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Reaction Products of Chlorine Dioxide

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Concern over the presence of trihalomethanes and other chlorinated by-products in chlorine-disinfected drinking water has led to extensive investigations of treatment options for controlling these by-products. Among these treatment options is the use of an alternative disinfectant such as chlorine dioxide. Although chlorine dioxide does not react to produce trihalomethanes, considerable evidence does exist that chlorine dioxide, like chlorine, will produce other organic by-products. The literature describes chlorinated and nonchlorinated derivatives including acids, epoxides, quinones, aldehydes, disulfides, and sulfonic acids that are products of reactions carried out under conditions that are vastly different from those experienced during drinking water treatment. Evidence is beginning to emerge, however, that some by-products in these categories may be produced. Certain specific volatile aldehydes and halogenated derivatives as determined by the total organic halogen parameter are among those by-products that have been measured.

Introduction

The study of organic compounds in drinking water continues to be of intense interest. Extensive work in this area of drinking water research started with the disclosure of the results of a 1974 study of New Orleans drinking water where source water contaminants were still found in treated drinking water (*1*). At about the same time, a different problem was described in two papers: trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane and bromoform) were found in finished drinking waters, but were not present at detectable concentrations in the source water (*2,3*). Indications were that the trihalomethanes were not typically source water contaminants but were formed during the chlorination/disinfection part of the treatment process.

Because of concern as to the significance of formation of chlorinated organic compounds during the water treatment process, the United States Environmental Protection Agency (USEPA) included the measurement of these four trihalomethanes in its National Organics Reconnaissance Survey (NORS) of drinking water from 80 selected cities (*4*). As a result of analysis of source and finished waters in that study, the occurrence of trihalomethanes in finished drinking water was demonstrated to be widespread and a direct result of the chlorination practice. A multitude of other studies has since confirmed these results. Furthermore, natural humic material was demonstrated to be precursor to trihalomethane formation and is present in virtually all source waters, indicating the ubiquity of the problem wherever chlorination is practiced (*5,6*).

Because of findings concerning the carcinogenicity of chloroform and the confirmation of the ubiquity of chloroform and other trihalomethanes in chlorinated drinking water, the USEPA has promulgated a regulation specifying a maximum contaminant level (MCL) of 0.10 mg/l. of total trihalomethanes (arithmetic sum of weight concentrations of $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$) (*7*). Utilities must use available knowledge and technology to adjust or change treatment processes to reduce higher concentrations to below the MCL.

Three treatment approaches that can be considered for preventing trihalomethanes from reaching the consumer (*8*) are: (a) remove precursor (humic material) before chlorination, (b) remove trihalomethanes after they are formed, and (c) change disinfectant. This paper concerns the third option only, specifically the use of chlorine dioxide as the alternate disinfectant and focusing on the possible influence of this treatment on the chemical contaminants in the finished water.

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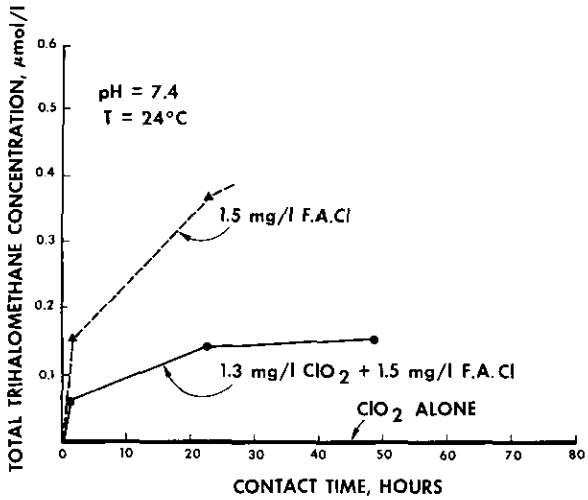

FIGURE 1. Trihalomethane formation in clarified Ohio River water by chlorine dioxide and excess free available chlorine. Data of Miltner (*9*).

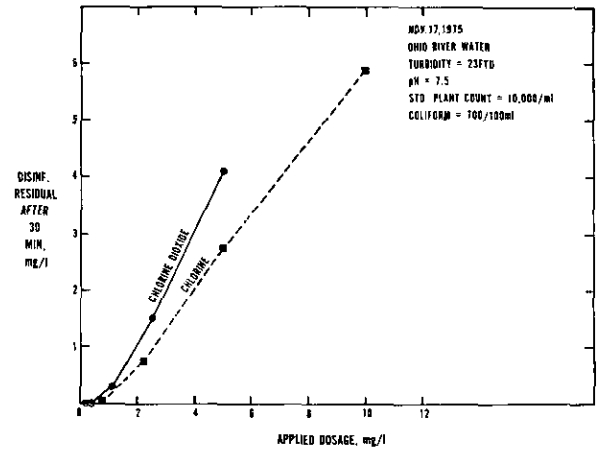

FIGURE 2. Comparison of chlorine dioxide and free chlorine demands for Ohio River water.

