ERRATA

page 22, line 2, delete "α-Napthol", include "α - Naphthol"

page 32, line 18, delete "humus", include "humic"

page 32, line 19, delete "bezenes", include "benzenes"

page 32, line 29, delete "cholrine", include "chlorine"

page 54, Table 3.1, line 4,

delete	"5	5,10,15	6,7,8,9"
include	"5	5	6,7,8"
include	"5	10	6,7,8,9"
include	"6.2	15	6,7,8"

page 54, Table 3.1, line 8, delete "6.2", include "5"

page 59, Table 3.4, line 3, column 4, delete "H.A.", include "F.A."

page 64, equation (6), delete "k", include "k_2"

page 69, line 2, delete "dehydroxyquinone", include "dihydroxyquinone"

page 73, equations (10) and (14), delete "k_2", include "k_2'"

page 75, Table 3.7, line 3, delete "1.689", include "1.89"

page 75, line 25, delete "stabe", include "stable"

page 79, line 1, delete "Humic Acid 5 $\mu g\ l^{-1}$", include "Humic Acid 5 $mg\ l^{-1}$"

page 83, Table 4.1, delete "April 78", include "April 79"

page 91, line 8 and line 9, delete "1978", include "1979"

page 107, equation (4), insert ")" after "$[Cl_2]_t$"

TRIHALOMETHANE FORMATION ARISING FROM THE CHLORINATION OF POTABLE WATERS

A thesis submitted to the University of London
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by

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A mi querida esposa

Delia

TRIHALOMETHANE FORMATION ARISING FROM THE CHLORINATION OF POTABLE WATERS

ABSTRACT

There is growing concern of the health effects associated with long term exposure to halogenated organics in potable water supplies resulting from the chlorination process. A review of the relevant literature concerning aqueous chlorination is presented with particular reference to the trihalomethanes.

Laboratory studies on the chlorination of upland water with a high content of organic matter (predominantly humic materials) and humic and fulvic fractions extracted from the Thames water were performed under controlled conditions of pH and temperature. Chlorine consumption and trihalomethane production were monitored. In the absence of bromide, chloroform was the main trihalomethane species produced. A 'bromide addition' experiment and the results from a survey of household potable waters showed that the percentage contribution of brominated trihalomethanes to total trihalomethane formation increases on increasing bromide concentration.

Trihalomethane analysis was performed using a direct aqueous injection technique (D.A.I.) developed by the author. This method permitted the indirect measurement of organohalide intermediates of the haloform reaction which have been designated the term 'residual' trihalomethane.

All the reactions involving chlorine and humic material produced dissolved and residual chloroform. The different sources of humic material show similar trends in the formation of dissolved chloroform and the formation and break down of the intermediates detected as residual chloroform. The lower molecular weight fulvic acid produced consistently less chloroform (dissolved and residual) than the higher molecular weight humic acid. pH was a dominant factor influencing both the production of total-chloroform (residual + dissolved) and the relative proportions of these components. The organohalide intermediates of the haloform reaction detected as residual chloroform break down slowly at ambient temperatures to produce dissolved chloroform is a reaction step which does not require the presence of chlorine. Results indicate that these intermediates contain trichloroacetyl groups (CCl_3CO-).

A linear relationship was found between chlorine consumption and total-chloroform production for both the upland water and the humic and fulvic acids. Chloroform formation, however, accounts for only a small proportion of the chlorine consumed. A relationship was also found between the UV/VIS absorption spectra of a water containing humic material and the total-chloroform produced. An empirical equation has been derived for predicting total-chloroform formation.

The result obtained from on-site investigations of trihalomethane production at a treatment plant under normal operating conditions were consistent with the result from the laboratory studies.

The chlorination of organic compounds containing a <u>meta</u>-dihydroxy moiety produced dissolved and residual chloroform. This is further evidence to support the hypothesis that this moiety is present in humic materials and is an active site responsible for trihalomethane formation.

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ABBREVIATIONS

kilometre	$(10^{3}m)$	km
centimetre	$(10^{-2}m)$	cm
millimetre	$(10^{-3}m)$	mm
nanometre	$(10^{-9}m)$	nm
litre		l
millilitre	$(10^{-3}l)$	ml
microlitre	$(10^{-6}l)$	μl
gram		g
millgram	$(10^{-3}g)$	mg
microgram	$(10^{-6}g)$	μg
second		s
minute		min
hour		hr
parts per million		ppm
Normal solution		N
milliequivalent		meq
kilojoule		KJ
Total-chloroform		$TCHCl_3$
Residual chloroform		$RCHCl_3$
Humic acid		HA
Fulvic acid		FA
Total organic carbon		TOC
Total organic chlorine		TOCl
Polychlorinated biphenyl		PCB
Polycyclic aromatic hydrocarbon		PAH
Diethyl-p-phenylenediamine		DPD
Aqueous		aq
Slow sand filtered		S.S.F.
Rapid gravity filtered		R.G.F.

Direct aqueous injection	DAI
Gas Chromatography	GC
Mass spectrometry	MS
Ultra violet	UV
Visible	VIS
Environmental Protection Agency	EPA
World Health Organization	WHO
Water Research Centre	WRC
United Nations	UN
United Kingdom	UK
United States	US

1. INTRODUCTION

Water disinfection usually involves the use of chlorine, which is unequalled as a general purpose disinfectant. The germicidal efficiency of chlorine has resulted in its widespread adoption with relatively little account having been taken until recently of its chemical reactions with other species in aqueous solution.

The industrialised nations have virtually eliminated the transfer of enteric diseases as a direct result of the disinfection of water supplies, and it is now considered normal by the populaion of these countries to have access to potable waters. The dramatic reduction of bacterial and viral infections has increased the percentage of deaths from cancer and cardiovascular disease in these societies which might be associated with environmental factors, factors which have both chemical and social implications.

The growing concern of the long term health effects of trace chlorinated organics present in potable water supply as a result of the chlorination process has increased the demand for their removal and stimulated research on the chemical aspects of water disinfection. This in turn has led to a reappraisal of the traditional methods of water disinfection.

It is a reflection on the unequal distribution of wealth between the developed and underdeveloped countries that as the industrialised nations are taking steps to control the formation of trace organics in water supplies as a result of water disinfection, two thirds of the world population (not including China) do not have access to water supplies free of enteric diseases(1).

The WHO has stated that "the chlorination of water supplies in developing countries is extremely important because biological pollution, namely the pollution of natural waters by excreta, presents the greatest problem in controlling water quality and the greatest threat to health"(1). Thus, as the United States is considering implementing regulations for the control of trihalomethanes and other organics in water supplies at a cost estimated to exceed one thousand million dollars(2) (in the US alone), the UN is initiating an ambitious programme to improve the standards and where necessary, to establish water supplies to over one thousand million people within 10 years(1,3).

The EPA's proposed regulation of a maximum 0.10 mgl^{-1} for total trihalomethane in drinking water$^{(4)}$ has been criticised as too ambitious and lacking a scientific basis for the decision that the present levels constitute a hazard to health$^{(2)}$. Furthermore, there is growing criticism of the recommended use of granular activated carbon for the removal of organics from potable waters$^{(5)}$ as many consider that granular activated carbon itself is a source of harmful chemicals$^{(2)}$ and that its implementation will only substitute one problem for another. It may also be argued that the money could be better spent on increasing the standards in other sectors which will have a more direct impact on public health than the removal of trace organics from water supplies, or that the efforts of the industrialised nations should be directed towards the assistance of the developing countries to eliminate enteric diseases by increasing the standards of water supply.

The EPA's stand in implementing the regulations on the levels of the trihalomethanes, which it considers to be by far the most widespread synthetic organic contaminants in drinking water$^{(6)}$, is to a certain extent political as the EPA has been given a mandate from Congress to "regulate contaminants on the basis that they may have adverse effects on human health and to do so even in the absence of absolute proof", proof which the EPA considers is seldom available$^{(6)}$. There is growing concern however that many of the organics produced after the chlorination of water supplies are mutagenic$^{(7)}$,carcinogenic$^{(8)}$ or both$^{(9)}$.

There is no doubt that the introduction of chlorination of water supplies as a disinfectant has resulted in a dramatic reduction in enteric diseases. On no account therefore, should the removal of trace organics resulting from the chlorination of water supplies jeopardize the present high standards of water disinfection, though it cannot be denied that the elimination of, or reduction in, the levels of chlorinated organics in potable waters will be beneficial to the environment and as a consequence improve, directly or indirectly, public health. Thus, more effort should be directed towards a better understanding of the chemical factors involved which may not only improve disinfection, which would have direct implications for the developing nations, but also help reduce the organic by-products resulting from such treatment.

1.1 CHEMICAL ASPECTS OF AQUEOUS CHLORINATION REACTIONS

The complexities of chlorine chemistry have in the past been examined where they directly affect the processes of water treatment as in, for example, the breakpoint phenomenon, which results from the reactions of chlorine with ammonia and its derivatives.

The necessity of using a wider range of source waters for potable supplies has increased the numbers of chemical compounds which are exposed to chlorination during water treatment. This is particularly significant in densely industrialised and populated lowland areas of high water reuse. It has become increasingly evident that there is a need to elucidate the chemical reactions taking place between chlorine and industrial pollutants, and compounds such as phenols have been studied. Upland waters, usually considered to be pure and wholesome, cannot be treated without consideration of the chemical aspects of chlorination, particularly where such waters are peaty, containing high levels of humic and fulvic materials.

As a result of the EPA's nationwide trihalomethane survey and the proposed limit of trihalomethane concentration in drinking water in the United States, research is currently centered on the relationships between trihalomethane formation and factors which influence their formation during water chlorination.

To obtain a better understanding of the factors involved in trihalomethane formation the following sections outline the complex nature of chlorine chemistry. A brief description of the behaviour of chlorine in solution is included as are sections on the chlorination of ammonia and aromatic hydrocarbons which have been the two most widely investigated aspects of chlorination chemistry. A final section reviews the relevant literature of trihalomethane chemistry.

1.1.1 Chlorine in Solution

The diversity of aqueous chlorination reactions stems from the ability of the chlorine molecule to either hydrolyse or disproportionate rapidly to establish the equilibria (1) and (2):-

$$Cl_2 + H_2O \xrightarrow{FAST} Cl_{2(aq)} = H^+ + Cl^- + HOCl \quad K_1 \qquad (1)$$

$$HOCl = H^+ + OCl^- \quad K_2 \qquad (2)$$

The equilibrium constants K_1 and K_2 lie in the ranges $(1.5 - 4.0) \times 10^{-4}$(10) and $(1.6 - 3.2) \times 10^{-8}$(11) respectively between 0°C and 25°C. Both the equilibria are pH dependent and thus the fractions of total chlorine (Cl_T) present as $Cl_{2(aq)}$, HOCl and OCl^- vary with pH as shown in Fig.1.1. As the hydrolysis of chlorine liberates H^+, increasing chlorine concentration reduces the fraction of Cl_T present as HOCl. Also the extent to which chlorine is hydrolysed increases with decreasing Cl_2 concentration or with the neutralization of liberated H^+.

The buffering capacity of natural waters (pH 6-9) ensures that the predominant oxidizing species present in chlorinated water are hypochlorous acid and hypochlorite ion, the proportion of each species depending on pH. It has been demonstrated(12) that under the conditions of normal chlorination practice only an insignificant fraction of Cl_T is present in the molecular form ($\sim 10^{-9} - 10^{10}$ ppm). Reaction kinetic studies have shown that chlorinating species other than HOCl and OCl^- are present and that under certain conditions they are more active in the chlorination process. The displacement of H^+ by Cl^+ in N-chlorination, for example, is dependent on the electrophilic character of the attacking chlorine containing species. An anticipated order of reactivity for a number of possible donors of Cl^+ has been suggested by Morris(13), who compiled the series by the substitution of Cl^+ for H^+ in an analogous table of acid strength:-

$$Cl^+ > H_2OCl^+ > Cl_2 > Cl_2O > AcOCl > HOCl > ROCl > H_2NCl > OCl^-$$

The existence of the chlorinium ion in water is now considered unlikely, largely as the result of the work of Swain and Crist(14), who found no kinetic evidence for the participation of Cl^+ in electrophilic substitution reactions. This result supported that of Belle and Gelles(15), whose thermodynamic calculations indicated that the existence of Cl^+ in aqueous solution was doubtful:-

$$Cl_{2(aq)} = Cl^+_{(aq)} + Cl^-_{(aq)} \rightarrow K \sim 10^{-40} - 10^{-60} \qquad (3)$$

This was in contrast to earlier work by de la Mare and Vernon(16), who postulated a chlorination step involving the chlorinium ion to explain kinetic data. Thermodynamic calculations have indicated(15) that

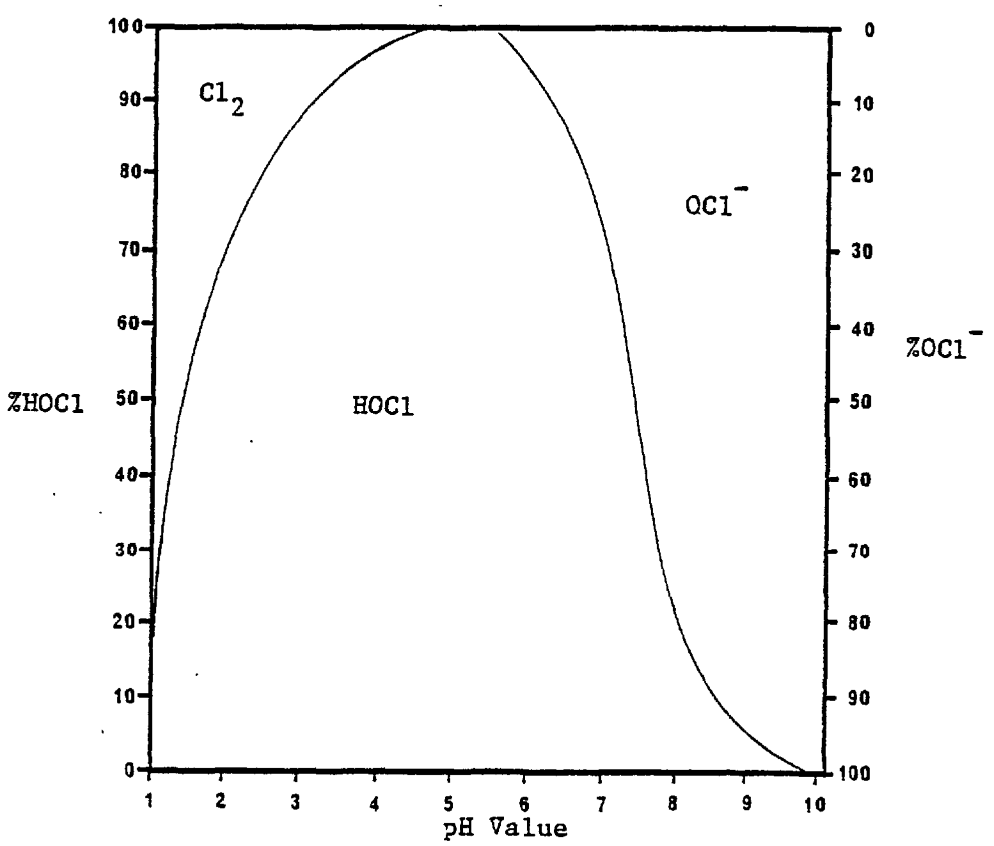


Figure 1.1 Effect of pH on HOCl dissociation

H_2OCl^+ would be more stable than Cl^+ but confirmed that this species also would only be present in insignificant concentrations during aqueous chlorination:-

$$Cl_2 + H_2O \; = \; H_2OCl^+ + Cl^- \qquad K \sim 10^{-30} \qquad (4)$$

Kinetic evidence, however, has indicated the participation of H_2OCl^+ in chlorination reactions and results in criticism of the proposed equilibrium constant values for equations (3) and (4)(17,18). It is generally accepted that the relatively unreactive hypochlorous acid is converted under certain conditions into more reactive chlorinating species:-

$$OCl^- + H^+ \; = \; HOCl \qquad (5)$$

$$HOCl + H^+ \; = \; H_2OCl^+ \qquad (6)$$

$$H^+ + HOCl + Cl^- = Cl_2 + H_2O \qquad (7)$$

$$2HOCl = Cl_2O + H_2O \qquad (8)$$

$$HOCl + AcOH = AcOCl + H_2O \qquad (9)$$

Other reactions, which do not appear to take part in the kinetics of chlorination but are significant as they contribute to the overall loss of chlorine, include:-

$$2HOCl + OCl^- = [H_2Cl_3O_3]^- \rightarrow 2H^+ + 2Cl^- + ClO_3^- \qquad (10)$$

The chlorate ion then reacts slowly at low pH with hydrochloric acid to form chlorine dioxide(19):-

$$2ClO_3^- + 4H^+ + 2Cl^- = Cl_2 + 2ClO_2 + 2H_2O \qquad (11)$$

Chlorine may also be lost by the decomposition of hypochlorous acid to form oxygen(20):-

$$HOCl = \tfrac{1}{2}O_2 + H^+ + Cl^- \qquad K = 10^{18} \qquad (12)$$

Although thermodynamically favourable reaction (12) is slow, particularly in the dark - the reaction rate being 50-200 times greater in sunlight. Hypochlorite ion disproportionates to form chlorate and perchlorate:-

$$3ClO^- = 2Cl^- + ClO_3^- \qquad K \sim 10^{27} \qquad (13)$$

$$4ClO^- = 3Cl^- + ClO_4^- \qquad K \sim 10^{26} \qquad (14)$$

Again, these reactions are thermodynamically favourable but very slow, slower even than reaction (12), and thus anions containing chlorine in such high oxidation states are not normally found in aqueous chlorine solutions. The disproportionation of OCl^- to form ClO_2^- is energetically more favourable than that of hypochlorous acid(21):-

$$2ClO^- = Cl^- + ClO_2^- \qquad K \sim 10^7 \qquad (15)$$

$$2ClOH = Cl^- + H^+ + HClO_2 \qquad K \sim 10^{-5} \qquad (16)$$

Table 1.1 Possible aqueous chlorine equilibria

REACTION		EQUILIBRIUM CONSTANT	REFERENCE
$Cl_2(g)$	$= Cl_2(aq)$	0.062	21
$Cl_2(aq)$	$= Cl^+ + Cl^-$	$10^{-40} - 10^{-60}$	15
$Cl_2(aq)$	$= H^+ + Cl^- + HOCl$	3.9×10^{-4}	10
$HOCl$	$= H^+ + OCl^-$	2.88×10^{-8}	11
$2HOCl$	$= Cl_2O + H_2O$	9.6 10^{-4} (0°C) 8.7 10^{-3} (20°C)	22 23
$Cl_2 + Cl^-$	$= Cl_3^-$	0.169	23
H_2OCl^+	$= H^+ + HOCl$	$\sim 10^3 - 10^4$ 4×10^{11}	19
$Cl_2 + H_2O$	$= Cl_2OH^- + H^+$	10^5	24
Cl_2OH^-	$= HOCl + Cl^-$	2×10^{-6}	24
$Cl_2 + H_2O$	$= H_2OCl^+ + Cl^-$	10^{-30}	17
$2HOCl$	$= Cl^- + H^+ + HClO_2$	10^{-5}	21
$2ClO^-$	$= Cl^- + ClO_2^-$	10^7	21
$3ClO^-$	$= 2Cl^- + ClO_3^-$	10^{27}	20
$4ClO^-$	$= 3Cl^- + ClO_4^-$	10^{26}	20
$2HOCl + OCl^- = [H_2Cl_3O_3]^- \quad 2H^+ + 2Cl^- + ClO_3^-$			
$2ClO_3^- + 4H^+ + 2Cl^- = Cl_2 + 2ClO_2 + 2H_2O$			

A comparison with the disproportion of other halogenated species is interesting. Hypobromite disproportionates moderately fast even at room temperature, thus solutions of BrO^- may only be produced and stored at 0°C. At 50-80°C quantitative yields of BrO_3^- are obtained:-

$$3Br_2 + 6OH^- = 5Br^- + BrO_3^- + 3H_2O \qquad (17)$$

The rate of disproprotionation of IO^- is so fast that the species is unknown in solution. How this affects halogenation by bromine or iodine at high pH is unknown. Table 1.1 lists known or postulated chlorine equilibria in aqueous solutions.

1.1.2 Reactivity of Chlorinating Species

Support for the existence of positive halogen containing species is provided by a direct comparison of the halogen substitution reaction with nitric acid nitration, the established mechanism of which involves the nitronium ion, NO_2^+ (25). The chlorinium ion, Cl^+, has been shown to be thermodynamically unstable(15) and its existence in aqueous solution is in doubt. There is no kinetic data to support the existence of Cl^+, the formation of H_2OCl^+ being of more significance in chlorination reactions. The overall rate of chlorination of anisole, $CH_3OC_6H_5$(AnH), for example, under acidic conditions(14) follows the rate equation:-

$$\frac{d[AnCl]}{dt} = k'[HOCl]^2 + k''[H_3O^+][HOCl]^2 + k''' [AnH][H_3O^+][HOCl] \qquad (18)$$

The reaction is carried out under conditions which suppress hypochlorite and chloride catalysis; and no term in the rate equation is consistent with a rate determining formation of chlorinium ion or with its involvement in the chlorination step. Those terms which are second order in HOCl describe the formation of chlorine monoxide in steps (19) and (20):-

$$2HOCl = Cl_2O + H_2O \qquad \text{(slow)} \qquad (19)$$

$$2HOCl + H_3O^+ = Cl_2O + H_3O^+ + H_2O \qquad \text{(slow)} \qquad (20)$$

$$Cl_2O + AnH = AnCl + HOCl \qquad \text{(fast)} \qquad (21)$$

while the term first order in HOCl may result from a termolecular reaction or a reaction of anisole with hypochlorous acidium ion, H_2OCl^+ (24):-

$HOCl + H_3O^+ + AnH \rightarrow AnCl + H_3O^+ + H_2O$ (slow) (22)

or:

$HOCl + H_3O^+ = H_2OCl^+ + H_2O$ (fast) (23)

$H_2OCl^+ + AnH \rightarrow AnCl + H_3O^+$ (slow) (24)

Kinetic data also indicate that free chlorine does not participate to any measurable extent in the reaction, having been suppressed by low concentrations of chlorine. Chlorination *via* a free radical mechanism is unlikely as p-AnCl always accounts for less than 68% of the AnCl product mixture, whereas the free radical chlorination of anisole by sulphonyl chloride at pH2 yields an AnCl mixture containing 80% p-AnCl.

Morris(12) calculated the relative reactivities for several forms of oxidizing chlorine species in dilute aqueous solutions at pH7. The comparison was made relative to HOCl and based on measured or predicted reaction rates of the reacting species with the same substrate at overall chlorine concentrations below 10^{-3}M (Table 1.2).

Table 1.2 Relative reactivities of chlorinating species

Species	Estimated Specific Reactivity	Fraction of Total Chlorine	Net Relative Reactivity
Cl_2	10^3	3×10^{-6}	0.003
HOCl	1	0.8	0.80
OCl	10^{-4}	0.2	0.00002
H_2OCl^+	10^5	10^{-8}	0.001
Cl_2O	2×10^5	3.2×10^{-8}	0.0064

The net relative reactivities indicate that at pH7 the dominant chlorinating species is hypochlorous acid, its greater concentration being more significant than the larger specific reactivities of chlorine or H_2OCl^+. In acid catalysed chlorination the increase in the concentrations of chlorine and H_2OCl^+ produces a corresponding increase in net relative reactivities to the extent that they become the dominant chlorinating species. The relative reactivity of chlorine monoxide, known to be a powerful chlorinating agent(22), and that of hypochlorous acid were calculated for reactions with allyl alcohol and ethyl crotonate(26). Such reactions, chlorine addition to a double bond, involve an electrophilic attack by the chlorinating species. The reactivity of chlorine monoxide was calculated to be 10^6-10^9 greater than that of HOCl, based on a chlorine monoxide equilibrium constant for reaction (19) of 10^{-3}(22). The low chlorine monoxide concentration signifies a low net relative reactivity, though at high chlorine concentrations, and at pH7, chlorine monoxide concentration may increase to the extent that it becomes significant in the chlorination step. There is no kinetic evidence to support this suggestion, however, in the chlorination of, for instance, phenols and amines, which are generally fast reactions. Thus, although chlorine monoxide might react rapidly with such species its slow formation would be rate determining, indicating that it is not a significant participant in such reactions.

1.1.3 Classification of Chlorination Reactions

The effects of chlorination on selected organic compounds under conditions similar to those in water disinfection have been studied(27); it was concluded that only ring structures with electron activating substituents or amino groups were chlorinated. The amino groups undergo conversion to organic chloramines rather than cleavage of the C-N bond. No chlorination of oxidation products were reported from the action of chlorine on organic acids.

Chlorination is further dependent on the type of substituents present and, in particular, on their effects in respect of electrophilic attack(28).

It is possible to classify chlorination reactions with organic compounds thus(29):-

(I) SUBSTITUTION REACTIONS

(a) Formation of N-chlorinated compounds
(b) Formation of C-chlorinated compounds

(2) ADDITION REACTIONS

(3) OXIDATION REACTIONS

1.1.4 Formation of N-Chlorinated Compounds

The presence of ammonia nitrogen and organic nitrogen in raw waters complicates chlorination of water supplies in as much as the relative amounts of these compounds present cause wide variations in chlorine requirement(30,31) and their chlorinated derivatives have mild oxidizing and chlorinating powers.

1.1.4.1 Chlorination of Ammonia

Ammonia, which is generally considered to be an indicator of pollution, is accepted as the main reactant with chlorine in raw waters causing a phenomenon now known as breakpoint chlorination(30,32,33). Essentially, chlorine reacts with ammonia in stepwise manner with the formation of chloramines, nitrogen trichloride and the evoluation of nitrogen with excess chlorine. This, in effect, removes ammonia from the system and is the main competing reaction with the chlorination of organics.

Chloramines, as mentioned earlier, have mild oxidising powers and will eventually chlorinate certain organics, the extent of this chlorination is not known but it has been reported that over prolonged contact periods, ring structures are chlorinated and oxidised by chloramines(27).

The formation of chloramines is rapid and in accordance with the following equations(34):-

$$NH_3 + HOCl = NH_2Cl + H_2O \qquad K = 3.6\times10^{9} \qquad (25)$$

$$NH_2Cl + HOCl = NHCl_2 + H_2O \qquad K = 1.33\times10^{6} \qquad (26)$$

$$NHCl_2 + HOCl = NCl_3 + H_2O \qquad (27)$$

With excess chlorine, the overall reaction becomes:-

$$2NH_3 + 3Cl_2 = N_2 + 6HCl \qquad (28)$$

The kinetics of ammonia chlorination will be discussed briefly as it is the predominant reaction in aqueous chlorination. The reaction between chlorine and ammonia can be considered as the replacement of H^+ by Cl^+, the rate of such a reaction should vary with electrophilic character of the chlorine species(12,13). Conversely, it may be considered as a nucleophilic attack of the nitrogen containing compounds on the chlorine species, thus an increase in the rate of reaction with increased basicity of the reactant nitrogen compounds is to be expected(12,13). The reaction between ammonia and chlorine is rapid, governed by second order kinetics(12,34):-

$$\frac{d[NH_2Cl]}{dt} = k[NH_3][HOCl] \qquad (29)$$

(where $k = 5.1 \times 10^6$ l mol^{-1} sec^{-1} at 25°C), and pH dependent; it is, therefore, considered to proceed *via* a bimolecular mechanism of chloramine formation. The rate attains a maximum at pH8, 99% of chlorine reacting withint 60 seconds(20). At pH5 and pH11, equilibrium is reached in 210 minutes and 50 minutes respectively.

The rate of reaction between monochloramine and chlorine is also second order but, for uncatalysed systems, very much slower than the corresponding ammonia reaction ($k = 3.4 \times 10^2$l mol^{-1} sec^{-1} at 25°C(12)). The reaction is greatly enhanced by H_3O^+ and acetic acid. The rate constant for acid catalysed reaction (k_2') is given by equation:-

$$k_2' = k_2\left[1 + k_{2H}[H^+] + k_{2A}[AcOH]\right] \qquad (30)$$

where $k_{2H} = 5 \times 10^4$

$k_{2A} = 2 \times 10^2$

The overall rate of reaction for acid catalysed systems is given by:-

$$\frac{d[NHCl_2]}{dt} = k_2'[NH_2Cl][HOCl]$$

$$= k_2[NH_2Cl][HOCl] + k_{2H}[NH_2Cl][HOCl][H^+] + k_{2A}[AcOH][HOCl][NH_2Cl] \qquad (31)$$

The first term is due to direct bimolecular reaction between chloramine and hypochlorous acid. The second term is analogous to the general reaction for substitution reactions with aromatics:-

$$HOCl + H^+ = H_2OCl^+ \qquad \text{(fast)} \qquad (32)$$

$$H_2OCl^+ + NH_2Cl = NHCl_2 + H_3O^+ \qquad \text{(slow)} \qquad (33)$$

or:

$$HOCl + H_3O^+ + NH_2Cl = NHCl_2 + H_3O^+ + H_2O \qquad \text{(slow)} \qquad (34)$$

The third term is probably due to the formation of acetyl hypochlorite and presents an interesting comparison with kinetic data obtained for chlorination of allyl alcohol(26), in which the formation of acetyl hypochlorite is rate determining, the acetyl hypochlorite reacting with the allyl alcohol as fast as it is formed. The chloramine reaction indicates the opposite, that acetyl hypochlorite formation is fast and the rate determining step being the chlorination of chloramine by acetyl hypochlorite.

These are the two most important reactions between ammonia and chlorine. Other reactions such as the formation of nitrogen trichloride, which tends to form mainly under acid conditions(12,33), or the disproportionation reaction of monochloramine do occur but at relatively low rates in neutral waters. At 25°C, hypochlorous acid reacts almost 10^4 times as rapidly with NH_2Cl as does NH_2Cl which is in accordance with the greater electrophilic nature of HOCl over NH_2Cl(12).

1.1.4.2 Chlorination of Organic Nitrogen

Dissolved nitrogen compounds in natural waters are mainly of biological origin(35-39) including amino acids, proteins and amines. The enzymic hydrolysis of proteins yields α-amino acids, which undergo further enzymic attack yielding ammonia and fatty acids. In natural waters, therefore, a variety of organic compounds differing in degree of hydrolysis is to be expected as is the gradual liberation of ammonia. Tara(40,41) studied the chlorination of organic nitrogen and observed that the loss of nitrogen during chlorination was a function of chlorine demand, contact time and the character of the nitrogen-containing species. It has been established that the presence of organic nitrogen in waters alters the classical breakpoint type clorination curve of ammonia. This plateau effect results in very little loss of nitrogen and the presence of an irreducible minimum residual chlorine level, which subsequently produces residuals of greater nuisance such as dichloramine and nitrogen trichloride.

The relationship between chlorination and nitrogen is given by the expression:-

$$D_t = D_1 \; t^n$$

where: D_1 = the chlorine demand after one hour contact
D_t = the chlorine demand after t hour contact
n = factor dependent on the reactivity of the nitrogen

Chlorine demand = Chlorine dose − Chlorine residual

Variation in n indicates the nature of the organic compound involved in the reaction with chlorine. The higher the value of the exponent, the more complex the organic compound. Well waters for example have exponents with values ranging from 0.01-0.05 while treated surface waters range from 0.1-0.2, showing an increase in organic nitrogen which is more resistant to chlorination.

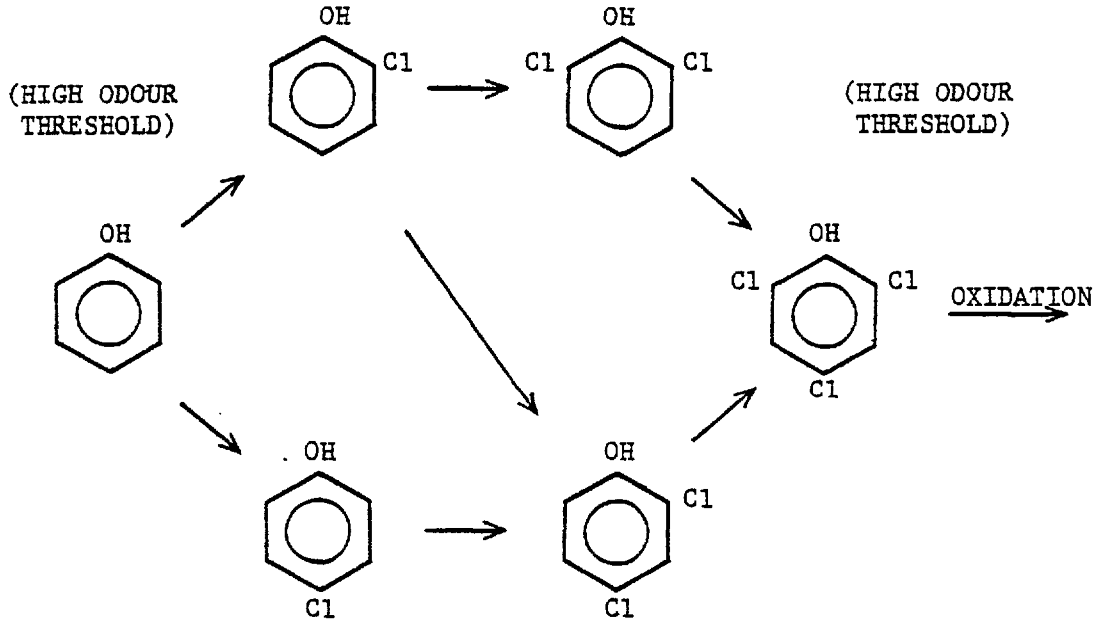
The reactivity of organic nitrogen towards chlorination was studied by Morris(12,42) in terms of simple amines, obtaining kinetic data on a number of these reactions giving an insight into the mechanisms of reaction and a comparison with the ammonia reactions.

This subject area has been discussed more fully in a recent report published by the Water Research Centre (OR14)(120).

1.1.5 Formation of C-Chlorinated Compounds (Aromatic Chlorination)

The problems of phenolic type compounds in waters giving rise to tastes and odours after chlorination have prompted extensive studies into the formation of chlorophenols. Bertschell et al(43) have isolated and identified a number of chlorophenols produced by the chlorination of phenol in dilute aqueous solution. A series of reactions was proposed (Scheme 1) to explain the phenomenon that excessive chlorination eventually destroys tastes and odours.

Scheme 1



The mechanism of reaction is electrophilic attack by hypochlorous acid on the phenoxide ion(44) such that:-

$$\frac{-d[HOCl]}{dt} = k[PhO^-][HOCl] \qquad (43)$$

This equation was established from observations that the rate of reaction increases and reaches a maximum as pH increases from near neutral. Soper(44) noted a change in reaction kinetics in the presence of hydrochloric acid to the extent that the rate of reaction became independent of phenol concentration:-

$$V = k[H^+][Cl^-][HOCl] \qquad (44)$$

and concluded that the rate determining step in the presence of hydrochloric acid is the formation of molecular chlorine:-

$$HCl + HOCl = Cl_2 + H_2O \qquad (45)$$

Phenol reacts with molecular chlorine faster than with hypochlorous acid, primarily because of the more electrophilic nature of molecular chlorine.

In the absence of chloride, but under acidic conditions, de la Mare(16,45) established a series of rate equations dependent on the reactivity of the aromatic system. This was based on earlier work by Derbyshire(46) who had established a rate equation for the chlorination of sodium benzyl sulphonate under acid conditions:-

$$\frac{-d[HOCl]}{dt} = k[ArH][H^+][HOCl] \qquad (46)$$

de la Mare applied this equation to aromatics with low reactivity such as benzene and toluene and proposed that for more reactive compounds such as phenol and anisole at low concentrations of hypochlorous acid and substrate, the reactions follow:-

$$\frac{-d[HOCl]}{dt} = k[HOCl] + k'[HOCl][H^+] \qquad (47)$$

The rate of reaction above a critical concentration becomes:-

$$\frac{-d[HOCl]}{dt} = k[HOCl] + k'[HOCl][H^+] + k''[HOCl][H^+][ArH] \qquad (48)$$

To explain these different equations, de la Mare proposed a series of equilibria:-

$$HOCl = Cl^+ + OH^- \qquad (49)$$

$$HOCl + H^+ = H_2OCl^+ \qquad (50)$$

$$H_2OCl^+ = Cl^+ + H_2O \qquad (51)$$

$$Cl^+ + ArH = ArCl + H^+ \qquad (52)$$

The rate equation (46) describes a reaction involving either H_2OCl^+ or Cl^+, in whith the rate determining step is either a termolecular reaction (HOCl, H^+ and ArH) or a reaction of the aromatic compounds with hypochlorous acidium ion or chlorinium ion. The rate of reaction at low aromatic and hypochlorous acid concentrations is independent of aromatic concentration. Rate determining steps for such a reaction are (53) and (55):-

$$HOCl \rightarrow Cl^+ + OH^- \qquad \text{(slow)} \qquad (53)$$

$$(HOCl + H^+ \rightarrow H_2OCl^+) \qquad \text{(fast)} \qquad (54)$$

$$H_2OCl^+ \rightarrow Cl^+ + H_2O \qquad \text{(slow)} \qquad (55)$$

On increasing the aromatic concentration above a critical level, a third term dependent on aromatic concentration appears. The aromatic concentration is high enough for direct reaction with H_2OCl^+ before the latter dissociates to form Cl^+:-

$$H_2OCl^+ + ArH \rightarrow ArCl + H_3O^+ \qquad (56)$$

though a termolecular reaction is also possible(14). Tbese hypotheses were based on chlorinium ion (Cl^+) which, as discussed earlier, is now considered unlikely in aqueous solutions.

An alternative mechanism that would correspond to equations (49-56), but not incorporate the formation of chlorinium ion, was proposed by Arotsky and Symmons(18) who based their criticism on the use by de la Mare of silver perchlorate to inhibit chlorine formation. There is a possibility that under the conditions used by de la Mare, $AgCl_2^+$ is formed:-

$$AgCl_{(s)} + H_2OCl^+ \overset{k_1}{=} AgCl_2^+ + H_2O \qquad (57)$$

$$AgCl_2^+ + ArH \xrightarrow{k_2} ArCl + AgCl_{(s)} + H^+ \qquad (58)$$

This would be in accord with the kinetic data if $k_2 > k_1$, i.e. k_1 rate determining, making the reaction independent of silver ions in solution and of aromatic substrate. de la Mare found no dependence of reaction on silver ion concentration.

Swain and Crist(14), in an attempt to resolve the discrepancies between kinetic data, which favour the formation of chlorinium ion and thermodynamic data which indicate that the formation of Cl^+ is unlikely in aqueous solution, established an alternative rate equation for anisole chlorination under similar conditions to de la Mare:-

$$\frac{d[AnCl]}{dt} = k'[HOCl]^2 + k''[H_3O^+][HOCl]^2 + k'''[AnH][H_3O^+][HOCl] \tag{59}$$

This equation was discussed earlier and it was shown that the first two terms, being second order in HOCl, are due to slow formation of chlorine monoxide and not the formation of chlorinium ion (Cl^+), $AgCl^+$ or Cl_2 since these processes would be first order in HOCl corresponding to the de la Mare equation.

Grimley(47) reported that at pH < 2 and at high chloride concentration, phenol is chlorinated *via* a rapid bimolecular reaction in which an intermediate is formed which, subsequently, decomposes *via* three parallel pathways: an H^+ ion and Cl^- ion dependent path, an H^+ ion dependent path and an H^+ ion and Cl^- independent path:-

$$Cl_2 + C_6H_5OH \rightarrow [Cl_2C_6H_5OH] \tag{60}$$

$$[Cl_2C_6H_5OH] \rightarrow Cl\ C_6H_4OH + H^+ + Cl^- \tag{61}$$

$$\frac{-d[Cl_2]}{dt}(aq) = k'[C_6H_5OH](aq) \tag{62}$$

and

$$\frac{-d[Cl_2C_6H_5OH]}{dt} = \left[k[H^+][Cl^-] + k'[H^+] + k''\right][Cl_2C_6H_5OH] \tag{63}$$

Lee observed that on chlorinating phenols in acid solutions, an unidentified intermediate was formed which slowly decayed(28). Kinetic information on the relative composition and reaction rates of chlorophenols in chlorinated waters(28.44) show that the maximum rate of chlorination is dependent on the acidity of the chlorophenol. The more acidic phenols display a shift in the position of the maximum towards lower pH values. The products of the rate constants and the acid dissociation constants for the compounds under chlorination were found to be constant and approximately equal to 10^{-4}, which is in agreement with previous phenolic chlorination data(44). More acidic phenols, containing electrophilic substituents have lower rates of reaction with corroborates the mechanism of electrophilic attack by the chlorinating species. In contrast to N-chlorination, the rate constants for phenol chlorination at pH values greater than 6 were found to be indpendent of ionic strength, concentration of buffer and chloride concentration. Carlsón et al(48) subjected a number of aromatics to chlorination at varying pH, again showing the dependence of rate on pH (Table 1.3). In this case, the pH adjustment was made by the addition of hydrochloric acid which is known to enhance chlorination by molecular chlorine(44) rather than by hypochlorous acid(28,44).

Substituent groups, such as $-OH$, $-NH_2$ or alkyls, tend to promote electrophilic substitution of the aromatic, whereas reaction is suppressed to nitrile, chloro or carbonyl substituents.

The position at which an aromatic compound undergoes substitution is not only dependent on substituents present but also on the nature of the chlorinating species. Activating groups towards the electrophilic attack will give rise mainly to o- and p-chloro derivatives the percentage of each being dependent on pH(19). During the chlorination of anisole(14), for example, as pH decreases the fraction of p-chloroanisole also decreases from 68% at 5×10^{-3} M H_3O^+ to 58% at 1 M H_3O^+ indicating a change in selectivity by the chlorinating species. The chlorination of toluene(17.49) in acetic acid by molecular chlorine gives an o-:-p ratio of 0.75, whereas chlorination by H_2OCl^+ in water yields a product ratio of 1.75.

Concern that PCBs were being formed during chlorination of waste waters containing biphenyls(50) led to studies on biphenyl chlorination chemistry(48,50,51,52). Chlorination, it was found, does occur at specifically active sites in the 2, 3 and 4 positions, the higher chlorinated isomers 2, 2'-; 2, 3'-; 3, 4', and 4,4'- being formed at high chlorine concentrations (500 ppm). From this work, Carlson concluded that polychlorinated aromatics in effluents were not produced by dilute aqueous chlorination, as the substitution of chlorine into an aromatic system immediately deactivates the ring from further electrophilic chlorination. Highly activated aromatics, such as phenol, however, will polychlorinate(28,43). Lee observed that chlorophenols tend to undergo oxidative ring rupture, the degree of oxidation being

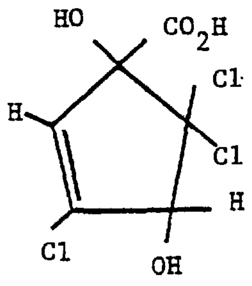
Table 1.3 Relative reaction rates of substituted aromatics(48)

Compound	pH		
	3 %Cl_2 uptake	7 %Cl_2	10.1 %Cl_2
Phenol	97.8	97.6	97.6
Anisole	80.7	11.4	2.6
Acetanilide	55.3	3.4	-
Toluene	11.1	2.9	-
Benzyl alcohol	2.3	-	-
Benzonitrile	2.1	-	-
Nitrobenzene	1.8	-	-
Chlorobenzene	1.8	-	-
Methyl benzoate	1.8	-	-
Benzene	1.5	-	-

Aromatic compounds 9.5 × 10^{-4}M; Chlorine initial (7.0 × 10^{-4}M) uptake after 20 minutes, 25°C

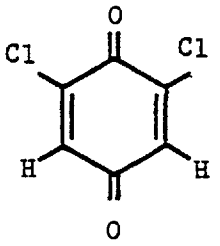
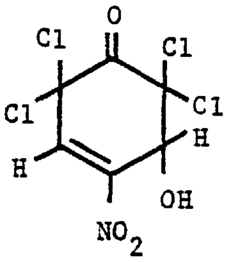
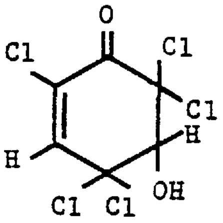
greater the more highly chlorinated the phenol.

