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REMOVAL OF CHLOROFORM FROM DRINKING WATER

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Lexington, Kentucky

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ABSTRACT

The overall objective of this investigation was to evaluate via laboratory experiments the technical feasibility of reducing trihalomethane levels in drinking water. Special attention was directed at the removal of chloroform since: (a) it is the only trihalomethane which has been shown to be carcinogenic in animal tests; and (b) this compound generally comprises the largest fraction of the total trihalomethane content of chlorinated waters in Kentucky. Trihalomethanes are present in municipal drinking waters due to the reaction of free chlorine with naturally occurring compounds, collectively called "precursors".

A variety of treatment processes and potential modifications (or additions) to existing treatment facilities were evaluated for precursor and trihalomethane removal. In-plant modifications which could be implemented at existing treatment facilities were evaluated initially since they require a minimal amount of capital expenditure and could be implemented within a short time frame. Unit treatment operations studied for precursor removal included: settling, alum-polymer coagulation, precipitive softening, ion-exchange softening, rapid sand filtration, adsorption with both powdered and granular activated carbon, and treatment with ozone and chlorine dioxide.

A survey of the trihalomethane levels at fifteen of Kentucky's larger water utilities was completed. While not a part of the original scope of this project, this information should assist local water utilities and health officials in assessing the State's current trihalomethane situation. Additional field studies were completed at two of Kentucky's water utilities to provide plant-scale data on: (a) the effectiveness of a shallow bed of granular activated carbon in removing trihalomethanes; (b) the reduction of trihalomethane levels by moving the point of pre-chlorination; and (c) the reduction in the formation of trihalomethanes during precipitive softening by converting free chlorine to chloramines prior to the addition of lime and soda ash.

Results from both field and laboratory studies indicate that water utilities can markedly reduce the level of trihalomethanes currently in drinking water. Such reductions can be made by a variety of approaches which include alteration of disinfection practices, in-plant modifications to enhance precursor removal, and addition of new treatment processes such as carbon adsorption, ozonation and so forth. Only granular activated carbon adsorption appeared capable of completely removing precursor compounds and thereby eliminate the subsequent formation of trihalomethanes upon chlorination.

Descriptors: Water Treatment*, Water Quality Control*, Activated Carbon
Water Purification, Clorination

Identifiers: Trihalomethanes

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The director and principal investigator of this project was Dr. John S. Zogorski who during the completion of this project was Assistant Professor of Environmental Engineering, University of Louisville. Dr. Zogorski is currently Associate Professor, School of Public and Environmental Affairs, Indiana University, Bloomington, Indiana 47401. Graduate research associates who were funded by the KWRRI grant included Robert L. Mullins, Jr. and George D. Allgeier. Others contributing to the research project were Steve Hubbs, Alan Arbuckle, Duane Wilding, Don Smith and Tim Kochert. The excellent typing and administrative support provided by Mrs. Penny Hoerter is gratefully acknowledged.

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INTRODUCTION

For almost half a century Americans have confidently relied upon their domestic water supply, assuming that drinking water was free of harmful contaminants. In November, 1974, the U.S. Environmental Protection Agency (EPA) announced officially that trace quantities of 66 organic chemicals were identified in the New Orleans drinking water supply (Anon., 1975). Several of the compounds identified were suspected carcinogens. Partially in response to the events surrounding New Orleans, the Congress of the United States passed legislation, section 1442a-9 of the safe drinking water act, that directed EPA to conduct a comprehensive study of public water supplies and drinking water sources to determine the nature, extent, sources and means to control contamination by chemicals or other substances suspected of being carcinogenic. In complying with this mandate by Congress, EPA and other organizations have initiated extensive research programs to answer the questions raised by Congress concerning suspected carcinogens in drinking water.

The occurrence of organics in drinking waters throughout the United States was intially monitored by EPA's National Organics Reconnaissance Study, NORS (Symons, 1975). The major findings of NORS were that small quantities of organics (precursors) were present in all of the 80 municipal water supplies sampled and that trihalomethanes (THM) were present in drinking waters as a direct result of chlorinating the water supply, as shown in the general reaction:

Chlorine + Precursors + Chloroform + Other Trihalomethanes

The precursors which react with chlorine to form chloroform and other trihalomethanes have not been identified specifically but are believed to be humic and fulvic acids, two groups of naturally occurring organic compounds resulting from the degradation of vegetation. As of July, 1977, a total of over 600 specific organic compounds have been definitely identified in various drinking water supplies. The majority of these organic compounds have not been examined for their potential chronic health effects.

A National Cancer Institute (NCI) report showed that chloroform caused cancer in rats and mice under laboratory test conditions (Anon., 1976a). In response to the NCI report, the United States Food and Drug Administration has banned the use of chloroform in human drugs, cosmetics, and food packaging. Also, the Administrator of EPA on March 29, 1976, released a public statement requesting that water utilities voluntarily take what steps they could to reduce the chloroform concentration in their particular drinking water.

Interim primary drinking water regulations for the control of organic chemical contaminants in drinking water were issued recently by EPA (Federal Register, February 9, 1978, p. 5756-5779). Among other regulations, a maximum concentration limit for total trihalomethanes was established at 100 μg/l (yearly average). The MCL for total trihalomethanes is initially applicable only to community water systems serving a population of greater than 75,000 people and which add a disinfectant to the water in any part of the treatment process. However, the language of EPA's organic regulations indicates clearly that small utilities will also have to meet a MCL standard for trihalomethanes in the near future.

As might be expected, the results of recent studies have raised serious questions about the overall quality of drinking water and have further illustrated the need for a better delineation between substances found in drinking waters and associated health effects. While the presence of trace amounts of organic substances in drinking water does not create any acute threat to public health or welfare, more research into the possible long-term health effects are certainly warranted. Studies are currently in progress in the United States to evaluate the health effects of substances identified in drinking water; most notable of these is the National Academy of Sciences' investigation, which should provide data to EPA for setting allowable levels of organic contaminants in drinking water (Anon., 1975). Numerous research projects have also been initiated to define the level of trihalomethanes in drinking waters (Rook, 1974; Bellar et al., 1974; Anon., 1975; Symons et al., 1975; Morris and Johnson, 1976; Rook, 1976; Lovett and McMullen, 1977; Young, 1977; and Zogorski and Wilding, 1977) and to evaluate the effectiveness of various treatment processes and in-plant modifications for the removal of trihalomethanes (Love, 1975; Anon., 1976; Clark et al., 1976; Hubbs, 1976; Symons, 1976; Babcock, 1977; Harms and Looyenga, 1977; O'Connor et al., 1977; Smith et al., 1977; Zogorski, 1977; and Zogorski and Wilding, 1977).

In summary, the occurrence of trihalomethanes in chlorinated drinking waters is widespread throughout the United States with at least one of these compounds being a known carcinogen. Steps to reduce public exposure to the trihalomethanes, especially chloroform, appears prudent and warranted provided they do not increase the risk of microbial contamination or other detrimental effects.

The overall objective of this investigation was to evaluate via laboratory experiments the technical feasibility of reducing trihalomethane levels in drinking water. Special attention was directed at the removal of chloroform since: (a) it is the only trihalomethane which has been shown to date to be carcinogenic in animal tests; and (b) this compound generally comprises the largest fraction of the total THM content of a chlorinated water.

A variety of treatment processes and potential modifications or additions to existing treatment facilities were evaluated for precursor and/or THM removal. In-plant modifications which could be implemented at existing treatment facilities were evaluated initially since they require a minimal amount of capital expenditure and could be implemented in a short time frame. Experiments were also conducted to define the THM and precursor removal efficiency of granular activated carbon. This unit treatment operation has not been widely used by water utilities to date. However, the recent regulations by EPA on organic contaminants has placed added pressure on water utilities to install granular activated carbon contactors to remove THM and synthetic organic chemicals.

A survey of the THM levels in fifteen of Kentucky's larger water utilities was completed. While not a part of the original scope of this project, this information should assist water utilities and health officials in assessing the state's current THM situation. Additional field studies were completed at two of Kentucky's water utilities to provide plant-scale data on: (a) the effectiveness of a shallow bed of granular activated carbon in removing THM; (b) the reduction of THM levels by moving the point of pre-chlorination; and (c) the reduction in the formation of THM during precipitive softening by converting free chlorine to chloramines prior to the addition of lime and soda ash.

EXPERIMENTAL EQUIPMENT, METHODS AND PROCEDURES

ANALYSIS OF TRIHALOMETHANES

Materials and Experimental Procedures

A model 5710A Hewlett Packard gas chromatograph (GC) was used for the analysis of trihalomethanes in drinking water. This chromatograph was equipped with dual flame ionization detectors and temperature programming. Gases used with this instrument included air, hydrogen, and nitrogen; all of which were purchased in the highest purity available from local dealers. Two identical six-foot long, 1/8 inch diameter, glass columns were used. These columns contained 80x100 mesh Chromosorb 101 resin (Supelco, Inc.). The GC unit was operated in a differential mode (A-B mode) and chromatograms were recorded via a SRG Sargent pen recorder.

Since small quantities of trihalomethanes are present in water supplies, a concentration step was used prior to GC analysis. Concentration of the trihalomethanes was accomplished with a model LSC-1 liquid concentrator which was purchased from the Tekmar Co., Cincinnati, OH. A 25 ml purging cell was built and used instead of the 10 ml unit supplied with the LSC-1 to increase the concentrator's sensitivity. After preliminary experimentation with the LSC and GC units, standard conditions for processing water samples for trihalomethane levels were established as follows:

LSC-1 Concentrator

sample volume = 25 ml
purge time = 10 min
purge setting = 40
desorb time = 12 min
desorb temp. = 180° C
desorb flow-rate = 28 ml/min

GC Unit

Attenuation = 1 x 1 (typically)
Mode = A-B
Injection port temp. = 200° C
Initial column temp. = 25° C
Detector temp. = 250° C
Temperature program = 80-200° C @ 8° C/min (typically)
Hold times @ 80° C = 4 min (for standard only)
Hold times @ 200° C = 0-4 min

Peaks on chromatograms were identified by their individual residence time, as well as by their residence time from the chloroform peak. Peak areas were measured manually using the triangulation technique. Standards were prepared daily and were analyzed in a manner identical to water samples. Each standard was prepared in an ethanol-water solution and typically contained chloroform, bromodichloromethane and chlorodibromomethane. The concentration of each compound in the standard was varied from season to season to closely reflect the content of these compounds in tap water.

All samples to be analyzed for trihalomethanes were collected in 60 or 120 ml serum bottles and were sealed with teflon coated septa. Prior to sealing about 0.1 g of sodium thiosulfate was added to remove any free residual chlorine. Samples were stored in a refrigerator until processing commenced. Most trihalomethane samples were processed within 7 days after the samples were returned to the lab.

Reproducibility

The reproducibility of the LSC-GC system was determined on two separate dates. The results of this evaluation for two tap water samples are shown in Table 1. The data indicate that reproducible results are attained with the LSC-GC system. Especially noteworthy are the coefficients of variation for chloroform, which were 5.8 and 4.5% on 8/20/76 and 12/2/76, respectively.

TABLE 1

Experimental Data Illustrating the Reproducibility of the U of L's GC Analyses of Trihalomethanes

Date	Replicate No.	Concentration (μg/l)	Remarks
		Chloroform	
8/20/76	1	103	$\overline{X} = 109\ \mu g/l$, $\sigma = 6.3\ \mu g/l$ and CV = 5.8%
8/20/76	2	112	
8/20/76	3	119	
8/20/76	4	108	
8/20/76	5	105	
12/2/76	1	24.3	$\overline{X} = 24.5\ \mu g/l$, $\sigma = 1.1\ \mu g/l$ and CV = 4.5%
12/2/76	2	25.7	
12/2/76	3	22.8	
12/2/76	4	25.1	
12/2/76	5	24.6	
		Bromodichloromethane	
8/20/76	1	28.	$\overline{X} = 28.2\ \mu g/l$, $\sigma = 4.4\ \mu g/l$ and CV = 15.5%
8/20/76	2	24.	
8/20/76	3	31.	
8/20/76	4	34.	
8/20/76	5	24.	
12/2/76	1	12.1	$\overline{X} = 12.2\ \mu g/l$, $\sigma = 0.4\ \mu g/l$ and CV = 3.7%
12/2/76	2	11.9	
12/2/76	3	12.9	
12/2/76	4	12.4	
12/2/76	5	11.9	
		Chlorodibromomethane	
8/20/76	1	5	
8/20/76	2	<4	
8/20/76	3	ND	
8/20/76	4	<4	
8/20/76	5	ND	
12/2/76	1	ND	
12/2/76	2	ND	
12/2/76	3	ND	
12/2/76	4	ND	
12/2/76	5	ND	

ND - not detected

NON-VOLATILE TOTAL ORGANIC CARBON ANALYSIS

General Description

Non-volatile total organic carbon (NVTOC) analyses were made with a Beckman 915 total organic carbon analyzer. This instrument provides rapid analysis of a microsample of aqueous solution for quantification of either of two parameters: (a) inorganic carbon (i.e. carbonates); and (b) total carbon (i.e. organic carbon plus inorganic carbon). The difference between the total carbon and inorganic carbon analyses yields the total organic carbon content of a sample.

For samples containing a high fraction of inorganic carbon, such as a potable water sample, it is customary to treat the water sample prior to analysis. This pretreatment step is done to remove carbonates from the water sample so that the sensitivity of the analyzer for organic carbon testing can be increased. As the water sample is purged with air (or nitrogen) to remove the inorganic forms of carbon that are present in a water sample, some of the more volatile organic compounds are also scrubbed. As such, the carbon analyses performed after stripping are termed "non-volatile". Thus, the terminology "non-volatile total organic carbon" or "non-purgeable total organic carbon" applies to water samples that are purged prior to injection into the Beckman analyzer.

Materials and Experimental Procedures

Samples for NVTOC analyses were collected in standard 300 ml BOD bottles and immediately returned to the laboratory where they were acidified with about 1.0 ml of concentrated hydrochloric acid. Samples were then stored in a refrigerator until the actual NVTOC analyses were performed.

Just prior to analysis, 150 ml of each water sample was aerated in a Waring laboratory blender (model 1120) for 1.5 minutes to remove carbonates. About 10-15 ml of each sample were then placed into sealed test tubes. A Hamilton syringe was used to accurately measure a 100 μg/l aliquot, which was injected directly into the Beckman analyzer. Two or three duplicate injections were made for each water sample. Reported NVTOC data are, therefore, the average of two or three replicates.

Reproducibility

Experiments were completed to define the reproducibility of the NVTOC test. The reproducibility of this test was determined using tap water sampled at the University of Louisville's laboratory. A large volume of water was drawn from a faucet and mixed completely. Ten 300 ml samples were then withdrawn and analyzed according to the procedures described above. The results of the ten replicates are given in Table 2. The arithmetic mean was 2.1 mg/l, with an observed range of 1.9-2.4 mg/l. The standard deviation and coefficient of variation for the 10 replicates were 0.2 mg/l and 9%, respectively. Both of these parameters are low, which indicates that reproducible NVTOC results can be attained with the Beckman TOC analyzer.

