The Placing of the Disinfection Stage in a Reclamation Plant to Reduce Haloform Formation*

O.O. HART
[WATER RESEARCH COMMISSION, P.O. BOX 824, PRETORIA, 0001]

Abstract

Chlorination of any water containing organic matter leads to the formation of various volatile halogenated hydrocarbons. The chlorination of reclaimed water from a well oxidized secondary sewage effluent results in lower concentrations of volatile halogenated hydrocarbons than from those derived from polluted surface waters due to the lower precursor content of reclaimed water. Various process configurations of a water reclamation plant were studied to optimize the positioning of the primary disinfection stage in the plant that would ultimately produce a minimum haloform concentration in the water distribution system. The pros and cons of ozone and chlorine as disinfectant with respect to haloform formation were also investigated. This study shows that precursor removal by activated carbon is only beneficial when at least 30 min hydraulic contact time is provided. The same applies for the removal of volatile halogenated hydrocarbons or the intermediate oxidation products of ozone and chlorine. The intermediate products formed by breakpoint chlorination with 45 min reaction time are more easily removed by activated carbon than those formed by 10 min ozone contacting. The process configuration for this particular reclamation plant that would ultimately produce the least volatile halogenated hydrocarbons in the distribution system, would be breakpoint chlorination followed by two-stage active carbon adsorption. It has also been established that a direct relationship exists between the bromide content of the water and the total yield of volatile halogenated hydrocarbons. Given a long enough reaction time all of the bromide present in the water will apparently be transformed to one or more species of volatile brominated hydrocarbon.

Introduction

The primary goal of any water purveyor is to provide a wholesome drinking water to the consumer. Disinfection to inactivate pathogenic micro-organisms is considered to be the most important unit operation in the water purification regime to achieve this goal. Throughout the world chlorine has been accepted as one of the most efficient and economic disinfectants of water supplies. For many decades no harmful effect on the public's health has been ascribed to the use of chlorine as disinfectant, except for the occasional taste problem derived from the chlorination of phenolic substances present in the raw water supply.

The situation changed drastically when improved analytical techniques for the detection of organic substances showed that the chlorination of water supplies may produce halogenated compounds that could be carcinogenic (National Cancer Institute, 1975, 1976). The discoveries by Rook (1974) and by Bellar, Lichtenburg and Kroner (1974) that the chlori-

---

*Paper presented at Symposium on "Disinfection of Water" organized by the National Institute for Water Research and the Institute of Water Pollution Control, CSIR Conference Centre, Pretoria, 16 November 1978.

nation of water supplies containing organic matter produces chloroform and other volatile organohalogens*, as well as a 1974 study of the New Orleans area water supply (U.S. Environmental Protection Agency, 1974), focused attention on the occurrence of these compounds in drinking water. Of these compounds that have been identified in the drinking waters of the United States, approximately 38% or 111 of 289 compounds were halogenated, (U.S. Environmental Protection Agency, 1976).

One volatile compound, chloroform, was present in the 100 $\mu g/dm^3$ range or less. In the Federal Republic of Germany, the highest chloroform concentration observed in drinking water, i.e. 52 $\mu g/dm^3$, was found within a limited distribution area in one city, (Sonneborn and Bohn, 1978). A survey of 27 different cities in Germany revealed that only chloroform was present above 1 $\mu g/dm^3$, while the concentration of the remaining haloforms fell within the ng/dm^3-range. This could be attributed to a philosophy in Germany (Kühn, Sontheimer, Steiglitz, Maier and Kurtz, 1978) that a groundwater source, that produced chemically and bacteriologically unobjectionable water due to the surrounding area of the wells and soil conditions, was always preferred to a source that required treatment and chlorination. By means of sandbank filtration, artificial percolation, and activated carbon and ozone treatment, it is ensured that the concentration of total organic material in the water is always below 2 mg/dm^3 total organic carbon (TOC). Tap water in Pretoria, South Africa, revealed a total VHH concentration of 65 $\mu g/dm^3$ with a chloroform content of 10,5 mg/dm^3. (Hart, 1978).

Concern about the health risks associated with the presence of VHH in drinking water supplies, led to extensive research to find ways of minimizing their concentrations in community supplies. Most efforts have been directed towards, either substituting ozone or chlorine dioxide for chlorine as the disinfectant, or changing points of chlorine application within the conventional water treatment plant (Symons, 1976; Harms and Looyenga, 1977; Young and Singer, 1977; Schwartz and Lancaster, 1977). Several investigators have demonstrated the effectiveness of delaying chlorination until after VHH precursors have been removed by conventional water treatment processes such as coagulation, flocculation and sedimentation (Harms and Looyenga, 1977; Young and Singer, 1977; Babcock and Singer, 1977). The use of granular activated carbon, either to remove precursors (Snoeyink, McCreary and Murin, 1977), or to remove VHH from drinking water (Weber, Pirbazari, Herbert and Thompson, 1977) has also been investigated.

When using secondary sewage effluent to reclaim potable water, it is obvious that a wide variety of organic precursors could be available for the formation of VHH. On the other hand, due to the variety of unit processes employed in water reclamation, the possibility exists to exploit various process configurations to produce a final water that would ultimately contain a minimum VHH concentration. Basic approaches to reduce drinking water VHH concentrations are: reducing precursor compounds; removing VHH after formation; and changing disinfectant. Two stage active carbon adsorption is a prerequisite for water reclamation, with the result that primary active carbon adsorption could be utilized to reduce precursors while secondary adsorption could be utilized to remove VHH after formation. Alternatively, the disinfection stage could be placed ahead of the two active carbon adsorption stages. In this study both possibilities were investigated. The third approach was also pursued *viz.*, by using either chlorine or ozone as disinfectant.

Formation of Volatile Organohalogens

It has been established that waters containing natural colour-producing organic materials yield volatile organohalogens upon chlorination (Rook, 1976) and that aqueous solutions of commercial humic acid behave similarly (Stevens, Slocum, Seeger and Robeck, 1978). Humic materials are complex polymers, which range in molecular weight from several hundred to ten or twenty thousand (Christman and Minear, 1971; Schnitzer and Kahn, 1972), and are composed of a variety of sub-units such as aromatic and alicyclic moeities containing alcoholic, carbonylic, carboxylic and phenolic functional groups (Steelink, 1963; Christman and Minear, 1971; Schnitzer and Kahn, 1972; Stevenson and Goh, 1972; Wershaw and Goldberg, 1972). Humus is normally fractionated into alkali-soluble and alkali-insoluble fractions, (Oden, 1919; Du Toit and Page, 1930). The insoluble fraction is referred to as humus coal or humin. The alkali-soluble fraction is categorized into three classes: (1) Fulvic acid, (2) Humic acid, and (3) Hymatomelanic acid. Babcock and Singer (1977) evaluated the chloroform potential of humic and fulvic acids and found that humic acid reacts with chlorine in a much more active way than fulvic acid, consuming 75% more chlorine and producing 117% more chloroform per unit of TOC and 23% more chloroform per unit of chlorine consumed. It seems, therefore, that humic acids are of greater importance than fulvic acids as far as precursors for the formation of VHH are concerned.

