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I am submitting herewith a thesis written by James C. Bird entitled "The Effect of Bromide on Trihalomethane Formation." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

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THE EFFECT OF BROMIDE ON TRIHALOMETHANE FORMATION

A Thesis
Presented for the
Master of Science
Degree
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James C. Bird
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ABSTRACT

A study was conducted to examine the effect of bromide on the formation and distribution of trihalomethanes in drinking water. Chlorination experiments were made under controlled laboratory conditions of bromide level, chlorine dose, pH, ionic strength, temperature, and organic precursor concentration. Two types of raw waters were chlorinated: pure humic acid solutions and filtered Tennessee River water. Resulting trihalomethane formations were monitored over 96 hour reaction periods.

The results indicated that bromide can be an important factor in THM formation. An increase in TTHM yield and a shift toward more brominated THMs was observed for an increase in initial bromide level. A decrease in the effect of chlorine dose on TTHM yield and distribution was noticed with an increase in initial bromide level. For a given level of bromide, a decrease in humic acid level was found to be associated with an increase in the amount of bromine THMs relative to the amount of chlorine THMs. Ionic strength was found to have no influence on TTHM yield or distribution for the levels of bromide examined. The effect of pH on TTHM yield was observed to be enhanced at higher levels of bromide. The temperature dependence on THM formation was found to be strongly influenced by the bromide level. The temperature dependence of $CHCl_3$ formation was found to decrease with an increase in bromide. The temperature dependence of $CHCl_2Br$ formation was found to be greatest at a level of bromide corresponding to its predominance in the TTHM distribution. The temperature dependence of $CHClBr_2$ formation was found to be greatest at a level of bromide corresponding to its predominance in the TTHM distribution. The tempera-

ture dependence of $CHBr_3$ formation was found to increase with an increase in bromide level. Similar bromide and temperature effects were observed with the chlorinations of Tennessee River water. In general, a first order computer simulation of THM formation did not give a good fit.

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I. INTRODUCTION

Since 1974 much interest has been generated concerning the presence of synthetic organic chemicals in drinking water. The most widespread occurring organic contaminants detected so far are four trihalomethanes: chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), and bromoform ($CHBr_3$). Since the discovery by Rook[1] that trihalomethanes (THMs) were produced by the chlorination process in drinking water, an extensive amount of research concerning their formation, levels of occurrence, and removal techniques has been acomplished. Proposed federal regulations by EPA on acceptable levels of THMs and other organics in drinking water have created significant economic and technical demands on the water treatment industry.

In the formation of THMs by the chlorination of drinking water, organic material in the raw water reacts with chlorine to form chloroform, and in the presence of bromide ions the three bromine containing THMs may also be formed. Chlorine oxidizes available bromide to a bromine species which can then react in the same manner as chlorine to form additional THMs. Although chloroform has been found to be the predominant THM species in most drinking waters, certain waters have shown high levels or even a predominance of the bromine THMs. These incidences have been linked to a high bromide content in the raw water. During a survey of THM levels in 33 Tennessee municipal water supplies, variations in the proportions of chloroform compared to the bromine THMs were observed. In certain cases, when the total trihalomethane (TTHM) value was low, a predominance of the bromine THMs was found. Initial interest in the present study was generated by these findings and one of the purposes of this study was to gain insight as to why there was so much variation in the distribution of THMs found in the Tennessee survey. Table 1 presents a summary of the ranges and distributions of THMs from this survey.

The emphasis of THM research has been on chloroform. Besides being the usual predominant species, research concerning the health hazards of chloroform is much more complete and implicating. The understanding of the bromine THMs is much less. Their behavior in formation and response to treatment schemes, and to what degree they differ from chloroform, are not well defined. Also it is possible that health effects research could conclude that the bromine THMs are more hazardous than chloroform, which would make their relatively low levels become more significant. Since bromide is a precursor to the THM reaction, it is important to understand its effects.

The objective of this research was to examine the effect of bromide on THM formation and distribution. This was accomplished by a series of lab scale chlorination experiments. Synthetic humic acid solutions were chlorinated under various controlled conditions of pH, ionic strength, temperature, chlorine dose, bromide level, and organic precursor concentration. Resulting THM formations were monitored over 96 hour reaction periods. Additional chlorinations were made using actual raw water samples from the Tennessee River instead of synthetic humic acid solutions. Initially, a comparison of raw water bromide levels with finished water THM levels was planned, but due to problems encountered in the available methods of bromide analysis, this was not successful.

Table 1. Finished Water THM Levels from Tennessee Survey

Compound	Range of Concentrations (ppb)	Percent of TTHM
$CHCL_3$	1.1 - 167.2	2.7 - 100
$CHCL_2Br$	0 - 76.8	0 - 87.6
$CHCLBr_2$	0 - 34.1	0 - 25.7
$CHBr_3$	0 - .1	0 - .5

II. LITERATURE REVIEW

Background Information

The present concern over synthetic organic compounds in drinking water stems largely from several studies reported in 1974. A study of New Orleans drinking water[2] reported a large number of known or suspected carcinogens occurring at detectable levels. Also in 1974, Rook[1] published results of an investigation in the Netherlands which showed THMs at significant levels immediately after, but not prior to, chlorination of drinking water. Another study reported by Bellar _et al._[3] reported finding THMs in U.S. drinking waters. Although not the only compounds detected, the THMs were the predominant contaminants measured. By December, 1974, the Safe Drinking Water Act was signed into law by President Ford (P.L. 93-523), giving EPA a directive for studies of levels of organic contaminants in U.S. drinking waters and to recommend corrective action to reduce levels of hazardous compounds. In 1975, Rook[4] presented a more detailed explanation of the formation of THMs, suggesting two groups of compounds, fulvic and humic acids, as being the main organic precursors responsible. Also in 1975, the EPA presented the results of the National Organics Reconnaissance Survey (NORS), reporting the occurrence of THMs in almost every finished water in the eighty cities surveyed, but only rarely in the raw waters.[5] Table 2 gives the ranges of THM levels measured from the survey. At the 1975 Conference on the Environmental Impact of Water Chlorination held in Oak Ridge, Tennessee, a number of presentations reported new findings concerning the THM issue.[6] Stevens _et al._[7] reported the results of a study of factors influencing THM formation including pH, organic precursor, type of

Table 2. Finished Water Analysis from the National Organics Reconnaissance Survey

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

Source: Symons, J. M., T. A. Bellar, J. K. Carswell, J. DeMarco, K. L. Kropp, G. G. Robeck, D. R. Seeger, C. J. Slocum, B. L. Smith, and A. A. Stevens, "National Organics Reconnaissance Survey", Journal American Water Works Association, 67:634 (1975).

disinfectant and temperature. The influences of these factors were evaluated by bench and pilot scale experiments, and some control applications for full scale water treatment plants were suggested.

In 1976, the National Cancer Institute published results of research showing that at higher doses chloroform could cause cancer in rats.[8] This was followed by an FDA ban on the use of chloroform as a food or drug additive.[9]

In June, 1977, the EPA issued the Interim Primary Drinking Water Regulations, but no Maximum Contaminant Level (MCL) for the THMs was included, pending completion of research on the health effects.[10] Revised Interim Standards were to be implemented based on the findings of a National Academy of Sciences review panel.[11] The Second Conference on the Environmental Impact of Water Chlorination in October, 1977 presented additional new findings on THM formation, methods of analyses, and treatment techniques.[12]

A proposed amendment to the Interim Primary Drinking Water Regulations was published in February, 1978.[13] Among other regulations, a maximum concentration limit for total trihalomethanes (TTHMs) was established at 100 ug/l (yearly average). This limit was designed to reduce the long term averaged exposure of the public to THMs via the drinking water supply. Water utilities under the regulations would be required to meet the standards, by modification of treatment schemes, change in disinfectant, or by installation of activated carbon filters.

As of April, 1979, no decision has been made concerning the implementation of the regulations concerning control of organic contaminants such as the THMs.[14] One likely approach may be to establish Maximum

Contaminant Levels (MCLs) for individual compounds and to allow the water suppliers to choose the method of compliance.

Trihalomethane Formation

The classical haloform reaction is generally accepted as being the reaction involved in the formation of THMs during drinking water treatment. Morris[15] described the haloform reaction as occurring generally in alkaline, aqueous solution with organic compounds containing the acetyl group ($CH_3\overset{O}{C}-$) or structures such as (CH_3CHOH-) that may be oxidized to the acetyl group. The overall reactions may be written:

$$CHCOR + 3HOX \longrightarrow CX_3COR + 3H_2O \tag{1}$$

$$CX_3COR + H_2O \longrightarrow CHX_3 + RCOOH \tag{2}$$

The reaction involves initial dissociation of a hydrogen and addition of the positive halogen to the resulting carbanion. Dissociation and addition are repeated until the methyl group is fully halogenated, which is then displaced by nucleophilic base attack and adds a hydrogen to yield the THM. The entire mechanism is written:

$$RCOCH_3 \longrightarrow R\overset{O}{C} = CH_2 + H^+ \tag{3}$$

$$R\overset{O}{C} = CH_2 + HOX \longrightarrow RCOCH_2X + OH^- \tag{4}$$

$$RCOCH_2X \longrightarrow R\overset{O}{C} = CHX + H^+ \tag{5}$$

$$R\overset{O}{C} = CHX + HOX \longrightarrow RCOCHX_2 + OH^- \tag{6}$$

$$RCOCHX \longrightarrow R\text{-}C = CX_2 + H^+ \tag{7}$$

$$RC = CX_2 + HOX \longrightarrow RCOCX_3 + OH^- \tag{8}$$

$$RCOCX_3 + OH^- \longrightarrow RCOOH + CX_3^- \tag{9}$$

$$CX_3^- + H^+ \longrightarrow CHX_3 \tag{10}$$

The initial enolization (rxn 3) is the rate-limiting step so that the entire sequence occurs at the same rate as the enol formation.

When hypochlorous acid is present, the product of the reaction will be chloroform. If bromide is also present, the hypobromous acid formed will generate the brominated THMs also. Rook[1] explained that the bromide is oxidized to hypobromous acid by hypochlorous acid when raw water is subjected to chlorination.

Symons _et al_.[5] concluded that the organic precursor level of the raw water is the major factor affecting the levels of THMs formed if the chlorine is not exhausted. Further research has concluded that the type of organic precursor is also very important. Rook[1] first proposed that naturally occurring humic substances in surface waters were precursors of THMs, using peat extracts as model precursors. In a later study, Rook[5] also demonstrated that THMs could be produced from other compounds, especially those that contained meta hydroxy aromatic rings. Stevens _et al_.[7] showed additional compounds that were THM precursors, suggesting the precursors are probably found in a mixture of humic substances and simpler compounds that contain the acetyl group. Morris and Baum[16] found other compounds with chemical structures that can react as ketones which could also serve as THM precursors. They suggested the importance of algal biomass and extracellular products as potential THM precursor material in raw water supplies. This was also reported by Hoehn _et al_..[17] Trussell and Umphres[18] presented a summary of functional groups which have been shown to form THMs, Figure 1.

Traditionally, chemists have categorized aquatic humus materials according to their physicochemical behavior. Black and Christman[19]

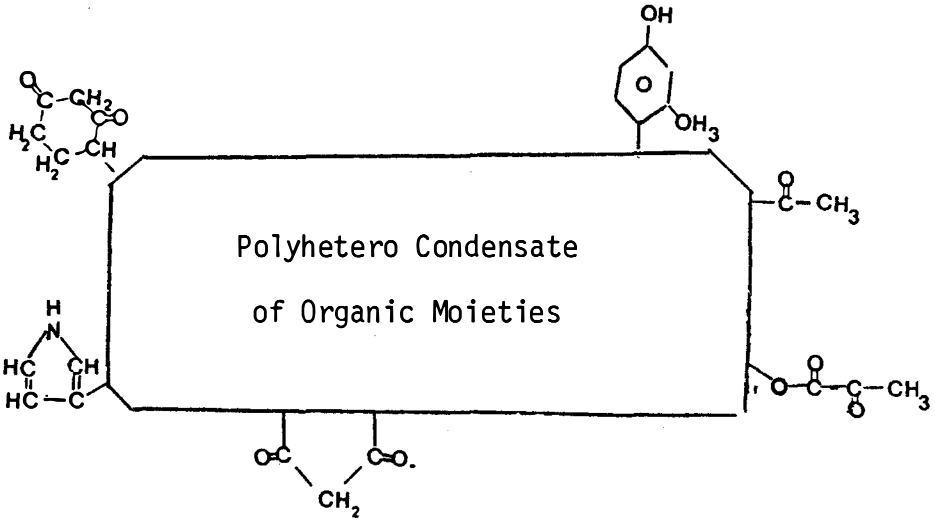

Figure 1. Model Humic Compound.

Source: Trussell, R.R. and M.D. Umphres, "Formation of Trihalomethanes," Journal American Water Works Association, 70:11, p. 608.

described a fractionization scheme based on the work of Oden[20] and Page,[21] in which the alkalai-soluble organic materials are divided into three classes: fulvic acids, humic acids, and hymamelanic acids. The molecular weight of the humic acids are the highest, probably 100,000 or higher, and the fulvic acids have the lowest, probably ranging between 100 and 1000. The data available concerning the distribution of aquatic humus classes in natural waters indicate that humic acids represent a much smaller fraction than the fulvic acids. However, more research on the distributions of humus materials will be needed before general statements can be made.

Several studies have examined the degree of reactivities of various compounds in THM reactions. The data indicate that humic material are much more reactive than low molecular weight compounds which also are THM precursors. Babcock and Singer[22] studied the relative chloroform formation of humic acids and fulvic acids, concluding that humic acids are much more reactive and give significantly higher THM yields upon chlorination.

Although chlorine dose can affect the levels of THMs produced, the relationship is more complicated than a simple linear one.[4,5,7,22] A free chlorine residual appears to be the most important factor concerning chlorine dose, but the level of the residual is not as crucial. Chloramines have not been found to produce measurable quantities of THMs.[23] Studies indicate that after chlorine satisfies an immediate chlorine demand from inorganics such as ammonia, sulfide, and iron (II), additional chlorine begins to react with available organics, including THM precursors.[18] It is at this point where available chlorine can affect the THM yield. Any chlorine in excess to that required to meet the immediate inorganic and short term organic demands does not appreciably increase THM yield. Although a chlorine residual is important in increasing THM formation, the amount of this residual is not so important.

Trihalomethane formation has been shown to be time dependent.[4] Although there is a rapid formation of THMs following contact with chlorine, an increase in yield has been found for over 24 hours.[4,7,24,25] Thus THM levels measured in the distribution system can be much higher than those found at the treatment plant immediately after chlorination. Studies have emphasized that the time of THM measurement is very important and must be considered when monitoring THM levels in drinking waters.[26]

The haloform reaction proceeds more rapidly at higher temperatures, and this has been observed in THM studies.[4,7,27] Stevens _et_ _al_.[7] attributed differences in seasonal THM levels largely to temperature variations. Zogorski[27] also found a temperature dependence for chloroform and bromodichloromethane. Hoehn and Randall,[28] in a two year study, did not find THM concentrations consistently higher with warmer temperatures, concluding that seasonal variations are determined by a number of factors including variation in precursor levels.

The effect of pH on THM formation has been illustrated by a number of investigators.[4,5,7,15,] Rook[4] explained that increasing the pH enhances enolization, which produces more reactive site on the precursor molecule. He observed a sharply increasing reaction rate with fulvic acids in the 9 to 10 pH region. Stevens _et_ _al_.[7] suggested that increasing the pH also may cause low molecular weight compounds, only reactive at higher pH, to enter the haloform reaction. He observed a thirty fold increase in the reaction rate of acetone with chlorine at pH 8.3 over that at pH 6.7. Morris and Baum,[16] using synthetic model compounds, found the chlorine demand to be less at higher pH, but the yields of chloroform about the same at high and low Phs. They suggested that the chlorination of organics proceeds as well at low pH as high pH, and only the final hydrolysis of the trihalogenated molecule requires an elevated pH.

Except for the development of THM formation curves from actual data, no quantitative descriptions of THM kinetics have developed. Because of the variation in organic precursors and the overall reaction complexities involved in natural waters, it has been difficult for researchers to accurately define and quantify the kinetics of THM reactions occurring in water treatment.

The Effect of Bromide

The formation of bromine containing THMs has been attributed to the oxidation of bromide in raw water by chlorine, followed by haloform reaction between the resulting bromine and organic precursors. The oxidation of bromide by chlorine was observed by Johannesson.[29] Whenever chlorine or hypochlorite is added to a water containing bromine ions, there is a rapid formation of hypobromous acid, according to the reaction:

$$Br^- + HOCl \longrightarrow HOBr + Cl^-$$

Other likely intermediates formed are Br_2, OBr^-, with some BrCl and $BrCl_5$. Farkas _et al._[30] and Lewin _et al._[31] studied the kinetics of reactions between hypochlorite and bromides in pure systems. The formation and stability of bromamines were investigated by Gorchev and Morris.[32]

Table 3 presents the possible oxidation states of bromide in water treatment with chlorine or ozone, computed from thermodynamic data. The reaction to bromate, although thermodynamically possible, proceeds only at a very slow rate, and probably is neglible in considerations of water treatment chemistry. Assuming complete oxidation to hypobromous acid and neglible formation of bromate, Figure 2 gives the ratio of different chlorine and bromine species at various pH values for and initial chlorine dose of .00020 M and initial bromide concentration of .0000020 M.[33] The HClO/HBrO ratio in the pH region 7 to 8 increases by an order of magnitude. In the alkaline region, pH 8 and higher, the concentrations of HOCl and HOBr drop to very low values. There the hypohalite species prevail.

Rook[1] noted the formation of bromine THMs and correctly attributed them to the presence of raw water bromide ions. Bunn *et al.*[34] observed the formation of THMs other than chloroform by a series of chlorination studies involving the addition of fluoride, chloride, iodide, and bromide to raw water samples followed by chlorination. Only chlorine, bromine, and iodine containing THMs were detected. The addition of bromide caused the most pronounced effect, with a shift in distribution and also an increase in THM yield. A study of THM levels in Concord, California pointed out this bromide effect.[35] During part of a continuous monitoring study of THM levels, drought conditions caused increasing salt water intrusion into the water source, with a corresponding increase in bromide levels. Although total organic carbon levels remained fairly constant, a dramatic increase in TTHM levels as well as a pronounced shift in distribution toward the bromine THMs were observed. As drought conditions and salt water intrusion subsided, a corresponding decrease in TTHMs and a shift back toward

Table 3. Oxidation States of Bromine and Chlorine

	(E_0 in Volts)
$O_3 + 2H^+ + 2e \longrightarrow O_2 + H_2O$	+ 2.07
$Cl_2 + 2e \longrightarrow 2CL^-$	+ 1.36
$HClO + H^+ + 2e \longrightarrow Cl^- + H_2O$	+ 1.49
$ClO^- + 2H^+ + 2e \longrightarrow Cl^- + H_2O$	+ 1.71
$ClO_3^- + 6H^+ + 5e \longrightarrow \frac{1}{2}Cl_2 + 3H_2O$	+ 1.47
$Br_2(aq) + 2e \longrightarrow 2Br^-$	+ 1.09
$HBrO + H^+ + 2e \longrightarrow Br^- + H_2O$	+ 1.33
$BrO^- + 2H^+ + 2e \longrightarrow Br^- + H_2O$	+ 1.60
$BrO_3^- + 6H^+ + 6e \longrightarrow Br^- + 3H_2O$	+ 1.44

Source: Rook, J. J., "Bromide Oxidation and Organic Substitution in Water Treatment", Journal Environmental Science and Health, A13(2), 91-116 (1978).

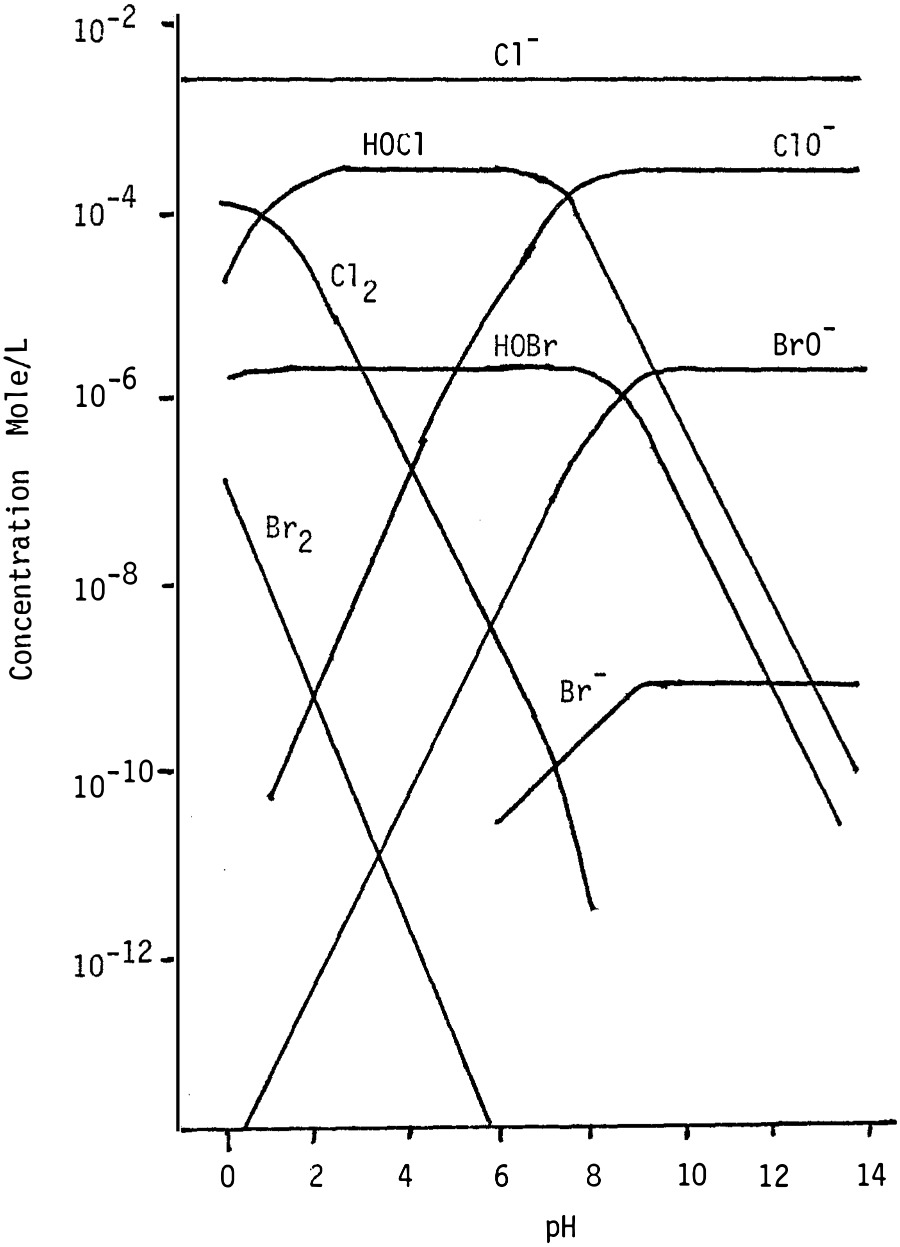

Figure 2. Concentrations of Aqueous Chlorine and Bromine Species as a Function of pH.

Source: Rook, J.J. "Bromide Oxidation and Organic Substitution in Water Treatment," Journal Environmental Science and Health, A13(2), 91-116 (1978).

chloroform was noticed. The increasing TTHM effect of bromide was further substantiated by a lab study in which raw water samples were collected at various locations in the Sacramento-San Joaquin Delta that had different degrees of salt water intrusion. The samples were subjected to standard conditions of chlorine dose and contact time. The results indicated increased TTHMs with increased levels of bromide. However, the total organic carbon levels of the sample varied also. A similar study by the East Bay Utility District in California indicated the same effect of bromide.[36] A comparison of two river sources of the water supply after chlorination showed that the one with salt water intrusion had much higher TTHM levels. Preliminary work by Trussell and Umphres[18] indicated the bromide effect by means of a comparison between a California ground water and the same water spiked with .5 mg/l of bromide. After chlorination, the spiked ground water formed higher TTHMs, and showed a possible faster reaction rate for THM formation.

A recent study published by Rook[33] presented an extensive description of the role of bromide in oxidation and substitution reactions in water treatment. Experiments involving combinations of chlorine and bromine indicated that chlorine preferentially acts as an oxidant while bromine reacts more as a halogenating agent. This conclusion explains the reason why the bromine to chlorine ratio in volatile by-products such as THMs is usually higher than the ratio of bromide originally present to chlorine added. Experiments with peat extracts as a model substance showed that with hypobromous acid a greater amount of bromoform was produced than the corresponding chloroform produced from the reaction with hypochlorous acid. When both halogens reacted in combination, the chloroform formation was suppressed and there was a shift toward brominated THMs. The results of a survey of raw and finished water conditions at a Rotterdam water treatment plant were also presented, shown in Table 4. The tendency toward more organic bromination with lower Cl/Br ratios can be seen.

Arguello <u>et al</u>.[37] in a one year study of THM levels and raw water conditions for fourteen water utilities, measured raw water bromide levels as well as finished water THMs. Most studies have not included successful raw water bromide measurements due to problems in the methods of analyses available. This particular study used ion chromatography to measure the bromide levels. A good correlation was found to exist between the concentration of inorganic bromide in the raw water and the amount of bromine in THMs in the finished water. In all cases examined, approximately five percent of the bromide in the raw water was found in the finished water THMs. These results are shown in Table 5.

Studies which have examined the distribution of THM species formed have reported dissimilar observations. Zogorski <u>et al</u>.[27], in a study of THM formation using chlorinated Ohio River water, reported that an increase in chlorine dose did not significantly increase bromine THM levels, as it did chloroform levels. The raw water bromide contents were apparently low, based on the reported bromine THM levels. Another study,[35] involving relatively high bromide levels in the raw water due to the effects of salt water intrusion, reported a noticeable decrease in bromoform along with an increase in chloroform with increasing chlorine doses. Another THM factor which has been described in opposing ways is the effect of pH. Kinman[38] <u>et al.</u> reported that observed concentrations of the

Table 4. Cl to Br Ratio in Haloforms in Rotterdam Treatment Plant

Sample Period	Chlorine Initial Dose (mg/l)	Chlorine Demand (mg/l)	Chlorine Residual ($x10^{-6}M$)	Bromide ($x10^{-6}M$)	Ratio, Cl/Br Inorganic	Ratio, Cl/Br Organic
1973	4	2.8	34	2	17	4.7
1974 (winter)	2.4	2.1	8.5	1.4	8	4.8
1974 (summer)	4.4	2.2	60	1.5	40	5.9

Source: Rook, J. J., "Bromide Oxidation and Organic Substitution in Water Treatment", Journal Environmental Science and Health, A13(2), 91-116 (1978).

Table 5. Concentration of Bromide in Raw Water Vs. Bromine in Trihalomethanes

City	Bromide in Raw Water, mg/L	Bromine in Trihalomethanes in Finished Water, μg/L	% Bromine Incorporated
1	N.D.	1	---
2a	0.3	17	5.6
2b	0.8	45	5.6
4	N.D.	2	---
5	N.D.	1	---
6	N.D.	1	---
8	N.D.	21	---
9	N.D.	1	---
10a	0.6	31	5.2
10b	0.3	14	4.7
10c	2.0	108	5.4
11	N.D.	1	---
13	N.D.	1	---

Source: Arguello, M. D., C. D. Chriswell, J. S. Fritz, L. D. Kissinger, K. W. Lee, J. J. Richard, and H. J. Svec, "Trihalomethanes in Water: A Report on the Occurrence, Seasonal Variations in Concentrations and Precursors of Trihalomethanes", (Accepted by Journal American Water Works Association for publication).

bromine THMs were not significantly influenced by pH in the range 7.5-9.0. Another study found that bromoform was the only THM which showed an increase with increased pH.[36] Again, these two studies involved raw waters with substantially different bromide levels. Zogorski et al.[27], in a study of the temperature effect on THM formation using settled Ohio River water, found a much greater temperature dependence for chloroform compared to bromodichloromethane, the only other THM monitored. One of the objectives of this thesis was to sort out these factors in relation to the bromide content of the raw water. These dissimilar trends observed regarding THM factors may be due to an added effect of the level of bromide.

Ozone is currently considered one of the most attractive alternatives to chlorine for disinfection. From a comparison of the oxidation potentials of ozone and bromine, it is concluded that bromide in the presence of ozone would be oxidized to bromine. In the presence of organic THM precursors, the reaction with bromine to form bromoform could be expected. Available data from completed studies, however, do not substantiate this hypothesis. Umphres et al.[39], evaluating the THMs formed by various oxidants in the presence and absence of bromide, reported no significant amounts of bromoform formed resulting from the ozonation of waters containing bromide. Symons et al.[40] reported no bromoform measured in raw water samples treated with ozone only. Rook[33] detected no brominated THMs after ozonating solutions containing bromide and organic THM precursors. However, he did indicate that other non-volatile brominated organics were formed, based on a mass balance of initial bromide, which were not detectable by the analytical methods used. Rook also suggested that preozonation followed by chlorination will shift the speciation so that more brominated THMs are formed. Trussell and Umphres[18] confirmed these observations in pilot scale studies involving preozonation.

An EPA study concerning the use of granular activated carbon for removal of THM precursors and THMs has found different degrees of effectiveness depending on the compound considered.[41] It was observed that precursor removal for chloroform by granular activated carbon was more effective than for the brominated THMs. However, for THM removal, chloroform was the least effectively removed THM, and had the fastest breakthrough time.

Besides bromide contribution from natural geologic sources and salt water intrusion, there are other significant sources resulting from human activity.[42] Two compounds are manufactured and used in large enough quantities to possibly make significant contributions to bromide levels in natural waters: Methyl bromide and ethylene dibromide. Methyl bromide is a widely used fumigant in mills, warehouses, railway boxcars, nurseries, and on agricultural crops. Soil fumigation is the major use, with frequent applications to tomatoes, strawberries, tobacco, ornamentals, and other crops. Most of the methyl bromide applied ends up in the soil, where it decomposes to inorganic bromide and can be readily leached out. Another major source of bromide is from ethylene dibromide, a gasoline additive used in leaded gasolines. Methyl bromide is formed by the degradation of ethylene dibromide during gasoline combustion, and has been detected at elevated concentrations in the exhaust of cars. In the atmosphere, methyl bromide decomposes by photolysis, in soils and food by methylation reactions, and in water by hydrolysis and enzymatically controlled reactions. Inorganic bromide residues commonly found in food are the result of methyl bromide decomposition. Other bromine containing compounds are primarily used as chemical intermediates in chemical manufacturing. In most applications, the bromine is converted to the inorganic bromide form before entry into the environment.

Trihalomethane Reduction Techniques in Water Treatment

The control of THM levels is a very site specific problem, and both the technical and economical feasibilities of minimizing THM levels depend upon the current treatment scheme, plant size, and raw water conditions. Based on a review of the literature, the following conclusions are presented:

1. Granular Activated Carbon (GAC) is not feasible for the effective reduction of THMs, because of poor affinities for these compounds and frequent regenerations required. Some success has been found for GAC applications to THM precursor removal.[23,41]
2. Substantial THM reductions may be achieved by changing the point of chlorination and optimum use of coagulation, flocculation, and sedimentation.[7,17,22,25,27,35,36,38,43,44,45]
3. Preozonation, depending on the specific situation being considered, may or may not be effective in reducing THM precursors.[33,39,40,46]

4. As alternative disinfectants to chlorine, neither ozone or chlorine dioxide produce THMs. More studies need to be completed to evaluate their potentials for producing other harmful by-products as well as their economic feasibilities.[33,39,40,46]

III. EXPERIMENTAL DESIGN

The objective of this study was to examine the effect of bromide on THM formation and distribution. This goal was met by a series of bench scale chlorination experiments using various conditions of bromide level, pH, chlorine dose, ionic strength, organic precursor concentration, and temperature.

Development of quantitative kinetic descriptions of THM formation was beyond the scope of this study. Consideration of all factors affecting the kinetics of THM formation would require a much more rigorous and extensive experimental matrix than was possible under the objective of this study. Furthermore, because the organic precursors of THMs are not fully understood or even identified, it would not be possible to obtain more than a rough empirical model, which would at best only apply to the specific chemical system used to develop the model. There may be so much variation in the basic organic substrate among water supplies that no useful generalizations could accurately predict THM formation, based on current knowledge of the subject.[18]

Chlorination Experiments

The effect of bromide on THM formation and distribution was studied by a series of bench scale chlorinations. An all glass and teflon reactor, Figure 3, was used for the primary reactions. In order to minimize loss of volatile reaction components, the reactor was designed with a moveable teflon cover. A complete mixed system was insured by means of a large magnetic stirrer. For each reaction, a measured volume of raw water solution was placed in the reactor.

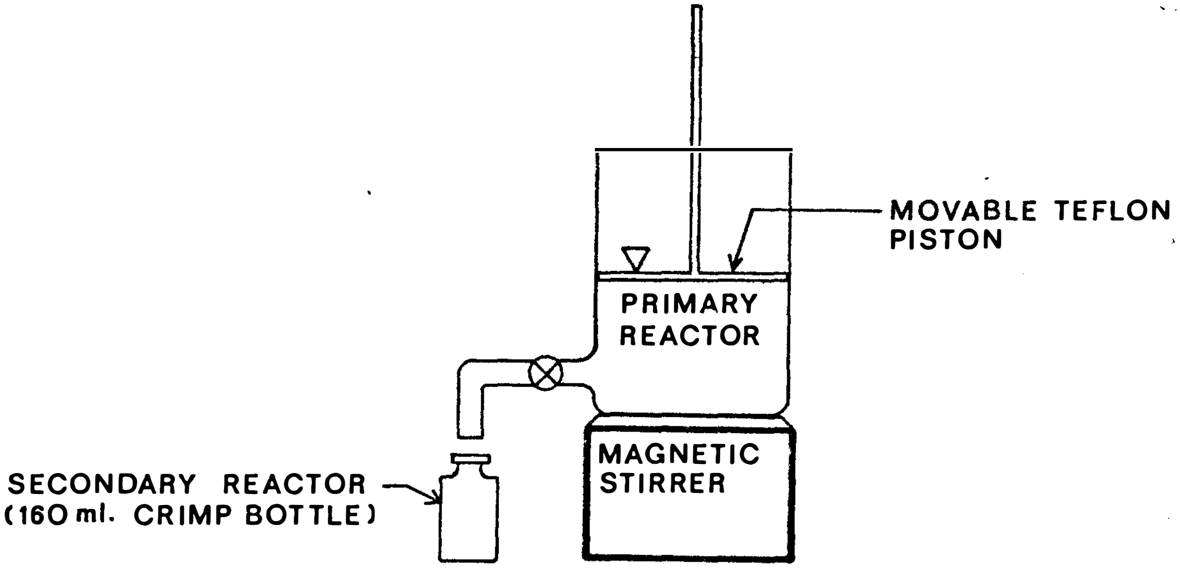

Figure 3. Reactor Design.

This solution was then chlorinated by an aliquot of sodium hypochlorite delivered by volumetric pipet. After two minutes of continuous mixing, a series of glass septum bottles were filled with the chlorinated solution and capped head space free by means of a teflon aluminum crimped seal. At designated times, 1 ml of 2N sodium thiosulfate solution was injected into the bottles to destroy the residual chlorine and thus quench the THM reaction. Simultaneously, corresponding samples from an unquenched bottle were taken for residual oxidant measurements. The sodium hypochlorite used in the chlorinations was prepared by bubbling chlorine gas (Research Purity Grade Matheson) into "organic free" water adjusted to pH 9.0 with NaOH. This stock chlorine solution was diluted and standardized. The entire reaction sequence was carried out in a constant temperature room to insure no variation in temperature during the reaction period. For each reaction, THM measurements were made at 1, 2, 4, 8, 24, 48, 72, and 96 hours and residual oxidant measurements were made at 0, 2, 4, 8, 24, 48, 72, and 96 hours. The reproducibility of the chlorination procedure used in the lab studies was evaluated by triplicate chlorinations under identical conditions. The results of this evaluation are shown in Table 6.

Glassware was rinsed with distilled, then deionized, then "organic free" water and heated in a 103 degree C. oven overnight prior to use. This cleaning procedure was followed to prevent possible THM contamination.

For synthetic solutions, humic acid (K & K Laboratories) was used as a source of THM organic precursor. A 17.5 liter batch was prepared for each series of experiments to minimize variation within

Table 6. Experimental Data Illustrating the Reproducibility of the Chlorination Procedure Used in the Laboratory Studies

	Concentration um/l			
Replicate	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
1	.063	.076	.090	.018
2	.074	.085	.097	.021
3	.078	.091	.106	.022
Mean	.072	.084	.098	.020
Standard Deviation	.008	.006	.006	.002
Coefficient of Variation %	10.8	9.8	8.2	10.4

a series. Each solution contained a measured amount of humic acid, phosphate pH buffer (.005M), and sodium sulfate for ionic strength adjustment. For pH adjustment, when required, either sulfuric acid or sodium hydroxide solutions were used. "Organic free" water was prepared from deionized, distilled water which had been purged with prepurified nitrogen for 24 hours. The prepared humic solution was allowed to stand overnight to insure adequate mixing and to achieve the desired reaction temperature. Prior to chlorinations, non-volatile total organic carbon (NVTOC) and pH measurements were made. Also, a sample blank of solution was analyzed for possible THM contamination.

For the actual raw water chlorinations, samples of settled Tennessee River water were filtered through .45 micron filters. No pH adjustments or phosphate buffer additions were made to the raw water samples. All experiments were carried out in a constant temperature room, with no exposure to sunlight.

For the synthetic humic acid solution experiments, standard conditions were:

Humic Acid:	1 mg/l
pH:	7.0
Chlorine Level:	5 mg/l
Bromide Level:	0 mg/l
Ionic Strength:	.015 M
Water Temperature:	20 degrees C.

One or more of the above parameters were varied in each experiment, with the remaining parameters held constant.

1. The effect of bromide concentration on THM formation and distribution at constant pH 7.0, 1.0 mg/l humic acid, .015 M ionic strength, 20 degrees C., and 5 mg/l chlorine was investigated by spiking individual solutions with 0, .01,

.02, .04, .10, .20, .40, 1.00, 2.00, and 4.00 mg/l bromide, prior to chlorination.

2. The effect of chlorine dose at different levels of bromide was examined by chlorinating solutions of 0, .033, .333 mg/l bromide with chlorine doses of 2.5, 5.0, and 10.0 mg/l.
3. The effect of humic acid level at different levels of bromide was investigated by preparing solutions of .5, 1.0, and 2.0 mg/l humic acid each at 0, .033, and .333 mg/l bromide and subsequently chlorinating.
4. The effect of pH at different levels of bromide was investigated by spiking solutions of pH 6.0, 7.0, 8.0, and 9.5 with 0, .033, .333 mg/l bromide, followed by chlorination.
5. The effect of ionic strength at different levels of bromide was investigated by preparing solutions of .015, .075, and .150 ionic strength. Ionic strength adjustments were made using sodium sulfate. For each ionic strength level, solutions were spiked with 0, .033, and .333 mg/l bromide and subsequently chlorinated.
6. The effect of temperature at different levels of bromide was investigated by chlorinating solutions of 0, .04, .40, and 4.0 mg/l bromide at 10, 20, and 30 degrees Celcius. These temperatures were maintained using a constant temperature room.