TRIHALOMETHANE POTENTIAL TEST (THMPT)

Materials and Experimental Procedures

A test was initiated in the Spring of 1977 to define the potential of water samples to form trihalomethanes under a standard set of experimental conditions. The test is termed a "trihalomethane potential test", THMPT, and was used extensively to monitor the level of precursors in natural waters. This test was also used to define the capability of various treatment processes for reducing precursor levels. The THMPT is an indirect measure of the concentration of precursors in a water sample and a direct measure of the potential of the same water to produce trihalomethanes.

In essence, steps in the THMPT consists of adjusting the pH value of the water sample to a predetermined value,

TABLE 2

EXPERIMENTAL DATA ILLUSTRATING THE REPRODUCIBILITY OF THE NVTOC TEST

Date	Replicate Number	NVTOC (mg/l)	Remarks
1/17/77	1	2.2	$\bar{x}$ = 2.1 mg/l σ = 0.2 mg/l CV = 9%
1/17/77	2	2.0	
1/17/77	3	2.0	
1/17/77	4	2.3	
1/17/77	5	2.1	
1/17/77	6	2.1	
1/17/77	7	2.4	
1/17/77	8	2.4	
1/17/77	9	1.9	
1/17/77	10	1.9	

placing the water sample in reaction vessels, adding a specific amount of free chlorine to each reactor, incubating the samples for a standard time period, and then measuring the concentration of THM at the conclusion of the incubation period. Environmental conditions selected for the THMPT were as follows:

Temperature = 30° C (incubator)
pH Value = 10.5 - 11.2
Initial Chlorine Dose = 10 mg/l
Incubation Time = 72 hours
Dilution of Sample = None
Number of THM Replicates = Two

A more detailed step-by-step description of the THMPT follows:

1. Obtain about one gallon of water and remove suitable aliquots for initial turbidity, chlorine residual, NVTOC, pH value, and THM analyses.
2. Pipette 1 ml of 0.1N NaOH into four 60 ml serum bottles. This should adjust the pH value into the 10.5 - 11.2 range.
3. Fill all four 60 ml serum bottles with the water to be tested. Seal and crimp each bottle. The bottles should be labeled as follows:

   1 bottle for initial pH value + Cl_2 residual

   1 bottle for terminal pH value + Cl_2 residual

   2 bottles for final THM analysis
4. Inject into all four bottles a concentrated chlorine solution via a Hamilton syringe to obtain an initial free chlorine dose of about 10 mg/l.
5. Immediately open the bottle labeled "initial pH value and chlorine residual" and perform these two tests.
6. Incubate the remaining three serum bottles in the dark at 30° C for a 72 hour period.
7. At the conclusion of the incubation period take the bottle labeled "final pH value and Cl_2 residual" and perform these two analyses. Also, inject 10 µl of a standard $Na_2S_2O_3$ solution into the two serum bottles designated for THM analysis.

8. Place the two bottles awaiting GC analysis into a refrigerator maintained at 5° C.
9. Perform the GC analysis for THM, as described previously, and record the results in the appropriate notebook.

When desired, water samples were centrifuged at 10,000 RPM for 12 minutes to remove particulate and colloidal matter. This step, if conducted, would occur between steps 2 and 3 of the overall THMPT procedure described above.

Reproducibility

The reproducibility of the THMPT was not determined as part of this study. However, replicates performed during the standard THMPT were typically within ± 10% of each other. A reasonable estimate for the coefficient of variation would be about 10-20 percent.

RESULTS AND DISCUSSION

FACTORS AFFECTING THE FORMATION OF TRIHALOMETHANES

Considerable insight into the many factors affecting the rate and extent of formation of trihalomethanes was gained in this investigation. Some of this information was derived indirectly as part of the THM sampling program. However, most of the information on the formation of THM was obtained via bench-scale studies. In these latter experiments either raw or settled Ohio River water was placed into a series of 60 ml (or 120 ml) serum bottles, chlorinated, incubated, fixed and analyzed for THM formed. Some of the water samples were pretreated so as to modify their pH value, suspended solids content, and so forth prior to placement into the serum bottles. Parameters which were evaluated in this manner for their influence on the formation of THM included: contact time, chlorine dosage, pH value, temperature, turbidity, and stability of precursors.

Chlorination Practice

The term "chlorination practices" denotes several different, yet influential parameters in the formation of trihalomethanes at water utilities. The first parameter is the amount of chlorine dosed, which is usually expressed in units of mass per unit time or volume (lbs/MG, mg/l, lbs/day, etc.). The second parameter is the point of chlorination within a particular treatment plant. The final parameter is chlorine contact time which, of course, is in practical situations related to the point of chlorination.

All three of the above chlorination practices are described in separate sub-sections below. It is recognized that in practical applications it is not always possible to completely separate the interaction of the above three aspects of chlorination.

Chlorine Dose - Bench-scale experiments showed that increased chlorine dosages resulted in increased formation of chloroform and total THM. This trend can be seen in Table 3, which lists THMPT data for chlorine dosages of 5 and 10 mg/l, each at six different pH values. Settled Ohio River water was used in these tests and was contacted with free chlorine for a period of 10 days. In summary, increased chloroform and total THM levels are expected if the chlorine dose is increased. This trend was demonstrated in this investigation and has been duplicated in field and laboratory studies elsewhere (Rook, 1975; Kinman, 1975; and Hoehn, 1977).

It is interesting to note that the concentration of $CHCl_2Br$ did not vary significantly with chlorine dosage in this investigation. The precise reason for this is unknown but similar trends have been observed at the Cincinnati Water Works (Kinman, 1976).

Point of Chlorination - There has been a great deal of success to date in reducing THM levels by moving the point of pre-chlorination. The observed reduction in THM levels is presumedly the cumulative effect of several factors most important of which are reduced contact time, reduced chlorine demand and reduced precursor concentration.

Movement of the point of pre-chlorination from the head of the pre-sedimentation basin to the start of the chemical coagulation process resulted in a 74% reduction in chloroform levels in Cincinnati's finished water (Kinman, 1976). The Huron Water Treatment plant in South Dakota also accomplished a similar reduction by moving the point of pre-chlorination further into its treatment scheme (Harms, 1977). Tom Love has also reported a noticeable decrease in the THMPT with movement of chlorination back to later stages in EPA's pilot water treatment plant (Love, 1976).

TABLE 3

EFFECT OF CHLORINE DOSAGE AND pH VALUE ON THE FORMATION OF CHLOROFORM AND BROMODICHLOROMETHANE[a]

pH Value[b]	Level of Trihalomethanes Formed at Selected Chlorine Doses, µg/l					
	Cl_2 Dose = 5 m/gl			Cl_2 Dose = 10 mg/l		
	$CHCl_3$	$CHCl_2Br$	Total	$CHCl_3$	$CHCl_2Br$	Total
5.9	46	16	62	62	20	82
6.9	69	30	99	88	27	115
7.6	76	30	106	100	26	126
8.3	98	30	128	118	25	143
9.9	129	16	145	184	26	210
10.9	105	NA	---	163	16	179

NA - Not analyzed.
a - Settled Ohio River water sampled on 11/10/76.
b - At termination of THMPT.

An important side-effect associated with moving the point of chlorination further back into the treatment scheme is that chlorine comes into contact with a higher quality water (i.e. lower Cl_2 demand). As such, less chlorine is needed to maintain a specified bacterial quality. It should be recognized, however, that any movement in points of chlorination must not jeopardize the bacteriological integrity of finished water.

Contact Time - As described in the preceeding subsection, movement of the points of chlorination back further into the treatment system may reduce the amount of THM formed. This phenomenon is, in part, a result of a shorter contact time between the precursor compounds and free chlorine. Research completed during the course of this investigation has documented that the formation of THM is not instantaneous, but rather, occurs over a period of several days. Further, the kinetics of the formation of THM are dependent upon various environmental parameters.

Several researchers have completed laboratory experiments to define the time dependence of the THM formation reaction. Studies have been completed by Rook (1974), Riley (1975), Symons (1976), Hoehn (1977) and by this research project. A predominant conclusion in each of these studies is that total THM and chloroform concentrations are increased with increased contact time between free chlorine and THM precursors. The dependence of THM levels with contact time is illustrated for settled Ohio River water in Table 4. As seen, the concentrations of both $CHCl_2Br$ and $CHCl_3$ were increased with increased contact time. Even after a three day contact period the experimental system still did not appear to have attained equilibrium.

Temperature

In general, all of the investigations completed to date agree that increased temperatures promote the formation of $CHCl_3$ and total THM. Bench-scale studies were

TABLE 4

INFLUENCE OF CUMULATIVE INCUBATION TIME ON THE FORMATION OF CHLOROFORM AND BROMODICHLOROMETHANE[a]

Cumulative Incubation Time[b], hours	THMPT, µg/l	
	$CHCl_3$	$CHCl_2Br$
0	0	0
13	32	15
16	35	15
20	48	19
38	42	17
44	57	25
84	51	34

a - Settled Ohio River water sampled on 11/10/76.

b - After addition of 7 mg/l of chlorine.

completed to accurately define the temperature dependence of settled Ohio River water. In these experiments aliquots of settled water (collected on 1/3/77) were incubated at three different temperatures, 7, 18 and 30°C, in the presence of free chlorine for a period of 7 days. The amount of chloroform produced increased from about 30 μg/l at 7°C to nearly 70 μg/l at 30°C. The least-squares line of best fit for the relationship between chloroform and water temperature was determined as:

$$C = -11.6 + .907\ T \qquad (R = 0.990)$$

where T is the water temperature in °F and C is the concentration of chloroform produced, μg/l.

During the period 1/11/77 - 6/10/77 water temperatures and THM levels of finished water (i.e. sampled from clearwell) were monitored occasionally. Results from this study also indicate a strong temperature dependence for $CHCl_3$ (about 1.3 μg/l per °F). Only a minor temperature dependence (about 0.2 μg/l per °F) was evident for $CHCl_2Br$. The least-square equations for these two trihalomethanes were defined as:

$$C_1 = -28.9 + 1.27\ T \qquad (R = 0.893)$$
$$C_2 = -3.6 + 0.216\ T \qquad (R = 0.668)$$

where C_1 and C_2 are the instantaneous concentrations in finished water of $CHCl_3$ and $CHCl_2Br$ in μg/l, respectively, and T is the instantaneous finished water temperature in °F.

The variation of $CHCl_3$ levels in Louisville tap water was also studied in relation to its dependence on temperature. For this purpose monthly average temperatures for Ohio River water were computed. Table 5 contains a listing of monthly averages for water temperature, $CHCl_3$ levels and other parameters. Linear regression analyses were performed with the results shown in Table 6. As evidenced by the high correlation coefficient, monthly average $CHCl_3$ concentrations in Louisville's drinking water are highly dependent upon ambient

TABLE 5

MONTHLY AVERAGES OF SELECTED WATER QUALITY PARAMETERS

Month/Year	Flowrate of Ohio River[a] (cfs)	Turbidity[b] (Units)	Total Hardness[b] (mg/l @ $CaCO_3$)	Temperature[b] (°F)	$CHCl_3$[c] (µg/l)
8/76	37,900	6.8	131	80	83
9/76	26,500	3.8	161	77	99
10/76	112,500*	42.4	126	64	58
11/76	68,880*	12.8	111	49	41
12/76	82,580*	22.2	118	41	27
1/77	40,920*	5.9	123	35	13
2/77	104,700*	30.7	129	36	27
3/77	253,700*	115.	112	46	42
4/77	200,000*	134.	116	57	49
5/77	76,360*	21.4	139	69	69
6/77	28,160*	6.9	143	77	63
7/77	53,100*	8.6	157	83	77
8/77	74,170*	21.6	147	81	77
9/77	44,870*	10.6	119	79	91
10/77	+	24.9	119	65	54

* - Provisional data.
\+ - Not available at present.
a - Provided by U.S. Geological Survey.
b - Of Ohio River water.
c - In U of L tap water.

TABLE 6

SUMMARY OF RELATIONSHIPS BETWEEN SEVERAL WATER QUALITY PARAMETERS AND OBSERVED CHLOROFORM CONCENTRATIONS AT U of L LABORATORY

Independent Parameter[a]	Least-Squares Linear Regression Equation	Correlation Coefficient (R)
Temperature (T)	$\overline{CHCl_3} = -27.0 + 1.37\ \overline{T}$	+0.936
Turbidity (TURB)	$\overline{CHCl_3} = 63.3 - 0.171\ \overline{TURB}$	-0.269
Flowrate of Ohio River (Q)	$\overline{CHCl_3} = 70.6 - .000143\ \overline{Q}$	-0.362
Total Hardness (TH)	$\overline{CHCl_3} = -67.3 + .963\ \overline{TH}$	0.611

[a] Monthly mean values for the period 8/1/76 - 10/31/77 were used in all regression equations.

water temperatures. The least-squares line of best fit was determined as:

$$\overline{C} = -27.0 + 1.37\ \overline{T} \qquad (R = 0.936)$$

where $\overline{C}$ is the monthly average $CHCl_3$ concentration in Louisville's drinking water, μg/l, and $\overline{T}$ is the corresponding monthly average water temperature for raw Ohio River water, ^oF.

pH Value

Many researchers have observed that the formation of THM is very dependent upon the pH value of the solution phase. The exact explanation for this occurrence has not been clearly elucidated to date for natural waters, although various mechanisms have been proposed (Morris, 1977). Studies on pH effects have been completed by Rook (1974, 1975), Kinman (1976), Stevens (1976), Symons (1976); Harms (1977), Morris (1977), as well as by this research team. In general, increased levels of chloroform are produced as the pH value is raised. A similar trend is found for total THM concentration, whereas the concentration of brominated haloforms may be independent of the pH value (Kinman, 1976).

Bench-scale potential tests were performed to document the effect of the pH value of Ohio River water on the formation of THM. Results from this preliminary experiment which was run on settled Ohio River water collected on 11/10/76 are presented in Table 3. In this study 120 ml aliquots of settled water were placed in serum bottles and then contacted with free chlorine for a period of 10 days. The pH value of each aliquot tested was adjusted with NaOH or HCl prior to its placement into the serum bottles so as to attain a spread of final pH values. Two series of bottles were incubated. One received a 5 mg/l initial dosage of free chlorine, while 10 mg/l of free chlorine was added to the second set. Shown in Table 3 is the dependence of the potential to form $CHCl_3$ versus final incubation pH values. The right half of the table is for the set that received the 10 mg/l chlorine dosage, whereas the left half corresponds to the set that received 5 mg/l of free chlorine. As noted very high correlations are apparent between $CHCl_3$ produced and residual pH values. As expected, higher concentrations of $CHCl_3$ were formed at elevated pH values. Table 3 also illustrates the dependence of $CHCl_2Br$ formed with pH value. The amount of $CHCl_2Br$ formed appears to be maximized in the 7-9 pH range, with a gradual dropoff on each side of this range. Needless to say, $CHCl_2Br$ concentrations do not exhibit a strong dependence with the pH value of the solution. Similar findings were reported by Kinman (1976) in his study of the Cincinnati water works. Namely, Kinman found that observed concentrations of $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$ were not significantly influenced by pH values in the 7.5-9.0 range.

