Chloral hydrate: Formation and removal by drinking water treatment

Lisa Barrott

ABSTRACT

Chloral hydrate (the hydrated form of trichloroacetaldehyde) is formed in water treatment as a by-product of the reaction between chlorine and naturally occurring organic material. Although a clear link between adverse health effects and levels of chloral hydrate in drinking water has not been established, the World Health Organisation (WHO) has set a Provisional Guideline Value of 10 μg l^{-1}. This paper reviews the potential for the formation and removal of chloral hydrate in drinking water treatment processes.

Two possible formation mechanisms for chloral hydrate are the reaction between amino acids and chlorine and the reaction between the aldehydes (formed when natural organic material is oxidised) and chlorine. Chloral hydrate can decay in alkaline conditions to give chloroform and in oxidising conditions to give trichloroacetic acid. Although the optimum conditions for the minimisation of trihalomethanes (THMs) may be different from the optimum conditions for the minimisation of chloral hydrate, the removal of organic precursors is common to both. Enhanced coagulation has the potential to reduce chloral hydrate levels in the treated water and to be the most efficient, convenient and cost effective method of reducing chloral hydrate levels in the treated water. Free chlorine is necessary for significant formation of chloral hydrate.

Key words | chloral hydrate, chlorination, disinfection by-products, enhanced coagulation, water treatment

Lisa Barrott
MWH,
201 Amersham Road,
High Wycombe,
Buckinghamshire HP13 5AJ,
UK
E-mail: *lisa.barrott@mwhglobal.com*

BACKGROUND

Chloral hydrate is formed as a by-product of the reaction between chlorine and naturally occurring organic material. Concern about the potential health effects of the by-products of chlorination has prompted the investigation of the possible association between exposure to these by-products and the incidence of human cancer, and more recently with adverse reproductive outcomes. Drinking water standards have been set for some of these chemicals, particularly the trihalomethanes (THMs), and the need for their regulation is generally accepted. The situation with regard to chloral hydrate is not so straightforward, but because of the concern over possible adverse health impacts, the World Health Organisation (WHO) has set a provisional guideline of 10 μg l^{-1}.

INTRODUCTION

The disinfection by-products produced when chlorine reacts with organic material include the trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs), chloropicrin and chloral hydrate. Chloral hydrate has not received as much attention as the THMs or the HAAs but it has been shown to be

present in drinking waters throughout the world. This paper reviews the formation and removal of chloral hydrate by drinking water treatment processes.

MECHANISM OF CHLORAL HYDRATE FORMATION: GENERAL

Although it is known that chloral hydrate is formed from the reaction between organic material and chlorine, the mechanism (or mechanisms) of formation are more difficult to identify because of the complex nature of organic material. Several mechanisms of formation are possible. However the studies carried out in this area show that chloral hydrate is also subject to decay and could better be described as an intermediate by-product. The studies show that chloral hydrate will decay to give other important disinfection by-products such as chloroform (a THM) and trichloroacetic acid (a HAA).

Many papers report investigations of the reactions between amino acids and chlorine to produce chloral hydrate. Amino acids can be oxidised during pre-chlorination to produce aldehydes and nitriles (Le Cloirec and Martin 1984). The presence of free and condensed amino acids in natural waters and known reaction pathways for the chlorination of amino acids strongly indicate that amino acids are potential precursors in the environment for disinfection by-products (DBPs), including chloral hydrate.

Formation of chloral hydrate from amino acids and nitrogen compounds

Trehy *et al*. (1987, 1989) suggested a pathway for the production of trichloroacetaldehyde from aspartic acid and also established that certain amino acids such as aspartic acid, tyrosine and tryptophan yield chloral hydrate when exposed to aqueous chlorine under conditions similar to those used in water treatment (Trehy *et al*. 1986). In the same paper the authors noted that chloral hydrate can be converted to chloroform and an important finding from the work was that the formation potential for chloroform appears to be different from the formation potential for chloral hydrate indicating that there are different precursors for these chlorination by-products.

In a similar study, Ueno *et al*. (1995) carried out a test that chlorinated three different types of humic acid (reagent, wastewater derived and soil-humic derived). Chloral hydrate was produced from all three sources, up to 4.4 $\mu g\ l^{-1}$. Ueno *et al*. also chlorinated various nitrogen compounds to investigate which disinfection by-products were formed. The results indicated that chloral hydrate can be produced from the chlorination of synthetic nitrogen-containing compounds and amino acids, with uracil and aspartic acid producing relatively high levels of chloral hydrate.

