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CHLORINATED ORGANICS: A REVIEW OF SOURCES
AND CONTRIBUTIONS TO THE GREAT LAKES
FROM MUNICIPAL AND INDUSTRIAL CHLORINATION
PRACTICES

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PRACTICES

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ABSTRACT

Laboratory chlorination studies indicate that the potential exists for many chlorinated organic compounds to be formed during wastewater disinfection. In many instances the chemical mechanisms involved are little understood (i.e., whether HOCl , OCl^- , H_2OCl^+ , or $\text{Cl}\cdot$ is the active species or some combination thereof). The pH of the reaction plays a major role in the type and degree of reaction since many of the reactions are acid catalysed while the haloform reaction is base catalysed. Laboratory chlorination of sewage effluents and cooling waters (especially superchlorination) results in a multitude of halogenated compounds, many of which do not appear to be found at appreciable concentrations under actual treatment plant chlorination conditions. The major fraction of chlorinated compounds in municipal effluents appears to be non-volatile, whereas the major fraction from cooling waters is reported to be volatile.

There have been no detailed monitoring studies of chlorinated organics in municipal waste treatment plant effluents or cooling water discharges, although some volatile halogenated organics have been identified in the cooling towers at the Oak Ridge Gaseous Diffusion Plant and the Kingston Steam Generating Plant.

Conservative estimates, based on laboratory chlorination studies, indicate that sewage treatment plants on the Great Lakes are responsible for an annual discharge of approximately 100 tonnes chlorinated organic compounds. Similar estimates for cooling waters yield a total discharge of 38.5 tonnes annually.

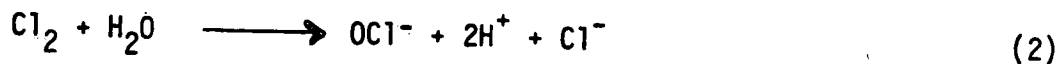
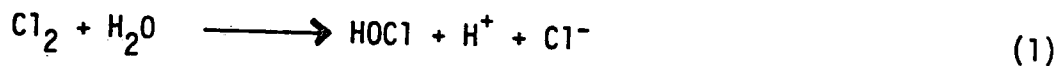
Industrial contributions of chloro-organics to the Great Lakes have been crudely estimated as 600 - 12,000 tonnes annually. The major fraction of these compounds arise from wood pulp processing in the paper industry. Hence, the contribution of chloro-organics from sewage treatment plants and cooling waters appear to be insignificant relative to the large industrial discharges.

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INTRODUCTION

The reactive species formed by the addition of chlorine to water can be summarized by the following two hydroxylation reactions:



Which of these reactions predominates depends on the pH. As illustrated in Table 1, at low pH reaction (1) predominates while at high pH reaction (2) is favoured. Free available chlorine is defined as the sum of Cl_2 , HOCl and OCl^- .

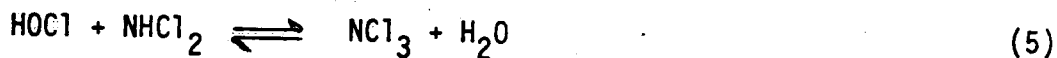
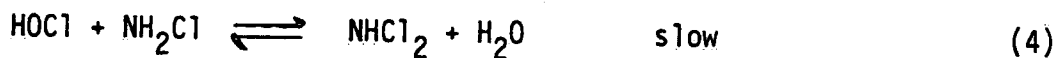
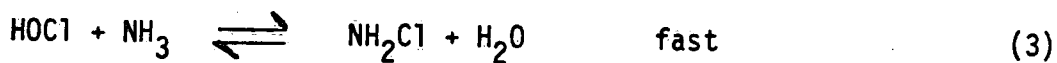
TABLE 1

<u>pH</u>	<u>% HOCl</u>	<u>% OCl⁻</u>
6	96	4
7	75	25
7.4	50	50
8	22	78
9	3	97

Other transient species that have been considered to be formed in aqueous solution include H_2OCl^+ , Cl^+ and Cl_3^- (Morris²⁰). According to Morris, H_2OCl^+ is probably the only one of these which is of any importance under conditions used for disinfection and could be the species

responsible for acid catalysis of many reactions of HOCl. However, Carlson and Caple (21) claim the chloronium ion, Cl^+ and the chlorine radical, $Cl\cdot$, are the two most significant active species.