Early results of work by Miltner (*9*) to monitor the time dependence of trihalomethane production after chlorine dioxide, chlorine, and chlorine dioxide with chlorine were separately applied to USEPA pilot plant settled water are shown in Figure 1. The upper curve represents the action of chlorine alone; the curve coincident with the abscissa represents the application of chlorine dioxide alone; and the curve between these two represents the action of chlorine to form trihalomethanes in the presence of chlorine dioxide. His results demonstrated two important points: (a) chlorine dioxide did not cause the formation of trihalomethanes at a near neutral treatment pH, although this formation has been reported in one instance to occur at pH 12 (*10*), and (b) chlorine dioxide plus excess chlorine (as is often the case in water treatment) caused formation of lower concentrations of trihalomethanes than the same amount of chlorine alone. Further, other in-house studies, as well as those reported by Roberts et al. (*11*), indicate a yet unexplained decrease in the trihalomethane yield as the ratio of applied ClO_2/Cl_2 increases. Therefore, with consideration only to minimizing trihalomethane formation, chlorine dioxide is a viable alternative to chlorine as a disinfectant in water treatment.

Chlorine dioxide has been widely used in Europe as an alternative to chlorine for drinking water disinfection for some time (*12*). Although these operations are considered successful with regard to disinfection, control of trihalomethanes through the use of chlorine dioxide has not been well documented in most places. The findings reported by Miltner have been borne out, however, at utilities in Hamilton, OH (*13*), Louisville, KY (*14*), Davenport, IA and Peoria, IL (*15*), and Contra Costa, CA (*16*). Consideration must still be given, however, to other by-products that may be formed by chlorine dioxide treatment.

Considerable evidence exists that chlorine dioxide reacts with organic material during water treatment and therefore is likely to produce by-products:

- Because chlorine dioxide is a good disinfectant, some reaction is taking place between the cell components of the organism and the chlorine dioxide.
- Chlorine dioxide is a strong oxidant, and surface waters exhibit a chlorine dioxide demand similar to that for chlorine (Fig. 2) (*8*).
- At applied chlorine dioxide concentrations higher than those in drinking water treatment and under different conditions, identifiable by-products of reactions with various organic materials have been isolated (*17,18*).
- Chlorine dioxide destroys phenolic compounds when the oxidant is used for taste and odor control in water supplies (*19*).
- Most importantly, as was shown earlier, the presence of chlorine dioxide reduces the formation of trihalomethanes by chlorine. This and other evidence obtained by Miltner (*9*) indicates that chlorine dioxide reacts with natural humic acid. This is not at all surprising because chlorine dioxide is used in the paper industry for delignification of wood pulp and is somewhat effective for reducing color in drinking water supplies.

Before an accurate estimate can be made of the relative safety of the two oxidants with regard to

the formation of organic by-products, a detailed investigation and identification of the products formed during disinfection with both chlorine and chlorine dioxide is necessary. The purpose of this paper is to consider briefly the possible organic by-products arising from the use of chlorine dioxide as a disinfectant in drinking water treatment, review available data demonstrating the presence of organic by-products, and briefly discuss the formation of inorganic end products unique to the use of chlorine dioxide. The paper is also intended to be an update of the state of knowledge presented earlier elsewhere (*20*). Presenting the reactions of chlorine dioxide in perspective with the reactions of chlorine when both are applied under the same circumstances is informative.

Organic Reactions of Chlorine Dioxide

Although the literature describing the organic reactions of chlorine dioxide is brief, numerous products of oxidation and chlorination by chlorine dioxide are described. However, the majority of this literature describes chlorinated and nonchlorinated derivatives, including acids, epoxides, quinones, aldehydes, disulfides, and sulfonic acids, that are products of reactions carried out under conditions vastly different from those experienced at water treatment plants. This paper discusses only a few reaction types that are known or suspected to be important in water treatment practice on the basis of some experimental evidence. A more complete review of chlorine dioxide chemistry is available elsewhere (*17,18*). The possible reactions with saturated aliphatic hydrocarbons, olefins, amines, and aromatic compounds (especially phenols) are in the group of likely reactions in dilute aqueous solution. In all examples presented for chlorine dioxide reactions, the authors claimed that the applied chlorine dioxide was free of chlorine or hypochlorite when applied.

Reactions with Saturated Aliphatic Hydrocarbons

No evidence exists that either chlorine dioxide or chlorine undergoes reactions with saturated aliphatic hydrocarbons under water treatment conditions. The question of whether or not free chlorine reacts with saturated aliphatic hydrocarbons in aqueous systems to form chlorinated derivatives frequently arises because of the presence of methane in many groundwaters, and the root name "methane" in "trihalomethane" implies to some that such reactions take place. Such reactions of free halogen with aliphatic hydrocarbons require a free radical mechanism, however, and are improbable in aqueous systems where chlorinated derivatives are formed. The trihalomethane formation can be more readily explained by the classical haloform reaction with methyl ketones. However, the classical haloform reaction is not the complete explanation because certain phenol derivatives, notably resorcinol, do react quite readily with aqueous chlorine to produce chloroform. The relationship of these reactions to those of humic materials with chlorine has been under intense investigation (*21*) and has been reported in part by Johnson (*22*). Reactions of humic materials with chlorine dioxide are discussed in more detail below.

Reactions with Alkenes

Chlorine can react with alkenes by addition across the double bond to produce saturated dichloro derivatives. A more likely course in aqueous systems, however, is to produce chlorohydrins by reaction with hypochlorous acid (*23*).

