.2.2 Protein and amino acids

There is little information on the ozonation of protein and amino acids, but they have been reported reactive. Short chain aliphatic amino acids, glycine and leucine, were reported to react with ozone to produce formaldehyde and glyoxylic or pyruvic acid respectively. Other amino acids are likely to react with ozone.

2.2.3 Carbohydrates

Carbohydrates were reported to react relatively slowly with ozone with the main degradation pathway via free radical reactions (Doré *et al* 1989). Some products were identified; ozonation of disaccharides caused scission of the glycosidic bond, eg glucose was produced from cellobiose (dimer of glucose) and glucose and galactose were products of the ozonation of lactose (dimer of glucose and galactose). Other products included aldonic acids.

2.2.4 Aliphatic compounds (hydrocarbons, acids, aldehydes, alcohols)

Alkanes were reported unreactive, whereas alkenes reacted readily with ozone by attack on the double bond to form aldehydes as the only observable products (Fielding *et al* 1987). Similarly, saturated aliphatic acids were found to be unreactive, whereas unsaturated acids reacted readily with ozone to produce aldehydes and acids (Fielding *et al* 1989, Reynolds *et al* 1989a, Al-Hayek *et al* 1989).

Primary alcohols reacted with ozone to produce aldehydes and acids; secondary alcohols formed ketones and acids (Laplanche and Martin 1984). Aliphatic aldehydes and aldehydo acids reacted to form acids (Caprio *et al* 1989, Glaze 1986).

2.2.5 Aromatic hydrocarbons

Little or no reaction with ozone was detected for hydrocarbons with one aromatic ring, such as toluene, xylene, ethylbenzene and diethylbenzene (Fielding et al 1989, Legube et al 1983). In contrast, hydrocarbons with more than one aromatic ring (PAHs, eg naphthalene, fluorene, phenanthrene, fluoranthene and pyrene) were consumed by ozone (Fielding et al 1989, Glaze 1986, Dreher and Klamberg 1988, Legube et al 1983, Helleur et al 1979).

A number of products were identified (see Table 1); these were mainly aromatic acids, aldehydes and hydroxy compounds, and only small amounts of ring fragmentation products (oxalic acid, formic acid).

2.2.6 Aromatic compounds (excluding hydrocarbons)

Phenolic compounds react rapidly with ozone to yield hydroxylated aromatic intermediates (eg polyhydroxybenzenes, quinones and hydroquinones) which undergo further oxidation with ring opening to give unsaturated aliphatic diacids or aldehydo acids. The latter may react further with ozone but at a slower rate (Legube et al 1981a and 1981b, Doré et al 1980, Brunet et al 1980). Brunet et al (1980) concluded that ring opening is part of the action of ozone on aromatic compounds, such as phenol, polyhydroxybenzenes, amines and phenoxyacetic acid derivatives, with the higher doses of ozone producing compounds with smaller numbers of carbon atoms.

Phenols may also react with ozone to form polymerised products with low solubility in water, via an oxidative coupling pathway (Chrostowski et al 1983 and Duguet et al 1985).

In a study on the decolorisation of hydroxyazo dyes with ozone, Matsui et al (1981) found that the reaction products of 4-phenylazo-1-naphthol were nitrogen, 1,4-naphthoquinone and phenol. Depending on the conditions used, the latter two substances are likely to react further with ozone as described above for phenols and quinones.

Ozonation of 1,2-benzenedioic acid (phthalic acid) was reported to lead to formation of hydroxy acids and products of ring rupture (El Dine et al 1984). Products of ring rupture were also identified from the ozonation of aniline (Gilbert 1983).

2.2.7 Heterocyclic compounds

Several heterocyclic compounds have been reported to react with ozone (Dreher and Klamberg 1988, Gauduchean 1987); products were mainly acidic and aldehydic heterocyclic compounds and short-chain acids. Aromatic or heterocyclic sulphur-containing compounds were produced from the ozonation of sulphur-containing heterocyclic compounds.

Doré et al (1989) reported that several purines and pyrimidines reacted with ozone, but no products were identified.

2.2.8 Surfactants

Linear alkyl benzene sulfonates were reported to be more reactive with ozone than linear alkyl sulfonates or aliphatic quaternary amino compounds (Fielding et al 1987). Nonylphenyl heptakis ethoxylate was consumed by ozone, but products were not identified (Fielding et al 1989). The unsaturated components of Prapagen WKT (ie dimethyl dialkyl and trimethyl alkyl ammonium chlorides in which some of the alkyl chains are unsaturated) reacted with ozone to form aldehydes and acids, whereas the saturated components were unreactive (Fielding et al 1989, Corless et al 1989).

2.2.9 Pesticides

The reactivity of pesticides and product formation was reviewed by Reynolds et al (1989b). The information from this review and from Fielding et al (1989) is summarised in Table 2. In general, the application of ozone could in many cases be beneficial by eliminating pesticides from water, since in general ozone is far more reactive than chlorine towards pesticides. However there is little information on the

**Table 2 - Reactivity of ozone with pesticides and products of their reactions
(summarised from a review by Reynolds *et al* 1989b and Fielding *et al* 1989)**

Compound	Pesticide concentration range (g l ⁻¹)	Pesticide consumption range (%)	Products
Chlorinated hydrocarbons			
Aldrin	20×10 ⁻⁶ - 2×10 ⁻³	0-100	dieldrin
DDT	2×10 ⁻⁶ - 2×10 ⁻³	<10- 94	-
Dieldrin	1.3×10 ⁻⁶ - 2×10 ⁻³	0- 99	-
Endosulphan I	17×10 ⁻³	0	-
Endosulphan II	17×10 ⁻³	12	-
Heptachlor	1×10 ⁻⁶ - 2×10 ⁻³	19-100	heptachlor epoxide
Heptachlor epoxide	4-17×10 ⁻³	6- 26	-
Lindane	9-149×10 ⁻³	0-100	-
Permethrin	10×10 ⁻⁶	>90	-
Organophosphorous pesticides			
DDTP	ni	ni	bis-(0,0 diethyl-thiono-phosphoryl disulphide and trisulphide
Dimefox	ni	ni	hexamethyl phosphoric triamide and its oxidation products (aldehydes)
Fenitrothion	120×10 ⁻⁶	40- 96	-
Fenthion	2.45×10 ⁻³	100	-
Malathion	6×10 ⁻⁶ - 123×10 ⁻³	35-100	Malaoxon, phosphoric acid, phosphate, succinic and phosphoric acid derivatives

Table 2 - Continued

Compound	Pesticide concentration range (g l ⁻¹)	Pesticide consumption range (%)	Products
Parathion	10×10 ⁻⁶ ~ 100×10 ⁻³	2-100	Paraoxon, sulphate, 2,4-dinitrophenol, picric acid, sulphuric acid, phosphoric acid
Methyl Parathion/ Metaphos	125×10 ⁻⁶	22- 95	Methyl paraoxon
Phosalone	ni	ni	bis(chloro-6-oxo-2-benzoxazolyl-3-methyl)-ether, hydroxymethyl-3-chlorobenzoxazolone, phosphoric acid
Phenoxyalkyl acid derivatives			
2,4-D	80×10 ⁻⁶ - 22×10 ⁻³	45-100	oxalic acid, glycolic acid, aldehydic compounds, chloride, carbon dioxide
MCPA	18×10 ⁻⁶ - 441×10 ⁻³	18-100	oxalic acid, glycolic acid, acetyl compound, 2-methyl-butenedioic acid, (1,2-dioxo)propoxy acetic acid,
4-chloro-2-methylphenyl			formate, 4-chloro-2-methylphenol, 4-chloro-salicyl aldehyde
MCPB	19×10 ⁻⁶	99	-
2,4,5-T	36×10 ⁻⁶	34	oxalic acid, glycolic acid, dichloromaleic acid, chloride, carbon dioxide
Organonitrogen compounds (carbamates)			
Propoxur/Baygon	44×10 ⁻³	99	-
Phenmedipham/Betanal	12×10 ⁻³	100	-

Table 2 - Continued

Compound	Pesticide concentration range (g l ⁻¹)	Pesticide consumption range (%)	Products
Carbaryl/Sevin	21×10 ⁻³	100	1-naphthol, naphthoquinone, phthalic anhydride, N-formyl carbamate of 1-naphthol
EPTC/Eptam	ni	ni	di-n-propylamine, nitrothiones, volatile carboxylic acids, carbon dioxide
SMDC/Vapam	58×10 ⁻³	>99	sulphate
Zineb	ni	ni	ethylene thiourea, sulphate

Organonitrogen compounds (heterocyclic N-compounds)

Amitrole	16×10 ⁻³	100	formamide, carbamic acid, 1,3,5-triazine, oxidised triazines
Atrazine	1-20×10 ⁻³	0-100	2-chloro-4-amino-6-isopropyl-amine-1,3,5-triazine, 2-oxo-4-ethylamino-6-isopropylamine-1,2-dihydro-1,3,5-triazine or 2-oxo-4-amino-6-isopropyl-amine-1,2-dihydro-1,3,5-triazine, 2,4-dioxo-6-isopropylamine-1,2,3,4-tetrahydro-1,3,5-triazine, 2,4,6-trioxo-hexahydro-1,3,5-triazine

Organonitrogen compounds (N-aryl N,N-dimethyl ureas)

Diuron	23×10 ⁻³	100	-
Fenuron	16×10 ⁻³	100	-

Table 2 - Continued

Compound	Pesticide concentration range (g l ⁻¹)	Pesticide consumption range (%)	Products
Fluometuron	23×10 ⁻³	100	-
Monuron	1×10 ⁻³	0-100	-
Phenolic compounds			
Dinobuton/Acrex	1-16×10 ⁻³	100	dinitrophenols, alcohols, nitrate
Dinocap/Karathane	1-18×10 ⁻³	100	dinitrophenols, alcohols, nitrate
Nitraphene	10×10 ⁻³	100	-
o-nitrophenol dinitro-o-cresol/ 2,4-dinitro-6-methyl phenol	20-99×10 ⁻³	100	nitrate
PCP	70×10 ⁻³	>99	chloride

ni: no information given

- products not identified or no products

presence or health effects of products from the ozonation of pesticides in drinking water. In the case of malathion and parathion it has been shown that more toxic compounds may be produced as a result of reaction with ozone (see Section 3.3.1).