For the Tennessee River water experiments, a batch sample of Tennessee River water was taken. After settling, the sample was filtered through a .45 micron filter. In anticipation of a higher chlorine demand, the chlorine dose was increased to 10 mg/l. The stock raw water had a NVTOC of 2.3 mg/L and a pH of 7.4. Besides filtration, no other treatment was made on the sample. The standard conditions were:

Water Temperature:	20 Degrees Celcius
Chlorine Dose:	10.0 mg/L
pH:	7.4
Bromide Level:	not determined

The effect of bromide level on THM formation was examined by spiking the river water with 0, .01, .02, .04, .10, .20, .40, 1.00, 2.00, and 4.00 mg/L bromide and chlorinating with 10.0 mg/L chlorine. The effect of temperature at different levels of bromide was investigated by chlorinating solutions of 0, .04, .40, and 4.00 mg/L bromide at 10, 20, and 30 degrees Celcius.

Individual experimental conditions for each chlorination experiment are presented in Table 7.

Analytical Methods

For THM analysis, a liquid-liquid extraction procedure reported by Henderson _et al_.[47] was used. Pentane was the extraction solvent. The samples were sealed in head space free teflon sealed vials and injected with measured portions of pentane, depicted in Figure 4. After addition of the pentane, the samples were put in a mechanical shaker (Controlled Environment Incubator Shaker, New Brunswick Scientific Co.) and extracted for 30 minutes at 200 r.p.m. before removal. From the extracted pentane layer a portion was withdrawn and injected into a

Table 7. Individual Experimental Conditions

	Humic Acid Studies					
Variation	Bromide (mg/l)	Humic Acid (mg/l)	pH	Temp. (C)	Ionic Strength	Chlorine (mg/l)
Bromide	0.000	1.0	7.0	20.0	.015	5.0
	0.010	1.0	7.0	20.0	.015	5.0
	0.020	1.0	7.0	20.0	.015	5.0
	0.040	1.0	7.0	20.0	.015	5.0
	0.100	1.0	7.0	20.0	.015	5.0
	0.200	1.0	7.0	20.0	.015	5.0
	0.400	1.0	7.0	20.0	.015	5.0
	1.000	1.0	7.0	20.0	.015	5.0
	2.000	1.0	7.0	20.0	.015	5.0
	4.000	1.0	7.0	20.0	.015	5.0
Humic Acid	0.000	0.5	7.0	20.0	.015	5.0
	0.033	0.5	7.0	20.0	.015	5.0
	0.333	0.5	7.0	20.0	.015	5.0
	0.000	1.0	7.0	20.0	.015	5.0
	0.033	1.0	7.0	20.0	.015	5.0
	0.333	1.0	7.0	20.0	.015	5.0
	0.000	2.0	7.0	20.0	.015	5.0
	0.033	2.0	7.0	20.0	.015	5.0
	0.333	2.0	7.0	20.0	.015	5.0
pH	0.000	1.0	6.0	20.0	.015	5.0
	0.033	1.0	6.0	20.0	.015	5.0
	0.333	1.0	6.0	20.0	.015	5.0
	0.000	1.0	7.0	20.0	.015	5.0
	0.033	1.0	7.0	20.0	.015	5.0
	0.333	1.0	7.0	20.0	.015	5.0
	0.000	1.0	8.0	20.0	.015	5.0
	0.033	1.0	8.0	20.0	.015	5.0
	0.333	1.0	8.0	20.0	.015	5.0
	0.000	1.0	9.5	20.0	.015	5.0
	0.033	1.0	9.5	20.0	.015	5.0

Table 7. (Continued)

Variation	Bromide (mg/l)	Humic Acid (mg/)	pH	Temp. (C)	Ionic Strength	Chlorine (mg/l)
Ionic Strength	0.000	1.0	7.0	20.0	.015	5.0
	0.033	1.0	7.0	20.0	.015	5.0
	0.333	1.0	7.0	20.0	.015	5.0
	0.000	1.0	7.0	20.0	.075	5.0
	0.033	1.0	7.0	20.0	.075	5.0
	0.333	1.0	7.0	20.0	.075	5.0
	0.000	1.0	7.0	20.0	.150	5.0
	0.033	1.0	7.0	20.0	.150	5.0
	0.333	1.0	7.0	20.0	.150	5.0
Chlorine Dose	0.000	1.0	7.0	20.0	.015	2.5
	0.033	1.0	7.0	20.0	.015	2.5
	0.333	1.0	7.0	20.0	.015	2.5
	0.000	1.0	7.0	20.0	.015	5.0
	0.033	1.0	7.0	20.0	.015	5.0
	0.333	1.0	7.0	20.0	.015	5.0
	0.000	1.0	7.0	20.0	.015	10.0
	0.033	1.0	7.0	20.0	.015	10.0
	0.333	1.0	7.0	20.0	.015	10.0
Temperature	0.000	1.0	7.0	10.0	.015	5.0
	0.040	1.0	7.0	10.0	.015	5.0
	0.400	1.0	7.0	10.0	.015	5.0
	4.000	1.0	7.0	10.0	.015	5.0
	0.000	1.0	7.0	20.0	.015	5.0
	0.040	1.0	7.0	20.0	.015	5.0
	0.400	1.0	7.0	20.0	.015	5.0
	4.000	1.0	7.0	20.0	.015	5.0
	0.000	1.0	7.0	30.0	.015	5.0
	0.040	1.0	7.0	30.0	.015	5.0
	0.400	1.0	7.0	30.0	.015	5.0
	4.000	1.0	7.0	30.0	.015	5.0

Table 7. (Continued)

Variation	Bromide (mg/l)	Tennessee River Studies Temp. (C)	Chlorine (mg/l)	pH
Bromide	0.000	20.0	10.0	7.4
	0.010	20.0	10.0	7.4
	0.020	20.0	10.0	7.4
	0.040	20.0	10.0	7.4
	0.100	20.0	10.0	7.4
	0.200	20.0	10.0	7.4
	0.400	20.0	10.0	7.4
	1.000	20.0	10.0	7.4
	2.000	20.0	10.0	7.4
	4.000	20.0	10.0	7.4
Temperature	0.000	10.0	10.0	7.4
	0.040	10.0	10.0	7.4
	0.400	10.0	10.0	7.4
	4.000	10.0	10.0	7.4
	0.000	20.0	10.0	7.4
	0.040	20.0	10.0	7.4
	0.400	20.0	10.0	7.4
	4.000	20.0	10.0	7.4
	0.000	30.0	10.0	7.4
	0.040	30.0	10.0	7.4
	0.400	30.0	10.0	7.4
	4.000	30.0	10.0	7.4

Varian 2100 Gas Chromatograph with a 10 uL syringe. A tritium foil electron capture detector was used. A six foot glass column filled with 10 % FFAP on 80/100 mesh Chromasorb AWA was used, with operating conditions of: Column, 100 degrees C., Injection Port, 150 degrees C., and Detector, 155 degrees C. The liquid-liquid extraction method was chosen due to the large number of samples that had to analyzed. Dibromoethane was used as an internal standard. The pentane used for the THM extractions was prepared with 54 ppb of dibromoethane. Aqueous standards of the four THMs were prepared, extracted, and analyzed using the same procedure as that for the samples. Figure 5 shows a standard curve, normalized using the internal standard. Figure 6 shows a THM chromatogram.

The variability of the pentane extraction/THM analysis procedure was determined by analyses of five replicate extractions. The results of the evaluation are illustrated in Table 8.

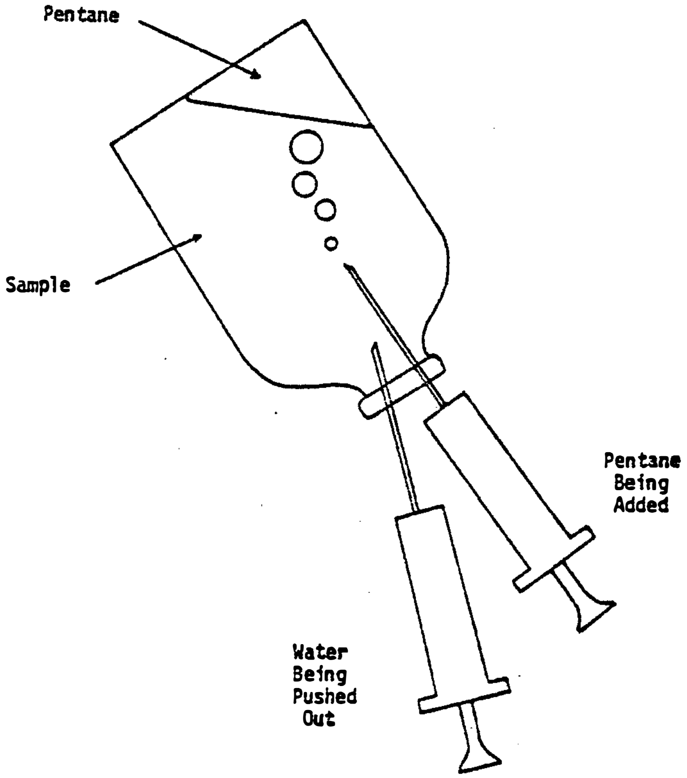

Figure 4. Extraction of Sample with Pentane.

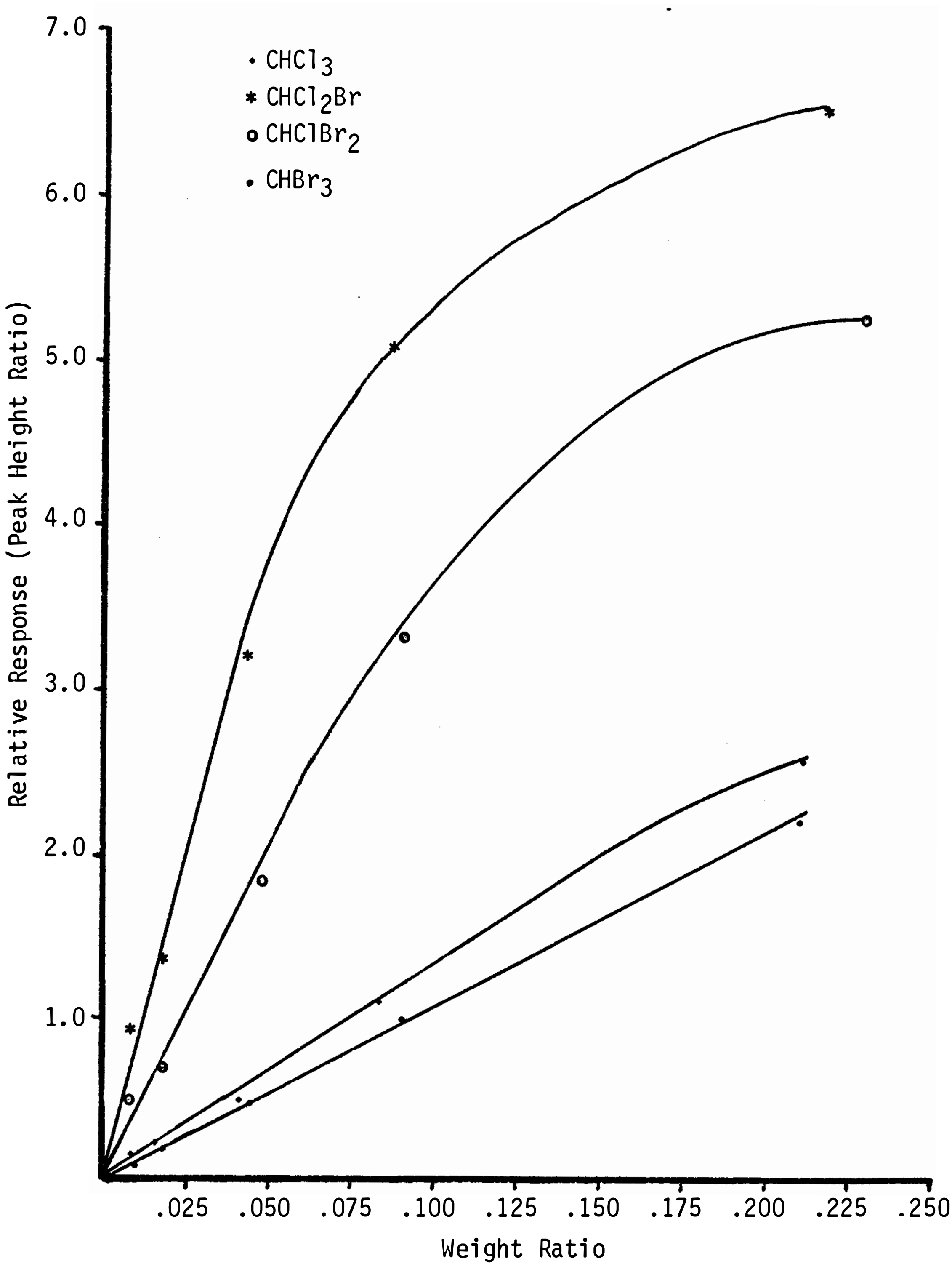

Figure 5. Normalized Trihalomethane Standard Curves.

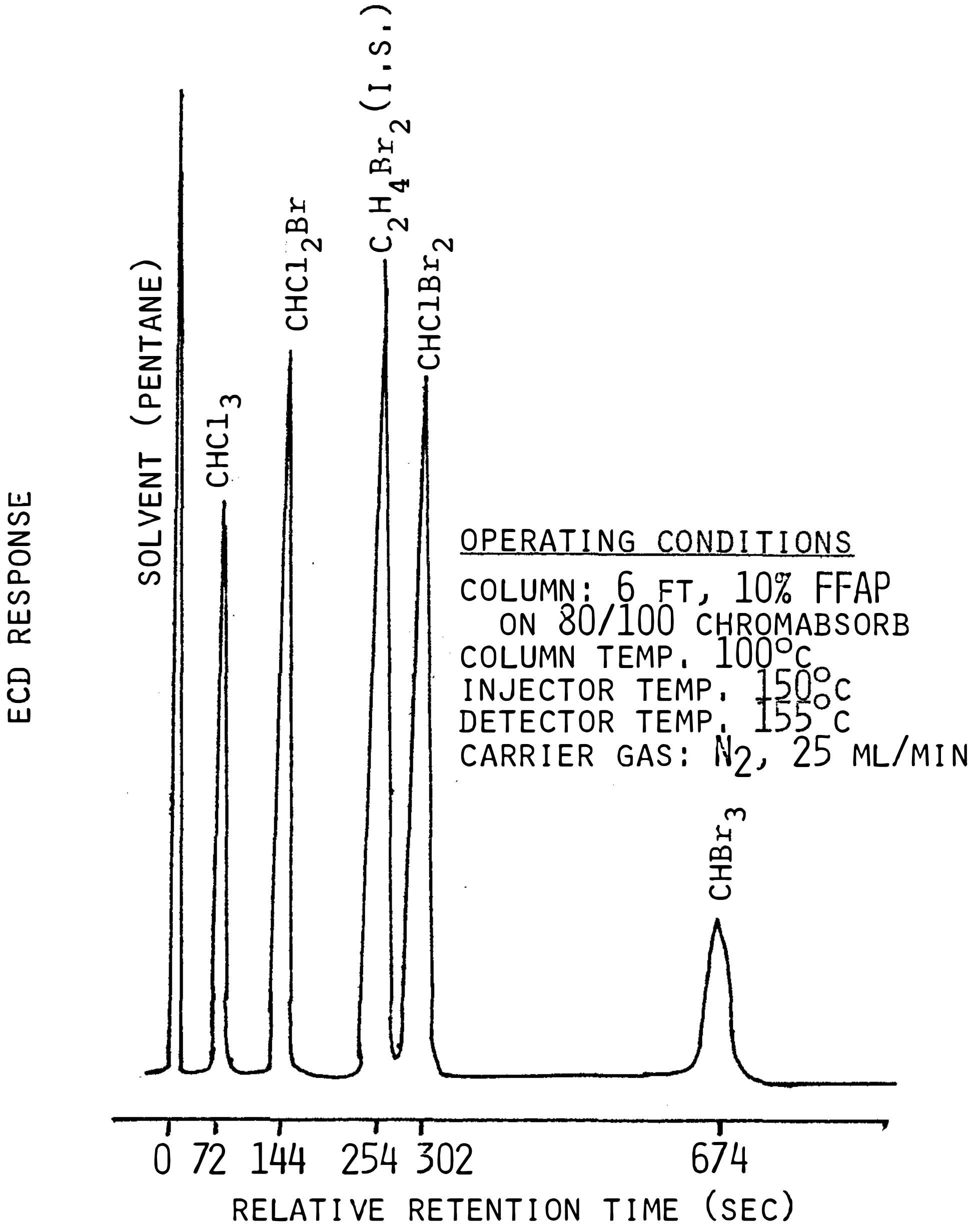

Figure 6. Sample Chromatogram of Standards.

Table 8. Experimental Data Illustrating the Reproducibility of the Pentane Extraction/THM Analysis Procedure

Replicate	Concentration			
	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
1	.063	.076	.092	.018
2	.067	.079	.094	.018
3	.060	.075	.090	.016
4	.059	.070	.087	.016
5	.062	.074	.090	.018
Mean	.062	.075	.091	.017
Standard Deviation	.003	.003	.002	.001
Coefficient of Variation %	5.0	4.4	2.9	6.4

Residual oxidant measurements were made using the iodometric method given in Standard Methods.[48] Because this method does not distinguish between chlorine and bromine, the total residual oxidant is measured as one parameter. The presence of bromide, which is oxidized by chlorine, may cause erroneous results using the iodometric method, unless a specific order of mixing the reagents is followed. Carpenter _et al._[49] attributed this error to the partial oxidation of iodide to iodate by hypobromous acid. Crecelius[50] recommended a mixing order listed in Standard Methods[48] that will prevent erroneous results. Because of the presence of large amounts of bromide in some of the experiments, this procedure was followed for all residual oxidant measurements.

Because of the relatively low levels of organic carbon present in the humic acid solutions and the Tennessee River water, pretreatment of the samples prior to TOC analyses was required. For samples containing a high fraction of inorganic carbon, pretreatment is required to achieve adequate sensitivity for the organic carbon fraction. This pretreatment involves acidifying the sample followed by purging with nitrogen to remove the inorganic carbon. During this purging, some of the more volatile organic compounds are also removed. Because of this, the carbon analysis performed after purging is termed "Non-volatile total organic carbon" (NVTOC). A Beckman 915 Total Carbon Analyzer was used for NVTOC analyses. The levels of NVTOC for the humic acid and Tennessee River samples were at the limits of detection for this instrument. The 1.0 mg/l humic acid solution and Tennessee River water had NVTOC measurements of .8 mg/l and 2.3 mg/l, respectively. For accurate measurements at these levels, a low level organic carbon instrument would have been required.

Two methods of bromide analysis were used, but neither method was adequate for the raw water samples being analyzed. An analysis procedure given in Standard Methods[51] was used, as well as another method given in a World Health Organization publication.[52] Both methods involve oxidizing the bromide with a chlorine species, followed by color development and subsequent colorimetric measurement. A Perkin-Elmer 190 Spectrophotometer was used for the colorimetric measurements. Different types of pretreatments were used in an attempt to improve the analyses, including filtration, concentration by evaporation in a water bath, and dry ashing at 550 degrees C. to remove organic interferences. It was concluded that interferences due to substances in the raw waters prevented successful bromide analyses at the low levels of bromide encountered. A new method of bromide anaysis has been found to be successful for even low level measurements in raw waters such as those examined in this study using ion chromatography. Unfortunately, at the time of this study, there was no access to an ion chromatograph.

IV. RESULTS AND DISCUSSION

Data Presentation

The complete data sets for each experimental run are presented in tabular form in Appendices A, B, and C. The concentration of each of the trihalomethane (THM) species is presented as micromoles per liter (um/l). Zero values represent samples below detection limits for the particular species at the dilution used for simultaneous analysis for the four THM species. Table 9 summarizes the location of these data sets in the appendices. Graphical representation of the data from Appendix B in the form of formation curves (TTHM vs. time) is contained in Appendix D. Table 10 provides a key to the variable sets represented in each of these figures for reference. The results of the residual chlorine measurements are presented in Appendix E.

Humic Acid Studies

Effect of Bromide

The experiments involving a variation in bromide level at constant humic acid level, chlorine dose, pH, ionic strength, and temperature clearly indicate several trends. A dramatic increase in TTHM yield with an increase in initial bromide level is observed. Table 11 presents this effect by a tabulation of percent increase in TTHM yield with an increase in bromide for the 96 hour samples. Figure 7 presents the relationship between the initial level of bromide and the resulting TTHM yield for the 96 hour samples. More than a two-fold increase

Table 9. Location of Data Sets in the Appendixes

EXPERIMENT	PAGE LOCATION IN APPENDIX A	PAGE LOCATION IN APPENDIX B	PAGE LOCATION IN APPENDIX C
Pure Humic Acid Studies			
Effect of Bromide Level	100	109	113
Effect of Chlorine Dose	101	109	114
Effect of Humic Acid Level	102	109	115
Effect of pH	103	110	116
Effect of Ionic Strength	104	110	117
Effect of Temperature	105	110	118
Tennessee River Studies			
Effect of Bromide Level	106	111	119
Effect of Temperature	107	111	120

A= Individual THM Species Concentrations, um/L

B= TTHM Concentrations, um/L

C= Percent of TTHM Contributed by Each THM Species
(i.e. A/B x 100)

Table 10. Summary of Appendix D, TTHM Formation Curves

EXPERIMENT	PAGE LOCATION IN APPENDIX D
<u>Pure Humic Acid Studies</u>	
Effect of Bromide Level	122
Effect of Chlorine Dose at 0 mg/L Br^-	123
Effect of Chlorine Dose at .033 mg/L Br^-	124
Effect of Chlorine Dose at .333 mg/L Br^-	125
Effect of Humic Acid Level at 0 mg/L Br^-	126
Effect of Humic Acid Level at .033 mg/L Br^-	127
Effect of Humic Acid Level at .333 mg/L Br^-	128
Effect of pH at 0 mg/L Br^-	129
Effect of pH at .033 mg/L Br^-	130
Effect of pH at .333 mg/L Br^-	131
Effect of Ionic Strength at 0 mg/L Br^-	132
Effect of Ionic Strength at .033 mg/L Br^-	133
Effect of Ionic Strength at .333 mg/L Br^-	134
Effect of Temperature at 0 mg/L Br^-	135
Effect of Temperature at .040 mg/L Br^-	136
Effect of Temperature at .400 mg/L Br^-	137
Effect of Temperature at 4.000 mg/L Br^-	138
<u>Tennessee River Studies</u>	
Effect of Bromide Level	139
Effect of Temperature at 0 mg/L Br^- Added	140
Effect of Temperature at .040 mg/L Br^- Added	141
Effect of Temperature at .400 mg/L Br^- Added	142
Effect of Temperature at 4.000 mg/L Br^- Added	143

Table 11. Initial Bromide Vs. Percent Increase in TTHMs from Humic Acid

Bromide Added (mg/L)	Reaction Time (hrs) 8	24	48	72	96
	% Increase over 0mg/L Br^-				
.01	1.5	2.9	4.4	4.0	5.8
.02	9.2	11.9	5.9	7.2	12.8
.04	27.5	22.3	12.3	12.9	19.4
.10	45.8	28.2	29.1	36.5	43.8
.20	61.8	46.5	43.8	51.4	49.6
.40	73.3	53.5	62.1	56.6	72.1
1.00	132.1	114.1	104.0	81.9	98.8
2.00	139.0	156.6	135.5	106.0	112.0
4.00	254.2	170.0	154.2	128.1	127.5

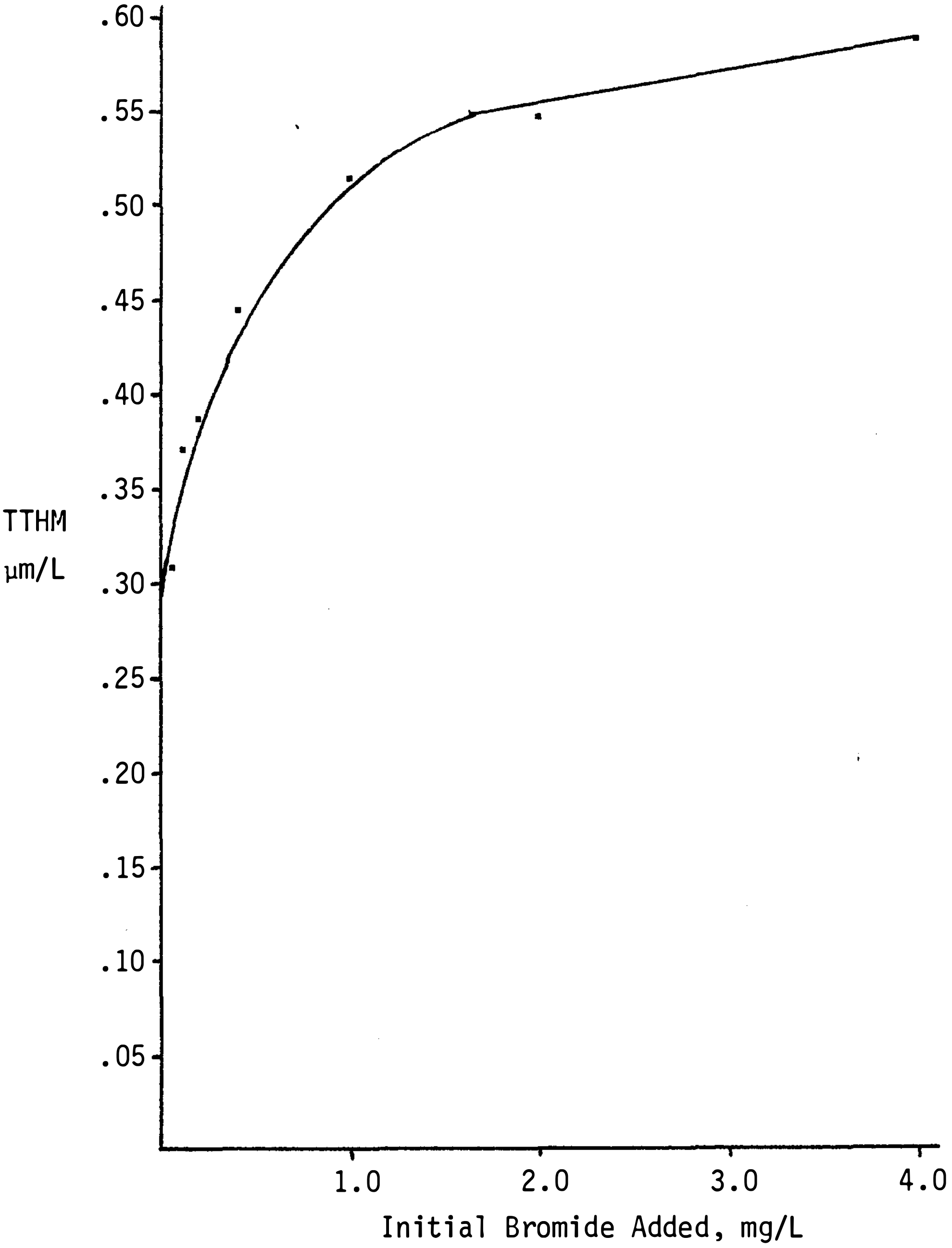

Figure 7. Initial Bromide Vs. TTHM Formation for 96 Hour Humic Acid Samples.

in TTHMs is observed at 4.0 mg/l initial bromide compared to 0 mg/l initial bromide. For a constant level of humic acid, the TTHM enhancement effect of bromide appears to begin to level off at the higher doses of bromide. This is probably due to a limiting effect of a given amount of humic acid available for reaction. With increasing levels of bromide, an increasing proportion of the total available organic precursors are used up.

This limiting effect of the humic acid level is also noticed in Figure 8, which illustrates the relationship between initial bromide added and the percent of the initial bromide added.

Another trend observed from the data is the shift in the distribution of THMs toward the more highly brominated species with an increase in initial bromide. Figure 9 illustrates the effect of bromide on the distribution of THM species. $CHCl_3$ shows a steady decrease in percent TTHMs with an increase in initial bromide. $CHClBr_2$ shows a peak in percent TTHM at about .2 mg/l initial bromide. $CHClBr_2$ shows a steady increase in percent TTHM with an increase in initial bromide. $CHBr_3$ shows a steady increase in percent TTHM with an increase in initial bromide.

For a constant initial chlorine dose, a variation in bromide changes the initial inorganic Cl/Br ratio. Figure 10 illustrates the relationship between these initial inorganic Cl/Br ratios and resulting THM Cl/Br ratios. This trend substantiates the finding that bromine is more reactive than chlorine in forming THMs.

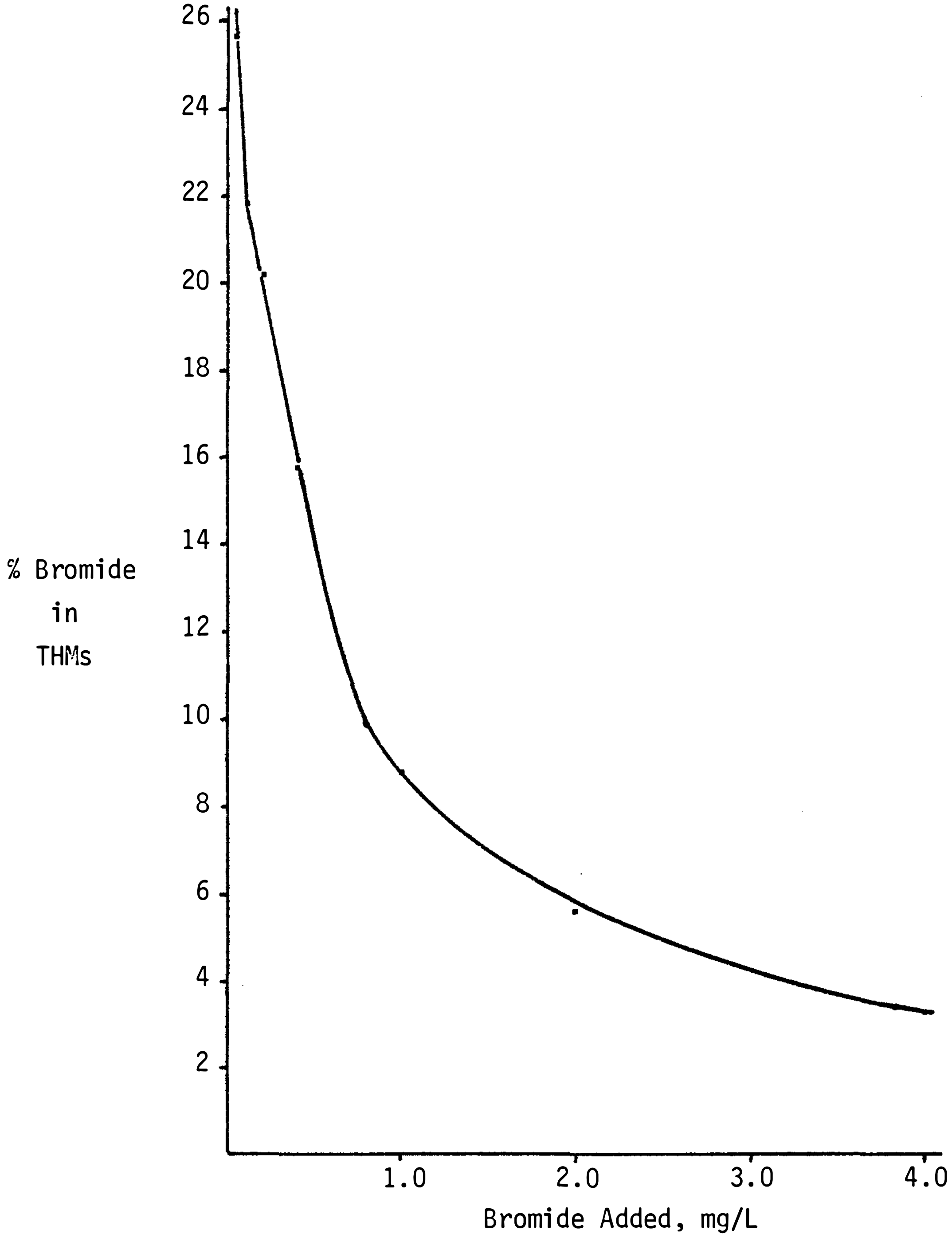

Figure 8. Initial Bromide Level Vs. % Bromide Incorporated into THMs.

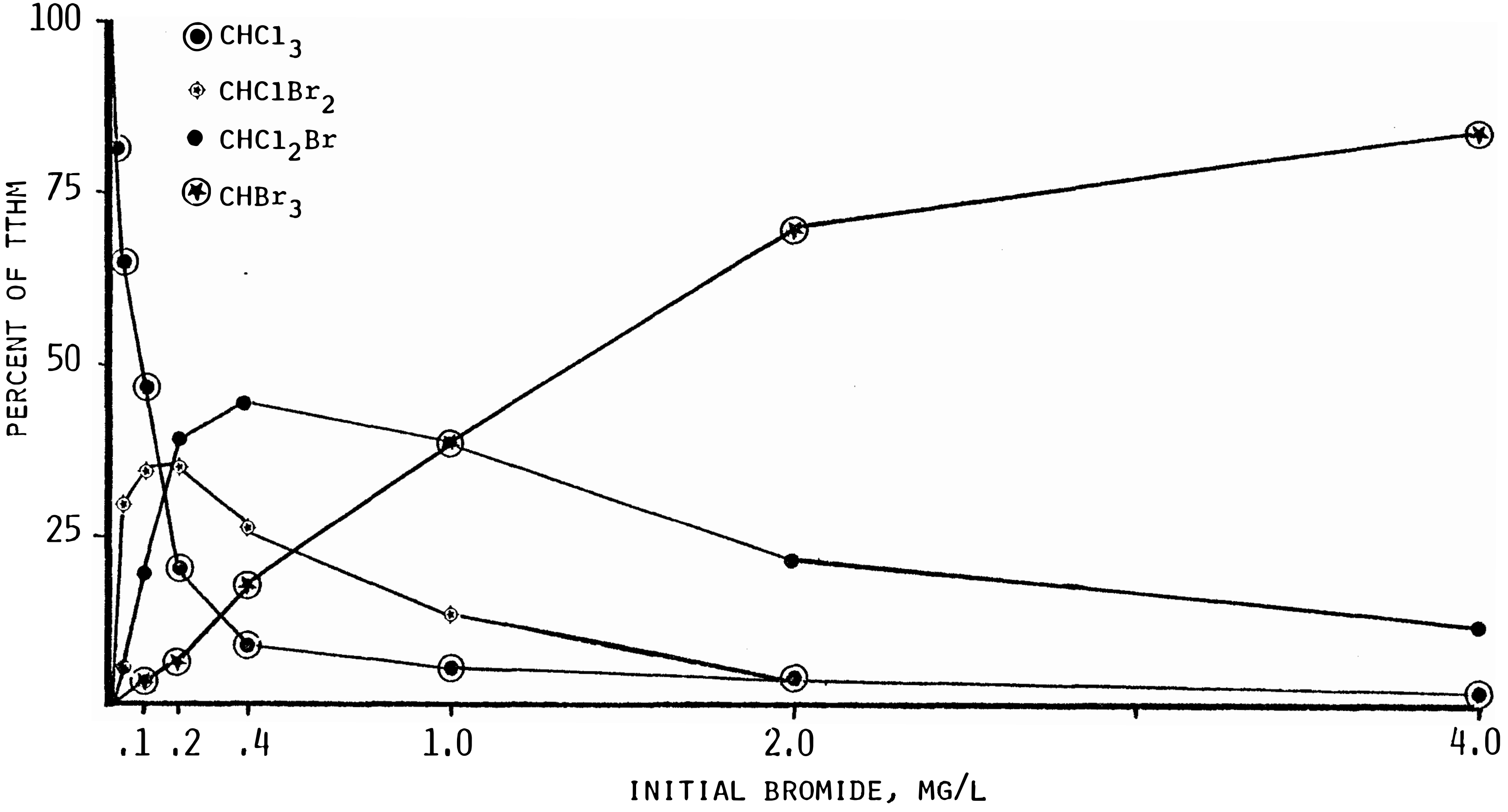

Figure 9. Initial Bromide Level Vs. Percent Distribution of THMs for 96 Hour Humic Acid Samples.

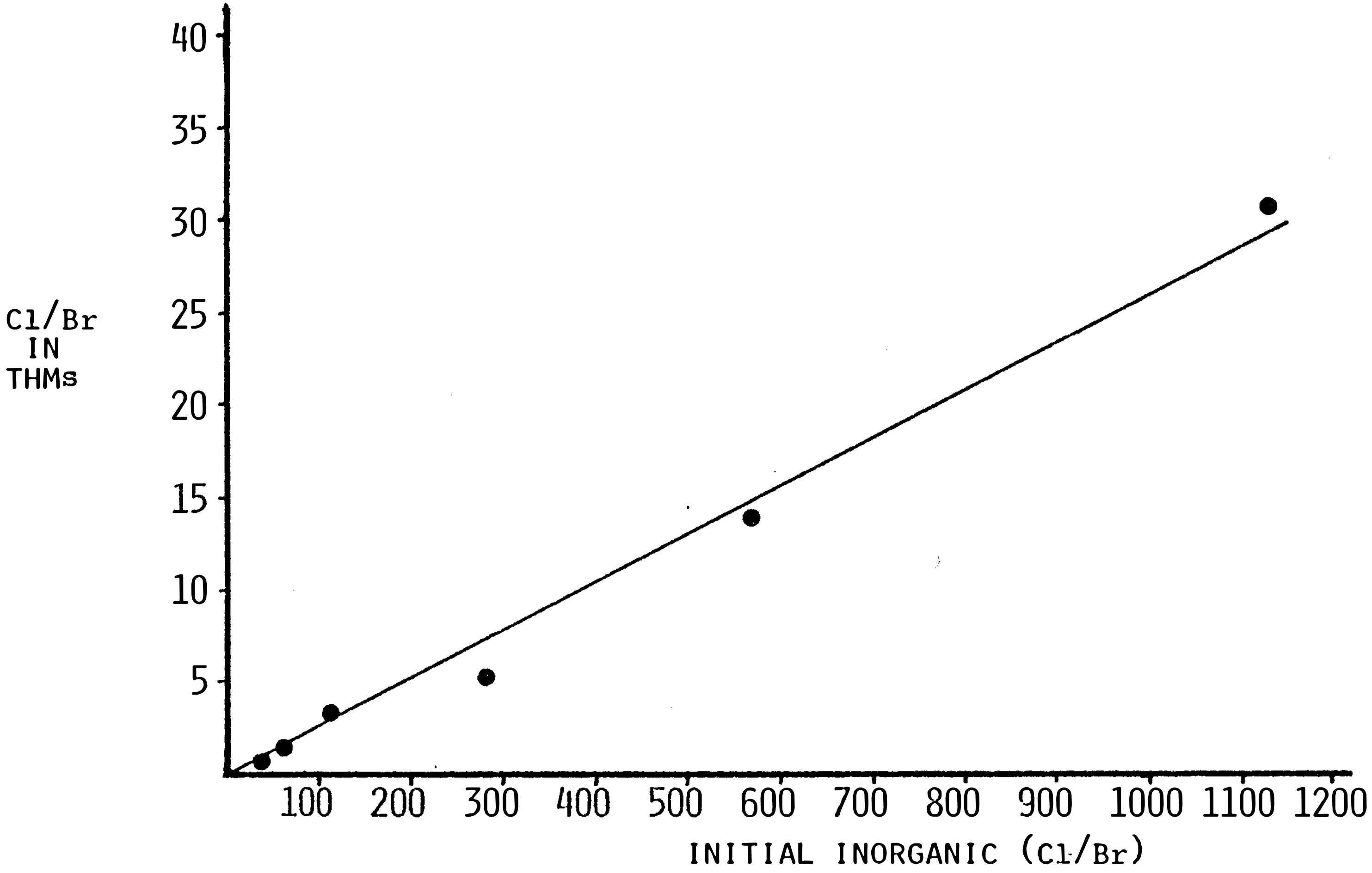

Figure 10. Initial Inorganic Cl/Br Ratios Vs. 96 Hour THM Cl/Br Ratios for a Variation in Initial Bromide.

