EFFECTIVENESS OF WATER TREATMENT METHODS FOR REMOVAL OF HALOFORMS AND THEIR PRECURSORS

by

Robert Paul Goode

Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE
in
Environmental Sciences and Engineering

APPROVED:

R. C. Hoehn, Chairman

C. W. Randall

P. H. King

March, 1977

Blacksburg, Virginia

LD
5655
V855
1977
G66
C.2

ACKNOWLEDGEMENTS

First and foremost, the author would like to take this opportunity to give thanks and praise to the Lord for providing strength in times of weakness (Philipians 4:13), patience and rest in times of anxiety (Philipians 4:6,7), and most of all for His unsurpassing love (I Corinthians 13).

In addition, the author would like to express his deep and sincere appreciation to Dr. R. C. Hoehn for all his invaluable instruction, guidance, and continuous constructive suggestions; to Dr. P. H. King for serving as a member on the author's committee and his continued encouragement and advice; to Dr. C. W. Randall for serving as a committee member; and to Mr. E. G. Willard for his extremely valuable laboratory assistance.

Special appreciation is extended to Linda, the author's wife, for her excellent typing of this thesis and her unceasing concern, patience, reassurance and prayers, and to Mr. and Mrs. E. T. Goode, the author's parents, and his immediate family for their unyielding support and encouragement.

The writer would like to thank the Virginia State Water Control Board for allowing the opportunity for his continued education with their financial support and to Mr. M. L. Meadows, a previous employee of the same, who was the initiator of this undertaking.

Finally, appreciation is extended to The Carborundum Company for their financial support given to this research by providing

all volatile organics analyses through Dr. Paul Taylor, California Analytical Laboratories and to Westvãco for providing activated carbon.

TABLE OF CONTENTS

		Page
	ACKNOWLEDGEMENTS	ii
	LIST OF FIGURES	vi
	LIST OF TABLES	ix
I.	INTRODUCTION	1
II.	LITERATURE REVIEW	3
	Humic Substances	3
	Humic Acid	3
	Documentation of Formation of Haloforms in Drink Water	9
	Tests for Volatile Organics	15
	Removal of Haloforms and Their Precursors	18
	Health Effects	20
	Future Needs	22
III.	MATERIALS AND METHODS	23
	Glassware Preparation	23
	Stock Solutions Preparations	24
	Testing Apparatus	26
	Color Measurements	26
	Sampling Technique	27
	Treatment Processes	27
IV.	RESULTS AND DISCUSSION	32
	Haloforms in Distilled Water and Simulated Lake Water	32
	Effects of Chlorine Contact Time	36
	Effects of Chlorine Dose and Humic Acid Concentration	41
	Effects of Routine Water Treatment (Coagulation, Flocculation, and Sedimentation)	46
	Effects of Powdered Activated Carbon Pretreatment	47
	Effects of Powdered Activated Carbon Contact Time	53

TABLE OF CONTENTS - Continued

		Page
IV.	RESULTS AND DISCUSSION - Continued	
	Effects of Powdered Activated Carbon Post-Treatment	55
	Effects of Sample Vial Pretreatment on Final Haloform Concentrations	60
V.	SUMMARY AND CONCLUSIONS	66
VI.	RECOMMENDATIONS	69
	BIBLIOGRAPHY	72
	Appendix A: Previous Studies	75
	Appendix B: Test Procedures and Results	82
	Appendix C: Sample Procedures and Analytical Results	112
	VITA	135
	ABSTRACT	

LIST OF FIGURES

Figure		Page
1.	The Structure of the Humic Acid Molecule According to Dragunov, 1948	5
2.	Water Treatment Plant Sampling Points	10
3.	Frequency Distribution of Trihalomethane Data	13
4.	Correlation of Total Trihalomethane and Nonvolatile Total Organic Carbon Concentrations	16
5.	Diagram Showing Scheme for Pretreatment of Distilled Water Used in Preparing Simulated Lake Water for Test Procedures H, J, and K	35
6.	Test Procedure "0" Designed to Evaluate the Contribution of Reactive Organics from Clay	37
7.	Variations in Chloroform ($CHCl_3$) and Chlorine Residuals During the First Four Hours of Contact Time Following Chlorination (with 5 mg/l Chlorine) of Distilled Water Containing Only 1 mg/l Humic Acid. Samples for Haloform Analysis were Dechlorinated at the Time of Collection (Test Procedure E)	39
8.	Variations in Chloroform ($CHCl_3$) and Chlorine Residuals During 96 Hours of Contact Time Following Chlorination (with 5 mg/l Chlorine) of Distilled Water Containing Only 1 mg/l Humic Acid. Samples for Haloform Analysis were Dechlorinated at the Time of Collection (Test Procedure E)	40
9.	Average Rate of Chlorine Uptake Compared to the Apparent Concentrations of Chloroform ($CHCl_3$) in Each Sample (Test Procedure E)	42
10.	Variations in Chloroform ($CHCl_3$) Concentrations with Increasing Concentrations of Humic Acid in the Test Water and Variations in Chlorine Dose. Samples Collected for Haloform Analysis were Dechlorinated after 30 Minutes Contact Time (Test Procedure F)	43

LIST OF FIGURES - Continued

Figure Page

11. A Comparison of Chloroform ($CHCl_3$) Concentrations Attained in Samples Dechlorinated After 30 Minutes Contact with Those in Samples Not Dechlorinated (Test Procedure F) 45

12. Variations in Concentrations of Chloroform ($CHCl_3$) with Varying Doses of Powdered Activated Carbon (PAC) Pretreatment for 30 Minutes Followed by Routine Water Treatment Processes and Post-Chlorination (Test Procedure A, Samples Dechlorinated After 30 Minutes). The Initial Humic Acid Concentration was 1 mg/l 49

13. Variations in Chloroform ($CHCl_3$) Concentrations with Varying Doses of Powdered Activated Carbon (PAC) Pretreatment for 30 Minutes Followed by Routine Water Treatment Processes and Post-Chlorination with 2 mg/l Chlorine. Analytical Differences Between Samples Dechlorinated after 30 Minutes and Those Not Dechlorinated are Shown (Test Procedure A). Water Initially Contained 1 mg/l Humic Acid 50

14. Variations in Chloroform ($CHCl_3$) Concentrations with Varying Doses of Powdered Activated Carbon (PAC) Pretreatment for 30 Minutes Followed by Post-Chlorination (Test Procedure H). Water Initially Contained 3 mg/l Humic Acid 52

15. Variations in Chloroform ($CHCl_3$) Concentrations with Increasing Times of Pretreatment up to Four Hours with 50 mg/l Powdered Activated Carbon (PAC) Followed by Routine Water Treatment and Post-Chlorination with 2 mg/l. Analytical Differences Between Samples Dechlorinated after 30 Minutes and Those Not Dechlorinated are Shown (Test Procedure C). Water Initially Contained 1 mg/l Humic Acid 56

16. Variations in Chloroform ($CHCl_3$) Concentrations with Increasing Times of Pretreatment up to 48 Hours with 50 mg/l Powdered Activated Carbon (PAC) Followed by Routine Water

LIST OF FIGURES - Continued

Figure Page

Treatment and Post-Chlorination with 2 mg/l. Analytical Differences Between Samples Dechlorinated after 30 Minutes and Those Not Dechlorinated are Shown (Test Procedure C). Water Initially Contained 1 mg/l Humic Acid 57

17. Variations in Chloroform ($CHCl_3$) Concentrations in Test Waters after Powdered Activated Carbon (PAC) Pretreatment Following Pre-chlorination with 2 mg/l and Routine Water Treatment Processes (Test Procedure B). Water Initially Contained 1 mg/l Humic Acid 59

18. Variations in Chloroform ($CHCl_3$) Concentrations with Varying Doses of Powdered Activated Carbon (PAC) Applied after Pretreatment with 10 mg/l Chlorine Followed by Routine Water Treatment Processes (Test Procedure J). Test Water Contained 3 mg/l Humic Acid 62

LIST OF TABLES

Table		Page
I.	Elementary Composition (%) of Humic Acids (HA) from Soils and other Sources	7
II.	Distribution of Oxygen in Humic Acids (HA)	8
III.	Trihalogenated Methane Content of Water from Water Treatment Plant	11
IV.	Initial Concentrations of Haloforms in the Distilled Water (DW) Utilized for Preparing the Simulated Lake Water (SLW)	34
V.	Analytical Results of Waters Produced by Test Procedure "O"	38
VI.	Removal of Precursor Material within the Visible Light Spectrum of 420 μm Prior to Chlorination	54
VII.	The Effectiveness of Water Treatment Processes and Post-Treatment with Varying Doses of Powdered Activated Carbon on Haloform Concentrations in Finished Water Samples	61
VIII.	A Comparison of Haloform Concentrations in Water Stored in Sample Vials Previously Washed Before Treatment in a Muffle Furnance and Those Treated Only in a Muffle Furnance	64

I. INTRODUCTION

For many years the American society has consumed the nation's public water supplies with confidence in their quality. However, with the recent findings of carcinogens and suspected carcinogens in drinking water, the "quality confidence" has been subject to question.

The term "volatile organics" has recently created much public concern with increased attention being given by federal authorities (e.g. United States Environmental Protection Agency) and researchers within the field. Volatile organics, especially the trihalogenated methanes (i.e. chloroform, bromoform, bromodichloromethane and dibromochloromethane) have been found in many of the public water supplies throughout the country (1, 2, 3, 4). Many of these compounds are designated as known and suspected carcinogens and have not only been blamed for cancer (5, 6, 7) but also for birth defects (8).

Volatile organics can be briefly defined as those low molecular weight organics which can be stripped from solution by sparging with an inert gas (e.g. helium, nitrogen). Their formation has been linked to chlorination during water treatment of raw water sources containing humic substances (i.e. humic and fulvic acids) (9, 10). The actual formation process has not been satisfactorily determined; however, the increase in trihalogenated methanes has been observed to occur between the time when the raw water enters the treatment process

and when the finished product is ready for consumption (2, 3, 4, 10).

Effective methods for the removal of the trihaloforms and their precursors are currently being sought. Also desired is a better understanding of the formation process of the haloforms as this could lead to a method of their control. Research is presently being expanded in both of these areas.

The research reported in this thesis focused on the effects of various treatment processes (i.e. chemical coagulation and flocculation, powdered activated carbon, and chlorination) on the removal of the precursor (i.e. humic acid) prior to chlorination and volatile organics removal subsequent to chlorination. It was hoped that this research would contribute to current water treatment technology by providing some insight into how best to solve the problem of high concentrations of volatile organics.

II. LITERATURE REVIEW

Humic Substances

Humic substances, which are known to be a precursor to the formation of volatile organics in drinking water (3, 9, 10) are widespread within the earth's environment (11, 12). However, even with their extensive distribution (e.g. soil, surface water, and groundwater), little is known about their origin, synthesis, chemical composition, and reactions.

Schnitzer and Khan (11) and Kononova (13) were quick to point out that most of the soil's organic matter is humic rather than nonhumic substances. Humic material, derived from the decomposition of plant and animal material (11, 13, 14), is leached from the surrounding soil into water where it remains relatively persistent due to its refractive nature.

Humic substances are classified in various ways (11, 13, 14); however, they are usually represented by three major categories: humic acid, fulvic acid, and humins. The humic acid represents the base-soluble fraction that can be extracted (i.e. precipitated) by acidification, whereas fulvic acids are both acid and base soluble. Humin represents the fraction that is insoluble in both dilute acid and base.

Humic Acid

Although it is generally agreed that humic substances originate

from the biological decomposition of plant and animal material, the actual synthesis of humic acids is still not well understood. Felbeck (15) stated four possible ways the formation of humic acids might occur (Appendix A). However, it is not known which hypothesis is more sound or even if they all occur simultaneously.

The fact that humic acids are base-soluble allows for their relatively easy isolation. Schnitzer and Khan (11), Kononova (13), and Weber and Wilson (16) discussed in excellent detail the methods for isolating these acids from soil and water.

Studies by Zamek and Arnold, Fuchs, Tissen and Kürschner, Flaig and Beutelspacher and Mehta, Dubach and Deuel [all cited by Kononova (13)] have provided information to show that the molecular weights of humic acids are highly variable, from several hundred to tens of thousands. Other studies cited by Schnitzer and Khan (11) have shown molecular weights even into the millions.

The complex humic acid is thought to consist of an aromatic ring, nitrogen-containing compounds in the forms of rings and peripheral chains, and possible reducing substances (13). Presently, a tentative model of humic acid is one by Dragunov cited by Kononova (13) (Figure 1). However, other researchers believe that any model proposed would only represent a temporary state (11). The loose structure of the molecule results from the oxygen bridges and other groups (i.e. -NH-, =N-, -S-, and $-CH_2-$) between the structural units.

The determination of functional groups within humic substances can provide information concerning their reactivity, whereas, their

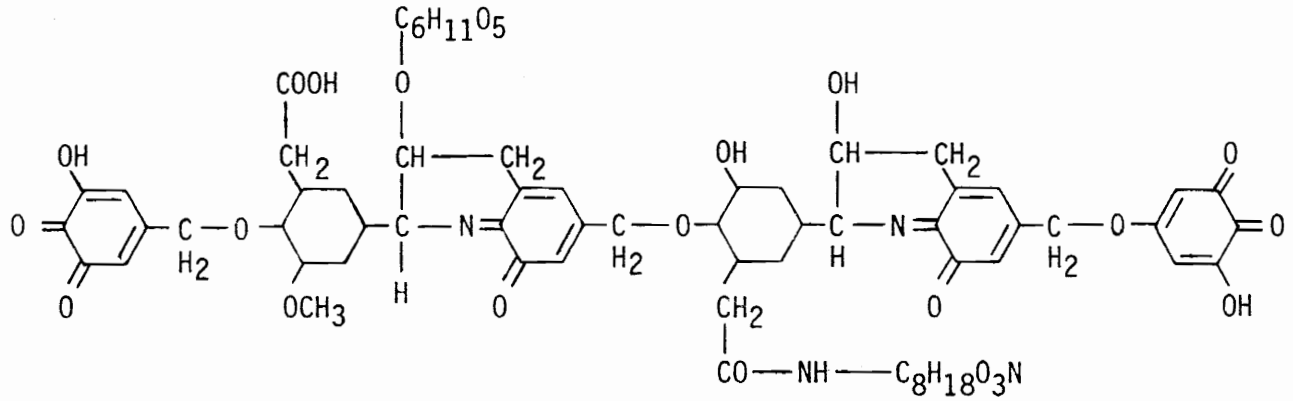


FIGURE 1. The structure of the humic acid molecule according to Dragunov, 1948 (after Schnitzer and Khan, Ref. 11).

complete analyses can yield information regarding their elemental makeup. As can be observed in Table I, the elemental composition of humic acids falls within fairly constant percentages.

Schnitzer and Khan (11) indicated that approximately 20-55 percent of the nitrogen contained within humic substances can be linked with amino acid nitrogen. However, a substantial part of the nitrogen is not released by acid hydrolysis. The unreleased nitrogen is thought to be either adsorbed firmly on or chemically bound to the humic substances.

Also pointed out by Schnitzer and Khan (11) is the fact that most of the oxygen is tied into oxygen-containing functional groups such as carboxyls, alcoholic and phenolic hydroxyls, carbonyls, and methoxyls. The bulk of the oxygen in these functional groups is contained within the carboxyl, phenolic hydroxyl, and carbonyl groups (see Table II).

The complexing of metal ions with humic acids has been discussed in detail by Schnitzer and Khan (11) and Wetzel (14). It has been demonstrated that the carboxyl, phenolic hydroxyl, and possibly the carbonyl and amine groups, take part in the complexing procedure. This complexing nature of humic acids and metal ions will be discussed later in more detail in the section entitled "Removal of Haloforms and Their Precursors."

The absorbance of humic substances within the visible spectrum [400-800 millimicrons (mμ)] generally yields an uncharacteristic spectrum. Schnitzer and Khan (11) indicated that the absorption of humic substances increases with various changes in structure and

TABLE I. Elementary Composition (%) of Humic Acids (HA) from Soils and other Sources (after Schnitzer and Khan, Ref. 11).

C	H	N	S	O
		Soil HA's		
56.4	5.5	4.1	1.1	32.9
53.8	5.8	3.2	0.4	36.8
56.7	5.2	2.3	0.4	35.4
56.4	5.8	1.6	0.6	35.6
60.4	3.7	1.9	0.4	33.6
60.2	4.3	3.6	-*	31.9
		Lake sediment HA		
53.7	5.8	5.4	-*	35.1
		Coal HA		
64.8	4.1	1.2	1.2	28.7
		Biologically synthesized HA's		
54.5	5.1	8.5	-*	31.9

*not determined

TABLE II. Distribution of Oxygen in Humic Acids (HA)
(after Schnitzer and Khan, Ref. 11).

Oxygen (%)	Percent of Oxygen					Percent oxygen accounted for
	Carboxyl	Phenolic OH	Alcoholic OH	Carbonyl	Methoxyl	
			Soil HA's			
32.9	43.8	10.2	13.6	21.4	1.5	90.5
36.8	26.1	24.9	15.2	7.8	-*	74.0
35.4	13.6	38.0	12.7	4.1	-*	68.4
35.6	42.2	24.7	0.9	23.4	-*	91.2
33.6	44.8	17.1	-*	14.8	1.4	78.1
			Coal HA			
28.7	49.1	16.2	-*	-*	9.4	74.4

*not determined

elemental makeup.

For a more in-depth study of the isolation, structure, and reactivity of humic substances, one is referred to Schnitzer and Khan (11) and Kononova (13).

Documentation of Formation of Haloforms in Drinking Water

Johannas J. Rook (9) of the Netherlands, one of the pioneers within the field, released the first major publication concerning the formation of trihalogenated methanes. He found that by passing clean uplands water through peat and chlorinating the extract, trihalogenated methanes were formed, especially chloroform. He postulated that the chlorine would oxidize any bromide in the water to bromine and that this process would enhance the formation of the high molecular weight brominated compounds. He also concluded that humic substances were the precursors and that their polyhydroxybenzene building blocks were responsible for the haloform reaction. Bellar et al. (10) documented the formation of trihalogenated methanes by water treatment processes by analysis of water as it passed through a water treatment plant. Their data showed that a definite increase in haloforms occurred through the plant. Figure 2 and Table III show their sampling points and results. Bellar et al. (10) noted that in comparison to the other trihalomethanes, chloroform was usually produced in the greatest concentration and also presented a possible method of its formation via the oxidation of ethanol. The National Organics Reconnaissance Survey (NORS) team, established by the United States Environmental Protection Agency (EPA), published

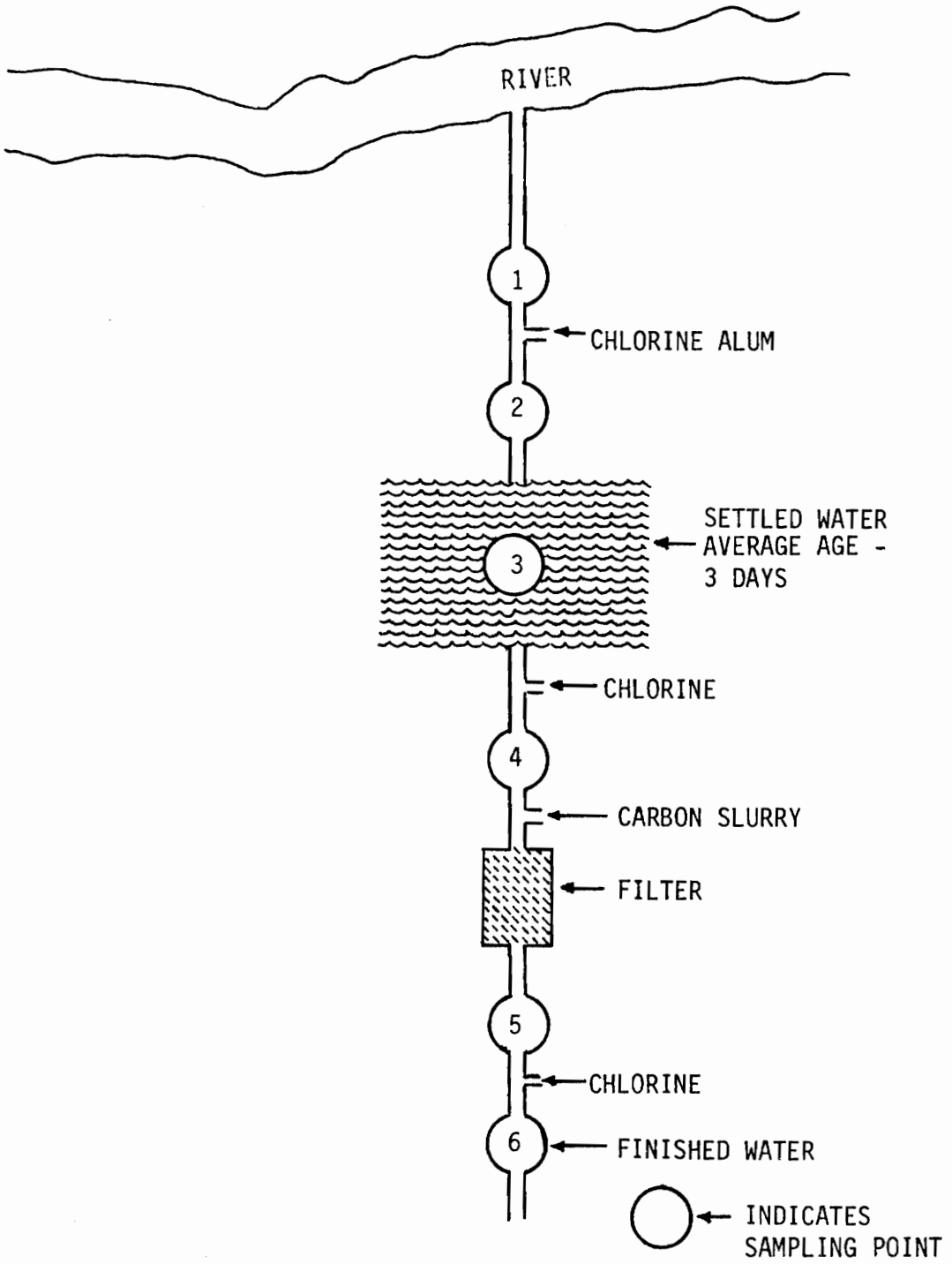


FIGURE 2. Water treatment plant sampling points (after Bellar et al., Ref. 10).

TABLE III. Trihalogenated Methane Content of Water from Water Treatment Plant (after Bellar et al., Ref. 10).

Sample Source	Sampling point	Free chlorine (ppm)	Concentration (ppb)		
			Chloroform	Bromodichloromethane	Dibromochloromethane
Raw river water	1	0.0	0.9	a	a
River water treated with chlorine and alum-chlorine contact time approximately 80 minutes	2	6	22.1	6.3	0.7
3-day-old settled water	3	2	60.8	18.0	1.1
Water flowing from settled area to filters[b]	4	2.2	127	21.9	2.4
Filter effluent	5	Unknown	83.9	18.0	1.7
Finished water	6	1.75	94.0	20.8	2.0

[a]None detected. If present, the concentration is < 0.1 ppb.

[b]Carbon slurry added at this point.

data from their study from which Symons (17) indicated an approximate frequency distribution of trihalomethanes being produced within drinking water supplies which also shows chloroform in the highest concentration (Figure 3).

Harris (5) of the Environmental Defense Fund not only demonstrated the occurrence of organics within the drinking water supply of the City of New Orleans but also tried to link the area's high incidence of cancer to the water supply. In partial response to Harris' findings, Congress passed an amendment [Section 1442 (a)(9)] to the Safe Water Drinking Act (P.L. 93-523). This section directed the Administrator of the EPA to make "a comprehensive study of public water supplies and drinking water sources to determine the nature, extent, sources of and means of control of contamination by chemicals or other substances suspected of being carcinogenic."

In accordance with Section 1442 (a)(9), the EPA conducted a joint federal/state survey of 80 selected water supplies throughout the nation (1, 2, 3). Region V of the EPA also conducted a survey within its jurisdiction of 83 selected water supplies (4). Both studies were conclusive in showing that organics were being formed upon chlorination of the raw water being utilized. Partial results of both EPA studies appear in Appendix A.

The literature (1, 2, 3, 19) mentions other studies that were conducted (some continuing as of November, 1976) to determine the contribution of chlorinated organics from domestic sewage treatment plant and industrial effluents and non-point source runoff. Jolley (18) of the Oak Ridge National Laboratory studied the formation and

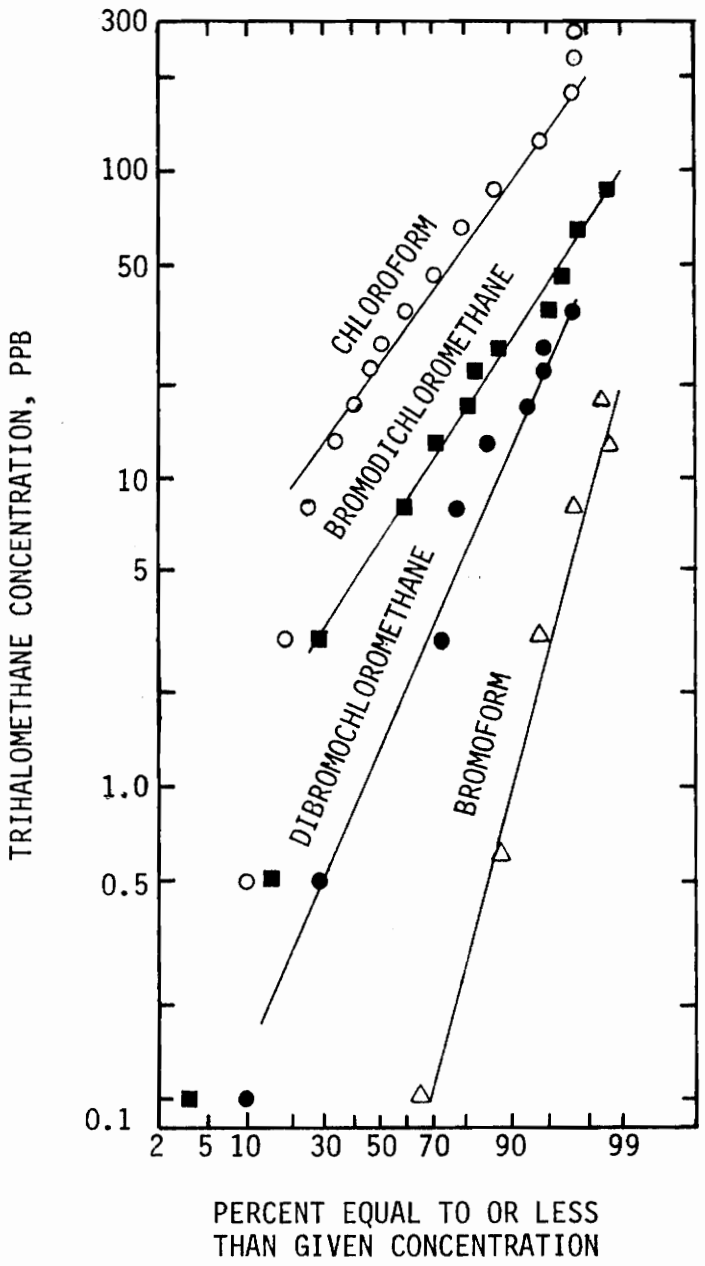


FIGURE 3. Frequency distribution of trihalomethane data (after Symons, Ref. 17).

identification of chlorinated organic compounds produced by the chlorination of domestic wastewater effluents. In addition to Jolley's work, the EPA personnel at the Southeast Environmental Research Laboratory examined the acid fraction of domestic wastewater (1, 3) whereas, Glaze (19) at North Texas State University studied the effects of super chlorination of domestic wastewater. From these studies, the only recognized or suspected carcinogenic compound found in the wastewater plant effluents, which is also found in drinking water supplies, was chloroform. It was noted, however, that the treatment plant effluent that contained chloroform received both domestic and industrial wastes.