The reactions of chlorine dioxide with alkenes are apparently very complex and produce a host of chlorinated and nonchlorinated products. Methyl oleate is reported to react at the double bond site to produce aldehydes, the epoxide, chlorohydrin, a dichloro derivative, and α-chloro and α-unsaturated ketones. The aldehyde formation seems to be subject to argument: Leopold and Mutton (*24*) reported aldehyde formation by chlorine dioxide cleavage of the double bond in triolein (the triglyceride of oleic acid), and Lindgren and Svahn (*25*) did not find aldehydes after chlorine dioxide reaction with methyl oleate.

Cyclohexene in aqueous mixture with pure chlorine dioxide has been shown by Lindgren and Svahn (*26*) to produce a similar complex mixture: adipic acid, cyclohexene-3-one, 3-chlorocylohexene, 1,2-epoxycyclohexane, *trans*-2-chlorocyclohexanol, 2-chlorocyclohexanone and *trans*-1,2-dichlorocyclohexane. Note that at least the last three of these products are the same as would be expected from reaction of cyclohexene with chlorine.

Reactions with Amines

Aqueous chlorine and chlorine dioxide react very differently with amines. Chlorine reacts with ammonia and primary and secondary amines to produce the well-recognized chloramines by replacement of hydrogen. Tertiary amines are a special case; their reaction with chlorine produces a chloramine and an aldehyde (*23*). Chlorine dioxide, however, does not react with ammonia and reacts only slowly with primary amines. In general, amines produce the

respective aldehydes upon reaction with chlorine dioxide in the following order of reactivity: tertiary > secondary >primary. Chlorine dioxide does not react with ammonia to form chloramines.

Reactions with Aromatic Compounds

The best known reactions of aqueous chlorine with aromatic compounds in the water treatment field are those that occur with phenols. Chlorine reacts rapidly with phenol to form 2- or 4-mono-; 2,4- and 2,6-di-, and 2,4,6-trichloro derivatives (*23,27*). These compounds are highly odorous and are slowly decomposed by excess chlorine. Other phenolics and substituted aromatics can also be chlorinated. The formation of odorous chlorophenols by chlorine treatment is one of the chief reasons that chlorine dioxide has been used as an alternative in drinking water disinfection applications (*19*).

Chlorine dioxide as usually used in drinking water treatment does not seem to cause formation of odorous compounds with phenol but, through a complex mechanism, forms quinones and chloroquinones, and when in excess, oxalic and maleic acids (*18*). As with alkenes, chlorine substitution in the products, however, is not entirely absent. Chlorine dioxide treatment of phenols can cause chlorine substitution or ring cleavage or both, depending on the particular phenol reacted and the conditions of the reaction. The chlorinated products formed by phenol reaction with chlorine dioxide will generally be of different structure and are either less odorous or are formed in much lower yield than those formed by phenol reaction with chlorine. In other reactions, chlorine dioxide reacts at pH 4 with vanillin to give the nonchlorinated β-formylmuconic acid monomethyl ester. Vanillyl alcohol reacts at low pH to produce both a chlorinated quinone and a nonchlorinated product of ring cleavage. Veratryl alcohol produces 4,5-dichloroveratrole. This is one of the products expected from chlorination of veratryl alcohol (*18*).

Some of the more detailed investigations of the reactions of chlorine dioxide with phenols have been accomplished by Glabisz and by Paluch at the Polytechnic University, Szczecin, Poland. A generalization for the reaction type (ring cleavage or ring retention with or without chlorine substitution) has been given by Glabisz (*28*). Glabisz states that, at least at concentrations of 1 mg/l. and above, reaction products of phenols form two characteristic groups. The first is the group in which the ring structure is retained and the end products are quinones. This group is made up of *p*-dihydric and monohydric phenols that are not *para*-substituted. The second group is characterized by those phenols that undergo ring cleavage to give carboxylic acids as end products. Examples include *para* alkyl phenols and *ortho* or *meta* dihydric phenols.

In general, monohydric phenols reacting with chlorine dioxide undergo chlorination along with oxidation, and those of the first group form the chloroquinones as well as chlorophenols. Glabisz considers this to be somewhat similar to the reaction of chlorine with these phenols. Although chlorine dioxide tends to favor oxidation over chlorination, the relative amounts of chlorinated versus oxidized products depend on the relative amounts of both chlorine dioxide used and phenols present. Excess chlorine dioxide favors oxidation.

Measured Individual Organic Compounds: EPA Studies

Because of the potential for undesirable by-product formation resulting from chlorine dioxide disinfection of drinking water, an in-house investigation was begun at the USEPA Cincinnati laboratory to determine if by-products of the type predicted by the literature (where reactions described were carried out at generally higher concentrations of chlorine dioxide and substrate) would prevail under drinking water disinfection conditions. This work was carried out in two phases: a search of gas chromatographic data for differences in purgeable compounds found in chlorine dioxide-treated and untreated waters, and development and use of a more elaborate analytical scheme, including evaporation under vacuum and derivatization, to detect products of a more diverse nature, specifically those expected from reactions of phenolic compounds.

Results of this work tend to support some of the general conclusions resulting from extrapolation of information in the literature given above.

Phase 1—Aldehydes. Two classes of compounds (amines and alkenes) were discussed earlier that could yield aldehydes as end products of chlorine dioxide oxidation under the proper reaction conditions. Although these aldehydes could react with chlorite (also present) at low pH to produce acids, these reactions should be slow at water treatment pH values.