The reaction of hypochlorite and phenol(53) under strongly alkaline conditions yields a polychlorinated alicyclic 5-membered ring system (A):



(A)

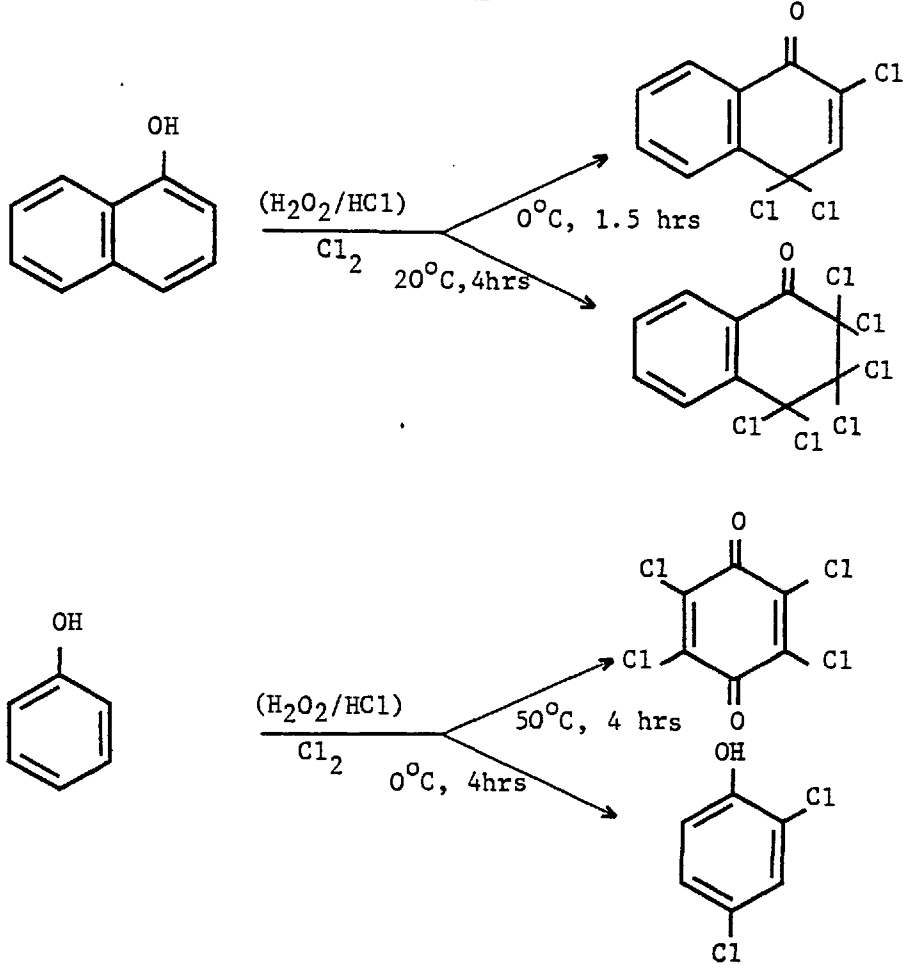
Under less drastic conditions(54), polychlorinated non-ring structures were isolated which are similar to the intermediates found during the formation of (A). p-Nitrophenol forms highly chlorinated products with the unexpected loss of the nitro groups in one of the products under acid conditions:-

No ring contraction occurs, but it is interesting to note in the formation of quinones a potential precursor to the haloform reaction is produced.

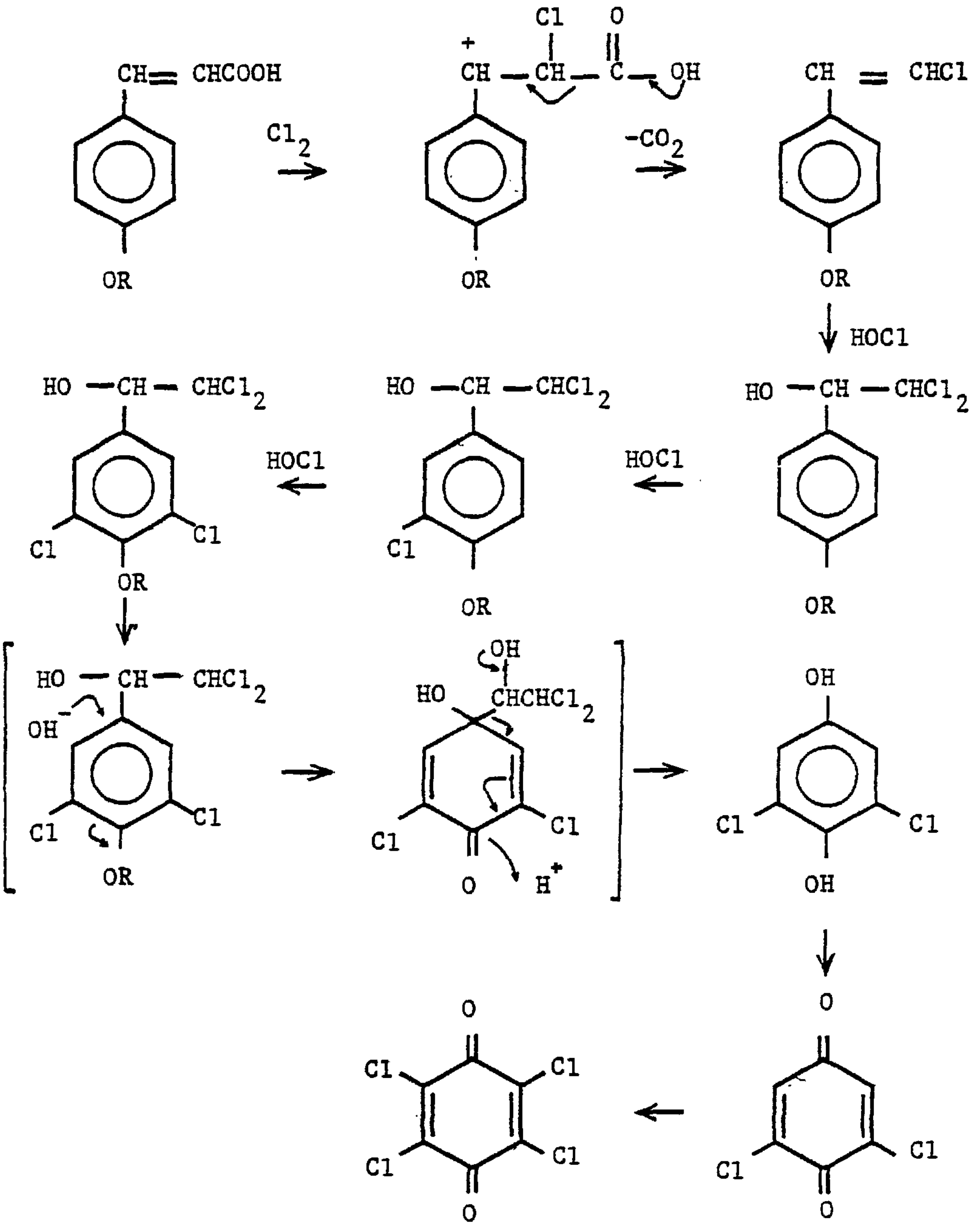
The rate of chlorination of many polyaromatics may be faster than for benzene or even phenol. Biphenyl is estimated to be 426 times

SCHEME 2



more reactive than benzene and phenanthracene has been measured to react 10^4 as fast(55) as benzene. α-Napthol yields higher chlorinated products than phenol under the same chlorination conditions(56) (H_2O_2/HCl - equivalent to molecular chlorine reaction) (Scheme 2).

Scheme 3



Hsu(57) has reported a detailed study of the chlorination of p-hydroxycinammic acids. In addition to oxidative chlorination, these naturally occurring phenyl-propanoid species also undergo chlorine substitution reactions in the side chains and the aromatic ring. Chlorination in the side chain is followed by decarboxylation and electrophilic substitution with the eventual elimination of the side chain. The final products of the reactions are chlorinated phenols and benzoquinones (Scheme 3).

This reaction may be compared with that of tyrosine, an α-amino acid, which also undergoes oxidative decarboxylation but, due to the amino group, tends to yield the corresponding nitrile derivative as the major product. The loss of the side chain and the eventual formation of quinones is similar to the reaction of p-nitrophenol.

Chlorination studies(58,59) on pyrene and benzo(ghi) perylene in dilute aqueous solutions have shown that polyaromatics are easily chlorinated with reaction rates of the same order of magnitude as compounds such as phenol. At pH above 6.5, the mechanism of PAH chlorination is first order in PAH and HOCl:-

$$\text{Rate} = k[\text{HOCl}][\text{PAH}] \qquad (64)$$

At pH 6, the rate becomes acid catalysed such that:-

$$\text{Rate} = k[\text{HOCl}][\text{PAH}] + k'[\text{HOCl}][\text{PAH}][\text{H}^+]^{0.2} \qquad (65)$$

the second term corresponding to the presence of H_2OCl^+ as a chlorinating species.

The rate for pyrene (k = 34.4 $l\ mol^{-1}\ s^{-1}$ at 20°C), compared to that phenol (k = 10 $l\ mol^{-1}\ s^{-1}$ at 25°C), indicates that these cholrination reactions are potentially competitive. Oxidation of PAH to quinones, which is the most likely route to break down of aromatic rings(60,61), has been noted after treatment with chlorine or chlorine dioxide(62).

1.1.6 Addition Reactions

Rates of reaction for this type of chlorination are generally slow(12) and might not be significant in water or waste water chlorination unless activated by substituent groups(19). Kinetic studies on chlorination of allyl alcohol in aqueous solutions(26) have suggested a rate equation of the form:-

$$\text{Rate} = k'[\text{HOCl}][C_3H_5OH] + k''[\text{HOCl}]^2 \qquad (66)$$

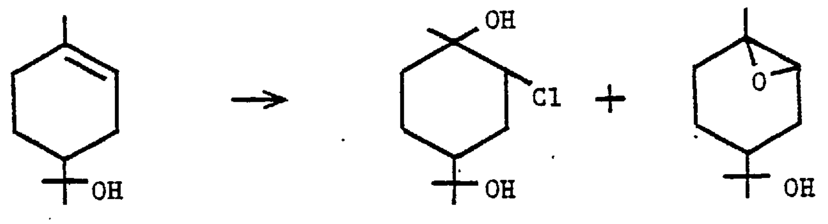
when: $k' \sim 2\ l\ mol^{-1}\ min^{-1}$ at pH 4.5

$k'' \sim 8\ l\ mol^{-1}\ min^{-1}$ at pH 4.5

These rate constants are in the region of 10^2-10^3 times lower than for phenol and 10^6 times lower than for ammonia and simple amines. The appearance of a second order term independent of allyl alcohol concentration indicates that chlorine monoxide formation is a rate determining step, chlorine monoxide reacting as fast as it is formed. At high chloride concentrations, it is possible that dichlorides are formed rather than chlorohydrins(52).

The chlorination of α-terpineol, a ubiquitous natural product, has been studied(63) in an attempt to identify any stable toxic chlorinated derivatives that might arise due to aqueous chlorination. Kinetic

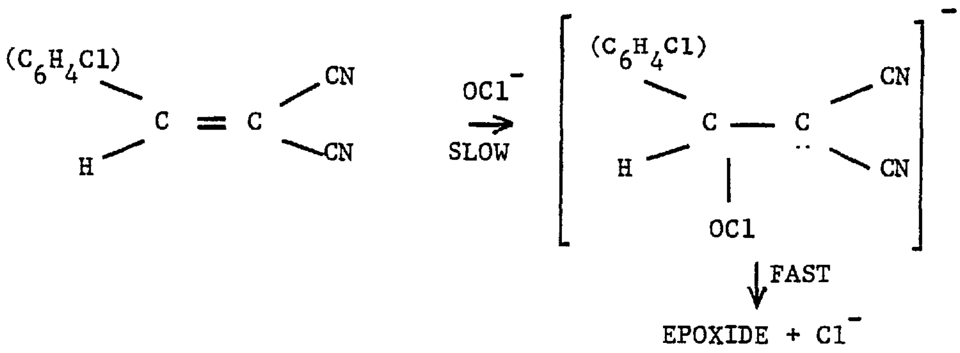
Sheme 4



α-terpineol (I) (II)

data is not available, but at high pH, the products formed are mainly (I) and (II) (Scheme 4), while at low pH, the main product formed is (I). The mechanism for epoxide formation appears to be *via* initial chlorination and subsequent elimination of HCl. For certain nitriles however, a mechanism for epoxide formation *via* nucleophilic oxygen attack by hypochlorite has been postulated$^{(64)}$ (Scheme 5). Whatever the mechanism epoxide formation is enhanced in alkaline solution, which is in accordance with general observations, that oxidation predominates over chlorination in alkaline solution$^{(19,65)}$.

Scheme 5



1.1.7 Oxidation Reactions

It has been claimed that oxidation is the predominant reaction of hypochlorous acid with organic species in natural and processed waters$^{(29)}$; such reactions normally involving carbohydrates and carbohydrate-related compounds. Several α-amino acids are oxidatively decarboxylated by hypochlorous acid to yield mixtures of the corresponding nitriles and aldehydes$^{(66)}$. A similar reaction has been observed for peptides with hypobromites under strong alkaline conditions$^{(67)}$. In general, the nature of the reaction with proteins, peptides and amino acids is dependent on pH$^{(65)}$, chlorination predominating in acid solutions while oxidation becomes more significant with increasing pH.

The pulp and textile industries make use of the effect of pH on the oxidising capacity of chlorine. During the bleaching process the breakdown of the natural product, cellulose, can be prevented if chlorination is carried out at low pH(68), as selective destruction of coloured substances takes place under these conditions with the minimum degradation of the fibre. As the pH is increased the oxidation capacity of the chlorine solution increases and is eventually capable of breaking down the cellulose structure. The attack reaches a maximum between pH7 and pH8 when the concentration of the chlorine species OCl^- and HOCl are equal(69).

The susceptibility of cellulose to degrade is attributed to the presence of hydroxyl and oxygen substituents at adjacent carbon atoms in the structure. This configuration results in an activated C-C bond which renders it susceptible to oxidation. The susceptibility of this configuration to oxidation is also considered as a route in aromatic ring fission, possibly *via* the formation of quinones.

1.1.8 Inter-Halogen Relationships

Improved germicidal activity has been observed during chlorination in waters containing bromide(70). This has been attributed to oxidation of bromide or iodide salts by chlorine producing the corresponding hypohalous acid(12,71):-

$$HOCl + X^- = HOX + Cl^- \quad \text{(when X = Br or I)} \qquad (67)$$

The hypohalous acid in acid conditions establishes an equilibrium with chloride(71,72):-

$$BrCl + H_2O = HOBr + HCl \quad (K = 2.94\times10^5 \text{ at } 0^\circ C \text{ for Br}) \, (68)$$

The presence of bromide, therefore, will give rise to not only chlorinated but also brominated compounds and as hypobromous acid is formed in preference to hypochlorous acid, the degree of bromination will be dependent on their relative concentrations. Studies on the relative rates of reaction of bromine chloride and of bromine with a variety of aromatic hydrocarbons shows that the reactivity of BrCl is on average greater than that of Br_2 by a factor of 20(73), but both yield only brominated compounds. Thus, bromine chloride acts solely as a brominating agent with aromatic compounds in electrophilic substitution reactions as hypobromous acid is the predominant electrophilic species in solution. In addition reactions BrCl is 100 times more reactive than Br_2(74).

Hypobromous acid has a lower dissociation constant than HOCl:-

$$HOBr \;=\; OBr^- + H^+ pK_A\ 8.7 \quad (HOCl,\ pK_A = 7.45) \qquad (69)$$

At pH8, 90% of bromine is present as HOBr, while for chlorine, only 19% is present as HOCl. The hypohalous acid is a more reactive halogenating agent than the hypohalite ion, which is reflected in the greater germicidal activity of bromine over chlorine at higher pH values(71). The rate of bromination when chlorinating bromide-containing waters is dependent not only on bromide concentration, but also on the rate of formation of hypobromous acid relative to the rate of chlorination of organics present.

1.1.9 Environmental Significance of Kinetic Data

The significance of laboratory kinetic data relative to environmental situations is complicated by the complex nature of waters. A model of the composition of chlorinated waters based on kinetic data for ammonia and simple amines has been reported(75). Various chloro-organics have been detected in sewage effluents(29,76-79), cooling waters(29) and potable waters(80,82) after chlorination, a number of which are listed in Tables 1,4, 1.5 and 1.6.

The detection of chloro derivatives of benzene and toluene at significant concentrations indicates that chlorination of relatively unreactive aromatics does occur. Most of the chloro-aromatic compounds, however, are derived from "activated" aromatic compounds, while the chloro-heterocyclic compounds have possible biological origin(29). The total concentration of non-volatile chloro-organics, which are formed after chlorination of sewage, accounts for less than 4% of the total input chlorine, most of the chlorine being converted to chloride(29). Glaze(78) found that the chlorination of sewage effluents with chlorine doses of ∿1500 mg/l for a contact period of one hour, produced a total organic-bonded chlorine concentration of 3000-4000 µg/l. Jolley(29)

Table 1.4 Chlorinated organics detected after the chlorination of sewage effluent and cooling waters(29)

Compound	Concn. µg/l
8-Chloroxanthine	1.5
5-Chlorouridine	1.7
5-Chlorouracil	4.0
2-Chlorobenzoic acid	0.3
3-Chlorobenzoic acid	0.6
4-Chlorobenzoic acid	1.1
3-Chloro-4-hydroxybenzoic acid	1.3
4-Chlorophenylacetic acid	0.4
4-Chloro-3-methylphenol	1.5
4-Chlororesorcinol	1.2

Table 1.5 Chlorinated organics detected after the chlorination of waste water effluent(76)

Compound	Concn. µg/l
Chlorocyclohexane	20
o-dichlorobenzene	10
p-dichlorobenzene	10
Chloroethylbenzene	21
Dichloromethoxytoluene	32
Trichloroethylbenzene	12
Tetrachlorophenol	30
Tetrachloromethoxytoluene	50

Table 1.6 Halogenated compounds detected in drinking water(80-82,125)

Bromodichloromethane
Bromoform
Chloroform
Chlorobenzene
Dibromochloromethane
Dichloroethane
1, 1-Dichloro - 2-Hexanone
Hexachlorocyclohexane
Hexachloroethane
Tetrachloromethane
Tetrachloroethylene

detected higher levels of chlorinated organics in colling waters originating from raw river water than in chlorinated sewage effluents. He attributed this to the fact that sewage effluents contain a much higher level of ammonia which, on chlorination, is converted to chloramines causing a reduction of free chlorine and an associated decrease in chlorinating potential. Studies(28) on the competitive chlorination of phenol and ammonia have shown that the rate of production of chloramine at pH8 and 20°C is two to three orders of magnitude greater than that for monochlorophenol. Murphy et al(27) found that the presence of ammonia drastically reduced the rate of phenol chlorination while Stevens et al(83), on chlorinating humic acid solutions in the presence of 5.2 mg/l of ammonia nitrogen, found that if breakpoint chlorination was not reached, a considerable reduction in trihalomethane formation occurred.

1.2 TRIHALOMETHANES

Interest in the formation of haloforms during the chlorination of water supply arose primarily from the work undertaken by Rook(84) who, in 1974, reported the presence of trihalomethanes in treated waters. Rook postulated that the precursors of the trihalomethanes were the humic materials in the water which react with the chlorine added for disinfection purposes. A subsequent survey in the United States on trihalomethanes in potable waters carried out by the EPA(79) concluded that chloroform is present in all waters after treatment with chlorine.

Considerable research has been reported in the past five years on trihalomethane formation in treated waters. The EPA survey, though, remains the most comprehensive source on the levels of the trihalomethanes in treated waters in the United States. No comparable survey has been carried out to establish the levels of the trihalomethanes in treated waters in the United Kingdom.

A survey in Germany involving 27 cities established considerably lower trihalomethane concentrations in treated waters compared to the levels in the United States (Table 1.7)(85). This difference in trihalomethane levels was attributed to the different approach in Germany in the use of chlorine as a disinfectant and not to dissimilarities in the quality of the water supply. Chlorine is used sparingly in Germany and is

Table 1.7 Main components of halogenated hydrocarbonds in drinking water, found in the US and in the Federal Republic of Germany

	Mean Concentration (μg/l)		
	USA[a]	Germany[b]	Germany[c]
Chloroform ($CHCl_3$)	21	2.5	6.4
Bromodichloromethane ($CHBrCl_2$)	6		3.4
Dibromomonochloromethane ($CHBr_2Cl$)	1		

[a] 80 cities
[b] 27 cities
[c] 12 cities

generally limited to doses of less than 1 mg l^{-1} (88,22) which is in contrast to the more liberal use of chlorine in the United States. The prime example of the high chlorine usage in the United States water treatment plants is the wide spread practice of pre-chlorination for the control of slime growth and as an initial stage of disinfection. This practice is the main cause for the production of the high trihalomethane concentrations found in United States finished waters. In view of this the EPA(87) recommended that pre-chlorination should be minimised if, as a result and without any detrimental effect on disinfection standards, trihalomethane levels in finished waters are reduced.

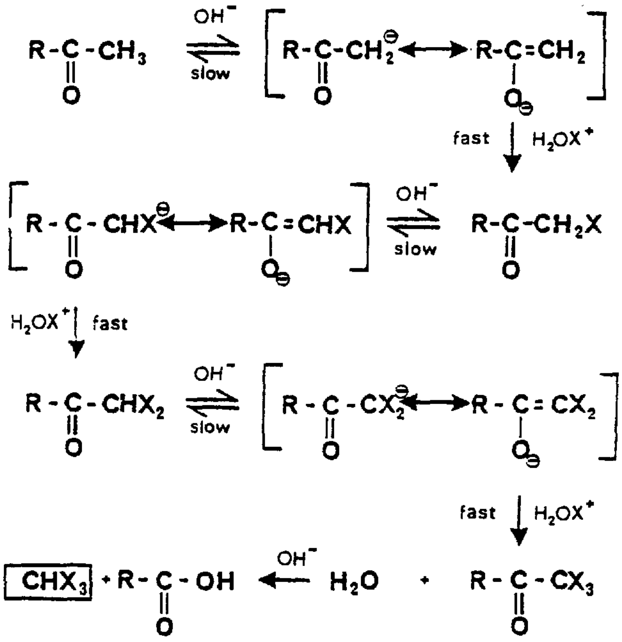
1.2.1 Trihalomethane Formation

It is now generally accepted that during water treatment, the chlorine added reacts with the humic material to produce chloroform, the levels of brominated trihalomethanes being enhanced when bromide is present in the raw water.

1.2.1.1 Haloform Reaction

The haloform reaction may be described as "the successive replacement of hydrogen by halogen on the α-carbon to a carbonyl group, followed by eventual hydrolysis to produce a trihalomethane (haloform) and generally a carboxylate" (Scheme 6)(89). The slow, rate determining, step is proton dissociation which is independent of halogen

Scheme 6



concentration(88). The rate of chloroform formation from acetone for example is pH dependent, the rate increasing on increasing the pH (83).

1.2.1.2 Precursors

Acetone was of particular interest during the initial investigation of precursors to chloroform because of its well-established haliform reaction. Stevens(83) compared the chlorination kinetics of acetone and humic acid and concluded that acetone would have to be present at concentrations in excess of 15 mg/l to account for the haloform levels measured in potable waters. The levels of acetone in source waters are generally too low to be significant in haloform production.

Chlorine gas(84) was also considered as a potential source of trihalomethane but was soon dismissed as no chloroform or bromoform could be detected in the gas using methods which would have given detection limits equivalent to 0.02 and 0.14 μg 1^{-1} respectively under normal chlorination procedures.

Although humic material is now generally accepted as the main precursor to chloroform, Morris(89) suggests that many other natural products which do not contain the meta dihydroxy moiety and which readily undergo the haloform reactions (as a result of their ability to form an active carbonion) must be considered when attempting to inhibit chloroform formation during water treatment.

Other potential substrates for haloform reaction were investigated by Rook(84). Hydroquinone, catechol, resorcinol and pyrogallol all yielded chloroform though the chloroform yields varied depending on the structure of the substrate. The rates of reaction were dependent on pH similar to the traditional haloform reactions with acetone(89). From these experiments Rook suggested(90) that the substrate structures most susceptible to trihalomethane production contain two hydroxyl or ketonic groups meta or beta- to each other. Resorcinol and 1, 3-cyclohexadione for example give much higher chloroform yields than acetone or 1, 2-cyclohexadione. Consequently as both humus and fulvic acids are based on polycondensates of di- and trihydroxyl bezenes containing 5%-10% glucosidic and peptide type N-bonds(31,91), Rook postulated that the amount of chloroform produced is based on the number of resorcinol type structures in a humic or fulvic acid molecule. From assumed structures for these acids(92) he calculated that the chloroform yield was equivalent to 0.2%-0.4% of the total carbon content (i.e. 1 carbon atom in 250-500 reacting to give chloroform). This agrees well with the reported trihalomethane yields from treated waters and on chlorinating humic and fulvic acids extracted from natural waters, ranging between 0.2% and 1.6% of the carbon content(82,84,93-96). The yield of chloroform will be greatly influenced by the cholrine dose, pH, temperature and other factors which control the kinetics of chloroform formation.

Babcock(94) reported that on chlorinating humic and fulvic acids, extracted from the same source, humic acid yielded greater amounts of chloroform than an equivalent amount of fulvic acid. Oliver found no difference in chloroform formation on chlorinating humic and fulvic acid though it is not clear whether these acids originated from the same source, an important factor when comparing the relative rates of chloroform formation between these two acid fractions.

Babcock(94) also observed that coagulation of humic and fulvic acids with Alum not only reduced the colour and TOC but also the chloroform yield per unit weight of acid, concluding that coagulation not only reduced precursors but in addition was selective in removing humic and fulvic acids most responsible for chloroform production.

Linear correlations between trihalomethane formation and total organic matter have been reported from laboratory studies(84,94,95) and data obtained from finished waters(94,97).

Carns(98) reported that the seasonal variations in trihalomethane formations, at a particular water works, correlated well with the humic content of the raw water, reaching a maximum during the winter months, when the organic content was high and a minimum during the summer months, when the organic content was low. This is in contrast to a report by Hohen(99) who found that the seaonsal variation in trihalomethane formation (at a different water works to Carns) showed only a low correlation with TOC levels which is surprising as the former correlated well with chlorine demand which reached a maximum during the summer months.

1.2.1.3 Bromide

The improved germicidal activity observed during chlorination of water supply containing bromide was attributed to the oxidation of bromide by chlorine to produce hypobromous acid (see Section 1.1.8). The hypobromous acid is involved in bromination reactions in a similar manner to hypochlorous acid.

On adding chlorine to waters containing bromide a mixture of hypobromous acid and hypochlorous acid are formed(69) which on reacting with the humic material present in the water produce the trihalomethanes; chloroform; bromodichloromethane; chlorodibromomethane and bromoform(100-102). The relative concentrations of these trihalomethanes will depend on the chlorinating conditions and the concentrations of bromide in the raw water. Kleopfer(102) observed that no chloroform was produced on chlorinating waters containing more than 2 mg l^{-1} bromide, all the trihalomethane being present as bromoform.

The presence of bromide is known to increase the formation of bromine containing trihalomethanes(100-102) and evidence exists that the yield of total trihalomethane formation is also increased as a consequence of the greater chemical reactivity of the hypobromous aicd compared to hypochlorous acid(69),

Lange(103) investigated the effect of salt water intrusion on trihalomethane levels at a water treatment plant. Tbe total trihalomethane concentration increased seven-fold as a result of salt water intrusion increasing the bromide concentration of the water supply from the normal 0.1 mg l^{-1} to 0.6 mg l^{-1}.

Hypohalous acid and other bromine containing species may be formed by oxidising agents other than chlorine. Ozonation of waters containing bromide have produced brominated trihalomethanes(98,104). Rook(96) has also observed that ozonation prior to chlorination will shift the speciation so that more brominated trihalomethanes are formed on chlorination. This was confirmed in pilot scale studies of preozonation resulting in a reduction of chloroform and bromodichloromethane concentrations and an increase in dibromochloromethane and bromoform concentrations(96).

1.2.1.4 Fluoride and Iodide

Chlorine is not capable of oxidising fluoride to hypofluorous acid and as a consequence fluoride is not involved in trihalomethane formation(102). Iodide in contrast is readily oxidised by chlorine to the corresponding hypohalous acid(105) which is then involved in the haloform reaction in a similar manner to hypochlorous and hypobromous acid(91,105).

Bunn(101) has shown that irrespective of the nature of the precursor any of ten possible trihalomethanes may be produced on chlorinating waters containing sufficient quantities of iodide and bromide. The Iodide concentration in natural waters, however, is generally too low to be of significance in trihalomethane formation. Thus the term 'trihalomethane' in the text refers only to the species; chloroform; bromodichloromethane; dibromochloromethane and bromoform.

1.2.1.5 Chlorine

As the reactions involving chlorine and humic material are complex the effect of chlorine dose on chloroform formation and the relationship between chlorine consumption and chloroform formation is not fully understood. Trussel(96) has recently reported a first order rate equation for chlorine consumption on chlorinating water containing humic material. Noack(106) however obtained a rate equation for chlorine consumption corresponding to a rapid initial second order relationship dependent on chlorine and humic acid (expressed in chlorine equivalents) concentrations and a slower secondary phase of reaction involving only the chlorine concentration, expressed as:

$$\frac{-d[Cl_2]}{dt} = k_1[Cl_2] + k[Cl_2][X]$$

where $[Cl_2]$ = chlorine concentration

$[X]$ = concentration of the more reactive reducing species (functional groups) of humic acid expressed in chlorine equivalents

Noack(106) also calculated the amount of chloroform produced per unit chlorine consumed on chlorinating 5 mg l^{-1} of humic acid at an initial chlorine concentration of 9 mg l^{-1} at pH6, pH7 and ph9.5, which gave values of $\Delta[CHCl_3]/-\Delta[Cl_2]$ equal to: 3.2×10^{-2}; 4.1×10^{-2} and 6.8×10^{-2}respectively.

It is unlikely that a general kinetic rate equation could be derived which would apply to all water independent of their nature and source.

If either humic material or chlorine become limiting there is a considerable reduction in the rate of chloroform formation, although chloroform formation may not cease altogether. Morris and Baum(89) reported that trihalomethane formation continues,when chlorine has been exhausted, upon increasing the pH. This was attributed to the formation, at low pH, of chlorinated intermediates that hydrolyze to form trihalomethanes once the pH is raised. Trussel(96) attempted to verify this but found no significant increase in trihalomethanes, on raising the pH after quenching the chlorine.

1.2.1.6 pH

Laboratory and water treatment plant investigations have shown that the rate of chloroform formation generally increases on increasing the pH consistent with a based catalysed haloform reaction. This is in contrast to the change in non-volatile TOCl which reduces on increasing the pH(107,108). Oliver(108) found that on chlorinating humic material the sum of the non-volatile organic chlorine and the volatile organic chlorine (including trihalomethanes) is constant and independent of pH.

1.2.1.7 Ammonia

The presence of ammonia considerably reduces trihalomethane formation. Stevens(82) observed that, in the presence of 5 mg l^{-1} of ammonia and if breakpoint chlorination was not reached, very low trihalomethane formation occurred. Any trihalomethane produced is a result of the presence of free chlorine as chloramines do not produce trihalomethanes(87).

1.2.2 Control of Trihalomethane Formation

The following sections outline the methods available for the control of trihalomethane formation in treated waters.

Following the EPA's nationwide survey of 80 cities(79) in the United States an arbitrary limit of 100 μg l^{-1} total trihalomethane in finished waters was proposed by the EPA(4) with a possible reduction of this limit within two years(109). The EPA considered that approximately ten percent of the treatment plants in the United States exceed the present limit(79).

To assist water supply agencies in reducing trihalomethane levels in finished waters the EPA issued a document(87) outlining the possible methods for the control of chloroform and other trihalomethanes based on the generally accepted view that trihalomethane formation is a result of chlorination reactions involving organic substances present in raw waters.

The methods for the control of trihalomethanes may be characterized as follows;

(1) Removal of trihalomethanes from finished waters

(2) Change to an alternative method of disinfection

(3) Reduce the precursors

(4) Change the existing chlorination practice

1.2.2.1 Removal of Trihalomethanes from Finished Waters

1.2.2.1.1 Powdered activated carbon

Powdered activated carbon has been found to be uneconomical in removing trihalomethanes on account of the unrealistically high doses required for effective treatment(87,103).

1.2.2.1.2 Granular activated carbon

Filtering the finished water through granular activated carbon removes not only trihalomethanes, but other chlorinated and non chlorinated organics(110), though the high removal efficiency is only maintained during the first two to three weeks of operation after which time break-through of the trihalomethanes and other volatile organic compounds occurs. The requirement for frequent regeneration of the activated carbon to maintain effective trhalomethane removal increases the cost of this treatment(87).

1.2.2.1.3 Aeration

Aeration has been considered an effective method for the removal of trihalomethanes and other volatile organic compounds. Lange(103) found that in practice aeration was ineffective in reducing trihalomethane to an acceptable level even at air to water ratios of 20:1. Furthermore, aeration does not eliminate the problem of trihalomethane formation as the residual chlorine will continue to react with the non-volatile humic material present in finished waters, resulting in further trihalomethane formation in the distribution system(87).

It should be noted that corrosion problems may be aggravated as a consequent of the increased oxygen content of the water following aeration(87).

1.2.2.1.4 Ozone

Uneconomically high ozone doses are required for the removal of trihalomethanes. Furthermore, ozonation of organic material in finished waters may result in by-products with unknown health effects(87).

1.2.2.2 Alternative Method of Disinfection

Several chemical reagents such as chlorine dioxide, ozone and chloramine may be used instead of chlorine for disinfection of water supplies. Their advantage over chlorine is that, when used as a disinfectant, and under the right conditions, these reagents do not produce trihalomethanes. Table 1.8 summarises and compares the disinfectant characteristics of these chemicals with chlorine(111).

Table 1.8 Summary of disinfectant characteristics (111)

	Chlorine	Ozone	Chloride Dioxide	Chloramines
Use and Generation	Widespread in US: offsite generation	Widspread outside US; onsite generation	Widespread outside US; onsite generation	Limited use; onsite generation
Biocidal Activity	Affected by pH: HOCl-3rd in activity; OCl-weak	Little pH influence; most active	Little pH influence; 2nd in activity	Affected by pH; $NHCl_2$-4th in activity; NH_2Cl-5th in activity
Measurement and Persistence of Residual	8 methods; HOCl and OCl^- not easily distinguished; persists	Titration method; does not persist	DPD and FACTS: Iodimetry, Mod. OT; amperometric titration; ClO_2 and ClO_2^- can be distinguished; certain by-products may interfere with DPD;persits-slowly changes to ClO_2^- and ClO_3^-	Amperometric titration; DPD; persists
By-products and end products				
Chemistry	Trihalomethanes, other chlorinated compounds, some odorous	Some, but not yet well characterized; no trihalomethanes	Some, but not yet well characterized; no trihalomethanes ClO_2^- and ClO_3^- are end products	Unknown; no trihalomethanes if no chlorine present
Health	$CHCl_3$ a carcinogen; epidemiology supports some adverse effect	None positive yet; still under study	None positive yet; both by-products and end products under study	None positive yet; studies beginning

1.2.2.3 Removal of Precursors

1.2.2.3.1 Chemical Oxidation

The chemical oxidation of humic material, present in natural waters, prior to chlorination may result in a reduction in the potential of these precursors to produce chloroform(97,119). This method of pretreatment, however, does not remove the humic material but chemically changes the active sites in the humic structure responsible for chloroform formation.

Chlorine dioxide treatment prior to chlorination is only moderately successful in reducing the trihalomethane precursors(87). Ozonation is more effective than chlorine dioxide though very high doses are required to produce a significant reduction in trihalomethane formation. Thus, although trihalomethane formation may be reduced by a chemical oxidation stage prior to chlorination(112,113) such treatment undoubtedly produces other by-products with unknown health effects.

1.2.2.3.2 Physico-chemical methods

The most effective method of reducing trihalomethane formation is to reduce the concentration of precursors prior to chlorination.

1.2.2.3.2.1 Granular activated carbon

Granular activated carbon filters are highly effective in removing organic material from waters. When fresh, the activated carbon will adsorb most trihalomethane precursors and produces a water with a low overall concentration of organic matter(87,113). Thus trihalomethane and hitherto unknown organic products are significantly reduced on chlorinating waters which have been filtered through granular activated carbon.

There are disadvantages, however, as the activated carbon must be regenerated frequently to prevent breakthrough and maintain the high removal efficiency of organic matter(87). The frequency of regeneration is dependent on the organic load on the filters.

1.2.2.3.2.2 Coagulation (Clarification)

Coagulation is a well-proven physico-chemical method for removing a substantial proportion of organic matter from water. A wide range of treatment efficiencies have been reported, ranging from 30% to 90% removal of TOC for both Al(III) and Fe(III) coagulants(97). Coagulation is not as effective as granular activated carbon in removing organic matter, particularly synthetic or non polar compounds(87), as much higher residual TOC levels remain after coagulation compared to granular activated carbon treatment.

Coagulation is more effective in removing the high molecular weight humic fractions than the low molecular weight organics from waters(96,114,115). Chlorination studies of humic and fulvic acids show that the higher molecular weight humic acid fraction produces more chloroform per unit weight of acid that the lower molecular weight fulvic acids(94,116). Coagulation, therefore, is selective in removing the precursors which readily produce trihalomethanes as a result of the greater removal efficiency of the high molecular weight humic fraction.

1.2.2.4 Changing the Existing Chlorination Practice

Attempts have been made to reduce trihalomethane formation in a number of water treatment works in the United States by modifying the existing treatment process. The results varied considerably depending on the type of treatment and the flexibility of the system to change without a deterioration of the prime requirements of the works, to produce a safe supply of potable water.

Prechlorination is the most obvious treatment stage to alter as this is probably the main cause of the high trihalomethane levels in United States finished waters(87). At a particular works trihalomethane formation was reduced by 50% on changing prechlorination from a single stage to a two stage process(97). Further reductions could only be achieved by granular activated carbon filtration or by changing the disinfectant. Harris(118) found that on relocating the prechlorination dose to a point after lime addition and subsequent recarbonation (to reduce the pH) resulted in a 75% reduction in chloroform concentration.

Other chlorinated products are formed apart from trihalomethanes on chlorinating natural waters. The advantages of chlorinating at a low pH in order to reduce trihalomethane formation is in doubt in view of the recent findings that total organic chlorine(108) and total-chloroform(116) concentrations are not significantly affected by changes in pH.

1.3 CRITERIA FOR STUDY

The main constituent of organic matter in natural waters is humic material characterised primarily as humic acid and fulvic acid. These acid fractions are considered to be precursors to trihalomethanes.

Any comparison of the reactivity of humic and fulvic acids must involve material extracted from the same source as waters from different areas may well contain differing types of these acid fractions. The work reported in Chapter 3 relates to the relative contribution of these acids fractions extracted from the River Thames(115), towards the chloroform formation upon chlorination under a range of conditions of temperature and pH. The purpose of these laboratory studies was to give an indication of the relative importance of the interacting parameters on both the rate and extent of chloroform production (total, residual and dissolved chloroform), and also to facilitate the development of appropriate experimental and analytical techniques.

The subsequent stage of investigations reported in Chapter 4 involve the chlorination of raw or partially treated water under similar laboratory conditions involving the humic acid and fulvic acids and to compare the results obtained with chloroform levels observed at a treatment works under normal operating conditions.

The complex structure of humic material has led to the use of 'model' compounds to elucidate the reaction mechanisms and parameters involved in trihalomethane formation. The work reported in Chapter 5 relates the chlorination of a number of 'model' compounds to investigate whether these compounds are truly representative of the basic structure of humic material.

Chapter 6 reports the data obtained from a survey of trihalomethane levels in household tap water in the London area. This survey was carried out to observe the extent and nature of trihalomethane formation in a distribution system.

2. EXPERIMENTAL METHODS

2.1 GENERAL ANALYTICAL METHODS

2.1.1 Chlorine Analysis

2.1.1.1 Iodometric Titration

Chlorine concentration (free and combined) was measured iodometrically using 25 ml samples as opposed to the 500 ml samples described in the UK standard method(120). This reduction in sample size was necessary because of the scale of reaction (1-2 litres) and the number of analyses required.

2.1.1.2 DPD Method

During on-site investigations at Lartington and on other occasions specified in the text, free and combined chlorine were analysed by the DPD method as described in the UK standard method(120).

2.1.1.3 Chlorine Electrode

A Delta Scientific chlorine electrode was evaluated for the continuous monitoring of free chlorine concentration, measured as HOCl.

The electrode required frequent calibration and was found to be unstable particularly at low chlorine concentrations and was therefore considered unsuitable for the purpose of this project.

2.1.2 pH

The pH was determined using a glass electrode coupled to an Orion 701 digital meter. The meter was calibrated prior to pH measurements using buffered solutions corresponding to the calibration range required.

2.1.3 Ultraviolet and Visible Spectra

The UV/VIS absorption spectra between the wavelengths 200 nm and 600 nm were obtained using a Pye Unicam SP8-100 spectrophotometer. The scanning speed was 2 mm sec^{-1} using a slit width of 0.5 nm. The cells used were quartz with a path length of 10 mm.

2.1.4 Colour

Colour measurements were carried out as described in the UV standard method using permanent glass standards in Nessler tubes calibrated in Hazen standard units (platinum equivalent) which were checked prior to use using standardised solutions.

2.1.5 Total Organic Carbon

Samples were sent for TOC analysis to the Water Research Centre (Medmenham Laboratories) UK.

2.1.6 Elemental Analysis

The humic and fulvic acids were analysed for carbon, nitrogen, hydrogen and chlorine content at the Water Research Centre (Medmenham Laboratories) UK, and more recently for carbon, nitrogen and hydrogen at the Micro Analytical Laboratory,Chemistry Department, Imperial College.

2.1.7 Bromide Analysis

Bromide analysis of Lartington water was carried out using the UV method recommended by the American Society for Testing and Materials(121).

2.1.8 Ammonia

Organic-free water was analysed for ammonia as described in the UK standard method(120).

2.2 TRIHALOMETHANE ANALYSIS

Although several analytical techniques for the analysis of trihalomethane in water have been reported all presently available methods are based on one of four basic techniques characterised as follows:-

(1) Head space

(2) Purge-and-trap

(3) Solvent extraction

(4) Direct aqueous injection

The first three methods of analysis involve a separation stage to extract the trihalomethane from the aqueous phase using either a solvent or a gas.

The head space technique(84,122-124) involves the partitioning of the trihalomethanes between the aqueous phase and the gaseous phase above the sample. A quantity of the head space is removed and injected directly into a gas chromatograph for analysis. To increase the transfer of trihalomethane into the head space the sample is generally heated to between 50°C and 90°C. In view of recent findings that organohalide intermediates breakdown at elevated temperatures to form the corresponding trihalomethane(116), this method may lead to further trihalomethane formation during analysis. The breakdown of the intermediates will be dependent on; the concentration of the organohalide intermediate; temperature; pH,and length of time the sample is heated.

The purge-and-trap technique(125-130) is the most commonly used method for the measurement of trihalomethanes, particularly in the United States, as a result of the EPA adopting this as a standard method during the nationwide survey(79). This method, developed by Bellar and Lichtenberg(126) involves the purging of trihalomethanes (and other volatile compounds) from the water sample using a purified gas such as nitrogen or helium. The gas is passed through an adsorbing material which traps and concentrates the volatile organic compounds. The compounds are then thermally desorbed from the trap and passed through a gas chromatographic column for separation and measurement.

Solvent extraction technique(131-134) involves the separation of the trihalomethanes from the water into an organic solvent followed by gas chromatographic analysis of the extract. A variety of different solvents may be used to extract the trihalomethanes from the water all of which have a specific extraction efficiency depending on the partition coefficient of the trihalomethane between the solvent and the water phase. By using a low solvent to water ratio the trihalomethanes are concentrated in the solvent. The solvent extraction method has been criticised for being susceptible to solvent interferences and erratic in the extraction efficiency. This method however is becoming more widely used in routine trihalomethane analysis because of its simplicity compared to the more involved and time consuming purging techniques.

Gas chromatography using direct aqueous injection (D.A.I.) for the analysis of trihalomethanes was first reported by Nicholson et al. in 1975(135).

Although this method does not involve a pre-treatment step to concentrate the trihalomethanes, the sensitivity of this technique is adequate for the quantitive determination of the trihalomethanes generally encountered in treated waters.

2.2.1 Choice of Analytical Method

The selection of a suitable analytical method for the determination of trihalomethanes in water was based on the requirements for a rapid and accurate analytical technique with the minimum of pretreatment stages.

The direct aqueous injection technique was considered the method most suitable to satisfy these requirements. However, a development stage prior to adopting D.A.I. as a standard method was necessary because of the limited amount of information on this technique and particularly in view of the preliminary investigations which indicated that breakdown of organohalide intermediates in the injection port of the chromatograph was occurring, giving higher than expected values of chloroform. A publication by Hammarstrand(136) was subsequently obtained in which he reported that D.A.I. tended to give higher values for chloroform concentration compared to the purge-and-trap technique, arriving at the same conclusion that the higher values obtained by D.A.I. are a result of breakdown in the injection port of the chromatograph of chloroform precursors.

Although the detection limit of D.A.I. technique is higher than the methods involving a preconcentration step this technique has proved very satisfactory as a fast and reliable method. Furthermore, the breakdown of organohalide intermediates in the injection port of the chromatograph has permitted a study of the effects of changing parameters on the formation of organohalide intermediates involved in the haloform reaction(116).

Nicholson et al. reported, in 1977(137), that the D.A.I. technique produces a value which is the maximum trihalomethane concentration attainable while the water is in the distribution system and that the combination of the purge-and-trap technique with D.A.I. gives both the free trihalomethanes and the total potential trihalomethanes content of a sample. More recently, Pfaender *et al.*(138) evaluated the D.A.I. method for the analysis of chloroform in drinking water confirming the reports by Nicholson that the D.A.I. technique gives higher values for chloroform than the purge method. Pfaender went one stage further, however, and noted that purging the water and reinjecting, a value for the 'residual chloroform' is obtained which, when subtracted from the original total chloroform concentration, yields a result comparable to chloroform as determined by the purge method. This method of distinguishing between 'residual' trihalomethane and 'free' or 'dissolved' trihalomethane is, in principle, the same as the method developed by the author.