Effect of Chlorine Dose

The results of the chlorine dose variation experiments indicate that the level of chlorine added can affect the TTHM yield and distribution of species. Figure 11 illustrates the relationship between chlorine dose and TTHM yield for the 96 hour samples. A non-linear relationship is indicated for the chlorine doses used. It appears that the effect of chlorine dose on TTHM yield is influenced by the level of bromide. Table 12 presents tabulations of the percent increase in TTHM yield with an increase in chlorine dose. The diminished effect of chlorine dose on TTHM yield at higher levels of bromide is probably related to competition between chlorine and bromine for a limited amount of humic acid. Since bromine is more reactive than chlorine, at higher initial bromide levels, a lower level of precursor is available to react with the available chlorine.

The level of chlorine dose also affects the distribution of TTHM species. Table 13 presents the percent TTHM distributions for the four THMs for the various combinations of Cl_2 and Br^-. For $CHCl_3$, at both levels of bromide, an increase in chlorine dose yields an increase in percent TTHM. For $CHCl_2Br$, at .033 mg/l Bromide, an increase in percent TTHM is observed. For $CHClBr_2$, for both levels of bromide, a decrease in percent TTHM is found with an increase in chlorine dose. For $CHBr_3$, a decrease in percent TTHM is observed with an increase in chlorine dose.

For a constant level of bromide, a variation in chlorine dose changes the initial inorganic Cl/Br ratio. Figure 12 illustrates the relationship between the initial inorganic Cl/Br ratios and the resulting

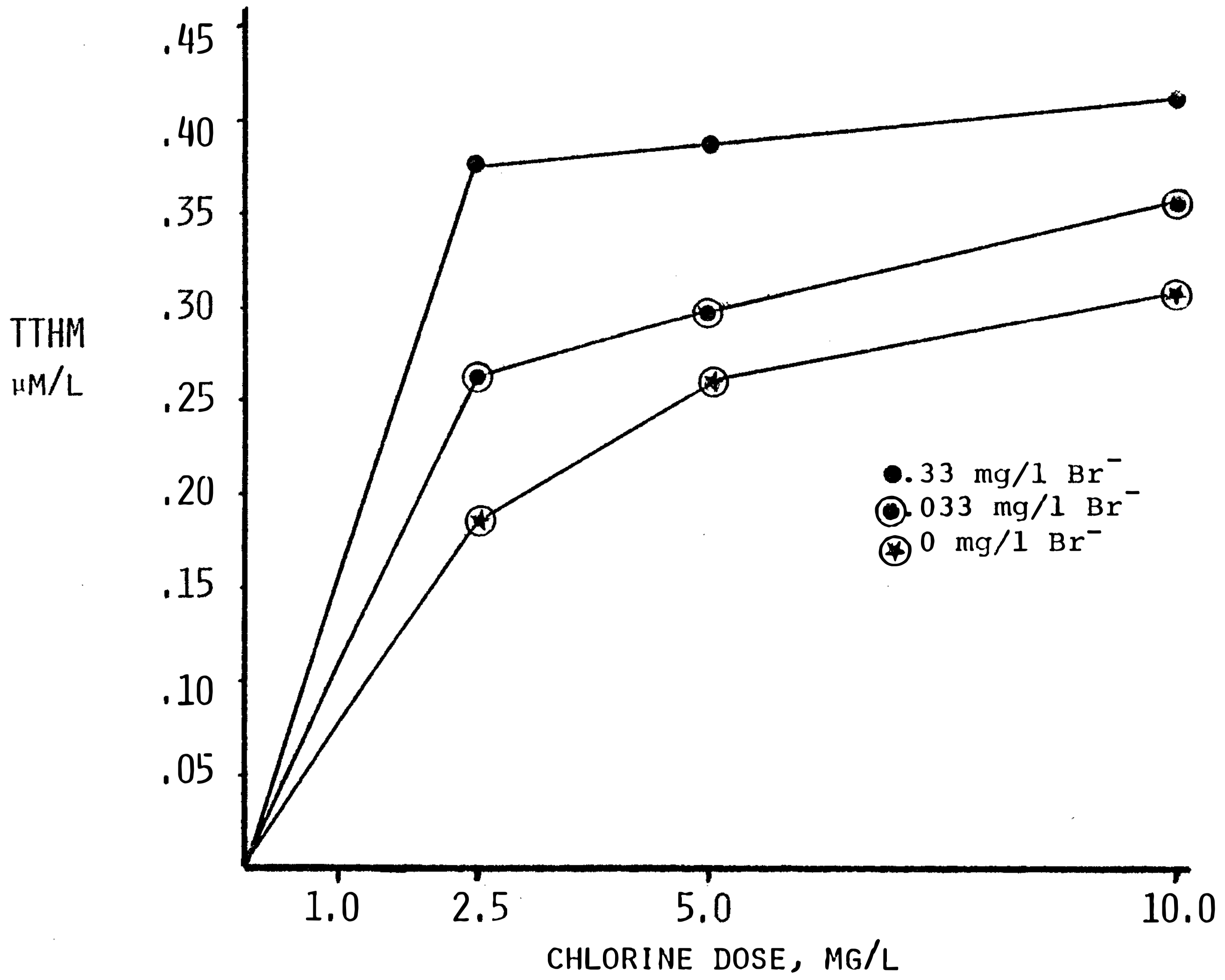

Figure 11. Chlorine Dose Vs. 96 Hour TTHMs.

Table 12. Chlorine Dose Vs. Percent Increase in TTHMs for the 96 Hour Samples

Chlorine Dose (mg/L)	Bromide (mg/l)	Over 2.5 mg/L Dose	Over 5.0 mg/L Dose
		% Increase in TTHMS	
5.0	0	39.5	----
10.0	0	64.9	18.2
5.0	.033	13.0	----
10.0	.033	16.0	2.7
5.0	.333	7.2	----
10.0	.333	8.5	1.9

Table 13. Percent Distribution of THMs for a Variation in Chlorine Dose, 96 Hour Samples

THM	Chlorine Dose, mg/L:	2.5		5.0		10.0	
	Bromide, mg/L:	.033	.333	.033	.333	.033	.333
		% of TTHM					
$CHCl_3$		67.6	7.2	71.3	12.9	73.4	15.8
$CHCl_2Br$		27.1	22.0	25.7	35.4	23.0	36.2
$CHClBr_2$		5.3	46.2	3.0	41.8	3.6	40.0
$CHBr_3$		----	24.7	----	9.9	----	8.0

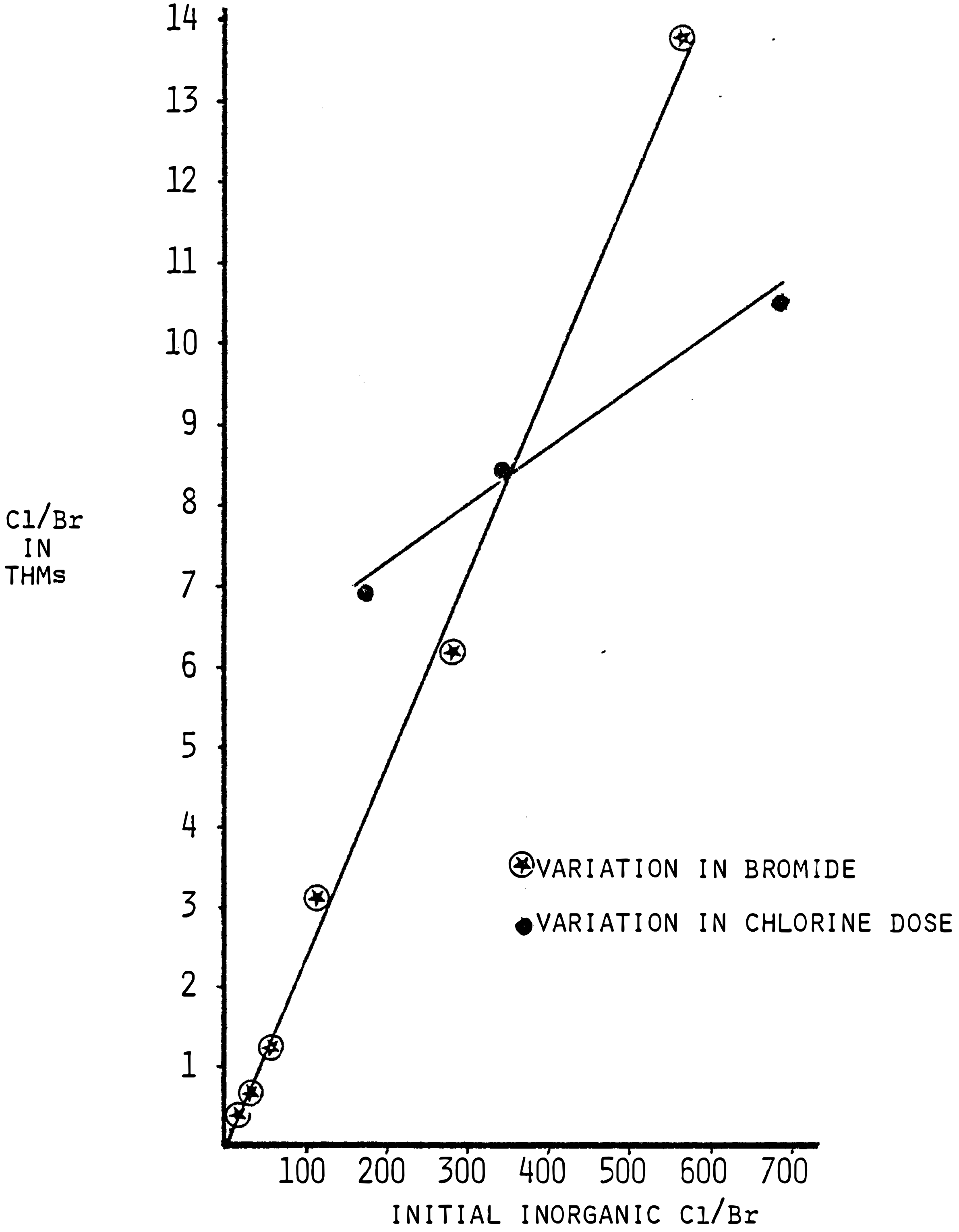

Figure 12. Initial Inorganic Cl/Br Ratios Vs. 96 Hour THM Cl/Br Ratios.

THM Cl/Br. This could be expected due to the lower reactivity of chlorine compared to bromine. The Cl/Br data from the chlorine variations at .333 mg/l bromide indicate the same trend but are not conclusive.

In summary, it appears that the relative effects of chlorine dose on TTHM yield and distribution are dependent on the level of the bromide. For a constant level of humic acid, the effect of increasing chlorine dose on TTHM yield is diminished at higher levels of initial bromide, due to increasing competition by bromine for the limited available organic precursors.

Effect of Humic Acid Level

The results of the variation in humic acid experiments indicate that at all levels of bromide an increase in humic acid causes an increase in TTHM yield. Figure 13 illustrates the relationship between humic acid level and TTHM yield for the 96 hour samples. Table 14 presents the TTHM distributions at 96 hours. For the levels of humic acid used, $CHCl_3$ shows a slight increase in percent TTHM with an increase in humic acid for both levels of initial bromide. $CHCl_2Br$ and $CHClBr_2$ show no conclusive trend for change in percent TTHM with variation in humic acid level. $CHBr_3$ shows a slight increase in percent TTHM with an increase in humic acid level. Table 15 indicates the percent increase in TTHM yield with an increase in humic acid levels.

The initial inorganic Cl/Br and resulting THM Cl/Br ratios are tabulated for the humic acid variation data in Table 16. Based on the Cl/Br data, it appears for a given initial inorganic Cl/Br

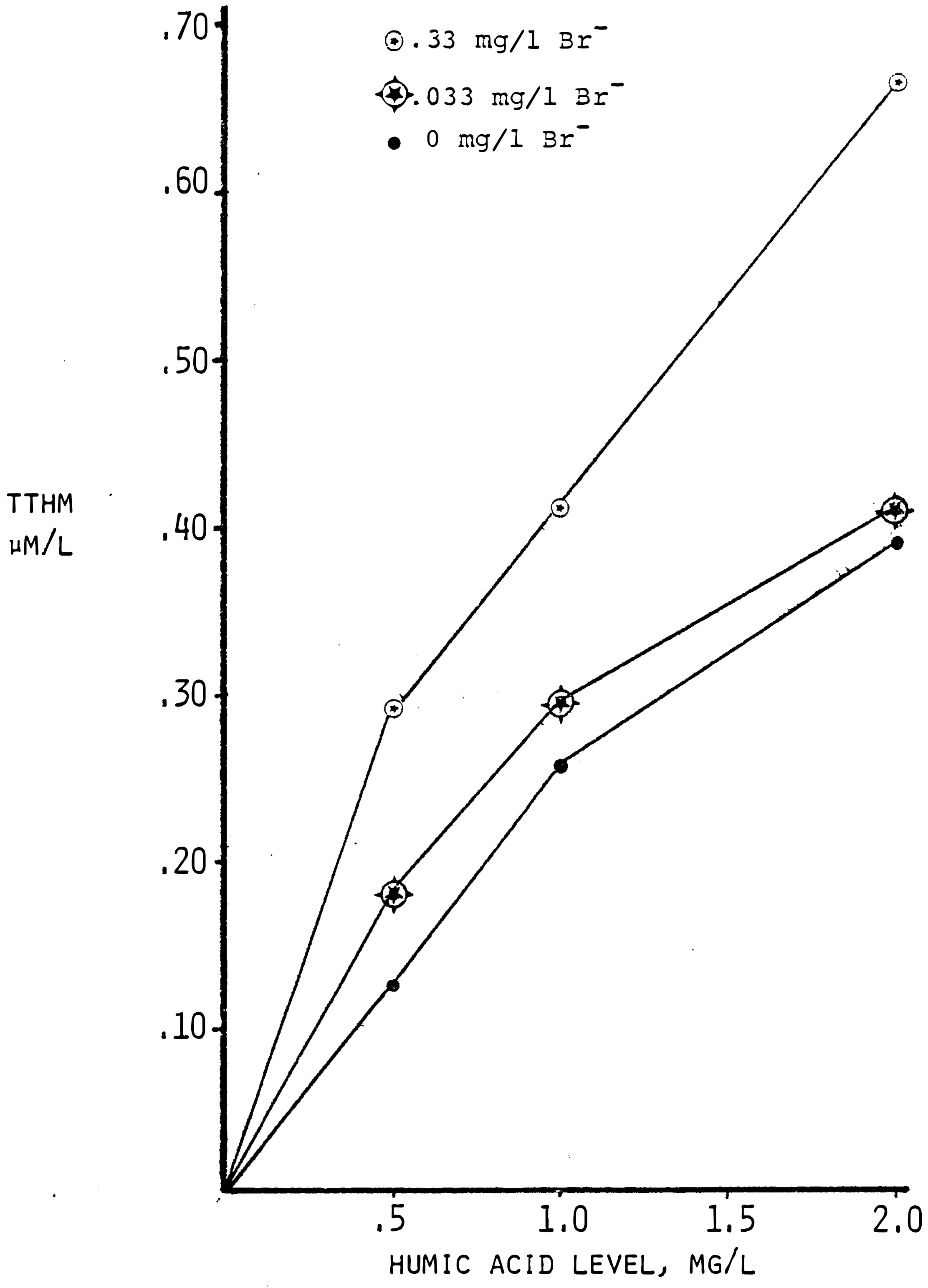

Figure 13. Humic Acid Level Vs. 96 Hour TTHMs.

Table 14. Percent Distribution of THMs for the Variation in Humic Acid 96 Hour Samples

THM	Humic Acid, mg/L:	.5		1.0		2.0	
	Bromide, mg/L:	.033	.333	.033	.333	.033	.333
		% of TTHM					
$CHCl_3$		63.5	12.3	71.3	14.4	75.2	15.0
$CHCl_2Br$		32.6	30.4	25.7	34.8	21.1	31.4
$CHClBr_2$		3.9	48.1	3.0	41.3	3.6	43.7
$CHBr_3$		----	9.2	----	9.7	----	9.9

Table 15. Humic Acid Level Vs. Percent Increase in TTHMs for the 96 Hour Samples

Humic Acid (mg/L)	Bromide (mg/L)	Over .5 mg/L Humic Acid Level	Over 1.0 mg/L Humic Acid Level
		% Increase in TTHMs	
1.0	0	106	---
2.0	0	213	51
1.0	.033	63	---
2.0	.033	128	39
1.0	.333	40	---
2.0	.333	128	63

Table 16. Cl/Br Ratios for 96 Hour Humic Acid Variation Samples

Humic Acid (mg/l)	Br^- (mg/l)	Initial Cl/Br	96 hour THM Cl/Br
.5	.033	343.9	6.40
1.0	.033	343.9	8.40
2.0	.033	343.9	9.60
.5	.333	34.4	.90
1.0	.333	34.4	1.00
2.0	.333	34.4	1.05

ratio, the resulting THM Cl/Br ratio is dependent on the level of humic acid. For a constant chlorine dose and level of bromide, the THM Cl/Br ratio decreases with a decrease in humic acid level. Since bromine is more reactive than chlorine, it is not as dependent on the level of humic acid. At the .33 mg/l bromide level, the change in THM Cl/Br associated with a change in humic acid level is not as pronounced, probably because at this level of bromide, bromine is more predominant in forming THMs. In conclusion, bromination resulting in THMs is not as dependent on the humic acid level as chlorination.

Effect of pH

The enhancement of TTHM formation at higher pH is observed for all levels of bromide examined. Figure 14 illustrates the relationship between pH and TTHM yield for the 96 hour samples. The overall increase in TTHMs with a increase in pH is found to be greater at higher bromide levels. For the experiments with no bromide added, a .08 um/l increase in TTHMs per pH unit is observed.

Table 17 presents the percent TTHM data for the 96 hour samples. The changes in distribution with pH are not conclusive.

An increase in pH is known to increase formation of haloforms by the classical haloform reaction. Although the nature of the reactions producing THMs from natural humics is not well understood, apparently the mechanism also involves a base-catylyzed step. Although the absolute rates of haloform formation depend on the initial rate of carbanion

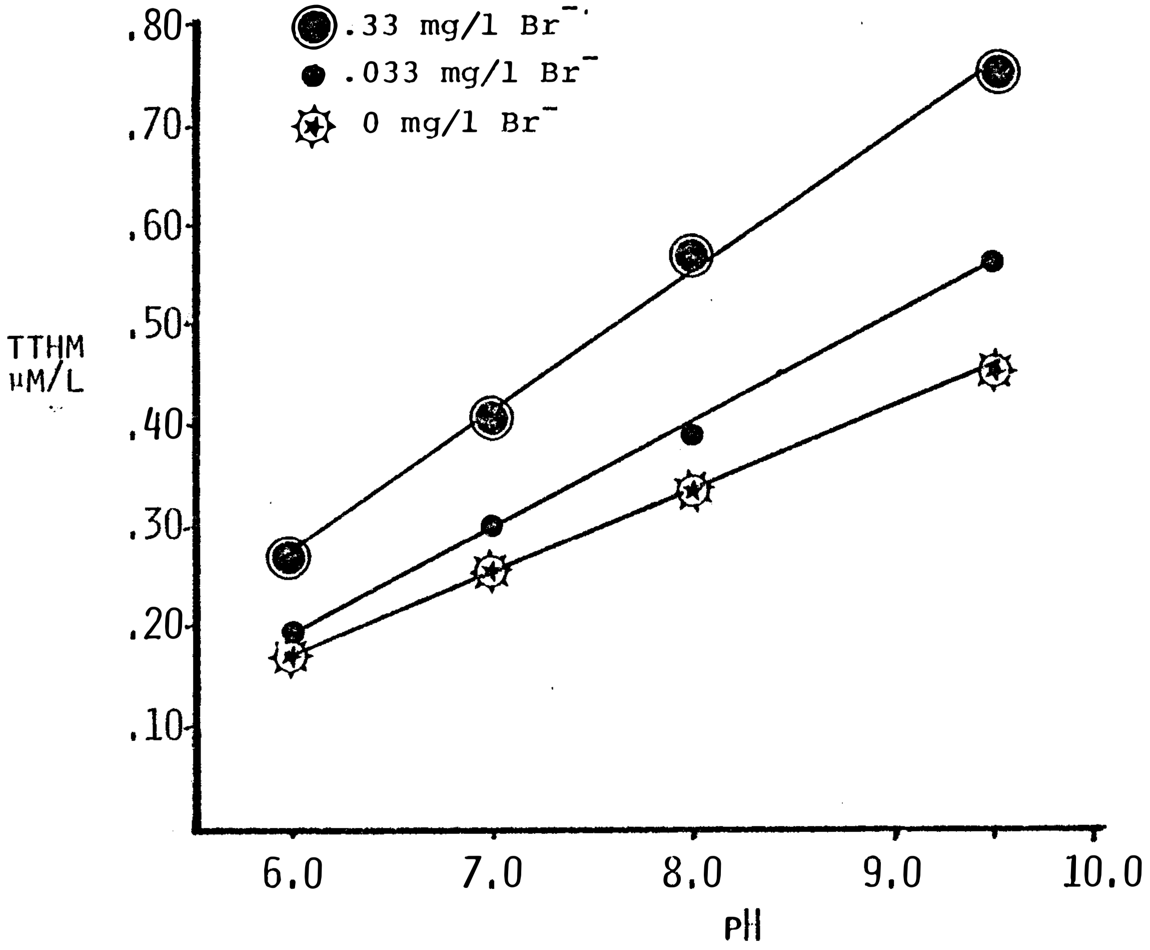

Figure 14. pH Vs. TTHM for 96 Hour Humic Acid Samples.

Table 17. Percent Distribution of THMs for the Variation in pH, 96 Hour Samples

THM	Br^-(mg/L)	pH 6.0 .033	 .333	pH 7.0 .033	 .333	pH 8.0 .033	 .333	pH 9.5 .033	 .333
				% of TTHM					
$CHCl_3$		69.3	18.5	71.3	12.9	17.9	11.9	72.6	12.3
$CHCl_2Br$		26.5	21.9	25.7	35.4	22.4	26.3	20.8	21.1
$CHClBr_2$		4.2	47.4	3.0	41.8	5.7	38.0	6.6	35.6
$CHBr_3$		----	12.2	----	9.9	----	23.8	----	31.0

formation, which is base-catalyzed, the resulting THMs formed are also dependent on the halogenation steps. The increased rate of reaction caused by an increase in pH coupled with the increased rate of halogenation by bromine would result in an overall enhancement in TTHM yield. This is apparent from data involving high pHs and also high levels of bromide.

In addition to the enhancement in THM formation due to the base-catalyzed effect caused by an increase in pH, another effect of pH on THM formation is possible. For a mixed system involving chlorine and bromine species, the concentrations of the individual halogen species are also dependent on pH. This was noted in Figure 2, Section II, page 15. For given initial bromide and chlorine levels, the concentrations of the resulting HOCl, OCl^-, HOBr, and OBr^- change with pH. Although the relative reactivities are not known for these halogen species for THM reactions, it is assumed that all four can participate in the halogenation steps.[15] Since the relative concentrations of these species change with pH, if their reactivities are different, an additional factor affecting THM formation and distribution caused by pH may exist. It is evident that the reactivities of chlorine species compared to bromine species are different, but the differences between the reactivities of the hypohalous acids compared to the hypohalites are not known. Such differences might explain some of the variation in percent TTHM distribution at different pHs. Again referring to Figure 2 in Chapter 2, it is noted that the pH region 6.0 to 9.5 is a very critical range in terms of relative concentrations of the chlorine and bromine species.

In summary, the effect of pH on THM formation may be due to two factors. First, the enhancement of THM formation due to the catalyzing effect of hydroxide ions on the THM reactions. Second, the effect of pH on the distribution of halogen species which are involved in THM reactions may cause a change in TTHM yield and distribution.

Effect of Ionic Strength

No significant effect of ionic strength on TTHM yield or distribution was observed. Table 18 and Table 19 present representative data of TTHM yields and distributions for the three ionic strengths examined. Since there are ionic species involved in the THM reaction, including forms of the halogens and organic precursors, an ionic strength effect might be expected.

The distribution of halogen species would be affected by a change in ionic strength. An increase in ionic strength would shift the equilibrium toward the ionic species of bromine and chlorine, of which only the hypohalites are capable of reacting to form THMs.

Although the THM reaction involved in water treatment chlorination is not well understood, it is assumed that it has a similar mechanism to that of the classical haloform reaction. If so, it could include base-catalyzed proton dissociations, carbanion intermediates, and electophilic attacks by halogen species. This would suggest a possible ionic strength effect.

Considering these possibilities for an ionic strength effect on the THM reaction, the lack of such an effect observed in these experiments may be due to the experimental conditions used. The use of

Table 18. Representative Percent Distribution Data for the Ionic Strength Experiments

THM	Time (hrs): Ionic Strength:	8 .015	.075	.150	48 .015	.075	.150	96 .015	.075	.150
					% of TTHMs					
					(.033 mg/L Br^-)					
$CHCl_3$		74.8	75.3	75.5	73.8	76.1	75.7	72.7	71.9	72.6
$CHCl_2Br$		20.6	19.6	20.2	22.6	20.3	20.2	24.1	25.0	24.3
$CHClBr_2$		4.5	5.1	4.3	3.6	3.6	4.1	3.1	3.1	3.1
$CHBr_3$		----	----	----	----	----	----	----	----	----
					(.333 mg/L Br^-)					
$CHCl_3$		17.7	18.3	19.4	15.0	14.5	14.0	12.9	12.7	12.7
$CHCl_2Br$		27.4	28.2	29.2	36.5	36.2	35.4	34.9	34.3	35.9
$CHClBr_2$		42.8	41.8	38.9	38.3	38.9	39.6	41.8	42.8	41.1
$CHBr_3$		12.1	11.7	12.5	10.1	10.4	11.0	10.4	10.2	10.2

Table 19. Representative TTHM Yield Data for the Variation in Ionic Strength Experiments

Ionic Strength	Reaction Time (hrs):	8			48			96		
	Bromide (mg/L):	0	.033	.333	0	.033	.333	0	.033	.333
						TTHM (µm/L)				
.015		.130	.155	.215	.210	.211	.326	.265	.295	.404
.075		.135	.158	.213	.208	.222	.337	.263	.292	.402
.150		.136	.163	.216	.213	.218	.328	.259	.288	.401

different pHs and a wider range of ionic strengths may have been necessary in order to observe an effect on THM reaction due to ionic strength. Under the conditions that were used the ionic strength effect may have been so slight as to not be significant.

Effect of Temperature

A substantial increase in THM yields with an increase in temperature was observed for all levels of bromide. Figures 15, 16, 17, 18, and 19 illustrate the relationships between temperature and the resulting $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, $CHBr_3$, and TTHM respectively. It appears that the temperature dependence of THM yield is affected by the level of bromide. $CHCl_3$ formation demonstrates a decreasing dependence on temperature with increasing bromide. $CHCl_2Br$ and $CHClBr_2$ appear to have maximum temperature dependences apparently at the levels of bromides that correspond to the predominances of these THMs. $CHBr_3$ formation demonstrates an increasing temperature dependence with increasing bromide. Within the temperature range examined and experimental error, fairly linear relationships between temperature and THM yield are observed. Table 20 presents the results of linear regressions on these relationships. Although not all of the linear regressions are statistically acceptable, for comparative purposes, the slopes (THM um/L/°C) illustrate the effect of bromide on THM temperature dependence. The lack of linearity observed in some cases may be due to the added variation from one or more of the factors affecting THM formation. For example, at the higher temperatures and higher bromide levels, a limitation due to the humic acid level may affect the THM yield. This the relationships illustrated may not be entirely the result of temperature dependences.

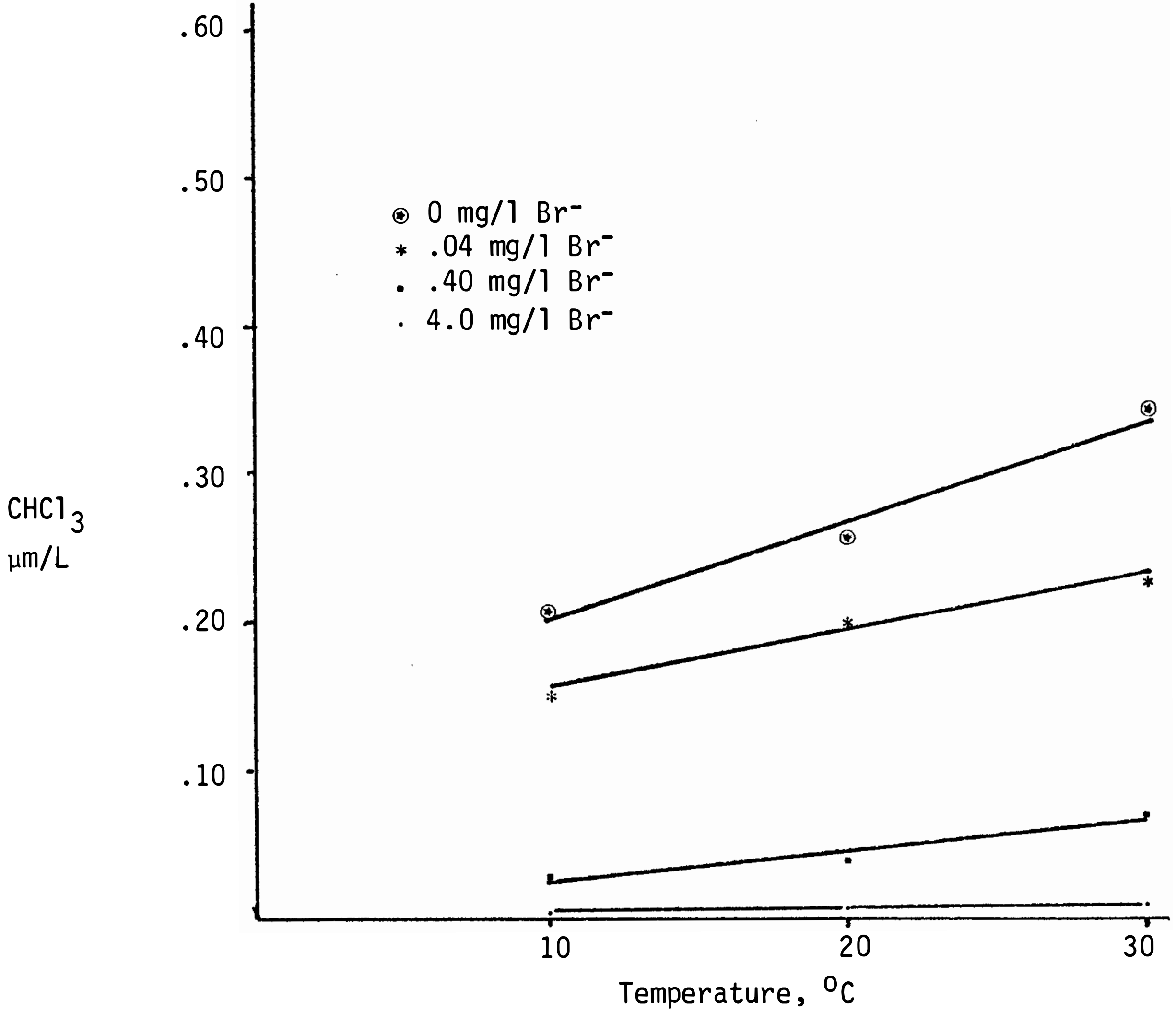

Figure 15. Temperature Vs. 96 Hour $CHCl_3$ Formation from Humic Acid.

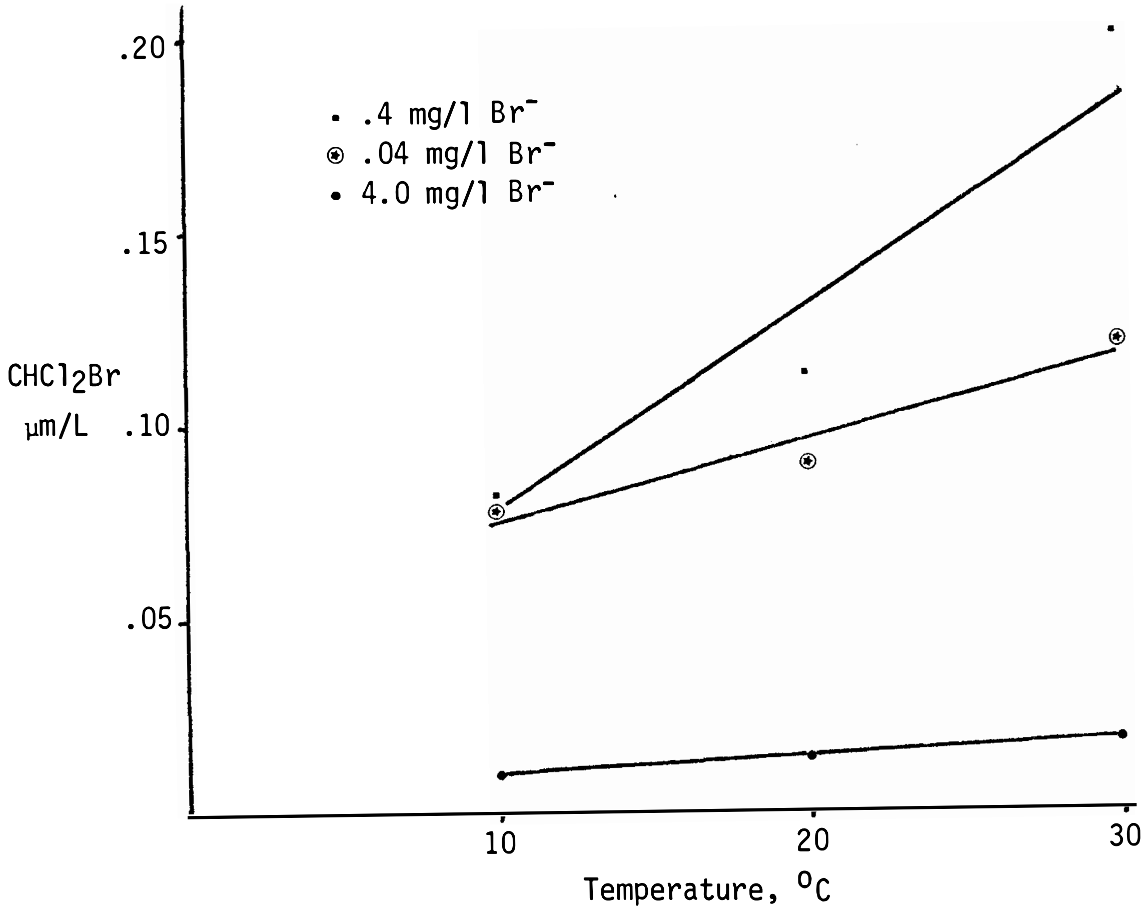

Figure 16. Temperature Vs. 96 Hour $CHCl_2Br$, Formation from Humic Acid.

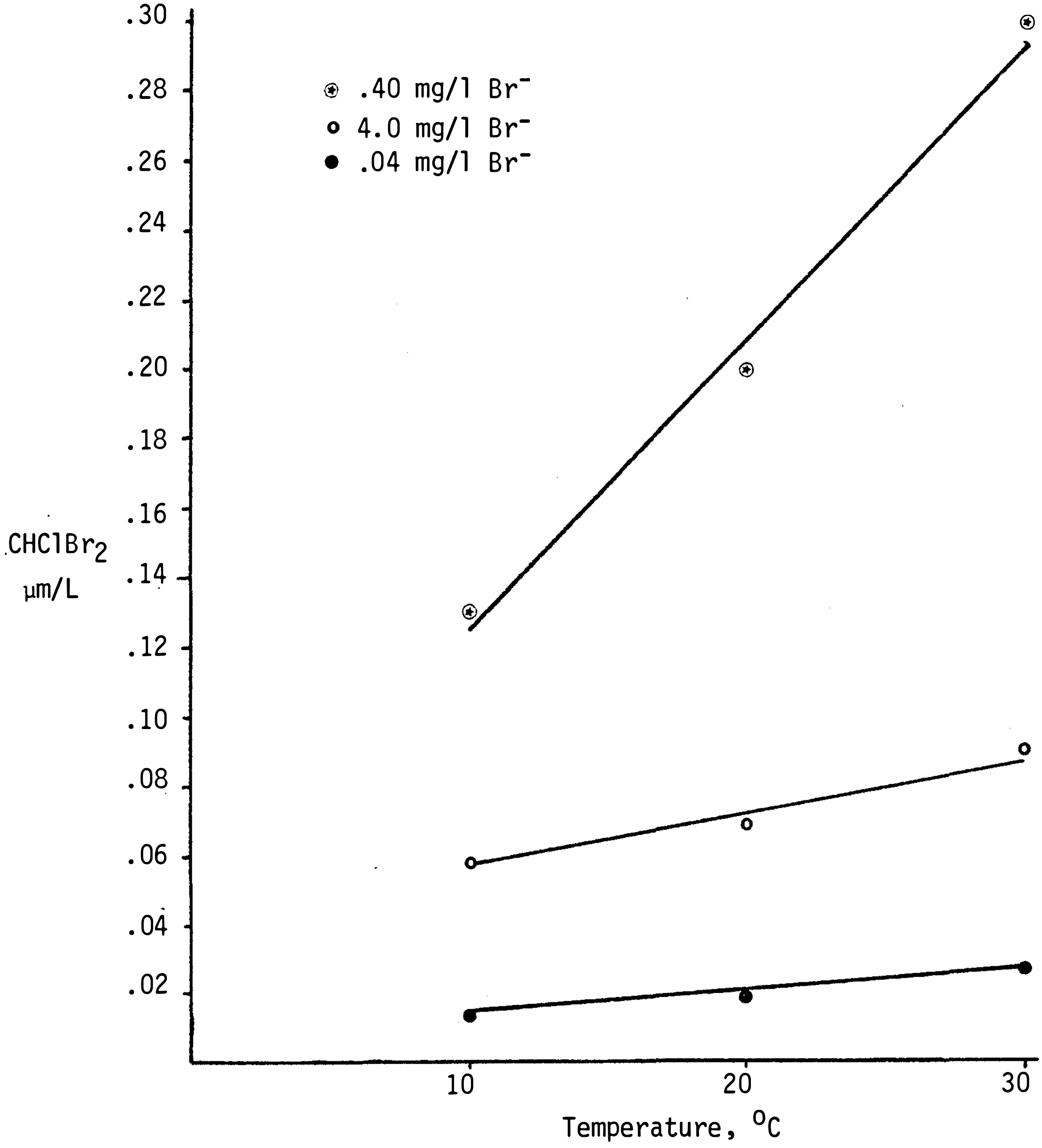

Figure 17. Temperature Vs. 96 Hour $CHClBr_2$ Formation from Humic Acid.