The Southeast Environmental Research Laboratory also conducted studies of industrial waste effluents (1, 3). Two suspected carcinogens found in drinking water supplies [chloroform and bis (2-chloroethyl) ether] were also found in chlorinated industrial effluents but not in domestic wastewater effluents. It has been noted, though, that the major source of chloroform within drinking water supplies results directly from chlorination of raw water; it is not present in significant quantities in industrial discharges (3).

The formation of trihalomethanes seems to be dependent on such variable factors as pH, temperature, time, and concentration. Research, especially by Rook (20) and Stevens et al. (21), seems to document this hypothesis.

Many modes of formation of the principal haloforms have been presented, yet, this area still needs to be examined in more detail. As stated, Rook (9) and Bellar et al. (10) gave possible methods for

the formation of trihalomethanes. Stevens et al. (21) concluded that the precursor to haloform production is humic substances but in conjunction with simple, low molecular weight compounds containing the acetyl group. Morris (22) also indicated the acetyl group as one of the possible reaction sites. Rook (20) recently published an article in which he described the formation process via enolization of aromatic rings with two hydroxyl groups in the meta position and cyclohexane rings with a specific configuration.

Tests for Volatile Organics

One principal test currently being utilized for the quantification of organics in drinking water is the Organics-Carbon Adsorbable (O-CA) test. The EPA Office of Toxic Substances (3) lists several advantages and disadvantages to the test and declares that the test's probable major shortcoming is that there is little confidence in its reliability as an index to the toxicity of the drinking water. One interesting disadvantage is that the test does not measure chloroform and some other organics of interest in drinking water! Bellar and Lichtenberg (23) discussed the determination of volatile organic compounds by use of the gas chromatograph. They stated a useful range for the test of from approximately 1 part per billion (ppb) to 2500 ppb with a lower limit of detection of 0.5 to 1.0 ppb for many compounds.

Besides the EPA (3), Cameron et al. (24) indicated the possible potential for the total organic carbon (TOC) test. However, the EPA further stated that many TOC tests are imprecise for measuring

carbon in the 0 to 5 milligrams per liter (mg/l) range, a range typical of finished drinking water. Some instruments capable of detecting TOC in this range must have the samples purged (e.g. nitrogen or helium), a process which removes some of the more important volatile organics (e.g. chloroform). It is noted, however, that not all TOC instruments require purging of the sample prior to analysis (e.g. Beckman Model 915A TOC Analyzer). The nonvolatile, total organic carbon (NVTOC) test also shows some promise; its detection limit is approximately 0.1 mg/l or less (3). Symons et al. (17) presented a graph which showed a fairly linear relationship between the raw water NVTOC concentration and the total trihalomethane (TTHM) concentration produced upon chlorination (Figure 4).

The common tests for organics as the biological oxygen demand (BOD) and the chemical oxygen demand (COD) do not provide the necessary accuracy. The EPA (3) stated that the BOD and COD tests are practically useless as they are inaccurate at low concentrations and measure significant inorganic portions. Besides pointing out precautionary measures to take while sampling for volatile compounds, Leithe (25) indicated that a reliable measure of the total of organic pollutants in the water can be obtained by the COD tests; however, this does not give an idea of elemental composition which is important. Hunter (26) pointed out the fact that the BOD test gives no idea as to the nature of the organic materials. Cameron et al. (24) indicated that the BOD test lacks precision when dealing with small amounts of carbon and the COD test gives fair precision but does not

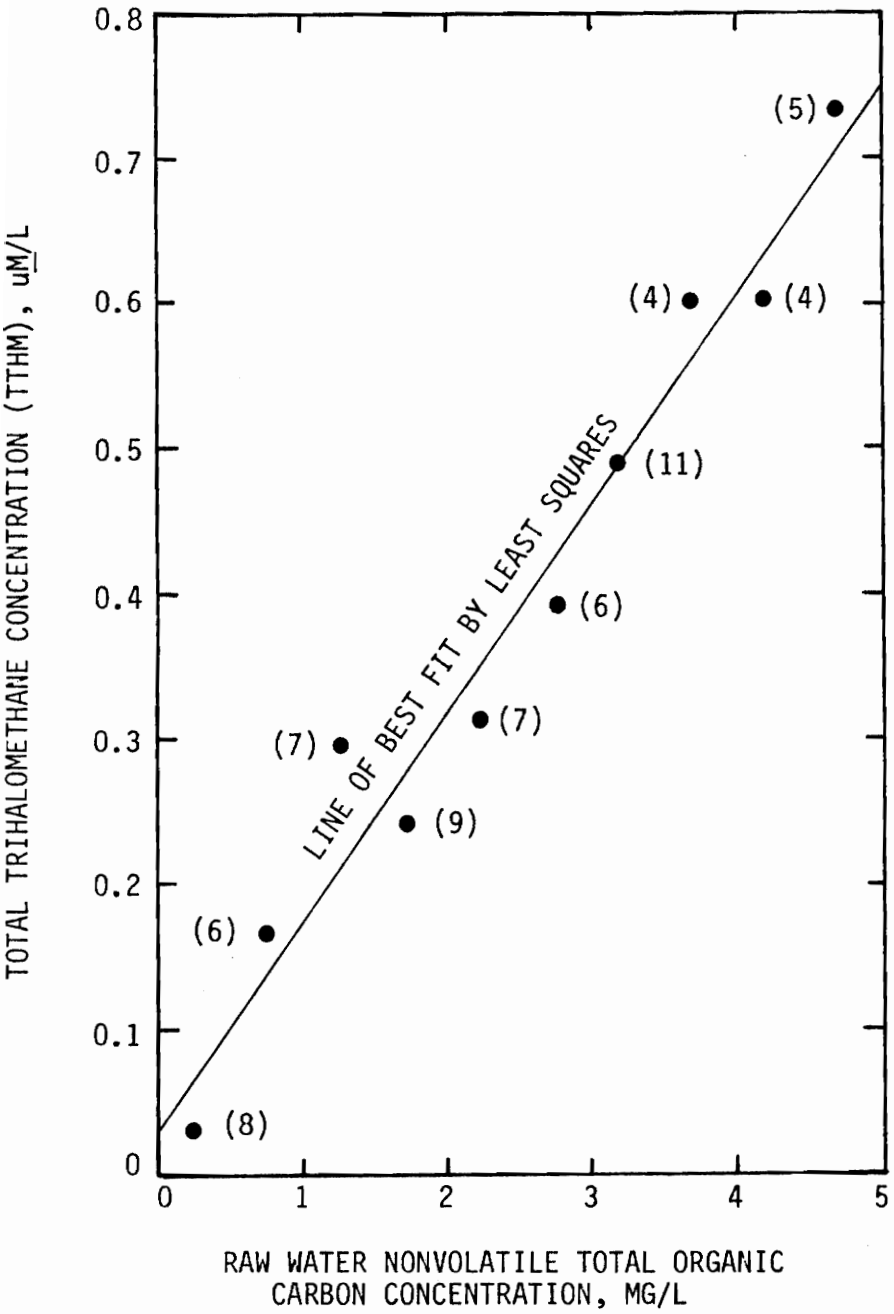


FIGURE 4. Correlation of total trihalomethane and nonvolatile total organic carbon concentrations. (No.) = number of supplies in NVTOC cell; 1 μM/l TTHM = 119 mg/l chloroform if only chloroform present. (After Symons et al., Ref. 17)

oxidize all the organic material.

Other tests referred to by the EPA (3) are the total oxygen demand (TOD), total organic chlorine (TOCl), and ultraviolet absorbance and fluoresence tests. The TOD test, as a surrogate parameter for volatile organics concentrations, is rejected by the EPA for the same reasons given for rejecting the BOD and COD tests. Chlorine-containing organic compounds are detected by the TOCl test, but, the test is incapable of measuring the total amount of organic chlorine in the water. Dobbs et al. (27) discussed the use of ultraviolet absorbance in monitoring the organic content of water. The EPA concluded that ultraviolet absorbance and fluoresence tests are dominated by the aromatic portion of the organics being measured. [The absorbance of humic substances increases with various changes in structure and elemental makeup (e.g. changes in the aromatic portion) (11).] They continued to say that these two tests also exclude chloroform and other low molecular weight chlorinated hydrocarbons.

Removal of Haloforms and Their Precursors

As stated previously, the effects of variables such as pH, temperature, time, and concentration are of extreme importance in the formation of trihalomethanes. The control of one or more of these also could provide the necessary means of efficient removal.

Humic acids can be removed to some extent by coagulation with salts of hydrolyzing metals (12, 20). Ong and Bisque (28) indicated that the effectiveness of various metal salts in coagulating humus

obeys the Schultze-Hardy rule (trivalent ions are more effective than divalent which are more effective than monovalent). They also found that the ferric sulfate was more effective as a coagulant than either ferric chloride or ferric nitrate.

Much of the past and present research in the area of volatile organics in drinking water involves the removal of trihalomethanes and their precursors via activated carbon, especially the granular form. The EPA has a pilot plant for treating unchlorinated Ohio River water for demonstrating how effectively precursor removal can be accomplished with granular activated carbon (GAC).

Besides examining possible methods of lowering the concentration of precursors, Rook (20) investigated haloform removal with GAC. He experienced an early breakthrough of the haloforms (two to three weeks). The EPA is studying the removal of trihalomethanes by passing tap water through GAC columns (3, 29). They found chloroform breakthrough after one month and complete column exhaustion within ten weeks. Medlar (30) contended that prefiltering the water with sand prior to using GAC would extend the carbon life and increase its efficiency; the European practice appears to substantiate this hypothesis. Further continuing studies concerning GAC are set forth in the progress report by Love et al. (29).

The use of powdered activated carbon (PAC) has been utilized in a few studies. The EPA stated that high doses of PAC (i.e. 100 mg/l) are required to remove at least 50 percent of the trihaloform precursors or the formed chloroform. Rook (20) indicated lower doses of PAC (i.e. 20-40 mg/l) for a significant effect on haloform

removal.

Aeration has been utilized for the purpose of stripping the trihalomethanes from the water. Rook's (20) results showed promise for its future use. The EPA, however, indicated that high gas-to-water ratios were required just to strip 50 percent of the chloroform and that future studies would include spray aeration rather than diffused-air aeration.

In studies cited by the EPA (3), the use of ozone for precursor removal did not prove effective. Massive doses (e.g. 350 times the disinfection dose) were required just to accomplish a 30 percent reduction in the trihalomethane precursors.

Health Effects

With the findings of trihalomethanes in drinking water supplies, concern has been raised over the possibility of some of these organics being carcinogenic. Since that time, much controversy has been raised over the idea of whether the organics cause cancer, genetic mutations, or birth defects.

As required by P.L. 93-523, the EPA arranged for a study to be conducted by the National Academy of Sciences (NAS) for the purpose of acquiring health data for setting maximum contaminant levels in drinking waters. The actual conditions of the study are outlined by the EPA in their December, 1975 Report to Congress (3).

In the wake of many claims that there is a link between the trihalomethanes and cancer, Foley and Missingham (31) have suggested that the concentrations in which the haloforms appear should not be

sufficiently high to cause bodily harm. They concluded that no health hazard exists.

The EPA Science Advisory Board prepared a report (32) concerning the organics being found in drinking water supplies and their carcinogenicity. The Board concluded that there exists some health risk from exposure to these organics through drinking water, yet, the actual risk is presently unquantifiable. Other studies are being conducted by the EPA (3) to determine the synergistic effects between the organics and toxicity, mutagenicity, and epidemiology.

Harris (5) of the Environmental Defense Fund made a study of the organics in the drinking water of New Orleans. His conclusion was that there is the possibility that the high incident of cancer in the New Orleans area could be linked to the drinking water; this was highly suggestive and could not be proved. Page et al. (6) published a paper on the Louisiana drinking water which supported the hypothesis of a link between carcinogens in drinking water and cancer mortality.

The Richmond Times Dispatch newspaper (8) printed an article which indicated that there is a possibility of birth defects from the organics within water supplies. "Positive" results were suggested from a study on mice.

One of the latest reports is one by the National Cancer Institute (NCI) (7). The study was definitely conclusive in showing that chloroform induced hepatocellular carcinomas (liver cancer) in mice and kidney tumors in rats. The NCI concluded its report by indicating that the results of the bioassay could not be directly extrapolated

to humans; however, because chloroform was a carcinogen in animals, the possibility of carcinogenicity in humans should not be ignored.

Future Needs

As seen in the literature, very little is presently known about the formation, reactivity, and toxicity of the trihalomethanes. The EPA (3), Morris (22), and Hoehn (33) pointed out many factors which need to be examined in further detail. Continued research is needed on precursor removal methods and on haloform formation and subsequent removal methods (e.g. moving chlorination application point, coagulation, GAC, PAC, ozonation, etc.). Further studies concerning the variable factors of pH, temperature, time, and concentration are necessary to more fully understand their relationships to haloform production and removal. The further examination of the toxicity of the organics is also desirable to determine if there is a real danger and to have a rational basis for setting limits on maximum allowable concentrations.

III. MATERIALS AND METHODS

The experimental procedures utilized in this research provided for various treatment schemes in the formation, reduction, and detection of volatile organics (VO), especially chloroform, within a simulated lake water. Concentrations of calcium hypochlorite [$Ca(OCl)_2$], humic acid, and powdered activated carbon (PAC) were varied along with the contact times of the hypochlorite and PAC and their point of addition within the treatment scheme. After treatment, the water color was analyzed spectrophotometrically and the samples were shipped to California Analytical Laboratory (Sacramento, California) for VO analysis by gas chromatography. Materials and procedures that were used are set forth in this section.

Glassware Preparation

All glassware used in the experimentation procedures, with the exception of the 50-milliliter (ml) sample vials, was cleaned shortly before use to remove organics by washing with hot chromic acid [prepared according to Standard Methods (34)] and rinsing first with tap water and then with distilled water.

The 50-ml glass sample vials (Hypo-Vials; Pierce Chemical Company, Rockford, Illinois) utilized for the study were capped with aluminum foil and placed in a muffle furnace set at 550 degrees Celsius (^{o}C) for approximately 20 minutes (min). This procedure allowed for the destruction or removal of any organic matter that

could possibly interfere with the analytical procedures. Upon removal from the furnace, the vials were immediately transferred to an oven adjusted to 103°C to slow the cooling process (and thus to prevent cracking of an excessive number of vials). After approximately 10-15 min in the oven, the vials, with the aluminum foil still in place, were placed in a desiccator and allowed to cool to ambient air temperature before being used.

A few of the glass sample vials were specially treated first by washing with a detergent (Alconox) and rinsing with tap water followed by distilled water. They were then rinsed with acetone and again with distilled water. Finally, the vials were capped with aluminum foil and treated by firing in a muffle furnace (550°C) as previously described.

Stock Solutions Preparations

Humic acid. Initially, 250 milligrams (mg) of powdered humic acid (supplied by The Carborundum Company) was added to approximately 100 ml of distilled water. Concentrated sodium hydroxide (NaOH) was used to raise the pH in the range of 12 to 14 which allowed the base-soluble humic acid to go into solution. After the humic acid was dissolved, the pH was adjusted to approximately 7.6 with sulfuric acid (H_2SO_4). The volume was then increased to 500 ml with distilled water, resulting in a stock solution of 0.5 mg/ml.

Sodium bicarbonate ($NaHCO_3$). This solution, utilized to provide alkalinity to the simulated lake water, was prepared by dissolving a large quantity of $NaHCO_3$ into distilled water. A 0.02 N H_2SO_4

solution was prepared and standardized as described by Standard Methods (34). One ml of the stock $NaHCO_3$ solution was then added to 999 ml of distilled water and this new solution's alkalinity [as mg/l calcium carbonate ($CaCO_3$)] was then determined as described by Standard Methods (34). Four ml of the stock $NaHCO_3$ solution diluted to one liter with distilled water provided an alkalinity from approximately 120-125 mg/l as $CaCO_3$.

Calcium hypochlorite. A stock solution of $Ca(OCl)_2$, the chlorinating agent, was prepared by placing a weighed portion of $Ca(OCl)_2$ [65 percent chlorine (Cl_2)] into a volumetric flask and diluting with distilled water. The stock solution was prepared to yield approximately 1 mg/ml chlorine as tested by amperometric titration.

Potassium ferrocyanide $K_4Fe(CN)_6$. The solution of $K_4Fe(CN)_6$, the dechlorinating agent, was prepared by adding six grams of $K_4Fe(CN)_6$ to a 200-ml volumetric flask. The flask was then filled to the 200-ml mark with distilled water to provide a solution concentration of 30 mg/ml.

Ferric sulfate $Fe_2(SO_4)_3$. The coagulating agent utilized in jar test procedures was $Fe_2(SO_4)_3$. The stock solution was prepared fresh daily by placing two grams of $Fe_2(SO_4)_3$ into a 200-ml volumetric flask and then filling with distilled water to the 200-ml mark. This solution provided 10 mg/ml.

Powdered activated carbon. One gram of PAC (Westvāco WV-G) was diluted to 100 ml in a volumetric flask. This suspension provided 10 mg/ml carbon.

Simulated lake water. This was prepared by adding to distilled water the desired volumes of humic acid solution (usually to provide 1 mg/l humic acid), $NaHCO_3$ solution to provide an alkalinity of approximately 120-125 mg/l as $CaCO_3$, and modeling clay (Stewart Clay Company, Inc.) to provide a turbidity from 25-30 nephelometric turbidity units (NTU) as measured by the Hach Turbidimeter Model 2100A.

In a few experiments, the distilled water used to prepare the simulated lake water was first treated with pulverized, granular activated carbon (GAC) [granular WV-G through a USG Standard Testing Sieve No. 200 (75 μm)] for about four hours. Afterwards, the treated water was filtered through a 0.45 μm Millipore filter.

Testing Apparatus

During the course of the research, coagulation and flocculation was carried out with a Phipps and Byrd jar test apparatus. The parameters measured included temperature, pH (Corning Scientific Instruments, Model 7), alkalinity [according to Standard Methods (34)], turbidity (Hach Turbidimeter Model 2100A), absorbance (Perkin-Elmer Double Beam Spectrophotometer, Coleman Model 124), and chlorine residual (Fischer-Porter Amperometric Titrator). The VO analysis was done according to the method described by Bellar and Lichtenberg (24); the replicability was approximately 1.0-2.0 ppb. Results for each individual treatment procedure appear in Appendix B.

Color Measurements

Using platinous cobalt chloride, various color concentrations were made according to Standard Methods (34). These samples were read on

the spectrophotometer for the purpose of being able to correlate a color unit to the various absorbance readings taken for humic acid concentrations. The graph showing this relationship appears as Appendix Figure B-1.

Sampling Technique

Just prior to collecting a sample for VO analysis, the aluminum foil was removed from the mouth of the glass 50-ml sample vial. The vial was then slowly filled to the neck with the sample and tapped against the desk to assure a bubble-free sample. Next, the vial was filled to overflowing so that a convex meniscus formed at the top. A Teflon-coated disc was carefully placed over the opening of the vial (Teflon side down); this displaced the excess sample. The aluminum cap was then placed over the disc and neck of the vial and tightly crimped with a crimping tool. Samples, after sealing by these procedures, were completely free of head space; however, a small bubble would form during refrigeration. (All samples were refrigerated at 2-3°C.) Prior to shipping to California, the vials were wrapped, placed into styrofoam shipping containers and packed in wet ice.

Treatment Process

The various treatment processes utilized in this study are briefly described in the following paragraphs. For a specific flow diagram of the treatment procedure, refer to Appendix B. In all cases, background samples were taken to determine if any VO were initially present.

Treatment procedure A. This procedure was used to evaluate the effects of VO precursor (i.e. humic acid) removal by pretreatment of the test water with varying doses (0-200 mg/l) of PAC. The effectiveness of the treatment was determined by the amount of VO formed in the PAC-treated samples by varying doses of chlorine (1-5 mg/l) after the completion of routine water treatment procedures.

Simulated lake water was first treated with varying doses of PAC for a period of 30 min while being stirred at 80 revolutions per minute (rpm) in the jar test apparatus. Next, the water was coagulated with $Fe_2(SO_4)_3$ (50 mg/l), flocculated, and settled. The decanted water was passed through a Reeve Angel grade 934 AH glass fiber filter in a Büchner funnel and separated into three parts and chlorinated with varying doses. After a 30-min contact time, all but one of the samples were dechlorinated with $K_4Fe(CN)_6$. The samples were then put into the vials, sealed, and refrigerated at 2-3°C.

Test procedure B. After prechlorinating the simulated lake water, the removal of the resulting VO was evaluated by applying varying PAC doses (0-200 mg/l) to the treated test water. Organic removal would be noted by the amount of VO found after treatment.

The simulated lake water was first prechlorinated with 2 mg/l chlorine and allowed a contact time of 30 min. The water was then coagulated [50 mg/l $Fe_2(SO_4)_3$], flocculated and settled. Equal volumes of decanted water were placed in vessels and one aliquot was dechlorinated. Varying doses of PAC were then added to each aliquot and allowed a 30-min contact time while stirring. After a designated contact time, the samples were passed through a 0.45 μm Millipore

filter to remove the carbon and then bottled, sealed, and refrigerated.

Test procedure C. By this treatment scheme, the effects of a single dose of PAC (50 mg/l) for varying contact times (up to 12 hours) on precursor removal were evaluated.

In this scheme, the simulated lake water was pretreated with PAC; however, the contact time for the carbon was varied. After a specified contact time, the water was coagulated [50 mg/l $Fe_2(SO_4)_3$], flocculated, settled, and passed through a Reeve Angel grade 934 AH glass fiber filter in a Büchner funnel. The water was then chlorinated with 2 mg/l chlorine and allowed a 30-min contact time. After treatment, two samples were collected, one was dechlorinated, and both were put into vials, sealed, and refrigerated.

Test procedure E. This experimental procedure was designed to demonstrate the influence of chlorine contact time on VO production.

A large jar of simulated lake water, which was devoid of clay, was dosed with 5 mg/l chlorine. Samples, which were taken over a time period of 10 min to 96 hours, were dechlorinated, placed in the vials, sealed, and refrigerated.

Test procedure F. The influence of varying concentrations of humic acid (0.25-3.0 mg/l) was examined by this test. The effects would be determined by the quantity of VO formed after treatment with varying doses of chlorine (1-5 mg/l).

Varying concentrations of humic acid were added to water containing only $NaHCO_3$. The water was then divided into three portions, chlorinated with different concentrations, and allowed a 30-min contact time, after which time all but one of the samples were dechlorinated. Samples were placed in vials, sealed, and refrigerated.

Test procedure H. In this test, the effects of varying PAC doses (0-200 mg/l) on precursor removal were evaluated.

Specially treated distilled water (PAC-treated) was used to prepare the simulated lake water, which contained 3 mg/l humic acid. Individual samples were treated with varying concentrations of PAC for 30 min while stirring at 80 rpm. After carbon treatment, each sample was coagulated [80 mg/l $Fe_2(SO_4)_3$], flocculated, settled, decanted, and divided into two equal parts. One part was chlorinated with 2 mg/l chlorine and the other with 10 mg/l chlorine. Both were allowed a 30-min contact time. The samples were then placed in vials, sealed, and refrigerated at 2-3°C. They were not dechlorinated.

Test procedure J. The effect of varying doses of PAC (0-100 mg/l) on prechlorinated and treated simulated lake water was examined by this testing procedure.

Distilled water (PAC-treated) was used to prepare the simulated lake water containing 3 mg/l humic acid. The water was then prechlorinated with 10 mg/l chlorine and allowed a 30-min contact time. Afterwards, the water was coagulated [80 mg/l $Fe_2(SO_4)_3$], flocculated, and settled. Varying doses of PAC were then added to

the decanted water and allowed a 30-min contact time while mixing at 80 rpm. After the proper contact time, the sample was divided and one half was dechlorinated. The split samples were passed through a 0.45 μm Millipore filter by gravity into the sample vials. When full, the vials were sealed, and refrigerated.

Test procedure K. With this test, the effects of chlorine dose on the production of VO in a sphagnum peat moss extract were examined.

Sphagnum peat moss was allowed to soak in distilled water (PAC-treated) to allowed for the extraction of humic and fulvic acids. The extract was then passed through a 0.45 μm Millipore filter to remove particulate matter. The concentrate was then added to more carbon-treated, distilled water until an absorbance equivalent to that of a 3 mg/l humic acid solution was obtained. Two samples of the water, which contained an approximate equivalent of 3 mg/l humic acid, were treated with 5 mg/l and 10 mg/l chlorine, respectively. After a 30-min contact time, the samples were placed in the vials without first being dechlorinated, sealed, and refrigerated.

