

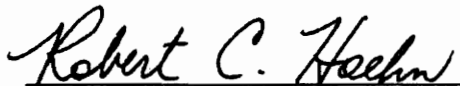
GRANULAR ACTIVATED CARBON PRETREATMENT
FOR THE
REMOVAL OF TRIHALOMETHANE PRECURSORS,

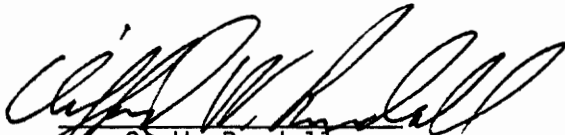
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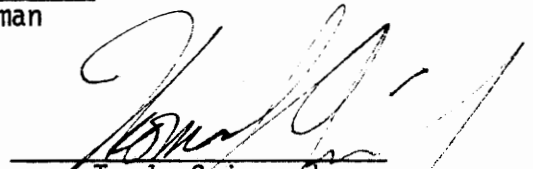
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I. INTRODUCTION

The problem of trihalomethanes (THMs) principally chloroform (CHCl_3) in drinking water was first recognized in 1974. Rook (1) in the Netherlands and Bellar et al. (2) in the United States published research data that showed that THMs are formed upon chlorination of natural waters (especially surface waters) and that the concentration of THMs increases with time as the water moves through the distribution system. In the same year, an EPA study of New Orleans drinking water (3) showed the presence of THMs and an array of other organic chemicals. Coincident with this was the release of an epidemiological study (4) that showed a correlation between the New Orleans water supply and a high incidence of cancer mortality in white males. This study was the acknowledged impetus for the passage of the Safe Drinking Water Act (PL93-523) in December, 1974.

To determine the significance of the New Orleans findings, the EPA initiated the National Organics Reconnaissance Survey of the water supplies of eighty cities. This confirmed the link between chlorinated surface water supplies and THMs (5). The National Organics Monitoring Survey (6) in late 1975 was initiated to study seasonal variations and the effect of various supplies and treatment processes on THM formation. In 1976 the National Cancer Institute released results of a carcinogenesis bioassay on rats and mice that showed chloroform to be an animal carcinogen (7). Human health effects of various types

are discussed in detail in the National Academy of Sciences report, "Drinking Water and Health" (8).

Mindful of the purpose and preventative nature of the Safe Drinking Water Act, and pushed along by a suit pressed in 1978 by the Environmental Defense Fund (EDF v. Costle, No. 75 2224, Feb. 10, 1978), the EPA published proposed regulations for the control of THMs and other organic contaminants in drinking water on February 9, 1978 (9). After voluminous public comment, the EPA published the regulations in their final form on November 28, 1979 (10). A maximum contaminant level (MCL) of 100 micrograms per liter ($\mu\text{g/l}$) of total THMs (TTHM) - the sum of the concentrations of CHCl_3 , CHCl_2Br , CHClBr_2 , and CHBr_3 - was established. Compliance or noncompliance of a utility with this regulation is determined on the basis of the average of four samples taken quarterly at different points in the distribution system served by the utility. A single sample with a concentration greater than 100 $\mu\text{g/l}$ is not necessarily a violation, nor is a concentration of 100 $\mu\text{g/l}$ to be construed to mean a safe level. The MCL is based primarily, by the EPA's own admission, on technological feasibility (10).

The components of natural waters that yield THMs upon chlorination are precursor materials. Humic and fulvic acids, the products of vegetative decomposition and the constituents primarily responsible for the color of natural waters, are believed to be the major types of precursor (11). The extracellular products of algae have also been demonstrated to have great potential for THM formation (12,13).

In general, the concentrations of THMs produced can be reduced three ways:

1. use of a disinfectant other than chlorine
2. removal of THMs after they are formed
3. removal of precursor materials prior to addition of chlorine.

Chlorine is firmly established for primary disinfection in public water supplies in the U.S. and an alternative with equally proven cost-effectiveness is not presently available. A preventative approach to THM formation is preferable to a "clean-up" technique to remove THMs after formation.

Under a grant from the Virginia Environmental Endowment a project was undertaken jointly by the Civil Engineering Department of VPI & SU and the Fairfax County Water Authority to investigate the effect of stormwater runoff on THM concentrations in a public water supply. The raw water source is the Occoquan Reservoir, an impoundment rapidly undergoing the process of eutrophication despite measures for the control of point source pollution (14). Urban runoff is a major problem and contributes significantly to the high organic content of the reservoir (14). One of the objectives of the project was to determine the effectiveness of ancillary water treatment processes such as ozonation and granular activated carbon (GAC) contact to reduce the THM-forming potential (THMFP) of the Occoquan Reservoir water.

This study was designed to evaluate the effectiveness of GAC pretreatment for the removal of THM precursors and to relate the quality of a water prior to chlorination to its THMFP. The rationale

for a pretreatment application of carbon is that a water treatment plant could add chlorine immediately after GAC contact and prior to standard coagulation, sedimentation, filtration processes. The chlorine contact time for disinfection purposes would then be essentially no different than the plant was designed to achieve using standard prechlorination practice. In addition to assuring adequate disinfection, the problems associated with fouling of plant basins and filters could be avoided.

A pilot scale set of three GAC contactors was designed to treat raw water at flow rates of 2, 4, and 6 gallons per minute in an upflow mode. The corresponding empty bed contact times (EBCT), based on the unexpanded bed depth of 7 feet, are 26, 13, and 6.6 minutes respectively. Twice weekly for thirteen weeks (June 27, 1979-September 26, 1979) 24-hour composite samples of the influent and three column effluents were collected. The samples were analyzed for pH, color, turbidity, total organic carbon (TOC), chlorine demand, and THM formation potential (THMFP) upon chlorination, to determine the effectiveness of the carbon for removal of THM precursor materials at varying contact times. Data to evaluate the quality of the reservoir water (algae counts, chlorophyll-a, rainfall, reservoir elevation) were collected. Correlations between water quality measurements and THMFP were investigated to assess their value for predicting the applicability of granular activated carbon pretreatment to a water and their subsequent value as operational parameters.

II. LITERATURE REVIEW

TRIHALOMETHANES

Occurrence and Distribution

The discovery that chlorination of natural waters results in the formation of trihalomethanes was first reported by Rook in 1974 (1). In that same year, Bellar et al. (2) reported the presence of THMs in drinking water produced by chlorination of both surface and groundwater. A study revealing the presence of THMs, as well as a multitude of other organic contaminants, in the drinking water supply of New Orleans (3) and a subsequent study linking that water supply to cancer incidence (4) contributed to a growing concern about the possible health effects of various contaminants in drinking water.

Section 1442(a)(9) of the Safe Drinking Water Act (PL 93-523) specifically mandated a nationwide survey of public water supply systems and sources "to determine the nature, extent, sources of, and means of control of contamination by chemicals suspected of being carcinogenic". From this came the National Organics Monitoring Survey (NORS) of eighty U.S. cities.

The objectives of NORS were to determine how widespread the presence of THMs was in water supplies in the United States, and to evaluate the effect of the raw water source and the water treatment practices employed upon the presence and concentration of THMs (5). The study confirmed the relationship between chlorination and THM formation. The highest THM concentrations were associated with

chlorination of surface water supplies, the practice of prechlorination, and the practice of water softening. Of the four major THMs, chloroform generally was found in the highest concentrations, with concentrations of the other three decreasing with the number of bromine substitutions on the carbon atom.

Following the NORS study, EPA conducted the National Organics Monitoring Survey (NOMS) to determine the occurrence and frequency of selected contaminants to establish data upon which to base an MCL or treatment requirement (6). Compounds to be studied were selected on the basis of their possible occurrence, the existence of relevant toxicological data, and the availability of an analytical method for their determination. The possibility that concentrations of general classes of compounds might be correlated with, and so valuable as an indicator of, the occurrence of specific contaminants was investigated. It was established that raw water contamination with organic chemicals was prevalent, but not to the extent of the occurrence of THMs in finished waters. The presence of specific compounds was not found to correlate well with the general water quality parameters studied, such as TOC and carbon-chloroform extract.

Health Effects

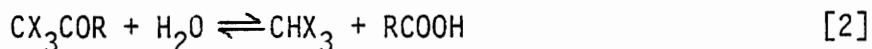
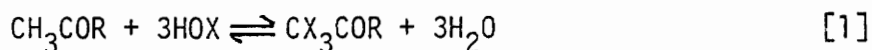
Trihalomethanes are the subject of concern from the standpoint of public health because chloroform has been shown to be an animal carcinogen (7). The National Academy of Sciences has accepted the value of the extrapolation of animal data from carcinogenicity testing

to man (8). Bromoform (CHBr_3) produced a positive carcinogenic response in a pulmonary adenoma bioassay on mice (15). The brominated THMs were demonstrated to have mutagenic activity in a bacterial assay using Salmonella (16). Organic residues isolated by reverse osmosis from drinking water were also found to have mutagenic activity (17).

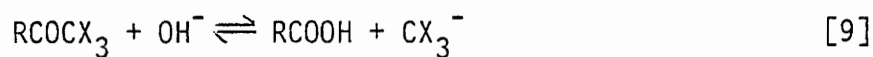
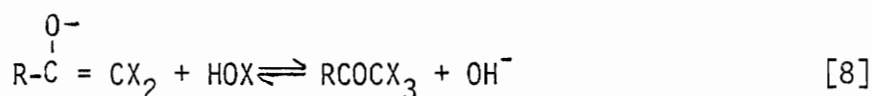
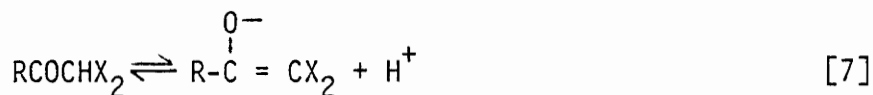
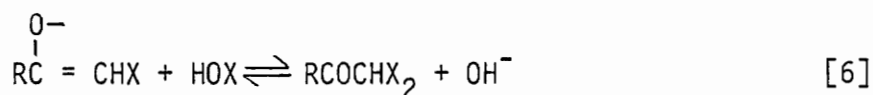
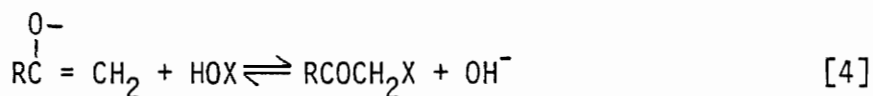
Epidemiological data from New Orleans linked that city's drinking water with cancer incidence (3). The risk of cancer of the gastrointestinal and urinary tract were found to be greater in areas with chlorinated drinking water (18). Cancer risk is believed to be a cumulative phenomenon (8), and so it is desirable to reduce human exposure to proven or suspected carcinogens wherever possible. The way in which the results of this study were interpreted was called into question at the time it was released, and is still controversial.

Trihalomethane Formation

The major reaction between aqueous chlorine and naturally occurring organic molecules in water that produces THMs is believed by many to be the haloform reaction (19,20,21). Organic compounds capable of this reaction are those that contain acetyl (CH_3CO) groups or those, such as secondary alcohols, that may be oxidized to acetyl groups. Under alkaline conditions the hydrogens of the terminal methyl groups are successively replaced by halogen atoms. The trisubstituted carbon bonded to the carbonyl group is then cleaved to yield a haloform and a carboxylic acid. The overall reaction is (19):



The proposed mechanism of the haloform reaction is (19):



A carbanion is formed upon dissociation of a hydrogen which adds a positive halogen. This repeats on the same carbon until it is fully halogenated. Nucleophilic base attack cleaves the CX_3^- group which then adds one hydrogen to form a trihalomethane. The first ionization step, the formation of an enol (reaction 3) is rate determining (22).

When chlorine is the only available halogen, CHCl_3 will be the haloform produced. The most common mixed halogen haloforms (CHCl_2Br , CHClBr_2 , and CHBr_3) result when bromine is available in the reaction solution. Bromide may occur naturally in waters or bromine may be a contaminant of commercially distributed chlorine. When hypochlorous acid (HOCl) is added to waters containing bromide, hypobromite is formed, and this oxidized halogen enters the haloform reaction (21,23). Iodine may become similarly involved, so that in all there are ten possible trihalomethanes (23).

When bromine is available, the proportion of CHCl_3 in the total THMs formed is substantially decreased and concentrations of the bromine-substituted THMs increase (23). Bromine substitution is favored over chlorine even in the presence of excess chlorine because bromine competes more effectively for reactive sites on the organic precursors possibly as a result of a faster substitution rate (24). There is evidence that bromide influences both the reaction rate and the reaction yield, the rate being faster in the presence of bromide (25). The yield of brominated THMs is proportional to the bromide concentration in the water (26).

Reactions other than the haloform reaction may be responsible for THM formation. Chlorination of diketones results in a more rapid rate of CHCl_3 production than the haloform reaction with simple ketones (21). Meta-dihydroxy substituted organic compounds also form THMs (27). Organic compounds containing the pyrrole ring (e.g. chlorophyll) yield THMs upon chlorination (20).

Carbanions formed in the mechanism of the haloform reaction may form organics other than THMs. Chlorination of model compounds usually does not result in the maximum theoretical yield of THMs, indicating the possible presence of partially oxidized intermediates or terminal products which may be chlorinated (20). Rook (27) produced twenty chlorinated organics from Rotterdam storage reservoir water. Many of these same compounds were reported by Glaze and Henderson (28) in chlorinated wastewater.

The kinetics of the classic haloform reaction are assumed to be zero order with respect to chlorine (22), but this assumption may not apply to complex systems such as natural waters. Research in this area has been limited and inconclusive. Trussel and Umphres (25) have reviewed the subject and proposed several possible models that incorporate chlorine residual and the concentration of precursor.

Effect of chlorine dose. The concentration of THMs formed has been shown to be dependent on a number of factors, one of which is chlorine dose. Chloroform concentration is proportional to the concentration of chlorine added up to the point where the chlorine demand of the solution is satisfied (24,29). According to Morris (19) chlorine demand is exerted during the conversion of available chlorine in solution to an inactive non-oxidizing form. Chlorine demand can provide an indirect measure of the THM-forming potential of a water because it always occurs as a result of the production of chlorinated organic chemicals (19). Chlorine demand may also

be exerted by certain inorganic compounds or elements. Chlorine in excess of demand forms a residual. Chlorine doses below those required to produce long-lasting chlorine residuals in the treated water result in substantially reduced levels of THMs (25). Excess free chlorine drives the haloform reaction far toward products (THMs) rather than various chlorinated intermediates which may be equally significant in terms of health effects and difficulty of removal (19).

Effect of reaction time. Trihalomethane concentrations have been shown to increase with increasing contact time between chlorine and precursor (11,21,29,30,31). As a result, when a free chlorine residual is maintained in the water distribution system, the reactions begun during treatment may continue so that THM concentrations will increase with increasing residence time in the system (31,32).

Effect of pH. The formation of THMs is strongly dependent upon pH, so that higher concentrations result at alkaline pH levels. The enolization step of the haloform reaction is facilitated by increased pH (21). In addition, the reactivity of some low molecular weight THM precursors is enhanced at higher pH levels (11). Active sites on the humic acid molecule are postulated to be more reactive at elevated pHs (11).

Because the lime softening process is carried out at an elevated pH, plants where this is practiced were shown to produce waters with especially high concentrations of THMs (5). Delaying chlorination until the pH has been readjusted to near neutral reduces THM formation

in the treatment plant (32). Morris and Baum (20) questioned the significance of this reduction, postulating that although low pH reduces THM formation, it does not stop the formation of chlorinated intermediates that only require an alkaline pH for hydrolysis.

Temperature effects. As is common for most chemical reactions, temperature has a profound effect on the rate of THM formation. Concentrations of THMs increase with increased temperatures (21,29). Changing temperature can partially account for the seasonal variation in THM concentrations in water supplies in which THM concentrations increase during the warmer months (11,26). Hoehn and Randall (33) found THM concentration to be inconsistent with temperature in a two-year study of the Occoquan Watershed, concluding that seasonal variation is dependant on a more complex set of factors, and that temperature effects may not only be associated with reaction rate.

Effect of precursor concentration. The concentration of THMs produced is also a function of the concentration of available precursor materials, which themselves vary seasonally (11,26). Chloroform concentration has been shown to be dependent to a degree upon precursor concentration (2,21), and it has been suggested that the organic content of the raw water may be the critical factor determining THMFP, provided the available chlorine is not limited (21).

An ideal method for measuring precursor concentration has not been found. In several studies, TOC concentrations were found to correlate well with THMFP (20,21), but other investigators (33) have failed to establish this relationship. Hoehn and Randall

(33) concluded that the more significant variable may be precursor type.

Methods for the Removal of Trihalomethanes

Trihalomethanes can be removed from water after they have been formed. This can be effected using adsorption on activated carbon or resins, oxidation with ozone (O_3), or aeration. Prohibitively expensive doses of powdered activated carbon (34) and ozone (34,35) have been shown to be required to achieve even partial removals of chloroform and other THMs. Aeration will remove as much as 90 percent of the THM concentration (34,36) but if a chlorine residual is maintained in the water leaving the treatment plant, the reaction will continue and THM concentrations will increase (37). THMs can be removed by resin adsorption, but these resins are too selective for more general treatment uses (38).

Granular activated carbon adsorption will remove THMs very effectively, but the capacity of the bed is quickly exhausted. Chloroform is the least well removed of the four THMs (39), the carbon's capacity being exhausted in as little as three weeks (21). GAC will also remove a broad spectrum of organic material and so has a more general application in water treatment. None of these methods is ideal, suggesting that the best approach to THM reduction is precursor removal to prevent their formation.

Trihalomethane Precursors

Humic substances in natural waters were first suggested as trihalomethane precursors by Rook (1). Since that time, research

has shown that various types of organic molecules found in natural waters will yield chloroform. Oliver and Lawrence (40) demonstrated that in addition to humic substances, sulfonated lignins, tannins, and phenolic compounds are precursors to THMs. Lower molecular weight organics containing acetyl groups were shown by Morris and Baum (20) to react with chlorine to yield chloroform. They also demonstrated that compounds containing the pyrrole ring (e.g. chlorophyll) and heterocyclic pigments (acetogenins) form chloroform upon reaction with chlorine. Algal metabolites and biomass have been shown to produce high yields of chloroform (12,13) and the chlorophyll-a concentration of natural water has been shown to correlate well with THM production (41).

Only a small fraction of the organic content of natural waters has been fully characterized. The majority of research has centered on low molecular weight, toxic chemicals and on organics responsible for tastes and odors in water. Macromolecules such as humic acids, polysaccharides, and proteins comprise the major portion of the organic material found in natural waters (42).

The primary source of organic matter is plant material. From this common source arises a great variety of compounds. The biological processes of plants produce synthetic units, metabolic intermediates, and end products, while the decomposition of plant material releases even more organic molecules to the water.

Humic substances. Humic substances are products of vegetative decomposition. They may be leached from the soil or introduced

directly into the water from decay of aquatic plants or floating leaves and debris. Humic substances have been divided into three major categories: humic acids, fulvic acids, and humatmelanic acids. These biologically resistant compounds, which differ in molecular size and solubility characteristics, are suggested sources of color in natural water (43).

Single compounds that make up the organic color of natural water were isolated and found to be very similar to the degradation products of "color solids" and the water soluble components of wood and soil (43). The relationship between color in natural waters and leaching of soil and forest debris was demonstrated by Sylvester et al. (44). The chlorine demand of a raw water was found to be proportional to its color, a result that suggests that color-imparting organics are precursors for chlorinated organics (45). Rook (21) found that storage of raw water containing high concentrations of humic substances did not decrease the THM-forming potential of that water, which suggests a biologically resistant precursor for THMs in the water he studied.

Humic substances can be chemically classified as polyhydroxy-methoxy carboxylic acids, and their oxidation products include α , β -dihydroxy or α -dihydroxy ketone configurations (46) characteristic of molecules that undergo the haloform reaction (20). Color in natural waters exists in large part as a colloidal suspension, and humic acids are likely to be associated with particulate matter.

Stevens et al. (11) demonstrated that THM formation reaction rates were similar in humic acid solutions and raw waters. This further confirmed the suggestion that naturally occurring humic substances are the precursors of trihalomethanes in surface water supplies.

Low molecular weight precursors. Low molecular weight organics containing the acetyl moiety can contribute to the THM-forming potential of a water. The extent of the participation of these compounds is critically pH-dependent. Stevens et al. (11) found that at pH 6.5, acetone was not a significant source of THM production but was important as a precursor at pH 11.5. They suggested that in a natural water both humic substances and low molecular weight materials are important precursors but that their relative contributions will be a function of pH.

Algal precursors. Both algal biomass and the extracellular products (ECP) of algae have been demonstrated to yield THMs upon chlorination (12,13). Algal ECP consists of soluble materials, metabolic intermediates and end products, that are released from living and intact algal cells. ECP was found to be a more significant precursor source than algal biomass, and chloroform yields from both groups were comparable to yields from humic substances (12,13). Chlorination of algal cultures yielded the highest levels of THMs when the cultures were in the exponential growth phase (12,13). Concentrations of chlorophyll, a common measure of algal activity in natural waters, were found by Hoehn et al. (41,47) to correlate well with THM production in the warmer months of 1975.

These authors suggested that humic substances are responsible for baseline levels of THMs produced all year, and that algae can be responsible for some of the seasonal increases observed in THMFP of surface waters.

Seasonal variation. The organic content of natural waters is derived from both allochthonous (from outside) and autochthonous (from within the aquatic system) sources, and so is subject to variation in the contribution of each source. Allochthonous organic material leached from soil and contributed by runoff will vary with rainfall (48). Autochthonous organic material produced by algae and other aquatic plants is subject to the variation in their growth cycles (48). Algal activity varies seasonally with a myriad of water characteristics such as pH, dissolved oxygen, temperature, and nutrient availability (48). Rainfall, and subsequent runoff, can contribute substantial amounts of nutrients (phosphorous and nitrogen) to a water supply (33). Short-term and seasonal variations in organic content result from environmental and biological changes in a highly complex system that make the organic materials present at any given time difficult to characterize or predict.