Formation of chloral hydrate from ozonated waters

The formation of aldehydes and other DBPs from the ozonation of water is well established (Murphy *et al*. 1993; Krasner *et al*. 1993; Weinberg *et al*. 1993). When these low molecular weight aldehydes are chlorinated they can produce THMs and chloral hydrate. The production of increased levels of chloral hydrate in plants that introduce ozone, in comparison with similar plants that do not include ozone, is well documented and a summary of these findings is presented in this paper.

Decay of chloral hydrate to form chloroform and trichloroacetic acid

Chloral hydrate is known to decompose in neutral, acidic and basic solutions to form chloroform. At a pH of 8 and temperature of 35°C, its half-life is 2 days (Luknitskii 1975). Keith *et al*. (1976) carried out a kinetic study of chloroform formation from chloral hydrate and found that conversion to chloroform was very slow.

Reckhow and Singer (1984) stated that chloral hydrate can undergo base catalysed hydrolysis and is considered to be a long-lived intermediate rather than an end product in the chlorination of natural organics. Chloral hydrate also undergoes oxidation to trichloroacetic acid at pH 7 in the presence of calcium hypochlorite (Plump 1948).

Thus chloral hydrate may be a precursor common to the two major DBPs: chloroform ($CHCl_3$) and TCAA (trichloroacetic acid).

Reckhow and Singer (1984) went on to state that, although the hydrolysis of chloral hydrate to form chloroform is too slow to be of significance, the importance of chloral hydrate as a trichloroacetic acid (TCAA) precursor at pH 7 merits investigation. The authors chlorinated a relatively concentrated solution of chloral hydrate (200 $\mu g\, l^{-1}$) to find that the rate of TCAA production was a constant 0.007 $\mu g\ l^{-1}\ h^{-1}$. If this value is compared with the high yield of TCAA and the low yield of chloral hydrate observed by Miller and Uden (1983) (who found about 40 $\mu g\, l^{-1}$ of chloral hydrate in a fulvic acid solution (5 $mg\, l^{-1}$ TOC, 25 $mg\, l^{-1}$ NaOCl) that was chlorinated at pH 7) it is apparent that chloral hydrate cannot account for a significant fraction of the TCAA formation. However the significance of this work is not in the production (slow) of chloroform but the decay of chloral hydrate over lengths of time which are found in the distribution system.

Miller and Uden (1983) also found that chloral hydrate formation in the chlorination of fulvic acid was dependent on pH with a steady increase in concentration from pH 4 up to a neutral pH at which point its concentration drops. At a pH of 10 no chloral hydrate is produced. The product of this decomposition was found to be chloroform. Their work also showed that the production of chloral hydrate was quite slow: from 0 to 10 minutes after chlorination the level of chloral hydrate increased steadily after which there was no further increase. An experiment to find out the effect of chlorine concentration on the formation of chloral hydrate showed that the level of chloral hydrate was proportional to the NaOCl:C ratio up to a ratio of 2 and then there was no further increase in the amount of chloral hydrate produced.

THE FORMATION OF CHLORAL HYDRATE AND OTHER DBPS BY WATER TREATMENT PROCESSES

In general the formation of DBPs is influenced by pH, contact time with the disinfectant, temperature and season, nature and concentration of natural organic matter (NOM), chlorine dose and residual and bromide concentration. All of the factors must be considered separately for each DBP when attempting to minimise the formation of a particular DBP.

The following sub-sections provide a review of the effects of water treatment processes on the levels of chloral hydrate in treated water.

The effect of chloramination

In a study reported in 1991, Dixon and Lee evaluated the effect of chloramine as a post-disinfectant. The chloraminated waters examined in their study exhibited lower mean levels of chloral hydrate than the chlorinated waters. The data was reviewed in terms of how much chloral hydrate was formed in the distribution system after leaving the treatment works. In the chlorinated waters it was found that chloral hydrate increased by 88% and the increase in chloral hydrate in the chloraminated waters was effectively arrested.

In the survey reported by Koch and Krasner (1989), two Californian works used free chlorine for initial disinfection and then used chloramines (via ammonia addition) as a final disinfectant before entering the distribution system. However during the period of the study one plant operated with concurrent addition of chlorine and ammonia at the head of the works so there was little free chlorine contact time. These results show that there was less chloral hydrate in the treated water at this plant that practised concurrent chloramination.

These studies strongly suggest that free chlorine is necessary for chloral hydrate formation.