A larger-scale experiment was also completed in this investigation team to further study the effect of pH value. In this experiment three identical five gallon carboys of settled Ohio River water were collected on 10/11/77. Varying amounts of NaOH were added among the three carboys so as to vary the pH value. Free chlorine was then added to produce an initial dosage of 10 mg/l after which mixing was promoted. A 100 ml aliquot was thereafter removed from each carboy and analyzed for initial pH value and free chlorine residual. Each carboy was then stored in the dark for 48 hours after which time samples were withdrawn from the middle of each jug for THM, chlorine and pH analyses. Results from this experiment are listed in Table 7. Again, the concentration of brominated THM was only slightly affected by the pH value of the solution. The rate of change of $CHCl_3$ formed was found to be about +40 μg/l per unit change in pH values. A value of about 21-22 μg/l per unit change in pH value was indicated from earlier studies (Table 3).

TABLE 7

RESULTS OF EXPERIMENTS ILLUSTRATING THE INFLUENCE OF pH VALUE ON THE FORMATION OF TRIHALOMETHANES

Reaction Vessel	Chlorine Dose (mg/l)	Chlorine Residual (mg/l)		pH Value		Concentration of Trihalomethanes[c], µg/l		
		Initial[a]	Final[b]	Initial[a]	Final[b]	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$
1	10.	5.5	3.3	7.3	7.3	56	25	8
2	10.	5.0	2.7	9.3	9.1	120	37	14
3	10.	4.8	2.2	10.6	10.6	189	36	13

a - Just after chlorine was added.
b - 48 Hours after chlorine addition.
c - Average of three replicate samples.

Stability of THM Precursors

A single bench-scale experiment was conducted as part of this investigation to determine the stability of precursors which react with free chlorine to form THM. It is believed that the majority of these precursors are naturally occurring compounds such as fulvic and humic acids, although no direct proof of this was attempted herein. Fulvic and humic substances are rather stable in natural waters and, as such, it was presumed that precursors associated with the THM formation reaction would also be stable.

To gain some understanding of the persistence of THM precursors a five gallon carboy of settled water was returned to the laboratory on 1/3/77 and allowed to stand in the dark for a 21 day period. At random time intervals the carboy was shaken and samples removed. The aliquots removed were immediately run for its potential to form THM, that is, a THMPT was completed. Table 8 lists the data collected in this preliminary assessment. For reason(s) which cannot be explained from this simple study, the amount of $CHCl_3$ appears to have increased during the first 14 days of storage after which a marked decrease occurred. In contrast, the levels of $CHCl_2Br$ formed remained relatively constant during the entire duration of the 21 day experiment. Further study is needed to verify the data found for $CHCl_3$ and to better understand the nature of precursor compounds.

Organic Carbon Content

A number of investigators have studied the influence of organic matter content, both naturally occurring and synthetically prepared solutions, on the formation of THM. Stevens (1976) demonstrated that increased humic acid concentrations yielded higher levels of total THM. Both Rook (1975) and Hoehn (1977) found similar trends specifically for chloroform. A total THM versus NVTOC correlation was published by Symons (1976) as part of the National Reconnaissance for Halogenated Organics. A positive correlation

TABLE 8

STABILITY OF PRECURSORS IN OHIO RIVER WATER

Storage Time Prior to Start of THMPT (days)	THMPT, μg/l $CHCl_3$	THMPT, μg/l $CHCl_2Br$
0	45	14
7	54	14
14	65	16
21	43	17

was found between total THM and NVTOC.

Treatment Chemicals

A variety of chemicals may be used for the purification of surface waters. Some of these chemicals were tested for their ability to react with chlorine to form trihalomethanes. That is, the research team considered the possibility that the THM in drinking water resulted from a reaction of chlorine with any of the other chemicals used (or an impurity in one of the chemicals used). After reviewing the data reported in Table 9 and other information, it is concluded that none of the chemicals tested (other than chlorine) resulted in a significant amount of THM production when added in the concentration range normally dosed. As such, it is concluded that the level of THM in chlorinated drinking waters results primarily from chlorine reacting with precursors already present in natural waters.

Suspended Solids (Turbidity) and Particle Size Breakdown

The influence of suspended and colloidal solids on the formation of THM from untreated surface waters has been reported by others. Stevens (1975) reported an 85-90% reduction in chloroform potential via gravity sedimentation. In contrast, Symons (1976) has documented a study in which only a 15% reduction in the potential to form $CHCl_3$ was recorded in a pilot water treatment plant. From a routine monitoring program on precursor levels in untreated Ohio River water (as part of this investigation) it was found that, on the average, about 20% of the $CHCl_3$ potential was associated with solids that were removeable via centrifugation. This average represents the difference between centrifuged and non-centrifuged THMPT completed on 14 different water samples. The observed range was 0-36%. In summary, a majority of the potential to form chloroform appeared to be associated with very fine colloidal and/or dissolved matter.

TABLE 9

EVALUATION OF CHEMICALS USED AT WATER TREATMENT PLANTS FOR THEIR POTENTIAL TO FORM CHLOROFORM UPON CHLORINATION

Laboratory Prepared Solutions[a]	Caustic Added	pH Value		Chlorine Residual			Trihalomethane Potential[e], μg/l	
		Start Incubation	End Incubation	Chlorine Dose	Start Incubation	End Incubation	$CHCl_3$	$CHCl_3$ Adjusted
Blank[f]	0.0	5.7	----	0.0	0.0	---	3	--
Blank[f]	0.0	4.5	4.4	5.0	5.0	3.2	5	2
NaOH	40[b]	11.1	11.0	5.0	---[d]	3.1	31	28
Lime	27[c]	11.2	11.0	5.0	---[d]	3.1	29	26
Lime, Alum	27[c]	11.1	11.0	5.0	---[d]	3.1	19	16
Lime, Polymer	27[c]	11.1	11.1	5.0	---[d]	3.0	28	25
Lime, Na_2CO_3	27[c]	11.1	11.0	5.0	---[d]	3.0	17	14
Lime, Alum, Polymer, Na_2CO_3	27[c]	10.9	10.9	5.0	---[d]	2.5	26	23
Lime, Na_2FSiO_2	27[c]	11.1	11.0	5.0	---[d]	2.7	26	23

a - Dosages:
Lime = 27 mg/l
NaOH = 40 mg/l
Polymer = 0.2 mg/l
Na_2CO_3 = 10.9 mg/l
Na_2FSiO_2 = 1.45 mg/l

b - 40 mg/l of reagent grade sodium hydroxide used for pH adjustment.

c - 27 mg/l of commercial grade lime used for pH adjustment.

d - All succeeding samples assumed to be 5.0 mg/l.

e - Samples incubated for 24 hours in the dark at room temperature.

f - Distilled water only.

To further explore this topic, Ohio River water (collected on 11/4/77) was treated in three different ways and analyzed subsequently for its ability to form THM. In this manner, the association of the $CHCl_3$ and total THM potential with particle size distribution could be derived. Standard THMPT were run on the following waters: (a) untreated Ohio River water; (b) settled Ohio River water; (c) centrifuged Ohio River water; and (d) chemically coagulated settled Ohio River water. A 24 hour settling time was used to obtain the settled Ohio River fraction. Centrifugation was done at 10,000 RPM for 12 minutes. Both alum and polymer were used to coagulate settled Ohio River water. Dosages were 100 and 5 mg/l, respectively. A Phipps and Bird stirrer was used to simulate coagulation with 3 minute period of rapid mixing, 15 minute period of slow mixing and a settling time of 1 hour. Tables 10 and 11 list the data collected from this bench-scale study. It is evident that the brominated species were not dependent upon the degree of treatment, whereas the amount of $CHCl_3$ and total THM formed were certainly influenced by the extent of treatment. For example, the $CHCl_3$ potential of untreated Ohio River water was reduced during gravity settling by only 10%, whereas coagulated settled water exhibited a 45% reduction. Similar trends were found for total THM with reductions of 8 and 39%, respectively.

The data just presented in Tables 10 and 11 was reorganized in order to illustrate the association of $CHCl_3$ and total THM potentials with particle size classification. Table 12 shows this breakdown and illustrates that as much as 85% of the potential to form THM was associated with fine colloidal and dissolved fractions. Of this 85% associated with essentially dissolved matter, about 25-35% was removed by chemical coagulation, flocculation, and sedimentation. Filtration prior to the initiation of the THMPT would be expected to further increase the observed percentage that

TABLE 10

LISTING OF DATA COLLECTED IN THE PARTICLE SIZE DISTRIBUTION EXPERIMENT

Type of Treatment/Water	NVTOC (mg/l)	Turbidity (NTU)	Chlorine Demand (mg/l)	Concentration of Trihalomethanes From THMPT, μg/l			
				$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	Total
Raw Water[a] - No Treatment	11.5	7.8	6.5	303	53	19	375
Settled Raw Water	11.9	4.8	5.0	273	52	19	344
Centrifuged Raw Water	9.5	1.4	6.8	262	43	15	320
Settled and Coagulated Raw Water[b]	8.2	1.0	6.0	167	44	19	230

a - Raw water collected on 11/4/77
b - 100 mg/l of alum and 5 mg/l polymer

TABLE 11

EFFICIENCY OF VARIOUS TREATMENT STEPS IN REDUCING NVTOC, TURBIDITY AND TRIHALOMETHANES

Type of Treatment (Type of Water)	Percent Reduction in Comparison to Raw Water (%)					
			Trihalomethane Potential			
	NVTOC	Turbidity	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	Total
Raw Water - No Treatment	-0-	-0-	-0-	-0-	-0-	-0-
Settled Raw Water	0.0	38.5	9.9	1.9	0.0	8.3
Centrifuged Raw Water	17.4	82.1	13.5	18.9	21.1	14.7
Settled and Coagulated Raw Water	28.7	87.2	44.9	17.0	0.0	38.7

TABLE 12

PERCENT BREAKDOWN OF SEVERAL WATER QUALITY PARAMETERS BY PARTICLE SIZE CLASSIFICATION

Size Range / Parameter	Suspended Solids		Fine Colloidal + Dissolved Solids
	Setteable	Non-Setteable	
$CHCl_3$ Potential	9.9	3.6	86.5
Total THM Potential	8.3	6.4	85.3
NVTOC	0.0	17.4	82.6
Turbidity	38.5	43.6	17.9

was removable via good coagulation practices.

Summary

Based upon the information just described it is certain that the levels of THM, especially $CHCl_3$, are dependent upon the chlorination practice employed at conventional water treatment plants and the environmental conditions present during chlorination. Water temperature is obviously a predominant factor in defining the amount of $CHCl_3$ formed. Particulate matter also has an enhancing effect, although certainly not as pronounced as water temperature. The NVTOC content of surface waters is probably also a contributing factor in the formation of THM although the exact impact of NVTOC remains to be systematically quantified. Finally, enhanced pH values in the presence of free chlorine greatly stimulates the production of $CHCl_3$ and total THM.

In summary, several environmental factors control the level to which THM are produced. The research results described herein provide a suitable, although certainly not perfect, data-base for extrapolating the qualitative effects of modifications to environmental conditions (during water treatment) upon expected THM levels in drinking waters.

SURVEY OF TRIHALOMETHANE LEVELS AT FIFTEEN WATER UTILITIES IN KENTUCKY

Plant Selection

Within the Commonwealth of Kentucky, there are 261 water treatment plants classified as municipally owned water utilities. Of these water companies, 158 draw their raw water from surface waters such as streams, rivers, and lakes. The remaining 103 utilities have wells which pump ground water from various aquifers throughout the state. The sampling of each of these 261 water treatment plants was not practical in conjunction with this project. Therefore, a manageable portion of this entire group was selected. Every effort was made to represent a statistically significant sample of the state's population. To accomplish this, a histogram was prepared to show the distribution of surface water plants among different ranges of daily production (Figure 1). A second histogram was prepared showing the population among the different ranges of plant production (Figure 2). Inspection of Figure 2 revealed that approximately 70% of Kentucky's population that is served by municipally owned water treatment plants uses water treated by utilities whose capacity ranges from 5 to 180 MGD. As shown in Figure 1, this range included 15 plants. By the extension of this range down to $\geq$ 2 MGD, seventeen additional plants are included. This total of 32 municipal water treatment plants represents approximately 80% of Kentucky's population (Figure 2).

In similar fashion, a set of histograms was prepared to determine the range of production capacity which would comprise a major portion of the state's populace served by municipally owned water utilities that use ground water as a source of supply. Figures 3 and 4 illustrate that 16 water plants of 1 or more MGD capacity provide for about 60% of the population supplied by municipal ground water treatment plants.

All of the plants with productions $\geq$ 1 MGD were then located on a map of Kentucky to illustrate their geographical distribution. To insure only reasonable travel expenses, the most distant plants (from Louisville) were eliminated. Then, to insure that the final plant selection was representative of a broad cross section of treatment practices, the remaining plants were grouped according to treatment schemes. Certain water treatment plants within the larger groups were eliminated to avoid excessive duplication.