In wastewater the situation is more complex. All three of the active species, Cl_2 , HOCl and OCl^- are strong oxidizing agents and will react strongly with any reducing compounds, such as hydrogen sulphide, carbohydrates, etc., present in the wastewater. When such oxidations have proceeded to virtual completion the active species start to react with ammonia or organic nitrogen containing compounds to form chloramines (combined chlorine).



When the weight ratio of chlorine to ammonia is less than 5:1, monochloramine is the predominant product (equ. 3). With a ratio of between 5:1 and 10:1, disproportionation occurs and dichloramine is formed (equ. 4) and above 10:1 (the approximate ratio for break point chlorination), some trichloroamine (equ.5) may be formed. Only after all these reactions have occurred will continued addition of chlorine produce free residual chlorine which will be available for disinfection.

The nature and concentrations of the reactive chlorine containing species are of primary importance in determining the formation and yield

of chlorinated organic compounds. Lee and Morris ⁽²⁾ have reported on the potential chlorinating ability of HOCl and Morris ⁽³⁾ has estimated that it is more effective than NH_2Cl by about 4 orders of magnitude. Since HOCl appears to be the major chlorinating species, the possible chemical reactions with organic constituents in aqueous solution must be examined. According to Jolley ⁽⁴⁾ these reactions may be grouped into three general categories:

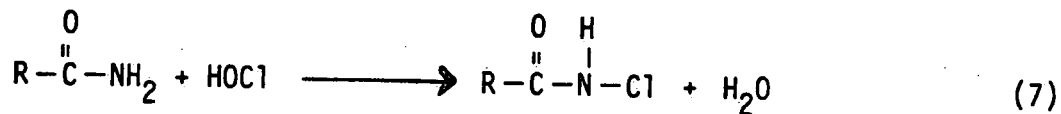
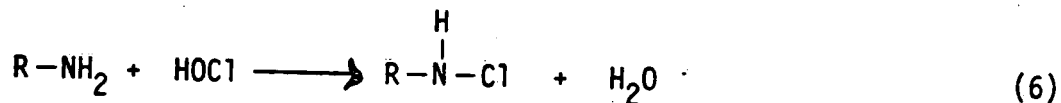
- a) Oxidation
- b) Substitution
- c) Addition

Jolley ⁽⁴⁾ has proposed that oxidation reactions may be the predominant type of reactions to occur in natural waters or effluents, although this has been disputed by Zaloum and Murphy ⁽⁵⁾. These latter authors quote unchanged values of TOC and COD before and after chlorination in support of their argument. However, they appear to be considering chloramines only since they assume all the chlorine to be in the combined form. Jolley ⁽⁶⁾ lists more than 20 carbohydrates, polyols and aliphatic organic acids which have been identified in primary domestic sewage and which would readily oxidize in the presence of HOCl. Most of these compounds were identified in the low μgL^{-1} range. Although these compounds probably contribute to the overall chlorine demand of effluents or cooling waters, they are unlikely to result in appreciable formation of chloro-organic compounds.

Substitution reactions can be conveniently divided into two groups:

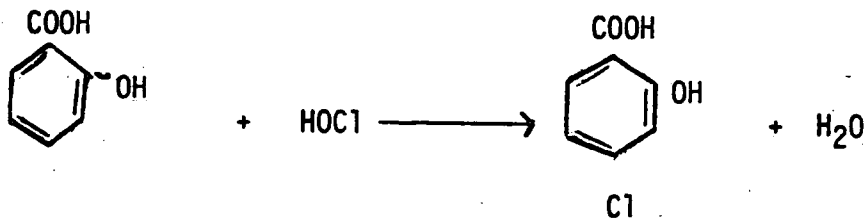
- i) those resulting in formation of N-chlorinated compounds;
- ii) those resulting in formation of C-chlorinated compounds.

The formation of N-chlorinated compounds has been reported by Morris (3). Pitt et al. (7) have identified numerous amides, amino acids, indoles, pyridine derivatives, purine derivatives and pyrimidine derivatives in sewage effluents. These compounds would be expected to react with aqueous chlorine in a similar way to ammonia.