2.3 OZONATION BY-PRODUCTS IN DRINKING WATER

Compared with the number of laboratory ozonation studies reported in the literature, there are relatively few studies of ozonation by-products in drinking water supplies. The by-products of concern in terms of their possible health effects appear to be mainly hydrogen peroxide, bromate, formaldehyde and other aldehydes, bromoform and other brominated organics. The US Environmental Protection Agency (US-EPA) have developed a list of disinfectants, chlorination by-products and ozonation by-products to serve as a basis for discussion for future legislation (Pontius 1990). The list includes formaldehyde and other aldehydes, organic acids, ketones, peroxides, quinones, chloral hydrate, chloropicrin and bromine-substituted compounds including bromoform, bromoacetic acids and dibromoacetonitrile. Maximum contaminant levels (MCLs) could be developed for some or all of the compounds listed, or for a few which could serve as surrogates for groups of compounds. Draft MCL goals (MCLGs) have been calculated for most, but health effects information is incomplete. In addition, bromate has been shown to cause cancer in experimental animals and this could become the limiting factor for the use of ozone in drinking water treatment (Bull and Kopfler 1990).

Low concentrations of hydrogen peroxide (H_2O_2) are produced during ozonation (Staehelin and Hoigné 1985). There are no data on concentrations in drinking water, but it seems likely that H_2O_2 would be consumed in reactions with ozone and other compounds in the water. Bromate can be produced during ozonation of bromide-containing water, but there is no information on the occurrence of bromate in drinking water. From a pilot plant study, McGuire *et al* (1990a) indicated that $60 \mu\text{g l}^{-1}$ could be produced if the bromide concentration in raw water were 1 mg l^{-1} .

Jacangelo *et al* (1989) reported an extensive study involving pilot plants at four different water utilities in the US, where the effect of ozonation on disinfection by-product formation was assessed. Incorporation of ozone in the treatment processes, in conjunction with chlorine as final disinfectant was generally effective at reducing total trihalomethanes, haloacetic acids, haloacetonitriles, and total organohalogen compounds in the final water. However, increases were observed in dibromochloromethane, bromoform, dibromoacetic acid, dibromoacetonitrile, formaldehyde, acetaldehyde, chloral hydrate, chloropicrin, and total haloketones.

In the same study, increases in aldehydes, chloropicrin and cyanogen chloride were observed in the final water when ozone and final disinfection with chloramine was used, instead of chlorine only. Ozone and chloramine, compared with chloramine only, resulted in increases in haloketones, aldehydes, chloropicrin, chloral hydrate and cyanogen chloride.

Lykins and Koffskey (1990) studied the effect of ozonation at a pilot plant where Mississippi river water was treated using pre-ozonation and final disinfection with either chlorine or chloramine. Preliminary results indicated that pre-ozonation combined with final chloramination was the most effective in minimising disinfection by-product (DBP) formation. Ozonation increased assimilable organic carbon, but this was subsequently removed by granular activated carbon treatment. Total organohalogen (TOX), in the raw water and TOX formation potential (ie TOX produced from final chlorination) were reduced as a result of ozonation. Trihalomethanes, halogenated acetic acids, chloroacetonitrile, chloral and chloroalkanes produced during final chlorination were present in the final water at lower concentrations when pre-ozonation was applied. Considerable reductions in contaminants originating from the raw water were achieved as a result of the use of ozone, for instance in atrazine, alachlor, total chlorinated hydrocarbon insecticides, total alkylbenzenes, alkanes, phthalates (although also reported as products of the ozonation of humic substances, see

Section 2.2.1), PAHs, chlorobenzenes and nitrobenzenes. However, increased concentrations of alkylaldehydes, chloropicrin and brominated organics in the final water resulted from the use of pre-ozonation.

Studies of ozonation by-products in drinking water were reported by Glaze et al (1989a and 1989b). The major ozonation by-products were aliphatic aldehydes, particularly formaldehyde and heptanal, carboxylic acids, aliphatic and alicyclic ketones. At a drinking water treatment plant where surface water treatment included pre-ozonation and final disinfection with chlorine, formaldehyde concentrations increased from less than $1.5 \mu\text{g l}^{-1}$ (ie not detected) in the raw water to $6-8 \mu\text{g l}^{-1}$ in the final water. The formaldehyde was first detected after the ozonation stage and remained at about the same concentration throughout the subsequent treatment stages. Formaldehyde concentrations between 7 and $12 \mu\text{g l}^{-1}$ were determined in final water at another plant where surface water treatment included pre-ozonation and final chlorination. At a drinking water treatment plant where surface water treatment included two ozonation stages and final disinfection with chloramine, formaldehyde concentrations increased from 3 to $25 \mu\text{g l}^{-1}$, whereas other aldehydes (C_2-C_7) increased from mostly below detection limit to concentrations ranging from 2 to $10 \mu\text{g l}^{-1}$. Although glyoxal and methylglyoxal were produced as a result of ozonation, these were not detected in the final water. Small amounts of formaldehyde were detected in a groundwater where treatment included ozonation and final chlorination.

An assessment of mutagenic activity as detected by bacterial test systems such as the Ames test has been applied extensively to investigate the presence of potentially carcinogenic compounds in chlorinated waters (Horth et al 1990, Meier 1988). Few studies have been carried out with ozonated waters and the results are variable. In some cases the mutagenicity of raw water was reduced as a result of ozonation (Kool and van Kreijl 1984, van der Gaag et al 1985, Cognet et al 1986, Glaze et al 1989a). Backlund et al (1985) found no production of mutagenicity as a result of ozonation of water with a high humic content and Miller et al (1986) detected no mutagenic activity in

pretreated, ozonated river water. However, Cognet *et al* (1986) and van Hoof *et al* (1985) reported the production of mutagenicity as a result of ozonation of water. The activity was of the direct-acting frame-shift type, as opposed to the base-pair substitution type which is produced as a result of chlorination (these terms describe the molecular events by which the DNA is altered to produce a mutation), indicating differences in the type of mutagens formed from the different disinfectants. The mutagenic activity was also dependent on raw water quality and ozone dose (highest activity at intermediate dose). It is possible that brominated methyl-hydroxyfuranones which are highly potent bacterial mutagens could be produced from ozonation where bromide is in the raw water (Horth *et al* 1991). Lykins and Koffskey (1990) reported a reduction in mutagenic activity in the final (chlorinated) water when pre-ozonation was used.

Overall, there appears to be less mutagenic activity produced from ozonation than from chlorination. However, the concentration techniques and mutagenicity assays were based mainly on techniques which are suitable for the concentration and determination of chlorination-derived mutagens and may not be suitable for ozonation by-products. Moreover, since there is no quantitative relationship between mutagenic activity in bacterial test systems and carcinogenicity in animal tests for different mutagens, it is not possible to infer that the health risk will be lower if the mutagenic activity is lower. A health risk assessment can only be made if the identity of the mutagens is known.

SECTION 3 - APPLICATION OF OZONE

Hyde and Zabel (1986) reviewed potential applications of ozone in the treatment of potable water. They listed the potential uses of ozone as: disinfection, taste and odour control, colour removal, organics removal, iron and manganese removal, algal removal and turbidity removal. They pointed out that as ozone can be used for so many processes, it was important to apply ozone at the correct place in the treatment process to achieve optimum performance and to avoid problems with downstream

processes or the distribution system. They stated that in general ozone should be applied at a stage where the ozone demand is lowest but before a, preferably biological, solid/liquid separation stage such as a slow sand or granular activated carbon (GAC) filter.

The following sections consider the various types of reactions in which ozone can take part, following which general conclusions are drawn regarding the best placement of ozonation to minimise unwanted side-effects. Section 4 reviews practical aspects of ozone installations. Because of the many potential applications of ozone, some plants employ multistage ozonation (Rice 1987). The types of plant configuration used for multistage ozonation are discussed in Section 4.1. This review is concerned specifically with ozone for disinfection. Advanced oxidation processes involving ozone, such as ozone with ultraviolet irradiation and ozone with hydrogen peroxide (Glaze *et al* 1987), are not included.

3.1 DISINFECTION ABILITY

Bourbigot (1990) cited research showing that a residual ozone concentration of 0.4 mg l^{-1} maintained for 4 minutes is sufficient for the destruction of a number of microorganisms, including viruses. To meet the ozone demand of the water and reach a residual concentration of 0.4 mg l^{-1} , about 60% of the total ozone dose is injected into the first compartment of the contactor. To apply a concentration \times time product, Ct , of $1.6 \text{ mg min l}^{-1}$, at least two compartments are used, with a total contact time of 10 minutes to compensate for imperfect mixing and contactor hydraulics.

Hyde and Zabel (1986) stated that a residual ozone concentration of 0.5 mg l^{-1} after 5 minutes contact is considered sufficient for bacterial disinfection and viral inactivation, provided the water is of low colour and turbidity. Disinfection is unaffected by ammonia or pH in the range 6.5 to 8.5 provided the colour is low. If the colour is high, longer contact times are required at high pH.

Peeters *et al* (1989) examined the ability of ozone to disinfect water containing 10^4 to 5×10^5 Cryptosporidium oocysts per ml, a level at least 1000 times higher than found in surface water. Ozone doses of 1.1 to 2.3 mg l⁻¹ with contact times of 6 to 8 minutes were sufficient to eliminate the infectivity of oocysts to mice. The authors stated that their conditions were similar to maintaining a residual ozone concentration of 0.4 mg l⁻¹ for 6 minutes, a Ct value of 2.4 mg min l⁻¹. Langlais *et al* (1990) studied the infectivity of ozonated water to rats. Ct values \leq 2.4 mg min l⁻¹ were insufficient to inactivate 3 log₁₀ (99.9%) of oocysts but a Ct value of 3.22 mg min l⁻¹ gave a 3 to 4 log₁₀ (99.9 to 99.99%) reduction of oocyst infectivity.

To maintain a required ozone concentration after a given contact time will require a lower applied ozone dose if the ozone demand of the water is low. It follows that lower ozone doses would be required if ozonation were conducted after ozone-consuming species (eg colour) had been removed. Considerable economies can result if the applied ozone dose can be reduced substantially (Legeron and Perron 1981).

3.2 EFFECT OF OZONE ON BY-PRODUCTS OF TERMINAL DISINFECTANT

By-products of ozonation are covered in Section 2. This section is concerned with the effects of pre-ozonation on by-product formation when terminal disinfection is conducted using a persistent disinfectant, such as chlorine or chloramine.

Naturally-occurring organic compounds in water, such as humic substances, produce a range of chlorinated organic compounds, including trihalomethanes (THMs), when chlorinated. Ozonation will have little effect on THMs once they have been produced (Rice 1980). Pre-ozonation has been considered as a means of reducing the formation of chlorinated disinfection by-products (DBPs). However, pre-ozonation can in practice lead to an increase or decrease in the formation of chlorinated DBPs; the final concentration depending on the concentration and characteristics of the original organics present, the treatment applied, the contact time between ozonation and chlorination, and the doses of

both chlorine and ozone (Hyde and Zabel 1986). Rice (1980) pointed out that the best approach for lowering the concentration of THMs ultimately produced upon chlorination is to remove as much as possible of the organic material from the water before addition of any oxidant.