Measurement of precursors. In 1959, Wilson (49) predicted that due to the diversity of functional groups that characterize the organic components of natural waters, specific chemical tests for them were not likely to be developed. Presently, in large measure, this prediction has been borne out. Methods for the characterization

of organic compounds in natural waters are largely for general groups or classes of compounds. The NORS study (5) investigated the use of non-purgeable total organic carbon concentration (NPTOC: the fraction of TOC remaining after acidification and CO₂ removal), ultraviolet (UV) absorbance, and fluorescence as surrogate indicators of the concentrations of THM precursors. Statistical analysis of the data generated in this study showed each to be a poor predictor. Although values for the three measurements were found to increase and decrease as did the THM concentrations, the percent of the variation in THM levels that could be explained using them was small. TOC has been used to measure organic content in studies of THM precursors (12,25), perhaps for lack of a more reliable or available method of measurement, with fairly good results. Humic substances can be a large fraction of the TOC in natural water (42). Color measurements have also been used because humic substances are largely responsible for color of natural waters (50). A large number of researchers have used THMFP as an indirect measure of available precursor concentrations (12,24,29,41,51,52,53). The problem with this measurement is that its determination requires seven days to complete and so is of no value as a predictive parameter or for operational purposes to control THM production by treatment modification.

Methods for Removal of Precursors

Organic compounds responsible for THM formation may be removed to varying degrees from water prior to chlorination by four basic

methods. Direct filtration treatment may be applied to low-turbidity waters. Coagulation with metal salts or polyelectrolytes removes organic material and turbidity. Chemical oxidation of precursor substances can reduce the THMFP of a water. Organic compounds may also be removed from water by carbon or resin adsorption.

Direct filtration. Application of this process to waters with low turbidity can be very effective in turbidity and color removal. Edzwald (51) investigated the effectiveness of this method on waters with different sources of organic content. Water from a lake whose primary source of organic matter was allochthonous was spiked with additional humic substances and tested for THMFP. Direct filtration was able to reduce the THMFP to the level of that of the unspiked water containing primarily lower molecular weight organic substances. This suggested that other treatment methods were needed for removal of these low molecular weight precursors. A water whose organic content was primarily autochthonous (from algae and aquatic vegetation) had a much higher THMFP, and direct filtration removal only 33-55 percent of the available precursors. Color removal was good in this case, which points to substances other than humic acids as precursors.

Coagulation. Several investigators have evaluated chemical coagulation as a method for precursor removal (29,35,40,51,53,54). Alum (aluminum sulfate) was found to effect removal not only of TOC in general, but also of selective portions of the TOC responsible for THMFP (29,40,53). Cationic polyelectrolytes were shown to

coagulate humic substances by Edzwald (51), who suggested that polyelectrolytes probably would not remove the lower molecular weight precursors unless the precursors have specific functional groups to interact with the cationic functional groups of the polymer.

Oxidation. Chemical oxidants other than chlorine can help to reduce concentrations of THM precursors. Potassium permanganate (KMnO_4) was 100 percent effective for removal of THMFP from solutions of model compounds (resorcinol, metadihydroxybenzoic acid) but only slightly (10-20 percent) effective on water from the Ohio River (24). Ozone oxidation has been shown to achieve variable degrees of THMFP reduction (21,25). Rook (21) postulated that this variation was due to the time between ozonation and chlorination of the water because ozonation produced an unstable intermediate that would not react with chlorine if it was not given sufficient time to decompose. Chlorine dioxide was demonstrated to be marginally effective in reducing THMFP (55).

Adsorption. Adsorption is perhaps the most promising method for removal of THM precursors. Several types of synthetic resin adsorbents have been demonstrated to be capable of precursor removal (56), but they pose problems with the chemical and waste disposal costs of regeneration. Powdered activated carbon (PAC) was unable to completely remove THMFP, but Symons and Stevens (52) suggest that PAC may be the solution to the THM problem where the THMFP of the water is only slightly in excess of the MCL. Granular activated carbon has been demonstrated to provide excellent precursor removal, proportional

to the EBCT, but the capacity of the bed is limited and would require periodic regeneration (52).

Measurement of Trihalomethanes

Trihalomethanes are analyzed in water samples by gas chromatography (GC), a method for the separation, identification, and quantification of the components in a mixture. Because trihalomethanes are volatile and only slightly soluble in water, they may be removed from the water for analysis by stripping with a gas or by extraction into a solvent. An aliquot of the mixture thus removed is volatilized in the injection port of the gas chromatograph and carried by a controlled flow of an inert carrier gas (such as N_2 or Ar/CH_4) through a column where the mixture is separated by the column packing material.

Various column packing materials may be used. Commercially available materials have been manufactured for different applications and may be quite specific as to the mixtures they are capable of separating. Column packing materials appear powdery but are actually spherical, solid-support material coated with a liquid. As the molecules of the mixture are forced over and between these particles in the column, they are selectively retarded based upon a number of properties, one of which is their solubility in the liquid phase. The more soluble the component of the mixture, the longer it is held on the column.

Carrier gas flow elutes each component from the column at a separate time that is proportional to its retention in the column, the retention time (t_R). Retention time is a characteristic of

the individual compound of the mixture and is used to identify the eluting component.

From the column, each component separated from the mixture passes through a detector which detects the presence and the amount of the substance eluting. Two types of detectors are commonly used: the flame ionization detector (FID), and the electron capture detector (ECD). The ECD is preferred because it is sensitive to lower concentrations of THMs; those that are commonly found in drinking water are in the $\mu\text{g/l}$ range.

The ECD contains a radioactive source which is continuously bombarding the carrier gas molecules as they pass, knocking electrons from the carrier gas molecule and producing an electrical current. As the component molecules pass through this electron stream, they interrupt the flow of electrons. This interference in the current is detected, amplified, and the signal activates a strip chart recorder.

The recorder receives a constant electrical signal from the detector when no component is eluting. This is recorded on a chart as a relatively straight line, the baseline. When the current is interrupted a peak results on the chart. The area under the peak is proportional to the degree of interference in the current, and to the amount of the component present in the mixture that produced the interference.

The peaks, valleys and baseline produced on the chart are known as a "chromatogram". Components may be identified by the time between

the midpoint of their peak and the time of injection of the mixture, t_R . The area under each curve on the chromatogram may be manually calculated or integrated by computer. Comparison of the area of the sample peak to that produced by a standard solution of known concentration is used to determine the concentration of the component in the original water sample. For a review of the fundamentals of gas chromatography, the reader is referred to Basic Gas Chromatography by McNair and Bonelli (57).

The EPA has developed specific procedures for the analysis of THMs in water samples that are required for use in monitoring programs for compliance with the MCL (10).

GRANULAR ACTIVATED CARBON

Activated carbon is carbon that has been treated by a controlled oxidation process designed to produce a porous structure with a large surface area. Adsorption is a surface phenomenon, and the area and condition of the carbon surface will affect the carbon's capacity for adsorption. When this capacity is reached, the activated carbon may be regenerated and reused. Although activated carbon has been used for many years in water treatment, removal of THM precursors and other organics from drinking water is a relatively new application.

Activation and Regeneration

Granular activated carbon is manufactured primarily from petroleum coke, bituminous coal, and lignite. GAC can also be

produced from cocoanut shells. The activation process has been reviewed by McGuire and Suffet (58). The raw material is dehydrated at 170°C. It then goes through a slow, stepwise, heat process of carbonization in the absence of oxygen. In the first stage, some of the carbonaceous material is driven off as carbon monoxide, carbon dioxide, and acetic acid. At temperatures of 270-280°C the second stage is carried out with decomposition byproducts such as tar and methanol. Carbonization is completed at temperatures of 400-600°C.

Decomposition products of the carbonization process are burned away in the presence of steam at 750-950°C. This procedure also clears the pore openings in the carbon. Activation is completed by the burning of amorphous carbon from the pores by continued application of steam and heat (to 950°C). The resultant product is carbon with a complex pore structure.

Regeneration is a very similar process involving steam and heat. The carbon is dried at 100°C to remove water and volatile substances. At 650-750°C, other adsorbed organics are pyrolyzed. The carbon surface is activated at 870-890°C with steam and controlled oxygen to burn the pyrolysis char from the carbon pores.

Adsorption Efficiency

Adsorbent characteristics. The raw materials and the process used to manufacture GAC determine its adsorption efficiency. The resulting carbon product has a microcrystalline structure of parallel graphite planes. These planes are stacked but their structure is unordered (59). Complete layers of fused carbon rings

are burned away, forming micropores. At the carbon surface of the walls of these micropores are located the adsorption sites (60). The structural characteristics that determine adsorptive efficiency are surface area and pore structure, the presence of surface oxides, and surface polarity, particle size, and hardness of the carbon.

The adsorptive capacity of a carbon is directly proportional to the carbon's surface area because adsorption is a surface phenomenon. Pore structure influences both the capacity and rate of adsorption. A balanced distribution of pore sizes is desirable for adsorption of the broadest size range of organics to be adsorbed. When this is the case, the rate of adsorption is generally higher (58).

Oxidized functional groups on the carbon surface change the surface polarity and reduce the adsorptive capacity. The pore surface of virgin carbon is nonpolar and has a high affinity for organic substances. Portions of the surface become polar when oxidized by ozone, chlorine, permanganate, or oxygen. Water is strongly adsorbed in these areas, constricting and blocking pore openings and reducing adsorption (61). In column studies, the adsorptive capacity of activated carbon decreased markedly as reduced chlorine adsorbed to the surface increased (36).

Surface area is a function of particle size. As particle size decreases, surface area is increased. Adsorption rate, in turn, is affected by particle size, increasing proportionally to the inverse of the square root of the particle diameter (62).

The hardness of activated carbon is an important structural characteristic from an economic standpoint. The ability of the carbon to withstand abrasion during backwashing and regeneration is related to the hardness. Carbon fines produced by abrasion can result in significant losses of carbon during the operational life of a column (58).

Adsorbate characteristics. A classification of the adsorbability of organic compounds based upon some characteristic such as molecular weight, functional groups, or solubility in water would be useful. Efforts to develop such a classification have met with little success. Aqueous solubility of organics provides the basis for the best general classification scheme (58). A major difficulty is the enormous variety of organic compounds in water, only 10-20 percent of which have been isolated by analytical techniques (63). Use of surrogate group measurements of organics such as NPTOC, total organic chlorine (TOCl), ultra-violet adsorbance at 254 nanometers (nm), chemical oxygen demand (COD), and fluorescence have been investigated for their relation to carbon adsorption. Only a few specific compounds have shown break-through patterns that correlate with those of the surrogate measurements (58).

Aqueous system characteristics. Temperature, pH, and the presence of dissolved solids or competing organic compounds in solution can effect adsorption. Adsorption is an exothermic process so that while adsorption capacity decreases with an increase in temperature (59), the rate of adsorption increases with temperature (62). These antagonistic effects tend to offset one another so that unless

temperature fluctuations are drastic, there is little net effect (62). Dissolved solids concentration and pH do not effect adsorption of most organic compounds in water of health significance because such compounds are primarily neutral molecules (58). The presence of a variety of organic compounds in solution can result in competition between compounds for adsorptive sites on carbon (64). This "chromatographic effect" was found to be significant in full scale operation of activated carbon columns when the applied water contained a great variety of organic compounds of differing affinity for carbon (36).

Adsorption Models

A number of mathematical models has been developed and applied to adsorption processes in an attempt to describe them quantitatively. McGuire and Suffet (58) have reviewed these for comparison. McGuire et al. (36) applied the Net Adsorption Energy model (NAE) to carbon adsorption and were able to correlate the amount of a compound adsorbed to its NAE. Interactions of three types of affinities involved in the complex process are described by this model: affinity of the solute for the adsorbent surface, affinity of the solute for the solvent, and affinity of the solvent for the adsorbent. The NAE of a compound is a function of these dispersion components, as well as molecular weight, density, and aqueous solubility of the compounds.

The kinetics of adsorption have been described by classic zero-, first-, and second-order models only with limited success (62). A second-order, reversible model was applied by Ishizaki and Cookson (65). They found a good fit with this model, showing that an

increase in surface oxides on the carbon decreased the rate of adsorption of selected compounds.

Applications in Water Treatment

Granular activated carbon is applied in drinking water treatment in the United States primarily for control of tastes and odors caused by organic substances. Experience with GAC for general or specific organic removal applications is largely European. GAC is used in columns or beds for continuous removal of organics, and allows higher adsorptive capacity than single applications of PAC and easier process control. Application in the granular form also facilitates removal of carbon for regeneration purposes.

GAC is most commonly incorporated into a water treatment scheme as replacement media in a rapid sand filter. Applied in this manner it can be effective for periods of years for taste and odor control (34). Experience with GAC contact for taste and odor control has limited value to applications for the control of THMs or their precursors. At seven of eight treatment plants using GAC as a filter/adsorber studied in NORS, the carbon was exhausted for removal of NVTOC and THMFP while still efficiently removing taste and odor (5). Fresh carbon added at one of the plants surveyed showed efficient removals of NVTOC and THMFP.

GAC will remove THMs from water effectively, but only for limited periods. Rook (21) showed a breakthrough in CHCl_3 from a carbon column after only seven days with twelve minutes EBCT.

Chloroform was reduced in Cincinnati tap water by at least 90 percent after three weeks when the EBCT was ten minutes (35). Bed life of carbon is slightly longer for removal of trihalomethanes other than CHCl_3 (39). The frequency of regeneration required if GAC is applied for THM removal would make this treatment technique prohibitively expensive for most waters.

GAC contact appears promising for the removal of THM precursors. Symons and Clark (39) reported THMFP (2-day) reductions of nearly 100 percent by carbon contact even after the carbon had been in service six months. McCreary and Snoeyink (66) showed that GAC would adsorb humic and fulvic acids, but the adsorption capacity and the extent of competitive adsorption varied with organic substances from different sources. Herzing (67) found that the type of carbon used and the type of natural organics in the water determined the extent of TOC removal by GAC. These variations in effectiveness of different carbons on different waters demonstrate the necessity of experimentation at each treatment plant to determine the optimum carbon and operating conditions for the water to be treated.

GAC applied as a sand replacement adsorber reduced the THMFP of a water to less than the MCL for nearly four and ten weeks at EBCTs of 6.5 and 24 minutes, respectively (51). Initially, precursor removal was nearly complete but decreased steadily with time in service. McCreary and Snoeyink (66) suggested that clarification preceding GAC contact helps reduce organic loading and extends bed life. Prior turbidity removal is important if the

GAC contactors are operated also as filters in the downflow mode to keep head loss to a minimum.

A discussion of the literature concerning the application of GAC as a pretreatment operation would be appropriate here. The literature reviewed, however, did not report the use of GAC in this application. In the study reported in this thesis, raw water was pretreated with GAC in an upflow mode to remove organic material by adsorption rather than by filtration.

III. MATERIALS AND METHODS

This project was intended to evaluate the effectiveness of granular activated carbon contact as a pretreatment for the removal of trihalomethane precursor materials, and to attempt to correlate trihalomethane formation potential to raw water quality. Three pilot-scale carbon contactors were operated in the upflow mode at two, four, and six gallons per minute (gpm) flow rates to treat raw water over a thirteen week period. Twice weekly, 24-hour composite samples of influent and effluent water were collected and analyzed for pH, turbidity, color, threshold odor number (TON), TOC, and THMFP. Once a week samples were analyzed for bacteriological quality and chlorine demand. Over the period of the project, the water quality in the Occoquan Reservoir was evaluated in terms of algae counts and chlorophyll-a concentration. Rainfall and reservoir elevation data were collected over the project period.

Pilot-Scale Carbon Contractors

Figure 1 is a schematic diagram of the pilot-scale carbon contactors and the associated piping and pumps. The contactors were constructed from 13 foot sections of one-foot diameter asbestos-cement pipe. All piping and pumps in contact with influent water were brass or copper to minimize organic contamination. Polyvinyl chloride piping was used to collect the discharge for disposal.

Each column was filled with seven feet of GAC: 3.5 feet of Westvaco (Covington, West Virginia) Nuchar WV-G (12x40 mesh) below

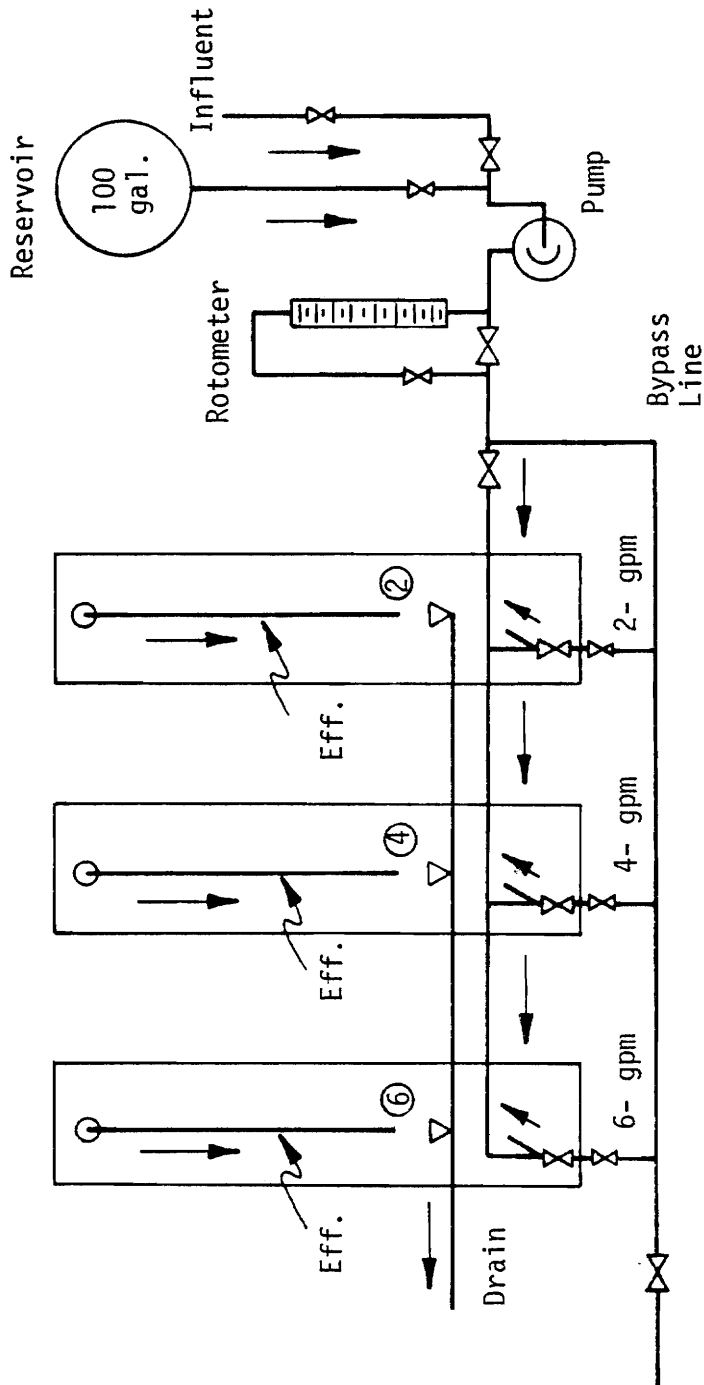


Figure 1. Schematic Diagram of Pilot-Scale Granular Activated Carbon Contactors

3.5 feet of Nuchar WV-DC (10x25 mesh). Two feet of gravel supported the carbon media and distributed the influent water. The columns had four feet of freeboard above the level of the unexpanded bed. The effluent pipe was located three feet above the unexpanded bed.

Nuchar WV-G is described by the manufacturer (68) as a hard carbon produced from bituminous coal and possessing a wide range of pore sizes. Pore sizes are predominantly transitional and macropores, making the carbon suitable for adsorption of both low- and high-molecular weight organics. Nuchar WV-DC (69) is a low density carbon with a large surface area and pore volume, especially suited for removal of large molecular weight organics. Table 1 lists the specifications and properties of both carbons.

Initially, the flow to the columns was controlled with a rotometer and globe valves. Clogging of the globe valves with sediment from the raw water necessitated a change to needle valves later in the project. Flow rates were measured using a bucket and stopwatch at regular intervals in conjunction with the sampling program.

The three columns were operated at hydraulic loadings of two, four, and six gpm, respectively. The corresponding EBCT's were 26, 13, and 6.6 minutes. The resulting bed expansions were 1.8, 2.0, and 2.6 percent. The columns were operated commencing June 26, 1979 and were taken out of service to be recharged on September 27, 1979.

An inadequate water supply provided by pumps used at start-up resulted in complete shutdown of Column 3 (6 gpm) from July 1

TABLE 1. Specifications and Properties of Westvaco
(Covington, West Virginia) Nuchar WV-G and
WV-DC (After Westvaco, ref. 67 and 68)

	WV-G	WV-DC
Iodine Number (mg/g)	1050 min	850 min
Particle Size (U.S. Sieve Series)	12x40	10x25
Oversize (%)	8.0 max	8.0 max
Undersize (%)	5.0 max	5.0 max
Surface Area (Nitrogen BET Method) (m^2/g)	1100 min	1500-1700
Apparent density (Kg/m^3)	433-465	240-288
Bed Density, Backwashed and Settled (Kg/m^3)	385-417	208-256
Mean Particle Diameter (mm)	0.90-1.20	1.1-1.4
Total Pore Volume (cm^3/g)	--	2.0-2.3

through July 13, when a new booster pump was installed. During this period, however, Columns 1 and 2 continued to operate.

The columns were backwashed 45 minutes each with filtered, dechlorinated finished water from the treatment plant on four occasions near the end of the period of operation as described in Table 2. This procedure failed to be effective in extending the bed life and the columns were taken out of service.