Through a lengthy process of postal and phone correspondence, a final list of 15 water treatment plants was selected. Each local water superintendent was guaranteed anonymity of results in exchange for their full cooperation

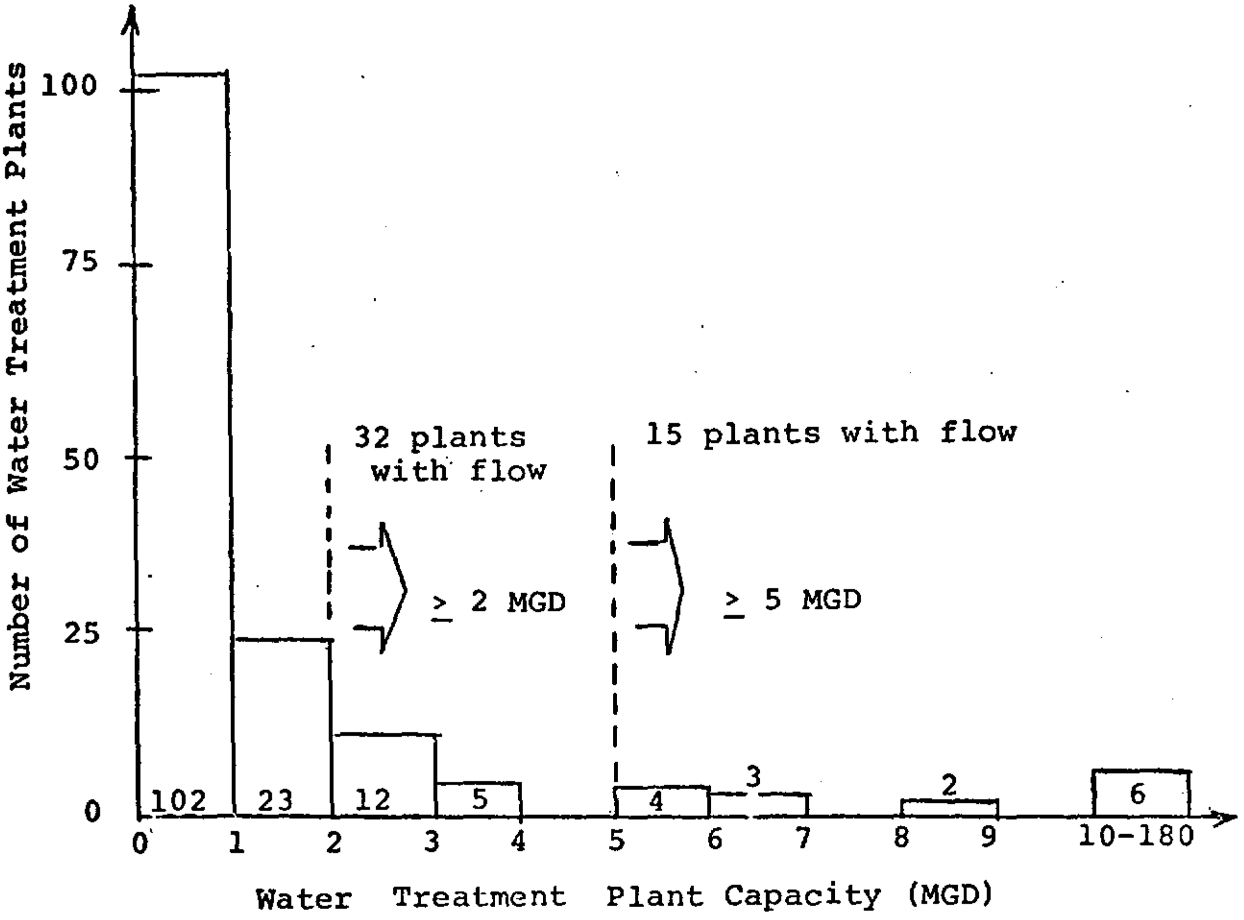

Figure 1 - Histogram of the Number of Water Treatment Plants Versus Production Capacity for Surface Water Supplies.

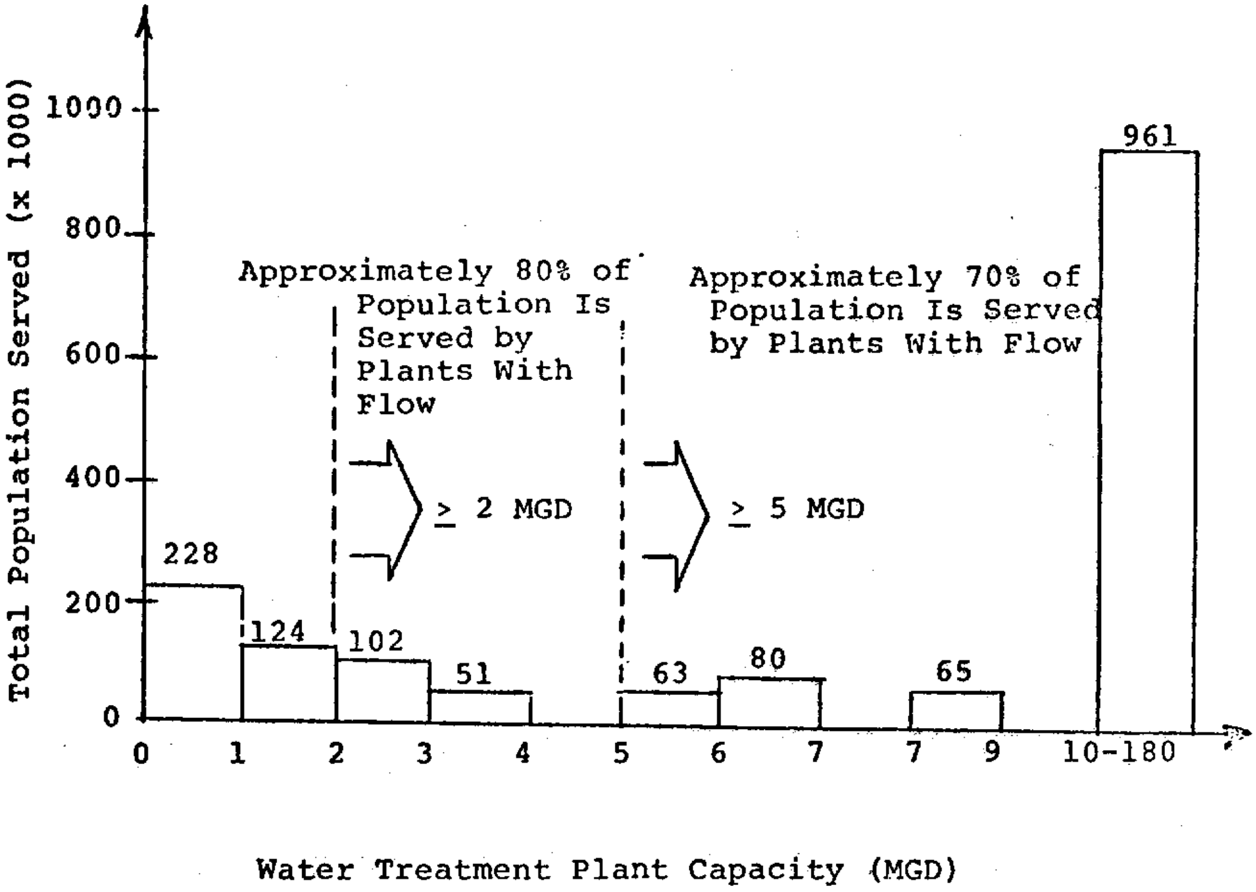

Figure 2 - Histogram of the Population Served Versus Production Capacity for Surface Water Supplies (Total Population Served = 1,674,000).

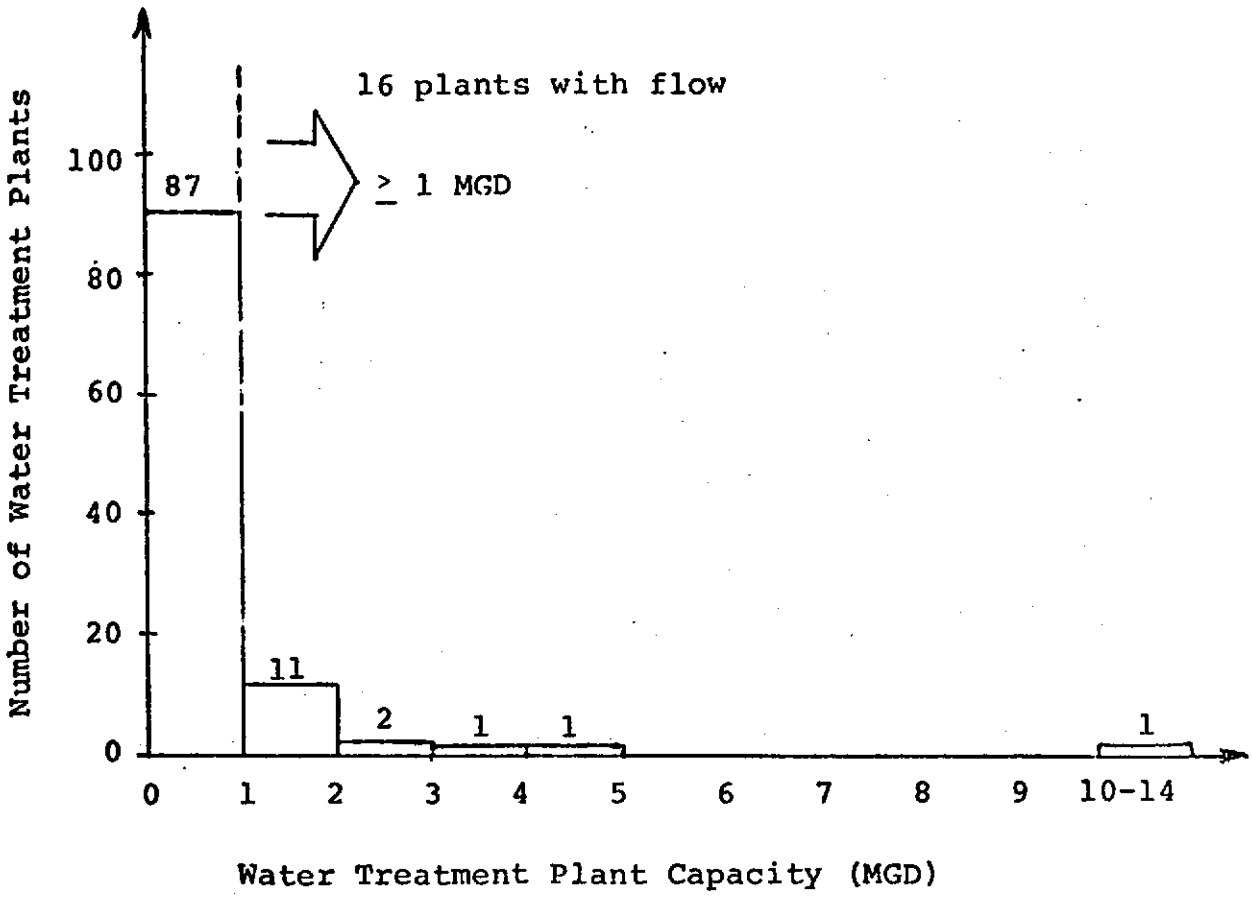

Figure 3 - Histogram of the Number of Water Treatment Plants Versus Production Capacity for Ground Water Supplies.

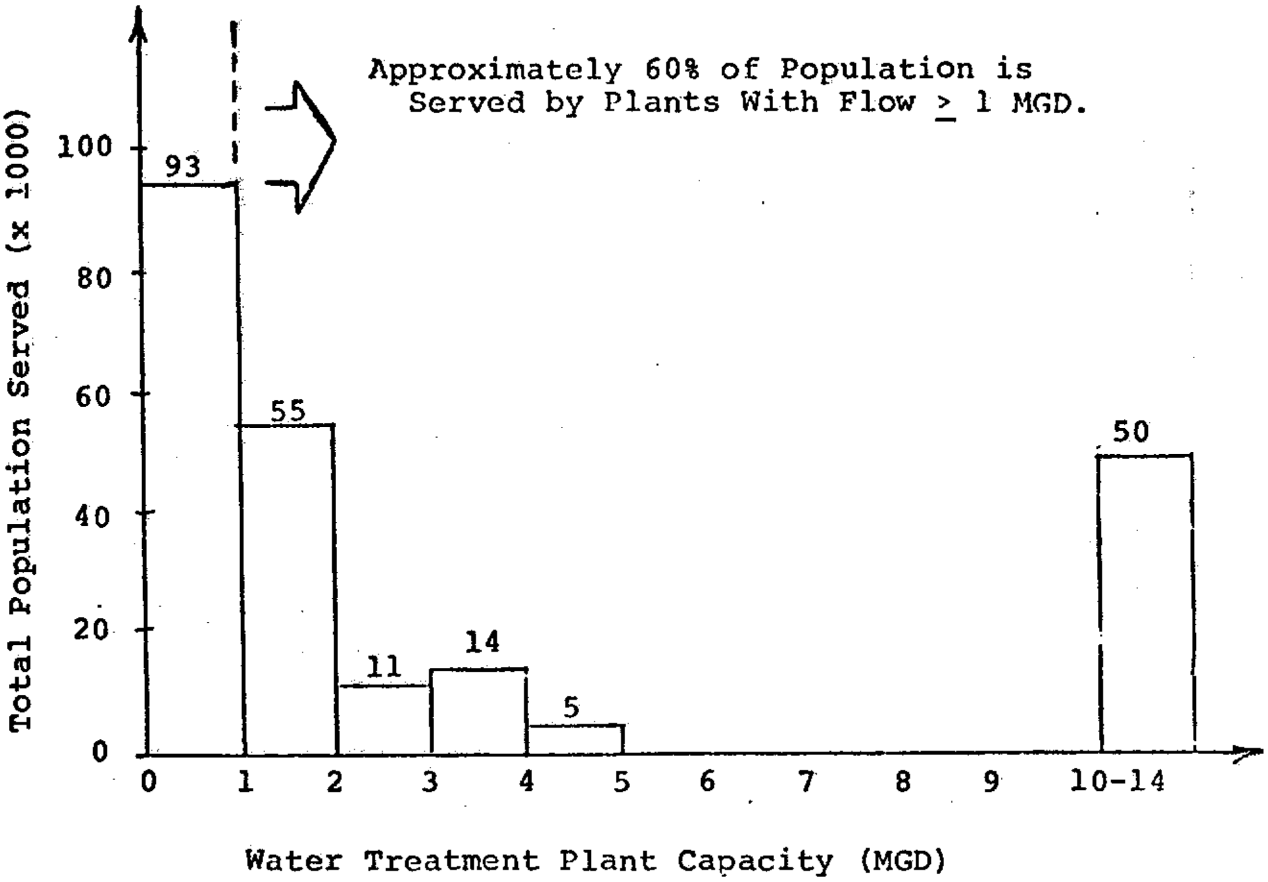

Figure 4 - Histogram of the Population Served Versus Production Capacity for Groundwater Supplies (Total Population Served = 227,300).

with the study (Appendix A).

Sampling Procedure

It was important to record sufficient supplementary data for each utility that was sampled so that the THM results could be interpreted meaningfully. To allow for rapid and complete data entry, three different forms were prepared and duplicated. Fifteen copies were made of each of the following: (a) water utility questionnaire; (b) treatment schematic; and (c) physical/chemical parameters. The water utility questionnaire was completed via an interview with the resident water superintendent. The first part of the questionnaire dealt with the official title of the water utility and the area and population served. The treatment plant's average daily production (MGD), raw water source, and average daily chlorine residual maintained in the clearwell were also included within this first section. The remainder of the questionnaire was a little more subjective in nature. This consisted of two questions related to the needs for future improvements and/or expansion for: (a) the water treatment plant proper; and (b) the distribution system. The answers to these questions gave an insight into the probabilities of future expansion.

The second form contained 10 separate subsections representing the different unit operations commonly found at water purification facilities. Information about basin size, and other specifications was placed in the appropriate subsection. Also, a list of chemicals used in each operation along with the daily dosages was prepared. As mentioned earlier in this section, data on treatment operations are instrumental in interpreting the results of THM analysis. The coagulant and disinfectant dosages were expressed in units of mg/l and listed for each of the water companies (Table 13).

The third and final data sheet was used to record the measurements taken both on site and back at the laboratory.