Doré et al (1988) studied the competing reactions which may occur when ozone is used as a pre-oxidant, followed by chlorination possibly in the presence of bromide ions and ammonia. Ozone can oxidise bromide to hypobromous acid which can react with organic precursors to produce brominated DBPs, even in the absence of a chlorination step (Glaze 1986). Based on a number of experiments, Doré et al (1988) concluded that pre-ozonation generally leads to a decrease in THM precursor concentration because of the degradation of sites in the precursor structures that are reactive to chlorine. They also showed that the decrease in THM concentration was enhanced by the presence of radical scavengers such as bicarbonate ion. Radical scavengers stabilise ozone in solution and favour direct ozonation reactions over indirect radical reactions (Section 2.1).

The effect of ozonation on the formation of selected DBPs was evaluated by studies at pilot or full scale at four treatment plants as described in Section 2.3 (Jacangelo et al 1989). In essence, the study evaluated the effects of changing from pre-chlorination or pre-chloramination to pre-ozonation followed by post-chlorination or post-chloramination. The extent to which final DBP concentrations were changed after introducing ozonation depended mainly on the final disinfectant; ozone followed by chloramines was more effective than ozone followed by chlorine in reducing the concentration of halogenated DBPs. Where secondary disinfection was applied prior to filtration, large increases in aldehyde concentrations were observed.

Robertson and Oda (1983) described pilot scale tests of the effect of ozone as a primary disinfectant, with chlorine or chloramine as a post-disinfectant, on chlorinated DBP formation. They ozonated surface water (Dissolved Organic Carbon concentration (DOC) 8 to 12 mg l⁻¹) with ozone doses from 0 to 20 mg l⁻¹, then applied chlorine or monochloramine

in a batch procedure. With chlorine as the post-disinfectant (free chlorine residual 0.5 mg l^{-1} after 30 minutes), up to 60% reduction in chloroform concentration could be achieved by replacing pre-chlorination with pre-ozonation. Ozone dose, delay time between ozone and chlorine dosing and storage time after chlorination had no significant effect on THM concentration. In the case of non-purgeable organic halide concentration (NPOX), a low ozone dose (2 mg l^{-1}) reduced NPOX but increasing ozone dose increased the NPOX towards the concentrations observed with prechlorination. When chloramine was used as the post disinfectant (0.5 mg l^{-1} combined chlorine after 30 minutes), negligible quantities of chloroform and NPOX were produced.

McGuire *et al* (1990b) evaluated DBP formation on a pilot plant incorporating pre-ozonation, coagulation, sedimentation and filtration. Both instantaneous DBPs (prior to final disinfection) and Simulated Distribution System DBPs (SDSDBP) after chlorination or chloramination were determined. Instantaneous DBPs are those formed immediately after disinfection whereas SDSDBPs are those formed after a period of standing, to simulate the residence time in distribution. Instantaneous DBPs in pre-ozonated samples (2 mg l^{-1} , 6 minute contact) were at or near detection limits with the exception of formaldehyde (9 to $18 \mu\text{g l}^{-1}$) and acetaldehyde (2 to $5 \mu\text{g l}^{-1}$). The SDSDBP results showed that chlorination produced substantially higher concentrations of THMs compared to ozone-chloramine; THM concentrations produced by chlorine and ozone-chlorine exceeded $100 \mu\text{g l}^{-1}$ (the US-EPA standard).

In summary, the use of ozone followed by chlorine may cause an increase or decrease in DBP concentrations. The use of ozone followed by chloramine has been shown to produce substantially lower DBP concentrations than when chlorine is used.

3.3 EFFECT OF OZONE ON DISSOLVED SUBSTANCES

3.3.1 Organic compounds

Section 2 provides a comprehensive review of the reactions of ozone with organic compounds. The following sections discuss some practical aspects of ozonation for the removal of organic compounds from water.

(a) Man-made chemicals

Ozonation will destroy a wide variety of pollutant chemicals. The major mechanisms involved are physical stripping (volatilisation) and chemical oxidation by ozone molecules (direct oxidation) and by free radicals (Gurol 1985). The overall removal efficiency is dependent on a number of factors including: the chemical reactivity of the compound, expressed by the reaction rate constant; the volatility of the compound, expressed by the Henry's law constant; the aqueous ozone concentration; the mass transfer characteristics of the reactor; and the chemical composition of the water.

Many studies on pollutant removal by ozonation have been reported and it would not be appropriate to attempt to summarise all of them here. In practice, the extent of pollutant removal is likely to be heavily influenced by background water quality and ozone-water contactor characteristics, as well as the intrinsic reactivity of the target compound(s). Direct ozonation reactions are highly specific and thus exhibit a wide range of reaction rate constants. Rate constants for a large number of compounds have been reported by Hoigné and Bader (1983a, 1983b). Nebel (1981) reported that materials readily oxidised by ozone include phenolics, detergents, certain pesticides, polycyclic aromatic hydrocarbons, proteins and amino acids. Malathion and parathion are two pesticides which can be oxidised completely by ozone but which proceed through intermediates which are more toxic than the parent compounds (Rice *et al* 1981).

Fronk (1987) and Clark *et al* (1988) presented the results of pilot ozonation experiments, using doses of 2 to 6 mg l⁻¹, to remove 29 organic chemicals from groundwater. Aromatic compounds and alkenes were removed well but alkanes were poorly removed. Removal efficiency for aromatics and alkenes improved with increasing dosage, and removal of some alkanes improved with increasing pH. Background total organic carbon (TOC) did not impair removal efficiency.

Any reaction of ozone with micropollutants could be regarded as a bonus to the primary aim of disinfection. In the absence of gross pollution, the quantity of ozone consumed by reaction with synthetic organic chemicals is likely to be negligible because of their low concentration in comparison with other ozone-consuming species, such as humic substances.

(b) Humic substances

The use of ozone for decolorisation of peaty waters is well documented (eg Bourbigot 1983). Ozonation of humic substances results in a shift in molecular weight distribution towards smaller molecules, a large decrease in UV absorbance but only a small reduction in DOC concentration (Amy *et al* 1988). Brunet *et al* (1982) reported about 50% reduction in UV absorbance but only 5 to 15% removal of TOC. Ozonation leads to an increase in polarity of dissolved organic matter, and an increase in biodegradability. A reduction in THM formation potential may result from ozonation, although contradictory results have been reported (Section 3.2).

Farvardin and Collins (1989) studied the effect of pre-ozonation on the coagulant demand of humic acid (20 mg l⁻¹), using ozone doses up to 5 mg l⁻¹. They obtained up to 30% reduction in the required dose of aluminium sulphate as a result of pre-ozonation. There was an optimum ozone dose above which the benefit of pre-ozonation was reduced, then eliminated and further ozonation became detrimental to the coagulation process. On the other hand Graham and Kotsani (1988) reported a negative effect of pre-ozonation (0.65 to 3 mg l⁻¹) on the aluminium sulphate

coagulation of a simulated upland water. For all ozone doses, the coagulant demand increased and the extent of colour removal by coagulation decreased compared with unozonated water.

Reckhow et al (1986) demonstrated that addition of bicarbonate at low concentrations (1 mM) enhanced the destruction of organohalide precursors by pre-ozonation. They suggested that plants treating low alkalinity coloured waters could consider installing a carbonation step prior to ozonation. Similar results were reported by Croué et al (1989). Bicarbonate (alkalinity) stabilises ozone in solution, thus favouring direct attack by ozone on the substrate rather than hydroxyl radical reactions.

Paillard et al (1989a) showed that alkalinity enhancement also improved the removal of manganese by ozonation of highly coloured water. They recommended that, to maximise organohalide precursor removal, alkalinity increase and ozonation should be applied at a point where the humic substance concentration is low, and be followed by filtration to remove iron and manganese precipitates and to allow biological degradation within the filter of assimilable organic carbon (AOC) generated during ozonation. The advantages of alkalinity increase to between 100 and 150 mg l⁻¹ (as CaCO₃) were under evaluation on a full-scale (20 × 10³ m³ d⁻¹) plant (Paillard et al 1989b). Following ferric chloride coagulation, lime and carbon dioxide were added to increase alkalinity after which ozone was dosed at 0.5 to 1 mg l⁻¹. Following sand filtration, a further ozone dose of 1.5 mg l⁻¹ was added, followed by chlorination.

The differing effects reported for the action of ozone on humic substances may be related to the alkalinity:TOC ratio in the raw water, a high ratio favouring direct reaction of ozone with humic substances. Clearly it would be necessary to establish by experiment whether pre-ozonation was beneficial or detrimental in any situation.

3.3.2 Inorganic species

Bourbigot (1983) summarised the effects of ozonation on a number of inorganic species. Iron(II) is rapidly oxidised to form iron(III) which precipitates as the hydroxide. Similarly manganese(II) is oxidised to manganese(IV) which rapidly forms manganese(IV) dioxide. An excess dose of ozone will oxidise manganese to manganese(VII) (permanganate) producing a pink coloration and the potential for subsequent deposition in distribution; manganese(VII) can be reduced by subsequent filtration with GAC or anthracite (Klein 1983). GAC filters used for this purpose are operated at high surface loadings (25 to 30 m h⁻¹) to avoid cake formation (Masschelein 1990).

In general, heavy metals are oxidised allowing their removal as oxides or hydroxides which are often insoluble. Cyanides are oxidised to the less toxic cyanates which in turn are slowly oxidised to carbon dioxide and nitrogen provided a sufficient ozone dose is applied. Ammoniacal nitrogen is not oxidised by ozone except at high pH (above 9).

Bromide ion is oxidised to form bromine, hypobromous acid and hypobromite ion; hypobromite ion decomposes back to bromide (Rice and Gomez-Taylor 1986). Excess ozone oxidises hypobromous acid and hypobromite ion to bromate ion. In the presence of ammonia, hypobromous acid and hypobromite ion react to form monobromamine which in turn can be oxidised to form nitrate and bromide ions. Ozone reacts slowly with hypochlorite ion producing chloride and chlorate ions. With chloramine, ozone reacts to produce chloride and nitrate ions. Chloride ion is not oxidised by ozone at any meaningful rate under drinking water treatment conditions. Nitrite is oxidised rapidly to nitrate.