Sampling program. Twice each week, 24-hour composite samples of the influent raw water and the effluent from each of the three contactors were collected. Beginning at 8 a.m., 250 milliliters (ml) of each sample was collected in a glass bottle every four hours until 4 a.m. the following morning. These six samples comprised the 24-hour composite for each sampling point, a total of 1.5 liters (L). Upon collection, the 250-ml samples were transferred to 2-L stoppered glass reagent bottles, one for each of the four sample points, and refrigerated. At each sampling time, prior to collection, the rate of flow of each contactor was checked and adjusted if necessary. The raw water sample line was flushed before the samples were collected. At 8 a.m. the first sampling day of each week, a bacteriological sample was collected for standard plate count (SPC) and total coliform analyses. Sampling and storage of this sample was carried out as described in Standard Methods for the Examination of Water and Wastewater, 14th ed. (70). Samples for physical and chemical analyses were allowed to come to room temperature prior to analysis.

TABLE 2. Pilot-Scale Carbon Contactors, Backwashing Schedule

Date	Column No.	Rate (gpm)	Duration (min)
9/4/79	1	1-8	45
	2	1-9	45
	3	1-10	45
9/13/79	1	4-8	45
	2	4-8	45
	3	4-9	45
9/21/79	1	4-9	45
	2	4-9	45
	3	4-9	45
9/26/79	1	4-10	45
	2	4-10	45
	3	4-10	45

General Physical, Chemical, and Biological Analyses

pH. Samples were analyzed for pH using a specific ion electrode as described in Standard Methods, method 424.

Color. The visual comparison method with platinum cobalt standards, method 204A, from Standard Methods was performed on samples that were first centrifuged for 15 minutes to remove turbidity so that a determination of true color was made.

Turbidity. Method 214A, the nephelometric method, described in Standard Methods was used.

T.O.N. Threshold odor number was determined according to method 206 from Standard Methods.

T.O.C. Total organic carbon was measured using the Dohrmann/Envirotech (Santa Clara, California) DC-54 Ultra Low Level Total Organic Carbon Analyzer System, designed for samples containing less than 10 mg/l carbon. Each sample was mixed with a solution of phosphoric acid and potassium persulfate. The instrument purges the sample with helium which carries CO₂ and the purgeable organic carbon (POC) through a CO₂ scrubber where the CO₂ is removed. The POC is pyrolyzed by a hydrogen-enriched nickel catalyst which reduces it to methane. The methane is detected by flame ionization and read from a digital display as mg/l carbon. The water sample containing the nonpurgeable organic carbon (NPOC) is driven through an ultra-violet reaction coil which completes the oxidation to CO₂. This CO₂ is converted to methane and detected as previously described

(71). All samples were analyzed at least twice and the average result reported.

Bacteriological quality. Samples for standard plate count and total coliforms were analyzed as outlined in Standard Methods, methods 907 and 909A, respectively.

Chlorine demand. Methods 410 and 409C (amperometric titration) in Standard Methods were used to analyze for chlorine demand. An initial chlorine dose of 25 mg/l was used, and the residual was determined after a 30 minute contact time.

Raw Water Algae Counts. Samples were shaken and an aliquot withdrawn and placed in a Sedgwick-Rafter cell. Identification and enumeration were done under a light microscope and reported as algae per ml.

Chlorophyll-a. Chlorophyll-a determinations were made using the trichromatic technique described in section 1002G of Standard Methods.

Trihalomethane Formation Potential

Sample Preparation

Glassware. Water samples to be analyzed for THMFP were not permitted to contact containers other than glass. All reagents used were stored in and pipetted with glass. Large pieces of glassware - such as beakers, reagent bottles and flasks - were washed with Alconox soap, rinsed once with tap water, twice with product water from a Milli-Q system (Millipore Corporation, Bedford, Mass.) and dried at 105°C for one hour. Smaller glassware such as hypovials,

extraction vials, and pipettes were washed with soap and rinsed, then soaked in acid, rinsed well with Milli-Q product water, and burned in a muffle furnace at 430°C for 60 minutes. Caps and seals that could not be placed in a muffle furnace were boiled in Milli-Q product water five minutes and dried for one hour at 105°C. Syringes for use in gas chromatography analyses were rinsed with high-purity solvent and then with sample before injections.

Sample chlorination. A 500-ml portion of each sample was measured and poured into a 1-L Erlenmeyer flask with a ground-glass stopper. To each flask was added an aliquot of a concentrated chlorine solution obtained from the treatment plant chlorinator. The solution was prepared by bubbling chlorine gas through plant effluent water. The strength of this chlorine solution was determined immediately before use by potassium iodide addition and titration with sodium thiosulfate according to the same procedure specified previously for chlorine demand.

Chlorine solution was added to each sample to obtain a 25 mg/l concentration initially. Chlorine demand testing indicated that 25 mg/l would provide a residual after seven days allowing the reaction to go to completion. The samples were mixed and placed in the dark at room temperature for thirty minutes. After this period, a 50-ml glass hypovial was filled with sample. To each was added three drops of a concentrated (4N) sodium sulfite solution to dechlorinate the sample and arrest THM formation. These samples dechlorinated after 30 minutes were then analyzed for trihalomethanes,

and reported as instantaneous THMs (ITHM). The remainder of the chlorinated samples were sealed in hypovials with teflon seals and aluminum caps and stored at room temperature in the dark for formation potential analysis after one, two, four, and seven days. The residual chlorine in each sample was determined by the DPD colorimetric method (72) at the time of the analysis.

Extraction. At the time of analysis all samples were dechlorinated with sodium sulfite prior to extraction. The extraction procedure was a modification of that of Glaze and Rawley (73). To 1 ml of high purity (Fisher Spectrograde) n-pentane in a 7-ml, screw-cap extraction hypovial with a Teflon seal was added 5 ml of the sample. The mixture was shaken vigorously by hand for one minute then allowed to stand undisturbed for a few minutes to allow separation of the layers.

Sample Analysis

A 2- μ l aliquot of the solvent layer in each sample extraction vial was withdrawn using a microsyringe and analyzed by gas chromatography using a modification of the method of Glaze and Rawley (73). The instrument used was a Perkin Elmer Model 900 gas chromatograph equipped with a ^{63}Ni electron capture detector (ECD). Instrument settings and conditions were as follows:

Injection port temperature - 200°C

Column - 3% FFAP on Gas Chrom Q, 80/100 mesh

Oven temperature - 90°C

Carrier gas - Ar/CH_4 @ 60 ml/min

Manifold temperature - 200°C

Detector temperature - 250°C

Components eluting were identified by comparison of retention times with those of standard solutions of each of the four THMs. Concentrations were calculated based on the response of a standard solution (prepared by volumetric dilution of each of the pure THMs into methanol and serial dilution in pentane) of all four THMs. A Columbia Scientific (Austin, Texas) computing integrator (Super-gator-3) was used to integrate the area under the peaks in the chromatogram, perform the calculations, and report the final concentrations in $\mu\text{g/l}$. The chromatogram was produced on a model 3047 Yokagowa (Tokyo, Japan) strip chart recorder. The response of the ECD over a range of 0-500 $\mu\text{g/l}$ of trihalomethanes was measured and a standard curve developed. The curve was sigmoid, showing the linear range of the detector to be 10-300 $\mu\text{g/l}$, gradually falling off to horizontal above 300 $\mu\text{g/l}$. Accuracy of the method was determined to be within the acceptable limits suggested by the EPA Quality Assurance program (Municipal Environmental Research Laboratory, Cincinnati, Ohio). On several occasions the samples were extracted and analyzed in replicate and were reproducible within a range of ± 2 percent.

IV. RESULTS

Data collected during this study were intended to answer the following three questions:

1. How effective is GAC pretreatment for removal of trihalomethane precursors?
2. How does this effectiveness vary with EBCT?
3. What correlations exist between measures of raw water quality and THMFP and can these characteristics be used as operational parameters for GAC pretreatment to indicate potential problem levels of THMs in the finished water?

Because the GAC columns were operated as upflow contactors, the organic materials removed were primarily soluble rather than particulate. The data represent the removal of soluble precursors more so than precursors associated with suspended particles in the water so that the relative importance of these two sources is reflected in the results.

While not an objective of the study, data were collected to evaluate the benefits of carbon pretreatment in terms of odor control and to assess the microbiological activity associated with GAC. Data presented in Table B6 show that GAC was effective in most instances for reducing odor. The efficiency of odor removal did not vary consistently as a function of flow rate. Data in Table B7 indicate that the GAC did support a community of bacteria and that bacterial counts in the effluent from the columns were in most cases as great or greater than those in the raw water.

TRIHALOMETHANE PRECURSOR REMOVAL

Trihalomethane Formation Potential

THMFP was used in this study as an indirect measure of the concentration of THM precursors in the water samples. Appendix A contains the results of these analyses.

Raw water samples. Figure 2 illustrates the ITHM and THMFP concentrations in chlorinated raw water samples. It can be seen that these concentrations remained fairly consistent during the period of the study. The relative proportions of ITHM and THMFP are summarized in Table 3. Raw water ITHM concentrations ranged from 80 $\mu\text{g/l}$ to 159 $\mu\text{g/l}$, and the mean value was 106 $\mu\text{g/l}$. Raw water THMFP was an average of 45 percent more than the raw water ITHM and ranged from 158 $\mu\text{g/l}$ to 257 $\mu\text{g/l}$, the mean value being 209 $\mu\text{g/l}$. Two peaks are most evident in the graph of raw water THMFP (Figure 2), occurring at days 75 through 78, and days 85 through 89. Three other noticeable increases correspond to days 33, 50, and 57. The correlation between these peaks and other water quality and hydrologic factors will be addressed later. Corresponding increases in raw water ITHM were not as pronounced.

Two-gpm contactor effluent. Table 4 summarizes the ITHM and THMFP data for the chlorinated raw water influent and the effluent of the 2-gpm GAC contactor. The THM concentrations produced upon chlorination of the effluent from the 2-gpm contactor are illustrated in Figure 3. Both ITHM and THMFP increased with time in service of the carbon contactor, approaching the corresponding raw water THMFP

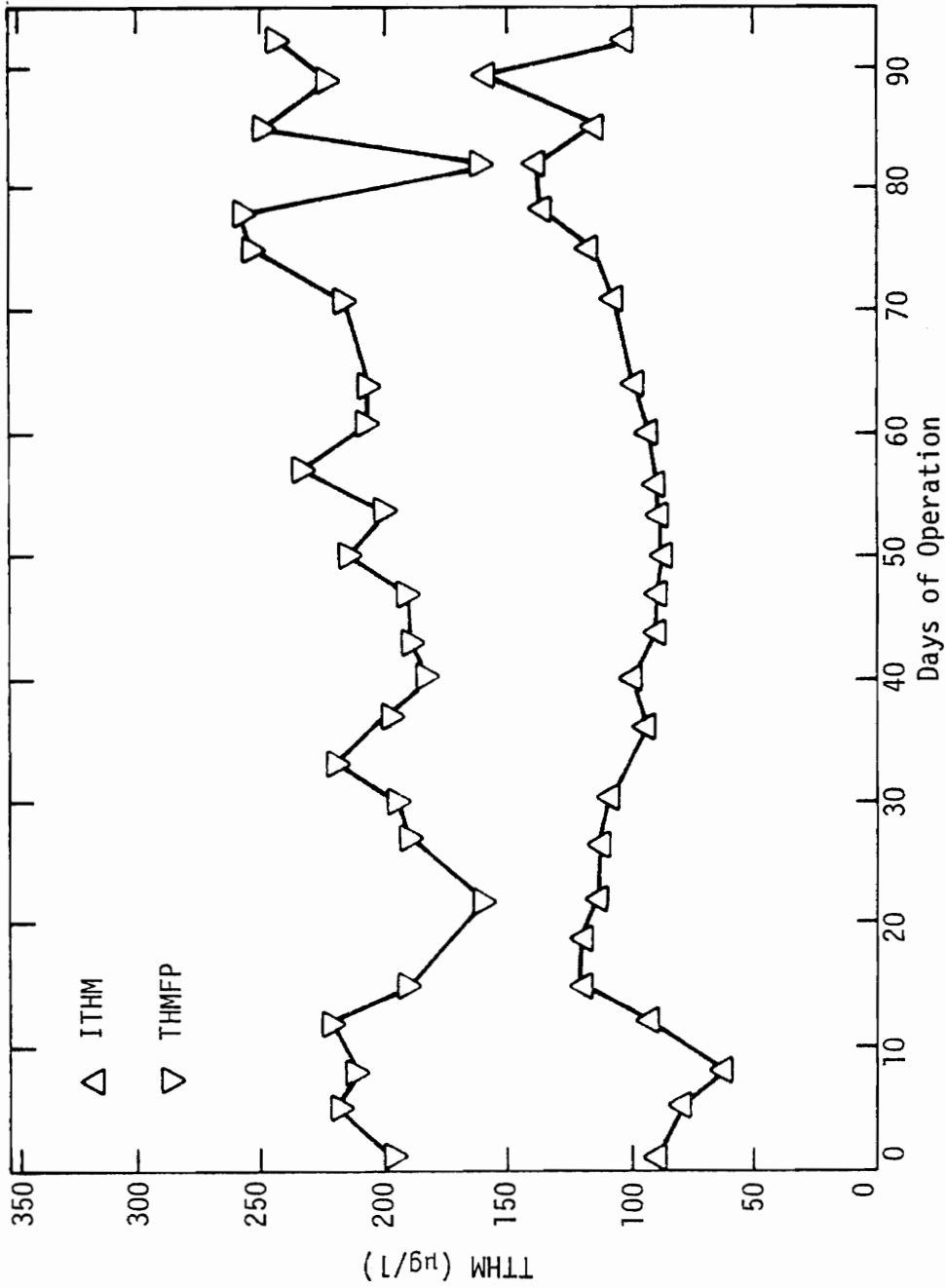


Figure 2. Total Trihalomethane (TTHM) Concentrations in Chlorinated Raw Water Samples After Thirty Minutes (ITHM) and Seven Days (THMFP).

TABLE 3. Percent Increase in Total Trihalomethane (TTHM) Concentrations in Chlorinated Raw Water and GAC Contactor Effluent Samples After Seven Days (June 27 - September 26, 1979)

Sample	$(1 - \frac{\text{Instantaneous TTHM}}{\text{7-Day TTHM}}) \times 100$	
	Mean	Standard Deviation
Raw	45.1	17.3
2-gpm Effluent	63.5	21.9
4-gpm Effluent	53.7	19.5
6-gpm Effluent	51.4	8.0

TABLE 4. Average Instantaneous (ITHM) and Seven-Day (THMFP) Total Trihalomethane Concentrations in Chlorinated Raw Water and GAC Contactor Effluent Samples (June 27 - September 26, 1979)

Sample	ITHM ($\mu\text{g/l}$)		THMFP ($\mu\text{g/l}$)	
	Mean	Standard Deviation	Mean	Standard Deviation
Raw	106	18.6	209	25.9
2-gpm Effluent	51	33.8	144	42.1
4-gpm Effluent	80	27.7	179	36.7
6-gpm Effluent	88	23.7	187	35.8

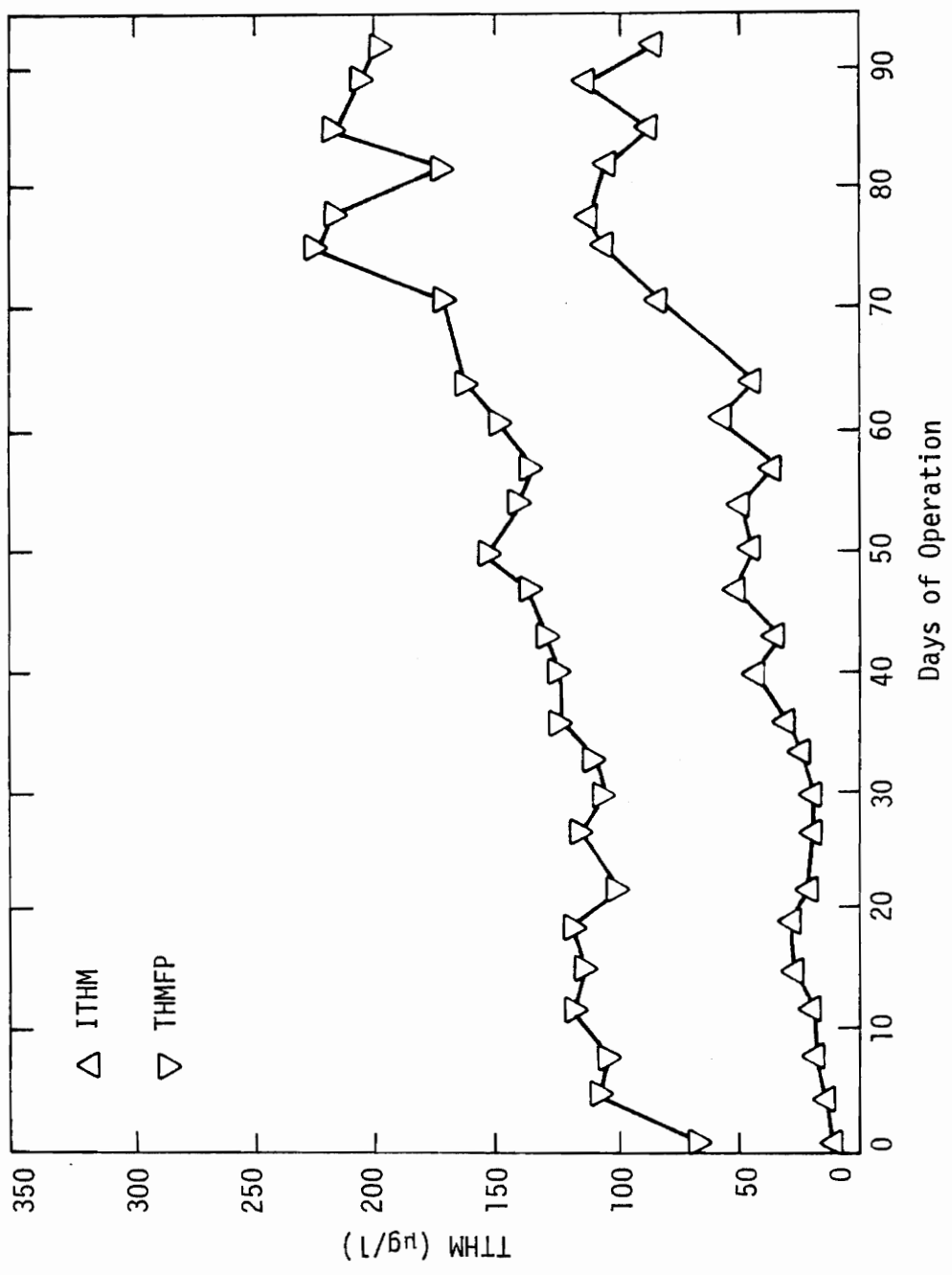


Figure 3. Total Trihalomethane (TTHM) Concentrations in Chlorinated 2-gpm Granular Activated Carbon Contactor Effluent Samples After Thirty Minutes (TTHM) and Seven Days (THMFP).

concentrations after seventy days of operation. None-the-less, ITHM and THMFP were reduced by GAC contact throughout the entire period of operation (92 days). The average THMFP removal in this column was 30.9 percent. A decrease in THMFP removal efficiency with time in service for the three GAC contactors is illustrated in Figure 4. Table 5 summarizes the removal of THMFP by the three GAC contactors.

ITHM concentrations produced in these samples averaged 51 $\mu\text{g/l}$, with a range of 11 $\mu\text{g/l}$ to 115 $\mu\text{g/l}$, and represented an average of 36.5 percent of the THMFP of the effluent water. THMFP concentrations ranged from 65 $\mu\text{g/l}$ to 226 $\mu\text{g/l}$. The average THMFP in these samples was 144 $\mu\text{g/l}$. Peaks in THMFP concentration corresponding to those that occurred in the THMFP of raw water samples late in the period of operation are apparent in Figure 3.

Figure 5 illustrates the total mass of THMFP adsorbed by the three carbon contactors with time in service. The 2-gpm contactor adsorbed nearly 0.14 pounds of THMFP over the 92 days of operation. The adsorptive capacity of the column was virtually nil when operation was terminated.

Four-gpm contactor effluent. Figure 6 shows the ITHM and THMFP concentrations produced by chlorination of the effluent of the 4-gpm contactor. Both these concentrations increased slightly with increasing time in service of the contactor. Figure 4 shows that the initial THMFP reduction by this GAC contactor was less than 20 percent and remained low throughout the study period, the average removal being 13.7 percent.

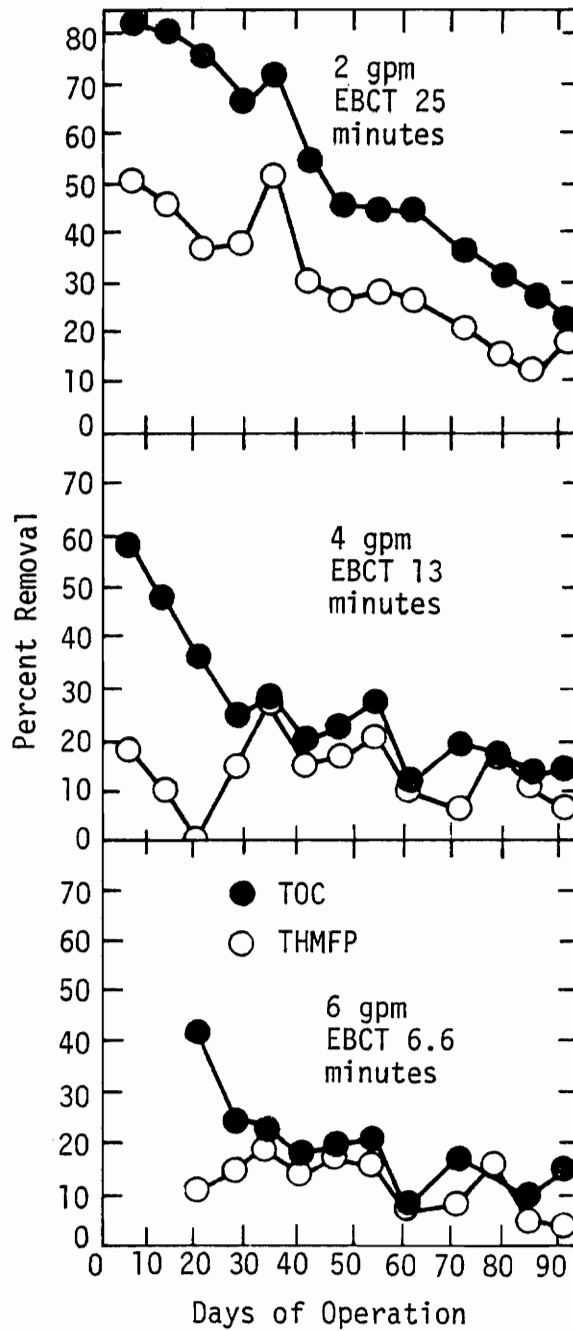


Figure 4. Percent Removal of Trihalomethane Formation Potential (THMFP) and Total Organic Carbon (TOC) by Granular Activated Carbon Contact at 2-, 4-, and 6-gpm Flow Rates.

