Environmental Health Sciences Center Task Force Review on Halogenated Organics in Drinking Water

by M. Deinzer,* F. Schaumburg,* and E. Klein†

The disinfection of drinking water by chlorination has in recent years come under closer scrutiny because of the potential hazards associated with the production of stable chlorinated organic chemicals. Organic chemical contaminants are common to all water supplies and it is now well-established that chlorinated by-products are obtained under conditions of disinfection, or during tertiary treatment of sewage whose products can ultimately find their way into drinking water supplies. Naturally occurring humic substances which are invariably present in drinking waters are probably the source of chloroform and other halogenated methanes, and chloroform has shown up in every water supply investigated thus far.

The Environmental Protection Agency is charged with the responsibility of assessing the public health effects resulting from the consumption of contaminated drinking water. It has specifically undertaken the task of determining whether organic contaminants or their chlorinated derivatives have a special impact, and if so, what alternatives there are to protect the consumer against bacterial and viral diseases that are transmitted through infected drinking waters. The impetus to look at these chemicals is not entirely without some prima facie evidence of potential trouble. Epidemiological studies suggested a higher incidence of cancer along the lower Mississippi River where the contamination from organic chemicals is particularly high. The conclusions from these studies have, to be sure, not gone unchallenged.

The task of assessing the effects of chemicals in the drinking water is a difficult one. It includes many variables, including differences in water supplies and the temporal relationship between contamination and consumption of the finished product. It must also take into account the relative importance of the effects from these chemicals in comparison to those from occupational exposure, ingestion of contaminated foods, inhalation of polluted air, and many others. The susceptibility of different age, genetic, and ethnic groups within the population must also be carefully considered. The present review discusses: the reasons for disinfection; the general occurrence of chlorinated organics in drinking water; the chemistry in the synthesis of chlorinated organics under aqueous conditions; and alternatives to chlorine for disinfection.

Introduction

In the United States, the majority of municipal water systems depend on ground water supplies, usually wells. These systems are more frequently found in smaller cities and serve less than 50% of the population. As a rule, ground waters contain relatively low levels of organic material and yield acceptable drinking water. Surface waters, usually rivers and lakes, are the most important source of drinking water, serving more than 150 million people in the United States (*1*).

* Environmental Health Sciences Center, Oregon State University, Corvallis, Oregon 97331.

† Gulf South Research Institute, New Orleans, Louisiana 70186.

Rivers are by far the most contaminated water sources. They contain viruses, bacteria, dissolved inorganic material, and large amounts of organic compounds. The organic contaminants usually originate from industrial and municipal discharges and the runoff from agriculture and urban areas. Large numbers of organic chemicals found in these waters can be traced to effluents from the manufacture of paper, plastics, explosives, synthetic fibers, petrochemicals, wood preservatives, synthetic rubbers, and others. Pesticides and fertilizers arise primarily from agricultural runoff. The bulk of the total organic carbon, however, probably falls in the category of humic substances, which arise from decaying vegetation (*1*) and are present in practically every water supply. Modern disinfection

methods have added pollutants to the natural and man-made organic contaminants that are already in the water.

Since early in the twentieth century, chlorination has been the method of choice for disinfection of water and wastewater. In recent years, several researchers (2–9) have found evidence that chlorine added as a disinfectant reacts with organic compounds in the water, producing very low concentrations of known and suspected carcinogens. Harris (10) attempted to show an epidemiologic link between the presence of such halogenated organic compounds in drinking water and the incidence of cancer, but several critics (11) feel he was unsuccessful. Nevertheless, the degree of danger presented by continual intake of low concentrations of these compounds is unknown. Because of this uncertainty, the consequences of chlorination deserve a careful scrutiny by everyone responsible for public health. The following is a review of the reasons for chlorination, the occurrence of chlorinated hydrocarbons, and the chemistry for their formation in water supplies.

The Need for Disinfection

Bacterial Diseases

The possibility of disease transfer by water was emphasized to Oregonians in 1975 when a clogged sewer line at Crater Lake National Park contaminated the water supply. Several hundred persons contracted enteritis as a result. Water can be the transferring vector for several bacterial diseases including typhoid, cholera, and paratyphoid (12). The infectious bacteria likely to be present in water are intestinal, arising from people with the active disease or from carriers. Pathogenic bacteria are usually highly specialized and cannot live well outside the host so that once discharged to sewers or rivers they begin to die off. Die-off, however, is slow enough for some organisms that it is possible for a person drinking water from a river polluted by sewage to ingest viable pathogens and become ill.

A relatively simple test, known as the coliform test, is used to determine the likely presence of pathogenic bacteria in the water. These bacteria are not generally pathogens, but the absence of any coliform bacteria is strong evidence that few, if any, pathogenic bacteria are present. A large coliform count, on the other hand, means that pathogens are very possibly present. Historically, the coliform count has been the principal test of drinking water quality.

Viral Disease

Recently there has been considerable concern about virus diseases in drinking water (13–25). It has been suggested that a variety of pathogenic viruses, including the causative agents for such well-known diseases as poliomyelitis and hepatitis, may be transferred via water. However, in very few cases of viral diseases has water been directly implicated as the transferring vector (21) but this is probably due to the extreme difficulty of detecting viruses in water. There is no standard test to detect viral pathogens in water. Virus concentrations in water are normally so low that it is necessary to concentrate them in some way. In addition, viruses can only be grown in living cells, which requires highly specialized techniques and a long time. In spite of the very limited amount of viral material, very small amounts of virus may be sufficient to infect a human (21), because the particles replicate themselves in cells. It must be remembered that the low concentrations do not confer protection because virus particles apparently survive in water over long periods and are not subject to the same kind of "die-off" effects that help control bacteria.

Bacterial disinfection schemes as generally used are not sufficiently effective against viruses to assure public health protection. In the past, lacking clear evidence of danger of viral disease transfer, it has not been felt necessary to design disinfection systems for virus deactivation. It seems likely that the potential danger of waterborne virus disease and the unknown consequences of halogenated organic compounds in water will lead to much broader water purification concepts in the future.

Higher Organisms

A few higher organisms including some protozoans can cause human illness and can be communicated by water. They do not usually present as great a problem as bacteria and viruses because their concentrations are much lower and their larger size makes them more easily removed during treatment.

Current Disinfection Practice

General

There are three major pathways by which waterborne diseases may be contracted. Pathogens may be ingested in drinking water, they may penetrate mucous membranes during contact with the water such as swimming, and they may be eaten

with shellfish or other organisms from polluted waters. There are two man-made lines of defense to prevent intake of pathogens in drinking water: (1) wastewater or sewage treatment; and (2) public water supply treatment. Dilution and die-off in the natural waterway also provide some protection. Pathogen removal during sewage treatment, prevention of sewage access to waterways, and dilution and die-off are the only ways of insuring the safety of water contact sports and eating marine organisms.

Wastewater Disinfection

Municipal wastewater is usually treated by removing settleable solids (primary treatment), biological removal of dissolved organics (secondary treatment), and disinfection. Physical-chemical treatment for removal of suspended solids and final effluent polishing may also be used. Primary and secondary treatment removes 93 to 99% of the bacteria (13) and 90 to 99.9% of the viruses (23) in domestic wastewater, but large concentrations of bacteria still remain. Physical-chemical treatment processes such as coagulation, filtration, and carbon adsorption remove various amounts of pathogens (15, 18, 23, 26). Coagulation followed by settling or filtration has been shown to be one of the most effective means of virus removal; it is more effective than chlorination.

The principal means of bacterial deactivation is disinfection. In almost all waste treatment plants in the United States disinfection depends upon chlorination (27). By varying the chlorine dose and contact time, the coliform concentration can be reduced to almost any desired level. In domestic sewage treatment plants, chlorination usually reduces the bacteria concentration 90 to 99% with a resulting coliform count of 100 to 10,000 per 100 ml (20).

Chlorination of wastewater involves the mixing of some form of chlorine with the wastewater followed by retention of the wastewater in a contact basin for a set period of time, usually 15 min to 1 hr, before discharge. Enough chlorine is added to maintain a certain residual chlorine concentration at the end of the contact time. Chlorine may be added in the gaseous form or else sodium or calcium hypochlorite, may be added. In either case hypochlorous acid is formed in the water. All three methods achieve the same disinfection and side reactions. Sodium hypochlorite is safer to handle and store, but chlorine gas is cheaper.

The actual chlorine disinfection mechanism is poorly understood. It is believed that disinfection does not require oxidative destruction of cells but results from some other reaction such as enzyme inhibition (28). A small portion of the chlorine added to water or wastewater actually reacts with bacteria.

The amount of chlorine used to disinfect wastewater is usually determined by measuring the total chlorine residual after a certain contact level. The total chlorine residual includes hypochlorous acid, hypochlorite ion, and chloramines. It can be measured by several methods. Due to its simplicity, the orthotolidine test is used in most wastewater treatment plants. Unfortunately, the orthotolidine is also the least accurate of the common residual chlorine analysis methods (29–32). Some of the more accurate methods include amperometric titration, the iodometric (starch-iodide) method, and the DPD or Palin's method (30–33).

Required residual chlorine concentrations in wastewater run as high as 1 mg/l. after 1 hr contact time. To insure that their residuals stay above the required level, many plant operators overchlorinate and have total chlorine residuals up to 3 or 4 mg/l. (32). Several researchers (29, 31, 34, 35) have reported that these chlorinated effluents are highly toxic to fish. The extent of formation of chlorinated organic compounds through overchlorination has not been established. Brungs (29) suggested a total chlorine residual concentration of 0.002 mg/l. as a maximum allowable continuous chlorine concentration that will not be toxic to the more sensitive aquatic organisms, trout and salmon.

Besides disinfection, chlorine has other less important uses in wastewater treatment. It can be added ahead of primary treatment or anywhere in the sewer system for odor control. It has been added to biological treatment processes to prevent bulking; i.e., to promote the separation of biological solids from the wastewater. It has been used to oxidize the sources of biochemical oxygen demand remaining after secondary treatment. Breakpoint chlorination can be used to remove ammonia.

Chlorine is used in wastewater treatment because it is effective, relatively easy to use, and inexpensive. Its use, however, presents toxicity problems to fish. In addition there is a newly recognized potential for long-term carcinogenic effects from the chlorinated organics formed during the chlorination process. It must be born in mind, however, that there may well be acute toxicity problems associated with the organic compounds in water as well, and in this respect, chlorination may be beneficial by degrading them into smaller molecules that are nontoxic or volatile or subject to attack by microorganisms. Therefore, assessments of hazards associated with organics in water cannot be limited to the chlorinated organics.

Water Supply Disinfection

The last line of defense against waterborne disease is the water treatment plant. Treatment of the public water supply has the dual goals of making the water safe and pleasant to drink. Making the water pleasant to drink requires the removal of excessive taste, odor, turbidity, and color. Making water safe to drink largely depends upon disinfection.

Water treatment processes vary widely, but the most common ones consist of some form of suspended solids removal such as coagulation, clarification, and/or filtration followed by chlorination. Sometimes chlorine is also added ahead of the suspended solids removal operations. Suspended solids removal renders the water more aesthetically appealing, removes many potentially harmful substances, and improves the effectiveness of chlorination. Chlorine is ineffective in water with high suspended solid concentrations because some bacteria and viruses are embedded in the particles and are thereby protected.

Chlorination of water supplies varies from chlorination of wastewater in that the drinking water has lower concentration of organic and nitrogenous compounds; the disinfection must be more complete, and regrowth of pathogens in the supply system must be prevented. At lower concentrations of organics and nitrogen compounds the chlorine demand to achieve a given residual in the water is lower. However, because the water must be safe to drink the coliform concentrations must be essentially zero and there must be a margin of safety consisting of a large chlorine residual to insure that few, if any, pathogens survive the treatment process. Virus removal is more important in drinking water than in wastewater treatment and requires much larger chlorine residuals than bacterial disinfection. It also requires better control of mixing and pH to insure that the most effective chlorine species, hypochlorous acid, predominates and reaches all of the water quickly (20, 24).

Once the water leaves the treatment plant, it is subject to possible contamination from other sources or regrowth of the few pathogens left after disinfection. To prevent these effects a chlorine residual is maintained throughout the distribution system. Free chlorine rapidly degrades, necessitating very heavy chlorination to maintain a residual in large distribution systems. Some water treatment plants intentionally add ammonia to form chloramines, which, though less effective disinfectants, will last much longer in a distribution system (36).

Occurrence of Chlorinated Hydrocarbons

The identification of C_1 and C_2 halocarbons in the finished drinking water of several cities in the U. S. poses a serious problem for agencies producing domestic water supplies. Studies on the origin of the halocarbons have identified the universally used chlorination procedure as a major source of the C_1 halocarbons. Since chlorination is so widely used to protect against waterborne transmission of infectious diseases, it is necessary to identify those process steps which intensify the halocarbon concentrations. The source of halocarbons cannot be restricted to the chlorination steps alone, since source waters in studies by the Surveillance and Analysis Branch, Lower Mississippi River Branch, U. S. Environmental Protection Agency (3), and other studies (37–48) have yielded a spectrum of halogenated hydrocarbons (Table 1). Thus one must consider the origin of halocarbons in the finished waters to be the result of complex variables which include halocarbon content in the source water, organics in the source waters subject to reaction with chlorine, and the process steps which use chlorine for the reduction of color, and as a bacteriocide.

The main sources of chloroorganics in drinking water have been ascribed to (49): (a) nonpoint sources such as airborne pesticides and solvents; (b) industrial effluents; (c) products from industrial wastewater chlorination; and (d) chlorination of natural organic matter in the source water. Many of the chloroorganics from the first three sources that have been identified in drinking water are shown in Table 1. The C_1 halocarbons generally considered to be derived from the latter sources are shown in Table 4.

Industrial and Municipal Sources of Chlorinated Organics

The recently published book by Keith (50) on the analysis of organic pollutants in water, presents a comprehensive survey of not only the identity of the compounds in drinking and source waters, but on the various aspects of sampling and analyses, as well. This book covers both the general spectrum of organic chemicals in water and some of the specifics with regard to the chlorinated compounds.

Many industrial processes generate chlorinated organic compounds. Chlorine is heavily used in the pulp and paper industry as a bleach. Power plants chlorinate cooling water to prevent the growth of microorganisms in cooling systems. Chlorine is used as a reagent by the chemical industry in the synthesis of an immense variety of industrial

Table 1. Chloroorganics found in the U. S. drinking water.

Compound	Probable use, source	Concentration range, μg/l.	Reference
Acetylene chloride			*37, 48*
Acetylene dichloride	Solvent, fermentation retardant		*3, 34, 48*
Aldrin	Pesticide		*44*
Bladex	Pesticide		*39*
Bromochlorobenzene			*39, 43*
Bromotrichloroethane			*48*
Carbon tetrachloride	Industrial, cleaning	0-5	*3, 39, 40, 48*
Chlordane	Pesticide		*39, 44*
Chlordene	Pesticide		*39*
Chlorobenzene	Manufacture of phenol, aniline	1-<5.0	*3, 39, 43*
Chloroethane	Manufacture of tetraethyllead		*48*
1,2-Bischloroethoxyethane	Refrigerant, solvent		*37, 39*
Chloroethoxy ether			*37, 39*
Bis-2-chloroethyl ether	Ethylene glycol manufacture intermediate	0.07–0.42	*3, 37, 38, 39, 43*
2-Chloroethyl methyl ether			*39*
Chlorohydroxybenzophenone			*38, 39*
Bis(2-chloroisopropyl)ether	Propylene glycol manufacture intermediate	0.18–1.58	*3, 38, 39*
Chloromethane	Refrigerant		*39, 48*
Chloromethyl ethyl ether			*3, 39, 43*
Chloromethyl ether			*39*
Chloromethylethyl ether			*39*
m-Chloronitrobenzene			*3, 39, 43*
2-Chloropropane			*48*
1-Chloropropene		<1.0	*6, 39*
Chloropyridine			*43*
3-Chloropyridine			*3, 39*
Chlorotoluene	Dyestuff intermediate, solvent, chemistry		*48*
Cyanogen chloride	Chemical synthesis		*39, 48*
DDE	Pesticide		*39, 44*
DDT	Pesticide	0.04	*39, 44, 45*
Dibromochloromethane		1.1 < 5	*39*
Dibromodichloroethane		0.33	*39*
Dichlorobenzene	Insecticide		*3, 43*
1,2-Dichlorobenzene	Solvent, insecticide, manufacture of dyes, other industrial uses		
1,3-Dichlorobenzene		0.01	*38, 39, 48*
1,4-Dichlorobenzene	Insecticide	1.0	*39, 48*
Dichlorobiphenyl	PCB component, dielectric fluid, plasticizer		*42*
Dichlorodifluoroethane	Refrigerant, propellant		*39*
1,2-Dichloroethane	Solvent	0.8	*3, 39, 48*
1,1-Dichloroethane	Extractant for heat-sensitive substances solvent		*48*
1,1-Dichloroethane (vinylidine chloride)	Food packaging		*48*
Cis-1,2-dichloroethene			*48*
Trans-1,2-dichloroethene			*48*
Dichloroethyl ether	Finish remover		*43*
Dichloromethane	Solvent, degreasing, cleaning	<5	*39, 48*
Dichlorofluoromethane			*48*
1,1-Dichloro-2-hexanone	Aerosol propellants	<1	*39*
Dichloroiodomethane			*48*
Dichloronitromethane			*48*
2-4-Dichlorophenol		36	*37, 39*
1,3-Dichloro-2-propanol			*42*
Dichloropropane	Solvent, cleaning fluid	<1	*6, 39, 40*
1,3-Dichloropropene	Soil fumigant	<1	*6, 39, 40*
Dieldrin	Pesticide	0.07–8.0	*39, 44*
Endrin	Pesticide	0.004–0.008	*39, 44*

Table 1. continued

Compound	Probable use, source	Concentration range, μg/l.	Reference
Heptachlor	Pesticide		39, 44
Heptachlor epoxide	Pesticide		39, 44
1,2,3,4,5,7,7-Heptachloronorbornene		0.06	39
Hexachlorobenzene	Organic synthesis		38, 39
Hexachlorobenzene	PCB component—dielectric fluid, plasticizer		42
Hexachloro-1,3-butadiene	Pesticide, solvent	0.06	15, 39
Hexachlorocyclohexane	Insecticide		39, 42, 44
Hexachloroethane	Explosives, solvent rubber vulcanizing accelerator	0.07	38, 39
Hexachlorophene	Germicidal soaps	0.01	39, 47
(2- or 1-Naphthyl) dichloromethane			40
Nitrotrichloromethane (chloropicrin)	Fungicide, nematicide		48
Octyl chloride			39
Pentachlorobiphenyl	From PCB mixture plasticizer, dielectric fluid		39, 42
Pentachlorophenol	Preservation of wood, starches, glues, herbicide (slime and algae control)	0.06	39, 47
1,1,3,3,3-Pentachloropropane			42
Pentachloropentene (isomers)			42
Pentachlorophenyl methyl ether			39
1,1,3,3-Tetrachloroacetone			39, 41
Tetrachloropropanes (isomers)			42
Tetrachlorobiphenyl	From PCB mixtures plasticizer, dielectric fluid		16, 39, 41, 42
1,1,1,2-Tetrachloroethane		0.11	39
Tetrachloroethylene	Dry cleaning, degreasing	0.41 < 5.0	6, 38, 39, 40, 43
Trichlorobiphenyl	From PCB mixture plasticizer, dielectric fluid		42
1,1,1-Trichloroacetone			42, 46
1,1,1-Trichloroethane	Cleaning cold metals and plastics		48
1,1,2-Trichloroethane	Solvent		39
Trichloroethane			40, 43
(1,1,2) Trichloroethylene	Industrial solvent extraction, organic chemicals intermediate		3, 39, 48
Trichlorofluoromethane	Refrigeration, aerosol propellant		39
Trichloroheptafluorobutane			42
Trichloropentafluoropropane			42
1,1,2-Trichloro-1,2,2-trifluoroethane			42
2,4,6-Trichlorophenol	Fungicide, bactericide preservative		39, 41
Trichloropropanes (isomers)			42
Vinyl chloride	Plastics industry, refrigerant, organic synthesis		48

chemicals. Many pesticides are chlorinated organics which after their use on a field find their way into streams and rivers. Because coliforms have been found in some industrial wastewaters (51), regulatory agencies may require chlorination of these waters as a precaution even though these are not related to human contamination.

