

**Evaluation of Activated Carbon Processes for Removing Trihalomethane Precursors from a
Surface Water Impoundment**

by

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(ABSTRACT)

A pilot plant study was conducted in Newport News, Virginia to investigate the effectiveness of powdered activated carbon [PAC] and granular activated carbon [GAC], with and without preoxidation, for reducing trihalomethane [THM] precursor concentrations in Harwood's Mill Reservoir water. Preoxidation with ozone followed by GAC is referred to as the "biological activated carbon" [BAC] process. This study showed that the GAC and BAC processes obtained the same level of organic removal; however, BAC would provide longer bed life and require less carbon than the GAC process. PAC treatment of alum coagulated water provided significantly higher TOC and THMFP removals than alum coagulation alone. The use of a preoxidant (ozone) with PAC slightly improved the organic removal efficiency. While treatment by PAC increased THMFP removals, it was not as efficient as the GAC and BAC processes. UV absorbance measured at 254 nm and TOC were found to be good surrogates for THMFP in the GAC column, but not in the BAC column.

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Chapter 1

INTRODUCTION

In 1984 the City of Newport News decided to proceed with plans to build a 25 million gallon per day (MGD) water treatment plant to meet present and future water consumption demands. The plant is to be constructed at the Harwood's Mill reservoir located in Newport News, Virginia. The conceptual design proposed by the consulting firm CH2M Hill Engineers included a year long pilot study to investigate various organic control options that could be employed at the new plant. These options were explored in anticipation of the Environmental Protection Agency (EPA) lowering the current maximum contaminant level (MCL) of 0.10 milligrams per liter (mg/L) for trihalomethanes (THM's) in the near future.

Harwood's Mill Reservoir is considered a "terminal reservoir" because it is the last of three reservoirs that receive water pumped from the Chickahominy River. The headwaters of the Chickahominy include a large area of swampy wetlands, an ideal source of humic substances, particularly fulvic acids, which constitute the majority of the trihalomethane precursors present in the reservoir. The Newport News Waterworks spent considerable time and money during 1981-1987 evaluating treatment alternatives to meet the current specified MCL.

Two of the organic-control options aimed at reducing THM precursors to be studied in the pilot plant program were powdered and granular activated carbon. The powdered activated carbon (PAC) was added in slurry form to the clarifier after coagulation while the granular activated carbon (GAC) was placed in columns immediately following the mixed media filters. Two sets of GAC columns were used to treat the filter effluent, one receiving ozonated water, the other receiving non-ozonated water. The application of ozone is reported to promote microbial activity and increase adsorption on the GAC, thus providing additional organic removal. This type of column is often referred to as biological activated carbon (BAC) columns. Both the GAC and BAC columns were monitored for their performance in removing organics, specifically THM precursors.

The principle investigation of this study was to compare the capabilities of the powdered, biological, and granular activated carbon to remove organics, specifically THM precursors.

The specific objectives of this research were:

1. To determine the breakthrough of the BAC and GAC for THM precursors.
2. To compare the BAC and GAC processes for removal of organic material, especially THM precursors.
3. To compare the performance of PAC to BAC and GAC in removing THM precursors.
4. To determine if PAC used in conjunction with alum coagulation was more effective at removing THM precursors than alum coagulation alone.
5. To determine if absorbance of ultraviolet light at 254 nm (UV254) or total organic carbon (TOC) could be used as accurate surrogate parameters for THM precursors.

Chapter 2

LITERATURE REVIEW

TRIHALOMETHANES

In the mid-1970's, it became known that one of the trihalomethanes (THM's), chloroform, is a potential carcinogen. Rook (1, 2) and Bellar et al. (3) presented evidence that THM's form after the chlorination of natural waters. On the basis of these studies and evidence that chloroform (a THM) is a potential carcinogen (4), the U.S. Environmental Protection Agency implemented regulations to restrict the amount of various organics in drinking water. A maximum contaminant level (MCL) of 0.10 (mg/l) was established for total THM's (5) in drinking water. This action initiated numerous research projects to develop new methods of reducing THM levels in water distribution systems.