The effect of ozonation

In a paper on the role of ozone in the formation and control of DBPs, Jacangelo *et al*. (1989) reported the studies carried out at four treatment utilities in the US. In a direct comparison of chlorine only versus ozone-chlorine disinfection in two utilities, the levels of chloral hydrate increased when ozone was introduced. This contrasted with the situation with THMs where levels increased in one utility and decreased in another. Levels

Table 1 | Positive or negative changes in disinfection by-products resulting from ozone addition at four utilities

	Treatment modifications						
	Chlorine–chlorine to ozone–chlorine Utility no.		Chloramines to ozone-chloramines Utility no.			Chlorine–chlorine to ozone–chloramines Utility no.	
	1	4[a]	2[b]	3[c]	4[d]	2[b]	4[e]
Trihalomethanes	—	NC	—	—	—	—	—
Haloacetic acids	—	NC	—	—	NC	—	—
Chloral hydrate	+	+	—	—	Small +	—	—

NC, no change.
[a]Pre-chlorine to pre-ozone before pre-chlorine.
[b]Utility 2 included 4 hours of contact time with free chlorine before NH_3 addition in the chlorine–chloramine scheme (pre-chlorine, post-ammonia); there was concurrent post chloramine addition in the ozone–chloramine scheme following the pre-ozone.
[c]Pre-chloramine to pre-ozonation-post chloramines.
[d]Pre-chloramine to pre-ozone before pre-chloramine.
[e]Pre-chlorine to pre-ozone before pre-chloramine.

of HAAs decreased after ozonation was introduced. A summary of the results obtained is given in Table 1.

The table shows that ozone in conjunction with chlorine or chloramines as the final disinfectant was generally effective in reducing concentrations of THMs and HAAs. However the picture with chloral hydrate is different. It is evident that the introduction of pre-ozonation before chlorine increases chloral hydrate levels. However chloral hydrate levels can increase or decrease when ozone is introduced before chloramination. Utility 2 demonstrates that the removal of the period of contact time with free chlorine reduced the chloral hydrate levels. Ozonation followed by chloramination is more effective in reducing chloral hydrate levels than ozone followed by chlorination. Levels of chloral hydrate with ozone followed by chloramination are lower than with chlorination alone.

Two pilot plants were used in a study to investigate the effects of water treatment processes on the formation of chloral hydrate (Xie and Reckhow 1992). The first pilot plant, West River, had three parallel process streams. The chloral hydrate formation potential or CHFP of the raw water was found to be 26 $\mu g\,l^{-1}$. (The CHFP is the chloral hydrate concentration found after chlorinating a water sample under standard conditions of chlorine, residual, temperature and pH.) The effects of the three process streams on the CHFP were as follows:

(a) After pre-ozonation in the direct filtration train, the CHFP increased to about 40 $\mu g\,l^{-1}$. Direct filtration with granular activated carbon (GAC)/sand, resulted in a CHFP of 8 $\mu g\,l^{-1}$ in the effluent.
(b) In the dissolved air flotation (DAF) train, pre-ozonation resulted in a CHFP of 38 $\mu g\,l^{-1}$. Subsequent DAF reduced the formation potential to 22 $\mu g\,l^{-1}$. Filtration through GAC/sand after DAF resulted in a formation potential of 8 $\mu g\,l^{-1}$.
(c) In the direct filtration/GAC adsorption train, direct filtration in full scale reduced the chloral hydrate concentration to 11 $\mu g\,l^{-1}$. Pre-ozonation increased the final (filtered) CHFP to 15 $\mu g\,l^{-1}$. GAC with different contact times of 4, 8, 12 and 16 minutes reduced the CHFP to 7, 5, 4 and 2 $\mu g\,l^{-1}$, respectively.

The second pilot plant gave similar results with the additional information that used GAC filters could reduce CHFP too, but not as much as the relatively new GAC. The authors concluded that ozonation consistently increased

Table 2 | Chloral hydrate levels in Canadian drinking water: 1993 (after Williams *et al*. 1997)

		Winter			Summer		
Treatment	**Site**	**Mean ($\mu g\ l^{-1}$)**	**Median ($\mu g\ l^{-1}$)**	**Range ($\mu g\ l^{-1}$)**	**Mean ($\mu g\ l^{-1}$)**	**Median ($\mu g\ l^{-1}$)**	**Range ($\mu g\ l^{-1}$)**
Chlorine–chlorine	Plant	2.2	1.4	< 0.1–13.8	4.3	2.9	< 0.1–14.7
	System	3.8	2.5	< 0.1–22.5	6.1	4.8	< 0.1–18.9
Chlorine–chloramine	Plant	1.2	0.8	< 0.1–3.2	3.9	3.3	0.3–15.1
	System	1.2	0.8	0.2–3.2	3.6	2.9	0.3–13.6
Ozone–chloramine	Plant	1.5	1.0	0.2–2.9	8.1	10.4	0.7–14.5
	System	2.2	1.9	0.2–5.8	8.4	5.6	0.2–20.1