These observations suggest that if certain organic substrates are present in a source water, chlorine dioxide treatment should cause an increase in the concentrations of the respective aldehydes. Preliminary results of some of our in-house work indicate that this may be occurring. Care must be taken, however, in interpreting the quantitative aspects of these data. These data were extracted from some early screening studies with chlorine dioxide in which gross treatment changes were sought.

The methods used in this phase are well docu-

mented elsewhere and will not be described in detail here. Briefly, the stock solutions of chlorine dioxide were prepared by oxidation of sodium chlorite; chlorine solutions from the pure gas, and standardization of both oxidants were by procedures selected in previous studies by Miltner (*9,29*). GC/MS analysis of reaction mixtures was by the purge-and-trap method exactly as described by Coleman (*30*). Coleman's method limited expected product identifications in this phase to only the most volatile species.

In the first part of the phase 1 study, two gas chromatograph/mass spectrometer (GC/MS) total ion current profiles (TICP) (Fig. 3) were obtained to indicate compounds purged from samples of Ohio River water. One sample had been treated with chlorine dioxide, and the other was untreated. Some compounds appear to be higher in concentration in the treated sample than in the untreated sample, and some new compounds appear in the treated sample. Many of these were identified as aldehydes by their respective mass spectra. Because the chlorinated compounds are present in such large concentrations compared to the aldehydes, apparent changes in aldehyde concentrations can be observed more clearly after additional data manipulation. A fragment ion common to the mass spectra of low molecular weight aldehydes, but not present in the mass spectra of the chlorinated compounds, was selected. The extracted ion current profile (EICP) for this ion, *m/e* 29, was then plotted (Fig. 4) for both treated and untreated river water, and the peaks corresponding to some aldehydes are labeled.

In computerized output GC/MS data, the largest peak in the profile is 100% of full scale, and other peaks are normalized to it. In these EICPs (Fig. 4), peak heights of diethyl ether (which also has an *m/e* 29 fragment) were adjusted to be equivalent, because diethyl ether was assumed not to change in concentration with treatment. The halogenated compounds are not represented in these plots, and the comparatively higher aldehyde peaks in the treated sample are clearly evident.

A similar set of chromatograms was obtained for an untreated source water (Ohio River) and a corresponding chlorinated tap water. The increase in chloroform concentration is obvious from the TICP (Fig. 5). The *m/e* 29 EICP does not show the obvious differences in aldehyde concentrations caused by chlorine dioxide treatment (Fig. 6). Although these samples are not necessarily derived from source water identical to that used in the ClO_2 treatment experiment (above), the results of the chlorination work are typical of those obtained in many replicate chlorination experiments performed over time using Ohio River water as a source.

As mentioned above, caution must be employed before generalizing from these screening studies. If aldehyde formation is considered important, considerably more analytical work is required to obtain

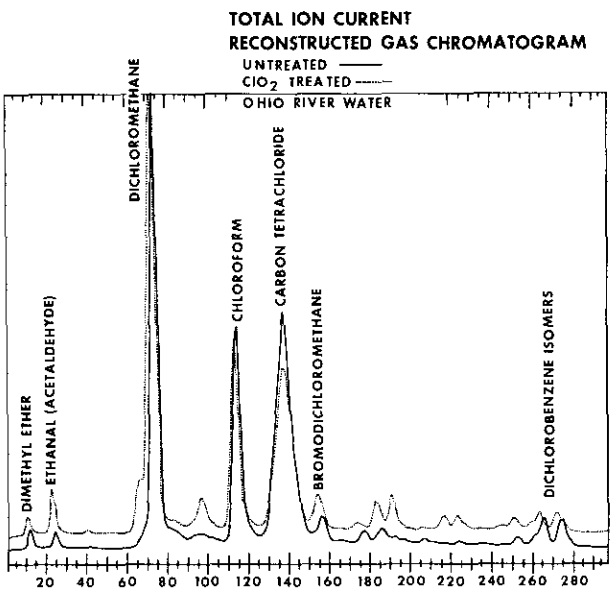

FIGURE 3. Volatile organic compounds in untreated and chlorine dioxide treated Ohio River water detected by GC/MS, total ion current profile.

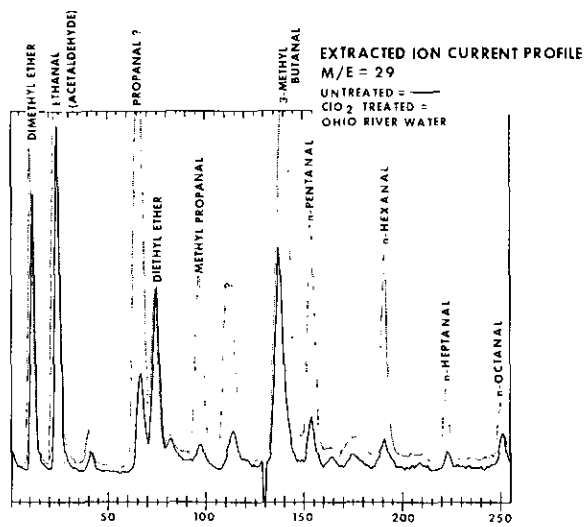

FIGURE 4. Volatile organic compounds in untreated and chlorine dioxide treated Ohio River water detected by GC/MS, *m/e* = 29 extracted ion current output.