Only four of the many possible THM's are included in the MCL. These include chloroform (CHCl_3), bromodichloromethane (CHBrCl_2), dibromochloromethane (CHClBr_2), and bromoform (CHBr_3). In most waters in the United States, the vast majority of the THM's are of the

chlorinated species. The most common precursor material for THM's is humic substances (6, 7), though other substances such as algae or their associated byproducts (8-12) may also contribute.

Humic Substances

Aquatic humic substances; consisting of humic, fulvic, and hymatomelanic acids; are the most common precursors for THM's and are present in almost every surface water source and some groundwaters. Upon reaction with chlorine, they form THM's and other halogenated organics (2, 6) . Humic and fulvic acids constitute the bulk of natural organic material present in surface waters (6). They may account for 85 to 90 percent of the total organic carbon, with fulvic acids usually representing the largest fraction (7). Humic substances are in especially high concentrations in surface waters which consist of wetlands and bogs, while much lower concentrations are generally found in groundwater sources.

Humic substances are derived from soil and decaying plant matter. They enter water supplies by leaching of plant organic material into water, leaching of soil fulvic and humic acids, lysis of algal remains, bacterial action on phytoplankton, or oxidation of organic material in the microlayer of surface water (7). Humic concentrations may vary widely on a seasonal basis. Heavy rains and the associated runoff will increase soil and sediment input, and vegetative growth and death will also contribute to changes in concentration.

Structure

The structure of fulvic and humic acids is similar. They are derived from essentially the same sources and each consist of carboxyl, hydroxyl, carbonyl, and phenolic hydroxyl functional

groups. Their molecular weight ranges from 500 to greater than 100,000 (6). Humic acids have fewer carboxyl groups and are larger in size than fulvic acid, thus making them less soluble. To isolate one from the other, humic acid is the fraction that precipitates below pH of 2.0, while fulvic acid is the fraction that remains in solution below pH of 2.0 (7).

Many research efforts have been aimed at trying to determine which fraction of humic substances forms the highest concentration of THM's. Treatment methods could then be aimed at removing that particular weight fraction. McCreary and Snoeyink (13) found that various molecular weight fractions of soil fulvic acid yielded approximately the same chloroform concentration; however, there were appreciable differences in chloroform production from soil humic acids and soil and leaf fulvic acids. Joyce et al. (14) found that the larger molecular weight fraction of fulvic acids ($> 10,000$), produced more chloroform than the smaller molecular weight fractions; however they found the reactivity to be dependent on the source of the humic substances. They also suggested that removing the higher molecular weight fulvics, which contain more carbon, would result in less THM production. In contrast, another study by Collins et al. (15) found that THM precursor reactivity increased with increasing molecular weight only up to 10,000. Above a molecular weight of 10,000 no significant increase in THM formation was observed. These contradictions indicate that the formation potential of humic materials is related to the source of the humics and not necessarily their size.

Algae and Extracellular Products

Algae and chlorophyll have also been found to be precursors for THM formation (10, 11, 12, 16). Although the amount of THM's that are formed from algae are not quite as large as that from humic substances, the amounts can be significant (12). Hoehn et al. (10) first reported that algal ECP could also be a THM precursor. They found that extracellular products of four

different algal species produced chloroform upon chlorination and the maximum yield was also provided during the exponential growth phase. Briley et al. (9) found that the genus *Anabaena* provided maximal levels of THM's during their exponential growth phase. The amounts produced were comparable to amounts generated from humic substances. Hoehn et al. (8) also found that high populations of heterotrophic organisms and algae that appear diurnally yield high amounts of THM's after treatment.