Temperature median 1°C in winter and 21°C in summer; plant samples taken after final disinfection; system samples taken from the approximate mid-point of the distribution system.

chloral hydrate precursors which could be removed by used GAC filters. A later study showed these GAC filters to be bioactive and this indicates that the precursors of chloral hydrate might be biodegradable and could be effectively removed by GAC and biodegradation.

In the 1-year study of DBPs in three treatment works in Canada (Williams *et al*. 1996; LeBel *et al*. 1997), low levels of chloral hydrate were found in two treatment plants, but significantly higher levels were found in water samples from the plant which used ozone-chlorine treatment (maximum of 23.4 $\mu g\ l^{-1}$ compared with 6.6 and 10.5 $\mu g\ l^{-1}$). There were lower levels of chloral hydrate during the cold water months than during the warm water months. The levels of chloral hydrate were not constant throughout the distribution system, with maximum levels seldom occurring at the end of the distribution system. With chorine-chloramine treatment the spatial variation was considerably more pronounced, with levels increasing in the distribution system to a maximum at the mid-point of the system and the lowest at the end. With ozone-chlorine treatment the chloral hydrate levels were considerably higher than at the other two plants. It was noteworthy that lower chloral hydrate levels were observed in February when the ozone was replaced with chlorine which suggests again that ozone treatment enhances chloral hydrate formation. During July to September when pre-chlorination was added to the treatment process, the chloral hydrate levels maximised at the treatment works and decreased with increasing distance from the plant. This suggests that the reaction that produces chloral hydrate was accelerated under the conditions of ozonation in combination with pre-chlorination and warm water temperatures.

In the related study carried reported by Williams *et al*. (1997) halogenated disinfection by-products were determined in Canadian drinking water supplies where chlorine was used at some stage in the treatment process. The study focused on 53 major municipalities across Canada. The disinfectants used at the plants were a mixture of pre-chlorination followed by post chlorination, pre-chlorination followed by chloramination and pre-ozonation followed by chlorination. The levels of chloral hydrate found in the waters are presented in Table 2.

Examination of the data shows that the relative positions of chlorine-chlorine and ozone-chloramine swap over in the summer months although levels in the chlorine-chloramine plants are always the lowest. This may be due to the non-concurrent addition of chloramines and the enhancement of ozonated chloral hydrate precursors in the summer months. Summer levels are significantly higher than winter levels and system levels are always higher than plant levels for the chlorine-chlorine systems. System levels are less than plant levels for chlorine-chloramine levels during the summer.

Table 3 | Chloral hydrate levels (3 day test) at various doses of chlorine dioxide

Chlorine dioxide dose (mg l^{-1})	Raw (μg l^{-1})	No ClO_2-post Cl_2 (μg l^{-1})	Pre-ClO_2-post Cl_2 (μg l^{-1})
2.0	22.8	16.1	14.1
3.0	16.1	11.3	8.2
4.0	23.5	Error	11.7
5.0	25.3	13.8	9.6

The objective of the work undertaken by Singer *et al*. (1994) was to evaluate the impact of ozonation on the formation of halogenated DBPs from subsequent chlorination and chloramination under various water quality conditions. The authors concluded that chloral hydrate formation on chlorination was adversely and dramatically affected by pre-ozonation in all cases (up to 60 μg l^{-1}).

Murphy *et al*. in 1993 studied the effect of pre-ozonation and biofiltration on DBPs. They showed that a significant percentage of dissolved organic carbon (DOC) is removed by these processes and aldehydes are removed during biotreatment. The data showed that the formation potentials of THMs, HAAs and chloral hydrate were reduced by as much as 70–80% using ozonation/biofiltration.

The effect of chlorine dioxide

Griese (1991) set up two pilot plants in parallel to compare the DBPs produced when chlorine dioxide was used as a pre-disinfectant with the DBPs produced when no pre-disinfectant was used. Both pilot plants used chlorine as a post disinfectant and had an intermediate filtration system.

During the study the chlorine dioxide pre-dose was gradually increased from 2 to 5 mg l^{-1}. The chloral hydrate levels produced by the two pilot plants are shown in Table 3. The raw figures in the table indicate the chloral hydrate formation potential.