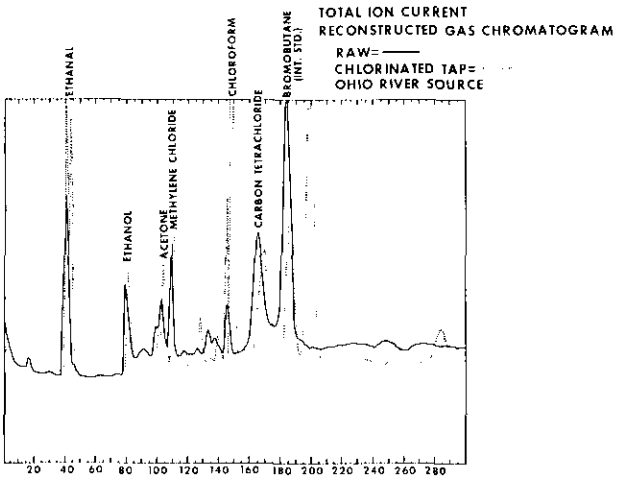

FIGURE 5. Volatile organic compounds in untreated and free chlorine treated Ohio River water detected by GC/MS, *total ion current profile.*

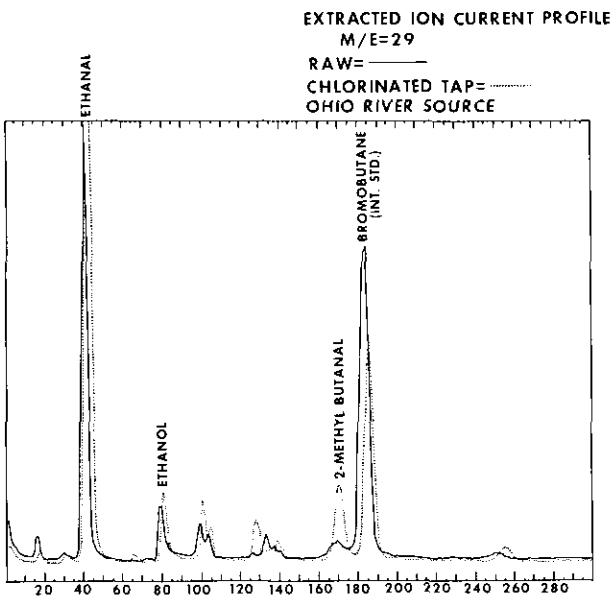

FIGURE 6. Volatile organic compounds in untreated and free chlorine treated Ohio River water detected by GC/MS, *m/e* = 29 extracted ion current profile.

a good quantitative estimation of these compounds and to adequately assess the magnitude and generality of the observed changes.

Phase 2—By-products from Phenol. Phenol was selected as the model compound for the beginning of the second phase primarily because of the supposed polyphenolic nature of humic materials, which are trihalomethane precursors that make up a large fraction of the organic material present in natural waters where trihalomethane formation is a problem (*31*).

Oxidant solutions were prepared for the second phase work in the same manner as for phase 1. After treatment of the phenol solutions, remaining oxidant residuals were chemically reduced with sodium sulfite. Concentrated ethyl ether extracts were chromatographed after treatment with diazomethane. Routine monitoring of reaction mixtures and quantitation of products was by flame ionization detection. Confirmation of identification was by GC/MS analysis of the same extracts. Spectral interpretation and GC retention times were all confirmed by comparison with authentic standards on the same instruments.

In one experiment, phenol was exposed to varying molar ratios of chlorine dioxide. The data (Table 1) show that chlorophenols were produced at low molar ratios (4/5) of chlorine dioxide to phenol. Higher ratios (14/5 and 14/1) did not produce chlorophenols but favored hydroquinone formation. This product distribution with varying oxidant/substrate ratio was expected to some extent based on the literature (*20,28,32,33*). Although odorous chlorophenolic materials can be avoided in drinking water through the use of chlorine dioxide (*18*), the data suggest that this may not occur if insufficient chlorine dioxide is used. Other expected organic by-products such as oxalic and maleic acids, and 2, 6- and 2,5-dichloro-*p*-benzoquinone, discussed earlier, were not immediately identifiable, although total organic carbon concentration data indicated that the phenol was not completely converted to carbon dioxide. To date, no compounds found in the phase 2 experiment nor similar compounds in this category that were not present in the untreated sample have been identified in chlorine dioxide-treated natural waters. Detection limits (calculated as phenol) were estimated to be in the range of 5 to 10 μg/l.

Extensive studies of humic and fulvic acid solutions are currently underway at the University of North Carolina where chlorine dioxide demand and chlorine dioxide degradation experiments are being carried out on aquatic humic materials. Reactions of chlorine dioxide with fulvic acids are apparently slower (or have lower long term oxidant demand) than those of chlorine, and degradation experiments with chlorine dioxide must be carried out initially under conditions designed to "force" the reactions (*34*).

Organic Halogen

Finding individual identifiable species from the chlorine dioxide treatment was not necessarily expected in this work because of the polymeric

Table 1. Products resulting from chlorine dioxide treatment of phenol.

