Effects of Disinfection on Organic Substances in Water (DWE 9005)

Progress Report to the Department of the Environment
January to September 1993
Sept-93 (J), RNRC 28/8/1
Interim Conclusions
Future work proposed.

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EFFECTS OF DISINFECTION ON ORGANIC SUBSTANCES IN WATER
(DWE 9005)

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Authors: J Hutchison, D Lunt, K Bailey and T Ogden

Contract Manager: M Fielding

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WRc plc, Henley Road, Medmenham, Marlow, Buckinghamshire SL7 2HD.
Telephone: Henley (0491) 571531
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SUMMARY

Work on the production of mutagenicity from the use of ozone has continued with an investigation of three different techniques for concentrating mutagenic fractions from water (diethyl ether extraction, Bond-Elut C18 cartridges and XAD-2 resin adsorption). A positive mutagenic response was obtained with diethyl ether extracts of both ozonated and unozonated humic acid. No response was observed after using either of the other techniques. Analysis of two known ozonation by-products and suspected mutagens (glyoxal and methylglyoxal) has indicated that none of the techniques utilised effectively isolates either compound from water. These results suggest that some of the techniques devised to isolate potentially mutagenic fractions from chlorinated drinking water, may not be suitable for more polar, highly water-soluble, ozonation by-products.

Investigations into the reaction of polyelectrolytes with ozone have been carried out. LT25, an anionic polyelectrolyte was shown to react with ozone by size exclusion chromatography, but no lower molecular weight products were detected by GC-MS. Similarly the reaction of ozone with a nonionic (LT20) and a cationic (LT24) polyelectrolyte did not result in the formation of any readily detectable low molecular weight products. It was, therefore, concluded that any products of the ozonation of polyelectrolytes are likely to be of relatively high molecular weight and/or very polar in nature and not amenable to analysis by GC-MS.

Further work on the formation of chloroacetic acids and THMs has shown that concentrations of these compounds increase with chlorine dose and chlorination time. Chlorination pH was an important factor in both TCA and THM formation - TCA being favoured at lower pH, THMs at higher pH. DCA formation was independent of pH. Results from distribution system samples suggest that concentrations of DCA and TCA can decrease in distribution. It is difficult, however, to predict the extent to which this will occur in a particular system. It seems unlikely, from the results obtained, that concentrations of DCA or TCA will increase within a distribution system.

A limited survey of bromate and bromide concentrations in samples taken from treatment works (ozonation and chlorination) and pilot-plants (ozonation) has been carried out. Results indicated that bromate could be formed under typical ozonation conditions at concentrations of 10-21 µg l⁻¹. The corresponding raw waters contained >100 µg l⁻¹ bromide. At sites where the raw water contained very low concentrations of bromide (<20 µg l⁻¹), no bromate was detected after ozonation. Bromate was detected (8 µg l⁻¹) in only one chlorinated final water - taken from a works using hypochlorite for disinfection. Bromate was also detected in samples of hypochlorite produced by on-site electrolytic generation, although no bromate was detected in final waters chlorinated using hypochlorite generated in this way.

Additional work on the production of bromate during on-site electrolytic generation of chlorine confirmed that bromate was formed during this process (concentrations in hypochlorite solutions analysed ranged from 2.8 to 21.8 mg l⁻¹). Bromate was detected in only two of the final waters analysed (at levels of 2 and 5 µg l⁻¹).
1. BACKGROUND

A large number of chemicals are produced at low concentrations during chlorination of drinking water. However, other oxidants/disinfectants, which could be used to replace chlorine, also result in by-product formation, but less is known about their identities and health effects. In addition to natural organic matter in the raw water, substances such as pesticides and water treatment chemicals also react with chlorine and ozone to produce by-products, most of which have not been evaluated in terms of their risks to health.

There is a trend in some European countries to avoid the use of chlorine to avoid the formation of undesirable by-products. New legislation on disinfection by-products (DBPs) is under consideration in the UK and a revision of the EC Drinking Water Directive (parameter 32, organochlorine compounds) is possible. The recently revised WHO Drinking Water Guidelines are now known and these set guideline values for a wide range of DBPs. Some of these levels could be exceeded in UK water supplies. More information is required on the possible implications of the new WHO guidelines and on the identity and health effects of by-products from the reactions of alternative disinfectants with organic substances and treatment chemicals. Models for DBP formation and relative chemical and microbiological risks are being developed in the US by the EPA. Similar models for the UK situation need to be evaluated.
2. OBJECTIVES AND PROGRAMME OF WORK

The objectives of the project are:

- To study the effects of disinfection of water by chlorine or ozone on a range of selected organic substances likely to occur as contaminants in water.
- To identify products of these reactions.
- To identify the by-products formed by the action of water treatment disinfectants on chemicals used in water treatment.
- To assess the occurrence of trichloroacetic acid and dioxins in chlorinated UK water supplies.
- To assess the generation of by-products and mutagens by water treatment disinfectants.
- To review developments likely to affect future legislation on disinfection by-products and implications for the UK, especially of the proposed new WHO guidelines for drinking water, and carry out appropriate investigations.
- To review and develop models covering disinfection by-product formation and chemical/microbial risks.