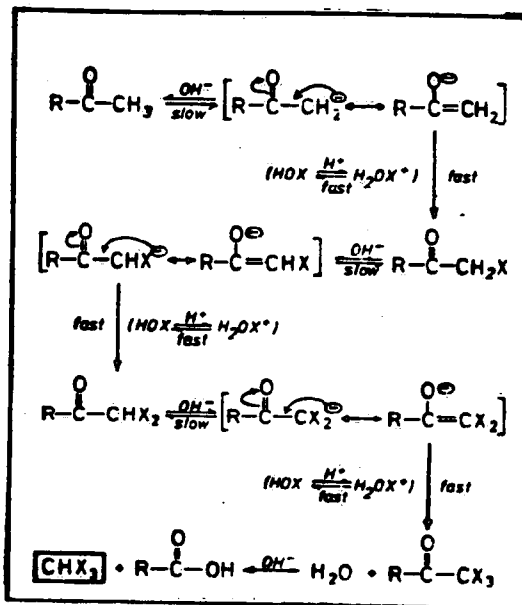


However, amines would be expected to react much faster to form N-chloro-derivatives than amides (3).

Substitution of chlorine into organic compounds to form C-chlorinated derivatives has been summarized by Jolley (4), Carlson et al. (8) and Morris (9). These reactions can either be conventional substitution, i.e., substitution of chlorine into aromatic or heterocyclic compounds or of the haloform reaction type. The latter reaction has been studied in detail in recent years in the chlorination of water (10,11), cooling water (12) and wastewater (13). The major precursors of the haloform reaction are now considered to be m-dihydroxy aromatic compounds - common building blocks of humic materials and low molecular weight methyl ketones (14). Examples of C-chlorinated derivative formation by conventional substitution and the haloform reaction are as follows:



CONVENTIONAL SUBSTITUTION



THE HALOFORM REACTION

During the past six years, studies of the formation of chlorinated organics during water and wastewater disinfection have proceeded along three directions:

- (a) Chlorination of model organic compounds in the laboratory.
- (b) Chlorination of sewage effluents or cooling waters in the laboratory.
- (c) Chlorination of effluents in sewage treatment plants under normal operating conditions.

These three areas will now be reviewed in turn - unfortunately (a) and (b) above have received considerably more attention than (c).

CHLORINATION OF MODEL ORGANIC COMPOUNDS

For a recent review of general chlorination reactions, the reader is referred to a report by R.C. Pierce⁽¹⁾. Numerous studies have been made on the chlorination of organic compounds (other than chloramines) which have either been identified as components of sewage effluents or predicted as possible components. Carlson et al.⁽⁸⁾ examined the interaction of several monosubstituted aromatics with low concentrations (7×10^{-4} M) of aqueous chlorine. The reactions followed recognized trends⁽²⁰⁾, i.e., aromatics containing activating substituents such as hydroxyl, ether, amine groups undergo electrophilic aromatic substitution faster than those containing electron withdrawing groups such as nitro, chloro, nitrile and carboxyl groups^(15,16,32). Phenol was shown to be an exception to this general rule in that it is readily chlorinated at high pH due to the formation of the phenolate anion. The

percentage of chlorine uptake of these substituted aromatic compounds as a function of pH is shown in Table 2.

TABLE 2
CHLORINE UPTAKE BY ORGANIC COMPOUNDS

$0.5 \pm 0.6 \times 10^{-4}$ M)	pH		
	3	7	10.1
	% Cl (uptake)	% Cl	% Cl
Phenol	97.8 + 0.1	97.6 + 0.1	97.6 + 0.2
Anisole	80.7 + 0.2	11.4 + 0.4	2.8 + 0.2
Acetanilide	55.3 + 0.5	3.4 + 0.2	-
Toluene	11.1 + 0.1	2.9 + 0.4	-
Benzylalcohol	2.3 + 0.2	-	-
Benzonitrile	2.4 + 0.2	-	-
Nitrobenzene	1.8 + 0.1	-	-
Chlorobenzene	1.8 + 0.1	-	-
Methylbenzoate	1.8 + 0.2	-	-
Benzene	1.5 + 0.1	-	-

Chlorine (7.0×10^{-4} M), 20 min, 25°C.

The concentration of chlorine used by these authors ($\approx 50 \text{ mg L}^{-1}$) is somewhat higher than normally experienced in a wastewater treatment plant but the molar ratio of organic:chlorine is reasonable. The 20 minute retention time is quite conservative. Carlson and Caple⁽²¹⁾ have studied the chlorination of unsaturated fatty acids (oleic acid), resin acids (abietic and dehydroabietic acids) and α -terpineol and

attempted to elucidate the chemical mechanisms involved.