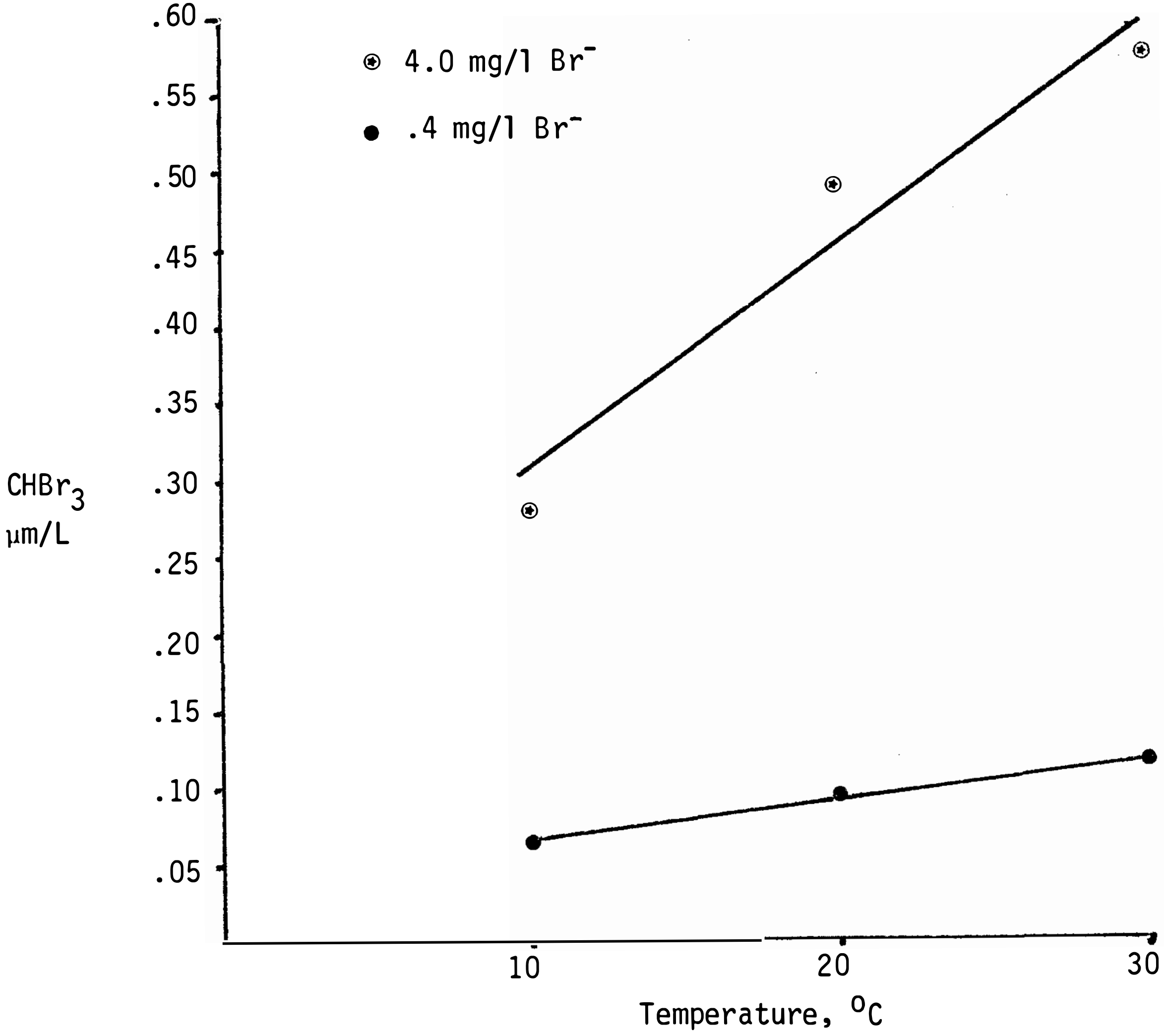

Figure 18. Temperature Vs. 96 Hour CHBr$_3$ Formation from Humic Acid.

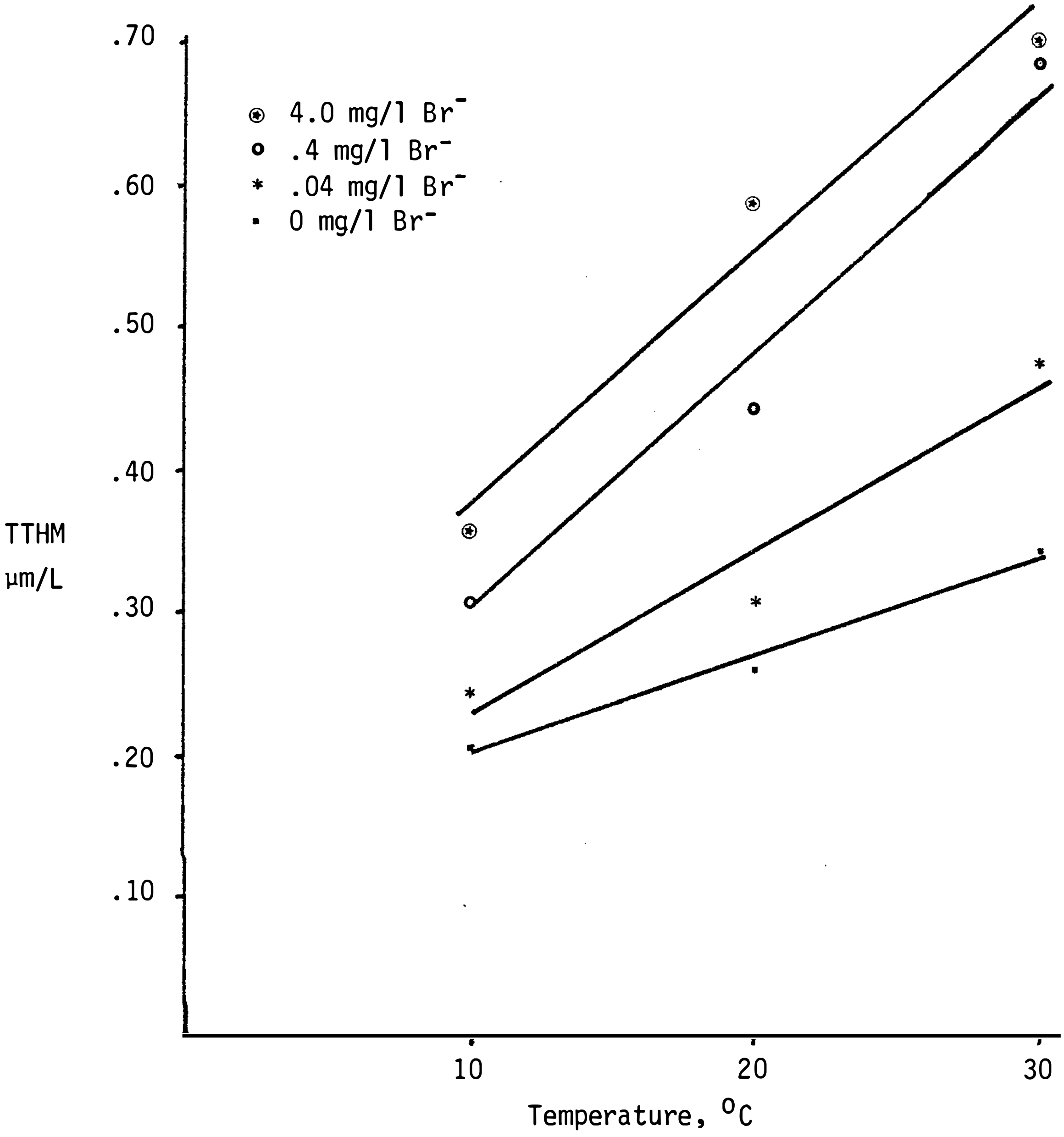

Figure 19. Temperature Vs. 96 Hour TTHM Formation from Humic Acid.

Table 20. Linear Regression Data for the Temperature Vs. THM Yield Relationships for the Humic Acid Experiments

THM	Br^- (mg/l)	Corr. Coef. (R)*	$\frac{\text{THM } (\mu m/l)}{^oC}$
$CHCl_3$	0	.9909	.0068
$CHCl_3$	.04	.9661	.0087
$CHCl_3$	.40	.9513	.0021
$CHCl_3$	4.00	1.000*	.0002
$CHCl_2Br$	.04	.9609	.0021
$CHCl_2Br$	.40	.9645	.0059
$CHCl_2Br$	4.00	1.000*	.0004
$CHClBr_2$	.04	.9966	.0007
$CHClBr_2$	.40	.9941	.0085
$CHClBr_2$	4.00	.9797	.0015
$CHBr_3$	.40	.9985*	.0027
$CHBr_3$	4.00	.9709	.0149
TTHM	0	.9909	.0068
TTHM	.04	.9693	.0116
TTHM	.40	.9874	.0191
TTHM	4.00	.9811	.0170

(*Significant at the 5% level)

The percent distribution data for the 96 hour samples are presented in Table 21. No conclusive evidence of a temperature effect on TTHM distribution is noticed.

Although both the initial based catalyzed reaction and subsequent halogenation steps involved in the THM reaction should be temperature dependent, the greatest effect of temperature is probably associated with the initial base catalyzed effect. Thus with an increase in temperature, a greater amount of THM intermediates are available for the halogenation steps, the products of which will depend on the relative and absolute levels of bromine and chlorine available for reaction.

In conclusion, the results of the temperature variation experiments indicate that the temperature dependence of THM formation is affected by the level of bromide. No conclusive evidence of a temperature effect on THM distribution is found.

Tennessee River Studies

The Tennessee River studies involved laboratory chlorinations of settled, filtered Tennessee River water. One batch of raw water was used for the chlorinations. The filtered Tennessee River sample had a NVTOC of 2.3 mg/l and a pH of 7.4.

Effect of Bromide

The experiments involving the effect of bromide indicate the same trends as the humic acid bromide experiments. Again, a dramatic increase in TTHMs as well as a shift in THM distribution is observed with an increase in added bromide. Table 22 demonstrates the increase in TTHM

Table 21. Percent Distribution Data for the Variation in Temperature Experiments Using Humic Acid

Temperature: (Celcius):	10			20			30		
Bromide (mg/L):	.04	.40	4.0	.04	.40	4.0	.04	.40	4.0
	% of TTHM								
$CHCl_3$	62.6	9.8	3.1	64.6	8.8	2.2	68.8	10.3	2.1
$CHCl_2Br$	32.1	26.8	2.8	29.2	25.5	2.4	25.5	29.1	2.6
$CHClBr_2$	5.3	42.5	16.4	6.2	44.8	11.8	5.7	43.6	12.9
$CHBr_3$	----	20.9	77.7	----	20.9	83.6	----	17.0	82.4

Table 22. Initial Bromide Vs. Percent Increase in TTHMs, Tennessee River Samples

Bromide Added mg/L	Reaction Time (hours) 8	24	48	72	96
	% Increase over 0mg/L Br^-				
.01	3.6	1.2	2.4	1.9	2.1
.02	7.9	6.3	5.7	4.4	6.2
.04	15.3	10.3	15.1	14.6	14.5
.10	21.9	25.1	20.3	17.3	14.8
.20	36.4	27.9	26.3	27.1	25.1
.40	47.1	38.2	40.2	42.7	43.3
1.00	71.2	57.0	62.1	65.3	67.8
2.00	82.7	81.6	85.8	90.5	88.4
4.00	84.1	96.7	99.4	100.1	99.5

yield by a tabulation of percent increase in added bromide. Figure 20 presents the relationship between the initial level of bromide and the resulting TTHM yield for the 96 hour samples. More than a twofold increase in TTHMs is observed at 4.0 mg/L initial bromide compared to no bromide added. Again, the TTHM enhancement effect due to bromide appears to level off at a higher level of Br^-. A shift toward the more highly brominated THM species with an increase in initial bromide is observed. Figure 21 illustrates the effect of bromide on THM distribution for the 96 hour samples. $CHCl_3$ shows a decrease in percent TTHM with an increase in initial bromide. $CHCl_2Br$ shows a peak in percent TTHM at about .4 mg/L bromide added. $CHClBr_2$ shows a peak in percent TTHM at about 1.0 mg/L bromide added. $CHBr_3$ shows a continuous increase in percent TTHM with an increase in bromide added. In a comparison of the peak percentages for $CHCl_2Br$ between humic acid and Tennessee River experiments, it is noticed that the levels of bromide at which these peak percentages occur are different. Likewise the levels of bromide for peak percentages of $CHClBr_2$ are different. These differences may be due to a difference in bromide demand. The river water could contain constituents not found in the pure humic acid solutions which could tie up bromide, such as ammonia, other inorganic reductants, or organic material. This could explain the higher levels of added bromide associated with the peak percents of TTHMs contributed by $CHCl_2Br$ and $CHClBr_2$.

Because the initial bromide level of the Tennessee River raw water was not determined, an evaluation of initial inorganic Cl/Br ratios was not possible.

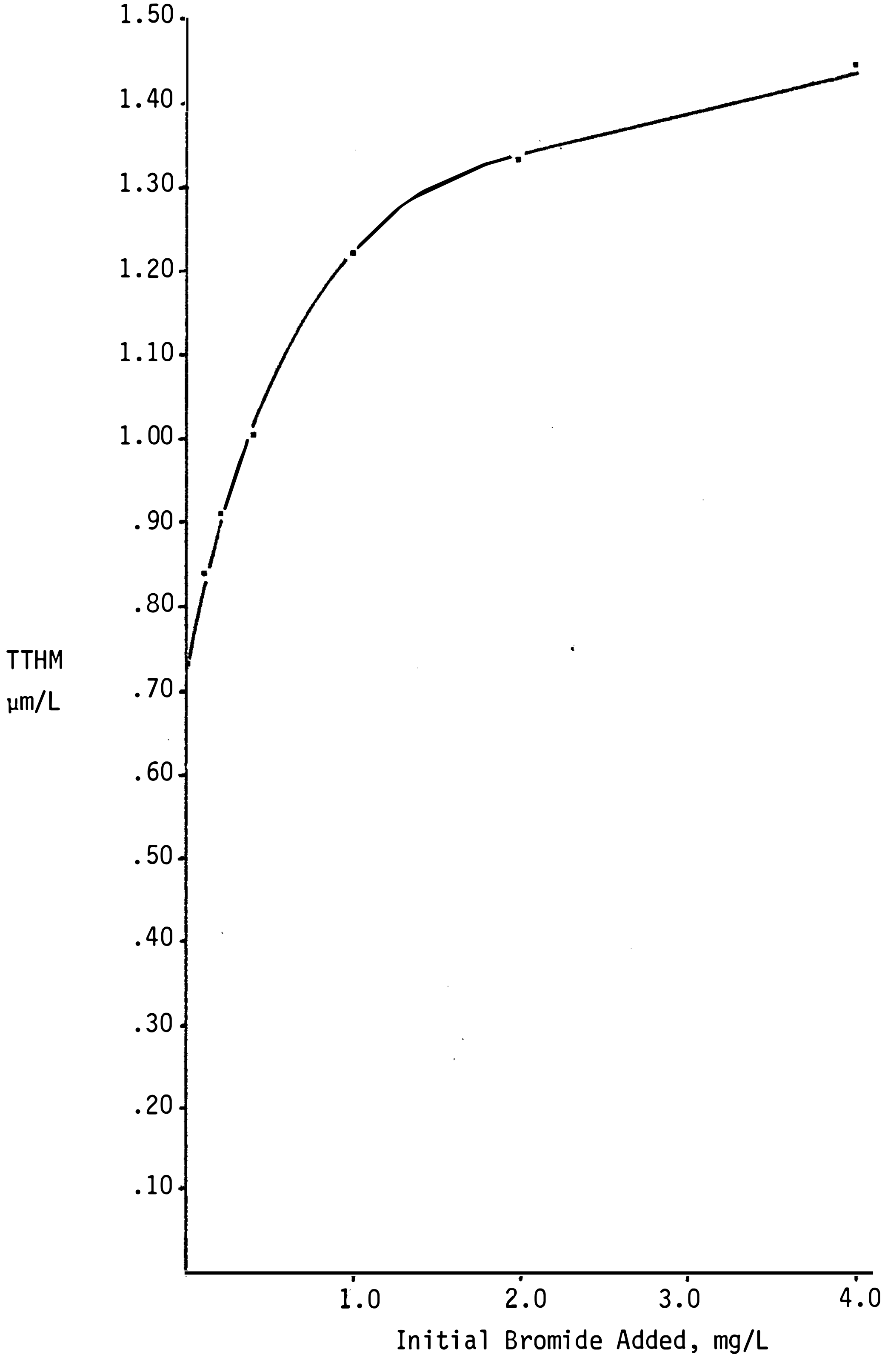

Figure 20. Bromide Added Vs. TTHM Formation for 96 Hour River Samples.

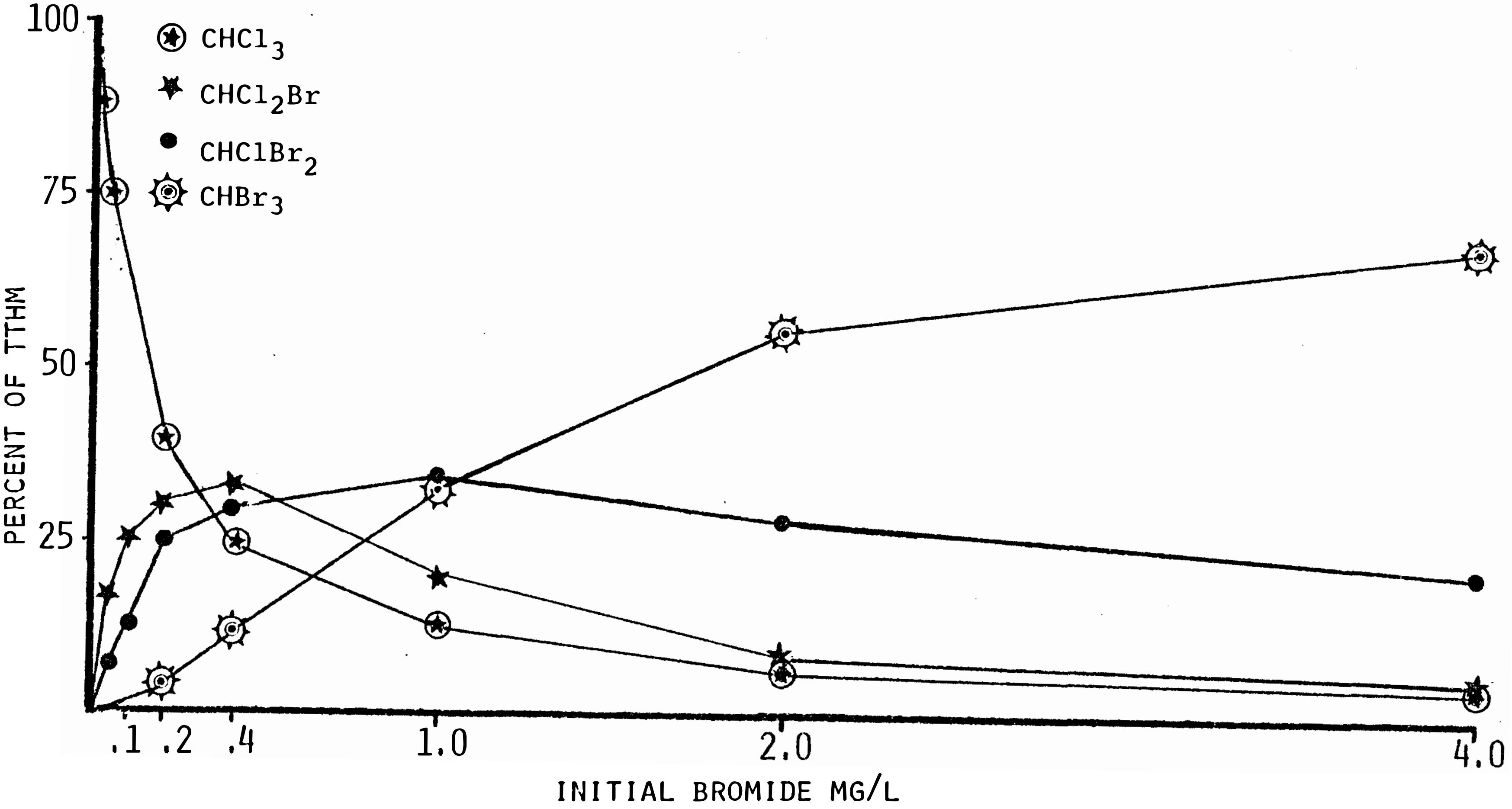

Figure 21. Initial Bromide Level Vs. Percent Distribution of THMs for 96 Hour Tennessee River Samples.

Effect of Temperature

As observed in the humic acid studies, the Tennessee River experiments involving a variation in temperature indicated a temperature effect on THM yield for all levels of bromide. Figures 22, 23, 24, 25, and 26 illustrate the relationship between temperature and the resulting $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, $CHBr_3$, and TTHMs respectively. Again, the relative effect of temperature on THM yield appears to be related to the level of bromide. Table 23 presents the results of linear regressions on these relationships. As with the humic acid studies, not all of the regressions are statistically significant, but a comparison of the slopes (THM, u m/l/^{o}C) of the regressions illustrate the effect of bromide on THM temperature dependence. The percent distribution data for the 96 hours samples are presented in Table 24. No conclusive evidence of a temperature effect on TTHM distribution is noticed.

Comparison with Previous Research

The general effects of organic precursor level, chlorine dose, pH, temperature, and bromide level on THM formation have all been reported by previous research. In most cases, a direct comparison of the results of this study with those of others is not possible because of differences in experimental conditions.

The effects of bromide on THM yield and distribution observed in this study compare with those found by Rook,[4] Bunn *et al*.[34], Lange and Kawcyznski,[35] Carns and Stinson,[36] and Trussell and Umphres.[18]

In this study, the effect of chlorine dose on THM formation was found to be dependent on the level of bromide. Rook[4] found an increase in

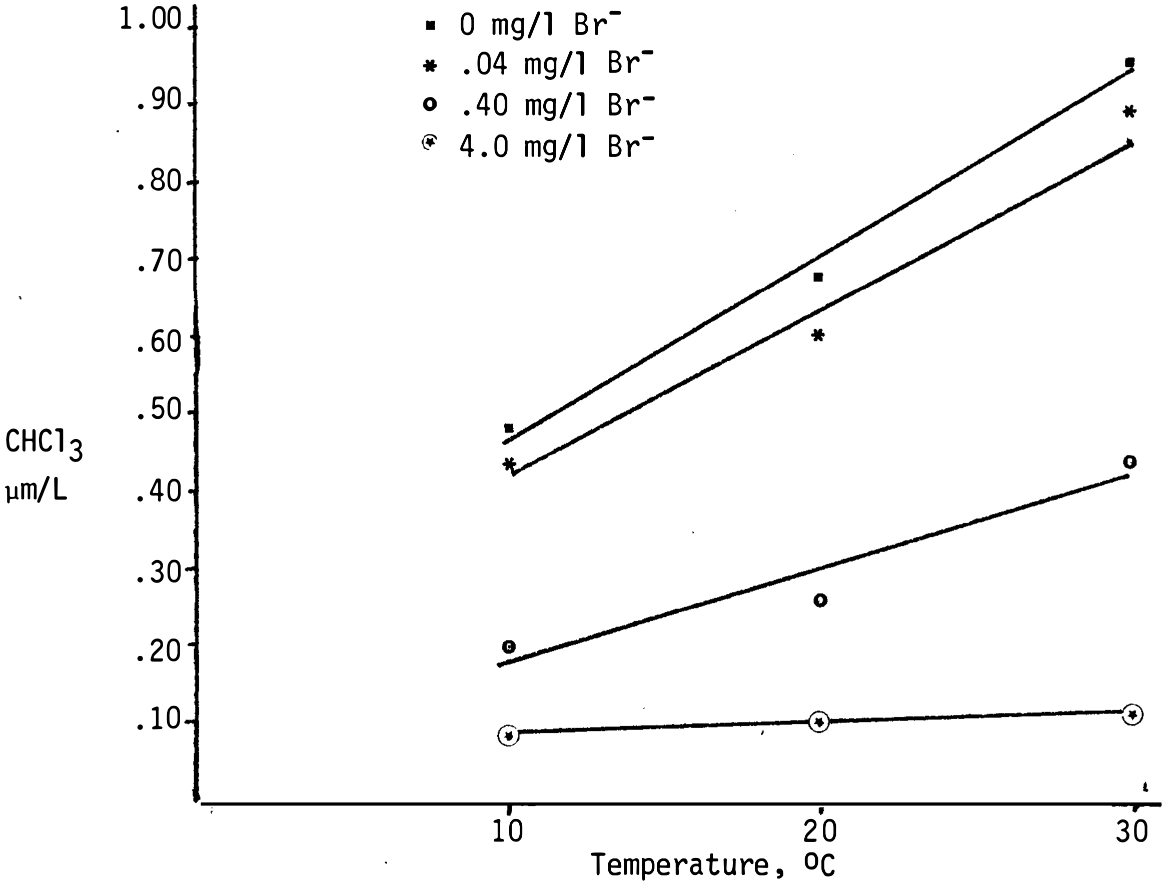

Figure 22. Temperature Vs. 96 Hour $CHCl_3$ Formation from Tennessee River Water.

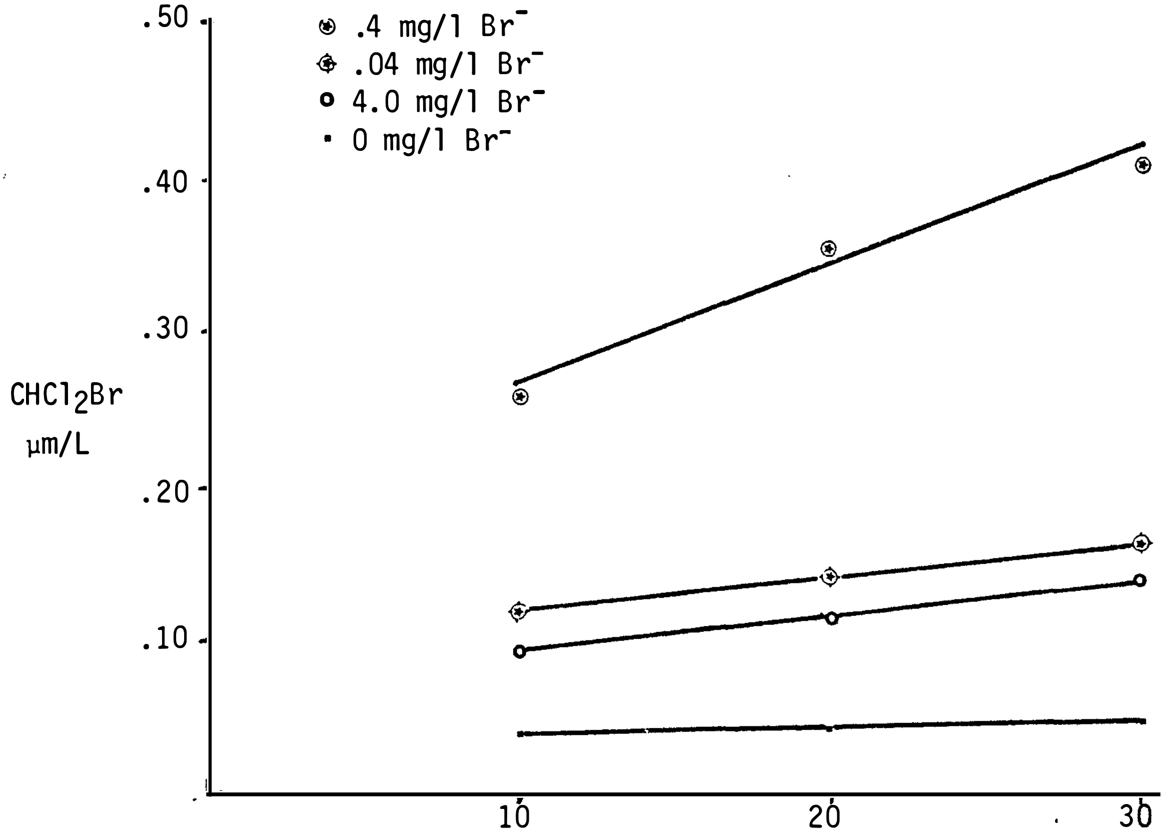

Figure 23. Temperature Vs. 96 Hour $CHCl_2Br$ Formation from Tennessee River Water.

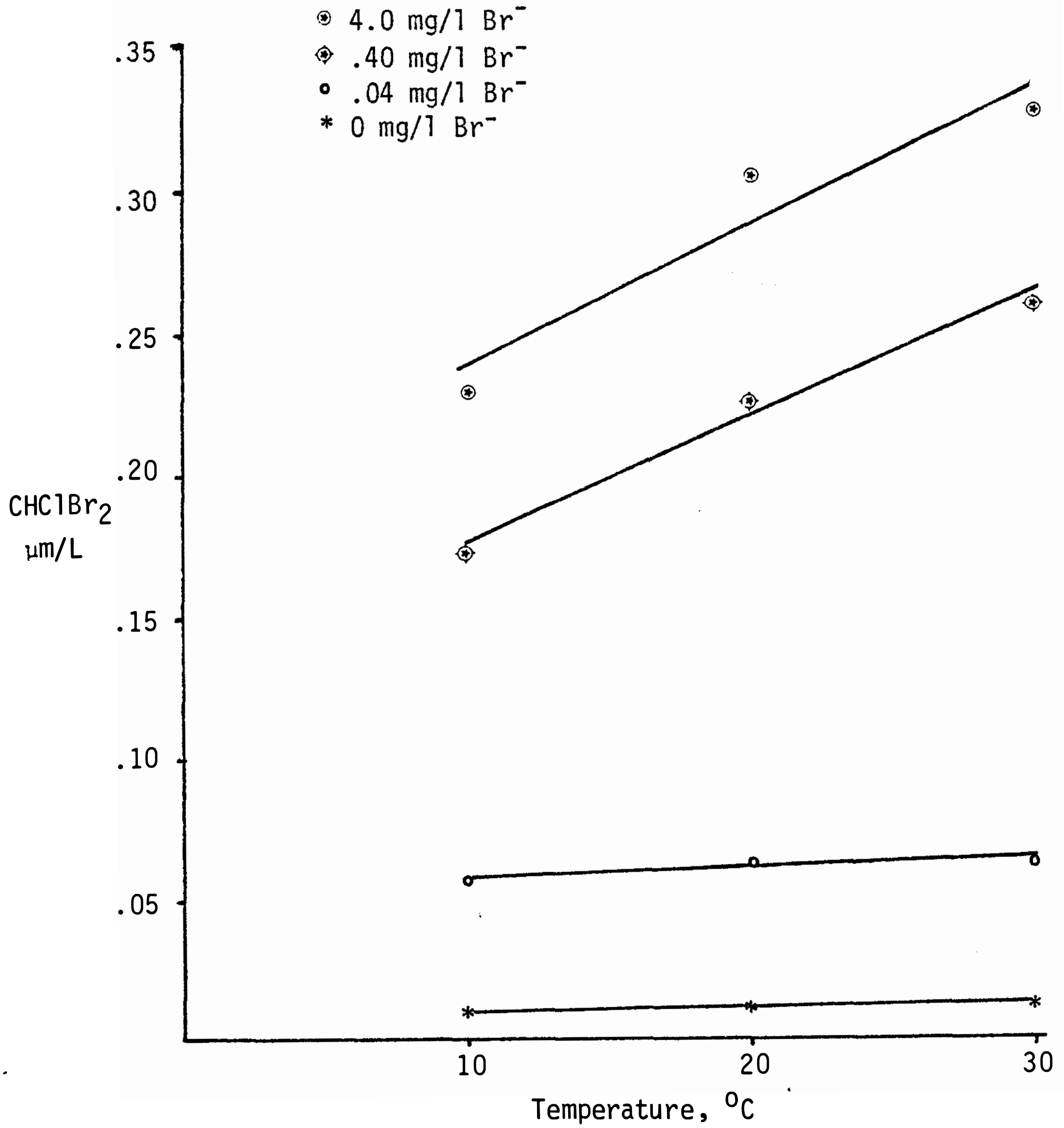

Figure 24. Temperature Vs. 96 Hour $CHClBr_2$ Formation for Tennessee River Water.

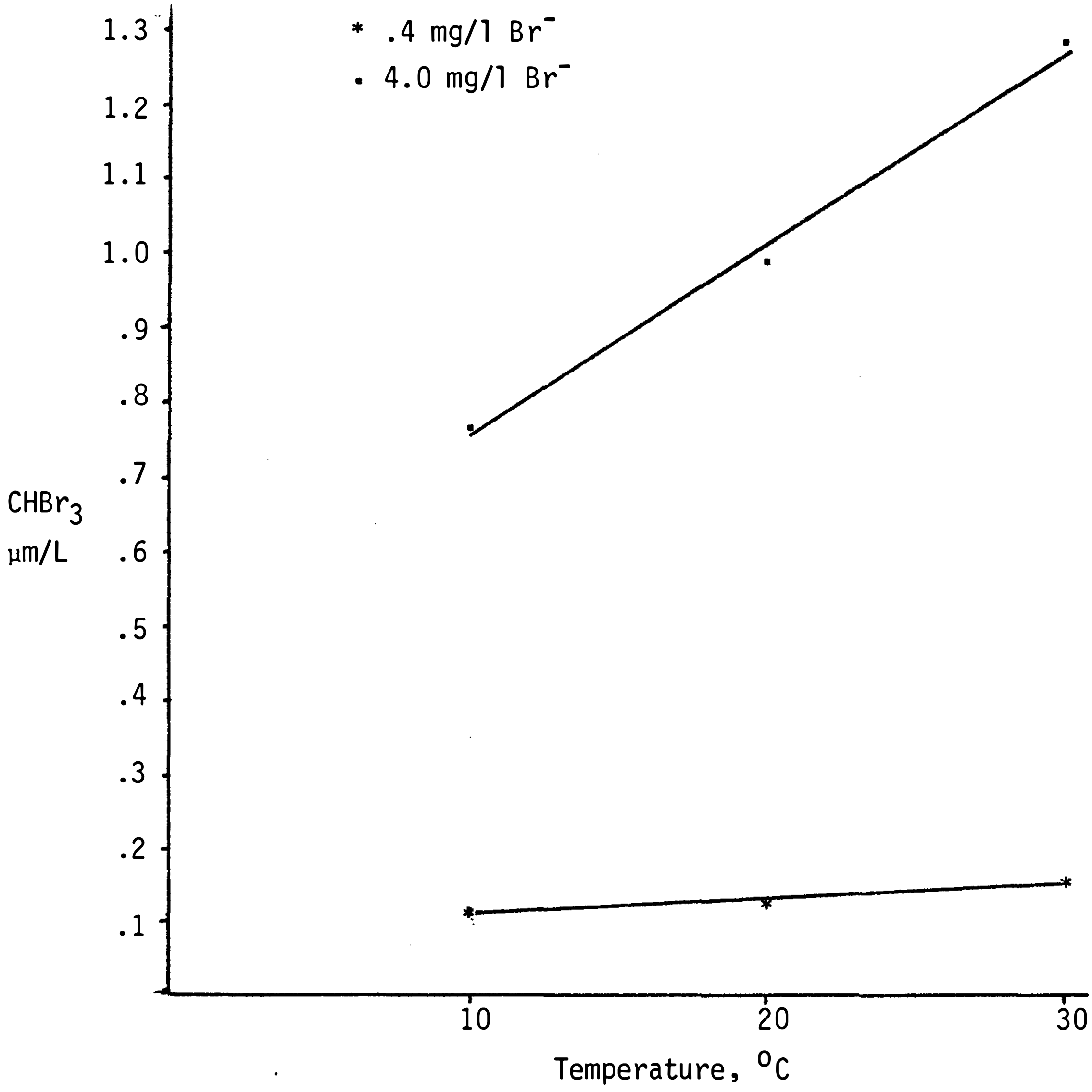

Figure 25. Temperature Vs. 96 Hour CHBr$_3$ Formation for Tennessee River Water.

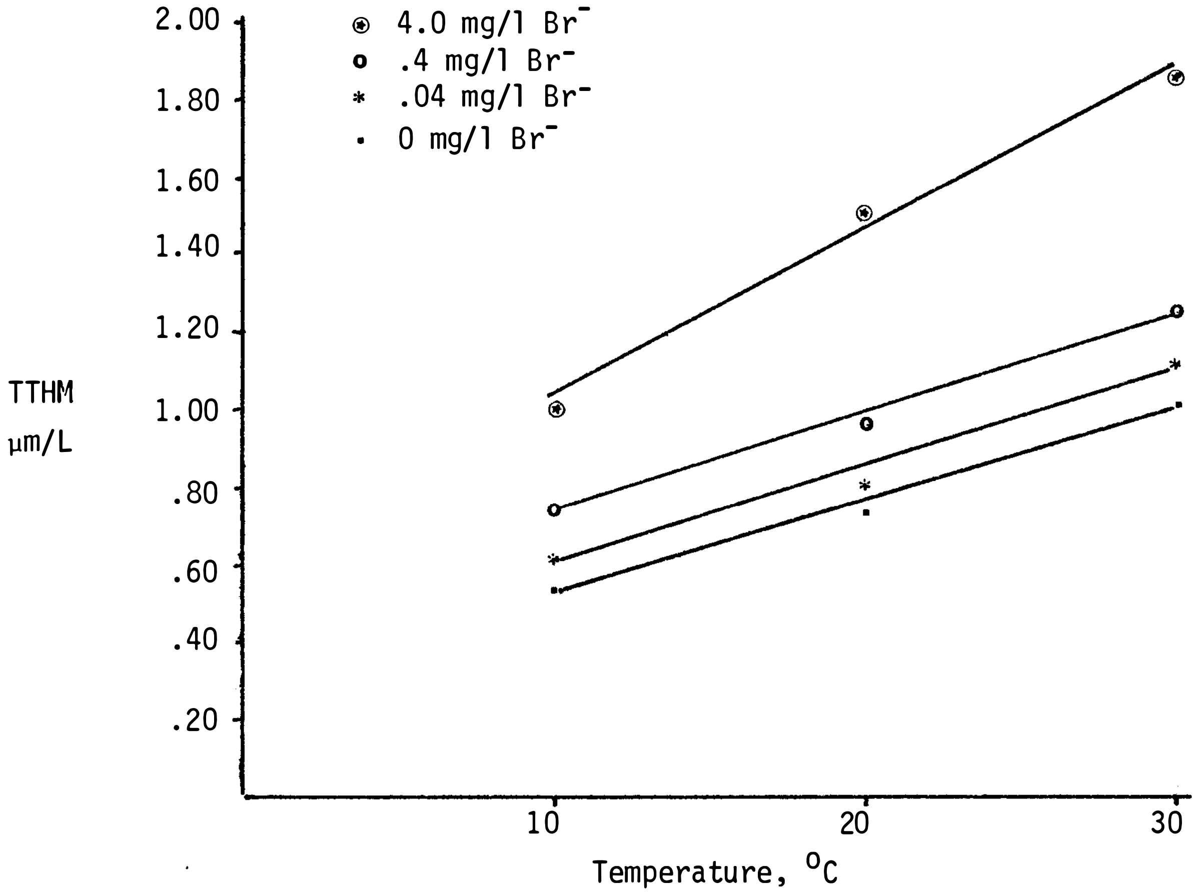

Figure 26. Temperature Vs. 96 Hour TTHM Formation from Tennessee River Water.