There is a tendency for the chloral hydrate levels to fall as the chlorine dioxide pre-dose is increased. The levels of chloral hydrate with no pre-disinfection were higher than when a chlorine dioxide pre-dose was used.

Removal of chloral hydrate precursors by enhanced coagulation

Dixon and Lee (1991) evaluated the effectiveness of optimum coagulation/delayed chlorination for DBP control at a test plant compared with an average of nine other typical plants that practised pre-chlorination. The test plant had a coagulation at a pH of 5.7 compared with a normal pH of 7.2. These conditions led to a total organic carbon (TOC) removal of 55% compared with 20% in the plants that practised conventional coagulation. Levels of most DBPs, including chloral hydrate, were found to be higher in the plants that used pre-chlorination compared with the test plant. However it was found that the formation of HAAs increased and the authors noted that treatment optimised to control certain DBPs enhances the formation of other undesirable DBPs.

Miltner *et al*. in 1994 compared the effect of enhanced coagulation and conventional coagulation on the removal of DBPs including chloral hydrate. Raw water samples from three different works were coagulated in jar tests, settled, dosed with chlorine and then stored for 24 hours before measuring the chloral hydrate levels. The results are presented in Table 4.

For comparison the raw water samples were dosed with chlorine and the chloral hydrate levels were measured so that the percentage removal of the precursors could be calculated.

The results show that enhanced coagulation does remove a higher percentage of chloral hydrate than conventional coagulation. In these tests conventional treatment was defined as the coagulant dose that resulted in settled turbidities below 1 NTU. Optimum treatment was defined as the lowest coagulant dose that resulted in best removal of TOC. For example one water used 45 mg l^{-1} alum in the conventional treatment compared with 75 mg l^{-1} in the optimum treatment.

Table 4 | The percentage removal of chloral hydrate precursors under conventional and optimum coagulation conditions

		Alum		Iron	
Name of treatment works	**Raw conc. ($\mu g\ l^{-1}$)**	**Conventional (%)**	**Optimum (%)**	**Conventional (%)**	**Optimum (%)**
East Fork Lake	35.6	59	72		
Great Miami River	20.2	30	66	41	73
Miami Whitewater Lake Water	24.5	22	56	51	58

In a similar study undertaken by Smith *et al*. in 1994, the authors investigated the ability of enhanced coagulation to remove organic precursors of halogenated disinfection by-products. The United States Environmental Protection Agency (USEPA) definition of enhanced coagulation is the coagulant dose at which an increase of 10 mg l^{-1} of coagulant does not reduce the TOC more than 0.3 mg l^{-1}. The baseline coagulation conditions in this test were the conditions used at the works where the water was obtained. It was found that CHFP levels were in the range 5–30 $\mu g\ l^{-1}$ for most raw and treated waters, with the exception of the higher TOC waters which had raw water CHFP values>50 $\mu g\ l^{-1}$. For the higher TOC waters, coagulation removed a substantial amount of the CHFP. The effect was less noticeable for the lower TOC waters. Enhanced coagulation removed more CHFP than baseline conditions for one water but had little effect on others, and caused an increase in CHFP compared with the baseline for others. Thus enhanced coagulation did not appear to be a viable treatment strategy for minimising chloral hydrate, but the enhanced conditions in the study carried out by Smith *et al*. used lower doses of coagulant at a different pH from the baseline. These different interpretations of enhanced coagulation lead to different and somewhat confusing results.

In general up to 60–80% of the formation potential for THMs and other chlorination DBPs can be removed by alum coagulation (Stevens *et al*. 1989). Stevens *et al*. carried out tests that showed that 6-day formation potentials at pH 7 produced about 25 $\mu g\ l^{-1}$ of chloral hydrate in the raw water and 8 $\mu g\ l^{-1}$ for alum treated water and the formation of chloral hydrate was time and pH dependent. Although chloral hydrate forms rapidly at basic pH values, the rate of hydrolysis at basic pH values exceeds the rate of formation. The authors concluded that the most important chemical variable in chlorination DBP formation is pH. Yields of nearly all halogenated organics including chloral hydrate, can usually be maximised or minimised by controlling the pH at which the various reactions occur.

Currently the USEPA recommends enhanced coagulation to minimise the formation of THMs and the US does not have a standard for chloral hydrate. This decision was based on the opinion of the USEPA on the fact that the maximum contaminant levels (MCLs) for total trihalomethanes (TTHMs) and HAAs and the treatment technique (i.e. enhanced coagulation/softening) will control for chloral hydrate as well as for other disinfection by-products. The above studies show that the optimum conditions for the minimisation of THMs are different in some aspects from the optimum conditions for the minimisation of chloral hydrate. However the removal of organic precursors is common to both. Careful consideration of the formation of all DBPs should be made in developing a strategy for the minimisation of chloral hydrate.