ClO_2/phenol mole/mole[b]	Yield from phenol, %[a]					
	o-Chloro-phenol	Phenol (recovered)	2,4-Dichloro-phenol	*p*-Chloro-phenol	*p*-Hydro-quinone	Total recovery
4/5	11	30	0.3	13	3.6	58
14/5	NF[c]	NF	NF	NF	7.2	7.2
14/1	NF	NF	NF	NF	45	45

[a]Reaction time, 4 hr.
[b]In mg/l., 4/5 = 43.5/75; 14/5 = 150/75; 14/1 = 164/16.
[c]None found.

Table 2. Reaction of humic acid with chlorine and chlorine dioxide.

Oxidant/C ratio, mole/mole	Cl_2/ClO_2 doses, mg/l.	Reaction time, hr	$CHCl_3$, μg/l.	Organic halogen, μg/l. as Cl^-
Cl_2/C				
1/3	3.8	1	39	198
5/3	19.4	1	32	278
ClO_2/C				
1/15	0.75	1	0.4	23
1/3	3.7	2	1.6	52.5

nature of the natural humic material in contrast to the monomeric phenol model. A pyrolysis technique was therefore used to measure the total substituted organic halogen (OX) on these high molecular weight nonvolatile materials (*35–37*). Experimental procedures performed prior to the OX analysis were essentially those referenced or described above. Humic acid solutions were prepared and buffered in the manner described by Stevens et al. (*5,38*). To investigate the possible formation of these higher molecular weight chlorinated species that could not be identified by gas chromatographic techniques, chlorine dioxide was added to humic acid at two different chlorine dioxide to carbon (ClO_2/C) ratios. To compare yields of substituted organic halogen, two reaction ratios with corresponding electron equivalents to chlorine were included in the experiment. That is, the molar ratios 1/15 and 1/3 selected for ClO_2/C correspond to the molar ratios 1/3 and 5/3, respectively, selected for chlorine (Table 2). The basis for this correspondence is that chlorine dioxide reducing to chloride requires five electrons per chlorine atom, whereas chlorine reducing to chloride requires only one electron per chlorine atom. These ratios were selected even though some portions of the chlorine dioxide are typically reduced only to chlorite.

According to the chlorination data (Table 2), with a 1-hr reaction time, the organic halogen yield is much higher than the chloroform yield and increases with chlorine dose, the chloroform concentration remaining essentially constant. Chlorine dioxide produced some (but less) organic halogen and, as expected, an insignificant concentration of chloroform. The trend toward less halogen substitution at the higher ClO_2/C ratio, observed with phenol, was not observed here; this experiment is not definitive, however, because a longer reaction time was allowed at the higher chlorine dose.

Factors influencing organic halogen yields from all disinfectants are currently under careful investigation in the USEPA Cincinnati laboratory. Partial results of these studies at two oxidant doses and 5 mg/l. sodium humate solution are shown in Tables 3 and 4. From Table 3 a general trend to decreasing organic halogen yield with increasing pH at the 10 mg/l. chlorine dioxide dose level at each temperature can be seen. No significant effect of temperature can be seen, probably because these reactions are essentially complete within the 2-hr reaction time (see below). Similar results are shown in Table 4 at the 20 mg/l. chlorine dioxide dose level. Somewhat higher organic halogen yields were observed at the higher chlorine dioxide dose.

In general, the organic halogen by-products of chlorine dioxide treatment were "instantaneously" formed at less than 7% of the maximum formed under similar conditions by chlorine. Concentrations of organic halogen from the chlorine dioxide reaction did not increase with time (up to 160 hr) beyond the initial sampling at 2 hr. This rapid formation of maximum organic halogen concentrations may correspond to the rapid initial oxidant demand reported by Colclough (*34*) also observed in

Table 3. Organic halogen formation with ClO_2 dose of 10 mg/l. to a 5 mg/l. sodium humate solution.

pH	Average organic halogen, μg/l.		
	4°C	20°C	36°C
5.4	26	23	25
7.3	10	10	9
11.5	ND[a]	ND	5[b]

[a]Not detected above blank value.
[b]Two positive of six samples.

Table 4. Organic halogen formation with ClO_2 dose of 20 mg/l. to a 5 mg/l. sodium humate solution.

pH	Average organic halogen, μg/l.		
	6°C	20°C	36°C
5.6	35	40	36
7.5	36	27	25
11.5	8	8	11

Table 5. Inorganic chlorine dioxide by-products.[a]

Species	Initial concentration		Final concentration		ClO_2 demand, %
	mg/l.	mg/l. as Cl^-	mg/l.	mg/l. as Cl^-	
ClO_2	1.5	0.8	0	0	–
ClO_2^-	–	–	0.7	0.4	50
ClO_3^-	–	–	0.4	0.2	25
Cl^-	17.9	17.9	18.1	18.1	25
Totals	–	18.7	–	18.7	100

[a]1.5 mg/l. ClO_2 added to Ohio River water which was coagulated, settled, dual-media filtered. Contact time was 42 hr; pH was 7.1.

these studies; this is in contrast to chlorine reactions, wherein a steady increase in organic halogen concentrations over a period of days is observed (*39*). In all cases, oxidant residual persisted for the duration of the experiment.