The programme of work for 1993/1994 is as follows:

- The likely implications of the new WHO guidelines will be reviewed and appropriate studies carried out. In particular, the formation of bromate during in situ generation of chlorine by electrolysis of brine will be investigated. In addition, follow up work on the occurrence and fate of chlorinated acetic acids will be undertaken, particularly fate in the distribution system and formation versus THMs under laboratory-simulated treatment conditions (pH, contact time and chlorine dose etc.).
- Development work carried out elsewhere in the area covered by the above will be critically reviewed and implications for the UK identified.
- The work on developing isolation/concentration techniques for maximising recovery of mutagens from the use of alternative disinfectants to chlorine (in particular ozone) will be continued and any detected mutagens identified.
- The availability of other bioassay techniques for detecting potentially hazardous DBPs in drinking water will be reviewed and potentially applicable methods identified.
- The identification of by-products from the action of disinfectants, especially ozone, on water treatment chemicals and specific water contaminants will be continued and the significance of detected by-products evaluated.
The developments in the US EPA on (i) modelling DBP formation in water treatment and (ii) microbial risks will be critically reviewed and attempts at deriving models for the UK situation begun. The latter will use existing information on incidence of pathogens in water sources, removal by treatment, resistance to disinfection, infective dose and impact on consumers.
3. OBJECTIVES FOR PERIOD JANUARY 1993 - SEPTEMBER 1993

The objectives of the work carried out in the period January to September 1993 were as follows:

- To examine a range of sample concentration techniques for the isolation of mutagens produced from ozonation.
- To investigate the reaction of ozone with polyelectrolytes.
- To determine the concentrations of chlorinated acetic acids in distribution systems.
- To investigate chlorinated acetic acid versus trihalomethane formation under a range of conditions (pH, contact time, chlorine dose).
- To undertake a limited survey of bromide and bromate concentrations in raw and treated waters (both chlorinated and ozonated).
- To review the potential for bromate formation during on-site electrolytic generation of chlorine.
- To carry out analysis of bromate concentrations in (i) hypochlorite produced by on-site electrolytic generation, and (ii) water disinfected using on-site generated hypochlorite.
4. RESULTS

4.1 Production of mutagenicity from ozonation

4.1.1 Introduction

Chlorination of drinking water can give rise to a number of mutagenic compounds, several of which have been identified in recent years (e.g. Meier et al. 1983, Fielding and Horth 1986). Several concentration techniques have been used to isolate the potentially mutagenic fraction from water prior to carrying out mutagenicity testing. Much of the previous work on the production of mutagenicity from the use of ozone (reviewed in WRc Report DoE 3298) has involved sample concentration techniques developed primarily for isolation of mutagens produced by chlorination. Ozonation is likely to produce more polar by-products, some of which may not be isolated effectively using these concentration techniques, resulting in an incomplete measure of the mutagenicity produced through the use of ozone. A number of isolation/concentration techniques were selected and used on ozonated humic acid samples to try and determine whether they effectively isolated any mutagenicity produced on ozonation. In addition, recoveries from each method were tested on two suspected mutagenic ozonation by-products, glyoxal and methylglyoxal, to try and quantify possible losses.

4.1.2 Mutagenicity of ozonated humic acid after sample concentration

Humic acid (20 mg l⁻¹; Fluka) was dissolved in phosphate buffer (5 mM, 2 l, pH 7) and ozonated for five minutes (ozone dose 8 mg l⁻¹ min⁻¹). Phosphate buffer (2 l) was also ozonated under the same conditions as a control. Residual ozone present after reaction was removed by aeration. Aliquots (1.8 l) of ozonated humic acid, ozonated buffer and an unozonated humic acid control were concentrated to a final volume of 10 ml using one of the following sample concentration techniques:

Solid phase extraction

C18 Bond-elut cartridges were pre-rinsed with dichloromethane, methanol and double-distilled water. The sample (360 ml) was filtered through each cartridge (five cartridges were used for each 1.8 l aliquot). The cartridges were eluted with methanol (10 ml per cartridge). The combined methanol extracts were evaporated to dryness and re-dissolved in acetone (10 ml).

Solvent extraction

Sodium chloride (25 g) was added to the sample (1.8 l) and the pH adjusted to 2 with sulphuric acid prior to extraction with diethyl ether (1 x 400 ml; 2 x 200 ml). The combined extracts were concentrated using a Kuderna-Danish apparatus, followed by nitrogen blow-down. The dried extracts were redissolved in acetone (10 ml).
XAD-2 macroreticular resin adsorption

XAD adsorption was carried out at both pH 7 and 2, using diethyl ether and acetone as eluting solvents at each pH. The XAD-2 resin was Soxhlet-extracted with methanol prior to use. The resin was poured as a slurry in methanol into a chromatography column and washed twice with the eluting solvent (25 ml). The resin was finally washed with phosphate buffer (5 mM; 25 ml; pH 7) for the pH 7 adsorption. For the pH 2 adsorption, the resin was initially washed with hydrochloric acid (1M; 25 ml). The sample (1.8 l) was passed through the column at a flow rate of 10-15 ml min\(^{-1}\). The resin was then eluted with either diethyl ether or acetone (50 ml). The diethyl ether eluates were evaporated to dryness and redissolved in acetone (10 ml); the acetone eluates were evaporated to 10 ml.

Mutagenicity testing on all the concentrated extracts was carried out using the microtitre fluctuation assay (Gatehouse 1978, Gatehouse and Delow 1979), with the Salmonella typhimurium tester strains developed by Ames et al. (1975). The samples were tested using both TA 100 and TA 98 strains (without metabolic activation), at a range of dose levels with appropriate negative and positive controls included in each assay. All assays were repeated at least once on a different day.

The results of the fluctuation assays were analysed using the Generalised Linear Interactive Model (GLIM) statistical package, which tests whether the variability exhibited by the observed number of revertant bearing wells is significantly greater than would be expected on the assumption of binomial variation. A probability value (p-value) is calculated that the observed results could have arisen by chance in the absence of a genuine dose effect. P-values equal or below 0.01 are taken to indicate significant mutagenicity.