2.2.2 Direct Aqueous Injection Gas Chromatographic Analysis

Trihalomethane analysis was performed on a Hewlett Packard 5713A gas chromatograph incorporating an electron capture detector, using, in order to facilitate rapid analysis, direct aqueous injection of 5 μl samples. Separation was achieved on a glass column, 4 mm × 1 m, packed with Chromosorb 101 (100-120 mesh) using 95% argon/5% methane as the carrier gas at a flow rate of 25 ml min^{-1}. The detector temperature was 300°C and that of the injection port 200°C. Column temperature was isothermal at 140°C for the analysis of chloroform and bromodichloromethane and 180°C for dibromochloromethane and bromoform. The detection limits under these conditions are; chloroform 1 μg l^{-1}; bromodichloromethane 0.5 μg l^{-1}; dibromochloromethane 1 μg l^{-1}; bromoform 1-2 μg l^{-1}. The accuracy of this technique is generally within ±5%. However, this is dependent on the consistency of breakdown of organohalide intermediates.

2.2.2.1 Nickel Powder

Inconsistent breakdown (or organohalide intermediates) in the injection port interfered with the accurate determination of residual chloroform concentrations. This was resolved by introducing fine nickel powder (0.3 - 0.4 g) prior to the glass wool packing at the injection port end of the analytical column, resulting in a 'cleaner' chromatogram and more consistent breakdown of the 'residual chloroform', which not only improved the accuracy of measurement but allowed the use of a Hewlett Packard 3880 integrator for quantification of results.

2.2.2.2 Chlorine Quenching

Prior to trihalomethane analysis, sodium thiosulphate was added to each sample to quench the residual chlorine. It has been suggested that thiosulphate interacts with organohalides. In the course of this work, however, thiosulphate addition has not been found to have any significant effect on the levels of trihalomethanes detected. A similar conclusion has recently been reported in the literature (143) with the recommendation that sodium thiosulphate be used as the quenching agent.

2.2.3 Dissolved and Residual Trihalomethanes

The high temperatures involved in the chromatographic analysis cause breakdown or transformation of, as yet, unidentified, organohalide intermediates to produce the corresponding trihalomethane. For chloroform, this intermediate is non-purgeable. The true dissolved chloroform concentration in a sample may be obtained, therefore, by a two stage analytical procedure:-

(a) Analysis before purging;

(b) Analysis after purging for 15 mins at a flow rate of 140 ml min^{-1} with white spot nitrogen.

The total chloroform level is determined by analysis (a). By purging the sample with nitrogen, any dissolved chloroform is stripped from solution. Thus the dissolved chloroform level is obtained from (a)-(b). The chloroform detected in step (b) is designated residual chloroform. This residual chloroform content proved of value in further investigations into the mechanisms of breakdown of these intermediate organohalide species.

The reduction of the injection port temperature to 140°C had little or not effect on the residual chloroform and bromodichloromethane levels. Heating a sample in a digester for 10 mins at 140°C caused a slight reduction in total-chloroform levels, possibly due to evaporative losses. No residual chloroform was present indicating that all the chloroform was removed by purging, and that complete breakdown of the dissolved organohalide intermediate had occurred in the digester at 140°C (this temperature being below that normally used in the injection port of the gas chromatograph).

Spiked samples were purged to obtain the required purging time for both chloroform and bromodiochloromethanes at levels normally found in chlorinated waters. Over 99% removal of bromodichloromethane and chloroform from spiked samples containing initially 30 μg l^{-1} and 100 μg l^{-1} respectively was achieved at a purging rate of 150 ml min^{-1} for 10 minutes (Appendix I, Fig. 13).

2.2.4 Solvent Extraction

Solvent extraction was used on occasions for the measurement of trihalomethanes in water samples. This was not a standard analytical method and is therefore described in the text when employed.

2.2.5 Preparation of Standard Trihalomethane Solutions

Difficulty was experienced when preparing standards for direct aqueous injection, primarily caused by the evaporative loss of the volatile haloforms, chloroform and bromodichloromethane. This gave rise to inconsistencies in calibration curves and required the selection of a suitable solvent which would minimise such evaporative losses. Methanol was chosen as this has a similar retention time to water on Chromosorb 101 under the chromatographic conditions employed. Calibration curves were prepared using the alcoholic solutions of chloroform, bromodichloromethane, dibromochloromethane and bromoform.

2.3 PREPARATION OF HUMIC AND FULVIC ACID STOCK SOLUTIONS

Humic and fulvic acid stock solutions were made up in organic-free water.

The pH of the organic-free water had to be raised to pH 9 to dissolve the humic and fulvic acids as these acid fractions are relatively insoluble under neutral or acid conditions. As these acids tend to reduce the pH on dissolving, the pH was monitored continuously and maintained at the required level by adding a solution containing sodium hydroxide (0.1N).

Stock solutions were not kept for more than 24 hours.

2.4 PREPARATION OF CHLORINE STOCK SOLUTIONS

Sodium hypochlorite was chosen as the chlorinating agent because it was convenient for preparation of reliable and repeatable standard solutions. Stock solutions were made up on the basis that sodium hypochlorite has the same oxidising capacity as a solution of molecular chlorine on a molar basis. Iodometric titration was used to standardise the stock solutions in terms of the 'free chlorine' concentration.

2.5 TEMPERATURE CONTROL

The reaction vessel was placed in a 40 litre glass tank containing an aqueous ethylene glycol solution maintained at the desired temperature using a Churchill Instruments thermocirculator (02 CTCU).

2.6 REACTION VESSEL - SAMPLING AND EVAPORATION LOSSES

Preliminary studies on the chlorination of humic acid revealed that a significant loss of haloforms occurred as the reaction progressed. This loss was attributed mainly to evaporation into the head space and subsequent diffusion out of the reaction vessel. Other factors which may contribute to such losses include: adsorption onto the glass walls of the vessel, hydrolysis, and further reactions of the trihalomethanes, though the significance of such factors for the overall loss is not known.

Evaporation rates of up to 6 μg l^{-1} for bromodichloromethane and 8 μg l^{-1} for chloroform per day were measured on spiked samples in glass stoppered flasks maintained at 10°C. Evaporation rate curves for chloroform are given in Appendix I, Fig. 8.

A sealed reaction vessel was, therefore, used to minimise the losses resulting from evaporation. Sampling was carried out by injecting nitrogen into the head space of the vessel, thus displacing water samples, which were collected and analysed for chlorine and the trihalomethanes.

The introduction of nitrogen into the reaction vessel to remove samples progressively lowers the chloroform concentration in the head space. This may cause a significant drop in dissolved chloroform concentration if the ratio of the water to head space volume is low, i.e. < 1, as further chloroform evaporation will occur to re-establish the equilibrium. Thus for a large reaction vessel and an increased scale of reaction the effect of sample removal on the water to headspace volume ratio will be minimised and consequently evaporative losses of chloroform from the solution (as a percentage of total dissolved chloroform) reduced.

During the initial investigations a one litre reaction vessel was used without stirring. Preliminary studies showed that the rate of trihalomethane formation is increased in the presence of light. It was therefore deemed necessary to wrap the reaction vessel with aluminium foil to prevent photolytically induced reactions.

Larger reaction vessels (2.5 litres) were used in subsequent investigations. Forced mixing of the reactions was considered necessary as a lack of mixing may lead to a spread of results during the initial rapid phase of chloroform production.

All the reported data on trihalomethane formation in the laboratory investigations are based on reactions carried out in the absence of light.

2.7 EXPERIMENTAL PROCEDURES

Organic-free water maintained at a constant temperature was spiked with humic acid or fulvic acid from stock solutions to give the required acid concentration and buffered at the desired pH.

Buffers were used sparingly (20% of the recommended concentration) to reduce any possible effects of ionic strength on the chlorination reaction while maintaining the buffering capacity of the solution.

Sodium hypochlorite was added from a stock solution to give the required initial free chlorine concentration. Samples were subsequently removed at intervals for both chlorine and trihalomethane analysis. The reaction was carried out in the absence of light.

The initial chlorine concentration of the reaction mixture containing humic material could not be calculated directly as the initial reaction between chlorine and humic material is fast. Known volumes of chlorine stock solution were added to organic-free water. The resulting chlorine concentrations were measured, and the data used to calculate the volume of stock solution required to give a known initial 'free chlorine' concentration.

During initial stages of investigations blanks were run concurrently. The rate of loss of chlorine in the absence of humic material was negligible compared to the rapid rate of reaction between chlorine and humic material.

2.7.1 Sampling - Trihalomethane Analysis

Samples were removed from the reaction vessel as described in Section 2.6 and collected in 5 ml glass volumetric flasks containing a crystal of sodium thiosulphate to quench the chlorine residual. The flask was filled to overflow, so that a meniscus formed, and capped with a rubber'suba-seal'. A 5 µl sample was withdrawn from the flask using a 10 µl syringe for gas chromatographic analysis by direct aqueous injection (Section 2.2.2). The 'suba-seal'was subsequently removed and the sample purged with white spot nitrogen prior to residual chloroform analysis (Section 2.2.3).

2.7.2 Sampling - Chlorine Analysis

Samples were removed from the reaction vessel as described in Section 2.6 and collected in a measuring cylinder containing a known volume of a potassium iodide/acetic acid solution. The rapid reaction between the free and combined chlorine and iodide (liberating iodine) terminates the chlorination reaction at the time of sampling. The iodine was subsequently analysed by the iodometric tritration method (Section 2.1.1.1). A similar procedure for quenching the chlorination reaction at the time of sampling was used for the DPD method.

2.8 REAGENTS

2.8.1 Trihalomethanes

The term 'trihalomethane' used in the text refers to the four trihalomethane species; chloroform, bromodichlormethane; debromochloromethane, and bromoform.

Analar grade chloroform and bromoform supplied by BDH, and bromodichloromethane and dibromochloromethane supplied by the Water Research Centre were used to make up standard solutions of the trihalomethanes.

2.8.2 Humic and Fulvic Acids

The humic and fulvic acids supplied by the Water Research Centre (Medmenham Laboratories) UK, were extracted from Thames water(115) in 1971.

The humic material present in natural waters may be classified as three fractions(4,5); humic acid; hymatomelanic acid, and fulvic acid. This classification is based on the solubility of the separate fractions in acids, bases and organic solvents.

The humic material in Thames water is composed of approximately: 4% humic acid; 13% hymatomelanic acid, and 83% fulvic acid. The technique used to extract these acids from the River Thames does not separate the hymatomelanic and humic acid fractions(115). Therefore, the humic acid used in this study is a combination of the humic and hymatomelanic fractions.

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The composition of the humic acid (% by weight) is:
C, 53.2; H, 4.7; N, 5.0; Cl, 5.3.

The composition of the fulvic acid (% by weight) is:
C, 55.7; H, 5.7; N, 2.0; Cl, ND.

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Humic acid: C, 47.6%; H, 4.2%; N, 4.8%

Fulvic acid:C, 52.4%; H, 5.2%; N, 2.1%

2.8.3 Methanol

Analar grade methanol was used to make up standard solutions of the trihalomethanes (Section 2.2.5). The methanol was analysed prior to each stage of standard preparation to screen the solvent for contamination. The solvent was discarded if carbon tetrachloride which has a retention time close to that of chloroform was present at a concentration which interfered with chloroform measurements.

2.8.4 Hexane

Analar grade hexane was selected as the extracting solvent on the occasions when solvent extraction technique was employed for the analysis of trihalomethanes.

The hexane was analysed prior to use to screen the solvent for contamination. Trihalomethane contamination could be reduced below the detection limit of the analytical technique employed by refluxing the hexane over potassium hydroxide pellets.

2.8.5 Organic-free Water

Organic-free water was prepared by distillation and subsequent refluxing over chromic acid and alkaline permanganate. The alkaline permanganate step was subsequently omitted with no noticeable effect on the results. No ammonia was detected in the organic-free water.

2.8.6 Sodium Hypochlorite

Sodium hypochlorite (BDH) low in bromine was used as the chlorinating agent.

2.8.7 Buffers

Buffering was carried out using phosphoric acid for pH 6-8 and boric acid/potassium chloride for pH 9, the pH in both cases being controlled by the addition of sodium hydroxide.

2.8.8 Sodium Thiosulphate

Analar grade sodium thiosulphate (BDH) was used to quench the chlorination reactions.

2.8.9 Potassium Bromide

Analar grade potassium bromide (BDH) was used in the bromide addition reactions.

3. CHLORINATION OF HUMIC AND FULVIC ACIDS

The work reported in this chapter relates to the relative contribution of the humic and fulvic acid fractions extracted from the River Thames,(115) towards trihalomethane formation on chlorination, under a range of conditions of pH and temperature.

Total, residual and dissolved chloroform determinations and chlorine consumption measurements were carried out over a 2-3 day period for each reaction. The chlorinating conditions employed for these reactions are summarised in Table 3.1.

Table 3.1 Summary of reaction conditions

Acid mg l^{-1}	Temp ^{o}C	pH	Chlorine (initial) mg l^{-1}
Humic 5	5,10,15	6,7,8,9	8
Fulvic			
5	5,10	6	8
5	10	7,8,9	8
6.2	15	6	8
25	10	7	4,8
Humic (Bromide addition) 5	10	7	8

3.1 RESULTS AND DISCUSSION

The chloroform data reported relate to chloroform measured as dissolved chloroform (as defined in 2.2.3), unless specifically described otherwise.

3.1.1 Temperature Effect on Chloroform Formation

The rate of chloroform production increases with increasing temperature, the increase between 5°C and 10°C being less than that between 10°C and 15°C (Appendix I, Figs. 1-4).

The ratios of chloroform concentration, after two days reaction between 8 mg l^{-1} of chlorine and 5 mg l^{-1} humic acid for 10°C and 5°C, and for 15°C and 10°C are given in Table 3.2.

The activation energy may be calculated from the Arrhenius equation assuming there is no change in the order of reaction within the temperature range 5°C-15°C. The activation energy for chloroform production is 20-30 KJ $mole^{-1}$. This value is similar to the activation energy previously determined by Harrison et al(58) for the reaction of chlorine with polycyclic aromatic hydrocarbons (PAH).

Table 3.2 Ratios of chloroform concentrations from humic acid after 2 days reaction

pH 6	$(CHCl_3)_{10^oC}/(CHCl_3)_{5^oC}$	=	1.15
pH 7	"	=	1.15
pH 8	"	=	1.15
pH 6	$(CHCl_3)_{15^oC}(CHCl_3)_{10^oC}$	=	1.29*
pH 7	"	=	1.28
pH 8	"	=	1.22

* Adjusted for 5 mg l^{-1} Humic Acid concentration

3.1.2 Effect of pH on Chloroform Formation

The rate of chloroform production is pH dependent and increases with pH for both humic (Fig. 3.1 and Appendix I, Fig. 5-6) and fulvic fractions (Fig. 3.2). The increase in chloroform production between pH 8 and pH 9 is less than that between pH 7 and pH 8, which is also less than that between pH 6 and pH 7 (Fig. 3.1 and Fig. 3.2). These differences in chloroform production are most significant during the first day of reaction, after which time all chloroform production curves approach linearity (particularly at lower pH, 6 and 7, and lower temperatures, 5°C and 10°C).

The effect of pH on residual chloroform formation is opposite to that observed for dissolved chloroform formation, in that there is a reduction in residual chloroform production on increasing pH from

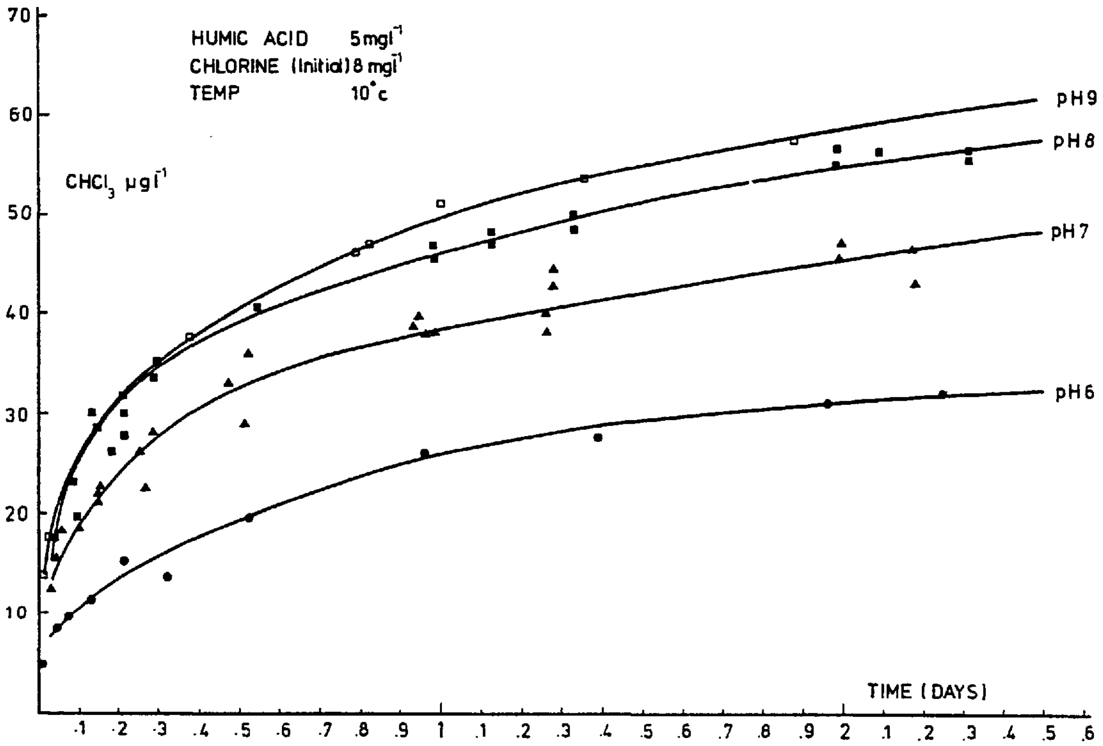


Fig. 3.1 Effect of pH on dissolved chloroform formation from humic acid at 10^{o}C

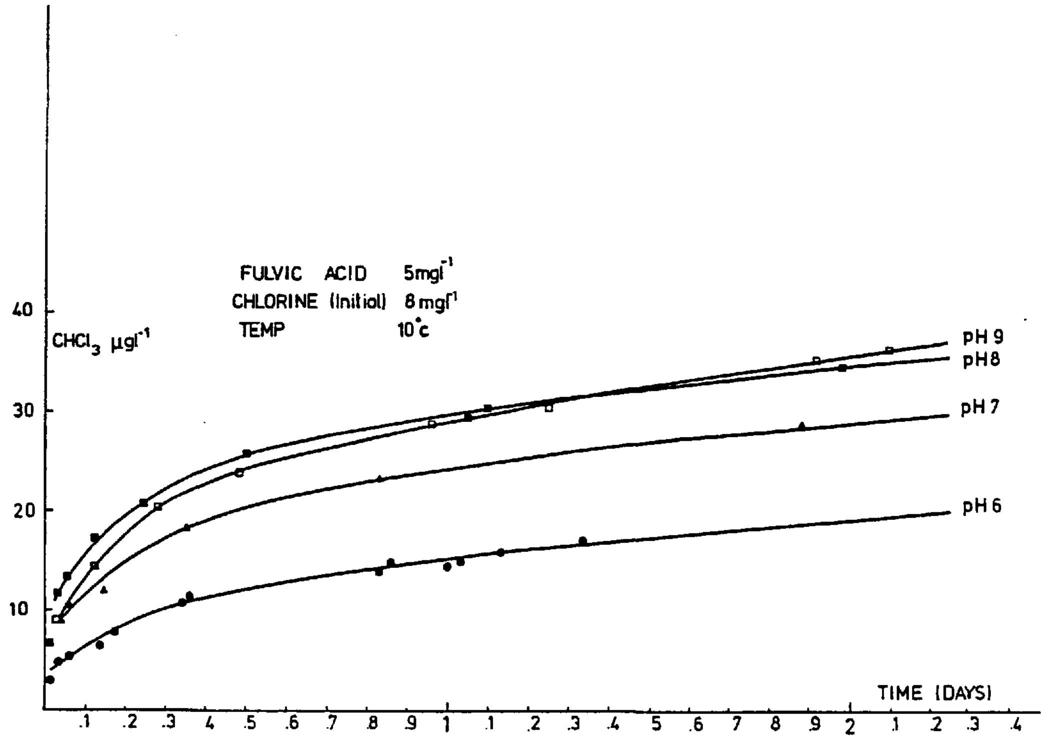


Fig. 3.2 Effect of pH on dissolved chloroform formation from fulvic acid at 10^{o}C

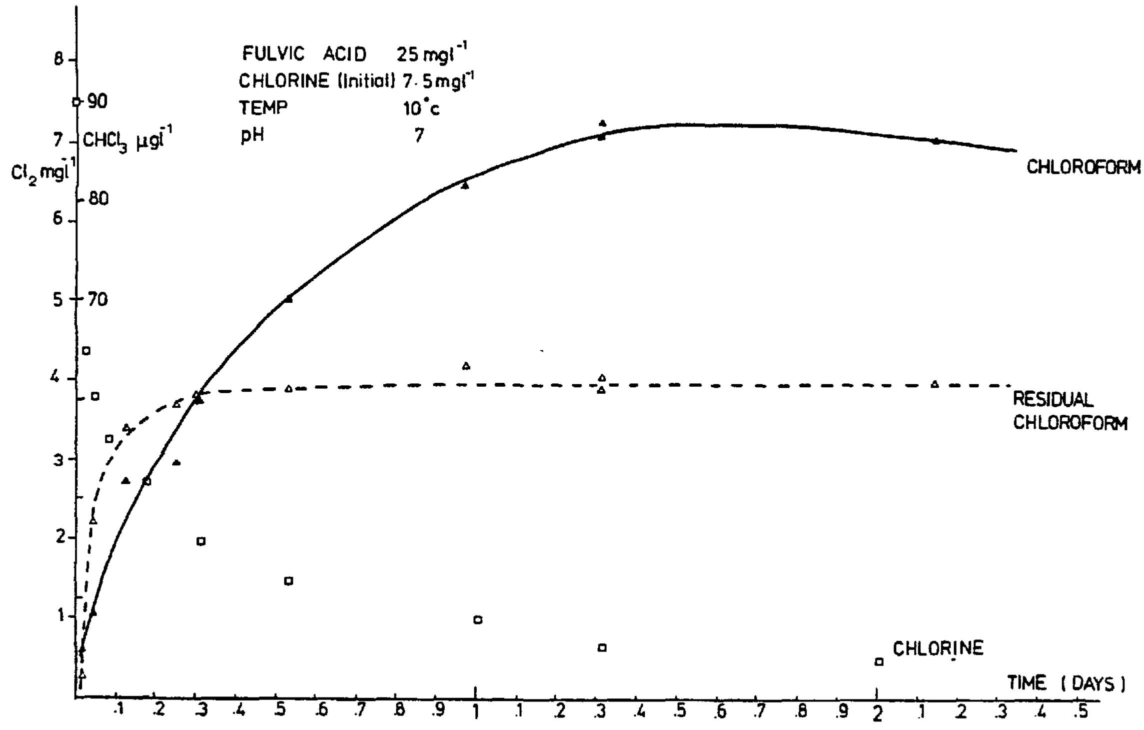


Fig. 3.3 Chloroform formation from fulvic acid (25 mg l^{-1}) at pH 7

7 to 9 for both humic acid (Fig. 3.4, Table 3.5) and fulvic acid (Fig. 3.5 and Table 3.6).

The trends in chloroform formation from humic and fulvic acids with variations in pH and temperature are similar. Furthermore, there is a definite relationship between the amounts of chloroform produced on chlorinating humic and fulvic fractions under similar reaction conditions. These relationships have been found to hold for chloroform levels measured after reaction times of both one and two days. The ratios of chloroform concentrations after one and two days reaction (8 mg l^{-1} chlorine, 5 mg l^{-1} humic or fulvic acid) for humic and fulvic acids are given in Table 3.3 and Table 3.4.

This may be a reflection of the similarity in structure between these two substrate fractions, which were extracted from the same source. Trussell(96) has recently reported similar findings. Oliver(95) found no difference in chloroform formation on chlorinating humic and fulvic acid though it appears that these acids did not originate from the same source. Humic and fulvic acid fractions are not clearly defined and their exact composition will be determined by the source from which they are extracted and by the nature of the extraction process.

The means of the ratios of chloroform produced from humic acid to that produced from fulvic acid, under similar reaction conditions, after one day (1.68) and after two days (1.64) are very similar.

Higher fulvic acid concentrations (25 mg l^{-1}) lead to rapid exhuastion of available chlorine (Fig. 3.3 and Appendix I, Fig. 7), and chloroform production is limited by the availability of chlorine. Over extended periods evaporation rates become significant (Appendix I, Fig. 8) leading to decreases in chloroform concentration (Appendix I, Fig. 9).

Table 3.3 Chloroform formation after 1 day

pH	Temperature (^{o}C)	Chloroform Conc. ($\mu g\ l^{-1}$) H.A.	F. A.	$\frac{(CHCl_3)^{H.A.}}{(CHCl_3)^{F.A.}}$	% of Mean
6	5	20.4	11.2	1.82	108
6	10	26.0	15.1	1.72	103
6	15	45.6*	19.7	(1.87)**	-
7	5	32.6	24.4	1.57	94
7	10	38.4			
7	15	51.0			
8	5	41.8	29.0	1.60	95
8	10	46.8			
8	15	57.6			
9	10	49.7	29.6	1.68	100
				Mean 1.68	

* At 15^{o}C Humic Acid concentrations 6.2 mg l^{-1}

** Ratio adjusted for Humic Acid concentration but not included in the determination of the mean ratio

Table 3.4 Chloroform formation after 2 days

pH	Temperature (°C)	Chloroform Conc. (μg l^{-1})		$\frac{(CHCl_3)^{H.A.}}{(CHCl_3)^{F.A.}}$	% of Mean
		H.A.	H.A.		
6	5	26.8	15.4	1.74	106
6	10	31.2	19.0	1.64	100
6	15	50.0*	22.9	(1.76)**	-
7	5	39.5			
7	10	45.4	29.3	1.57	95
7	15	58.0			
8	5	48.0			
8	10	55.0	34.6	1.59	97
8	15	67.0			
9	10	58.6	35.8	1.64	100
				Mean 1.64	

* At 15°C Humic Acid concentration 6.2 mg l^{-1}

** Ratio adjusted for Humic Acid concentration but not included in the determination of the mean ratio

3.1.3 Residual Chloroform

The effect of pH on residual chloroform from humic acid is shown in Appendix I, Fig. 10 and Fig. 3.4 for reactions carried out at 5°C and 10°C respectively, and in Fig. 3.5 for fulvic acid at 10°C. The effect of pH is opposite to that observed for dissolved chloroform, in that there is a reduction in residual chloroform production on increasing pH, reaching a maximum between pH 6 and pH 7.

The kinetics of residual chloroform formation from humic acid and fulvic acid are similar, both giving characteristic curves for residual chloroform formation between pH 7 and pH 9, involving two stages; an initial rapid phase within the first 5-7 hours of the reaction, followed by a slow near linear secondary phase. This initial phase of the reaction yields over 80% of the total residual chloroform intermediates produced over a 2 day period, while over the same time

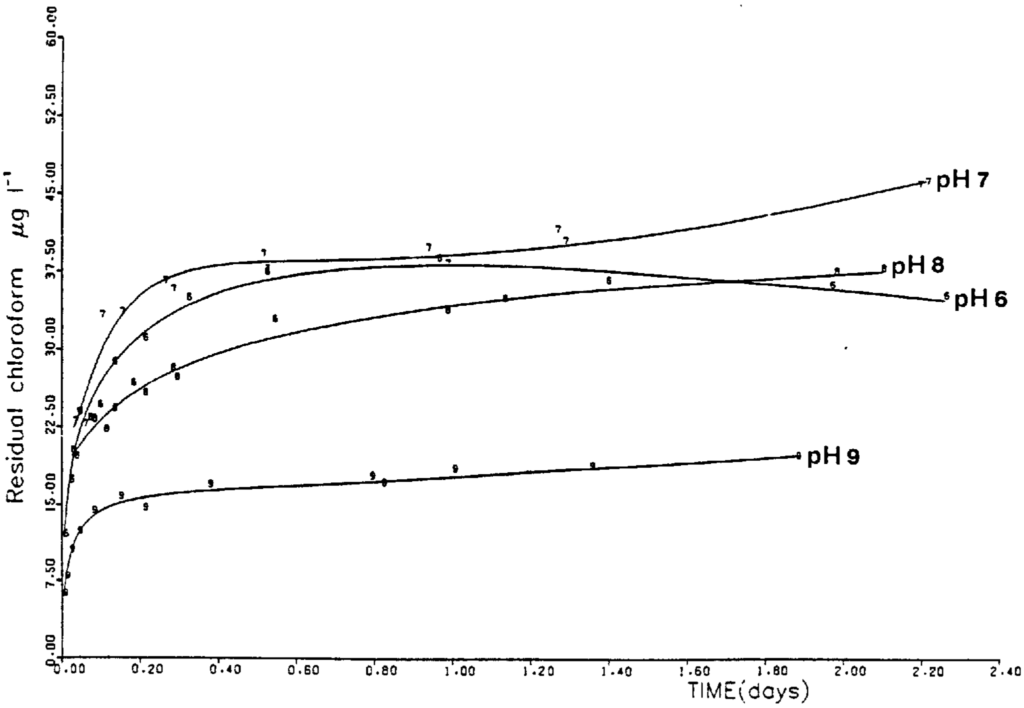


Fig. 3.4 Effect of pH on residual chloroform formation from humic acid at 10°C

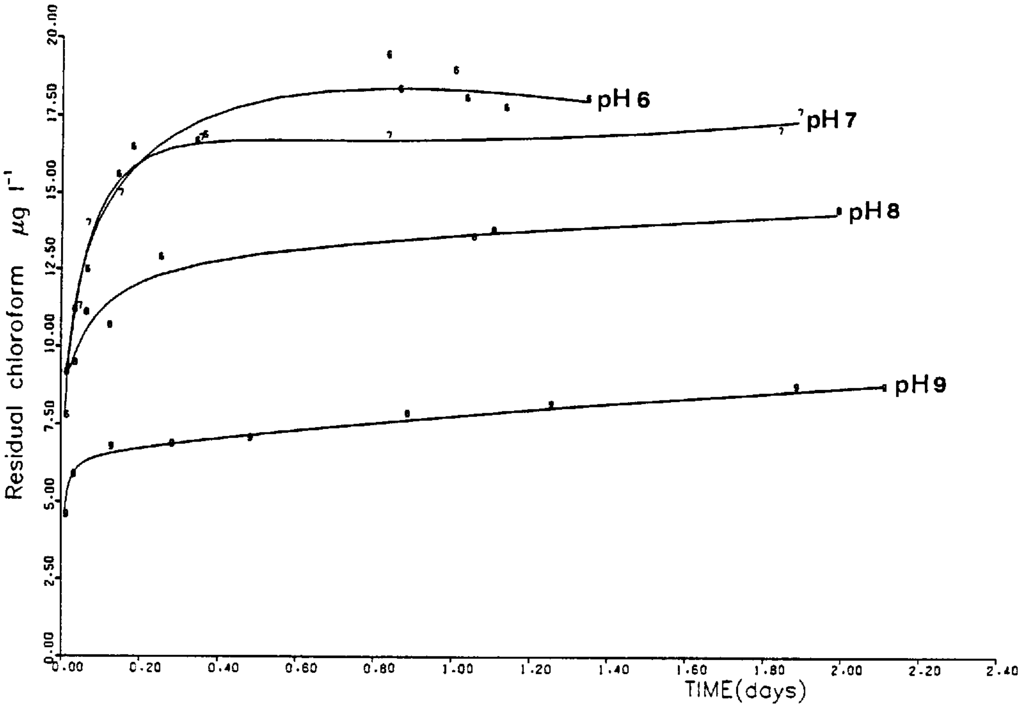


Fig. 3.5 Effect of pH on residual chloroform formation from fulvic acid at 10°C

interval, only 50% of the chloroform in solution has been formed. This two stage reaction is compatible with the rate of fall of chlorine concentration.

Rook(93) has noted a similar change in reaction kinetics in chloroform formation (not residual chloroform) on chlorinating fulvic acids, the phase change occurring within the first 15 minutes of the reaction. Side reactions with quinones after exhaustion of meta-dihydroxylated benzene moieties and the decrease in residual chlorine concentration as the reaction progressed were suggested to explain the changes in kinetics to a slow secondary phase of chloroform formation.

At pH 6 the rate of residual chloroform formation from both acid fractions does not follow the characteristic curves obtained under neutral or alkaline conditions. This may be a result of a change in mechanism and kinetics of the haloform reaction, or other reactions involving organohalide intermediates, under acid conditions.

Figure 3.6 and Fig. 3.7 represent residual chloroform formation in terms of the percentage contributions to total chloroform formation for humic and fulvic acids respectively. The percentage contribution of residual chloroform to total chloroform varies throughout the reaction. During the initial stages of reaction the percentage contribution of residual chloroform is high, followed by a slow but constant decrease after 5 to 7 hours of reaction. The rate of change in percentage contribution after this time appears to be independent of pH.

Though the residual chloroform concentration at pH 6 is lower than or equal to the residual chloroform concentration at pH 7 for humic acid (Fig. 3.6) and fulvic acid (Fig. 3.7), in terms of the percentage contribution of residual chloroform to total chloroform there is a near linear decrease between pH 6 and pH 9 for both acid fractions. The levels of total-chloroform, dissolved chloroform, residual chloroform and the percentage contribution of dissolved and residual chloroform to total chloroform after 1 day or reaction at 10°C are given in Table 3.5 and Table 3.6 for humic and fulvic acid respectively.

It is interesting to note that a similar dependence on pH has been reported(107,108) for TOCl formation, indicating that either the contribution of residual chloroform to the TOCl value may be substantial or that the dependence on pH of the reactions involving non

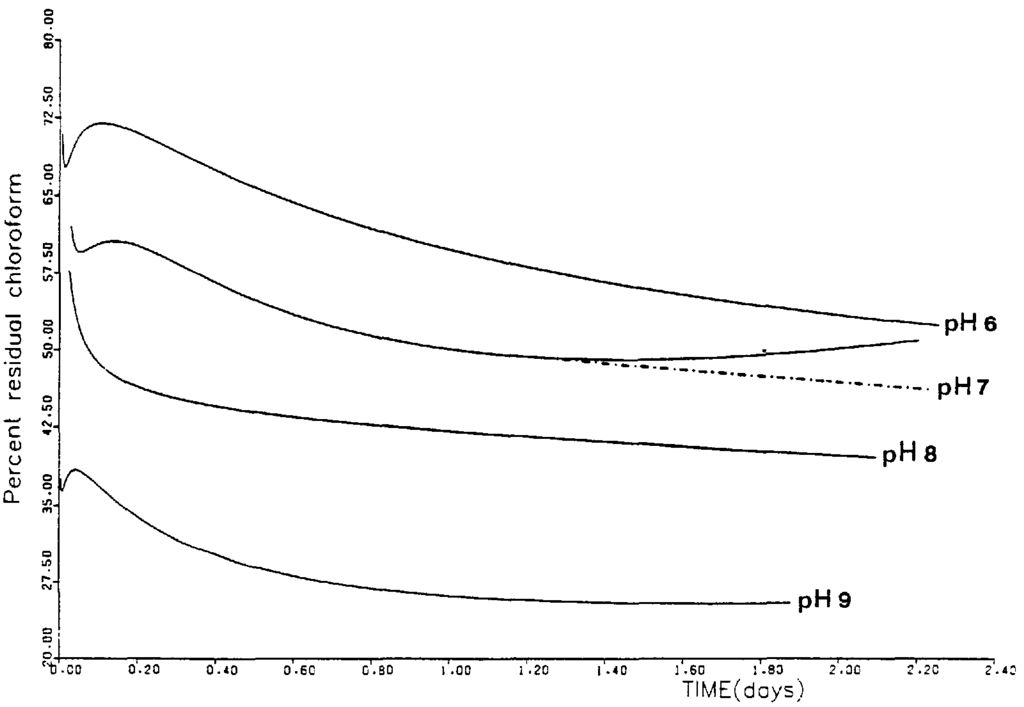


Fig. 3.6 Percentage change in residual chloroform from humic acid at 10°C

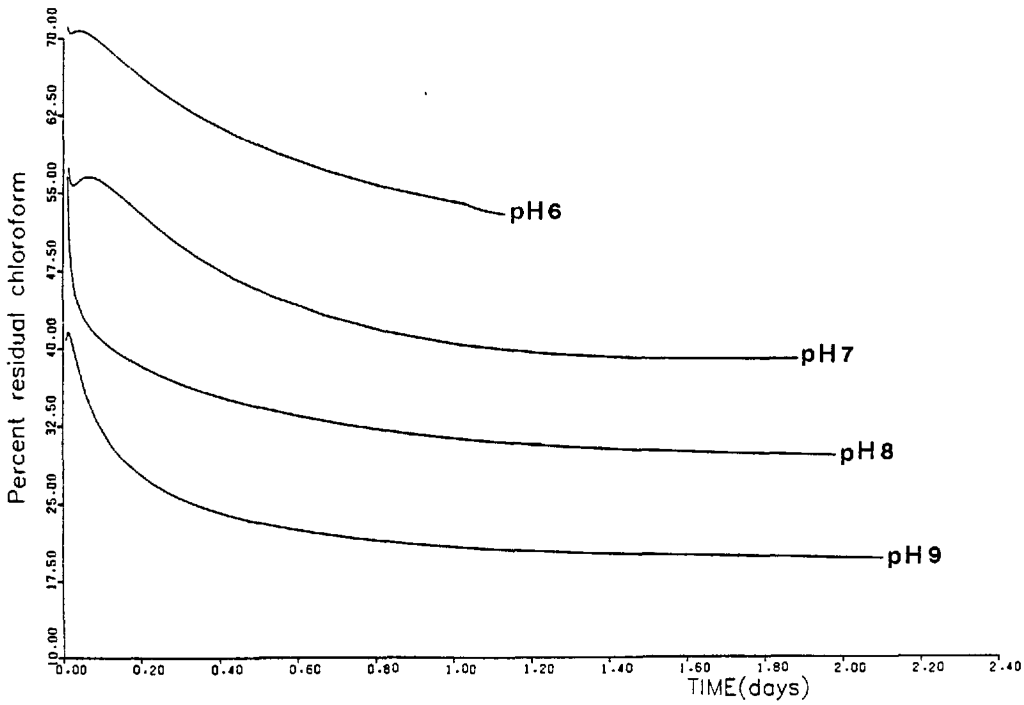


Fig. 3.7 Percentage change in residual chloroform from fulvic acid at 10°C

volatile C-chlorination is similar to those reactions involved in the formation of the organohalide intermediates detected as residual chloroform on chromatographic analysis using D.A.I.

Table 3.5 Total, dissolved and residual chloroform concentrations (μg l^{-1}) after 2 days reaction at 10°C from humic acid

pH	Total $CHCl_3$	Residual $CHCl_3$ (% of total)	Dissolved $CHCl_3$ (% of total)
6	67.5	36.5 (54)	31 (46)
7	87	42 (48)	45 (52)
8	92.5	37.5 (40)	55 (60)
9	79	20 (25)	59 (75)

Table 3.6 Total, dissolved and residual chloroform concentrations (μg l^{-1}) after 2 days reaction at 10°C from fulvic acid

pH	Total $CHCl_3$	Residual $CHCl_3$ (% of total)	Dissolved $CHCl_3$ (% of total)
6	37	18 (49)	19 (51)
7	47.3	18 (38)	29.3 (62)
8	49.1	14.5 (29)	34.6 (71)
9	44.5	9 (20)	35.5 (80)

3.1.3.1 Breakdown of Organochlorine Intermediates

It should be stressed at this point that although the residual chloroform concentration is produced by break down of chlorinated compounds on heating in the gas chromatograph, not all of these intermediates will necessarily break down to form chloroform or the relevant trihalomethane at ambient temperatures.

In the following discussion it will be assumed that all dissolved chloroform is produced *via* the breakdown of chlorinated intermediates detected as residual chloroform on chromatographic analysis by D.A.I. Thus, if dissolved chloroform is produced at ambient temperatures via the hydrolytic breakdown of the organohalide intermediates then;

$$\frac{d[CHCl_3]}{dt} = k_2[OH^-][RCHCl_3] \qquad (1)$$

where $[RCHCl_3]$ = residual chloroform concentration

After 12 hours (0.5 days) of reaction the residual chloroform concentration is approximately constant as, at this point in time, a steady state is reached in which the rate of formation of residual chloroform equals the rate of breakdown of residual chloroform to produce dissolved chloroform. Thus, the rate of change of residual chloroform equals zero;

$$\frac{d[RCHCl_3]}{dt} = 0 \qquad (2)$$

and as

$$\frac{d[TCHCl_3]}{dt} = \frac{d[RCHCl_3]}{dt} + \frac{d[CHCl_3]}{dt} \qquad (3)$$

where $[TCHCl_3]$ = total-chloroform concentration

then

$$\frac{d[TCHCl_3]}{dt} = \frac{d[CHCl_3]}{dt} \qquad (4)$$

The rate of total-chloroform formation and dissolved chloroform formation is approximately linear at this point, thus;

$$\frac{d[TCHCl_3]}{dt} = \frac{d[CHCl_3]}{dt} = K \qquad (5)$$

Substituting into equation (1) and rearranging

$$[RCHCl_3] = \frac{K}{k\,[OH^-]} \qquad (6)$$

The limiting value of residual chloroform concentration at the steady state is inversely proportional to the hydroxide ion concentration, thus on increasing pH there is a fall in the limiting value of the residual chloroform concentration when the steady state is reached.

3.1.4 Chlorine Dose and Chloroform Formation

The production of chloroform and the consumption of chlorine have been monitored with time over a range of temperatures and pH. The trends observed for humic and fulvic fractions with variations in these parameters have been found to be similar.

Chlorine consumption generally increased with increasing pH for both humic (Fig. 3.8 and Appendix I, Fig. 11-12) and fulvic (Fig. 3.9) fractions, reaching a maximum at pH 8 with a decrease in consumption between pH 8 and pH 9.

When considering the reaction of humic or fulvic acid with chlorine in aqueous solution to produce chloroform it is essential to note that this is a minor reaction. As indicated by the data reported here, approximately 1% of the chlorine consumed and only 0.2-0.3% of the carbon content (by weight) of the humic or fulvic fraction reacts to produce chloroform. These data are in good agreement with previously reported trihalomethane yields for the chlorination of fulvic or humic acids(18,19).

Chlorine consumption curves have been monitored for reactions containing 25 mg l^{-1} fulvic acid with chlorine doses of between 1 and 9 mg l^{-1} by both iodometric and DPD(120) methods. The total available chlorine curves have shown good agreement; additionally, the DPD method has enabled the determination of the contribution of chloramines to the total chlorine measured. This experiment has revealed that there is a rapid reaction of chlorine with the nitrogen content of the fulvic material to produce chloramines. At low chlorine doses this reaction leads to a rapid exhaustion of free chlorine. Independent of the original chlorine concentration and pH a fixed amount of chlorine reacts rapidly (within 10-20 minutes) to yield chloramines (0.3-0.4 mg l^{-1}).