IV. RESULTS AND DISCUSSION

The main objectives of this research were to study the effects of various treatment processes and their respective placement in the treatment scheme on the removals of both the precursors of volatile organics in the simulated lake water (i.e. containing humic acid) and the volatile organics themselves after they were formed following chlorination. In this chapter, the results of the individual tests are presented and discussed. Appendix Table B-I presents a description of the individual tests and Appendix Table C-I presents the results of the haloform analyses for the samples associated with each test. These test results are presented sequentially as they were performed during the course of this project. However, in the following sections, the results and discussion are presented according to the type treatment applied to evaluate one or more specific conditions.

Haloforms in Distilled Water and Simulated Lake Water

A major problem, discovered near the end of this project, was that the distilled water used in preparing the simulated lake water (i.e. distilled water plus bicarbonate, clay, and humic acid) contained from 19 to 26 parts per billion (ppb) chloroform ($CHCl_3$) with an average of 22 ppb. However, after the simulated lake water was prepared, concentrations remaining ranged from 2 to 9 ppb (average 6 ppb), a phenomenon attributed to losses by volatilization and,

possibly, by adsorption to the clay. Table IV shows the analytical results of samples of the distilled water and simulated lake water.

An attempt was made to remove the haloform contamination from the distilled water used in preparing the simulated lake water for test procedures H, J, and K by treating it with powdered activated carbon (PAC). The treatment scheme is shown in Figure 5. Aliquots designated Sample 1 and Sample 2 in the figure (sample series "Z", Appendix C) contained, respectively, 2 and 32 ppb $CHCl_3$, indicating that while the haloform concentration could be reduced by the treatment, some reactive organic remained that would yield high concentrations of haloform upon chlorination. It is possible that the act of stirring the water for four hours, and not PAC-treatment, caused the loss (by volatilization) of the $CHCl_3$. Another possible reason for the high $CHCl_3$ concentration in the chlorinated sample is that the membrane filters contributed a reactive organic. However, tests on other samples taken during the course of this project were not filtered yet did not contain lesser concentrations of haloforms. Therefore, it was surmised that the distilled water contained a substance that could react with chlorine to yield $CHCl_3$. The only problem created by the presence of this unknown organic substance was that it made it difficult to assess the exact levels of $CHCl_3$ caused specifically by the reactions of chlorine on the various humic acid concentrations used in the test waters throughout this study. The assumptions were made that the chlorine-reactive organic that yielded $CHCl_3$ was present in all experiments and that its presence did not invalidate comparisons of the results involving the

TABLE IV. Initial Concentrations of Haloforms in the Distilled Water (DW) Utilized for Preparing the Simulated Lake Water (SLW) and in the SLW Itself.

Sample Number	Concentration of Chloroform (ppb)	Concentration of Bromodichloromethane (ppb)
AO-1 (DW)	21	-
AO-2 (SLW)	9	-
AO-3 (SLW)	5	-
BO-1 (SLW)	7	-
BO-2 (SLW)	6	-
CO-1 (SLW)	2	-
CO-2 (SLW)	5	-
EO-0 (DW)	19	1
FO-1 (DW)	26	3
OO-1* (SLW)**	8	-

*can be compared with sample EO-1 as this was the same distilled water utilized to prepare this sample

**contained no humic acid

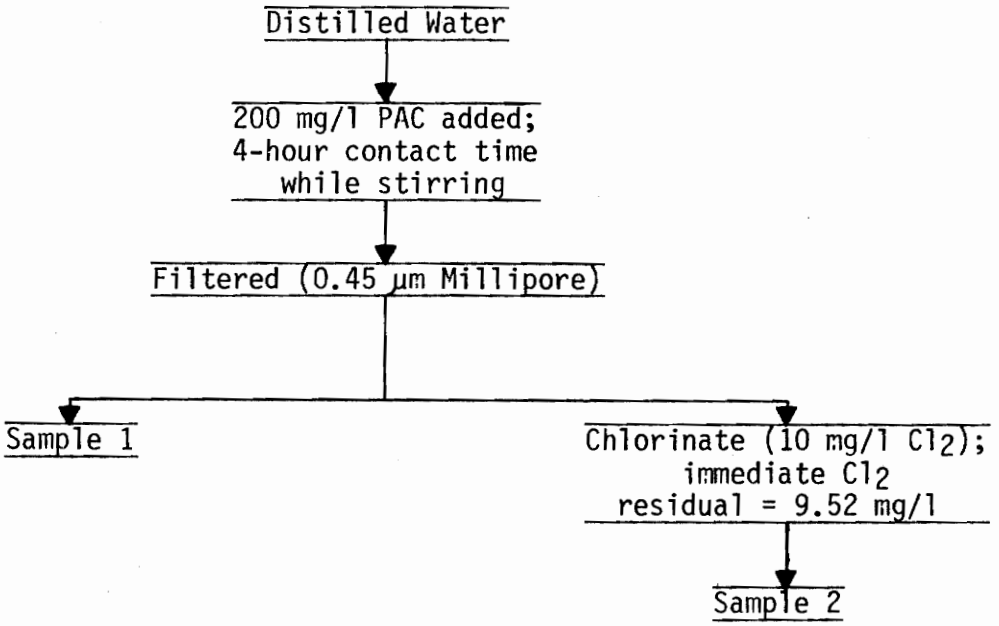


FIGURE 5. Diagram showing scheme for pretreatment of distilled water used in preparing simulated lake water for test procedures H, J, and K (see Appendix C). (Test Procedure Z)

various treatment schemes used throughout the study.

An additional test (designated "O-Series") was designed to determine if there was a contribution of reactive organics, which could have resulted in the formation of haloforms, by the clay used in preparing the simulated lake water. Figure 6 is a schematic of the treatment, and Table V shows the results of analytical tests performed. It is obvious from the results that the clay did not contribute significant quantities of organics, if any, which upon chlorination would yield $CHCl_3$. In fact, the difference of 6 ppb between the two samples was much less than that observed when the distilled water, chlorinated and unchlorinated, was analyzed (32 and 2 ppb, respectively, in sample series "Z", Appendix C).

Throughout the study, the pH and temperature of the test waters remained relatively constant. (See Appendix B.) Rook (20) and Stevens et al. (21) identified these as variables that can influence haloform production.

Effects of Chlorine Contact Time

Test procedures designated "E" were designed to evaluate the effects of chlorine contact time on volatile organics production. Results of this experiment are shown in Figures 7 and 8. Figure 7 shows the data collected during the first four hours of the chlorine contact period, and it can be seen that the production of $CHCl_3$ is quite rapid within the first 30 minutes. It should be noted that initially the $CHCl_3$ concentration in the test water was quite high (19 ppb) and the rapid production of $CHCl_3$ may have resulted from the

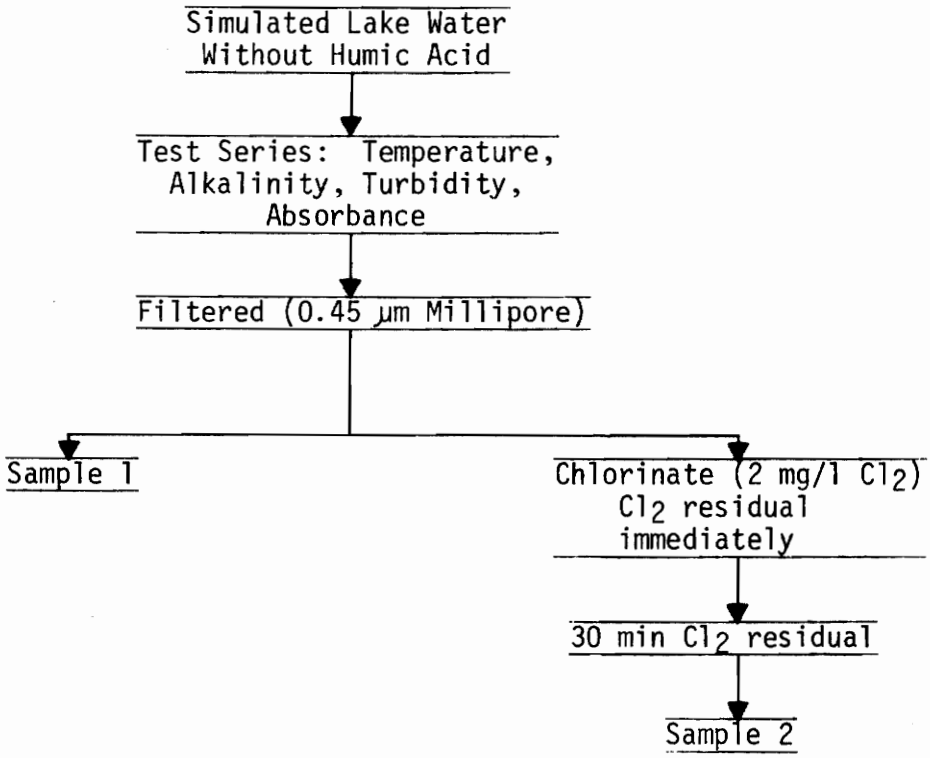


FIGURE 6. Test Procedure "O" designed to evaluate the contribution of reactive organics from clay.

TABLE V. Analytical Results of Waters Produced by Test Procedure "O".

Parameters	Sample Number	
	00-1	00-2
Temperature (^{o}C)	23	28
Alkalinity (as mg/l $CaCO_3$)	128	128
Turbidity (NTU)	27	27
Absorbance @ 420 mμ (filtered through 0.45 μm Millipore)	0.019	0.019
Cl_2 residual (mg/l)	NA	2.19
30 min Cl_2 residual (mg/l)	NA	1.88
$CHCl_3$, ppb	8	14

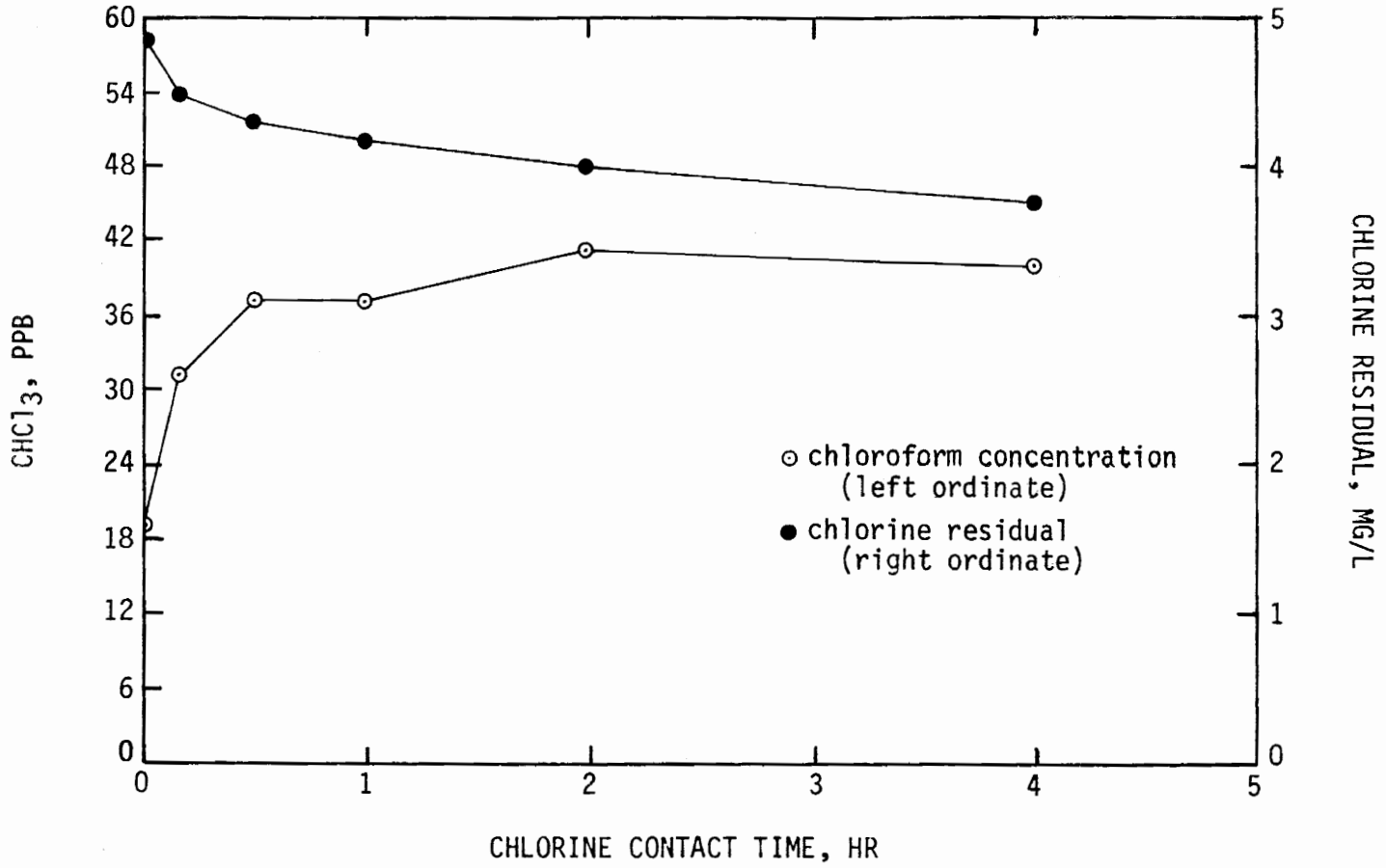


FIGURE 7. Variations in chloroform ($CHCl_3$) and chlorine residuals during the first four hours of contact time following chlorination (with 5 mg/l chlorine) of distilled water containing only 1 mg/l humic acid. Samples for haloform analysis were dechlorinated at the time of collection (test procedure E).

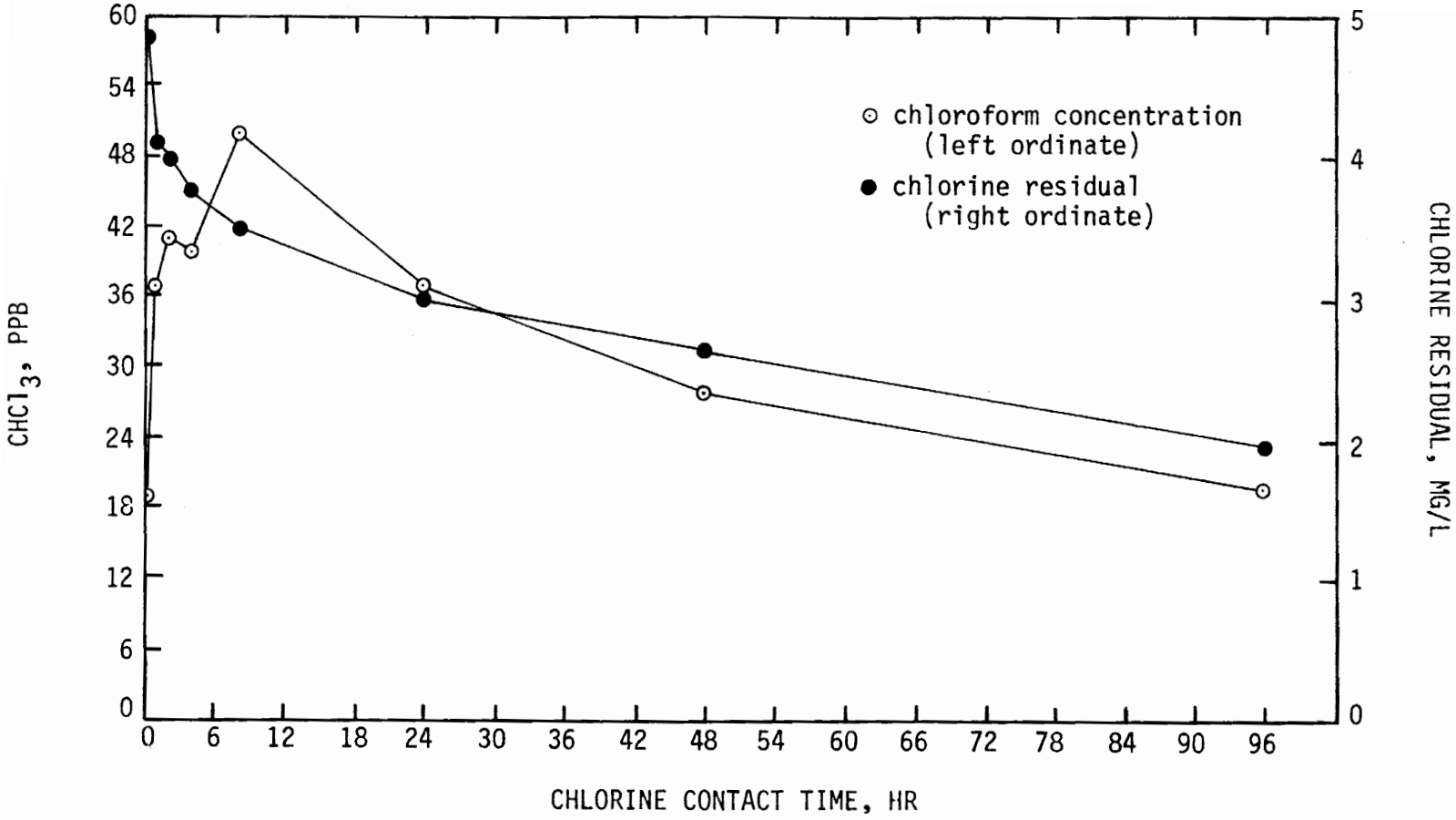


FIGURE 8. Variations in chloroform ($CHCl_3$) and chlorine residuals during 96 hours of contact time following chlorination (with 5 mg/l chlorine) of distilled water containing only 1 mg/l humic acid. Samples for haloform analysis were dechlorinated at the time of collection (test procedure E).

reaction of chlorine with the unidentified organic present in the distilled water rather than with the humic acid. However, as will be shown later, increasing the humic acid concentration does increase the level of $CHCl_3$ production upon chlorination.

Figure 8 shows that the peak $CHCl_3$ concentration (50 ppb) was observed eight hours after chlorination, though the maximum may actually have been attained between 6 and 24 hours. The jar in which the tests were conducted was left exposed to the atmosphere during the contact period, so it is likely that the losses observed beyond eight hours were a result of volatilization of the $CHCl_3$. It is possible that some of the $CHCl_3$ formed during the first eight hours was lost by volatilization and that the observed maximum concentration would have been higher had the samples been contained in air-tight vessels.

Note from Figure 8 that throughout the test period, considerable chlorine remained, indicating that the apparent rates of $CHCl_3$ production were caused by the difference in availability of chlorine-reactive sites on the humic acid molecules that result in $CHCl_3$ production. This phenomenom is illustrated by Figure 9, though the reason for the sudden increase in the apparent $CHCl_3$ concentration at eight hours is not known. It is possible that some unidentified factor affected the relative rates of production and loss from the system to cause the apparent increase at that time.

Effects of Chlorine Dose and Humic Acid Concentration

Figure 10 shows the effect of increasing chlorine doses on the

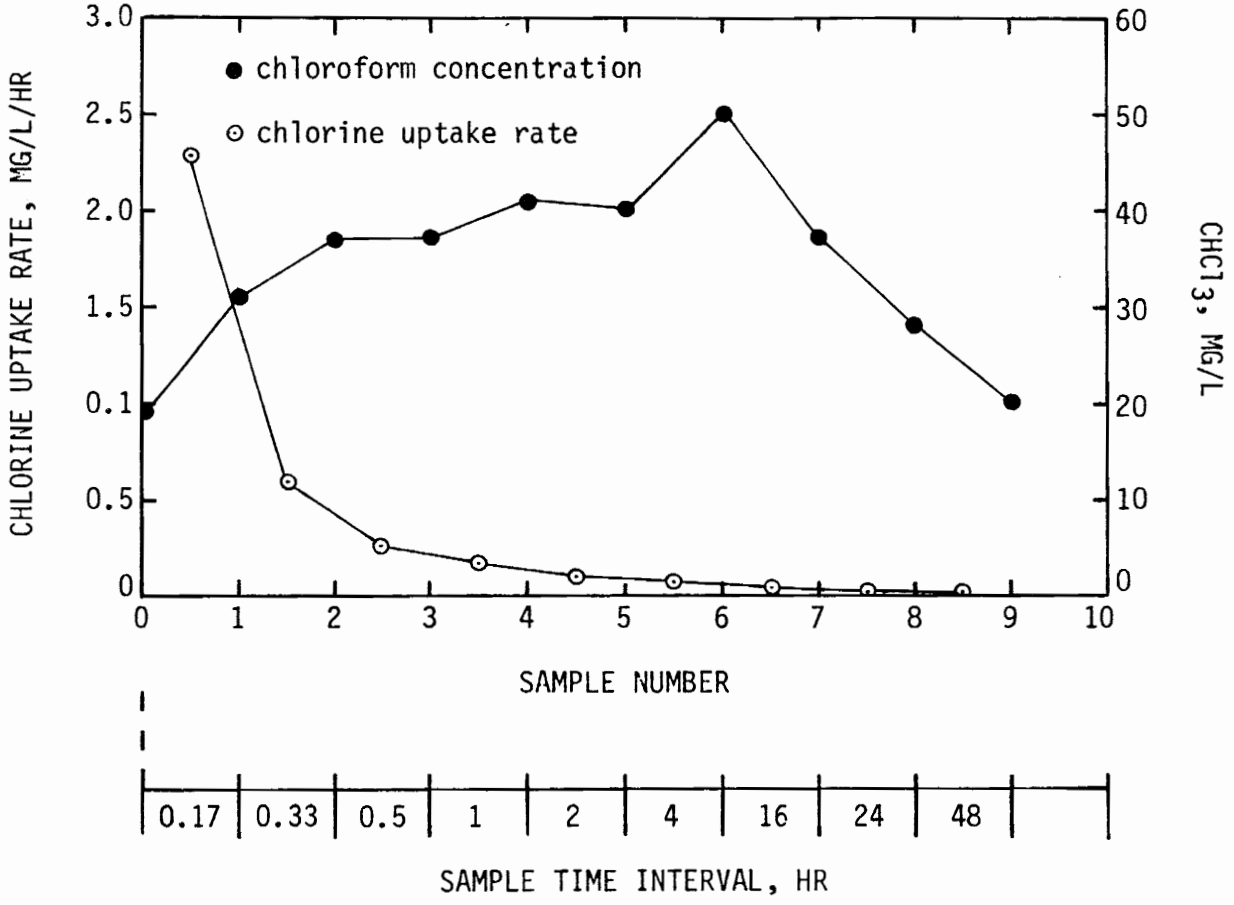


FIGURE 9. Average rate of chlorine uptake compared to the apparent concentrations of chloroform ($CHCL_3$) in each sample (test procedure E).

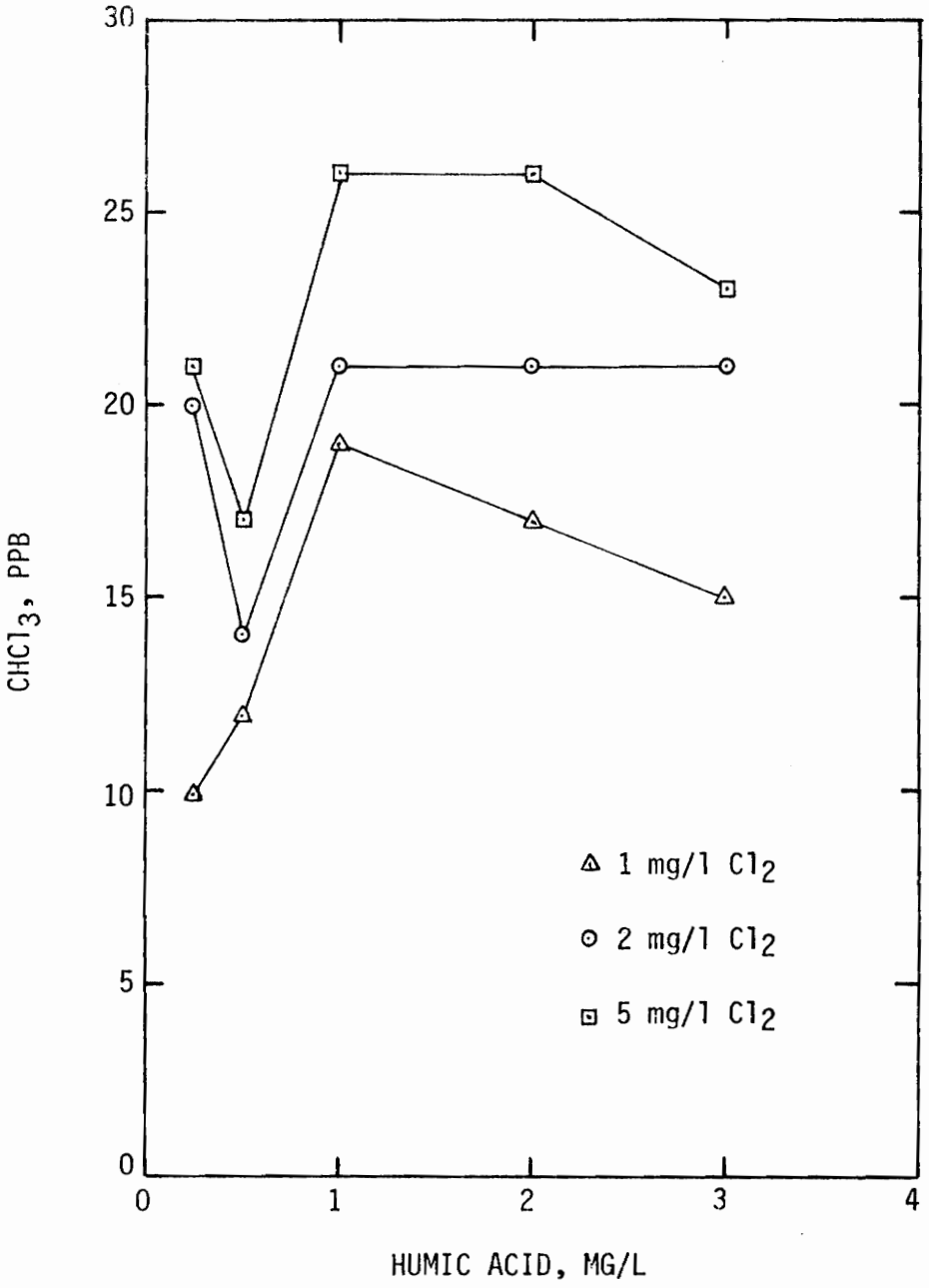


FIGURE 10. Variations in chloroform ($CHCL_3$) concentrations with increasing concentrations of humic acid in the test water and variations in chlorine dose. Samples collected for haloform analysis were dechlorinated after 30 minutes contact time (test procedure F).

production of $CHCl_3$ in water containing varying quantities of humic acid (test procedure F). The maximum humic acid concentration in these tests was 3 mg/l. Waters containing more were impossible to coagulate. The data indicate that a significant increase in $CHCl_3$ concentration occurred at all chlorine levels when the humic acid concentration was varied from 0.5 to 1.0 mg/l. The higher $CHCl_3$ concentrations observed for samples containing 0.25 mg/l humic acid and chlorinated with 2 and 5 mg/l chlorine, respectively, cannot be readily explained. Perhaps the more significant feature of Figure 10, however, is that the $CHCl_3$ concentrations that developed in waters containing a fixed humic acid concentration varied directly with the chlorine dose. This observation is not surprising, however, as the kinetics of chemical reactions predict that the concentrations of products vary proportionally with the concentrations of the reactants.