Table 23. Linear Regression Data for the Temperature Vs. THM Yield Relationships for the Tennessee River Experiments

THM	Br^- (mg/l)	Corr. Coef. (R)*	$\frac{\text{THM } (\mu m/l)}{^oC}$
$CHCl_3$	0	.9953	.0235
$CHCl_3$	.04	.9873	.0227
$CHCl_3$	.40	.9592	.0119
$CHCl_3$	4.00	.9998*	.0013
$CHCl_2Br$	0	.9820	.0005
$CHCl_2Br$	.04	.9997*	.0022
$CHCl_2Br$	.40	.9880	.0074
$CHCl_2Br$	4.00	.9997*	.0023
$CHClBr_2$	0	1.000*	.0001
$CHClBr_2$	.04	.9245	.0003
$CHClBr_2$	.40	.9893	.0043
$CHClBr_2$	4.00	.9522	.0049
$CHBr_3$	.40	.9878	.0022
$CHBr_3$	4.00	.9972*	.0259
TTHM	0	.9952	.0241
TTHM	.04	.9901	.0253
TTHM	.40	.9968	.0257
TTHM	4.00	.9999*	.0345

*(Significant at the 5% Level)

Table 24. Percent Distribution Data for the Variation in Temperature Experiments Using Tennessee River Water, 96 Hour Samples

THM	Temperature, C.	10				20				30			
	Bromide, mg/L	0	.04	.40	4.0	0	.04	.40	4.0	0	.04	.40	4.0
		% of TTHM											
$CHCl_3$		90.7	70.9	26.5	7.0	92.7	74.5	26.4	6.4	94.1	79.1	34.5	5.9
$CHCl_2Br$		7.4	19.8	35.2	8.0	5.8	17.7	36.8	7.6	4.7	14.8	32.5	7.5
$CHClBr_2$		1.9	9.3	23.4	19.7	1.5	7.8	23.6	20.4	1.2	5.7	20.7	17.7
$CHBr_3$		----	----	14.9	65.3	----	----	13.1	65.6	----	----	12.3	69.0

chlorine dose increased TTHM yield, of which about 50% were brominated THMs. Zogorski _et al._[27] found chlorine dose to affect $CHCl_3$ yield, but not $CHCl_2Br$ yield. In his work, apparently the level of initial bromide was relatively low. Lange and Kawcyzaski found that as chlorine dose increased there was a THM shift to more chlorinated THMs and less brominated THMs, but that the TTHM in μg/l remained the same. However, a conversion to um/l indicates that an increase in chlorine dose did increase the TTHM yield. In their work the initial levels of bromide were relatively high. The difference in chlorine dose trends observed among these studies may be due to differences in initial bromide levels, based on the results of this present study.

The effect of humic acid level on THM formation has been demonstrated by Stevens, _et al_.[7] The TTHM yields measured in the present study for humic acid levels used are comparable to those measured in Steven's work.

The effect of pH found in the present study compare with that reported by Stevens, _et al_,[7] who examined the change in $CHCl_3$ with a change in pH from 6.5 to 11.5. By calculation, a .08 um/l increase per pH unit was found, which is the same rate of change in the present study for no initial bromide added. Zogorski _et al._[27] observed an increase in $CHCl_3$ with an increase in pH, but no significant change in $CHCl_2Br$ with an increase in pH. Lange and Kawcyznski,[35] in a study of a raw water containing a relatively high bromide content, found that an increase in pH only increased $CHBr_3$ formation. Again, the level of initial bromide may explain the different trends found by these studies, based on the results of the present study.

Keeping in mind the effect of bromide on THM temperature dependence found in this study, the temperature effect results agree well with those reported in previous research. Stevens et al.[7] reported the temperature dependence of $CHCl_3$ using humic acid solutions. By calculation, this dependence was about (.04 um/l $CHCl_3$ ^{o}C) which is within the range reported for $CHCl_3$ in the present study. Zogorski et al.[27], in a study using Ohio River water, found a strong temperature dependence for $CHCl_3$ (.020 um/l $CHCl_3$ ^{o}C), with a much smaller temperature dependence for $CHCl_2Br$ (.002 um/l $CHCl_2Br$ ^{o}C). A relatively low initial bromide content is apparent, based on the THM distributions reported. These behaviors are consistent with the conclusions of the temperature effects in the present study, taking into consideration the bromide effect on temperature dependence.

Comparison of THM Formation With First Order Reaction Kinetics

The THM formation curves resulting from the chlorination experiments suggested that THM kinetics might be approximated by a simple first order kinetic model. Based on the measured THM data, computer simulations of THM formation were developed. A non-linear least squares approximation method was utilized, assuming simple first order kinetics. The expression used was:

$$THM_{(t)} = THM_{(f)}(1 - e^{-kt})$$

where $THM_{(t)}$ = THM value at time (t)

$THM_{(f)}$ = Final THM value

k = rate constant, hr^{-1}

t = time, hrs.

Comparisons of the predicted THM formation curves based on first order fits and the actual measured THM formation curves indicated that generally first order kinetics do not accurately describe THM formation. The trend observed in most of the comparisons is illustrated in Appendix F, Figure 49. In general, the predicted THM values overestimated the measured values during the earlier portion of the 96 hour reaction period, and underestimated the measured values during the later portion. A comparison of the rate constants (k) for the various experiments did not indicated any simple trends, probably because the first order model was not a good approximation.

An indepth analysis of the kinetics of THM formation was beyond the scope of this thesis. However, such a study could be very valuable, and the data from this thesis could be used for such a purpose.

V. SUMMARY AND CONCLUSIONS

The purpose of this study was to examine the effect of bromide on THM formation. Lab-scale chlorinations using humic acid solutions were made under controlled conditions of humic acid level, ionic strength, pH, chlorine dose, and temperature under varying conditions of initial bromide. THM formations were monitored over 96 hour reaction periods. Similar experiments were made using Tennessee River water under varying conditions of initial bromide and temperature.

The significant conclusions derived from this study are:

1. Bromine is more reactive than chlorine in forming THMs.
2. The level of bromide has an effect on TTHM yield and distribution.
3. The relative effect of pH on TTHM yield is dependent on the level of bromide.
4. Chlorination resulting in THMs is more dependent on the level of humic acid than bromination resulting in THMs.
5. The relative effect of pH on TTHM yield is dependent on the level of bromide.
6. The temperature dependence of $CHCl_3$ formation decreases with an increase in initial bromide.
7. The temperature dependence of $CHCl_2Br$ formation is greatest at the level of bromide corresponding to the predominance of $CHCl_2Br$ in the TTHM distribution.
8. The temperature dependence of $CHClBr_2$ formation is greatest at the level of bromide corresponding to the predominance of $CHClBr_2$ in the TTHM distribution.

9. The temperature dependence of $CHBr_3$ formation increases with an increase in initial bromide.
10. The kinetics of THM formation are not well approximated by a simple first order model, based on the measured THM data from this study.

Recommended Further Studies

Based on the results of this study, the following recommendations for further study are presented:

1. A study involving the comparison of raw water bromide levels (in addition to other known THM factors) to finished water THMs.
2. An extensive survey of raw water bromide levels and their fluctuations. (Using ion chromatography for bromide analysis)
3. A kinetic study of THM formation involving varying levels of bromide, extensive and accurate monitoring of initial TOC, totol organic chlorine and bromine, and the THMs. Computer simulations based on higher order kinetic models could then be more readily utilized and verified.
4. A study identifying additional non-THM halogenated organics formed in the chlorination of drinking water.
5. A study involving actual raw water instead of humic acid solutions, similar to the present study.

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APPENDIXES

APPENDIX A

THM DATA

Table 25. THM Data for the Effect of Bromide Level from Humic Acid

	Reaction Time (hrs.)							
Br$^-$ (mg/L)	1	2	4	8	24	48	72	96
				$CHCl_3$ (um/L)				
00.00	0.066	0.091	0.117	0.131	0.170	0.203	0.249	0.258
.01	.065	.087	.114	.120	.159	.192	.237	.251
.02	.063	.080	.110	.119	.157	.175	.217	.237
.04	.056	.065	.094	.113	.140	.147	.184	.199
.10	.046	.057	.065	.082	.096	.103	.148	.171
.20	.028	.034	.036	.051	.063	.072	.078	.078
.40	.018	.023	.029	.030	.030	.033	.036	.039
1.00	.015	.021	.024	.027	.028	.028	.028	.032
2.00	.012	.018	.021	.024	.025	.025	.025	.026
4.00	.004	.005	.007	.008	.010	.012	.012	.013
				$CHCl_2Br$ (um/L)				
00.00	.000	.000	.000	.000	.000	.000	.000	.000
.01	.005	.006	.011	.011	.014	.017	.019	.019
.02	.008	.013	.017	.020	.029	.036	.046	.049
.04	.018	.028	.033	.044	.057	.069	.083	.090
.10	.020	.036	.042	.064	.071	.097	.121	.127
.20	.024	.035	.042	.064	.071	.097	.121	.127
.40	.020	.028	.038	.051	.066	.089	.108	.113
1.00	.010	.011	.023	.030	.029	.051	.055	.068
2.00	.006	.009	.011	.014	.018	.021	.027	.024
4.00	.004	.005	.005	.007	.008	.010	.013	.014
				$CHClBr_2$ (um/L)				
00.00	.000	.000	.000	.000	.000	.000	.000	.000
.01	.000	.000	.001	.002	.002	.003	.003	.003
.02	.002	.002	.003	.004	.004	.004	.004	.005
.04	.003	.008	.010	.010	.011	.012	.014	.019
.10	.015	.028	.037	.045	.051	.062	.071	.073
.20	.035	.049	.064	.071	.092	.106	.137	.147
.40	.045	.069	.086	.104	.119	.143	.175	.199
1.00	.043	.073	.098	.117	.134	.147	.173	.205
2.00	.038	.059	.069	.076	.097	.107	.110	.118
4.00	.022	.037	.039	.041	.054	.063	.064	.069
				$CHBr_3$ (um/L)				
00.00	.000	.000	.000	.000	.000	.000	.000	.000
.01	.000	.000	.000	.000	.000	.000	.000	.000
.02	.000	.000	.000	.000	.000	.000	.000	.000
.04	.000	.000	.000	.000	.000	.000	.000	.000
.10	.000	.000	.000	.000	.000	.000	.000	.000
.20	.010	.012	.013	.016	.018	.021	.025	.025
.40	.023	.034	.039	.042	.046	.064	.071	.093
1.00	.049	.065	.093	.130	.173	.188	.197	.208
2.00	.080	.131	.173	.199	.296	.325	.351	.379
4.00	.119	.177	.242	.277	.387	.431	.479	.491

Table 26. THM Data for the Effect of Chlorine Dose

		Reaction Time (hrs.)							
		1	2	4	8	24	48	72	96
Cl (mg/L)	Br^- (mg/L)								
			$CHCl_3$ (um/L)						
2.5	0000	.056	.063	.099	.122	.135	.140	.162	.185
5.0	0000	.066	.091	.117	.137	.170	.203	.249	.258
10.0	0000	.085	.117	.158	.175	.204	.224	.290	.305
2.5	.033	.040	.044	.065	.085	.086	.111	.152	.177
5.0	.033	.051	.069	.107	.116	.149	.167	.199	.211
10.0	.033	.057	.083	.119	.175	.230	.251	.266	.273
2.5	.333	.016	.018	.022	.023	.024	.025	.026	.027
5.0	.333	.015	.021	.034	.037	.044	.048	.051	.052
10.0	.333	.023	.028	.039	.048	.057	.060	.063	.065
			$CHCl_2Br$ (um/L)						
2.5	0000	.000	.000	.000	.000	.000	.000	.000	.000
5.0	0000	.000	.000	.000	.000	.000	.000	.000	.000
10.0	0000	.000	.000	.000	.000	.000	.000	.000	.000
2.5	.033	.010	.014	.027	.030	.040	.052	.064	.071
5.0	.033	.014	.024	.026	.030	.034	.048	.072	.076
10.0	.033	.015	.022	.035	.038	.045	.050	.071	.070
2.5	.333	.011	.018	.025	.038	.040	.064	.081	.083
5.0	.333	.025	.035	.042	.065	.068	.093	.140	.143
10.0	.333	.024	.036	.047	.073	.076	.105	.143	.149
			$CHClBr_2$ (um/L)						
2.5	0000	.000	.000	.000	.000	.000	.000	.000	.000
5.0	0000	.000	.000	.000	.000	.000	.000	.000	.000
10.0	0000	.000	.000	.000	.000	.000	.000	.000	.000
2.5	.033	.002	.004	.006	.006	.008	.012	.014	.014
5.0	.033	.003	.005	.006	.007	.008	.012	.014	.014
10.0	.033	.002	.004	.007	.007	.008	.009	.011	.011
2.5	.333	.036	.053	.074	.102	.108	.143	.173	.174
5.0	.333	.046	.059	072	.089	.114	.130	.154	.169
10.0	.333	.039	.053	.068	.100	.111	.124	.161	.165
			$CHBr_3$ (um/L)						
2.5	0000	.000	.000	.000	.000	.000	.000	.000	.000
5.0	0000	.000	.000	.000	.000	.000	.000	.000	.000
10.0	0000	.000	.000	.000	.000	.000	.000	.000	.000
2.5	.033	.000	.000	.000	.000	.000	.000	.000	.000
5.0	.033	.000	.000	.000	.000	.000	.000	.000	.000
10.0	.033	.000	.000	.000	.000	.000	.000	.000	.000
2.5	.333	.014	.025	.031	.040	.050	.063	.086	.093
5.0	.333	.015	.018	.021	.026	.030	.035	.037	.040
10.0	.333	.008	.010	.015	.023	.026	.027	.033	.033

Table 27. THM Data for the Effect of Humic Acid Level

Humic Acid (mg/L)	Br^- (mg/L)	Reaction Time (hrs.) 1	2	4	8	24	48	72	96
				$CHCl_3$ (um/L)					
0.50	0000	.027	.045	.063	.106	.119	.126	.125	.125
1.00	0000	.066	.091	.117	.191	.207	.223	.249	.258
2.00	0000	.097	.165	.175	.300	.325	.358	.373	.391
0.50	.033	.024	.041	.057	.096	.100	.104	.110	.115
1.00	.033	.061	.069	.107	.176	.199	.207	.209	.211
2.00	.033	.080	.132	.167	.284	.307	.309	.309	.310
0.50	.330	.014	.020	.024	.028	.031	.033	.034	.036
1.00	.330	.019	.028	.043	.052	.054	.054	.059	.059
2.00	.330	.018	.027	.081	.094	.096	.096	.098	.100
				$CHCl_2Br$ (um/L)					
0.50	0000	.000	.000	.000	.000	.000	.000	.000	.000
1.00	0000	.000	.000	.000	.000	.000	.000	.000	.000
2.00	0000	.000	.000	.000	.000	.000	.000	.000	.000
0.50	.033	.005	.009	.015	.015	.022	.033	.045	.059
1.00	.033	.014	.024	.026	.030	.044	.048	.072	.076
2.00	.033	.019	.039	.039	.053	.058	.065	.087	.087
0.50	.330	.012	.026	.049	.069	.072	.088	.089	.089
1.00	.330	.025	.035	.062	.105	.128	.133	.140	.143
2.00	.330	.038	.058	.102	.191	.203	.205	.211	.210
				$CHClBr_2$ (um/L)					
0.50	0000	.000	.000	.000	.000	.000	.000	.000	.000
1.00	0000	.000	.000	.000	.000	.000	.000	.000	.000
2.00	0000	.000	.000	.000	.000	.000	.000	.000	.000
0.50	.033	.002	.003	.004	.005	.005	.007	.007	.007
1.00	.033	.003	.005	.006	.007	.008	.009	.009	.009
2.00	.033	.004	.009	.009	.009	.011	.012	.014	.015
0.50	.330	.015	.023	.035	.040	.059	.086	.093	.141
1.00	.330	.046	.059	.072	.089	.114	.130	.154	.169
2.00	.330	.058	.101	.103	.150	.197	.257	.292	.292
				$CHBr_3$ (um/L)					
0.50	0000	.000	.000	.000	.000	.000	.000	.000	.000
1.00	0000	.000	.000	.000	.000	.000	.000	.000	.000
2.00	0000	.000	.000	.000	.000	.000	.000	.000	.000
0.50	.033	.000	.000	.000	.000	.000	.000	.000	.000
1.00	.033	.000	.000	.000	.000	.000	.000	.000	.000
2.00	.033	.000	.000	.000	.000	.000	.000	.000	.000
0.50	.330	.005	.010	.012	.013	.019	.023	.025	.027
1.00	.330	.015	.018	.021	.026	.030	.035	.035	.040
2.00	.330	.019	.025	.029	.035	.054	.060	.066	.066

Table 28. THM Data for the Effect of pH

pH	Br^- (mg/L)	Reaction Time (hrs) 1	2	4	8	24	48	72	96
				$CHCl_3$ (um/L)					
6.0	0000	.052	.072	.103	.115	.147	.160	.168	.172
7.0	0000	.066	.091	.117	.131	.170	.203	.249	.258
8.0	0000	.072	.142	.183	.228	.259	.279	.308	.333
9.5	0000	.086	.191	.217	.263	.353	.400	.432	.454
6.0	.033	.045	.056	.079	.086	.109	.119	.128	.131
7.0	.033	.051	.069	.107	.116	.149	.167	.199	.211
8.0	.033	.061	.091	.125	.148	.229	.253	.269	.279
9.5	.033	.085	.114	.140	.197	.271	.339	.388	.408
6.0	.333	.014	.017	.025	.031	.039	.046	.048	.050
7.0	.333	.019	.028	.033	.037	.040	.044	.049	.052
8.0	.333	.020	.023	.044	.052	.065	.066	.067	.067
9.5	.333	.029	.036	.056	.064	.079	.085	.089	.092
				$CHCl_2Br$(um/L)					
6.0	0000	.000	.000	.000	.000	.000	.000	.000	.000
7.0	0000	.000	.000	.000	.000	.000	.000	.000	.000
8.0	0000	.000	.000	.000	.000	.000	.000	.000	.000
9.5	0000	.000	.000	.000	.000	.000	.000	.000	.000
6.0	.033	.012	.019	.025	.029	.045	.048	.049	.050
7.0	.033	.014	.024	.026	.030	.034	.048	.072	.076
8.0	.033	.029	.035	.045	.055	.063	.074	.083	.087
9.5	.033	.030	.039	.048	.065	.081	.098	.103	.117
6.0	.333	.015	.018	.019	.026	.046	.045	.046	.059
7.0	.333	.025	.035	.042	.065	.068	.093	.140	.143
8.0	.333	.028	.044	.045	.064	.072	.094	.144	.148
9.5	.333	.040	.053	.067	.093	.109	.123	.149	.158
				$CHClBr_2$ (um/L)					
6.0	0000	.000	.000	.000	.000	.000	.000	.000	.000
7.0	0000	.000	.000	.000	.000	.000	.000	.000	.000
8.0	0000	.000	.000	.000	.000	.000	.000	.000	.000
9.5	0000	.000	.000	.000	.000	.000	.000	.000	.000
6.0	.033	.003	.004	.005	.006	.007	.008	.008	.008
7.0	.033	.004	.005	.006	.007	.008	.009	.009	.009
8.0	.033	005	.010	.013	.014	.015	.018	.020	.022
9.5	.033	.008	.012	.019	.024	.034	.036	.037	.037
6.0	.333	.032	.052	.061	.074	.094	.116	.122	.128
7.0	.333	.046	.059	.072	.089	.114	.130	.154	.169
8.0	.333	.054	.074	.077	.123	.174	.183	.206	.214
9.5	.333	.068	.095	.131	.172	.213	.232	.255	.266
				$CHBr_3$ (um/L)					
6.0	0000	.000	.000	.000	.000	.000	.000	.000	.000
7.0	0000	.000	.000	.000	.000	.000	.000	.000	.000
8.0	0000	.000	.000	.000	.000	.000	.000	.000	.000
9.5	0000	.000	.000	.000	.000	.000	.000	.000	.000
6.0	.033	.000	.000	.000	.000	.000	.000	.000	.000
7.0	.033	.000	.000	.000	.000	.000	.000	.000	.000
8.0	.033	.000	.000	.000	.000	.000	.000	.000	.000
9.5	.033	.000	.000	.000	.000	.000	.000	.000	.000
6.0	.333	.014	.016	.020	.025	.028	.030	.032	.033
7.0	.333	.015	.018	.021	.026	.030	.035	.037	.040
8.0	.333	.040	.049	.053	.083	.119	.129	.131	.134
9.5	.057	.081	.092	.117	.181	.197	.197	.217	.232

Table 29. THM Data for the Effect of Ionic Strength

		Reaction Time (hrs.)							
Ionic Strength	Br- (mg/L)	1	2	4	8	24	48	72	96
		$CHCl_3$ (um/L)							
.015	0000	.071	.095	.119	.130	.164	.210	.241	.265
.075	0000	.075	.092	.118	.135	.160	.208	.257	.263
.150	0000	.069	.094	.118	.136	.169	.213	.260	.259
.015	.033	.060	.068	.107	.116	.147	.163	.208	.215
.075	.033	.061	.073	.107	.119	.154	.169	.192	.210
.150	.033	.063	.075	.117	.123	.152	.165	.194	.209
.015	.033	.021	.029	.035	.038	.046	.049	.051	.052
.075	.333	.024	.027	.036	.039	.047	.049	.050	.051
.150	.333	.017	.029	.036	.042	.046	.046	.047	.051
		$CHCl_2Br$ (um/L)							
.015	0000	.000	.000	.000	.000	.000	.000	.000	.000
.075	0000	.000	.000	.000	.000	.000	.000	.000	.000
.150	0000	.000	.000	.000	.000	.000	.000	.000	.000
.015	.033	.015	.025	.026	.031	.032	.045	.069	.073
.075	.033	.014	.023	.026	.031	.032	.045	.069	.073
.150	.033	.014	.024	.027	.033	.034	.044	.069	.070
.015	.333	.022	.034	.039	.059	.094	.119	.129	.141
.075	.333	.025	.036	.042	.060	.098	.122	.134	.138
.150	.333	.029	.035	.043	.063	.091	.116	.130	.144
		$CHClBr_2$ (um/L)							
.015	0000	.000	.000	.000	.000	.000	.000	.000	.000
.075	0000	.000	.000	.000	.000	.000	.000	.000	.000
.150	0000	.000	.000	.000	.000	.000	.000	.000	.000
.015	.033	.003	.005	.006	.007	.008	.008	.009	.009
.075	.033	.003	.005	.006	.007	.008	.008	.009	.009
.150	.033	.003	.005	.006	.008	.008	.009	.009	.009
.015	.333	.044	.060	.078	.092	.116	.125	.162	.169
.075	.333	.043	.061	.071	.089	.114	.131	.155	.172
.150	.333	.052	.056	.072	.084	.113	.130	.155	.165
		$CHBr_3$ (um/L)							
.015	0000	.000	.000	.000	.000	.000	.000	.000	.000
.075	0000	.000	.000	.000	.000	.000	.000	.000	.000
.150	0000	.000	.000	.000	.000	.000	.000	.000	.000
.015	.033	.000	.000	.000	.000	.000	.000	.000	.000
.075	.033	.000	.000	.000	.000	.000	.000	.000	.000
.150	.033	.000	.000	.000	.000	.000	.000	.000	.000
.015	.333	.014	.018	.023	.026	.029	.033	.037	.042
.075	.333	.014	.018	.020	.025	.030	.035	.039	.041
.150	.333	.016	.018	.021	.027	.030	.036	.039	.041

Table 30. THM Data for the Effect of Temperature from Humic Acid

Temp (C^o)	Br^- (mg/L)	Reaction Time (hrs.)							
		1	2	4	8	24	48	72	96
				$CHCl_3$ (um/L)					
10	0000	.042	.075	.091	.112	.139	.169	.188	.206
20	0000	.066	.091	.117	.131	.170	.203	.249	.258
30	0000	.109	.157	.185	.212	.318	.330	.339	.342
10	0.04	.039	.055	.079	.092	.119	.130	.140	.152
20	0.04	.046	.065	.094	.113	.140	.147	.184	.199
30	0.04	.091	.117	.168	.199	.295	.309	.320	.327
10	0.40	.013	.017	.019	.021	.024	.028	.029	.030
20	0.40	.018	.023	.029	.030	.030	.033	.036	.039
30	0.40	.031	.039	.048	.062	.067	.069	.071	.071
10	4.00	.003	.004	.005	.006	.008	.009	.010	.011
20	4.00	.004	.005	.006	.008	.010	.012	.012	.013
30	4.00	.007	.009	.010	.012	.013	.014	.015	.015
			$CHCl_2Br$ (um/L)						
10	0000	.000	.000	.000	.000	.000	.000	.000	.000
20	0000	.000	.000	.000	.000	.000	.000	.000	.000
30	0000	.000	.000	.000	.000	.000	.000	.000	.000
10	0.04	.012	.022	.027	.033	.049	.060	.070	.078
20	0.04	.018	.023	.033	.044	.057	.069	.083	.090
30	0.04	.029	.045	.054	.076	.109	.116	.118	.121
10	0.40	.017	.024	.032	.039	.051	.060	.073	.082
20	0.40	.020	.028	.038	.051	.066	.089	.108	.113
30	0.40	.039	.051	.071	.110	.157	.180	.191	.200
10	4.00	.003	.004	.005	.006	.007	.008	.009	.010
20	4.00	.004	.005	.006	.007	.008	.010	.013	.014
30	4.00	.008	.011	.012	.014	.016	.017	.017	.018
			$CHClBr_2$ (um/L)						
10	0000	.000	.000	.000	.000	.000	.000	.000	.000
20	0000	.000	.000	.000	.000	.000	.000	.000	.000
30	0000	.000	.000	.000	.000	.000	.000	.000	.000
10	0.04	.003	.005	.006	.008	.010	.011	.012	.013
20	0.04	.003	.008	.010	.010	.011	.012	.014	.019
30	0.04	.005	.010	.014	.017	.023	.026	.027	.027
10	0.40	.038	.059	.067	.085	.095	.111	.123	.130
20	0.40	.045	.069	.086	.104	.119	.143	.175	.199
30	0.40	.077	.100	.124	.146	.238	.277	.291	.300
10	4.00	.018	.027	.030	.034	.042	.048	.052	.059
20	4.00	.022	.037	.039	.041	.054	.063	.064	.069
30	4.00	.034	.042	.047	.054	.077	.083	.086	.090
			$CHBr_3$ (um/L)						
10	0000	.000	.000	.000	.000	.000	.000	.000	.000
20	0000	.000	.000	.000	.000	.000	.000	.000	.000
30	0000	.000	.000	.000	.000	.000	.000	.000	.000
10	0.04	.000	.000	.000	.000	.000	.000	.000	.000
20	0.04	.000	.000	.000	.000	.000	.000	.000	.000
30	0.04	.000	.000	.000	.000	.000	.000	.000	.000
10	0.40	.020	.028	.033	.037	.041	.053	.060	.064
20	0.40	.023	.034	.039	.042	.046	.064	.071	.093
30	0.40	.028	.043	.060	.076	.092	.107	.110	.117
10	4.00	.104	.159	.180	.199	.232	.248	.262	.279
20	4.00	.119	.177	.242	.277	.307	.387	.431	.491
30	4.00	.152	.209	.300	.311	.493	.547	.560	.576

Table 31. THM Data for the Effect of Bromide Level from Tennessee River Water.

	Reaction Time (hrs.)							
Br^- (mg/L)	1	2	4	8	24	48	72	96
			$CHCl_3$ (um/L)					
0000	.197	.258	.283	.337	.529	.588	.634	.676
0.01	.192	.250	.276	.325	.504	.569	.610	.655
0.02	.184	.239	.259	.310	.490	.551	.584	.630
0.04	.171	.224	.235	.287	.460	.551	.584	.630
0.10	.148	.189	.198	.247	.449	.479	.492	.510
0.20	.105	.147	.163	.199	.282	.317	.343	.360
0.40	.070	.105	.127	.134	.187	.212	.237	.254
1.00	.034	.046	.059	.082	.105	.122	.140	.157
2.00	.025	.033	.040	.052	.065	.079	.087	.096
4.00	.016	.020	.030	.039	.060	.065	.068	.072
			$CHCl_2Br$ (um/L)					
0000	.008	.012	..017	.020	.031	.035	.038	.042
0.01	.015	.023	.028	.043	.059	.064	.069	.072
0.02	.027	.034	.046	.065	.087	.087	.095	.108
0.04	.039	.049	.064	.097	.120	.125	.141	.142
0.10	.058	.074	.087	.125	.181	.192	.208	.217
0.20	.080	.099	.110	.148	.232	.250	.279	.284
0.40	.101	.124	.144	.187	.270	.310	.336	.354
1.00	.069	.083	.099	.127	.170	.192	.217	.243
2.00	.030	.039	.047	.067	.089	.100	.111	.115
4.00	.022	.027	.032	.044	.073	.079	.084	.086
			$CHClBr_2$ (um/L)					
0000	.003	.005	.007	.008	.010	.011	.011	.011
0.01	.004	.006	.008	.010	.014	.016	.017	.017
0.02	.010	.014	.017	.019	.029	.032	.034	.036
0.04	.016	.024	.028	.037	.049	.054	.058	.063
0.10	.029	.040	.055	.068	.078	.087	.096	.105
0.20	.053	.079	.102	.127	.179	.198	.205	.227
0.40	.082	.099	.111	.148	.237	.259	.287	.311
1.00	.127	.156	.175	.221	.320	.362	.194	.423
2.00	.094	.121	.150	.185	.250	.300	.356	.384
4.00	.087	.104	.121	.140	.224	.241	.274	.307
			$CHBr_3$ (um/L)					
0000	.000	.000	.000	.000	.000	.000	.000	.000
0.01	.000	.000	.000	.000	.000	.000	.000	.000
0.02	.000	.000	.000	.000	.000	.000	.000	.000
0.04	.000	.000	.000	.000	.000	.000	.000	.000
0.10	.001	.003	.005	.005	.005	.005	.005	.005
0.20	.008	.015	.021	.024	.036	.039	.041	.041
0.40	.023	.035	.048	.068	.094	.108	.115	.126
1.00	.092	.129	.157	.195	.300	.352	.378	.400
2.00	.195	.236	.297	.363	.631	.699	.747	.771
4.00	.240	.308	.380	.449	.764	.879	.941	.989

Table 32. THM Data for the Effect of Temperature from Tennessee River Water

		Reaction Time (hrs.)							
Temp (^{o}C)	Br$^-$ (mg/L)	1	2	4	8	24	48	72	96
			CHCl$_3$ (um/L)						
10	0000	.135	.204	.238	.284	.319	.376	.421	.480
20	0000	.197	.258	.283	.337	.529	.588	.634	.676
30	0000	.254	.393	.451	.630	.820	.894	.927	.951
10	0.04	.118	.138	.184	.231	.320	.362	.399	.434
20	0.04	.171	.224	.235	.287	.460	.517	.554	.598
30	0.04	.280	.362	.454	.524	.772	.837	.860	.889
10	0.40	.057	.068	.082	.105	.148	.167	.180	.195
20	0.40	.070	.105	.127	.134	.187	.212	.237	.254
30	0.40	.104	.139	.190	.237	.320	.379	.411	.433
10	4.00	.017	.025	.030	.039	.050	.063	.071	.082
20	4.00	.025	.033	.040	.052	.065	.079	.087	.096
30	4.00	.042	.044	.049	.065	.078	.089	.100	.109
			CHCl$_2$ Br (um/L)						
10	0000	.008	.010	.012	.017	.024	.030	.035	.039
20	0000	.008	.012	.017	.020	.031	.035	.038	.042
30	0000	.012	.016	.220	.029	.038	.043	.046	.048
10	0.04	.031	.040	.052	.079	.093	.106	.113	.121
20	0.04	.039	.049	.064	.097	.120	.125	.141	.142
30	0.04	.047	.056	.078	.110	.146	.157	.162	.165
10	0.40	.069	.083	.107	.130	.186	.215	.241	.260
20	0.40	.101	.124	.144	.187	.270	.310	.336	.354
30	0.40	.138	.174	.217	.282	.342	.379	.397	.408
10	4.00	.026	.034	.043	.056	.070	.079	.085	.093
20	4.00	.030	.039	.047	.067	.089	.100	.111	.115
30	4.00	.032	.045	.059	.080	.104	.119	.132	.139
			CHClBr$_2$ (um/L)						
10	0000	.002	.003	.005	.006	.008	.009	.009	.010
20	0000	.003	.005	.007	.008	.010	.011	.011	.011
30	0000	.003	.006	.008	.010	.012	.012	.012	.012
10	0.04	.012	.017	.027	.034	.040	.046	.052	.057
20	0.04	.016	.024	.032	.037	.049	.054	.058	.063
30	0.04	.021	.029	.048	.052	.060	.063	.064	.064
10	0.40	.044	.059	.070	.091	.129	.148	.159	.173
20	0.40	.053	.079	.102	.127	.179	.198	.205	.227
30	0.40	.070	.094	.124	.159	.217	.229	.235	.259
10	4.00	.073	.088	.103	.119	.172	.199	.217	.230
20	4.00	.087	.104	.121	.140	.224	.241	.274	.307
30	4.00	.102	.127	.150	.184	.270	.299	.311	.329
			CHBr$_3$ (um/L)						
10	0000	.000	.000	.000	.000	.000	.000	.000	.000
20	0000	.000	.000	.000	.000	.000	.000	.000	.000
30	0000	.000	.000	.000	.000	.000	.000	.000	.000
10	0.04	.000	.000	.000	.000	.000	.000	.000	.000
20	0.04	.000	.000	.000	.000	.000	.000	.000	.000
30	0.04	.000	.000	.000	.000	.000	.000	.000	.000
10	0.40	.017	.026	.039	.050	.073	.086	.099	.110
20	0.40	.023	.035	.048	.068	.094	.108	.115	.126
30	0.40	.033	.045	.060	.087	.119	.133	.148	.154
10	4.00	.211	.252	.309	.377	.592	.654	.704	.763
20	4.00	.240	.308	.380	.449	.764	.879	.941	.989
30	4.00	.303	.360	.485	.578	.926	1.072	1.210	1.282

APPENDIX B

TTHM DATA

Table 33. TTHM Data for the Humic Acid Studies

		Reaction Time (hrs.)							
		1	2	4	8	24	48	72	96
		Effect of Bromide Level TTHM (um/L)							
Br^- (mg/L)									
0.00		0.066	0.091	0.117	0.131	0.170	0.203	0.249	0.258
.01		0.070	0.093	0.126	0.133	0.175	0.212	0.259	0.273
.02		0.073	0.095	0.130	0.143	0.190	0.215	0.267	0.291
.04		0.077	0.101	0.137	0.167	0.208	0.228	0.281	0.308
.10		0.081	0.121	0.144	0.191	0.218	0.262	0.340	0.371
.20		0.097	0.130	0.155	0.212	0.249	0.292	0.377	0.386
.40		0.106	0.154	0.192	0.227	0.261	0.329	0.390	0.444
1.00		0.117	0.170	0.238	0.304	0.364	0.414	0.453	0.513
2.00		0.136	0.217	0.274	0.313	0.436	0.478	0.513	0.547
4.00		0.149	0.224	0.293	0.333	0.459	0.516	0.568	0.587
		Effect of Chlorine Dose TTHM (um/L)							
Cl (mg/L)	Br^- (mg/L)								
2.5	0000	0.056	0.063	0.099	0.122	0.135	0.140	0.162	0.185
5.0	0000	0.066	0.091	0.117	0.137	0.170	0.203	0.249	0.258
10.0	0000	0.085	0.117	0.158	0.175	0.204	0.224	0.290	0.305
2.5	.033	0.052	0.062	0.098	0.121	0.134	0.175	0.230	0.262
5.0	.033	0.068	0.098	0.139	0.153	0.191	0.224	0.280	0.296
10.0	.033	0.074	0.109	0.161	0.180	0.234	0.249	0.288	0.304
2.5	.333	0.077	0.114	0.152	0.203	0.222	0.295	0.366	0.377
5.0	.333	0.101	0.133	0.169	0.217	0.256	0.306	0.382	0.404
10.0	.333	0.094	0.127	0.169	0.244	0.270	0.316	0.400	0.412
		Effect of Humic Acid Level TTHM (um/L)							
Humic Acid (mg/L)	Br^- (mg/L)								
0.50	0000	0.027	0.045	0.063	0.106	0.119	0.126	0.125	0.125
1.00	0000	0.066	0.091	0.117	0.191	0.207	0.223	0.249	0.258
2.00	0000	0.097	0.165	0.175	0.300	0.325	0.358	0.373	0.391
0.50	.033	0.031	0.053	0.076	0.116	0.127	0.144	0.162	0.181
1.00	.033	0.078	0.098	0.139	0.213	0.251	0.264	0.290	0.296
2.00	.033	0.103	0.180	0.215	0.346	0.376	0.386	0.410	0.412
0.50	.330	0.046	0.079	0.120	0.150	0.181	0.230	0.241	0.293
1.00	.330	0.105	0.140	0.198	0.272	0.326	0.352	0.390	0.411
2.00	.330	0.133	0.211	0.315	0.470	0.550	0.618	0.667	0.688

Table 33. (Continued)

Reaction Time (hrs.)

Effect of Ionic Strength

TTHM (μm/1)

Ionic Strength	Br^- (mgl/L)	1	2	4	8	24	48	72	96
.015	0000	0.071	0.095	0.119	0.130	0.164	0.210	0.241	0.265
.075	0000	0.175	0.092	0.118	0.135	0.160	0.208	0.257	0.263
.150	0000	0.069	0.094	0.118	0.136	0.169	0.213	0.260	0.259
.015	.033	0.078	0.098	0.139	0.155	0.189	0.221	0.285	0.295
.075	.033	0.078	0.101	0.139	0.158	0.194	0.222	0.270	0.292
.150	.033	0.080	0.104	0.150	0.163	0.194	0.218	0.272	0.288
.015	.333	0.101	0.141	0.175	0.215	0.285	0.326	0.379	0.404
.075	.333	0.106	0.142	0.169	0.213	0.289	0.337	0.373	0.402
.150	.333	0.114	0.138	0.172	0.216	0.280	0.328	0.371	0.401

Effect of pH

TTHM (μm/L)

pH	Br^- (mg/L)	1	2	4	8	24	48	72	96
6.0	0000	0.052	0.072	0.103	0.115	0.147	0.160	0.168	0.172
7.0	0000	0.066	0.091	0.117	0.131	0.170	0.203	0.249	0.258
8.0	0000	0.072	0.142	0.183	0.228	0.259	0.279	0.308	0.333
9.5	0000	0.086	0.191	0.217	0.263	0.353	0.400	0.432	0.454
6.0	.033	0.060	0.079	0.109	0.121	0.161	0.175	0.185	0.189
7.0	.033	0.069	0.098	0.139	0.153	0.191	0.224	0.280	0.296
8.0	.033	0.095	0.136	0.183	0.217	0.307	0.345	0.372	0.388
9.5	.333	0.123	0.165	0.207	0.286	0.386	0.473	0.528	0.562
6.0	.333	0.075	0.103	0.125	0.156	0.207	0.237	0.248	0.270
7.0	.333	0.105	0.140	0.168	0.217	0.252	0.302	0.380	0.404
8.0	.333	0.142	0.190	0.219	0.322	0.430	0.472	0.548	0.563
9.5	.333	0.194	0.265	0.346	0.446	0.582	0.637	0.710	0.748

Effect of Temperature

TTHM (μm/L)

Temp. (C^{o})	Br^- (mg/L)	1	2	4	8	24	48	72	96
10	0000	0.042	0.075	0.091	0.112	0.139	0.169	0.188	0.206
20	0000	0.066	0.091	0.117	0.131	0.176	0.203	0.249	0.258
30	0000	0.109	0.157	0.185	0.212	0.318	0.330	0.339	0.342
10	0.04	0.054	0.082	0.112	0.133	0.178	0.201	0.222	0.243
20	0.04	0.067	0.101	0.137	0.167	0.208	0.228	0.281	0.308
30	0.04	0.125	0.172	0.236	0.292	0.427	0.451	0.465	0.475
10	0.40	0.088	0.128	0.151	0.182	0.211	0.252	0.285	0.306
20	0.40	0.106	0.154	0.192	0.227	0.261	0.329	0.390	0.444
30	0.40	0.175	0.233	0.303	0.394	0.554	0.633	0.663	0.688
10	4.00	0.128	0.194	0.220	0.245	0.289	0.313	0.333	0.359
20	4.00	0.149	0.224	0.293	0.333	0.379	0.472	0.520	0.587
30	4.00	0.201	0.271	0.369	0.391	0.599	0.661	0.678	0.699

Table 34. TTHM Data for the Tennessee River Studies

Reaction Time (hrs.)