A positive mutagenic response (with both strain TA 100 and TA 98, without metabolic activation) was only obtained with ozonated and unozonated humic acid after sample concentration using diethyl ether extraction (Table 4.1). Both these samples gave responses that were significant at the 0.1% level (i.e. this result would only occur by chance 1 in a 1000 times). With both bacterial strains ozonation of the humic acid appeared to increase the level of mutagenic activity slightly. The ozonated and unozonated humic acid show a slightly higher level of activity with bacterial strain TA 98. All the samples concentrated by solid-phase extraction and XAD-2 resin adsorption were non-mutagenic when tested with bacterial strains TA 98 and TA 100 without metabolic activation.
<table>
<thead>
<tr>
<th>Method of concentration</th>
<th>pH</th>
<th>Sample</th>
<th>TA 100</th>
<th>TA 98</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid-phase extraction</td>
<td>7</td>
<td>ozonated buffer</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>(Bond-Elut C18)</td>
<td></td>
<td>ozonated humic acid</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>unozonated humic acid</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Solvent extraction</td>
<td>2</td>
<td>ozonated buffer</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>(diethyl ether)</td>
<td></td>
<td>ozonated humic acid</td>
<td>S(0.304)*</td>
<td>S(0.701)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>unozonated humic acid</td>
<td>S(0.140)</td>
<td>S(0.435)</td>
</tr>
<tr>
<td>XAD-2 resin adsorption</td>
<td>2</td>
<td>ozonated buffer</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>(ether elution)</td>
<td></td>
<td>ozonated humic acid</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>unozonated humic acid</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>XAD-2 resin adsorption</td>
<td>2</td>
<td>ozonated buffer</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>(acetone elution)</td>
<td></td>
<td>ozonated humic acid</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>unozonated humic acid</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>XAD-2 resin adsorption</td>
<td>7</td>
<td>ozonated buffer</td>
<td>NS</td>
<td>NS</td>
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<tr>
<td>(ether elution)</td>
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<td>NS</td>
<td>NS</td>
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<tr>
<td></td>
<td></td>
<td>unozonated humic acid</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>XAD-2 resin adsorption</td>
<td>7</td>
<td>ozonated buffer</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>(acetone elution)</td>
<td></td>
<td>ozonated humic acid</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>unozonated humic acid</td>
<td>NS</td>
<td>NS</td>
</tr>
</tbody>
</table>

Notes:

S = Significant at 0.1% level
NS = Dose effect not significant
*( ) = Slope
The limited results obtained from this study suggest that solvent extraction may recover more of the mutagenic fraction than the other two techniques used. However, the positive mutagenic response with unozonated humic acid is surprising. A similar result was obtained when high concentrations of humic acids were tested without any sample preconcentration (WRc Report DoE 3298). It is possible that this apparent mutagenicity in the unozonated samples could be due to histidine in the humic acid solution, which would be reflected as differences in the histidine-limited yield of bacteria in the test (Forster et al. 1983). Ozonation does seem to increase mutagenicity, although the positive results obtained for the unozonated samples do make it difficult to draw any firm conclusions.

4.1.3 Application of concentration techniques to aldehydes

Aldehydes, including glyoxal and methylglyoxal, have been identified as reaction products of the ozonation of humic acids (Ueno et al. 1989) and known models of humic acid chemical structure such as 1,3-dihydroxynaphthalene and p-hydroxybenzaldehyde (Sayato et al. 1987, Matsuda et al. 1991, 1992). Glyoxal and methylglyoxal have been reported to contribute up to 90% of the total mutagenicity of ozonated p-hydroxybenzaldehyde (Matsuda et al. 1991). These compounds were therefore selected as suitable representative compounds to use in order to determine whether the concentration techniques described in Section 4.1.2 were likely to be effective at isolating potentially mutagenic ozonation by-products.

Humic acid solution (20 mg L\(^{-1}\)) was ozonated (see Section 4.1.2) and the concentrations of glyoxal and methylglyoxal determined by the PFHBA derivatisation method (Scilimenti et al. 1991). The ozonated humic acid solution was then concentrated using each of the techniques described above in turn (to isolate the organic fraction), and the aqueous fractions remaining re-analysed for glyoxal and methylglyoxal.

Glyoxal and methylglyoxal were present in the ozonated humic acid solution (Table 4.2). No significant change in these levels was observed after the sample concentration step (Table 4.2), indicating that these particular mutagenic ozonation by-products were not isolated and recovered by the techniques used. The fact that these two compounds, both known ozonation by-products and suspected mutagens, are not effectively isolated using any of the three concentration methods used, does suggest that some of the methods available for isolation of the mutagenic fraction from water will not necessarily be suitable for more polar, highly water-soluble, ozonation by-products. The positive mutagenic response obtained from the ozonated humic acid solution (solvent extracted) suggests that some mutagenicity is isolated by this method, although the results have to be treated with caution given that a positive response was also seen with the unozonated sample (Section 4.1.2).
### Table 4.2 Glyoxal and methylglyoxal concentrations in ozonated humic acid before and after sample concentration

<table>
<thead>
<tr>
<th>Method of sample concentration</th>
<th>pH</th>
<th>Glyoxal (μg l⁻¹)</th>
<th>Methylglyoxal (μg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid-phase extraction (Bond-Elut C18)</td>
<td>7</td>
<td>7.6</td>
<td>8.2</td>
</tr>
<tr>
<td>Solvent extraction (diethyl ether)</td>
<td>2</td>
<td>9.4</td>
<td>9.1</td>
</tr>
<tr>
<td>XAD-2 resin adsorption (ether elution)</td>
<td>7</td>
<td>9.2</td>
<td>8.6</td>
</tr>
</tbody>
</table>

### 4.1.4 Summary

Mutagenic activity was detected in diethyl ether extracts of both ozonated and unozonated humic acid solutions. The reasons for the mutagenic response in the unozonated humic acid are difficult to explain, but there did appear to be some increase in mutagenic activity after ozonation. Mutagenic activity was not detected in the extracts isolated by either Bond-Elut C18 cartridges or XAD-2 resin adsorption. Analysis of ozonated humic acid solution before and after ‘isolation’ of an organic fraction by the three techniques investigated, revealed that glyoxal and methylglyoxal (two known ozonation by-products and suspected mutagens) were not isolated by any of the methods used. These findings support the view that some of the techniques devised to isolate potentially mutagenic fractions from chlorinated drinking water may not be suitable for some of the more polar, highly water-soluble, by-products likely to be produced from the use of ozone in water treatment.