It is also known that many reactions are time-dependent, and Figure 11 shows that to be true in the haloform-production reactions. Additional samples collected during test procedure F (just discussed) for haloform analysis were not dechlorinated before storage and subsequent shipment to the analytical laboratory. Several weeks elapsed before the samples were analyzed, and it is assumed that the haloform-production reaction had reached completion. The data clearly show that a 30-minute contact time is insufficient to produce maximum concentrations of $CHCl_3$. The time to reach maximum, as indicated by data just presented (Figure 8, e.g.), probably is between 6 and 24 hours.

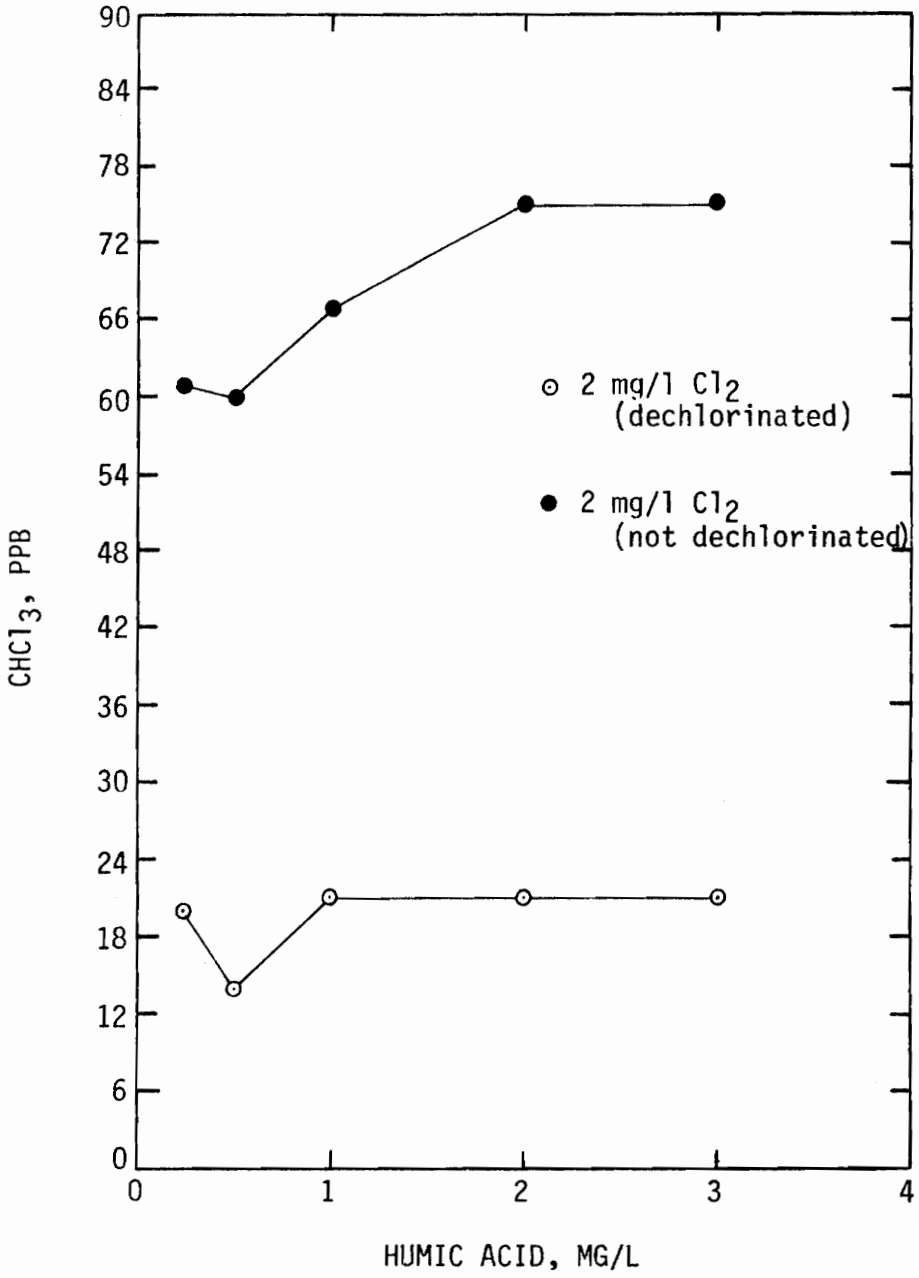


FIGURE 11. A comparison of chloroform ($CHCl_3$) concentrations attained in samples dechlorinated after 30 minutes contact with those in samples not dechlorinated (test procedure F).

In one test (Procedure K, Appendices B and C), a water extract of peat moss was substituted for the commercially available humic acid. The test water was prepared by diluting the extract with distilled water until the absorbance was equivalent to that produced by 3 mg/l humic acid. Treatment of two portions, with 5 and 10 mg/l chlorine (without dechlorination) produced, respectively, 98 and 209 ppb $CHCl_3$ and 2 and 6 ppb $CHBrCl_2$ (bromodichloromethane). Obviously, the nature of the carbon source influences the absolute magnitude of the volatile organics concentration.

The phenomenon of increased haloform production with increasing chlorine dose in samples containing the same humic acid concentration was observed in all tests where these conditions prevailed [experimental series A, F, H, and J (Appendices B and C)]. The significance of these data from a practical point of view is that when prechlorination is practiced in a water treatment plant, it usually is with sufficient dosages to carry a residual through the entire treatment process. As the quality of surface waters deteriorates, there usually is more organic matter present and the prechlorination dose necessarily is increased. If a nominal treatment time is eight hours, sufficient time is available to permit the development of substantial concentrations of $CHCl_3$. Bellar et al. (10) observed this phenomenon in a water treatment plant they studied.

Effects of Routine Water Treatment (Coagulation, Flocculation, and Sedimentation)

Results of several experiments that were part of different

series of tests in this study can be examined to demonstrate the effectiveness of coagulation [with $Fe_2(SO_4)_3$ in this instance] followed by flocculation and sedimentation. Two samples, H1-2 and J1-2, both initially contained clay and 3 mg/l humic acid. Sample J1-2 was chlorinated with 10 mg/l chlorine and did not undergo any further routine treatment while sample H1-2 was post-chlorinated with the same dose after routine water treatment processes. Neither sample was dechlorinated prior to shipment to the laboratory for analysis. Sample J1-2 contained 256 ppb $CHCl_3$, 5 ppb $CHBrCl_2$, and 1 ppb $CHBr_2Cl$ (dibromochloromethane), while sample H1-2 contained only 37 ppb $CHCl_3$ and 1 ppb $CHBrCl_2$, 85 percent less haloforms produced just through the use of routine water treatment processes.

A comparison between samples E0-2 and A1-4, which contained only 1 mg/l humic acid also is possible. Sample E0-2 was chlorinated with 5 mg/l chlorine while sample A1-4 received the same chlorine dose only, in this case, as a treatment following coagulation, flocculation, and sedimentation. In both these tests, the chlorine contact time was restricted to 30 minutes, and the samples were dechlorinated after that time. The analyses showed that sample E0-2 contained 37 ppb $CHCl_3$ and 1 ppb $CHBrCl_2$, while sample A1-4 contained only 8 ppb $CHCl_3$, 79 percent less haloforms again just by routine water treatment processes.

Effects of Powdered Activated Carbon Pretreatment

Powdered activated carbon (PAC) was used as an initial treatment

for haloform-precursor removal in three test series--A, C, and H. In these tests, carbon treatment was followed by coagulation, flocculation, and settling, then chlorination. Unfortunately, no samples for haloform analyses were taken between the times when PAC and coagulant were added. Therefore, there is no precise measure of how well the PAC performed alone in reducing precursor concentration. However, evaluations of PAC performance can be made if it is assumed that the effectiveness of the routine water treatment process in all tests was the same. This evaluation is possible, permitting that assumption, because the concentrations of applied PAC varied from 0 to 200 mg/l and for varying lengths of time in the pretreatment phase.

Figures 12 and 13, depicting data derived from test procedure A, show that the minimum effective dose of PAC prior to treatment by routine water treatment process was 30 mg/l when the humic acid concentration in the test water was 1 mg/l. The remaining concentrations of haloforms, even after post-chlorination with as much as 5 mg/l, was quite small, and the decrease in $CHCl_3$ concentration per unit PAC applied was also quite small. The fact that there were small differences in $CHCl_3$ concentrations in samples dechlorinated after 30 minutes contact and those not dechlorinated indicates that most of the precursors were removed by the combination of PAC and routine water treatments.

It may be that the effect of the PAC shown in the preceding figures is merely to increase the efficiency of flocculation and

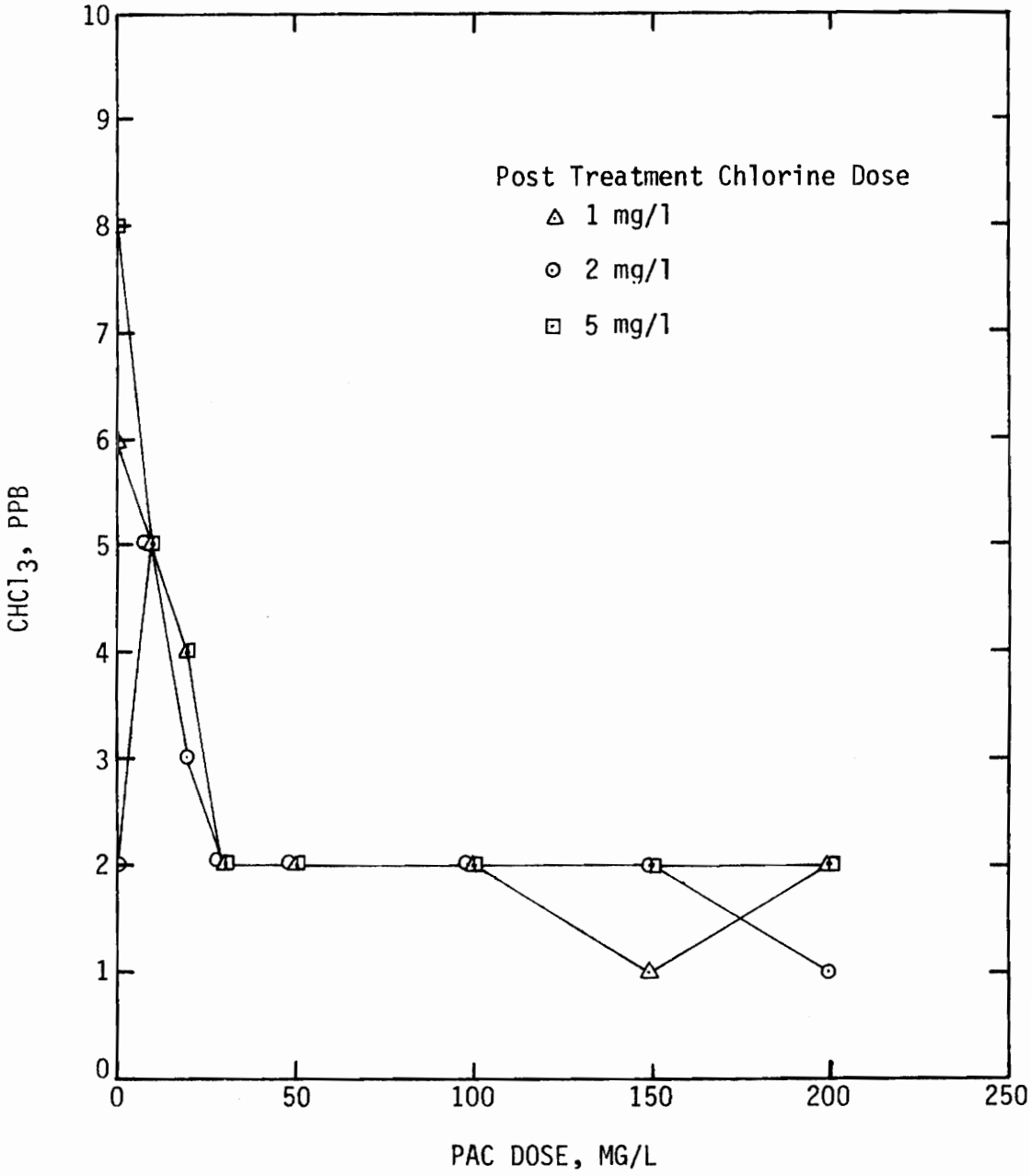


FIGURE 12. Variations in concentrations of chloroform ($CHCl_3$) with varying doses of powdered activated carbon (PAC) pretreatment for 30 minutes followed by routine water treatment processes and post-chlorination (test procedure A, samples dechlorinated after 30 minutes). The initial humic acid concentration was 1 mg/l.

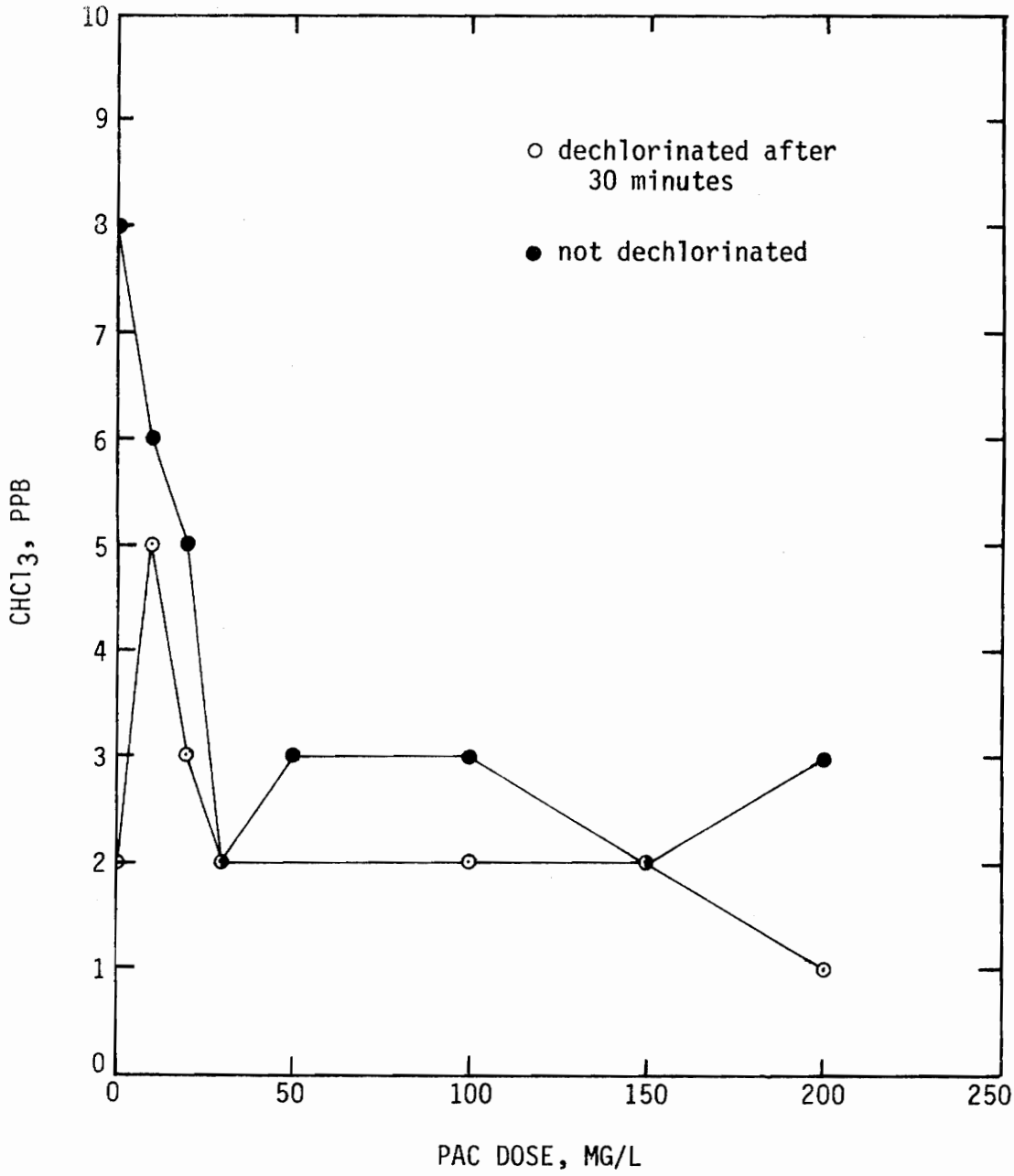


FIGURE 13. Variations in chloroform ($CHCl_3$) concentrations with varying doses of powdered activated carbon (PAC) pre-treatment for 30 minutes followed by routine water treatment processes and post-chlorination with 2 mg/l chlorine. Analytical differences between samples dechlorinated after 30 minutes and those not dechlorinated are shown (test procedure A). Water initially contained 1 mg/l humic acid.

settling. Appendix Table B-III shows that there was a somewhat downward trend in final turbidity with increasing PAC dose. The effect could be one of the PAC causing floc particles to increase in weight and cause better settling.

Results similar to those just presented were seen in test procedure H. A low concentration of PAC (50 mg/l) was required for maximum removal of haloform precursors. (See Figure 14.) The additional removal realized by increasing the PAC dose to concentrations greater than 50 mg/l was insignificant. One spurious data point (at 200 mg/l PAC, 10 mg/l Cl_2) was believed to have resulted from the sample's high turbidity (12 NTU's). Floc was trapped in the sample and probably contained some adsorbed precursor material. (The samples in this series were not filtered.) Over a period of time, the chlorine remaining in the sample probably reacted with the entrapped material, causing an increase in the $CHCl_3$ concentration.

The results of tests performed in series H (Figure 14) show better than those previously presented (Figures 12 and 13) that the carbon effectively removed precursor material. This difference was accentuated by the generation of higher $CHCl_3$ concentrations from remaining precursor material upon chlorination with a higher dose (10 mg/l) in series H than was used in series A experiments, and also by the increased initial humic acid concentration in the test waters from 1 to 3 mg/l. It appears that PAC may prove to be a more effective pretreatment as the quality of the water worsens

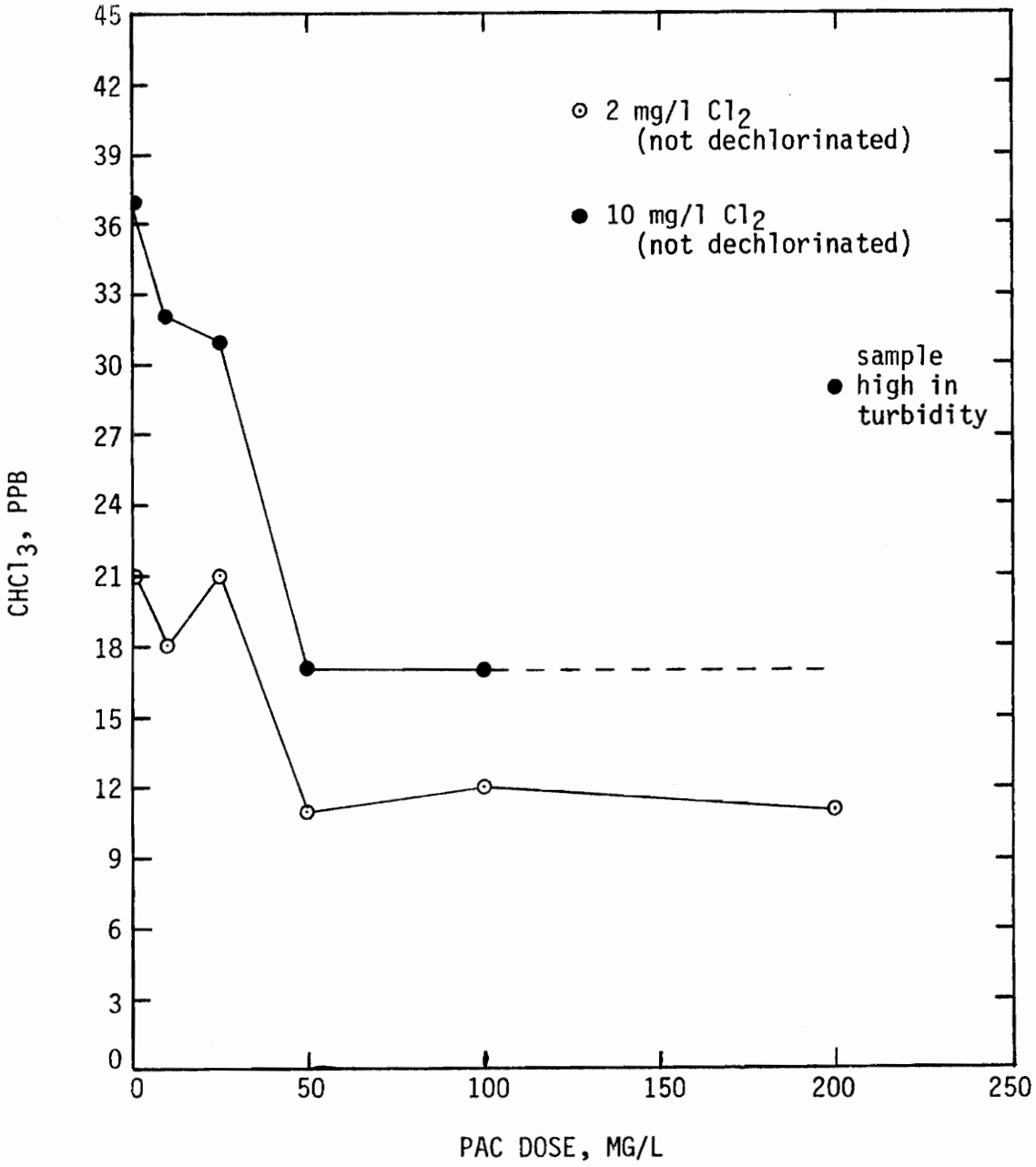


FIGURE 14. Variations in chloroform ($CHCl_3$) concentrations with varying doses of powdered activated carbon (PAC) pretreatment for 30 minutes followed by post-chlorination (test procedure H). Water initially contained 3 mg/l humic acid.

(i.e. if the total organic carbon concentration and chlorine demand both increase).

If PAC is effective in removing haloform precursors, it is yet unclear why it was ineffective in removing them from the distilled water used in these studies. Recall that $CHCl_3$ in PAC-treated distilled water, after chlorination with 10 mg/l, increased from 2 to 32 ppb. It is possible that the organic(s) involved differed from humic acid insofar as its adsorption characteristics were concerned. Table VI presents the absorbances of test waters in series A and H before and after treatment. The high concentrations of $CHCl_3$ that developed after chlorination, even when the removal of humic acid (indicated by absorbance) was complete are a further indication that the distilled water did, in fact, contain some poorly adsorbable material that reacted readily with the chlorine to produce $CHCl_3$. Rook (20) did report that low concentrations of PAC are effective for removing haloform precursors, yet it is doubtful that PAC concentrations between 30 and 50 mg/l can be considered low. Further studies need to be conducted to determine whether those haloform-precursor organics that are indigenous to natural waters are, in fact, removed by PAC and, if so, the use of PAC in water treatment may provide an alternative for water treatment plants that cannot afford to treat water with granular activated carbon beds.

Effects of Powdered Activated Carbon Contact Time

Test procedure C was used to demonstrate the effects of a

TABLE VI. Removal of Precursor Material within the Visible Light Spectrum of 420 mμ Prior to Chlorination.

Sample Number	Initial Absorbance	Final Absorbance	Percent Removal	Chloroform Concentration (nondechlorinated sample) (mg/l)
A1 - (1-4)	0.200*	0.065	68	8
A2 - (1-4)	0.200*	0.045	78	6
A3 - (1-4)	0.200*	0.048	76	5
A4 - (1-4)	0.103	0.085*	17	2
A5 - (1-4)	0.103	0.032	69	3
A6 - (1-4)	0.103	0.048	53	3
A7 - (1-4)	0.103	0.038	63	2
A8 - (1-4)	0.103	0.015	85	3
H1 - (1-2)	0.200	0.000	100	37
H2 - (1-2)	0.200	0.000	100	32
H3 - (1-2)	0.200	0.000	100	31
H4 - (1-2)	0.200	0.000	100	17
H5 - (1-2)	0.200	0.000	100	17
H6 - (1-2)	0.200	0.000	100	29

*considered high readings from spectrophotometer

constant dose (50 mg/l) of PAC for varying contact times when it was applied as a pretreatment for precursor removal. Figure 15 shows results for the first four hours of treatment and Figure 16 shows results for the entire test period of 48 hours. It was necessary to prepare a new batch of test water for samples treated for four hours and longer, and the initial $CHCl_3$ in this batch was higher than in the first (2 vs. 5 ppb). The increase in residual $CHCl_3$ concentration at four hours evident in Figures 15 and 16 was due, no doubt, to that unidentified haloform precursor that interfered throughout this entire project. Absorbance data presented in Appendix Table B-VII show that humic acid removals during these studies were greater than 80 percent.