THM Formation

The haloform reaction has been proposed as one possible mechanism involved in the formation of THM's in drinking water (2). The haloform reaction is a base-catalyzed series of halogenating and hydrolysis reactions. It usually involves a methyl ketone group or compounds oxidizable to that structure (16). Free chlorine or bromine reacts with a terminal methyl group to successively replace the hydrogen atoms with halogen atoms. The trisubstituted methyl group is cleaved so that the resulting products are a haloform and a carboxylate ion. (17). Rook (18) has proposed a pathway for the degradation of fulvic acid to THM's based on this reaction.

Because chlorine oxidizes inorganic bromide ions to bromine, the halogenated methyl group may contain a mixture of chlorine and bromine atoms. The effect of other halogens (specifically bromine) in water and how it affects the formation of THM's has been reviewed by several investigators (19-21). Bromine is more effective than chlorine as a halogenating agent. The reaction rate between bromine and humic material is much faster than that between chlorine and humic material, even at low temperatures. The bromide ion in water is oxidized to hypobromous acid in water, a reaction that can explain the appearance of brominated methanes. The degree of bromine substitution on the methyl group will be a function of the amount of bromide ion in the water. Brominated THM's are quite prevalent in

Europe and in many places in the United States, especially in locations near the ocean, where groundwater contains high concentrations of bromide.

Trihalomethane formation is dependent upon several conditions, most notably the amount of humic substances present in raw water and the point of chlorine application in the water treatment process can make tremendous impacts. When raw water is chlorinated, 50 to 70 percent of the THMFP will have developed before the water exits the settling tanks (22). Postponing chlorination until after coagulation and clarification may still result in a substantial THM concentration.

Other factors may strongly influence the THM-formation rate. The chlorine dose, temperature, and pH are three important ones. Increased doses of chlorine will increase the THM concentration formed in the distribution system (6, 23). Elevated temperatures can increase the rate of THM formation. Most utilities experience their highest concentration of THM's during the summer months, and in contrast, THM formation is much less pronounced during the winter (24). The formation rate of THM's also increases with increasing pH (6, 25). As mentioned earlier, the haloform reaction is base catalyzed, therefore, higher pH's will result in higher THM concentrations. The reason is that halogenated intermediates that form during chlorination are cleaved from the parent molecule at a faster rate if the pH is increased (16). Treatment systems that employ lime softening often experience large THM concentrations because of the high pH.

Toxicological Effects

The THM that causes the most concern for health officials is chloroform, which generally constitutes the largest fraction of THM's in the majority of the United States (21). A study by the United States National Cancer Institute (4) found that chloroform was directly related to

tumor formation and this study provided the impetus for the 100 µg/L MCL for THM's imposed by the EPA in 1979. The other brominated THM's are generally not in sufficient quantities to raise serious alarms over health in the United States, however in Europe there is considerable concern because of higher brominated THM concentrations (19).

Lappenbusch (26) reported that a chloroform concentration of 25 µg/L in drinking water will result in a lifetime population risk of developing cancer of one in 5,000. He suggested a concentration in the water of less than 30 µg/L. The National Academy of Sciences specified a cancer risk estimate of 170 cancers induced by chloroform per 1,000,000 people per µg/L over a lifetime (26).

The degree of carcinogenicity of chloroform to humans is still questioned by some scientists and disputes over the methods used to obtain results in the National Cancer Institute study have prompted other studies in recent years. Reitz, et al. (27) and Pereira, et al. (28) found that chloroform is most likely a tumor promoter and not a tumor initiator. Another study (29) found that chloroform actually inhibits the formation of tumors, though the researchers believed these results were different from the National Academy of Sciences report because the methods employed were different. The exact link chloroform provides in cancer-promoting activity is still not known.

GRANULAR ACTIVATED CARBON

Activated carbon is a porous material containing a tremendously large surface area for its size. Tiny pores, created during its "activation", honeycomb throughout its structure. It is within these pores that carbon adsorbs the majority of the organics found in water and

wastewater. Two forms are used in the water treatment industry: granular activated carbon (GAC) and powdered activated carbon (PAC).