TABLE 5. Percent Reduction in Trihalomethane
Formation Potential (THMFP) by GAC
Contact (June 27 - September 26, 1980)

Sample	$(1 - \frac{\text{Sample THMFP}}{\text{Raw Water THMFP}}) \times 100$	
	Mean	Standard Deviation
2-gpm Effluent	30.9	16.5
4-gpm Effluent	13.7	10.5
6-gpm Effluent	10.2	5.5

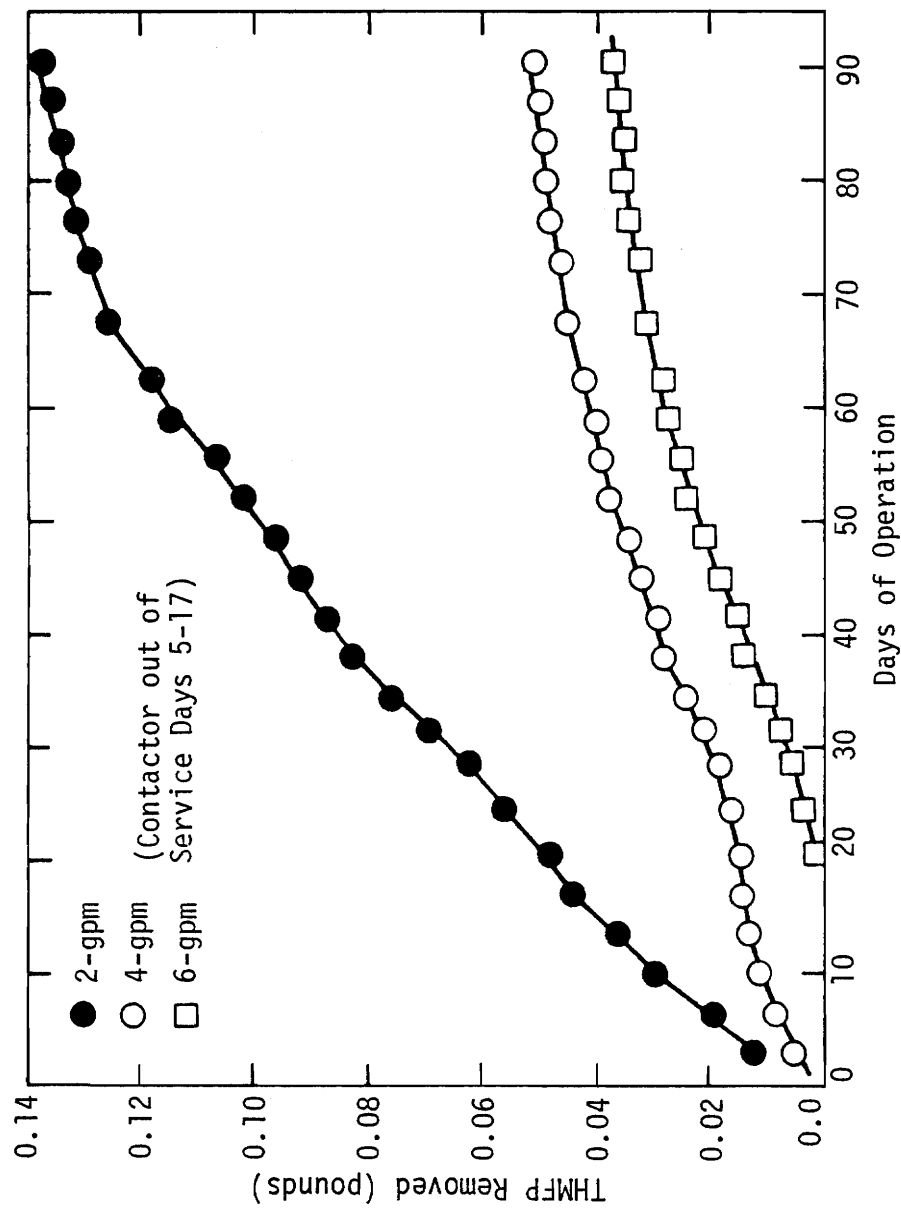


Figure 5. Mass of Trihalomethane Formation Potential (THMFP) Removed by Granular Activated Carbon Contact at 2-, 4-, and 6-gpm with time in Service of the Carbon Contactors.

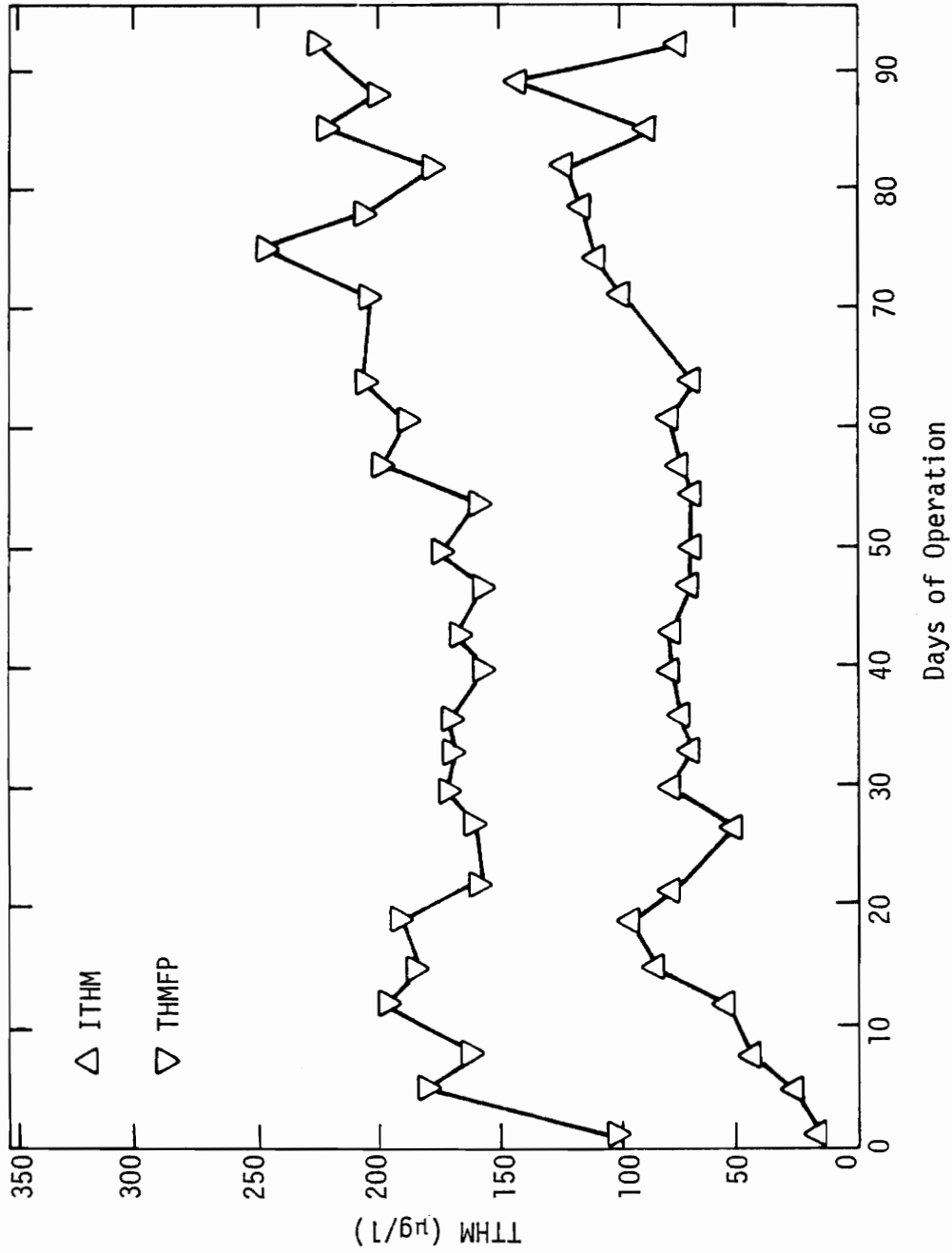


Figure 6. Total Trihalomethane (TTHM) Concentrations in Chlorinated 4-gpm Granular Activated Carbon Contactor Effluent Samples After Thirty Minutes (ITHM) and Seven Days (THMFP).

ITHM concentrations varied from a high of 143 $\mu\text{g/l}$ to a low of 15 $\mu\text{g/l}$, averaging 80 $\mu\text{g/l}$. THMFP concentrations were an average of 53.7 percent greater and averaged 179 $\mu\text{g/l}$. From Figure 6, it can be seen that the peaks in THMFP concentration corresponding to those observed in the raw water THMFP were present but to a lesser degree.

Figure 5 illustrates that the total mass of THMFP adsorbed by the 4-gpm contactor was considerably less than that adsorbed by the 2-gpm contactor. The column's capacity of approximately 0.05 pounds had been reached after 75 days in service.

Six-gpm contactor effluent. THM concentrations in the effluent of the 6-gpm contactor are shown in Figure 7. This contactor was out of service for a period of thirteen days at the beginning of the study period. It can be seen from this figure that both ITHM and THMFP concentrations were very nearly as great as those in chlorinated raw water samples. The average ITHM concentration was 88 $\mu\text{g/l}$ and the average THMFP concentration was 187 $\mu\text{g/l}$ during the study period. Similar peaks in the THMFP of this water and raw water were observed.

Figure 4 shows that THMFP removal at this hydraulic loading was just over ten percent initially and remained fairly consistent over the study period. The average THMFP removal for the period was 10.2 percent. Figure 5 shows that the carbon adsorbed only 0.04 pounds of THMFP before it was exhausted.

Total Organic Carbon

TOC was measured in this study to provide an indication of the organic content of the samples and to serve as a surrogate measure

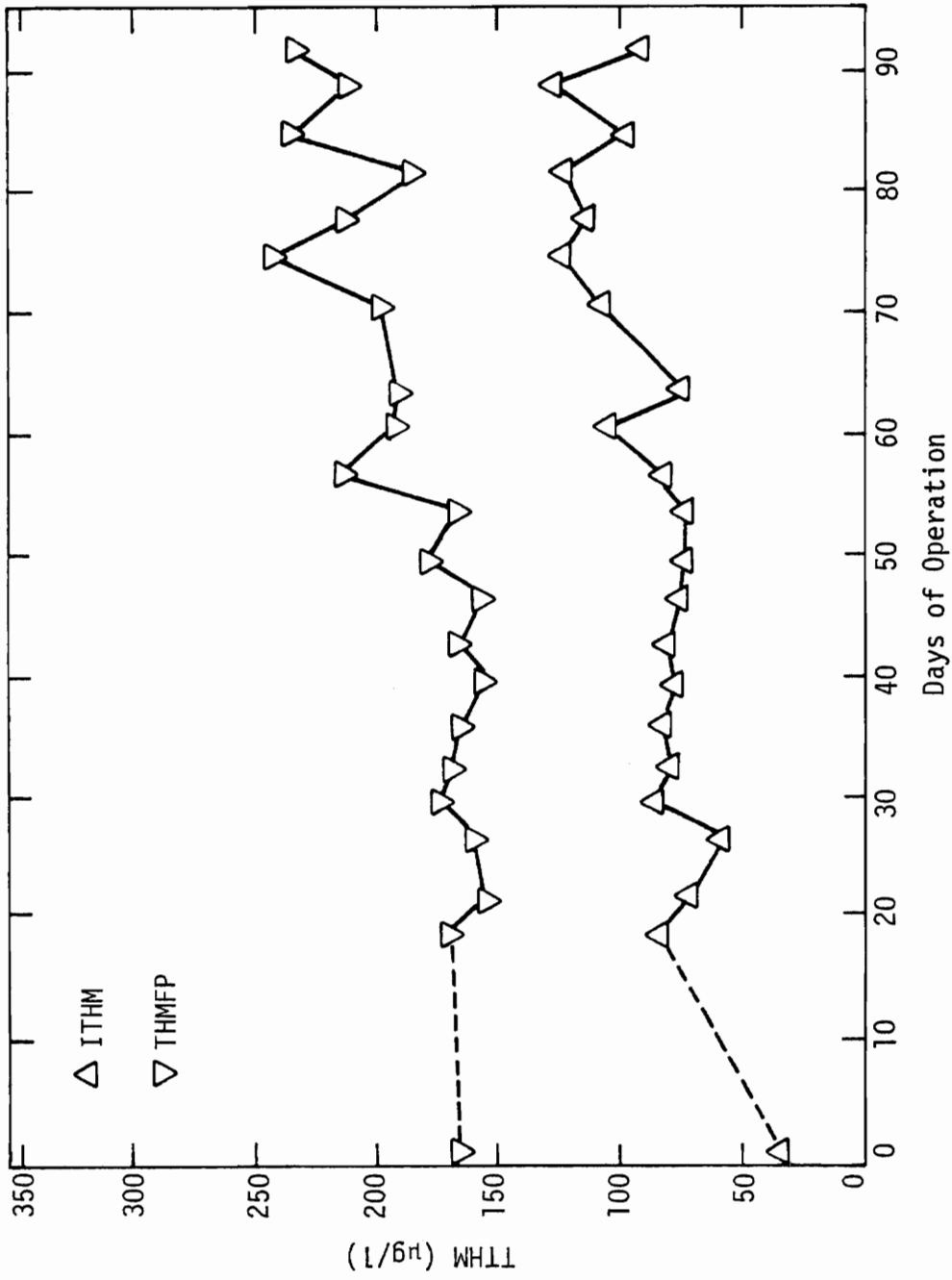


Figure 7. Total Trihalomethane (TTHM) Concentrations in Chlorinated 6-gpm Granular Activated Carbon Contactor Effluent Samples After Thirty Minutes (ITHM) and Seven Day (THMFP).

of THM precursor concentration. Data from these analyses are presented in Appendix B, Table B1.

Raw water samples. Concentrations of TOC in the raw water are plotted in Figures 8, 9, and 10, for purposes of comparison to the TOC in the effluents of the three GAC contactors. The TOC concentration in the raw water remained fairly consistent until after day 65 when it started increasing, peaking on day 75, and remaining high for the remainder of the study period. Raw water TOC concentrations ranged from 4.9 mg/l to 10.3 mg/l, the average concentration being 6.9 mg/l. Table 6 summarizes TOC concentrations in the raw water and GAC contactor effluent samples.

Two-gpm contactor effluent. Figure 8 illustrates the TOC concentrations in the effluent of the 2-gpm contactor. As can be seen, effluent TOC increased during the period of study, and approached the level of TOC in the raw water. The sharp increase in raw water TOC after day 65 was also evident in the effluent.

Figure 4 illustrates the decline in removal of TOC by GAC contact with increasing time in service. TOC removal was 82 percent initially and decreased steadily to a low of 23 percent. Average TOC removal over the period of operation was 54.8 percent. Table 7 summarizes the TOC removal achieved by GAC contact.

Figure 11 represents the total mass of TOC adsorbed by the GAC during the study period. When operation was terminated, a total of eight pounds of TOC had been adsorbed. The shape of the curve does

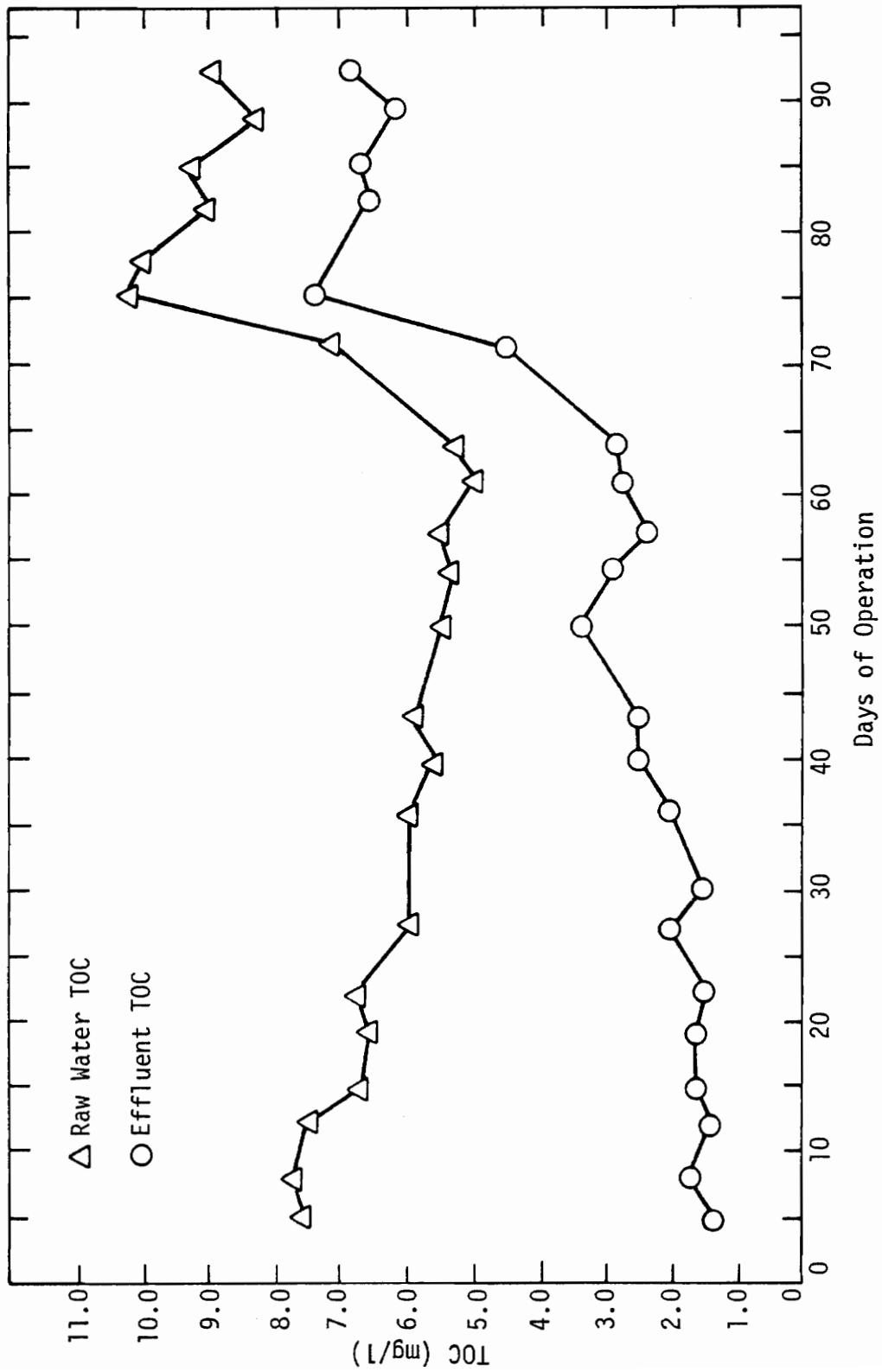


Figure 8. Total Organic Carbon (TOC) Concentrations in Raw Water and 2-gpm Granular Activated Carbon Contactor Effluent Samples.

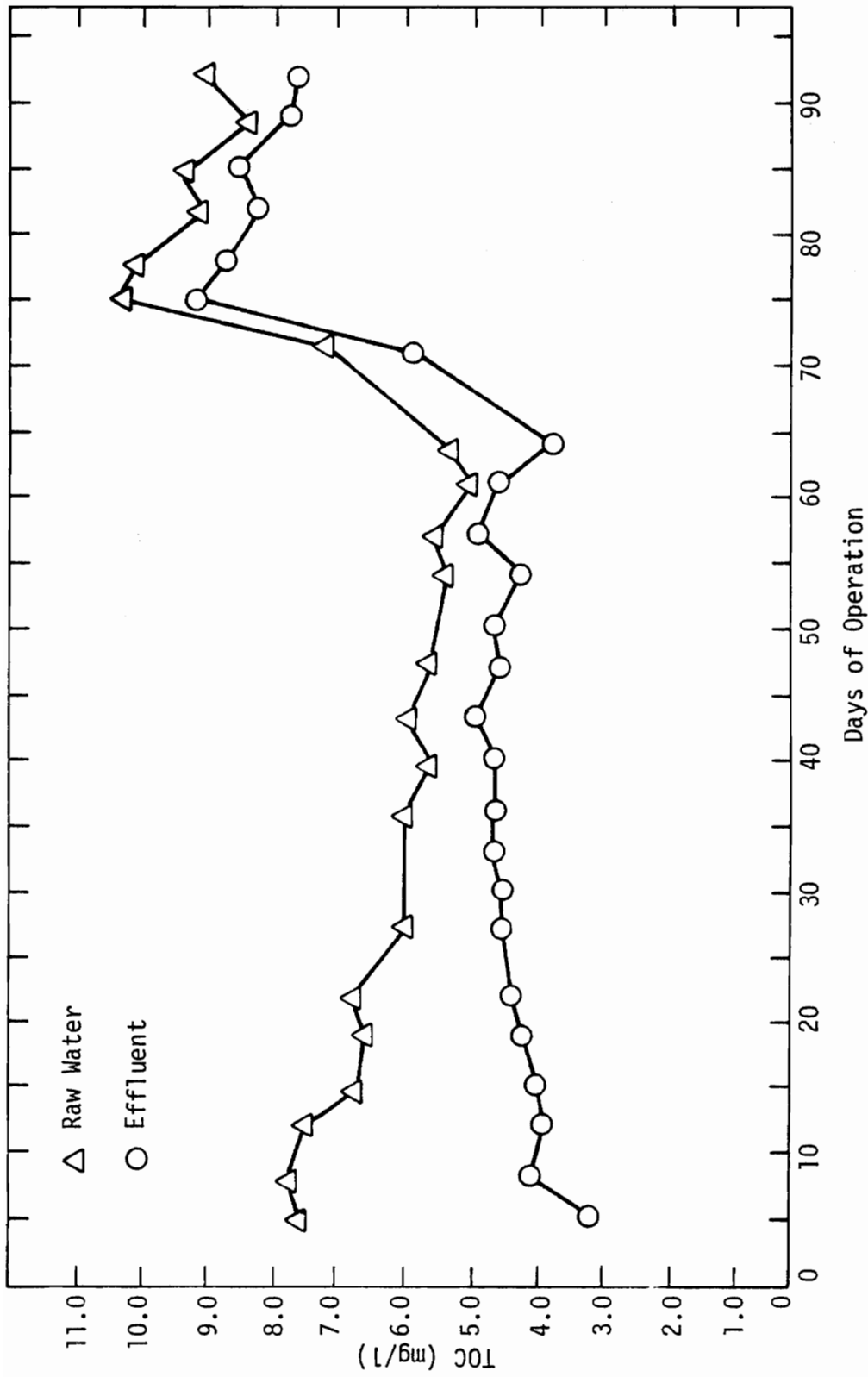


Figure 9. Total Organic Carbon (TOC) Concentrations in Raw Water and 4-gpm Granular Activated Carbon Contactor Effluent Samples.