The structure of humic acid is exceedingly complex but for the purpose of this discussion a simplified model of the humus molecule as suggested by Trussel (1978) is shown in Figure 1. The humus molecule can be thought of as a huge amorphous mass of polyhetero condensate with certain functional groups protruding from its surface which react with chlorine to produce VHH. The course of the classical haloform reaction by

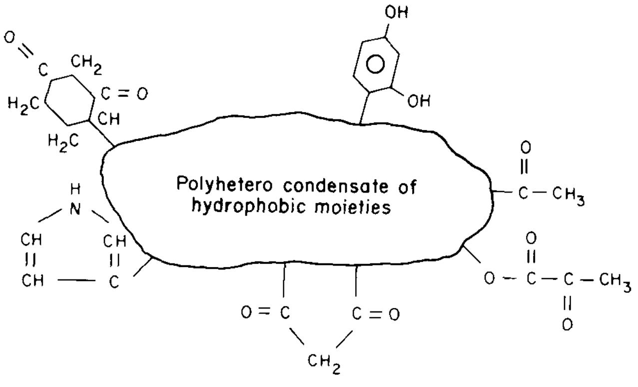

Fıgure 1
Model humic compound

---

*Numerous volatile and non-volatile organohalogen compounds are formed when water containing organic material is chlorinated. The volatile organohalogens are normally quantified by gas chromatographic, electron capture responsive halogenated hydrocarbons. For the purpose of this study six of the volatile halogenated hydrocarbons (VHH) were identified in relation to retention time data. They are: carbon tetrachloride (CCl_4); chloroform ($CHCl_3$); ethylene tetrachloride (C_2Cl_4); bromodichloromethane ($CHBrCl_2$); dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$).

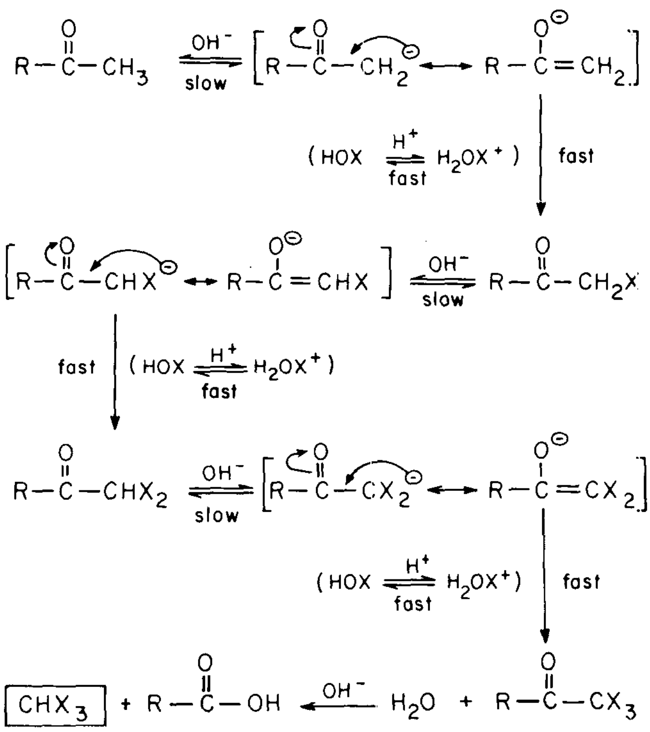

Figure 2
The reaction pathway of the haloform reaction

which VHH are formed is outlined in Figure 2 (Morris and Baum, 1978). Essentially the reaction consists of a base-catalysed series of alternate hydrolyses and halogenation steps. The rate of the overall reaction under usual laboratory conditions is determined by the first step namely the rate of ionization of the methyl ketone.

With the exception of the ketone groups, the functional groups illustrated in Figure 1 are generally those which more rapidly execute that first ionization step, especially the meta-hydroxy aromatic rings (Rook, 1977).

In view of the ubiquitous occurrence of organohalogens in chlorinated drinking waters all over the world, it is plausible that waterborne humic materials are a primary reaction precursor. It has been reported that humic substances comprise 50% of the soluble organic matter in sewage effluents (Rebhun and Manka, 1971; Manka, Rebhun, Mandelbaum and Bortinger, 1974), and 90% soluble organic matter in surface waters (Junk and Stanley, 1975). The difference in humic substance concentration between sewage effluents and surface waters could, therefore be the reason for the lower total VHH production between chlorinated reclaimed water and surface water (Hart, 1978). Considering the possible health implications of haloforms in drinking waters, it is incumbent on the scientist to develop and refine treatment technologies which will minimize the formation of such compounds during reclamation or conventional water treatment, as well as the removal of such compounds once formed.

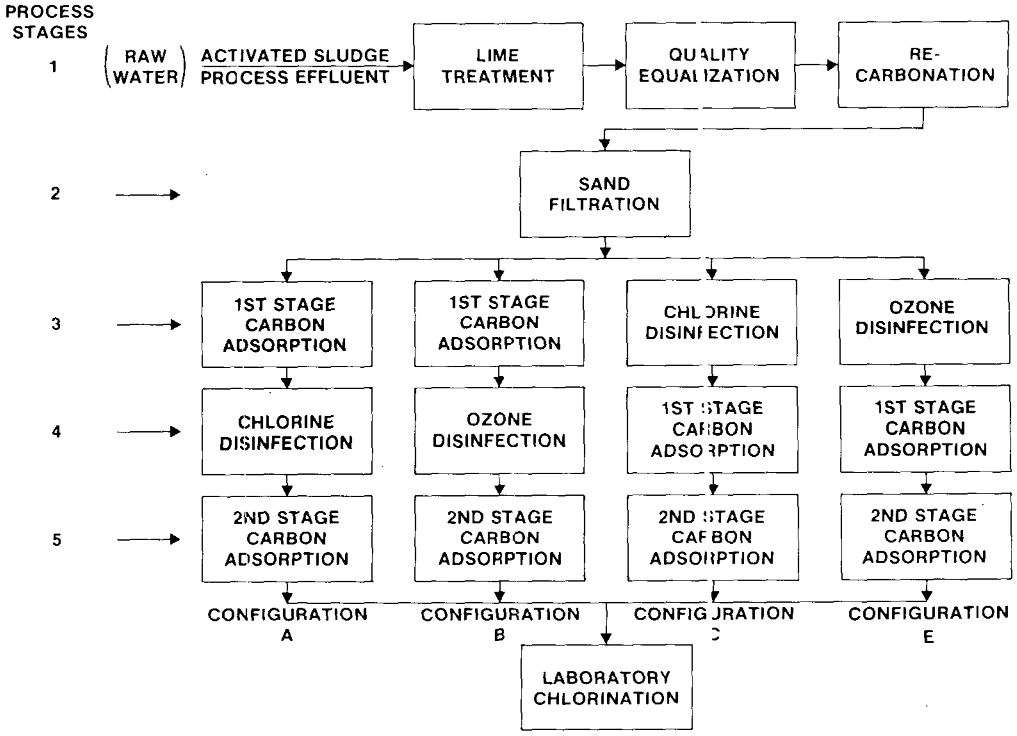

Figure 3
Process configurations studied

Experimental

Four different process configurations were investigated at the 4 500 m^3/d Stander water reclamation plant (SWRP), Pretoria. The process configurations studied are shown in Figure 3. The pH after lime treatment was kept at 11,2 ± 0,1 while the pH at the recarbonation stage was adjusted to 7,0 ± 0,3 with carbon dioxide.

For each configuration the plant was operated for one week to reach equilibrium after process modifications. On the 8th day a 24 h representative sample was obtained by collecting a constant flow sample stream (approximately 0,1 dm^3/min) in a large container. The flow throughout the plant was kept constant by using constant flow regulators between all the process stages. Retention times in the various unit processes were considered when the sample stream was turned on to obtain an approximate plug flow representative sample. Samples of 20 dm^3 were collected and filtered through a sterile 0,45 μm millipore membrane into sterile containers to prevent suspended matter exerting a chlorine or ozone demand. The samples were then stored at 5°C.