Carbon has been noted for its special adsorptive properties since the late 18th and early 19th century when European scientists discovered that charcoal would decolorize solutions (30). Based on this ability, charcoal was immediately used in the sugar refining industry, and its growth for the next 100 years was limited to that. It was not until the turn of the 20th century that modern commercial activated carbon was developed. Its publicity as an adsorbent of chlorine gas in World War I sparked continued development. For the next 60 years, its use in the United States' water and wastewater treatment industry was generally limited to taste- and odor-control and for decolorization of water (31). Powdered activated carbon was most common because it could be employed on a temporary basis and, therefore, was more economical. Granular activated carbon was not looked upon as a viable treatment technique for removing organics in the drinking water industry until the 1970's.

Adsorption

Adsorption is the mechanism by which activated carbon removes organics from water. A thorough review of the subject has been provided by Montgomery (32). The process of adsorption can be best described as a surface phenomenon that occurs at the interface of the solid and liquid surfaces. The attractive forces of a fluid molecule (adsorbate) and a solid surface (adsorbent) interact such that the fluid molecule attaches to the solid surface. These forces may include physical, chemical, and/or electrical attractions, with the most common being physical or chemical attractions (32). Chemical adsorption, or chemisorption, is less common and involves chemical reactions between the adsorbate and the adsorbent such that strong covalent bonds, which are difficult to break are formed.

Physical adsorption usually involves an adsorbate of low solubility being attracted to the carbon's surface by electrostatic forces. The electrostatic force consists of dipole-dipole interactions, van der Waals forces and hydrogen bonding (32). Typically, organic molecules are nonpolar and thus are less stabilized by hydrogen bonding and dipole-dipole interactions in solution. The more nonpolar the molecule the less soluble it is in an aqueous solution. The nonpolar adsorbent (activated carbon) and the nonpolar molecule are attracted to each other by their van der Waals forces (32).

These attractive forces may be broken if an adsorbate that exhibits a stronger attraction to the adsorbent appears. The adsorbate that is more strongly attracted will remove the weakly held adsorbate. This phenomenon is known as "competitive adsorption or desorption". Various researchers (33-36) have found that desorption of halogenated compounds, specifically THM's, can occur after a period of time. Desorption of chloroform may occur when the influent concentration is suddenly decreased or when a competitive species appears in the influent. Thacker et al. (33) found that CHBrCl_2 could be competitive with CHCl_3 . Another study (34) demonstrated that the CHCl_3 concentration in the effluent can exceed that in the influent when low influent levels follow high levels (reequilibrium). The authors suggested that the chlorine changed the GAC adsorptive properties, specifically decreasing the adsorption capacity, and allowing deeper penetration of the bed depth by the lower concentration of organics.

Ozone has been found in some cases to promote competitive adsorption between the background organic matrix and the organohalides in solution (35). Likewise, Summers and Roberts (36) observed the desorption of chloroform from GAC columns when preozonation was practiced (36).

Adsorption of humics onto carbon is dependent upon many factors including pH, initial concentration of humic material, carbon dosage, and particle size of carbon (37). The pH of water entering the GAC was found to influence the adsorption characteristics significantly. Semmens et al. (38) demonstrated that as the pH of the influent water decreases to pH 5.0, the

Semmens et al. (38) demonstrated that as the pH of the influent water decreases to pH 5.0, the adsorption capacity of GAC for total organic carbon (TOC) and THM precursors increased. As the pH increased to 7.0, the organic removal deteriorated rapidly. Similarly, soil fulvic acid adsorption onto GAC increased with decreasing solution pH (13).