The most important reactions of ozone with inorganic substances are likely to be those involving iron and manganese, bromide and ammonia. If iron and/or manganese are present, filtration following ozonation is essential to remove precipitated solids. The presence of bromide will lead to the formation of bromate or hypobromous acid; the latter will react with organics to produce brominated DBPs. Addition of ammonia at

the ozonation stage can be used to hinder brominated DBP formation by reacting with hypobromous acid and hypobromite ion to form monobromamine (Rice 1990, Daniel et al 1990). Ammonia is not removed by ozonation, and would need to be removed by biological nitrification subsequent to ozonation.

3.4 EFFECT OF OZONE ON SUSPENDED SOLIDS

One of the reported benefits of pre-ozonation is a reduction in turbidity and/or coagulant demand due to a so-called "microflocculation" effect (Bourbigot 1983). A variety of mechanisms have been invoked to explain this phenomenon, for example oxidation of metal cations or oxidation of humic substances adsorbed on particle surfaces, leading to a decrease in colloidal stability of the particles (Dowbiggin and Singer 1989). In some cases, however, ozonation has been reported to have negligible or adverse effects on particle removal.

Dowbiggin and Singer (1989) examined ozone-induced destabilisation of alumina particles (130 mg l^{-1}) in the presence of humic substances (0.4 mg C l^{-1}) and calcium ions. In the absence of calcium, ozone (0 to 1 mg l^{-1}) had no effect on particle stability. In the presence of calcium (up to 1 mM), ozone was found to significantly reduce particle stability. Ozonation did not change the partitioning of organic carbon between the particulate and dissolved phases, suggesting that oxidation and solubilisation of adsorbed organic material was not responsible for the decrease in particle stability. Overall, it was concluded that ozone could act as a coagulant aid for the destabilisation of organic material.

Experiments by Grasso and Weber (1988) showed that the nature and chemistry of both the particulate matter and the dissolved organic matter play important roles in ozone-induced particle destabilisation. They reported substantial differences in behaviour between 'synthetic' humic acid solutions and river water. On the basis of their analyses, they concluded that polymerisation of organics by ozone followed by adsorption and inter-particle bridging could be responsible for particle destabilisation.

Kreft *et al* (1990) used a pilot plant incorporating pre-ozonation, coagulation (ferric sulphate plus cationic polymer), sedimentation and filtration to evaluate the effects of pre-ozonation on particulate removal and coagulant demand. The tests were conducted on lake water with 4 to 5 mg l⁻¹ TOC, alkalinity 100 to 140 mg l⁻¹ as CaCO₃, and turbidity 3 to 22 NTU. Pre-ozonation gave significant reductions in filtered water turbidity and higher removals of 5 to 10 µm particles compared to no pre-ozonation; the optimum ozone dose was about 2 mg l⁻¹. Pre-ozonation also reduced the coagulant dose required to achieve target filtered water turbidity (0.2 NTU) by 40%. With pre-ozonation, high filtration rates (>24 m h⁻¹) could be used without compromising filtrate quality or filter production.

Bourbigot (1990) summarised the results of pilot and full-scale studies of pre-ozonation at the Choisy-le-Roi treatment plant. Pre-ozonation (0.3 to 1.2 mg l⁻¹) increased the removal of turbidity and UV absorbance after coagulation and sedimentation but did not improve DOC or TOC removal. Above the optimum dose (0.8 mg l⁻¹), floc settling velocity was reduced.

Rice (1990) considered that ozone-induced particle destabilisation occurs by charge neutralisation and argued that the use of high ozone doses would lead to charge reversal and restabilisation of the particles. Further, he stated that excessive ozonation might solubilise organic matter associated with particles, leading to an increase in DOC concentration. He concluded that, with turbid raw waters, "over oxidation" in a pre-ozonation stage would not aid turbidity removal and might increase the dissolved organics concentration.

The ozone doses required to maintain a Ct value sufficient to inactivate oocysts of Cryptosporidium (see Section 3.1) would be much higher than those suggested for pre-ozonation. Pre-ozonation using such high doses could lead to problems such as particle stabilisation, DOC release, increase in coagulant demand and reduction in floc settling velocity.

3.4.1 Algal removal

Algal removal is often cited as one of the uses of ozone. Pre-ozonation can increase significantly the removal of algae by rapid gravity filtration, especially if a small dose of coagulant is added prior to filtration (Hyde and Zabel 1986).

Hyde and Zabel (1986) reported pilot plant experiments on pre-ozonation ahead of slow sand filtration which showed that ozone reduced the level of algal activity in the water above the filter, resulting in longer run lengths. However, with high influent algal loads, ozone had little effect on filter run length but prevented breakthrough of algae.

Ozone has been shown to be effective in destroying algal toxins (Hiisvirta and Lahti 1990). A pre-ozonation dose of 1.0 mg l^{-1} , followed by coagulation and filtration, completely eliminated $55 \mu\text{g l}^{-1}$ of microcystin (hepatotoxin of Microcystis aeruginosa) in laboratory tests. Oscillatoria agardhii hepatotoxin behaved similarly.

Pilot-scale (100 l h^{-1}) tests were conducted using a fresh Microcystis aeruginosa bloom spiked into raw water to give a toxin concentration of $50 \mu\text{g l}^{-1}$. Pre-ozonation (1.0 to 1.5 mg l^{-1}) reduced the toxin concentration by 90%; a total reduction of 99% was achieved by pre-ozonation followed by coagulation, sedimentation and filtration.

A recent development is "ozoflotation", in which ozonation and flotation are combined (Bourbigot 1990). This process is reported to be particularly suited to the treatment of algal-laden eutrophic waters.

3.5 GENERATION OF ASSIMILABLE ORGANIC CARBON

All disinfectants but especially ozone have been shown to increase the concentration of AOC in water (Packham 1989). AOC is that fraction of the total organic carbon content (TOC) which can support the growth of microorganisms in water. The observed increase in AOC following ozonation results from the breakdown of non-biodegradable compounds into simpler molecules including amino acids, aliphatic carboxylic acids and

various carbohydrates. The degree of AOC increase will depend on the nature of the organics present, the ozone dose and contact time, and water quality parameters such as pH, alkalinity and temperature (Rice 1990).

High concentrations of AOC in treated waters can give rise to problems with taste, odour and turbidity levels as well as unsatisfactory heterotrophic plate counts (HPC) in the distribution system. Schalekamp (1986) recorded the large increase in bacterial counts which occurred in the water supply to Zurich when ozonation was installed to replace chlorination at the Lengg plant; the deterioration of quality in distribution contributed to a decision to close down the ozonation facility. Problems of bacterial aftergrowths were also experienced in the Antwerp water supply (Masschelein 1985).

Legube et al (1989) examined the ozonation of aqueous solutions of fulvic acid isolated from water. The rate of ozone consumption was rapid during the first few minutes of reaction and ozonation led to an increase in lower molecular weight compounds, an enhancement of carboxyl content and aldehyde formation. To assess biodegradability, a fulvic acid solution (5 mg C l^{-1}) was ozonated (0 to 3 mg l^{-1}) and inoculated with secondary effluent. Dissolved organic carbon concentrations measured over 28 days revealed a substantial increase in biodegradability after ozonation, the extent of mineralisation increasing with ozone dose. GAC filtration of ozonated fulvic acid gave greater DOC removal than GAC treatment of un-ozonated fulvic acid or GAC filtration under sterile conditions.

Van der Kooij et al (1989) presented data on AOC concentrations measured at various stages of treatment in a number of full-scale plants in the Netherlands. The AOC concentration increased linearly with ozone dose up to 1 mg O_3 per mg DOC. The AOC increased linearly with decrease in UV absorbance, suggesting that AOC compounds were produced from UV-absorbing substances such as humic substances. Biological filtration reduced AOC concentrations but not always to the same level as before

ozonation. AOC concentration was found to decrease in distribution, accompanied by increased HPC; the greatest AOC decrease and highest HPC was observed with the highest AOC concentration.

Because of the generation of AOC, as well as the possibility of precipitation of iron and manganese, it is generally accepted that ozonation should be followed by sand or GAC filtration, with terminal disinfection using chlorine, chloramines or chlorine dioxide to control bacterial and animal aftergrowth in distribution (Hyde and Zabel 1986).

A few European plants practise ozonation without terminal disinfection (Rice et al 1981) but only where the ozonated water is of low TOC and AOC. Hyde and Zabel (1986) listed the following requirements which should be met if ozone is to be used as the sole disinfectant: clean, leak-free distribution system; TOC below 0.2 mg l^{-1} ; absence of ammonia; water temperature below 15°C ; residence time in distribution less than 1 day; iron $<0.05 \text{ mg l}^{-1}$ and manganese $<0.02 \text{ mg l}^{-1}$.

European treatment practice often includes biological filtration; disinfectant residuals are not maintained throughout the plant so filters become biologically active. AOC, which increases after ozonation, decreases through the filter as it is utilised by microorganisms attached to the filter media (McGuire et al 1990b). A small amount of final disinfectant is added to prevent regrowth in the distribution system.

McGuire et al (1990b) reported pilot plant studies using pre-ozonation, coagulation, sedimentation and anthracite-sand filtration. AOC, elevated by ozonation, returned to raw water concentrations if no disinfectant residual was maintained through the filter. In addition, aldehydes, formed during ozonation, were removed in the biologically active filters.

Glaze et al (1989a) identified a large number of ozonation by-products following pre-ozonation (1 to 4 mg l^{-1}) of two surface waters at a full-scale treatment plant (Section 2.3). The principal DBPs were

aldehydes, fatty acids and ketones. Comparison of samples taken before and after flocculation with ferric chloride and cationic polymer and direct rapid gravity sand filtration (13 m h^{-1}) showed that a substantial number of compounds were removed by flocculation and filtration. Thus, a reduction in the concentration of biodegradable compounds (AOC) was achieved by non-biological treatment.

Zabel (1985) reported pilot plant data showing that slow sand filtration was very effective in removing AOC. Ozonation caused a large increase in AOC, but slow sand filtration reduced the concentration to below that in the influent water. Bourbigot (1990) stated that ozonation followed by slow sand filtration is the most effective means of biologically removing organic carbon.

Thus, to prevent problems in distribution as a result of elevated AOC concentrations, filtration should be provided following ozonation unless the water is of very low organic carbon concentration. GAC filters (empty bed contact time 15 to 20 minutes) are the most effective for AOC removal (Rice 1990); GAC/sand filters and sand or anthracite filters are less effective. Slow sand filters are also highly effective for AOC removal. In addition to filtration, a persistent disinfectant should be applied as a terminal disinfectant to protect the distribution system.

3.6 OPTIMUM PLACEMENT OF OZONATION

By considering the reactions of ozone that may cause unwanted side-effects, as discussed above, it is possible to list the main factors which will influence the placement of ozone in the treatment sequence.