Effect of Bromide Level TTHM (µm/L)

Br^- (mg/L)	1	2	4	8	24	48	72	96
0000	0.208	0.275	0.307	0.365	0.570	0.634	0.683	0.729
0.01	0.211	0.279	0.312	0.378	0.577	0.649	0.696	0.744
0.02	0.221	0.287	0.322	0.394	0.606	0.670	0.713	0.744
0.04	0.226	0.297	0.327	0.421	0.629	0.730	0.783	0.835
0.10	0.236	0.306	0.345	0.445	0.713	0.763	0.801	0.837
0.20	0.246	0.340	0.396	0.498	0.729	0.804	0.868	0.912
0.40	0.276	0.363	0.430	0.537	0.788	0.889	0.975	1.045
1.00	0.322	0.414	0.490	0.625	0.895	1.028	1.129	1.223
2.00	0.344	0.431	0.534	0.667	1.035	1.178	1.301	1.366
4.00	0.365	0.459	0.563	0.672	1.121	1.264	1.367	1.454

Effect of Temperature TTHM (µm/L)

Temp (°C)	Br^- (mg/L)	1	2	4	8	24	48	72	96
10	0000	0.145	0.217	0.255	0.307	0.351	0.415	0.465	0.529
20	0000	0.208	0.275	0.307	0.365	0.570	0.634	0.683	0.729
30	0000	0.269	0.415	0.479	0.669	0.870	0.949	0.985	1.011
10	0.04	0.161	0.195	0.263	0.344	0.453	0.514	0.564	0.612
20	0.04	0.226	0.297	0.331	0.421	0.629	0.696	0.753	0.803
30	0.40	0.348	0.447	0.580	0.686	0.978	1.057	1.086	1.118
10	0.40	0.187	0.236	0.298	0.376	0.536	0.616	0.679	0.739
20	0.40	0.247	0.343	0.421	0.516	0.730	0.828	0.893	0.961
30	0.40	0.345	0.452	0.591	0.765	0.998	1.120	1.191	1.254
10	4.00	0.327	0.399	0.485	0.591	0.884	0.995	1.077	1.168
20	4.00	0.382	0.484	0.588	0.708	1.142	1.299	1.413	1.507
30	4.00	0.479	0.576	0.743	0.907	1.378	1.579	1.753	1.859

APPENDIX C

THM DISTRIBUTION DATA

Table 35. THM Distribution Data for the Effect of Bromide Level from Humic Acid

	Reaction Time (hrs.)							
Br^- (mg/L)	1	2	4	8	24	48	72	96
			$CHCl_3$ (% of TTHM)					
0.00	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
.01	92.9	93.5	90.5	90.2	90.9	90.6	91.5	91.9
.02	86.3	84.2	84.6	83.2	82.6	81.4	81.3	81.4
.04	72.7	64.4	68.6	67.7	67.3	64.5	65.5	64.6
.10	56.8	47.1	45.1	42.9	44.0	39.3	43.5	46.1
.20	28.9	26.2	23.2	24.1	25.3	24.7	20.7	20.2
.40	17.0	14.9	15.1	13.2	11.5	10.0	9.2	8.8
1.00	12.8	12.4	10.1	8.9	7.7	6.8	6.2	6.2
2.00	8.8	8.3	7.7	7.7	5.7	5.2	4.9	4.8
4.00	2.7	2.2	2.2	2.4	2.2	2.3	2.1	2.2
			$CHCl_2Br$ (% of TTHM)					
0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.01	7.1	6.5	8.7	8.3	8.0	8.0	7.3	7.0
.02	11.0	13.7	13.1	14.0	15.3	16.7	17.2	16.8
.04	23.4	27.7	24.1	26.3	27.4	30.3	29.5	29.2
.10	24.7	29.8	29.2	33.5	32.6	37.0	35.6	34.2
.20	24.7	26.9	27.1	34.9	30.5	31.8	36.3	35.2
.40	18.9	18.2	19.8	22.5	25.3	27.1	27.7	25.5
1.00	8.5	6.5	9.7	9.9	8.0	12.3	12.1	13.3
2.00	4.4	4.1	4.0	4.5	4.1	4.4	5.3	4.4
4.00	2.7	2.2	1.7	2.1	1.7	1.9	2.3	2.4
			$CHClBr_2$ (% of TTHM)					
0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.01	0.0	0.0	0.8	1.5	1.1	1.4	1.2	1.1
.02	2.7	2.1	2.3	2.8	2.1	1.9	1.5	1.7
.04	3.9	7.9	7.3	6.0	5.3	5.3	5.0	6.2
.10	18.5	23.1	25.7	23.6	23.4	23.7	20.9	19.7
.20	36.1	37.7	41.3	33.5	36.9	36.3	36.3	38.1
.40	42.5	44.8	44.8	45.8	45.6	43.5	44.9	44.8
1.00	36.8	42.9	41.2	38.5	36.8	35.5	38.2	40.0
2.00	27.9	27.2	25.2	24.3	22.2	22.4	21.4	21.6
4.00	14.8	16.5	13.3	12.3	11.8	12.2	11.3	11.8
			$CHBr_3$ (% of TTHM)					
0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.02	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.04	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.20	10.3	9.2	8.4	7.5	7.2	7.2	6.6	6.5
.40	21.7	22.1	20.3	18.5	17.6	19.5	18.2	20.9
1.00	41.9	38.2	39.1	42.8	47.5	45.4	43.5	40.5
2.00	58.8	60.4	63.1	63.6	67.9	68.0	68.4	69.3
4.00	79.9	79.0	82.9	83.2	84.3	83.5	84.3	83.6

Table 36. THM Distribution Data for the Effect of Chlorine Dose

		Reaction Time (hrs.)							
Cl (mg/L)	Br^- (mg/L)	1	2	4	8	24	48	72	96
		$CHCl_3$ (% of TTHM)							
2.5	0000	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
5.0	0000	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
10.0	0000	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
2.5	.033	76.9	71.0	66.3	70.2	64.2	63.4	66.1	67.6
5.0	.033	77.0	76.1	73.9	75.0	77.4	76.3	71.5	73.4
10.0	.033	20.8	15.8	14.5	11.3	10.8	8.5	7.1	7.2
2.5	.333	14.9	15.8	20.1	17.1	17.2	15.7	13.4	12.9
10.0	.333	25.5	28.3	27.9	29.9	28.1	33.2	35.7	36.2
		$CHCl_2Br$ (% of TTHM)							
2.5	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5.0	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10.0	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.5	.033	19.2	22.6	27.6	24.8	29.9	29.7	27.8	27.1
5.0	.033	20.6	24.5	18.7	19.6	17.8	21.4	25.7	25.7
10.0	.033	20.3	20.2	21.7	21.1	19.2	20.1	24.7	23.0
2.5	.333	14.3	15.8	16.4	18.7	18.0	21.7	22.1	22.0
5.0	.333	24.8	26.3	24.9	30.0	26.6	30.4	36.6	35.4
10.0	.333	25.5	28.3	27.8	29.9	28.1	33.2	35.7	36.2
		$CHClBr_2$ (% of TTHM)							
2.5	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5.0	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10.0	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.5	.033	3.8	6.5	6.1	5.0	6.0	6.9	6.1	5.3
5.0	.033	4.4	5.1	4.3	4.6	4.2	4.0	3.2	3.0
10.0	.033	2.7	3.7	4.3	3.9	3.4	3.6	3.8	3.6
2.5	.333	46.8	46.5	48.7	50.2	48.6	48.5	47.3	46.2
5.0	.333	45.5	44.4	42.6	41.0	44.5	42.5	40.3	41.8
10.0	.333	41.5	41.7	40.2	41.0	41.1	39.1	40.3	40.0
		$CHBr_3$ (% of TTHM)							
2.5	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5.0	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10.0	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.5	.033	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5.0	.033	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10.0	.033	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.5	.333	18.2	21.9	20.4	19.7	22.5	11.4	23.5	24.7
5.0	.333	14.9	13.5	12.4	12.0	11.7	11.4	9.7	9.9
10.0	.333	8.5	7.9	8.9	9.4	9.6	8.5	8.3	8.0

Table 37. THM Distribution Data for the Effect of Humic Acid Level

Humic Acid (mg.L)	Br^- (mg/L)	Reaction Time (hrs.) 1	2	4	8	24	48	72	96
		$CHCl_3$ (% of TTHM)							
0.50	0000	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
1.00	0000	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
2.00	0000	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
0.50	.033	77.4	77.4	75.0	82.8	78.7	72.2	67.9	63.5
1.00	.033	78.2	70.4	77.0	82.6	79.3	78.4	72.1	71.3
2.00	.033	77.2	73.3	77.7	82.1	81.6	80.1	75.4	75.2
0.50	.330	30.4	24.3	20.0	18.7	17.1	14.3	14.1	12.3
1.00	.330	18.1	20.0	21.7	19.1	16.6	15.3	15.1	14.4
2.00	.330	13.5	12.8	25.7	20.0	17.5	15.5	14.7	15.0
		$CHCl_2Br$ (% of TTHM)							
0.50	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1.00	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.00	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.50	.033	16.1	17.0	19.7	12.9	17.3	22.9	27.8	32.6
1.00	.033	17.9	24.5	18.7	14.1	17.5	18.2	24.8	25.7
2.00	.033	18.4	21.7	18.1	15.3	15.4	16.8	21.2	21.1
0.50	.330	26.1	32.9	40.8	46.0	39.8	38.3	36.9	30.4
1.00	.330	23.8	25.0	31.3	38.6	39.3	37.8	35.9	34.8
2.00	.330	28.6	27.5	32.4	40.6	36.9	33.2	31.6	31.4
		$CHClBr_2$ (% of TTHM)							
0.50	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1.00	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.00	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.50	.330	6.5	5.7	5.3	4.3	3.9	4.9	4.3	3.9
1.00	.330	3.8	5.1	4.3	3.3	3.2	3.4	3.1	3.0
2.00	.330	3.9	5.0	4.2	2.6	2.9	3.1	3.4	3.6
0.50	.330	32.6	29.1	29.2	26.7	32.6	37.4	38.6	48.1
1.00	.330	43.8	42.1	36.4	32.7	35.0	36.9	39.5	41.1
2.00	.330	43.6	47.9	32.7	31.9	35.8	41.6	43.8	43.7
		$CHBr_3$ (% if TTHM)							
0.50	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1.00	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.00	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.50	.033	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1.00	.033	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.00	.033	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.50	.330	10.9	12.7	10.0	8.7	10.5	10.0	10.4	9.2
1.00	.330	14.3	12.9	10.6	9.6	9.2	9.9	9.5	9.7
2.00	.330	14.3	11.8	9.2	7.4	9.8	9.7	9.9	9.9

Table 38. THM Distribution Data for the Effect of pH

pH	Br⁻ (mg/L)	Reaction Time (hrs.) 1	2	4	8	24	48	72	96
		$CHCl_3$ (% of TTHM)							
6.0	0000	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
7.0	0000	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
8.0	0000	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
9.5	0000	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
6.0	.033	75.0	70.9	72.5	71.1	67.7	68.0	69.2	69.3
7.0	.033	73.9	70.4	77.0	75.8	78.0	74.6	71.1	71.3
8.0	.033	64.2	66.9	68.3	68.2	74.6	73.3	72.3	71.9
9.5	.033	69.1	69.1	67.6	68.9	70.1	71.7	73.5	72.6
6.0	.333	18.7	16.5	20.0	19.9	18.8	19.4	19.4	18.5
7.0	.333	18.1	20.0	19.6	17.1	15.9	14.6	12.9	12.9
8.0	.333	14.1	12.1	20.1	16.1	15.1	14.0	12.2	11.9
9.5	.333	14.9	13.6	16.2	14.3	13.6	13.3	12.5	12.3
		$CHCl_2Br$ (% of TTHM)							
6.0	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
7.0	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8.0	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
9.5	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6.0	.033	5.0	5.1	4.3	4.6	4.2	4.0	3.2	3.0
7.0	.033	5.8	5.1	4.6	5.0	4.3	4.6	4.3	4.2
8.0	.033	5.3	7.4	7.1	6.5	4.9	5.2	5.4	5.7
9.5	.033	6.5	7.3	9.2	8.4	8.8	7.6	7.0	6.6
6.0	.333	42.7	50.5	48.8	47.4	45.4	48.9	49.2	47.4
7.0	.333	43.8	42.1	42.9	41.0	45.2	43.0	40.5	41.8
8.0	.333	38.0	38.9	35.2	38.2	40.5	38.8	37.6	38.0
9.5	.333	35.1	35.8	37.9	38.6	36.6	36.4	35.9	35.6
		$CHClBr_2$ (% of TTHM)							
6.0	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
7.0	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8.0	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
9.5	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6.0	.033	20.0	24.1	22.9	24.0	28.0	27.4	26.5	26.5
7.0	.033	20.3	24.5	18.7	19.6	17.8	21.4	25.7	25.7
8.0	.033	30.5	25.7	24.6	25.3	20.5	21.4	22.3	22.4
9.5	.033	24.4	23.6	23.2	22.7	21.0	20.7	19.5	20.8
6.0	.333	20.0	17.5	15.2	16.7	22.2	19.0	18.5	21.9
7.0	.333	23.8	25.0	25.0	30.0	27.0	30.8	36.8	35.4
8.0	.333	19.7	23.2	20.5	19.9	16.7	19.9	26.3	26.3
9.5	.333	20.6	20.0	19.4	20.9	18.7	19.3	21.0	21.1
		$CHBr_3$ (% of TTHM)							
6.0	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
7.0	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8.0	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
9.5	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6.0	.033	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
7.0	.033	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8.0	.033	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
9.5	.033	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6.0	.333	18.7	15.5	16.0	16.0	13.5	12.7	12.9	12.2
7.0	.333	14.3	12.9	12.5	12.0	11.9	11.6	9.7	9.9
8.0	.333	28.2	25.8	24.2	25.8	27.7	27.3	23.9	23.8
9.5	.333	29.4	30.6	26.6	26.2	31.1	30.9	30.6	31.0

Table 39. THM Distribution Data for the Effect of Ionic Strength

		Reaction Time (hrs.)							
Ionic Strength	Br^- (mg/L)	1	2	4	8	24	48	72	96
			$CHCl_3$ (% of TTHM)						
.015	0000	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
.075	0000	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
.150	0000	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
.015	.033	76.9	69.4	77.0	74.8	77.8	73.8	73.0	72.9
.075	.033	78.2	72.3	78.0	75.3	79.4	76.1	71.1	71.9
.150	.033	78.8	72.1	78.0	75.5	78.4	75.7	71.3	72.6
.015	.333	20.8	20.6	20.0	17.7	16.1	15.0	13.5	12.9
.075	.333	22.6	19.0	21.3	18.3	16.3	14.5	13.4	12.7
.150	.333	14.9	21.0	20.9	19.4	16.4	14.0	12.7	12.7
			$CHCl_2Br$ (% of TTHM)						
.015	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.075	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.150	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.015	.033	19.2	25.5	18.7	20.6	18.0	22.6	23.9	24.1
.075	.033	17.9	22.8	18.7	19.6	16.5	20.3	25.6	25.0
.150	.033	17.5	23.1	18.0	20.2	17.5	20.2	25.4	24.3
.015	.333	21.8	24.1	22.3	27.4	33.0	36.5	34.0	34.9
.075	.333	23.6	25.4	24.9	28.2	33.9	36.2	35.9	34.3
.150	.333	25.4	25.4	25.0	29.2	32.5	35.4	35.0	35.9
			$CHClBr_2$ (% of TTHM)						
.015	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.075	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.150	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.015	.033	3.8	5.1	4.3	4.5	4.2	3.6	3.2	3.1
.075	.033	3.8	5.0	4.3	5.1	4.1	3.6	3.3	3.1
.150	.033	3.8	4.8	4.0	4.3	4.1	4.1	3.3	3.1
.015	.333	43.6	42.6	44.6	42.8	40.7	38.3	42.7	41.8
.075	.333	40.6	43.0	42.0	41.8	39.4	38.9	40.2	42.8
.150	.333	45.6	40.6	41.9	38.9	40.4	39.6	41.8	41.1
			$CHBr_3$ (% of TTHM)						
.015	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.075	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.150	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.015	.033	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.075	.033	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.150	.033	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
.015	.333	13.9	12.8	13.1	12.1	10.2	10.1	9.8	10.4
.075	.333	13.2	12.7	11.8	11.7	10.4	10.4	10.5	10.2
.150	.333	14.0	13.0	12.2	12.5	10.7	11.0	10.5	10.2

Table 40. THM Distribution Data for the Effect of Temperature from Humic Acid

		Reaction Time (hrs.)							
Temp (°C)	Br⁻ (mg/L)	1	2	4	8	24	48	72	96
		$CHCl_3$ (% of TTHM)							
10	0000	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
20	0000	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
30	0000	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
10	0.04	72.2	67.1	70.5	69.2	66.9	64.7	63.1	62.6
20	0.04	68.7	64.4	68.6	67.7	67.3	64.5	65.6	65.5
30	0.04	72.8	68.0	71.2	68.2	69.1	68.5	68.8	68.8
10	0.40	14.8	13.3	12.6	11.5	11.4	11.1	10.2	9.8
20	0.40	17.0	14.9	15.1	13.2	11.5	10.0	9.2	8.8
30	0.40	17.7	16.7	15.8	15.7	12.1	10.9	10.7	10.3
10	4.00	2.3	2.1	2.3	2.4	2.8	2.9	3.0	3.1
20	4.00	2.7	2.2	2.0	2.4	2.6	2.5	2.3	2.2
30	4.00	3.5	3.3	2.7	3.1	2.2	2.1	2.2	2.1
		$CHCl_2Br$ (% of TTHM)							
10	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
20	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
30	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10	0.04	22.2	26.8	24.1	24.8	27.5	29.9	31.5	32.1
20	0.04	26.9	27.7	24.1	26.3	27.4	30.3	29.5	29.2
30	0.04	23.2	26.2	22.9	26.0	25.5	25.7	25.4	25.5
10	0.40	19.3	18.8	21.2	21.4	24.2	23.8	25.6	26.8
20	0.40	18.9	18.2	19.8	22.5	25.3	27.1	27.7	25.5
30	0.40	22.3	21.9	23.4	27.9	28.3	28.4	28.8	29.1
10	4.00	2.3	2.1	2.3	2.4	2.4	2.6	2.7	2.8
20	4.00	2.7	2.2	2.0	2.1	2.1	2.1	2.5	2.4
30	4.00	4.0	4.1	3.3	3.6	2.7	2.6	2.5	2.6
		$CHClBr_2$ (% of TTHM)							
10	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
20	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
30	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10	0.04	5.6	6.1	5.4	6.0	5.6	5.5	5.4	5.3
20	0.04	4.5	7.9	7.3	6.0	5.3	5.3	5.0	6.2
30	0.04	4.0	5.8	5.9	5.8	5.4	5.8	5.8	5.7
10	0.40	43.2	46.1	44.4	46.7	45.0	44.0	43.2	42.5
20	0.40	42.5	44.8	44.8	45.8	45.6	43.5	44.9	44.8
30	0.40	44.0	42.9	40.9	37.1	43.0	43.8	43.9	43.6
10	4.00	14.1	13.9	13.6	13.9	14.5	15.3	15.6	16.4
20	4.00	14.8	16.5	13.3	12.3	14.2	13.3	12.3	11.8
30	4.00	16.9	15.5	12.7	13.8	12.9	12.6	12.7	12.9
		$CHBr_3$ (% of TTHM)							
10	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
20	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
30	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10	0.04	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
20	0.04	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
30	0.04	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10	0.40	22.7	21.9	21.9	20.3	19.4	21.0	21.1	20.9
20	0.40	21.7	22.1	20.3	18.5	17.6	19.5	18.2	20.9
30	0.40	16.0	18.5	19.8	19.3	16.6	16.9	16.6	17.0
10	4.00	81.3	82.0	81.8	81.2	80.3	79.2	78.7	77.7
20	4.00	79.9	79.0	82.6	83.2	81.0	82.0	82.9	83.6
30	4.00	75.6	77.1	31.3	79.5	82.3	82.8	82.6	82.4

Table 41. THM Distribution Data for the Effect of Bromide Level from Tennessee River Water

	Reaction Time (hrs.)							
Br^- (mg/L)	1	2	4	8	24	48	72	96
			$CHCl_3$ (% of TTHM)					
0000	94.7	93.8	92.2	92.8	92.7	92.8	92.8	92.7
0.01	91.0	89.6	88.5	86.0	87.3	87.7	87.6	88.0
0.02	83.3	83.3	80.4	78.7	80.9	82.2	81.9	81.4
0.04	75.7	75.4	71.9	68.2	73.1	75.5	74.6	75.4
0.10	62.7	61.8	57.4	55.5	63.0	62.8	61.4	60.9
0.20	42.7	43.2	41.2	40.0	38.7	39.4	39.5	39.5
0.40	25.4	28.9	29.5	25.0	23.7	23.8	24.3	24.3
1.00	10.6	11.1	12.0	12.1	11.7	11.9	12.4	12.8
2.00	7.3	7.7	7.5	7.8	6.3	6.6	6.7	7.0
4.00	4.4	4.4	5.3	5.8	5.4	5.1	5.0	5.0
			$CHCl_2Br$ (% of TTHM)					
0000	3.8	4.4	5.5	5.5	5.4	5.5	5.6	5.8
0.01	7.1	8.2	9.0	11.4	10.2	9.9	9.9	9.7
0.02	12.2	11.8	14.3	16.5	14.4	13.0	13.3	14.0
0.04	17.3	16.5	19.6	23.0	19.1	17.1	18.0	17.0
0.10	24.6	24.2	25.2	28.1	25.4	25.2	26.0	25.9
0.20	32.5	29.1	27.8	29.7	31.8	31.1	32.1	31.1
0.40	36.6	34.2	33.5	34.8	34.3	34.9	34.5	33.9
1.00	21.4	20.0	20.2	20.3	19.0	18.7	19.2	19.9
2.00	8.7	9.0	8.8	10.0	8.6	8.5	8.5	8.4
4.00	6.0	5.9	5.7	6.5	6.5	6.3	6.1	5.9
			$CHClBr_2$ (% of TTHM)					
0000	1.4	1.8	2.3	2.2	1.8	1.7	1.6	1.5
0.01	1.9	212	2.6	2.6	2.4	2.5	2.4	2.3
0.02	4.5	4.9	5.3	4.8	4.8	4.8	4.7	4.7
0.04	7.1	8.1	8.6	8.8	7.8	7.4	7.4	7.5
0.10	12.3	13.1	15.9	15.3	10.9	11.4	12.0	12.5
0.20	21.5	23.2	25.8	25.5	24.6	24.6	23.6	24.9
0.40	29.7	27.3	25.8	27.6	30.1	29.1	29.4	29.8
1.00	39.4	37.7	35.7	35.4	35.8	35.2	34.9	34.6
2.00	27.3	28.1	28.1	27.7	24.2	25.5	27.4	28.1
4.00	23.8	22.7	21.5	20.8	20.0	19.1	20.0	21.1
			$CHBr_3$ (% of TTHM)					
0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.02	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.04	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.10	0.4	1.0	1.4	1.1	0.7	0.7	0.6	0.6
0.20	3.3	4.4	5.3	4.8	4.9	4.9	4.7	4.5
0.40	8.3	9.6	11.2	12.7	11.9	12.1	11.8	12.1
1.00	28.6	31.2	32.0	31.2	33.5	34.2	33.5	32.7
2.00	56.7	55.2	55.6	54.4	61.0	59.3	57.4	56.4
4.00	65.8	67.1	67.5	66.8	68.2	69.5	68.8	68.0

Table 42. THM Distribution Data for the Effect of Temperature from Tennessee River Water

		Reaction Time (hrs.)							
Temp (C°)	Br^- (mg/L)	1	2	4	B	24	48	72	96
			$CHCl_3$	(% of TTHM)					
10	0000	93.1	94.0	93.3	92.5	90.9	90.6	90.5	90.7
20	0000	94.7	93.8	92.2	92.3	92.8	92.7	92.8	92.7
30	0000	94.4	94.7	94.2	94.2	94.3	94.2	94.1	94.1
10	0.04	73.3	70.8	70.0	67.2	70.6	70.4	70.7	70.9
20	0.04	75.7	75.4	71.0	68.2	73.1	74.3	73.6	74.5
30	0.04	80.5	81.0	78.3	76.4	78.9	79.2	79.2	79.5
10	0.40	30.5	28.8	27.5	27.9	27.6	27.1	26.5	26.5
20	0.40	28.3	30.6	30.2	26.0	25.6	25.6	26.5	26.4
30	0.40	30.1	30.8	32.1	31.0	32.1	33.8	34.5	34.5
10	4.00	5.2	6.3	6.2	6.6	5.7	6.3	6.6	7.0
20	4.00	6.5	6.8	6.8	7.3	5.7	6.1	6.2	6.4
30	4.00	8.8	7.6	6.6	7.2	5.7	5.6	5.7	5.9
			$CHCl_2Br$	(% of TTHM)					
10	0000	5.5	4.6	4.7	5.5	6.8	7.2	7.5	7.4
20	0000	3.8	4.4	5.5	5.5	5.4	5.5	5.6	5.8
30	0000	4.5	3.9	4.2	4.3	4.4	4.5	4.7	4.7
10	0.04	19.3	20.5	19.8	23.0	20.5	20.6	20.0	19.8
20	0.04	17.3	16.5	19.3	23.0	19.1	18.0	18.7	17.7
30	0.04	13.5	12.5	13.4	16.0	14.9	14.9	14.9	14.8
10	0.40	36.9	35.2	35.9	34.6	34.7	34.9	35.5	35.2
20	0.40	40.9	36.2	34.2	36.2	37.0	37.4	37.6	36.8
30	0.40	40.0	38.5	36.7	36.9	34.3	33.8	33.3	32.5
10	4.00	8.0	8.5	8.9	9.5	7.9	7.9	7.9	8.0
20	4.00	7.9	8.1	8.0	9.5	7.8	7.7	7.9	7.6
30	4.00	6.7	7.8	7.9	8.8	7.5	7.5	7.5	7.5
			$CHClBr_2$	(% of TTHM)					
10	0000	1.4	1.4	2.0	2.0	2.3	2.2	1.9	1.9
20	0000	1.4	1.8	2.3	2.2	1.8	1.7	1.6	1.5
30	0000	1.1	1.4	1.7	1.5	1.4	1.3	1.2	1.2
10	0.04	7.5	8.7	10.3	9.9	8.8	8.9	9.2	9.3
20	0.04	7.1	8.1	9.7	8.8	7.8	7.8	7.7	7.8
30	0.04	6.0	6.5	8.3	7.6	6.1	6.0	5.9	5.7
10	0.40	23.5	25.0	23.5	24.2	24.1	24.0	23.4	23.4
20	0.40	21.5	23.0	24.2	24.6	24.5	23.9	23.0	23.6
30	0.40	20.3	20.8	21.0	20.8	21.7	20.4	19.7	20.7
10	4.00	22.3	22.1	21.2	20.1	19.5	20.0	20.1	19.7
20	4.00	22.8	21.5	20.6	19.8	19.6	18.6	19.4	20.4
30	4.00	21.3	22.0	20.2	20.3	19.6	18.9	17.7	17.7
			$CHBr_3$	(% of TTHM)					
10	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
20	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
30	0000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10	0.04	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
20	0.04	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
30	0.04	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10	0.40	9.1	11.0	13.1	13.3	13.6	14.0	14.6	14.9
20	0.40	9.3	10.2	11.4	13.2	12.9	13.0	12.9	13.1
30	0.40	9.6	10.0	10.2	11.4	11.9	11.9	12.4	12.3
10	4.00	64.5	63.2	63.7	63.8	67.0	65.7	65.4	65.3
20	4.00	62.8	63.6	64.6	63.4	66.9	67.7	66.6	65.6
30	4.00	63.3	62.5	65.3	63.7	67.2	67.9	69.0	69.0

APPENDIX D

TTHM FORMATION CURVES

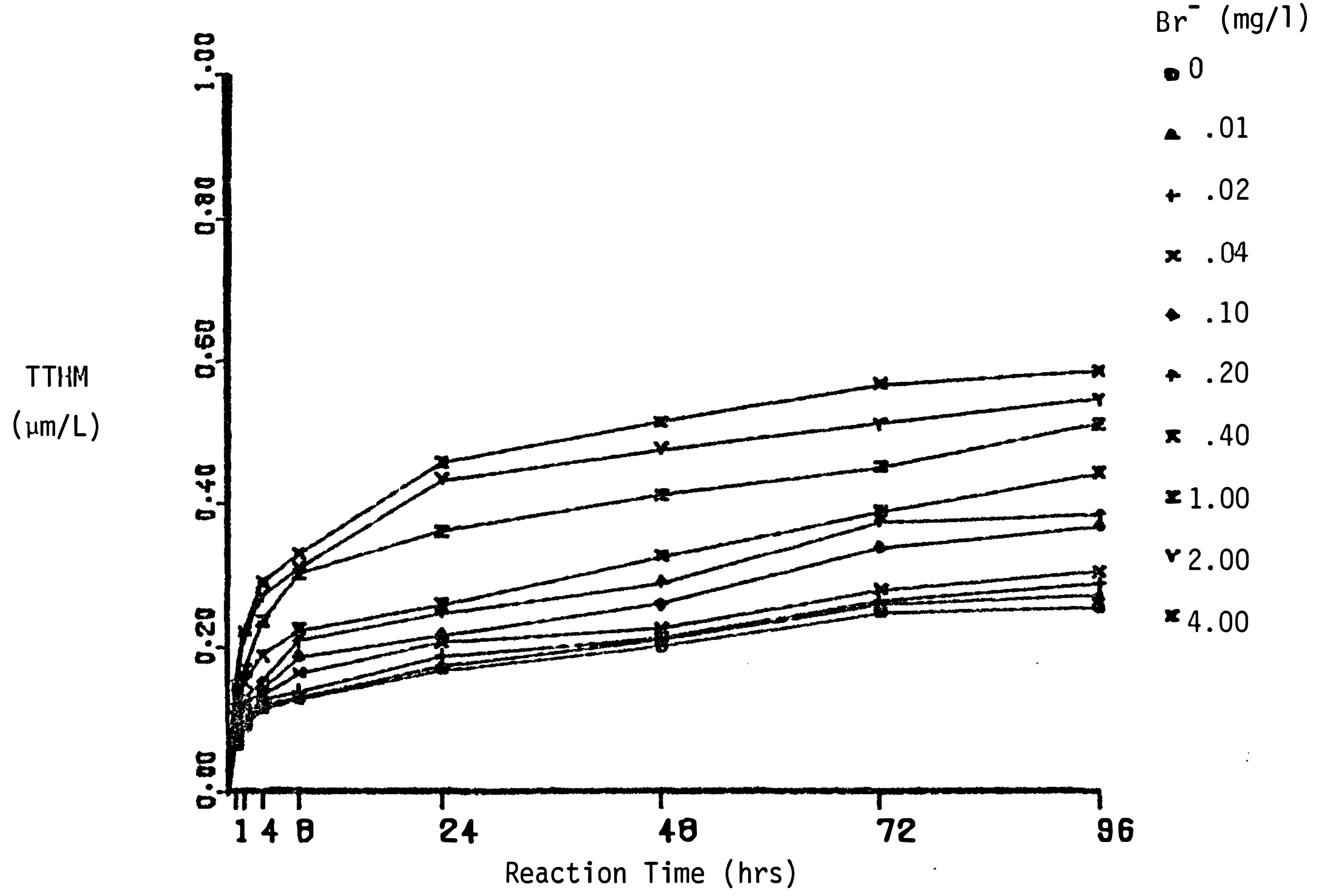

Figure 27. The Effect of Bromide on TTHM Formation from Humic Acid.

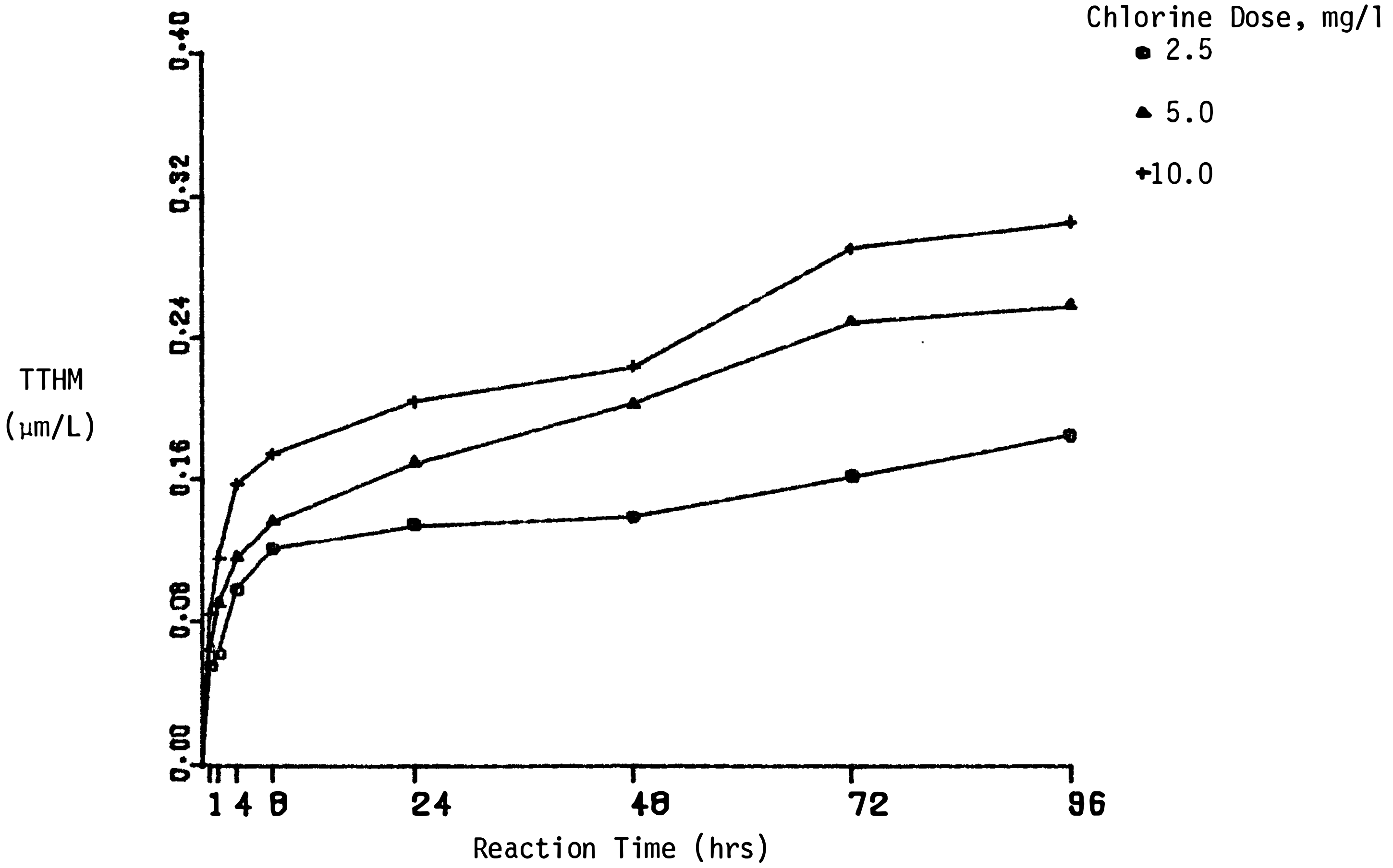

Figure 28. Effect of Chlorine on TTHM Formation at 0 mg/L Bromide.

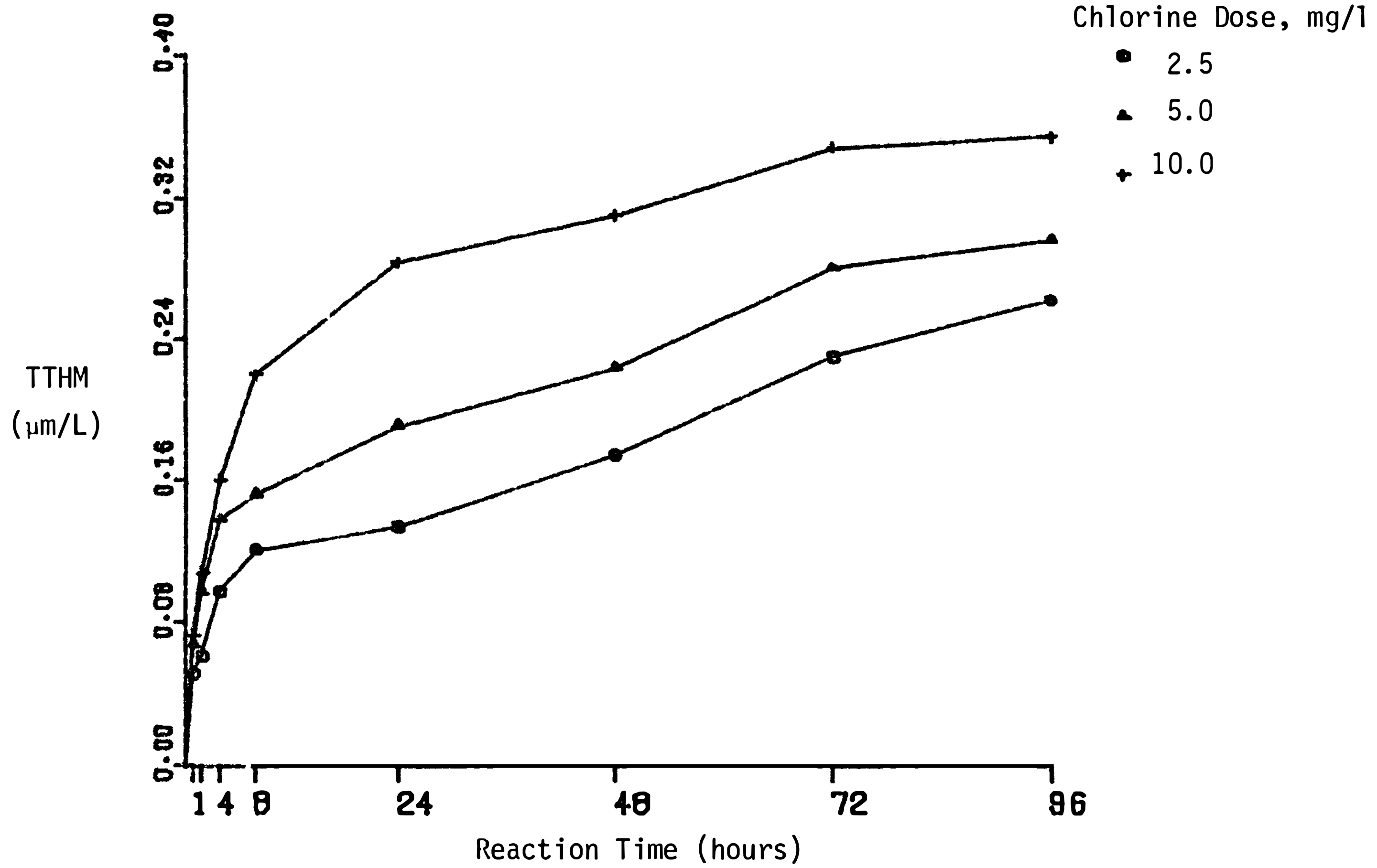

Figure 29. Effect of Chlorine Dose on TTHM Formation at .033 mg/L Bromide.