The chlorine demand of the second-stage active carbon adsorption effluent (which was 1,4 mg/dm^3 Cl_2 for all four configurations) was satisfied by adding sufficient chlorine to ensure a free chlorine level of 1,0 ± 0,1 mg/dm^3 after 2,5 min contact time. The concentrated chlorine solution contained approximately 1 250 mg Cl_2/dm^3 and was prepared by bubbling chlorine gas through double glass distilled water.

Samples of 5 dm^3 were then chlorinated by addition of the appropriate volume of concentrated chlorine solution and 300 cm^3 bottles were filled to the brim with the solution. The bottles were sealed with aluminium-lined caps. The chlorination reaction was allowed to continue at room temperature for various time intervals, after which the reactions were stopped by the addition of a few crystals of ascorbic acid. The bottles were again sealed and stored at 5°C before analysis. The reaction times were 2,5, 5, 10, 25, 50, 100, 250, 500, 1 000, 2 500, 5 000 and 10 000 min.

Volatile halogenated hydrocarbon compounds were extracted as described by Van Rensburg, Van Huysteen and Hassett (1978). Quantitative analyses were performed on a Hewlett Packard 5710A gas chromatograph equipped with a Hewlett Packard 5671A autosampler. A Ni-63 electron capture detector with a 3 m x 6,3 o.d. x 2,5 mm i.d. glass column packed with 15% XF1150 on chromosorb W-AW (800 — 100 mesh) was used. The column and inlet temperature was 90°C, the detector temperature 250°C, the carrier gas an argon/methane mixture (95% : 5%) and the flow rate 20 cm^3/min.

The autosampler was controlled by a Hewlett Packard 3352B data system and programmed to wash the syringe 10 times with solvent, then to rinse the syringe with the sample a further 10 times and finally to inject a 5 mm^3 aliquot on to the column. Compounds were identified in relation to retention time data and quantitative results obtained from peak areas calibrated by extraction of a standard water solution.

The SWRP utilized four carbon columns forming two parallel trains, each containing two stages in series. The hydraulic retention time in each stage was 15 min, giving a total of 30 min. The beds were the fixed-bed, downflow type. The carbon in all four columns were regenerated before the commencement of the experiment. The plant was operated continuously for approximately three months (7 September — 30 November, 1977) during which period the following configurations were studied:

Configuration	Unit processes	Period (1977)
A7	R—SF—C1—Cl_2—C2—F	15/9 to 21/9
B7	R—SF—C1—O_3—C2—F	23/9 to 29/9
C7	R—SF—Cl_2—C1—C2—F	17/10 to 23/10
E7	R—SF—O_3—C1—C2—F	21/11 to 23/11

R = raw water (activated sludge effluent)
SF = sand filtration effluent
C1 = 1st stage active carbon effluent
C2 = 2nd stage active carbon effluent
Cl_2 = breakpoint chlorination effluent
O_3 = ozone reactor effluent
F = plant effluent after final chlorination

The following notation is used to depict a specific sample:

B7C1 = the effluent from the 1st stage active carbon column during the B7 configuration run.

Results and Discussion

Effect of Precursor Removal

When considering the removal of organics from water it is implicit that adsorption on activated carbon be considered, that is for the removal of precursor compounds as well as removal of halogenated compounds, either formed or already present in the raw water. The two stage active carbon adsorption system as applied at the SWRP is ideally suited for the investigation of both these objectives. There is a substantial amount of information available regarding the efficiency of active carbon for removing taste and odour compounds from drinking water, as well as for a variety of organic substances from industrial and municipal wastewaters (Weber, 1972; 1974a; 1974b; Weber and Ying, 1977). The removal efficiency however, of trace amounts of low molecular weight haloforms in competition with high concentrations of high molecular weight humic substances might be extremely low. To evaluate the effectiveness of activated carbon for removal of haloforms and typical wastewater compounds, Weber, *et al.*, (1977) determined the adsorption equilibrium and rate characteristics for the following haloforms: chloroform, bromodichloromethane, carbon tetrachloride, and bromoform; as well as for the following organic compounds; phenol, p-bromophenol, p-toluene sulfonate and dodecyl benzene sulfonate. It was concluded that the adsorption capacities for the low molecular weight VHH at the concentration levels of interest are significantly different from those of higher-molecular-weight compounds. The chemical character of these types of substances, coupled with their higher concentrations, lead to different adsorption characteristics than those of VHH which are important in water treatment.

The question is, while active carbon can remove low-molecular-weight VHH, what effect would the presence of other organic constituents, especially high molecular weight humic substances, have on VHH removal efficiency.

To determine the effect of precursor removal under operating conditions at the SWRP, the following process configurations together with the ensuing laboratory chlorination experiments were considered: configuration A7 versus C7, i.e. breakpoint chlorination with and without precursor removal and configuration B7 versus E7, i.e. ozone disinfection with and without precursor removal. With respect to VHH removal by active carbon, the following is relevant: within the treatment plant an increase in all the VHH is observed after the 1st stage active carbon adsorption (Table 1 A7Cl, B7Cl), i.e. before chlorination or ozonation. The VHH concentrations are, however, very low, of the order 0,2 μmol carbon for the total VHH. Ozonation has practically no effect on VHH occurrence within the plant, whereas breakpoint chlorination ($C7Cl_2$) increases the total VHH by more than an order of magnitude, whereupon the first stage active carbon reduces the total μmol carbon by 81 per cent and the second stage active carbon by another 61 per cent. It can be seen from Table 1 that bromodichloromethane and dibromochloromethane are more effectively adsorbed than chloroform.

Precursor removal has a marked effect on VHH formation within the plant. Breakpoint chlorination of A7Cl effluent, containing 3,2 mg/dm^3 TOC produces a total μmol carbon yield of 0,12 per cent while breakpoint chlorination of C7SF effluent containing 4,4 mg/dm^3 TOC produces a total μmol carbon yield of 0,46 per cent. (The total μmol carbon yield is equal to the sum of the total μmol carbon of all six VHH minus the total μmol carbon in the water before chlorination, times 100, divided by the μmol precursor carbon. The μmol precursor carbon is the μg/dm^3 TOC divided by the molecular weight of carbon.)

When considering the effect of precursor removal on the formation of VHH with time, the percentage yield of each VHH as well as that of the total is of importance. Because retention times within a distribution system after final chlorination can vary from hours to days, the formation rates of individual VHH would be informative with respect to interaction between oxidants and the various VHH. The carbon yield for chloroform, bromodichloromethane, dibromochloromethane and bromoform is shown in Figures 4 to 7 for the various configurations.

Precursor removal results in higher yields for all four VHH up to 5 000 min, whereafter the three bromo-VHH produced higher yields (compare Figures 4, 6 and 5, 7). The phenomena could not be ascribed to the fact that precursors were removed in configuration A7 but rather that breakpoint chlorination created new precursors that could not be removed by only 15 min active carbon contact time. Furthermore, the total μmol carbon concentrations in both the A7C2 and C7C2 effluents were practically the same. In the case of ozonation (Figures 5 and 7) only chloroform showed a marked increase up to 1 000 min with precursor removal. From the latter it can be concluded that the type of precursors formed by breakpoint chlorination could more easily be removed by active carbon than precursors formed by ozonation.