Inorganic By-Products

As noted above, when chlorine dioxide reacts with organic compounds to oxidize them, the by-product chlorite (ClO_2^-) is formed. Furthermore, as chlorine dioxide disproportionates in water, both chlorite and chlorate (ClO_3^-) are formed as by-products. The relative proportion of these by-products was determined during a study reported elsewhere by Miltner (*29*), in which 1.5 mg/l. of chlorine dioxide was added to Ohio River water that had been treated in a pilot plant. The data in Table 5 show that approximately 50% of the original chlorine dioxide was converted to chlorite, about 25% to chlorate, and approximately 25% to chloride. Thus, when chlorine dioxide is used as an alternative disinfectant, the health significance of inorganic anions other than chloride (the sole major inorganic by-product of chlorine treatment) must be considered. These inorganic by-products are unique to chlorine dioxide.

Summary

Inspection of the available literature reveals that a detailed investigation of the aqueous organic chemistry of chlorine dioxide and systematic identification of products formed during water disinfection has not been considered. This must be done before an informed assessment can be made of the relative safety of using chlorine dioxide as a disinfectant alternative to chlorine.

Although trihalomethanes are generally not formed by the action of chlorine dioxide, the products of chlorine dioxide treatment of organic materials are oxidized species, some of which also contain chlorine. The relative amounts of species types may depend on the amount of chlorine dioxide residual maintained and the concentration and nature of the

organic material present in the source water. The trend toward lower concentrations of chlorinated by-products with increasing ClO_2 concentration, which was observed with phenols, has not been observed with natural humic materials as measured by the organic halogen parameter. Organic halogen concentrations have been shown to increase with increasing chlorine dioxide dose, but are much lower than those observed when chlorine is applied.

Aldehydes have been detected as apparent by-products of chlorine dioxide oxidation reactions in a surface water that is a drinking water source. Some other nonchlorinated products of chlorine dioxide treatment may be quinones and epoxides. The extent of formation of these moieties within the macromolecular humic structure is also still unknown.