It is probable that the effectiveness of routine water treatment processes in removing precursors was extremely good and did not permit an evaluation of the effects of PAC above. The gradual decrease in $CHCl_3$ observed after four hours was most likely a result of volatilization of the compound as the samples were continuously stirred. As in other tests reported thus far, differences in $CHCl_3$ concentration between samples dechlorinated and those sent away for analysis without dechlorination, show the time-dependency of the haloform reaction.

Effects of Powdered Activated Carbon Post-Treatment

An attempt was made in two series of tests (B and J, Appendices B and C) to evaluate the effectiveness of PAC in removing haloforms from water once they had been produced by chlorination during water

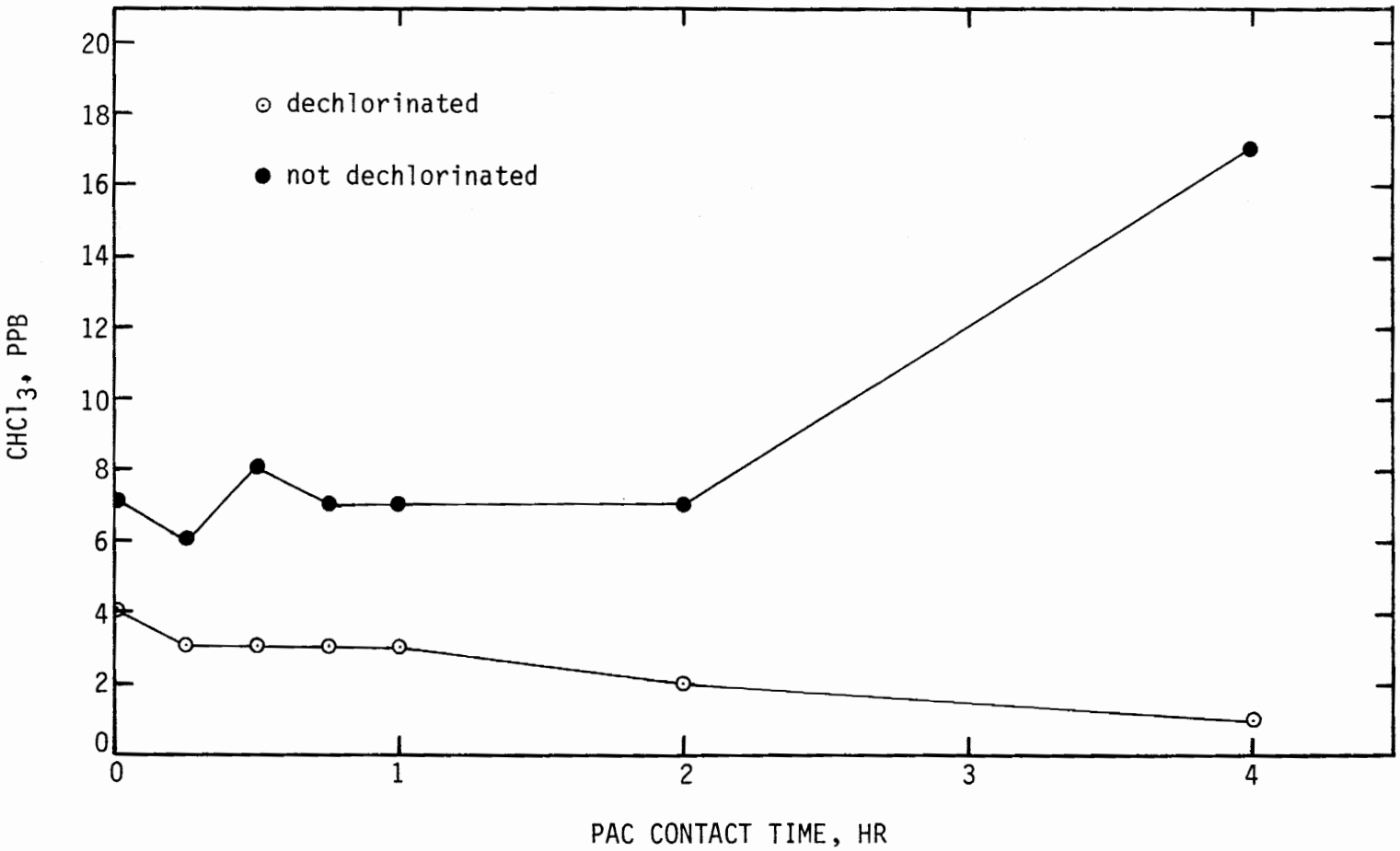


FIGURE 15. Variations in chloroform ($CHCl_3$) concentrations with increasing times of pre-treatment up to four hours with 50 mg/l powdered activated carbon (PAC) followed by routine water treatment and post-chlorination with 2 mg/l. Analytical differences between samples dechlorinated after 30 minutes and those not dechlorinated are shown (test procedure C). Water initially contained 1 mg/l humic acid.

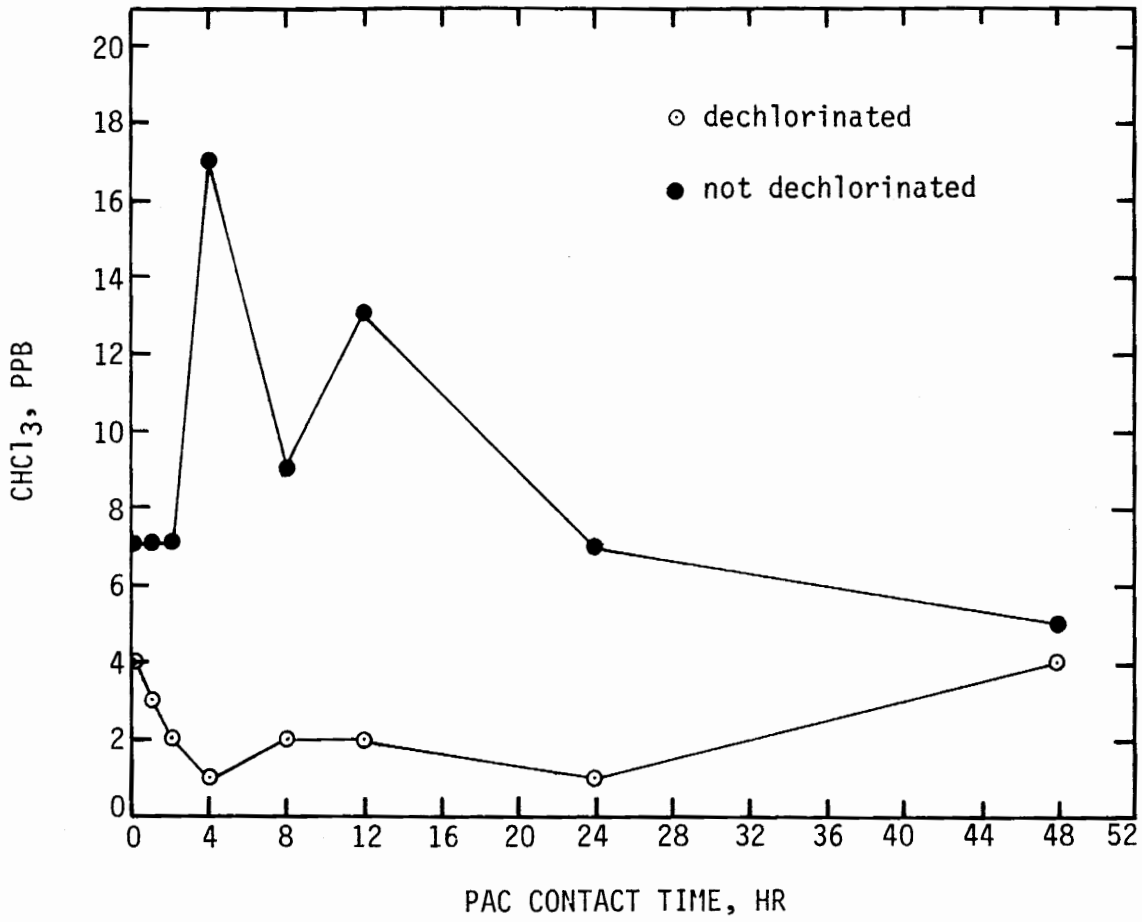


FIGURE 16. Variations in chloroform ($CHCl_3$) concentrations with increasing times of pretreatment up to 48 hours with 50 mg/l powdered activated carbon (PAC) followed by routine water treatment and post-chlorination with 2 mg/l. Analytical differences between samples dechlorinated after 30 minutes and those not dechlorinated are shown (test procedure C). Water initially contained 1 mg/l humic acid.

treatment. In the B series of tests, water containing 1 mg/l humic acid was chlorinated with 2 mg/l, then treated by routine water treatment before being treated with varying doses of PAC. Treatment applied during test series J was similar except the water contained 3 mg/l humic acid and prechlorination was with 10 mg/l chlorine. As will be shown, an unfortunate feature of these experiments was that not enough time was provided for maximum haloform production between the times when chlorine and coagulant were added. As had been shown earlier, the haloform concentration increases to a maximum during approximately the first eight hours of chlorine contact. In these studies (B and J) less than an hour was provided for contact with chlorine, and during about half of that time, the water was being flocculated and settled. The importance of the time factor is once again manifested by comparing the haloform concentrations formed in samples J1-1 and J1-2, which were chlorinated samples of stock water containing 3 mg/l humic acid. The first sample was dechlorinated after 30 minutes, but the second was permitted to react to completion. The results were, respectively, 19 and 256 ppb $CHCl_3$.

Figure 17 shows the results of the B series of experiments. Based on results presented earlier when PAC was a pretreatment (see Figure 13), one would have to conclude that the majority of the "removal" of haloforms was actually a removal of precursors during flocculation and settling before the haloform reaction could go to completion. In one phase of test series B, the PAC was added to settled water samples without dechlorination. When the PAC treatment was 50 mg/l and greater, all the residual chlorine was removed by

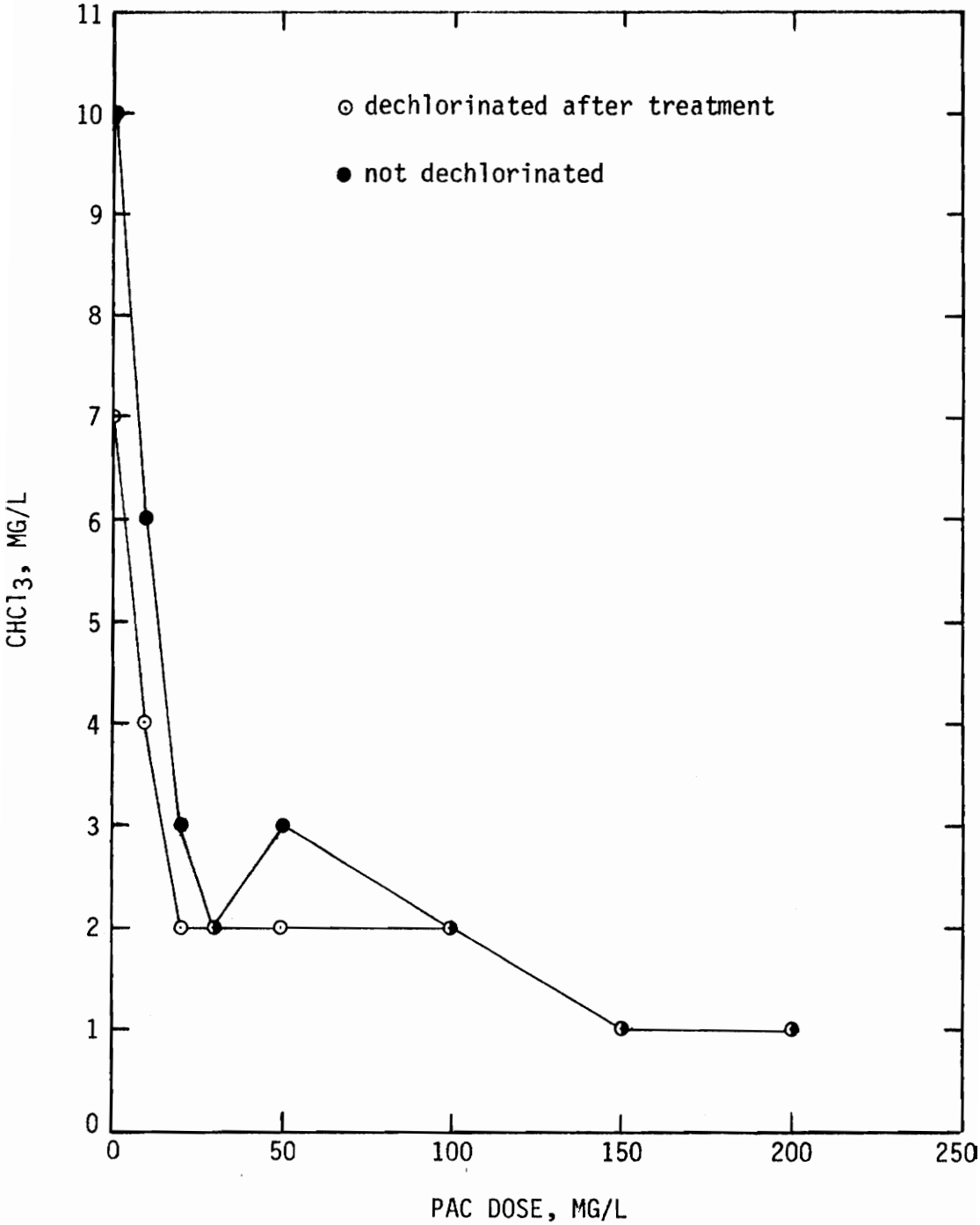


FIGURE 17. Variations in chloroform ($CHCl_3$) concentrations in test waters after powdered activated carbon (PAC) pretreatment following prechlorination with 2 mg/l and routine water treatment processes (test procedure B). Water initially contained 1 mg/l humic acid.

adsorption, thus effectively stopping the haloform reaction. The effect, then, most likely was not one of $CHCl_3$ adsorption by PAC.

The effects of PAC were more easily discerned from the J-series' results. Table VII is a summary of the data showing clearly what was stated eariler, namely that most of the "removal" that occurred actually was a removal of precursors before the haloform reaction could be completed. Sample J1-4 shows that flocculation and settling alone produced an 86 percent reduction in $CHCl_3$, but some effects of carbon are seen in these experiments. By increasing the PAC dose to 50 mg/l, the $CHCl_3$ was reduced to 3 ppb, approximately 10 percent of the quantity present after coagulation, flocculation and settling. Because the chlorine dose in this series of experiments was much higher than in the B-series, the carbon did not remove the residual chlorine. Hence, it can be assumed that the removals observed with increasing doses of PAC (Figure 18) were either caused by adsorption 1) of formed $CHCl_3$ or 2) of precursor material not removed by coagulation, flocculation and settling. There was a marked decrease in the absorbance of samples treated with PAC, a fact that tends to support the latter explanation for the effectiveness of PAC.

Effects of Sample Vial Pretreatment on Final Haloform Concentrations

During the course of this study, the 50-ml glass bottles used to contain samples shipped to California for analysis were routinely treated in a muffle furnace before use. There was some concern as to whether this was sufficient treatment to remove any organic material

TABLE VII. The Effectiveness of Water Treatment Processes and Post-Treatment with Varying Doses of Powdered Activated Carbon on Chloroform Concentrations in Finished Water Samples.

	Sample Number					
	J1-2	J1-4	J2-2	J3-2	J4-2	J5-2
Maximum Chloroform Concentration (ppb) after Prechlorination with 10 mg/l	256	256*	256*	256*	256*	256*
Treatment						
Coagulation Flocculation and Settling	No	No	Yes	Yes	Yes	Yes
PAC Dose (mg/l)	0	0	10	25	50	100
Final Chloroform Concentration (ppb) after Treatment	-	35	23	11	3	3
Percent Reduction in Chloroform Generation	-	86	91	96	99	99

*assumed to be approximately the same as J1-2 as the same stock simulated lake water containing 3 mg/l humic acid was used.

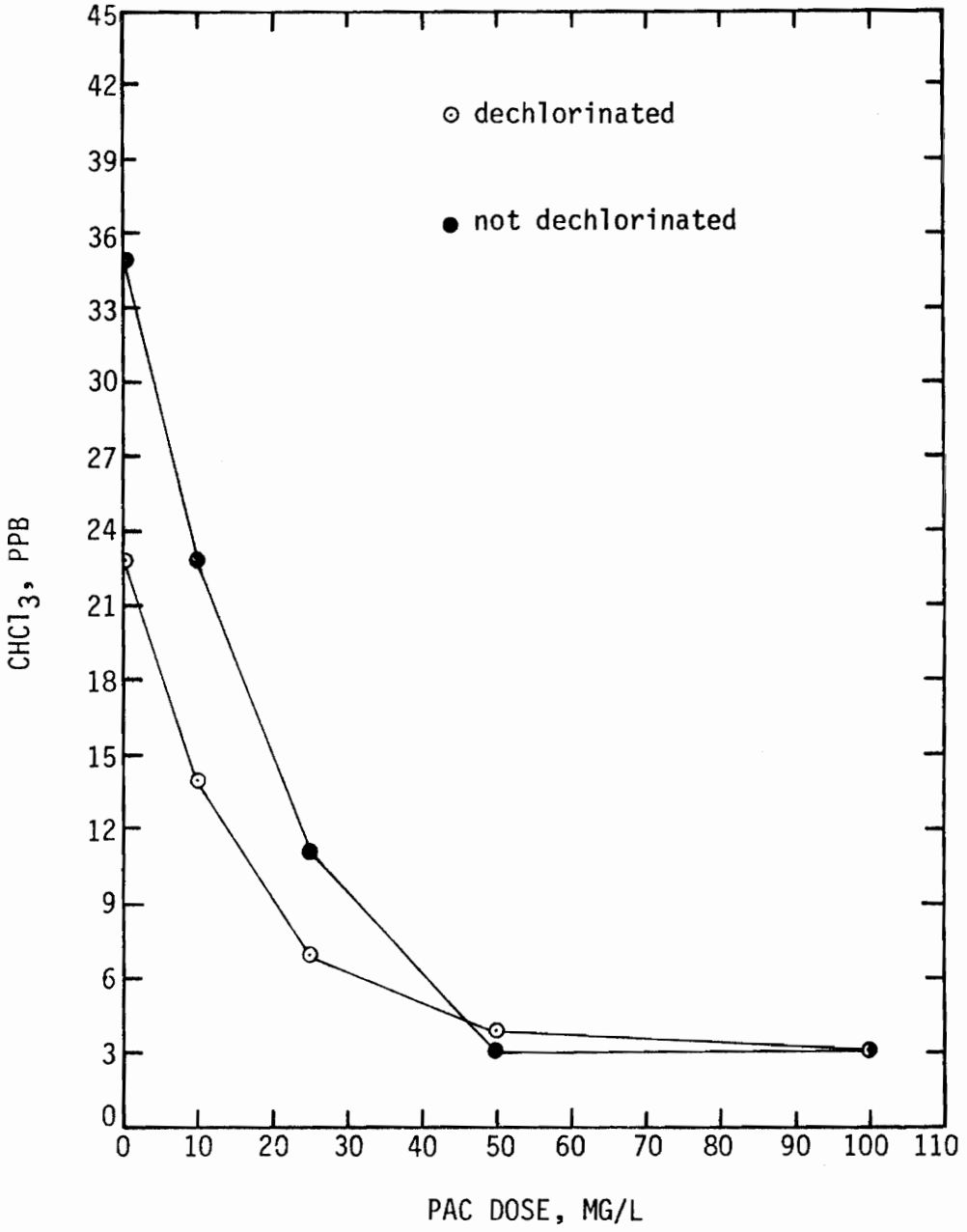


FIGURE 18. Variations in chloroform ($CHCl_3$) concentrations with varying doses of powdered activated carbon (PAC) applied after pretreatment with 10 mg/l chlorine followed by routine water treatment processes (test procedure J). Test water contained 3 mg/l humic acid.

that might be present on the glass, material that could react with chlorine to generate $CHCl_3$. To determine the sufficiency of the heat treatment, several samples were shipped for analysis in two containers--one, a glass bottle receiving only heat treatment and another, a glass bottle having first been washed by an elaborate procedure involving detergent and solvents and then heat-treated in the muffle furnace. Table VIII shows the results of 11 tests, and it is clear that the differences in haloform concentrations between the pairs was random and insignificant. Therefore, the heat-treatment in a muffle furnace is regarded as adequate for preparation of glassware to remove possible interfering organic matter.

TABLE VIII. A Comparison of Haloform Concentrations in Water Stored in Sample Vials Previously Washed Before Treatment in a Muffle Furnace and Those Treated Only in a Muffle Furnace.
*(S-Suffix = Specially Washed Samples)

Sample Number	Concentration of Chloroform (ppb)	Concentration of Bromodichloromethane (ppb)
C7-1	1	-
C7-1S	1	-
C7-2	17	-
C7-2S	20	-
C8-1	2	-
C8-1S	2	-
C8-2	9	<1
C8-2S	10	<1
C9-1	2	<1
C9-1S	2	<1
C9-2	13	<1
C9-2S	11	<1
EO-9	20	-
EO-9S	23	-

TABLE VIII. - Continued

Sample Number	Concentration of Chloroform (ppb)	Concentration of Bromodichloromethane (ppb)
F5-1	15	2
F5-1S	19	2
F5-2	21	2
F5-2S	21	2
F5-3	75	2
F5-3S	77	2
F5-4	23	<1
F5-4S	22	1

*See Methods and Materials Chapter for details of washing procedure

V. SUMMARY AND CONCLUSIONS

The objective of this research was to study the effects of various water treatment processes and their respective position within the treatment scheme on the removal of haloform precursors and on the haloforms themselves subsequent to their formation.

A simulated lake water containing humic acid was prepared and treated in various ways by powdered activated carbon; coagulation, flocculation, and settling; and chlorination. Various analyses, including temperature, pH, alkalinity, absorbance, and chlorine residual, were performed in the laboratory throughout the treatment processes. Samples were shipped to California Analytical Laboratory for volatile organic analysis.

The results of this study supported those from past studies in that it showed humic acid to be a precursor to volatile organics. The data indicated that humic acid could be effectively removed by coagulation, flocculation, and settling, however, it can be even further removed by powdered activated carbon in the range of 30 to 50 mg/l.

During the study, it was observed that the chlorine concentration had more effect on volatile organic formation than the humic acid concentration. The reaction between the chlorine and the humic acid was not instantaneous. Haloform concentrations continue to increase for up to eight or more hours after chlorine is applied.

Significant conclusions derived from this study are:

1. The maximum haloform concentration generated in a water containing sufficent quantities of haloform precursor organics is both time and chlorine concentration dependent. Maximum haloform concentrations required at least eight hours for development in room temperature.
2. The reactant that appeared to be limiting in most of the studies appeared to be chlorine rather than humic acid. Treatment with from 1 to 5 mg/l chlorine for 30 minutes caused increased haloform production in waters containing up to 1 mg/l humic acid, but no additional effect was seen by increasing the humic acid to 3 mg/l.
3. The most effective treatment for reducing the final concentrations of haloforms in finished water was the removal of haloform precursors by coagulation, flocculation, and sedimentation. As high as 85 percent reduction was noted by this treatment alone. This treatment appeared to be most effective when the pretreatment with chlorine was minimized and when the water contained less humic acid.
4. Powdered activated carbon is effective in removing haloform precursors when applied either as a pre- or post treatment at dosages of from 30 to 50 mg/l. It appears that the greatest effect of carbon in these studies was in removing precursors before the chlorine

could react with them and not in removing haloforms themselves once they were formed.

It appears, then, from the results of this study that the most effective treatment to insure minimum concentrations of haloforms in finished water is that precursors be removed by some process before chlorine is applied. If the water is a surface water, then chlorination should be preceded by coagulation, flocculation, settling, and possible powdered activated carbon treatment. However, if prechlorination is necessary, the treatment by routine processes as rapidly as possible after the initial dosing with chlorine will insure reasonably low levels of haloforms in finished water.

VI. RECOMMENDATIONS

In future laboratory studies, the following changes in test procedures would make comparisons of data much easier:

1. Sufficient time should be allowed between experiments to provide an opportunity to examine the haloform results to determine the best structure of subsequent experiments.
2. It should be assured that proper and well matched cylinders are utilized for the spectrophotometer. Consistent and reliable absorbance data could then be obtained.
3. The distilled water should be pretreated more carefully so that upon chlorination, haloforms are not generated. This yields more reliable data and facilitates easier analysis of results.
4. To give a better indication of the effectiveness of precursor removal by the PAC, the following procedure would be utilized:

   Chlorinate the simulated lake water to determine the maximum generation of haloforms. Using the same stock "lake" water (unchlorinated), pretreat with PAC (vary doses and/or contact times). Chlorinate the treated water with the same and/or varying doses and sample without dechlorination.

5. To determine the effectiveness of PAC or haloform removal subsequent to its formation, the following would be utilized:

   Chlorinate the simulated lake water to determine the maximum concentration of haloforms generated. Chlorinate a second batch of "lake" water with the same and/or varying doses and let stand for approximately 12 hours for the maximum generation of haloforms. Treat the water with PAC of varying doses and/or contact times and sample without dechlorination.

6. To determine the effectiveness of coagulation, flocculation, and settling on precursor and/or haloform removal, the same procedures discussed in numbers 3 and 4 above would be incorporated except coagulation, flocculation, and settling would be used in place of the PAC.

7. In test procedure E where the generation of haloforms with time was being determined, samples would be taken more frequently with time and there would also be a reduction in the time required for taking samples (e.g. approximately 24 hours). A couple of runs could also be made to better determine the test reliability.

8. Dechlorination of samples within test procedures for determining removal efficiencies would not be utilized. This would allow for the maximum generation of haloforms

and, therefore, it is believed that a better determination of removal efficiencies could be made.

BIBLIOGRAPHY

1. "Suspect Carcinogens in Water Supplies." Environmental Protection Agency, Office of Research and Development Interim Report (April, 1975).

2. "Preliminary Assessment of Suspected Carcinogens in Drinking Water." Environmental Protection Agency, Office of Toxic Substances Interim Report to Congress (June, 1975).

3. "Preliminary Assessment of Suspected Carcinogens in Drinking Water." Environmental Protection Agency, Office of Toxic Substances Report to Congress (December, 1975).