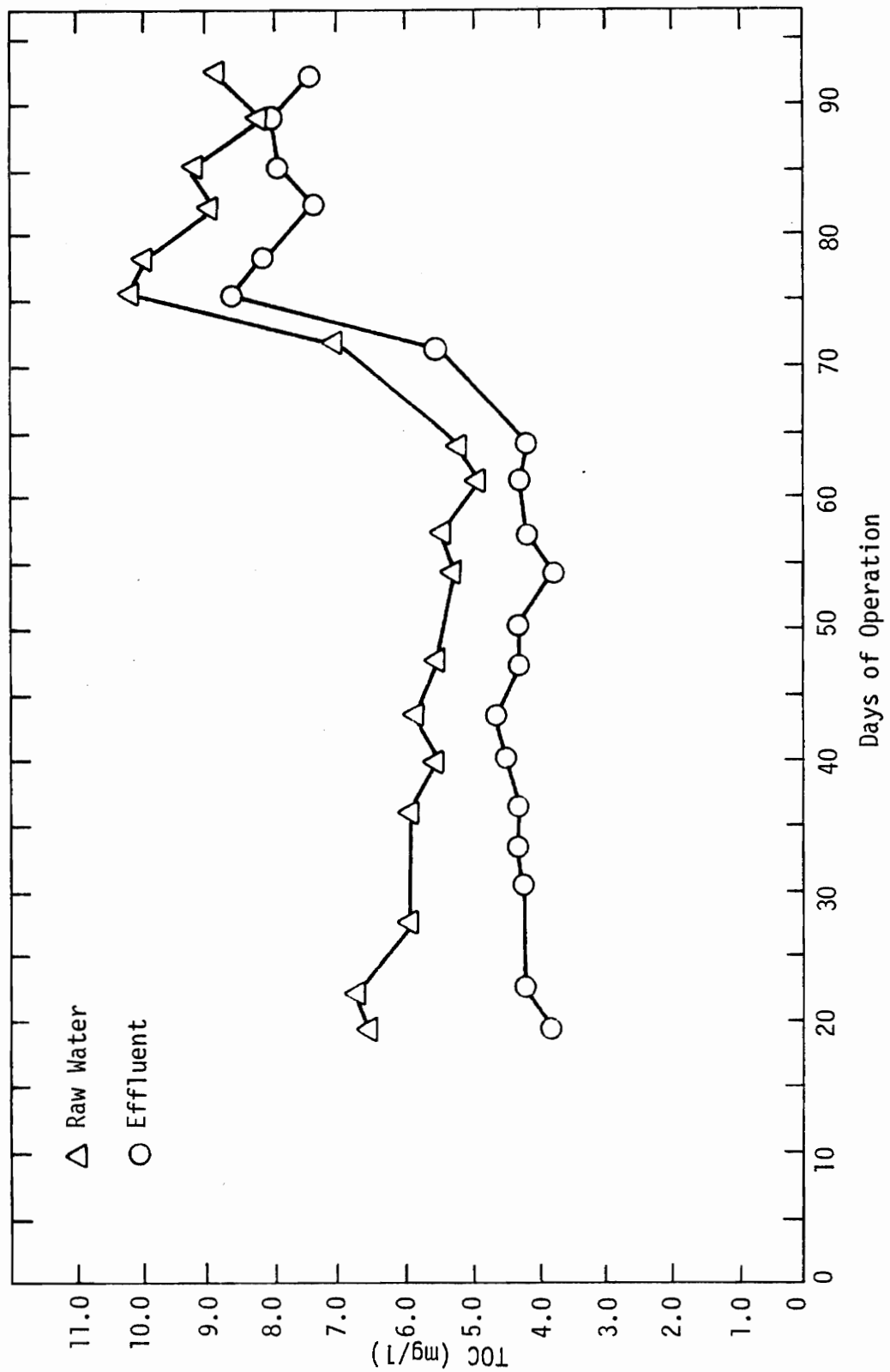


Figure 10. Total Organic Carbon (TOC) Concentrations in Raw Water and 6-gpm Granular Activated Carbon Contactor Effluent Samples.

TABLE 6. Total Organic Carbon (TOC) Concentrations in Raw Water Influent and GAC Contactor Effluent Samples (June 27 - September 26, 1979).

Sample	TOC (mg/l)	
	Mean	Standard Deviation
Raw	6.9	1.6
2-gpm Effluent	3.2	2.0
4-gpm Effluent	5.2	1.7
6-gpm Effluent	5.6	1.8

TABLE 7. Percent Removal of Total Organic Carbon (TOC) by GAC Contact
(June 27 - September 26, 1979)

Sample	Percent Removal	
	Mean	Standard Deviation
2-gpm Effluent	54.8	20.2
4-gpm Effluent	25.9	12.6
6-gpm Effluent	23.0	12.4

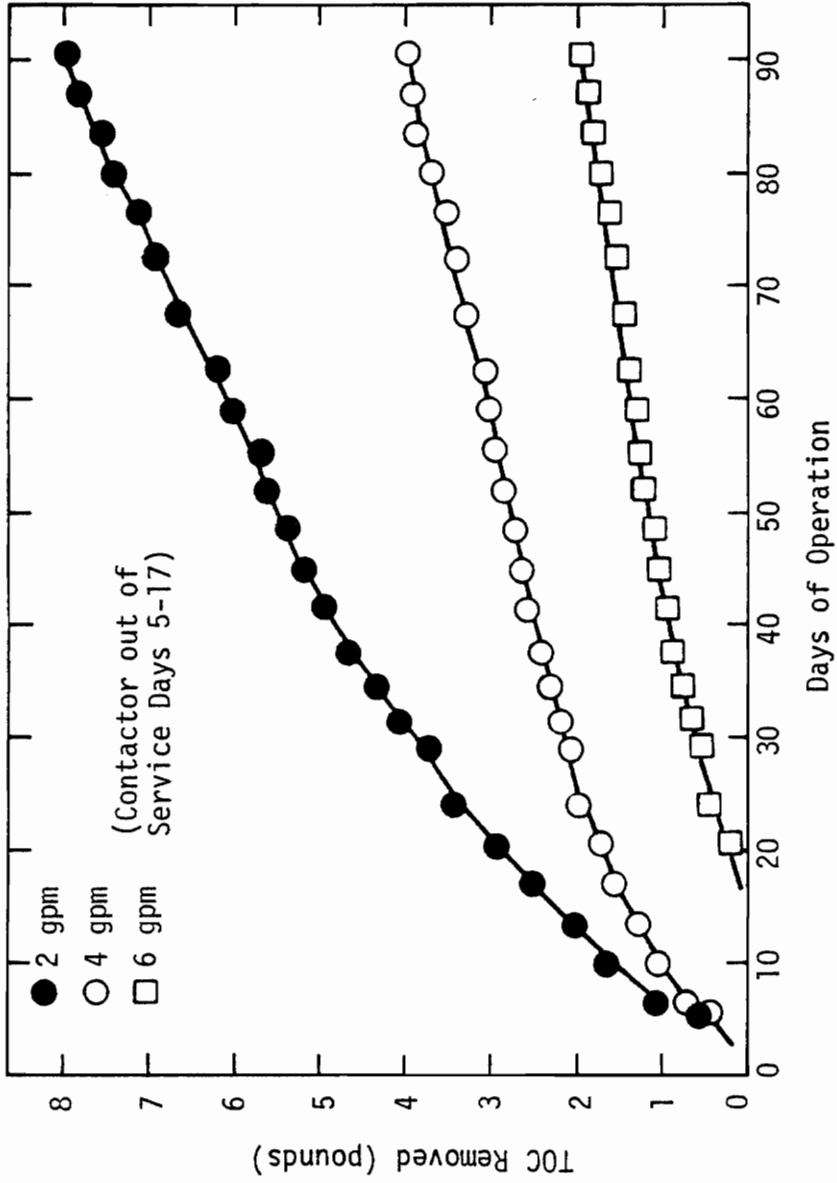


Figure 11. Mass of Total Organic Carbon (TOC) Removed by Granular Activated Carbon Contact at 2-, 4-, and 6-gpm with Time in Service of the Carbon Contactors.

not indicate with certainty that the column's capacity had been reached at that time.

Four-gpm contactor effluent. TOC concentrations in samples of effluent water from the 4-gpm contactor are shown in Figure 9. Although some reduction in TOC was evident in all samples, the concentrations of TOC in the effluent rapidly approached those of the raw water. Effluent TOC concentrations increased with the raw water concentrations after day 65. TOC concentrations in the effluent from this contactor ranged from 3.2 mg/l to 8.7 mg/l, and the average concentration for the period of operation was 5.2 mg/l.

Figure 4 illustrates the percent removal of TOC by GAC contact at a 4-gpm rate of flow. Initially 58 percent of the influent TOC was removed, but the removal efficiency decreased rapidly, averaging 25.9 percent over the period of operation. When operation was terminated, the carbon in this contactor had adsorbed four pounds of TOC, as is shown in Figure 11.

Six-gpm contactor effluent. GAC contact at this flow rate removed some TOC throughout the period of operation. Figure 10 shows that there was not a great difference in TOC concentration in the raw water and the effluent from the GAC contactor. The TOC concentration in the effluent increased markedly after day 65 concomitantly with the increased TOC in the raw water. The average TOC concentration in the effluent samples was 5.6 mg/l. The range over the study period was 3.7 mg/l to 9.1 mg/l.

Almost two pounds of TOC had been adsorbed by the carbon in this contactor when operation was ended (Figure 11). Figure 4 shows that TOC removal was initially 41 percent and decreased rapidly with time in service. The average TOC removal achieved was 23 percent.

Color

Color measurements in raw and GAC treated samples are listed in Appendix B, Table B5. Color removal by GAC contact is summarized in Table 8. GAC contact at EBCTs of 26, 13, and 6.6 minutes (2-, 4-, and 6-gpm) reduced raw water color an average of 35.1, 17.5, and 14.2 percent, respectively. Color in the effluent samples ranged from 20 to 120 color units. As might be expected, color removal by GAC contact decreased with time in service of the GAC contactors.

Turbidity

Although the carbon contactors were operated in an upflow mode, flow rates were not sufficiently high to allow all of the turbidity in the effluents to pass. Turbidity was removed to some degree from raw water at all flow rates used in this study. Raw water turbidity measurements are illustrated in Figure 12. After day 60 they increased dramatically, peaking on days 75 and 89. Effluent turbidity showed corresponding increases. On several occasions late in the study effluent turbidity exceeded the turbidity in the raw water. Appendix B, Table B4, contains turbidity data for all samples collected during the study.

Table 8. Color Removal by GAC Contact
(June 27 - September 26, 1979)

Sample	Percent Color Removal	
	Mean	Range
2-gpm Contactor	35.1	9-62
4-gpm Contactor	17.5	0-55
6-gpm Contactor	14.2	0-55

EFFECTS OF EMPTY BED CONTACT TIME

The three GAC contactors were operated at 2-, 4-, and 6-gpm with corresponding EBCTs of 26, 13, and 6.6 minutes. Differences in removal of THMFP, TOC, color, and turbidity were observed at the different EBCTs.

Trihalomethane Formation Potential

Table 4 summarizes the THM data for the three carbon contactor effluents. The highest concentrations were found in the effluent samples from the 6-gpm contactor which had the shortest EBCT, 6.6 minutes. Lower concentrations were produced in samples collected from the 4-gpm contactor which had an EBCT of 13 minutes. The lowest THM concentrations were achieved by an EBCT of 26 minutes in the 2-gpm contactor.

Correspondingly, the best removal (30.9 percent) of THMFP was effected by the 2-gpm contactor. Table 5 summarizes the percent removal by the three contactors. The average removal observed in the column with 13 minutes EBCT was less than half that in the 2-gpm contactor, 13.7 percent. The least effective THMFP removal corresponded to the shortest EBCT. At 6.6 minutes EBCT, an average of only 10.2 percent of the THMFP was removed. Figure 4 illustrates the percent removal of THMFP at the three EBCTs. From this figure it can be seen that not only was the percent removal reduced at shorter EBCTs, but also the efficiency of the contactor decreased more rapidly with time in service.

Table 3 summarizes the relative proportions of ITHM and THMFP at different flow rates and corresponding EBCTs. The ITHM concentration was 54.9 percent of the THMFP in the raw water samples. After GAC contact at 2-gpm (26 minutes EBCT) the ITHM was only 36.5 percent of the THMFP of the water. It appears from the data that as EBCT was reduced, the ITHM was a greater percentage of the THMFP. Represented another way, the percent increase in TTHM over the seven-day period of chlorine contact was greatest in samples from the GAC columns with the longer EBCT's. The significance of this observation will be addressed in the Discussion chapter.

Figure 5 shows how the mass of THMFP adsorbed by GAC varied with EBCT. At a flow rate of 6-gpm (EBCT of 6.6 minutes), the total THMFP adsorbed was less than that observed at longer EBCTs. A much greater mass of THMFP was adsorbed by GAC at 2-gpm (EBCT of 26 minutes), nearly three times that adsorbed at the 4-gpm flow rate.

Total Organic Carbon

The concentration of TOC in the effluent also varied with the time the water was in contact with the carbon. At slower flow rates and longer EBCTs, the TOC concentration that was present in the effluent was lower. Table 6 summarizes the TOC data, and shows 1) that the 2-gpm contactor effluent TOC concentrations were the lowest, an average of 3.2 mg/l and 2) that the TOC in the 6-gpm contactor effluent was the highest, an average of 5.6 mg/l. As with THMFP, the reduction of TOC by GAC contact was greatest at the longest EBCT.

Table 7 summarizes the removal of TOC by the three GAC contactors.

Figure 11 shows that the total mass of TOC adsorbed in the three GAC contactors was directly related to EBCT. At 26 minutes EBCT, TOC adsorbed was nearly twice that at 13 minutes EBCT and four times that at 6.6 minutes EBCT.

Color Removal

Color removal also varied with EBCT, and was greatest at longer EBCTs. Color removal data are summarized in Table 8. Color removal was variable during the study period, but in general it decreased with time in service of the carbon contactors at all EBCTs. The maximum color removal achieved was 62 percent. Table B5 contains color data for the study period.

Turbidity Removal

Some removal of turbidity was achieved by all three GAC contactors. As was expected, more turbidity was permitted to pass through the beds at higher flow rates. Raw water turbidity removals were 44.9, 28.3, and 17.9 percent at flow rates of 2-, 4-, and 6-gpm, respectively. Turbidity removal was variable over the period at all EBCTs. Late in the study, some effluent samples had higher turbidities than the raw water. Table B4 contains turbidity measurements recorded during the study.

WATER QUALITY AND THMFP

Total Organic Carbon

Raw water TOC (Figures 8, 9, and 10) remained fairly consistent until it increased sharply after day 65. It does not noticeably increase and decrease correspondingly with raw water THMFP, except during the final three weeks of the study when both concentrations reached their maximum. The data did not illustrate that there was a dependable, predictive relationship between TOC concentrations and corresponding THMFP concentrations.

Color

Figure 12 shows the variation in raw water color during the study. Until after approximately sixty days, the color of the raw water remained at a fairly consistent level. Raw water color increased dramatically after that time, reaching two peak values on days 75 and 89. The average raw water color was 56 color units. The maximum color observed was 130 color units.

Color values had much the same relationship to THMFP concentrations as did TOC concentrations. They did not fluctuate in a corresponding manner except during the time the peak values were observed at days 57, and especially at day 75 and 89.

Turbidity

Raw water turbidity also was maximal on days 75 and 89. The turbidity of the raw water was fairly constant throughout the period of study prior to day 60. It increased slightly on day 33 and

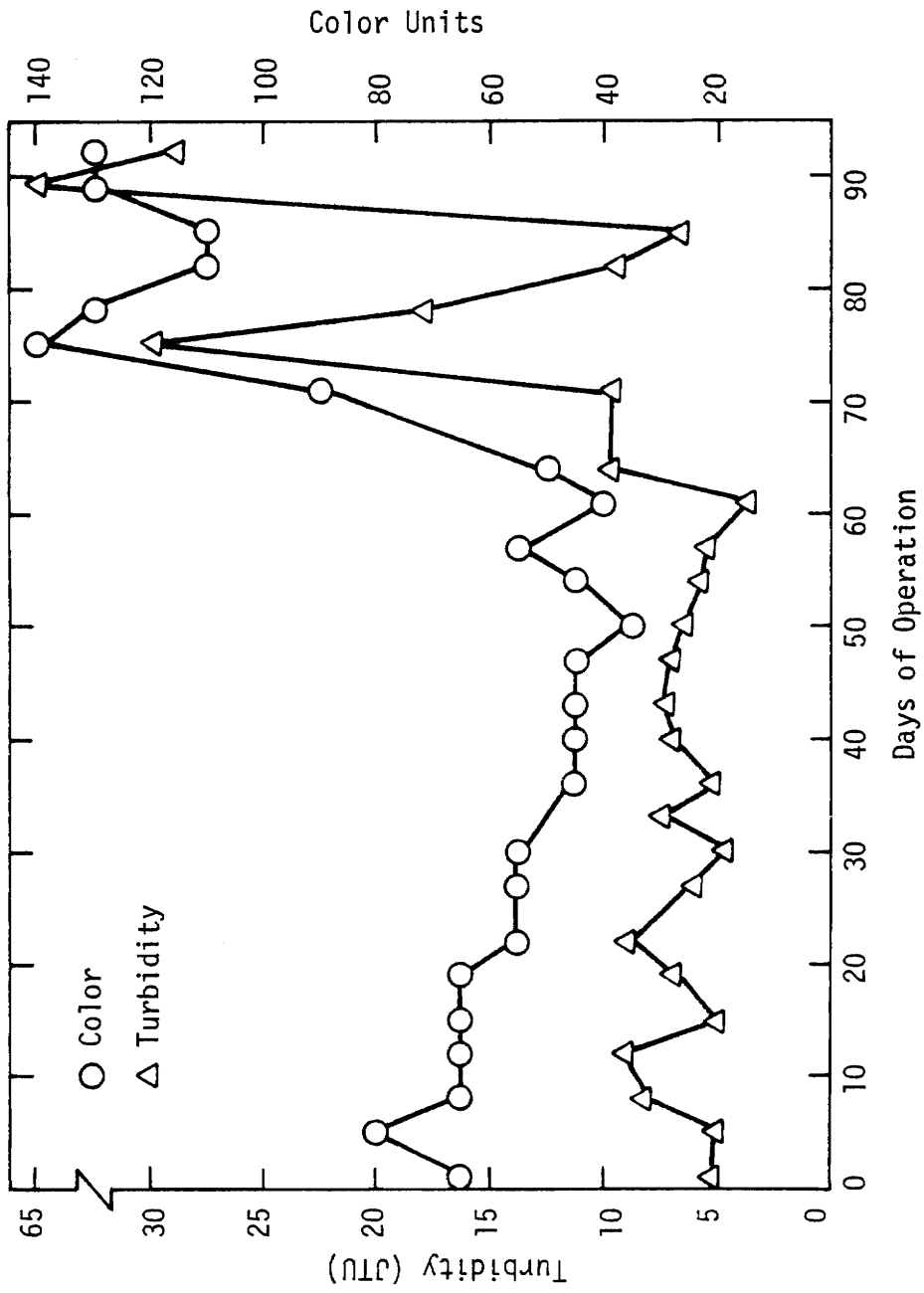


Figure 12. Raw Water Turbidity and Color Measurements During the Period of Operation (June 27 - September 26, 1979).

corresponded to a slight increase in raw water THMFP on that day as well.

ITHM concentrations corresponded much less well with increased turbidity than did THMFP concentrations. Table 3 shows that ITHM concentrations represented less of the THMFP in samples with higher turbidity (i.e. raw water and effluent samples from the higher flow rate contactors). The highest percentage of influent turbidity was removed by the 2-gpm contactor, and the ITHM produced in those samples comprised a smaller proportion of the THMFP than was observed in either the raw water or the other two contactor effluents.

Figure 4 shows that when the GAC contactors were achieving high removals of TOC, the removals of THMFP were not as high. This effect was not so pronounced in the 2-gpm contactor as it was in the 4-gpm and 6-gpm contactors. These two higher-rate contactors passed greater amounts of turbidity and THMFP as well.