The chlorination of biphenyl (8,17) and naphthalene (17) has also been studied in detail due to relatively easy recognition of chlorinated isomers and the concern over possible PCB and PNC formation in treatment plants known to receive biphenyl and naphthalene (16,17). Smith et al. (17) reported that chlorinated biphenyls and chlorinated naphthalenes formed readily at room temperature with the extent of reaction depending upon pH and the molar ratio of hydrocarbon:chlorine. In a 500 mgL⁻¹ non-homogeneous suspension of biphenyl they identified the predominant products as 2-chlorobiphenyl, 4-chlorobiphenyl, 2,2'-dichlorobiphenyl and 2,4'-dichlorobiphenyl. In 50% saturated solutions of biphenyl, Carson et al. (21) reported the above products and significant concentrations of 3,4-dichlorobiphenyl and 4,4'-dichlorobiphenyl at low or neutral pH. Unfortunately, neither authors extended their study to true treatment plant conditions. In the case of naphthalene, Smith (17) identified the 1,2-dichloro- and 1,4-dichloro-isomers plus four other undefined products (isomers?) and an undefined tetrachloro-naphthalene. Similar products were observed in both 500 mgL⁻¹ suspensions and 10 mg L⁻¹ solutions.

Murphy et al. (18) and Usenik and Murphy (19) have grouped representative organics into groups which are "easily chlorinated", "chlorinated under vigorous conditions" and "not chlorinated" as follows:

TABLE 3

Ease of chlorination of selected organics

Easily Chlorinated	Chlorinated under Vigorous Conditions	Not Chlorinated
Phenols	Carboxylic Acids	Alcohols
Amines	Nitrobenzene	Methyl Ketone
Aldehydes	Benzonitrile	Urea
Ketones		Furan
Pyrrole		Thiophene

Compounds in the table were evaluated by measurement of chlorine uptake during aqueous chlorination rather than by identification of specific chlorinated product. Molar ratios of between 1:1 and 3.5 were used. The conclusion drawn supported those of Carlson *et al.*⁽⁸⁾ in that only those ring structures with electron activating substituents are likely to be chlorinated under conditions employed during wastewater disinfection. The presence of ammonia retarded the uptake of chlorine through the formation of less oxidative chloramines but given sufficient contact time, both aromatic structures and amino acids could be chlorinated in the presence of ammonia. With sufficient contact period, ring structures were both chlorinated and oxidized even by NH_2Cl but excess free chlorine was required for the oxidation of amino acids.

Reinhard et al. (22) have examined the possibility of chlorinated hydrocarbons originating from the chlorination of petroleum-derived compounds in aqueous solution. Specifically they studied the aqueous chlorination of aromatic fraction of diesel fuel over 1, 30 and 70 hours. Products were identified using gas-chromatographic-mass spectrometric analysis. Major products include 2-chloromesitylene and chloronaphthalene derivatives after one hour chlorination; chlorinated benzene derivatives, 2,5-dichloromesitylene and chlorinated indane derivatives after 30 hours and chlorinated benzene derivatives, 2-chloromesitylene and dichlorobenzene derivatives after 70 hours chlorination. In addition some other non-chlorinated oxidation products were generated.

The formation of halomethanes by the haloform reaction has been studied in detail by a number of researchers (10,14,23-25). The general consensus is that most compounds containing the *m*-dihydroxy aromatic moiety or low molecular weight methyl ketones will form haloforms upon chlorination. Since many natural organic compounds (or their degradation products) contain *m*-dihydroxy groupings, the formation of volatile halomethanes can be expected during chlorination of many natural waters and effluents. Compounds which have been shown to produce chloroform, bromodichloromethane, chlorodibromomethane, carbon tetrachloride, or bromoform, include humic acid (10,24,25) fulvic acid (10,24), tannic acid (24,25), glucose (25), vanillic acid (25), gallic acid (25), lignosulphonic acid (24) and amino acids (24). Of these precursors, humic and fulvic acids are the most abundant in effluent and hence contribute most to the total volatile organo-halogens. The brominated compounds arise from traces of bromide which become oxidized by chlorine to bromine and then via the haloform reaction to brominated or chlorobrominated methanes. The haloform reaction is strongly pH dependent: the total yield at pH 11 being approximately 3 times that at pH 7 (24).