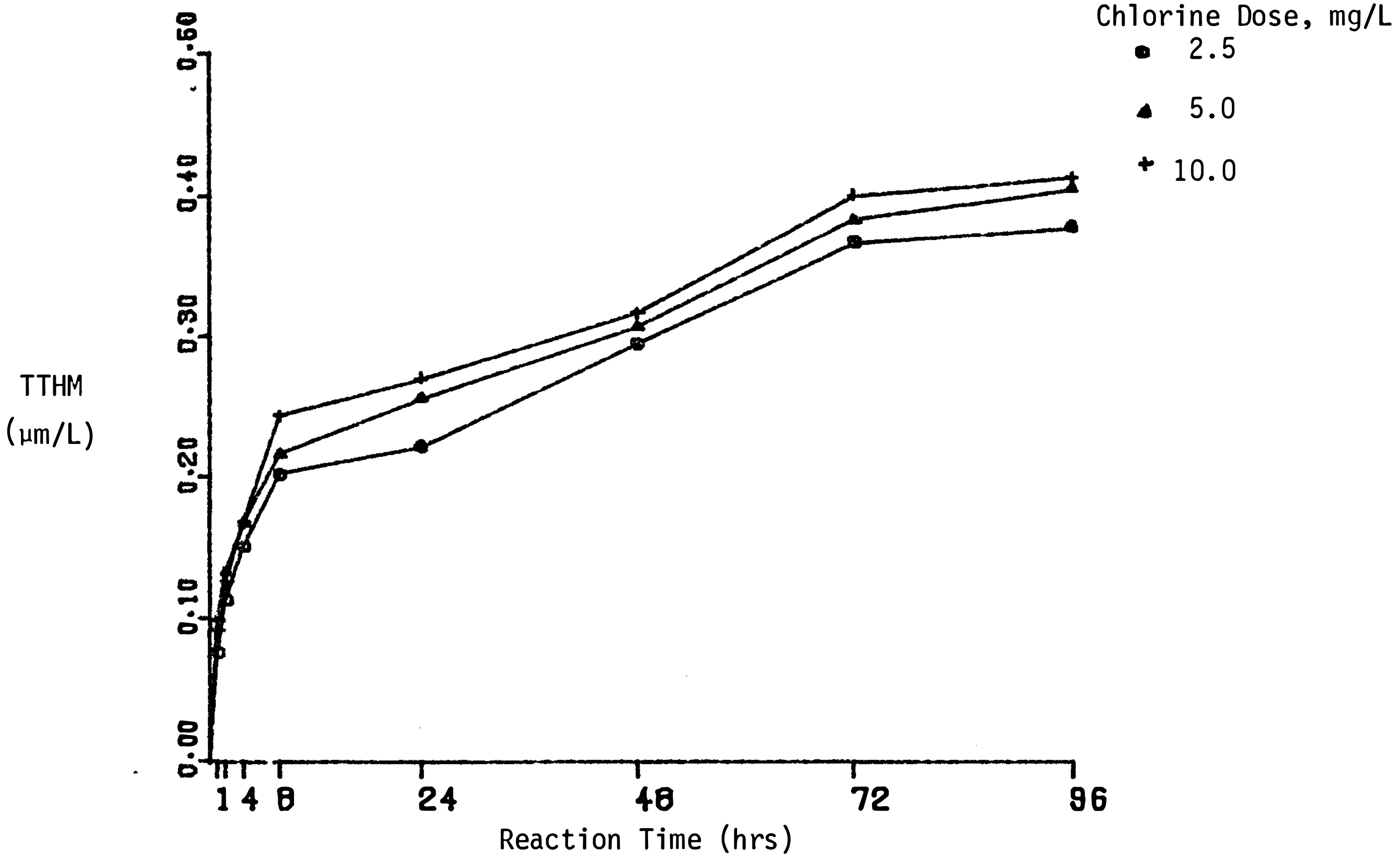

Figure 30. Effect of Chlorine Dose on TTHM Formation at .333 mg/L Bromide.

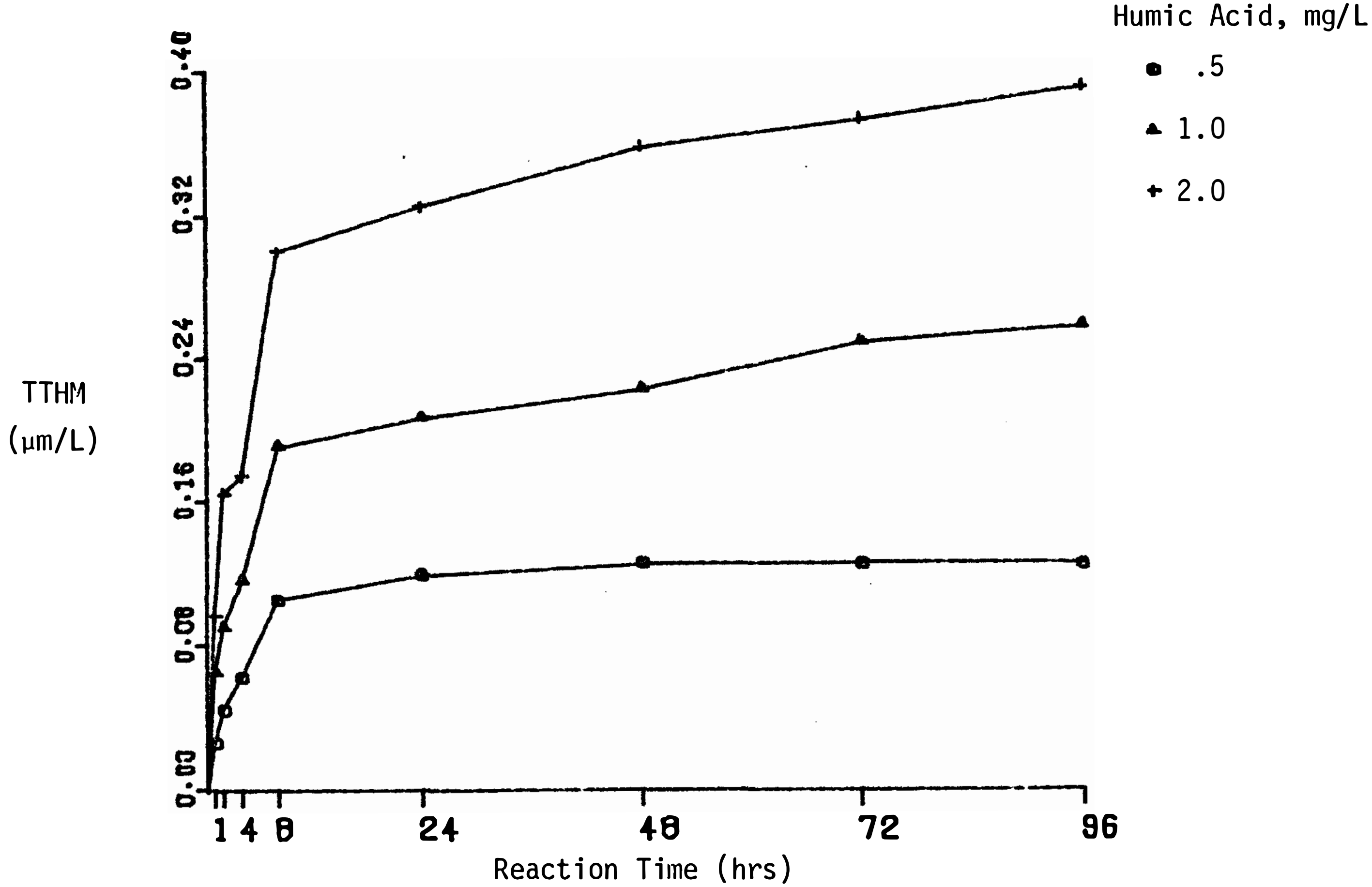

Figure 31. Effect of Humic Acid on TTHM Formation at 0 mg/L Bromide.

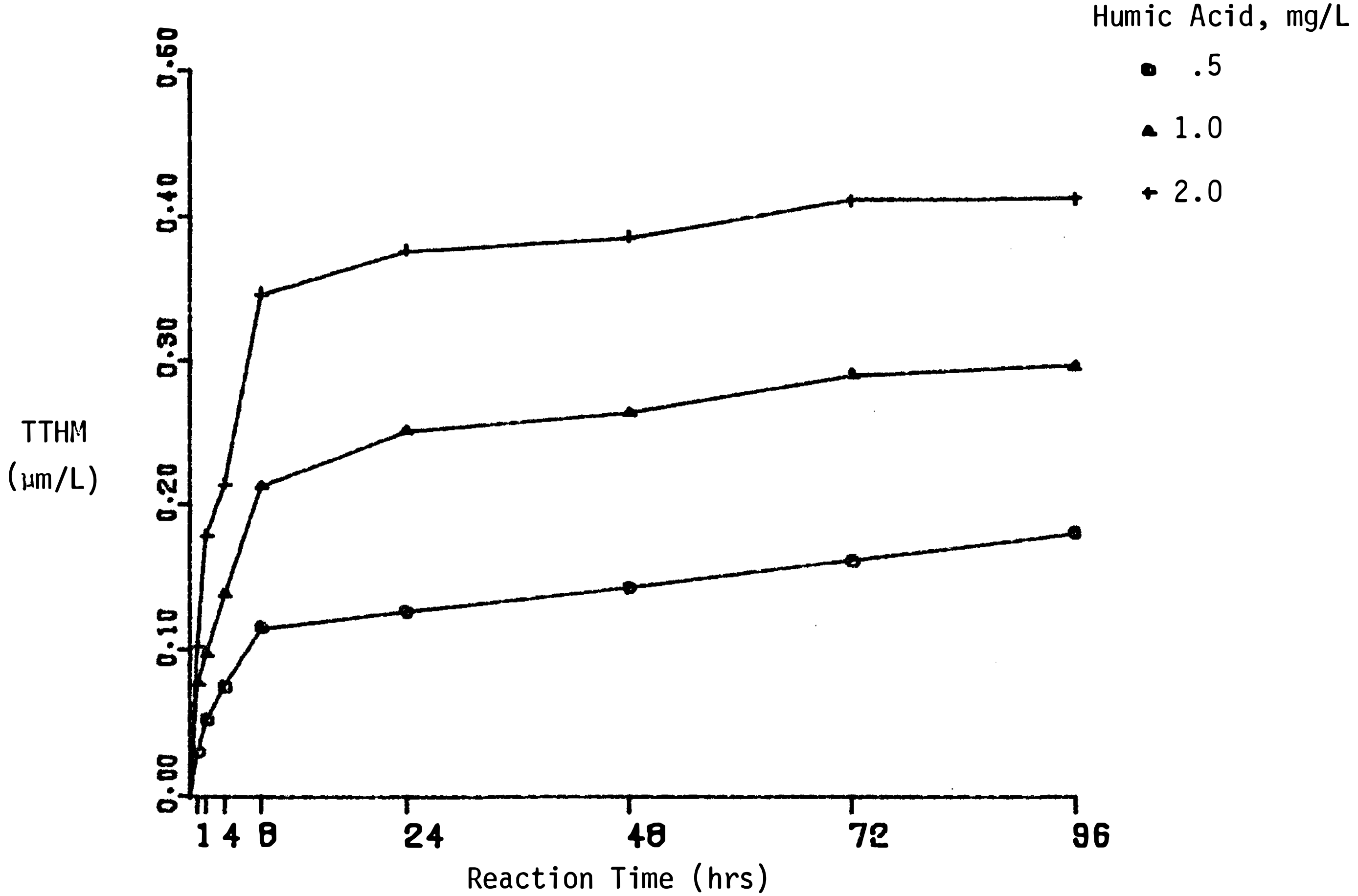

Figure 32. Effect of Humic Acid Level on TTHM Formation at .033 mg/L Bromide.

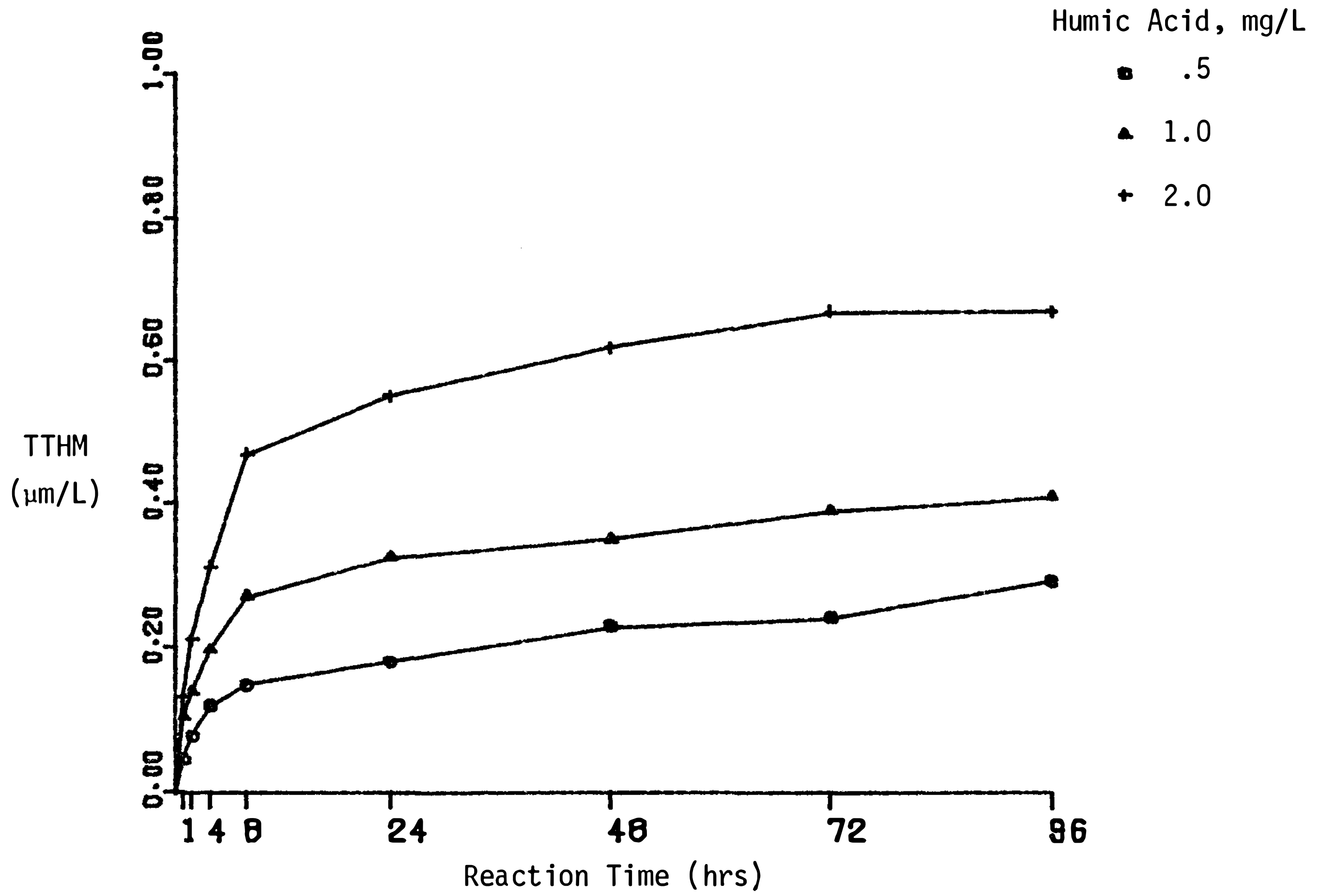

Figure 33. Effect of Humic Acid Level on TTHM Formation at .333 mg/L Bromide.

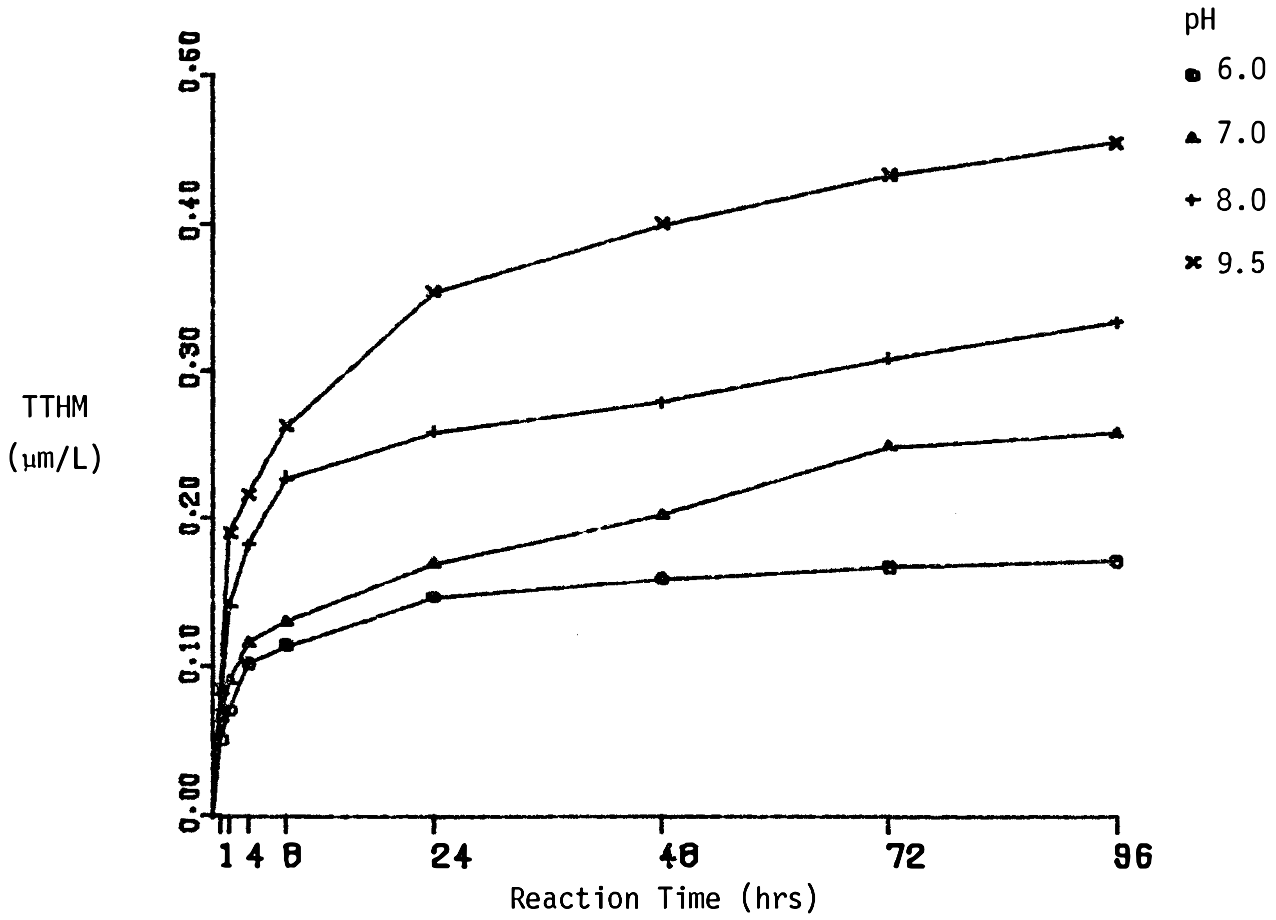

Figure 34. Effect of pH on TTHM Formation at 0 mg/L Bromide.

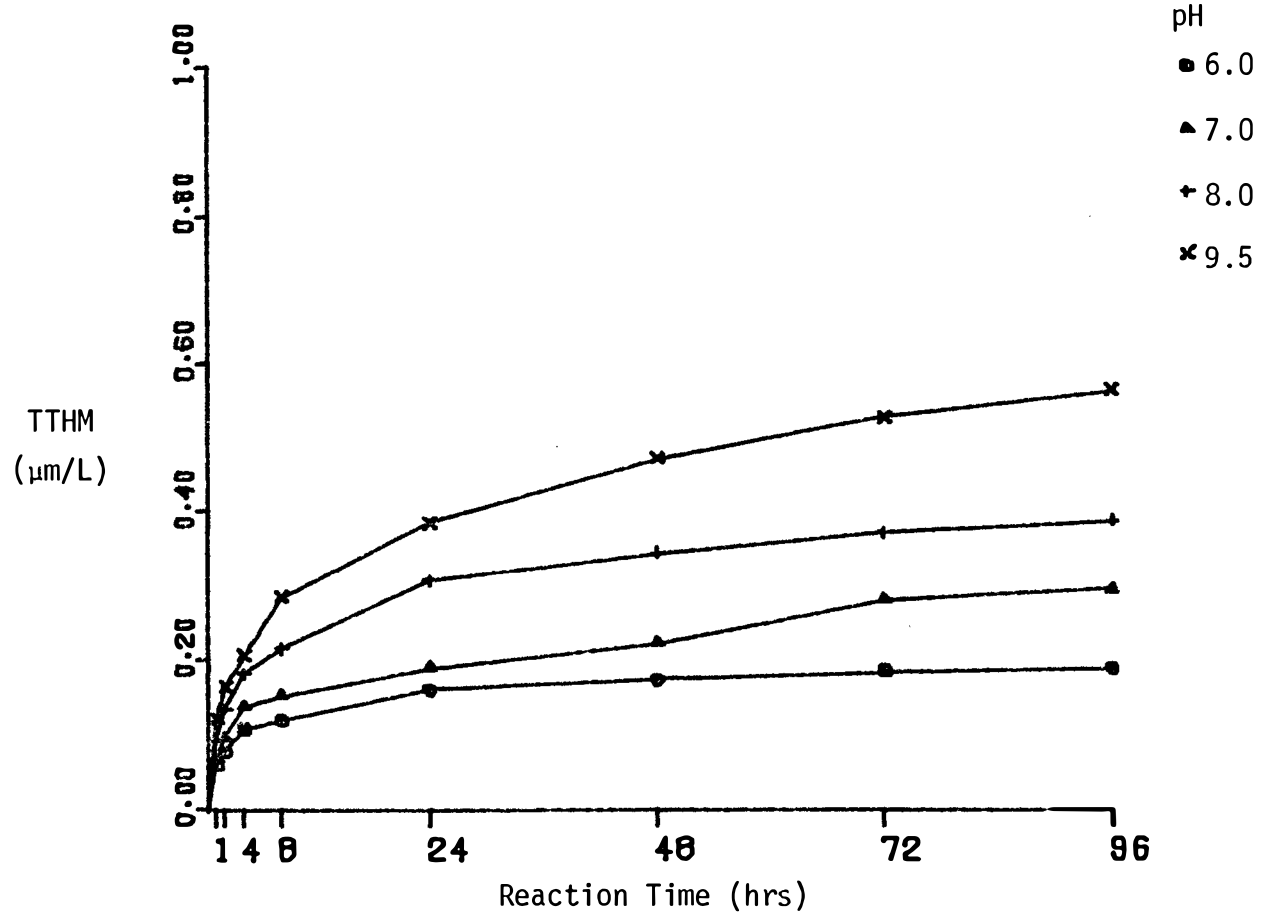

Figure 35. Effect of pH on TTHM Formation at .033 mg/L Bromide.

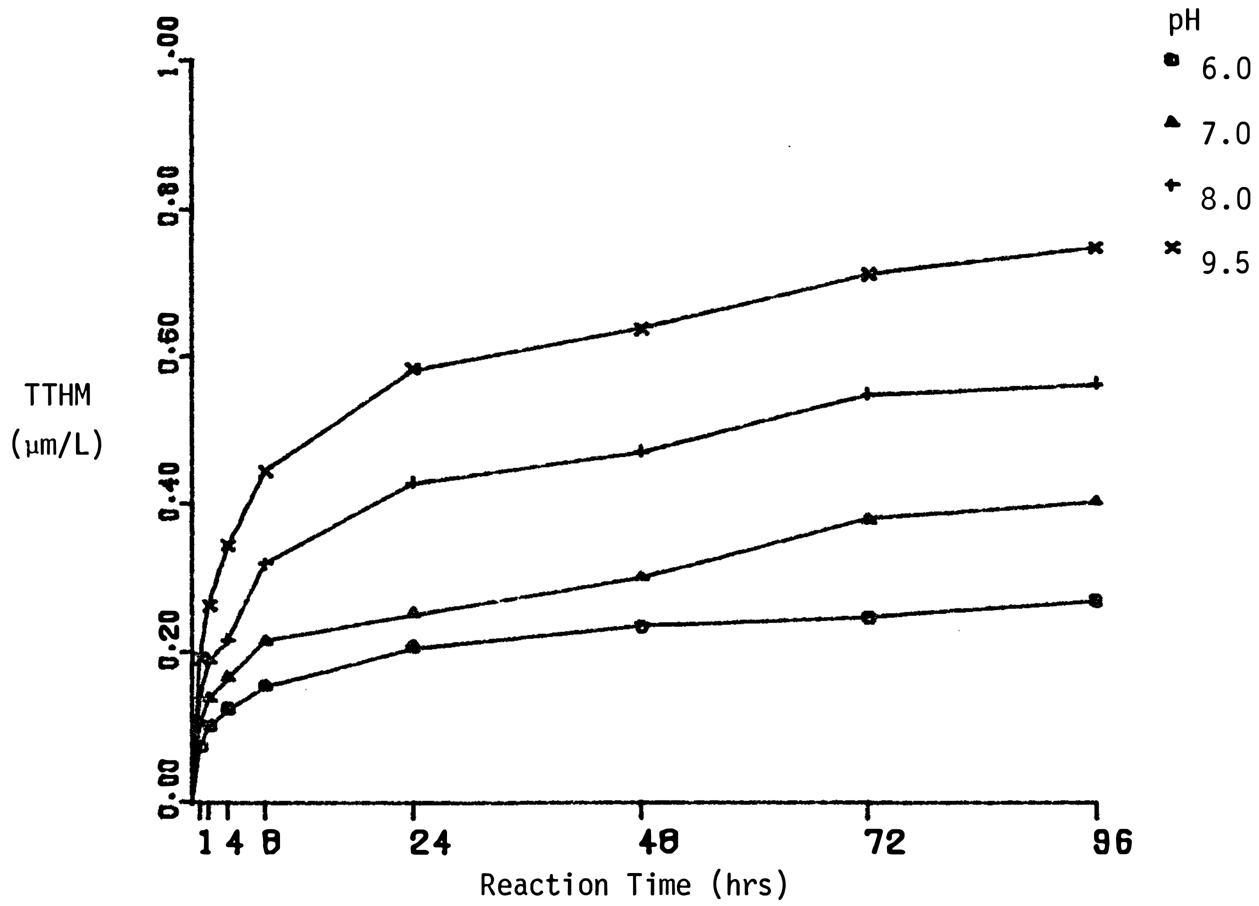

Figure 36. Effect of pH on TTHM Formation at .333 mg/L Bromide.

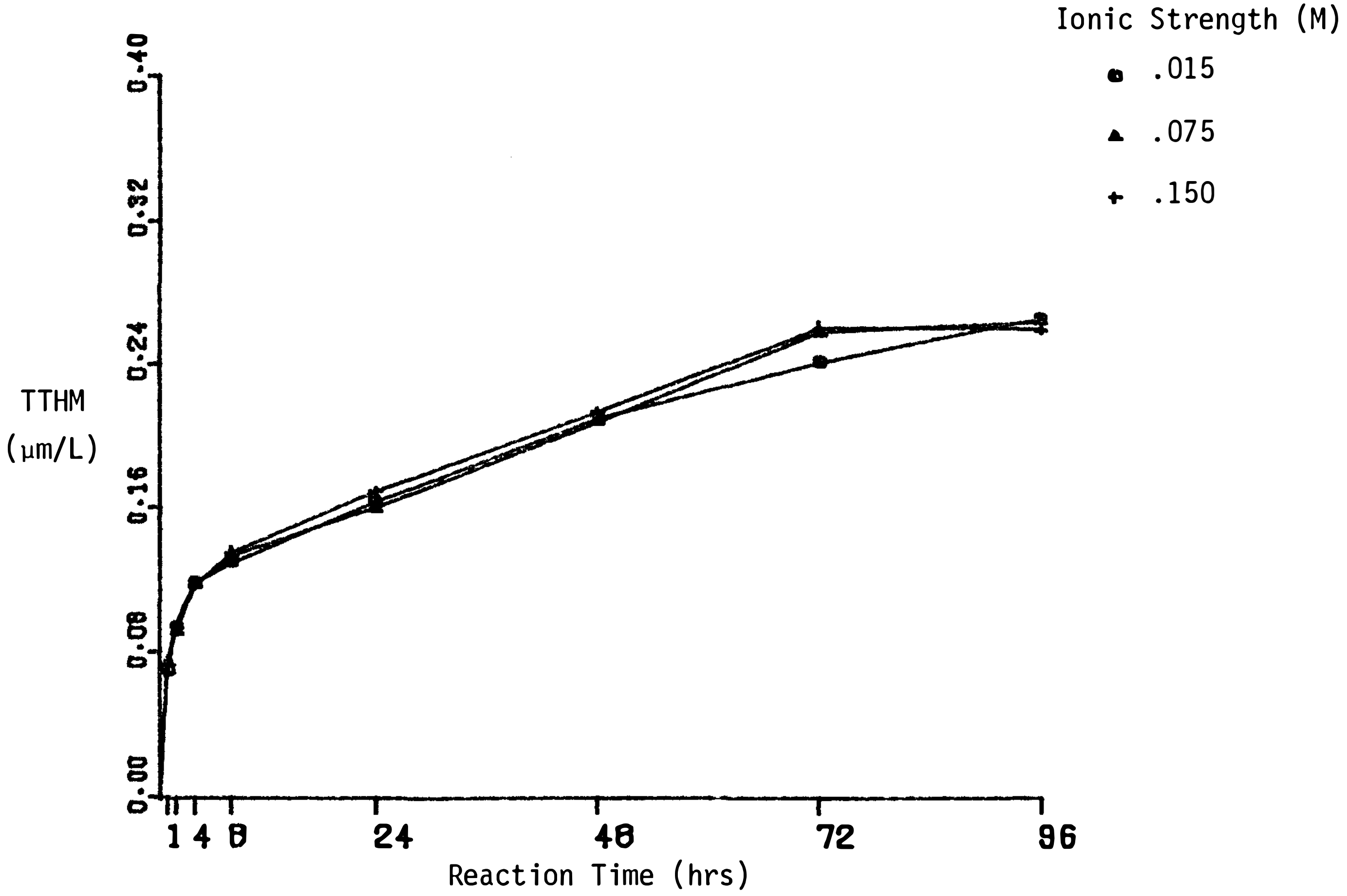

Figure 37. Variation in Ionic Strength at 0 mg/L Bromide.

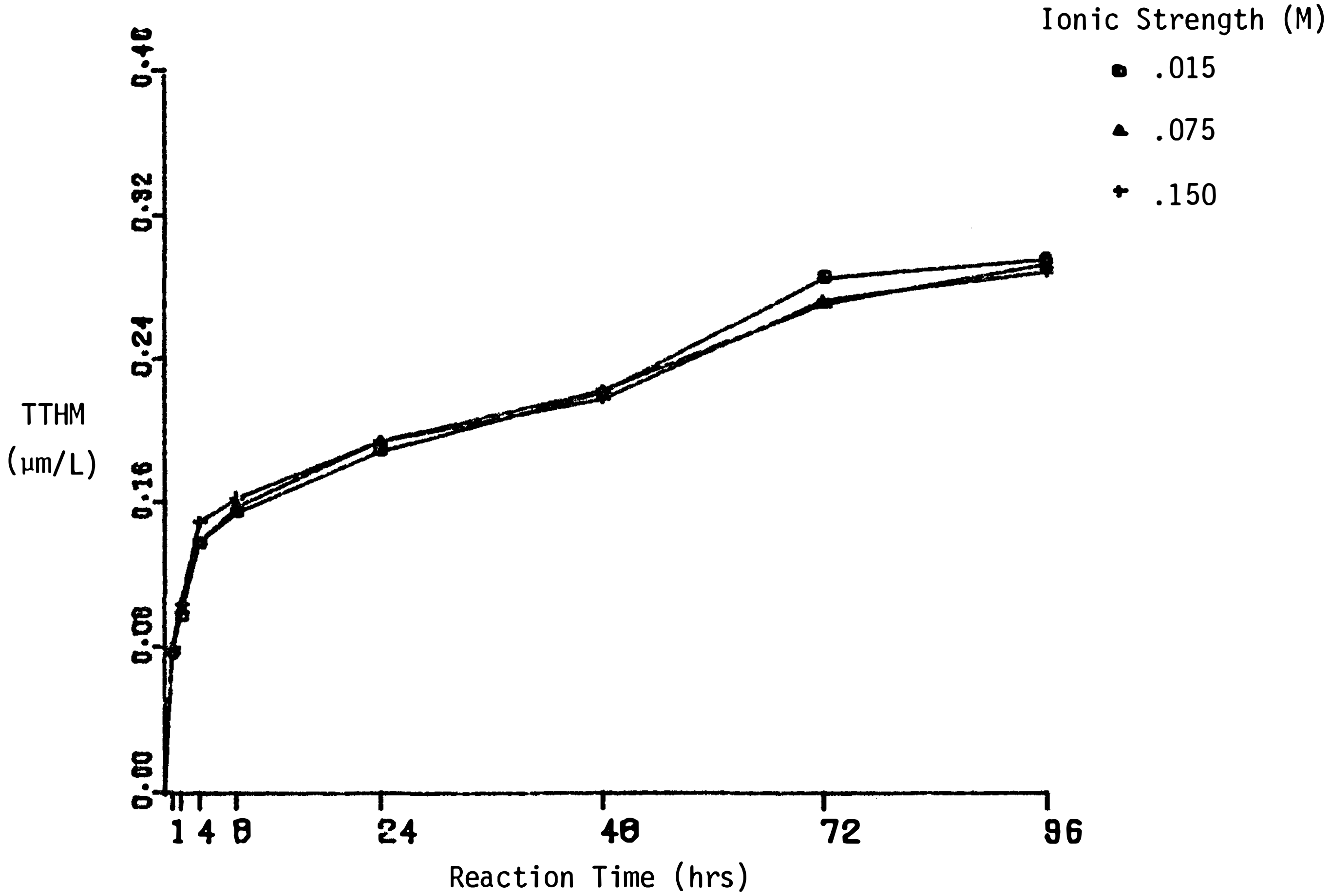

Figure 38. Variation in Ionic Strength at .033 mg/L Bromide.

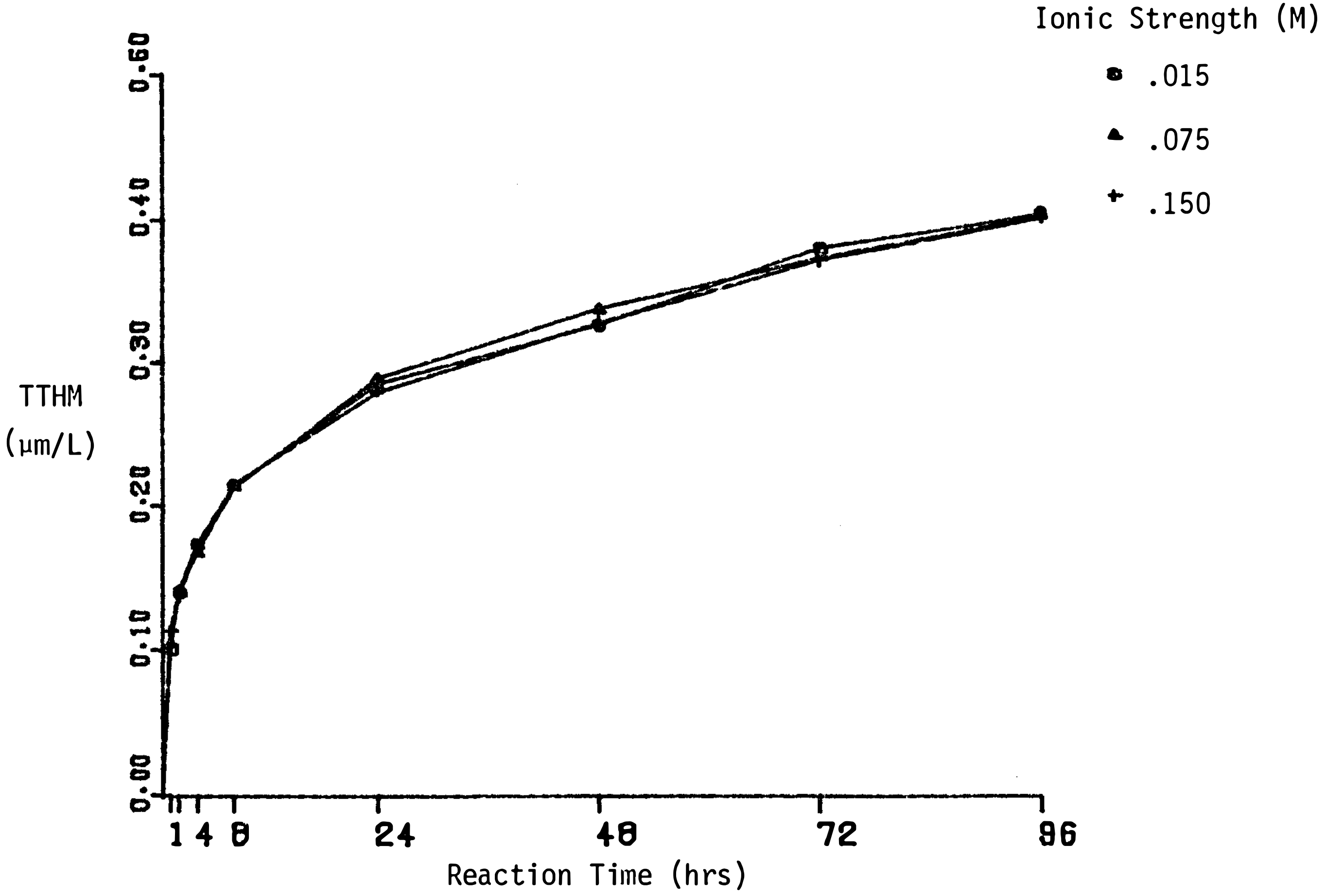

Figure 39. Variation in Ionic Strength at .333 mg/L Bromide.