This chloramine level remains relatively constant falling only to 0.2-0.3 mg l^{-1} after 30 hours. With initial chlorine doses of 4 mg l^{-1} and 2 mg l^{-1}, free chlorine was reduced to 0.05 mg l^{-1} after 80 minutes and 0.1 after 60 minutes respectively, whilst in both cases chloramine concentrations had reached a maximum of 0.3 mg l^{-1} after

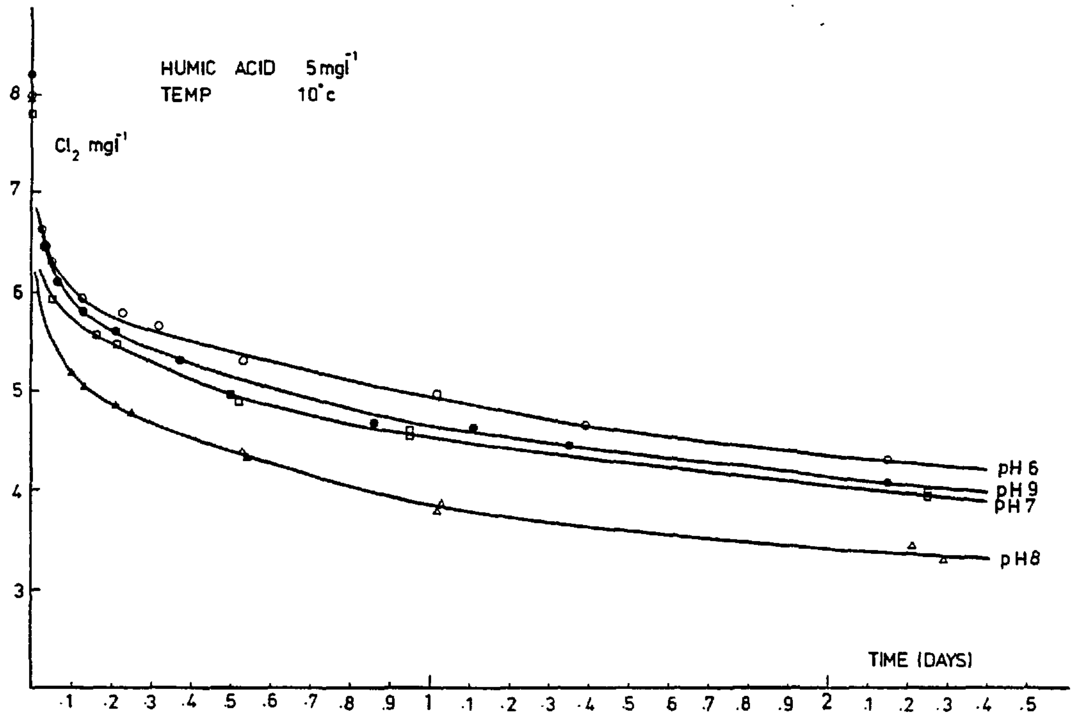


Fig. 3.8 Change in chlorine concentration on chlorinating humic acid at $10^{\circ}C$

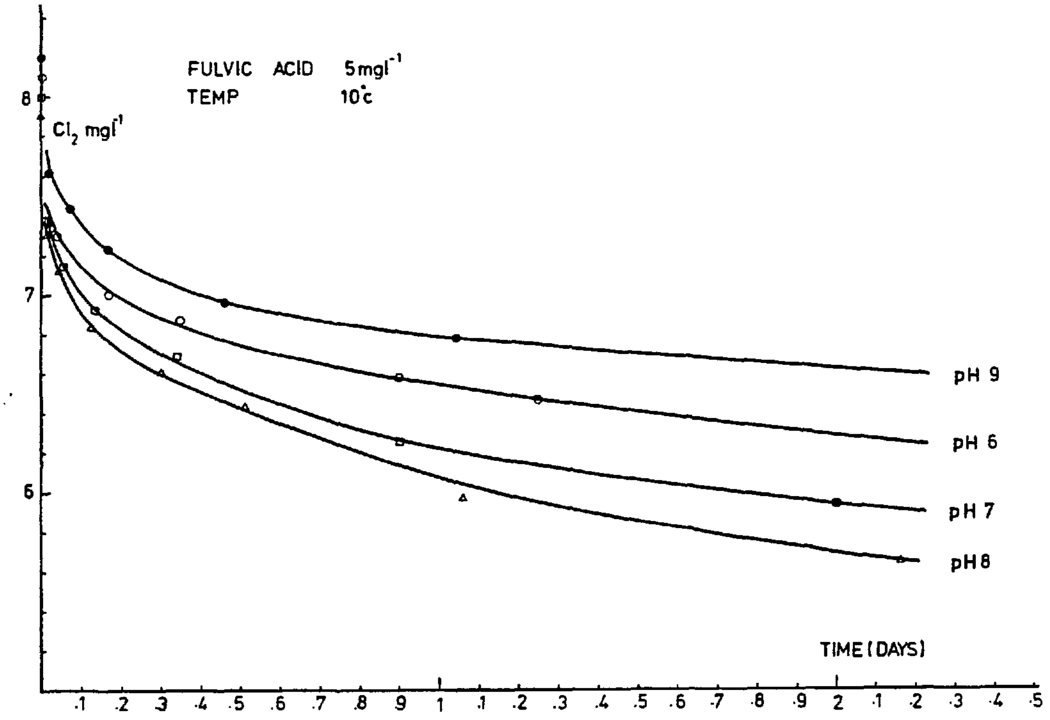


Fig. 3.9 Change in chlorine concentration on chlorinating fulvic acid at $10^{\circ}C$

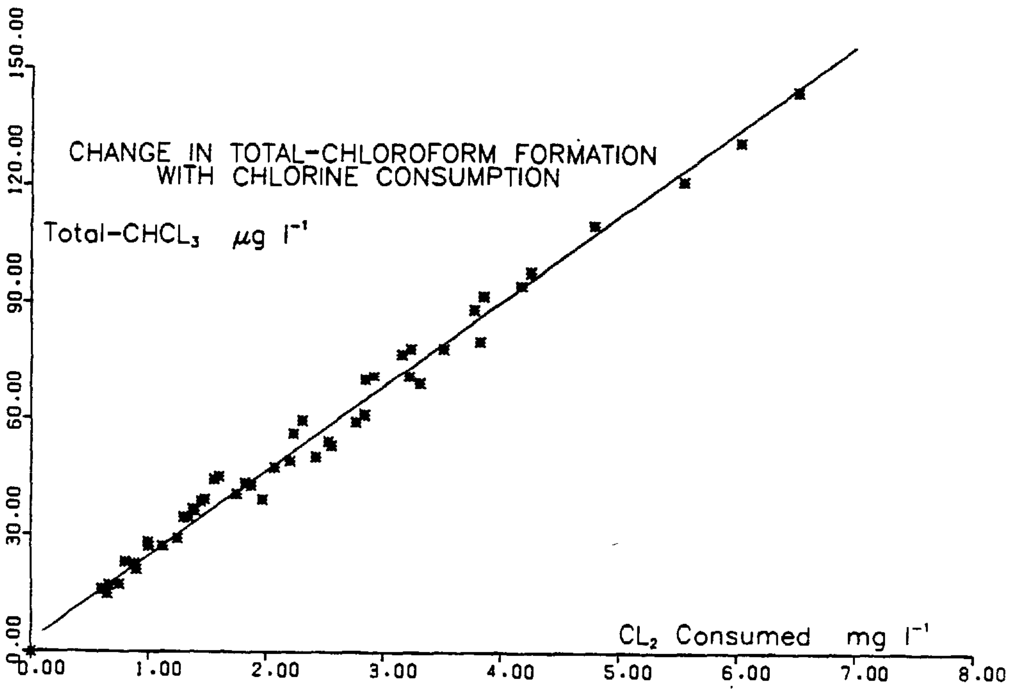


Fig. 3.10 Change in total-chloroform formation with chlorine consumption

40 minutes and remained constant up to 100 minutes. Thus this competitive reaction to yield chloramines may well limit haloform production under such conditions. Stevens et al.(83) on chlorinating humic acid solutions in the presence of 5.2 mg 1^{-1} of ammonia nitrogen, found that if breakpoint chlorination was not reached, a considerable reduction in trihalomethane formation occurred.

Figure 3.10 shows the change in total-chloroform concentration (residual and dissolved chloroform) with chlorine consumption for both humic and fulvic acids over a range of conditions, which may be expressed as:-

$$(TCHCl_3)_t = 0.022\{(Cl_2)_o - (Cl_2)_t\} \qquad (7)$$

where $(TCHCl_3)_t$ = Total Chloroform concentration (mg l^{-1}) at time t
$(Cl_2)_t$ = Chlorine concentration (mg l^{-1}) at time t
$(Cl_2)_o$ = Initial chlorine concentration (mg l^{-1})

The lower chlorine consumption by fulvic acid compared to humic acid is compensated for by a lower yield of dissolved and residual chloroform.

3.1.5 Total-Chloroform

Total-chloroform equals the sum of residual chloroform and dissolved chloroform.

The overall chloroform reaction may be represented by equations (8) and (9), which involve the formation and subsequent breakdown of intermediates detected as residual chloroform ($RCHCl_3$).

$$F.A./H.A. + yCl_2 \xrightarrow[OH^-]{k_1} RCHCl_3 \qquad (8a)$$

$$RCHCl_3 \xrightarrow[OH^-]{k_2} CHCl_3 \qquad (8b)$$

As discussed in the previous section the residual chloroform concentration reaches a limiting value as the steady state is reached between the rate of formation and the rate of breakdown of residual chloroform. The concentration of residual chloroform at the steady state is inversely proportional to the hydroxide ion concentration.

The haloform reaction involves the successive substitution of hydrogen by halogen at the α-carbon to a carbonyl group and subsequent hydrolysis to produce a haloform. The slow, rate determining, step for simple acetyl containing compounds is proton dissociation, a step which is dependent on pH but independent of halogen concentration. The rate of reaction increases with increasing pH. The reaction may be either acid or base catalysed, though under acid conditions there is a change in mechanism. For more complex organic compounds hydrolysis is the rate determining step as steric hinderance becomes a dominating factor.

Humic and fulvic acids have complex structures which will undoubtedly undergo more complicated 'haloform reactions' than simple organic compounds. Chloroform formation may involve dehydroxyquinone structures and other active double bonds, provided that these sites give rise to acetyl groups on oxidation. Chloroform formation from sites which react readily with chlorine to produce acetyl groups may follow the classical haloform reaction. Oxidation though may well become the rate determining step once these sites are exhausted.

If the breakdown of intermediates is rapid no residual chloroform would be detected. The presence of residual chloroform indicates that the hydrolysis of the organohalide intermediates containing a trihalide group is slow and possibly dependent on factors such as steric hinderance, mesomeric and inductive effects.

Total-chloroform formation may be characterised as follows;

(a) A rapid initial phase of total-chloroform formation from sites which readily produce acetyl groups. These reactions may follow the classical haloform reaction, the rate determining step being proton dissociation which is greatly influenced by pH.

(b) An intermediate phase involving sterically hindered or deactivated sites that follow the classical haloform reaction but which also include rate determining steps involving not only proton dissociation but the chlorinating species (HOCl or H_2OCl^+).

(c) A slower secondary phase of total-chloroform formation involving an initial oxidation step of active sites to form acetyl groups which subsequently undergo the haloform reaction. The oxidation step of the active sites may be the rate determining step for such reactions.

Figure 3.11 shows the formation of total-chloroform on chlorinating humic and fulvic acid at 10°C for reactions carried out at pH 7, pH 8 and pH 9. It is evident that the rate of total-chloroform formation is not significantly affected by pH compared to the formation of dissolved chloroform. Total-chloroform formation therefore does not follow the classical haloform reaction in terms of its dependence on pH.

The rapid phase (a) and the intermediate phase (b) are to a certain extent mutually exclusive, as on decreasing the pH, phase (a) will slow down, as a result of the lower hydroxide ion concentration, but may be compensated for by an increase in phase (b) as a result of the increase in HOCl and H_2OCl^+ concentration at the lower pH.

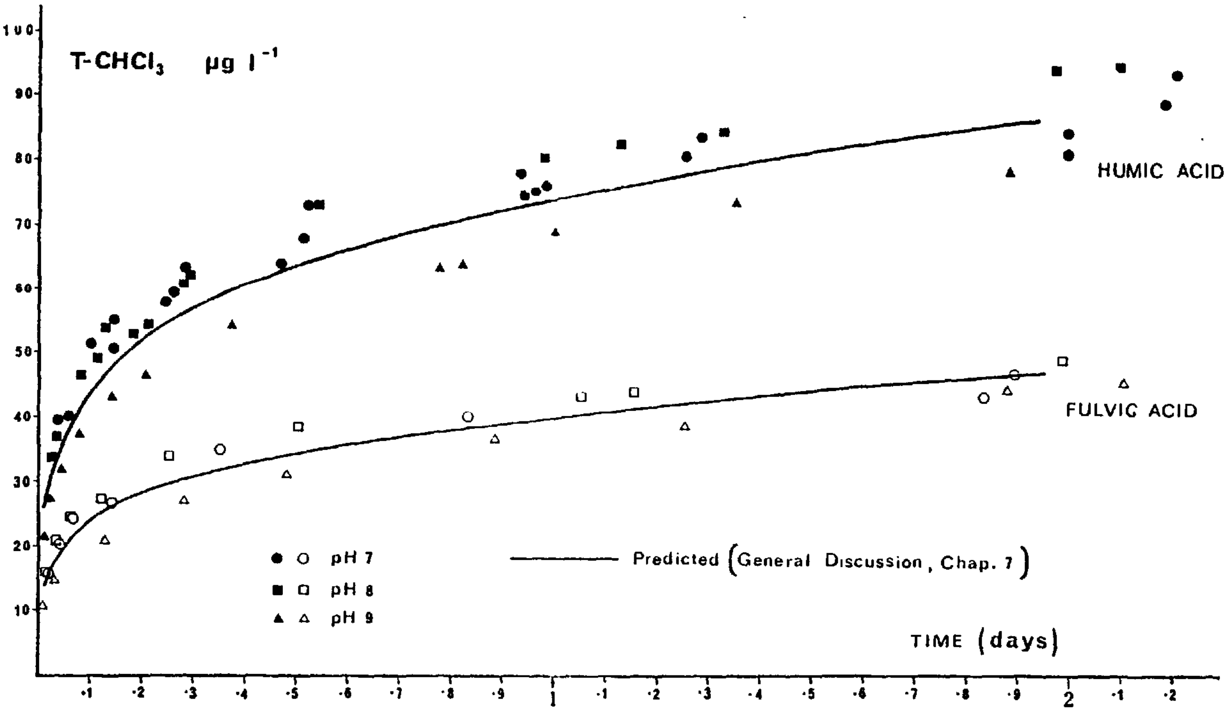


Fig. 3.11 Effect of pH on total-chloroform formation from humic and fulvic acids (5 mg l^{-1}) at 10°C. Predicted values based on empiricial equation (Chapter 7)

The slower phase (c) of total chloroform formation involves an initial oxidation step of active sites. The chlorine species OCl^- does not have the chlorinating capacity of HOCl but is effective oxidising agent, thus both the chlorine species HOCl and OCl^- are involved in the oxidation step. This secondary phase therefore is dependent on the total chlorine ($HOCl + OCl^-$) concentration, which of course does not vary with pH.

3.1.6 Rates of Reaction

A first order dependence of the rate of chlorine consumption on chlorine concentration during reaction with humic acid has recently been reported(13).

It is doubtful whether the derivation of a general rate equation for both chlorine consumption and haloform formation is possible, due to the complexity of the reactions and the variations in the structure of humic substances present in different waters. A rate equation may, however be formulated for a specific source of water to predict the effect of changing the chlorination conditions on haloform formation and chlorine consumption.

The reported data were derived from experiments designed to examine the variation of chloroform production over a wide range of reaction conditions. Experimental design was not such as to facilitate rigorous kinetic interpretation. Selection of appropriate groups of data does, however, permit a simple representation of the kinetics involved.

The overall chloroform reaction may be represented by equations (8) and (9), which involve the formation and subsequent breakdown of intermediates detected as residual chloroform ($RCHCl_3$). The rates of residual chloroform and dissolved chloroform formation are given by equations (10) and (1) respectively. Equation (3) is the rate of total-chloroform formation which is equal to the sum of the rates of formation of residual and dissolved chloroform.

As shown by Fig. 3.9 the overall chlorine consumption for fulvic acid after 2 days reaction is not greater than 25% of the initial chlorine dose. Thus it may be assumed that, under these conditions, chlorine remains in excess throughout the reaction.

At constant pH a pseudo first-order rate equation may be derived for the rate of total-chloroform formation dependent on the fulvic acid concentration (equation 12) or, more correctly, dependent on the number of acetyl groups and active sites available for the haloform reaction. For a given quantity of fulvic acid in excess chlorine, the haloform concentrations will reach a limiting value. This maximum haloform concentration is a measure of the acetyl groups and active sites in the acid structure which give the haloform reaction. Therefore, the effective fulvic acid concentration, may be represented in terms of this limiting chloroform concentration by equation (13). Substituting this equation into equation (12) and integrating gives equation (15).

The two basic assumptions for these equations are:-

(a) Chlorine is in excess.

(b) All chloroform is produced <u>via</u> intermediates measured as residual chloroform.

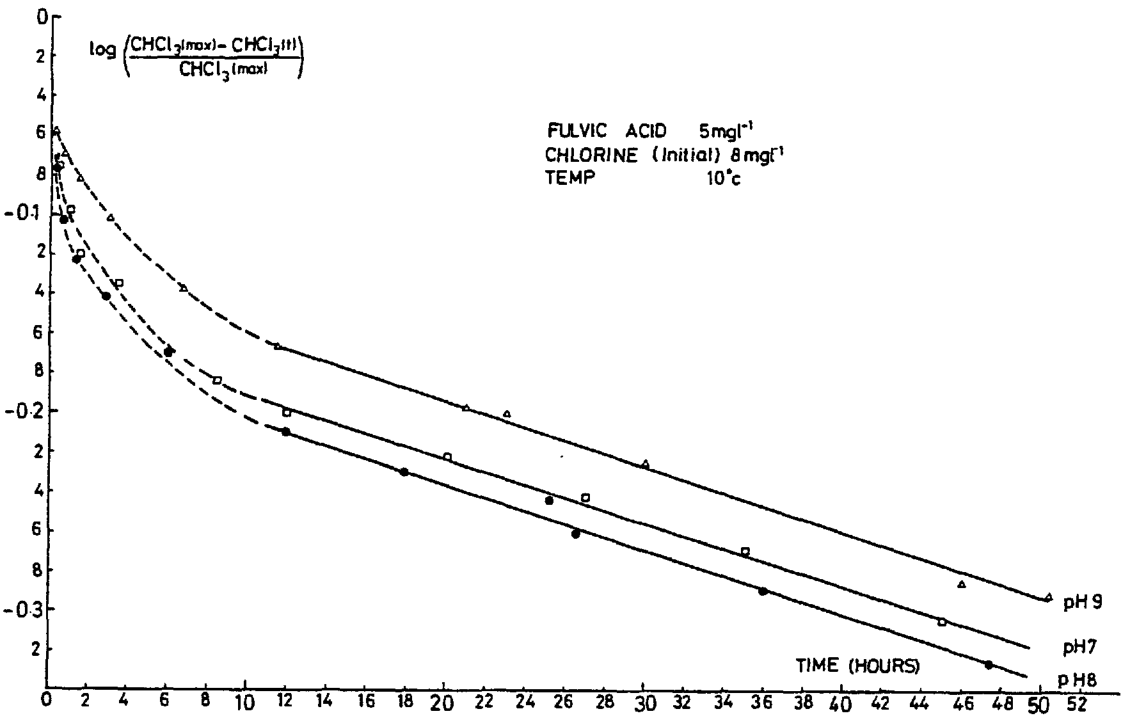


Fig. 3.12 Pseudo first-order plot of total-chloroform formation

The calculation of the rate constant k_1'' has not been attempted as the value $(TCHCl_3)_{max}$ has not been determined. An arbitrary but realistic value of 100 µg l^{-1} may be assumed for $(TCHCl_3)_{max}$ and the above equation plotted (Fig. 3.12). The equation gives straight line plots for pH 7, 8, and 9 after 8 hours of reaction. The initial rate of total-chloroform formation is fast and does not follow the first order rate equation.

$$F.A. + yCl_2 \underset{OH^-}{\overset{k_1}{\rightarrow}} RCHCl_3 \qquad (8b)$$

$$RCHCl_3 \underset{OH^-}{\overset{k_2}{\rightarrow}} CHCl_3 \qquad (9b)$$

where $RCHCl_3$ = Residual Chloroform

F.A. = Fulvic acid

$$\frac{d(RCHCl_3)}{dt} = k_1(F.A.)^x(Cl_2)^y(OH^-)^z - k_2(RCHCL_3) \qquad (10)$$

From equations (1) and (3)

$$\frac{d(CHCl_3)}{dt} = k_2(RCHCl_3)$$

$$\frac{d(TCHCl_3)}{dt} = \frac{d(RCHCl_3)}{dt} + \frac{d(CHCl_3)}{dt}$$

where $(TCHCl_3)$ = Total-Chloroform

$$\frac{d(TCHCl_3)}{dt} = k_1(F.A.)^x(Cl_2)^y(OH^-)^z \qquad (11)$$

for constant (Cl_2) and (OH^-)

$$\frac{d(TCHCl_3)}{dt} = k_1'(F.A.)^x \qquad (12)$$

for a first order rate equation $x = 1$

$$(F.A.)_t^* \propto (TCHCl_3)_{max.} - (TCHCl_3)_t \qquad (13)$$

where $(F.A.)_t^*$ = effective fulvic acid concentration at time t

$$\frac{d(TCHCl_3)}{dt} = k_1''((TCHCl_3)_{max} - (TCHCl_3)_t) \qquad (14)$$

integrating equation (14) gives,

$$\ln\left(\frac{(TCHCl_3)_{max} - (TCHCl_3)_t}{(TCHCl_3)_{max}}\right) = -k_1'' \, t \qquad (15)$$

3.1.7 UV/VIS Absorption Spectra and Total-Chloroform Correlation

The U.V. absorption of humic acid is greater than for fulvic acid signifying a higher degree of unsaturation or delocalisation associated with the greater complexity of these molecules. The greater number of active sites in the humic acid molecule gives rise to an increased potential for oxidation and subsequent trihalomethane formation.

A correlation is tentatively proposed between the ratios for total-chloroform formation by these acids and the integral of the U.V./VIS. absorption between the wavelengths 600-240 nm (the region where C = C and C = 0 absorb being 400-200 nm) at pH 7 (Table 3.7).

Table 3.7 Total-chloroform formation and U.V./VIS adsorption

Acid Conc.	Ratio Abs.Integral H.A./F.A. 600–240 nm	Ratio Total-$CHCl_3$ H.A./F.A.			
		pH 6	pH 7	p H 8	pH 9
5 mg l^{-1}	1.689	1.82	1.89	1.85	1.76
20 mg l^{-1}	1.97*	-	-	-	-

* No significant change in the ratio of the absorption integral at 20 mg l^{-1}

3.1.8 Reaction Scheme

A reaction scheme involving a minimum of two possible pathways to chloroform may be outlined. There is a fast initial step which forms an intermediate, $(CHCl_3)_A$*, which is detected as residual chloroform.

The breakdown of this residual to form chloroform is slower than its formation and is pH dependent (Path 1). There is a second path (Path 2) leading to chloroform formation, which involves a slow oxidation stage followed by a chlorination stage to form the intermedaites, $(CHCl_3)_B$*, possibly via quinones, as suggested by Rook(90). This intermediate also decomposes to yield chloroform at normal temperatures in a reaction which is also pH dependent.

The intermediates A and B are characterised by the difference in the ease with which they break down to yield chloroform. Some simple acetyl containing compounds will form trihalo intermediates which decompose slowly depending on temperature, pH and steric hindrance, as these factors affect the rate of hydrolysis(88). There are trihaloacetyl derivatives which are quite stabe at ambient temperatures due to steric hindrance(88), and decompose to form the corresponding trihalomethane only under more drastic conditions.

It is implicit from a general consideration of reaction mechanisms that the production of chloroform from humic or fulvic materials will involve reaction intermediates. If such intermediates were short-lived and the end-product, chloroform, was produced rapidly under the full range of process conditions used in water disinfection

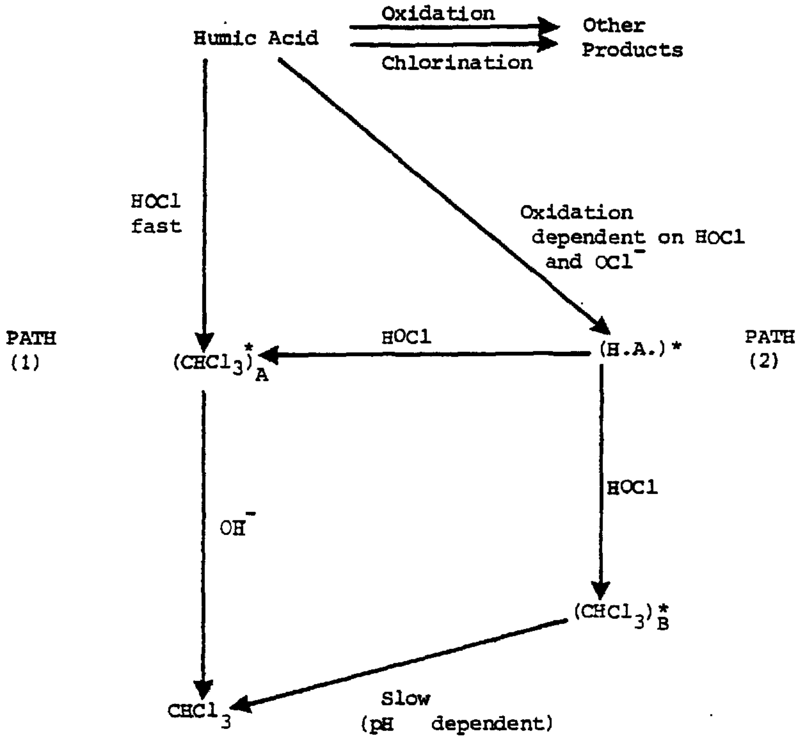


Fig. 3.13 Reaction scheme to chloroform formation

with chlorine, a knowledge of the reaction mechanisms and the nature of the intermediate species would be of limited practical value and would constitute only an academic interest. Indications from the data reported here and from the observations of other authors are: that this is not the case; that the basic reaction system is complex and that it is further complicated by the presence of such species as bromide, ammonia and amines.

The presence of bromide in waters undergoing chlorination(100) has been shown to give rise to organically bound bromine in addition to increasing the brominated haloforms produced. At bromide levels of 2 ppm, no chloroform was detected, all the haloform being present as bromoform(102).

3.1.9 Bromodichloromethane

Brominated haloforms were not expected to be formed, as sodium hypochlorite, low in bromine, was being used as a chlorinating agent in these preliminary humic acid reactions. Relatively high bromodichloromethane (up to 15 μg l^{-1}) levels were, however, detected on certain occasions. Like chloroform, these were composed of distinct dissolved and residual components. The rate of removal of 'apparent bromodichloromethane' by purging was not in agreement with rates obtained for spiked samples (Appendix I, Fig. 13). Further, only 30% of the bromodichloromethane could be solvent extracted into hexane while spiked samples gave extraction efficiencies of over 90%. These anomalies in extraction and purging efficiencies indicated the presence of a volatile halogenated compound which, on heating, breaks down to form bromodichloromethane.

Further evidence that this is an intermediate is obtained by observing the effect of pH on the formation of 'apparent bromodichloromethane', Appendix I, Fig. 14,which decreases on increasing the pH in a similar manner to the formation of residual chloroform.

The fact that the bromodichloromethane intermediate is purgeable in contrast to the corresponding chloroform intermediate is interesting. No conclusion, however, can be arrived at until mass spectrometric data are obtained to elucidate the nature of this intermediate.

3.1.10 Bromide Addition

In order to observe the effect of bromide on trihalomethane formation a solution containing 450 μg l^{-1} of bromide and 5 mg l^{-1} of humic acid, buffered at pH 7 and maintained at 5°C was chlorinated at an initial concentration of 8 mg l^{-1}.

At the time the bromide addition experiment was carried out there were no available data on bromide concentrations in Thames water. The spiked bromide concentration of 450 μg l^{-1} was therefore based on reported levels(70) from various waters of up to 1 mg l^{-1}. Recent analyses, however, show that bromide concentrations in Thames water generally range between 90 μg l^{-1} and 120 μg l^{-1} (139).

Table 3.8 shows the effect of 450 µg l^{-1} bromide on total, residual and dissolved trihalomethane formation. It is apparent that although total-chloroform formation is reduced, the overall trihalomethane concentration, in terms of molar concentrations, is greatly enhanced by the presence of bromide.

The bromide is oxidised by chlorine to hypobromous acid (and possibly other oxybromine species) which is subsequently involved with hypochlorous acid in competitive haloform reactions. Figure 3.14 shows the percentage distribution, in terms of molar concentration, of the trihalomethanes produced after 42 hours of reaction under the chlorinating conditions employed, and the percentage distribution present in tap water samples within the London area (Chapter 6). At 450 µg l^{-1} of bromide, dibromochloromethane is the predominant trihalomethane produced.

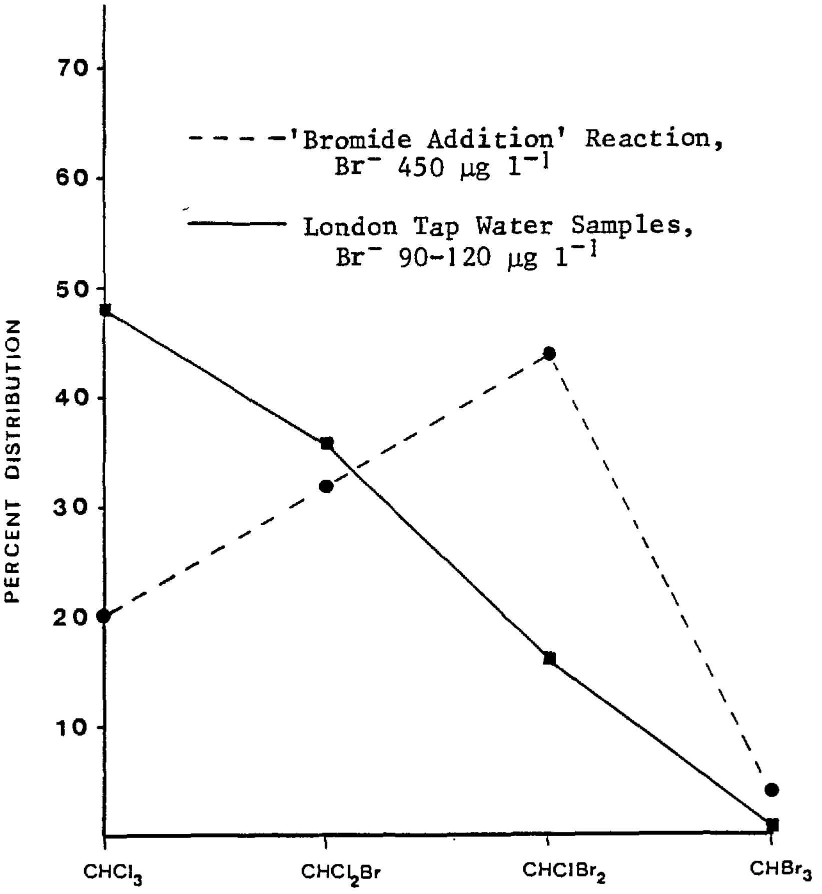


Fig. 3.14 Total-trihalomethanes percent distribution (molar) for 'bromide addition' reaction and tap water samples within the London area (Chapter 6)

Table 3.7 Effect of bromide on trihalomethane formation (humic acid 5 μg l^{-1}; chlorine (initial) 8 mg l^{-1}; bromide 450 μg l^{-1}; pH 7; temperature 10°C)

Time hrs	$CHCl_3$ (μg l^{-1})			$CHCl_2Br$ (μg l^{-1})			$CHClBr_2$ (μg l^{-1})			$CHBr_3$ (μg l^{-1})		
	Tot.	Res.	Diss.	Tot.	Res.	Diss.	Tot.	Res.	Diss.	Tot.	Res.	Diss.
0.25	8	3	5	7	3	4						
1.0	11	4	7	13	8	5	32	9.5	22	5	2	3
19	26	14	13	48	14	34	97	36	60	12	3.5	8.5
42	36	18	18	74	16	58	134	41	93	16	3.5	12.5
Molar Concns. (Total)	0.3×10^{-6}			0.45×10^{-6}			0.64×10^{-6}			0.06×10^{-6}		
% Contribution (molar)	20			32			44			4		

Total molar concentration after 42 hrs 1.45×10^{-6}

Total molar concentration (no bromide) 0.64×10^{-6}

4. CHLORINATION OF AN UPLAND WATER - LABORATORY and ON-SITE STUDIES

4.1 INTRODUCTION

The work reported in Chapter 3 has dealt with the production of chloroform during the chlorination of humic and fulvic acids under controlled conditions. These laboratory studies gave indications of the relative importance of the interacting parameters on both the rate and extent of chloroform production, and also facilitated the development of appropriate experimental and analytical techniques.

It was not possible to determine the applicability of the results obtained to the process of chlorination as practiced in the water industry. The humic and fulvic materials used had been extracted from the Thames(115) and stored dry for an extended period before being dissolved in 'purified' water prior to reaction. The partition between humic and fulvic fractions was therefore defined by the extraction procedure. The effect of storage was not known, nor was there any indication as to how representative these species were of humic substances in general.

The work reported here has involved the chlorination of raw or partially treated water under similar laboratory conditions to those used previously, and comparison of the results obtained with chloroform levels observed at a treatment works, under normal operating conditions. Particular attention has been paid to the role of the residual chloroform, which may not be detected by other analytical techniques but which can constitute an appreciable proportion of the eventual total chloroform produced during treatment and distribution.

A suitable source water for these studies was required to contain high concentrations of humic material which would produce high levels of the trihalomethanes on chlorination; thus facilitating the observation of the effect of changing parameters on their formation. Lowland waters tend, in general, to be low in humic content. Trihalomethane production in such waters is also complicated by the presence of ammonia and organic amines, which may undergo rapid, competitive, reactions with chlorine. Upland waters on the other hand satisfy the above requirements as this type of water generally contains a high level of humic material and has a low ammonia content.

An upland water treated at the works of the

Northumbria Water Authority was selected for study. Normal operation at the works is designed to ensure that the final water leaving the plant contains enough free chlorine for a residual to be present throughout an extended distribution system. The high chlorine demand means that the chlorine dosing level for disinfection is high. approximately 2.5 mg l^{-1} to 3 mg l^{-1}. The high organic content of the water coupled with the required chlorine dosing level leads to a substantial amount of chloroform formation. The low bromide content (10 μg l^{-1}), generally associated with upland waters is reflected in the low concentrations of the brominated trihalomethanes produced on chlorination. Dibromochloromethane and bromoform were not detectable by D.A.I. and bromodichloromethane concentrations were less than 5% of the chloroform concentration.

4.1.1 Treatment Works Operation

The demand for an aesthetic water requires that the colour of water be reduced to an acceptable level prior to distribution. Not all the water through the works is treated for the removal of colour, one third of the flow is slow sand filtered which, though ineffective in reducing the colour, serves in removing gross debris and suspended material.

The bulk of the water, approximately two thirds of the total flow is chemically treated for colour removal by the addition of ferrous sulphate (Copperas) which is oxidised by chlorine to ferric sulphate at pH 4.5 to pH 5 for effective coagulation. The flocs are settled and the clarified water 'polished' by rapid gravity filters. The reduction in TOC is 70-80% with a greater than 95% reduction in colour.

The water from the rapid gravity filters is mixed with the slow sand filtered water prior to chlorination. The chlorine dose is approximately 2.5 mg l^{-1} to 3 mg l^{-1}, after which lime is added to increase the pH from pH 6 to pH 9. The contact period is approximately 40 minutes, though, as the contact tank also serves as a balancing tank, the contact time may vary depending on the diurnal water requirements. Figure 4.1 is a flow diagram of the treatment plant showing the sampling points.

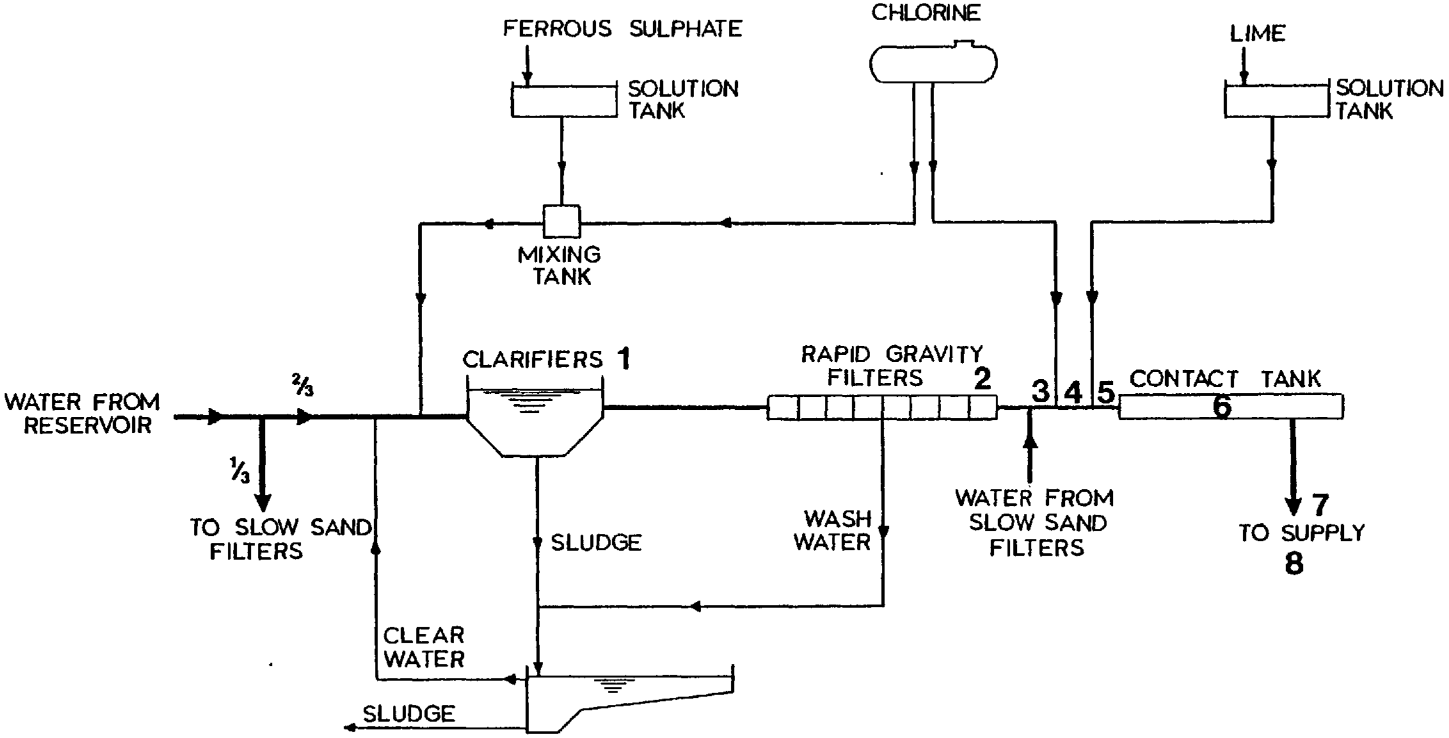


Fig. 4.1 Treatment Plant - Flow Diagram (sampling points (1) - (8))

4.2 RESULTS AND DISCUSSION

4.2.1 Initial Laboratory Studies on Slow Sand Filtered Water

Samples were collected on 2 November 1978 from treatment works. 60 litres of slow sand filtered water were collected in 10 litre aspirators from a sampling point in the works laboratory. All samples were transferred on 2 November from the aspirators to 2.5 l bottles and stored at 3°C. A 200 ml sample from each aspirator and a sample of rapid sand filtered water were sent to WRC on 3 November for T.O.C. analysis. U.V. analysis, colour estimation (Hazen value) and pH determination were performed on a composite sample (S.S.F. (Nov. 78), Table 4.1).

Table 4.1 water analyses

Water	TOC mg l^{-1}	Colour Hazen Value	pH Range	Abs. Integral (Arbitrary Units)
S.S.F. (Nov. 78)	10.5	180-200	7.0-7.5	766
R.G.F. (Nov. 78)	2.1	5	4.5-5.0	-
Mixed S.S.F./R.G.F. (1 : 3) (Nov. 78)	4.8	-	7.0	293
S.S.F. (April 78)	5.7	95	7.0-7.2	447
Final (April 78)	3.5	50	7.0-9.5	214

The rate of chloroform formation is pH dependent, increasing from pH 6 to pH 8 followed by a slight fall at pH 9 (Figs. 4.2-4.6). This is in contrast to the corresponding residual chloroform concentration which decreases on increasing the pH from pH 6 to pH 9 (Figs. 4.2-4.5 and Fig. 4.7).

The high humic content of the water rapidly consumes the chlorine, only 10% of the intial concentration remaining after 3 hours for pH 7 and pH 8 and 5 hours for pH 6 and pH 9. The rate of chlorine

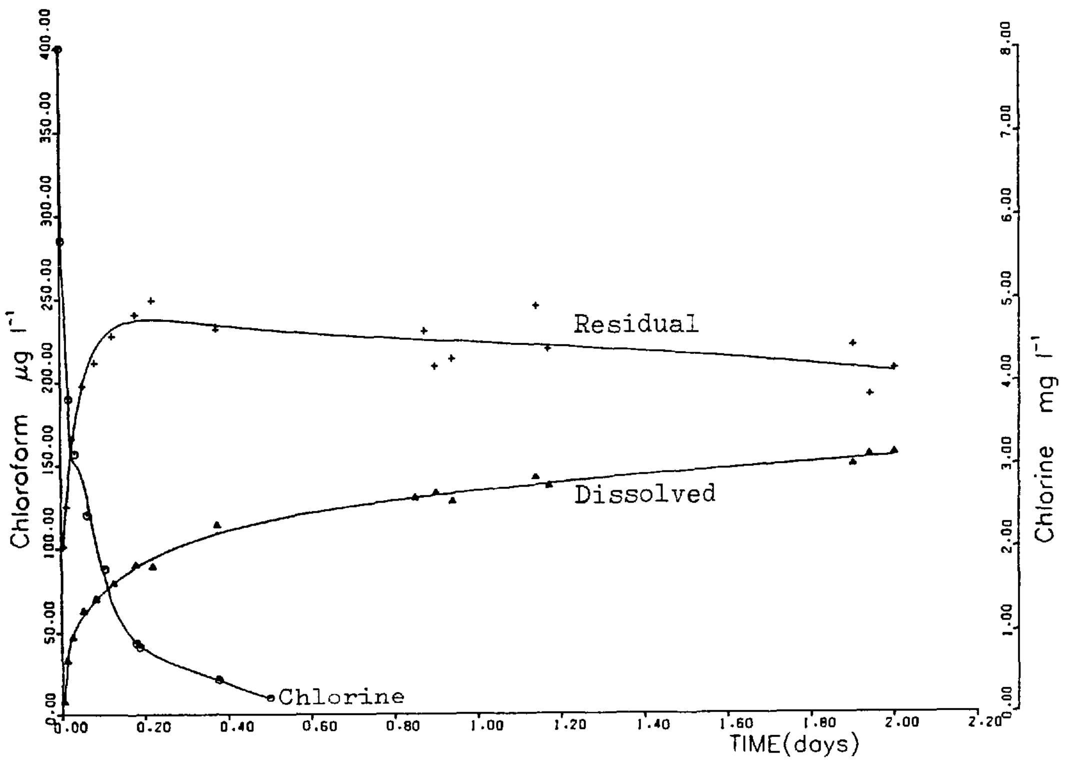


Fig. 4.2 Chlorination of S.S.F. water at pH 6 (Chlorine Int. Concn. 8 mg l^{-1})

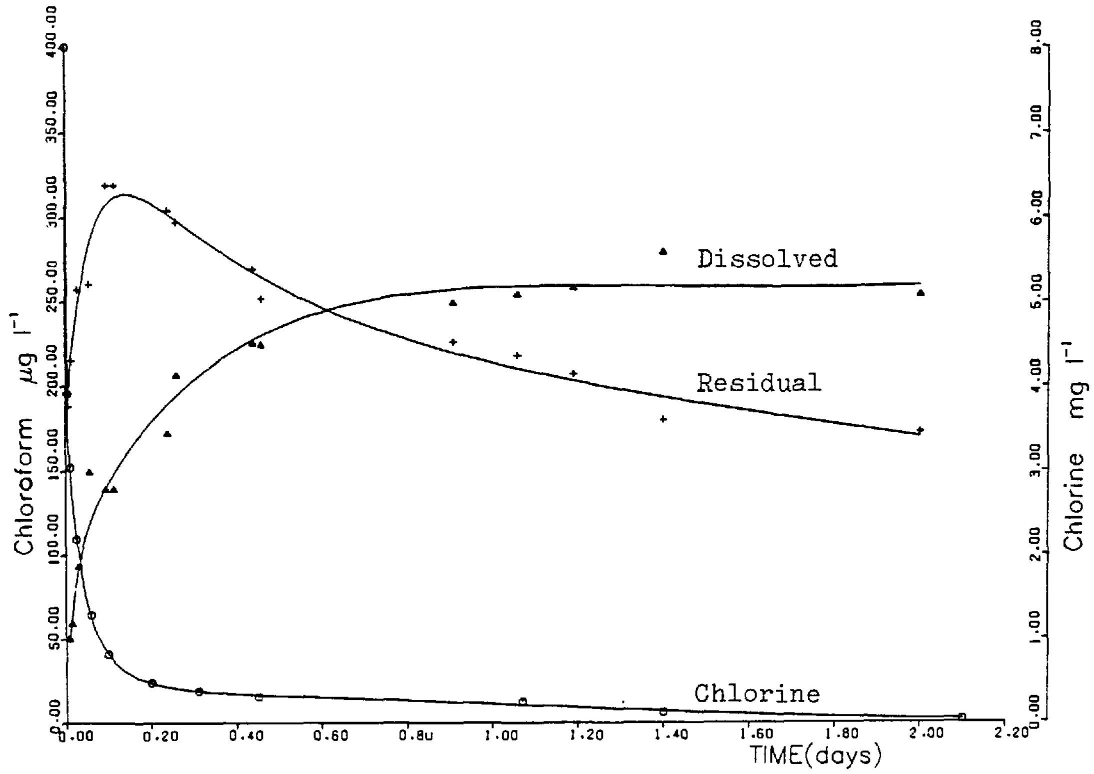


Fig. 4.3 Chlorination of S.S.F. water at pH 7 (Chlorine Int. Concn. 8 mg l^{-1})

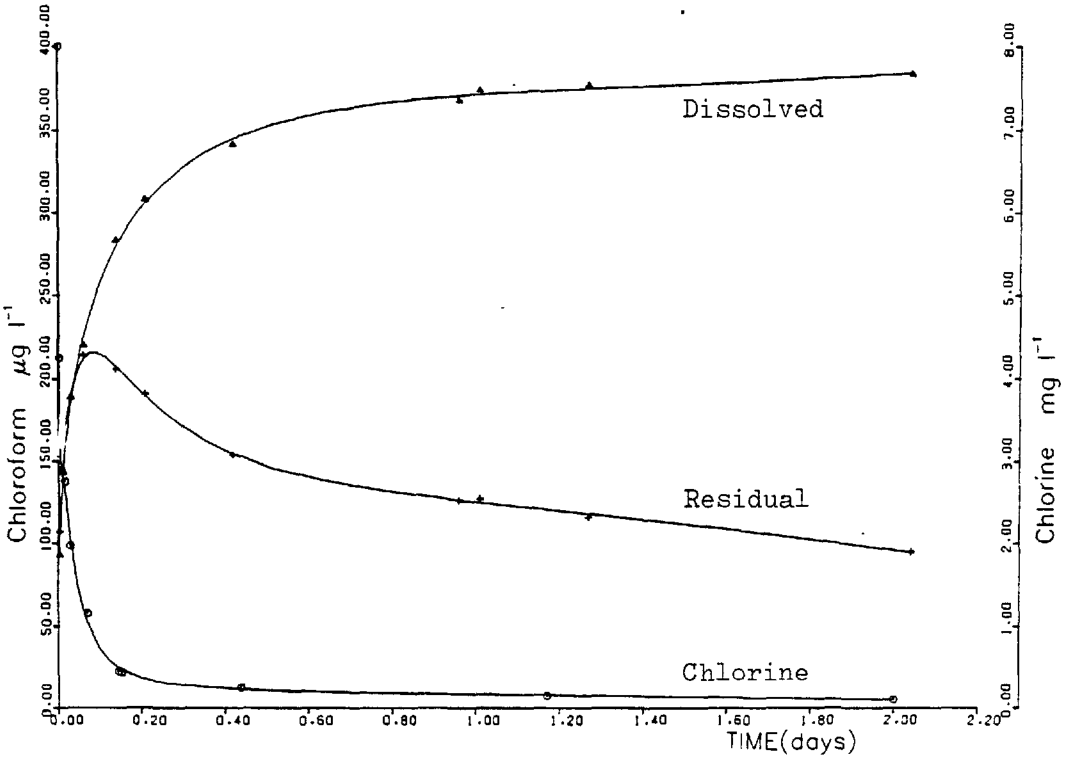


Fig. 4.4 Chlorination of S.S.F. water at pH 8 (Chlorine Init. Concn. 8 mg l^{-1})