4. "Region V Joint Federal/State Survey of Organics and Inorganics in Selected Drinking Water Supplies." Environmental Protection Agency, Region V Draft (June, 1975).

5. Harris, R. H., "The Implications of Cancer-Causing Substances in Mississippi River Water." Environmental Defense Fund Report Submitted to James A. Moreau, Councilman-at-Large, New Orleans, La. (November 6, 1974).

6. Page, T., Harris, R. H., and Epstein, S. S., "Drinking Water and Cancer Mortality in Louisiana." Science, 193, 55 (1976).

7. "Report on Carcinogenesis of Chloroform." National Cancer Institute (March 1, 1976).

8. "Water Supplies, Defects Linked." Richmond Times Dispatch Newspaper (May 31, 1976).

9. Rook, J. J., "Formation of Haloforms During Chlorination of Natural Waters." Water Treatment and Examination 23, 234 (1974).

10. Bellar, T. A., Lichtenberg, J. J., and Kroner, R. C., "The Occurrence of Organohalides in Chlorinated Drinking Waters." Reference No. EPA-670/4-74-008 Environmental Protection Agency (November, 1974).

11. Schnitzer, M., and Khan, S. U., Humic Substances in the Environment. Marcel Dekker, Inc., New York, N.Y. (1972).

12. Mangravite, F. J., Jr., Buzzell, T. D., Cassell, E. A., Matijević, E., and Saxton, G. B., "Removal of Humic Acid by Coagulation and Microflotation." Journal American

Water Works Association, 67, 88 (1975).

13. Kononova, M. M., Soil Organic Matter. 2nd English Edition Pergamon Press, Oxford, Conn. (1966).

14. Wetzel, R. G., Limnology. W. B. Saunders Company, Philadelphia, Pa. (1975).

15. Felbeck, G. T., Jr., "Chemical and Biological Characterization of Humic Matter." In Soil Biochemistry, 2, 55. A. D. McLaren and J. Skujins [Eds.] Marcel Dekker, Inc., New York, N.Y. (1971).

16. Weber, J. H., and Wilson, S. A., "The Isolation and Characterization of Fulvic Acid and Humic Acid from River Water." Water Research, 9, 1079 (1975).

17. Symons, J. M., Bellar, T. A., Carswell, J. K., Dellar, J., Dropp, K. L., Robeck, G. G., Seeger, D. R., Sloccum, C. J., Smith, B. L., and Stevens, A. A., "National Organics Reconnaissance Survey for Halogenated Organics." Journal American Water Works Association, 67, 634 (1975).

18. Jolley, R. L., "Chlorination Effects on Organic Constituents in Effluents from Domestic Sanitary Sewage Treatment Plants." Oak Ridge National Laboratory Publication No. ORNL-TM-4290 (October, 1973).

19. Glaze, W. H., and Henderson, J. E., IV, "Formation of Organochlorine Compounds from the Chlorination of a Municipal Secondary Effluent." Journal Water Pollution Control Federation, 47, 2511 (1975).

20. Rook, J. J., "Haloforms in Drinking Water." Journal American Water Works Association, 68, 279 (1976).

21. Stevens, A. A., Slocum, C. J., Seeger, D. R., and Robeck, G. G., "Chlorination of Organics in Drinking Water." To be Published in Proceeding of Conference on the Environmental Impact on Water Chlorination, Oak Ridge National Laboratory, Oak Ridge, Tenn. (October 22-24, 1975).

22. Morris, J. C. "Formation of Halogenated Organics by Chlorination of Water Supplies." Reference No. EPA-600/1-75-002 Environmental Protection Agency, Office of Research and Development (March, 1975).

23. Bellar, T. A., and Lichtenberg, J. J., "The Determination of Volatile Organic Compounds at the µg/l Level in Water by Gas Chromatography." Reference No. EPA-670/4-74-009 Environmental Protection Agency (November, 1974).

24. Cameron, C. D., Hoehn, R. C., and Strimaitis, J. R., "Organic Contaminants in Raw and Finished Water." Journal American Water Works Association, 66, 519 (1974).

25. Leithe, B. W., Analysis of Organic Water Pollutants. Ann Arbor Science Publishers, Inc., Ann Arbor, Mich. (1973).

26. Hunter, J. V., "Origin of Organics from Artificial Contamination." In Organic Compounds in Aquatic Environments. S. J. Faust and J. V. Hunter [Eds.], Marcel Dekker, Inc., New York, N.Y. (1971).

27. Dobbs, R. A., Wise, R. H. and Dean, R. B., "The Use of Ultraviolet Absorbance for Monitoring the Total Organic Carbon Content of Water and Wastewater." Water Research, 6, 1173 (1972).

28. Ong, H. L., and Bisque, R. E., "Coagulation of Humic Colloids by Metal Ions." Soil Science, 106, 220 (1968).

29. Love, O. T., Jr., Carswell, J. K., Stevens, A. A., and Symons, J. M., "Evaluation of Activated Carbon as a Drinking Water Treatment Unit Process." Environmental Protection Agency National Environmental Research Center Progress Report (March, 1975).

30. Medlar, S., "Operating Experiences with Activated Granular Carbon." Water and Sewage Works, 122, 70 (1975).

31. Foley, P. D., and Missingham, G. A., "Monitoring of Community Water Supplies." Journal American Water Works Association (1976).

32. "A Report: Assessment of Health Risk from Organics in Drinking Water." Environmental Protection Agency, Hazardous Materials Advisory Committee, Science Advisory Board (May 20, 1975).

33. Hoehn, R. C., "Comparative Disinfection Methods." Journal American Water Works Association, 68, 302 (1976)

34. "Standard Methods for the Examination of Water and Wastewater." 13th Edition, American Public Health Association, Washington, D.C. (1971).

APPENDIX A

Previous Studies

FELBECK'S HYPOTHESES

(After Felbeck, Ref. 15)

"(1) The plant alteration hypothesis. Those fractions of the plant tissue that are resistant to microbial attack, especially the lignified tissues, are altered more or less superficially in the soil to produce humic substances. According to this view the nature of the original plant compound strongly influences the nature of the final humic substance. The higher-molecular-weight humin then represents the first stages of humification followed by subsequent microbial attack to degrade the humin to humic acid, then fulvic acid, and finally mineralization to CO_2 and H_2O. However, depending on the nature and size of the original plant molecule, lower-molecular-weight humic substances could also be found initially with microbial mineralization following.

(2) The chemical polymerization hypothesis. Plant material is degraded microbially to small molecules, which are absorbed by the microbes as sources of carbon and energy. The microbes synthesize various products, usually phenols and amino acids, which are excreted into the surrounding medium where chemical oxidation and polymerization to humic substances take place. According to this hypothesis the nature of the original plant tissue has no effect on the kind of humic substances finally

FELBECK'S HYPOTHESES - Continued

produced.

(3) The cell autolysis hypothesis. Humification is thought to be the product of the autolysis of plant and microbial cells after the death of a cell. The product is a heterogeneous substance formed by the random condensation and polymerization of cellular debris (such as sugars, amino acids, phenols, other aromatic compounds, and so on) that are converted to free radicals by autolytic enzymes released on the death of the cell.

(4) The microbial synthesis hypothesis. The early stages of microbial attack on plant tissues are seen to be the same as in the chemical polymerization hypothesis in that a microbe utilizes the plant tissue only as a source of carbon and energy. However, the microbe synthesizes various high-molecular-weight humus-like compounds intracellularly and these compounds are only released to the soil when the microbe dies and its cells are lysed. According to this view the higher-molecular-weight compounds represent the first stages of humification followed by extracellular microbial degradation to humic acid, fulvic acid, and final mineralization."

TABLE A-I. - Raw Water Analysis (Based on 79 Samples) from EPA's 80 City Survey (after EPA, Ref. 2).

	Number of Locations Detected	Range of Concentrations (ppb)
None Detected	30	-
Chloroform	45	0.1 - 0.9 (16)*
Bromodichloromethane	6	0.2 - 0.8 (11)*
Dibromochloromethane	0	- (3)*
Bromoform	0	-
1,2-Dichloroethane	11	0.2 - 3
Carbon Tetrachloride	4	2 - 4

*One additional location received raw water prechlorinated by a nearby industry. This water contained 16 ppb of chloroform, 11 ppb bromodichloromethane, and 3 ppb dibromochloromethane.

TABLE A-II. - Finished Water Analysis (Based on 79 Samples) from EPA's 80 City Survey (after EPA, Ref. 2).

Compound	Number of Locations Detected	Range of Concentrations (ppb)
Chloroform	79	0.1 -- 311
Bromodichloromethane	76	1.8 -- 116
Dibromochloromethane	70	0.4 -- 100
Bromoform	25	1.0 -- 92
Carbon Tetrachloride	10	2.0 -- 3
1,2-Dichloroethane	26	0.2 -- 6

TABLE A-III. - Summary of Analytical Results (Volatile Organics) from Region V Survey (after EPA, Ref. 2).

Chemical Formula & Name	Percent of Samples Giving Positive Results		Mean Concentration (ppb)		Mean Concentration (ppb)	
	Finished Water	Raw Water	Finished Water	Raw Water	Finished Water	Raw Water
$CHCL_3$ - Chloroform	95	27	20	1.0	366	94
$CHBrCL_2$ - Bromodi-chloromethane	78	5	6	1.0	91	11
$CHBr_2Cl$ - Dibro-mochloromethane	60	2	1	1.0	14	1.4
$CHBr_3$ - Bromoform	14	0	1	1.0	7	1.0
CCl_4 - Carbon Tetrachloride	34*	18	2*	1.0	26*	20
CH_2Cl_2 - Methylene chloride	8	1	1	1.0	7	1
$C_2H_4Cl_2$ - 1,2-Dichloroethane	13	14	1	1.0	26	15

*Those samples from Minnesota may have been contaminated by being exposed to laboratory air containing carbon tetrachloride.

TABLE A-IV. - Volatile Organic Compound Concentrations (10 Highest) from Region V Survey (after EPA, Ref. 2).

	Concentration (ppb)			
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$
Fremont, Ohio	366	18	1.4	0
Bessemer Township, Mich.	312	4	0	0
Fairmount, Minn.	200	31	0.7	0
Chester, Ill.	182	17	1.1	0
Dundee, Mich.	170	26	2	0
Bowling Green, Ohio	160	27	5	0
Warren, Ohio	138	19	0.8	0
Breckenridge, Minn.	128	15	0	0
Piqua, Ohio	102	10	0.7	0
Bedford, Ind.	84	12	0.8	0.8

APPENDIX B

Test Procedures and Results

Note: All absorbance data recorded for stock water characterization and sample series are at 420 mμ after passage through a 0.45 μm Millipore filter.

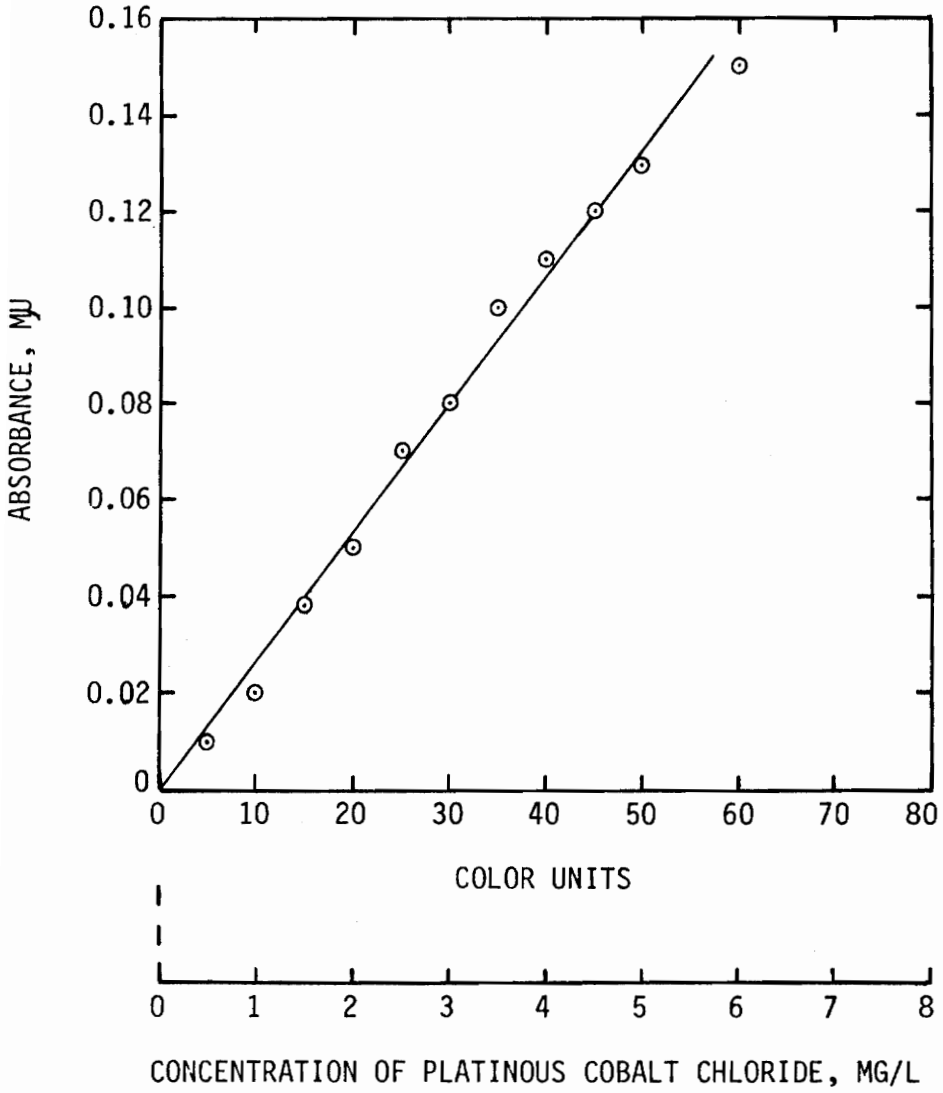


FIGURE B-1. The variation in absorbance with the concentration of platinous cobalt chloride and equivalent color units.

TABLE B-I. - Treatment Applied in the Various Tests

Treatment	Test Procedure							
	A	B	C	E	F	H	J	K
1. Humic Acid								
a. Concentration Varied					X			
b. Concentration Fixed	X	X	X	X		X	X	X
2. Prechlorination		X		X			X	
3. Carbon Treatment								
a. Concentration Varied	X					X		
b. Contact Time Varied			X					
4. Coagulation, Flocculation and Sedimentation	X	X	X			X	X	
5. Filter (Grade 934 AH Reeve Angel Glass Fiber Filter in Büchner Funnel)	X		X					
6. Dechlorination		X		X				
7. Carbon Post-treatment, Concentration Varied		X					X	
8. Dechlorination							X	
9. Filter (0.45 μm Millipore)		X		X			X	
10. Chlorination								
a. Concentration Varied	X				X	X		X
b. Concentration Fixed			X					
11. Final Dechlorination of Selected Samples	X		X		X			

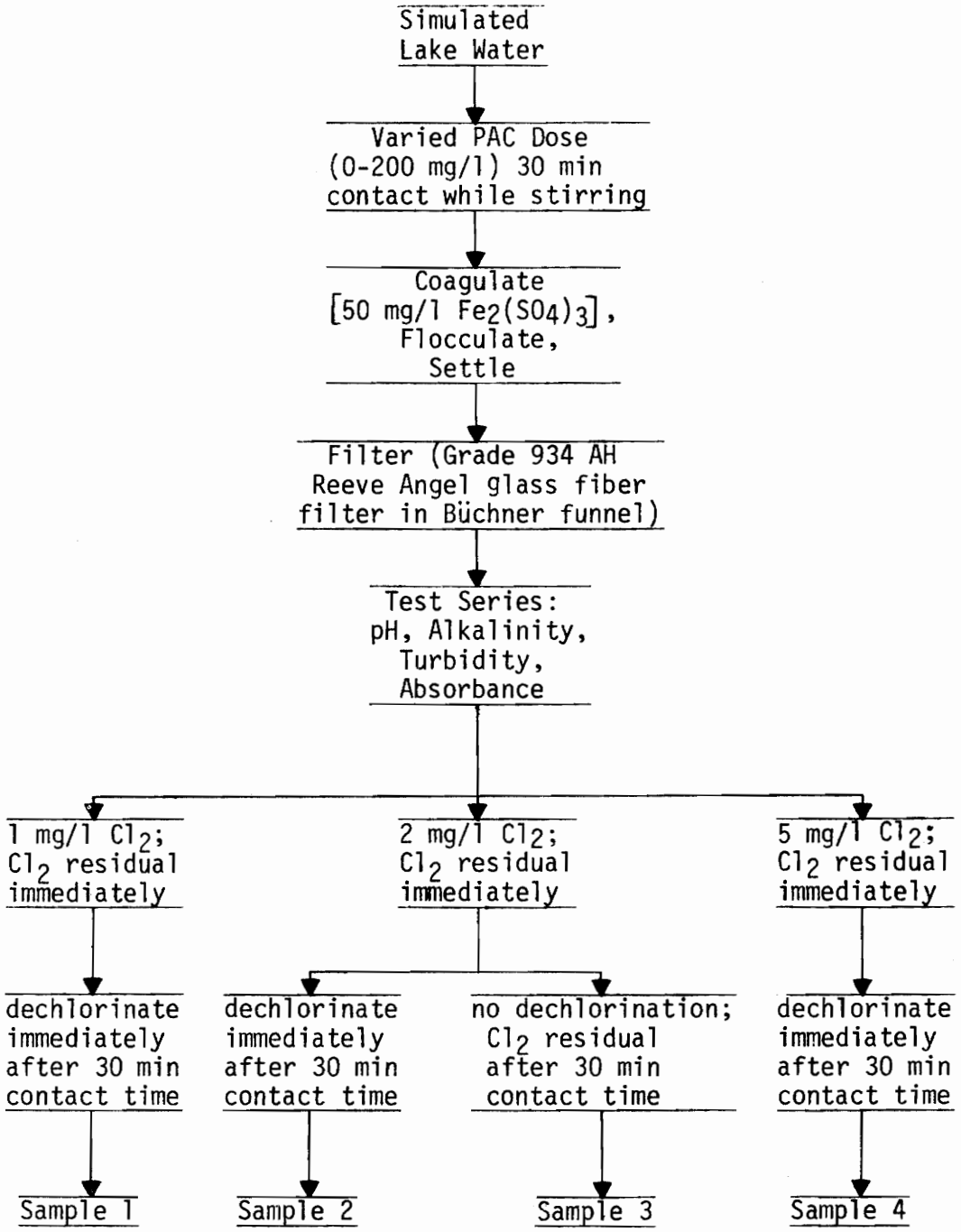


FIGURE B-2. - Test Procedure A

TABLE B-II. - Stock Water Characterization

Stock Water	Parameters					
	Temperature (°C)	pH	Alkalinity (as mg/l $CaCO_3$)	Turbidity (NTU)	Absorbance (@ 420 mμ)	Color Units
Sample Series A1 - A3	28	8.3	124.5	30	0.20	-
Sample Series A4 - A8	26	8.2	122.0	26	0.103	38

TABLE B-III. Sample Series Characterization

Parameters	Sample Series							
	A1 (1,2, 3,4)	A2 (1,2, 3,4)	A3 (1,2, 3,4)	A4 (1,2, 3,4)	A5 (1,2, 3,4)	A6 (1,2, 3,4)	A7 (1,2, 3,4)	A8 (1,2, 3,4)
PAC Dose (mg/l)	0.0	10	20	30	50	100	150	200
pH	6.8	6.8	6.8	6.7	6.7	6.6	6.7	6.7
Alkalinity (as mg/l $CaCO_3$)	94.6	94.6	93.4	93.4	94.6	94.6	94.6	92.1
Turbidity (NTU)	2.0	2.0	2.0	1.3	1.5	1.5	1.0	1.0
Absorbance (@ 420 mu)	0.065	0.045	0.048	0.085	0.032	0.048	0.038	0.015
Color Units	25	17	18	32	12	18	14	6
Initial Cl_2 Residual (mg/l)								
1 mg/l	0.98	1.05	0.98	1.05	1.06	1.0	0.98	1.0
2 mg/l	1.88	1.97	1.91	2.0	2.1	2.03	1.94	1.89
5 mg/l	4.69	4.88	4.91	5.1	4.92	4.81	4.79	5.02
30 min Cl_2 Residual (mg/l)								
2 mg/l	1.53	1.81	1.77	1.75	1.83	1.84	1.73	1.55

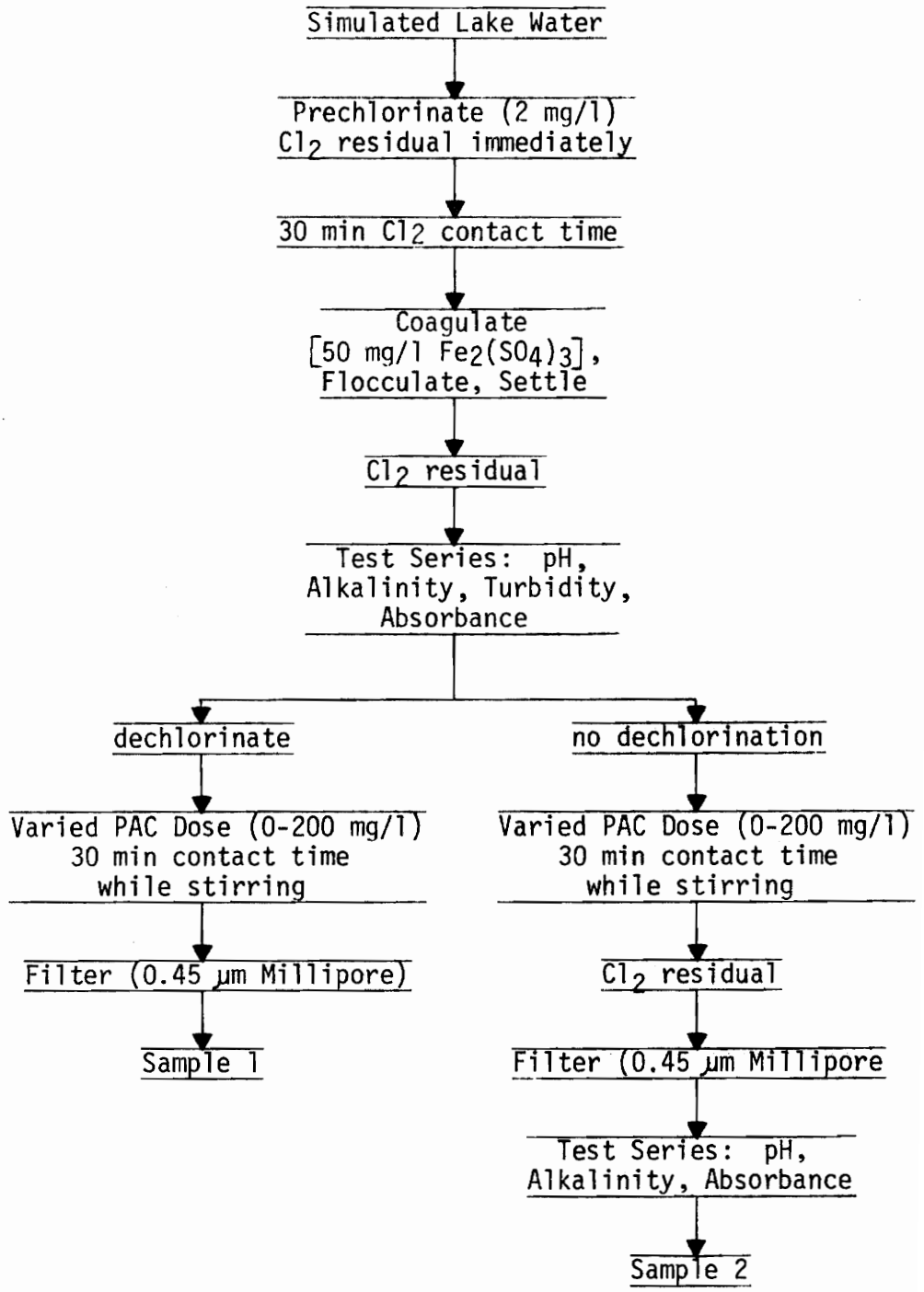


FIGURE B-3. - Test Procedure B

TABLE B-IV. - Stock Water Characterization

Stock Water	Parameters					
	Temperature (°C)	pH	Alkalinity (as mg/l $CaCO_3$)	Turbidity (NTU)	Absorbance (@ 420 mμ)	Color Units
Sample Series B1 - B4	28	8.6	119.5	26	0.085	32
Sample Series B5 - B8	28	8.6	120.8	27	0.11	38

TABLE B-V. Sample Series Characterization

Parameters	Sample Series							
	B1 (1,2)	B2 (1,2)	B3 (1,2)	B4 (1,2)	B5 (1,2)	B6 (1,2)	B7 (1,2)	B8 (1,2)
Initial Cl_2 Residual (mg/l)	1.90	2.00	1.99	1.88	1.93	2.10	1.88	1.86
Cl_2 Residual after Sedimentation (mg/l)	1.10	1.19	1.14	1.27	1.28	1.26	1.18	1.15
pH	6.7	6.9	6.9	6.8	6.7	6.6	6.6	6.8
Alkalinity (as mg/l $CaCO_3$)	93.4	94.6	92.1	92.1	94.6	94.6	94.6	94.6
Turbidity (NTU)	3.4	3.9	2.0	2.5	3.1	3.9	2.8	2.7
Absorbance (@ 420 mμ)	0.02	0.008	0.015	0.004	0.0	0.0	0.003	0.002
Color Units	8	3	6	2	0	0	1	1
Carbon Dose (mg/l)	0.0	10	20	30	50	100	150	200
Final Cl_2 Residual (mg/l)	-	0.26	0.03	0.04	0.0	0.0	0.0	0.0

TABLE B-V. - Continued

Parameters	Sample Series							
	B1 (1,2)	B2 (1,2)	B3 (1,2)	B4 (1,2)	B5 (1,2)	B6 (1,2)	B7 (1,2)	B8 (1,2)
Total Cl_2 Contact Time (min)								
Sample 4	73	97	75	80	85	85	78	80
Sample 2 (to Cl_2 Residual)	75	132	110	113	118	120	115	115
Test Series (Sample 2)								
pH	-	7.2	7.3	7.1	6.9	7.0	7.2	7.1
Alkalinity (as mg/l $CaCO_3$)	-	91.2	89.6	89.6	93.4	94.6	94.6	94.6
Absorbance (@ 420 mμ)	-	0.002	0.0	0.0	0.0	0.0	0.0	0.0
Color Units	-	1	0	0	0	0	0	0