Removal of chloral hydrate precursors by membrane filtration

Siddiqui *et al*. (2000) evaluated a range of nanofiltration modules to determine the rejection of DBP precursors

from low turbidity surface waters. They established that dissolved organic carbon, trihalomethane formation potential, haloacetic acid formation potential and chloral hydrate formation potential rejections averaged 90, 97, 94 and 86%, respectively. Microfiltration provided virtually no DBP precursor removal.

Removal of chloral hydrate by GAC

In an extensive study carried out by Hartman *et al*. in 1991, tests on the effect of GAC on the removal of DBP precursors were divided into two phases: in Phase 1 the point of chlorine application was upstream of the GAC and in Phase 2 it was downstream. Thus in Phase 1 the GAC was presented with both DBPs and DBP precursors. Tests in Phase 1 showed that THM precursors were removed effectively at the start of the runs and this effectiveness gradually decreased with time until a steady state plateau was reached. Results with chloral hydrate in Phase 2 showed that the use of GAC did reduce the formation of chloral hydrate through precursor removal and that longer contact time with GAC resulted in additional precursor removal. The GAC empty bed contact time (EBCT) had an effect on the chloral hydrate formation potential, with higher EBCT (21 min) giving lower levels of CHFP.

In the study carried out by Dixon and Lee (1991), the data indicated that the removal of chloral hydrate by GAC is significantly influenced by EBCT. Virgin GAC with an EBCT of 8.7 minutes achieved only 56% removal of CHFP. In contrast a 2.75-year-old GAC with an EBCT of 12.5 minutes achieved a removal of 75% of CHFP. The authors concluded that given sufficient contact time, GAC offers an effective long-term option for control of chloral hydrate.

Removal of chloral hydrate precursors by other methods

Krasner *et al*. (1993) presented the results of pilot tests with biologically active filters for removal of aldehydes. In this paper Krasner *et al*. state that the aldehydes produced with ozonation may be regulated at a later date and that pre-ozonation can increase the formation of certain halogenated DBPs, for example chloral hydrate, upon oxidation. Krasner *et al*. report a study that shows that acetaldehyde can undergo chlorination substitution to yield chloral hydrate. Although acetaldehyde was not specifically studied by Krasner *et al*., formaldehyde was and was found to be removed at 50 and 80% across biologically active GAC beds at varying EBCTs of up to 4.2 minutes.

In a related article, biologically active GAC filters were shown to be an effective means of aldehyde removal (Weinberg *et al*. 1993) in a survey of 11 full-scale and pilot-plant treatment works. Weinberg *et al*. concluded that aldehydes were formed in all the water treatment plants that were included in his study, the majority of which included an ozonation stage. The plant surveys indicated that the aldehydes were removed by filters that possess an active biomass and that filter rate and history of the filters may have an effect on the removal.

CONCLUSIONS

Two possible formation mechanisms for chloral hydrate are the reaction between amino acids and chlorine and the reaction between aldehydes (formed when natural organic material is ozonated) and chlorine. Chloral hydrate can decay in alkaline conditions to give chloroform and in oxidising conditions to give trichloroacetic acid. Thus chloral hydrate can be viewed as an intermediate in the formation of both THMs and HAAs. However the main pathway for the formation of chloroform is different from the pathway for the formation of chloral hydrate and different precursors are involved. Experiments have shown that the formation of trichloroacetic acid from chloral hydrate is slow and it is not the principal mechanism for the formation of this HAA.

The decay of chloral hydrate to give chloroform is enhanced at alkaline pH with the rate of decay exceeding the rate of formation. Alkaline conditions will minimise the final levels of chloral hydrate but will promote the formation of THMs; some studies have shown that the optimum conditions for the minimisation of THMs are

different in other aspects from the optimum conditions for the minimisation of chloral hydrate. However the removal of organic precursors is common to both. Careful consideration of the formation and minimisation of all DBPs should be made in developing a strategy for the minimisation of chloral hydrate. The higher pH levels necessary to promote the decay of chloral hydrate is in conflict with the recommended upper pH limit of 8 for effective disinfection with chlorine.

The use of chloramine as a disinfectant reduces the formation of chloral hydrate compared with chlorine. The introduction of pre-ozonation before chlorine increases chloral hydrate levels or chloral hydrate formation potential. Many studies have shown that ozonation consistently increases chloral hydrate precursors.