- * In general, the ozone demand should be as low as possible at the point of ozone application in order to use less ozone and generate less AOC.
- * To minimise DBP formation, the organics concentration should be as low as possible prior to adding any oxidants, and oxidant doses should be low.

- * High ozone doses and/or long contact times should not be used for pre-ozonation to avoid particle stabilisation and DOC release.
- * Wherever ozone is placed, it should be followed by at least one filtration stage, for removal of precipitates and AOC.
- * Biological filtration (ie in the absence of disinfectant) will reduce AOC and possibly DBP concentrations.

Considering the above factors, general recommendations can be made on the optimum placement of ozone based on raw water and plant type.

3.6.1 Groundwaters (and good quality surface waters)

This category of water is considered to be of low turbidity, and low organic content. Additionally, there is probably minimal existing treatment plant other than chlorinators and pumps.

For this category of water, ozone would be deployed in the pre-ozonation mode. This would require the provision of ozone generation and contacting equipment for primary disinfection, and the use of existing chlorination equipment to provide a disinfectant residual in supply.

With water of low organic content, AOC generation should not be problematical, and terminal chlorination should be sufficient to prevent aftergrowth problems in distribution.

If iron and/or manganese removal is presently practised, for example by chlorination or aeration followed by filtration, ozone can be used for their precipitation, utilising the filters as at present. In the case of manganese, it could be advisable to provide a layer of GAC on top of the sand filter to reduce permanganate if it is formed.

3.6.2 Surface waters - coagulation plants

With surface waters, with relatively high TOC concentrations, several factors govern the placement of ozone. Firstly, a substantial reduction in TOC is desirable prior to ozonation to reduce the ozone dose required for disinfection, reduce DBP formation and reduce AOC enhancement. Secondly, at least one stage of filtration needs to be provided following ozonation, to act as a biological filter for AOC reduction.

These factors dictate that ozonation should be conducted after the removal of as much TOC as possible by coagulation; ie ozonation should be conducted after sand filtration but an additional stage of GAC filtration should be provided for AOC reduction. Alternatively, ozonation could be conducted on the settled (or floated) water, prior to filtration as is practised at two US plants (Tate 1990); pilot scale evaluation of this option would be required.

In the case of direct filtration plants, eg pressure filtration plants, an additional (GAC) filtration stage would need to be provided. It would be inadvisable to attempt to use pre-ozonation in this situation on waters which are commonly highly coloured and of low alkalinity, without first conducting extensive pilot-scale tests. The use of pre-ozonation, at the doses that would be required for disinfection, could have a number of undesirable consequences including increased coagulant demand, high DBP concentrations and high AOC concentrations. Therefore, it is recommended to install a second filtration stage, preferably biological GAC, after the existing filters with ozonation conducted between the two stages of filtration. Alternatively, for moderately coloured waters, it might be possible to replace coagulation treatment with two-stage ozonation, as practised at the Tullich plant (see Section 4.1).

Terminal disinfection should be provided to protect the distribution system; to minimise chlorinated DBP formation, chloramination might be preferable to chlorination.

3.6.3 Surface waters - slow sand filtration plants

Slow sand filtration plants generally treat water of moderate turbidity and colour. Although ozonation will generate some AOC, slow sand filtration has been shown to be an effective means of AOC removal (Zabel 1985). Therefore pre-ozonation should be applied ahead of the slow sand filters, but after pre-filters if those are present. Terminal disinfection should be provided.

SECTION 4 - REVIEW OF RECENT PRACTICE

4.1 EUROPEAN PRACTICE

Bourbigot (1990) provided an overview of recent European practice. For disinfection, the aim was generally to have an ozone residual of 0.4 mg l^{-1} after 4 minutes contact; this would provide a concentration \times time product, Ct , of $1.6 \text{ mg min l}^{-1}$. In practice, designers aimed for a total contact time of 10 minutes to overcome problems of short circuiting in contactors. Ozonation was widely used for intermediate oxidation prior to slow sand filtration to facilitate increased filtration rates or before biological GAC filters. Pre-ozonation was employed to remove iron and manganese, algae, colour, taste and odour, and to promote "microflocculation". Multistage ozonation was becoming widely adopted to optimise conditions for each contaminant to be removed.

Masschelein (1990) reviewed various practical aspects of European ozone installations. Post-ozonation for disinfection remains one of the main aspects of European treatment schemes. The method of contacting generally involves the use of porous pipes or disks (pore size 50 to 100 μm) and repeated contacting in baffled chambers. The diffusers are installed under 4 to 6 m of water and should produce bubbles about 4 mm in diameter. In conventional contact columns, the downflow velocity of the water is 4 to 5 mm s^{-1} . The ozonised air is injected under sufficient pressure to overcome the headloss associated with the water

column and dispersion system (about 0.7 bar); the headloss of the immersed porous diffusers should be 300 to 500 mm water gauge. With adequately pre-treated water, the average gas flow remains below 10% of the water flow with an ozone concentration in air of 20 mg l^{-1} . The maximum total dose is usually below 4 mg l^{-1} . The hydraulic residence time is typically designed to be between 8 and 20 minutes.

Masschelein (1990) also considered pre-ozonation. He stated that experience from different plants shows that pre-ozonation and intermediate ozonation should not exhaust the ozone demand of the water, as the desired effects are achieved with lower doses. Generally, a dose of 0.1 to 0.2 mg ozone per mg TOC is required but increased temperature and low alkalinity can increase the dose required by accelerating the self decomposition of ozone. In pre-ozonation schemes, contacting systems under positive pressure, such as ejectors, should be avoided as the water can become supersaturated with oxygen and nitrogen, resulting ultimately in foam formation. Consequently, low counter-pressure turbines are the preferred mode of injection where diffusers cannot be used due to the risk of clogging.

Masschelein (1985) described a number of Belgian drinking water plants which employed ozonation. Most plants used post-ozonation, with or without pre-ozonation. In one plant (Notmeir) filtered water was ozonised in four consecutive contact chambers, each of four minutes residence time. The operational criterion was to maintain a residual ozone concentration of 0.5 mg l^{-1} for 16 minutes. At another plant (Tailfer), ozonation was used as part of a complicated treatment process involving prechlorination, chlorine dioxide, coagulation, chlorination, sedimentation and filtration, ozonation, chloramination, blending with other (disinfected) waters, and chlorine dioxide prior to distribution. Masschelein reported that bacterial aftergrowth in distribution had been a problem in the absence of post-disinfection. Consequently, this phenomenon, as well as the formation of chlorinated DBPs, had led to a reconsideration of treatment sequences and the location of ozonation.

Beck et al (1986) reported on the use of pre-formed monochloramine as a post disinfectant following ozonation at Sjaelso in Denmark. Surface water with a high organics content (TOC 12 mg l⁻¹) was treated by flocculation, sedimentation and rapid gravity filtration, ozonation (2 mg l⁻¹) followed by biologically-active GAC filtration. Pre-formed monochloramine was applied at 0.2 to 0.3 mg l⁻¹ immediately following the GAC as a precaution against bacterial release from the GAC. Final disinfection of a mixture of treated waters was achieved with a dose of 0.1 to 0.2 mg l⁻¹ pre-formed monochloramine.

Schalekamp (1986) reviewed the development of oxidation and disinfection practices at a number of plants supplying the city of Zurich, Switzerland. Current practice was to use pre-ozonation, intermediate ozonation and terminal disinfection using chlorine or chlorine dioxide. Ozonation was always followed by some form of biological filtration to reduce AOC concentrations.

Zabel (1985) described the two UK plants which were then using ozone. At Durleigh (30×10^3 m³ d⁻¹), reservoir water with high colour, manganese concentration and algal counts was treated by microstraining, chlorination, ozonation, coagulation, filtration and chlorination. Pre-chlorination was used to reduce oxidant demand, after which ozone was dosed at 3 to 5 mg l⁻¹ into two countercurrent contact chambers, the first with a residence time of 2 minutes and the second 20 minutes. Effective colour, turbidity and taste and odour removal were reported. At Tullich (10×10^3 m³ d⁻¹), impounded upland water (colour 40 °Hazen, turbidity 3 NTU, iron and manganese each 0.1 mg l⁻¹) was treated by microstraining, pre-ozonation, rapid sand filtration, intermediate ozonation (disinfection stage), chlorination and pH increase. Raw water colours varying from 15 to 50 °Hazen had been reduced to <5 °Hazen with ozone doses from 1.7 to 5.0 mg l⁻¹, depending on the raw water quality.

Multistage ozonation is becoming increasingly common in European plant designs (Bourbigot 1990). The use of multiple stages enables each to be optimised (dose, contact time etc) for each specific treatment objective. Generally, pre-ozonation is achieved by recycling the

off-gas from a later stage of ozonation. Two UK plants have recently been designed with two-stage ozonation: Littleton (Bristol Waterworks Co) with intermediate ozonation for taste and odour removal and post-ozonation for disinfection, and Campion Hills (Severn Trent Water Ltd) with pre-ozonation and intermediate ozonation for reduction of organics and disinfection (Bourbigot 1990).

Rice (1987) reviewed the application of multiple-stage ozonation in drinking water treatment plants in Europe. At Rouen-la-Chapelle, polluted groundwater is treated by pre-ozonation, sand filtration, GAC filtration, ozone for disinfection and post chlorination. Pre-ozonation oxidises iron and manganese; these are removed during the biological sand filtration which also nitrifies ammonia to nitrate. The GAC adsorbers also operate as biological units and complete the oxidation of ammonia. At Valence Mauboule, pre-ozonation is employed for manganese removal from groundwater, followed by coagulation and sand filtration (5 m h^{-1}), post ozonation and final chlorination. The Louveciennes plant also treats groundwater by microstraining, pre-ozonation (for iron and manganese removal), biological nitrification, ozonation, biological filtration through sand and GAC, and chlorine dioxide for disinfection. At Mulheim, river water is pre-ozonated (at the point of coagulant addition), settled, filtered and ozonised. After dual media filtration, the water is passed through GAC filters and finally chlorinated.

Nastorg (1980) described the use of tri-ozonation at the Mery-sur-Oise plant in France treating river Oise water. The treatment process comprised pre-ozonation; reservoir storage (48 hours); flocculation, sedimentation and sand filtration; ozonation; GAC filtration; ozonation and terminal chlorination. This arrangement superseded one in which the pre- and intermediate ozonation stages and GAC filtration were absent but pre-chlorination was used. The tri-ozonation treatment led to a significant improvement in bacterial quality in distribution (Bourbigot *et al* 1984).

4.2 NORTH AMERICAN PRACTICE

Tate (1990) provided a comprehensive overview of ozone installations for drinking water treatment in North America. A questionnaire survey was used to establish: plant information; details of ozone application; ozone generation, contactor and destruct systems; capital and running costs; and experience.