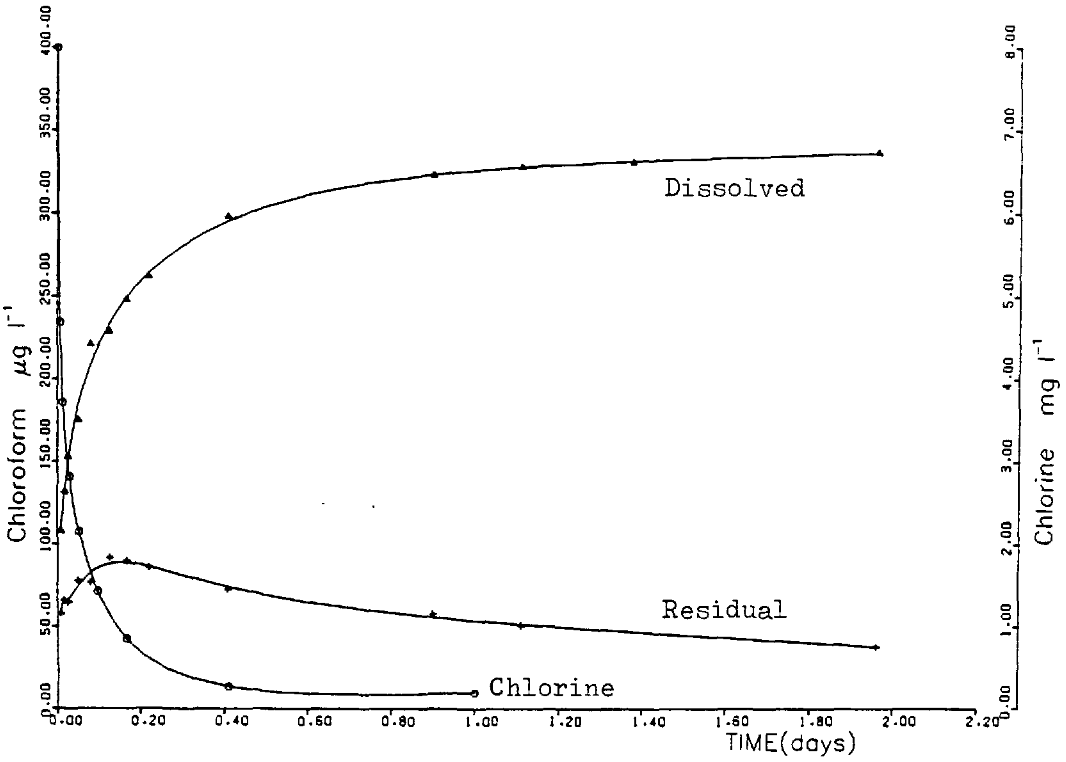


Fig. 4.5 Chlorination of S.S.F. water at pH 9 (Chlorine Init. Concn. 8 mg l^{-1})

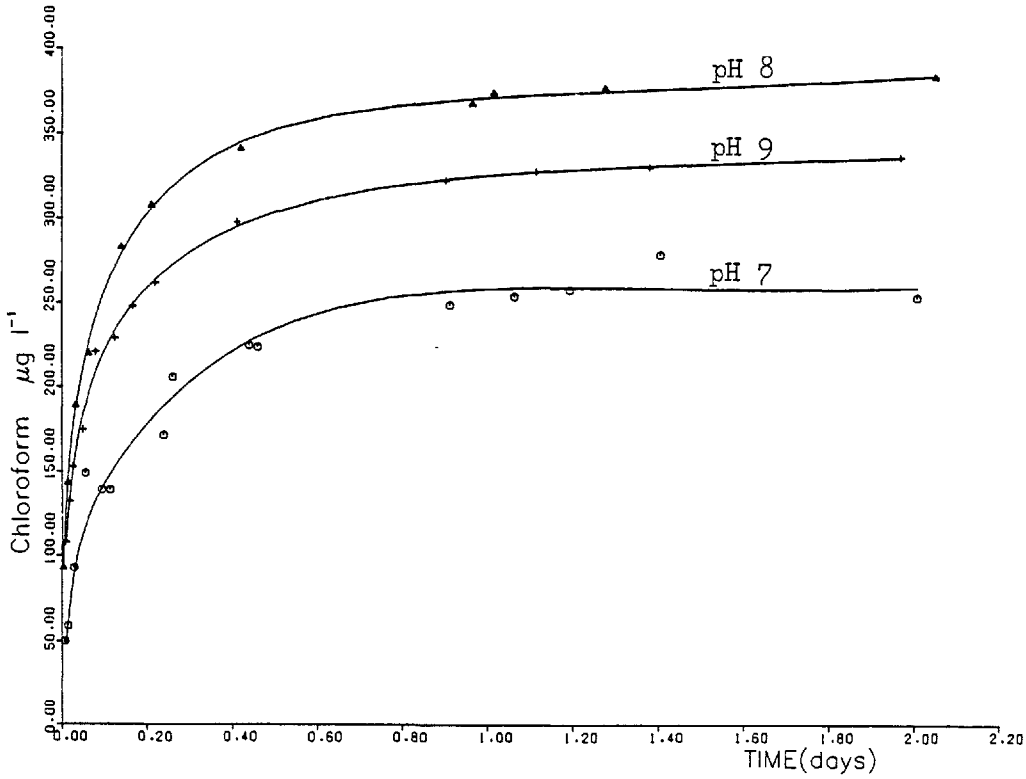


Fig. 4.6 Effect of pH on dissolved chloroform formation from S.S.F. water

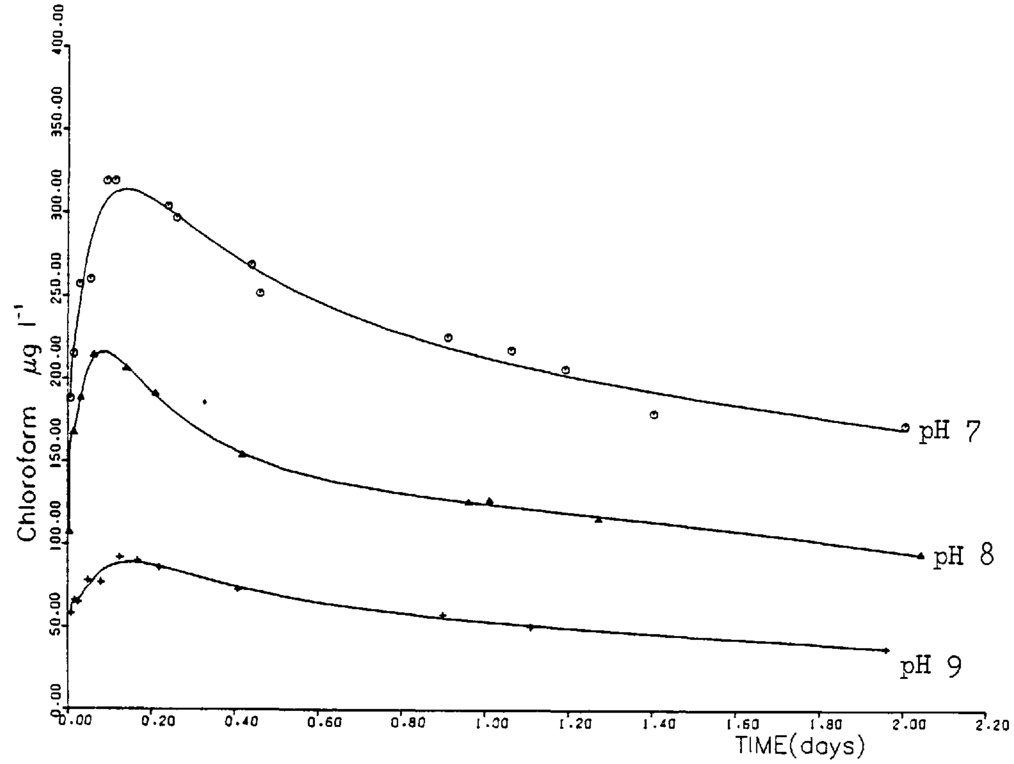


Fig. 4.7 Effect of pH on residual chloroform formation from S.S.F. water

consumption reaches a maximum at pH 8 consistent with the maximum rate of chloroform formation.

Residual chloroform formation reaches a maximum when the chlorine concentration falls below 1 mg l^{-1} (Figs. 4.2-4.5). The kinetics of the formation and decay of residual chloroform vary depending on whether the reaction is carried out under acid or neutral/alkaline conditions. Figure 4.7 shows the formation and decay of residual chloroform at pH 7, pH 8 and pH 9. Although the levels of residual chloroform are different, the trends in the formation and decay of residual chloroform are similar over this range of pH, involving an initial rapid rate of formation in the presence of excess chlorine which, as the chlorine becomes limiting, is followed by an initial rapid decay and subsequent near linear fall in residual chloroform concentration.

The maximum residual chloroform concentration is reached at a steady state when the rate of formation of residual chloroform equals the rate of loss of residual chloroform. The limiting value of residual chloroform is inversely proportional to the hydroxide ion concentration (c.f. section 3.1.3.1) thus,

$$[RCHCl_3] \propto \frac{1}{[OH^-]} \qquad (1)$$

The steady state is reached because of the limiting chlorine concentration, thus if it is assumed that no residual chloroform is produced within a short period of the steady state having been reached then,

$$\frac{d[RCHCl_3]}{dt} = -k_2\ [OH^-][RCHCl_3] \qquad (2)$$

Substituting for $[RCHCl_3]$ gives

$$\frac{d[RCHCl_3]}{dt} = -N \qquad (3)$$

which is independent of pH. Thus the observed rate of fall of residual chloroform is equal to the rate of dissolved chloroform formation and independent of pH. It is evident from figure 4.6 and figure 4.7 that the rate of dissolved chloroform formation and decay of residual chloroform become independent of pH (between pH 7 and pH 9) after a steady state had been reached. The rate of break down of organochlorine intermediates however is dependent on their susceptibility to undergo hydrolytic break down. The value of N therefore will vary with time as the more readily hydrolysed intermediates break down rapidly compared to the intermediates which are sterically hindered or deactivated as a result of mesomeric or inductive effects.

Under acid conditions (pH 6) there appears to be a change in the kinetics of residual chloroform formation (Fig. 4.2). The rate of formation is slower than for pH 8 (Fig. 4.4) with no distinct maximum,only a slow linear decay as the chlorine concentration falls below 1 mg l^{-1}.

The dissolved chloroform concentration as a percentage of the total-chloroform increases between pH 6 and pH 9; at pH 6 only 36% of the total-chloroform is present as dissolved chloroform increasing to 86% at pH 9, after 2 days of reaction.

Figure 4.4 and Figure 4.8 show the effect of reducing the initial chlorine concentration from 8 mg l^{-1} to 4 mg l^{-1}, on residual and dissolved chloroform formation. The initial rate of chloroform formation is fast but slows down rapidly as the chlorine concentration becomes limiting. Reducing the initial chlorine concentration from 8 mg l^{-1} to 4 mg l^{-1} at pH 8 leads to a reduction in tota-chloroform produced from 62 µg/mg Cl_2 consumed to 35 µg/mg Cl_2 consumed.

To observe the effect of dilution on chloroform formation, slow sand filtered water was mixed with rapid gravity filtered water at a ratio of 1:2 in accordance with final water at the works, and chlorinated at pH 8 at an initial chlorine concentration of 4 mg l^{-1} (Fig. 4.9). Total-chloroform produced per unit chlorine consumed is increased compared to undiluted slow sand filtered water at the same initial chlorine concentration, from 35 µg/mg Cl_2 consumed, to 55 µg/mg Cl_2 consumed. This indicates that the initial reactions, which at low initial chlorine concentrations rapidly limit the available chlorine, are not directly involved in the formation of trihalomethanes. However, the initial reactions may be a pre-requisite to the eventual formation of trihalomethanes, as total-chloroform produced per unit chlorine consumed is independent of the humic content in so far as the chlorine concentration does not become the limiting factor.

There is no distinct maximum in the residual chloroform concen-

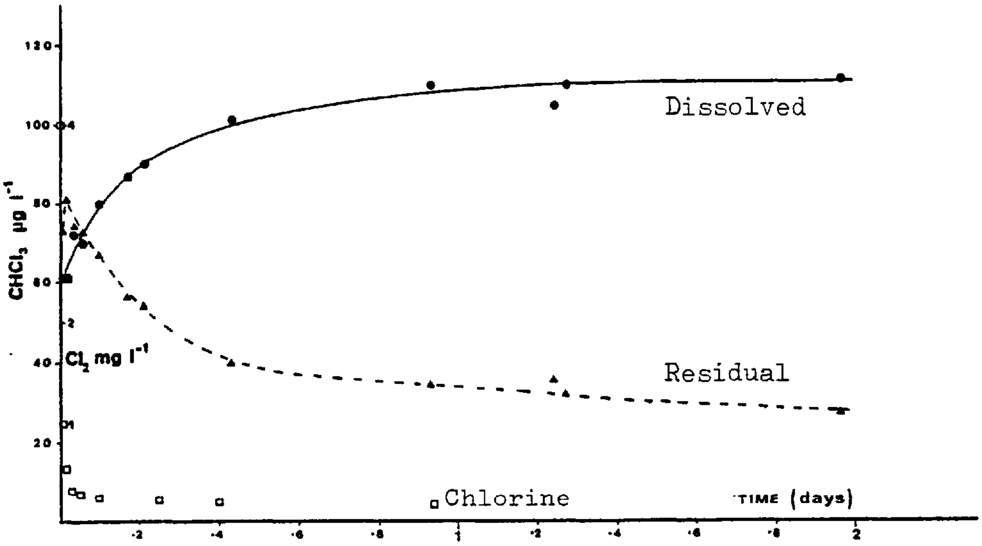


Fig. 4.8 Chlorination of S.S.F. water at pH 8 (Chlorine Init. Concn. 4 mg l^{-1})

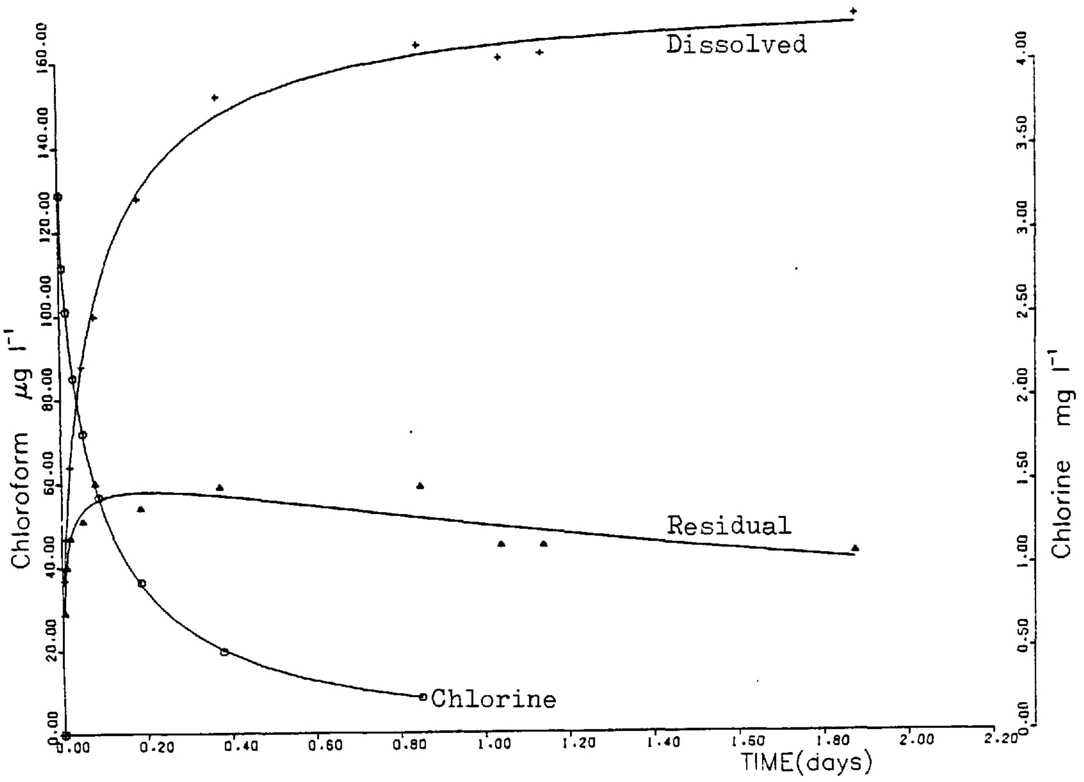


Fig. 4.9 Chlorination of mixed S.S.F./R.G.F. (1:2) water at pH 8 (Chlorine Init. Concn. 4 mg l^{-1})

tration in diluted slow sand filtered water compared to undiluted slow sand filtered water as the steady state between the rate of formation and rate of break down of residual chloroform is maintained because of the continued presence of chlorine resulting from the lower rate of chlorine consumption.

4.2.1.1 Break down of Organochlorine Intermediates

The rate of decay of the residual chloroform, after chlorine has been exhausted, is equal to the rate of increase in dissolved chloroform indicating that the organohalide intermediates, detected as residual chloroform might break down at ambient temperatures to produce dissolved chloroform.

This has been verified in the laboratory by quenching excess chlorine with sodium thiosulphate in a chlorinated sample after a reaction time of 5 hours at pH 8, removing dissolved chloroform by purging and determining the residual chloroform concentration. After the addition of hexane to the sample and sealing the vessel at ambient temperature for 2 days, analysis of the hexane layer revealed that although, the total chloroform (i.e. in both the hexane extract and aqueous sample) had not changed, about 42% could be found in the hexane. Thus the organochlorine intermediates, detected as residual chloroform and which are insoluble in the hexane had broken down at ambient temperature to produce chloroform even in the absence of chlorine. This suggests that the intermediate is a trichloroacetyl derivative, the hydrolysis of this intermediate being the rate determining step in chloroform formation, a step which does not require the presence of chlorine.

The rate of break down of the intermediate varies throughout the reaction depending on its nature. Samples taken during the initial stages of reaction show a rapid decay (approximately 1.5 $\mu g\ l^{-1}$/10 min) followed by a much slower fall in residual chloroform concentration. In contrast, samples taken after 1-2 days of reaction give a much slower overall rate of decay of residual chloroform (approximately 0.5 $\mu g\ l^{-1}$/10 min).

Humic material contains sites which vary in their ease of oxidation, chlorination and hydrolysis. Steric hindrance and possibly mesomeric effects at these sites greatly influence the rate of hydrolysis of the trichloracetyl group. The initial rapid phase in the break down of the intermediate is probably a result of easily cleaved sites, the more sterically hindered sites which are more resistant to hydrolysis at ambient temperatures require more drastic conditions, such as those encountered in the injection port of the gas chromatograph.

4.2.2 Investigations at the Treatment Works

Final water was sampled in the works laboratory through a 6 mm diameter copper pipe connected to the outlet main with a residence time of the water in the sampling pipe of less than 3 minutes. Chloroform, chlorine and pH determinations were carried out on the final water during each day of the sampling period, 26 March 1978 to 5 April 1978.

Total-chloroform levels varied between 65 μg l^{-1} and 100 μg l^{-1} during the sampling period (Fig. 4.10(a)-(c)). This variation in total-chloroform formation may be accounted for by changes in: the contact time, organic content of the treated water, chlorine dose, and pH, as these parameters influence the haloform reaction.

4.2.2.1 Contact Time

Changes in the contact time occur as a result of the contact tank being used to balance out diurnal variations in the flow. The rate of chloroform formation in the initial stages of chlorination is fast, therefore any changes in the contact time will have a significant effect on the chloroform concentration in the final water.

4.2.2.2 Organic Content

The organic content of the raw water varies considerably during the year, reaching a maximum of approximately 220 Hazen units in November and December and a minimum of 80 Hazen units in June. The changes from month to month are gradual. TOC measurements on slow sand filtered water sampled on the 2 December 1978 did not vary by more than ±6%, nor was there any significant change in colour of raw water during the period of on-site study.

On occasions a rapid rise in the Hazen value of the final water was observed as a result of 'plugs' of highly coloured turbid water. These 'plugs' were of short duration, the colour of the final water return-

Fig. 4.10(a) Relationship between total, residual, dissolved chloroform, pH and chlorine (free and combined) in Lartington final water with time

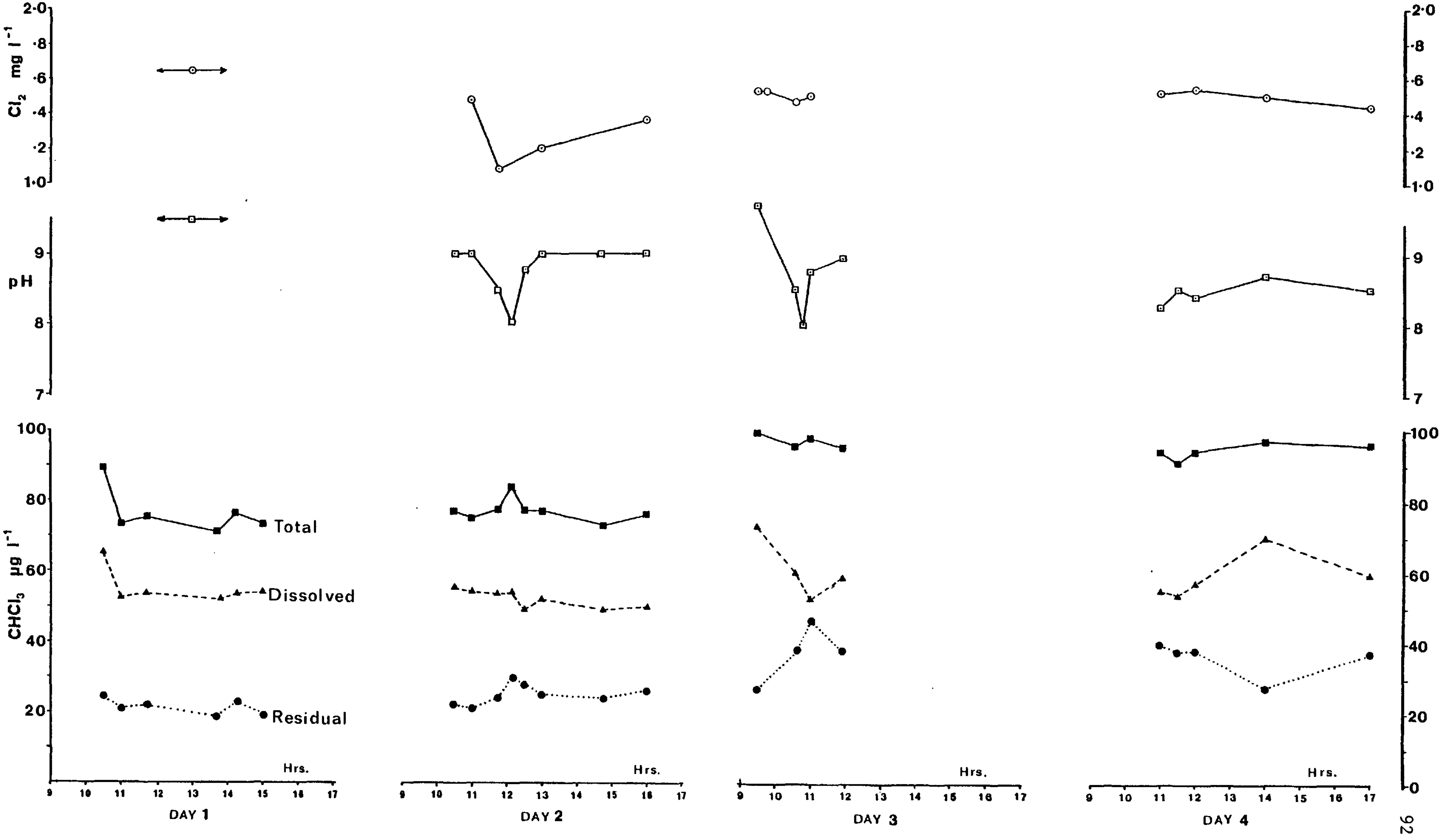


Fig. 4.10(b)

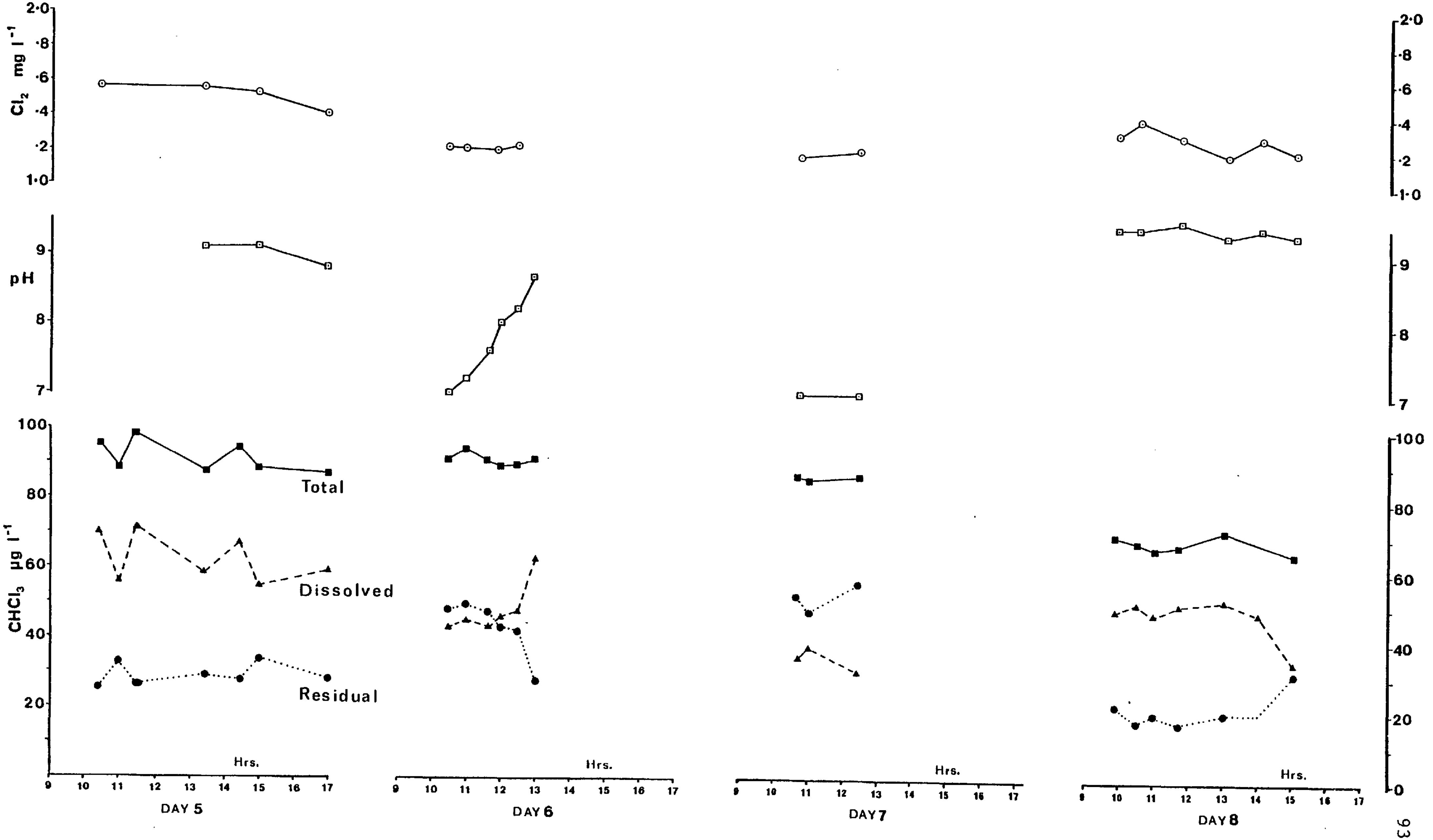
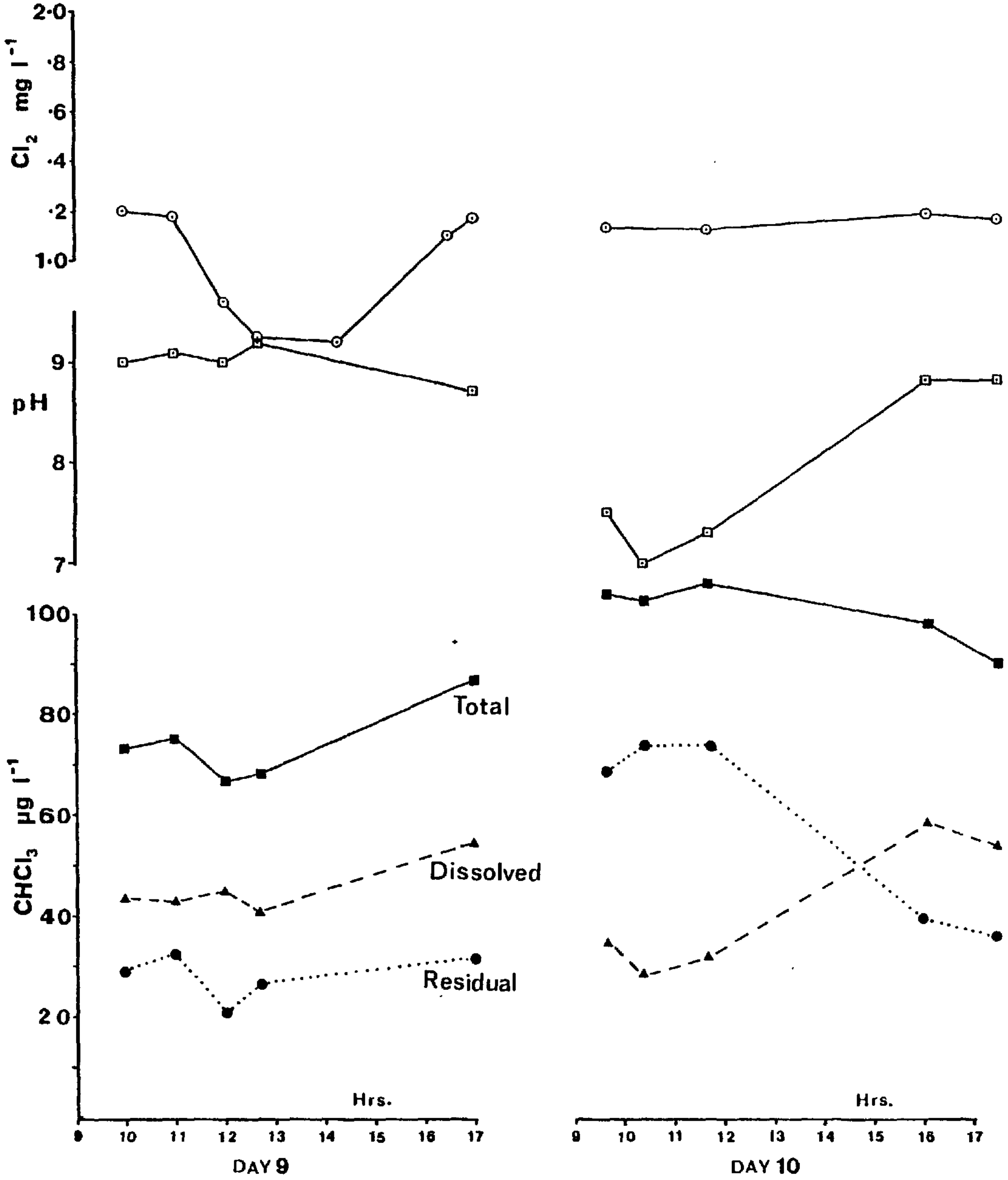

Cl$_2$ mg l^{-1}
2·0
·8
·6
·4
·2
1·0
pH
9
8
7
100
80
60
40
20
0
CHCl$_3$ µg l^{-1}
Total
Dissolved
Residual
Hrs.
9
10
11
12
13
14
15
16
17
DAY 5
DAY 6
DAY 7
DAY 8

Fig. 4.10(c)


Cl$_2$ mg l^{-1}
2·0
·8
·6
·4
·2
1·0
pH
9
8
7
CHCl$_3$ µg l^{-1}
100
80
60
40
20
Total
Dissolved
Residual
Hrs.
9
10
11
12
13
14
15
16
17
DAY 9
Hrs.
9
10
11
12
13
14
15
16
17
DAY 10

ing rapidly to normal. Fluctuations in the organic content and thus the colour of the final water on a day to day basis, may be attributed to possible changes in the performance of the chlorinated copperas treatment or the variation in the relative contribution of rapid gravity filtered and slow sand filtered waters to the final water.

4.2.2.3 Chlorine Dose

The rate of chloroform formation may be influenced by the initial chlorine concentration. Data on the chlorine dosing levels at the works were unobtainable as the chlorine dose for disinfection is not measured directly but altered depending on the chlorine residual level in the final water. Furthermore, the chlorine required for both the copperas treatment and for disinfection is supplied from one bulk chlorine storage tank, so dosing levels could not be obtained from daily chlorine consumption based on chlorine levels in the storage tank.

An estimated initial chlorine concentration of 3 mg l^{-1} was obtained based on the overall consumption of chlorine and the level of chlorination required for effective copperas treatment. This value is in good agreement with the calculated initial chlorine concentration of 2.5-3.0 mg l^{-1} based on chlorine consumption experiments performed on site and in the laboratory.

The fluctuations in the chloroform concentration of the final water may be a result of poor mixing during the initial stages of chlorination through the prolonged contact period should minimise such fluctuations.

4.2.2.4 pH

The effect of pH on total-chloroform formation at the works is consistent with the data obtained from previous laboratory studies. Figure 4.11 is a plot of the measured total-chloroform concentration against the corresponding pH level in the final water and shows a fall in the total-chloroform concentration above pH 8. The majority of samples of final water contained less than 1.5 mg l^{-1} total chlorine residual but on a few occasions the chlorine concentration in the final water rose above 1.5 mg l^{-1}, probably as a result of a higher chlorine dosing level, and was generally associated with a high total-chloroform concentration.

The spread of results may be caused by a combination of the factors mentioned above, though, as can be seen from Figure 4.11, pH is the dominant single factor which affects the total;chloroform concentration in the final water as was shown to be the case for the previous laboratory studies.

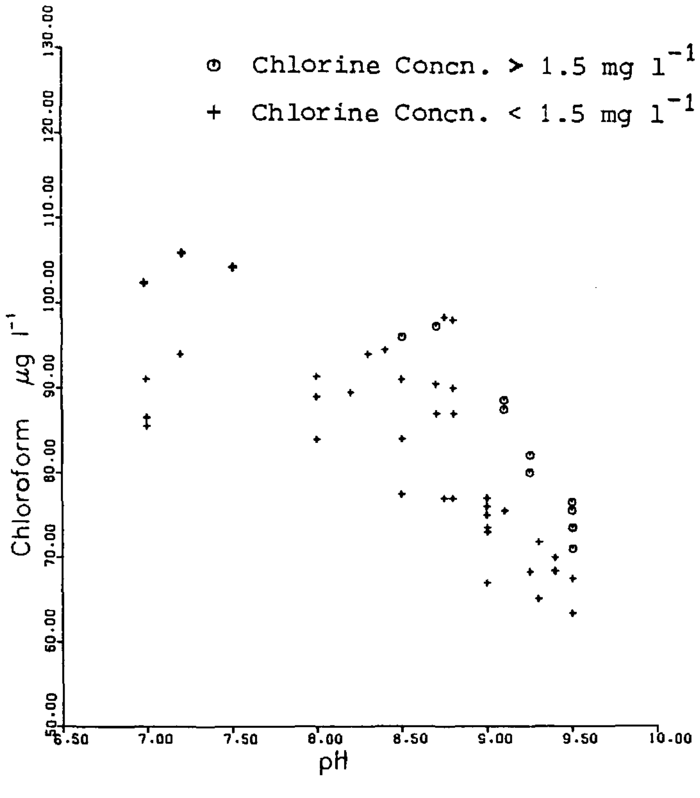


Fig. 4.11 Change in total-chloroform concentration with pH of final water

pH is also the main factor affecting the relative proportions of residual and dissolved chloroform concentrations for these waters, which is again consistent with the results obtained from both laboratory investigations on the upland water and the humic and fulvic acids isolated from Thames water.

4.2.3 Jar and Tap Tests

4.2.3.1 Jar Test

To simulate trihalomethane formation in the distribution main 250 ml samples of final water were stored in the dark and the reaction followed over a period of 4-5 hours (Fig. 4.12 and Fig. 4.14). The temperature of the samples rose rapidly (over 2 hours) from 3°C (final water in the main) to near room temperature (∿12°C). The effect of temperature on the rate of chloroform formation was examined by comparing the chloroform concentration of samples stored outside to maintain the temperature at 3°C and samples stored in the laboratory.

4.2.3.2 Tap Test

An alternative simulation of trihalomethane formation during distribution was obtained by shutting off the final water sampling tap in the works laboratory. Again the water temperature rose though not to the same extent as was observed with the glass jars. Samples taken at regular intervals over a period of 4-5 hours showed the formation of chloroform and the corresponding fall in chlorine concentration with time (Fig. 4.13, 4.15, Appendix II, Fig. 1). Bromodichloromethane concentrations were found to be less than 5% of the chloroform concentration with dibromochloromethane and bromoform not detectable by D.A.I.

Comparison of the results obtained from the Jar and the Tap tests demonstrated a significant discrepancy between the two systems in the rates of both chloroform formation and chlorine consumption; the rates for both processes being appreciably higher in the Tap than in the Jars. As the Jar samples generally reached higher temperatures than the tap samples, temperature was not considered to be a major contributing factor towards the observed variation in the rates of chloroform formation and chlorine consumption between these two types of test.

The pH of the samples was monitored and found to be unstable

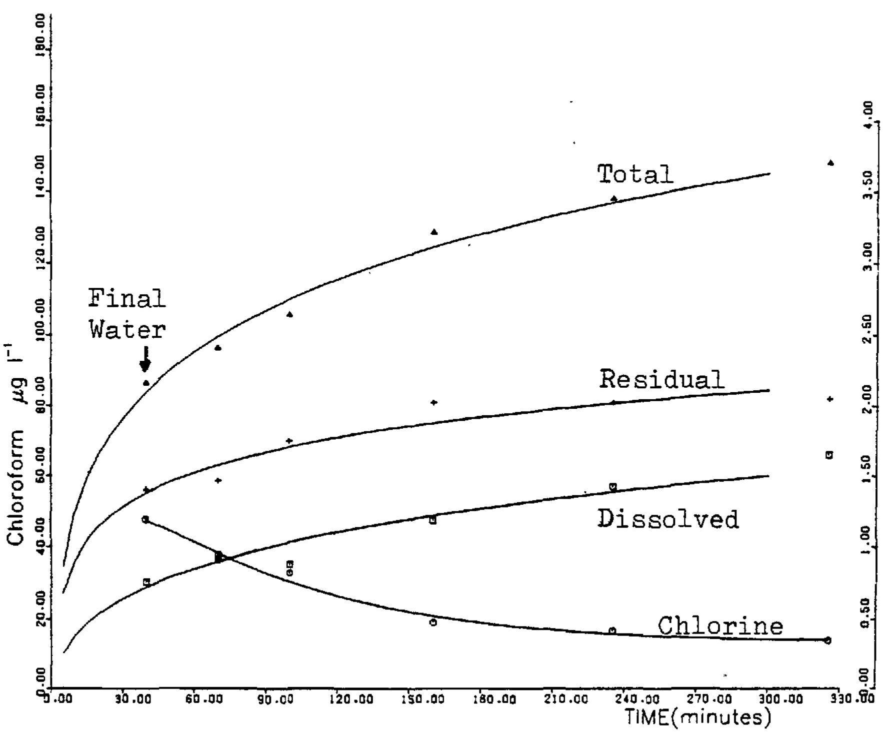


Fig. 4.12 Total, residual and dissolved chloroform formation and chlorine consumption Jar test No. 1 (Initial pH 7)

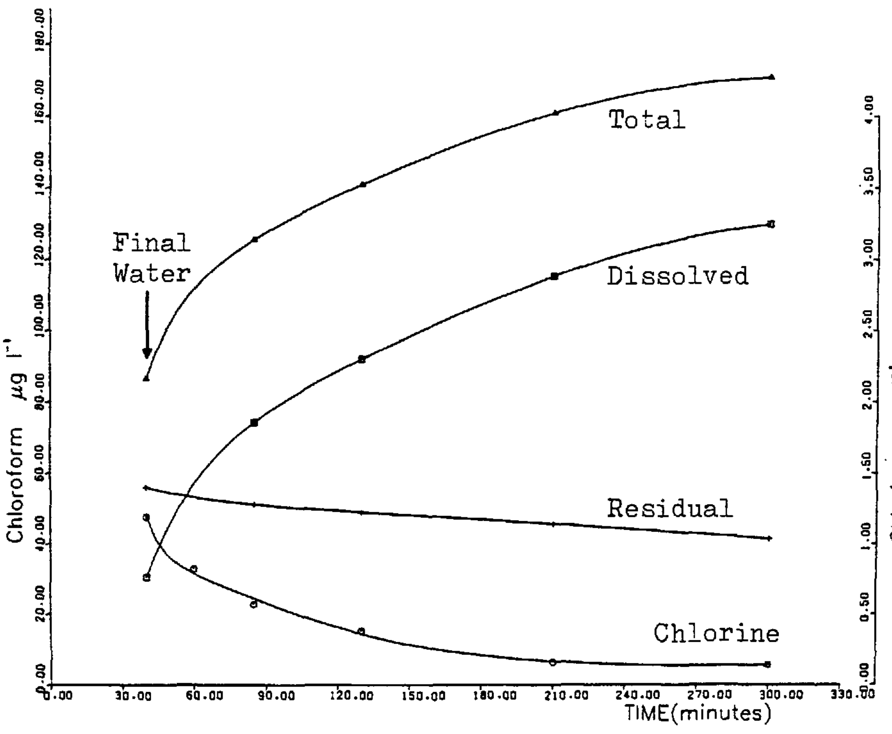


Fig. 4.13 Total, residual and dissolved chloroform formation and chlorine consumption in Tap test No. 1 (Initial pH 7)

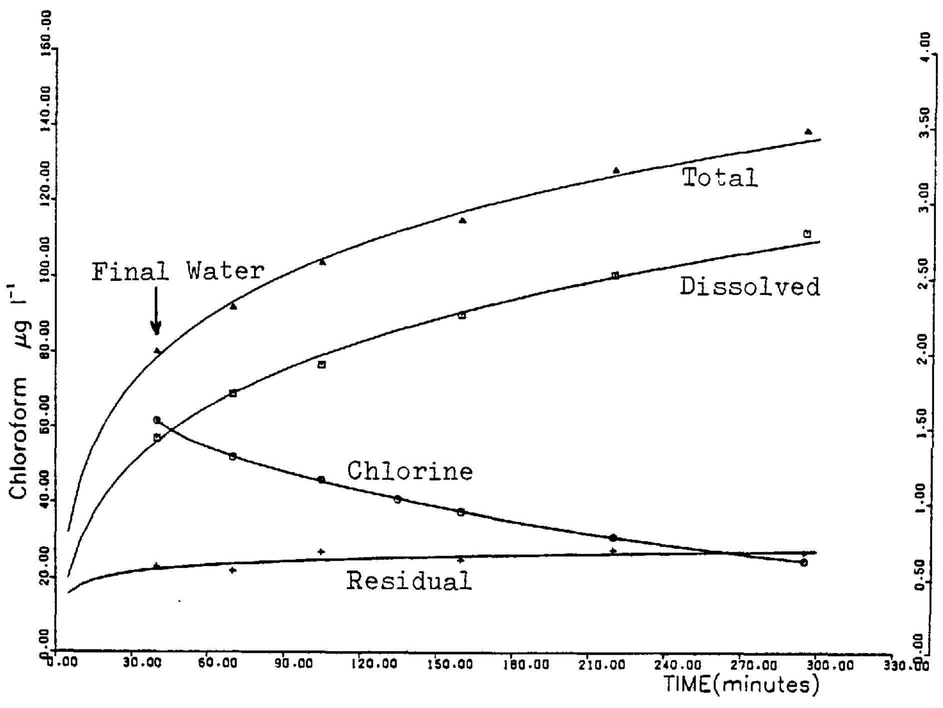


Fig. 4.14 Total, residual and dissolved chloroform formation and chlorine consumption in Jar test No. 2 (Initial pH 9)

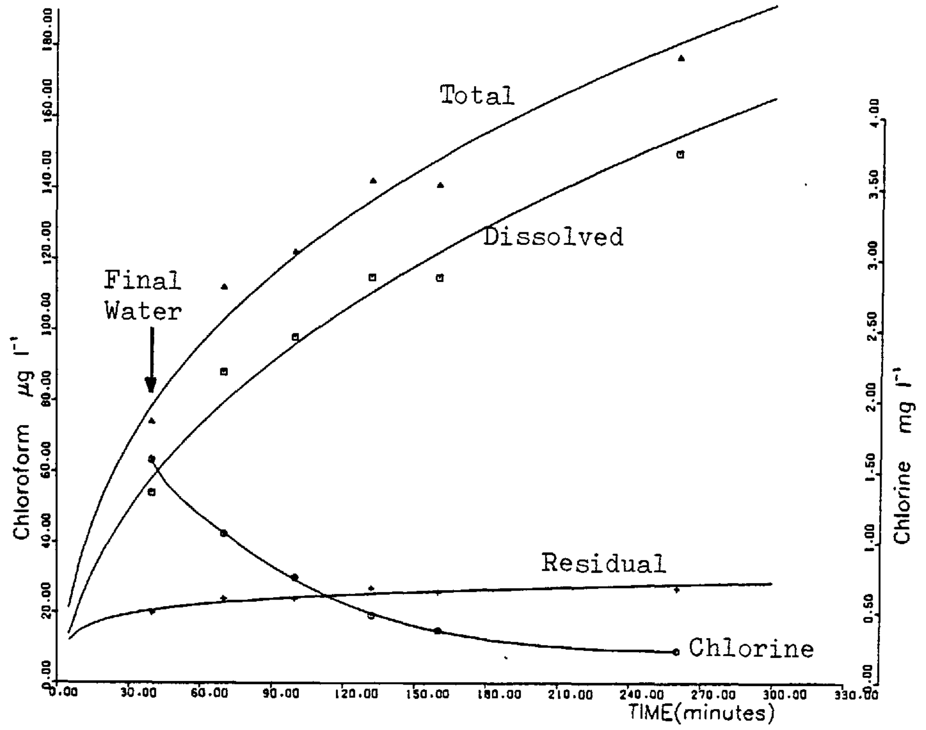


Fig. 4.15 Total, residual and dissolved chloroform formation and chlorine consumption in Tap test No. 2 (Initial pH 9.5)

particularly in the Tap test. A small fall in pH occurred after 4 hours of reaction in the Jar tests on final water at pH 7 (No. 1) and pH 9 (No. 2). The Tap tests showed a fall in pH from 9.5 to pH 8.75 after 4 hours in Tap test No. 2 (Fig. 4.15) and an increase in pH from pH 8.75 to pH 9.0 after 6 hours in Tap test No. 3 (Appendix II, Fig. 1). Tap test No.1, which was run concurrently with Jar test No. 1, showed an increase in pH from pH 7 to pH 8 after 6 hours (Fig. 4.13).