Table 2 is an abbreviated list of the major chloroorganics released into the environment through manufacturing. United States production and the estimated release rate clearly show that introduction of chloroorganics into the environment from this source is enormous (52).

At least 17 chloroorganic compounds of the 25 listed in Table 2 have been identified in drinking water. The priorities for these compounds were established on the basis of the following criteria (52): (a) production and industrial waste; (b) use pattern; (c) persistence; (d) dispersion tendency; (e) conversion under biotic and abiotic conditions; and (f) biological consequences. This list may be incomplete for establishing a background. For example, the relatively soluble pentachlorophenol, with a national output of 50 million pounds per year (53), is not shown and PCP has been identified in drinking waters (Table 1).

Table 2. Major chloroorganics released into the environment[a]

	Present in drinking water?	Priority environmental impact	Rank as human health hazard	U.S. production, lb × 10⁶	Estimated release rate, lb × 10⁶
Allyl chloride		51	8	295.0	4.4
Carbon tetrachloride	X	4	5	234.7	38.7
Chlorinated paraffins	X	25	48	48.8	50.3
Bis(2-chloroethyl) and bis(2-chloropropyl) ethers	X	42	33	N.A.	N.A.
Chloroform	X	5	7	234.7	38.7
Chloroprene		62	11	402.0	6.0
o-Dichlorobenzene	X	45	66	62.4	27.1
p-Dichlorobenzene	X	38	60	77.3	70.8
Dichlorobenzidine		35	17	4.6	0.01
Dichlorodifluoromethane		1	32	439.2	445.8
1,3-Dichloropropene 1,2-Dichloropropane }mixture	X	10	43	60.0	60.6
Ethyl chloride	X	34	61	575.5	34.6
Ethylene dichloride	X	23	40	8,600.0	458.0
Hexachlorobenzene	X	6	25	1.3	1.32
Hexachlorobutadiene	X	8	23	8.0	7.3
Methyl chloride	X	12	45	453.5	16.7
Methylene chloride	X	33	50	471.3	366.9
Perchloroethylene	X	44	14	734.2	562.0
Polyhalogenated biphenyls	X	3	9	30.0	30.3
Poly(vinyl chloride)		40	67	4,258.0	4,238.8
1,1,1-Trichloroethane		24	21	440.7	284.5
Trichloroethylene	X	50	37	426.7	429.5
Trichlorofluoromethane		2	28	299.6	274.1
Vinyl chloride	X	48	20	5,088.5	146.5
Vinylidine chloride		71	11	402.0	6.0

[a] Data of Stephenson (52).

Tertiary treatment of sewage is a rich source of stable chloroorganic compounds (Table 3). Some of these derivatives are probably of industrial origin, while many others are formed in the treatment process. Jolley (8) has demonstrated the importance of chloroorganic synthesis in the chlorination of sewage. A total of 17 stable chlorocarbon compounds, principally chlorinated aromatics and some chlorinated nucleotides was reported. One of the chief difficulties in the identification of these compounds is their high solubility in water. Chloronucleic acids; chloroguanine, chlorocaffeine, etc., which were formed under Jolley's conditions, have not been identified in drinking water because the analytical methods (GC-MS) are specific for compounds which are relatively insoluble in water.

The work of Glaze and co-workers (54) illustrates the importance of the chlorination of typical industrial organic complexes and solvents in sewage. Several of these chlorinated derivatives; i.e.,

chloroform, dibromochloromethane, o-dichlorobenzene, p-dichlorobenzene, and 1,1,3,3-tetrachloroacetone have been identified in drinking water (Tables 1 and 4).

Chlorine also reacts by a variety of mechanisms with the other organic compounds. Most of these are oxidation-reduction type reactions with the chlorine reduced to chloride salts. Some of the chlorine reacts to produce stable chlorinated organics (8). The concentration of dissolved and suspended organic material in biologically treated effluents is commonly less than 100 mg/l. (55). It is common to add about 10 mg/l. chlorine to wastewater so both reactants are at very low concentrations. The concentrations of halogenated organics that result are on the order of a few micrograms per liter (8). But sewage water can or does eventually enter the source for finished waters, and it is important to consider the chlorinated products that arise from this source.

Table 3. Chloroorganics found in sewage.

Compound	Reaction type	Source	Reference
Chloroalkyl acetate			(54)[a]
2-Chlorobenzoic acid	Electrophilic aromatic substitution	Intermediate in manufacture of fungicides and dyes preservative for glues, paints	(8)[b]
3-Chlorobenzoic acid	Electrophilic aromatic substitution		(8)
4-Chlorobenzoic acid	Electrophilic aromatic substitution		(8)
8-Chlorocaffeine	(N) substitution		(8)
Chlorocumene	Electrophilic aromatic substitution		(54)
Chlorocyclohexane	Substitution		(54)
Chloroethylbenzene	Electrophilic aromatic substitution		(54)
Chloroform[c]	Substitution	Solvent, fire extinguishers, rubber industry	(54)
6-Chloroguanine	Substitution		(8)
3-Chloro-4-hydroxybenzoic acid	Electrophilic aromatic substitution		(8)
4-Chloromandelic acid			(8)
Chloro-α-methylbenzylalcohol			(54)
3-Chloro-2-methyl-but-l-ene			(54)
4-Chloro-3-methyl-phenol	Electrophilic aromatic substitution	Antiseptic, disinfectant	(8)
2-Chlorophenol	Electrophilic aromatic substitution		(8)
3-Chlorophenol	Electrophilic aromatic substitution		(8)
4-Chlorophenol	Electrophilic aromatic substitution		(8)
4-Chlorophenylacetic acid	Electrophilic aromatic substitution		(8)
4-Chlororesorcinol	Electrophilic aromatic substitution		(8)
5-Chlorosalicylic acid			(8)
5-Chlorouracil	(N) substitution		(8)
5-Chlorouridine	(N) substitution		(8)
8-Chloroxanthine	(N) substitution		(8)
Dibromochloromethane[c]	Substitution (haloform)		(54)
Dichloroacetate derivative			(54)
Dichloroaniline derivative			(54)
Dichloroaromatic derivative			(54)
o-Dichlorobenzene[c]	Electrophilic aromatic substitution	Solvent, insecticide, manufacture of dyes, metal polishes, etc.	(54)
p-Dichlorobenzene[c]	Electrophilic aromatic substitution	Kills moths, roaches and others; preserves furs, woolen cloths, rugs	(54)
Dichlorobutane	Substitution		(54)
Dichlorobis(ethoxy)benzene			(54)
Dichloroethylbenzene			(54)
Dichloromethoxytoluene			(54)
Dichloro-α-methylbenzyl alcohol			(54)
Dichlorotoluene	Electrophilic aromatic substitution	Manufacture of benzylalde-hyde and cinnamic acid	(54)
Hexachloroacetone	Substitution		(54)
N-Methyltrichloroaniline			(54)
Pentachloroacetone	Substitution		(54)
Tetrachloroacetone[c]	Free radical(?) substitution		(54)
Tetrachloroethylstyrene			(54)
Tetrachloromethoxytoluene	Electrophilic aromatic substitution		(54)
Tetrachlorophenol	Electrophilic aromatic substitution		(54)
Tetrachlorophthalate derivative			(54)
Trichlorobenzene	Electrophilic aromatic substitution		(54)
Trichlorocumene			(54)
Trichlordimethoxybenzene	Electrophilic aromatic substitution		(54)
Trichloroethylbenzene	Electrophilic aromatic substitution		(54)
Trichloro-N-methylanisole			(54)
Trichloro-α-methylbenzyl alcohol			(54)
Trichlorophenol	Electrophilic aromatic substitution	2,4,5-Fungicide, bactericide 2,4,6-Fungicide, bactericide, preservative	(54)
Trichlorophthalate derivative			(54)
Trichloromethylstyrene			(54)

[a] Data of Glaze et al. (54). Sewage treatment plant, Denton, Texas, Conditions: superchlorination, 2,000 mg/l. chlorine.

[b] Data of Jolley, (8). Conditions: primary and secondary treatment: tagged with ^{36}Cl 2.4-6.0 mg/l. chlorine. [c] Identified in drinking water as well (Tables 1 and 2).

Table 4. Volatile halogenated organic compounds determined in 80 cities across the United States.

Compound	Concentration range, $\mu g/l$	References
Bromodichloromethane	0–116	2, 3, 5, 38, 40
Bromoform	0–92	2, 3, 38
Chloroform	<0.1–311	2, 3, 5, 40
Chlorodibromomethane	0–100	2, 5, 38, 40
1,2-Dichloroethane	0–6	2

Water Disinfection as a Source of Halocarbons

One of the earliest reports showing the presence of trihalomethanes in drinking water was that of Kleopfer and Fairless (38). Using the older CCE; i.e., carbon-chloroform extractable, method to recover nonpolar organic chemicals from a municipal drinking water supply on the Ohio River, these investigators found bromodichloromethane, $CHBrCl_2$, dibromochloromethane, $CHBr_2Cl$, and bromoform, $CHBr_3$. Several other chlorinated hydrocarbons, including bis(2-chloroethyl) ether, and bis(2-chloroisopropyl) ether, were also present. These two compounds were shown to be present in the raw intake water prior to chlorination and were believed to be of industrial origin further upstream.

Several other early studies showed chlorinated organic compounds in municipal drinking water supplies that could conceivably have arisen from the treatment process. For example, chlorinated phenols, and 1,1,3,3-tetrachloroacetone was reported in Cincinnati's drinking water (41). Chlorinated hydrocarbons, including chloroform were also reported in drinking water in Europe (56, 57), although as frequently happened in earlier studies, investigators were skeptical of their own results and in this case chloroform (57) was considered to be a possible contaminant from the laboratory.

The distinction between chloroorganics originating in the source waters from upstream effluents and from reactions between chlorine and organic compounds during disinfection was not generally accepted or even recognized until very recently, despite the fact that soon after chlorine disinfection became common practice in 1922, it was suggested that chlorine does react with organic matter to produce chloroorganics (58). It wasn't until Jolley's definitive studies reported in 1973 (8) on the chlorination of sewage using radioactive chlorine, that the formation of stable chloroorganics under these conditions was generally accepted. Several additional studies involving tertiary treatment of sewage have confirmed these findings.

Rook in 1974 (9) and more recently (59) reported the results of his studies which indicated that chloroform and a series of C_1 halocarbons were formed in Rotterdam as a result of chlorine addition to the source water. He was able to demonstrate that the chloroform did not originate as a contaminant in the chlorine, and that reactions between chlorine and naturally-occurring solutes such as humic or fulvic acids in the water led to all of the variants of the haloform reaction. Rook's results also indicated that all of the halocarbons were C_1 derivatives. The significance of this conclusion is that all higher homologs must have originated with the source water. It is rather surprising that the yield of halocarbons was only 0.4%, based on the total organic carbon content of the source water.

However, the analyses in these studies were restricted to headspace volumes, which would preclude the identification of other chlorinated hydrocarbons that were highly water soluble and/or had low volatilities at ambient temperature. It has been known for some time, for example, that phenolics will chlorinate in water under the conditions in a water treatment plant (60). One can thus speculate that other organics having low volatilities and perhaps molecular weights high enough to escape analysis by head-space methods could have been present in the water supply. Unfortunately, there are no methods available for the identification of trace levels of organically linked halogens, in the presence of a large excess of ionic chloride.

A study by Bellar et al. (5) in the same year supported the conclusions of Rook. Bellar demonstrated that chloroform, bromoform, and the mixed chlorobromoforms were formed during the chlorination of water. Bellar attributed the products to the haloform reaction between chlorine and ethanol (found in the Ohio River source water used), but this reaction sequence has not been well established.

In June of 1975 (48) the EPA released a prepublication copy of some results from their National Organics Reconnaissance Survey (NORS). This part of the study was concerned with the occurrence of volatile organics in drinking water from five cities, preselected to represent a cross section of the nation's drinking water supplies. These supplies were located in: Miami, Florida, which is representative of ground water containing natural organics such as humic acids; Seattle, Washington, a surface water supply containing natural organics; Ottumwa, Iowa, a surface water with agricultural wastes; Philadelphia, Pennsylvania, a surface water containing municipal wastes; and Cincinnati, Ohio, a surface water containing industrial wastes. This excellent study, which was carried out with great pains to

insure qualitative accuracy, and the detection of low levels of pollutants provides the most convincing evidence of the degree to which the nation's drinking waters are contaminated, not only with a general spectrum of organics, but with a broad range of chloroorganics as well. A total of 72 volatile organics were identified at one or more of the five locations.

Five of the compounds were halogenated aromatics and 33 were halogenated aliphatics. The sum of these two classes of compounds represented 53% of the total. The chlorinated organics that were common to all five cities were chloroform, bromodichloromethane, dibromochloromethane, chloromethane, and dichloromethane. The presence of halomethanes has become characteristic of chlorinated drinking water, and in a separate study (2) 80 municipal waters across the nation were analyzed for chloroform, bromodichloromethane, dibromochloromethane, bromoform, and carbon tetrachloride (Table 4). 1,2-Dichloroethane was also measured. Chloroform was found in all of them, with a concentration range of <0.1–311 ppb. Even the cleanest waters, which contained <0.05 ppm total organic carbon (TOC), probably the detection limit for the TOC analyzer, contained a detectable amount of chloroform. Bromodichloromethane was found in all but one of the supplies, and dibromochloromethane was found in all but eight of them. The other four compounds were found in fewer drinking waters, although all of them were detected in a least several of the samples.

These results were later criticized by Fritz (56), who noted that chloroform, bromodichloromethane, chlorodibromomethane, and bromoform increased in concentration after sampling and during storage for several days. A method for stabilizing the concentration of halomethanes by the addition of ascorbic acid to the water sample, was subsequently reported (57). But EPA scientists issued a statement in the form of a letter to the editor of Chemical and Engineering News (63) acknowledging the possibility that concentrations do increase on storage, but defended the protocol for the Nationwide Organics Reconnaissance Survey (NORS) (64), on the basis that a sample more representative of the actual water consumed by the public would be obtained by allowing the concentration of halomethanes to build up under storage for several days.

The source of the bromine to make the brominated compounds is not entirely clear at this point. Rook (9) investigated the possibility that chlorine gas used in his experiments contained either bromine or impurities of brominated methane. He found neither. It is possible that lead bromide from auto emissions, which is fairly soluble and may subsequently be washed into surface waters (65), is a source of bromide ion.

The relationship between volatile organic compounds, i.e., the halomethanes, and the total organic carbon content in the water is demonstrated by the EPA data from the survey of 80 cities. The relationship is weak, but definitely present. A regression analysis gave the relationship:

$$\log y = 1.14 + 0.21x$$

where y is the nonvolatile total organic carbon in (mg/l.) and x, the volatile halomethane constituents (in μg/l.). The halomethane content is the sum of chloroform, bromodichloromethane, dibromochloromethane, bromoform, 1,2-dichloroethane, and carbon tetrachloride. The correlation coefficient was 0.62 and the square of this value is 0.39, which means that 39% of the variation in the concentration of halomethanes is explained on the basis of the organic carbon content. A similar relationship has been developed by Symons et al. (64). The data in this treatment were divided into cells with a 0.5 ppm nonvolatile total organic carbon (NVTOC) concentration range in each cell. A correlation coefficient of 0.98 was obtained. However, this treatment was criticized and a correlation coefficient of 0.74 was obtained (66). It thus seems clear that a statistical correlation exists and a method for control of volatile halomethanes is the reduction of the organic contaminants which directly produce these compounds on chlorination. Elimination of substances such as humic acids, methyl ketones, ethanol, etc., that undergo the haloform reaction would be expected to reduce the concentration.