In the US, as of June 1990 there were 14 operational ozonation plants, 11 under construction and 14 in design or tender stages. Of the 39 plants, ozonation was installed as a retrofit to 15 existing plants. Ozone was being installed in response to existing or anticipated water quality issues. Approximately 82% of the plants treated surface water, the remainder groundwater; most surface water plants employed ozone for more than one reason.

The predominant location for ozone application is pretreatment (raw water prior to coagulation and flocculation), followed by post sedimentation (prefiltration) and post filtration. Eleven plants employ ozone in more than one location and twenty two use only pre-ozonation. Two groundwater treatment plants employ ozone as the sole treatment, one for volatile organics and the other for colour removal. One reason for the use of pre-ozonation is good quality raw water (low turbidity, TOC and coliform count) which has low ozone demand. Pre-ozonation enables ozone to be used as a powerful oxidant for disinfection, DBP control and taste and odour removal, whilst also enhancing the performance of downstream processes through the "microflocculation" effect (Section 3.4).

Plants using ozone post sedimentation might do so because of a lowered ozone demand after sedimentation or the ability to convert part of an existing sedimentation tank into an ozone contactor. The two plants where ozone is applied post filtration have GAC as a filter medium, and post filtration ozonation. Of the 15 plants retrofitting ozone to an existing plant, 10 reported multiple application points and 5 used pretreatment only.

Information on feed gas, generators and contactors is provided. Most plants use air as the feed gas, and there is an increasing trend towards the use of medium frequency generators. Ozone contactors are predominantly of the over/under baffled basin type. Ozone doses are 0.5 to 17 mg l⁻¹ (most <5 mg l⁻¹), contact time 4 to 30 minutes, contactor depth 3 to 9 metres, and ozone transfer efficiency 85 to 98%. A majority (82%) of installations had conducted pilot-scale testing prior to installing ozonation.

Tate (1990) also listed several large ozonation plants in Canada and provided details on a few. The Charles J Des Bailleets plant, serving Montreal, treats river water where the average raw water quality is: turbidity 4 NTU, TOC 3 mg l⁻¹ and total coliforms 350 per 100 ml. Ozone is used primarily for disinfection and colour removal, and also for DBP control. Ozone is applied post filtration at doses from 1.7 to 3.0 mg l⁻¹ into an 8 metre deep over/under baffled tank with a mass transfer efficiency of 80% and theoretical detention time of 8 minutes.

Ozone was added to an existing plant in Quebec (Pierrefonds) in 1976, to control taste and odour. Ozone is dosed post filtration at 1.5 mg l⁻¹ into an over/under baffled basin, 6 metres deep with a detention time of 4 minutes. Another plant (Sherbrooke) uses microstrainers and ozonation to treat surface water. The Roberval plant uses pre-ozonation for disinfection, in contrast to most Canadian applications where ozone is added after filtration.

Rosenbeck and Badhuin (1990) described the application of ozonation for treatment of groundwater contaminated with coliform bacteria (normally <75 colonies per 100 ml). The design criteria for the plant were based on achieving a Ct product of 6.0, for inactivation of Giardia cysts, and a flow of 3.8×10^3 m³ d⁻¹. An ozone system incorporating a turbine diffuser contactor was selected because it was available as a 'package', it operated under a negative pressure, it was adaptable to small treatment plants, it was reliable and could be packaged into a limited area. The ozonator provided a dose of 3.0 mg l⁻¹ to a series of two turbine diffuser contactors, each with a detention time of 2 minutes.

Ozonated water passed to a baffled storage tank (30 to 45 minute detention) and was chlorinated to achieve a 0.2 mg l^{-1} residual before pumping into supply. Tracer tests revealed serious short-circuiting in the contactors but, by adjustments to the ozone dose, it was possible to take advantage of the retention time in the storage tank to achieve the required Ct value.

Fung *et al* (1990) described a plant in which ozonation and coagulation are carried out concurrently for colour removal from a surface water of colour approximately 30°Hazen . The plant treats $760 \times 10^3 \text{ m}^3 \text{ d}^{-1}$. Aluminium sulphate (7 mg l^{-1}) and cationic polymer (1.7 mg l^{-1}) are dosed into the raw water which passes to the ozone contactor where ozone (1.8 mg l^{-1}) is introduced using a submerged turbine diffuser. The total residence time in the contactor is 21 minutes and the ozone transfer efficiency is at least 92%. The dosed water flows first to a tank where flotation occurs, and then to anthracite/sand filters operated at 15 m h^{-1} . Chlorine (2.9 mg l^{-1}) is added at the filter inlet to precipitate manganese. Following filtration, the water is chloraminated ($2.1 \text{ mg l}^{-1} \text{ Cl}_2$, $1.0 \text{ mg l}^{-1} \text{ NH}_3$) and sodium hydroxide is added for pH adjustment before the water enters supply.

At the Los Angeles Aqueduct Filtration plant, treating $2270 \times 10^3 \text{ m}^3 \text{ d}^{-1}$, pre-ozonation was reported to lead to higher filtration rates, shorter flocculation time, lower coagulant doses and lower distribution system THM concentrations (Christie and Stolarik 1990). Good quality surface water (turbidity 1.2 to 2.0 NTU, TOC 1.7 to 2.6 mg l^{-1}) is screened then dosed with ozone at up to 1.5 mg l^{-1} with a contact time of 5 minutes. Ferric chloride and cationic polymer are applied with rapid mixing, then mechanical flocculation is applied for 8 minutes before the water is filtered through single media anthracite filters at a rate of 33 m h^{-1} . Chlorine is applied as the final disinfectant.

4.3 INSTALLATION OF OZONATION FACILITIES

4.3.1 Process selection

It is generally recommended that pilot-scale, or at least bench-scale, testing is conducted prior to installing ozonation at new or existing plants. Rice (1990) presented a procedure for such tests to evaluate ozonation as a process for treating different types of raw water. His approach is based on attempting to take advantage of as many potential benefits of ozonation other than disinfection, and then determining how an ozone plant should be configured to achieve those goals. His approach can be summarised as follows:

- a) With high turbidity waters, determine the ozone doses necessary to minimise (i) turbidity and (ii) DOC. For low turbidity, low DOC waters, select single-stage pre-ozonation.
- b) If doses (i) and (ii) are coincident, as expected for good quality surface waters and groundwaters, single-stage pre-ozonation followed by direct filtration is indicated.
- c) If doses (i) and (ii) are not coincident, pre-ozonation using low ozone dose and contact time should be used for turbidity reduction. A second ozonation stage should be used for oxidation of organics.
- d) Optimise ozonation for primary disinfection.
- e) Determine whether advanced oxidation processes are required for organics removal.
- f) Select biological filtration step to mineralise AOC.
- g) Conduct pilot study to confirm choice and establish design criteria.

Whilst recognising that it may be appropriate to take advantage of ozone for solving water quality problems other than disinfection, it is considered that Rice's approach is not directly applicable in the present context where ozone is being considered to solve a particular water quality problem, in the majority of cases at existing plants where alternatives to ozone are already in operation to solve other water quality problems.

Here, it is recommended that the ozonation plant should be designed primarily to achieve elimination of Cryptosporidium, and the point of ozone application should be selected on the basis given in Section 3.6. It can then be decided whether to use ozone for secondary purposes, and if so, Rice's approach (given above) can be used to determine whether single or multiple-stage ozone addition is required. However, particularly with existing plants, it should be clearly established that the use of ozone for subsidiary objectives is technically and economically effective with respect to existing (or alternative) treatments. Also, it should be noted that the relatively high ozone dose required for Cryptosporidium elimination may be above the optimum for other purposes. Testing of proposed plant designs and configurations by pilot-scale evaluation is strongly recommended.

The ozonation system will need to meet a set of process criteria which define the requirements to meet the treatment targets. Detailed criteria need to be established for at least:

- * Application point(s); single or multistage.
- * Required ozone dose and transfer efficiency.
- * Contact time.
- * Ozone feed gas concentration and generation technique.
- * Range of ozone concentration in the gas.

- * Contactor design parameters; depth, width, length, number of compartments, compartments for ozone injection.
- * Gas to liquid ratio and gas loading rate to each compartment.
- * Dissolution system.
- * Basic control philosophy.

Once the process criteria have been established, plant design can commence. It is to be expected that the process criteria will be modified as design details are developed.

4.3.2 Design considerations

Ozone, being unstable, is generated on-site by silent electrical discharge through oxygen-containing gas. In general, an ozone plant consists of a gas preparation plant, an ozone generator, an ozone-water contacting stage and an ozone off-gas destruction device.

(a) Gas preparation plant

The feed gas to an ozone generator must be dry (maximum dewpoint -60 °C at 1 atm), free of particulates, and cool. Moisture in the feed gas reduces the amount of ozone generated per unit power input and increases maintenance costs. Dust collects in the ozoniser tubes and slowly reduces ozone generation efficiency. Feed gases include ambient air, high purity oxygen, recycled off-gas with oxygen make-up and oxygen-enriched air. These gases require various levels of treatment to achieve the necessary quality (Robson et al 1990).

Ambient air is the most common feed gas and can be prepared by ambient, low, medium or high pressure systems. All air preparation systems include compression devices, desiccant driers, filters and moisture traps; aftercoolers, refrigerant driers and pressure-reducing valves may be used in specific systems. Air preparation systems should also include flow measurement and dewpoint monitoring.

Several stages of gas filtration are used to remove particles. Dust, oxidised metals and other particles are removed by inlet filters and additional filtration is provided at the inlet and outlet of the desiccant drying unit. To avoid contamination by lubricating oil, which reduces the capacity of desiccant driers, gas compression is achieved by application of a water ring compressor or an oil-free screw compressor. "Oil-free" positive displacement compressors have been used on a number of small installations in the US but some have leaked oil into the system (Robson *et al* 1990).

The type of desiccant drier may be dictated by the capacity of the ozone system. Pressure swing adsorption (heatless) systems are normally employed with systems generating up to 4 kg h^{-1} , whilst thermally regenerated systems are generally used for larger systems (Robson *et al* 1990). The pressure swing system is relatively easy to operate and maintain owing to its simplicity. With thermally regenerated driers, an external heat source may be preferable to in-bed heating which tends to give localised heating leading to stress cracks, burning of the desiccant and corrosion. Thermally regenerated systems require suitable instrumentation and controls to prevent overheating which could damage the media.

(b) Ozone generator

An ozone generator element consists of two electrodes separated by an air space and a dielectric (insulation) layer. An efficient cooling system is required to minimise the decomposition of ozone, achieve maximum efficiency of the ozoniser and prevent damage to the dielectric.