### 4.2 Ozonation of polyelectrolytes

#### 4.2.1 Introduction

Three polyelectrolytes, LT25 (an anionic polyacrylamide), LT24 (a cationic polyacrylamide) and the nonionic polyacrylamide, LT20 (all obtained from Allied Colloids Ltd) were chosen for investigation in this study because of their wide use in the UK water industry.

#### 4.2.2 Experimental

Standards and samples were prepared by dissolving the polyelectrolytes in distilled water to form stock solutions which were then diluted as appropriate.
Polyelectrolyte solutions (10 mg l\(^{-1}\)) were ozonated with approximately 25 mg l\(^{-1}\) ozone over a period of 12 minutes. A high polyelectrolyte concentration (far in excess of that likely to be found in water) was chosen so that direct analysis was possible (i.e. without any sample pre-concentration). A correspondingly high ozone dose was therefore used.

LT25, the anionic polyacrylamide, was analysed using size exclusion chromatography (SEC) as described by Leung et al. (1987). This method utilises the total exclusion of polyelectrolytes from the column packing so the polyelectrolyte elutes as a sharp quantifiable peak at the void volume of the column. The other polyelectrolytes were not analysed directly - total organic carbon (TOC) and total organic nitrogen (TON) measurements on the polyelectrolyte solutions were used to assess whether any mineralisation had occurred.

Aliquots of the unozonated and ozonated polyelectrolyte solutions were analysed for the following:

(a) Non-polar products - dichloromethane extraction under acidic (pH 2) and neutral (pH 7) conditions, followed by GC-MS analysis of the concentrated extracts.

(b) Polar products - diethyl ether extraction (pH 2), methylation with diazomethane, followed by GC-MS analysis.

(c) Aldehydes - the PFBHA derivatisation method (Sclimenti et al.) was used, followed by GC-ECD analysis.

4.2.3 Results

SEC of LT25 solutions before and after ozonation revealed an apparent change in the structure of the polyelectrolyte (Figure 4.1). The characteristic polyelectrolyte peak (A) which eluted at seven minutes in unozonated samples was absent after ozonation and an additional peak (B) of apparently lower molecular weight, eluting after approximately 12 minutes, appeared. In order to monitor the degradation of peak A and formation of peak B, samples were taken at one minute intervals during the reaction. Analysis of these samples showed peak A broadening in the first few minutes of ozonation, and to have disappeared completely after four minutes. Peak B first appeared in the third minute of ozonation and its retention time was seen to increase with further ozonation.
Figure 4.1  SEC analysis of LT25 before (t=0) and after ozonation (t=1 - t=12 min). Peak A = unreacted LT25; Peak B = product of ozonation
GC-MS analysis of the fractions obtained by dichloromethane and diethyl ether extraction revealed no significant differences between the extracts from the ozonated and unozonated samples. Similarly, no aldehydes were found in the ozonated polyelectrolyte samples that were not present in the unozonated samples.

TOC and TON measurements on the unozonated and ozonated polyelectrolytes indicated that little or no mineralisation of the polyelectrolytes had occurred after ozonation.

4.2.4 Discussion

SEC analysis of LT25 revealed that ozonation clearly resulted in a physical change to the polyelectrolyte, but it is unclear whether this change is due to the breaking of inter/intramolecular bonds, thus lowering the molecular weight, or to an adjustment in charge density which could have a similar effect.

Increased peak retention times for ozonated polymers when analysed by SEC has been noted by many authors (Saponkanaporn and Gehr 1989, Mallevialle et al. 1984, Suzuki et al. 1978). Gehr and Saponkanaporn (1990) ozonised samples of polyacrylamide and deduced that the apparent molecular weights of the compounds had been reduced from $5 \times 10^6$ to less than $1 \times 10^6$. There are three possible explanations for the appearance of later eluting peaks:

(a) Depolymerisation, in which ozone acts either directly or through an intermediate (e.g. hydroxyl radical) to break the polymer chain into smaller fragments, would result in smaller molecules and also increased molecular polarity due to partial oxidation.

(b) Breakage of inter and intramolecular bonds may alter the shape and size of the molecule sufficiently to change its retention time when analysed by SEC.

(c) The formation of polar functional groups may cause the compounds to adsorb more strongly onto the SEC column. This would result in longer elution times, but the structure of the polymer may not be significantly changed.

It is possible that the actual mechanism is a combination of all three, and possibly other mechanisms.

Several studies (Suzuki et al. 1979, Mallevialle et al. 1984, Gehr and Saponkanaporn 1990) report little or no loss of organic carbon, evolution of carbon dioxide or change in nitrogen speciation after reaction with ozone. Saponkanaporn and Gehr (1989) found that the total peak areas of the polyelectrolyte and impurity peaks were constant when the polyelectrolytes were ozonated at pH 3 and pH 6. These findings would appear to indicate that the polyelectrolyte is transformed to a lower molecular weight without any loss of amine, significant oxidation or mineralisation. However, there is an indication that during ozonisation at pH 9, mineralisation of the polyelectrolyte may occur. At this pH the total peak area of the polyelectrolyte and impurity peaks was found to have decreased by 50% (Saponkanaporn and Gehr 1989).
Suzuki et al. (1978) used viscosity studies to investigate the effect of ozone on the polyelectrolyte at pH 2 and pH 10. These indicated that the polyelectrolyte chains were broken at pH 10 but not at pH 2, with the chains being broken in proportion to the amount of ozone consumed. From similar studies Gehr and Saponkanaporn (1990) concluded that at all pHs the reaction involved main chain cleavage (depolymoerisation), although they found that ozonated polyelectrolytes had a substantially decreased flocculating efficiency, suggesting that ozonation also causes a decrease in charge density of the polymers. Analysis of the ozonation products by IR, $^{13}$C NMR and UV caused Suzuki et al. (1978) to speculate that ozonation causes the formation of a new functional group in the polyelectrolyte chain, possibly an aldehyde or ketone. The authors suggest that this group combines with the amide group to produce an unspecified ring structure.