The adsorptive capacity of activated carbon to remove different molecular weight substances is dependent in part upon the pore volume associated with the different carbon pore sizes (39). Lee et al. (39) reported that the adsorption capacity and rate of uptake for a given humic substance increases as the molecular weight decreases. Thus, the smaller weight fractions of THM precursors can more easily enter the micropores of the activated carbon and be adsorbed. Similar results have been found by other investigators (13, 40). The lower molecular weight fractions of a given humic or fulvic acid are the most adsorbable while high molecular weight substances ($> 40,000$) are the least adsorbable.

Other types of adsorbents have been studied as possible alternatives to GAC including carbonaceous resins and polymeric adsorbents. However, for removal of THM precursors or halogenated organics, GAC is superior (41, 42).

Properties of Activated Carbon

The source material used for generating activated carbon is important in determining the resulting adsorptive capacity and many studies have been conducted to determine the suitability of various materials. The most commonly used materials are bituminous coal, lignite, coconut shells, wood, and pulp mill residues (43).

Important properties in selecting a an activated carbon include: capacity, hardness, permeability, and solubility of the adsorbate (43). Capacity is important in that it determines the amount of adsorbate that can be adsorbed from solution. Activated carbon has a large

surface area (600 - 1800 m²/g) which can be attributed to its porous structure. By changing the activating conditions, the distribution of macropores and internal micropores will be affected. Macropores (> 100 angstroms) provide access to micropores (< 100 angstroms) which are of molecular dimensions (31). The majority of the surface area is provided by the micropores, and it is here that most of the adsorption occurs. The capacity of the carbon is important in determining the time available between regenerations. Carbon hardness is important in keeping losses accrued during regeneration and transportation of the carbon to a minimum. Carbon permeability is important when considering the build-up of head loss during operation and bed expansion in backwash. The solubility of the adsorbate is also important in selecting a carbon. The effectiveness of carbons to remove adsorbates from solution is dependent on the solubility of the adsorbate. As mentioned earlier, less soluble organics are more easily removed. Thus, it is essential to choose a carbon that will efficiently remove the desired organic at its solubility point.

Activation and Regeneration of Carbon

The process of "activating" carbon results in an increase in the adsorptive capacity by providing a high degree of porosity and surface area. The "regeneration" process restores carbon, which has had its adsorption sites depleted, to its original state of high porosity and surface area. The activation or regeneration process can be accomplished one of two ways. The most popular method employs the use of a furnace to heat the carbon to very high temperatures. It is basically a three step process: drying, carbonization, and activation (31, 43). The alternate method employs chemical oxidation which involves the use of chemicals to dehydrate and oxidize the carbon.

Heat Regeneration

The regeneration of activated carbon is the process of removing all adsorbed materials so that the carbon is restored approximately to its virgin state. The steps involved in regenerating carbon are essentially the same as in activating carbon. Initially, the carbon is dried at 300°F to remove water. The temperature is then raised between 900°F and 1400°F where 75 to 90 percent of the organic adsorbates are volatilized. The remaining adsorbates are left as a char on the carbon. To remove these, selective oxidation using steam heat at 1500°F to 1800°F is used. At this point the regenerated carbon is essentially restored to its original state (31). GAC losses of six percent per cycle can be assumed for post-filter adsorbers (44); however, losses as high as 16 to 19 percent have been experienced (45).

Four basic types of furnaces are employed to thermally regenerate carbon. These include the multiple hearth furnace, rotary kilns, fluidized bed furnace, and the infrared furnace. The multiple hearth furnace is most commonly applied while the fluidized bed furnace is quickly gaining acceptance (43, 46).

Chemical Regeneration

The chemical regeneration of activated carbon is far less common and involves the use of chemicals to remove organic material from the carbon. Various chemicals used in the treatment of spent activated carbon include phosphoric acid, potassium hydroxide, and zinc chloride (32).