TABLE 13

SUMMARY OF WATER QUALITY ANALYSES PERFORMED AS PART OF THE STATE THM SURVEY

Water Utility			THM Levels[a] (µg/l)				Physical/Chem. Parameters[c]				Chemical Dosages (mg/l)				
											Chlorine				
Plant Number	Plant Size (MGD)	Raw Water Source	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	TTHM[b]	pH	Temp (°C)	Cl_2 Res (mg/l)	TOC (mg/l)	Pre	Post	Total	Alum	Lime
1	1.7	Ohio River Alluvium	TR	TR	TR	<15	7.7	19	1.2	2.0	---	---	1.8	----	----
2	0.95	Ohio River Alluvium	TR	TR	TR	<15	7.2	17	0.7	---	---	---	0.7	----	----
3	9.3	Med. River, Trib., of Ohio	55	5	ND	60	7.2	25	2.7	---	3.6	1.4	5.0	22.7	8.5
4	9.5	Ohio River	45	15	TR	>60	7.9	26	>3.0	3.2	5.3[d]	2.1	7.4	42.4	35.2
5	9.0	Ohio River	40	10	TR	>50	7.6	26	1.9	1.7	4.7	0.5	5.2	18.0	3.3
6	2.5	Long, Narrow Impoundment, Shallow	130	10	ND	140*	7.9	24	1.4	5.4	4.8	1.4	6.2	26.4	14.4
7	1.2	Med. Size Creek, Somewhat Turbid.	50	15	TR	65	7.6	27	2.6	5.1	10.0	2.5	12.5	40.0	15.0
8	1.1	Small Stream-Fed Lake	60	10	TR	>70	7.1	27	1.6	4.4	4.2	1.1	5.3	37.2	17.0
9	2.0	Ohio River Alluvium (well)	TR	TR	TR	<15	8.2	17	0.6	2.1	2.7	1.8	4.5	4.5	39.0
10	1.5	Med. Size Spring Into Small Reservoir	20	15	TR	>35	7.3	21	1.4	3.0	2.4	1.6	2.0[e]	24.3	18.2
11	1.7	Creek-Fed Med. Size Lake	85	10	ND	95*	7.7	27	>3.0	7.5	10.6	1.4	12.0	42.4	21.2
12	6.0	Med. Size River Highly Turbid.	75	15	ND	90*	7.2	26	2.3	7.1	4.7	1.6	6.3	Occas.	Polymer
13	1.0	Med. Size River Highly Turbid.	40	10	ND	50	7.5	25	1.9	5.0	4.0	1.9	5.9	78.0	13.0
14	3.3	Large Lake	100	10	ND	110*	7.9	27	1.4	5.4	3.9	10.2	14.1	Occas.	Occas.
15	180.0	Ohio River	80	10	TR	>90*	8.5	18	1.4	4.3	4.2	1.0	5.2	12.0	14.4

a - Finished water, ND = not detected, TR = Trace <5.
b - Total trihalomethanes.
c - Finished Water Values.
d - Partial ClO_2 dosage.
e - Pre-Chlorination rarely used with post-chlorination, average value given.

Whereas the temperature (raw and finished) and chlorine residual (finished only) were performed during the site visitation, 300 ml bottles were filled for later analysis of NVTOC levels (raw and finished). Duplicate samples were taken in sealed serum bottles for both raw and finished water trihalomethane content. The results of these physical and/or chemical analyses are reported for each of the fifteen utilities in Table 13.

Discussion of Results

In as much as they are similar studies, this survey was modeled after the EPA National Organics Reconnaissance Survey (NORS) of halogenated organics. The similarity applies to its purpose as well as its format. Therefore this state survey, like the NORS study, seeks to establish a data base of THM levels as affected by different treatment operations as well as environmental conditions. This, as opposed to providing plant-scale data to substantiate a number of research hypotheses, would obviously require more than a single grab sample. Nevertheless, the results from this limited survey suggest several generalizations.

As one instance, the chlorine demand (dose minus residual) was plotted in the NORS study versus total THM to yield a positive correlation. It has been postulated (Symons, 1975) that a measure of precursor utilization may be a relatively constant fraction of the free chlorine uptake (Cl_2 demand). Therefore, the finished water THM levels should follow the chlorine demand assuming that chlorine is in excess and that other environmental factors remain constant. When the clorine demand was plotted versus TTHM for the fifteen water utilities surveyed in the present study, a modest positive correlation was observed ($R = 0.067$).

Taking into account the influence of total chlorine dose, the single most influential factor remaining was the source and quality of raw water supply. Water sources which contain low concentrations of THM precursors will obviously lead to a reduced formation of THM. Consequently, those utilities which use ground water (plant numbers 1, 2, 9 and 10) were found to exhibit the lowest levels of finished water THM. In contrast, plant numbers 6 and 12 (moderate Cl_2 dosages) drew from highly turbid and/or colored waters. Research on the origin of THM precursors points to surface runoff containing decayed materials (leached from humis). In the case of plant number 6 a shallow impoundment is used as a raw water source and is subject to a great deal of agricultural runoff (source of precursor material). Therefore, it is not surprising to note that the chloroform level for plant number 6 was 130 μg/l. Unless provisions can be made to draw from an alternate water body, little can be done to reduce the inevitable THM formation due to disinfection. Perhaps a shift in the point of pre-chlorination to after clarification could reduce the THM somewhat. Similarly, plant number 12 must contend with a precursor-laden raw water source, but in this case, the source is a highly turbid river. The large quantities of silt and other particulate matter in this water supply presumedly results from soil erosion. Frequently, precursors associate with particulate and colloidal material. Consequently, this river carries high levels of precursors which later form THM upon chlorination at the water treatment plant (≈75 μg/l). Again, to reduce the final THM concentrations at plant 12 pre-chlorination should be located after the majority of the suspended solids and colloids have been removed (i.e., at the head of the sand filters).

From the data listed in Table 13 it is obvious that ground water supplies yielded lower THM levels than surface water supplies. Presumedly, the trend results due to the lower content of precursors in ground water supplies. However, the potential beneficial effects of lower chlorine dosages, shorter contact times, lower temperatures, absence of suspended solids and other similar factors associated with ground waters cannot be completely overlooked. Unfortunately, most of the water utilities in Kentucky that currently use surface water supplies cannot switch to a ground water supply because the latter resource is unavailable in sufficient supply to meet current demands. As such, these water treatment plants must utilize in-plant modifications and/or new treatment systems to reduce the level of THM to acceptable levels. A brief review of the total THM data in Table 13 shows that five of the twelve surface water supply plants surveyed had levels of THM either at or above EPA's recently promulgated interim standard.

BENCH-SCALE TREATMENT EXPERIMENTS

The research team evaluated in the laboratory several unit treatment operations. The overall goal of these experiments was to define the efficiency of each treatment operation in the removal of trihalomethanes and/or precursor compounds. Significant results from these studies are described herein. A more complete description of these experiments will be contained in the Master of Engineering thesis yet to be prepared by the graduate students performing these experiments.

Simulated Treatment Scheme Studies

A series of experiments were completed to determine the general effectiveness of various treatment processes and treatment schemes for the removal of precursors. Because of the design of these studies, information can also be derived concerning the potential benefit(s) of moving the point of pre-chlorination back further into the treatment system. In essence, these experiments consisted of treating Ohio River water via a variety of treatment processes. After each treatment step an aliquot of water was removed and a THMPT completed. In this manner both the cumulative and incremental effectiveness of treatment systems in reducing the $CHCl_3$ potential was assessed.

Four treatment plants were selected for simulation and are illustrated in Figure 5. As shown these simulated treatment plants included collectively the following unit operation: pre-sedimentation, chemical coagulation, precipitive softening, ion-exchange softening, rapid sand filtration, granular activated carbon (GAC) filtration and powdered activated carbon (PAC) addition in conjunction with chemical coagulation. The dosages of chemicals were 12 mg/l of alum, 18 mg/l of lime, 11 mg/l of soda ash and 8 mg/l of PAC. The location in the treatment schemes where these chemicals were dosed is indicated in Figure 5. Fixed beds of granular activated carbon and cationic exchange resin were used. Each filter was 3.0 feet in depth and was operated in a continuous downflow mode at a conventional surface loading rate of about 2.0 gpm/ft^2.

Results from the THMPT are listed in Table 14 in which the $CHCl_3$ potential is reported in both μg/l and percent reduction (from the THMPT identified for raw Ohio River water). Several observations can be made concerning the reduction in $CHCl_3$ potential. First, the chloroform potential of Ohio River water was reduced by about 34% in a treatment system consisting of pre-sedimentation, chemical coagulation, precipitive softening and filtration. That is, the chloroform potential of filtered water (i.e., water that was settled, chemically coagulated, precipitive softened, and filtered) was only 66% (142/216) of that found for untreated Ohio River water (216 μg/l). This information is listed in Table 14 under treatment experiment I. It should be noted that the THMPT reported for coagulated water (Raw - Set - Coag entry in Table 14) was higher than raw water and is presumed to be an eronious reading since more detailed studies on chemical coagulation clearly indicate that such an increase should not occur. As such, the entry for coagulated water was not used in calculating the percent reductions of $CHCl_3$ potential shown in Table 14.

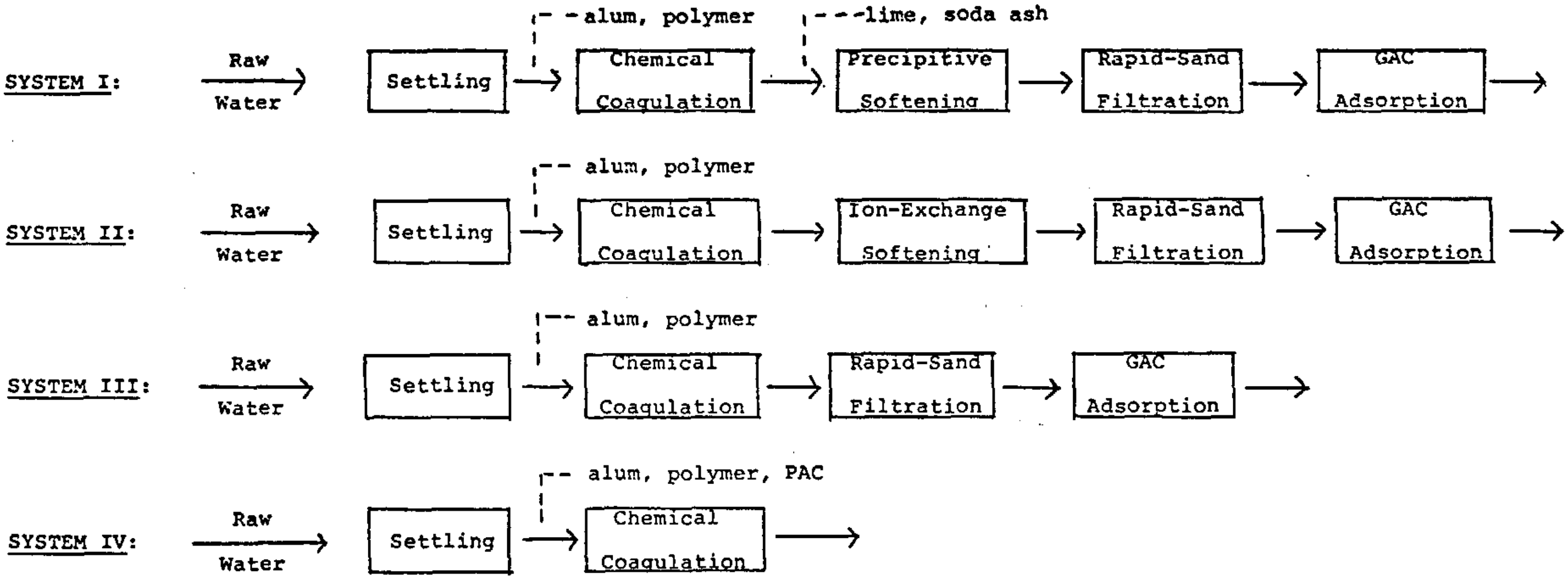

Figure 5 - Flow Diagrams of Simulated Treatment Plants.

TABLE 14

REDUCTION IN THE POTENTIAL TO FORM CHLOROFORM UPON SUBSEQUENT CHLORINATION FOR SEVERAL TREATMENT SCHEMES

Treatment Experiment	Extent of Treatment[a]	Chloroform Potential		
		(µg/l)	% Reduction	Cumulative % Reduction
I	a) RAW	216	----	----
	b) RAW, SET,	202	6.5	6.5
	c) RAW, SET, COAG,	238	0.0	6.5
	d) RAW, SET, COAG, PS,	180	10.2	16.7
	e) RAW, SET, COAG, PS, RSF	142	17.6	34.3
	f) RAW, SET, COAG, PS, RSF, GAC	9	61.6	95.9
II	a) RAW	216	----	----
	b) RAW, SET,	202	6.5	6.5
	c) RAW, SET, COAG,	238	0.0	6.5
	d) RAW, SET, COAG, IE	202	0.0	6.5
	e) RAW, SET, COAG, IE, RSF	160	19.4	25.9
	f) RAW, SET, COAG, IE, RSF, GAC	29	60.6	86.5
III	a) RAW	216	----	----
	b) RAW, SET,	202	6.5	6.5
	c) RAW, SET, COAG,	238	0.0	6.5
	d) RAW, SET, COAG, RSF	153	22.7	29.2
	e) RAW, SET, COAG, RSF, GAC	26	58.8	88.0
IV	a) RAW	216	----	----
	b) RAW, SET,	202	6.5	6.5
	c) RAW, SET, COAG-PAC	194	3.7	10.2

a - Abbreviations are as follows: RAW = Untreated Water; SET = Settled Water; COAG = Chemical Coagulation; PS = Precipitative Softening; RSF = Rapid Sand Filtration; GAC = Granular Activated Carbon; IE = Ion Exchange Softening; and PAC = Powdered Activated Carbon.

It is important to note that sand filtration was apparently very effective in reducing $CHCl_3$ potential. Both coagulated and softened waters had relatively high turbidities (2.6 and 4.6 turbidity units). The lab scale sand filter appeared to do a good job in removing the floc carried over from chemical coagulation and precipitive softening. Presumedly, the removal of this floc resulted in the lower $CHCl_3$ potential in filtered water. It should be emphasized that the 34% cumulative reduction in the $CHCl_3$ potential was obtained for treatment conditions that may not be optimal for the removal of precursors. Presumedly, this percentage could be increased further by optimizing each unit operation (coagulation, softening, and filtration). An inherent assumption in this evaluation is that in actual practice chlorination would not be practiced until after filtration.