A few studies indicate that acrylamide is decomposed by oxidation with ozone. Croll et al. (1974) reacted a 6 µg l$^{-1}$ solution of acrylamide with 3 mg l$^{-1}$ ozone for 30 minutes at pH 7 and obtained 100% removal of the acrylamide. Mallevialle et al. (1984) found that the removal of acrylic acid and acrylamide was rapid during ozonation. HPLC analysis of the products showed the formation of two peaks. However these would not be identified by GC-MS analysis. Gehr and Saponkanaporn (1990) measured acrylamide after ozonation of a 50 mg l$^{-1}$ polyelectrolyte solution (containing 0.05 mg l$^{-1}$ acrylamide) and found that acrylamide was almost totally removed after 30 minutes ozonation at pH 6. Degradation of the polymer therefore did not result in production of the monomer; furthermore ozone mineralised the acrylamide already present.

4.2.5 Summary

SEC analysis before and after ozonation showed that the anionic polyelectrolyte LT25 did react with ozone. Extraction of the solution after ozonation, followed by analysis by GC-MS and GC-ECD, did not reveal any lower molecular weight reaction products. Similarly, ozonation of a nonionic (LT20) and cationic (LT24) polyelectrolyte did not produce any readily detectable, low molecular weight compounds. It seems likely that the products of ozonation are of high molecular weight and/or very polar in nature.

4.3 Occurrence and formation of haloacetic acids

4.3.1 Introduction

A report detailing the results from the studies (up to the end of 1992) into haloacetic acids has been produced recently (WRc Report DoE 3286). This work has largely concentrated on the production of dichloroacetic acid (DCA)and trichloroacetic acid (TCA), both of which are present as by-products in a wide range of chlorinated drinking water. In terms of their widespread occurrence and the levels found, DCA and TCA can be compared to trihalomethanes (THMs). Both DCA and TCA are included in the revision of the WHO Guidelines for drinking water (to be published in late 1993), with guideline values of 50 and 100 µg l$^{-1}$ respectively. In addition, the US EPA are likely to set standards for individual or total haloacetic acids (or both). Based on the data obtained to date, in terms of the UK position, DCA and TCA concentrations in most chlorinated waters would be
below the WHO guideline values, but levels in some waters could exceed either the DCA or TCA guideline value (or both). Where high levels of DCA and TCA are being produced, there would seem to be some possibility of reducing the concentrations produced through modification of the treatment process.

Further laboratory studies were undertaken to investigate the production of DCA and TCA under varying chlorine dose, chlorination time and pH. Production of THMs was also monitored, allowing an assessment of the relative formation of two major groups of chlorination by-products under a range of conditions. Additional work was also carried out looking at the fate of DCA and TCA in the distribution system.

4.3.2 Formation of chloroacetic acids and THMs

All the laboratory studies into chloroacetic acid and THM formation were carried out using Thames river water (filtered). The extraction procedure and analysis details have been reported previously (WRc Report DoE 3286).

Effect of chlorine dose

The levels of DCA, TCA and THMs produced under a range of chlorine doses are given in Table 4.3. As expected the concentrations of all the compounds analysed increased with chlorine dose although, with the exception of TCA, there was little change in concentrations formed with chlorine doses of 5 and 10 mg l\(^{-1}\).

<table>
<thead>
<tr>
<th>Cl(_2) dose (mg l(^{-1}))</th>
<th>DCA (µg l(^{-1}))</th>
<th>TCA (µg l(^{-1}))</th>
<th>CHCl(_3) (µg l(^{-1}))</th>
<th>CHCl(_3)Br (µg l(^{-1}))</th>
<th>CHClBr(_2) (µg l(^{-1}))</th>
<th>CHBr(_3) (µg l(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>&lt;1.0</td>
<td>2.0</td>
<td>&lt;0.4</td>
<td>&lt;0.2</td>
<td>&lt;0.5</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>1</td>
<td>11.7</td>
<td>7.9</td>
<td>11.2</td>
<td>3.1</td>
<td>&lt;0.5</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>2</td>
<td>19.3</td>
<td>20.5</td>
<td>33.2</td>
<td>17.1</td>
<td>6.3</td>
<td>0.6</td>
</tr>
<tr>
<td>5</td>
<td>42.3</td>
<td>38.1</td>
<td>50.2</td>
<td>22.0</td>
<td>6.9</td>
<td>0.4</td>
</tr>
<tr>
<td>10</td>
<td>42.6</td>
<td>47.8</td>
<td>52.6</td>
<td>21.8</td>
<td>6.5</td>
<td>&lt;0.4</td>
</tr>
</tbody>
</table>

Effect of chlorination time

Thames river water was chlorinated with 5 mg l\(^{-1}\) chlorine for varying lengths of time. The levels of DCA, TCA and THMs increased with increasing reaction time (Table 4.4).
Table 4.4  Effect of chlorination time on the formation of chloroacetic acids and THMs