While it has been shown that many organic compounds react with chlorine at near neutral pH and ambient temperature, a large number do not react or react very slowly under these conditions (26). However, when illuminated with ultraviolet light, many of these compounds which do not react with chlorine under strictly thermal conditions, will form chlorinated compounds. Oliver and Carey (27) showed that in the case of ethanol, the primary hydroxyl radical attack occurs at the α -carbon atom and hence acetic acid and acetaldehyde were the major products with only small amounts of 2-chloroethanol and 2-chloroacetaldehyde being formed. For n-butanol, however, only 34% of the hydroxyl radical attack was at the α -carbon and consequently more chlorinated products were formed, such as 2-chloro-n-butanol. The weight percent uptake of chlorine by aqueous solution of butanol is summarized in Table 4.

TABLE 4

Wt. % Organic Chlorine in Products of n-Butanol Solutions Containing 0.01 M Chlorine After 30 Min Irradiation at 350 nm

N-Butanol Concn . mol/L	Wt. % of organic chlorine		
	pH 4	pH 7	pH 10
0.001	11.1	7.2	0.4
0.005	13.2	9.0	0.3
0.010	16.5	15.4	0.3

Kobayashi and Okuda (26) list about 50 organic compounds and group them in terms of relative reactivity with chlorine in the presence and absence of UV irradiation. These photolysis reactions could be quite significant since many sewage treatment plants disinfect their effluents in open-air tanks exposed to sunlight.

From the above discussion of laboratory studies of the chlorination of organic compounds, it is evident that the potential exists for many chlorinated organic compounds to be formed during wastewater disinfection. It is also evident that in many instances the chemical mechanisms involved are little understood. The pH of the reaction plays a major role in the type and degree of reaction since many of the reactions are acid catalysed while the haloform reaction is base catalysed.

LABORATORY CHLORINATION OF EFFLUENTS AND COOLING WATERS

Many studies have been carried out in which secondary sewage treatment plant effluents have been chlorinated in the laboratory and the products examined. Although such experiments could be expected to represent 'real-life' chlorination, the conditions chosen by many of the authors are far in excess of those used in secondary treatment.

Glaze and Peyton (28) reported that chlorination of wastewater results in a decrease of the mean molecular weight of the organic constituents of almost exactly one-half. They also found a very similar reduction during raw-water chlorination (analogous to cooling water). The chlorination conditions used in these experiments was $740 \text{ mg } \ell^{-1}$

residual of chlorine and a contact time of two weeks at 5°C. It is, therefore, unlikely that sewage treatment plant conditions would produce anything like the 50% reduction reported here, although super-chlorination has been suggested for specific applications, such as the oxidative stabilization of wastewater and sludge by-products (29).

Both Glaze and Co-workers (13,30,40) and Jolley et al. (4,6,31,39) have reported on the formation of chlorinated organic compounds resulting from the disinfection of sewage effluents. While initial studies tended to identify chlorinated products in terms of the number of gas-chromatographic peaks obtained, more recent studies have identified the peaks either by matching GC retention times or by confirmation with mass spectrometry. Glaze & Henderson (13) obtained well in excess of 100 gas chromatogram peaks when they chlorinated a secondary effluent from Denton, Texas, with 1500 mg L⁻¹ chlorine. Many of the peaks they predicted were mixtures of two or more compounds and 36 of these peaks were not present before chlorination. Their results are summarized in Table 5:

These compounds range from chloroform to substituted aromatics, however, it is evident that not all of the chlorinated aromatics are derived from "activated" aromatics as predicted by Morris (20). Glaze & Henderson cite the chloroderivatives of benzene, toluene and benzyl alcohol as examples of "inactivated" aromatic moieties. Although these products resulted from the super-chlorination of effluents, some of them were the same as those generated by chlorination with 10 mg L⁻¹ chlorine (30).