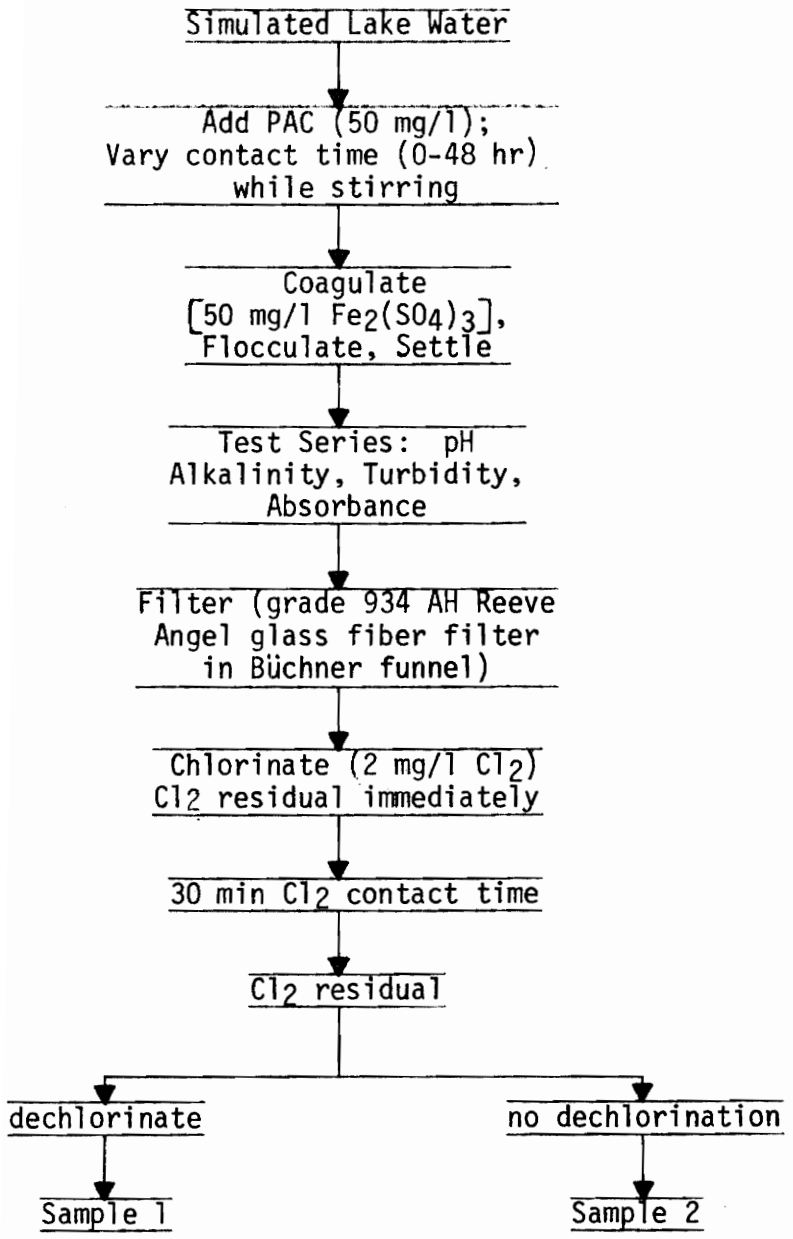


FIGURE B-4. - Test Procedure C

TABLE B-VI. - Stock Water Characterization

Stock Water	Parameters					
	Temperature (°C)	pH	Alkalinity (as mg/l $CaCO_3$)	Turbidity (NTU)	Absorbance (@ 420 mμ)	Color Units
Sample Series C1 - C6	28	8.5	125.7	28	0.10	38
Sample Series C7 - C11	28	8.4	122.0	26	0.068	26

TABLE B-VII. - Sample Series Characterization

Parameters	Sample Series					
	C1 (1,2)	C2 (1,2)	C3 (1,2)	C4 (1,2)	C5 (1,2)	C6 (1,2)
PAC Contact Time (hr)	0.0	0.25	0.50	0.75	1.0	2.0
pH	6.9	6.9	6.9	6.8	6.95	6.9
Alkalinity (as mg/l $CaCO_3$)	94.6	97.1	97.1	97.1	98.4	99.6
Turbidity (NTU)	3.4	2.5	2.5	2.5	1.8	2.7
Absorbance (@ 420 mμ)	0.01	0.005	0.002	0.01	0.002	0.0
Color Units	4	2	1	4	1	0
Cl_2 Residual (mg/l)	1.79	1.89	1.82	1.87	1.90	2.04
30 min Cl_2 Residual (mg/l)	1.03	1.36	1.33	1.20	1.24	1.42

TABLE B-VII. - Continued

Parameters	Sample Series				
	C7 (1,1S,2,2S)	C8 (1,1S,2,2S)	C9 (1,1S,2,2S)	C10 (1,2)	C11 (1,2)
PAC Contact Time (hr)	4.0	8.0	12.0	24.0	48.0
pH	7.1	6.8	6.9	6.8	6.8
Alkalinity (as mg/l $CaCO_3$)	94.6	94.6	94.6	122.0	99.6
Turbidity (NTU)	1.6	2.2	1.3	1.6	1.7
Absorbance (@ 420 mu)	0.01	0.0	0.008	0.013	0.018
Color Units	4	0	3	5	7
Cl_2 Residual (mg/l)	2.03	1.98	1.89	1.95	1.85
30 min Cl_2 Residual (mg/l)	1.42	1.56	1.52	1.47	1.48

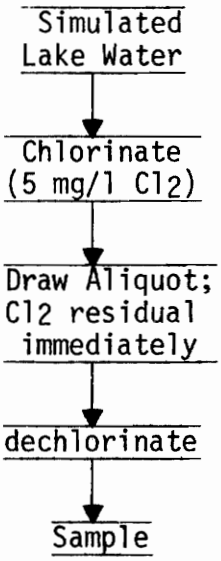


FIGURE B-5. - Test Procedure E

TABLE B-VIII. - Stock Water Characterization

Stock Water	Parameters					
	Temperature (°C)	pH	Alkalinity (as mg/l $CaCO_3$)	Turbidity (NTU)	Absorbance (@ 420 mμ)	Color Units
Sample Series EO-1 to EO-9	27	8.5	127.0	0.5	0.08	30

TABLE B-IX. - Sample Series Characterization

Parameters	Sample Series								
	EO-1	EO-2	EO-3	EO-4	EO-5	EO-6	EO-7	EO-8	EO-9 EO-9S
Initial Cl_2 Residual (mg/l)	4.85	-	-	-	-	-	-	-	-
Total Cl_2 Contact Time (hr)	0.16$\overline{6}$	0.5	1.0	2.0	4.0	8.0	24.0	48.0	96.0
Cl_2 Residual after Contact Time (mg/l)	4.47	4.28	4.15	3.98	3.78	3.49	2.98	2.65	1.95

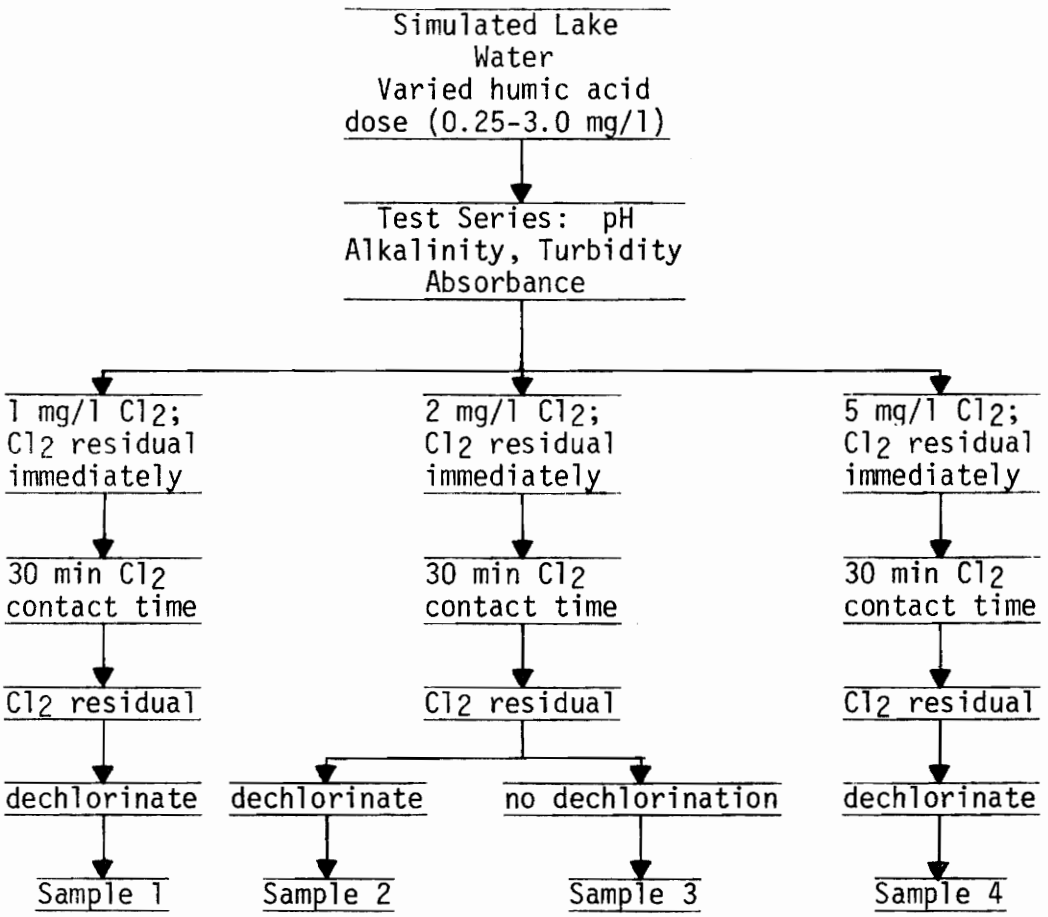


FIGURE B-6. Test Procedure F

TABLE B-X. Sample Series Characterization

Parameters	Sample Series				
	F1 (1,2,3,4)	F2 (1,2,3,4)	F3 (1,2,3,4)	F4 (1,2,3,4)	F5 (1,1S,2,2S 3,3S,4,4S,5,5S)
Humic Acid Conc. (mg/l)	0.25	0.5	1.0	2.0	3.0
pH	8.6	8.4	8.7	8.7	8.6
Alkalinity (as mg/l $CaCO_3$)	123.3	124.5	122.0	123.3	124.5
Turbidity (NTU)	0.2	0.2	0.2	0.3	0.3
Absorbance (@ 420 mμ)	0.022	0.038	0.05	0.075	0.065
Color Units	8	14	19	28	24
Cl_2 Residual (mg/l)					
1 mg/l	1.17	1.10	1.07	1.01	1.02
2 mg/l	1.94	2.19	2.07	1.94	1.75
5 mg/l	5.42	5.21	5.03	4.95	5.05
30 min Cl_2 Residual (mg/l)					
1 mg/l	1.05	0.93	0.97	0.83	0.80
2 mg/l	1.84	1.94	1.86	1.67	1.42
5 mg/l	5.26	4.93	4.70	4.44	4.82

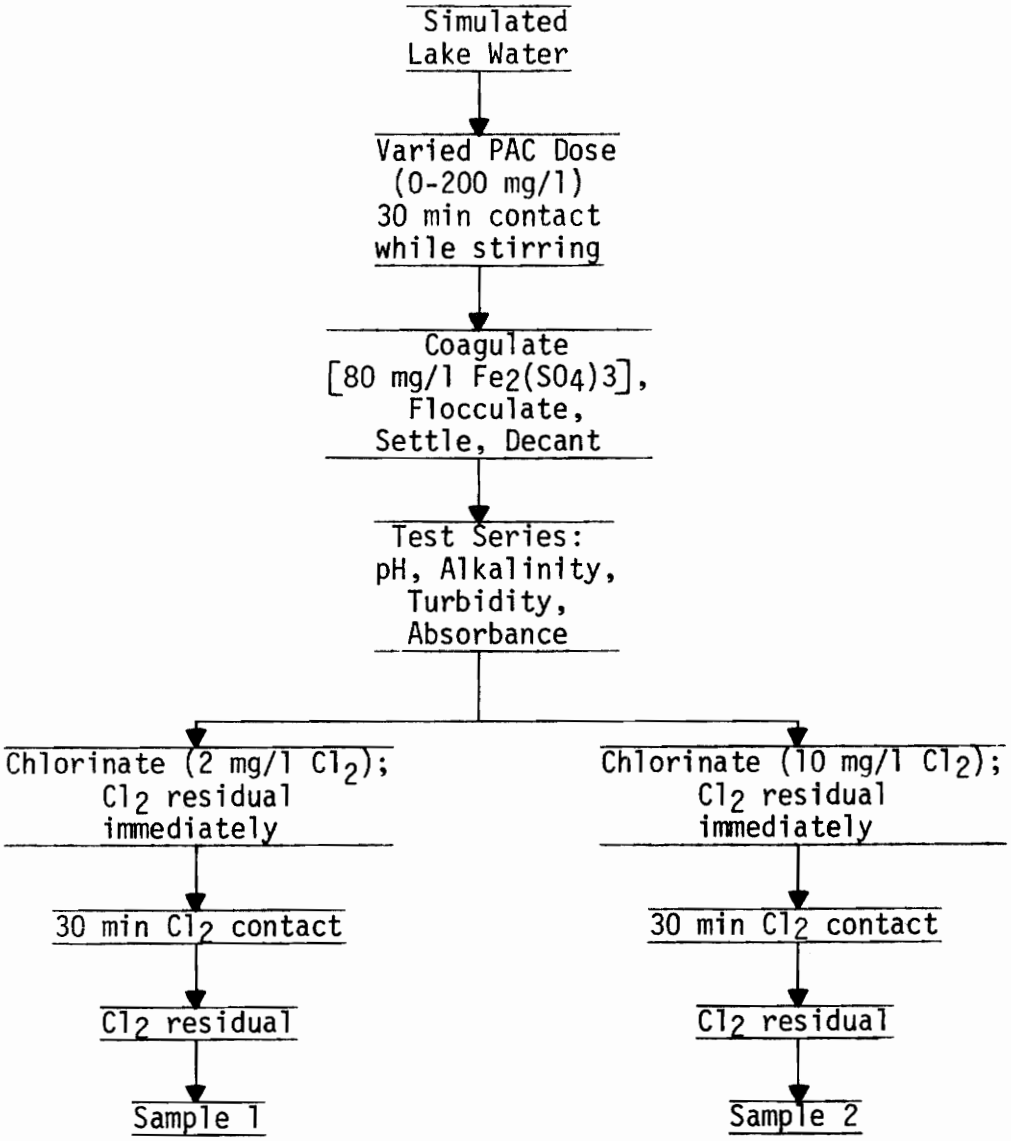


FIGURE B-7. - Test Procedure H

TABLE B-XI. - Stock Water Characterization

Stock Water	Parameters					
	Temperature (°C)	pH	Alkalinity (as mg/l $CaCO_3$)	Turbidity (NTU)	Absorbance (@ 420 mμ)	Color Units
Sample Series H1 - H6	27	8.5	120	31	0.20	-

TABLE B-XII. - Sample Series Characterization

Parameters	Sample Series					
	H1 (1,2)	H2 (1,2)	H3 (1,2)	H4 (1,2)	H5 (1,2)	H6 (1,2)
PAC Dose (mg/l)	0.0	10	25	50	100	200
pH	6.5	6.5	6.3	6.4	6.4	6.5
Alkalinity (as mg/l $CaCO_3$)	77.5	77.5	65.0	67.5	72.5	77.5
Turbidity (NTU)	1.5	1.2	5.6	5.2	7.0	12.0
Absorbance (@ 420 mμ)	0.0	0.0	0.0	0.0	0.0	0.0
Color Units	0	0	0	0	0	0
Cl_2 Residual (mg/l)						
2 mg/l	2.29	2.07	2.07	2.03	2.0	1.98
10 mg/l	9.30	9.83	10.02	10.03	10.05	10.15
30 min Cl_2 Residual (mg/l)						
2 mg/l	1.90	1.75	1.27	1.65	1.72	1.56
10 mg/l	9.26	9.80	9.85	9.86	9.65	9.53

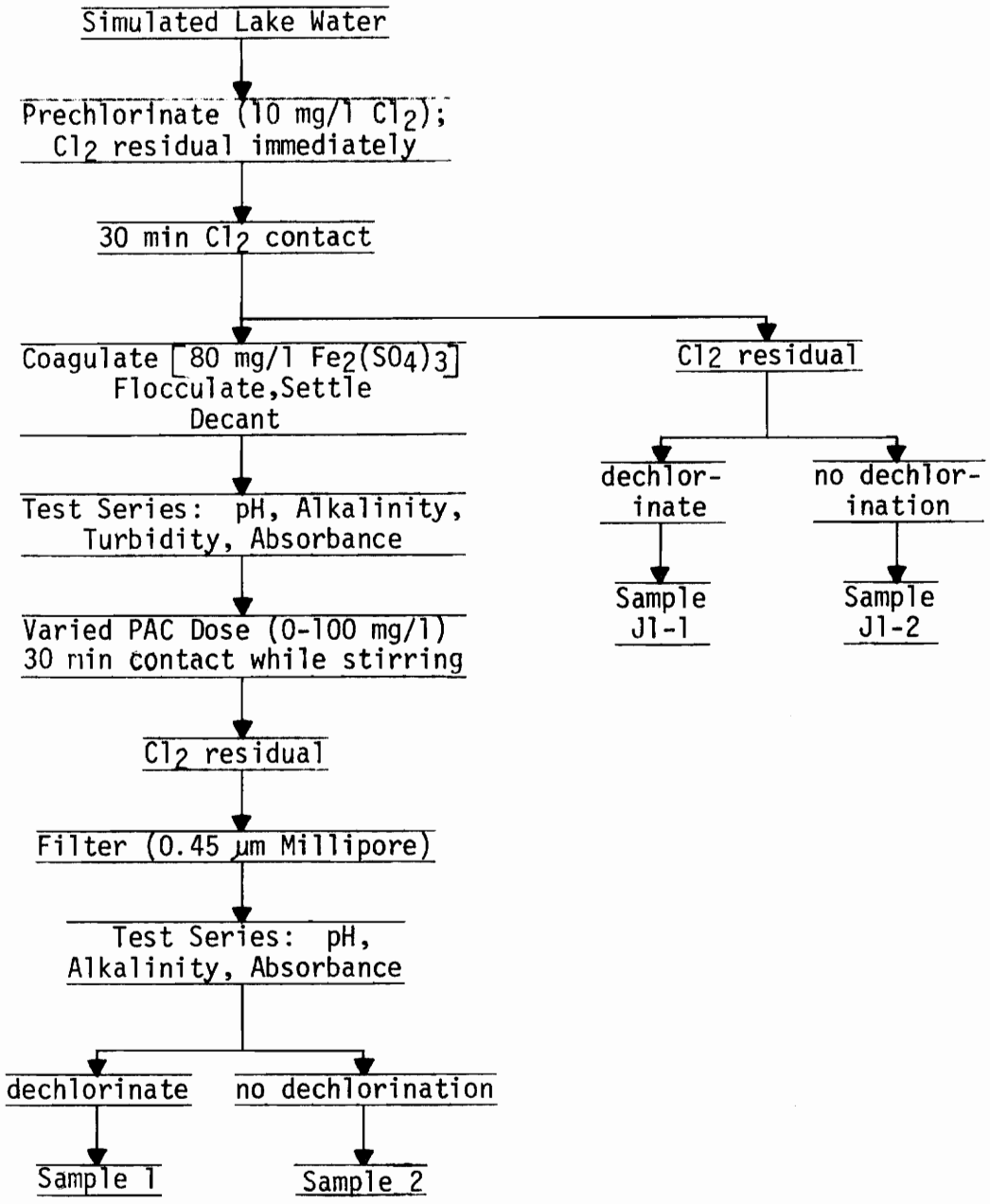


FIGURE B-8. - Test Procedure J

TABLE B-XIII. - Stock Water Characterization

Stock Water	Parameters					
	Temperature (°C)	pH	Alkalinity (as mg/l $CaCO_3$)	Turbidity (NTU)	Absorbance (@ 420 mμ)	Color Units
Sample Series J1 - J5	27	7.9	117.5	31	0.19	-

TABLE B-XIV. - Sample Series Characterization

Parameters	Sample Series				
	J1 (1,2,3,4)	J2 (1,2)	J3 (1,2)	J4 (1,2)	J5 (1,2)
Initial Cl_2 Residual (mg/l)	8.35	9.48	9.85	10.2	9.98
30 min Cl_2 Residual (mg/l)	7.50	-	-	-	-
pH	6.5	-	7.0	6.6	6.7
Alkalinity (as mg/l $CaCO_3$)	72.5	-	50.0	65.0	70.0
Turbidity (NTU)	-	-	2.5	7.6	2.6
Absorbance (@ 420 mμ)	0.005	-	0.075	0.045	0.04
Color Units	2	-	28	17	15
PAC Dose (mg/l)	0.0	10	25	50	100
Final Cl_2 Residual (mg/l)	6.79	4.6	1.45	0.3	0.02
Cl_2 Contact Time (min)	85	110	105	110	105
pH	-	7.2	7.2	7.3	7.2
Alkalinity (as mg/l $CaCO_3$)	-	70.0	67.5	62.0	67.5
Absorbance (@ 420 mμ)	-	0.0	0.025	0.012	0.01

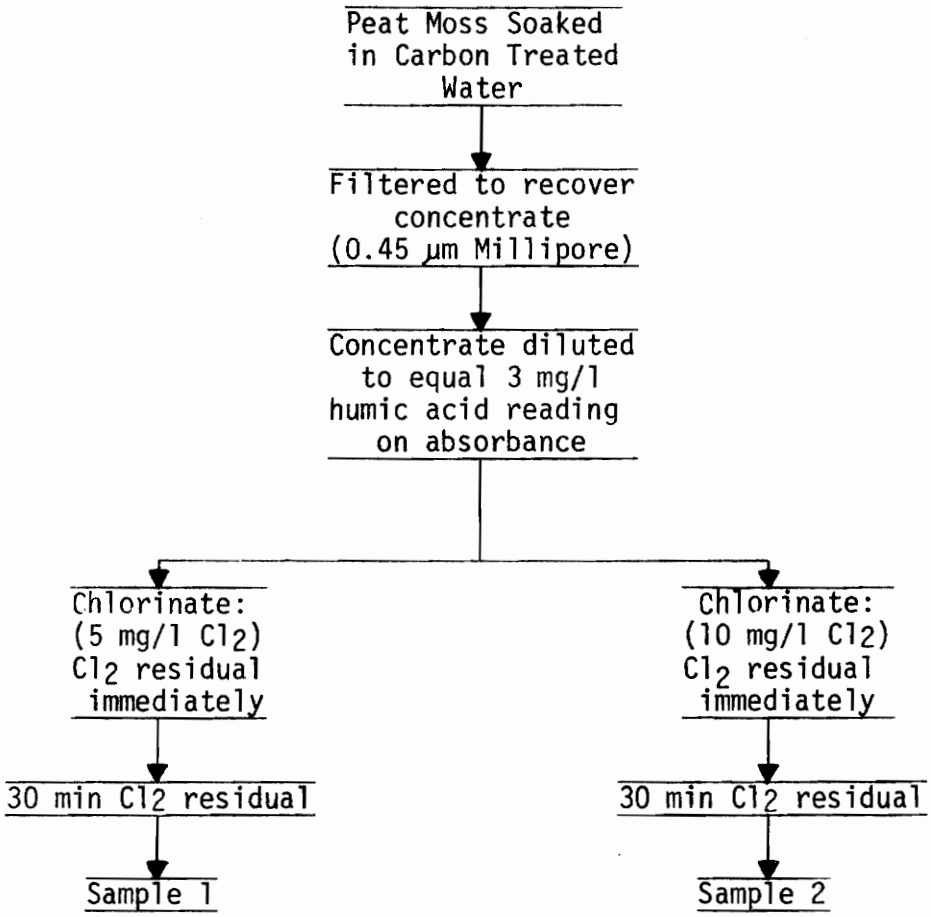


FIGURE B-9. - Test Procedure K

TABLE B-XV. - Sample Series Characterization

Parameters	Sample Series	
	KO-1	KO-2
Absorbance (@ 420 mμ)	0.218	0.218
Color Units	-	-
Cl_2 Residual (mg/l)		
5 mg/l	4.05	NA
10 mg/l	NA	8.38
30 min Cl_2 Residual (mg/l)		
5 mg/l	1.68	NA
10 mg/l	NA	5.67