<table>
<thead>
<tr>
<th>Reaction time</th>
<th>DCA (µg l⁻¹)</th>
<th>TCA (µg l⁻¹)</th>
<th>CHCl₃ (µg l⁻¹)</th>
<th>CHCl₂Br (µg l⁻¹)</th>
<th>CHClBr₂ (µg l⁻¹)</th>
<th>CHBr₃ (µg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;0.4</td>
<td>&lt;0.2</td>
<td>&lt;0.5</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>5 min</td>
<td>4.9</td>
<td>4.8</td>
<td>28.7</td>
<td>11.7</td>
<td>3.2</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>15 min</td>
<td>7.9</td>
<td>9.0</td>
<td>29.9</td>
<td>12.8</td>
<td>3.5</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>30 min</td>
<td>11.4</td>
<td>17.2</td>
<td>35.7</td>
<td>15.3</td>
<td>4.3</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>60 min</td>
<td>15.8</td>
<td>24.1</td>
<td>41.9</td>
<td>18.2</td>
<td>5.1</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>2 hours</td>
<td>17.6</td>
<td>27.3</td>
<td>48.6</td>
<td>22.2</td>
<td>6.0</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>4 hours</td>
<td>23.5</td>
<td>33.5</td>
<td>55.5</td>
<td>24.9</td>
<td>7.0</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>6 hours</td>
<td>28.7</td>
<td>40.1</td>
<td>54.8</td>
<td>24.8</td>
<td>7.3</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>24 hours</td>
<td>48.1</td>
<td>55.2</td>
<td>66.3</td>
<td>29.2</td>
<td>9.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Effect of chlorination pH

River water samples were chlorinated (5 mg l⁻¹; 2 hours) at a range of pH values (6, 7, 8 and 9). The concentrations of DCA, TCA and THMs produced at each pH are shown in Table 4.5. The concentration of both TCA and CHCl₃ was dependent on the chlorination pH (Figure 4.2), with the formation of TCA being favoured at lower pH values, whereas that of CHCl₃ is favoured at higher pH. Similar results have been reported before (Reckhow et al. 1990) and would seem to favour the supposition that TCA and CHCl₃ originate, at least in part, from the same intermediates, with the ratio of products formed dependent on pH. It is interesting to note that their combined concentrations was greatest at pH 7. In contrast to TCA, the amount of DCA formed appeared independent of pH, suggesting that the two chloroacetic acids are formed via different reaction pathways.
Figure 4.2  Effect of pH on the formation of TCA and CHCl₃
Table 4.5  Effect of pH on the formation of chloroacetic acids and THMs

<table>
<thead>
<tr>
<th>pH</th>
<th>DCA (µg l⁻¹)</th>
<th>TCA (µg l⁻¹)</th>
<th>CHCl₃ (µg l⁻¹)</th>
<th>CHCl₂Br (µg l⁻¹)</th>
<th>CHClBr₂ (µg l⁻¹)</th>
<th>CHBr₃ (µg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>22.3</td>
<td>45.5</td>
<td>24.2</td>
<td>13.6</td>
<td>3.4</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>7</td>
<td>22.9</td>
<td>44.2</td>
<td>43.8</td>
<td>18.6</td>
<td>4.9</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>8</td>
<td>23.7</td>
<td>32.7</td>
<td>40.3</td>
<td>18.4</td>
<td>5.3</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>9</td>
<td>26.7</td>
<td>26.0</td>
<td>43.9</td>
<td>17.5</td>
<td>5.9</td>
<td>&lt;0.4</td>
</tr>
</tbody>
</table>

4.3.3  Fate of DCA and TCA in the distribution system

The fate of DCA and TCA in the distribution system has been investigated previously (WRc Report DoE 3286). On that occasion, two distribution systems were studied with samples being taken of the water leaving the treatment works and at various points around the system. The results showed that the concentrations of both DCA and TCA could alter between leaving the treatment works and reaching the consumer. On occasions, a substantial reduction in both DCA and TCA concentrations were observed, but this was not observed in all the samples analysed. In the light of these results, it was decided to carry out further studies. Four distribution systems were selected and samples taken from the works and at three points in the system. It should be emphasised that all the samples were collected on the same day, and therefore no attempt was made to cover any variation in the concentrations of DCA and TCA in water leaving the works.

The results from this study (Table 4.6) again showed that concentrations of both DCA and TCA can decrease within a distribution. The concentration of DCA appears to decrease more rapidly than that of TCA, which agrees with previous data from distribution systems, as well as results from laboratory studies into the respective stabilities of DCA and TCA. On occasions (e.g. GR1 to GR2) the decrease in DCA concentration is very great (71.1 to 5.5 µg l⁻¹). As reported previously, it seems that TCA is more stable in distribution, although it too shows some significant reductions (e.g. GR1 to GR4, falling from 56.5 to 7.4 µg l⁻¹). In other systems (BR and PW) it is present at similar concentrations in water leaving the works and in consumers taps. It is difficult to draw any final conclusions from this latest study, but it does confirm the findings previously reported (WRc Report DoE 3286). It does seem that in general concentrations of both DCA and TCA decrease in distribution, but other factors (peculiar to individual systems and water types) may be significant. It should be noted that the GRI sample exceeds the WHO guideline value for DCA.
### Table 4.6  DCA and TCA concentrations in distribution systems