TABLE 5

Chlorinated organics in wastewater effluent (Denton, Texas) identified by gas chromatography/mass spectrometry methods

Compound	Concentration (µg/L)
Chloroform	--
Dibromochloromethane	--
Dichlorobutane	27
3-chloro-2-methylbut-1-ene	285
Chlorocyclohexane	20
Chloroalkyl acetate	--
o-dichlorobenzene	10
tetrachloroacetone	11
p-dichlorobenzene	10
Chloroethylbenzene	21
Pentachloroacetone	30
Hexachloroacetone	30
Trichlorobenzene	--
Dichloroethylbenzene	20
Chlorocumene	--
N-methyl-trichloroaniline	10
Dichlorotoluene	--
Trichlorophenol	--
Chloro-a-methyl benzyl alcohol	--
Dichloromethoxytoluene	32
Trichloromethylstyrene	10
Trichloroethyl benzene	12
Dichloro-a-methyl benzyl alcohol	10
Dichloro-bis(ethoxy)benzene	30
Dichloro-a-methyl benzyl alcohol	--
Trichloro-a-methyl benzyl alcohol	25

TABLE 5 (continued)

Compound	Concentration (ug/L)
Tetrachlorophenol	30
Trichloro-a-methyl benzyl alcohol	50
Trichlorocumene	--
Tetrachloroethylstyrene	--
Trichlorodimethyloxybenzene	--
Tetrachloromethoxytoluene	40
Dichloroaniline derivative	13
Dichloroaromatic derivative	15
Dichloroacetate derivative	20
Trichlorophthalate derivative	--
Tetrachlorophthalate derivative	--

Jolley (6,31) also identified numerous specific chlorinated products during chlorination of effluents from the Oak Ridge Municipal Sewage treatment plant. These are shown in Table 6 together with an estimate of their concentration. These compounds were studied with the ^{36}Cl tracer, high resolution chromatographic technique developed by Jolley (33) in which the effluent is chlorinated with ^{36}Cl and then separated into molecular constituents by high-resolution, anion exchange chromatography and detection of the ^{36}Cl containing species by liquid scintillation counting.

TABLE 6

Tentative Identification and Concentration of Chlorine-Containing
Constituents in Chlorinated Effluents *

Identification	Concentration of Organic Compound ($\mu\text{g/liter}$)
5-Chlorouracil	4.3
5-Chlorouridine	1.7
8-Chlorocaffeine	1.7
6-Chloroguanine	0.9
8-Chloroxanthine	1.5
2-Chlorobenzoic acid	0.26
5-Chlorosalicylic acid	0.24
4-Chloromadnelic acid	1.1
2-Chlorophenol	1.7
4-Chlorophenylacetic acid	0.38
4-Chlorobenzoic acid	1.1
4-Chlorophenol	0.69
3-Chlorobenzoic acid	0.62
3-Chlorophenol	0.51
4-Chlororesorcinol	1.2
3-Chloro-4-hydroxy-benzoic acid	1.3
4-Chloro-3-methyl-phenol	1.5

* Chlorination Conditions: $3.2 \mu\text{g L}^{-1}$ chlorine as hypochlorite, 45 minute retention time.

Sievers et al.⁽³⁴⁾ have reported on the generation of volatile organic compounds by treatment of secondary sewage effluent with chlorine but note that there is often a marked difference between plant and laboratory chlorination. In some cases, plant chlorination resulted in increased levels of aromatic hydrocarbons (i.e., toluene, o-, m- and p-xylenes and styrene) whereas laboratory chlorination resulted in chlorotoluene and chloroxylene species.

The chlorination of sea water has been studied by Bean et al.⁽³⁵⁾ under conditions similar to those expected in cooling water treatment. Samples of chlorinated sea water were obtained from a continuous-flow system at the Battelle-Northwest Marine Research Laboratory. The sea water was relatively pristine (1 mg L⁻¹ organic carbon) and chlorine (as NaOCl) was added to 1-2 mg L⁻¹ active chlorine: retention time was two hours. The principal component found in all sea water samples was bromoform with lesser amounts of dibromochloromethane and dichlorobromomethane. Interestingly, chloroform was not present in significant concentrations in any of the samples. A list of all the products identified by GC-MS is given in Table 7.

TABLE 7

Components Identified in Chlorinated Sea Water

1. Bromoform	10. Dimethylnaphthalenes
2. Trimethylbenzene	11. Bromonaphthalene
3. Naphthalene	12. Bromomethylnaphthalenes
4. Bromotrimethylbenzene	13. Bromobiphenyls and Bromodimethylnaphthalenes
5. 2-Methylnaphthalene	14. Phenanthrene
6. 1-Methylnaphthalene	15. Bromotrimethylnaphthalene
7. Biphenyl	16. Phthalate Esters
8. Bromotetralin	17. Pyrene
9. Bromotetramethylbenzene	18. Bromoacetal

From this work the authors concluded that the concentrations of non-polar and presumably lipophilic halogenated components generated by the low-level chlorination of relatively pristine sea water appear to be very low (in the ng L^{-1} range), except for the haloforms. The latter were reported as high as $30 \mu\text{g L}^{-1}$.