Several of the chlorinated organics formed are possible carcinogens, but little is known of their effects on humans at such low concentrations. Gehrs (7) demonstrated toxic effects to fish eggs for two chlorinated organic compounds at the levels found in wastewaters, and Dowty and co-workers showed that at least two chlorinated compounds; i.e., tetrachloroethylene and carbon tetrachloride, present in drinking water were present in human plasma (6). No solid evidence is yet available, however, on the possible dangers of these compounds to human health.

Analytical Methods and Their Limitations

The procedures used to examine water supplies for their organic contaminants have been constantly evolving over the years, and even now are by no means comprehensive. Perhaps the most important water analytical methodology involves analysis for organohalides. Among the reasons for this is the

availability of halogen specific gas chromatographic detectors, and the easily identifiable chlorine isotope clusters in mass spectra. Nevertheless, identification of these compounds at the microgram per liter and nanogram per liter level remains a difficult task, and perhaps only a small fraction of the compounds actually present have been identified.

To discuss this topic in the context of the present report, we must recognize the historic trend in this subject. Organic halocarbon analyses, prior to 1970, dealt primarily with pesticides and their residues. Most of the analytical methods for their detection relied on the very nonpolar nature of these agents, and on organic extraction steps to concentrate the solutes, followed by chromatographic separations (TLC, columns, etc.) to isolate classes of compounds on the basis of common polarity. Confirmation and identification of unknown organic compounds was generally performed with gas chromatography using either the flame ionization detectors (FID) for the ppm range, or electron capture (EC) detectors for the ppb range. These two procedures are not well suited for broad screening analytical programs for unknown organic compounds in water samples. Numerous compounds are usually detected which cannot be identified, or else there are unknown compounds which cause interference problems when searching for specific contaminants.

Since the reports of Bellar (5) and Rook (9) interest has centered on identification of relatively insoluble, highly volatile halocarbons. The method presently used for analysis of volatile organic compounds is a modification (48) of the Bellar technique (67) and is frequently referred to as VOA (volatile organic analysis). This method involves purging the volatile organics from the water sample with pre-purified nitrogen directly into a gas chromatograph. It should be noted incidentally, that it was during the development of this analytical method for volatile organics by Bellar and his co-workers that the omnipresence of chloroform and the other halomethanes in chlorinated drinking water was discovered although the presence of halomethanes and other chlorinated hydrocarbons had been suggested earlier.

The McAuliffe (68) headspace analysis has been used successfully to provide gaseous samples that contain not only the halocarbons, but also aliphatic and aromatic compounds having the requisite vapor pressures above their aqueous solutions. These sampling preparations, coupled with the sensitivity of electron capture detectors, or the specificity of coulometric detectors that convert the halogen to ionic halide, now provide quite reliable analyses at the ppb level for this group of volatile and insoluble halocarbons. Two recent papers (69, 70) report a simple extraction procedure with a hydrocarbon solvent followed by electron capture GLC for halomethane analysis. Detection levels of 0.1 μg/l. were obtained.

The more highly water soluble halocarbons and the less volatile compounds cannot be determined by these techniques. Even the steam stripping methods of Lassiter et al. (6, 40) have not revealed substantial numbers of halocarbons subject to chromatographic elution. It is very probable that until liquid chromatographic separations can be routinely coupled to mass spectrometry, there will not be significant improvement in the comprehensiveness of the analyses of organics in water. Halogenated carbohydrates, chlorinated peptides, humic acid derivatives, and chlorinated hydrophilic heterocycles will not have sufficient thermal stability or volatility to permit separations by gas chromatography. Thus alternate means of concentration and separation must first be developed if such water soluble species are to be identified. Similarly, on current GC columns, chlorinated derivatives of unsaturated fatty acids are not detected without prior derivatization.

The class of organics which consists of compounds having a relatively limited solubility in water, absence of strong functional groups, and a finite vapor pressure can be isolated and identified by combination GC/MS methods. However, these methods require extensive "clean-up" if useful mass spectra are to be obtained. At present very few reports of such analyses are in the literature, presumably because of the extensive separation and preparation effort that such samples demand. Substituted aromatics, aliphatics, and even heterocyclic compounds of relatively low volatility can be isolated from organic extracts of water samples. These require preliminary column separations, as in pesticide analyses, to provide mixtures which can be resolved on either low liquid phase, or capillary columns. The series of reports by EPA (48) describe several analytical procedures, although the extent of prechromatography separations has been limited in their work.

Presently, a solid data base concerning the identities and amounts of organics and chloroorganics in water is lacking, largely because the present techniques cannot easily measure compounds that are not volatile, and relatively nonpolar. Yet, it is generally believed that the greatest proportions— perhaps 90% or more—of the organic matter in water is highly polar, nonvolatile, and very water-soluble (71). Most of this material is believed to consist of humic substances which are polymeric aromatic poly(hydroxymethoxycarboxylic acids). Nevertheless, recent studies have shown that reverse osmosis with cellulose acetate and nylon membranes can concentrate as much as 93% of the

total organic carbon in drinking waters (41, 42). Final recoveries from the concentrate using extraction and adsorption procedures, however, have not exceeded 35% (42).

One of the major requirements in the analyses of halocarbons is the development of an organic chlorine analysis method, in analogy to the total organic carbon analysis. The analyst who attempts to establish that his method for separation and identification of halocarbons is valid, has no independent measure of total organic halogen content in the starting sample. Present methods which attempt to oxidize all of the organics and then search for ionic halogen cannot effect a satisfactory preliminary removal of ionic species. For example, an aqueous sample with a total organic carbon level of 1 ppm may have present 100 ppm of ionic chloride. If the 1 ppm organic compound level contains 1% organic chlorine, the analyst must be able to reduce the ionic burden to less than 0.1 ppb if his subsequent assay for organic halogen is to have even a 10% reliability. Naturally, this reduction of ionic halogen must be accomplished without significant loss of organic solutes in the sample.

To summarize the problem at this time, we can divide the range of possible organohalides as follows: (1) water-insoluble, volatile, compounds; (2) water-soluble, low volatility compounds; (3) water-insoluble, low volatility compounds.

Volatile, water-insoluble compounds can be measured by head space analyses, concentration on resins, and sometimes by direct analysis of the sample. The detection methods are based on gas chromatographic separations, followed by relatively specific detectors, including mass spectrometers.

Water-soluble, low volatility compounds are generally not identified by present methods. Their analysis will probably be dependent on coupling of liquid chromatographs to mass spectrometers.

Water-insoluble, low volatility compounds, such as organic halides can be detected by present methods, but require extensive concentrations and sample preparations. The GC/MS methods available are the most informative of the techniques applied thus far, but few comprehensive analyses have been reported, perhaps because of the high cost of such analyses.

The limitations in the analytical methods are thus a real barrier to a complete understanding of the organic chemicals and their reactions in water. The possible approaches to these problems have by no means been exhausted. The emphasis in analytical methodology has been placed mostly on instrumental techniques, while bioassays have received relatively little attention. Compound class specific radioimmune assays, for example, would be very useful.

Chlorination Chemistry

The ever-increasing numbers of nonchlorinated organic compounds present in drinking water compiled by EPA raises the obvious question whether these compounds are resistant to chlorination, or just escaped chlorination from strictly dynamic considerations. In the discussion of the chemistry and reactions of classes of organic compounds, an attempt was made to assess the potential for chlorinating these compound classes with hypochlorous acid solutions. One would predict that many of the compounds identified in drinking waters are subject to some degree of chlorination except possibly the aliphatic hydrocarbons, and even these may be chlorinated if free radical processes are involved.

Each compound, however, must be reviewed separately, unless a free energy relationship can be established for the class as a whole. Aromatic compounds, for example, can be activated by electron-donating functional groups such as phenols and cresols and are easily chlorinated, while the deactivated nitroaromatic rings are relatively resistant. But relationships of this type are not always possible, and the enormous complexity of the organic content in water makes it difficult to come up with the useful generalizations.

In addition, any discussions of chlorination chemistry must include a consideration of the effects of temperature. Reaction rates, yields, and product distribution will be markedly influenced by relatively small changes in temperature, and the effects of temperature on solubility properties of the organic precursors or the particulate matter to which they may be sorbed and on which they may react may also be important. The dynamics involving reaction rates, precursor and product solubility, chlorine demand, and product disappearance or decomposition which are all influenced by temperature, makes the problem extremely complex, and simple predictions of the events taking place are highly unlikely. Mathematical models that take into account these variables could be helpful.
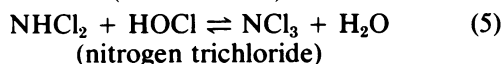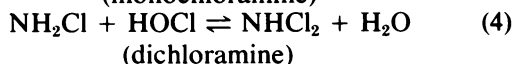
Chlorine Species in Solution

The chemistry of chlorine in water has been well established to involve the initial formation of hypochlorous acid [Eq. (1)] which dissociates to give the hypochlorite ion [Eq. (2)] (72).

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad (1)$$

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad (2)$$

The equilibrium constant K for Eq. (1) is 3.94 × 10^{-4} at 25°C (73), and the reaction proceeds quickly. The equilibrium and concentrations of various chlorine-containing species are both temperature and pH dependent. Jolley (8) has calculated that chlorine at a concentration of 1 mg/l. water at a pH of 7.5 and 25°C will produce the following species: $Cl_2 = 8 × 10^{-15}M$, $Cl^- = 1.4 × 10^{-5}M$, $HOCl = 7.0 × 10^{-6}M$, and $OCl^- = 7.0 × 10^{-6}M$. In other words under normal water treatment conditions most of the chlorine is in the form of hypochlorous acid and hypochlorite ion and only a negligible amount is in the form of molecular chlorine.

At pH values less than 6.5 hypochlorous acid is largely undissociated. Above pH = 8.0 it is largely dissociated (13). Krusé et al. (20) showed that hypochlorous acid gives better virus and bacteria disinfection than the same concentration of hypochlorite ion. White (24) confirms this. Thus, lower pH is preferable.

Most wastewaters contain significant amounts of ammonia, which will react with chlorine to form chloramines (33).

$$NH_3 + HOCl \rightleftharpoons NH_2Cl + H_2O \quad (3)$$
(monochloramine)
$$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O \quad (4)$$
(dichloramine)
$$NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O \quad (5)$$
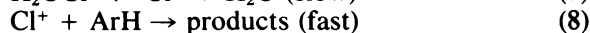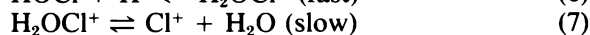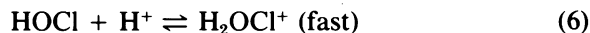(nitrogen trichloride)

Though not as rapid as the dissociation of hypochlorous acid, the reaction with ammonia is fast. It usually occurs before a significant amount of disinfection has taken place (8). The predominating chloramine depends on the wastewater pH and the relative amounts of chlorine and ammonia (33). Monochloramine and dichloramine are normally present in chlorinated wastewaters, but very little nitrogen trichloride is ever found. The available oxidizing power of monochloramine and dichloramine is roughly the same as it is for hypochlorous acid (74) and mono- and dichloramine have some disinfecting strength, but much less than that of hypochlorous acid or hypochlorite ion. They require several hours contact time compared to only a few minutes for hypochlorous acid (33) for the same disinfection effectiveness. At high concentrations of ammonia, bromoamines should also be present (75).

When the chlorine dosage exceeds approximately ten times the concentration of ammonia nitrogen by weight, a process known as the breakpoint reaction occurs (76). By a series of reactions most of the ammonia nitrogen is oxidized to nitrous oxide or nitrogen gas. Beyond the breakpoint most of the chlorine added is present as hypochlorous acid or hypochlorite ion. Below the breakpoint most of it is in the form of chloramines. The breakpoint reaction is significant because it removes ammonia from wastewaters and it makes available free chlorine (HOCl or OCl$^-$) with its better disinfectant powers.

Chlorination Mechanisms of Organic Compounds

The exact mechanism involved in chlorination of organic species by hypochlorous acid has been the subject of considerable conjecture during the past 30 years and several excellent reviews have been written on the subject (77, 78). Chlorination studies with hypochlorous acids have been carried out under a variety of conditions making it difficult to decide on a unique mechanism. Initial proposals invoked the electrophilic chlorinium ion (Cl$^+$) analogous to the nitronium ion (NO$_2^+$) (79) that occurs in nitration reactions. The chlorinium ion was expected to be the most reactive of chlorinating species. Kinetic experiments in aqueous solutions at room temperature showed that chlorination of olefins and aromatics were dependent on HOCl, and H$_3$O$^+$ concentrations, but independent of substrate concentration, which is consistent with a proposed rate-limiting formation of the chlorinium ion (80–82) as shown in Eqs. (6)–(8). The rate expression is given by Eq. (9). For less reactive substrates such as benzene, toluene, and sodium benzyl sulfonate the presence of sulfuric or perchloric

$$HOCl + H^+ \rightleftharpoons H_2OCl^+ \text{ (fast)} \quad (6)$$
$$H_2OCl^+ \rightleftharpoons Cl^+ + H_2O \text{ (slow)} \quad (7)$$
$$Cl^+ + ArH \rightarrow \text{products (fast)} \quad (8)$$
$$- d[HOCl]/dt = k[HOCl] + k'[HOCl][H^+] \quad (9)$$

acids was shown to be necessary (83, 84), which is consistent with the formation of a reactive hypochlorous acidium ion (H$_2$OCl$^+$). These reactions were shown to be dependent on the substrate concentration for which the rate expression, Eq. (10), holds.

$$-d[HOCl]/dt = k[ArH][HOCl][H^+] \quad (10)$$

Isotope effects, however, in H$_2$O and D$_2$O, were not consistent with the rate-limiting formation of the hypochlorous acidium ion (85) and thermodynamic considerations (86) for the dissociation of chlorine (Cl$_2$) in water showed that the chlorinium ion[Cl$^+$] concentration is so low under conditions where the substrate concentration is not kinetically important, that chlorination cannot occur at a measurable rate via this species. The chlorinium ion concentration [Cl$^+$] was estimated to be about $10^{-40}M$ after correction for ligand field stabilization of the cations in water (77).

Over the years several other proposals have been advanced including the participation of free chlorine (Cl_2) generated from the chloride ion (Cl^-) (87)

$$HOCl + H^+ + Cl^- \rightarrow Cl_2 + H_2O \qquad (11)$$
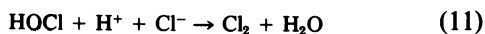
in reactions involving zeroth-order substrate concentrations [Eq. (11)], or the rate-limiting isomerization involving a hydrated chlorinium ion [Eq. (12)] (88).

$$\begin{array}{c} H \searrow \quad + \qquad\qquad + \\ \qquad O - Cl \rightarrow H - Cl - OH \\ H \nearrow \end{array} \qquad (12)$$
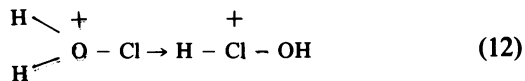
This species is not believed to be a very favorable chlorinating agent (78), and the former can be ruled out on the basis of kinetic experiments, including those showing partial rate factors for zeroth-order chlorination by Cl_2 in acetic acid that give ratios of chlorotoluene isomers much different than does acidified hypochlorous acid in water (88).

Under conditions of zeroth-order substrate concentrations; i.e., in the presence of perchloric acid to suppress hypochlorite catalysis and excess anisole as substrate, an acid dehydration of hypochlorous acid to chlorine monoxide (Cl_2O) was proposed as the rate-limiting step (89). At low acidity the rate expression involves a second-order term for hypochlorous acid which could also be interpreted as involving chlorine monoxide. None of the kinetic data, however, supported the formation of the chlorinium ion. The participation of chlorine monoxide as a chlorinating agent had been proposed much earlier (90, 91), and this species is more attractive under neutral pH conditions where its formation from hypochlorite ion can be represented by Eq. (13).

$$ClO^- + HOCl + H^+ \rightarrow Cl_2O + H_2O \qquad (13)$$
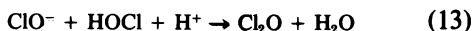
The present view is that several chlorine or oxychlorine species may be involved in rapid equilibria in the chlorination of organic chemicals in water. These include hypochlorous acid (HOCl), hypochlorite ion (OCl^-), chlorine monoxide (Cl_2O), trichloride ion (Cl_3^-), and hypochlorous acidium ion (H_2OCl^+) (92). In addition there are other irreversible reactions that occur at neutral pH; notably the formation of chlorate ion (ClO_3^-) which is slowly oxidized to the perchlorate ion (ClO_4^-) by hypochlorous acid [Eq. (14)].

$$2HOCl + OCl^- \xrightleftharpoons[]{K_{eq}} [H_2Cl_3O_3^-] \rightarrow$$
$$2H^+ + 2Cl^- + ClO_3^- \qquad (14)$$
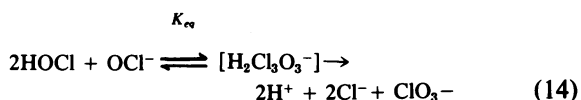
Morris (93) has defined the relative importance of these chlorinating species. The net relative reactivities r under a given set of conditions is a sum of the products of the estimated temperature dependent specific reactivity (r_i) and the fraction (f_i) of the total chlorine-containing species and is given by:

$$r = \Sigma \, r_i f_i \qquad (15)$$

The net relative activities for chlorine products in water at pH 7.0 and 15°C are shown in Table 5. The variation in the electrophilic behavior of a chlorinating species will depend on the nucleophilicities of the substrate. Under acidic conditions, the participation of the hypochlorous acidium ion (H_2OCl^+) will make a greater contribution to the total chlorine and hence in its net relative activity. Clearly, under neutral conditions hypochlorous acid is the predominant chlorinating precursor regardless of the mechanism or intermediates in the reaction.
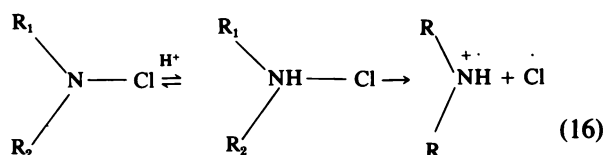
Table 5. Estimated net reactivities of forms of active chlorine at pH 7, 15°C[a].