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Sample source</th>
<th>Distance from works (km)</th>
<th>DCA (µg l⁻¹)</th>
<th>TCA (µg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GR1</td>
<td>treatment works</td>
<td>0</td>
<td>71.1</td>
<td>56.5</td>
</tr>
<tr>
<td>GR2</td>
<td>service reservoir</td>
<td>NA</td>
<td>5.5</td>
<td>30.4</td>
</tr>
<tr>
<td>GR3</td>
<td>service reservoir</td>
<td>NA</td>
<td>1.0</td>
<td>12.2</td>
</tr>
<tr>
<td>GR4</td>
<td>service reservoir</td>
<td>NA</td>
<td>&lt;1.0</td>
<td>7.4</td>
</tr>
<tr>
<td>PW1</td>
<td>treatment works</td>
<td>0</td>
<td>25.2</td>
<td>24.8</td>
</tr>
<tr>
<td>PW2</td>
<td>service reservoir</td>
<td>19</td>
<td>14.3</td>
<td>16.8</td>
</tr>
<tr>
<td>PW3</td>
<td>consumer tap</td>
<td>24</td>
<td>13.0</td>
<td>18.2</td>
</tr>
<tr>
<td>PW4</td>
<td>consumer tap</td>
<td>28</td>
<td>12.9</td>
<td>18.3</td>
</tr>
<tr>
<td>BR1</td>
<td>treatment works</td>
<td>0</td>
<td>18.0</td>
<td>15.3</td>
</tr>
<tr>
<td>BR2</td>
<td>consumer tap</td>
<td>1</td>
<td>&lt;1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>BR3</td>
<td>consumer tap</td>
<td>2</td>
<td>3.2</td>
<td>11.9</td>
</tr>
<tr>
<td>BR4</td>
<td>consumer tap</td>
<td>5</td>
<td>2.6</td>
<td>15.0</td>
</tr>
<tr>
<td>DA1</td>
<td>treatment works</td>
<td>0</td>
<td>8.5</td>
<td>3.2</td>
</tr>
<tr>
<td>DA2</td>
<td>gravity feed tank</td>
<td>24</td>
<td>9.5</td>
<td>2.8</td>
</tr>
<tr>
<td>DA3</td>
<td>service reservoir</td>
<td>40</td>
<td>8.9</td>
<td>3.1</td>
</tr>
<tr>
<td>DA4</td>
<td>consumer tap</td>
<td>72</td>
<td>1.4</td>
<td>3.1</td>
</tr>
</tbody>
</table>

NA = data not available

#### 4.3.4  Summary

The findings confirm the results reported previously (WRc Report DoE 3286), as well as providing data on the formation of THMs in addition to those for DCA/TCA. Concentrations of both chloroacetic acids and THMs increased with chlorine dose and chlorination time. Chlorination pH was an important factor in both TCA and THM formation (TCA being favoured at lower pH, THMs at higher pH). The difference in the effect of chlorination pH on the formation of TCA and CHCl₃ is significant and would be an important factor in any consideration of pH control as a means of limiting the formation of TCA.

Results from distribution system samples again suggest that concentrations of both DCA and TCA can decrease significantly in distribution, but it is difficult to predict the extent to which this will occur in a particular system. It does seem from the data obtained during this study, as well as the previous work, that it is unlikely that DCA or TCA concentrations will increase within a distribution system.
4.4 Bromate

4.4.1 Introduction

The increase in recent years in the use of ozone in drinking water treatment has led to concern about the possible formation of harmful by-products. Of particular concern is bromate, which can be formed from the ozonation of raw waters containing bromide. Bromate is a suspected carcinogen and is included in the revised WHO Guidelines for drinking water. The WHO have set a provisional guideline value of 25 $\mu$g l$^{-1}$, taking account of some of the analytical problems associated with the determination of bromate at low levels in drinking water. Based on the use of low dose extrapolation models, an upper 95% confidence limit risk of 1 in $10^5$ of the population (a factor commonly used when deriving guideline values) gives rise to a value of 3 $\mu$g l$^{-1}$. It should be noted that the presumed analytical problems have been largely resolved.

It is possible at least in principle that the use of chlorine could give rise to significant levels of bromate in drinking water. Work carried out during the last reporting period, involving laboratory chlorination studies, provided evidence that direct oxidation of bromide by chlorine to form bromate is unlikely under typical treatment conditions (WRc Report DoE 3298). Bromate has, however, been detected in commercial hypochlorite solutions (Bolyard et al. 1992), and it is possible that bromate could be present in final water disinfected using hypochlorite. The use of on-site electrolytic chlorine generation is another potential source of bromate, since the brine used in the generator cells will inevitably contain bromide, which can undergo electrolysis to form bromate.

A limited survey of bromide and bromate in raw and treated waters (both chlorinated and ozonated) was undertaken. Samples of chlorinated water were collected from treatment works using gas chlorination, commercial hypochlorite or on-site generated hypochlorite. The results of this survey have been reported as part of a review on bromate (WRc Report DoE 3397 - The Formation of Bromate during Drinking Water Disinfection). The main findings are summarised below. Additional work has subsequently been carried out looking at the formation of bromate from the use of on-site electrolytic chlorine generation. The findings from that study are being reported elsewhere (WRc Report DoE 3533), but the conclusions are included below.

4.4.2 Bromate and bromide survey

The main findings from the survey were:

1. Bromate is formed under typical ozonation conditions. Concentrations of 10-21 $\mu$g l$^{-1}$ were detected in treated waters. The corresponding raw waters contained 120-160 $\mu$g l$^{-1}$ bromide. At sites where the raw water contained very little bromide (<20 $\mu$g l$^{-1}$), no bromate was detected after ozonation.

2. Bromate (8 $\mu$g l$^{-1}$) was only detected in one chlorinated final water - taken from a treatment works using hypochlorite for disinfection. Bromate was also detected in samples of hypochlorite produced by on-site electrolytic generation, although no
bromate was detected in final waters chlorinated using hypochlorite generated in this way. The use of hypochlorite would seem to be the most likely source of bromate in chlorinated drinking water.

4.4.3 Bromate from on-site electrolytic generation of chlorine

The conclusions from this study were as follow:

1. Bromate is formed during on-site generation of hypochlorite. The concentrations found in hypochlorite samples ranged from 2.8 to 21.8 mg l⁻¹. The upper end of this range approaches the theoretical maximum (calculated by assuming all the bromide likely to be present in the brine solution is converted to bromate).