The above discussion illustrates what a multitude of halogenated compounds could be formed during sewage effluent disinfection. It is also evident that, although these compounds are formed during laboratory chlorination, many of them are not formed at appreciable concentrations under treatment plant chlorination conditions. The next section will deal only with those compounds that have been identified in plant disinfected effluents or cooling waters.

PLANT CHLORINATION OF EFFLUENTS AND COOLING WATERS

Studies of the chlorinated organic component of effluents and cooling water which have undergone disinfection with chlorine under normal plant operating conditions are, unfortunately, far fewer than those involving laboratory chlorination ⁽³⁶⁾. Laboratory super-chlorination leads to much higher concentrations of halogen-containing species which, in turn, makes detailed analysis more feasible. Obviously some of the investigations discussed in the previous section in which the chlorination conditions were realistic ⁽³¹⁾, should be representative of real plant situations.

The presence of low volatility chloro-organics in cooling towers and once-through systems has been reported by Jolley et al. (37). Three cooling water systems were evaluated, the cooling tower at Oak Ridge Gaseous Diffusion Plant (ORGDP), the cooling tower of the High Flux Isotope Reactor (HFIR) at Oak Ridge, and the once-through cooling system at the Kingston Steam Generating Plant (KSGP). Both the ORGDP and the HFIR units operate under closed-cycle conditions with make-up water contributing only about 3% of the total flow. The chlorination conditions and the haloform production for these two systems are given in Table 8.

TABLE 8
Cooling Tower Parameters and Volatile Halogenated Organic Production for HFIR and ORGDP

	HFIR	ORGDP
Cooling Capacity, MWe	121	2060
Cooling Water		
Flow rate (gpd)	37×10^6	324×10^6
Makeup (gpd)	1.0×10^6	9.0×10^6
Chlorine, feed (ppm)	0.5	1.0
Chlorine, continuous (ppm)		0.3 - 0.5
Chlorine	2	
Feed or Makeup Water ^c		
Chloroform (ppb)	120 - 137	86
Bromodichloromethane (ppb)	5 - 15	7
Dibromochloromethane (ppb)	0.2 - 0.4	1
Bromoform (ppb)	0.1	ND
Tower Basin Water		
Chloroform (ppb)	1-38 ^a	12-31 ^b
Bromodichloromethane (ppb)	0.2-1.6	0.9-3
Dibromochloromethane (ppb)	ND	1
Bromoform (ppb)	ND	ND
Chloroform Production (lb/day)	~1.1	~6.5
Chloroform Loss (lb/day)	~0.8	~4.9
Bromodichloromethane Production	trace	trace
Dibromochloromethane Production	trace	trace
Bromoform Production	trace	trace

a Chlorinated weekly to 2 ppm calculated chlorine dose; b Chlorinated continuously to 0.5 ppm chlorine residual; ND Not detected; c Chlorinated

The KSGP uses 100,000 to 125,000 gpm cooling water through each of its 9 condensers. The water is chlorinated 30 minutes daily with 0.2 ppm free chlorine residual (0.5 ppm total residual). The condensers are chlorinated sequentially so that the discharged chlorinated coolant is diluted with unchlorinated water within the discharge canal. The concentration of haloforms in the discharge channel was 5 ppm as opposed to 1 ppm in the feed water. The authors estimated the annual production of chloroform at about 1 ton. They then extrapolated the results on a national basis and estimated a total production of 100-200 tons per year in the U.S. from all electric power stations.

Garrison et al.⁽⁴¹⁾ carried out a detailed analysis of many of the organic components in domestic wastewaters. The only reported effect of chlorination (in terms of generation of chloro-organics) was the formation of chlorocyclohexane, 1,1,1,2-tetrachloromethane, pentachloroethane, hexachloroethane, and five other unidentified compounds. No indication of the concentrations involved were included in the report and indeed the identification of some of the components was not confirmed.