The most pronounced reductions in $CHCl_3$ potential were obtained with the filter of granular activated carbon. In each of the first three treatment experiments the GAC filter accounted for approximately two-thirds of the observed reduction in total $CHCl_3$ potential. More importantly the GAC filter was able to remove precursors present in Ohio River water and thereby lower the $CHCl_3$ potential into the 10-30 μg/l range. It should be stressed that the environmental conditions under which the THMPT was completed are extremely favorable for the formation of $CHCl_3$. As such, it is unlikely that the effluent from a fresh GAC filter would upon chlorination have $CHCl_3$ levels as high as 30 μg/l. In summary, granular activated carbon was capable of significantly reducing the level of precursors and, therefore, a marked reduction in $CHCl_3$ potential was observed. In contrast, the addition of an 8 mg/l dosage of powdered activated carbon was ineffective in reducing the chloroform potential (See treatment scheme IV in Table 14).

Chemical Coagulation

Experiments were initiated to determine more precisely the efficiency of chemical coagulation in removing precursors present in surface waters. These studies were completed with one liter water samples using a Phipps & Bird stirrer which is capable of coagulating six samples simultaneously. By adjusting the rotation speed of the paddles the unit operations of rapid mixing (coagulation), slow mixing (flocculation), and settling (gravity sedimentation) were simulated. Again, the experimental procedure was to chemically coagulate Ohio River water under a variety of experimental conditions (i.e., pH values, alum and polymer dosages, etc.) and then to subject aliquots of the treated waters to THM potential tests. Two different potential tests were completed on each aliquot. The "standard" THMPT (See page 9) was run both with and without adjustment of the initial pH value into the 10.5-11.2 range. The THMPT with pH adjustment provides data on the maximum potential to produce $CHCl_3$ and total THM, whereas the THMPT run without initial pH value adjustment gives a more representative indication of THM concentrations expected under plant operating conditions.

Variation in the potential to form THM under a variety of alum and polymer dosages is shown in Table 15. It is evident from Table 15 that both alum and polymer are capable of reducing the potential to form THM, although the magnitude of the effectiveness of each coagulant varies with dosage and THM species. For example, reductions in the $CHCl_3$ potential (with pH adjustment) that resulted when the alum dosage was increased from 0-20 and 0-100 mg/l were 18 and 48%, respectively. Corresponding reductions in the total THM potential for these same dosages were 12 and 40%, respectively. Thus, it appears that large dosages of alum alone would be required to enhance significant removals of precursors during the chemical coagulation process. It is significant to note that the data reported in Table 15 only

TABLE 15

INFLUENCE OF CHEMICAL COAGULATION ON THE POTENTIAL TO SUBSEQUENTLY FORM TRIHALOMETHANES[a]

Dosage of Chemicals (mg/l)		Trihalomethane Potential, µg/l							
alum	polymer	$CHCl_3$[b]	$CHCl_3$[c]	$CHCl_2Br$[b]	$CHCl_2Br$[c]	$CHClBr_2$[b]	$CHClBr_2$[c]	Total THM[b]	Total THM[c]
0.0	0.0	125	81	5	31	1	7	131	119
5.0	0.0	124	81	12	32	6	7	142	120
20.0	0.0	102	57	12	26	6	7	120	90
100.0	0.0	65	25	13	16	6	6	84	47
0.0	0.0	125	81	5	31	1	7	131	119
0.0	0.25	100	68	8	20	3	8	111	96
0.0	1.00	90	77	8	24	3	9	101	110
0.0	5.00	95	76	8	21	3	9	106	106
0.0	0.0	125	81	5	31	1	7	131	119
5.0	0.25	86	88	15	28	9	6	110	122
20.0	1.00	70	62	16	25	10	5	96	90
100.0	5.00	53	28	17	16	11	3	81	47

a - Coagulated at a neutral pH value.
b - From a standard THMPT with an initial pH adjustment into 10.5-11 range.
c - From a standard THMPT except no initial pH adjustment.

describes the chemical coagulation process and not the effect of chemical coagulation followed by granular filtration. Based upon data previously reported in Table 14 (on filtration), it is reasonable to expect that the combined influence of coagulation, flocculation, sedimentation and filtration to be substantially more efficient for precursor removal than simply the chemical coagulation process for reasons mentioned previously.

Data is also presented in Table 15 for coagulation with polymer only and for alum/polymer coagulation. As shown, coagulation with polymer alone is not as effective in removing precursors in comparison to coagulation with alum alone. However, the joint use of alum and polymer does appear to enhance somewhat the removal of precursors above and beyond that accomplished by either alum or polymer alone. For example, data for the THMPT conducted with pH adjustment show the following percent reductions, in comparison to untreated Ohio River water:

Coagulant	$CHCl_3$ Potential	Total THM Potential
alum (20 mg/l)	18	12
polymer (1.0 mg/l)	28	24
alum and polymer (20 and 1.0 mg/l)	44	33

The influence of the pH value under which coagulation occurs was also studied in regards to removal of precursors. Table 16 lists the results from these THMPT tests. In all of these coagulation studies the dosages of alum and polymer were kept constant at 12.1 and 0.2 mg/l, respectively. Results for the THMPT with pH adjustment suggest that optimum precursor removal occurs over the pH 6-8 range, although the observed results for the alkaline range were only about 6-8% higher than those observed in the neutral range.

TABLE 16

REDUCTION IN THE POTENTIAL TO FORM TRIHALOMEHTANES VIA CHEMICAL COAGULATION AT VARIOUS pH VALUES[c]

pH Value During Coagulation	Trihalomethane Potential, µg/l							
	$CHCl_3$[a]	$CHCl_3$[b]	$CHCl_2Br$[a]	$CHCl_2Br$[b]	$CHClBr_2$[a]	$CHClBr_2$[b]	Total THM[a]	Total THM[b]
5.0	135	40	7	ND	1	ND	143	40
6.0	100	37	6	11	1	6	107	54
7.0	102	73	5	18	1	6	108	97
8.0	104	83	5	17	1	7	110	107
9.0	109	89	5	17	1	9	115	115
10.0	112	115	3	19	1	9	116	143

a - From a standard THMPT with an initial pH adjustment into 10.5-11.2 range.
b - From a standard THMPT except no initial pH adjustment was made.
c - Dosages of alum and polymer were 12.1 and 0.2 mg/l, respectively.

Coagulation in the acidic range, however, resulted in considerably higher potentials to form both $CHCl_3$ and total THM.

Powdered Activated Carbon (PAC) Adsorption

Results from preliminary studies (See Table 14) suggested that PAC was not effective for the removal of precursors at conventional dosages (i.e. 10 mg/l). A subsequent PAC experiment was completed to determine if THM precursors could be removed at higher carbon dosages. In this experiment, six one liter samples of Ohio River water were treated with varying amounts of Hydrodarco-HDB PAC under identical mixing conditions. The dosage of PAC was varied from 0-1,000 mg/l and mixing was provided by a Phipps & Bird stirrer operating at 100 RPM. After 30 minutes of contact with the PAC, the water samples were centrifuged to remove the adsorbent and suspended matter. Subsequently, each clarified water sample was subjected to a THMPT analysis with the results shown in Table 17. As shown, PAC dosages of 50 mg/l are required to obtain roughly a 50 percent reduction in the potential to form chloroform. Increasing the carbon dosage beyond 100 mg/l appears to have little incremental return for removing precursors. Further, it appears that as much as 20% of the THM precursors are non-adsorbable, at least by the adsorbent tested in this experiment.

The implementation of PAC for removing THM precursors from natural waters cannot be clearly elucidated from the single experiment just described. Additional studies should be completed to define optimum environmental conditions (of adsorbate, adsorbent and contacting methods) for the removal of THM precursors with PAC. Such a study was beyond the scope of this project. In summary, the data listed in Table 17 and reported elsewhere (Love, 1975) does illustrate that PAC can remove some, but certainly not all, of the THM precursors. PAC dosages considerably above those frequently used for taste and odor control may be required to effect significant precursor removals. As such, PAC adsorption is

TABLE 17

PRECURSOR REMOVAL VIA POWDERED ACTIVATED CARBON (PAC) ADSORPTION[a]

Dosage of PAC (mg/l)	Chloroform Potential[b] (μg/l)	(% Removal)
0	236	0
10	215	9
25	170	28
50	127	46
100	85	64
1,000	48	80

a - Hydrodarco HDB powdered activated carbon.

b - THMPT for chloroform only with initial pH adjustment prior to chlorination into the 10.5-11.2 range.

not a panaceia for the complete reduction of chloroform formation at water utilities. However, PAC may be appropriate in situations where only partial precursor removal is acceptable or for situations where intermittent THM problems occur. This may be especially true for small water utilities where simplicity in treatment operations is highly desirable.

Chlorine Dioxide and Ozone

A potential treatment modification that indicates promise towards the overall goal of chloroform reduction involves the use of ozone and possibly chlorine dioxide as a primary disinfectant instead of pre-chlorination. Addition of ozone or chlorine dioxide could occur to either raw, settled, coagulated and other waters and would then be followed by filtration and minimal post-chlorination. Symons (1975) has shown that neither ozone or chlorine dioxide react with precursors to form trihalomethanes. The use of chlorine dioxide at water utilities, however, may be limited by EPA to a maximum dosage of 1.0 mg/l due to potential health problems associated with chlorites. As such, the utilization of ozone as an alternative primary disinfectant in place of pre-chlorination appears to be favored at this time.

Bench-scale research with both chlorine dioxide and ozone have been completed in the principal investigators laboratory in conjunction with another project. Only a brief summary of the significant conclusions and observations from this work is included herein. The reader is referred to two recent articles which describe these results in more detail (Hubbs, 1976; and Zogorski, 1977).

The ability of ozone to chemically oxidize chloroform and other trihalomethanes was determined by Hubbs (1976). Neither chlorine or ozone were capable of oxidizing chloroform at conventional dosages (i.e. $\leq$ 5 mg/l). Presumedly, the oxidants reacted more readily with other matter present in natural waters. The effect of conventional dosages of chlorine and ozone on THM precursor levels has also been determined.

In essence, Hubbs (1977) found that the addition of ozone did reduce the potential of surface waters to subsequently form THM upon chlorination. This trend is illustrated in Table 18 which shows the influence of several ozone dosages to pre-settled Ohio River water on the potential to form chloroform. Mr. Hubbs cautioned, however, that the precursor removal accomplished by ozonation (in his experiment) was also attainable by good pre-sedimentation and coagulation practices. Thus, the addition of ozone to existing treatment facilities may not produce significant reductions in precursor levels, above and beyond THM precursor removals currently accomplished. This finding does not suggest that the use of ozone (or chlorine dioxide) when used as an alternative to pre-chlorination will be ineffective in reducing the levels of THM subsequently formed when the water is post-chlorinated. Rather, it simply denotes that ozonation was incapable of removing that fraction of precursors which are not removed by conventional treatment practices (pre-settling, chemical coagulation, precipitive softening, PAC adsorption, or sand filtration). The implication of course, is that some THM will form as a result of post-chlorination in water treatment schemes that utilize alternative pre-disinfectants. However, the level of THM formed in such schemes should be considerably less than water treatment schemes using both pre- and post-chlorination for reasons discussed previously (See pages 13 - 16).

Granular Activated Carbon (GAC) Adsorption

The use of GAC at water utilities is not widespread at present, although the applicability of GAC adsorption technology for reducing the level of organic matter from drinking water is well documented. A majority of the plant scale uses of GAC at water utilities in the U.S. has been for taste and odor problems. Considerably fewer utilities have installed GAC contactors for the removal of synthetic organic chemicals. Prior to 1975, essentially nothing was known

TABLE 18
(After Hubbs, 1976)
EFFECT OF OZONATION OF PRE-SETTLED OHIO RIVER WATER ON THE POTENTIAL TO FORM CHLOROFORM

Ozone Dosage (mg/l)	Chloroform Potential	
	µg/l	% Reduction[a]
0	50[b]	0
1	46	8
2	38	24
4	32	36
6	26	48
8	26	48

a - In comparison to the chloroform potential of un-ozonated settled water

b - Estimated value

concerning the removal of THM and THM precursors from drinking waters. The most recent interim primary regulations for the control of organic chemical contaminants in drinking water (Federal Register - February 9, 1978), however, has mandated considerably more interest in the usage of GAC at municipal water utilities. In fact, the new regulations may require the installation of GAC treatment at all water utilities serving a population greater than 75,000 people whose water source is subjected to possible contamination by synthetic organic chemicals. As such, many utilities will be evaluating GAC for the removal of both THM and synthetic organic chemicals.

Information was collected as part of this investigation on the efficiency of GAC for the removal of THM and THM precursors only. The effectiveness of GAC for the removal of the myriad of synthetic organic chemicals which might be present in a polluted surface or ground water supply was not envisioned as part of this investigation, although the necessity of conducting such research in light of EPA's recent regulations are clearly demonstrated.

A series of three distinct experiments were completed as part of this study to ascertain knowledge on the adsorption phenomena of THM and THM precursors by GAC. The specific goals of the adsorption experiments were: (a) define the approximate height of the mass transfer zone for the removal of trihalomethanes; (b) perform bench-scale column tests on various commercially available adsorbents to illustrate their relative performance in the removal of trihalomethanes and THM precursors in the trihalomethane formation reaction; and (c) field test GAC for trihalomethane, NVTOC, and precursor removal. Results collected to define the mass transfer properties of the THM-GAC system for a fixed-bed contactor have been reported elsewhere (Smith et al., 1977) and, therefore, only a brief summary will be presented herein. Eight adsorbents have also been tested on a side-by-side basis for their effectiveness in THM removal. Because of the significance of this information, details and associated results of this experiment is described herein. Finally, a field study of a GAC installation in Kentucky was made to gain insight into the performance of GAC in removing THM under plant-scale conditions. Results from this latter experiment are described in the next major section of this report.

Mass Transfer Parameters - Four brands of GAC were tested initially to gain insight into the performance of GAC in removing THM and THM precursors, and to obtain data on the mass transfer characteristics of the GAC-THM system. Briefly, these experiments consisted of passing water thru a fixed bed of GAC and recording the breakthrough of THM and precursors in the effluent from each column. The breakthrough curves were in turn used to calculate parameters which collectively describe the mass transfer properties of a GAC contactor. The reader is referred to the recent publication by Smith et al. for a more detailed description of these experiments.

Results from these preliminary studies demonstrate that chloroform and other trihalomethanes can be removed from water supplies via commercially available adsorbents. Each of the four brands of granular activated carbon that were tested were capable of decreasing the concentration of trihalomethanes below the limit of analytical detection.

The kinetics of adsorption of chloroform and other trihalomethanes by GAC in a fixed-bed contactor were rapid. As such, high levels of adsorptive efficiency are attainable in shallow beds of carbon. For example, adsorptive efficiency at initial breakthrough of 80-90% is expected for a 3.0 foot depth of granular carbon being operated at a conventional surface loading rate (i.e. 2 gpm/ft). A higher efficiency could presumedly be attained by increasing the depth of adsorbent, decreasing the surface loading rate and by otherwise optimizing the adsorptive properties of GAC for trihalomethanes.