A wide range of generator types is available (low, medium, high frequency; air, water, dual media generator cooling; horizontal and vertical glass tube, glass plate, ceramic plate dielectrics). Typically, generators are specified to produce a stated quantity of ozone at a designated percentage of the maximum rated power capacity of the generator. The voltage applied to the dielectric tubes can then be limited to a point which will allow an operating safety margin below the

breaking point of the dielectric. The installed capacity should be sufficient to ensure that the generator is not required to operate at above 75% of its rated capacity for prolonged periods (Robson et al 1990).

Ease of maintenance is an important factor in generator selection. Maintenance will be required on the generator, power supply units and cooling fluid supply system. Small systems would tend to favour low frequency water-cooled units while larger systems could justify medium or high frequency generators with chilled water cooling systems.

(c) Ozone-water contactor

For primary disinfection and oxidation, fine bubble diffuser, multiple-stage contactors are most frequently used. Many other types of contactors could be used depending on feed water characteristics, point of ozone application and site constraints. These include: turbine mixers with positive or negative gas pressure; injectors with positive or negative gas pressure; packed columns; spray chambers; and various recently developed techniques (Robson et al 1990). Ejectors and aspirating turbines have been used in preference to fine bubble diffusers for raw and unfiltered waters.

Predictable operational problems and maintenance must be considered in the selection and design of ozone contactors. Sufficient headspace (freeboard) must be provided to prevent froth, foam or float being carried into the off-gas system. Foam sprays and demisters should be provided upstream of the ozone destruct system.

The relationship of the ozone generator building and the contactor should be carefully considered. If direct viewing of the contactor interior is required, this can be achieved with viewing ports in the contactor walls and viewing galleries between pairs of contactors.

(d) Ozone destructor

Excess ozone in the atmosphere is detrimental to human, animal and plant life and an upper limit of 0.1 ppm in the surrounding air has been set by the Health and Safety Executive. Most ozone plants require an ozone destruct system to remove the residual ozone from the off-gas leaving the ozone contactor.

Destruction units are of two types: thermal, generally used in Europe; and catalytic units which are commonly employed in the US. The method of off-gas destruction should be selected considering simplicity and ease of maintenance as well as cost-effectiveness. Plant-specific features may favour one type of destruct unit or recycling of the off-gas back to the treatment process. Even after the destructor, the vent stack should discharge at an elevation higher than the normal work area, and its orientation with respect to building ventilation intakes and prevailing winds should be considered.

The relatively high doses of ozone that would be required to deal with contamination by Cryptosporidium could result in high residual ozone concentrations in water leaving the contactor. To prevent release of dissolved ozone into the atmosphere, plant designs incorporate one or all of the following:

- a) sufficient free-fall at the outlet of the contactor to assist in degassing and removal of ozone;
- b) allocation of sufficient detention time to facilitate dissipation of the residual ozone within the contactor; and
- c) covered downstream channels and tanks to contain emissions.

Other methods may need to be considered for retrofits (Section 4.3.3(a)).

(e) Dose control

Ozoniser operation and control for drinking water disinfection is normally based on residual dissolved ozone concentration as the control measurement. Changes to the ozone dose are effected by changing the applied voltage. Louboutin (1985) described the automatic control of an ozonation plant using ozone in water monitors to measure residual ozone concentration in the contactor outlet. A programmable logic controller was used to control the ozone plant to achieve set-point ozone concentrations. MacKay (1985) described a hierarchical process control system which used residual ozone concentration measurements to calculate total ozone requirement, select the most power-efficient equipment configuration and control the flow of ozonised air to each contactor in a two-stage ozonation plant.

If there were a means available to determine when oocysts might be present then, in principle, it would be possible to employ ozonation only when oocysts were present or anticipated, ie to apply ozonation intermittently. No reference to this mode of operation was found in the literature. If intermittent ozonation were practised, primary disinfection would need to be provided by chlorine or chloramine at times when ozonation was suspended; the chlorination or chloramination plant would need to have sufficient capacity for this duty as opposed to terminal disinfection to protect the distribution system. In certain situations, chloramine might be judged to be insufficiently powerful for primary disinfection.

Intermittent ozonation might also affect the operation of a biological GAC process. The operation of GAC in a biological mode (ie after ozonation) is reported to increase GAC life between regenerations (Rice et al 1981); conversely GAC life might be shortened by suspending ozonation. Biological GAC might be by-passed when ozonation was suspended.

Intermittent operation of ozonation facilities would, of course, decrease operating costs by lowering the average ozone dose; however the impact on amortised costs would be proportionately smaller because the same capacity ozone plant would need to be installed irrespective of its frequency and duration of use (Section 4.4). The impact of suspending ozonation on planned maintenance programmes and plant manning levels would need to be considered. Some components of the ozonation plant, for example porous plate diffusers and pressure-swing driers, might require continuous air purge even when ozone generation was suspended.

Overall, the concept of employing intermittent ozonation has both advantages and disadvantages; the merits of discontinuous operation would need to be considered in the light of local circumstances. It should also be noted that continuous operation of the ozonation plant would provide a margin of safety against Cryptosporidium.

(f) Additional considerations

Stainless steel (304L or 316L) is the material of choice for ozonised gas distribution and dissolution systems. Selection of gaskets, valve seats and other non-metallic material must be considered carefully. The possibility that ozonised gas could backflow upstream of the ozone generator means that ozone resistant materials should be used for piping, valves and fittings immediately upstream of the generator, as well as downstream.

The noise generated by the ozone plant should be addressed, and consideration given to isolation of equipment in sound suppression rooms or enclosures. Pressure relief of oxygen plants or compressors and driers generate noise. Cooling water pumps and electrical gear are less severe noise problems. Noise from other equipment can be reduced by enclosures, acoustical panels or louvres, or physical separation.

In terms of safety, production of ozone can be stopped immediately by interrupting the power supply to the generator. A primary safety consideration is to install ambient ozone analysers in the generator

room, at destruct vent units, and any other location where leaks could occur. These analysers should signal automatic generator shutdown and activate exhaust fans to vent the room air to the outside. The Health and Safety Executive has specified that ozone-in-air monitors must be installed in the ozone generation room. Safe entry into the contactor chambers should be provided for maintenance purposes, and the generator should be earthed and vented before servicing. The maximum concentration of ozone in air permitted continuously in the working environment is 0.1 ppm, with a maximum short-term exposure limit of 0.3 ppm (Health and Safety Executive Guidance Note EH38, 1983).

The level of system reliability and redundancy required depends in part on the treatment objective which ozone is required to achieve at a specific site. Disinfection will demand a higher level of reliability than eg taste and odour control. In general, it is advisable to be able to meet the design capacity with the largest item of any equipment being out of service. Another reliability consideration is the power supply; ozone systems are often excluded from emergency power supplies owing to their high power demand. However, emergency chlorination should be available if ozone is being used as the primary disinfectant.

4.3.3 Retrofit considerations

Retrofitting an existing treatment plant with an ozone facility will present complexities which would not normally be encountered in designing a new plant. The final plant arrangement is likely to be a compromise between meeting the objectives of installing ozonation and physical and process constraints of the existing plant. The factors which need to be considered (Bellamy et al 1990) are discussed below.

(a) Process considerations

The first stage in the project will be to establish design criteria. Initial criteria can be chosen on the basis of recommendations and/or experience. The final process criteria, which provide a description of the process requirements necessary to meet the treatment objectives,

will have to be developed within the constraints of existing facilities. For example, to achieve a target disinfection C_t , it may be necessary to use a higher ozone dose to accommodate a shorter detention time caused by limited space availability for the contactor. It may also be necessary to accept and allow for reduced ozone transfer efficiency if an existing shallow tank is to be used as a contactor. The items to be included in the final process criteria are listed in Section 4.3.1.

The application of ozone may have implications for downstream processes. Bellamy *et al* (1990) discussed the problems which may occur if ozonation is conducted between sedimentation and filtration. Although that point of ozone addition is not particularly recommended in this report, it should be noted that the presence of ozone and agitation in the contactor could adversely affect floc filterability and filter efficiency, and cause gas binding of the filter media. Similar considerations apply to placing ozonation ahead of sedimentation.

Limited hydraulic head and site constraints can lead to ozone being carried out of the contactor and into the next treatment process. It would be undesirable for ozone to be released into a covered building and it might be necessary to remove excess ozone by dosing hydrogen peroxide into the contactor effluent to accelerate the decomposition of ozone; any residual hydrogen peroxide would be expected to dissipate rapidly (Section 2.3). Alternatively, a mechanical or vacuum degassing system could be employed.

Retrofitting may expose existing facilities to ozone in water that were not originally designed for that purpose. The compatibility of construction materials needs to be evaluated where this situation occurs. Corrosive action is concentrated at gas-liquid interfaces. Concrete cover over reinforcing steel (minimum 5 cm recommended), piping, equipment, gaskets, seals, coating and lining materials must all be considered.

Ozonation can lead to scum or foam formation, which are likely to collect in the contactor and downstream channels. Facilities for scum removal should be provided in or after the ozone contactor if this constitutes an operational or aesthetic problem. The installation of scum removal facilities might require modifications to existing structures.

Where generation of AOC is a potential problem but site considerations dictate that it is not possible to install or utilise biological filtration as recommended in Section 3.6, Bellamy *et al* (1990) suggested changing the operation of existing filters, eg by reducing the filtration rate and replacing the sand with GAC, to accentuate biological treatment.

(b) Site considerations

The development of a retrofit design will be strongly influenced by existing facilities and the available site. These considerations are highly site-specific, but some general areas of concern can be identified.

The most obvious site consideration is determining the locations for the contactor, ozone building and power facilities. Basic siting criteria include the size of the site, the closeness to process interfaces, and interference with existing structures and utilities such as water, power and chemicals. Other factors to be considered include proximity to control room and operator accessibility; access and drainage; interference with existing structures, eg foundations; and aesthetics such as visual impact and noise impact.

The location of the ozone contactor could be restricted by the hydraulic profile in the plant as most plants are designed with minimum headloss between processes. If ozonation is to be installed in an area with limited available head, it needs to be considered whether upstream or downstream modifications can be made to accommodate the contactor; whether pumping to the contactor is an acceptable alternative; and

whether process criteria can be modified to allow installation at a different location. If the water surface elevation is increased as a result of changing the hydraulic profile, the effect on existing structures must be reviewed.

The control system philosophy for the ozone equipment and process can be based either on compatibility with an existing process control system, or on renovating the entire plant control system. Methods of integrating into an existing system require careful consideration. The capacity of an existing computer-based process control system could be exceeded if computer control were desired for the ozonation system.