Species	Estimated specific activity	Fraction of total chlorine	Net relative activity
Cl_2	10^3	3×10^{-6}	0.003
HOCl	1	0.80	0.80
OCl^-	10^{-4}	0.20	0.00002
H_2OCl^+	10^5	10^{-8}	0.001

[a] Taken from Morris (93).

Rosenblatt (92) concluded that oxidation potentials have only limited use and can best explain reactivities of organic chemicals with chlorinating species if electron transfer equilibria are involved. Reactions of organics with different chlorine species, including Cl_2, H_2OCl^+, Cl_2O, OCl^-, ClO_4^-, and ClO_2, are difficult to predict, since in addition to one and two electron transfer processes, they may involve electrophilic and nucleophilic reactions, charge transfer complex formation, oxidation reactions, N-demethylation reactions, and others.

Rosenblatt has also suggested the possibility of free radical species participating in chlorination reactions. The chlorammonium ion results from reaction of chloramines in acidic solutions (94) yielding a chlorine atom [Eq. (16)]:

$$\begin{array}{c} R_1 \searrow \qquad\qquad R_1 \searrow \qquad\qquad\qquad R \searrow \\ \quad N - Cl \xrightleftharpoons[]{H^+} \quad NH - Cl \rightarrow \quad \overset{+\,\cdot}{N}H + \overset{\cdot}{Cl} \\ R_2 \nearrow \qquad\qquad R_2 \nearrow \qquad\qquad\qquad R \nearrow \end{array} \qquad (16)$$

Triethylenediaminechlorammonium ion (92, 95) and triethylchlorammonium (92, 96) ions yield corresponding radical cations, and chlorine atoms.

Free radical chlorinations may be particularly important in the presence of ultraviolet light (97).

The possible reactions that broad classes of organic chemicals can undergo with aqueous chlorine was reviewed by Morris (98). It was concluded that there were only two reaction types that are significant under these conditions, and they include: (1) electrophilic aromatic chlorination, and (2) electrophilic chlorine addition to activated double bonds. The majority of chlorinated compounds that appear in drinking water (Table 1) fall into these two reaction classes. Several government publications have also appeared which report the results of studies on the chlorination of a broad spectrum of organic compounds in aqueous solutions (99–103).

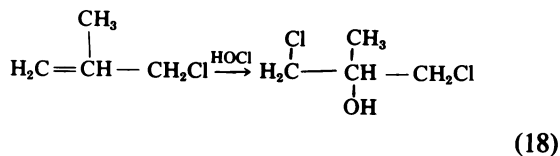## Hypochlorous Acid Reactions with Multiple Bonds

Hypochlorous acid can add to double bonds, yielding simple addition products called chlorohydrins (104–108). The following mechanism has been proposed (106) for the stepwise addition reaction.

$$\text{C=C} + Cl_2 \rightarrow \overset{Cl^+}{\text{C—C}} \xrightarrow{H_2O} \overset{Cl}{-\text{C—C}}_{OH} \quad (17)$$
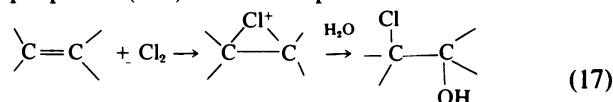
The direction of addition indicates attack by an electrophilic species despite the fact that the existence of Cl^+ in solution has been ruled out (89, 92). Chlorine, however, does exist in the positive state in $Cl-Cl$, Cl^+OH_2, and $Cl-OH$ (109), and the addition of the positive species results in formation of the stabilized cyclic alkane chloronium ion followed by addition of the basic anion, usually OH^-, but sometimes Cl^-.

The trans-stereospecificity is a result of the cyclic alkene chloronium ion. The formation of a chlorohydrin opens a route to further oxidation. Thus, addition of hypochlorous acid to olefins could conceivably yield methyl ketones which would subsequently undergo the haloform reaction. Addition to unsymmetrical olefins will produce the two possible isomers.

The products of the reaction of hypochlorous acid have been shown to be dependent on temperature, concentration of HOCl, and pH. In the reaction of allyl chloride with hypochlorous acid, for example, maximum yields of glycerol dichlorohydrins are obtained at low temperatures and low concentration of HOCl (110). 1,3-Dichloro-2-methyl isopropanol is formed readily and from methylallyl chloride in the presence of hypochlorous acid (110, 112). Generally, one should expect that olefins will react under water treatment conditions in the presence of HOCl.

$$\underset{\text{H}_2\text{C}=\text{CH}}{\overset{\text{CH}_3}{|}}-\text{CH}_2\text{Cl} \xrightarrow{\text{HOCl}} \underset{\text{H}_2\text{C}}{}\overset{\text{Cl}}{\underset{\text{OH}}{\overset{|}{-}}\text{CH}}\overset{\text{CH}_3}{\underset{}{|}}-\text{CH}_2\text{Cl}$$

(18)

Hypochlorous Acid Reactions with Aromatic Compounds

Aromatic compounds are readily chlorinated under the conditions used for the chlorination of water. The incorporation of chlorine follows the trends of activation of the aromatic ring. An aromatic compound with electron donating groups (such as $-OH$, $-OR$, $-NH_2$, $-R$) as substituents are more reactive and will incorporate chlorine more readily than aromatics with electron withdrawing groups (such as $-NO_2$, $-COOH$, $-COOR$, $-x$). The electron donating groups direct halogens generally to the ortho and para positions, while electron-withdrawing groups (except halogens) direct chlorine to the meta position, but there are exceptions to this rule. There is a reversal of direction when the salts of benzoic acid or aromatic amines are formed. This reversal is associated with the appearance of electrical charge; positive in the case of amines and negative in benzoic acid. The activated aromatics react readily with hypochlorous acid, while the less reactive aromatics require acid catalysis. Nonaromatic oxidation products can also be formed.

Carlson et al. (113) have investigated the reactions of monosubstituted aromatics under wastewater renovation conditions. Their results showed the trend expected from principles of aromatic electrophilic substitution reactions. Phenol and anisole and aromatics with other activating groups react readily under these conditions while nitrobenzene, chlorobenzene, benzonitriles, etc., show very little reactivity. Benzene itself is unreactive. At higher pH the reactivity with hypochlorous acid diminishes and at pH 7 only phenol reacts completely within 20 min at 25°C. Anisole incorporated 11% chlorine, and toluene only 2.9%. Similar results were reported by Barnhart and Campbell (100). Benzene, toluene, ethylbenzene, nitrobenzene, and benzoic acid showed no evidence of reacting with chlorine in aqueous solution at pH 7.4 in a 24-hr test period. Phenol, m-cresol, aniline, and hydroquinone, on the other hand, reacted readily. Similarly, hydroxycinnamic acid reacted to form chlorinated styrenes and chlorinated quinone (103).
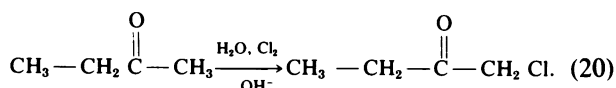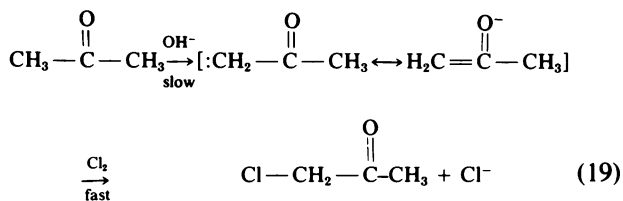
Monochlorinated aromatic carboxylic acids and aldehydes react readily with aqueous sodium

hypochlorite (*114*). Many of these types of compounds; e.g., vanillic acid p-hydroxybenzaldehyde, vanillin, etc. are present in kraft mill effluents (*115, 116*), and should be considered potential sources of chlorinated by-products in drinking water.
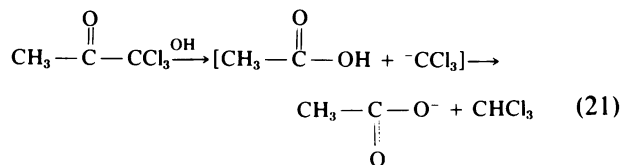
Hypochlorous acid chlorinates thiophene very easily (*117*), although the sulfur atom is in part oxidized to sulfate. Pyrrole also reacts readily with chlorine (*117*). Pyridine is very aromatic with a resonance energy of 28 kcal/mole or about the same order as benzene (36 kcal/mole) (*118*). As a result, it resists attack by electrophilic reagents, and chlorination proceeds only with difficulty. One report (*102*) suggests that pyridine reacted with a chlorox solution with a chlorine residual of 20 ppm. However, this same study concluded that phenol was not very reactive, and there is, therefore, some question about these results. Unlike the parent compound, 3-hydroxy and 2, 3-, and 4-aminopyridines, react under mild conditions, forming mono and dihaloderivatives in aqueous solution (*118*). Furans, as a rule, decompose more readily under halogenation conditions, although bromo addition products are obtained, which again illustrates the tendency of aromatic compounds of lower resonance energy (16 kcal/mole) to add halogen rather than to undergo electrophilic substitution (*118*). Polynuclear aromatic hydrocarbons appear to undergo reactions with hypochlorous acid under water treatment conditions, but the products apparently have not been identified (*119, 120*). This is important, however, since these PAHs are present in drinking water (*42*).

The Haloform Reaction

It has been known for many years that methyl ketones or compounds capable of being oxidized to methyl ketones will react with halogen under basic conditions to give haloforms (*122*). The rate of the reaction is proportional to the concentrations of both the ketone and the base, but not the concentration of the chlorine. This suggests the mechanism shown in Eq. (19) (*105*):

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{slow}]{OH^-} [:CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \leftrightarrow H_2C=\overset{O^-}{\overset{\|}{C}}-CH_3]$$

$$\xrightarrow[\text{fast}]{Cl_2} \quad Cl-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + Cl^- \qquad (19)$$

$$CH_3-CH_2\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[OH^-]{H_2O, Cl_2} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2 Cl. \quad (20)$$
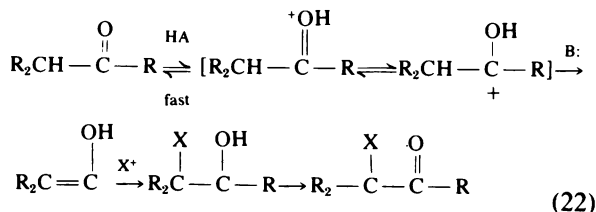
The rupture of the α C-H bond accounts for a good portion of the activation energy. The rate diminishes when an electron-donating group (such as an alkyl group) is substituted for an α-hydrogen. This is demonstrated by the preferential attack at the less substituted site in unsymmetrial ketones. The presence of an electron-withdrawing substituent accelerates the reaction, so that a monohalo ketone is not isolable, but reacts even faster to form the di- and trihalo ketone. In the presence of base, the trihalo derivative is finally cleaved (the haloform reaction) (*121*) yielding the haloform or in the present case, chloroform.

$$CH_3-\overset{O}{\overset{\|}{C}}-CCl_3 \xrightarrow{OH} [CH_3-\overset{O}{\overset{\|}{C}}-OH + {}^-CCl_3] \longrightarrow$$

$$CH_3-\overset{}{\underset{O}{\overset{|}{C}}}-O^- + CHCl_3 \qquad (21)$$

Besides the reactions with ethanol, acetaldehyde, and methyl ketones, various substituted quinones, hydroquinone, catechol, resorcinol, pyrogallol, phloroglucinol, and even di- or trimethylamines may give the haloform reaction, as do the humic substances which are present in water as the result of plant decay (*9, 59*).

For chlorination in the presence of acid, whose rate also is dependent on substrate and acid concentrations but not chlorine concentration, the proposed mechanism (*105*) is given in Eq. (22).

$$R_2CH-\overset{O}{\overset{\|}{C}}-R \underset{\text{fast}}{\overset{HA}{\rightleftharpoons}} [R_2CH-\overset{{}^+OH}{\overset{\|}{C}}-R \rightleftharpoons R_2CH-\overset{OH}{\overset{|}{C}}-R] \overset{B:}{\longrightarrow}$$

$$R_2C=\overset{OH}{\overset{|}{C}} \xrightarrow{X^+} R_2\overset{X}{\overset{|}{C}}-\overset{OH}{\overset{|}{C}}-R \longrightarrow R_2-\overset{X}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-R$$

$$(22)$$

The acid protonates the carbonyl, forming the conjugate acid, which draws the electron density away from the α C-H bond, thus weakening it. This is easier than the reorganization of charge around the α carbon to form a double bond, as in base. In acid, the presence of an electron-donating group accelerates the reaction, causing halogenation at the more substituted site.

An electron withdrawing substituent would retard the rate, making the isolation of the monohalo ketone possible in acid which is not the case in base. The α halogenation of other molecules containing carbonyls (acids, esters, aldehydes) is also possible by the same mechanisms (although carboxylic acids cannot be base-catalyzed).

In a comprehensive study by Stevens et al. (*123*), humic substances have been shown to be important precursors for halomethane formation. The rates of formation of halomethanes in surface waters upon chlorination are similar to the rates when commercial humic acid in distilled water is treated with chlorine. In addition, these investigations showed that coagulated and/or filtered raw water yield considerably less chloroform. Although acetone reacts much less rapidly with chlorine at neutral pH (*100, 123*), it could be a significant precursor at high pH. These studies serve to illustrate the rate dependency of trihalomethane formation under varying treatment conditions, including solubilities, pH, temperatures, and condition of raw water with respect to particulates to which precursors may be sorbed. Generally, methyl ketones or oxidizable precursors of methyl ketones should be considered potential sources of chloroform.

Rook (*59*) recently reported the results of his studies with fulvic acids and model substrates. From these studies he has concluded that the activated metadihydroxybenzene structures in humic substances are important for the formation of chloroform and a number of other halogenated products, including methylene chloride, the brominated methanes, tetrachloroacetone, and higher homologs, chloral, dichloro- and trichloroacetic acids [Eq. (23)]. The products obtained will depend on whether the reaction proceeds by cleavages a, b, or c. Some of these products, tetrachloroacetone


(23)
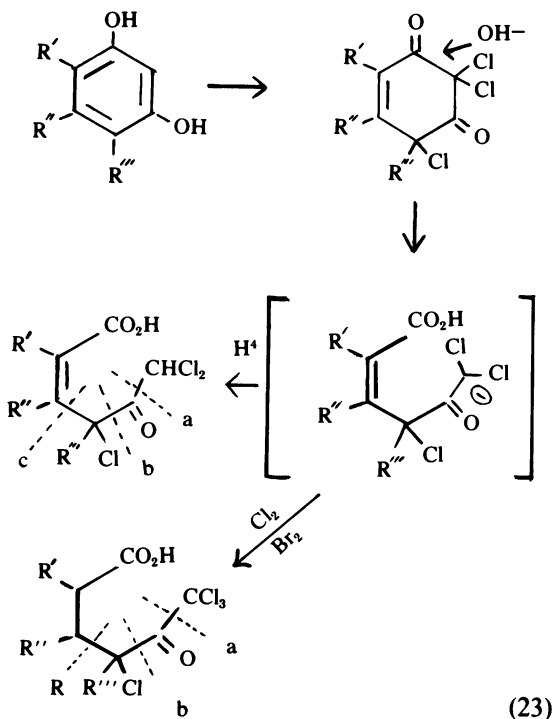
(*41, 55*) for example, had previously been difficult to rationalize on the basis of the usual base-catalyzed haloform reaction.

Reactions of Amines With Hypochlorous Acid

The chemistry of the chloramines, derived from ammonia under aqueous conditions has been important in water treatment, primarily because of the longer residence time of chloramine over hypochlorous acid for residual disinfection capacity. Several reviews have dealt with both the chemistry and disinfection qualities of the chloramines (*8, 124*). Monochloramine, dichloramine, and trichloramine are formed in a stepwise fashion when ammonia reacts with hypochlorous acid (*33,124*) [Eq. (3)–(5)], and the ratio of products is dependent on the pH of the final solutions (*125-127*). Under acidic conditions nitrogen trichloride is formed while under alkaline conditions, monochloramine is favored. The ratio of monochloramine to dichloramine increases rapidly with an increase in pH from 5 to 9 (*128*) and at pH 7.0 the ratio is approximately 0.65 (*8, 129*). The equilibrium involved is given by Eq. (24).

$$2NH_2Cl + H^+ \rightleftharpoons NH^+_4 + NHCl_2 \qquad (24)$$
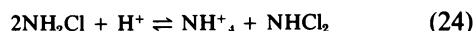
with an equilibrium constant $K = 6.7 \times 10^5$ at 25°C. The measured rate of chloramine formation is also influenced by the pH of the medium with a maximum rate at pH 8.3 for monochloramine formation. The rate of chloramine formation is second order (*130*) and is given by Eq. (25).

$$d[NH_2Cl]/dt = k[NH_3][HOCl] \qquad (25)$$
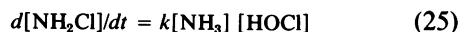
The half-life for a second order reaction is dependent on the initial concentration of the reactants, and so the rate of chloramine formation can only be determined with knowledge of the initial conditions. The rate, however, for monochloramine formation is so fast at pH 8.3 that it cannot be experimentally measured (*130*). The rate falls off rapidly at both high and low pH values and from extrapolation of these results it was shown that at typical hydrogen ion, chlorine, and ammonia concentrations of potable water supplies the reaction is virtually complete within one minute.