The type of container may be a significant factor in the observed differences in results between these tests as glass vessels were used in the jar tests and copper in the tap tests (because of the copper sampling pipe). Samples returned to Imperial College for further studies on chloroform formation showed that copper has a marked effect on the rate of chlorine consumption, though, in contrast to the tap tests, there was no increase in the rate of chloroform formation associated with the high rate of chloroform consumption during laboratory experiments in the presence of copper.

4.2.3.3 Temperature Effect on the Rate of Chloroform Formation

Jar tests carried out at different temperatures by storing outside at 3°C and inside at 12°C showed a fall in the rate of chloroform formation by approximately 10% for the sample maintained at the lower temperature. The corresponding levels of residual chloroform remained constant, although as a percentage of the total-chloroform there is an effective increase in residual chloroform concentration on reducing the temperature which is consistent with the increased stability of organohalide intermediates at lower temperature.

4.2.4 Other Sites

Samples were collected from various other points within the treatment works for the determination of trihalomethanes, pH and chlorine concentration. From these data the increase in chloroform concentration through the plant can be followed (Fig. 4.1 and Table 4.2). Samples were taken:

(a) during clarification,
(b) after rapid gravity filtration,
(c) prior to chlorine treatment,
(d) prior to lime addition (after chlorine dosing),
(e) during retention in the contact tank (10-15 minutes contact).

The chlorine added during the chlorinated copperas treatment, not only oxidises the ferrous sulphate to ferric sulphate but reacts with the humic material to produce chloroform. For effective coagulation the pH is maintained between pH 4.5 and pH 5 which is reflected in the high proportion of residual chloroform, from samples taken during clarification and after rapid gravity filtration. The total-chloroform concentration is low at this stage even though the chlorine dose is approximately 10 mg l^{-1} as the rate of chlorine formation is slow relative to the rapid reaction between chlorine and ferrous sulphate.

The chloroform concentration after rapid gravity filtration fluctuated between 25 μg l^{-1} and 50 μg l^{-1} during the sampling period as a result of variations in the operating conditions of the chlorinated copperas treatment. Residual chloroform still predominated over dissolved chloroform at this stage.

After rapid gravity filtration the treated water (67%) is mixed with slow sand filtered water (33%) diluting the chloroform and removing the last traces of combined residual chlorine present in the rapid gravity filtered (RGF) water. The mixed RGF and slow sand filtered (SSF) water is subsequently chlorinated prior to lime addition. The total chlorine residual concentration at the sampling point immediately after chlorination varied considerably ranging between 1 mg l^{-1} and 4.4 mg l^{-1} as a result of incomplete mixing. After lime addition the dissolved chloroform concentration starts to incresae relative to the residual chloroform, consistent with the increase in pH. The sampling point in the contact tank, after approximately 15 minutes contact, shows a significant increase in total-chloroform formation and a stable chlorine concentration.

4.2.4.1 Outside Sampling Points

Samples taken at two points along the distribution system at and reservoir at 5 km and 10 km respectively

Table 4.2 Chloroform and total chlorine concentrations at different stages of treatment and distribution

Sampling Site	Mean $CHCl_3$ µg l^{-1}			No. of Samples	Tot.Chlorine Residual Range(mg l^{-1})
	Tot.	Res.	Dis.		
1. Clarification	33	28	5	1	-
2. R.G.F.	36	27	9	9	0.05-0.1
3. Mixed R.G.F./S.S.F. (Prior to Cl_2)	28	23	5	3	N.D.
4. After Chlorine	43	20	23	4	1.0-4.4
5. After Lime	42	11	31	2	1.3-2.5
6. Contact tank (15 mins retention)	63	31	32	12	1.5-2.3
7. Final Water (40 mins.retention)	84	32	52	63	1.0-1.7
8. Distribution System (a) 3 hrs retention (estimated)	129	26	103	7	0.2-0.8
(b) 4 hrs retention (estimated)	138	35	103	10	0.2-0.35

from the works showed significant increases in total and dissolved chloroform concentrations and a reduction in the chlorine concentration from levels in the final water leaving the works (Table 4.2).

The retention time of the water in the distribution main to thses sampling points is estimated to be 3 hours to .   and 4 hours to

reservoir. Taking into account the reduced temperature of the water in the main, these levels of total, residual and dissolved chloroform as well as the chlorine consumption are in good agreement with Jar tests carried out in the laboratory.

4.2.5 Further Laboratory Investigations

Samples of mixed rapid gravity filtered and slow sand filtered water (final water prior to chlorination) were returned to Imperial

College for further laboratory investigations on chloroform formation at chlorine doses similar to those encountered at the treatment works. Chlorination was carried out on buffered samples at pH 7 and pH 9 to cover the pH range normally encountered at the works (Figs. 4.16-4.18).

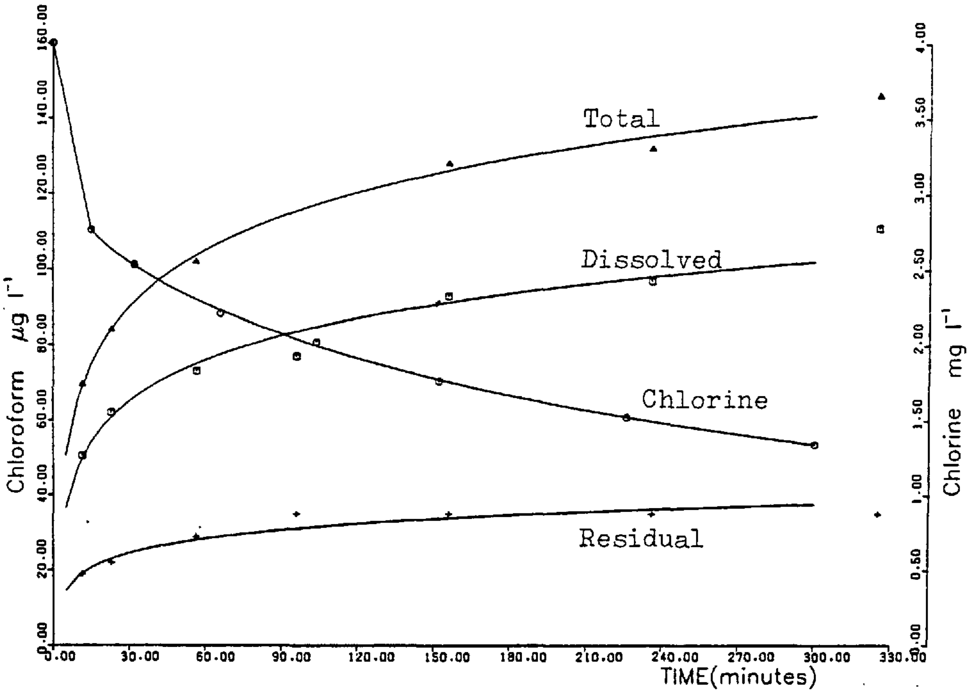


Fig. 4.16 Chlorination of mixed S.S.F./R.G.F. water at pH 9 at an initial chlorine concentration of 4 mg l^{-1}

There is good agreement, during the initial stages of chlorination on the rates of chloroform formation between these samples and the Jar tests carried out at the works. After 2 hours of reaction however, the rate of chloroform formation in the laboratory samples slows down relative to the rates obtained from the Jar tests. The samples had been stored for 3 weeks at 4°C prior to chlorination with no visible deterioration.

After 6 weeks of storage the remaining samples visibly deterio-

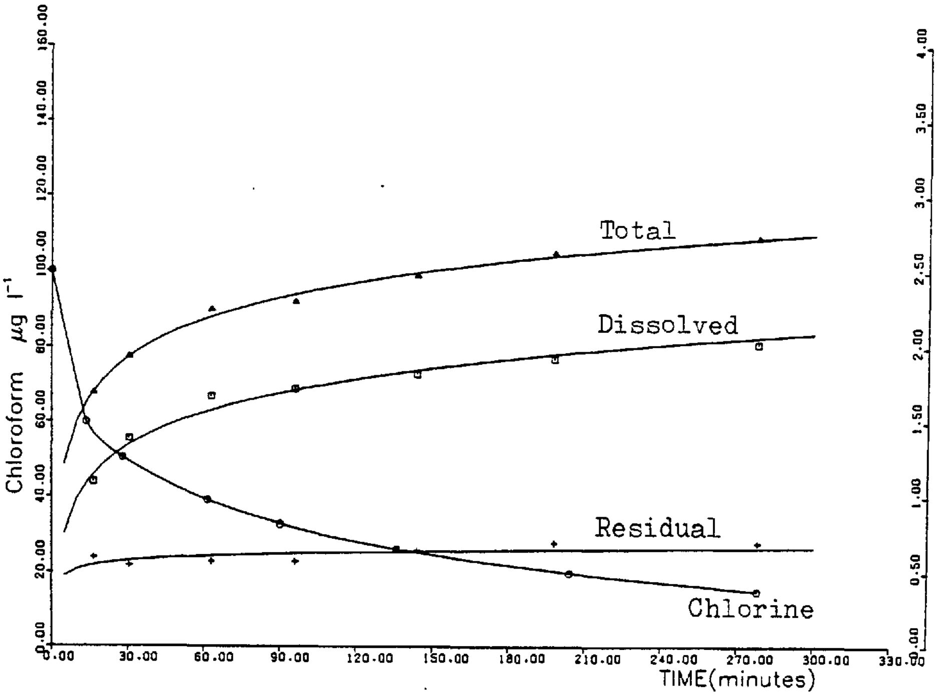


Fig. 4.17 Chlorination of mixed S.S.F./R.G.F. water at pH 9 and an initial chlorine concentration of 2.5 mg l^{-1}

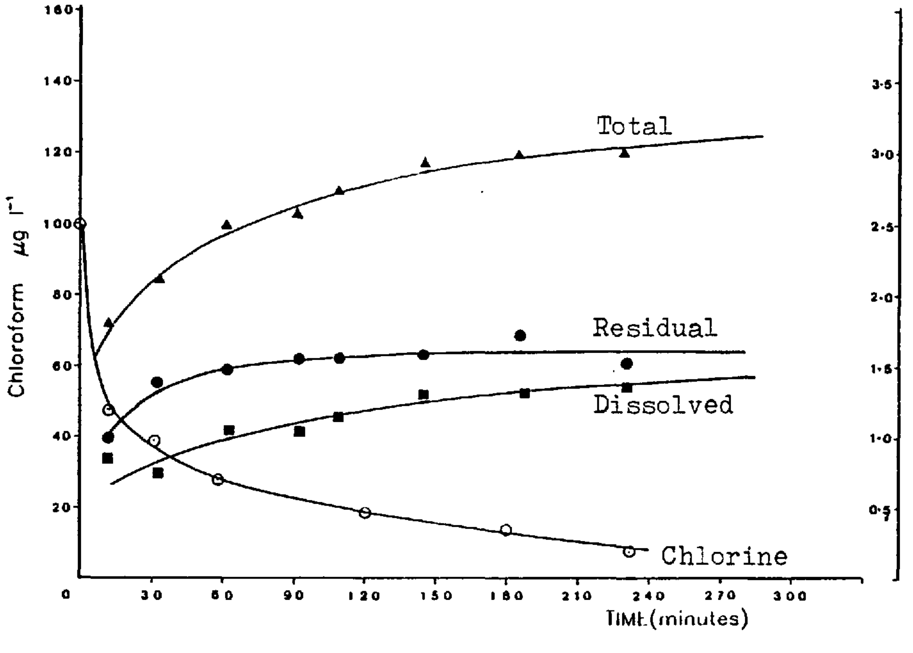


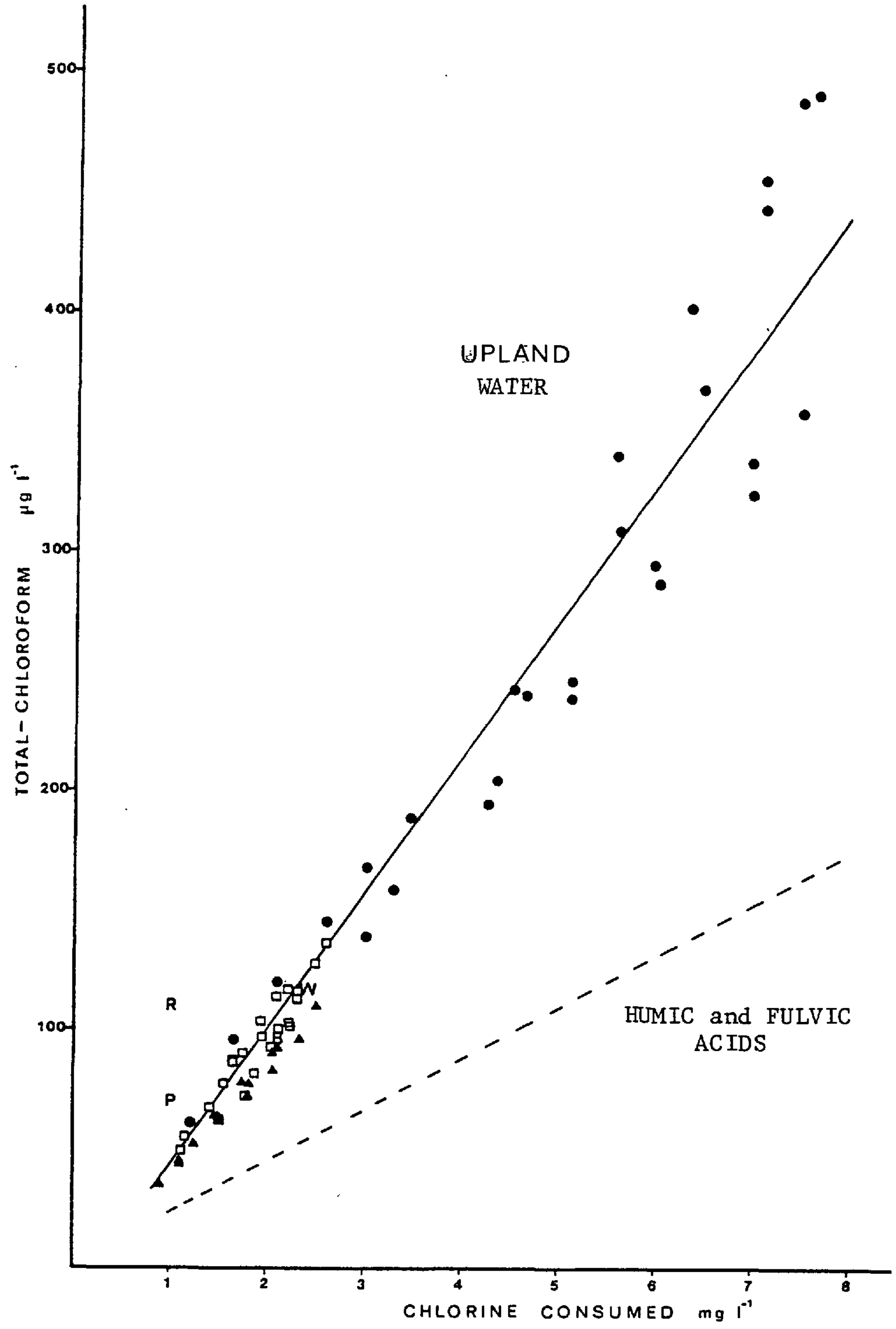
Fig. 4.18 Chlorination of mixed S.S.F./R.G.F. water at pH 7 and an initial chlorine concentration of 2.5 mg l^{-1}

rated with the appearance and precipitation of small light flocs. Chlorination of these samples gave lower rates of chloroform formation than for the Jar tests and for those samples stored for only 3 weeks (Appendix 2, Fig. 2-3). This change in character of the water on storage is in contrast to earlier work on slow sand filtered water which showed no visible sign of deterioration or any effect on the rate or chloroform formation on storing for 6 weeks. On mixing the two types of waters (S.S.F. and R.G.F.) the chlorinated copperas treated water may destabilize the humic material present in the slow sand filtered water causing a gradual decrease in the potential for chloroform formation.

The laboratory experiments carried out in glass vessels showed the same characteristic chlorine consumption curves obtained from the glass jar tests at the works. To observe the effect of copper on the rate of chloroform formation and loss of chlorine, copper gauze was added to a sample and chlorinated at pH 9. The rate of chlorine consumption is increased by the presence of copper as a result of copper/chlorine reactions, and correlates well with the observed fall in chlorine concentration in the tap tests. The rapid loss of chlorine in the tap tests is associated with a corresponding increase in the rate of chloroform formation. This was not the case in the laboratory reactions in the presence of copper which gave a fall in the rate of chloroform formation consistent with the rapid loss of chlorine (Appendix II, Fig. 4). Chloroform formation is therefore not involved persé in the copper/chlorine reactions though in the tap tests the increase in the rate of chloroform formation appears to be a direct consequence of the reaction between copper and chlorine. The anomaly between the results of these two tests may be explained if the copper in the tap tests is coated with humic material, as a result of prolonged contact with high organic containing water. This humic material is subsequently involved in the surface reaction of chlorine with copper.

4.2.6 Total-Chloroform Formation and Chlorine Consumption

Figure 4.19 shows the change in total-chloroform formation with chlorine consumption over a range of chlorinating conditions. The data were obtained from the laboratory studies and the on-site investigations. The relationship between total-chloroform formation and chlorine consumption is linear and may be expressed as:



R = Resorcinol
P = Phlorizin

Fig. 4.19 Change in total-chloroform formation with chlorine consumption for upland water and humic and fulvic acids

$$[TCHCl_3]_t = L([Cl_2]_o - [Cl_2]_t - 0.014 \qquad (4)$$

where $[TCHCl_3]_t$ = Total-chloroform concentration (mg l^{-1}) at time t
$[Cl_2]_t$ = Chlorine concentration (mg l^{-1}) at time t
$[Cl_2]_o$ = Initial chlorine concentration.

The constant, L, varies by ±15% from the mean value of 0.056, depending on pH. For slow sand filtered water (sampled November 1978), L is equal to 0.049 for pH 6 and pH 9 and 0.064 for pH 7 and pH 8, the latter pH values producing the maximum total-chloroform per unit chlorine consumed. The effect of pH on L became more marked on increasing the concentration of humic material. Equation (4) is only applicable if chlorine is present at a concentration greater than 0.5 mg l^{-1} and if the humic material has not been exhausted. During the initial stages of reaction, chlorine is consumed without the formation of total-chloroform, which starts to be produced at a critical chlorine consumption value of approximately 0.25 mg l^{-1}.

4.2.7 UV/VIS Absorption Spectra and Total-Chloroform Concentration

Table 4.3 shows the ratio of the UV/VIS absorption integral between the wavelengths 600-240 nm for slow sand filtered water, and slow sand filtered water diluted 3 fold with rapid gravity filtered water, to the final water, prior to chlorination. Figure 4.20 shows the UV/VIS Absorption Spectra for, S.S.F. (November 1978), S.S.F. (April 1979), mixed S.S.F./R.G.F. (November 1978) and R.G.F. (April 1979) waters.

Studies of humic and fulvic acids showed that a relationship exists between the UV/VIS absorption integral and the total-chloroform produced by the corresponding humic fractions extracted from Thames water (Table 4.3). For mixed S.S.F./R.G.F. (1:2) water the increase in total-chloroform is consistent with the increase in the UV/VIS adsorption integral, measured in arbitrary units, and the TOC value. For undiluted S.S.F. water, however, the increase in UV/VIS adsorption integral is consistent only with the <u>mean</u> increase in total-chloroform formation over the pH range pH 6 to pH 9, with a variation of ±20%. This variation is a result of the effect of pH on the rate of total-chloroform formation.

Table 4.3 UV/VIS absorption integral, TOC and total-chloroform correlations

Water	S.S.F.(Nov. 78) F.W.(April 79)	Mixed S.S.F. + R.G.F.(1:2)(Nov.78) F.W. (April 79)
UV/VIS Abs.Int. Ratio	3.6	1.37
TOC Ratio	3	1.38
T-$CHCl_3$ Ratio		
1 hr	3.7 ±20%	1.41
2 hr	3.75 ±20%	1.48

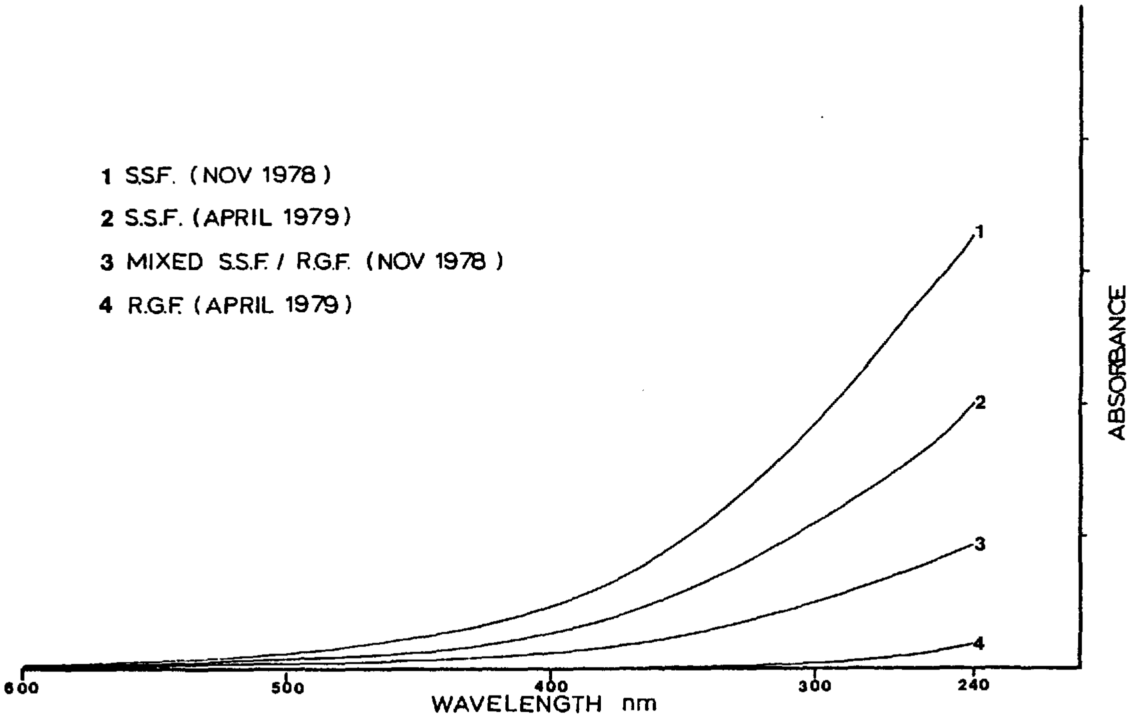


Fig. 4.20 UV/VIS absorption spectra for various types of water

For undiluted S.S.F. water the increase in total-chloroform is not proportional to the increase in TOC as this water contains a greater proportion of high molecular weight humic material than the final water which is made up of 67% R.G.F. water. R.G.F. water contains a high proportion of low molecular weight humic material with a lower number of active sites. Thus the final water produces less total-chloroform per unit weight of organic material than S.S.F. on raw waters.

4.2.8 Effect of Chlorinated Copperas Treatment on Residual Chloroform

The measurement of dissolved chloroform by direct aqueous injection relies on the non-purgability of the organohalide intermediates which are detected as residual chloroform after breakdown during G.C. analysis.

The stability and resistance toward purging of these organohalide intermediates is dependent on the nature and therefore source, of the humic material present in the water. The organohalide intermediates produced on chlorinating the slow sand filtered water were less stable than the intermediates from the fulvic and humic acids extracted from Thames water. The latter produced a stable residual chloroform with no apparent loss on purging. The rate of breakdown in the absence of chlorine was slow and only detectable after prolonged storage at ambient temperatures. In contrast, the chlorination of the slow sand filtered water produced substantial amounts of residual chloroform which reached a maximum concentration within a few hours of reaction and subsequently decaysed to form chloroform as the chlorine concentration fell below 1 mg l^{-1}. On quenching the chlorine, the fall in residual chloroform concentration varied depending on the time of sampling. After 5 hours of reaction the rate of decay was greater than after 24 hours of reaction, changing from 1.6 μg l^{-1}/10 min to 0.5 μg l^{-1}/10 min respectively.

The on-site investigations at the works on chloroform levels in the final water not only verified the instability of these intermediates which breakdown to form dissolved chloroform but also showed that under certain conditions the residual chloroform is 'purgable.' As the purging rate is low compared to that of chloroform such losses may not be significant at high pH levels when the residual chloroform concentration is low relative to the dissolved chloroform concentration. This may not be the case at low pH levels as the relative residual chloroform concentration is high thus any loss as a result of breakdown or by direct evaporation will significantly alter the calculated chloroform concentrations.

The final water at is made up of 67% rapid gravity filtered water and 33% slow sand filtered water, with approximately 30% of the TOC content of the final water having undergone chemical treatment. The effect of chemical treatment on thehumic material may explain the observed differences in the behaviour of the residual chloroform between the on-site investigations and the laboratory studies on slow sand filtered water.

The removal of humic material by coagulation during chlorinated copperas treatment is a result of a chemical reaction between the humic material (anionic polyelectrolyte) and the hydrolysed ferric ion (cationic polyelectrolyte). These polyelectrolytes are involved in a charge neutralisation reaction with the formation and subsequent precipitation of insoluble complexes.

Narkis and Rebhun(114) showed that there is a direct relationship between the required dose of cationic polyelectrolyte for effective coagulation and the equivalent concentration of carboxylic acid and phenolic groups present in the humic or fulvic fraction, and concluded that these groups are directly involved in the charge neutralization reaction between the humic material and the coagulant. Hall and Packham(144) observed that humic acids are more readily coagulated than fulvic acids as a significant proportion of the fulvic acid could not be removed by coagulation. Rook(90) on comparing the removal efficiency of TOC and colour using a ferric coagulant observed that, for the same coagulant dose, the percentage removal of colour is greater than the percentage removal of TOC.

Rook's work is consistent with the view that the high molecular weight humic acid fraction containing a high proportion of phenolic and carboxylic groups per unit weight compared to fulvic acid fractions are more effectively removed by cationic polyelectrolytes. The greater removal efficiency of humic acid which is more coloured per unit weight than thelower molecular weight fulvic acid fraction results in a greater reduction of colour compared to the corresponding reduction in TOC.

It is evident, therefore, that the chemical and physical properties of coagulation, or more specifically the chlorinated copperas treatment, determines the nature of the uncoagulated residual organic matter. Chloroform measurements on rapid gravity filtered water show that the humic content has undergone chlorination which demonstrates that not all the chlorine added during chlorinated copperas treatment reacts with the ferrous sulphate. The bleaching effect of chlorine on the residual organic matter coupled with the low pH levels may further reduce the colour of the rapid gravity filtered water and thus increase the discrepancy between the efficiency of colour removal and TOC removal.

The colour of the water after rapid gravity filtration is less than 5 Hazen units which when mixed with slow sand filtered water (2:1) reduces the colour and TOC of the latter by approximately 50% and 40% respectively. This results in the final water containing a relatively high proportion of low molecular weight organic matter compared to the slow sand filtered or raw waters.

The purgability of the residual chloroform in the final water may be a result of the volatility of the organochloro intermediates from the low molecular weight organic fraction. Thus the loss of residual chloroform on purging final water is greater than the loss from slow sand filtered water.

5. MODEL COMPOUNDS

5.1 INTRODUCTION

Since the discovery by Rook and the subsequent EPA survey that the chlorination of water supplies containing humic material produces trihalomethanes, attention has been focussed on the basic structure of the humic material present in natural waters in an attempt to elucidiate the active sites involved in the haloform reaction.

Rook(93) investigated the formation of chloroform from 'model compounds', so called because of their structural similarity to those compounds reported as degradation products of humic and fulvic acids. On chlorinating a number of polyhydroxy-aromatic compounds and diketo-alicyclic compounds Rook concluded that the meta-dihydroxy-aromatic configurations are the structures most susceptible to the haloform reaction, and that it is the presence of these sites in the humic and fulvic structures which is responsible for trihalomethane formation.

To explain the observation that chloroform formation from fulvic acid occurs in two stages, a rapid initial phase within the first 15 minutes followed by a secondary slow phase, Rook postulated that this secondary stage was a result of slow oxidative disruptions of alpha - chlorinated quinonoid intermediates(93).

Morris and Baum(89) however, suggest that a variety of organic substances other than humic and fulvic acids should be considered as possible precursors to the trihalomethanes, as structures apart from m-dihydroxy moieties are liable to undergo the haloform reaction on chlorination as a result of their ability to form active carbanions.

On chlorinating the natural product syringaldehyde at various values of pH, Morris and Baum(89) observed that the overall chlorine consumption was equal at high and low pH. The breakdown of the intermediates to form chloroform however occurred more readily at high pH. They concluded that the high yield of chloroform at high pH is a result of the increase in rate of hydrolysis of the intermediates and not an increase in the rate of the chlorination stage of the haloform reaction.

Rook(93) used the proposed mechanistic pathway for the degradation of pentachlororesorcinol given by Hoye to explain the formation of chloroform and other halogenated compounds in chlorinated waters (Fig. 5.1).

R_1, R_2 and R_3 represent the main structure of the fulvic or humic materials. Cleavage at III(a) gives rise to CH_2Cl_2 which has been detected in chlorinated waters and cleavage at IV(a) yields chloroform. A similar mechanism applied to a para-dihydroxy species could yield trichloroethylene but would probably require more rigorous conditions.

This proposed mechanism for chloroform formation from resorcinol should result in the formation of a straight chain ketoacid after ring rupture. The involvement of the carbon atom between the two hydroxyl groups in ring structures containing dihydroxy moieties, such as resorcinol, has been verified by Christman(140) who analysed the products formed on chlorinating resorcinol. He observed that ring contraction occurs forming a cyclopentene derivative with the loss of the carbon, as chloroform, between the two hydroxyl groups. In view of this finding Christman challenged Rook's hypothetical mechanism as it is inconsistent with the observation that ring contraction occurs forming a cyclopentene derivative and not, as Rook proposed, a straight chain ketoacid.

5.2 OBJECTIVE OF MODEL COMPOUND CHLORINATION

The chloroform yields reported by Rook, Christman and Morris on chlorinating model compounds refer to dissolved chloroform.

The measurement of dissolved chloroform from humic and fulvic acids using the D.A.I. technique has shown that an intermediate stage in the haloform reaction exists with the presence of organohalide intermediates detected as residual chloroform. If model compounds are to be considered as indicators of the mechanisms involved in the formation of chloroform from humic and fulvic acids, then the haloform reaction from such compounds should also involve an intermediate stage producing organohalide intermediates which breakdown on chromatographic analysis by D.A.I. to give residual chloroform.

A series of experiments was undertaken to verify whether pyrogallol, phlorizin and resorcinol produce residual chloroform (Fig. 5.2). The chlorination conditions for these experiments are summarized in Table 5.1.

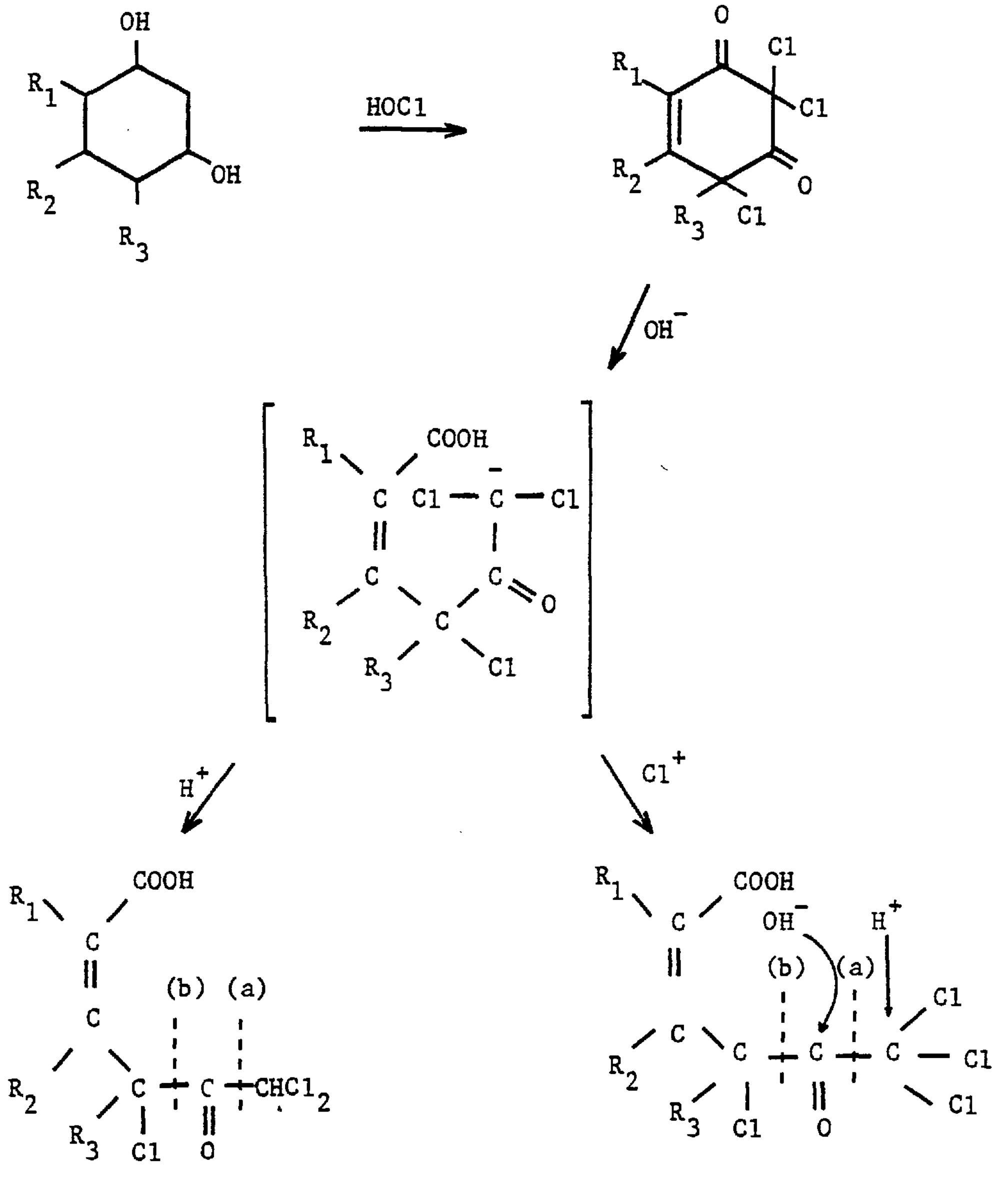
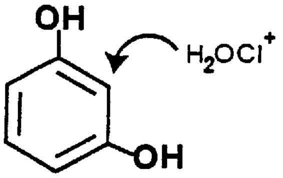
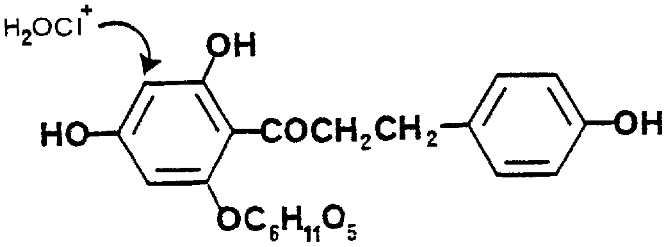


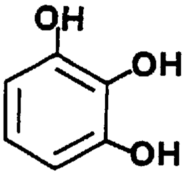
Fig. 5.1 Mechanistic pathway proposed by Rook for the degradation of a meta-dihydroxy moiety(93)



RESORCINOL



PHLORIZIN



PYROGALLOL

Fig. 5.2 Resorcinol, phlorizin and pyrogallol. Possible mode of attack by H_2OCl^+ on ortho-carbon atom activated by the meta-dihydroxy moiety

Chlorine may be considered in excess for all reactions as the molar chlorine to precursor ratio was approximately 140:1.

Table 5.1 Summary of reaction conditions

Compound	Concn. mole l^{-1}	pH	Cl_2 initial mg l^{-1}	temp °C
Pyrogallol	1×10^{-6}	7	10	10
Phlorizin	1×10^{-6}	7,9	10	10
Resorcinol	1×10^{-6}	4,7,9	10	10

5.3 RESULTS AND DISCUSSION

5.3.1 Total-Chloroform

Dissolved chloroform and residual chloroform were produced on chlorinating pyrogallol,phlorizin and resorcinol. The molar yields of total chloroform after 4 hours of reaction were: pyrogallol 7%, phlorizin 50%, and resorocinol 80% relative to the theoretical molar yields. The theoretical chloroform yield is dependent on the number of available carbon atoms in the precursor capable of involvement in the haloform reaction.

As discussed in Section 5.1, compounds containing a *meta*-dihydroxy moiety readily undergo the haloform reaction. Thus as these compounds contain two hydroxyl groups in the 1, 3 position the theoretical molar yield of chloroform from these compounds is equal to 1 mole/mole of precursor as only one carbon atom in these structures is sufficiently activated by the hydroxyl groups and in the correct position (Scheme 5.1) to undergo the haloform reaction. In the case of pyrogallol however, the hydroxyl group of the *ortho* carbon atom interferes with the haloform reaction and consequently only a low yield of total-chloroform is produced on chlorination, *via* unknown mechanistic pathways.

5.3.1.1 Total-Chloroform and Chlorine Consumption

If the reaction between the chloroform precursor containing a *meta*-dihydroxy group and chlorine goes to completion with the formation of chloroform, CO_2 and water then the following stoichiometric equations may be written for resorcinol and phlorizin. For resorcinol,

$$C_6H_6O_2 + 12HOCl \rightarrow CHCl_3 + 5CO_2 + 4H_2O + 9Cl^- + 9H^+ \quad (1)$$

and phlorizin,

$$C_{21}H_{24}O_{10} + 43HOCl \rightarrow CHCl_3 + 20CO_2 + 13H_2O + 40Cl^- + 40H^+ \quad (2)$$

According to equations (1) and (2) the theoretical molar ratios of total chloroform produced to total chlorine consumed in terms of mg:mg are 0.14:1 (1:12) and 0.039:1 (1:43) for resorcinol and phlorizin respectively. The observed ratios in terms of mg total-chloroform produced:mg chlorine consumed are equal to 0.11:1 for resorcinol and 0.071:1 for phlorizin. The ratio for resorcinol shows agreement with the theoretical value with the chlorine consumed approaching the theoretical chlorine demand of 12. This indicates that under the chlorinating conditions employed the reaction between chlorine and resorcinol goes to completion after only 4 hours of reaction producing over 80% of the theoretical yield of chloroform.

The reaction between chlorine and phlorizin is more complicated than the resorcinol reaction. The chlorine consumed is only 50% of the stoichiometric requirements from equation (2), indicating that, unlike resorcinol, phlorizin is more resistant to oxidation as the reacton has not gone to completion, with the continued presence of partially oxidised intermediates, some of which may be chlorinated. Furthermore, although the total-chloroform produced per unit chlorine consumed is higher than the theoretical value of 0.039:1 (1:43) the molar yield of total-chloroform does not exceed the theoretical chloroform yield.

5.3.2 Dissolved Chloroform

Table 5.2 shows the effect of pH on total chloroform, residual chloroform and dissolved chloroform, formation from resorcinol and phlorizin and the percentage contribution of residual and dissolved chloroform to total-chloroform, after 4 hours of reaction.

On chlorinating phlorizin both the rates of dissolved chloroform and total chloroform formation decrease from pH 7 to pH 9. This is in contrast to the chlorination of resorcinol which shows the

Table 5.2 Chloroform formation from resorcinol and phlorizin after 4 hours reaction

Compound	pH	Molar Concn.	$CHCl_3$ $\mu g\ l^{-1}$ (% of Total)		
			Tot.	Res.	Diss.
Resorcinol	4	1×10^{-6}	73	71 (97)	2 (3)
	7	1×10^{-6}	96.7	60 (62)	36.7 (38)
	9	1×10^{-6}	95.0	19 (20)	76 (80)
Phlorizin	7	1×10^{-6}	109	50 (46)	59 (54)
	9	1×10^{-6}	56	20 (36)	36 (64)

characteristic increase in dissolved chloroform on increasing the pH consistent with a base catalysed haloform reaction.

Other authors have also observed a decrease in the rate of chloroform formation on chlorinating organic compounds which give the haloform reaction. Morris reported that on chlorinating phloroacetophenone a fall in the rate of chloroform formation occurred on increasing the pH from pH7 to pH11. Similar results were obtained by Rook(93) for phloroglucinol, 1-hydroxy-3-methoxybenzene and 3-hydroxybenzoic acid.

This deviation from the classical base catalysed haloform reaction is not surprising as chloroform formation is a minor reaction involving only a small proportion of the total chlorine consumed. On changing the pH the relative proportions of the chlorine species is altered and, as a consequence, so too is the chlorinating and oxidising capability of the chlorine. Such changes will affect the kinetics of other, more important reactions involving chlorine which may as a result indirectly affect the haloform reaction.

Changes in the relative kinetics of reaction involving chlorine may also be affected by the chlorine dose, as chloroform yields vary depending on the initial Cl_2/C ratio.