Chloral hydrate levels can increase when ozone is introduced before chloramination too if the chloramination is not concurrent. However ozonation followed by chloramination is more effective in reducing chloral hydrate levels than ozone followed by chlorination. Levels of chloral hydrate with ozone followed by chloramination are lower than with chlorination alone. Ozone-chloramine can result in low levels of chloral hydrate provided that the chlorine addition is well managed and there is little free chlorine contact time. Free chlorine is necessary for significant levels of chloral hydrate to be formed. The use of chlorine dioxide as a pre-disinfectant can also decrease the levels of chloral hydrate. Chloral hydrate levels fall as the chlorine dioxide pre-dose is increased.

Biologically active GAC filters can remove precursors of chloral hydrate. The removal of precursors by GAC is highly dependent on the EBCT. Several studies have shown that it is possible to remove the aldehyde precursors to chloral hydrate (produced on the ozonation of water) by using a biologically active filter.

Enhanced coagulation can reduce chloral hydrate compared with conventional coagulation, although the definition of enhanced coagulation must be carefully interpreted. Misinterpretations of this term have led to confusing results in the literature. Enhanced coagulation involves optimising the coagulant dose, coagulation pH, mixing time and energy and mixing conditions. However high doses of alum at a reduced pH do have the potential to reduce chloral hydrate levels in the finished water. Adapting the existing coagulation processes to provide enhanced coagulation has the potential to reduce all DBPs without the need for any extra treatment processes. It has the potential to be the most efficient, convenient and cost effective method of reducing DBP levels, including chloral hydrate, in the treated water.

REFERENCES

Dixon, K. L. & Lee, R. G. 1991 Disinfection by-products control: A survey of American system treatment plants. *Annual Conference Proceedings, American Water Works Association, Water Research for the New Decade*. Philadelphia, Pennsylvania, 23–27 June, pp. 265–287.

Griese, M. H. 1991 Pilot plant optimization of the chlorine dioxide treatment process for disinfection by-product reduction. *Annual Conference Proceedings, American Water Works Association, Water Research for the New Decade*. Philadelphia, Pennsylvania, 23–27 June, pp. 97–128.

Hartman, D. J., DeMarco, J., Metz, D. H., Himmelstein, K. W. & Miller, R. 1991 Disinfection by-products precursor removal by GAC and alum coagulation. *Annual Conference Proceedings, American Water Works Association, Water Research for the New Decade*. Philadelphia, Pennsylvania, 23–27 June, pp. 193–252.

Jacangelo, J. G., Patania, N. L., Reagan, K. M., Aieta, E. M., Krasner, S. K. & McGuire, M. J. 1989 Ozonation: Assessing its role in the formation and control of disinfection by-products. *J. Am. Wat. Wks Assoc.* **81**(8), 74–84.

Keith, L. H., Garrrison, A. W., Allen, F. R., Carter, M. H., Floyd, T. L., Pope, J. D. & Thruston, Jr, A. D. 1976 Identification of organic compounds in drinking water from thirteen US cities. In: Keith, L. H. (ed.) *Identification and Analysis of Organic Pollutants in Water*. Ann Arbor Science Publishers, Ann Arbor, Michigan, pp. 329–373.

Koch, B. & Krasner, S. W. 1989 Occurrence of disinfection by-products in a distribution system. *Annual Conference Proceedings, American Water Works Association, Dedicated to Excellence*. Los Angeles, California, 18–22 June, pp. 1203–1230.

Krasner, S. W., Sclimenti, M. J. & Coffey, B. M. 1993 Testing of biologically active filters for removing aldehydes formed during ozonation. *J. Am. Wat. Wks Assoc.* **85**(5), 62–71.

Le Cloirec, C. & Martin, G. 1984 Evolution of amino acids in water treatment plants and the effect of chlorination on amino acids. In: Jolley, R. L., Bull, R. J., Davies, W. P., Katz, S., Roberts, Jr, M. H. & Jacobs, V. A. (eds) *Water Chlorination: Chemistry, Environmental Impact and Health Effects*, Vol. 5. Lewis Publishers, Chelsea, Michigan, Chapter 65.

Lebel, G. L., Benoit, F. M. & Williams, D. T. 1997 A one year survey of halogenated disinfection products in the distribution system

of treatment plants using three different disinfection processes. *Chemosphere* **34**(11), 2301–2317.

Luknitskii, F. I. 1975 The chemistry of chloral. *Chem. Rev.* **75**(3), 259–289.