Chlorophyll-a Concentrations and Algal Counts

Available chlorophyll-a data for the period of study illustrated in Figure 13, were not abundant. The data are tabulated in Appendix C, Table C1. It is difficult to relate the observed concentrations of chlorophyll-a to the THMFP produced in the raw water. On day 78, near the time when THMFP was maximal, chlorophyll-a was 9.5 $\mu\text{g/l}$. Measurements for several weeks prior to that are not available, so it is difficult to interpret the importance of that concentration. While 9.5 $\mu\text{g/l}$ is a relatively high concentration, it is not atypical during the summer months in the reservoir.

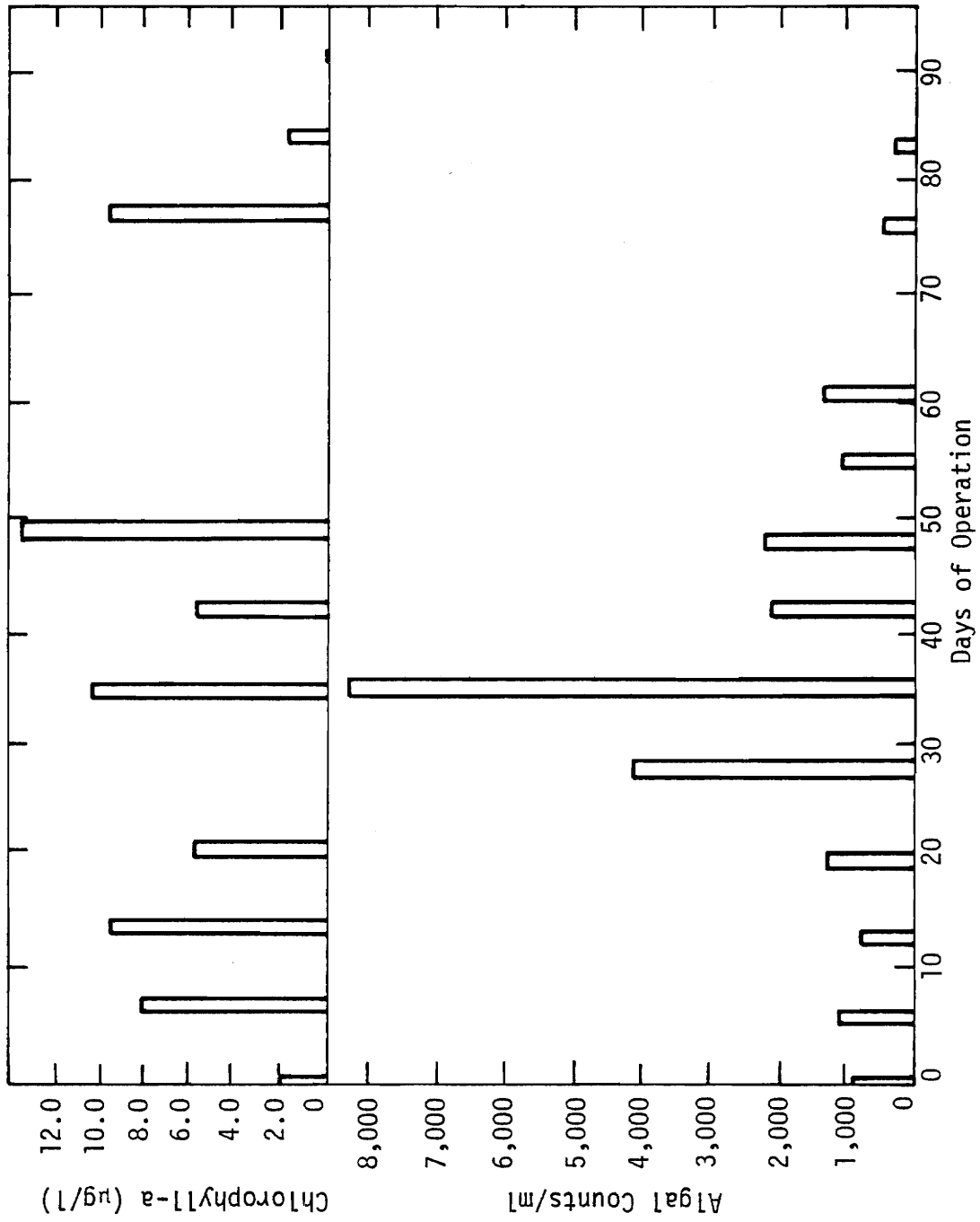


Figure 13. Reservoir Algal Counts and Chlorophyll-a Concentrations During the Period of Operation (June 27 - September 26, 1979).

Only one algal bloom period was evident during the study period. Algal counts in the reservoir are represented in Figure 13 and tabulated in Appendix C, Table C2. The maximum algae count of 8323 cells/ml corresponded to a slight increase in raw water THMFP. The large increases in THMFP on days 75 and 89 did not correspond to increases in algal populations.

Rainfall and Reservoir Stage

Rainfall data and measurements of reservoir stage are tabulated in Appendix C, Tables C3 and C4, respectively. Fluctuations in these two measurements correspond well. Increases in rainfall were followed shortly in time by a rise in reservoir surface elevation. These increases in water level correspond to the majority of peaks in THMFP at days 33, 50, 57, and especially 75 and 89. As has been reported previously, increases in other water quality measurements such as color, turbidity, and TOC also were noted on these days. The significance of these correlations will be discussed in the following section.

V. DISCUSSION

GAC PRETREATMENT FOR TRIHALOMETHANE PRECURSOR REMOVAL

The results of this study demonstrated that GAC pretreatment was effective for the removal of THM precursors. In addition, GAC was effective in reducing the THMFP, TOC, and color of raw water, all of which are associated in one way or another with concentrations of precursor substances. It is emphasized that this study was undertaken to evaluate the effectiveness of GAC for precursor removal in general, and not with a view to its applicability specifically for meeting the newly-promulgated MCL of 100 $\mu\text{g/l}$ TTHM. However, some indication can be drawn from the data regarding the usefulness of GAC pretreatment for complying with the MCL and will be addressed.

The maximum removal of THM precursors (as measured by THMFP) attained in this study was slightly greater than 80 percent. Precursor removal efficiency diminished steadily with time in service of the GAC columns, a phenomenon demonstrated by other studies reported in the literature (21,51). The minimum observed THMFP concentration was 65 $\mu\text{g/l}$, produced in water pretreated with GAC at a flow rate of 2 gpm.

The THMFP of the effluents from the three GAC contactors increased steadily during the study period as the capacity of the carbon for adsorbing precursors was decreased. As the adsorbed mass of THMFP and TOC (Figures 5 and 11) increased, the percent reduction in THMFP and TOC (Figure 4) decreased. This same result

has been observed in other research (21). On a weight basis, the best removal of TOC observed was 74 mg/g GAC. GAC removed a maximum of 1.3 mg THMFP per gram of GAC (Table 9). This removal is significantly less than that reported by Wood and DeMarco (74); however, it should be noted that the nature and concentration of precursors in the raw water treated in that study were quite different as well.

Figure 3 shows that GAC pretreatment may have been capable of producing an effluent water quality good enough to be in compliance with the THM MCL up to approximately 40 days in service at a flow of 2 gpm under summer conditions. This suggestion is based on the specification by the EPA (10) that compliance with the MCL would be based on a number of samples collected quarterly from various points in a water supplier's distribution system. Assuming that most tap water in the United States has a residence time in the distribution system of less than seven days (the period of chlorine contact used to define THMFP), THM concentrations in the chlorinated effluent water from this contactor would have likely met the MCL. It may be reasonably expected that worst-case conditions in terms of some of the factors affecting THM production, for example temperature and organic content of the raw water, occur during the summer. As a result, if GAC pretreatment is effective under these conditions, it shows promise for THM control year-around.

Comparison of Figures 3, 6, and 7 with Figure 2 shows that the THMFP of the GAC contactor effluents fluctuated in a manner similar to that of the raw water. This same pattern of fluctuation was

TABLE 9. Removal of Trihalomethane Formation Potential (THMFP) and Total Organic Carbon (TOC) by GAC by Weight (June 27 - September 26, 1979)

Flow Rate (gpm)	<u>mg TOC Removed</u> g GAC	<u>mg THMFP Removed</u> g GAC
2	74	1.3
4	36	0.5
6*	17	0.4

*6-gpm contactor was out of service July 1 - July 13, 1979.

observed in the removal of TOC by GAC (Figures 8, 9, and 10). This relationship indicates that the effectiveness of GAC is such that the effluent quality will vary with the quality of the influent and may not be assumed to decrease only as a function of time in service.

The data from this study suggest that GAC was effective for the removal of THM precursors that react readily with chlorine (i.e. those responsible for ITHM concentrations) more so than for those precursors which react more slowly (i.e. those responsible for THMFP concentrations). Figure 2 shows that the ITHM concentration in a sample was not a constant proportion of the THMFP of that sample. ITHM concentrations cannot be relied upon to predict the THMFP concentration which will be produced. One possible explanation is the existence of two types of precursor materials, one type responsible for production of ITHM concentrations, and another type which requires several days to react completely with available chlorine to produce THMFP concentrations. Differing relative concentrations of these two types of precursors could be responsible for the different ITHM/THMFP ratios observed among different samples.

The suggestion that GAC pretreatment is selective for the removal of ITHM-forming precursors is implicit in the data displayed in Table 3. Comparison of the relative proportions of ITHM and THMFP concentrations shows that the GAC contactor effluent samples had a smaller relative proportion of ITHM-forming precursors than the raw water. While Table 5 shows that THMFP was reduced by GAC contact at all flow rates used in this study, Table 3 indicates that compounds that

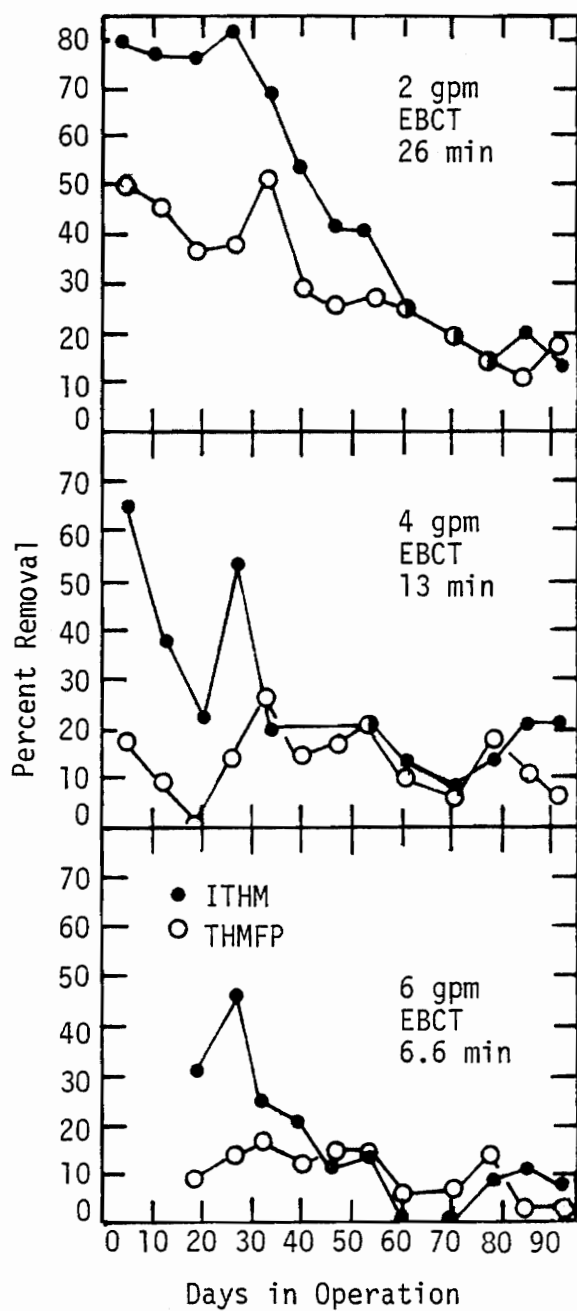


Figure 14. Percent Removal of Trihalomethane Formation Potential (THMFP) and Instantaneous Trihalomethanes (ITHM) by Granular Activated Carbon Contact at 2-, 4-, and 6-gpm Flow Rates

readily react to form THMs were removed to a greater extent than those that react more slowly.

Some suggestion of the characters of these two types of precursors with regard to whether they are soluble or associated with particulate matter in the water can be drawn from the data. Figure 4 shows that at flow rates of 4-gpm and 6-gpm, GAC contact was selective for the removal of TOC that was not responsible for THMFP. While the removals of TOC were relatively great, corresponding THMFP removals were not. This is not evident from the data for the 2-gpm contactor. At the higher flow rates, not only was the fraction of the TOC responsible for THMFP passing through the bed, these columns were also passing larger amounts of the influent turbidity (Table B4). This suggests that organic material associated with particulate matter in the water may have been responsible for a large fraction of the THMFP of the column effluents.

Figure 14 shows that the percent removal of ITHM by the three GAC contactors parallels the removal of TOC much more closely than that of THMFP. Selectivity for non-precursor TOC is not evident in the case of the removal of ITHM precursors. The GAC contactors were designed primarily as adsorbers rather than filters and as such were more efficient for removing adsorbable organics than filterable particulates. This further substantiates the contention that most precursors removed by GAC contact are those responsible for ITHM rather than THMFP and that these are most likely soluble rather than particulate forms.

EFFECTS OF EMPTY BED CONTACT TIME

GAC pretreatment at a flow rate of 2 gpm consistently produced the best quality effluent in terms of THMFP, TOC, and color. In addition, the effluent quality of the 2-gpm contactor did not decrease as rapidly with increasing time in service as did that of the 4- and 6-gpm contactors. The greatest mass of both TOC and THMFP was removed by the 2-gpm contactor.

The results of this study indicate that GAC pretreatment of Occoquan Reservoir water at a flow rate of 2 gpm or less was necessary to produce an effluent water with a THMFP in the range to comply with MCL. At 4 and 6 gpm, the THMFP of the effluent was equal to or greater than 100 $\mu\text{g/l}$ throughout the study period. At both these flow rates, even the ITHM concentrations were in excess of 100 $\mu\text{g/l}$ at times. Of course, these data evaluate GAC contact as the sole treatment process used, but if GAC pretreatment was used in conjunction with standard coagulation, sedimentation, and filtration the effluent quality would surely be further improved.

The best removal of THMFP and TOC on a weight basis (Table 9) was achieved at 2 gpm. Figures 5 and 11 show that GAC was adsorbing greater quantities of both THMFP and TOC at 2-gpm than at 4 or 6 gpm. The capacity of GAC at the higher flow rates was reached more quickly than at 2 gpm. Furthermore, the differences in the capacities were not proportional to the flow rates, a fact that indicates that some non-adsorptive property (such as filtration capacity) of the columns was responsible for improving the 2-gpm contactor's performance.

It is obvious from the data represented in Figures 3-11 and Tables 3-8 that the performance of the GAC in terms of effluent quality decreased as flow rate increased. It is interesting to note that effluent quality and GAC performance was not a linear function of flow rate. The 2-gpm contactor produced a significantly better effluent quality than either the 4- or 6-gpm contactors which were not in most cases greatly different from one another in terms of effluent quality and carbon performance. It should be noted that backwashing the GAC contactors late in the period of operation did not extend the bed-life or significantly improve the performance of the contactors.

WATER QUALITY AND THMFP

No measure of water quality was found to have a predictive relationship to THMFP. Several characteristics (TOC, color, turbidity) exhibited the same general pattern of fluctuation as THMFP over the period of study (Figures 3, 8, and 12). Because these characteristics did fluctuate together, it is impossible to single out the one whose effect was the most significant.

These water quality characteristics are interrelated in a complex cause-and-effect relationship with each other and other factors (algal populations, chlorophyll-a concentrations, rainfall) involved in the natural processes of surface water systems. The data clearly show that a substantial rainfall occurring after day 70 was followed by a rise in reservoir surface elevation due to runoff (Tables C3 and C4). Concomitantly, the turbidity, color, and TOC of the raw water

increased (Figures 8 and 12). An increase in THMFP also occurred at this time (Figure 2). Algal populations were not observed to increase (Figure 13), indicating that the effect of rainfall and runoff in this instance did not stimulate their growth. In turn, this indicates that algae probably were not responsible for the increased THMFP concentrations observed during that period of time.

VI. SUMMARY AND CONCLUSIONS

The objectives of this study were to evaluate the effectiveness of granular activated carbon (GAC) pretreatment for the removal of trihalomethane (THM) precursors, to determine if this effectiveness varies with empty bed contact time (EBCT), and to attempt to correlate various measures of raw water quality to the trihalomethane formation potential (THMFP) of the water. Raw water from the Occoquan Reservoir was treated by upflow GAC contact at flow rates of two, four, and six gallons per minute (gpm), corresponding to EBCTs of 26, 13, and 6.6 minutes, respectively. The column effluents and the influent raw water were chlorinated and analyzed for THMs after chlorine contact times of 30 minutes, one, two, four, and seven days.

Influent raw water and the three contactor effluents were analyzed for total organic carbon (TOC), color, and turbidity to determine the relationship between these water quality characteristics and THMFP. The GAC contactors were operated for thirteen weeks, from June 27 to September 26, 1979, and the effectiveness of GAC contact was found to diminish with time in service of the carbon contactors. During the period of operation chlorophyll-a concentrations and algal populations in the reservoir, rainfall, and reservoir surface elevation were monitored to determine what relationship exists between these characteristics and the THMFP of the reservoir water.

The significant conclusions that may be drawn from the results of this study are:

1. Precursors of THMs (as measured by THMFP and TOC) can be removed from untreated surface water by granular activated carbon contact. The most effective removals on a weight basis were achieved at a flow of 2 gpm. During the thirteen week study, THMFP removal was 1.3 mg/g carbon and TOC removal was 74 mg/g carbon.
2. The degree to which THM precursors were reduced by GAC contact was directly related to EBCT. Removals of THMFP and TOC were greatest at an EBCT of 26 minutes (averaging 30.9 and 54.8 percent, respectively), less at an EBCT of 13 minutes (averaging 13.7 and 25.9 percent, respectively) and least at an EBCT of 6.6 minutes (averaging 10.2 and 23.0 percent, respectively).
3. GAC contact (in the range of flow rates studied) in an upflow mode appeared to be selective for the removal of the fraction of THM precursors in the raw water responsible for the THM concentrations produced in thirty minutes of chlorine contact time (ITHM). Those precursors responsible for the additional THM concentrations produced after thirty minutes and up to seven days of chlorine contact (THMFP) appear to have been associated with particulate matter (turbidity) in the raw water which, due to the upflow design of the system, was in large measure (55 to 82 percent) passing through the contactors, or larger molecular weight substances which were not well adsorbed by the carbon used.
4. Direct correlations between THMFP and the turbidity, color, TOC, chlorophyll-a concentrations, and algal counts in the raw water could not be established by the data collected during this study.

Rainstorms and resulting runoff late in the period of operation resulted in the concomitant increases in the color, turbidity, and TOC concentrations of the raw water. Which of these three factors was most responsible for the resultant increase in THMFP is not clear. It is likely that all three are related to the concentration of available THM precursors, as well as to each other, so that a single parameter cannot be reliably used to predict the THMFP of a water.

VII. RECOMMENDATIONS FOR FURTHER RESEARCH

The results of this study suggest that raw water turbidity may play a significant role in the trihalomethane formation potential of the water. Research to answer the following questions would help to verify this suggestion and evaluate its significance in terms of water treatment practices to control trihalomethane formation potential:

1. What effect do coagulation, flocculation, and sedimentation have on the THMFP of a water and the relative proportions of THMFP and ITHM concentrations produced upon chlorination of that water?
2. Do coagulation, flocculation, and sedimentation further reduce the THMFP of a water when applied subsequent to GAC contact?