Table 5.3 compares the percentage molar yield of chloroform and residual chloroform from resorcinol and phlorizin obtained in this laboratory at a Cl_2/C ratio of 140:1, giving a maximum chloroform yield of 63% at pH9, which is lower than the yields reported by Rook

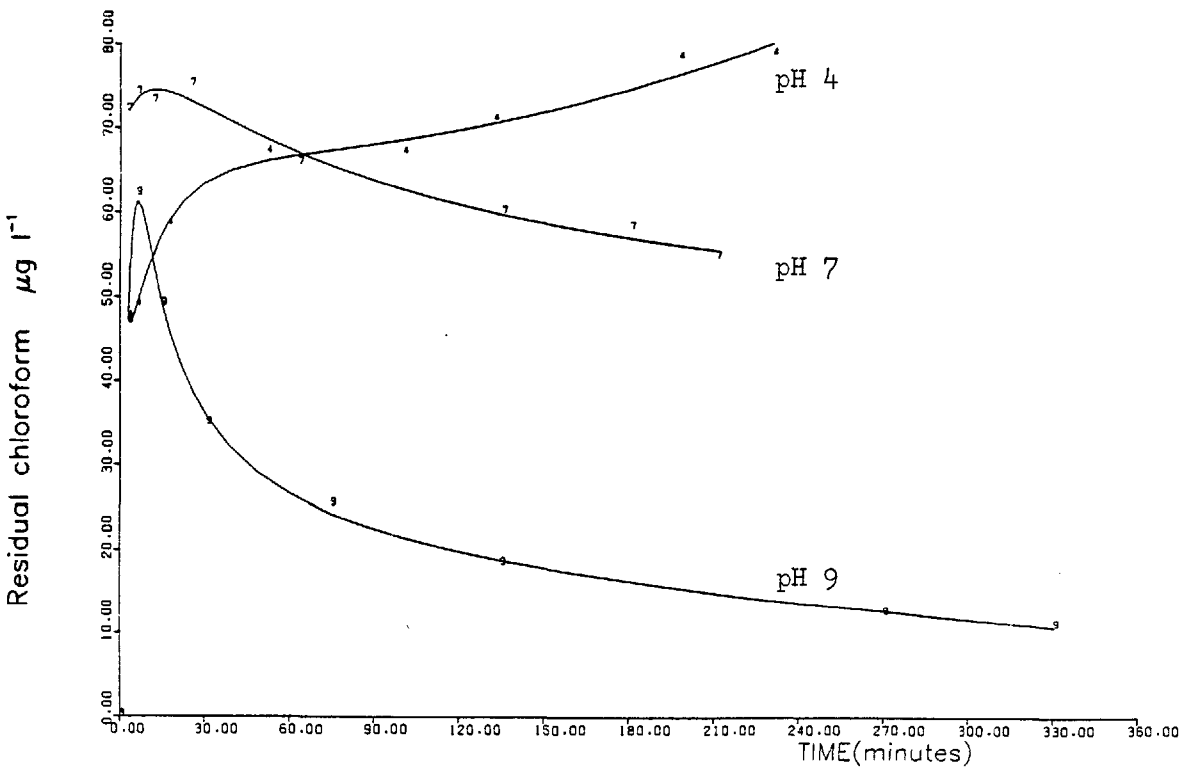


Fig. 5.3 Effect of pH on residual chloroform from resorcinol at 10°C

Table 5.3 Chloroform molar yields (percentage) after 4 hours reaction

Compound	Molar Concn.	pH 4		pH 7		pH 9		Rook(93)		Christman(140)
		Res.	Diss.	Res.	Diss.	Res.	Diss.	pH 7	pH 11	pH 7
Resorcinol	1×10^{-6}	59%	2%	50%	31%	15%	63%	75%	80%	100%
Phlorizin	1×10^{-6}	-		41%	50%	17%	30%	90%	-	-
Pyrogallol	1×10^{-6}	-		-		5%	2%	0%	7%	-

and Christman. Christman indicated that the discrepency between his 100% yield of chloroform (dissolved chloroform) from resorcinol at a Cl_2/C ratio of 1.14:1 and the 75-80% yield obtained by Rook, at a Cl_2/C ratio of 6-8:1, may be a result of the different Cl_2/C ratios.

Thus, a change in the parameters such as pH and chlorine dose may have a significant effect on the rate of formation of chloroform and, as a consequence, on the overall yield of this product. The exact effect, however, of these parameters on the various reactions involving chlorine will be dependent on the structure and the number of active groups, or sites, present in the organic compounds.

Resorcinol and phlorizin show the characteristic increase in the percentage contribution of dissolved chloroform to total chloroform formation on increasing the pH which have been observed for both 'Thames' water and Lartington water. This is probably a result of the decreasing stability with increasing pH of the organohalide intermediates, containing a trihaloacetyl group, which are involved in the haloform reaction.

5.3.3 Residual Chloroform

The effect of pH on residual chloroform formation is opposite to that observed for dissolved chloroform in that there is a reduction in residual chloroform formation on increasing the pH.

On chlorinating resorcinol and phlorizin both the percentage molar yield (Table 5.3) and the % contribution (Table 5.2) of residual chloroform increase on decreasing the pH.

Figure 5.3 (c.f. Fig. 4.7) shows the change in residual chloroform concentration with time on chlorinating resorcinol at pH 4, pH 7 and pH 9. At pH 4 over 90% of the total-chloroform is present as residual chloroform falling to 20% at pH 9, after 4 hours of reaction. At pH 7 and pH 9 the residual chloroform concentration reaches a maximum within the first few minutes of reaction. This is followed by a decay in residual chloroform concentration, the rate being dependent on pH. At pH 7 the decay is not as marked as at pH 9, reflecting the low rate of hydrolysis of the organohalide intermediate at the lower pH. At pH 4 the rate of hydrolysis of the intermediate is so slow that there is virtually no breakdown of this residual chloroform intermediate.

5.3.3.1 Breakdown of Residual Chloroform

To test whether residual chloroform break down at ambient temperatures to produce dissolved chloroform a sample was taken after 75 minutes of reaction of resorcinol with chlorine at pH 9 and the chlorine quenched. 1 ml of hexane was added to 5 mls of sample, the sample bottle sealed and shaken for 1 minute. The hexane fraction was subsequently analysed for chloroform to give the dissolved chloroform concentration, and the water fraction analysed for the hexane insoluble residual chloroform. The sample bottle was shaken for a further minute after standing at room temperature for 6 hours and chloroform analysis of the two fractions repeated. The results are given in Table 5.4 which show that residual chloroform breaks down at ambient temperatures and in the absence of chlorine to produce dissolved chloroform .

Table 5.4 Breakdown of residual chloroform from resorcinol in the absence of chlorine

Time	$CHCl_3$ μg l^{-1}		
	Tot.	Res.	Diss.
Initial (75 mins. Reaction Chlorine quenched)	92	25	67
After 6 hrs standing (20°C)	93	6	87

6. TRIHALOMETHANE SURVEY

A survey of trihalomethane levels in household potable water supplies from 7 sites (Table 6.1) in the London area was undertaken to establish the nature and extent of formation of the four trihalomethanes under study; chloroform; bromodichloromethane; dibromochloromethane, and bromoform. An additional site within the East Surrey Water Company area was included in the survey. The survey was carried out between November and December 1978.

6.1 INTRODUCTION

The EPA's nationwide survey in 1975 in the United States established that the total trihalomethane concentrations in treated waters was related to the organic content of the water in so far as sufficient chlorine was added during treatment to create a chlorine residual. The reported range of concentrations of the four trihalomethanes (from 80 cities) was chloroform < 0.1 μg l^{-1} to 311 μg l^{-1}; bromodichloromethane not detectable to 116 μg l^{-1}; bromochloromethane not detectable to 100 μg l^{-1}, and bromoform not detectable to 92 μg l^{-1}. The median concentration of three of those compounds were chloroform 21 μg l^{-1}; bromodichloromethane 6 μg l^{-1}, and dibromomethane 1.2 μg l^{-1}. Bromoform was found in only 30% of the supplies surveyed.

This variation in trihalomethane levels arising from the chlorination of water supplies was dependent on the quality of the raw water and the unit processes employed during treatment.

Laboratory studies have shown that chloroform is the predominant trihalomethane produced on chlorinating 'pure' solutions of humic and fulvic acids extracted from Thames water. If bromide is added to these 'pure' solutions and the solutions subsequently chlorinated the formation of the brominated trihalomethanes is greatly enhanced. This increase in brominated trihalomethanes formation is a result of the oxidation of bromide by chlorine to hypobromous acid and possibly other oxybromide species. Hypobromous acid then acts as a halogenating agent and is involved in the haloform reaction in a similar manner to hypochlorous acid. Thus, on chlorinating waters containing humic material in the absence of bromide, all the trihalomethane produced is present as chloroform. On increasing the bromide concentration, however,

Table 6.1 Location of sampling sites

Site No.	Location (Area)	No. of Samples
(1)	Chelsea	8
(2)	Fulham	3
(3)	Islington	6
(4)	Imperial College	8
(5)	East Ham	4
(6)	Brixton	3
(7)	Ealing	1
(8)	Caterham (East Surrey Water Company)	2

there is a shift towards the brominated species. This shift in favour of the brominated species will increase on increasing the bromide concentration until all the trihalomethane produced is present as bromoform. water for example, which contains less than 10 µg l^{-1} of bromide produces over 95% chloroform and less than 5% bromodichloromethane of the total trihalomethane concentration (Dibromochloromethane and bromoform were not detectable by the D.A.I. chromatographic technique).

6.2 SAMPLING

The choice of the eight sites in the survey was based on the regular availability of samples from research students and members of staff in the Public Health section.

To facilitate sampling and analysis the containers chosen were 5 ml glass vials sealed with PTFE'mininert caps'. Each sample vial contained a small crystal of sodium thiosulphate to quench the chlorine residual remaining in the water. Samples were taken from the cold water taps connected directly to the main, as trihalomethane losses may occur as a result of evaporation from water stored in cisterns or tanks. The vials were filled to overflow so that a miniscus formed taking care that no headspace formed on capping.

It was noted that small bubbles formed if the vials were not kept in the dark after sampling. Thus the vials were wrapped in aluminium foil to reduce the formation of bubbles and to inhibit photolitically induced reactions.

The design of the mininert caps allows 5 µl samples to be syringed directly out of the vial for analysis by the direct aqueous injection chromatographic technique.

6.2.1 Trihalomethane Analysis

Trihalomethane analysis was carried out as described in section 2.2.2. Samples were extracted directly from the sample vial using a 10 µl syringe.

6.3 RESULTS

Table 6.2 shows the mean total-chloroform, total-bromodichlormethane, total-dibromochloromethane and total-bromoform from sites (1)-(7) in the London area and for site (8) in the East Surrey Water Company area. Bromoform concentration was generally below the detection limit of 2 µg l^{-1} for the D.A.I. chromotographic technique.

Dissolved chloroform accounts for 80-90% of the total-chloroform concentration. The percentage is higher for bromodichloromethane which account for 90-95% of the total-bromodichloromethane concentration. The dibromochloromethane concentrations were generally too low to give any significance to the residual dibrmochloromethane measurements after purging.

To examine the hourly variations in trihalomethane concentration site no 4 was sampled every hour for eight hours. The variation was not greater than 5% which is within the percentage error of the analytical technique.

In terms of the percentage weight distribution chloroform and bromodichloromethane are the predominant trihalomethanes produced although in terms of molar concentration,chloroform is the highest contributor to total trihalomethane formation. In comparison to the London area the water from site no 8, which is supplied by the East Surrey Water Company, contains virtually no trihalomethanes. This area is supplied by mixed well and surface water. The treatment of surface water consists of coagulation and softening followed by filtration through both sand and carbon. This degree of treatment will have a marked effect in reducing the TOC content of the water and consequently on trihalomethane formation. However, the effect of such treatment on reducing the bromide concentration may not be significant.

Table 6.2 Mean total-trihalomethane concentrations for sites (1)-(8)

Site No.	T-$CHCl_3$ ($\mu g\ l^{-1}$)	T-$CHCl_2Br$ ($\mu g\ l^{-1}$)	T-$CHClBr_2$ ($\mu g\ l^{-1}$)	T-$CHBr_3$ ($\mu g\ l^{-1}$)
(1)	12	13	7.5	<2
(2)	12	13.5	8.5	<2
(3)	12	11	7.5	<2
(4)	14	17	9.8	<2
(5)	28	32.5	19.6	3
(6)	17	16	7.5	<2
(7)	22	16	6.5	<2
(8)	N.D.	1.5	2	3
Mean Molar Concns. Site Nos.(1)-(7)	0.139×10^{-6}	0.103×10^{-6}	0.046×10^{-6}	$\sim0.004\times10^{-6}$
% Contribution of Mean (Molar)	48	35	16	1

6.4 DISCUSSION

Although the survey of trihalomethane levels in the complex water distribution system of the London area was based on a limited number of sites and over a limited period of time, the data obtained do indicate the extent of trihalomethane formation resulting from the chlorination of water originating from the Thames Valley area.

The Thames Water Authority uses a variety of different sources to make up the overall water requirements of the London area, abstracting water not only from the River Thames but also from the River Lee and Wells, the latter contributing nearly 20% to the total.

Other factors further complicate the distribution system such as the Thames-Lee transfer main which carries water from the River Thames to the north of London when it is mixed with water from the River Lee prior to treatment and distribution. These factors make it very difficult, if not impossible, to assess the source of water to a particular site.

The observed similarities of the trihalomethane concentrations between the sites was not expected in view of the complex water distribution system. The percentage distribution of the trihalomethanes and the total trihalomethane concentration do not vary significantly between sites. All the samples from site no 5 gave the highest trihalomethane concentrations.

Just as total trihalomethane formation is related to the concentration of humic material and the chlorine dose, the percentage distribution of the trihalomethanes produced is related to the bromide concentrations in the raw water. Thus, Thames water, which contains between 90 $\mu g\ l^{-1}$ and 120 $\mu g\ l^{-1}$ of bromide(139), produces a higher percentage of bromide containing trihalomethanes but a lower total trihalomethane concentration-compared to Lartington water which contains approximately 10 $\mu g\ l^{-1}$ of bromide.

Although the source of bromide present in natural waters is still uncertain, there are indications that man's activities may contribute significantly to bromide contamination of surface waters. The higher bromide concentrations in Thames water relative to water may be associated with the highly urbanized and industrialized areas within the Thames water catchment area. Further research though is needed to establish whether waters containing high bromide concentrations are specifically associated with these highly urbanized or industrialized lowland regions.

7. GENERAL DISCUSSION

Although there is insufficient data available to enable the determination of a complete reaction mechanism, a scheme for chloroform formation from humic materials is presented in Chapter 3. It is apparent that more than one route to chloroform is possible and that the relative rates and extent to which any one route is followed will depend on a large number of reaction parameters.

A key factor in the formation of trihalomethanes is the presence of active sites, capable of undergoing the haloform reaction, within the organic structure. Structural investigations of humic materials have shown that humic and fulvic acids contain phenolic-OH groups(139). Chlorination studies of 'model compounds' containing such groups indicate that the meta-dihydroxy moiety is the configuration most susceptible to the haloform reaction(90). However, the proportion of the phenolic-OH groups in the humic structure present as meta-dihydroxy moieties is not known.

The use of the D.A.I. technique for the measurement of dissolved chloroform produced from the model compounds; phlorizin and resorcinol, revealed the presence of organochlorine intermediates, detected indirectly as residual chloroform. These intermediates were found to breakdown slowly at ambient temperature to produce dissolved chloroform in a reaction step which did not require the presence of chlorine but which was pH dependent as the rate of dissolved chloroform formation increased and the residual chloroform concentration decreased on increasing the pH.

This suggests, therefore, that dissolved chloroform formation is the result of hydrolytic attack on the organochlorine intermediate. It is considered that this intermediate contains a trichloroacetyl group (CCl_3CO-). This hypothesis is based on the specific nature of the haloform reaction and the capability of such groups to hydrolyse with the formation of the corresponding trihalomethane without the requirement of further halogenation.

This is further supported by comparing the behaviour of these intermediates with trihaloacetyl derivatives formed by the stepwise halogenation of ketones. The hydrolytic breakdown of trihaloacetyl derivatives from simple acetyl containing compounds to produce the corresponding trihalomethane is generally a rapid reaction under alkaline conditions. However, trihaloacetyl derivatives arising from organic compounds which sterically hinder hydrolytic attack have been isolated during slow breakdown under acid conditions.(88)

Thus the rate of trihalomethane formation is not only dependent on the rate of chlorination of active sites susceptible to the haloform reaction but also on the stability of the trihaloacetyl derivative.

There is a striking similarity in the nature and behaviour of the intermediates produced from the model compounds examined (Fig. 5.1) and the intermediates from humic materials (Fig. 4.7), although in more specific terms the rate of formation and breakdown of the latter are significantly slower. This is probably the consequence of the greater complexity of the humic structure which will undoubtedly be influential on the kinetics of trihalomethane formation as many of the sites which have the potential to undergo the haloform reaction may be deactivated. This may occur if the active sites are sterically hindered by the large complex humic structure which interferes with halogenation and hydrolytic attack or, if the sites are influenced by the proximity of deactivating groups within the humic structure.

Studies of humic and fulvic acids show that in the presence of excess chlorine the residual chloroform concentration becomes constant. This indicates that a steady state is reached in which the rate of formation of the intermediates is equal to the rate of breakdown. In the case of water, however, the high organic content rapidly reduced the chlorine concentration resulting in a gradual fall in residual chloroform concentration after a maximum had been reached, when the rate of breakdown exceeded the rate of formation of the intermediates. Furthermore, on quenching the chlorine, or when the chlorine concentration became limiting the increase in dissolved chloroform concentration corresponded to the fall in residual chloroform concentration.

It may be concluded, therefore, that the organohalide intermediates from humic material detected by D.A.I. as residual chloroform breakdown to produce dissolved chloroform, at ambient temperature, in a reaction step which does not require the presence of chlorine but which is greatly enhanced by increasing the pH in a similar manner to the model compound intermediates.

As the breakdown of these intermediates in the injection port of the gas chromatograph is not a controlled reaction, care must be taken when attempting to interpret residual chloroform concentrations as an indirect measure of the organohalide intermediates. It is not known for example whether all the intermediates produced by the haloform reaction will necessarily breakdown even under the extreme conditions encountered in the injection port. Residual chloroform measurements may therefore correspond to only a proportion of the intermediates actually present, thus underestimating the trihalomethane potential. Alternatively, the residual chloroform measurements may overestimate the trihalomethane potential if other reaction pathways which do not produce trihalomethanes become dominant at ambient temperature.

During the development stage of the D.A.I. technique residual chloroform measurements were subject to variations. This was corrected for by introducing nickel powder in the injection port of the gas chromatograph which, not only increased the reproducibility of residual chloroform measurements, but also improved the resolution of the chromatography.

The mechanism by which the nickel powder affects the breakdown of the intermediates is uncertain. However, it may act both as a catalyst,and produce 'hot spots' for rapid volatilisation of the water resulting in a more consistent and rapid breakdown of the intermediates.

Breakdown of the intermediates is obviously far slower at ambient temperature compared to temperatures encountered in the injection port. The stability of the intermediates (at ambient temperature) depends on the location of the corresponding active site within the humic structure with respect to steric hindrance and inductive effects. Thus the intermediates from humic materials vary in the ease of breakdown to the extent that residual chloroform has been detected in quenched samples even after prolonged storage.

Total-chloroform formation (residual and dissolved chloroform) reaches a maximum between pH 7 and pH 8, consistent with the maximum rate of chlorine consumption, for the humic and fulvic acids and Lartington water. Dissolved chloroform, however, is enhanced by increasing the pH which, as already discussed, is considered to be the result of an increase in hydrolytic attack on the organohalide intermediates containing a trihaloacetyl group. If all the dissolved chloroform produced is the result of hydrolytic breakdown of these intermediates then the rate of total-chloroform formation is equal to the rate of organohalide intermediate formation. Consequently the maximum rate of total-chloroform formation in terms of pH dependence, corresponds to the maximum rate of intermediate formation.

The reaction mechanisms which influence the rate of residual chloroform formation may be similar to the mechanisms which control the kinetics of the chlorination of phenol (to produce chlorinated phenols) as both reactions are influenced by the phenolic-OH groups (meta-dihydroxy moieties in the case of trihalomethane formation) and reach a maximum rate between pH 7 and pH 8.

The rate of reaction between chlorine and phenol is dependent on the product of the hypochlorous acid (HOCl) and the phenoxide concentration(44). The phenoxide ion activates the aromatic ring towards electrophilic attack to a greater degree than the undissociated hydroxyl group which predominates under acid conditions. The effect of pH on hypochlorous acid is opposite in that there is a decrease in concentration on increasing the pH. Consequently the maximum rate of chlorination occurs at approximately pH 8 when the product of hypochlorous acid and phenoxide concentration is at a maximum.

Dissociation of the hydrogen ion from the phenolic-OH groups present in the humic structure start between pH 6 and pH 7.(114) The dissociation is complete at pH 9. At this pH the activation of the humic structure is at a maximum with respect to electrophilic attack by hypochlorous acid at the corresponding active sites of the meta-dihydroxy moieties. Thus maximum rate of total-chloroform formation occurs between pH 7 and pH 8 when the product of the effective phenoxide ion concentration of the humic material and hypochlorous acid concentration reaches a maximum, similar to the chlorination of phenol.

This undoubtedly is an over simplification of the reaction as other factors associated with the complex humic structure will exert their influence on the kinetics of this reaction.

Although chloroform formation accounts for only 1-5% of the overall chlorine consumed, a linear relationship was found between the total-chloroform produced and the chlorine consumed for the humic and fulvic acids and water. This may be explained if the kinetic order for chloroform formation and other reactions involving chlorine are similar. However, another more plausible explanation is that the chlorine reacts primarily as an oxidising agent at sites which produce trihalomethane as a by-product, the rate determining step for trihalomethane formation being the oxidation reaction.

This, however, contradicts the previous analogy of total-chloroform formation with the chlorination of phenol. It is probable therefore that chloroform formation is the result of a number of reaction steps involving oxidation and chlorination reactions and finally, hydrolytic breakdown of trihaloacetyl intermediates. The relative importance of these steps on the kinetics of trihalomethane formation is dependent on the location and nature of specific active sites.

The measurement of TOCl in addition to dissolved chloroform, residual chloroform and total chlorine consumption would be required to establish the relative importance of oxidation and C-chlorination reactions.

It is interesting to note that TOCl measurements have shown that C-chlorination is reduced on increasing the pH(107,108). This is similar to the effect of pH on residual chloroform concentration.

The humic and fulvic acids used in this study were obtained from the same source, the Thames, and their relative compositions determined by the constraints of the procedure used to isolate them. The similar trends in chloroform production reflects the similarity of the basic structure of these acid fractions which are the product of polycondensation reaction involving natural organic compounds present in the soil(139). It is the very nature and source of these compounds which ultimately define the basic structure of the humic material present in natural waters. Thus, a quantitative comparison of the relative reactivities of humic and fulvic acids is only valid if the acid fractions originate from the same source .

The higher molecular weight humic acids are generally more coloured and more susceptible to coagulation as a result of the greater number of active sites per unit weight than the lower molecular weight fulvic acids. It is not surprising therefore that humic acids produce a higher yield of chloroform per unit weight than the lower molecular weight fulvic acids as chloroform formation is also dependent on the number of active sites present in the organic structure. These sites however must contain or give rise to a suitable moiety for trihalomethane formation to occur as the haloform reaction is highly specific to configuration which contains an acetyl group.

Trihalomethane formation does not necessarily depend on the carbon content of the organic material as the governing factor in trihalomethane yield is determined by the presence of specific active site in the organic structure. Comparing the yield of chloroform for the model compounds phlorizin, pyrogallol and resorcinol for example, shows this to be the case as the yield is not dependent on the carbon content but on the active site which has the potential to undergo the haloform reaction. For these compounds the active site is considered to be the meta-dihydroxy moiety as this configuration makes the alpha carbon highly active towards electrophilic attack.

Assuming therefore that trihalomethane formation results primarily from meta-dihydroxy (or quinoid) moieties the proportion of phenolic-OH or quinoid groups present in the meta configuration may be estimated, based on reported equivalent weight values for these groups in humic and fulvic acid(139). These values range between 2 and 6 meq./g of humic material for phenolic hydroxyl groups and 0.6 and 1 meq./g of humic material for quinoid groups. The observed total-chloroform produced from humic and fulvic acids and water is equivalent to approximately 1 in 20 of these groups present in the meta position.

Chlorination studies on waters show general agreement with work on humic and fulvic acids extracted from the Thames. In both cases total-chloroform formation may be represented by an empirical equation:

$$[\mathrm{TCHCl_3}]t_{\mathrm{min}} = Kt^{x}_{\mathrm{min}} \qquad (1)$$

where $x = 0.227 \pm 5\%$.

The constancy of x indicates that the mechanisms and rate determining steps involved in total-chloroform formation are independent of the source of humic material and that the nature or active sites of the organic matter in these different waters may be similar with respect to chloroform formation. The value of K, however, will vary depending on the concentration of humic material, though not necessarily in relation to TOC, as the governing factor in chloroform formation is not the carbon content of the humic material but the number of active sites present.

The humic and fulvic acids, which make up the humic material in natural waters, differ in the number of active sites per unit weight. Humic acids contain a higher percentage of active sites than the lower molecular weight fulvic acids. This difference in the number of active sites not only affects the coagulation of these acids, as discussed in Section 4.2.7 , but, as shown by chlorination studies of humic and fulvic acids extracted from Thames water, the lower molecular weight fulvic acid produces consistently less total chloroform per unit weight of acid than the higher molecular weight humic acid.

An indirect measure of the active sites present in the humic structure may be obtained from the UV/VIS absorption integral (Section 4.2.6). This integral was found to be proportional to total-chloroform formation.

Although chloroform formation is only a minor reaction involving humic material with chlorine in aqueous solution a linear relationship was found between the total-chloroform produced and the chlorine consumed (Sections 3.1.4 and 4.2.5). The amount of total-chloroform produced (mg) per unit chlorine consumed (mg), L, varied depending on the source of humic material, with water having a higher value (0.056) than the humic and fulvic acids from Thames water (0.022). Not surprisingly, however, the model compound resorcinol gave a higher value of L (L = 0.1) than the humic materials.

If meta-dihydroxy moieties are the main active sites in humic materials for the haloform reaction, it is considered doubtful that a natural water containing humic and fulvic acids will exceed the value of 0.1 given by resorcinol, as this compound is the simplest basic aromatic unit for such a configuration.

L might therefore be considered as a measure of the reactivity of the humic material with respect to chloroform formation. This value may also represent the proportion of active sites which, on reacting with chlorine are involved in the haloform reaction.

Thus, K may be redefined as being related to the proportion of the total number of available active sites present in the water which, on chlorination undergo the haloform reaction. Therefore,

$$K \propto (\text{Abs.Integral}) \times (L) \tag{2}$$

where (Abs.Integral) is a measure of the total number of active sites in the water to be chlorinated

and (L) is a measure of the proportion of those sites which, on reacting with chlorine, undergo the haloform reaction.

Thus, the total-chloroform produced ($\mu g\ l^{-1}$) in time t (min) is given by equation (3)

$$[TCHCl_3]_t = k(\text{Abs.Integral})(L)t^{0.227} + z \tag{3}$$

where $k = 2.9$

z = total-chloroform concentration ($\mu g\ l^{-1}$) prior to chlorination.

The value of k, equal to 2.9, was obtained by fitting equation (3) to the total-chloroform produced from slow sand filtered water using the corresponding UV/VIS absorption integral value of 766 (arbitrary units) for slow sand filtered water and the mean value of L equal to 0.056 for these waters.

Table 7.1 compares the predicted total-chloroform concentration, calculated from equation (3) and the observed total-chloroform concentration after 60 minutes and 120 minutes of reaction for various types of water. As the value of L is the same for all waters tested, changes in total-chloroform formation are directly related to changes in the UV/VIS absorption integral of the various waters.

Table 7.1 also compares the observed total-chloroform concentration after 60 minutes and 48 hours of reaction with the values obtained from equation (3) for humic and fulvic acids using the value of k based on water data. Figure 3.11 shows a good fit between the increase in total-chloroform concentration from humic and fulvic acids over a 2 day reaction period and the calculated values from equation (3).

Table 7.1 Observed and predicted total-chloroform concentrations

Water	Predicted T-$CHCl_3$($\mu g\ l^{-1}$)		Observed T-$ChCl_3$($\mu g\ l^{-1}$)	
	1 hr	2 hrs	1 hr	2 hrs
S.S.F. (Nov. 78) 10°C	315	369	244-400	290-450
F.W. (April 78) 5°C, z = 25	101	115	95	115
Mixed S.S.F./R.S.F. (Nov. 78) 10°C, z = 15	136	156	134	158
	1 hr	48 hrs	1 hr	48 hrs
Humic Acid 5 mg l^{-1}, 10°C	36	87	37	94
Fulvic Acid 5 mg l^{-1}, 10°C	19	46	20	46
	1 hr	13 hrs	1 hr	13 hrs
Fulvic Acid 25 mg l^{-1}, 10°C x = 0.156	76	112	86	131

However, equation (3) is not applicable to fulvic acid at a concentration of 25 mg l^{-1}. This was due to a change in the value of the exponent, x, to 0.156 which is lower than the value obtained for water, and humic and fulvic acid at a concentration of 5 mg l^{-1}. This indicates that the exponent, x, is constant only over a limited range of concentration of humic material, the range depending on the source of water. The reason for this change is not known. However, as x is related to the mechanisms and rate determining steps involved in total-chloroform formation it would appear that a change in the kinetics of the haloform reaction occurs at the higher concentrations of humic material.

Equation (3) is based on reactions with humic materials from only two types of waters. Further studies on other source waters are necessary in order to examine whether equation (3) is applicable as a general equation for total-chloroform formation, irrespective of the source, and if so, to determine the limitations of such an equation.

The bromide addition experiments and the results from the London tap water survey have shown that the presence of bromide increases the formation of brominated trihalomethanes. Thus equation (3) is only applicable to waters containing low bromide concentrations and if total-chloroform accounts for over 90% of total-trihalomethane formation.

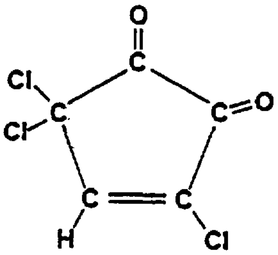
The results from the bromide addition experiment indicate that bromide might enhance trihalomethane formation, acting possibly as a catalyst in the haloform reaction, as there is an increase in the overall trihalomethane concentration relative to the chlorination of bromide free humic acid solutions. Bromoform formation however remains relatively low with the increase in brominated trihalomethanes corresponding to bromodichloromethane and dibromochloromethane. Thus it appears that in the presence of both hypochlorous and hypobromous acids the haloform reaction produced primarily the trihalomethane species, bromodichloromethane and dibromochloromethane. The percentage distribution of the trihalomethanes is dependent on the hypobromous acid to hypochlorous acid ratio.

It is evident from the work reported here that a better understanding of the factors involved in trihalomethane formation may be obtained by considering total-trihalomethane formation rather than limiting the observations to dissolved trihalomethanes as measured by the conventional solvent extraction, purge-and-trap, or head space analytical techniques. Furthermore, it is considered that residual trihalomethane should be included in proposed limits on trihalomethane levels in potable water supplies, such as the 100 $\mu g\ l^{-1}$ total trihalomethane (dissolved) standard currently being considered in the United States. This should be done not only because of the possible adverse health effects associated with long-term exposure to these unstable organohalide intermediates but also as this would take into account any further trihalomethane formation which may occur as a result of breakdown of these intermediates during the distribution of potable water supplies.

The present recommended analytical methods in the United States and United Kingdom are of limited value as these techniques are only suitable for the measurement of dissolved trihalomethanes (and other volatiles). However, D.A.I. has proved a quick and reliable method for dissolved trihalomethane analysis and as a method for the indirect measurement of organohalide intermediates detected as residual trihalomethane. In view of this,D.A.I. is a viable alternative to the recommended methods giving not only the extent of chlorination with respect to triahlomethane formation but - as there is a striking similarity between the effect of pH on residual chloroform concentration and the reported effect of pH on TOCl measurements - a possible indication to overall C-chlorination.

An important point has arisen from these studies with respect to the growing use of gas chromatography/mass spectrometry for the identification of chlorinated compounds in potable waters resulting from the chlorination process. The D.A.I. analytical technique has revealed the presence of organohalide intermediates of the haloform reaction which, although relatively stable at ambient temperature, break down reapidly on heating. It is probable therefore that other chlorinated organic compounds, not necessarily associated with the haloform reaction, are also liable to break down or transform on heating.

Christman used a GC/MS analytical method to identify the products resulting from the chlorination of resorcinol(141) (Section 5.1). The main product he observed, in addition to chloroform,was a five membered ring structure which, as Christman pointed out, was inconsistent with the proposed mechanistic pathway given by Rook involving ring rupture and the formation of a straight chain ketoacid (Chapter 5). The work presented in Chapter 5 shows that on chlorinating resorcinol an organochlorine intermediate containing probably a trichloroacetyl group is produced which breaks down even in the absence of chlorine to produce chloroform. This is in accordance with Rook's proposed mechanistic pathway but not with Christman's five membered ring structure 3,5,5-trichlorocyclopentene-3-ene-1,2-dione, as such a structure would required further halogenation



if chloroform is to be produced. As the reaction products were subjected to temperatures ranging between 100°C and 300°C during gas chromatographic separation, it is considered that the product identified by Christman as a cyclopentene derivative may have been formed during GC/MS analysis.

Due consideration must therefore be taken of possible break down or transformation of organohalide compounds when attempting to interpret GC/MS data as this analytical technique generally subjects the compounds to high temperatures to procure effective chromatographic separation.

8. SUMMARY AND CONCLUSIONS

1. Direct aqueous injection (D.A.I.) gas chromatography is a rapid and reliable method for the analysis of the trihalomethanes; chloroform; bromodichloromethane; dibromochloromethane, and bromoform, in potable water supplies. This analytical technique gives the dissolved and residual trihalomethane concentrations.

2. Residual trihalomethane is the result of breakdown in the injection port of the gas chromatograph of unstable organohalide intermediates of the haloform reaction.

3. Chloroform was the most abundant trihalomethane species produced on chlorinating water and humic and fulvic acids (extracted from Thames water). This was the result of both the low bromide content of these waters, and the use of sodium hypochlorite, low in bromine, as the chlorinating agent in the laboratory studies. Furthermore, there was no significant difference in the percentage contribution of brominated trihalomethanes to total trialomethane produced (<5%) between the laboratory studies on slow sand filtered water and final water at the water treatment plant (using industrial chlorine gas). It is therefore considered that the formation of bromodichloromethane in water (dibromochloromethane and bromoform not detectable) is due primarily to the presence of bromide in the raw water and not the result of bromine contamination of the chlorinating agent.

4. Bromide is oxidised by hypochlorous acid to hypobromous acid which is subsequently involved in the haloform reaction. The percentage contribution of brominated trihalomethanes to total trihalomethane formation increases on increasing bromide concentration in the raw water. Thus, water with an initial bromide concentration of approximately 10 μg l^{-1} produced over 95% of the total trihalomethane as chloroform and less than 5% as bromodichloromethane, whilst London potable waters contained 48% of the total trihalomethanes as chloroform and 52% as brominated trihalomethanes from raw waters containing between 90 μg l^{-1} and 120 μg l^{-1} of bromide.

At high chlorine to bromine ratios bromoform formation does not increase significantly. The increase in brominated trihalomethanes is associated primarily with increases in bromodichloromethane and dibromochloromethane formation.

5. Dissolved and residual chloroform formation increase on increasing temperature.

6. Dissolved chloroform formation increases on increasing the pH which is consistent with the general base catalysed haloform reaction. In contrast residual chloroform concentration decreases as a result of the higher rate of breakdown of organochlorine intermediates on increasing pH. Total-chloroform formation (residual + dissolved chloroform) reaches a maximum between pH 7 and pH 8. These trends were observed for the humic and fulvic acids and [illegible] water. If it is assumed that all the dissolved chloroform is produced <u>via</u> the breakdown of organochlorine intermediates, detected as residual chloroform, then the rate of total-chloroform formation is a direct measure of the overall rate of organochlorine intermediate formation. Thus, under these circumstances it may be stated that the rate of formation of these intermediates reaches a maximum between pH 7 and pH 8.

7. The organohalide intermediates break down slowly at ambient temperature to produce the corresponding trihalomethane in a reaction step which does not require the presence of chlorine.

In the case of chloroform formation, breakdown of the intermediates is the result of hydrolytic attack on an active carbon atom which contains the pre-requisite number of chlorine atoms for chloroform formation. Chloroform may continue to be produced in the distribution system or in samples even after free or residual chlorine have been exhausted or quenched. The specific nature of the haloform reaction coupled with these observations leads to the conclusions that these intermediates contain a trichloracetyl group (CCl_3CO-).

8. All the reactions involving humic material produced dissolved and residual chloroform. The different sources of humic material show similar trends in the formation of dissolved chloroform, and the formation and breakdown of the intermediates detected as residual

chloroform. Dissimilarities however do exist, as water produced not only a less stable intermediate than the intermediates from the humic material extracted from Thames water, but also a higher overall yield of chloroform and a greater overall chlorine consumption per unit weight of organic material. If account is taken for the possible 'aging' of the humic and fulvic acids, which were extracted from Thames water in 1971, the results indicate that 'fresh' humic material might be more reactive towards chlorine and produce higher levels of the trihalomethanes.

9. Model compounds containing meta-dihydroxy moieties produce dissolved chloroform and residual chloroform. Similar trends were observed in the formation of dissolved chloroform and breakdown of the organochlorine intermediates, with respect to pH, for the model compound resorcinol and humic materials. This similarity is further evidence to support the hypothesis that meta-dihydroxy moieties are present in the humic structure and are the active sites involved in the haloform reaction. However, more specifically, the rate of dissolved chloroform formation and breakdown of the intermediates from the model compounds are much faster than the observed rates for humic material. This slowing down of the haloform reaction is considered to be the result of deactivation of the active sites in the humic structure by steric hindrance, mesomeric or inductive effects.

Active sites in the humic structure other than meta-dihydroxy moieties may possibly be involved in the haloform reaction. It is therefore probable that more than one reaction pathway is involved in chloroform formation. The stability of the organochlorine intermediates will vary throughout the reaction depending on the degree of deactivation of the specific active sites involved in the haloform reaction.

10. Total-chloroform formation may be characterised as follows:-

(a) A rapid initial phase of total-chloroform formation from sites which contain, or readily produce, acetyl groups. These reactions may follow the classical haloform reaction, the rate determining step being proton dissociation which is greatly influenced by pH.

(b) An intermediate phase involving sterically hindered or deactivated sites that follow the classical haloform reaction but which also include rate determining steps involving not only proton dissociation but the chlorinating species (HOCl or H_2OCl^+).

(c) A slower secondary phase of total-chloroform formation involving an initial oxidation step of active sites to form acetyl groups or derivatives which subsequently undergo the haloform reaction. The oxidation step of the active sites may be the rate determining step for such reactions.

11. A linear relationship was established between total-chloroform formation and overall chlorine consumption for humic and fulvic acids and water. The amount of total-chloroform produced per unit chlorine consumed (L) for humic material extracted from Thames water and water is equal to 0.022 and 0.056 respectively, with the model compounds resorcinol giving the highest value of L equal to 0.1. Assuming that meta-dihydroxy moieties are the main active sites for the haloform reaction it is considered that the chlorination of a natural water containing humic material will not exceed the value of L given by resorcinol as this compound is the simplest aromatic unit containing such a configuration.

12. The higher molecular weight humic acid fraction produces higher levels of dissolved and residual chloroform that the low molecular weight fulvic acid fraction. This is due to the greater number of active sites associated with the more complex humic acid structure. Thus total-chloroform formation from a source water which varies in humic content is not necessarily directly proportional to TOC content of the water but is dependent on changes in the molecular weight fraction of the humic material.

13. A relationship was established between total-chloroform formation and the UV/VIS absorption intergral. The absorption integral is considered to be a measure of the active sites of the humic material present in the water.

14. A general empirical equation for total-chloroform formation has been derived which is applicable to the humic and fulvic acids and water, involving the total-chloroform produced per unit chlorine consumed (L) and the UV/VIS absorption intergral (Abs. Integral).

$$[\mathrm{TCHCl_3}]_t = 2.9(\mathrm{Abs.Integral})(L)t_{\mathrm{min}}^{0.227}$$

15. Any pre-treatment of waters which affects the molecular weight distribution of the humic material will as a consequent change the amount of chloroform produced per unit weight of organic material.

16. pH is the single most important parameter which affects total, residual and dissolved chloroform formation. A reduction in pH prior to chlorination in order to reduce dissolved chloroform formation will, as a result, increase the concentration of residual chloroform.

17. It is evident from these studies that a better understanding of the factors which influence chloroform production from humic materials has been established. The conclusions have been based not only on results from laboratory studies of humic materials extracted from Thames water and a natural water containing humic material but also from on-site investigations at a water treatment plant under normal operating conditions.

The 'bromide addition' experiment and the results from the survey of household water supply in the London area demonstrated the importance of bromide on the haloform reaction and its effect on the formation of the brominated trihalomethane species. Trihalomethane production in water supplies must be kept in perspective as the haloform reaction is a minor reaction between chlorine and humic material accounting for only 1-5% of the total chlorine consumed.

On the basis of this research programme a number of new areas of research should be investigated:-

(a) A number of organohalide compounds have been identified in water supplies though generally at concentrations one or two orders of magnitude below trihalomethane levels. These studies have shown that organohalide intermediates of the haloform reaction are relatively stable and persist in water distribution systems.

It is clearly not feasible to examine the health risks associated with long term exposure to each individual compound particularly as the toxicological tests on compounds at low concentrations are generally inconclusive. Furthermore, even if a high risk factor can be related to a specific halogenated organic compound there would be little advantage in selectively removing that offending compound.

A more realistic approach to establishing potential health risks associated with the chlorination process might be obtained by relating these risks to total organic halogen levels in potable waters. However, as chlorine can act both as a chlorinating agent and an oxidising agent a greater understanding is required of the overall chlorine reactions with humic materials in relation to the extent of C-chlorination.

(b) Because of the importance of bromide on the haloform reaction, the effect of varying bromide and chlorine concentration on the percentage distribution of the individual trihalomethanes species should be investigated.

(c) On-site studies showed that chlorinated copperas treatment (coagulation) might be specific in removing those humic materials most susceptible to trihalomethane formation. Treatment processes involving coagulation, flocculation, filtration and activated carbon should be investigated in terms of their effect on the molecular weight distribution of the humic material and the resulting trihalomethane formation.