Three characteristics of the mass transfer zone for the chloroform-activated carbon system were calculated. These parameters include: (a) the height of the mass transfer zone, H_{MTZ}; (b) the rate of movement of the mass transfer zone, R_{MTZ}; and (c) the fractional capacity of the adsorbent within the mass transfer zone, ϕ. Collectively, these three parameters describe the adsorbate-adsorbent interaction which occurs in a fixed-bed contactor. Table 19 contains data on these mass transfer parameters for three of the activated carbons tested in this study. These data are only applicable for the system studied. It is significant to note, however, that the height of the mass transfer zone was shallow (0.7-0.9 ft.) which indicates a rapid interaction between the adsorbent and adsorbate but fell in the 0.02-0.04 feet per day range. If applicable to field conditions, these data suggests that a 3 foot depth of granular activated carbon could effectively remove chloroform for a period of 6-15 weeks before regeneration would be necessary. In summary, the mass transfer characteristics of the THM-GAC systems are generally favorable with a shallow mass transfer zone and a high fractional capacity. The adsorptive capacity of GAC for the removal of THM in the microgram per liter range is low, in 0.05 - 0.2% by weigh range, which will be reflected in actual applications by the rapid exhaustion of shallow beds of this adsorbent.

<u>Evaluation of Eight Adsorbents</u> - A more detailed study on the removal of THM by GAC was completed during the summer of 1977. These tests were completed in the laboratory with the feed to each column being Louisville tap water. As such, the concentration of THM in the influent stream to each column varied from day to day in a manner similar to what

TABLE 19

MASS TRANSFER ZONE PARAMETERS FOR SEVERAL ADSORBENTS

Adsorbent	Characteristics of Mass Transfer Zone ϕ	 H_{MTZ} (ft)	 R_{MTZ} (ft/day)
Columibia LCK	0.5	0.7	0.04
Filtrasorb 400	0.4	0.9	0.03
Nuchar WV-W	0.6	0.8	0.02

might be expected under actual plant-scale conditions. Eight adsorbents were selected for testing, seven of which were brands of GAC. Table 20 shows the adsorbents tested and associated physical properties. As noted, adsorbents from a variety of suppliers and source materials were included in this evaluation.

The experimental design for this more comprehensive study is described in Table 21. This table lists the size, depth and amount of each adsorbent studies. Also described are the dimensions of the carbon columns, hydraulic parameters and mode of operation. The nature and frequency of samples collected to describe the performance of each adsorbent is given in Table 22. Each of the adsorbents in this study was specially prepared to avoid any possible air-binding problems and initial backwashing. The adsorbents were sifted to a 16 x 20 mesh size (except XE-340). Each adsorbent was then washed and dried to remove fines which might have otherwise clogged the column. Thereafter, approximately one-half meter of the pre-treated adsorbent was weighed. Before placing the adsorbent into its appropriate columns, the measured amount of adsorbent was boiled in deionized water to wet the pores of the adsorbent and to drive off trapped gases. The carbon slurries were allowed to cool to room temperature and then were carefully placed into the 2.54 cm diameter columns. Shortly thereafter a tap water line was connected to the eight columns and the experimental testing was commenced.

An extremely voluminous quantity of data was collected during the course of this experiment. Parameters listed in Table 22 were collected for both the influent and effluent of each column. From this information breakthrough curves were prepared for chloroform, bromodichloromethane, total THM, chlorine, NVTOC and THM precursors. The cumulative amount of these parameters adsorbed by each of the eight adsorbents was calculated at various volumes of water treated.

TABLE 20

PROPERTIES OF ADSORBENTS STUDIED[a]

TYPE OF CARBON	PURCHASED MESH SIZE	SOURCE MATERIAL	APPARENT DENSITY[b]	SURFACE AREA[c]
Filtrasorb 400	12 x 40	Lignite	0.40	1125[d]
Nuchar WV-W	12 x 40	Bituminous Coal	0.58	850
XE-340	20 x 50	Synthetic Carbonaceous Resin	0.60	400
Hydrocarco 1030	10 x 30	Lignite	0.37	650
Columbia LCK	12 x 28	Coal	0.46	1200
Nuchar WV-G	12 x 40	Bituminous Coal	0.44	1100
Barnebey-Cheney	12 x 30	Nut Shell	0.50	950[d]
Witco 950	8 x 30	Petroleum	0.55	1050[d]

a - Refer to Appendix B for further information.
b - Apparent density has units of gm/cc.
c - Surface area, reported by manufacturer, m^2/gm.
d - Average value.

TABLE 21

EXPERIMENTAL SETUP OF BENCH-SCALE GRANULAR ADSORPTION INVESTIGATION

EXPERIMENTAL PARAMETER	COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6	COLUMN 7	COLUMN 8
Type of Adsorbent	Filtrasorb 400	Witco 950	Nuchar WV-W	XE-340	Hydrocarco 1030	Columbia LCK	Nuchar WV-G	Barneby-Cheney
Size of Adsorbent (mesh)	16 x 20	16 x 20	16 x 20	16 x 20	16 x 20	16 x 20	16 x 20	16 x 20
Size of Adsorbent (mm)	1.0	1.0	1.0	0.6	1.0	1.0	1.0	1.0
Amount of Adsorbent (g)	111.7990	93.6667	119.2045	130.7500	89.2749	102.3760	94.4699	117.1716
Depth of Adsorbent (m)	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46
Column Diameter (cm)	2.54	2.54	2.54	2.54	2.54	2.54	2.54	2.54
Mode of Operation	Downflow Cont.	Downflow Cont.	Downflow Cont.	Downflow Cont.	Downflow Cont.	Downflow Cont.	Downflow Cont.	Downflow Cont.
Static Head (m)	1.33	1.33	1.33	1.33	1.33	1.33	1.33	1.33
Flow Rate (lpm/m^2)	172.26	172.26	172.26	172.26	172.26	172.26	172.26	172.26
Temperature (°C)	18-30	18-30	18-30	18-30	18-30	18-30	18-30	18-30
Surface Area (m^2/g)	1050-1200	1000-1100	850	400	650	1200	1100	900-1000
Avg. Surface Area/Volume (m^2/cm^3)	543	422	437	226	250	530	448	480

TABLE 22

SAMPLING PROGRAM FOR BENCH-SCALE GRANULAR ADSORPTION INVESTIGATIONS

PARAMETER	SAMPLE TYPE	FREQUENCY	REMARKS
NVTOC	Composite	Daily, M-F	60 ml/day
THMPT	Composite	Daily, M-F	60 ml/day
pH Value	Grab	Twice Weekly	-
Cl_2	Grab	Twice Weekly	-
Temperature	Grab	Daily	Inflow + One Effluent
Flowrate	-	Daily	Once Per Day
THM	Grab	3-4/Week Inflow	Duplicates
THM	Grab	Twice Weekly Effluents	-

The THM data was condensed still further with the results presented in Table 23. In essence, Table 23 contains most of the useful information derived from this study with respect to the THM adsorptive properties of these adsorbents. Included for each brand of adsorbent at three arbitrary breakpoints are: (a) the bed volumes passed; (b) the amount of $CHCl_3$ adsorbed; (c) the amount of $CHCl_3$ adsorbed per unit weight of adsorbent; and (d) the amount of $CHCl_3$ adsorbed per unit volume of adsorbent.

A new experimental adsorbent, XE-340, was included for evaluation in this study. This adsorbent has been designed specifically for the removal of small organic molecules, such as chloroform, and therefore may have certain advantages over GAC for the removal of trihalomethanes. As shown in Table 23, this adsorbent did not reach the 0.1 breakthrough point and, therefore, could not be compared directly with the other adsorbents tested. Pre-designed flowrate (See Table 21) could not be maintained thru the bed of XE-340 with the gravity-flow system used in this experiment. Based upon the information in Table 23, the adsorptive properties of the various brands of GAC were classified into three qualitative categories - fair, average and good. It should be emphasized that the data listed in Table 23 are for a single study of one water supply only. As such, it is conceivable for an adsorbent which is classified as "good" in this investigation to be classified as "average" or "fair" for another water source and vice versa. Until comprehensive testing of various brands of GAC is completed elsewhere, the transferability of the findings from this comparative evaluation to other water supplies should not be attempted unless tests are completed to justify such usage.

Both Filtrasorb 400 and Nuchar WV-G were classified in the fair category for removing chloroform from Louisville's drinking water. Both of the adsorbents reached 90% chloroform breakthrough about 4,000 bed volumes earlier than the

TABLE 23

SUMMARY OF THE ADSORPTIVE PROPERTIES OF SEVERAL ADSORBENTS FOR THE REMOVAL OF CHLOROFORM

Carbon Type	Breakthrough Point	Bed Volumes Treated[a]	Chloroform Adsorbed[b]	Chloroform Adsorbed / Weight Adsorbent[c]	Chloroform Adsorbed / Column Volume[d]
Filtrasorb 400	0.10	2,650	23.6	2.11×10^{-4}	98.3
	0.50	5,700	58.7	5.25×10^{-4}	245
	0.90	7,350	69.8	6.24×10^{-4}	291
Nuchar WV-G	0.10	2,300	18.7	1.98×10^{-4}	77.9
	0.50	4,150	32.3	3.42×10^{-4}	135
	0.90	7,200	51.5	5.45×10^{-4}	215
Nuchar WV-W	0.10	2,300	18.4	1.54×10^{-4}	76.7
	0.50	6,000	56.3	4.72×10^{-4}	235
	0.90	12,700	95.8	8.04×10^{-4}	399
Hydrodarco 1030	0.10	1,800	12.7	1.42×10^{-4}	52.9
	0.50	6,400	57.1	6.40×10^{-4}	238
	0.90	13,800	91.7	10.30×10^{-4}	382
Columbia LCK	0.10	3,000	26.5	2.59×10^{-4}	110
	0.50	6,200	64.5	6.30×10^{-4}	269
	0.90	11,500	92.4	9.02×10^{-4}	385
Witco 950	0.10	3,400	44.1	4.71×10^{-4}	184
	0.50	8,000	107.1	11.40×10^{-4}	446
	0.90	11,000	115.0	12.30×10^{-4}	479
Barnebey-Cheney PC-1	0.10	3,000	19.8	1.69×10^{-4}	82.5
	0.50	7,950	76.2	6.50×10^{-4}	318
	0.70*	15,000	120.0	10.24×10^{-4}	517
XE-340	(This resin did not reach 0.10 breakthrough and therefore could not be compared with the other adsorbents studied.)				

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a - 1 bed volume = 0.232 liters.
b - milligrams.
c - milligrams/milligrams.
d - grams/meter^3.
* - Note that this is 70% breakthrough; not 90%.

other adsorbents tested. The adsorbents were also compared based upon the amount of chloroform adsorbed at various breakthrough points. Here, too, Filtrasorb 400 and Nuchar WV-G had inferior performance records with neither adsorbent removing over 70 mg of chloroform at 90% breakthrough. These observations indicate that in treating Louisville's drinking water both Filtrasorb 400 and Nuchar WV-G have lower adsorptive capacities for chloroform removal and, therefore, would need to be regenerated more frequently in comparison to the other brands of GAC tested.

Three adsorbents were denoted as average in their ability to continually remove chloroform from drinking water. Included were Nuchar WV-W, Hydrodarco 1030 and Columbia LCK. With regards to the quantity of water treated, all three adsorbents were within a 2,000 bed volume range of one another. Hydrodarco 1030 was the best performer in this regard having treated 13,800 bed volumes at the 90% breakthrough point. However, all three adsorbents were remarkedly similar in terms of the amount of chloroform adsorbed at this same breakthrough point. Cumulative amounts of chloroform removed were 91.7, 92.4 and 95.8 g for Hydrodarco 1030, Columbia LCK and Nuchar WV-W, respectively. The performance characteristics of these three adsorbents is clearly superior to that indicated for Filtrasorb 400 and Nuchar WV-G.

The last group of adsorbents were those classified as good for the removal of chloroform. These included Witco 950 and Barnebey-Cheney PC-1. The latter carbon was the best performer on a bed volume treated per unit time basis having treated 15,000 bed volumes at the 70% breakthrough point. In comparison, Witco 950 treated 11,000 bed volumes at the same point of breakthrough. With regards to their adsorptive properties, both Barnebey-Cheney PC-1 and Witco 950 exhibited a superior characteristics than the other five brands of GAC tested. At the 50% breakthrough point the amounts of chloroform adsorbed were 76.2 and 107.1 mg, respectively. As shown in Table 23, the experiment was terminated before Barnebey-Cheney PC-1 reached the 90% breakthrough point. However, the cumulative amount of chloroform adsorbed by this GAC at the 70% breakthrough point was 120 mg (See Table 23). In comparison, it is estimated that Witco 950 adsorbed about 110 mg at this breakthrough point.

In summary, all seven brands of GAC tested were capable of reducing chloroform levels by more than 95% at the start of the experiment. Over the two month period of testing, however, the adsorbent varied markedly in their ability to remove THM from Louisville's drinking water. Barnebey-Cheney PC-1 was overall the best performer when 90% breakthrough was tolerated, whereas Witco 950 had superior adsorptive properties at the 50% breakthrough point.

PLANT-SCALE TREATMENT STUDIES

Field tests were made at a water utilities in Kentucky to ascertain the efficiency of in-plant changes on the amount of THM in finished water. Similar studies were also done at another utility which employs GAC adsorption in its treatment plant. The overall intention of the latter investigation was to define the approximate on-line time and performance of a GAC filter for removing trihalomethanes. Significant findings from these field tests are described in Table 24. The reader is referred to several recent publications which contain further details on the in-plant modifications described in Table 24 (Hubbs, et al., 1977; Zogorski, 1977; and Zogorski, et al., 1977).

In-Plant Modifications to Treatment Processes

Several comprehensive field investigations were completed at a surface water treatment plant to demonstrate that reduction in THM levels can be accomplished by modifications to chlorination practices. This water utility draws its raw water from the Ohio River. The raw water is then

TABLE 24

CHLOROFORM LEVELS AT A UTILITY EMPLOYING GAC FILTERS

Date	Influent[a]	Effluent[a]	Effluent / Influent
10/18/77	32	2	0.06
11/11/77	56	6	0.11
11/19/77	26	14	0.54
11/25/77	30	16	0.53
12/1/77	20	10	0.50
12/9/77	16	16	1.00
12/13/77	18	12	0.67

a - Units are µg/l.

settled in large reservoirs for a period of approximately 24 hours. Historically, breakpoint chlorination was accomplished in the influent well of the pre-sedimentation basin. Effective February, 1976, the continuous addition of chlorine at the head of the settling reservoir was discontinued as a means to reduce the amount of chloroform in finished water. A shock dosage of 40 LBS/MG of chlorine is added once per month at this location, however, to control biological growth within this basin.