The total carbon yield for the four configurations are shown in Figure 9. Up to 5 min reaction time no difference is observed for configurations A7 and C7. Thereafter, and up to 10 000 min reaction time, more VHH is formed with precursor removal ahead of the disinfection stage. The same applies for configurations B7 and E7 except that no difference is observed up to 500 min.

TABLE 1
OCCURRENCE OF VOLATILE ORGANOHALOGENS THROUGHOUT RECLAMATION PLANT

Configu= ration	Sampling point	μg /dm^3						Total μ mol C	TOC mg/dm^3
		CCl_4	$CHCl_3$	C_2Cl_4	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$		
A7	R	0,197	1,304	0,430	0,047	0,051	0,074	0,219	8,0
	SF	0,163	1,016	0,285	0,076	0,056	0,079	0,169	6,1
	C1	0,208	1,285	0,385	0,121	0,034	0,127	0,221	3,2
	Cl_2	0,210	1,323	0,354	1,548	2,718	1,586	0,546	2,1
	C2	0,166	0,875	0,237	0,091	0,079	0,262	0,159	1,6
	F	0,046	1,331	0,022	0,344	0,509	1,712	0,277	2,0
B7	R	0,309	2.130	0.775	0,084	0,071	0,103	0,366	7,6
	SF	0,234	1,237	0,372	0,083	0,051	0,107	0,211	5,1
	C1	0,240	1,315	0,385	0,170	0,135	0,351	0,242	1,2
	O_3	0,237	1,258	0,391	0,157	0,096	2,609	0,343	1,0
	C2	0,233	1,213	0,369	0,138	0,047	0,061	0,209	0,6
	F	0,288	1,247	0,351	0,332	0,912	3,090	0,423	1,2
C7	R	0,026	1,275	0,004	0,015	0,039	0,001	0,133	7,0
	SF	0,004	0,473	0,015	0,021	0,014	0,001	0,053	4,4
	Cl_2	0,040	6,957	0,023	9,116	5,681	0,548	1,728	4,6
	C1	0,049	2,192	0,026	1,057	0,287	0,063	0,325	2,1
	C2	0,022	1,181	0,010	0,022	0,021	0,023	0,126	2,0
	F	0,022	1,505	0,013	0,778	1,633	1,567	0,381	2,6
E7	R	0,011	0,468	0,016	0,022	0,008	0,001	0,052	6,3
	SF	0,007	0,474	0,005	0,035	0,013	0,019	0,053	4,1
	O_3	0,004	0,437	0,004	0,045	0,019	0,023	0,050	3,0
	C1	0,004	0,654	0,001	0,256	0,088	0,062	0,093	1,5
	C2	0,003	0,451	0,007	0,001	0,037	0,106	0,054	0,7
	F	0,012	1,343	0,005	0,601	1,324	1,946	0,364	1,3

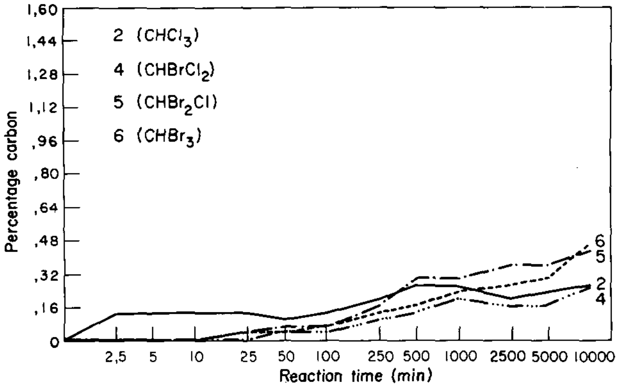

Figure 4
Carbon yield in VHH for configuration A7

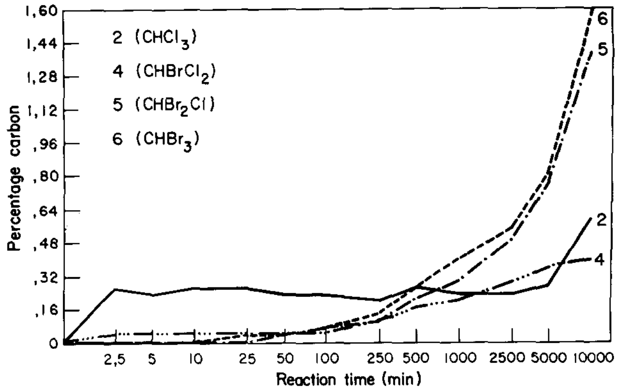

Figure 5
Carbon yield in VHH for configuration B7

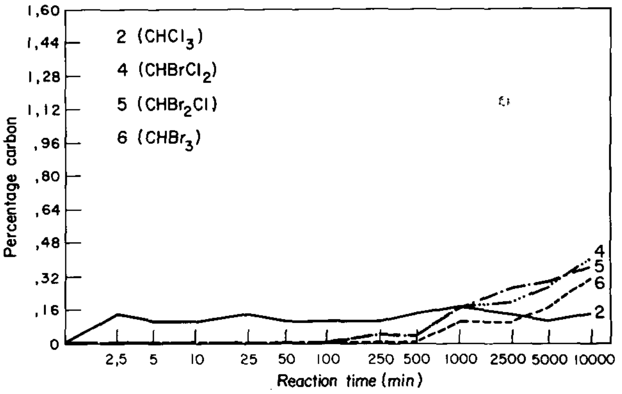

Figure 6
Carbon yield in VHH for configuration C7

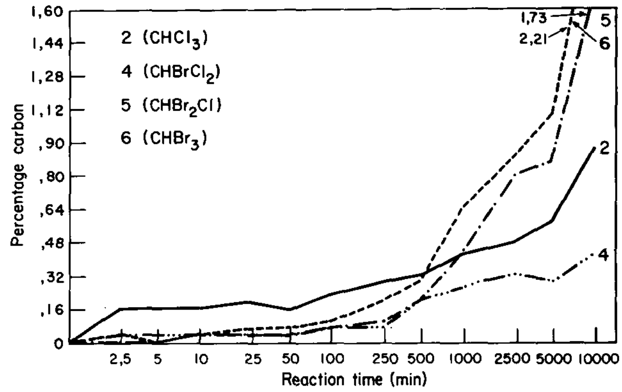

Figure 7
Carbon yield in VHH for configuration E7

It could be concluded that:

1. Activated carbon effectively reduces VHH even in the low concentration range. A 93 per cent reduction in total VHH was observed after 30 min contact with an initial concentration of 22 $\mu g/dm^3$ total VHH.

2. Precursor removal is only effective when at least 30 min active carbon contact time is allowed.

3. Precursors formed by breakpoint chlorination are more effectively removed by active carbon than those formed by ozonation.

Effect of Ozonation

According to Heist (1973), ozone is capable of oxidizing practically any organic compound to carbon dioxide, however, the reaction may take many hours and large amounts of ozone. The results of the ozonation of a mixture of low molecular weight organic compounds demonstrated that new stable products can be formed during ozonation of wastewaters and that not all of the low molecular weight organics are oxidized completely to carbon dioxide and water (Elia, Clark, McGinnis, Cody and Kinman, 1978). The decrease in TOC observed, indicated that approximately 30 per cent of the organic species in a hospital effluent were completely oxidized. However, when ozone treatment of water is combined with an activated carbon biological filter it has been found that the humic acid precursors of chlorinated organics can be removed to a large extent (Kühn, Sontheimer, Stieglitz, Maier and Kurtz, 1978). On the other hand, ozonalysis of water organics generally results in more polar molecules due to the formation of carboxylic acids, cathecols, aldehydes, etc. (Bailey, 1972; Benedek, 1977), and this in all probability would lessen equilibrium carbon adsorption capacity. It has been speculated that ozone, in addition to aldehydes and acids, can produce epoxides which may be carcinogens (Menzel and Pryor, 1976).