2. Detectable concentrations of bromate were found in two final waters analysed. These corresponded to the two hypochlorite solutions containing the highest concentrations of bromate. The concentration of bromate present in a particular final water will be a function of the concentration in the hypochlorite and the chlorine dose.

3. It is very unlikely that the provisional WHO guideline for bromate of 25 μg l⁻¹ would be exceeded through the use of on-site generated hypochlorite alone. If a lower value (e.g. 5 or 10 μg l⁻¹) is adopted at a later date, then it is feasible that exceedances could occur.

4. A major factor in determining the level of bromate present in hypochlorite is likely to be the bromide concentration in the brine entering the generator cell. This will be determined by a combination of the original bromide content of the salt and the strength of the brine. The brine strength is likely to vary significantly in different systems, and in some cases is increased to maintain a pre-determined hypochlorite concentration in the outlet stream (normally 0.7-0.9% chlorine).

5. Other variations in operating procedures could affect the amount of bromide converted to bromate. These include cell voltage, current density, operating temperature and residence time in the generator cell. To a certain extent all these parameters will be inter-related, and whilst it is difficult to predict the effect of changes in any one of them on bromate production, it is likely that any increase in one or other parameter is likely to favour bromate production.

6. Loss of efficiency, possibly through deterioration of the electrode surface or poor feed water quality, may be overcome through an increase in cell voltage, which is likely to result in more bromate formation. Increasing brine concentration is another option (see 2 above).

7. Storage of on-site generated hypochlorite does not seem to result in significant increase in bromate concentrations, suggesting that most of the bromate is formed through electrolysis of bromide, rather than oxidation by chlorine (either in the generator cell or in the storage tank).
8. The type of on-site generating system does not seem to be important in determining the level of bromate formed. Three systems were sampled during this study, but no one type was found to produce more bromate than the others. All the systems sampled are based on essentially the same cell design (electrodes etc.) and operate under broadly similar conditions. Any variations in bromate production due to slight variations in cell design are likely to be outweighed by other variations (e.g. brine strength, cell voltage).
5. **INTERIM CONCLUSIONS**

Three concentration techniques have been used to isolate the mutagenic fraction from ozonated humic acid solutions (diethyl ether extraction, Bond-Elut C18 cartridges and XAD-2 resin adsorption). Mutagenic activity was only detected in the diethyl ether extracts of the ozonated and unozonated humic acid solution. The reasons for the mutagenic activity in the unozonated humic solutions are not clear. There did appear to be an increase in mutagenic activity after ozonation.

Analysis of ozonated humic acid solutions before and after carrying out the three concentration techniques, revealed that glyoxal and methylglyoxal (two known ozonation by-products and suspected mutagens) were not isolated by any of the methods used. This suggests that some of the techniques developed to isolate potentially mutagenic fractions from chlorinated drinking water may not be suitable for more polar, highly water-soluble, by-products of ozonation.

The anionic polyelectrolyte LT25 reacts with ozone. No lower molecular weight reaction products were detected by GC-MS. Similarly, ozonation of a nonionic (LT20) and cationic (LT24) polyelectrolyte did not result in any readily detectable low molecular weight products. It seems likely that the products of the ozonation of polyelectrolytes are high molecular weight or very polar in nature.

Concentrations of DCA, TCA and THMs formed through the chlorination of River Thames water, were found to increase with chlorine dose and chlorination time. Chlorination pH was an important factor in both TCA and THM formation (TCA favoured at lower pH, THMs at higher). DCA formation was independent of pH.

Results from distribution system samples suggest that concentrations of TCA and DCA decrease in distribution. It is difficult, however, to predict the extent to which this will occur in a particular system. It appears unlikely that either DCA or TCA concentrations will increase within a distribution system.

Bromate is formed under typical ozonation conditions. Concentrations of 10-21 µg l\(^{-1}\) were detected in treated waters. The corresponding raw waters contained 120-160 µg l\(^{-1}\) bromide. At sites where the raw water contained very little bromide (<20 µg l\(^{-1}\)), no bromate was detected after ozonation.

Bromate (8 µg l\(^{-1}\)) was only detected in one chlorinated final water - taken from a treatment works using hypochlorite for disinfection. Bromate was also detected in samples of hypochlorite produced by on-site electrolytic generation, although no bromate was detected in final waters chlorinated using hypochlorite generated in this way. The use of hypochlorite would seem to be the most likely source of bromate in chlorinated drinking water.

Additional work on the production of bromate during on-site electrolytic generation of chlorine confirmed that bromate was formed during this process (concentrations in hypochlorite solutions analysed ranged from 2.8 to 21.8 mg l\(^{-1}\)). Bromate was detected in only two of the final waters analysed (at levels of 2 and 5 µg l\(^{-1}\)).
6. WORK PROPOSED FOR THE NEXT REPORTING PERIOD

The likely implications of the revised WHO Guidelines for drinking water (due to be published in October 1993) will be reviewed. Work being carried out elsewhere in relation to the new guidelines will be critically reviewed and implications for the UK identified. Areas where further research is required will be identified and appropriate studies carried out.

Investigations into the production of mutagenicity from ozonation will focus on possible inconsistencies in the test results (such as the positive response from unozonated humic acid). Additional methods for the isolation of mutagenic fractions will be investigated, with emphasis being placed on those likely to maximise the recovery of polar ozonation by-products.

The availability of bioassay techniques, other than bacterial mutagenicity testing, for detecting potentially harmful disinfection by-products in drinking water will be reviewed.

The development in the US of models to predict DBP formation during water treatment and microbial risks will be critically evaluated and attempts at deriving models for the UK situation will be started.
REFERENCES