It was shown that the variation of reaction rate with pH is general for amines (*130*). Depending on whether the mechanism involves ionic or neutral species, the reaction rate would be expected to diminish at low pH, because the base is consumed in either mechanism.

$$NH_4^+ + OCl^- \rightleftharpoons NH_2Cl + H_2O \qquad (26)$$
$$NH_3 + HOCl \rightleftharpoons NH_2Cl + H_2O \qquad (27)$$
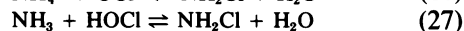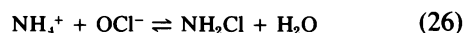
Similarly at high pH the acids are removed, and a mechanism involving both neutral and ionic species is not plausible.

The above mechanisms are kinetically indistinguishable. On the basis that the reaction rates for several amines, including ammonia, methylamine, and dimethylamine are approximately proportional to their base strengths, a nucleophilic displacement of hydroxide by the amine was proposed involving a cyclic transition state. Edward and Soper (131), however, favored the ionic mechanism because of better donor properties of the hypochlorite ion.

In one sense, there is an advantage to having chloroamines formed. Although chloroamines are poor oxidizing agents and not as effective in disinfection as are nonaminated chlorines, they may be somewhat less likely to act as chlorinating reagents for carbon. As Jolley has noted (132), chloramines are aminating agents, and usually require basic conditions to react with alcohols or phenols (133, 134). They can, however, add to activated double bonds and react with carbonyl groups to give chloramines (134).

Free energy correlations have been developed by Higuchi and coworkers (135–139) for the chlorination of amines and amides. The chlorine potential for N-chlorinated derivatives has been defined as:

$$pK_{cp} = -\log K_{cp} \qquad (28)$$

where K_{cp} is the equilibrium constant for the following type of equilibria:

$$R_2NCl + H_2O \rightleftharpoons R_2NH + HOCl \qquad (29)$$
$$R_3{}^+NCl + H_2O \rightleftharpoons R_3{}^+NH + HOCl \qquad (30)$$
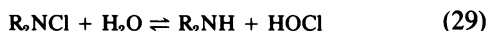
The chlorine potential is the free energy difference between the reactants and products and values for various amines can be determined experimentally if the pK_{cp} for one amine is known, because of the following equilibrium:

$$YN + XN-Cl \rightleftharpoons XN + YN-Cl \qquad (31)$$
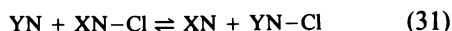
Higuchi and Haseguwa (139) showed that the exchange does not involve hypochlorous acid as an intermediate. The pK_{cp} values are thus considered to be valid and several of these values are shown in Table 6. These results show the relative tendency for amines to chlorinate, and allow predictions of equilibrium ratios of various chloramines in solution. From the values shown in Table 6, reactions between secondary amines and hypochlorous acid go virtually to completion and this was demonstrated with dimethylamine which was converted in less than one-half hour under water chlorination conditions (100).

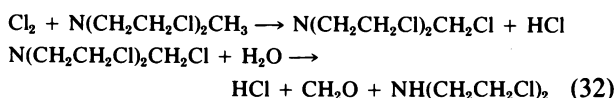The chlorination of aliphatic tertiary amines involves α and β positions along the carbon chains to

Table 6. pK_{cp} Values for various chloramines.[a]

| Donor (XN-Cl)[b]	pK_{cp} at pH 7.0
N-Chlorodimethylamine	11.18
N-Chlorodiethylamine	11.26
N-Chlorodipropylamine	11.16
N-Chloro-disopropylamine	9.77
N-Chlorodibutylamine	11.18
N-Chlorobutylmethylamine	11.16
N-Chloropiperidine	11.93
N-Chloromorpholine	12.62

[a] Data from Higuchi et al. (137).
[b] N-Chlorosuccinimide was used as acceptor throughout.

give intermediates in oxidation reactions. Methyl bis (2-chloroethyl)amine reacts with Cl_2 in aqueous solution to give formaldehyde and bis(2-chloroethyl)amine (140) [Eq. (32)]. Higher doses of chlorine also give glyoxal, chloral, glyoxalic, and glycollic acids, presumably through the intermediate α-chlorination products.

$$Cl_2 + N(CH_2CH_2Cl)_2CH_3 \longrightarrow N(CH_2CH_2Cl)_2CH_2Cl + HCl$$
$$N(CH_2CH_2Cl)_2CH_2Cl + H_2O \longrightarrow$$
$$HCl + CH_2O + NH(CH_2CH_2Cl)_2 \qquad (32)$$

The α-chlorination products are more rapidly hydrolyzed than the β-chlorination products.

Kinetic studies show that the chlorammonium ion is involved in the interaction of hypochlorous acid and trimethylamine. The rate is also somewhat dependent on the concentration of the free amine base (141). These and other data are consistent with a mechanism suggested by Bohme and Krause (142) in which hydrogen halide is abstracted from the chlorammonium ion by another free amine to give a dipolar structure [Eq. (33)]. The secondary amine formed in the overall reaction is expected to under-

$$\longrightarrow HCHO + R_2NH_2{}^+ \quad Cl^-$$

$$(33)$$
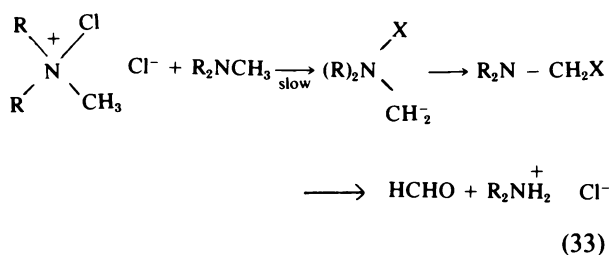
go chlorination to give the secondary chloramine. The possible formation of chlorine atoms from chlorammonium salts should also be considered (92, 95) particularly under ultraviolet radiation.

The relative rates of chlorination of nitrogen compounds generally appear to be related to their basicity since amines chlorinate more rapidly than amides (143, 144). The chlorination rates of amides and acetamides is also a function of the pH of the solution (143). As the pH increases the reaction rate

increases. These results led to the view that N-chlorination of anilides involves the hypochlorite ion. The chlorination rate of N-methylacetamide is also accelerated by the presence of acids at constant pH (146).

Reactions of Amino Acids With Hypochlorous Acid

The products formed from the reaction of α-amino acids and hypochlorous acid appear to be temperature, concentration, and in particular pH dependent. The predominant reactions are chlorination of the amine group and oxidative decarboxylation to give the corresponding aldehydes with elimination of carbon dioxide and ammonia (147) [Eq.(34)]. The formation of chloroamines predominates under acid conditions while oxidation to the aldehyde occurs primarily under neutral or alkaline conditions (148, 149).

$$R - \underset{\underset{NH_2}{|}}{C}H - CO_2H \xrightarrow{HOCl} R - CHO + NH_3 + CO_2 \qquad (34)$$
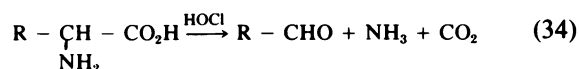
The formation of nitriles under these conditions is also important (150). A mixture of both aldehydes and nitriles are formed from hypochlorous acid at pH 3.0-3.5. L-Phenylalanine produces 95% phenylacetonitrile and 5% phenylacetaldehyde and L-glutamic acid gives the nitrile and aldehyde, as major and minor products, respectively. α-Tyrosine produces mostly ring-chlorinated nitriles and aldehydes. 3-Chloro-4-hydroxy phenylacetonitrile is the predominant product. This occurs under both acidic and neutral conditions (151).

Oxidative decarboxylation would appear to be the predominant course under the buffered conditions of typical water supplies. Glycine, serine, tyrosine, lysine, and arginine react with hypochlorite solution at pH 8.0 to produce the corresponding aldehydes although the yields of the products have not been reported (151). Oxidative decarboxylation of cystine and cysteine occurs presumably forming the aldehydes at pH 8.0, but it has not been shown that oxidation at the sulfur atoms occurs, as it does under acidic conditions.
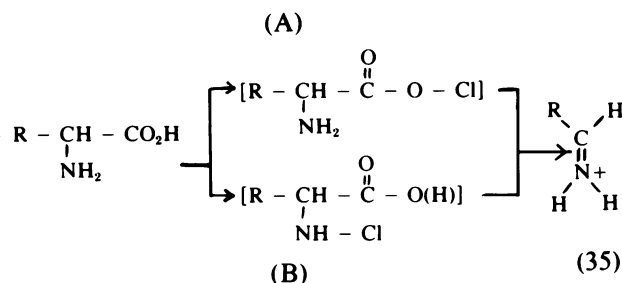
Chlorination under conditions of typical wastewater disinfection shows that amino acids with aromatic rings yield ether extractable oxidation products (152). Tyrosine and phenylalanine reportedly yielded aldehydes, while histidine forms the nitrile. In another simulated water study, tyrosine yielded chlorinated benzonitrile (100). In fact several other α-amino acids, including phenylalanine, leucine, isoleucine, and tryptophan yielded nitriles as well. Alanine, aspargine, methionine, glutamic acid,

glutamine, threonine, valine, cystine, and glycine reportedly react with hypochlorous acid under these conditions, but did not yield ether extractable oxidation products. The possible formation of the N-chloramine derivatives was apparently not investigated. The normal decrease in pH of an unbuffered reaction mixture containing amino acids and hypochlorous acid (153) makes this likely. Typical water supplies on the other hand are well buffered and a pH of 7.0–8.5 is their normal range. The products obtained, therefore, under nonbuffered conditions are open to some question.

The presence of bromide ion in drinking water also poses questions as to whether hypobromous acid causes oxidation of amino acids. It has been shown (146) that the reaction conditions and products formed are similar to those from hypochlorous acid oxidation. General oxidation reactions for the amino acids have been reviewed, and aldehydes are the usual products (154). The cross-chlorination and oxidation of amino acids by chloramines present may also be important. Chloramine T produces the same products; i.e., aldehydes and chloramino acids from amino acids as does hypochlorous acid (155, 156).

The mechanism for the chlorination and oxidation of amino acids has not been clearly established although the intermediacy of the N-chloro or N, N-dichloroamine derivatives was invoked at the outset (147). Certain observations were used as evidence to support the formation of an intermediate (149), and these included: (a) large quantities of amino acids consumed less available chlorine than smaller quantities, which would suggest chlorination and subsequent oxidation with excess hypochlorous acid, and (b) a definite maximum at the theoretical point when a chloroamino derivative would appear on the amino acid–hypochlorite curves, particularly under neutral or slightly acidic conditions. The relative instability of the chloroamine derivatives would have prevented their isolation.

The intermediacy of the chloramine derivative is now generally accepted in the oxidation of amino acids (157). There is some question as to the nature of the intermediate since there are two possibilities [Eq. (35)].

(A)

$$R - \underset{\underset{NH_2}{|}}{C}H - CO_2H \longrightarrow \begin{cases} [R - \underset{\underset{NH_2}{|}}{C}H - \overset{\overset{O}{\|}}{C} - O - Cl] \\ \\ [R - \underset{\underset{NH-Cl}{|}}{C}H - \overset{\overset{O}{\|}}{C} - O(H)] \end{cases} \longrightarrow \underset{\underset{H}{|}}{\overset{R}{\underset{|}{C}}} \underset{H}{\overset{H}{\underset{|}{N^+}}} \qquad (35)$$

(B)

The enamine once formed could lead to the aldehyde or the nitrile. The chlorimino derivative as an intermediate requires the presence of active α-hydrogens (*158*). The involvement of this species was opened to question when it was shown that α-dimethylaminoisobutyric acid which has no active α-hydrogens can also be oxidized to acetone and dimethylamine on treatment with hypochlorous acid (*159-162*). Labeling studies also show that the hydrogen atom on the α-carbon atom of the amino acid cannot be involved; at least not under neutral or basic conditions (*163*).

Reactions of Nucleic Acids With Hypochlorous Acid

The halogenation of nucleic acids has been studied since the beginning of the century (*164*). The color reaction between bromine and pyrimidine bases (*165*) has been developed into an analytical procedure, and DNA and RNA apparently are altered when treated with sodium hypochlorite at pH 7.0 as evidenced by the decrease in the optical density of their absorbing maxima (*166*). Moreover, an acid hydrolyzate of bacteria yielded 5-chloropyrimidines after reaction with sodium hypochlorite (*167*).

Bromination of the pyrimidine bases or their nucleosides produces the 5-bromo derivative with the 5,6-double bond intact (*168*). 5-Halo derivatives are obtained under anhydrous acidic (*169, 170*), aqueous acidic (*171*), and photocatalytic (*172*) conditions. Uracil and its riboside, uridine, react with a sodium hypochlorite at pH 7.0 to give 5-chloro derivatives (I) and (II), respectively, and cytosine and cytodine likewise give the 5-chloro derivatives (*166*).

5-Chlorouracil
I

5-Chlorouridine
II

The mechanisms for the halogenation of pyridine bases have been studied in some detail. Wang (*173*) suggested that bromination of uracils involves addition of hypobromous acid across the 5,6-double

bond which subsequently undergoes a slow acid catalyzed elimination to give the 5-bromouracils. In excess hypobromous acid, this product can subsequently brominate further to give the 5,5-dibromouracil addition product. This reaction is suppressed when uracils are substituted by the nitrogen positions as, for example, in uridine where the mono bromo derivative predominates (*171*)

The reaction between aqueous hypochlorous acid and cytosine has also been studied in some detail (*174*). Cytosine (VI) undergoes initial *N*-chlorination to give VII, and this derivative is subsequently converted to the 5-chloro compound after acid catalyzed dehalogenation. The 5-chloro derivatives can react further to give the 4*N*,5-dichloro derivatives.

VI VII VIII

In addition to 4N- and 5-chlorocytosine, the product mixture at high concentrations of hypochlorous acid has been shown to contain unstable chlorohydrins IX and X.

IX X

Jolley et al. have identified several chlorinated purines, pyrimidines, and nucleosides in chlorinated sewage (*8, 175, 176*). Among these were 5-chlorouracil, 5-chlorouridine, 8-chlorocaffeine, 6-chloro-2-aminopurine, and 8-chloroxanthine. Chlorine reportedly also reacts with pyrimidine and purine derivatives in nucleic acids, yielding smaller fragments (*177*). 5-Chlorocytosine and 5-chlorouracil were isolated.

Reaction of Phenols With Hypochlorous Acid

The reactions of phenol with chlorine have been extensively investigated with respect to water quality because of the strong taste and odor problems which result from these reactions. Phenol reacts

with aqueous hypochlorite solutions to give various amounts of chlorine substitution and this has been known since as early as 1883 (*177*). The taste due to the chlorination of phenols in water supplies was at first attributed to the formation of 2-chlorophenol (*178*). Subsequent studies, however, showed that the taste could not be attributed solely to any single monochlorinated phenol (*179*). Burttschell et al. (*179*) showed that several mono-, di-, and tri-chlorophenols were formed, several of which were strongly organoleptic. The chlorinated products are formed sequentially giving a succession of higher substitution products. The yields, tastes, and odors for the isomers are shown in Table 7.

Table 7. Yields, tastes, and odors due to chlorination of phenol.

| | | Geometric means of thresholds, ppb | |
	Yields, %	Taste	Odor
Phenol	1–2	> 1000	> 1000
2-Chlorophenol	2–5	4	2
4-Chlorophenol	2–5	> 1000	250
2,4-Dichlorophenol	20	8	2
2,6-Dichlorophenol	25	2	3
2,4,6-Trichlorophenol	40–50	> 1000	> 1000

There was no evidence for the formation of any other chlorination products which were not substituted in the *ortho* or *para* positions. However, oxidation products are formed and these results were later confirmed by Lee and Morris (*180*) who showed that direct oxidation was involved between dichlorophenols and hypochlorous acid. Ingels and Ridenour (*181*) had earlier suggested that di-chloroquinone (XI) was the main oxidation product causing taste and odor problems. While the contribution to taste and odor by this compound is not ruled out, it seems on the basis of the work by Burttschell et al. (*179*) the dichlorophenols are the most important contributors. Ettinger and Ruckhoft (*182*) showed that taste and odor goes through a maximum with chlorine concentration and then diminishes during superchlorination. The ultimate fate of the chlorophenols is formation of 2,4,6-trichlorophenol and several oxidation products. These products are much less organoleptic.

Under aqueous acidic conditions, Cresol reacts with hypochlorous acid to give 5- and 6-chlorocresol, 5,6-dichlorocresol, trichlorocresol, and their respective *o*-benzoquinones. Oxalic, methylfumaric, and trichloro-β-methylmuconic acids and 3,5-dichloro-4-methyl-*o*-benzoquinone
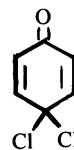
XI

are also formed (*183*). The respective catechols were proposed to be the intermediates in the formation of the quinones.

The reaction kinetics for the chlorination of phenols have been discussed in detail (*60, 179*). Soper and Smith (*184*) showed that the kinetics are second-order and these investigators and Lee and Morris (*181*) have interpreted the reaction to involve hypochlorous acid, and the phenolate ion. The relative rates of reaction

$$\text{rate} = k_{obs} [\text{HOCl}] [\text{ArO}^-] \qquad (36)$$

are dependent on both the pK_a of the phenolic compound and/or the pH of the solution. The data of Soper and Smith (Fig. 1) reveal that the more acidic phenols are chlorinated at a slower rate, and Lee and Morris (*180*) have shown that the reaction rate for a particular phenol increases with pH to a maximum and then diminishes as expected from Eq. (36). The maximum reaction rate constants are observed at pH 7–9 or at about the pH of typical water supplies.
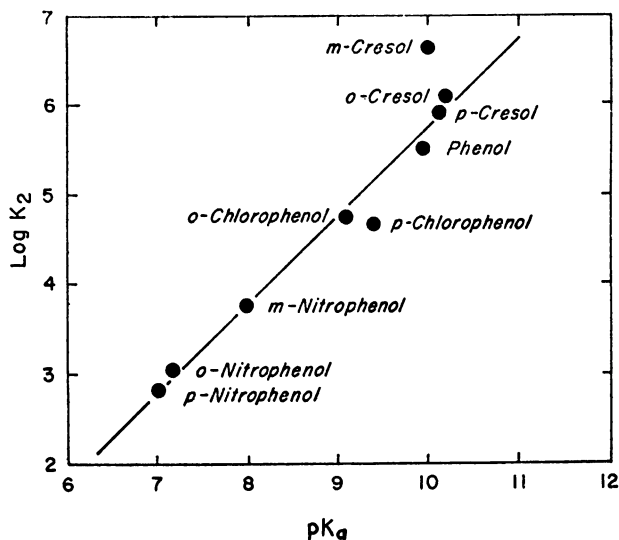

FIGURE 1. Chlorination rates of phenol by hypochlorite as a function of pK_a at 25°C.