The fact that ozonation of the Rhine and Lake Constance waters, (Stieglitz, Roth, Kühn and Legger, 1976; Maier and Mäckle, 1976) resulted in an increase in total VHH formation after chlorination, is of interest to the placement of the ozonation stage in a water reclamation plant. Rook (1976) speculates that ozone blocked reactive sites of the precursor molecule but found that the length of time between the ozonation stage and chlorination appeared to have had an effect on ozone's ability to reduce haloform formation. It was concluded that the organic precursor had gradually lost ozonides or that new reactive methylketones might have been formed. Trussel (1978) suggests the formation of unstable products following ozonation which will not react with chlorine as long as the chlorine is added before they have had time to decompose. Another possible reason for the increased formation of haloforms might be the creation of new oxidants with ozonalysis, especially when bromides are present, the formation of new precursors and the slowness of the haloform reaction.

The effect that ozone has on the formation of VHH after final chlorination might better be understood when the reaction chemistry of ozone with organics and inorganics in water is considered. Hoigné and Bader (1978) recently proposed a reaction model to describe the primary oxidants initiated by ozone. The reaction sequence is shown in Figure 8 and described as follows: "On the one hand, during ozonation, part of the ozone (O_3) dissolved in water reacts directly with the solutes M. Such 'direct reactions' are highly selective and often rather slow (minutes). On the other hand, part of the ozone added decomposes before it reacts with solutes and before it is stripped off. This decomposition leads to free radicals. Among these, the OH radicals belong to the most reactive oxidants known to occur in water. OH can easily oxidize all types of organic contaminants and many of the inorganic solutes ('radical-type reactions'). They are therefore consumed in fast reactions (micro-seconds) and exhibit little substrate selectivity. Only a few of their reactions are of specific interest in water treatment processes. Measured oxidations in model solutions indicate up to 0,5 mol OH formed per mole of ozone decomposed. The higher the pH, the faster the decomposition of ozone which is catalyzed by hydroxide ions (OH^-). The decomposition is additionally accelerated by an auto-catalyzed sequence of reactions in which radicals formed from decomposed ozone act as chain carriers. Some types of solutes react with OH radicals under formation of secondary radicals ($R^\cdot$) which still act as chain carriers. Others, for instance bicarbonate ions, transform the primary radicals to inefficient species (ϕ) and thereby act as inhibitors of the chain reaction. Therefore, the rate of the decomposition of ozone in wastewater depends on the pH of the water as well as on the solutes present. The overall effect initiated by ozonation is a superposition of the 'direct reaction' and the 'radical-type reaction'." It was further concluded by Hoigné and Bader (1978) that a large part of the oxidation effects by ozone could be expected to be the result of secondary oxidants produced from decomposed ozone. This effect would further be enhanced by lowering the pH because the lower the pH the more ozone becomes available during ozonation.

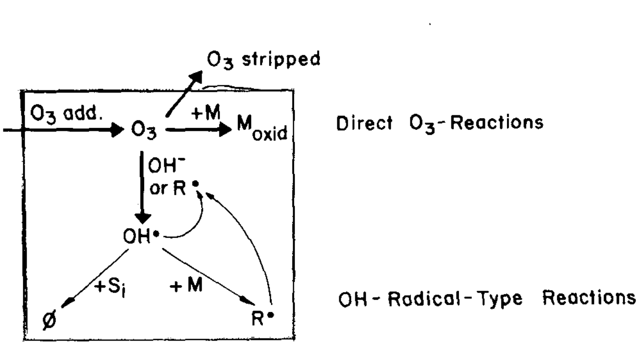

Figure 8
Reaction sequence of ozone in water (Hoigné & Bader, 1978)

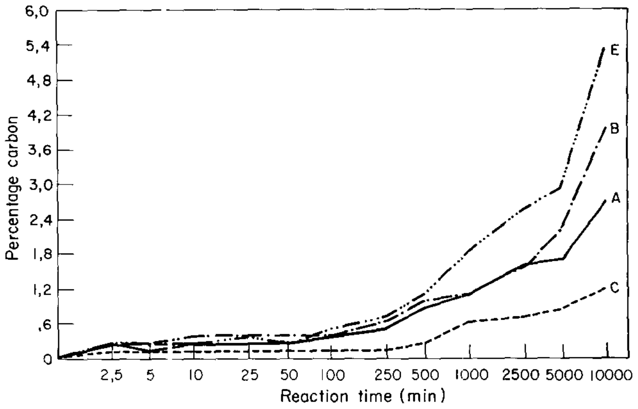

Figure 9
Carbon yield in total VHH for config. A7, B7, C7 & E7

The conclusions by Hoigné and Bader (1978) are substantiated by the results of the present study. Much more total VHH is formed (10 000 min after final chlorination) when using ozone as disinfectant compared to chlorine under all conditions of this experiment. The total carbon yield by the six VHH for all four configurations is shown in Figure 9.

From 2,5 to 10 000 min reaction time the C2 effluent from configurations B7 and E7 produced more VHH upon chlorination than those of configurations A7 and C7. A drastic increase in VHH formation is observed after approximately four hours contact time for configurations B7 and E7. This is further evidence that secondary oxidation products are formed upon ozonation which are only partly removed by subsequent active carbon adsorption. With or without precursor removal the products of ozonation result in the same amount of VHH being formed up to 500 min contact time after final chlorination. Thereafter, VHH formation increases with time indicating that precursor removal has a beneficial effect on the ultimate production of VHH, when ozone is used as disinfectant.

Effect of Bromide

It is becoming increasingly recognised that when waters containing bromides are chlorinated the ensuing VHH production is markedly influenced by the bromide concentration (Rook, 1974; Kleopfer, 1976; Lange and Kawczynski, 1978). The presence of bromide not only influences the yield of VHH (mmol TOC in VHH/mol TOC) but also the reaction rate. Various reaction pathways have been suggested when chlorine is added to water containing bromide and organic compounds. Carpenter and Macalady (1978) chlorinated sea water containing natural bromide and suggest that bromide is oxidised to a mixture of hypobromous acid and hypobromite ion with the possibility that hypobromous acid disproportionates into bromate and other oxidation states. The reaction between bromide and hypochlorite ion as suggested by Weszelsky (1957) and modified by Van der Meulen (1957) is:

$$Br^- + 3ClO^- \rightarrow BrO_3^- + 3Cl^-$$

Szabo and Csanyi (1957) suggest that the reaction takes place in two main steps:

$$2Br^- + Cl_2 \rightarrow Br_2 + 2Cl^-$$

$$Br_2 + H_2O \rightarrow BrOH + H^+ + Br^-$$

$$BrOH + Cl_2 \rightarrow BrCl + HOCl$$

and

$$3BrOH \rightarrow BrO_3^- + 3H^+ + 2Br^-$$

$$BrCl + 2Cl_2 \rightarrow BrCl_5$$

$$BrCl_5 + 3H_2O \rightarrow BrO_3^- + 6H^+ + 5Cl^-$$

Bromate ion could, however, not be detected by Macalady, Carpenter and Moore (1977) in chlorinated sea water, unless the solutions were exposed to sunlight. If bromate ion is only formed under these conditions (chlorination of sea water containing 65 mg/dm^3 bromide and in the presence of sunlight) it is doubtful whether bromate plays a significant role in the formation of haloform under normal chlorination conditions of surface water or sewage effluents (0,01 to 1 mg/dm^3 bromide and in the absence of sunlight).