Miller, J. W. & Uden, P. C. 1983 Characterization of nonvolatile aqueous chlorination products of humic substances. *Environ. Sci. Technol.,* **17**(3), 150–157.

Miltner, R. J., Nolan, S. A., Dryfuse, M. J. & Summers, R. S. 1994 The control of DBPs by enhanced coagulation. *Water Quality: Proceedings American Water Works Association Annual Conference*, 1994, New York, pp. 721–735.

Murphy, B., Amy, G., Siddiqui, M. & Adams, J. 1993 Ozone-induced conversion of DBP precursors (DOC) to biodegradable by-products (BDOC). *Annual Conference Proceedings, American Water Works Association Research,* San Antonio, Texas, 6–10 June, pp. 389–416.

Plump, R. E. 1948 Preparation of trichloro-aliphatic carboxylic acids. *Chem. Abstr.* **42**, 7320e.

Reckhow, D. A. & Singer, P. C. 1984 Mechanisms of organic halide formation during fulvic acid chlorination and implications with respect to preozonation. In: Jolley, R. L., Bull, R. J., Davies, W. P., Katz, S., Roberts, Jr, M. H. & Jacobs, V. A. (eds) *Water Chlorination: Chemistry, Environmental Impact and Health Effects*, Vol. 5. Lewis Publishers, Chelsea, Michigan, Chapter 96.

Siddiqui, M. Amy, G., Ryan, J. & Odem, W. 2000 Membranes for the control of natural organic matter from surface waters. *Wat. Res.* **34**(13), 3355–3370.

Singer, P. C., Harrington, G. W., Cowman, G. A., Smith, M. E., Schechter, D. S. & Harrington, L. J. 1994 Impact of ozonation on the formation of chlorination and chloramination by-products. *Water Research: Proceedings American Water Works Association Annual Conference*, 1994. New York, pp. 921–940.

Smith, L. A., Dietrich, A. M., Mann, P. D., Hargette, P. H., Knocke, W. R., Hoehn, R. C. & Randtke, S. J. 1994 Effects of enhanced coagulation on halogenated disinfection byproduct formation potentials. *Water Research: Proceedings American Water Works Association Annual Conference*, 1994, New York, pp. 635–652.

Stevens, A. A., Moore, L. A. & Miltner, R. J. 1989 Formation and control of non-trihalomethane by-products. Formation and control of non-trihalomethane disinfection by-products. *J. Am. Wat. Wks Assoc.* **81**(8), 54–60.

Trehy, M. L., Yost, R. A. & Miles, C. J. 1986 Chlorination byproducts of amino acids in natural waters. *Environ. Sci. Technol.* **20**(11), 1117–1122.

Trehy, M. L., Yost, R. A. & Miles, C. J. 1987 Amino acids as potential precursors for halogenated by-products formed on chlorination of natural waters. Paper presented at the *194th ACS National Meeting, Division of Environmental Chemistry, American Chemical Society, Washington DC*, Vol. 27(2), pp. 582–584.

Trehy, M. L., Yost, R. A. & Miles, C. J. 1989 Amino acids as model compounds for halogenated by-products formed on chlorination of natural waters. In: *Biohazards of Drinking Water Treatment*. Lewis Publishers, Chelsea, Michigan, pp. 133–140.

Ueno, H., Nakamuro, K., Moto, T. & Sayato, Y. 1995 Disinfection by-products in the chlorination of organic nitrogen compounds: possible pathways for the formation of disinfection by-products. *Water Supply* **13**(3/4), 171–176.

Weinberg, H. S., Glaze, W. H., Krasner, S. W. & Sclimenti, M. J. 1993 Formation and removal of aldehydes in plant that use ozonation. *J. Am. Wat. Wks Assoc.* **85**(5), 72–85.

Williams, D. T., LeBel, G. L. & Benoit, F. M. 1996 *A One-Year Survey of Halogenated Disinfection By-Products in the Distribution System of Treatment Plants using Three Different Disinfection Processes*. Environmental Health Directorate Report, Health Canada, 96-EHD-206.

Williams, D. T., LeBel, G. L. & Benoit, F. M. 1997 Disinfection by-products in Canadian drinking water. *Chemosphere* **34**(2), 299–316.

Xie, Y. & Reckhow, D. A. 1992 Formation and control of trihaloacetaldehyde in drinking water. *Proceedings Water Quality Technology Conference Part II, Toronto, Ontario, Canada, 15–19 November*, pp. 1499–1511.

First received 10 March 2003; accepted in revised form 2 July 2004