BIOLOGICAL ACTIVATED CARBON

The Biological Activated Carbon (BAC) process is frequently misinterpreted. It does not refer to a carbon that is biological in nature. It refers to the degradation of organics that occur due to a biological population on the granular activated carbon. The actual BAC process is defined as a simultaneous combination of GAC adsorption and aerobic biological oxidation of organic materials (43). The major difference between the BAC and GAC processes is that ozone is applied immediately before the GAC columns in the BAC process. The oxidant makes organic compounds more biodegradable and it may improve adsorption onto the carbon even if microbial degradation is not significant. Glaze and Wallace (47) proposed two mechanisms to account for the removal of organic materials in BAC columns: 1) physical adsorption, which dominates the early stages of adsorption and decreases as the adsorption sites are filled, and 2) microbial degradation, which becomes more dominant as time progresses and the column reaches long-term, quasi steady-state performance (47).

Europeans have much more experience in using ozone with GAC, and they have had relatively good results with it (48). One of the more famous European treatment processes using ozone and GAC is the Mulheim process. It incorporates ozone-GAC followed by a slow-sand filter. The process removes 60-80 percent of the organochlorine compounds present (49).

Microbial populations on activated carbon can be quite active in oxidizing organics; however, growth is slow and little biomass is produced (50). Bacterial growth may remove as much as 24 percent of TOC in a BAC column over a period of 200 days (51). Microbial populations on GAC, once established, are very similar until environmental changes cause fluctuations of steady state. Most biological isolates found on the GAC and its effluent can be placed into two broad groups: gram negative rods unable to ferment glucose and spore forming gram positive rods. These include members of the genera *Pseudomonas*, *Acinetobacter*, *Achromobacter*,

Chromobacterium, Micrococcus, and Bacillus (52). To determine the activity of biological populations on activated carbon, oxygen uptake (50) or inorganic carbon evolution (47) measurements have been used, even though their as predictors of bioactivity is questioned (53).

Enhancement of GAC with Ozone

Microbiological activity has most often been cited as the main mechanism for the long-term steady-state performance of BAC columns; however, another mechanism has been proposed by Peel and Benedek (54). They propose a dual-rate, kinetic model that contributes the long-term quasi steady-state removal of TOC to both slow adsorption kinetics and microbial degradation. They maintain that after the early stages of adsorption, 50 to 80 percent of the carbon's capacity is exhausted and that the remaining adsorptive capacity is exhibited slowly over a long period of time. It is believed that the initial adsorption phase occurs in the macropores where diffusion rates are relatively unhindered, while the slow adsorption occurs in the micropores where diffusion rates are considerably more restricted.

Ozone may enhance slow adsorption by improving the kinetics of dissolved organic carbon adsorption. It breaks down large precursor molecules to smaller ones, thus improving the adsorption kinetics in the micropores (55). An ozone dose of 1.0 mg ozone/mg carbon before the activated carbon was found to be optimum for increasing the adsorption of humics from solution (56). However, ozone is not always necessary for this phenomenon to occur. Miller et al. (45) found that after the initial GAC adsorption sites were saturated, TOC removals stabilized at 40 percent and remained at this quasi steady-state for many months. It was thought that slow adsorption or biodegradation was occurring, although no ozone was applied before the GAC.

The amount of THM precursor or organic removal that slow adsorption or microbial degradation may account for is subject to much discussion. Maloney et al. (57) found that slow adsorption accounted for 20 percent of the TOC removed while biological degradation accounted for 9 to 16 percent. It appears therefore that the benefits derived from BAC is a combination of increased adsorption and microbial degradation.

Ozone has been known to effectively remove taste and odors for many years (58). Researchers have found that at sufficiently high doses, ozone may serve as a powerful oxidant and disinfectant but the ozone residual in water is short-lived and does not provide continuous disinfection as does chlorine. For ozone to be an effective oxidant, sufficient concentrations and contact times must be provided. In the BAC process, ozone is added at a dose that partially oxidizes organics but does not disinfect.

Ozone provides two direct benefits as a preoxidant in the BAC process: 1) It partially oxidizes many of the large, non-biodegradable organics into products that are biodegradable and 2) it aerates the water and provides a source of oxygen for the biological population (35, 36, 59, 60). Preozonation has been found to enhance biological growth on activated carbon in addition to improving organic removal (61).