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APPENDIX I

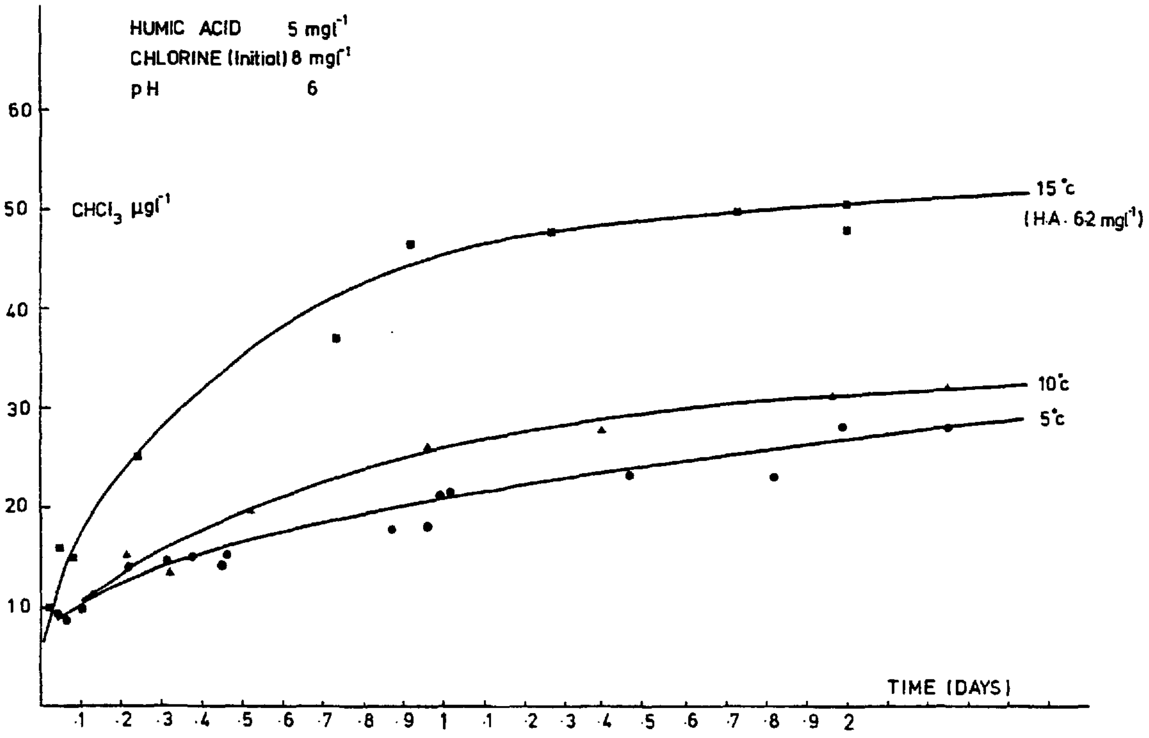

Fig. 1 Effect of temperature on dissolved chloroform formation from humic acid at pH 6

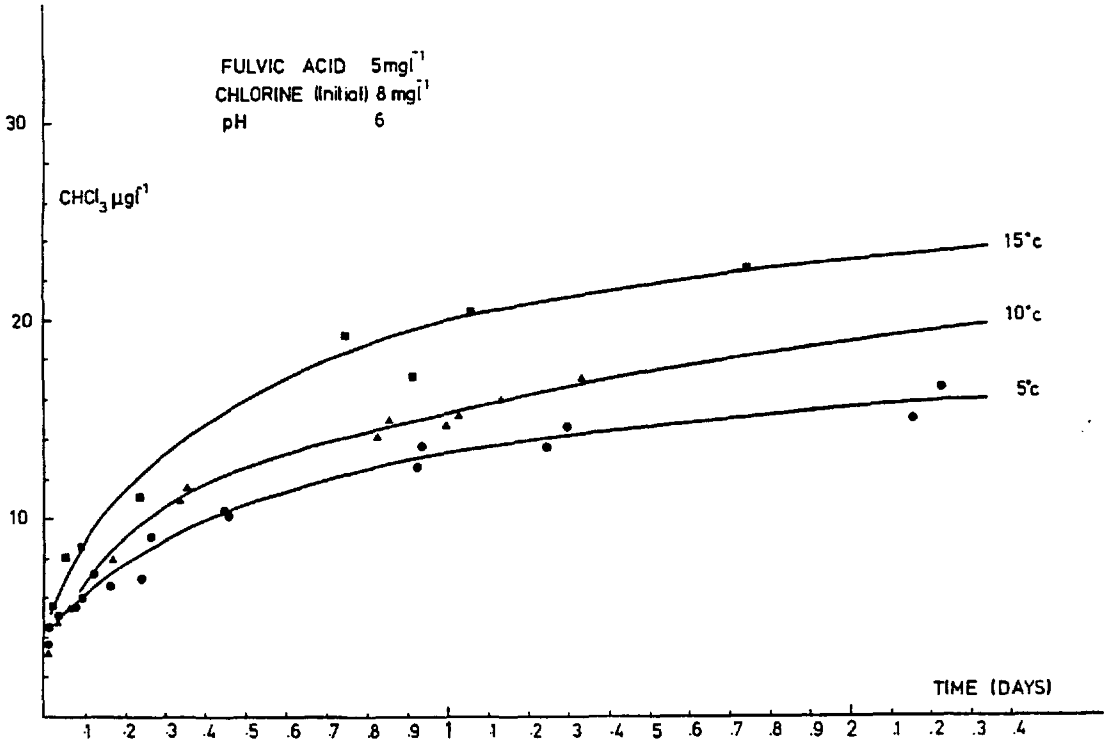

Fig. 2 Effect of temperature on dissolved chloroform formation from fulvic acid at pH 6

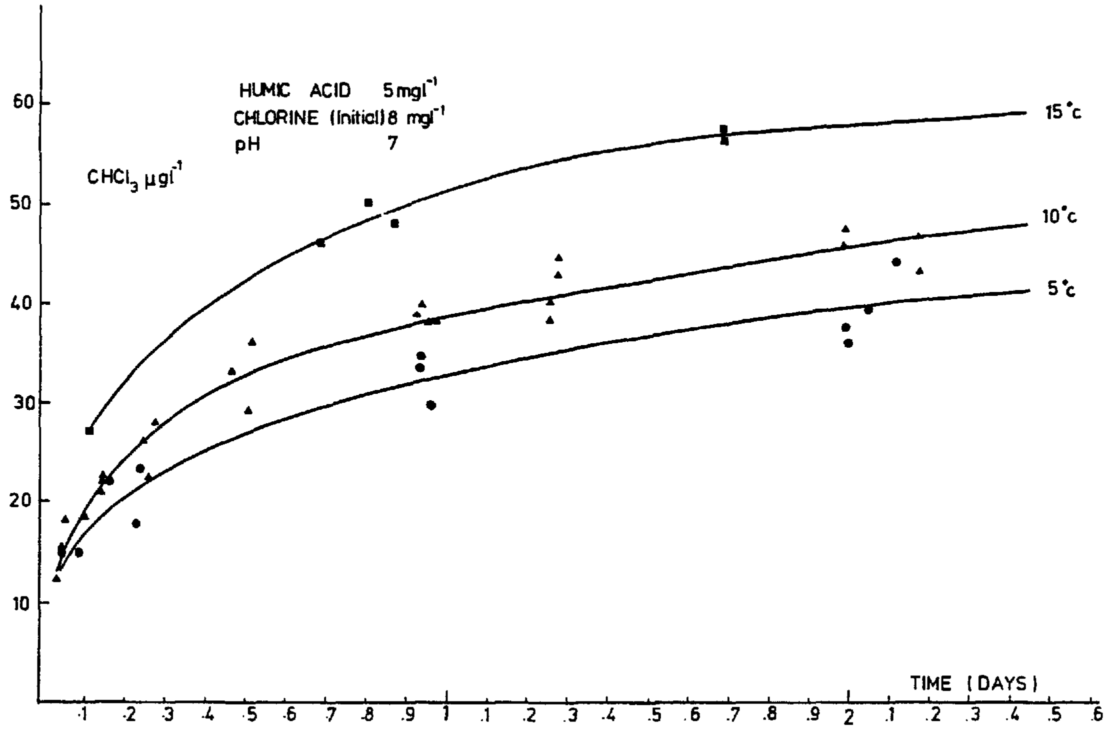

Fig. 3 Effect of temperature on dissolved chloroform formation from humic acid at pH 7

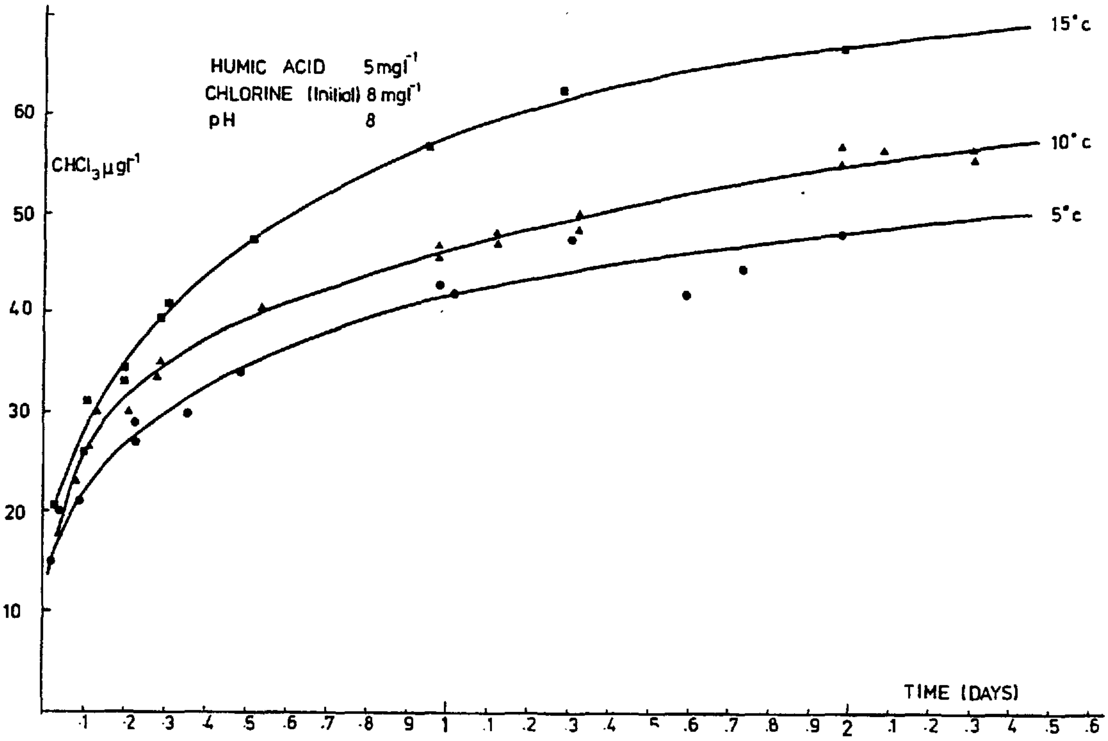

Fig. 4 Effect of temperature on dissolved chloroform formation from humic acid at pH 8

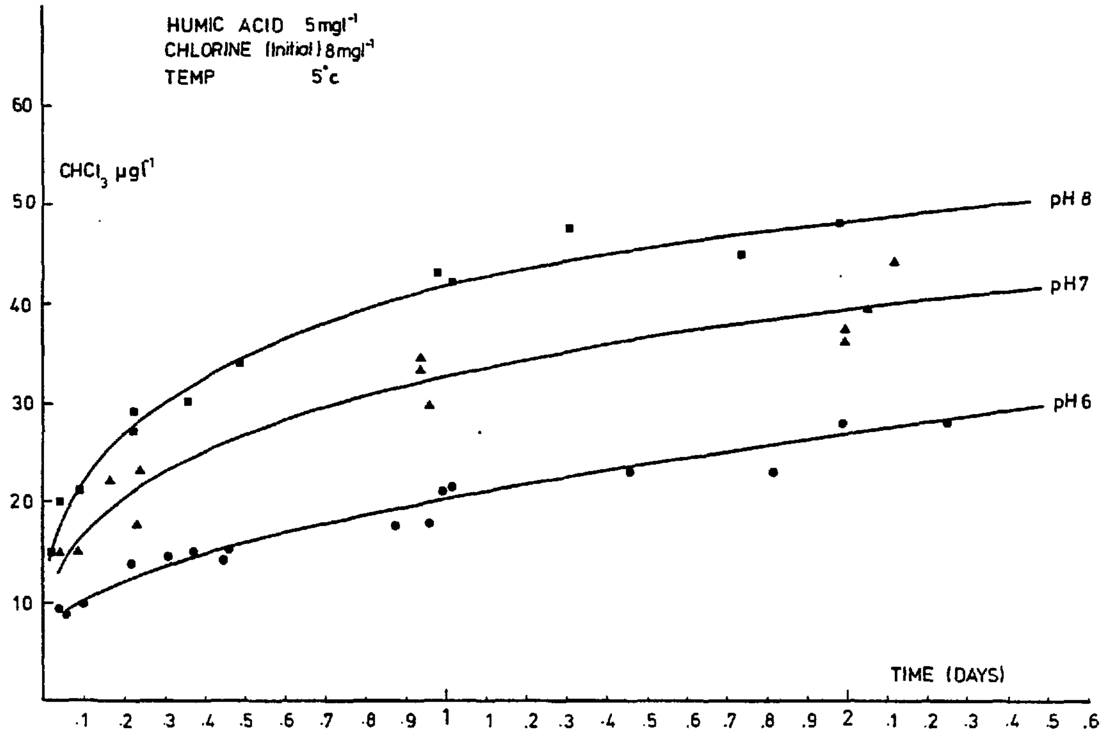

Fig. 5 Effect of pH on dissolved chloroform formation from humic acid at 5^{o}C

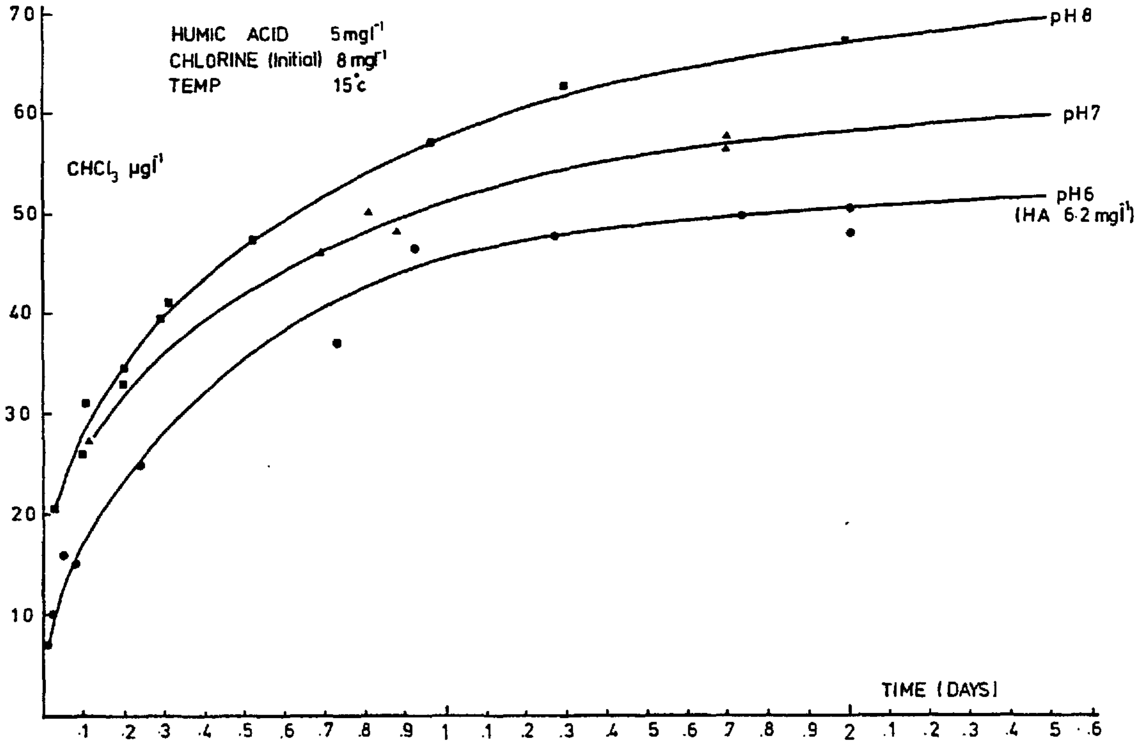

Fig. 6 Effect of pH on dissolved chloroform formation from humic acid at 15^{o}C

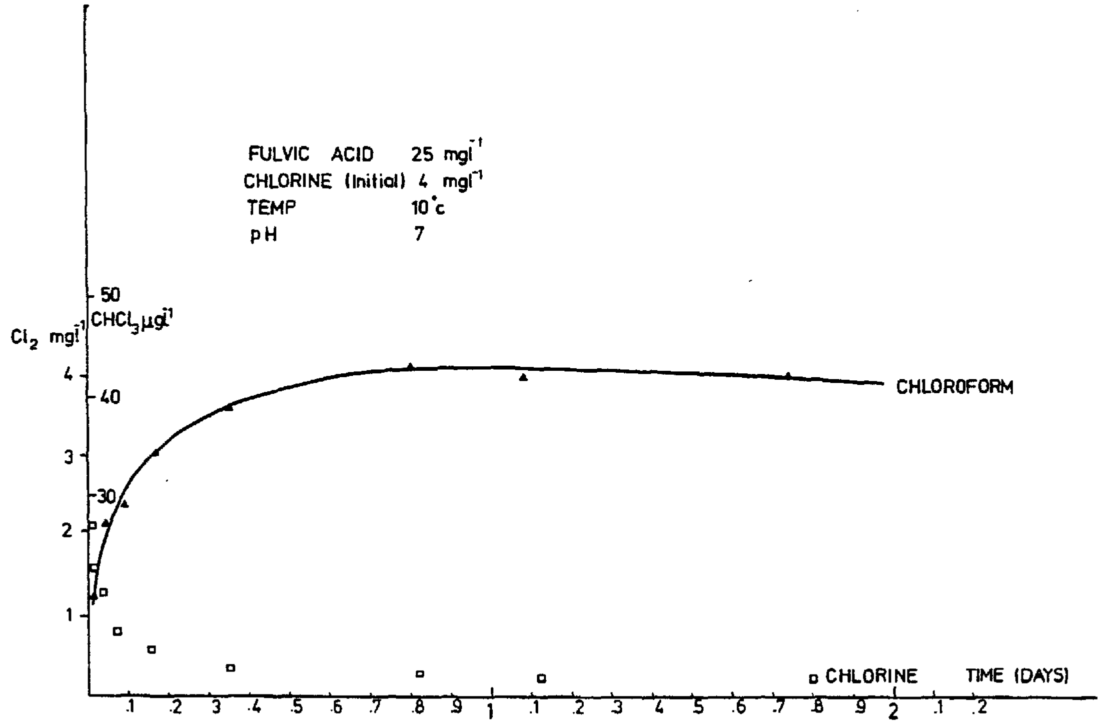

Fig. 7 Change in chlorine concentration and dissolved chloroform formation on chlorinating fulvic acid at 25 mg l^{-1}

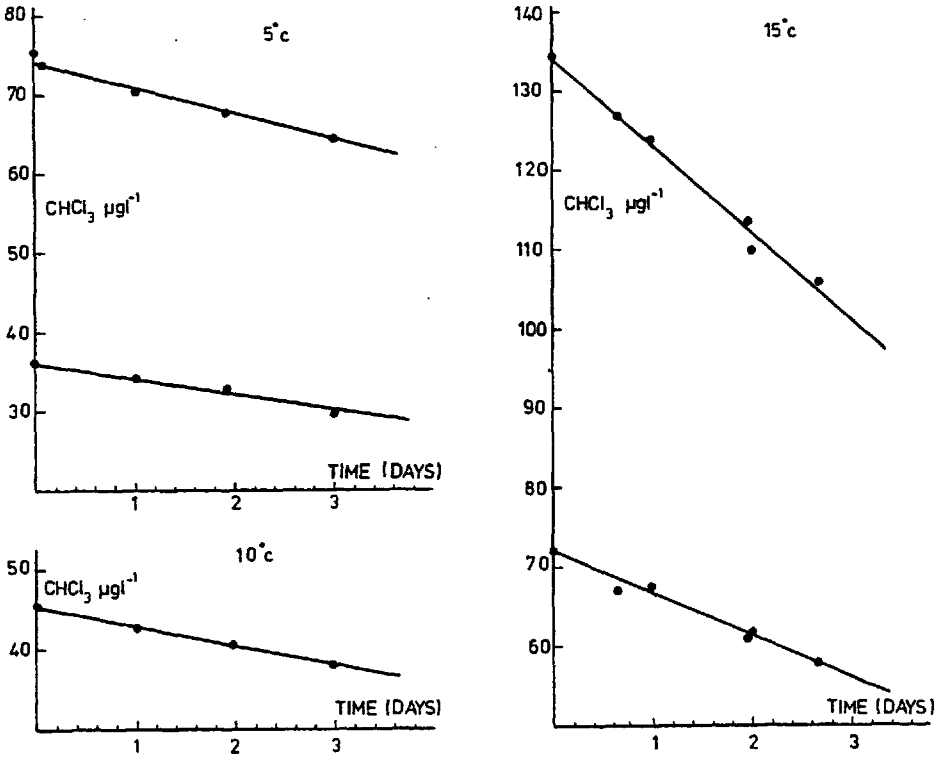

Fig. 8 Evaporation rates

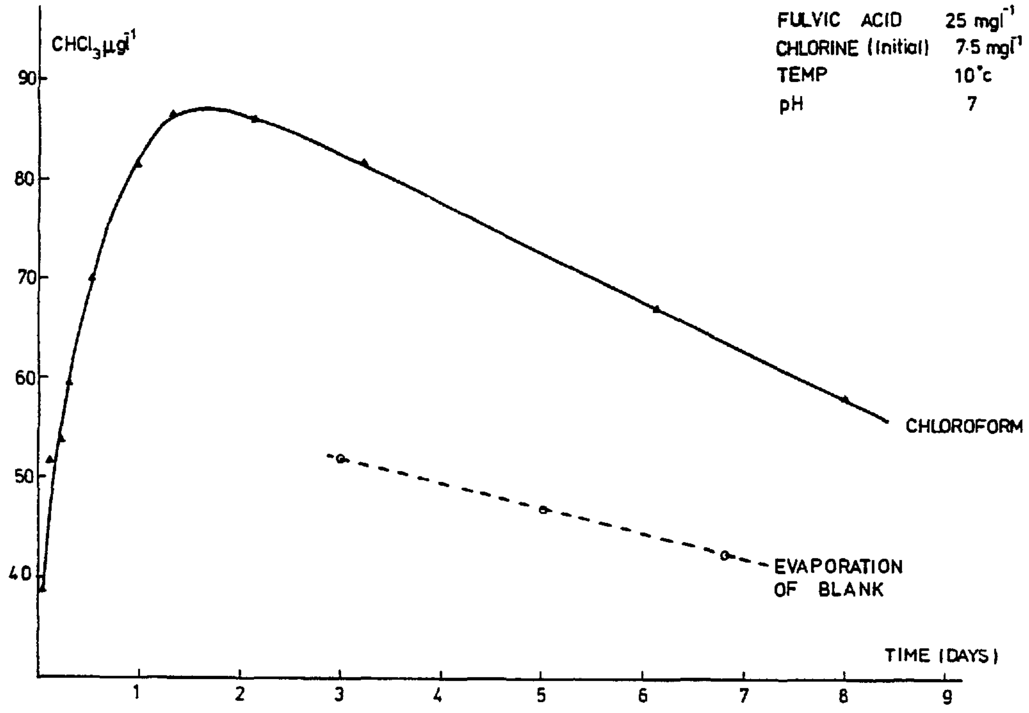

Fig. 9 Formation and subsequent evaporation of dissolved chloroform on chlorinating fulvic acid at 25 mg l^{-1}

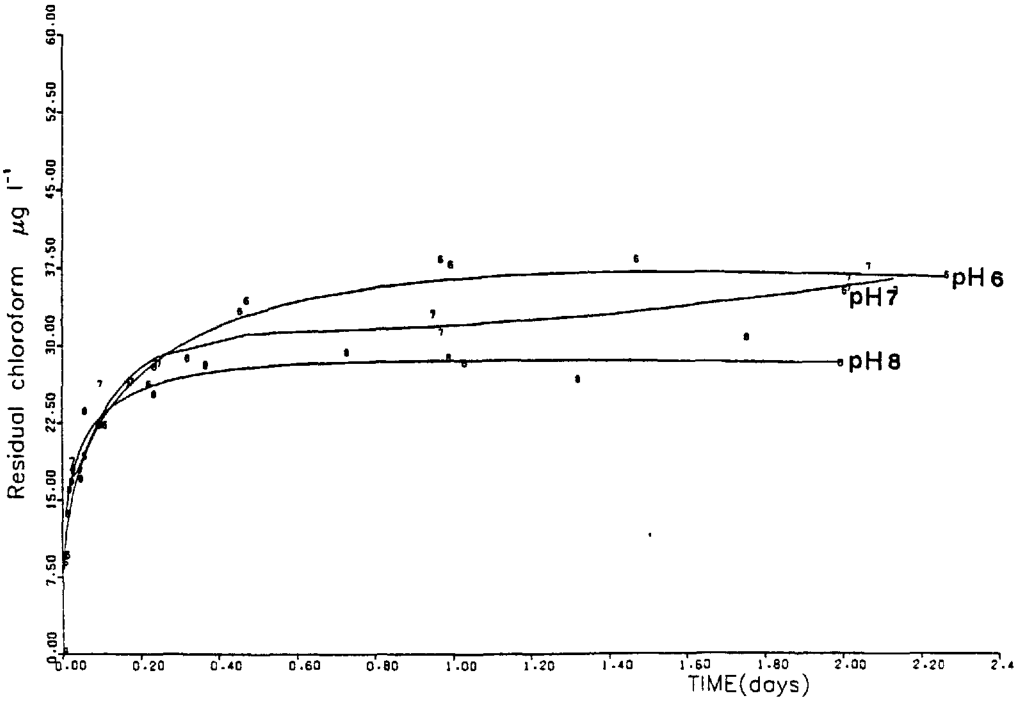

Fig. 10 Effect of pH on residual chloroform formation from humic acid at 5°C

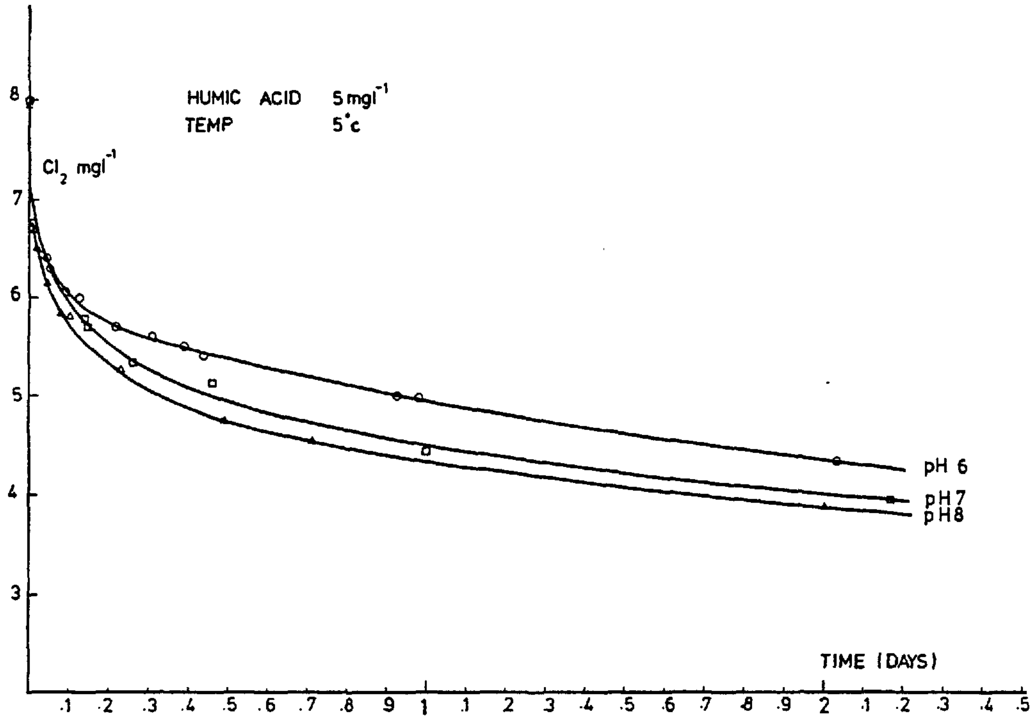

Fig. 11 Change in chlorine concentration on chlorinating humic acid at $5^{\circ}C$

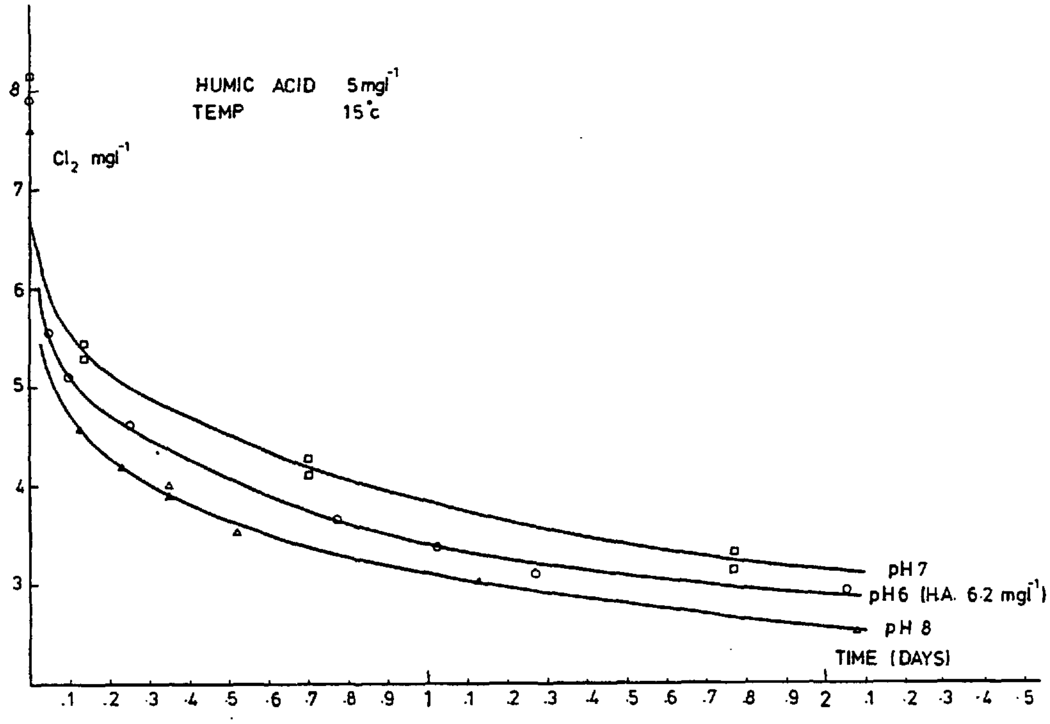

Fig. 12 Change in chlorine concentration on chlorinating humic acid at $15^{\circ}C$

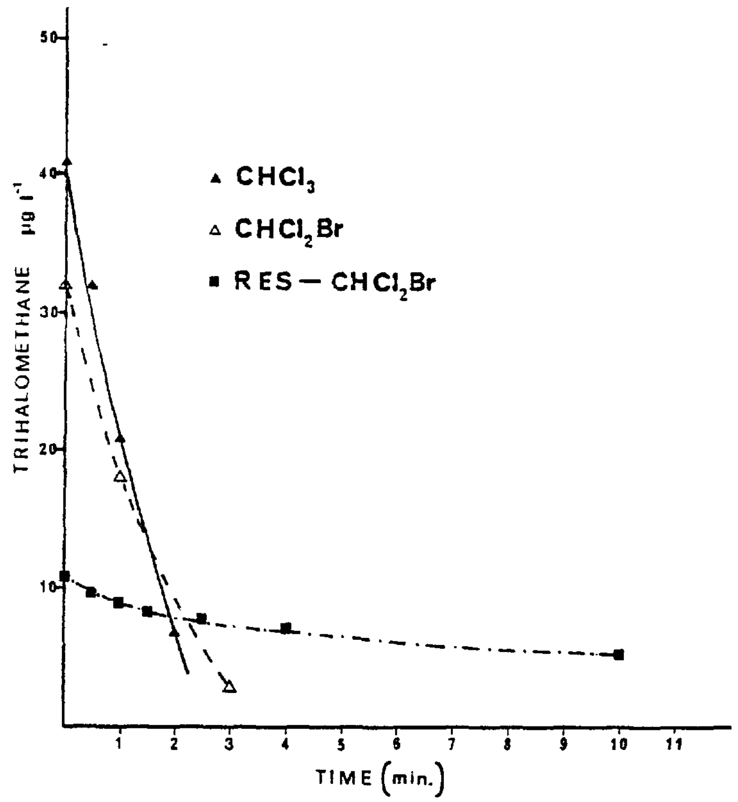

Fig. 13 Purging rates for chloroform, bromodichloromethane' and 'apparent bromodichloromethane'

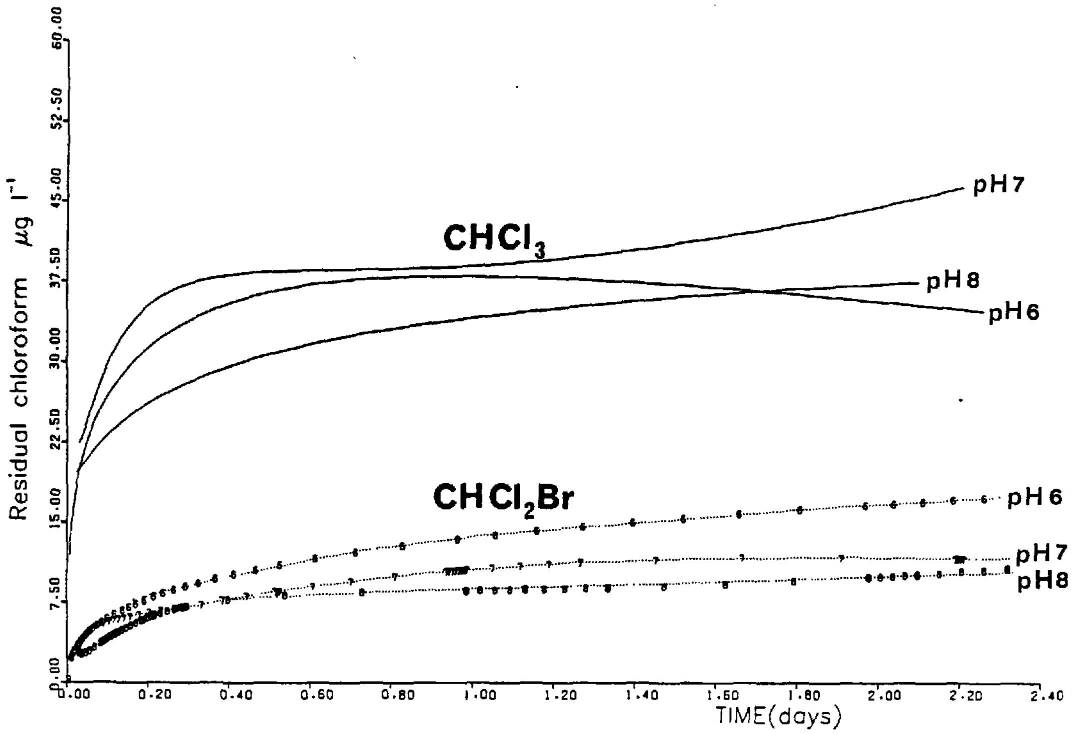

Fig. 14 Effect of pH on residual chloroform and 'apparent bromodichloromethane' from humic acid at $10^{\circ}C$

APPENDIX II

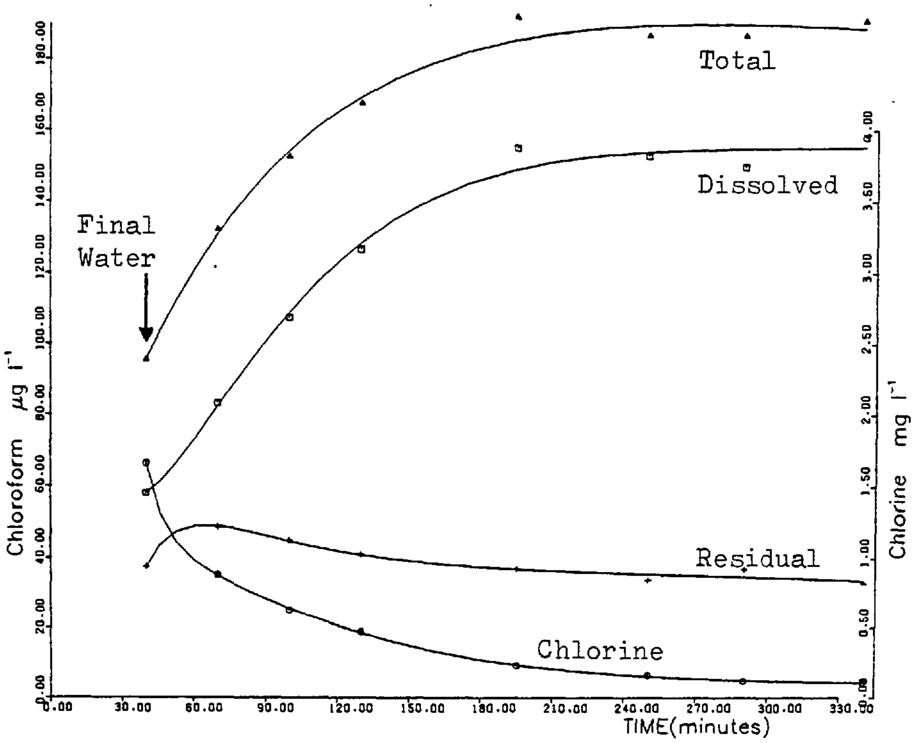

Fig. 1 Total, residual and dissolved chloroform formation and chlorine consumption in Tap test No. 3 (Initial pH 8.75)

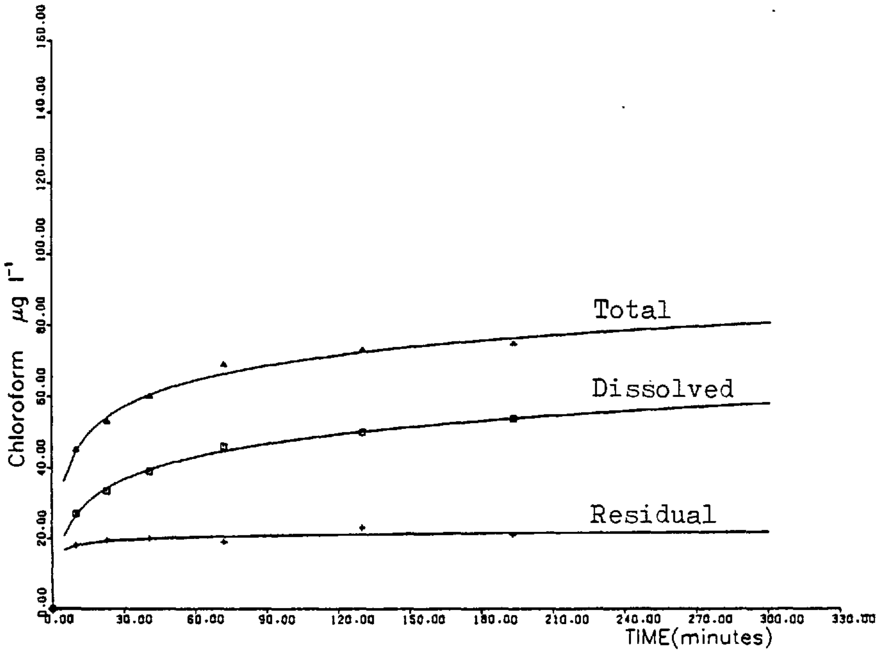

Fig. 2 Chlorination of mixed S.S.F./R.G.F. water after 6 weeks storage. Initial chlorine concentration 2.5 mg l^{-1}, pH 9

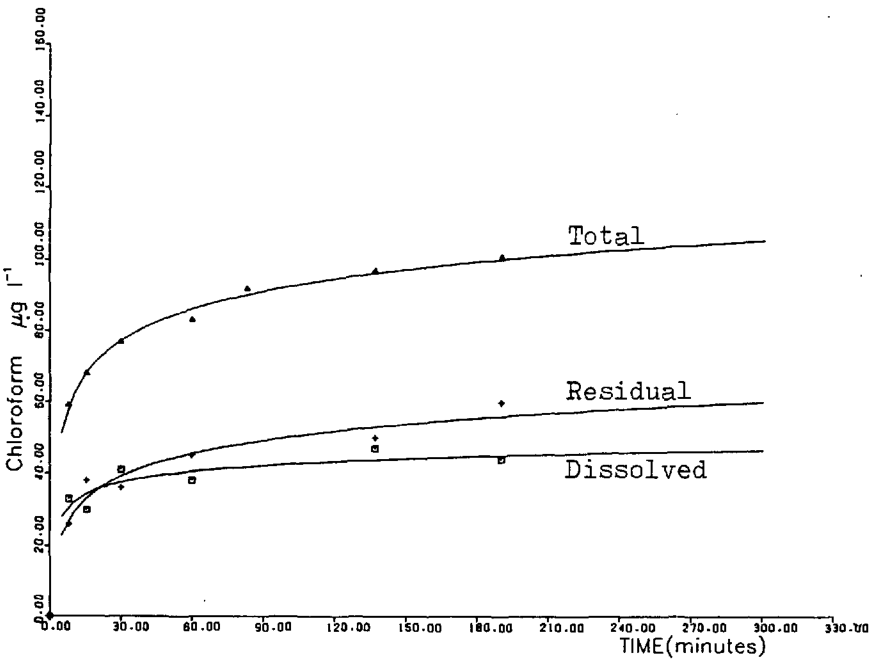

Fig. 3 Chlorination of mixed S.S.F./R.G.F. water after 6 weeks storage. Initial chlorine concentration 2.5 mg l^{-1}, pH 7

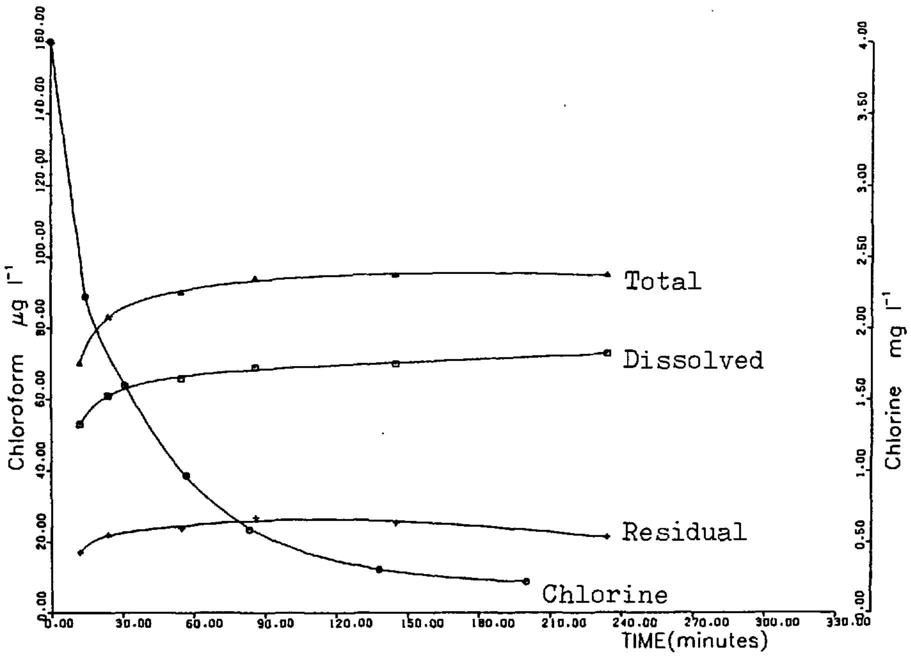

Fig. 4 Chlorination of mixed S.S.F./R.G.F. water in the presence of copper. Initial chlorine concentration 4 mg l^{-1}, pH 9

APPENDIX III

List - Program for curve fitting using Chebyshev polynomial

```
    PROGRAM FA(INPUT,OUTPUT,DATA,TAPE5=DATA,TAPE6=OUTPUT,TAPE10)
   DIMENSION XX(100),YY(100),X(100),Y(100),W(100),AK(7)
   DIMENSION XAV(100)
   DIMENSION F(100)
   DIMENSION CC(100),DD(100)
    DIMENSION EE(100),GG(100),AKK(7)
   DIMENSION AA(100),BB(100),Z(100),P(100)
   DIMENSION E(100),G(100)
     DIMENSION  X(100),Y(100)
    LL=100
   K=6
   KPLUS1=K+1
   IFAIL=0
   DO 10 N=1,LL
   READ (5,*)   XX(N),YY(N),II
   WRITE(6,700)  N,XX(N),YY(N)
   W(N)=1
   M=N
   IF (II.EQ.1) GO TO 15
10 CONTINUE
15 CONTINUE
   CALL ALTER (XX,YY,E,G,AK,W,M)
    M2=M-1
   CALL DOG(E,G,X,Y,M)
   DO 20 N=1,M2
   XAV(N)=0.5*(X(N)+X(N+1))
   W(N)=1
20 CONTINUE
   X1=X(1)
   XM=X(M)
   D=XM-X1
   DO 30  N=1,M2
   XCAPR=((XAV(N)-X1)-(XM-XAV(N)))/D
   CALL E02AEF (KPLUS1,AK,XCAPR,FIT,IFAIL)
   IF (IFAIL.NE.0) WRITE(6,500) IFAIL
   F(N)=FIT
30 CONTINUE
   CALL ANTI (XAV,F,AA,BB,M2)
   DO 31 N=1,M
   K=2*N-1
   CC(K)=E(N)
   DD(K)=G(N)
   W(K)=1
31 CONTINUE
   DO 32 N=1,M2
   K=2*N
   CC(K)=AA(N)
   DD(K)=BB(N)
   W(K)=1
32 CONTINUE
   L=2*M-1
   II=0
   DO 33 K=1,L
   IF (K.EQ.L) II=1
   WRITE(6,400)  CC(K),DD(K),II
   WRITE(10,400) CC(K),DD(K),II
33 CONTINUE
```

```
100 FORMAT(F5.3,5X,F5.2,5X,I1)
200 FORMAT (10X,F7.3,10X,F7.3,10X,I1)
300 FORMAT(1H,F5.2,5X,F5.2)
400 FORMAT (10X,F7.3,10X,F7.3,10X,I1)
500 FORMAT(1X,I2)
600 FORMAT(1H,I2,10X,F7.3,10X,F7.3,10X,F7.3)
700 FORMAT (1H,I2,15X,F7.3,15X,F7.3)
    STOP
    END
    SUBROUTINE DOG(XX,YY,X,Y,M)
    DIMENSION X(100),Y(100),XX(100),YY(100)
    DO 32 N=1,M
    X(N)=ALOG10(XX(N))
    Y(N)=ALOG10(YY(N))
 32 CONTINUE
    RETURN
    END
    SUBROUTINE ANTI(X,Y,Z,P,M)
    DIMENSION  X(100),Y(100)
    DIMENSION Z(100),P(100)
    DO 33 N=1,M
    Z(N)= 10**X(N)
    P(N)=10**Y(N)
 33 CONTINUE
    RETURN
    END
    SUBROUTINE ALTER(XX,YY,E,G,AK,W,M)
      DIMENSION  X(100),Y(100)
      DIMENSION W(100),WORK1(3,100),WORK2(2,7),A(7,7),S(7)
    DIMENSION XX(100),YY(100)
    DIMENSION AK(7)
    DIMENSION F(100),AA(100),BB(100),C(100),DD(100)
    DIMENSION E(100),G(100),YYY(100)
    NROWS=7
    N=1
    K=6
    IFAIL=0
    KPLUS1=K+1
    CALL DOG (XX,YY,X,Y,M)
    DO 20 IPLUS1=1,KPLUS1
     CALL E02ADF (M,KPLUS1,NROWS,X,Y,W,WORK1,WORK2,A,S,IFAIL)
      IF(IFAIL.NE.0)  WRITE(6,500) IFAIL
     I=IPLUS1-1
    WRITE(6,200) I
    DO 25 JPLUS1=1,KPLUS1
    WRITE (6,300) A(IPLUS1,JPLUS1)
 25 CONTINUE
 20 CONTINUE
    DO 16 IPLUS1=1,KPLUS1
    AK(IPLUS1)=A(KPLUS1,IPLUS1)
 16 CONTINUE
    X1=X(1)
     XM=X(M)
    D=XM-X1
    N=0
     DO 30 N=1,M
    XCAPR=((X(N)-X1)-(XM-X(N)))/D
    CALL E02AEF(KPLUS1,AK,XCAPR,FIT,IFAIL)
    IF (IFAIL.NE.0) WRITE(6,500) IFAIL
    YYY(N)= FIT
    WRITE(6,300) X(N),YYY(N)
 30 CONTINUE
```

```
      CALL ANTI (X,YYY.E,G.M)
      DO 26 N=1,M
      RED=G(N)-YY(N)
      WRITE(6,600) N,E(N),G(N),RED
   26 CONTINUE
  100 FORMAT(F4.2,5X,F5.1,5X,I1)
  200 FORMAT (7H DEGREE,I4,26H    J   CHEBYSHEV COEFF A(J))
  300 FORMAT(1H,F5.2,5X,F5.2)
  500 FORMAT(1X,I2)
  600 FORMAT (1H,I2,10X,F7.3,10X,F7.3,10X,F7.3)
      RETURN
      END
```

Program used in conjunction with graphics program for figures,

Chapter 3	3.4 - 3.7
Chapter 4	4.2 - 4.9, 4.12 - 4.17
Chapter 5	5.3
Appendix I	10, 14
Appendix II	1 - 4