Morris (1978) explained that whenever chlorine or hypochlorite is added to a water containing bromide there is a rapid formation of hypobromous acid (HOBr) according to the reaction:

$$Br^- + HOCl \rightarrow HOBr + Cl^-$$

The resulting HOBr is also an electrophilic agent, but one that tends generally to react much more extensively and rapidly with organic matter than HOCl. The bromide regenerated in the reduction of HOBr is readily reoxidized by residual HOCl and thus serves as a catalyst in oxidation reactions. The overall result is an enhanced reactivity exhibited by the addition of chlorine to waters containing bromide ion.

In addition to the formation of HOBr and BrO$^-$ there is the possibility that interhalogen compounds are formed when water containing bromide is chlorinated. Pungor, Burger and Schulek (1958) have presented spectroscopic evidence for the existence of chloride ion complexes of bromine chloride in aqueous solution. These interhalogen compounds, are in effect, still halogens, although electronegativity difference render them somewhat more polar in character than the molecular halogens themselves (McMorris and Yost, 1952). They behave as oxidizing agents and undergo hydrolysis according to the reaction:

$$XX^- + H_2O \rightleftharpoons H^+ + X^- + HOX$$

where X$^-$ is the more electronegative halogen.

Bromine chloride would therefore hydrolise as follows:

$$BrCl + H_2O \rightleftharpoons H^+ + Cl^- + HOBr$$

Bromine chloride will add to ethylenic double bonds and react rapidly with aromatic and olefinic compounds (McMorris, 1952; Carpenter and Macalady, 1978).

According to the literature, the more effective oxidants to be expected when chlorinating water containing bromide would be hypobromous acid, hypobromite ion and bromine chloride. The reactivity of these species containing bromide with organics under various pH conditions, will determine the variety of brominated or mixed chlorobromo compounds formed when waters containing bromide are chlorinated. The presence of bromides in sewage effluents necessitates an evaluation of the role played by bromide in the ultimate VHH production in reclaimed water. The type of disinfectant and the position of this unit process in the reclamation plant will, to a great extent, determine the type of bromo oxidants formed and their concentrations in the distribution system.

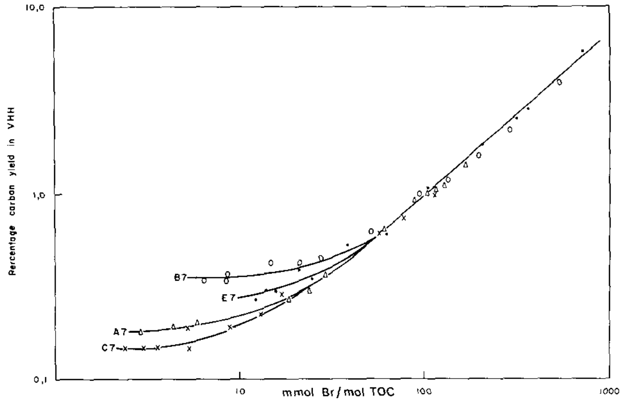

Figure 10
Influence of bromide on the yield of VHH

To evaluate the effect of bromide on the yield of VHH, Figure 10 was prepared from the bromide content of the haloforms developed after final chlorination under the conditions of this experiment and the percentage yield of carbon in the total VHH for all four configurations studied. The ordinate represents the percentage yield of VHH carbon per precursor carbon present in the C2 effluents and the abscissa represents the ratio between the millimoles of bromide present in the VHH formed after final chlorination and the moles of carbon in the C2 effluents.

For a ratio of mmol/Br to mol/TOC greater than 55 a linear relationship exists between the percentage carbon yield and bromide present in the VHH irrespective of the pretreatment. The yield of carbon for lower ratios is dependent on the pretreatment or process configuration before final chlorination. From Table 2 it can be seen that the bromide content of the C2 effluents from the two configurations where chlorine is used as disinfectant (A7, C7), is considerably lower than those of the ozone configurations, with C7 much lower than A7.

TABLE 2
YIELD OF BROMIDE IN VHH

Configuration	Br in C2 nmol Br	Br in VHH nmol Br	Yield %
A7	626	22,5	3,6
B7	2 628	25,0	1,0
C7	25	23,6	94,4
E7	2 127	39,9	1,9

It could be inferred that the chloro-bromo-organic oxidation products formed during the 45 min contact time in the breakpoint chlorination tank and subsequently removed by active carbon adsorption, are responsible for this lower bromide content of the A7C2 and C7C2 effluents. Further evidence that

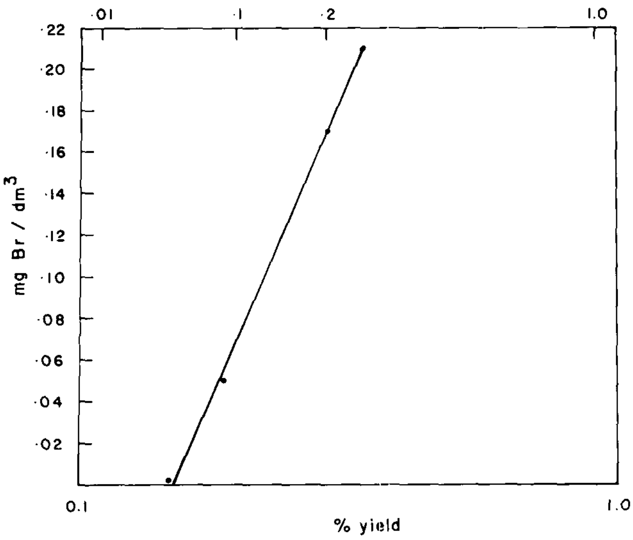

Figure 11
Effect of bromide concentration on VHH yield

the bromo oxidants react more rapidly with the organic material than the chloro-oxidants is shown in Figure 11 where a direct relationship is found between the bromide content of the C2 effluents and the total VHH yield within the first 2,5 min contact time.

The short contact time in the ozone reactor is possibly responsible for the lower VHH removal by active carbon. The higher VHH yield during the first 100 min after chlorination of B7C2 as against E7C2, as shown in Figure 10, explains this assumption.

When considering the effect of time and bromide concentration in the C2 effluents it seems from Table 2 and Figure 10 that the bromination reaction will continue until practically all of the bromide is transformed to bromo-VHH. At the start of the laboratory chlorination, the C7C2 effluent contained only 25 nmol bromide. After 10 000 min (approx. 1 week) 94 per cent of this bromide was in the form of bromo-VHH. Figure 10 indicates that the bromo-VHH will continue to increase if longer reaction time is allowed. This substantiates the explanation by Morris (1978) that the bromide serves as a catalyst in the oxidation reaction. The following reaction sequence can be expected:

$$CHCl_3 + HOBr \rightleftharpoons CHBrCl_2 + HOCl$$

$$CHBrCl_2 + HOBr \rightleftharpoons CHBr_2Cl + HOCl$$

$$CHBr_2Cl + HOBr \rightleftharpoons CHBr_3 + HOCl$$

This trend in the increase of bromo-VHH with time occurs at the expense of the chloro-VHH. Figure 12, indicating the bromine to chlorine mole ratio in the total VHH for all configurations studied, substantiates this tendency.

It is concluded that the bromide present in water to be chlorinated, although not a precursor in itself, plays a substantial role in the ultimate VHH content of the finished water. Hypobromous acid, hypobromite ion and bromine chloride react more rapidly with organic compounds and especially VHH precursors than any of the chlorine equivalents. The bromo-VHH formed are more easily removed by active carbon than the chloro-VHH as was also shown by Rook (1976) (see Table 1).