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APPENDIX A

TRICHALOMETHANE CONCENTRATIONS IN CHLORINATED
RAW WATER INFLUENT AND GAC (WESTVACO NUCHAR
WV-G AND WV-DC) CONTACTOR EFFLUENT SAMPLES

TABLE A1. Instantaneous Trihalomethane Concentrations in Chlorinated Raw Water Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				TTHM
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	
6-27-79	1	82	5	1	ND*	88
7-1-79	5	76	4	<1	ND	80
7-4-79	8	91	5	<1	ND	96
7-8-79	12	82	6	4	ND	92
7-11-79	15	112	6	3	ND	121
7-15-79	19	114	6	3	ND	123
7-18-79	22	104	6	4	ND	114
7-23-79	27	103	6	4	ND	113
7-26-79	30	100	8	1	ND	109
7-29-79	33	94	7	ND	ND	101
8-1-79	36	85	6	1	ND	92
8-5-79	40	93	7	<1	ND	100
8-8-79	43	85	7	1	ND	93
8-12-79	47	83	7	1	ND	91
8-15-79	50	79	7	1	ND	87
8-19-79	54	84	6	<1	ND	90
8-22-79	57	85	6	ND	ND	91
8-27-79	61	81	7	5	ND	93
8-29-79	64	91	8	ND	ND	99
9-5-79	71	96	5	7	ND	108
9-9-79	75	110	4	4	ND	118
9-12-79	78	126	5	5	ND	136
9-16-79	82	130	4	5	ND	139
9-19-79	85	110	4	<1	ND	114
9-23-79	89	152	5	1	ND	159
9-26-79	92	100	3	<1	ND	103

*Not Detected

TABLE A2. One-Day Trihalomethane Concentrations in Chlorinated Raw Water Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	TTHM
6-27-79	1	146	12	2	ND*	160
7-1-79	5	--	--	--	--	--
7-4-79	8	161	11	2	ND	174
7-8-79	12	172	12	2	ND	186
7-11-79	15	178	13	2	ND	193
7-15-79	19	153	14	2	ND	169
7-18-79	22	155	14	<1	ND	169
7-23-79	27	134	13	2	ND	149
7-26-79	30	146	16	1	ND	163
7-29-79	33	146	18	1	ND	165
8-1-79	36	137	16	1	ND	154
8-5-79	40	157	20	1	ND	178
8-8-79	43	143	19	1	ND	163
8-12-79	47	163	21	1	NC	185
8-15-79	50	159	18	1	ND	178
8-19-79	54	137	20	1	ND	158
8-22-79	57	148	18	1	ND	167
8-27-79	61	126	18	1	ND	145
8-29-79	64	173	18	1	ND	192
9-5-79	71	134	12	1	ND	147
9-9-79	75	195	8	2	ND	205
9-12-79	78	227	10	2	ND	239
9-16-79	82	146	7	1	ND	154
9-19-79	85	180	9	1	ND	190
9-23-79	89	194	9	1	ND	204
9-26-79	92	179	8	1	ND	188

*Not Detected

TABLE A3. Two-Day Trihalomethane Concentrations
in Chlorinated Raw Water Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	TTHM
6-27-79	1	--	--	--	--	--
7-1-79	5	180	14	1	ND*	195
7-4-79	8	--	--	--	--	--
7-8-79	12	196	15	1	ND	211
7-11-79	15	--	--	--	--	--
7-15-79	19	175	15	1	ND	191
7-18-79	22	--	--	--	--	--
7-23-79	27	147	17	1	ND	165
7-26-79	30	173	20	1	ND	194
7-29-79	33	166	21	1	ND	188
8-1-79	36	--	--	--	--	--
8-5-79	40	154	22	1	ND	177
8-8-79	43	156	22	1	ND	179
8-12-79	47	121	19	1	ND	141
8-15-79	50	154	21	1	ND	176
8-19-79	54	157	21	1	ND	179
8-22-79	57	142	21	1	ND	164
8-27-79	61	142	20	1	ND	163
8-29-79	64	--	--	--	--	--
9-5-79	71	--	--	--	--	--
9-9-79	75	182	9	2	ND	193
9-12-79	78	--	--	--	--	--
9-16-79	82	140	7	1	ND	148
9-19-79	85	--	--	--	--	--
9-23-79	89	214	11	<1	ND	225
9-26-79	92	--	--	--	--	--

*Not Detected

TABLE A4. Four-Day Trihalomethane Concentrations in Chlorinated Raw Water Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				TTHM
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	
6-27-79	1	154	14	ND*	ND	168
7-1-79	5	--	--	--	--	--
7-4-79	8	155	13	1	ND	169
7-8-79	12	195	16	1	ND	212
7-11-79	15	203	14	<1	ND	217
7-15-79	19	167	15	1	ND	183
7-18-79	22	--	--	--	--	--
7-23-79	27	163	17	1	ND	181
7-26-79	30	159	21	1	ND	181
7-29-79	33	163	22	1	ND	186
8-1-79	36	162	22	1	ND	185
8-5-79	40	166	24	1	ND	191
8-8-79	43	--	--	--	--	--
8-12-79	47	174	22	1	ND	197
8-15-79	50	154	22	1	ND	177
8-19-79	54	178	23	1	ND	202
8-22-79	57	157	19	1	ND	177
8-27-79	61	163	15	1	ND	179
8-29-79	64	--	--	--	--	--
9-5-79	71	199	16	1	ND	216
9-9-79	75	258	13	1	ND	272
9-12-79	78	235	12	2	ND	249
9-16-79	82	144	7	1	ND	152
9-19-79	85	221	13	1	ND	235
9-23-79	89	229	13	2	ND	244
9-26-79	92	193	11	1	ND	205

*Not Detected

TABLE A5. Seven-Day Trihalomethane Concentrations (THMFP)
in Chlorinated Raw Water Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				TTHM
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	
6-27-79	1	181	15	<1	ND*	196
7-1-79	5	203	15	1	ND	219
7-4-79	8	196	15	ND	ND	211
7-8-79	12	205	15	1	ND	221
7-11-79	15	185	15	1	ND	201
7-15-79	19	175	13	<1	ND	188
7-18-79	22	143	15	1	ND	159
7-23-79	27	164	24	1	ND	189
7-26-79	30	169	24	1	ND	194
7-29-79	33	195	24	1	ND	220
8-1-79	36	182	23	1	ND	206
8-5-79	40	156	24	1	ND	181
8-8-79	43	165	25	1	ND	191
8-12-79	47	166	23	1	ND	190
8-15-79	50	189	24	1	ND	214
8-19-79	54	176	22	1	ND	199
8-22-79	57	214	21	2	ND	237
8-27-79	61	181	25	1	ND	207
8-29-79	64	--	--	--	--	--
9-5-79	71	197	20	1	ND	218
9-9-79	75	241	13	1	ND	255
9-12-79	78	237	19	1	ND	257
9-16-79	82	150	7	1	ND	158
9-19-79	85	234	14	2	ND	250
9-23-79	89	208	14	1	ND	223
9-26-79	92	231	12	1	ND	244

*Not Detected

TABLE A6. Instantaneous Trihalomethane Concentrations in Chlorinated 2-gpm GAC Contactor Effluent Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				TTHM
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	
6-27-79	1	10	1	ND*	ND	11
7-1-79	5	13	2	ND	ND	15
7-4-79	8	15	3	ND	ND	18
7-8-79	12	15	5	ND	ND	20
7-11-79	15	22	5	ND	ND	27
7-15-79	19	25	4	<1	ND	29
7-18-79	22	17	4	ND	ND	21
7-23-79	27	15	4	ND	ND	19
7-26-79	30	15	5	1	ND	21
7-29-79	33	22	4	ND	ND	26
8-1-79	36	26	5	<1	ND	31
8-5-79	40	38	5	<1	ND	43
8-8-79	43	29	6	<1	ND	35
8-12-79	47	46	6	<1	ND	52
8-15-79	50	41	5	<1	ND	46
8-19-79	54	45	5	1	ND	51
8-22-79	57	32	4	1	ND	37
8-27-79	61	47	8	11	4	69
8-29-79	64	41	5	ND	ND	46
9-5-79	71	77	5	3	ND	85
9-9-79	75	97	4	5	ND	106
9-12-79	78	106	4	4	ND	114
9-16-79	82	100	4	2	ND	106
9-19-79	85	84	4	<1	ND	88
9-23-79	89	110	5	<1	ND	115
9-26-79	92	83	3	1	ND	87

*Not Detected

TABLE A7. One-Day Trihalomethane Concentrations in
Chlorinated 2-gpm GAC Contactor Effluent Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	TTHM
6-27-79	1	20	5	1	ND*	26
7-1-79	5	--	--	--	--	--
7-4-79	8	37	10	2	ND	49
7-8-79	12	44	11	1	ND	56
7-11-79	15	65	12	3	ND	80
7-15-79	19	58	12	1	ND	71
7-18-79	22	51	12	2	ND	65
7-23-79	27	55	9	ND	ND	64
7-26-79	30	44	10	1	ND	55
7-29-79	33	62	10	1	ND	73
8-1-79	36	68	11	1	ND	80
8-5-79	40	95	14	1	ND	110
8-8-79	43	89	18	2	ND	109
8-12-79	47	109	17	1	ND	127
8-15-79	50	107	14	1	ND	122
8-19-79	54	92	16	1	ND	109
8-22-79	57	73	13	1	ND	87
8-27-79	61	83	14	1	ND	98
8-29-79	64	120	13	1	ND	134
9-5-79	71	105	10	2	ND	117
9-9-79	75	163	7	1	ND	171
9-12-79	78	207	8	1	ND	216
9-16-79	82	164	9	1	ND	174
9-19-79	85	158	8	1	ND	167
9-23-79	89	159	8	1	ND	168
9-26-79	92	179	8	1	ND	188

*Not Detected

TABLE A8. Two-Day Trihalomethane Concentrations in Chlorinated 2-gpm GAC Contactor Effluent Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	TTHM
6-27-79	1	--	--	--	--	--
7-1-79	5	180	14	1	ND*	195
7-4-79	8	--	--	--	--	--
7-8-79	12	59	13	4	ND	76
7-11-79	15	--	--	--	--	--
7-15-79	19	80	14	5	ND	99
7-18-79	22	--	--	--	--	--
7-23-79	27	72	12	1	ND	85
7-26-79	30	70	12	1	ND	83
7-29-79	33	72	12	1	ND	85
8-1-79	36	--	--	--	--	--
8-5-79	40	92	15	1	ND	108
8-8-79	43	96	17	2	ND	115
8-12-79	47	86	15	1	ND	102
8-15-79	50	91	11	1	ND	103
8-19-79	54	109	17	1	ND	127
8-22-79	57	77	15	1	ND	93
8-27-79	61	99	16	1	ND	116
8-29-79	64	--	--	--	--	--
9-5-79	71	--	--	--	--	--
9-9-79	75	164	9	1	ND	174
9-12-79	78	--	--	--	--	--
9-16-79	82	150	9	1	ND	160
9-19-79	85	--	--	--	--	--
9-23-79	89	185	10	1	ND	196
9-26-79	92	--	--	--	--	--

*Not Detected

TABLE A9. Four-Day Trihalomethane Concentrations in Chlorinated 2-gpm GAC Contactor Effluent Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	TTHM
6-27-79	1	--	--	--	--	--
7-1-79	5	--	--	--	ND*	--
7-4-79	8	56	12	5	ND	73
7-8-79	12	66	12	2	ND	80
7-11-79	15	96	13	1	ND	110
7-15-79	19	85	13	1	ND	99
7-18-79	22	--	--	--	--	--
7-23-79	27	87	13	1	ND	101
7-26-79	30	75	14	2	ND	91
7-29-79	33	82	14	2	ND	98
8-1-79	36	93	15	2	ND	110
8-5-79	40	106	16	1	ND	123
8-8-79	43	91	18	2	ND	111
8-12-79	47	130	18	1	ND	149
8-15-79	50	113	17	1	ND	131
8-19-79	54	125	18	1	ND	144
8-22-79	57	97	18	2	ND	117
8-27-79	61	107	13	ND	ND	120
8-29-79	64	--	--	--	--	--
9-5-79	71	165	13	<1	ND	178
9-9-79	75	224	11	1	ND	236
9-12-79	78	210	11	1	ND	222
9-16-79	82	145	8	1	ND	154
9-19-79	85	195	11	1	ND	207
9-23-79	89	209	11	1	ND	221
9-26-79	92	172	10	1	ND	183

*Not Detected

TABLE A10. Seven-Day Trihalomethane Concentrations (THMFP) in Chlorinated 2-gpm GAC Contactor Effluent Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				TTHM
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	
6-27-79	1	53	8	4	ND*	65
7-1-79	5	203	15	<1	ND	108
7-4-79	8	84	15	4	ND	103
7-8-79	12	100	16	3	ND	119
7-11-79	15	95	15	3	ND	113
7-15-79	19	--	--	--	--	--
7-18-79	22	80	17	3	ND	100
7-23-79	27	98	17	1	ND	116
7-26-79	30	87	16	2	ND	105
7-29-79	33	93	16	2	ND	111
8-1-79	36	106	15	2	ND	123
8-5-79	40	106	18	1	ND	125
8-8-79	43	107	21	2	ND	130
8-12-79	47	120	17	1	ND	138
8-15-79	50	137	18	1	ND	156
8-19-79	54	124	17	1	ND	142
8-22-79	57	120	15	2	ND	137
8-27-79	61	--	--	--	--	--
8-29-79	64	--	--	--	--	--
9-5-79	71	159	13	<1	ND	172
9-9-79	75	216	10	<1	ND	226
9-12-79	78	196	11	<1	ND	217
9-16-79	82	161	8	1	ND	170
9-19-79	85	204	12	1	ND	217
9-23-79	89	196	11	1	ND	208
9-26-79	92	189	8	1	ND	198

*Not Detected

TABLE A11. Instantaneous Trihalomethane Concentrations in Chlorinated 4-gpm GAC Contactor Effluent Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	TTHM
6-27-79	1	13	2	<1	ND*	15
7-1-79	5	24	3	ND	ND	27
7-4-79	8	38	6	ND	ND	44
7-8-79	12	48	5	ND	ND	53
7-11-79	15	74	6	3	ND	83
7-15-79	19	88	6	ND	ND	94
7-18-79	22	63	6	4	ND	73
7-23-79	27	46	5	ND	ND	51
7-26-79	30	72	7	1	ND	80
7-29-79	33	63	6	<1	ND	99
8-1-79	36	69	6	1	ND	76
8-5-79	40	72	6	1	ND	79
8-8-79	43	71	7	1	ND	79
8-12-79	47	64	6	1	ND	71
8-15-79	50	63	7	ND	ND	70
8-19-79	54	64	6	<1	ND	70
8-22-79	57	71	5	<1	ND	76
8-27-79	61	67	8	5	ND	80
8-29-79	64	65	5	ND	ND	90
9-5-79	71	89	5	4	ND	98
9-9-79	75	99	4	6	ND	109
9-12-79	78	109	4	3	ND	116
9-16-79	82	118	3	2	ND	123
9-19-79	85	86	3	<1	ND	89
9-23-79	89	138	5	<1	ND	143
9-26-79	92	77	3	<1	ND	80

*Not Detected

TABLE A12. One-Day Trihalomethane Concentrations in Chlorinated 4-gpm GAC Contactor Effluent Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				TTHM
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	
6-27-79	1	45	8	ND*	ND	53
7-1-79	5	--	--	--	--	--
7-4-79	8	108	12	2	ND	122
7-8-79	12	129	13	3	ND	145
7-11-79	15	138	15	3	ND	156
7-15-79	19	125	14	3	ND	142
7-18-79	22	131	14	1	ND	146
7-23-79	27	107	13	1	ND	121
7-26-79	30	117	15	1	ND	133
7-29-79	33	116	15	1	ND	132
8-1-79	36	110	14	1	ND	125
8-5-79	40	132	18	1	ND	151
8-8-79	43	129	18	1	ND	148
8-12-79	47	134	18	1	ND	153
8-15-79	50	132	17	1	ND	150
8-19-79	54	110	16	1	ND	127
8-22-79	57	123	16	1	ND	140
8-27-79	61	117	17	1	ND	135
8-29-79	64	164	16	1	ND	181
9-5-79	71	119	10	5	ND	134
9-9-79	75	181	8	1	ND	290
9-12-79	78	211	9	1	ND	221
9-16-79	82	169	9	1	ND	179
9-19-79	85	168	9	1	ND	178
9-23-79	89	158	7	1	ND	166
9-26-79	92	162	7	1	ND	170

*Not Detected

TABLE A13. Two-Day Trihalomethane Concentrations in Chlorinated 4-gpm GAC Contactor Effluent Samples

Date	Day of Operation	Trihalomethane Concentration (µg/l)				
		CHCl ₃	CHCl ₂ Br	CHClBr ₂	CHBr ₃	TTHM
6-27-79	1	--	--	--	--	--
7-1-79	5	120	11	3	ND*	134
7-4-79	8	--	--	--	--	--
7-8-79	12	151	15	3	ND	169
7-11-79	15	--	--	--	--	--
7-15-79	19	152	18	3	ND	173
7-18-79	22	--	--	--	--	--
7-23-79	27	119	15	1	ND	135
7-26-79	30	139	17	1	ND	157
7-29-79	33	131	18	1	ND	150
8-1-79	36	--	--	--	--	--
8-5-79	40	129	19	1	ND	149
8-8-79	43	139	20	1	ND	160
8-12-79	47	103	17	1	ND	121
8-15-79	50	128	17	1	ND	146
8-19-79	54	127	16	1	ND	144
8-22-79	57	117	16	1	ND	134
8-27-79	61	141	14	1	ND	156
8-29-79	64	--	--	--	--	--
9-5-79	71	--	--	--	--	--
9-9-79	75	161	9	1	ND	171
9-12-79	78	--	--	--	--	--
9-16-79	82	149	9	1	ND	159
9-19-79	85	--	--	--	--	--
9-23-79	89	178	10	1	ND	189
9-26-79	92	--	--	--	--	--

*Not Detected

TABLE A14. Four-Day Trihalomethane Concentrations in
Chlorinated 4-gpm GAC Contactor Effluent Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				TTHM
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	
6-27-79	1	58	14	ND*	ND	72
7-1-79	5	--	--	--	--	--
7-4-79	8	113	14	2	ND	129
7-8-79	12	160	17	2	ND	179
7-11-79	15	177	17	3	ND	197
7-15-79	19	156	17	1	ND	174
7-18-79	22	166	19	1	ND	186
7-23-79	27	141	15	1	ND	157
7-26-79	30	138	19	1	ND	158
7-29-79	33	138	19	1	ND	158
8-1-79	36	140	19	1	ND	160
8-5-79	40	140	19	1	ND	160
8-8-79	43	130	22	1	ND	153
8-12-79	47	145	16	1	ND	162
8-15-79	50	134	18	1	ND	153
8-19-79	54	141	19	1	ND	161
8-22-79	57	147	22	1	ND	171
8-27-79	61	141	14	1	ND	156
8-29-79	64	166	24	1	ND	191
9-5-79	71	174	13	1	ND	188
9-9-79	75	240	11	1	ND	252
9-12-79	78	210	11	1	ND	222
9-16-79	82	154	9	1	ND	164
9-19-79	85	208	13	1	ND	222
9-23-79	89	214	11	1	ND	226
9-26-79	92	172	10	1	ND	183

*Not Detected

TABLE A15. Seven-Day Trihalomethane Concentrations (THMFP) in Chlorinated 4-gpm GAC Contactor Effluent Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				TTHM
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	
6-27-79	1	83	11	3	ND*	97
7-1-79	5	161	16	3	ND	180
7-4-79	8	145	11	3	ND	159
7-8-79	12	180	15	2	ND	197
7-11-79	15	162	17	3	ND	182
7-15-79	19	--	--	--	--	--
7-18-79	22	139	17	1	ND	157
7-23-79	27	139	19	1	ND	159
7-26-79	30	148	21	1	ND	170
7-29-79	33	145	21	1	ND	167
8-1-79	36	151	18	1	ND	170
8-5-79	40	133	20	1	ND	153
8-8-79	43	145	22	1	ND	168
8-12-79	47	138	18	1	ND	157
8-15-79	50	154	20	1	ND	175
8-19-79	54	138	17	1	ND	156
8-22-79	57	181	17	1	ND	199
8-27-79	61	--	--	--	--	--
8-29-79	64	--	--	--	--	--
9-5-79	71	186	17	<1	ND	203
9-9-79	75	233	11	1	ND	245
9-12-79	78	194	11	1	ND	206
9-16-79	82	165	9	1	ND	175
9-19-79	85	208	13	1	ND	222
9-23-79	89	188	11	1	ND	200
9-26-79	92	215	10	1	ND	226

*Not Detected

TABLE A16. Instantaneous Trihalomethane Concentrations in Chlorinated 6-gpm GAC Contactor Effluent Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	TTHM
6-27-79	1	28	3	<1	ND*	31
7-1-79	5	--	--	--	--	--
7-4-79	8	--	--	--	--	--
7-8-79	12	--	--	--	--	--
7-11-79	15	--	--	--	--	--
7-15-79	19	74	5	3	ND	82
7-18-79	22	64	6	3	ND	73
7-23-79	27	50	5	3	ND	58
7-26-79	30	79	7	1	ND	87
7-29-79	33	67	6	1	ND	74
8-1-79	36	76	7	<1	ND	83
8-5-79	40	71	6	<1	ND	77
8-8-79	43	75	7	<1	ND	82
8-12-79	47	70	6	1	ND	77
8-15-79	50	68	7	1	ND	76
8-19-79	54	68	5	1	ND	74
8-22-79	57	78	5	<1	ND	83
8-27-79	61	92	8	6	2	108
8-29-79	64	70	5	ND	ND	75
9-5-79	71	101	6	4	ND	111
9-9-79	75	115	4	6	ND	125
9-12-79	78	112	4	3	ND	119
9-16-79	82	120	4	3	ND	127
9-19-79	85	93	4	<1	ND	97
9-23-79	89	121	5	1	ND	127
9-26-79	92	89	3	<1	ND	92

*Not Detected

TABLE A17. One-Day Trihalomethane Concentrations in Chlorinated 6-gpm GAC Contactor Effluent Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				TTHM
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	
6-27-79	1	100	13	2	ND*	115
7-1-79	5	--	--	--	--	--
7-4-79	8	--	--	--	--	--
7-8-79	12	--	--	--	--	--
7-11-79	15	--	--	--	--	--
7-15-79	19	113	14	3	ND	130
7-18-79	22	122	13	1	ND	136
7-23-79	27	100	11	1	ND	112
7-26-79	30	125	13	1	ND	139
7-29-79	33	120	16	<1	ND	136
8-1-79	36	113	16	1	ND	130
8-5-79	40	127	16	1	ND	144
8-8-79	43	133	19	1	ND	153
8-12-79	47	141	16	1	ND	158
8-15-79	50	135	18	1	ND	154
8-19-79	54	111	16	1	ND	128
8-22-79	56	132	16	1	ND	149
8-27-79	61	114	16	1	ND	131
8-29-79	64	172	19	1	ND	192
9-5-79	71	119	12	5	ND	136
9-9-79	75	179	8	1	ND	188
9-12-79	78	219	9	1	ND	229
9-16-79	82	172	9	1	ND	182
9-19-79	85	175	9	1	ND	185
9-23-79	89	177	8	1	ND	186
9-26-79	92	178	8	1	ND	187