The processing of textile wastes in a municipal sewage treatment plant was studied by Tincher⁽³⁸⁾. Textile processing facilities use and discharge a wide range of organic and inorganic compounds which come in contact with chlorine or chlorine-containing compounds either during waste treatment or in textile processing operations. Reported experiments suggest that chlorination of some species can occur but the only significant increase between influent and effluent was for the 2-monochloro isomer of biphenyl. The other isomers either did not change or decreased within the chlorination unit. Concentrations for the 2-monochloro isomer were $2.8 \mu\text{g L}^{-1}$ for the influent and $17.2 \mu\text{g L}^{-1}$ for the effluent.

If the same exercise is carried out using Glaze's superchlorination data in Table 5, the total chloro-organic discharge is 36X larger. This is an unrealistically high figure but it does illustrate the necessity of avoiding excess chlorination.

In the case of cooling water from thermal generating stations, Jolley's data for the haloform production at the Kingston Steam Generating Plant can be used to estimate the total loading of haloforms to the Great Lakes. Total discharge of cooling water from the four generating stations on the Canadian side of the Great Lakes is 1.7×10^6 gpm. These stations usually chlorinate to 0.5 ppm residual for a period of 30 minutes twice each day (approximately twice the dose at the KSGP). The total production of haloforms is hence about 3.5 tonnes/year. This is assuming that doubling the chlorine dose will result in a doubling of haloform concentrations. Obviously this figure does not include any non-volatile chloro-organics that might be produced. The corresponding U.S. contribution is ≈ 35 tonnes/year.

Combining the contributions from sewage treatment plants and cooling waters gives a total discharge of about 20 tonnes of chlorinated organics per year into the Great Lakes from the Canadian side and 118 tonnes/year from the U.S. It must be stressed that these figures are extremely rough estimates. It is unfortunate that there is no reliable data available on the levels of chlorinated organics discharged from sewage treatment plants or cooling waters. Industrial contributions of chloro-organics to the Great Lakes have been crudely estimated as 600 - 12,000 tonnes annually*. (500 - 10,000 tonnes/year from Canadian sources and 100-2,000 from United States sources). The major

* Based on estimates of total consumption of chlorine and 1% to 20% conversion to chloro-organics of medium molecular weight. The 1% to 20% conversion is for the pulp and paper industry, the exact value depending on the bleaching process employed and the efficiency of the operation.

GENERAL DISCUSSION AND CONCLUSIONS

It is apparent from the above three sections that, although a lot of information is available on the aqueous chlorination of organic compounds, including those likely to be present in sewage effluents, very little has been reported on the qualitative or quantitative determination of chloro-organics in actual effluents. Hence any assessment of environmental impact of chlorinated organic compounds arising from wastewater treatment plants or cooling water discharges is very difficult without some rather gross assumptions.

The total volume of secondary sewage effluent discharged into the Canadian side of the Great Lakes has been estimated at 476 mgd. If this figure is combined with the sum of the organo-chlorine concentrations reported by Jolley in Table 6, an estimate of the total expected loading to the Great Lakes can be calculated.

Total discharge	=	789×10^9 L/year
Total chloro-organic concentration	=	$20.7 \mu\text{g L}^{-1}$
∴ Annual loading	=	$20.7 \times 789 \cdot 10^3 = 16.33 \times 10^6$ g/yr or 16.3 tonnes

This is probably a conservative estimate since Jolley's chlorination conditions were only 32 mg L^{-1} chlorine with a 45 minute retention time and the compounds listed in Table 6 are the identified chloro-organics and not the total chloro-organics.

fraction of these compounds arise from wood pulp processing in the paper industry. Hence, the contribution of chloro-organics from sewage treatment plants and cooling waters appear to be insignificant relative to the large industrial discharges.

Very little is known concerning environmental and public health significance of chloro-organics in lakes and rivers, although it is well established that hydrophobic chlorinated compounds tend to biomagnify along the food chain. It is also not known for sure whether the compounds remain in solution or adsorb onto sediments, although one would expect much of the material to readily adsorb onto sediments or suspended particulates. Reliable analytical data are needed on the discharge and ultimate fate of chloro-organics together with an assessment of the toxicological effects to both aquatic and terrestrial organisms.

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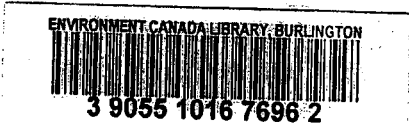
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