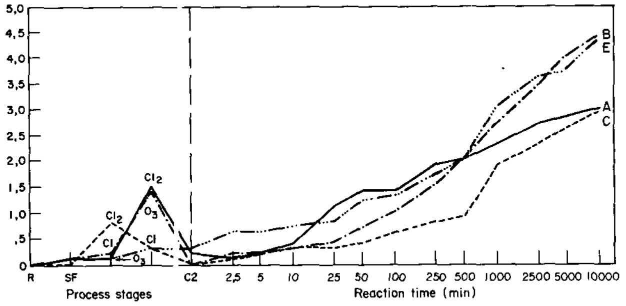

Figure 12
Bromine to chlorine mole ratio in total VHH for configurations A7, B7, C7 & E7

Keeping all other factors such as pH, TOC concentration, chlorine concentration, temperature, sunlight and pretreatment constant, the bromide content of the water will determine the ultimate VHH concentration. The mole ratio of bromide to TOC could be used to calculate the ultimate VHH to be expected under a constant set of experimental conditions.

Conclusions

When water is to be reclaimed from secondary sewage effluents an essential precondition should be the assurance that the finished water shall at all times contain less potential harmful substances and at lower concentrations than normally found with conventionally treated polluted surface waters. The engineer and scientist have at their disposal the most modern equipment and a number of physical-chemical unit processes to achieve this goal. With the present scare about the ubiquitous presence of halogenated hydrocarbons in drinking waters various process configurations of the SWRP were investigated to determine what effect the position of the disinfection stage and the type of disinfectant had on the ultimate VHH formation. Some of the more important factors that might be expected to influence the rate of VHH formation as well as the ultimate concentration are the following:

- Activated carbon is effective in removing VHH precursors and thereby reducing the ultimate VHH concentration, provided a contact time of at least 30 min is allowed before or after the disinfection stage.

- Activated carbon is effective in removing VHH but again on condition that at least 30 min contact time is allowed.

- The precursors formed by breakpoint chlorination are more easily removed by active carbon adsorption than those formed by ozonation.

- When comparing ozone versus chlorine as disinfectant, **invariably** more VHH are formed after final chlorination **when** using ozone as disinfectant, no matter what process configuration is employed. There could be a few reasons for this phenomena. The reaction time of 10 min through the ozone reactor is too short for active carbon removable substances to be formed. An additional retention time of 0,5 to 1 h might result in less ultimate VHH production. The oxidants formed by ozone and not removed by active carbon are much more reactive than those formed by chlorine with a resultant higher VHH yield.

- The bromide content of the water not only enhances the reactivity of the oxidants, but is also responsible for an ultimate higher VHH yield, the higher the bromide concentration.

- The mole ratio of bromide to TOC in the water can be used to calculate the ultimate VHH concentration to be expected under a given set of experimental conditions.

- Given a long enough reaction time, apparently all of the bromide present in the water will be transformed to one or more species of bromo VHH.

- To achieve the primary goal of water reclamation, namely, to provide a drinking water that will contain less potentially harmful organic substances than most conventional water supplies, the design engineer of a water reclamation plant has many tools at his disposal. One is the correct placing of the disinfection stage in the reclamation plant process unit sequence. By oxidizing as much organic material as possible to readily detectable compounds and then removing these substances by active carbon adsorption, he has won more than half the battle. From the results of this experiment breakpoint chlorination ahead of the two active carbon adsorption stages is the preferred process sequence and disinfectant to assure the lowest possible VHH production in the distribution system.

Acknowledgements

A special word of thanks goes to the personnel of the Stander Water Reclamation Plant for the operation of the plant and to Miss L. Slabbert for sample preparation. In addition, the analytical services of the Water Quality Division of the National Institute for Water Research (NIWR) are much appreciated. This paper is published by permission of the Director of the NIWR.

References

BABCOCK, D. & SINGER, P. (1977) Chlorination and Coagulation of Humic and Fulvic Acids, *Proceedings 97th Annual American Water Works Association Conference,* Anaheim, California.

BAILEY, P.S. (1972) in Evans, F.L. *Ozone in Water and Waste Water Treatment.* Ann Arbor, Michigan: Ann Arbor Science Publishers Inc.

BELLAR, T.A., LICHTENBURG, J.J. & KRONER, R.C. (1974) The Occurrence of Organohalides in Finished Drinking Waters. *J. Amer. Water Works Ass.* **66** 703–706.

BENEDEK, A. (1977) *The Effect of Ozone on Activated Carbon Adsorption* — A mechanistic Analysis of Water Treatment Data Presented at 101 Symposium on Advanced Ozone Technology Toronto, Ontario.

CARPENTER, J.H. & MACALADY, D.L. (1978) Chemistry of Halogens in sea water in Jolley, R.L. *Water Chlorination: Environmental Impact and Health Effects.* Vol 1, Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc. 439 p.

CHRISTMAN, R.F. & MINEAR, R.A. (1971) *Organic Compounds in Aquatic Environments,* New York: Marcel Dekker, Inc.

DU TOIT, M. & PAGE, H. (1930) Studies on the Carbon and Nitrogen Cycles in Soil, III. The Formation of Natural Humic Matter. *J. Agr. Sci.* **20** 478.

ELIA, V.J., CLARK, C.S., McGINNIS, K.T., CODY, T.E. & KINMAN, R.L. (1978) Ozonation in a Wastewater Reuse System. Examination of Products formed. *J. Wat. Poll. Con. Fed.* **50** 1729–1732.

HARMS, L.L. & LOOYENGA, R.W. (1977) Chlorination Adjustment to Reduce Chloroform Formation. *J. Amer. Water Works Ass.* **69**(5) 258–262.

HART, O.O. (1978) Operational and Control Aspects in Water Reclamation. *Prog. Wat. Tech.* **10** 65–80.

HEIST, J.A. (1973) Ozone Oxidation of Wastewater Contaminants, *Water Am. Inst. Chem. Eng.* 456–467.

HOIGNÉ, J. & BADER, H. (1978) Ozone Initiated Oxidations of Solutes in Wastewater. A Reaction Kinetic Approach. *Prog. Wat. Tech.* **10**(5/6) 657–671.

JUNK, G.A. & STANLEY, S.E. (1975) *Organics in Drinking Water,* Part 1. Listing of identified chemicals. Ames Laboratory, Ames, Iowa. 84 p.

KLEOPFER, R. (1976) Analysis of Drinking Water for Organic Compounds in Leith, L. *Identification and Analysis of Organic Pollutants in Water,* Ann Arbor, Michigan. Ann Arbor Science Publishers 399.

KÜHN, W., SONTHEIMER, H., STEIGLITZ, L., MAIER, D. and KURTZ, R. (1978) Use of Ozone and Chlorine in Water Utilities in the Federal Republic of Germany. *J. Am. Water Works Assn.* **70** 326–331.

LANGE, A. & KAWCZYNSKI, E. (1978) Experiences at Contra Costa County Water District. *Proceedings of Water Treatment Forum VII Organics in Domestic Water Supplies,* California — Nevada Section AWWA. Palo Alto, California.

MACALADY, D.L., CARPENTER, J.H. & MOORE, C.A. (1977) Sun-light-Induced Bromate Formation in Chlorinated Seawater. *Science,* **195** 1335–1337.

MAIER, D. & MÄCKLE, H. (1976) "Wirkung von Chlor auf natürliche und ozonte organische Wasserinhaltsstoffe. *Vom Wasser* **47** 379–397.