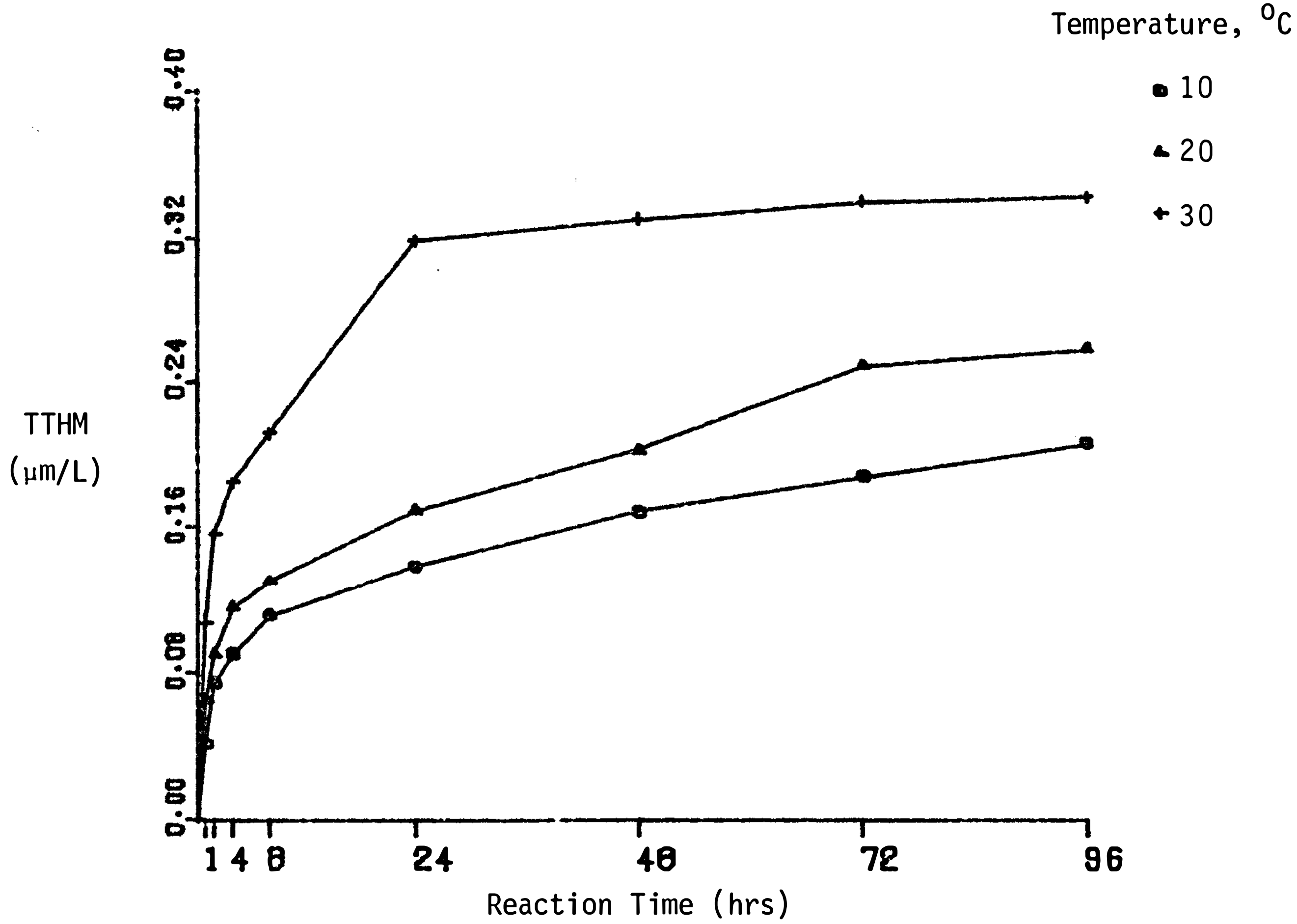

Figure 40. Effect of Temperature on Humic Acid TTHM Formation at 0 mg/L Bromide.

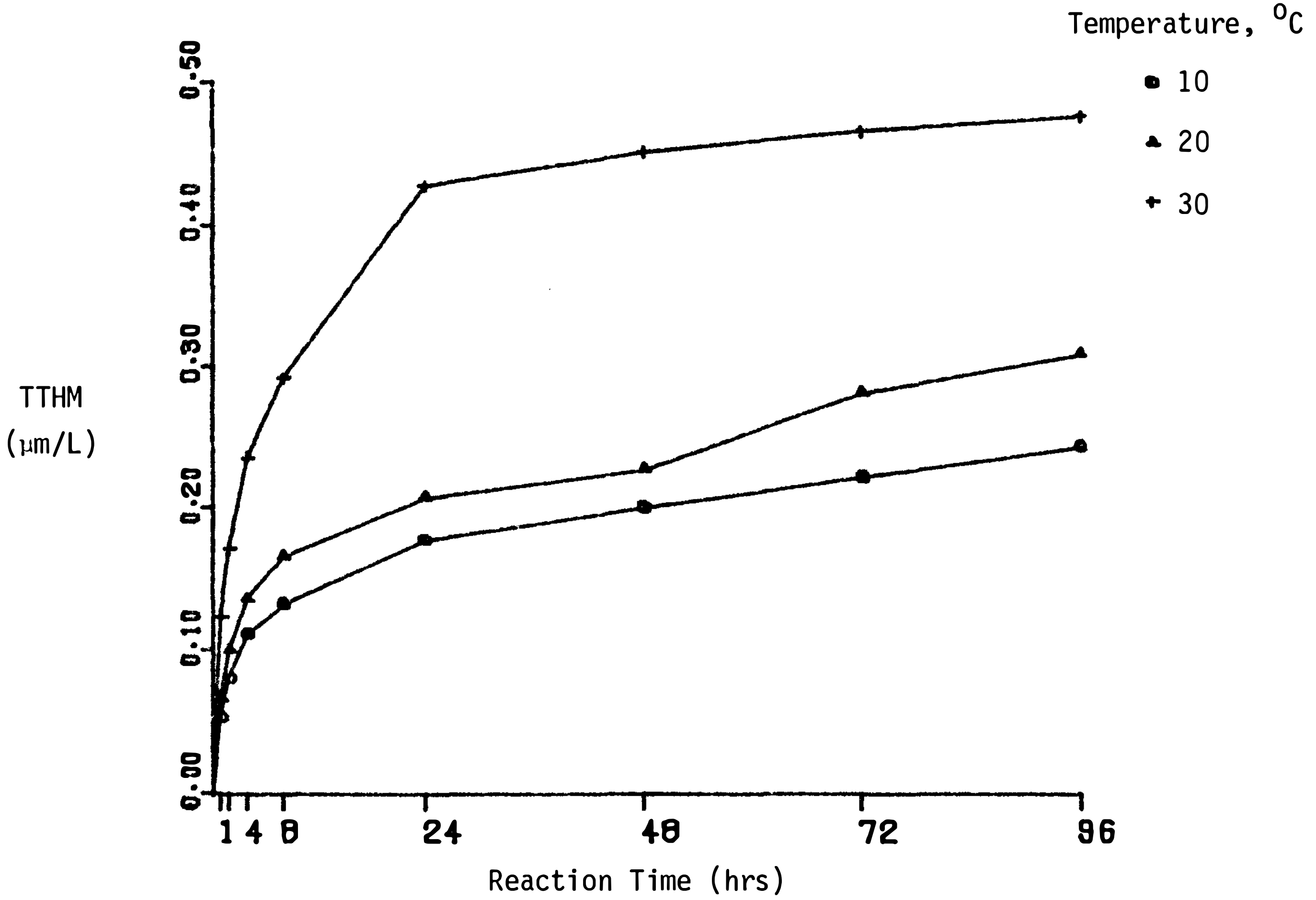

Figure 41. Effect of Temperature on Humic Acid TTHM Formation at .04 mg/L Bromide.

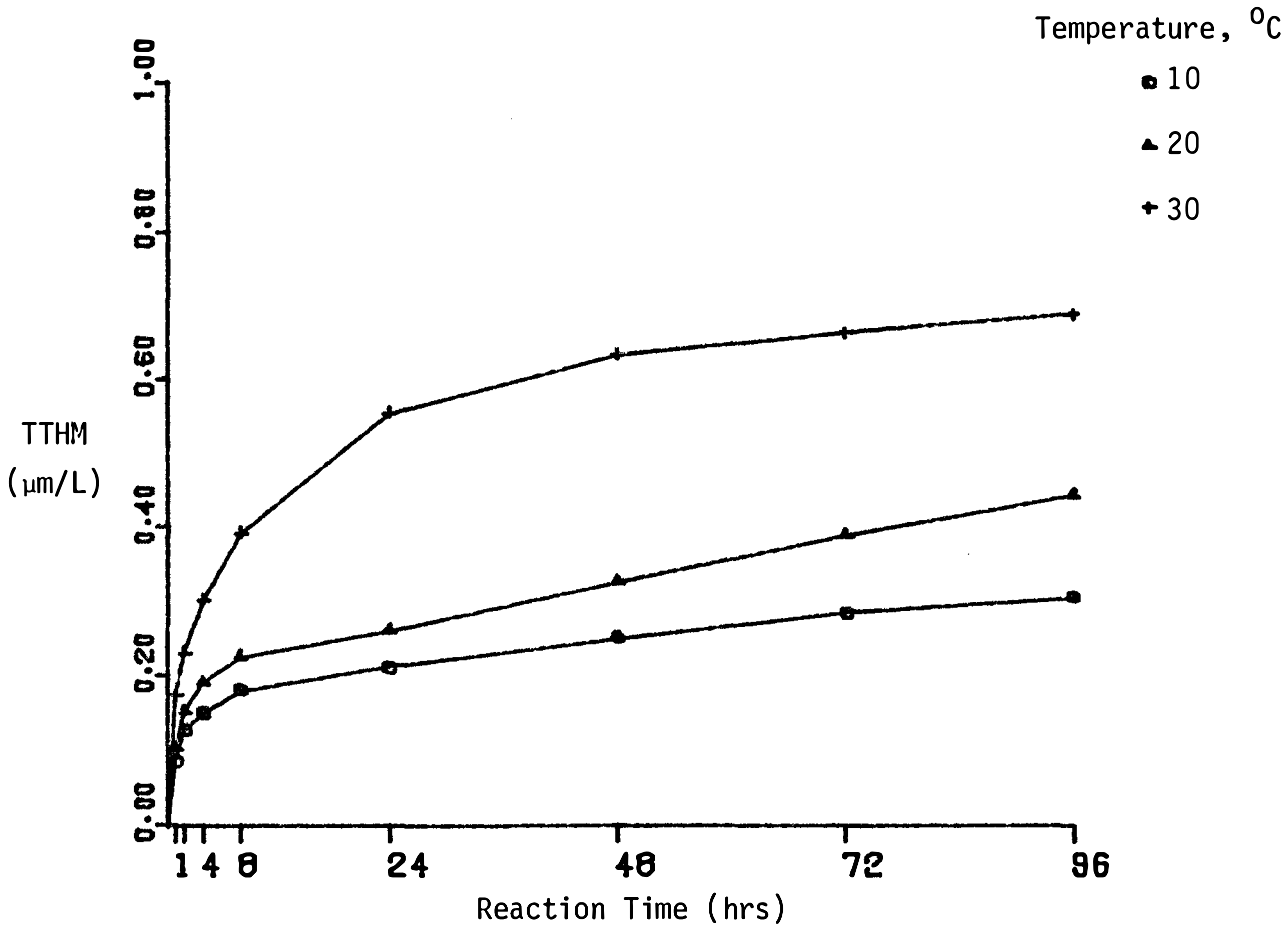

Figure 42. Effect of Temperature on Humic Acid TTHM Formation at .40 mg/L Bromide.

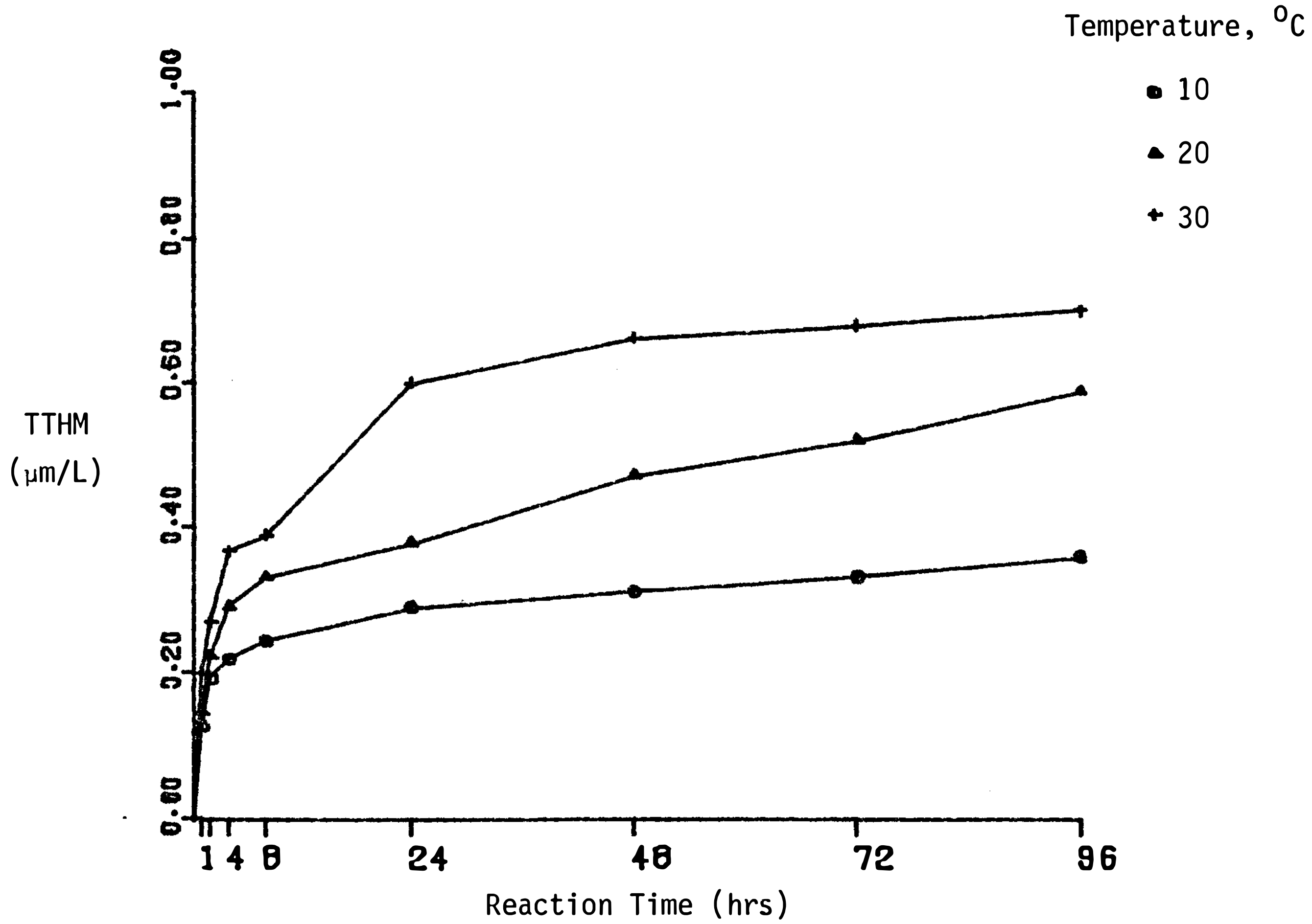

Figure 43. Effect of Temperature on Humic Acid TTHM Formation at 4.0 mg/L Bromide.

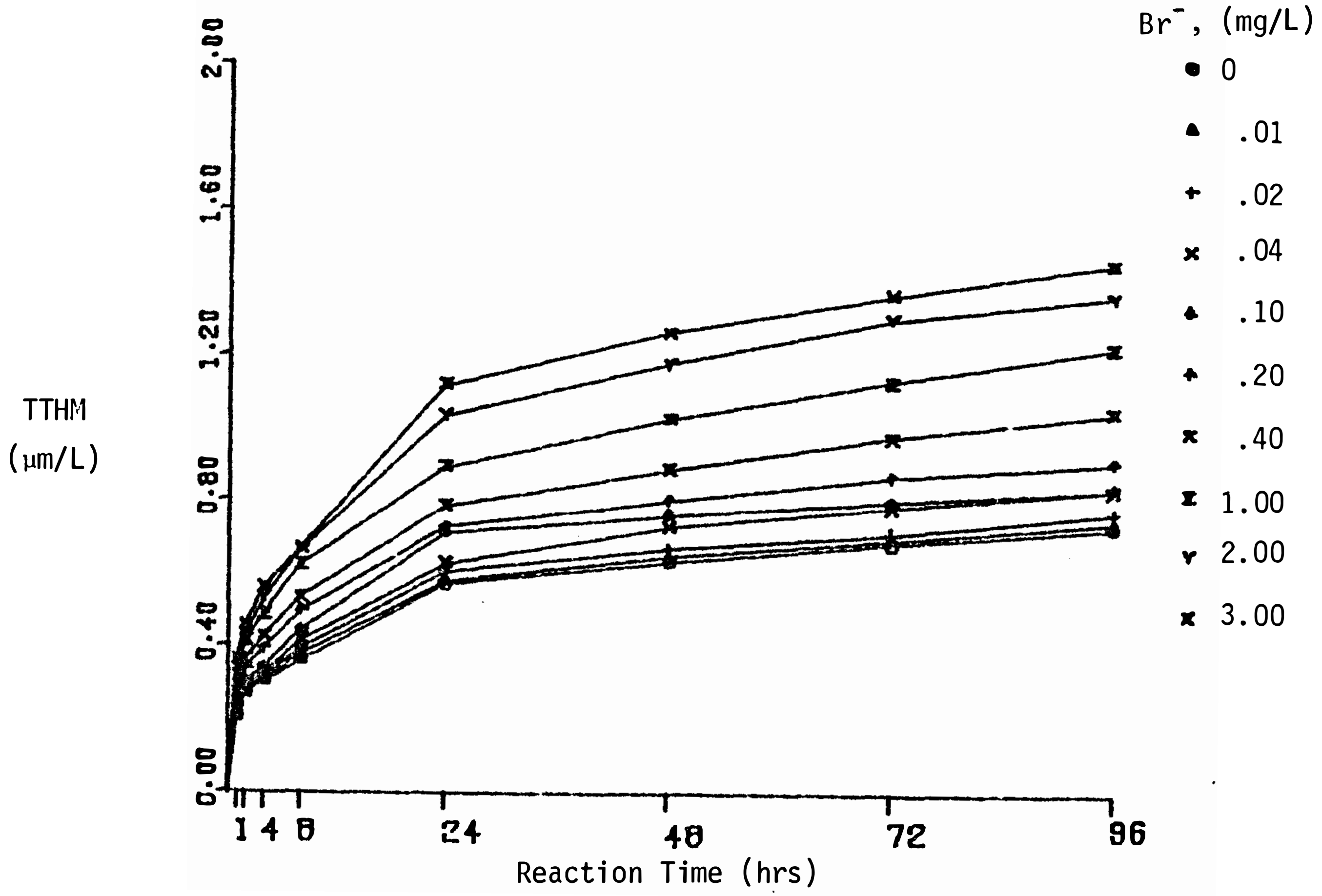

Figure 44. The Effect of Bromide on TTHM Formation from Tennessee River Water.

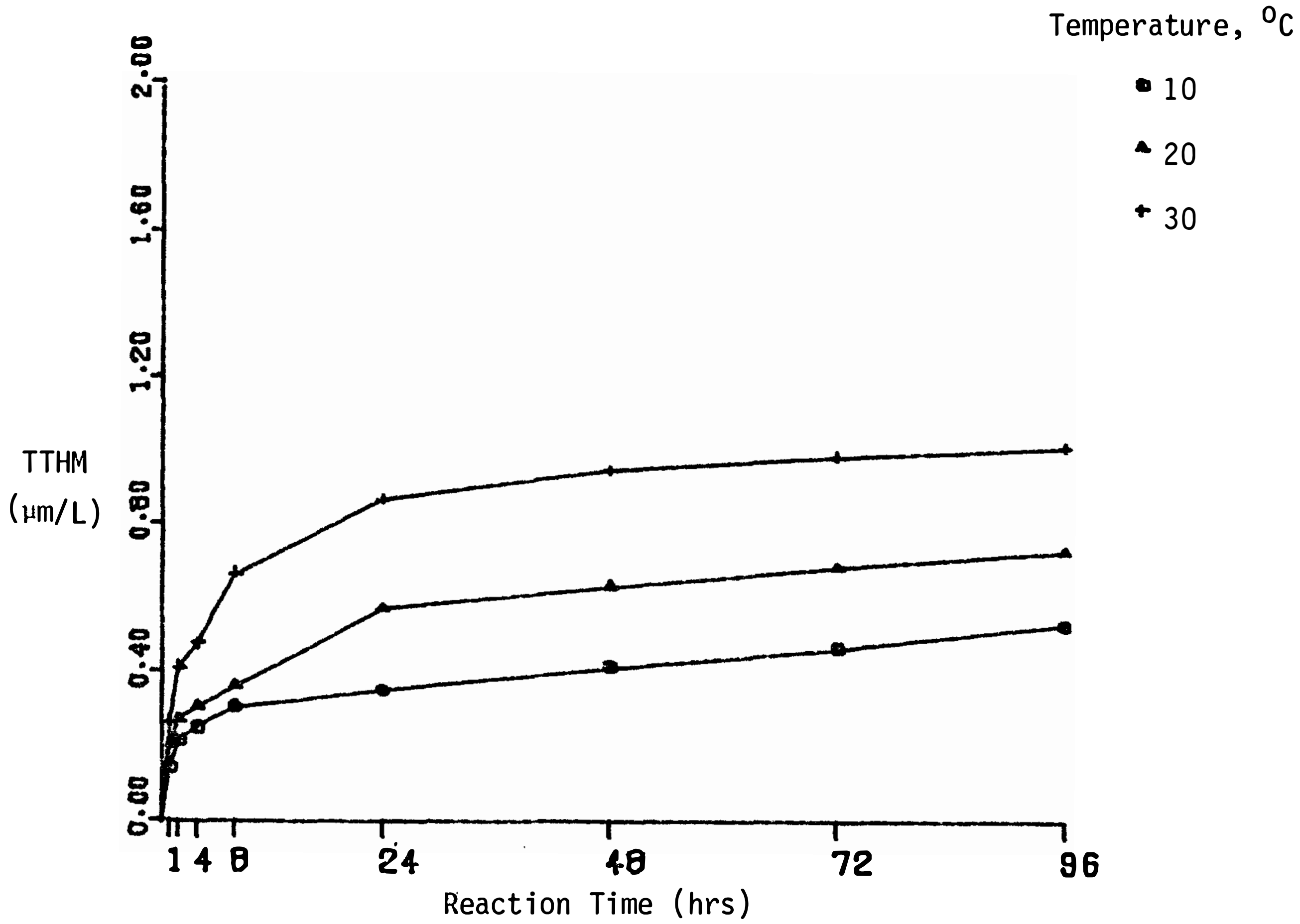

Figure 45. Effect of Temperature on Tennessee River TTHM Formation at 0 mg/L Bromide.

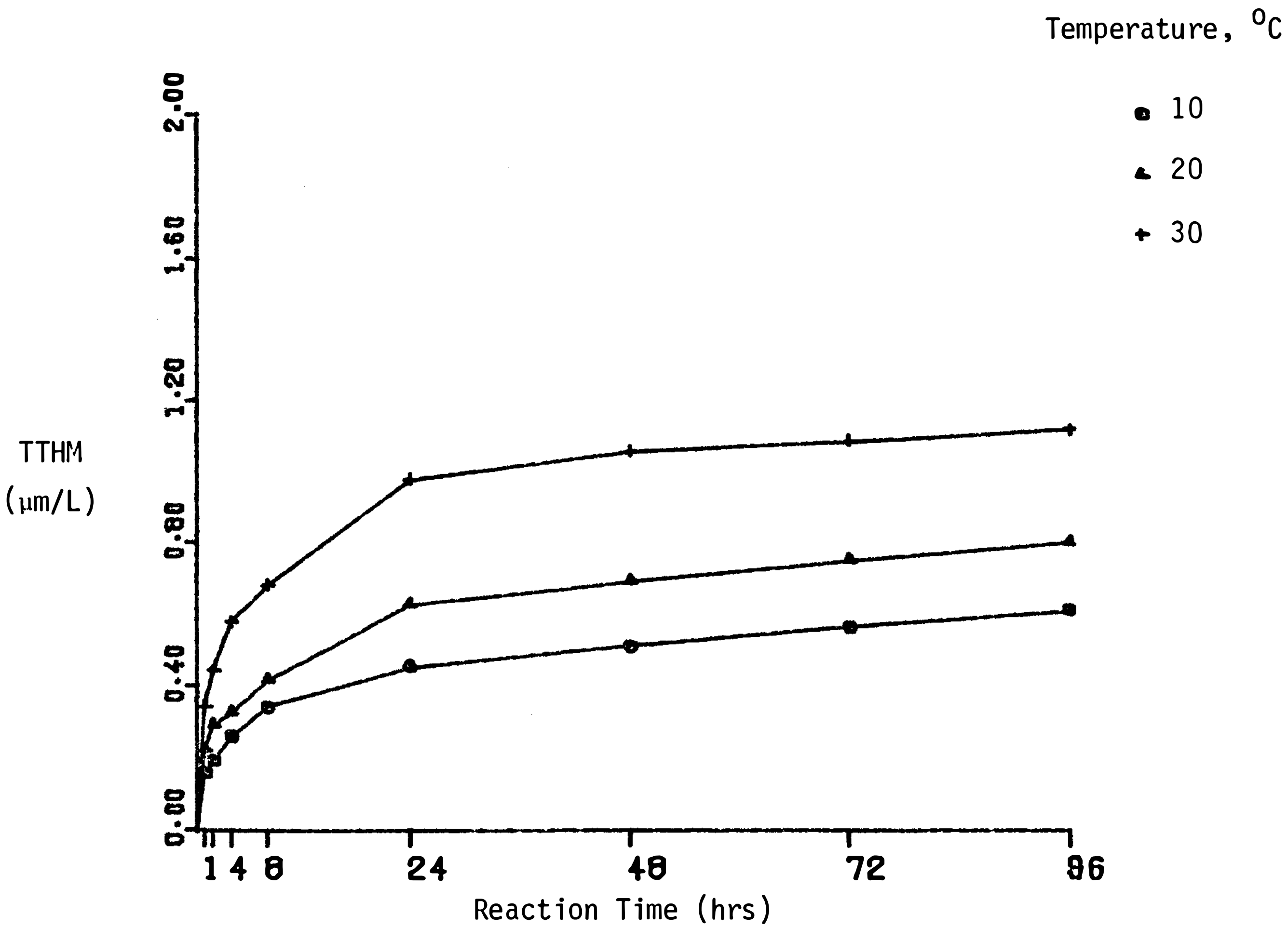

Figure 46. Effect of Temperature on Tennessee River TTHM Formation at .04 mg/L Bromide.

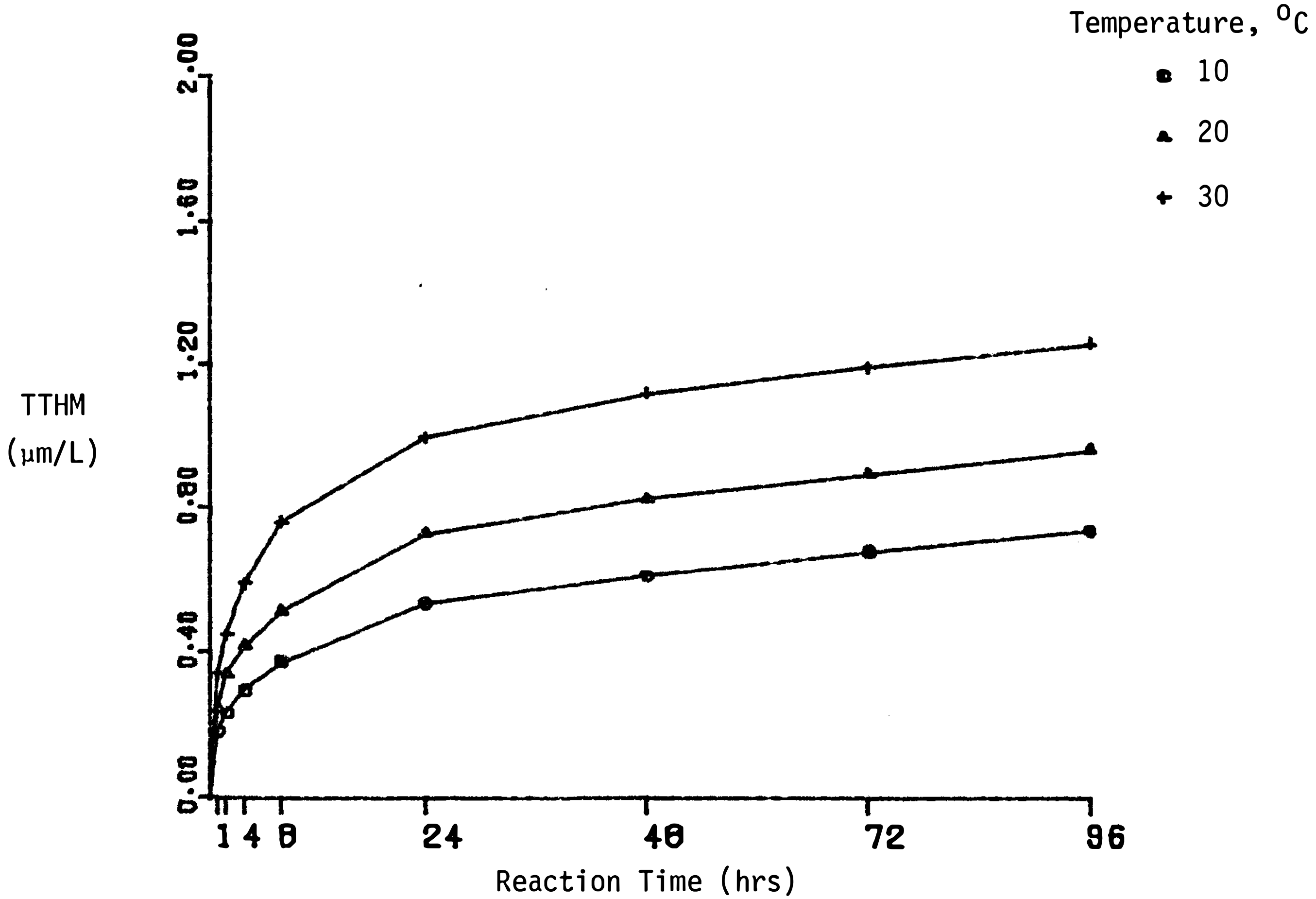

Figure 47. Effect of Temperature on Tennessee River TTHM Formation at .40 mg/L Bromide.

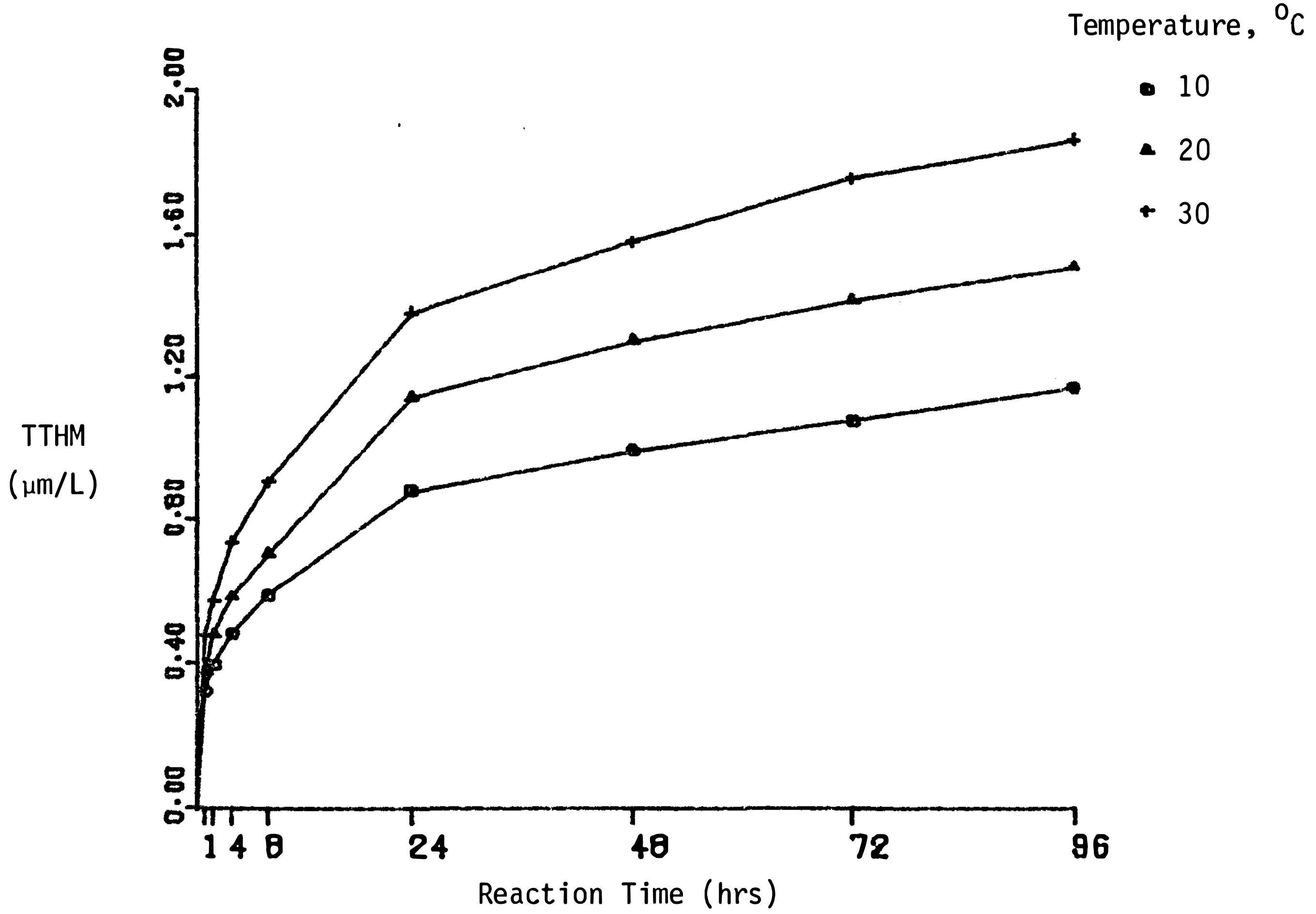

Figure 48. Effect of Temperature on Tennessee River TTHM Formation at 4.0 mg/L Bromide.

APPENDIX E

RESIDUAL OXIDANT DATA

Table 43. Residual Oxidant Data

Experimental Conditions	Reaction Time (hrs)						
	0	4	8	24	48	72	96
Humic Acid Studies							
Humic Acid, mg/L							
.5	4.85	4.65	4.53	4.25	4.14	4.00	3.90
1.0	4.75	4.23	4.00	3.77	3.50	3.39	3.24
2.0	4.65	3.80	3.60	3.47	3.15	2.72	2.60
Chlorine Dose mg/L							
2.5	2.26	1.85	1.53	1.29	1.03	.87	.80
10.0	9.68	9.35	9.01	8.65	8.38	8.24	8.08
pH							
6.0	4.79	4.33	4.09	3.88	3.62	3.49	3.39
7.0	4.75	4.23	4.00	3.77	3.50	3.39	3.24
8.0	4.58	4.14	3.71	3.50	3.35	3.18	3.07
9.5	4.28	3.75	3.32	3.30	3.25	3.10	2.95
Temperature, deg. C.							
10	4.79	4.40	4.18	3.94	3.70	3.60	3.52
30	4.70	4.10	3.85	3.50	3.36	3.21	3.05
Bromide, mg/L							
0	4.75	4.23	4.00	3.77	3.50	3.39	3.24
.033	4.71	4.12	3.92	3.68	3.42	3.33	3.20
.040	4.71	4.12	3.88	3.64	3.34	3.25	3.18
.333	4.62	3.96	3.70	3.42	3.23	3.10	2.97
.400	4.57	3.92	3.67	3.37	3.19	3.06	2.95
4.000	4.48	3.75	3.33	3.01	2.88	2.75	2.60
Tennessee River Studies							
0	5.75	5.29	5.10	4.79	4.50	4.33	4.20
.04	5.74	5.25	5.05	4.75	4.46	4.30	4.18
.40	5.70	5.00	4.78	4.43	4.27	4.15	4.01
4.00	5.60	4.12	3.48	3.17	2.95	2.81	2.69
Temperature, deg. C.							
10	5.80	5.44	5.21	4.95	4.80	4.68	4.60
30	5.66	5.09	4.90	4.52	4.34	4.19	4.08

APPENDIX F

COMPARISON OF MEASURED AND PREDICTED THM FORMATION CURVES

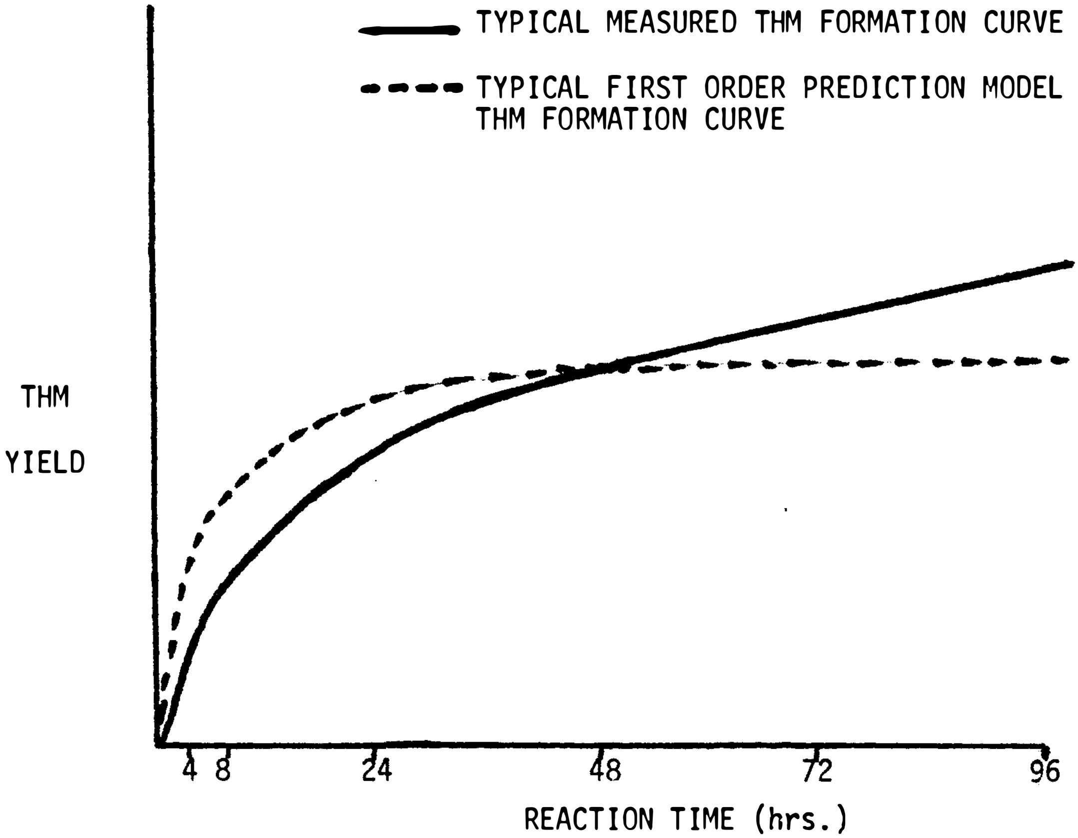

Figure 49. Comparison of Typical Measured THM Formation Curve Vs. First Order Prediction Model THM Formation Curve.

VITA

James Christy Bird was born in Lakeland, Florida, on April 5, 1953. He graduated from Santa Fe High School in Lakeland, Florida, in June 1971. The following September he entered the University of South Florida. In March 1974 he transferred to the University of Florida where he received a Bachelor of Science degree with a major in Chemistry in June 1975. In January 1976 he began study toward a Master's degree at the University of Tennessee. In June 1976 he accepted a staff position at Santa Fe Community College in Gainesville, Florida. In September 1977 he re-entered the Graduate School at the University of Tennessee, and received the Master of Science degree with a major in Environmental Engineering in August 1979. He is a member of the American Water Works Association.