REFERENCES

1. Draft Analytical Report, New Orleans Area Water Supply Study, Lower Mississippi River Facility, Slidell, La. 1974.
2. Rook, J. J. Formation of haloforms during chlorination of natural waters. Water Treat. Exam. 23 (Part 2): 234 (1974).
3. Bellar, T. A., Lichtenberg, J. J., and Kroner, R. C. The occurrence of organohalides in chlorinated drinking water. J. Am. Water Works Assoc. 66: 703 (1974).
4. Symons, J. M., Bellar, T. A., Carswell, J. K., DeMarco, J., Kropp, K. L., Robeck, G. G., Seeger, D. R., Slocum, C. J., Smith, B. L., and Stevens, A. A. National organics reconnaissance survey for halogenated organics. J. Am. Water Works Assoc. 67: 634 (1975).
5. Stevens, A. A., Slocum, C. J., Seeger, D. R., and Robeck, G. G. Chlorination of organics in drinking water. J. Am. Water Works Assoc. 68: 615 (1976).
6. Rook, J. J. Haloforms in drinking water. J. Am. Water Works Assoc. 68: 168 (1976).
7. Federal Register, 44 (No. 231): 68624-68707 (November 29, 1979); 45, No. 49: 15542-15547 (March 11, 1980).
8. Symons, J. M., Stevens, A. A., Clark, R. M., Geldreich, E. E., Love, O. T., Jr., DeMarco, J. Treatment Techniques for Controlling Trihalomethanes in Drinking Water. USEPA, Cincinnati, 1981, EPA-600/2-81-156.
9. Miltner, R. J. The Effect of Chlorine Dioxide on Trihalomethanes in Drinking Water, M. S. Thesis, University of Cincinnati, Cincinnati (1976).
10. Kuhn, W., and Sontheimer, H. Treatment: Improvement or deterioration of water quality. Presented at: Water Supply and Health, Noordwijkerhout, The Netherlands, August 27-29, 1980.
11. Roberts, P. V., Aieta, E. M., Berry, J. D., Chow, B. M. Chlorine Dioxide for Wastewater Disinfection: A Feasibility Evaluation, Technical Report No. 251, Department of Civil Engineering, Stanford University, Stanford, 1980.
12. Miller, W. G., Rice, R. G., Robson, C. M., Scullin, R. L., Kuhn, W. and Wolf, H. An Assessment of Ozone and Chlorine Dioxide Technologies for Treatment of Municipal Water Supplies, U.S. Environmental Protection Agency, Cincinnati, 1978, EPA 600/2-78-147.
13. Augenstein, H. W. Use of chlorine dioxide to disinfect water supplies. J. Am. Water Works Assoc. 66: 716 (1974).
14. Hubbs, S. A., Guers, M., and Siria, J. Plant-scale examination and control of a ClO_2-chloramination process at the Louisville water company. In: Water Chlorination: Environmental Impact and Health Effects, Vol. 3, R. L. Jolley, W. A. Brungs, and R. B. Cumming (Eds.), Ann Arbor Science Publishers, Ann Arbor, Mich., 1980.
15. Blanck, C. A. Trihalomethane reduction in operating water treatment plants. J. Am. Water Works Assoc. 71: 525-528 (1979).
16. Lange, A. A., and Kawczynski, E. Controlling organics - the Contra Costa County Water District. J. Am. Water Works Assoc. 70: 653-659 (1978).
17. Morris, J. C., Christman, R. F., Glaze, W. H., Helz, G. R., Hoehn, R. C., and Jolley, R. L. The chemistry of disinfectants in water: reactions and products. In: Drinking Water and Health, National Academy of Sciences, Washington, D.C., 1980, pp. 139-249.
18. Gordon, G., Kieffer, R. G., and Rosenblatt, D. H. The chemistry of chlorine dioxide. In: Progress in Inorganic Chemistry, Vol. 15, S. J. Lippard (Ed.), Wiley-Interscience, New York, 1972, p. 201.
19. White, G. C. Handbook of Chlorination, Van Nostrand Reinhold Co., New York, 1972, p. 604.
20. Stevens, A. A., Seeger, D. R., and Slocum, C. J. Products of chlorine dioxide treatment of organic materials in water. In: Proceedings-Ozone/Chlorine Dioxide Oxidation Products of Organic Materials, R. G. Rice and J. A. Cotruvo, Eds., Ozone Press International, Cleveland, 1978, p. 383.
21. Christman, R. F., Johnson, J. D., Norwood, D. L., Liao, W. T., Hass, J. R., Pfaender, F. K., Webb, M. R., and Bobenrieth, M. J. Chlorination of Aquatic Humic Substances, U.S. Environmental Protection Agency, Cincinnati, 1981, EPA 600/2-81-016; NTIS Accession No. PB 81-161952.
22. Johnson, J. D. Reaction products of humic substances with chlorine. Environ. Health Perspect. 46: 63-72 (1982).
23. Morris, J. C. Formation of Halogenated Organics by Chlorination of Water Supplies, U. S. Environmental Protection Agency, Washington, D. C., 1975, EPA 600/1-75-002.
24. Leopold, B., and Mutton, D. B. The effect of chlorinating and oxidizing agents on derivatives of oleic acid. Tappi 42: 218 (1959).
25. Lindgren, B. O., and Svahn, C. M. Reactions of chlorine dioxide with unsaturated compounds, II, Methyl oleate. Acta Chem. Scand. 20: 211 (1966).
26. Lindgren, C. O., and Svahn, C. M. Chlorine dioxide oxidation of cyclohexene. Acta Chem. Scand. 19: 7 (1965).
27. Burtschell, R. H., Rosen, A. A., Middleton, F. M., and Ettinger, M. B. Chlorine derivatives of phenol causing taste and odor. J. Am. Water Works Assoc. 51: 205-214 (1959).
28. Glabisz, U. The Reactions of Chlorine Dioxide with Components of Phenolic Wastewaters - Summary, Monograph 44, Polytechnic University, Szezecin, Poland, 1968.
29. Miltner, R. J., Measurement of chlorine dioxide and related products. In: Proceedings, AWWA Water Quality Technology Conference, San Diego, Dec. 6-7, 1976, Am. Water Works Assoc., Denver, 1977, paper 2A-5.
30. Coleman, W. E., Lingg, R. D., Melton, R. G., and Kopfler, R. C. The occurrence of volatile organics in five drinking water supplies using gas chromatography/mass spectrometry. In: Identification and Analysis of Organic Pollutants in Water, L. H. Keith (Ed.), Ann Arbor Science, Ann Arbor, Mich., 1976, p. 305.
31. Christman, R. F., and Ghassemi, M. Chemical nature of organic color in water. J. Am. Water Works Assoc. 58: 723-741 (1966).
32. Dence, C. W., and Sarkanen, K. V. A proposed mechanism for the acidic chlorination of softwood lignin. Tappi 43: 87 (1960).
33. Dence, C. W., Gupta, M. K., and Sarkanen, R. V. Studies on oxidative delignification mechanisms, Part II. Reactions of vanillyl alcohol with chlorine dioxide and sodium chlorite. Tappi 45: 29 (1962).
34. Colclough, C. A., Johnson, J. D., Christman, R. F. Organic reaction products of chlorine dioxide and natural fulvic acids. Proceedings, Fourth Conference on Water Chlorina-

tion: Environmental Impact and Health Effects, October 1981, Pacific Grove, in press.

35. Dressman, R. C., Najar, B. A., and Redzikowski, R. The analyses of organohalides (OX) in water as a group parameter. Proceedings 7th Annual AWWA Water Quality Technology Conference, American Water Works Assoc., Denver, 1980, p. 69.
36. *Takahashi, Y. Analysis techniques for organic carbon and* organic halogen. Proc. EPA/NATO-CCMS-Conference on Adsorption Techniques, (1979), U.S. Environmental Protection Agency, Washington, D.C., in press.
37. Kuhn, W., and Sontheimer, H. Analytic determination of chlorinated organic compounds with temperature-programmed pyrohydrolysis. Wasser 41: 1 (1975).
38. Stevens, A. A., and Symons, J. M. Measurement of trihalomethane and precursor concentration changes occurring during water treatment and distribution, J. Am. Water Works Assoc. 69: 546-554 (1977).
39. *Kuhn, W., and Sander, R. Formation and behavior of polar* organic chlorine compounds. In: Oxidation Techniques in Drinking Water, USEPA, Washington, D.C., 1979; EPA-570-9-79-020; NTIS Accession No. PB 301313/AS, p. 161.