Pre-settled water is fed via gravity to chemical coagulation. The flowrate to each of the coagulation units is monitored via venturi meters. Aqueous chlorine is fed at this point and shortly thereafter alum and polymer are added. Design retention times for flocculation and settling are 30 minutes and 6 hours, respectively. Coagulated water is then fed into a softening system consisting of several flocculation-sedimentation trains. A simple lime softening process is utilized to treat the influent water when the hardness exceeds 140 mg/l. During softening the pH value is raised to 10.0 and is held at this level for about 6 hours. The chemical stability of water leaving the softening basins is controlled by adjusting the pH value with lime when softening is not utilized or by adding gaseous carbon dioxide when softening is necessary. A saturation index of 0.2 usually requires that the water leaving the treatment facility has a pH value of 8.5. Following the softening system, water is applied to dual-media filters rated at 3 gpm/ft^2. The filtration media consists of 24 inches of sand topped with 6 inches of anthracite. Backwashing is necessary once every 60 hours. Chlorine and fluoride are added to filtered water at the influent to the clearwell. Typically, a chlorine residual of 1.8 mg/l free and 0.2 mg/l combined is carried into the distribution system.

<u>Movement in Point of Pre-Chlorination</u> - The addition of chlorine periodically at the head of the pre-sedimentation

basins affords the opportunity to quantify the effect THM levels of moving the point of chlorination farther back into the treatment system. Movement of the point of pre-chlorination to the head of chemical coagulation, instead of at the influent to the pre-sedimentation reservoirs, reduces the contact time of chlorine in the plant by about 24 hours. Also, chlorine is now added to a higher quality water containing lesser amounts of suspended matter, which in turn results in lower chlorine dosages being applied at the head of coagulation to obtain the same bacteriological quality. As described previously (page 13), alterations to the chlorination practice such as those just described are expected to reduce the concentration of THM present in finished water.

The magnitude to which THM levels were reduced by moving the point of pre-chlorination was determined from two field studies. The first investigation was completed in October, 1976 and the second in March, 1977. Analysis of the data collected during these two studies suggests that moving the point of pre-chlorination has reduced the concentration of $CHCl_3$ (and therefore total trihalomethanes) in finished water by as much as 40-50%. Similar but less pronounced data are evident for $CHCl_2Br$. In conclusion, it is apparent that the change in pre-chlorination was indeed warranted and has had a positive impact in reducing THM levels in finished water at this water utility.

Elimination of Free Chlorine During Precipitive Softening

As a means of further reducing THM in finished water at this utility, studies were initiated in October, 1977 to quantity the impact of eliminating free chlorine during precipitive softening. Prior studies at this water treatment plant clearly showed that as much as 50% of the chloroform in finished water was formed in the softening basins due to the presence of free chlorine and elevated pH values. As such, the possibility of diminishing the level of THM in tap water by stopping the THM reaction at the head of the softening process appeared promising and potentially significant. To test this hypothesis, ammonia was fed at the head of several of the softening trains in an attempt to convert free chlorine, which was carried over from the chemical coagulation basins, to combined chlorine prior to raising the pH value into the 10.0-10.5 range. Several softenign trains were operated without ammonia addition and, therefore, servedas controls in this study. After reaching steady-state conditions, water samples were collected from various locations within both the ammoniated and non-ammoniated softening basins and subsequently analyzed for THM levels. The data show that the concentration of $CHCl_3$ and total THM in the softening train receiving ammonia remained relatively constant as water passed through the slow-mix and settling basins. In contrast, $CHCl_3$ and total THM levels showed a definite increase as water moved through the treatment basins not receiving ammonia. That is, the formation of THM within the softening basin receiving NH_3 was nearly stopped, whereas the control basins continued to show increasing levels of THM illustrating that the THM formation reaction was on-going.

The reduction of THM levels attributable to the ammoniation process was determined by comparing THM levels in ammoniated and non-ammoniated samples. Results showed the following average reductions over a 7-day sampling period:

• $CHCl_3$	28 μg/l
• $CHCl_2Br$	8 μg/l
• $CHClBr_2$	3 μg/l
• Total THM	37 μg/l

That is, the softening basins receiving ammonia exhibited considerably lower THM levels. In summary, the addition of ammonia at the head of the precipitive softening process was capable of stopping the THM formation reaction and thereby reducing the concentration of THM in finished water. Ammoniation as indicated reduced the level of THM in finished water by about 33%, in comparison to when this plant was maintaining a free chlorine residual during softening.

Granular Activated Carbon Filter

The effective life of granular carbon filters in removing THM under plant scale conditions was determined by studies completed at a water treatment plant where conventional rapid sand filters have been converted to granular activated carbon filters. The carbon filters were originally installed in 1970 as a means of eliminating taste and odor problems. In the Fall of 1977 the old carbon media was replaced with about 30 inches of Filtrasorb 300 GAC. The research team observed the changeover process and were permitted to collect aliquots of filtered and non-filtered water at various intervals thereafter. In this manner, the adsorptive and breakthrough properties of Filtrasorb 300 were determined upon plant-scale operating conditions.

The raw water source for this water treatment plant is a medium size tributary to the Kentucky River. Treatment at this facility is conventional, with the exception of GAC filters. Raw water is pumped up to the plant where it is pre-chlorinated. Copper sulfate is added occasionally as an algicide. Alum and lime are added next and mixing occurs in the pipe lines leading to a single flocculation basin. From the flocculation basin, water flows to one of two sedimentation basins. After settling, fluoride is added and the flow is split to four GAC filters. Once filtration through GAC has been accomplished, the water flows to a clearwell where soda ash and chlorine are added.

A number of trihalomethane (THM) samples were taken at the changeover and a field sampling program was completed. Influent and effluent samples to the new filters were taken immediately after installation. Three weeks after this, the team returned and left a number of sample bottles such that

that plant operators could sample the filters on a weekly basis. Table 24 summarizes the results of chloroform data collected in association with this survey. As shown, the granular activated carbon filters operated for almost 6-8 weeks before becoming exhausted for chloroform removal. This finding is in agreement with data reported previously by EPA and other field investigations. Specifically, the adsorptive capacity of commercial brands of activated carbon is quite low, in the order of 0.05-0.2% by weight and, therefore, frequent regeneration will be needed when this adsorbent is used in conventional filter boxes (depth of about 30 in). The regeneration cycle can be lengthened, of course, by operating these units at lower surface and organic loading rates, by increasing the depth of adsorbent, by optimizing the environmental factors affecting the adsorption process, and by an integrated combination of the three prior methods. The regeneration cycle could also be extended by installing new carbon contactors with depths of 20-30 feet, although the capital cost of such installations may be prohibited in many circumstances.

CONCLUSIONS

Based on the findings of this investigation the following specific conclusions are made:

Factors Affecting the Formation of Trihalomethanes

1. Increased chlorine dosage was found to enhance the concentration of $CHCl_3$ and total THM formed. In contrast, the quantity of $CHCl_2Br$ produced was independent of the level of chlorine added.

2. Total THM, $CHCl_3$ and $CHCl_2Br$ concentrations were all increased with increased contact time between free chlorine and precursors present in settled Ohio River water.

3. Both laboratory and field monitoring studies illustrated that higher water temperatures promote increased formation of $CHCl_3$. Levels of $CHCl_3$ formed from Ohio River water were highly correlated with water temperature ($R \geq 0.90$). The dependence of $CHCl_3$ potential was found to be about 1.0-1.4 µg/l per °F. The temperature dependence of $CHCl_2Br$ was considerably less in the order of about 0.2 µg/l per °F.

4. Increased levels of $CHCl_3$ were produced as the pH value of Ohio River water increased. A direct linear relationship was found between the amount of $CHCl_3$ formed and the pH value with a rate of change of about 40 µg/l per pH unit. The calculated correlation coefficient was ≥ 0.99. The potential to form $CHCl_2Br$ upon chlorination was maximized in the 7-9 pH value range with a gradual dropoff on either side of the above range.

5. Precursor compounds remained in Ohio River water even after a 21 day storage time attesting that these compounds are extremely stable in natural waters.

6. Chemicals used at water treatment plants in the concentration range normally dosed did not contribute significant amounts of THM upon chlorination. As such, the observed levels of THM in finished water result almost exclusively from chlorine reacting with precursors present in natural waters.

Survey of THM Levels in Fifteen Water Utilities in Kentucky

7. The GC-LSC methodology for measuring the levels of trihalomethanes in drinking waters was reproducible and completely satisfactory for concentrations exceeding about 5 μg/l.

8. A modest positive correlation was observed (R = 0.67) between the total THM content and chlorine demand for the 15 utilities sampled.

9. Water utilities which use ground water as their water supply were found to contain the lowest level of THM, whereas surface water supplies containing high concentrations of turbidity and/or color contained the highest concentration of THM. Five of the twelve plants that used a surface water supply contained total THM levels above the 100 μg/l drinking water standard recently issued by EPA.

Bench-Scale Treatment Studies

10. In a simulated treatment study it was found that the $CHCl_3$ potential of filtered coagulated water was only 66% of that found for untreated Ohio River water. The unit treatment operation of sand filtration was found to be a significant factor in the removal of precursors indicated above.

11. The most pronounced reduction in $CHCl_3$ potential of four treatment systems studied was obtained with a fixed-bed filter of granular activated carbon. The GAC filter was very efficient in removing precursors present in Ohio River water and thereby lowered the $CHCl_3$ potential into the 10-30 μg/l range. Collectively, the treatment scheme of pre-sedimentation, chemical coagulation, flocculation, settling, sand filtration, and GAC filtration removed better than 95% of the precursors present in a surface water supply.

12. Both alum and polymer were capable of reducing the potential of untreated Ohio River water to form $CHCl_3$ and other THM, although the magnitude of each coagulants effectiveness varied with coagulant dosage. Unfortunately, however, large dosages of either alum or polymer are required to obtain substantial precursor removals. The pH value range 6-8 was found to be optimum for the removal of precursors via alum/polymer coagulation.

13. A detailed experiment for delineating the association of precursors with particle size distribution showed that (for Ohio River water collected on 11/4/77) 85%

of the $CHCl_3$ and total THM potentials was associated with fine colloidal and dissolved matter, with the remaining 15% associated with settleable and non-settleable suspended solids. Between 25-35% of the precursors associated with dissolved matter were removable via chemical coagulation, flocculation and sedimentation. Presumedly, further precursor removal could be accomplished by good filtration practices.

14. Witco 950 and Barnebey-Cheney granular activated carbons exhibited superior adsorptive properties for the removal of THM in comparison to several other brands of adsorbents. A short mass transfer zone was found ($\leq$ 1.0 ft.) for all of the adsorbents tested. Nuchar WV-W, Hydrodarco 1030 and Columbia LCK all exhibited similar adsorptive properties; measurably below that for Witco 965, however. The adsorptive capacity of GAC for chloroform was quite low, in the order of 0.05-0.12 percent by weight and, therefore, frequent regeneration of the adsorbent will be required if shallow beds of GAC are used to treat drinking watres.

15. Ozonation was effective in reducing the $CHCl_3$ potential of pre-settled water. An ozone dose of 6-8 mg/l resulted in a 50% reduction in the $CHCl_3$ potential. It should be noted, however, that a large fraction, if not all, of the above indicated removal currently occurs via chemical coagulation and precipitive softening. This latter observation was apparent from ozone's inability to influence the $CHCl_3$ potential of coagulated and softened waters.

16. Neither ozone or chlorine dioxide in conventional dosages were effective in oxidizing trihalomethanes.

17. Powdered activated carbon (PAC) removed some, but certainly not all, of the precursors associated with the formation of THM. Dosages of PAC above those frequently used for taste and odor control will probably be required to effect significant precursor removals. For example, in a single experiment, a 50 mg/l dosage of PAC was required to obtain a 50% reduction in the potential to form chloroform.

Plant-Scale Studies

18. Based upon two detailed studies, it was concluded that moving the point of chlorination from the head of pre-sedimentation reservoirs to the head of the coagulation process significantly reduced the concentration of $CHCl_3$ in finished water. A 40-50% reduction was indicated in each of the two field studies.

19. Ammoniation at the head of precipitive softening ceased the THM formation reaction and markedly reduced the level of THM in softened water. Average reductions in THM concentrations due to ammoniation were:

• $CHCl_3$	28 μg/l
• $CHCl_2Br$	8 μg/l
• $CHClBr_2$	3 μg/l
• Total THM	37 μg/l

20. An in situ investigation of a 30-inch fixed-bed filter of granular activated carbon showed that such a unit could remove chloroform for between 6-8 weeks before regeneration would be needed. This short on-time is a direct result of the low adsorptive capacity of GAC for chloroform.

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SPEED SCIENTIFIC SCHOOL
JAMES BRECKENRIDGE SPEED FOUNDATION
ENVIRONMENTAL ENGINEERING

George D. Allgeier
Dept. of Chemical &
Environmental Engineering
Speed Scientific School
University of Louisville
Louisville, KY 40208

Dear Sir:

A motion was passed at the last annual meeting of the Kentucky-Tennessee section of AWWA, Chattanoga, TN, endorsing a state-wide sampling program for the presence of chloroform and other trihalomethanes in water supplies serving Kentucky and Tennessee. In conjunction with a project supported by the Kentucky Water Resources Research Institute and under the direction of Dr. John S. Zogorski, Assistant Professor of Environmental Engineering at the University of Louisville, I am conducting just such a survey to determine trends in trihalomethane levels among various schemes of water treatment.

Therefore, it would be very helpful if I were allowed to tour and collect samples at your water facility. Please notify us prior to July 22, 1977, indicating whether or not you would like to participate and, if possible, include a brief description of the treatment that your water receives.

Please feel free to write or call me at the address given, if you have any questions. The results of our analysis for your respective plant will be forwarded to you. Further, the identity of each individual water treatment company and its results will be kept anonymous within all reports and published materials to maintain complete confidentiality.

Your assistance in this valuable research will be greatly appreciated.

Thank you,

George D. Allgeier

George D. Allgeier
Research Assistant

GDA/pjh

APPENDIX B

ADSORBENTS SELECTED FOR EVALUATION IN BENCH-SCALE EXPERIMENTS

TRADE NAME	MANUFACTURER	ADDRESS
Filtrasorb 400	Calgon Corporation, Pittsburgh Activated Carbon Division	P.O. Box 1346, Pittsburgh, PA, 15230
Nuchar WV-W	Westvaco, Chemical Division	Covington, VA, 24426
XE-340*	Rohm and Haas Company	Independence Mall West Philadelphia, PA, 19105
Hydrodarco 1030	ICI United States Inc. Chemical Division	Wilmington, Del., 19897
Columbia LCK*	National Carbon Co., Union Carbide Corporation, Carbon Products Div.	270 Park Avenue New York, NY 10017
Nuchar WV-G	Westvaco, Chemical Division	Covington, VA 24426
Barnebey-Cheney	Barnebey-Cheney Corporation	Cassady at Eight Columbus, OH 43216
Witco 950	Witco Chemical Corporation	227 Park Avenue New York, NY 10017

* - Not a mass produced adsorbent.