*Not Detected

TABLE A18. Two-Day Trihalomethane Concentrations in Chlorinated 6-gpm GAC Contactor Effluent Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	TTHM
6-27-79	1	--	--	--	--	--
7-1-79	5	--	--	--	--	--
7-4-79	8	--	--	--	--	--
7-8-79	12	--	--	--	--	--
7-11-79	15	--	--	--	--	--
7-15-79	19	136	16	3	ND*	155
7-18-79	22	--	--	--	--	--
7-23-79	27	118	16	1	ND	135
7-26-79	30	147	16	1	ND	164
7-29-79	33	137	16	1	ND	154
8-1-79	36	--	--	--	--	--
8-5-79	40	128	18	1	ND	147
8-8-79	43	143	20	1	ND	164
8-12-79	47	106	18	1	ND	125
8-15-79	50	130	19	1	ND	150
8-19-79	54	130	17	1	ND	148
8-22-79	57	128	17	1	ND	146
8-27-79	61	132	17	1	ND	150
8-29-79	64	--	--	--	--	--
9-5-79	71	--	--	--	--	--
9-9-79	75	172	9	2	ND	183
9-12-79	78	--	--	--	--	--
9-16-79	82	171	10	1	ND	182
9-19-79	85	--	--	--	--	--
9-23-79	89	200	10	1	ND	211
9-26-79	92	--	--	--	--	--

*Not Detected

TABLE A19. Four-Day Trihalomethane Concentrations in Chlorinated 6-gpm GAC Contactor Effluent Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	TTHM
6-27-79	1	--	--	--	--	--
7-1-79	5	--	--	--	--	--
7-4-79	8	--	--	--	--	--
7-8-79	12	--	--	--	--	--
7-11-79	15	--	--	--	--	--
7-15-79	19	142	15	1	ND*	158
7-18-79	22	--	--	--	--	--
7-23-79	27	140	15	1	ND	156
7-26-79	30	143	20	1	ND	164
7-29-79	33	139	18	1	ND	158
8-1-79	36	141	19	1	ND	161
8-5-79	40	139	19	1	ND	159
8-8-79	43	130	19	1	ND	150
8-12-79	47	149	17	1	ND	167
8-15-79	50	138	19	1	ND	158
8-19-79	54	145	19	1	ND	165
8-22-79	57	141	19	1	ND	161
8-27-79	61	142	14	1	ND	157
8-29-79	64	--	--	--	--	--
9-5-79	71	187	16	1	ND	204
9-9-79	75	241	12	1	ND	254
9-12-79	78	217	11	1	ND	229
9-16-79	82	155	8	1	ND	164
9-19-79	85	210	12	1	ND	223
9-23-79	89	218	10	1	ND	229
9-26-79	92	181	11	1	ND	193

*Not Detected

TABLE A20. Seven-Day Trihalomethane Concentrations (THMFP) in Chlorinated 6-gpm GAC Contactor Effluent Samples

Date	Day of Operation	Trihalomethane Concentration ($\mu\text{g/l}$)				
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3	TTHM
6-27-79	1	146	16	4	ND*	166
7-1-79	5	--	--	--	--	--
7-4-79	8	--	--	--	--	--
7-8-79	12	--	--	--	--	--
7-11-79	15	--	--	--	--	--
7-15-79	19	--	--	--	--	--
7-18-79	22	137	18	1	ND	156
7-23-79	27	140	19	1	ND	160
7-26-79	30	152	22	1	ND	175
7-29-79	33	147	20	1	ND	168
8-1-79	36	155	19	1	ND	165
8-5-79	40	134	20	1	ND	155
8-8-79	43	146	21	1	ND	168
8-12-79	47	138	17	1	ND	156
8-15-79	50	159	21	1	ND	181
8-19-79	54	148	19	1	ND	168
8-22-79	57	194	18	1	ND	213
8-27-79	61	--	--	--	--	--
8-29-79	64	--	--	--	--	--
9-5-79	71	182	16	1	ND	199
9-9-79	75	228	12	2	ND	242
9-12-79	78	201	12	1	ND	214
9-16-79	82	176	8	1	ND	185
9-19-79	85	224	12	1	ND	237
9-23-79	89	199	11	1	ND	211
9-26-79	92	222	11	2	ND	235

*Not Detected

APPENDIX B

RESULTS OF CHEMICAL, PHYSICAL, AND BIOLOGICAL
ANALYSES OF RAW WATER INFLUENT AND
GAC (WESTVACO NUCHAR WV-G AND WV-DC)
CONTACTOR EFFLUENT SAMPLES

TABLE B1. Total Organic Carbon Concentrations in Raw Water Influent and GAC Contactor Effluent Samples

Date	Day of Operation	Total Organic Carbon (mg/l)			
		Raw	2-gpm Effluent	4-gpm Effluent	6-gpm Effluent
6-27-79	1	--	--	--	--
7-1-79	5	7.6	1.4	3.2	--
7-4-79	8	7.8	1.7	4.1	--
7-8-79	12	7.5	1.4	3.9	--
7-11-79	15	6.7	1.6	4.0	--
7-15-79	19	6.6	1.6	4.2	3.8
7-19-79	22	6.8	1.5	4.4	4.2
7-23-79	27	6.0	2.0	4.5	4.5
7-26-79	30	6.0	1.5	4.2	4.5
7-29-79	33	6.0	1.7	4.3	4.6
8-1-79	36	6.0	2.0	4.3	4.6
8-5-79	40	5.6	2.5	4.5	4.6
8-8-79	43	5.9	2.5	4.7	4.9
8-12-79	47	5.6	3.0	4.3	4.5
8-15-79	50	5.5	3.4	4.3	4.6
8-19-79	54	5.3	2.9	3.8	4.2
8-22-79	57	5.5	2.3	4.2	4.8
8-26-79	61	4.9	2.7	4.3	4.5
8-29-79	64	5.3	2.8	4.2	3.7
9-5-79	71	7.0	4.4	5.6	5.8
9-9-79	75	10.3	7.4	8.7	9.1
9-12-79	78	10.0	--	8.2	8.6
9-16-79	82	9.0	6.5	7.4	8.1
9-19-79	85	9.3	6.7	8.0	8.4
9-23-79	89	8.2	6.1	8.1	7.6
9-26-79	92	8.8	6.8	7.5	7.5

TABLE B2. Raw Water Influent and GAC Contactor
Effluent Sample Chlorine Demands

Date	Day of Operation	Chlorine Demand (mg/l)			
		Raw	2-gpm Effluent	4-gpm Effluent	6-gpm Effluent
8-1-79	36	10.0	7.5	8.3	9.0
8-8-79	43	11.1	7.9	8.5	4.2
8-15-79	50	10.2	11.5	12.7	12.9
8-22-79	57	10.7	9.6	10.0	9.6
8-29-79	64	9.3	8.5	8.7	8.9
9-5-79	71	10.0	8.1	8.7	9.1
9-12-79	78	12.9	12.9	10.6	11.5
9-19-79	85	--	9.3	9.9	15.0
9-26-79	92	12.2	10.2	10.5	11.0

TABLE B3. pH of Raw Water Influent and GAC
Contactor Effluent Samples

Date	Day of Operation	pH			
		Raw	2-gpm Effluent	4-gpm Effluent	6-gpm Effluent
6-27-79	1	6.7	7.2	7.2	--
7-1-79	5	6.9	7.3	7.2	--
7-4-79	8	6.9	7.1	7.0	--
7-8-79	12	6.7	7.2	7.1	--
7-11-79	15	7.0	7.2	7.1	--
7-15-79	19	6.7	7.1	7.0	6.8
7-18-79	22	7.0	7.2	7.1	7.2
7-23-79	27	7.1	7.4	7.2	7.1
7-26-79	30	6.9	7.2	7.1	7.2
7-29-79	33	7.1	7.4	7.2	7.2
8-1-79	36	7.2	7.4	7.3	7.3
8-5-79	40	7.2	7.3	7.3	7.2
8-8-79	43	7.3	7.6	7.4	7.4
8-12-79	47	7.0	7.2	7.2	7.2
8-15-79	50	7.0	7.3	7.2	7.2
8-19-79	54	6.9	7.1	7.1	7.0
8-22-79	57	7.4	7.5	7.4	7.3
8-27-79	61	7.0	7.3	7.1	7.2
8-29-79	64	7.2	7.5	7.3	7.2
9-5-79	71	7.1	7.4	7.2	7.2
9-9-79	75	7.0	7.2	7.0	6.9
9-12-79	78	6.9	7.0	6.8	6.9
9-16-79	82	7.0	7.2	7.0	7.0
9-19-79	85	7.2	7.2	7.2	7.0
9-23-79	89	6.9	7.3	7.0	7.0
9-26-79	92	7.0	7.1	7.0	7.0

TABLE B4. Turbidity Measurements of Raw Water Influent and GAC Contactor Effluent Samples

Date	Day of Operation	Turbidity (NTU)			
		Raw	2-gpm Effluent	4-gpm Effluent	6-gpm Effluent
6-27-79	1	5.2	4.2	4.7	--
7-1-79	5	5.1	3.7	4.0	--
7-4-79	8	8.3	5.1	6.4	--
7-8-79	12	9.0	4.3	4.9	--
7-11-79	15	5.0	2.7	3.5	--
7-15-79	19	7.0	4.1	4.0	4.8
7-19-79	22	8.0	3.5	4.6	5.0
7-23-79	27	6.0	3.1	4.1	3.4
7-26-79	30	4.7	2.1	2.7	3.0
7-29-79	33	7.5	2.8	3.5	4.0
8-1-79	36	5.3	2.5	3.2	3.4
8-5-79	40	7.0	2.8	4.6	4.5
8-8-79	43	7.3	2.4	6.4	6.4
8-12-79	47	7.1	2.4	5.4	5.3
8-15-79	50	6.5	2.4	3.6	4.1
8-19-79	54	5.8	1.6	2.7	4.0
8-22-79	57	5.5	1.6	3.5	4.7
8-26-79	61	3.6	2.6	2.2	6.4
8-29-79	64	9.8	2.4	13.0	16.0
9-5-79	71	9.7	7.0	8.8	9.3
9-9-79	75	30.0	21.0	30.0	27.0
9-12-79	78	18.0	21.0	16.0	20.0
9-16-79	82	9.5	6.8	8.0	10.0
9-19-79	85	6.7	5.1	6.0	6.1
9-23-79	89	65.0	41.0	56.0	57.0
9-26-79	92	29.0	23.0	26.0	26.0

TABLE B5. True Color Measurements of Raw Water
Influent and GAC Contactor Effluent Samples

Date	Day of Operation	True Color Units			
		Raw	2-gpm Effluent	4-gpm Effluent	6-gpm Effluent
6-27-79	1	65	25	35	--
7-1-79	5	80	35	45	--
7-4-79	8	65	35	45	--
7-8-79	12	65	35	45	--
7-11-79	15	65	35	45	--
7-15-79	19	65	35	45	55
7-19-79	22	55	25	45	35
7-23-79	27	55	30	45	45
7-26-79	30	55	25	45	45
7-29-79	33	55	25	35	45
8-1-79	36	45	25	35	35
8-5-79	40	45	30	40	40
8-8-79	43	45	25	40	35
8-12-79	47	45	30	35	25
8-15-79	50	35	30	35	40
8-19-79	54	45	30	20	20
8-22-79	57	55	25	45	45
8-26-79	61	40	30	35	45
8-29-79	64	50	35	45	45
9-5-79	71	90	55	70	90
9-9-79	75	140	120	110	110
9-12-79	78	130	110	110	110
9-16-79	82	110	90	110	110
9-19-79	85	110	100	110	110
9-23-79	89	130	110	120	120
9-26-79	92	130	110	110	110

TABLE B6. Threshold Odor Number and Characterization of Raw Water Influent and GAC Contactor Effluent Samples

Date	Day of Operation	Threshold Odor Number/Characterization			
		Raw	2-gpm Effluent	4-gpm Effluent	6-gpm Effluent
6-27-79	1	50M*	2DF**	4Df	--
7-1-79	5	24M	8Df	8Df	--
7-4-79	8	35M	4M	6M	--
7-8-79	12	17M	4M	4M	--
7-11-79	15	35M	4M	6M	--
7-15-79	19	35Df	6Df	8M	8Df
7-19-79	22	17M	3M	3M	1.4M
7-23-79	27	17M	2M	8M	2M
7-26-79	30	4M	1M	17M	2M
7-29-79	33	8Df	1.4Df	3Df	3Df
8-1-79	36	12M	3M	3M	3M
8-5-79	40	8Df	1Df	1.4Df	2Df
8-8-79	43	35M	2Df	3Df	8Df
8-12-79	47	17M	1.4M	4M	2M
8-15-79	50	50Df	4Df	4Df	3Df
8-19-79	54	17Df	24Df	4Df	3Df
8-22-79	57	24M	1.4M	4M	6M
8-26-79	61	35M	12M	24M	12M
8-29-79	64	12Df	1Df	4Df	6Df
9-5-79	71	6M	4M	4M	50M
9-9-79	75	17M	4M	3M	4M
9-12-79	78	12M	1M	4M	6M
9-16-79	82	12Bs	1.4M	4M	6Df
9-19-79	85	12M	12M	2Bs***	4Bs
9-23-79	89	50Bs	12Bs	4M	4M
9-26-79	92	8M	12M	2M	2M

*Musty **Disagreeable, Fishy ***Balsamic, Sweet

TABLE B7. Standard Plate Count and Total Coliform
Results for Raw Water Influent and GAC
Contactor Effluent Samples

Date	Day of Operation	Standard Plate Count/ml			
		Raw	2-gpm Effluent	4-gpm Effluent	6-gpm Effluent
8-6-79	41	83	89	260	230
8-13-79	48	510	1800	1500	1700
8-20-79	55	2100	1900	3900	3800
8-27-79	61	3200	5500	8900	18000
9-4-79	70	2900	2000	2900	2700
9-5-79	71	2900	2800	2100	1600
9-10-79	76	6200	8300	3800	3800
9-17-79	83	1200	1200	1600	2200
9-23-79	90	61000	12000	42000	82000
Total Coliform/100 ml					
8-6-79	41	65	40	60	60
8-13-79	48	240	20	47	47
8-20-79	55	30	6	6	6
8-27-79	61	100	100	0	100
9-4-79	70	180	100	0	50
9-5-79	71	750	150	250	100
9-10-79	76	1500	500	0	6500
9-17-79	83	100	260	245	440
9-23-79	90	16800	4000	12200	27600

APPENDIX C

RESERVOIR WATER QUALITY DATA

TABLE C1. Occoquan Reservoir Chlorophyll-a
Concentrations During the Period
of Operation

Date	Day of Operation	Chlorophyll-a ($\mu\text{g/l}$)			3-Station* Average
		Station RE10	Station RE05	Station RE01	
6-26-79	--	12.0	5.8	11.0	9.6
7-3-79	7	5.8	5.8	12.0	7.9
7-10-79	14	5.8	5.8	17.0	9.5
7-17-79	21	5.8	5.8	5.8	5.8
7-31-79	35	12.0	12.0	5.8	10.0
8-7-79	42	5.8	5.8	5.8	5.8
8-14-79	49	5.8	29.0	5.8	13.5
9-11-79	77	17.0	5.8	5.8	9.5
9-18-79	84	5.8	0.0	0.0	1.9
9-25-79	91	0.0	0.0	0.0	0.0

*Occoquan Watershed Monitoring Program Sample Stations:

R 10 Jacob's Rock
R 05 Sandy Run
R 01 Dam

TABLE C2. Occoquan Reservoir Algae Counts
for the Period of Operation

Date	Day of Operation	Algae Average Count/ml	Dominant Genus
6-25-79	--	951	<u>Scenedesmus</u> , <u>Sphaerocystis</u>
7-2-79	6	1187	<u>Scenedesmus</u> , <u>Sphaerocystis</u>
7-9-79	13	800	<u>Scenedesmus</u> , <u>Sphaerocystis</u>
7-6-79	20	1265	<u>Sphaerocystis</u>
7-24-79	28	4190	<u>Sphaerocystis</u>
7-31-79	35	8323	<u>Scenedesmus</u> , <u>Sphaerocystis</u>
8-7-79	42	2088	<u>Sphaerocystis</u>
8-13-79	48	2216	<u>Golenkinia</u>
8-20-79	55	1051	<u>Scenedesmus</u> , <u>Crucigenia</u>
8-27-79	61	1316	<u>Golenkinia</u>
9-10-79	76	495	<u>Anabaena</u> , <u>Aphanizomenon</u>
9-17-79	83	382	--

TABLE C3. Dam Area Rainfall Measurements
During the Period of Operation

Date	Day of Operation	Rainfall (inches)	Date	Day of Operation	Rainfall (inches)
6-24-79	--	0.09	8-11-79	46	1.15
6-28-79	2	0.05	8-12-79	47	1.12
6-30-79	4	0.57	8-19-79	54	0.55
7-1-79	5	0.16	8-21-79	56	0.38
7-4-79	8	0.48	8-24-79	59	0.35
7-10-79	14	0.01	8-25-79	60	0.09
7-11-79	15	0.01	8-26-79	61	0.56
7-12-79	16	0.01	8-27-79	62	1.75
7-13-79	17	0.13	8-29-79	64	0.01
7-14-79	18	0.05	9-2-79	68	0.03
7-21-79	25	0.05	9-3-79	69	0.27
7-23-79	27	0.02	9-5-79	71	2.98
7-24-79	28	0.05	9-6-79	72	0.04
7-25-79	29	0.06	9-7-79	73	0.06
7-28-79	32	0.66	9-13-79	79	0.34
7-29-79	33	0.03	9-21-79	87	3.42
8-2-79	37	0.10	9-22-79	88	0.52
8-5-79	40	0.14	9-28-79	--	0.07
8-8-79	43	0.40	9-29-79	--	0.03
8-10-79	45	0.08	9-30-79	--	0.24

TABLE C4. Occoquan Reservoir Elevation
During Period of Operation

Date	Day of Operation	Reservoir Elevation (ft)	Date	Day of Operation	Reservoir Elevation (ft)
6-26-79	--	120.0	7-16-79	20	119.7
6-27-79	1	120.0	7-17-79	21	119.6
6-28-79	2	120.0	7-18-79	22	119.6
6-29-79	3	119.9	7-19-79	23	119.5
6-30-79	4	119.9	7-20-79	24	119.4
7-1-79	5	120.0	7-21-79	25	119.3
7-2-79	6	120.1	7-22-79	26	119.3
7-3-79	7	120.1	7-23-79	27	119.2
7-4-79	8	120.0	7-24-79	28	119.1
7-5-79	9	120.1	7-25-79	29	119.1
7-6-79	10	120.0	7-26-79	30	119.1
7-7-79	11	120.0	7-27-79	31	119.0
7-8-79	12	120.0	7-28-79	32	118.9
7-9-79	13	119.9	7-29-79	33	118.9
7-10-79	14	119.9	7-30-79	34	119.1
7-11-79	15	119.8	7-31-79	35	119.3
7-12-79	16	119.7	8-1-79	36	119.4
7-13-79	17	119.7	8-2-79	37	119.5
7-14-79	18	119.6	8-3-79	38	120.1
7-15-79	19	119.6	8-4-79	39	120.3

TABLE C4. (cont.)

Date	Day of Operation	Reservoir Elevation (ft)	Date	Day of Operation	Reservoir Elevation (ft)
8-5-79	40	120.2	9-1-79	67	120.0
8-6-79	41	120.0	9-2-79	68	119.8
8-7-79	42	120.0	9-3-79	69	119.5
8-8-79	43	119.9	9-4-79	70	119.0
8-9-79	44	119.9	9-5-79	71	118.6
8-10-79	45	119.8	9-6-79	72	123.9
8-11-79	46	119.8	9-7-79	73	123.4
8-12-79	47	119.9	9-8-79	74	121.0
8-13-79	48	120.5	9-9-79	75	120.6
8-14-79	49	120.4	9-10-79	76	120.3
8-15-79	50	120.1	9-11-79	77	120.1
8-16-79	51	120.1	9-12-79	78	120.1
8-17-79	52	120.0	9-13-79	79	120.1
8-18-79	53	120.0	9-14-79	80	119.8
8-19-79	54	119.9	9-15-79	81	119.7
8-20-79	55	120.0	9-16-79	82	119.6
8-21-79	56	120.1	9-17-79	83	119.3
8-22-79	57	120.4	9-18-79	84	119.0
8-23-79	58	120.2	9-19-79	85	118.6
8-24-79	59	119.9	9-20-79	86	118.2
8-25-79	60	120.4	9-21-79	87	117.8
8-26-79	61	121.1	9-22-79	88	121.9
8-27-79	62	121.0	9-23-79	89	123.3
8-28-79	63	121.2	9-24-79	90	121.0
8-29-79	64	120.0	9-25-79	91	120.5
8-30-79	65	120.4	9-26-79	92	120.3
8-31-79	66	120.2	9-27-79	--	120.2

VITA

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Karen B. Carter

GRANULAR ACTIVATED CARBON PRETREATMENT
FOR THE
REMOVAL OF TRIHALOMETHANE PRECURSORS

by

Karen Blake Burnett Carter

(ABSTRACT)

Granular activated carbon (GAC) pretreatment was evaluated for the removal of trihalomethane (THM) precursors from a surface water supply, the Occoquan Reservoir, in northern Virginia. The carbon contactors were operated in the upflow mode at flow rates of 2, 4, and 6 gpm which provided empty bed contact times (EBCT) of 26, 13, and 6.6 minutes, respectively. Reservoir raw water quality data was collected to determine what relationship existed between these measurements and the trihalomethane formation potential (THMFP) of the reservoir water.

The results indicated that THM precursors, as measured by total organic carbon (TOC) and THMFP, could be removed from an untreated surface water supply by GAC contact. The degree to which THM precursors were removed was directly related to EBCT, the most effective being 26 minutes (2 gpm).

GAC contact appeared to be selective for the removal of those precursors responsible for instantaneous THM concentrations i.e., those produced within a thirty minute chlorine-contact period. Those precursors responsible for THM concentrations produced after thirty

minutes and for up to seven days thereafter (herein designated THMFP) appeared to be associated either with particulate matter in the raw water or with larger molecular weight organic substances which were not well adsorbed by the carbon.

There were no discernible direct correlations between THMFP and the turbidity, color, TOC, chlorophyll-a concentration and algal populations in the raw water. Runoff from a rainstorm late in the period of study resulted in increases in raw water color, turbidity, and TOC concentrations, but it was impossible to determine which of these factors was responsible for the increased raw water THMFP that occurred at the same time.