Classical mechanistic arguments can be used to explain these results. At high pH the hypochlorite ion [Eq. (37)] which is not a good chlorinating agent (Table 5) is formed, and at low pH the phenolate ion is absent. Electron-withdrawing groups on the aromatic ring which cause phenols to be more acidic, also make them less susceptible to electrophilic attack and thus result in smaller second-order rate constants.

$$HOCl \rightleftharpoons H^+ + OCl^{\ominus} \qquad (37)$$

Reactions of Other Classes of Organic Compounds With Hypochlorous Acid

Discussions of the reactions of hypochlorous acids with organic compounds are usually limited to discussions of chlorination of amines, addition reactions in unsaturated systems, and the electrophilic substitution reactions of aromatic compounds (185, 186). The possibilities for reactions with other compound classes, however, must also be considered.

It appears that only a few other examples have been investigated. Simple alcohols such as isopropanol, methanol, and tert-butanol do not seem to react readily (100), although the possibility for oxidation of the primary and secondary alcohols should not be ruled out. Carboxylic acids as well as long chain fatty acid esters which are known to be present in water supplies (41, 187, 188) are not expected to be very reactive. Linoleic and oleic acids, despite the presence of double bonds reportedly did not react at all with aqueous chlorine (102). Lignins react to yield highly chlorinated derivatives (103), and reducing sugars are oxidized by hypochlorite (8), as are amino sugars (143).

Degradation and Disappearance

Chlorinated organics are as a rule very stable; the nonbiodegradability of many chlorinated organic pesticides has been well publicized. McConnell et al. (189) indicate that the one and two carbon halogenated organics such as those EPA (3) detected in drinking water degrade photolytically for the most part. Most of the lower molecular weight chlorinated organics have low solubilities in water and are readily transferred from water to the atmosphere, where they are subject to rapid photolytic degradation by sunlight. McConnell et al. (189) reported that microorganisms are generally believed to be incapable of degrading the one and two carbon chlorinated organics. However, mammals can degrade these compounds to chlorinated acetic acids, which can be further degraded by micro-organisms.

McConnell et al. (189) also state that chemical breakdown in water does occur but is extremely slow, having half lives of several years. The authors could find no reference to the likely degradation routes of those higher molecular weight chlorinated organics found by Jolley (8) in chlorinated sewage. Similarly, the authors could find no reference to the significance of adsorption as a disappearance mechanism for chlorinated organics in the environment.

Alternative Chlorination Procedures

Better Control

The hazards to fish of residual chlorine and the potential long term carcinogenic effect on man of chlorinated organics has led to the consideration of alternatives to the heavy use of chlorine. There are a number of ways to reduce the danger associated with chlorine while retaining it as the principal disinfectant. Following the maxim "if a little is good, a lot must be better," many treatment plant operators overchlorinate. A group of ten waste treatment plants in the Tualatin river basin in Oregon reported annual average chlorine residuals for July 1973 to July 1974 ranging from 1.3 to 3.4 mg/l. with most of the values around 2 mg/l. (190). Peak chlorine residuals during the year were much higher. In a study of 20 waste treatment plants in Illinois, Snoeyink and Markus (32) reported chlorine residuals in effluents as high as 4 mg/l. Where chlorination is required, a chlorine residual of 0.5 to 1 mg/l. is usually required by state regulatory agencies. The amount of chlorine used as a disinfectant could be greatly reduced if the actual residuals were kept near these levels and not allowed to go significantly higher. This would not eliminate the hazards of chlorine and chlorinated organics, but it would definitely reduce them.

Most water and wastewater treatment plant operators use the o-tolidine test to measure the total chlorine residual. This method gives values much lower than the total chlorine residual measured by more accurate tests such as the amperometric method. General use of one of the more accurate tests of chlorine residual could reduce the amount of chlorine used and thus the amount of chlorinated organics formed.

The use of a certain minimum required chlorine residual may be ineffective in achieving the desired disinfection of wastewater. Krusé et al. (20) showed that the degree of disinfection depended greatly on the pH of the water, the method of mixing after

chlorine addition, the turbidity, and the ammonia concentration. Chlorine disinfects wastewaters low in ammonia, faster and more effectively than water with high ammonia concentrations. When added to water with a pH less than 5, chlorine is present as hypochlorous acid, rather than hypochlorite ion. The acid is a more effective disinfectant but yields lower chlorine residuals from the same dose than hypochlorite ion in alkaline waters. Hypochlorite and chloramines give practically no virus kill, where hypochlorous acid had a significant virucidal effect (191). The work by Jolley (8) suggests that hypochlorous acid produces no more chlorinated organics than hypochlorite ion. Hypochlorous acid, hypochlorite ion, and chloramines all react in the measurement of total chlorine residual but have different disinfecting capabilities. A microbiological test or a measurement of free chlorine concentrations might give a better indication of disinfections efficiency than the total chlorine residual. Flash mixing, low pH, low turbidity, and low ammonia concentration all improve disinfection effectiveness without changing the chlorine residual.

Disinfection Not Always Necessary

There is a clear need for disinfection of water supplies to protect the public health, but a similar need for disinfection of wastewater is not universally evident. Secondary waste treatment removes most of the pathogens in sewage. If the receiving water provides a great deal of dilution, is not used for swimming, and shellfish are not harvested from it, it would seem unnecessary to disinfect wastewater before discharge. Such logic led the Environmental Protection Agency to reconsider their requirement of disinfection of all sewage effluents by 1977 and to propose that their requirement be rescinded (192, 193). If enacted as proposed, the amended EPA rules will permit the states to determine on a water quality basis if disinfection of the effluent of a given treatment plant is necessary.

There is very limited evidence that pathogens in waters used for swimming present a hazard. Water Quality Criteria 1972 (194) recommend no criteria for coliform levels in waters used for swimming. Based on the limited epidemiological data it would seem logical to disinfect treated sewage discharged to waters used for swimming, but it is difficult to set a maximum allowable coliform concentration for these effluents. Shellfish and some other marine organisms may concentrate pathogens present in the water. It would thus seem advisable to disinfect discharges that increase the coliform concentration of waters where shellfish are harvested.

Many sewage treatment plants discharge to waters, which for at least part of the year present no danger of disease transfer at all. Chlorination under these circumstances, as during the winter months, may not be justified.

Dechlorination

A final means of reducing the hazards presented by chlorination is to dechlorinate after chlorination. This has little application to water treatment because it eliminates the safety of a chlorine residual in the distribution system. For wastewaters it has potential since a chlorine residual in effluents has no purpose per se but is only used as an indicator of sufficient disinfection. Sulfur dioxide or thiosulfate can be added to dechlorinate water or activated carbon can be used to remove chlorine. These treatments have no apparent ill effects on the receiving water and do eliminate the problem of residual chlorine toxicity to fish (32, 35). However, there is little reason to believe that dechlorination will reduce the amount of chlorinated organics formed.

Alternatives to Chlorination

Ozone

There are several disinfection alternatives that avoid the use of chlorine. The most prominent among these is ozonation. Ozone is electrolytically produced at the treatment plant and mixed with the water or wastewater (27). Like chlorine, ozone has a high oxidation potential and acts as a rapid and effective disinfectant (19). It has seen limited use in the past in the U. S., but it is widely used in Europe, especially for treatment of water supplies (27). Several pilot plant scale studies of ozone use have been done in the U. S. (195). A full-scale demonstration plant using ozone, sonics, and chlorination to disinfect wastewater was built at Indiantown, Florida (196). Two other cities in the U. S.; Strasburg, Pennsylvania and Whiting, Indiana, use ozone for at least part of their water treatment (195).

Ozone has many advantages over chlorine. It is a much more effective virucide. Kinman (197) describes several studies demonstrating 99% virus kills by ozone in seconds. Katzenelson et al. (19) and Keller et al. (195) reported rapid bacteria and virus kills utilizing ozone. Ozone has no residual. For wastewater disinfection this is a benefit, since there is no toxicity to fish. For water supply disinfection, it eliminates the safety of a residual and is thus a disadvantage. Ozone will remove many tastes and odors; a definite advantage for water

treatment. When used in wastewater treatment plants, ozone acts as a tertiary treatment stage by oxidizing the small amounts of chemical oxygen demand remaining after biological treatment. Ozone application tends to float suspended solids, aiding their removal (27).

The principal disadvantage of ozone is cost. The EPA (198) estimates the cost of ozone disinfection for a 10 MGD wastewater treatment plant to be 3.49¢/1000 gal as compared to chlorine disinfection costs of 1.42¢/1000 gal. Others have made similar cost comparisons and arrived at similar results (27, 197, 199). Ozone is expensive because it takes large amounts of energy to generate it and the capital cost for the generating equipment is high (197). The second disadvantage of ozone for water treatment is the lack of a residual to prevent regrowth or contamination in the distribution system. Since ozone has no residual, it is difficult to monitor the degree of disinfection being achieved. Since ozone must be generated on site, the amount of maintenance and repair work necessary is usually greater than with chlorine. Like chlorine, ozone is highly toxic in air so precautions must be taken to prevent its release (197). A review by Kinman (197) summarizes the advantages and disadvantages of ozone. Ozone is likely to be used to a greater extent in the future due to the shortcomings of chlorine, but it is unlikely it will replace chlorine completely. Some plants are currently being designed utilizing a combination of chlorine and ozone in an attempt to obtain the advantages of both.

Bromine Chloride

One of the newest, most promising alternative disinfectants is bromine chloride. It is as effective as chlorine and can be handled in the same manner (198). The bromamines formed when ammonia is presented are much stronger disinfectants than chloramines, especially against viruses. The process is currently in the development stage so accurate information on costs and the formation of halogenated organics is not yet available. Predicted bromine chloride disinfection costs for a 10 MGD plant are 3.04¢/1000 gal. The nature of the compound suggests that halogenated organics will be as much of a problem with bromine chloride as with chlorine. Bromamines are less stable in water than chloramines so bromine chloride should not present as great a hazard to fish as chlorine.

Chlorine Dioxide

Chlorine dioxide is a powerful disinfectant and has been used successfully in several places. Augenstein (200) reported successful use of chlorine

dioxide where chlorine caused objectionable tastes and odors. Bernarde et al. (201) studied the kinetics of disinfection by chlorine dioxide and found it to be extremely rapid. Chlorine dioxide is produced by mixing solutions of sodium chlorite and chlorine. This must be done on site. Cost estimates vary; Augenstein (200) estimates that chlorine dioxide costs 50% more than chlorine and the EPA (198) estimates a 13-fold increase. No research has been done in the area, but it is likely that chlorine dioxide would produce similar amounts of halogenated organics as chlorine and pose a similar toxicity problem for marine organisms.

Bromine and Iodine

Bromine and iodine are effective disinfectants reacting in a manner similar to chlorine. They are discussed briefly by the EPA (198). They are safer to handle than chlorine since they are not gases at room temperature. They retain good disinfecting strength at higher pH, where chlorine loses much of its strength. Their principal disadvantage is cost, bromine costing roughly 3.5 times as much as chlorine and iodine roughly 18 times as much. As mentioned in the discussion of bromine chloride, halogenated organics are likely to result from treatment with bromine. Iodine does not react as readily with the organics in water and so would present a lesser problem.

Permanganate

Hamilton (202) states that potassium permanganate has been used for taste and odor control in water treatment and for disinfection of newly laid mains. The author found no reference to its use as a water disinfectant to replace chlorine. It seems unlikely that such a use is feasible given the strong color and toxicity of permanganate.

Lime

Heavy lime applications are sometimes used to remove suspended solids from wastewaters. Lime will also disinfect wastewater if enough is added to bring the pH to 11.5 or 12.0 (198). Disposal costs for the large amounts of inorganic sludge produced are high. Advantages of the technique are that it can be used in water with high organic concentrations, will remove some organics and phosphorus, and is effective over a wide temperature range.

Heat

A number of physical processes have potential as alternatives to chlorination. Most obvious among

these is the use of heat. Water can be disinfected by pasteurization, and this is often done in homes when water supplies become temporarily contaminated. On a large scale, the energy costs are prohibitive. Energy costs alone for heat disinfection would be approximately 100 times the total cost of chlorination.

Coagulation

A more feasible physical disinfection technique is to add coagulants so that the pathogens can be filtered or will settle out. York and Drewry (25) reported > 99% virus removal with several coagulants. Sobsey et al. (23) noted excellent coliform removal and better virus deactivation than can be achieved by chlorination. Coagulation is not as reliable as chlorination and does not have a residual effect so it alone is not adequate for water supply disinfection. Coagulation-filtration followed by chlorination is common in water treatment. Coagulation alone may be a viable alternative to chlorination for disinfection of wastewaters. Cost estimates of coagulation for disinfection purposes were not available.

Membrane Processes

It is possible to disinfect wastewater by membrane processes, more commonly known as reverse osmosis and ultrafiltration. Membranes with smaller pore sizes are necessary to remove viruses. The capital cost, membrane replacement cost and pumping cost due to the large head loss make this method far more expensive than chlorination. Membrane processes produce a very "clear" effluent and may in certain cases be economically feasible as a combined tertiary treatment and disinfection. They are insufficient for water treatment because they produce no residual effect.

Ionizing Radiation

There has been considerable discussion of gamma radiation as a possible disinfectant (198). Murphy (203) used cobalt 60 to disinfect up to 25,000 Imperial gallons/day of secondary effluent. Radiation forms none of the byproducts formed by chlorination and it can break down some of the organics in the water. Ballantine et al. (204) gave rough cost estimates for various radiation disinfection methods ranging from 66¢ to over $1.00/1000 gal as compared to 2¢/1000 gal for chlorine. Some of the least costly methods such as the use of spent fuel rods from reactors from reactors or reactor loops are unproven and entail a fairly high radiation exposure

risk. Ballantine et al. (204) estimated that to disinfect the water from one 10 MGD plant would require all the ^{60}Co available in 1969 when the article was written. Other possible radioactive isotopes would be in similar short supply. Due to cost, safety, and supply factors it is unlikely widespread disinfection by ionizing radiation will be utilized in the near future.

Sonics

Heckroth (196) reports the use of sonic vibration in conjunction with ozone as disinfectants in a plant constructed in Indiantown, Florida and maintains that the sonic vibration greatly improves disinfection. Kinman (197) argues that Heckroth's data do not show improved disinfection with sonic vibration. No work has been done with sonic vibration as the principal disinfectant. Energy costs for sonic vibration are known to be high, but a more exact cost analysis is not available.

Ultraviolet Radiation

Ultraviolet light destroys cells by causing a biochemical change in essential molecules (200). Ultraviolet disinfection systems that emit most of their energy at the optimum disinfection wavelength have been developed and are in use for treatment of many small water systems, used in such applications as hotels or single industrial installations. A demonstration plant at St. Michaels, Maryland, showed that ultraviolet light will provide good disinfection of secondary wastewaters. In order to be effective, ultraviolet radiation must penetrate the water. Because turbidity or color in the water will reduce the effectiveness of ultraviolet radiation, it may be necessary to include tertiary treatment such as sand filtration before ultraviolet disinfection. A 2 MGD wastewater treatment plant under construction at Rochester, New York will use ultraviolet disinfection preceded by sand filtration. EPA (200) estimates the cost for ultraviolet disinfection at a 10 MGD plant to be 2.7¢/1000 gal.

Conclusion

Because it is reliable, inexpensive, and easy to control, chlorine has become the dominant method of water and wastewater disinfection. There is currently considerable concern about the safety of continued heavy use of chlorine. Chlorination has been shown to produce potentially carcinogenic, halogenated organics. The chlorine residual itself is highly toxic to marine organisms.

Future action should proceed along two lines: (1) reduction of chlorine usage to the minimum necessary, utilizing alternative disinfection schemes where possible; and (2) further investigation to determine the true significance of the problem and to perfect alternative disinfection methods.

The first course of action, to reduce chlorine usage, will require reconsideration of existing state regulations. It might be advisable to institute a maximum chlorine residual as well as a minimum in wastewater effluents. States such as Oregon, which require high chlorine residuals for all waste treatment plants should consider whether their values criteria may be more stringent than is necessary for the desired disinfection. Some plants may not require disinfection at all or may require it only during certain times of the year due to high dilution and low contact opportunity. More accurate tests for chlorine residual than the orthotolidine test should be used. Disinfection requirements for wastewater treatment should be based on microbiological tests rather than total residual chlorine analysis alone since one chlorine residual level can correspond to various degrees of disinfection efficiency depending on how chlorination is accomplished and how effective the treatment prior to disinfection is. Disinfection requirements not based on a specific chlorine residual are especially important for those plants using a disinfection method other than chlorination.

The chlorine residual concentration in receiving waters should also be regulated to protect marine life. When it exceeds the levels safe for the desired organisms outside of a defined mixing zone, then dechlorination or alternative disinfection techniques should be required of plants discharging wastewater to the affected receiving waters.

The foremost goal of further investigations will be to determine the significance of the chlorinated organics formed during chlorination. The degree of hazard presented by the small concentrations of chlorinated organics formed must be determined. The reaction conditions that encourage or discourage chlorination of organics must be elucidated. It must be shown if the amounts of chlorinated organics formed by water and wastewater chlorination are significant when compared to the amounts from other sources such as industry.

Current knowledge is sufficient to show the extreme toxicity of chlorine residuals to marine life. Further investigations related to chlorine residual toxicity should determine what amounts of chlorine can be discharged to specific receiving waters without endangering the most sensitive species present.