An ozonation system will need to blend-in architecturally with the existing site. Air feed systems typically require two storeys in height for maintenance of desiccant drier systems. It may be desirable to screen ozone destruct units and electrical gear from view. These constraints have interrelationships with both individual site characteristics and site selection.

(c) Site utilities

The addition of ozone will affect power, air and water supplies, and drainage. The most significant impact, in terms of land requirements, capital and operating costs, will be on electrical power requirements.

The addition of ozone will create a large increase in power consumption, principally by the ozone generators but also by auxiliary systems such as compressors, driers, cooling water pumps and ozone destruct units. The energy consumption for ozone production from air is generally in the range 25 to 30 kWh kg⁻¹ of ozone produced, of which 15 to 20 kWh kg⁻¹ is for the generator itself. As an example of the increase in power consumption this can cause, retrofitting ozone (40 kg h⁻¹) to an existing plant (230×10^3 m³ d⁻¹) nearly tripled the power requirements from 875 kW to 2565 kW, without any increase in plant throughput (Bellamy *et al* 1990). Plant power distribution, including transformers and switchgear, may need to be upgraded. The need to operate the ozone

system during emergencies also needs to be addressed in terms of emergency power requirements. It may be considered acceptable to operate with chlorination only during emergencies.

Compressed air facilities may already be present on site for filter air-scour, instruments and valve actuators. If a diffuser system is used in the ozone contactors, purge air is desirable to prevent diffuser plugging when the contactors are full but out of service. This additional demand may cause the capacity of the existing compressors to be exceeded, and the existing system may have to be expanded, dedicated purge compressors installed, or the air-purge function linked with the generator air supply (if an air-feed system is used).

Ozone generators are only about 5% efficient, such that 95% of the applied energy input is lost as heat. This creates a significant cooling requirement, usually satisfied by water in either open or closed loop cooling circuits, depending on the quality and quantity of water available. As an example, the 40 kg h⁻¹ ozone plant referred to above required 11×10^3 m³ d⁻¹ of cooling water.

In addition to the drainage modifications which might normally be required during site modifications, drainage of the ozone contactors needs special consideration. Contactor basins are commonly 6 metres deep, often requiring drainage pumps. Ozone resistant materials are required for equipment and pipework; this applies also to sample and scum drainage.

It will most probably be necessary for treatment plants to remain in operation during the construction of the ozonation facilities. Careful attention should be given to scheduling, sequencing, and planning of shutdowns, connections to process streams, power supplies and other interfaces. It needs to be defined whether existing systems need to remain in operation at all times, and, if not, the allowable extent and frequency of shutdowns.

4.4 COSTS OF OZONATION

Installation of ozonation facilities will incur both capital and operating costs. Capital costs are due to the ozone generation system and building, the contactor, pumping plant (if re-pumping is required), and provision of power and cooling water services. Direct operating costs include electricity, cooling water, costs of re-pumping (if necessary) and repairs and maintenance.

Hyde and Walker (1985) provided a means of estimating the capital and operating costs for ozone systems for the treatment of potable water. The cost functions provided have been used to calculate costs (at Q4 89 prices) for a range of plant capacities, ozone doses and contact times. The results, given in Table 3, show that the amortised cost of ozonation varies from less than 1 p m⁻³ to over 5 p m⁻³, depending principally on plant capacity and ozone dose; contact time has a relatively small impact on both capital and operating costs.

Care should be taken in using estimated costs, as local factors may have a large impact on actual costs. This will be particularly true for retrofits, where the cost model may not account for all the costs that would be incurred. Nevertheless, the costs given in Table 3 provide tentative figures for budget purposes.

The effect of intermittent operation of the ozonation facility (Section 4.3.2 (e)) would be to reduce operating costs, and the magnitude of the effect can be gauged from the operating cost data given in columns 5 and 6 of Table 3. The effect of intermittent dosing (effectively reducing the average dose) would have a proportionately greater effect on overall costs for larger plants, because with smaller plants the amortised capital cost makes a greater contribution to the overall cost.

Table 3 - Estimated costs of ozonation (Q4 89 prices)

Capacity $10^3 \text{ m}^3 \text{ d}^{-1}$	Dose mg l^{-1}	Contact time minutes	Capital cost £K	Operating cost £K y^{-1}	Operating cost p m^{-3}	Total amortised cost p m^{-3}
5	1	5	438.5	17.3	0.9	3.7
		10	461.7	18.0	1.0	3.9
		20	494.2	19.0	1.0	4.2
	5	5	557.3	32.3	1.8	5.3
		10	580.6	33.0	1.8	5.5
		20	613.0	34.1	1.9	5.7
	50	1	1078.0	66.8	0.4	1.0
		10	1148.2	69.1	0.4	1.1
		20	1246.1	72.2	0.4	1.2
100	5	5	1810.3	202.6	1.1	2.3
		10	1880.5	204.9	1.1	2.3
		20	1978.4	208.0	1.1	2.4
	1	5	1602.3	115.9	0.3	0.8
		10	1700.2	119.1	0.3	0.9
		20	1836.8	123.4	0.3	0.9
	5	5	2870.1	381.3	1.0	2.0
		10	2968.0	384.4	1.1	2.0
		20	3104.6	388.8	1.1	2.0

Notes

Calculations assume that 3 ozone generators are installed (1 as duty standby), and that re-pumping to a head of 5 metres is required after the ozone contactor. Electricity costs are taken as 6 p kWh^{-1} , and cooling water is assumed to cost 2 p m^{-3} . Mechanical plant is assumed to have a 15 year life, and civil structures 30 years. An interest rate of 10% and a test discount rate of 5% are assumed

SECTION 5 - DISCUSSION

The use of ozone in drinking water treatment appears to be beneficial in some cases by achieving a reduction in the concentrations of many of the by-products of final disinfection with chlorine. However, increased concentrations of some compounds, such as formaldehyde, acetaldehyde, chloral hydrate and other aldehydes, bromoform, dibromoacetic acid, dibromoacetonitrile, chloropicrin, haloketones and probably bromate in final water have been reported. In some cases, increased mutagenic activity resulting from ozonation has been reported, though the information is inadequate and the compounds responsible for the activity have not been identified. More information is needed on the identity and concentrations of ozonation by-products in drinking waters and their toxicological effects. In particular, the presence of bromate and formaldehyde in drinking water may be of concern, as well as the numerous aldehydes for which there is insufficient toxicological information. The above compounds are currently under consideration for future drinking water legislation by the US-EPA. Bromate is of particular interest since recent studies indicate the possibility of a very low drinking water standard (Bull and Kopfler 1990).

Studies of the reactivity of ozone with organic substances indicate that the concentrations of many raw water contaminants may be reduced substantially as a result of their reaction with ozone. A considerable number of products of such reactions have been identified while many are unknown. Although the laboratory studies can give useful indications of the likely reactivity of organic substances and by-products to be expected, there is a need to verify the studies at pilot plants or at drinking water treatment plants; very little information of this type is available.

The health effects of by-products of ozonation formed from naturally occurring organic material and from reactions with man-made contaminants in raw water need to be evaluated and risks assessed. However, as with chlorination, the by-products formed by ozonation are present at low concentrations in drinking water and any potential risks to health are

probably low. Consequently, there appears at present to be no reason on health grounds why ozonation should not be employed for elimination of Cryptosporidium.

Because of the number of potential reactions in which ozone can take part, the best point for application of ozone as a disinfectant needs careful consideration to avoid undesirable side-effects and the consumption of ozone in unwanted reactions. In general terms, ozone should be applied for disinfection at a late stage in the treatment sequence to minimise side reactions, to minimise the formation of organic by-products including AOC, and to reduce the required ozone dose.

The application of high doses of ozone to waters with high TOC concentrations should, in general, be avoided. To reduce the required ozone dose, by-product formation and AOC generation, as much TOC as possible should be removed, eg by coagulation, prior to ozonation. Additionally, biological treatment to reduce AOC should be provided.

Unless the water being treated is of low organic content (eg a groundwater) some form of biological treatment (filtration) will be needed following ozonation for the removal of AOC. Biological filtration needs to be provided also to enable nitrification of ammonia, which is not oxidised by ozone. Ozonation will oxygenate the water, providing the oxygen required for biological nitrification. The ideal means of providing biological filtration is to utilise or install slow sand filters or GAC filters operated in a biological mode. In practice, some compromise may be necessary, and it might be necessary to utilise existing sand filters for this purpose.

The addition of ozone to an existing plant imposes several constraints and considerations which would not be present with new plant designs. Retrofitting ozone requires careful choice of process criteria and verification using pilot tests. The impact on, and interaction with, existing plant, processes and utilities require careful consideration and planning.

SECTION 6 - CONCLUSIONS AND RECOMMENDATIONS

1. The use of ozone appears to be beneficial in some cases by achieving a reduction in the concentrations of certain raw water contaminants and by-products of final chlorination.
2. Ozone reacts with many natural and man-made organic compounds in water to form a variety of by-products.
3. Increased concentrations of formaldehyde, acetaldehyde, chloral hydrate and other aldehydes, bromoform, dibromoacetic acid, dibromoacetonitrile, chloropicrin and haloketones, and the likely presence of bromate in final water have been reported to result from the use of ozone, compared with chlorine only.
4. Laboratory studies on the destruction of organic substances by ozone and product formation should be verified by tests on pilot or full scale plants.
5. In some cases, increased mutagenic activity resulting from ozonation has been reported, though the information is inadequate and the compounds responsible for the mutagenic activity in drinking water have not been identified.
6. There is relatively little information on the identity, concentration and health effects of ozonation by-products found in drinking water. The formation of bromate in particular needs further investigation. The health effects of ozonation by-products need to be assessed, though the risk to the consumer is likely to be small.
7. The potential risks to health posed by ozonation by-products so far identified are not sufficient to preclude the use of ozonation for elimination of Cryptosporidium.

8. Careful placement of ozone in the treatment sequence is required to avoid undesirable side-effects.
9. Disinfection using ozone should be conducted at a late stage in the treatment process to reduce competing reactions, by-product formation and ozone consumption.
10. The application of ozone to surface waters will generate significant increases in assimilable organic carbon (AOC) concentration, with the potential for bacterial aftergrowths in distribution systems.
11. Biological filtration needs to be provided to reduce excessive AOC concentrations; either slow sand filtration or granular activated carbon filters would be suitable.
12. A persistent disinfectant residual should be provided using chlorine or chloramine before the water enters the distribution system.
13. Installing ozone at an existing treatment plant may be problematic with regard to existing plant, processes and site utilities.
14. Final process design will reflect a compromise between initial design criteria and plant and process constraints.

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