MANKA, J., REBHUN, M., MANDELBAUM, A. & BORTINGER, A. (1974) Characterization of Organics in Secondary Effluents. *Environ. Sci. Technol.* **8** 1017–1020.

McMORRIS, J. & YOST, D.M. (1952) In Moeller T: *Inorganic Chemistry* New York. John Wiley & Sons Inc. 966 p.

MENZEL, D.B., PRYOR, W. (1976) *Free Radicals in Biology.* Vol II New York: Academic Press.

MORRIS, J.C. (1978) The chemistry of aqueous chlorine in relation to Water chlorination, in Jolley, R.L. *Water Chlorination: Environmental Impact and Health Effects.* Vol. I. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc. 439 p.

MORRIS, J.C. & BAUM (1978) Precursors and Mechanisms of Haloform Formation in the Chlorination of Water Supplies, in Jolley, R.L. Gorcher, H., Hamilton, Jr. D.H. *Water Chlorination: Environmental Impact and Health Effects.* Vol. 2. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc. 909 p.

NATIONAL CANCER INSTITUTE (1975) List of Chemicals that cause Cancer in Man. *House of Representatives Hearings, Subcom-mittee of the Committee on Appropriations, March, 1975.* Department of Labour, Health, Education and Welfare. U.S. Government Printing Office, Washington, D.C. 85 p.

NATIONAL CANCER INSTITUTE (1976) Report on the Carcinogenesis Bioassay of Chloroform. National Technical Information Service, Washington D.C.

ODEN, S. (1919) Humic Acids. *Kolloidchem. Beineftc.* **11** 75.

PUNGOR, E., BURGER, K. & SCHULEK, E. (1958) Interhaloid complexes in Aqueous Solution. *J. Inorg. Nucl. Chem.* **11** 56.

REBHUN, M. & MANKA, J. (1971) Classification of Organics in Secondary Effluents. *Environ. Sci. Technol.* **5** 606–609.

ROOK, J.J. (1974) Formation of Haloforms During Chlorination of Natural Waters. *Water Treatment Exam.* **23** 234–243.

ROOK, J.J. (1976) Haloforms in Drinking Water. *J. Am. Water Works Assoc.* **68** 168–172.

ROOK, J.J. (1977) Chlorination Reactions of Fulvic Acids in Natural Waters. *Environ. Sci. Technol.* **11** (5) 478–482.

SCHNITZER, M. & KAHN, S.U. (1972) *Humic Substances in the Environment* New York. Marcel Dekker, Inc.

SCHWARTZ, M. & LANCASTER, E.A. (1977) Studies in Ozone and Chlorine for Water Treatment and Disinfection. *Proceedings American Water Works Association Disinfection Seminar,* Paper No. 4. Presented at the 97th American Water Works Association Conference, Anaheim, California.

SNOEYINK, V.L., McCREARY, J.J. & MURIN, J. (1977) Activated Carbon Adsorption of Trace Organic Compounds. Office of Research and Development U.S. Environmental Protection Agency, Cincinnati, Ohio.

SONNEBORN, M. & BOHN, B. (1978) Formation and Occurrence of Haloforms in Drinking Water in the Federal Republic of Germany, in Jolley, R.L., Gorchev, H., Hamilton, Jr. D.H. *Water Chlorination: Environmental Impact and Health Effects.* Vol. 2. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc. 909 p.

STEELINK, C. (1963) What is Humic Acid. *J. Chem. Educ.* **40** 379–385.

STEVENS, A.A., SLOCUM, C.J., SEEGER, D.R. & ROBECK, G.G. (1978) Chlorination of Organics in Drinking Water, in Jolley, R.L. *Water Chlorination: Environmental Impact and Health Effects.* Vol. 1. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc. 439 p.

STEVENSON, F.J. & GOH, K.M. (1972) Infrared Spectra of Humic and Fulvic Acids and their Methylated Derivatives: Evidence for Nonspecificity of Analytical Methods for Oxygen Containing Functional Groups. *Soil Sci.* **113** 334–345.

STIEGLITZ, L., ROTH, W., KÜHN, W. & LEGGER, W. (1976) Das Verhalten von Organohalogenverbindungen bei de Trinkwasseraufbereitung, *Vom Wasser* **47** 347–77.

SYMONS, J.M. (1976) Interim Treatment Guide for the Control of Chloroform and Other Trihalomethanes. Water Supply Research Division, Municipal Environmental Protection Agency, Cincinnati, Ohio.

SZABO, Z.G. & CSANYI, L. (1957) In *Volumetric Analysis,* New York: Interscience Publishers, Inc. 254 p.

TRUSSEL, R.R. (1978) Factors influencing the formation of trihalomethanes. *Proceedings of Water Treatment Forum VII, Organics in Domestic Water Supplies,* California — Nevada Section, AWWA. Palo Alto, California.

U.S. ENVIRONMENTAL PROTECTION AGENCY (1974) Lower Mississippi River Facility, New Orleans Area Water Supply Study (Draft Analytical Report), Slidell, Louisiana.

U.S. ENVIRONMENTAL PROTECTION AGENCY (1976) List of Organic Compounds Identified in Drinking Water in the United States, January 1. Health Effects Research Laboratory, Cincinatti, Ohio.

VAN DER MEULEN, J.H. (1957) In *Volumetric Analysis,* New York: Interscience Publishers, Inc. 254 p.

VAN RENSBURG, J.F.J., VAN HUYSTEEN, J.J. & HASSETT, A.J. (1978) A Semi-Automated Technique for the Routine Analysis of Volatile Organohalogens in Water Purification Processes. *Water Research* **12** 127–131.

WEBER, W.J. Jr., PIRBAZARI, M., HERBERT, M. & THOMPSON, R. (1977) Effectiveness of Activated Carbon for Removal of Volatile Halogenated Hydrocarbons from Drinking Water, in Barchardt, J.A. Cleland, J.K., Redman, W.J., Olivier, G. *Viruses and Trace Contaminants in Water and Wastewater.* Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc. 249 p.

WEBER, W.H., Jr. (1972) *Physiochemical Processes for Water Quality Control.* New York: Wiley Interscience. 640 p.

WEBER, W.H., Jr. (1974a) Purification of Industrial Effluents with Activated Carbon. Proceedings, *NTA Advanced Study Institute: Scientific Aspects of Sorption and Filtration Methods for Water Purification.* Institute for Atom Energi, Kjeller, Norway.

WEBER, W.J. Jr. (1974b) The Prediction of the Performance of Activated Carbon for Water Treatment. *Activated Carbon in Water Treatment.* The Water Research Association, Medmenham, Marlow, Bucks.

WEBER, W.J. Jr., & YING, W. (1977) Integrated Biological and Physiochemical Treatment for Reclamation of Wastewater, paper presented at *International Conference on Advanced Treatment and Reclamation of Wastewater,* Johannesburg.

WERSHAW, R.R. & GOLDBERG, M.C. (1972) Interaction of Organic Pesticides with Natural Organic Polyelectrolytes, in Faust, S.D. *Fate of Organic Pesticides in the Environment. Advances in Chemistry Series.* Nr. 111 American Chemical Society, Washington D.C.

WESZELSZKY, VON J. (1957) In *Volumetric Analysis,* New York: Interscience Publishers, Inc. 254 p.

YOUNG, J.S. & SINGER, P.C. (1977) Chloroform Formation in Public Water Supplies: A Case Study. *Proceedings 97th Annual American Water Works Association Conference,* Anaheim, California.