Considerable research and development is necessary to define and perfect alternatives to chlorina-tion. It will also be necessary to investigate the potential side effects of these disinfection methods as well. For instance, what are the reactions and effects of sulfur dioxide used to dechlorinate? Does it affect fish or produce any stable hazardous compounds? Does it affect the production of chlorinated organics?

There is room for improvement in the design of ozonators and the regulation of the amounts needed. Since ozone degrades rapidly, it is not possible to control ozonation by measuring the residual, so some other monitoring method must be developed.

Some of the new alternate disinfection methods need to be demonstrated on a full scale. These include ultraviolet disinfection of wastewater, bromine chloride, coagulation, and sonic vibration.

Epidemiological investigations are necessary to determine the amount of disinfection necessary. Is the residual chlorine required in water distribution systems necessary? European cities who use ozone have no such residual. Is disease transfer more frequent as a result? What is the danger presented by viruses in water? There is even a shortage of epidemiological data on the likelihood of contracting a disease through water contact such as swimming. Current regulations for wastewater disinfection are based primarily on educated guesses as to the required disinfection. It should be possible to develop some scientific method of determining the disinfection necessary to reduce the danger of disease transfer to an acceptable level.

The current information available concerning the hazards of chlorine are not cause for alarm. These hazards are much less significant than the hazards of no disinfection. Current knowledge does suggest that we need to investigate the chlorination process and its products much more closely. Meanwhile we should reduce chlorine usage to only that amount that is necessary to protect the public health. As with everything else in an ecosystem, too much of a good thing can be dangerous.

REFERENCES

1. Robeck, G. Introductory comments. N. Y. Acad. Sci. Conference on Aquatic Pollutants and Biological Effects With Emphasis on Neoplasia. EPA, The Barbizan-Plaza Hotel Theater, New York, September 27–29, 1976.
2. Environmental Protection Agency. EPA results of national drinking water survey. Environmental News (News Release), April 18, 1975.

3. Environmental Protection Agency. Industrial pollution of the lower Mississippi River in Louisiana. U. S. Environmental Protection Agency, Region VI, Dallas, Texas, April, 1972, PB 229 814.

4. Anonymous. Ozone can help clean water and air. Environ. Sci. Technol. 9: 618 (1975).

5. Bellar, T. A., Lichtenberg, J. J., and Kroner, R. C. The occurrence of organohalides in chlorinated drinking waters. J. Am. Water Works Assoc. 66: 703 (1974).

6. Dowty, B., Carlisle, D., and Laseter, J. L. Halogenated hydrocarbons in New Orleans drinking water and blood plasma. Science 187: 75 (1975).

7. Gehrs, C. W., et al. Effects of stable chlorine-containing organics on aquatic environments. Nature 249 (5458): 675 (1974).

8. Jolley, R. L. Chlorination effects on organic constituents in effluents from domestic sanitary sewage treatment plants. Oak Ridge National Laboratory, ORNL-TM-4290, Oak Ridge, Tennessee, October 1973.

9. Rook, J. J. Formation of haloforms during chlorination of natural waters. Water Treatment and Examination 23 (Part 2): 234 (1974).

10. Harris, R. H. and Epstein, S. S. Drinking water and cancer mortality in Louisiana. Science. 193: 55, 1976.

11. Gart, J. J., and Terone, R. E. The Implication of Cancer-Causing Substances in Mississippi River Water. Unpublished review of a report by R. H. Harris: January 1975.

12. Miller, R. W. Carcinogens in drinking water. Pediatrics. 57(4): 462 (1976).

13. Metcalf and Eddy, Inc. Wastewater Engineering. McGraw-Hill Book Co. New York, 1972.

14. Berg, G. Removal of viruses from sewage, effluents and waters. WHO Bull. No. 49: 451 (1973).

15. Brown, T. S., Malina, J. F., Jr., and Moore, B. D. Virus removal by diatomaceous earth filtration. Part 2. J. Am. Water Works Assoc. 66: 735 (1974).

16. Cookson, J. R., Jr. Virus and water supply. J. Am. Water Works Assoc. 66: 707 (1974).

17. Culp, R. L. Breakpoint chlorination for virus inactivation. J. Am. Water Works Assoc. 66: 699 (1974).

18. Culp, R. L. Virus and bacteria removal in advanced wastewater treatment. Public Works 102 (6): 84 (1971).

19. Katzenelson, E., Kletter, B., and Shuval, H. I. Inactivation kinetics of viruses and bacteria in water by use of ozone. J. Am. Water Works Assoc. 66: 725 (1974).

20. Krusé, C. W., et al. Improvements in terminal disinfection of sewage effluents. Water Sewage Works 120 (6): 57 (1973).

21. McDermott, J. H. Virus problems and their relation to water supplies. J. Am. Water Works Assoc. 66: 693 (1974).

22. Malina, J. F., et al. Poliovirus inactivation by activated sludge. J. Water Pollut. Control Fed. 47: 2178 (1975).

23. Sobsey, M. D., et al. Virus removal and inactivation by physical-chemical waste treatment. J. ASCE Environ. Eng. Div. 99 (EE3): 245 (1973).

24. White, G. C. Disinfection: present and future. J. Am. Water Works Assoc. 66: 689 (1974).

25. York, D. W., and Drewry, W. A. Virus removal by chemical coagulation. J. Am. Water Works Assoc. 66: 711 (1974).

26. Morrison, S. M., Martin, K. L., and Humble, D. E. Lime disinfection of sewage bacteria at low temperature. Government Reports Announcement 74 (9): 130 (1974).

27. McCarthy, J. J., and Smith, C. H. A review of ozone and its application of domestic wastewater treatment. J. Am. Water Works Assoc. 66: 718 (1974).

28. Friberg, L. Quantitative studies on the reaction of chlorine with bacteria in water disinfection. Acta Pathol. Microbiol. Scand. 38: 135 (1956).

29. Brungs, W. A. Effects of residual chlorine on aquatic life. J. Water Pollut. Control Fed. 45: 2180 (1973).

30. Collins, H. F., and Deaner, D. G. Sewage chlorination versus toxicity—a dilemma? J. ASCE Environ. Eng. Div. 99 (EE6): 761 (1973).

31. Servizi, J. A., and Martens, D. W. Preliminary survey of toxicity of chlorinated sewage to sockeye and pink salmon. Progress Report No. 30, International Pacific Salmon Fisheries Commission, New Westminster, B. C., Canada, 1974.

32. Snoeyink, V. L., and Markus, F. I. Chlorine residuals in treated effluents. Water Sewage Works 121 (4): 35 (1974).

33. White, G. C. Handbook of Chlorination. Van Nostrand Reinhold, New York, 1972.

34. Martens, D. W., and Servizi, J. A. Acute toxicity of municipal sewage to fingerling sockeye salmon. Progress Report No. 29, International Pacific Salmon Fisheries Commission, New Westminster, B. C., Canada, 1974.

35. Stone, R. W., Kaufman, W. J., and Horne, A. J. Long-term effects of toxicity and biostimulants on the water of central San Francisco Bay. California State Water Resources Control Board Publication 51, 1974.

36. Sletten, O. Halogens and their role in disinfection. J. Am. Water Works Assoc. 66: 690 (1974).

37. Burnham, A. K., et al. Trace organics in water—their isolation and identification. J. Am. Water Works Assoc. 65: 722 (1973).

38. Kleopfer, R. D., and Fairless, B. J. Characterization of organic components in a municipal water supply. Environ. Sci. Technol. 6: 1036 (1972).

39. Mullaney, J. L., and Tardiff, R. G. Inventory of organics presently identified in drinking water. I. In: Preliminary Assessment of Suspected Carcinogens in Drinking Water. R. G. Tardiff et al., Eds., Interim Report to Congress. Appendices. EPA, Washington, D. C., June 1975, p. 1.

40. Dowty, B. J., Carlisle, D. R., and Lassiter, J. L. New Orleans drinking water sources tested by gas chromatography-mass spectrometry. Environ. Sci. Technol. 9: 762 (1975).

41. Deinzer, M., Melton, R., and Mitchell, D. Trace organic contaminants in drinking water: their concentration by pressure osmosis. Water Res. 9: 799 (1975).

42. Kopfler, F. C., et al. Extraction and identification of organic micro pollutants—reverse osmosis method. Ann. N. Y. Acad. Sci. 298: 20 (1977).

43. Miller, S. S. Are you drinking biorefractories, too? Environ. Sci. Technol. 7: 14 (1973).

44. Schafer, M. L., et al. Pesticides in drinking water: waters from the Mississippi and Missouri Rivers. Environ. Sci. Technol. 3: 1261 (1969).

45. West, I. Pesticides as Contaminants. Arch. Environ. Health 9: 626 (1964).

46. Suffet, I. H., Brenner, L., and Silver, B. Identification of 1,1,1-trichloroacetone (1,1,1-trichloropropanone) in two drinking waters: a known precursor in haloform reaction. Environ. Sci. Technol. 10: 1273 (1976).

47. Buhler, D. R., Rasmusson, M. E., and Nakaue, H. S. Occurrence of hexachlorophene and pentachlorophenol in sewage and water. Environ. Sci. Technol. 7: 929 (1973).

48. Coleman, W. E., et al. The occurrence of relative organics in five drinking water supplies using GC/MS. In: Identification and Analysis of Organic Pollutants in Water, 1st ed., L. H. Keith, Ed., Ann Arbor Science Publishers, Ann Arbor, Michigan, 1976.

49. Symons, G. E., and Henderson, K. W. Disinfection—where are we? J. Am. Water Works Assoc. 69: 148 (1977).

50. Keith, L. H. Identification and Analysis of Organic Pollutants in Water. Ann Arbor Science Publishers, Ann Arbor,

Michigan, 1976.

51. Owens, E. Private communication to F. Schaumburg, September 1975.

52. Stephenson, M. E. An approach to the identification of organic compounds hazardous to the environment and human health. Paper presented at International Symposium on Chemical and Toxicological Aspects of Environmental Quality, Munich, Germany, September 9, 1975.

53. U. S. International Trade Commission. Synthetic Organic Chemicals, United States Production and Sales. USITC Publication 776, 1974, p. 185.

54. Glaze, W. H., and Henderson, J. E., IV. Formation of organochlorine compounds from the chlorination of a municipal secondary effluent. J. Water Pollut. Control Fed. 47: 2511 (1975).

55. Painter, H. A. Chemical, physical, and biological characteristics of wastes and waste effluents. In: Water and Water Pollution Handbook. Vol. 1, L. L. Ciacco, Ed., Marcel Dekker, New York, 1971, pp. 329-364.

56. Grob, K. Organic substances in potable water and in its precursor. Part 1. Methods for their determination by gas-liquid chromatography. J. Chromatogr. 84: 255 (1973).

57. Novak, J., et al. Analysis of organic constituents present in drinking water. J. Chromatgr. 76: 45 (1973).

58. Donaldson, W. Observations on chlorination tastes and odors. Eng. Contracting Waterworks Monthly, 58: 74 (Nov. 1922).

59. Rook, J. J. Chlorination reactions of fulvic acids in natural waters. Environ. Sci. Technol. 11: 478 (1977).

60. Lee, C. F. Kinetics of reactions between chlorine and phenolic compounds. In: Principles and Applications of Water Chemistry, S. D. Faust and J. V. Hunter Eds., Proc. Rudolfs Res. Conf., 4th, John Wiley, New York, 1967, p. 54.

61. Fritz, J. S. Analyses of drinking water may be in error. Chem. Eng. News 54 (16): 35 (1976).

62. Kissinger, L. D., and Fritz, J. S. Analytical Notes—Analysis of Drinking Water for Haloforms. J. Am. Water Works Assoc. 68: 435 (1976).

63. Stevens, A. A., and Kopfler, F. C. Analyzing drinking water. Chem. Eng. News 54 (26): 5 (1976).

64. Symons, J. M., et al. National Organics Reconnaissance Survey for halogenated organics. J. Am. Water Works Assoc. 67: 634 (1975).

65. Laxen, D. P. H., and Harrison, R. M. The highway as a source of water pollution: an appraisal with the heavy metal lead. Water Res. 11: 1 (1977).

66. Singer, P. C., Lawler, D. L., and Babcock, D. B. Notes and comments. J. Am. Water Works Assoc. 68: 452 (1976).

67. Bellar, T. A., and Lichtenber, J. J. Determining volatile organics at microgram-per-litre levels by gas chromatography. J. Am. Water Works Assoc. 66: 739 (1974).

68. McAuliffe, C. GC determination of solutes by multiple phase equilibration. Chem. Technol. 1: 46 (1971).

69. Mieure, J. P. A rapid and sensitive method for determining volatile organohalides in water. J. Am. Water Works Assoc. 69: 60 (1977).

70. Richard, J. J., and Junk, G. A. Liquid extraction for the rapid determination of halomethanes in water. J. Am. Water Works Assoc. 69: 62 (1977).

71. Garrison, A. W. Analysis of organic compounds in water to support health effects studies. Ann. N. Y. Acad. Sci. 298: 2 (1977).

72. Hahn, W., and Stroh, R. In: Methoden der Organischen Chemie. Vol. 5, Part 3. E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1962.

73. Connick, R. E., and Chia, Y. T. The hydrolysis of chlorine and its variation with temperature. J. Amer. Chem. Soc. 81: 1280 (1959).

74. Moore, E. W. Fundamentals of chlorination of sewage and waste. Water Sewage Works 98: 130 (1951).

75. Ingols, R. S., et al. Bactericidal studies of chlorine. Ind. Eng. Chem. 45: 996 (1953).

76. Pressley, T. A., Bishop, D. F., and Roan, S. G. Ammonia-nitrogen removal by breakpoint chlorination. Environ. Sci. Technol. 6: 622 (1972).

77. Arotsky, J., and Symons, M. C. R. Halogen cations. Quart. Rev. 16: 282 (1962).

78. Berliner, E. The current state of positive halogenating agents. J. Chem. Educ. 43: 124 (1966).

79. Ingold, C. K. Structure and Mechanism in Organic Chemistry. Cornell University Press, Ithaca, N. Y., 1969, Chap. VI.

80. de la Mare, P. B. D., Hughes, E. D., and Vernon, C. A. Mechanism of aromatic halogenation; the chlorine cation, Cl^+. Research (London), 3: 192 (1950).

81. de la Mare, P. B. D., Hughes, E. D., and Vernon, C. A. Reactions of chlorine cations with olefins. Research (London) 3: 242 (1950).

82. de la Mare, P. B. D., Ketley, A. D., and Vernon, C. A. The kinetics and mechanisms of aromatic halogen substitution. Part I. Acid-catalyzed chlorination by aqueous solutions of hypochlorous acid. J. Chem. Soc. 1954: 1290.

83. de la Mare, P. B. D., et al. The kinetics and mechanisms of aromatic halogen substitution. Part VII. Some experiments relating to the halogenation of toluene and t-butybenzene. J. Chem. Soc. 1958: 2756.

84. Derbyshire, D. H., and Waters, W. A. An acid-catalyzed chlorination by means of hypochlorous acid. J. Chem. Soc. 1951: 73.

85. Swain, C. G., and Ketley, A. D. The chlorinium ion as an intermediate in chlorination of aromatic compounds by hypochlorous acid. J. Amer. Chem. Soc. 77: 3410 (1955).

86. Bell, R. P., and Gelles, E. The halogen cations in aqueous solution. J. Chem. Soc. 1951: 2734.

87. Kupinskaya, G. V., and Shilov, E. A. The chlorine cation as an agent for chlorination in an aqueous solution. Dokl. Akad Nauk SSSR 131: 570 (1960); Chem. Abstr. 57: 9711 (1962).

88. de la Mare, P. B. D., and Ridd, J. H. Aromatic Substitution. Academic Press, New York, 1959.

89. Swain, L. G., and Crist, D. R. Mechanisms of chlorination by hypochlorous acid. The last of chlorinium ions, Cl^+. J. Amer. Chem. Soc. 94: 3195 (1972).

90. Shilov, E. A., Kanyaev, N. P., and Otmennikova, A. P. Kinetics of the addition of hypochlorous acid to double bonds. III. Hypochlorous acid and ethylene. J. Phys. Chem. (U.S.S.R.) 8: 909 (1936); Chem. Abstr. 31: 2075 (1937).

91. Shilov, E. A. The chlorine cation as a chlorination agent in aqueous solution. Dokl. Akad. Nauk SSSR 84: 1001 (1952); Chem. Abstr. 46: 9958 (1952).

92. Rosenblatt, D. H. Chlorine and oxychlorine species reactivity with organic substances. In: Disinfection Water and Wastewater. J. D. Johnson, Ed., Ann Arbor Science Publishers, Ann Arbor, Mich., 1975, pp. 249-276.

93. Morris, J. C. The chemistry of aqueous chlorine in relation to water chlorination. In: Proceedings of the Conference on the Environmental Impact of Water Chlorination, R. L. Jolley Ed., Oak Ridge National Laboratory, Oak Ridge, Tennessee, October 22-24, 1975, p. 27.

94. Neale, R. S., and Walsh, M. R. New aspects of the Hofmann-Loeffler N-chloramine rearrangement in acetic acid. J. Amer. Chem. Soc. 87: 1255 (1965).

95. Rosenblatt, D. A., Demek, M. M., and Davis, G. T. Oxidations of amines. XI. Kinetics of fragmentation of triethylenediamine chlorammonium cation in aqueous solution. J. Org. Chem. 37: 4148 (1972).

96. Horner, L., and Podschus, G. (1951). Reply on the above inquiry. Angew Chem. 63: 531 (1951).

97. Meiners, A. F., and Morriss, F. V. The light-catalyzed oxidation of starch with aqueous chlorine. J. Org. Chem. 29: 449 (1964).

98. Morris, J. C. Formation of halogenated organics by chlorination of water supplies (a review). EPA-600/1-75-002, PB-241 511, 1975.