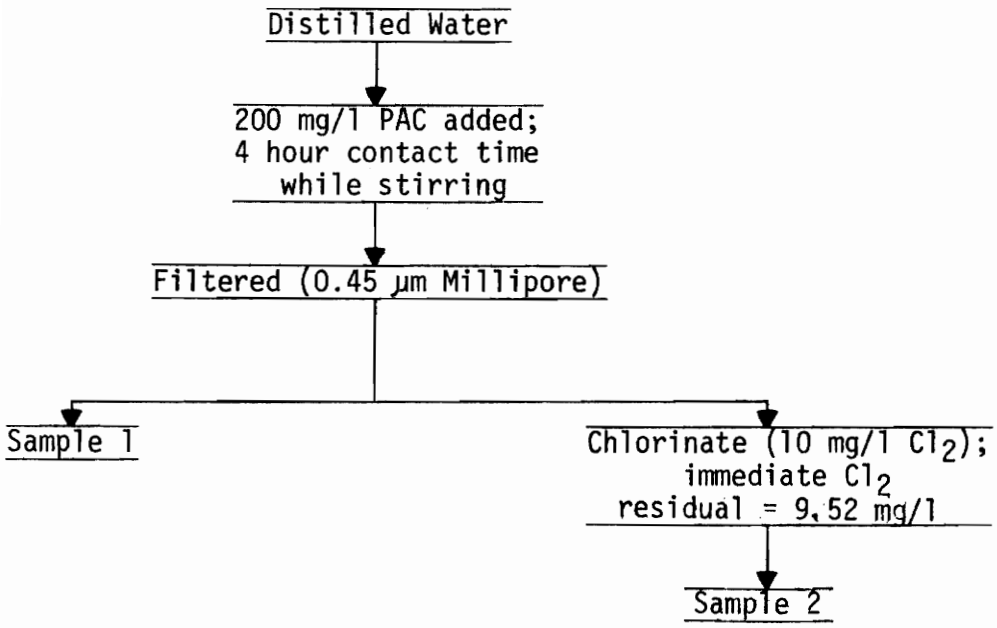


FIGURE B-10. - Test Procedure Z

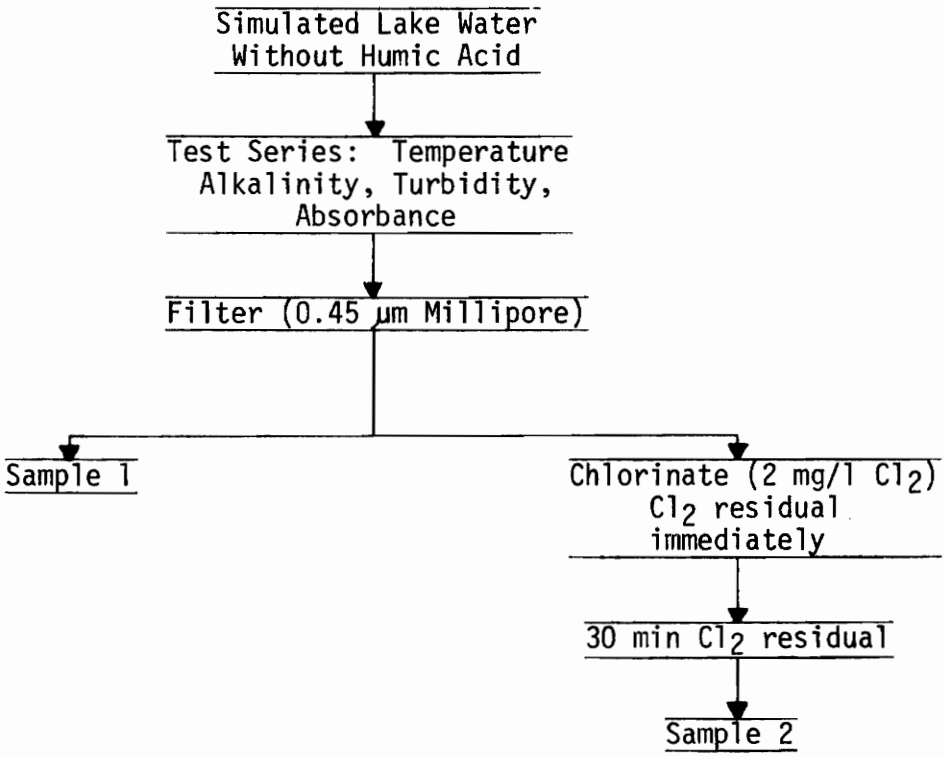


FIGURE B-11. - Test Procedure "O"

TABLE B-XVI - Sample Series Characterization

Parameters	Sample Series	
	00-1	00-2
Temperature (^{o}C)	28	28
Alkalinity (as mg/l $CaCO_3$)	128	128
Turbidity (NTU)	27	27
Absorbance (@ 420 mμ)	0.019	0.019
Color Units	7	7
Cl_2 Residual (mg/l)	NA	2.19
30 min Cl_2 Residual (mg/l)	NA	1.88

APPENDIX C

Sample Procedures and Analytical Results

TABLE C-I. - Sample Procedures and Resultant Haloform Concentrations

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
AO-1	Distilled water used in preparing stock simulated lake water	21
AO-2	First batch of simulated lake water with 1 mg/l humic acid; no treatment; no chlorination	9
AO-3	Second batch of simulated lake water with 1 mg/l humic acid; no treatment; no chlorination	5
A1-1	Simulated lake water with 1 mg/l humic acid; no carbon pretreatment; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934 AH Reeve Angel glass fiber filter in Büchner funnel; chlorinate with 1 mg/l; 30-minute chlorine contact time; dechlorination	6
A1-2	Same as A1-1 except chlorinated with 2 mg/l; no dechlorination	8
A1-3	Same as A1-1 except chlorinated with 2 mg/l; 30-minute chlorine contact time; dechlorination	2
A1-4	Same as A1-1 except chlorinated with 5 mg/l; 30-minute chlorine contact time; dechlorination	8

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
A2-1	Simulated lake water with 1 mg/l humic acid; pretreatment for 30 minutes with 10 mg/l PAC; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934 AH Reeve Angel glass fiber filter in Büchner funnel; chlorinated with 1 mg/l; 30-minute chlorine contact time; dechlorination	5
A2-2	Same as A2-1 except chlorinated with 2 mg/l; no dechlorination	6
A2-3	Same as A2-1 except chlorinated with 2 mg/l; 30-minute chlorine contact time; dechlorination	5
A2-4	Same as A2-1 except chlorinated with 5 mg/l; 30-minute chlorine contact time; dechlorination	5
A3-1	Simulated lake water with 1 mg/l humic acid; pretreatment for 30 minutes with 20 mg/l PAC; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934 AH Reeve Angel glass fiber filter in Büchner funnel; chlorinated with 1 mg/l; 30-minute chlorine contact time; dechlorination	4

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
A3-2	Same as A3-1 except chlorinated with 2 mg/l; no dechlorination	5
A3-3	Same as A3-1 except chlorinated with 2 mg/l; 30-minute chlorine contact time; dechlorination	3
A3-4	Same as A3-1 except chlorinated with 5 mg/l; 30-minute chlorine contact time; dechlorination	4
A4-1	Simulated lake water with 1 mg/l humic acid; pretreatment for 30 minutes with 30 mg/l PAC; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934 AH Reeve Angel glass fiber filter in Büchner funnel; chlorinated with 1 mg/l; 30-minute chlorine contact time; dechlorination	2
A4-2	Same as A4-1 except chlorinated with 2 mg/l; no dechlorination	2
A4-3	Same as A4-1 except chlorinated 2 mg/l; 30-minute chlorine contact time; dechlorination	2
A4-4	Same as A4-1 except chlorinated with 5 mg/l; 30-minute chlorine contact time; dechlorination	2

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
A5-1	Simulated lake water with 1 mg/l humic acid; pre-treatment for 30 minutes with 50 mg/l PAC; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934 AH Reeve Angel glass fiber filter in Büchner funnel; chlorinated with 1 mg/l; 30-minute chlorine contact time; dechlorination	2
A5-2	Same as A5-1 except chlor-inated with 2 mg/l; no dechlorination	3
A5-3	Same as A5-1 except chlor-inated with 2 mg/l; 30-minute chlorine contact time; dechlorination	2
A5-4	Same as A5-1 except chlor-inated with 5 mg/l; 30-minute chlorine contact time; dechlorination	2
A6-1	Simulated lake water with 1 mg/l humic acid; pre-treatment for 30 minutes with 100 mg/l PAC; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934 AH Reeve Angel glass fiber filter in Büchner funnel; chlorinated with 1 mg/l; 30-minute chlorine contact time; dechlorination	2

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
A6-2	Same as A6-1 except chlorinated with 2 mg/l; no dechlorination	3
A6-3	Same as A6-1 except chlorinated with 2 mg/l; 30-minute chlorine contact time; dechlorination	2
A6-4	Same as A6-1 except chlorinated with 5 mg/l; 30-minute chlorine contact time; dechlorination	2
A7-1	Simulated lake water with 1 mg/l humic acid; pretreatment for 30 minutes with 150 mg/l PAC; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934 AH Reeve Angel glass fiber filter in Büchner funnel; chlorinated with 1 mg/l; 30-minute chlorine contact time; dechlorination	1
A7-2	Same as A7-1 except chlorinated with 2 mg/l; no dechlorination	2
A7-3	Same as A7-1 except chlorinated with 2 mg/l; 30-minute chlorine contact time; dechlorination	2
A7-4	Same as A7-1 except chlorinated with 5 mg/l; 30-minute chlorine contact time; dechlorination	2

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
A8-1	Simulated lake water with 1 mg/l humic acid; pre-treatment for 30 minutes with 200 mg/l PAC; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934 AH Reeve Angel glass fiber filter in Büchner funnel; chlorinated with 1 mg/l; 30-minute chlorine contact time; dechlorination	2
A8-2	Same as A8-1 except chlor-inated with 2 mg/l; no dechlorination	3
A8-3	Same as A8-1 except chlor-inated with 2 mg/l; 30-minute chlorine contact time; dechlorination	1
A8-4	Same as A8-1 except chlor-inated with 5 mg/l; 30-minute chlorine contact time; dechlorination	2
B0-1	First batch of simulated lake water with 1 mg/l humic acid; no treatment; no chlorination	7
B0-2	Second batch of simulated lake water with 1 mg/l humic acid; no treatment; no chlorination	6
B1-1	Simulated lake water with 1 mg/l humic acid; pre-chlorination with 2 mg/l; 30-minute chlorine contact	10

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
	time; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; no dechlorination; no carbon post treatment; filtered through 0.45 μm Millipore	
B1-2	Same as B1-1 except dechlorinated after coagulation, flocculation and settling	7
B2-1	Same as B1-1 except for post treatment for 30 minutes with 10 mg/l PAC; filtered through 0.45 μm Millipore	6
B2-2	Same as B1-1 except dechlorinated; post treatment for 30 minutes with 10 mg/l PAC; filtered through 0.45 μm Millipore	4
B3-1	Same as B1-1 except for post treatment for 30 minutes with 20 mg/l PAC; filtered through 0.45 μm Millipore	3
B3-2	Same as B1-1 except dechlorinated; post treatment for 30 minutes with 20 mg/l PAC; filtered through 0.45 μm Millipore	2
B4-1	Same as B1-1 except for post treatment for 30 minutes with 30 mg/l PAC; filtered through 0.45 μm Millipore	2

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
B4-2	Same as B1-1 except dechlorinated; post treatment for 30 minutes with 30 mg/l PAC; filtered through 0.45 μm Millipore	2
B5-1	Same as B1-1 except for post treatment for 30 minutes with 50 mg/l PAC; filtered through 0.45 μm Millipore	3
B5-2	Same as B1-1 except dechlorinated; post treatment for 30 minutes with 50 mg/l PAC; filtered through 0.45 μm Millipore	2
B6-1	Same as B1-1 except for post treatment for 30 minutes with 100 mg/l PAC; filtered through 0.45 μm Millipore	2
B6-2	Same as B1-1 except dechlorinated; post treatment for 30 minutes with 100 mg/l PAC; filtered through 0.45 μm Millipore	2
B7-1	Same as B1-1 except for post treatment for 30 minutes with 150 mg/l PAC; filtered through 0.45 μm Millipore	1
B7-2	Same as B1-1 except dechlorinated; post treatment for 30 minutes with 150 mg/l PAC; filtered through 0.45 μm Millipore	1

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
B8-1	Same as B1-1 except for post treatment for 30 minutes with 200 mg/l PAC; filtered through 0.45 μm Millipore	1
B8-2	Same as B1-1 except dechlorinated; post treatment for 30 minutes with 200 mg/l PAC; filtered through 0.45 μm Millipore	1
C0-1	First batch of simulated lake water with 1 mg/l humic acid; no treatment; no chlorination	2
C0-2	Second batch of simulated lake water with 1 mg/l humic acid; no treatment; no chlorination	5
C1-1	Simulated lake water with 1 mg/l humic acid; no carbon pretreatment; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934 AH Reeve Angel glass fiber filter in Büchner funnel; chlorinated with 2 mg/l; 30-minute chlorine contact time; dechlorination	4
C1-2	Same as C1-1 except no dechlorination	7
C2-1	Simulated lake water with 1 mg/l humic acid; pretreatment for 0.25 hour with	3

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
	50 mg/l PAC; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934 AH Reeve Angel glass fiber filter in Büchner funnel; chlorinated with 2 mg/l; 30-minute chlorine contact time; dechlorination	
C2-2	Same as C2-1 except no dechlorination	6
C3-1	Simulated lake water with 1 mg/l humic acid; pretreatment for 0.5 hour with 50 mg/l PAC; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934 AH Reeve Angel glass fiber filter in Büchner funnel; chlorinated with 2 mg/l; 30-minute chlorine contact time; dechlorination	3
C3-2	Same as C3-1 except no dechlorination	8
C4-1	Simulated lake water with 1 mg/l humic acid; pretreatment for 0.75 hour with 50 mg/l PAC; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934 AH Reeve Angel glass fiber filter in Büchner funnel; chlorinated with 2 mg/l; 30-minute chlorine contact time; dechlorination	3

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
C4-2	Same as C4-1 except no dechlorination	7
C5-1	Simulated lake water with 1 mg/l humic acid; pretreatment for 1 hour with 50 mg/l PAC; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934 AH Reeve Angel glass fiber filter in Büchner funnel; chlorinated with 2 mg/l; 30-minute chlorine contact time; dechlorination	3
C5-2	Same as C5-1 except no dechlorination	7
C6-1	Simulated lake water with 1 mg/l humic acid; pretreatment for 2 hours with 50 mg/l PAC; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934 AH Reeve Angel glass fiber filter in Büchner funnel; chlorinated with 2 mg/l; 30-minute chlorine contact time; dechlorination	2
C6-2	Same as C6-1 except no dechlorination	7
C7-1	Simulated lake water with 1 mg/l humic acid; pretreatment for 4 hours with 50 mg/l PAC; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934	1

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
	AH Reeve Angel glass fiber filter in Büchner funnel; chlorinated with 2 mg/l; 30-minute chlorine contact time; dechlorination	
C7-1S	Same as C7-1 except sample put in specially treated bottle	1
C7-2	Same as C7-1 except no dechlorination	17
C7-2S	Same as C7-1 except no dechlorination and sample put in specially treated bottle	20
C8-1	Simulated lake water with 1 mg/l humic acid; pretreatment for 8 hours with 50 mg/l PAC; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934 AH Reeve Angel glass fiber filter in Büchner funnel; chlorinated with 2 mg/l; 30-minute chlorine contact time; dechlorination	2
C8-1S	Same as C8-1 except sample put in specially treated bottle	2
C8-2	Same as C8-1 except no dechlorination	9,<1
C8-2S	Same as C8-1 except no dechlorination and sample put in specially treated bottle	10,<1

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
C9-1	Simulated lake water with 1 mg/l humic acid; pretreatment for 12 hours with 50 mg/l PAC; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934 AH Reeve Angel glass fiber filter in Büchner funnel; chlorinated with 2 mg/l; 30-minute chlorine contact time; dechlorination	2,<1
C9-1S	Same as C9-1 except sample put in specially treated bottle	2,<1
C9-2	Same as C9-1 except no dechlorination	13,<1
C9-2S	Same as C9-1 except no dechlorination and sample put in specially treated bottle	11,<1
C10-1	Simulated lake water with 1 mg/l humic acid; pretreatment for 24 hours with 50 mg/l PAC; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934 AH Reeve Angel glass fiber filter in Büchner funnel; chlorinated with 2 mg/l; 30-minute chlorine contact time; dechlorination	1,<1
C10-2	Same as C10-1 except no dechlorination	7,<1

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
C11-1	Simulated lake water with 1 mg/l humic acid; pretreatment for 48 hours with 50 mg/l PAC; coagulation with 50 mg/l $Fe_2(SO_4)_3$, flocculation and settling; filtered through grade 934 AH Reeve Angel glass fiber filter in Büchner funnel; chlorinated with 2 mg/l; 30-minute chlorine contact time; dechlorination	4, <1
C11-2	Same as C11-1 except no dechlorination	5, <1
E0-0	Distilled water used in preparing stock simulated lake water	19, 1
E0-1	Simulated lake water with 1 mg/l humic acid and no clay; chlorination with 5 mg/l; sample after 10 minutes chlorine contact time; dechlorination	31, 1
E0-2	Same as E0-1 except sample after 30 minutes chlorine contact time; dechlorination	37, 1
E0-3	Same as E0-1 except sample after 1 hour chlorine contact time; dechlorination	37, 1
E0-4	Same as E0-1 except sample after 2 hours chlorine contact time; dechlorination	41, 2
E0-5	Same as E0-1 except sample after 4 hours chlorine contact time; dechlorination	40, 1

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
EO-6	Same as EO-1 except sample after 8 hours chlorine contact time; dechlorination	50
EO-7	Same as EO-1 except sample after 24 hours chlorine contact time; dechlorination	37
EO-8	Same as EO-1 except sample after 48 hours chlorine contact time; dechlorination	28
EO-9	Same as EO-1 except sample after 96 hours chlorine contact time; dechlorination	20
EO-9S	Same as EO-9 except sample put in specially treated bottle	23
FO-1	Distilled water used in preparing stock simulated lake water	26, 3
F1-1	Simulated lake water with 0.25 mg/l humic acid and no clay; chlorination with 1 mg/l; 30-minute chlorine contact time; dechlorination	10
F1-2	Same as F1-1 except chlorination with 2 mg/l; 30-minute chlorine contact time; dechlorination	20, 2
F1-3	Same as F1-2 except no dechlorination	61, 2
F1-4	Same as F1-1 except chlorination with 5 mg/l; 30-minute chlorine contact time; dechlorination	21, 2

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
F2-1	Simulated lake water with 0.5 mg/l humic acid and no clay; chlorination with 1 mg/l; 30-minute chlorine contact time; dechlorination	12, 1
F2-2	Same as F2-1 except chlorination with 2 mg/l; 30-minute chlorine contact time; dechlorination	14, 1
F2-3	Same as F2-2 except no dechlorination	60, 1
F2-4	Same as F2-1 except chlorination with 5 mg/l; 30-minute chlorine contact time; dechlorination	17, 1
F3-1	Simulated lake water with 1 mg/l humic acid and no clay; chlorination with 1 mg/l; 30-minute chlorine contact time; dechlorination	19, 2
F3-2	Same as F3-1 except chlorination with 2 mg/l; 30-minute chlorine contact time; dechlorination	21, 2
F3-3	Same as F3-2 except no dechlorination	67, 2
F3-4	Same as F3-1 except chlorination with 5 mg/l; 30-minute chlorine contact time; dechlorination	26, 2
F4-1	Simulated lake water with 2 mg/l humic acid and no clay, chlorination with	17, 2

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
	1 mg/l; 30-minute chlorine contact time; dechlorination	
F4-2	Same as F4-1 except chlorination with 2 mg/l; 30-minute chlorine contact time; dechlorination	21, 1
F4-3	Same as F4-2 except no dechlorination	75, 1
F4-4	Same as F4-1 except chlorination with 5 mg/l; 30-minute chlorine contact time; dechlorination	26, 1
F5-1	Simulated lake water with 3 mg/l humic acid and no clay; chlorination with 1 mg/l; 30-minute chlorine contact time; dechlorination	15, 2
F5-1S	Same as F5-1 except sample put in specially treated bottle	19, 2
F5-2	Same as F5-1 except chlorination with 2 mg/l; 30-minute chlorine contact time; dechlorination	21, 2
F5-2S	Same as F5-2 except sample put in specially treated bottle	21, 2
F5-3	Same as F5-2 except no dechlorination	75, 2
F5-3S	Same as F5-3 except sample put in specially treated bottle	77, 2

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
F5-4	Same as F5-1 except chlorination with 5 mg/l; 30-minute chlorine contact time; dechlorination	23, <1
F5-4S	Same as F5-4 except sample put in specially treated bottle	22, <1
H1-1	Simulated lake water with 3 mg/l humic acid; no carbon pretreatment; coagulation with 80 mg/l $Fe_2(SO_4)_3$, flocculation and settling; chlorinated with 2 mg/l; no dechlorination	21, 2
H1-2	Same as H1-1 except chlorinated with 10 mg/l; no dechlorination	37, 1
H2-1	Simulated lake water with 3 mg/l humic acid; pretreatment for 30 minutes with 10 mg/l PAC; coagulation with 80 mg/l $Fe_2(SO_4)_3$, flocculation and settling; chlorinated with 2 mg/l; no dechlorination	18, 1
H2-2	Same as H2-1 except chlorinated with 10 mg/l; no dechlorination	32, 1
H3-1	Simulated lake water with 3 mg/l humic acid; pretreatment for 30 minutes with 25 mg/l PAC; coagulation with 80 mg/l $Fe_2(SO_4)_3$, flocculation and settling; chlorinated with 2 mg/l; no dechlorination	21, 1

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
H3-2	Same as H3-1 except chlorinated with 10 mg/l; no dechlorination	31, 1
H4-1	Simulated lake water with 3 mg/l humic acid; pretreatment for 30 minutes with 50 mg/l PAC; coagulation with 80 mg/l $Fe_2(SO_4)_3$, flocculation and settling; chlorinated with 2 mg/l; no dechlorination	11, 1
H4-2	Same as H4-1 except chlorinated with 10 mg/l; no dechlorination	17, <1
H5-1	Simulated lake water with 3 mg/l humic acid; pretreatment for 30 minutes with 100 mg/l PAC; coagulation with 80 mg/l $Fe_2(SO_4)_3$, flocculation and settling; chlorinated with 2 mg/l; no dechlorination	12, 1
H5-2	Same as H5-1 except chlorinated with 10 mg/l; no dechlorination	17, 1
H6-1	Simulated lake water with 3 mg/l humic acid; pretreatment for 30 minutes with 200 mg/l PAC; coagulation with 80 mg/l $Fe_2(SO_4)_3$, flocculation and settling; chlorinated with 2 mg/l; no dechlorination	11, 1
H6-2	Same as H6-1 except chlorinated with 10 mg/l; no dechlorination	29, 1

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
J1-1	Simulated lake water with 3 mg/l humic acid; chorination with 10 mg/l; 30-minute chlorine contact time; dechlorination	19,<1
J1-2	Simulated lake water with 3 mg/l humic acid; chlorination with 10 mg/l; no dechlorination	256, 5, 1
J1-3	Simulated lake water with 3 mg/l humic acid; pre-chlorination with 10 mg/l; 30-minute chlorine contact time; coagulation with 80 mg/l $Fe_2(SO_4)_3$, flocculation and settling; no carbon post treatment; filtered through 0.45 μm Millipore; dechlorination	23,<1
J1-4	Same as J1-3 except no dechlorination	35, 3
J2-1	Same as J1-3 except for post treatment for 30 minutes with 10 mg/l PAC; filtered through 0.45 μm Millipore; dechlorination	14, 2
J2-2	Same as J2-1 except no dechlorination	23,<1
J3-1	Same as J1-3 except for post treatment for 30 minutes with 25 mg/l PAC; filtered through 0.45 μm Millipore; dechlorination	7,<1
J3-2	Same as J3-1 except no dechlorination	11,<1

TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
J4-1	Same as J1-3 except for post treatment for 30 minutes with 50 mg/l PAC; filtered through 0.45 μm Millipore; dechlorination	4, <1
J4-2	Same as J4-1 except no dechlorination	3, <1
J5-1	Same as J1-3 except for post treatment for 30 minutes with 100 mg/l PAC; filtered through 0.45 μm Millipore; dechlorination	3, <1
J5-2	Same as J5-1 except no dechlorination	3, <1
K0-1	Peat moss soaked in carbon treated distilled water, filtered through 0.45 μm Millipore; diluted to equal 3 mg/l humic acid reading on absorbance; chlorinated with 5 mg/l; no dechlorination	98, 2
K0-2	Same as K0-1 except chlorinated with 10 mg/l; no dechlorination	209, 6
Z0-1	Distilled water treated for about 4 hours with 200 mg/l PAC; filtered through 0.45 μm Millipore; no chlorination	2, <1
Z0-2	Same as Z0-1 except chlorinated with 10 mg/l; no dechlorination	32, <1
00-1	Simulated lake water with no humic acid; filtered through	8

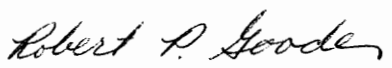
TABLE C-I. - Continued

Sample Number	Treatment	Final Haloform Concentration ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$)
	0.45 μm Millipore, no chlorination	
00-2	Same as 00-1 except chlorinated with 2 mg/l; no dechlorination	14

VITA

Robert P. Goode was born September 2, 1950 in Palatka, Florida. He received his primary and secondary education in the Prince George County Public Schools, graduating from Prince George High School, Prince George, Virginia in June, 1968.

He entered Virginia Polytechnic Institute and State University in September, 1968 and was graduated in June, 1973 with a Bachelor of Science in General Science. After graduation, he was employed by the Virginia State Water Control Board's Tidewater Regional Office. In September, 1975, he entered the Graduate School of Virginia Polytechnic Institute and State University and has been working towards completing the requirements for a Master of Science in Environmental Sciences and Engineering.



EFFECTIVENESS OF WATER TREATMENT METHODS FOR REMOVAL OF HALOFORMS AND THEIR PRECURSORS

by

Robert Paul Goode

(ABSTRACT)

Using a simulated lake water containing humic acid, various combinations of water treatment processes were utilized to determine their effect on precursor removal and haloform removal subsequent to their formation.

Laboratory tests, including temperature, pH, alkalinity, absorbance, and chlorine residual, were performed throughout the treatment process. Samples were collected and shipped to California Analytical Laboratory for volatile organic analysis.

The results of this study supported those from past studies in that it showed humic acid to be a precursor to volatile organics. The data indicated that effective precursor removal could be achieved by coagulation, flocculation, and sedimentation, especially when followed by doses of activated carbon in the range of 30-50 mg/l.

It was also observed that the chlorine concentration had more effect on the production of volatile organics than the humic acid concentration. The reaction between humic acid and chlorine was not instantaneous as haloform concentrations continued to increase

for up to eight or more hours after chlorination.

The data appear to show that the most effective treatment to insure minimum concentrations of haloforms in finished waters is precursor removal prior to chlorination. If the raw water is a surface water, then coagulation, flocculation, and sedimentation, and possible powdered activated carbon treatment, should proceed chlorination. However, if prechlorination is necessary, chlorination should be rapidly succeeded by the routine water treatment processes which would insure reasonably low haloform levels in finished water.