99. Sforzolini, G. S., et al. Decontamination of water contaminated with polycyclic aromatic hydrocarbons (PAH). I. Action of chlorine and ozone on PAH dissolved in doubly distilled and in de-ionized water. Igiene Moderna 66(3): 309 (1974) Translation, Oak Ridge National Laboratory, ORNL-tr-2960.

100. Barnhart, E. L., and Campbell, G. R. Effect of Chlorination on Selected Organic Chemicals. EPA-12020 EXG PB 211-160, March 1972.

101. Shimizu, Y. Plant Phenols and Related Organic Compounds in Public Water Sources, Their Relationship to Chlorination. OWRR-A-041-RI, PB-223 566/1, July 1973.

102. Stoveken, J. Ozone and Chlorine Degradation of Wastewater Pollutants. OWRR-A-017-VT, PB-238 365, June 1974.

103. Shimizu, Y. Plant Phenols and Related Organic Compounds in Public Water Sources, Their Relationship to Chlorina-274, July 1973.

104. Bianchini, J. P., and Gaydoe, E. M. Stereoisomer identification resulting from the addition of hypochlorous, hydrochloric, and hydrobromic acids to di- and tri-substituted allenic hydrocarbons. C. R. Hebd. Seances Acad. Sci., Ser. C; Chem. Abstr. 83: 57910q (1975).

105. Gould, E. S. Mechanisms and Structure in Organic Chemistry. Holt, Rinehart, and Winston, New York, 1959, pp. 790.

106. Liberles, A. Introduction to Theoretical Organic Chemistry. Macmillan Co., New York, 1968.

107. Craw, D. A. The kinetics of chlorohydrin formation. V. The reaction between hypochlorous acid and crotonic acid in buffered solutions at 25° and 35°. J. Chem. Soc. 1954: 2510.

108. Craw, D. A. The kinetics of chlorohydrin formation. VI. The reaction between hypochlorous acid and tiglic acid at constant pH. J. Chem. Soc. 1954: 2515.

109. Zollinger, H. Hydrogen isotope effects in aromatic substitution reactions. Adv. Phys. Org. Chem. 2: 163 (1964).

110. Sharifov, G. S., et al. Effect of the ratio of starting components on the formation of glycerol dechlorohydrins. Khim. Prom. (12) 890 (1975); Chem. Abstr. 84: 73316b (1976).

111. Kiryu, T. β-Methylglycerol dichlorhydrin. Japan. Pat. 72 38,409 (1972); Chem. Abstr. 78: 15495z (1973).

112. Muehlstaedt, M., Shulze, K., and Winkler, G. Production of 1,3-dichloro-2-methyl-2-propanol. J. Prakt. Chem. 317: 166 (1975); Chem. Abstr. 82: 124637a (1975).

113. Carlson, R. M., et al. Facile incorporation of chlorine into aromatic systems during aqueous chlorination process. Environ. Sci. Technol. 9: 674 (1975).

114. Hopkins, C. Y., and Chisholm, M. J. Chlorination by aqueous sodium hypochlorite. Can. J. Res. B24: 208 (1946).

115. Webb, R. G., et al. Current Practices in GC/MS Analysis of Organics in Water. Environmental Protection Agency, Corvallis, Oregon, EPA-R2-73-277, August 1973, p. 91.

116. Keith, L. H. Identification of organic compounds in unbleached treated kraft mill wastewaters. Environ. Sci. Technol. 10: 555 (1976).

117. Morten, A. A. The Chemistry of Heterocyclic Compounds. McGraw-Hill, New York, 1946.

118. Katritzky, A. R., and Lagowski, J. M. The Principles of Heterocyclic Chemistry. Academic Press, New York, 1968.

119. Harrison, R. M., Perry, R., and Wellings, R. A. Chemical kinetics of chlorination of some polynuclear aromatic hydrocarbons under conditions of water treatment processes. Environ. Sci. Technol. 10: 1156 (1976).

120. Harrison, R. M., Perry, R., and Wellings, R. H. Effect of water chlorination upon levels of some polynuclear aromatic hydrocarbons in water. Environ. Sci. Technol. 10: 1151 (1976).

121. Berliner, J. F. T. The chemistry of chloramines. J. Am. Water Works Assoc. 23: 1320 (1931).

122. Fuson, R. C., and Bull, B. A. The haloform reaction. Chem. Rev. 15: 275 (1934).

123. Stevens, A. A., et al. Chlorination of organics in drinking water. J. Am. Water Works Assoc. 68: 615 (1976).

124. Fair, G. M., et al. The behavior of chlorine as a water disinfectant. J. Am. Water Works Assoc. 40: 1051 (1948).

125. Corbett, R. E., Metcalf, W. S., and Sapor, F. G. Studies of N-halogen-compounds. Part IV. The reaction between ammonia and chlorine in aqueous solutions, and the hydrolysis constants of chloroamines. J. Chem. Soc. 1953: 1927.

126. Chapin, R. M. Dichloro-amine. J. Amer. Chem. Soc. 51: 2112 (1929).

127. Chapin, R. M. The influence of pH upon the formation and decomposition of the chloro-derivatives of ammonia. J. Amer. Chem. Soc. 53: 912 (1931).

128. Moore, E. M. Fundamentals of chlorination of sewage and waste. Water Sewage Works 98: 130 (1951).

129. Baker, R. J. Types and significance of chlorine residuals. J. Am. Water Works Assoc. 51: 1185 (1959).

130. Weil, I., and Morris, J. C. Kinetic studies on the chloramines. I. The rates of formation of monochloramine, N-chlormethylamine, and N-chlordimethylamine. J. Amer. Chem. Soc. 71: 1664 (1949).

131. Edmond, C. R., and Sopor, F. G. The mechanism of formation of dialkylchloroamines from hypochlorous acid. J. Chem. Soc. 1949: 2942.

132. Jolley, R. L., et al. Chlorination of organics in cooling waters and process effluents. Proceedings of the Conference on the Environmental Impact of Water Chlorination. Oak Ridge National Laboratory, Oak Ridge, Tennessee, October 22-24, 1975, p. 115.

133. Theilacker, W., and Wegner, E. Organic syntheses using chloramine. In: Newer Methods of Preparative Organic Chemistry. Foerst, W., Ed., Vol. 3, Academic Press, New York, 1964, p. 303.

134. Kovacic, P., Lowery, M. K., and Field, K. W. Chemistry of N-bromamines and N-chloramines. Chem. Rev. 70: 639 (1970).

135. Higuchi, T., Ideda, K., and Hussain, A. Mechanisms and thermodynamics of chlorine transfer among organochlorinating agents. Part III. Autocatalytic pathway between N-chloro succinimide and chloramine-T. J. Chem. Soc. (B) 1968: 1031.

136. Pitman, I. H., et al. Prediction of chlorine potentials of N-chlorinated organic molecules. J. Chem. Soc. (B) 1969: 1230.

137. Higuchi, T., Hussain, A., and Pitman, I. H. Mechanism and thermodynamics of chlorine transfer among organohalogenating agents. Part IV. Chlorine potentials and rates of exchange. J. Chem. Soc. (B) 1969: 626.

138. Dawn, H. S., et al. N-chlorosaccharin as a possible chlorinating reagent: structure, chlorine potential and stability in water and organic solvents. J. Pharm. Sci. 59: 955 (1970).

139. Higuchi, T., and Hasegawa, J. Rate of exchange of chlorine between dimethylchloramine and succinimide. J. Phys. Chem. 69(3): 796 (1965).

140. Crane, C. W., et al. The chlorination of methyldi-2-(chloroethyl)amine and related compounds. J. Chem. Soc. 1946: 827.

141. Ellis, A. J., and Soper, F. G. Studies of *N*-halogeno-compounds. Part VI. The kinetics of chlorination of tertiary amines. J. Chem. Soc. 1954: 1750.

142. Bohme, H., and Krause, W. Zur Kenntnis der Halogenadditionsprodukte tertiärer Amine und ihrer thermischen Zersetung. Chem. Ber. 84: 170 (1951).

143. Sandford, P. A., Nafziger, A. J., and Jeanes, A. Reaction of sodium hypochlorite with amines and amides: a new method for quantitating amino sugars in monomeric form. Anal. Biochem. 42: 422 (1971).

144. Soper, F. G. The rate of transformation of acetyl-chloroaminobenzene into *o*- and *p*-chloroanilides as a measure of the catalytic power of the hydrochloric acid. J. Phys. Chem. 31: 1192 (1927).

145. Pryde, D. R., and Soper, F. G. The interaction of anilides and hypochlorous acid. J. Chem. Soc. 1931: 1510.

146. Mauger, R. P., and Soper, F. G. Acid catalysis in the formation of chloroamides from hypochlorous acid. *N*-Chlorination by hypochlorite ions and by acyl hypochlorites. J. Chem. Soc. 1946: 71.

147. Langheld, L. Uber das Verhalten von α-Aminosauren gegen Natriumhypochlorit. Chem. Ber. 42: 2360 (1909).

148. Wright, N. C. The action of hypochlorites on amino acids and proteins. Biochem. J. 20: 524 (1926).

149. Wright, N. C. The action of hypochlorites on amino acids and proteins. The effect of acidity and alkalinity. Biochem. J. 30: 1661 (1936).

150. Pereira, W. E., et al. Chlorination studies. II. The reaction of aqueous hypochlorous acid with α-amino acids and dipeptides. Biochim. Biophys. Acta 313: 170 (1973).

151. Kantouch, A., and Abdel-Fattah, S. H. Action of sodium hypochlorite on α-amino acids. Chem. Zvesti 25: 222 (1971).

152. Murphy, K. L., Zaloum, R., and Fulford, D. Effect of chlorination practice on soluble organics. Water Res. 9: 389 (1975).

153. Norman, M. F. The oxidation of amino acids by hypochlorite. I. Glycine. Biochem. J. 30: 484 (1936).

154. Greenstein, J. P., and Winitz, M. Chemistry of the Amino Acids, Vol. 2, Wiley, New York, 1961, p. 1318.

155. Wieland, T., et al. In: Methoden der Organischen Chemie, 4th ed. Vol. XI/2, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1958, p. 322.

156. Dakin, H. D. The oxidation of amino acids to cyanides. Biochem. J. 10: 319 (1916).

157. van Tamelen, E. E., Haarstad, V. B., and Orvis, R. L. Hypohalite induced oxidative decarboxylation of α-amino acids. Tetrahedron 24: 687 (1968).

158. Wieland, H., and Bergel, F. Über den Mechanismus der Oxydationsvorgange. VIII. Zum oxydativen Abbau der Aminosauren. Liebigs Ann. 439: 196 (1924).

159. Bergel, F., and Boltz, K. Über die Autoxydation von Aminosaurederivaten an Tierkohle und Hamin. I. Hoppe-Seylers Z. Physiol. Chem. 215:25 (1933).

160. Bergel, F., and Boltz, K. (1933). Autoxydation von Aminosaurederivaten und ihr Abbau durch Ozon. II. Hoppe-Seylers Z. Physiol. Chem. 220: 20 (1933).

161. Bergel, F. Uber die ´Dehydrierbarkeit der α-N-Methylaminoisobuttersaure. Hoppe-Seylers Z. Physiol. Chem. 223: 66 (1934).

162. Herbst, R. M., and Clarke, H. T. Oxidation of amino acids by silver oxide. J. Biol. Chem. 104: 769 (1934).

163. Spenser, I. D., Crawhall, J. C., and Smyth, D. G. Oxidative decarboxylation of amino acids. Chem. Ind. (London) 1956: 796.

164. Johnson, T. B., and Jones, C. O. I. Researches on pyrimidins: some 5-iodopyrimidin derivatives; 5-iodocytosin. J. Biol. Chem. 1: 305 (1905).

165. Soodak, M., Pircio, A., and Cerecedo, L. R. A colorimetric method for the estimation of uracil and cytosine. J. Biol. Chem. 181: 712 (1949).

166. Hayatsu, H., Pan, S. K., and Ukita, E. T. Reaction of sodium hypochlorite with nucleic acids and their constituents. Chem. Pharm. Bull. 19: 2189 (1971).

167. Prat, R., Nofre, C., and Cier, A. Effet de l'hypochlorite de sodium sur les constituants pyrimidiques des bactéries. C. R. Acad. Sci. (Paris) 260 (5): 4859 (1965).

168. Levene, P. A., and LaForge, F. B. Über die Hefe-Nucleinsäure. V. Die Struktur der Pyrimidin-Nucleoside. Chem. Ber. 45: 608 (1912).

169. Visser, D., Dittmer, K., and Goodman, I. The synthesis of 5-chlorouracil and 5-bromouracil nucleosides. J. Biol. Chem. 171: 377 (1947).

170. Fukuhara, T. K., and Visser, D. W. Pyrimidine nucleoside antagonists. J. Biol. Chem. 190: 95 (1951).

171. Banerjee, S., and Tee, O. S. Reinvestigation of the mechanism of bromination of uracil and its *N*-methyl derivatives. J. Chem. Soc. Chem. Commun. 1974: 535.

172. Fukuhara, T. K., and Visser, D. W. Cytidine derivatives. J. Amer. Chem. Soc. 77: 2393 (1955).

173. Wang, S. Y. Chemistry of pyrimidines. I. The reaction of bromine with uracils. J. Org. Chem. 24: 11 (1959).

174. Patton, W., et al. Chlorination Studies. I. The reaction of aqueous hypochlorous acid with cytosine. Biochem. Biophys. Res. Commun. 48: 880 (1972).

175. Jolley, R. L. Chlorine-containing organic constituents in chlorinated effluents. J. Water Pollut. Control Fed. 47 (3): 601 (1975).

176. Jolley, R. L., et al. Determination of Chlorination Effects on Organic Constituents in Natural and Process Waters Using High Pressure Liquid Chromatography. Oak Ridge National Laboratory, FLD: 07D Conf. 751150-2 (1975).

177. Chandelon, Th. Ueber die durch Einwirkung alkalischer Hypochlorite auf Phenol gebildenten Chlorphenole. Chem. Ber. 16: 1749 (1883).

178. Adams, B. A. Substances producing taste in chlorinated water. Water Water Eng. 33(387): 109 (1931).

179. Burttschell, R. H., et al. Chlorine derivatives of phenol causing taste and odor. J. Am. Water Works Assoc. 51: 205 (1959).

180. Lee, G. F., and Morris, J. C. Kinetics of chlorination of phenol-chlorophenolic tastes and odors. Int. J. Air Water Pollution 6: 419 (1962).

181. Ingols, R. S., and Ridenour, G. M. The elimination of phenolic tastes by chloro-oxidation. A suggested explanation of the mechanism of reactions in the chlorination process. Water Sewage Works 95: 187 (1948).

182. Ettinger, M. B., and Ruchhoft, C. C. Effect of stepwise chlorination on taste- and odor-producing intensity of some phenolic compounds. J. Am. Water Works Assoc. 43 (7): 561 (1951).

183. Gess, J. M. Reactions of cresol with aqueous acidic chlorine. Ph.D. Thesis, Syracuse University, 1970. Diss. Abstr. Int. 31: 5258-B (1971).

184. Soper, F. G., and Smith, G. F. The halogenation of phenols. J. Chem. Soc. 1926: 1582.

185. Hine, J. Physical Organic Chemistry, 2nd ed., McGraw-Hill, New York, 1962, pp. 221, 358.

186. Roberts, J. D., and Caserio, M. C. Basic Principles of Organic Chemistry, W. A. Benjamin, New York, 1964, pp. 670, 791.

187. Mueller, H. F., Larson, T. E., and Ferretti, M. Chromatographic separation and identification of organic acids. Anal.

Chem. 32: 687 (1960).

188. Murtaugh, J. J., and Bunch, R. L. Acidic components of sewage effluents and river water. J. Water Pollution Control Fed. 37: 410 (1965).

189. McConnell, G., Ferguson, D. M., and Pearson, C. R. Chlorinated hydocarbons and the environment. Endeavour 34: 13 (1975).

190. Unified Sewerage Agency, Operation and Quality Control Division, Washington County, Oregon. Annual Report, July 1974.

191. White, G. C. Handbook of Chlorination. Van Nostrand Reinhold, New York, 1972.

192. Quarles, J. Environmental Protection Agency. Notice, Domestic Wastewater Disinfection Secondary Treatment. Fed. Register 40 (159): 34524 (August 15, 1975).

193. Quarles, J. Proposed Rule Change (40 CFR Part 133), Environmental Protection Agency, Secondary Treatment Information. Fed. Register 40(159): 34522 (August 15, 1975).

194. National Academy of Sciences–National Academy of Engineering. Water Quality Criteria 1972, U. S. Environmental Protection Agency, Washington, D. C., EPA-R3-73-033 1972.

195. Keller, J. W., Morin, R. A., and Schaffernoth, T. J. Ozone Disinfection pilot plant studies at Laconia, N. H. J. Amer. Water Works Assoc. 66: 730 (1974).

196. Heckroth, C. W. Sonics plus ozone, a winner? Water Wastes Eng. 11 (6): 41 (1974).

197. Kinman, R. N. Water and wastewater disinfection with ozone: a critical review. CRC Crit. Rev. Environ. Control 1975: 141 (Jan. 1975).

198. Environmental Protection Agency. Disinfection of wastewater. Task Force Report, July 1975.

199. Monti, R. P., and Silberman, P. T. Wastewater system alternates: what are they . . . and what they cost. Water Wastes Eng. 11 (5): 40 (1974).

200. Augenstein, H. W. Use of chlorine dioxide to disinfect water supplies. J. Am. Water Works Assoc. 66: 716 (1974).

201. Benarde, M. A., et al. Kinetics and mechanism of bacterial disinfection by chlorine dioxide. Appl. Microbiol. 15: 257 (1967).

202. Hamilton, J. J. Potassium permanganate as a main disinfectant. J. Am. Water Works Assoc. 66: 734 (1974).

203. Murphy, K. L. Gamma radiation as an effective disinfectant. Water and Pollution Control 112 (4): 24 (1974).

204. Ballantine, D. S., et al. The practicality of using atomic radiation for wastewater treatment. J. Water Pollution Control Fed. 41 (Part I): 445 (1969).