A general consensus of researchers is that ozone significantly reduces the amount of UV-absorbing materials present in the water (56, 59, 62, 63). The actual effect ozone will have on destroying THM precursors, which absorb UV quite well, is dependent upon the nature of the humic substances and characteristics of the water when ozone is applied (62). Ozone has been shown to remove from 5-15 percent of the THM precursor material entering the GAC column (47). Kaastrup and Brattebo (56) showed that ozone before GAC can improve the TOC removal by an additional 10 percent over that achieved by absorption alone.

Other reports do not proclaim ozone as being as efficient at removing THM precursors. Glaze et al. (64) found that ozonation in conjunction with GAC provided longer bed service times;

however, ozone alone did not produce noticeable benefits. Argaman et al. (65) found that ozone removed color quite effectively at a dose of 5 mg/L, however, little or no reduction in THM precursors was seen. Also, Malley et al. (55) found that ozone at low doses (2 mg/L) did not significantly improve total organic halogen precursor removal in BAC processes.

A possible detriment to the use of ozone are the organic byproducts of ozonation. Toxic species, which are not removed by GAC or destroyed by post chlorination may form (66). Low ozone doses with short contact times produced some cytotoxic compounds that were not present before ozonation. Stronger doses with longer contact times did not produce these compounds.

THM PRECURSOR REMOVAL BY COAGULATION AND PAC

Granular activated carbon is used primarily as a tertiary treatment method to lower the level of THM's below an already reduced value. In many instances, the life of the carbon filter can be lengthened considerably if it is preceded by effective primary treatment. If coagulation is effective, GAC or BAC may not be needed in many cases. If THM levels are above the MCL of 0.10 mg/L only at certain times of the year, then temporary applications of PAC may be adequate.

Alum Coagulation

Clarification is important in removing large amounts of humic particulate matter. Alum coagulation with filtration is effective in achieving high levels of turbidity removal while simultaneously removing large fractions of the THM precursors (8, 15). To achieve optimum THM removal with alum coagulation, it may be necessary to adjust the pH. Various investigators report that the optimum pH for removing THM precursors was between pH 5.0 and 6.0 (25, 40, 63, 67). At increasing pH's the removal efficiency markedly worsened (68).

If GAC treatment is required, various studies indicate that prior alum treatment will markedly extend the carbon bed life (69, 70). This is due to an interaction between the aluminum species and the organic molecules (71). It is believed that the THM precursor is adsorbed onto alum floc after neutralization of its negative charges (39).

Preozonation before coagulation may improve the removal of organics and turbidity. Ozone has been found to enhance coagulation by increasing the number of large particles at the expense of smaller ones. It is believed that this is due to the reduction of negative charges on the organic molecules. Ozone has been found to be most effective at acidic pH's (72). An optimum ozone dose may even allow a reduction in the amount of coagulant used. (73). Amy et al. (74) found that preozonation before coagulation reduced levels of THM precursors from as little as one percent to as high as 68 percent. The large variation was due to the source of the water which dictated the efficiency of THM precursor removal.

Not all investigators advocate the use of ozone before alum coagulation. Reckhow and Singer (75) found that ozone can aid in the coagulation of turbidity yet it hindered the removal of THM precursors by alum coagulation. Although ozone did destroy some THM precursors, it lowered the efficiency of alum coagulation to remove the remaining ones.

Powdered Activated Carbon

PAC was first employed to treat tastes and odors at the Hackensack Water Company in New Milford, New Jersey (24). This successful application led to its use at other plants and made it a cost-effective treatment for tastes and odors. Recently, it has also been used to remove organic materials. PAC will effectively remove THM precursors; however, it may require continuous addition at high doses, which in turn produces large amounts of sludge. The combination of these two factors would most likely make PAC cost-prohibitive as a year round treatment option.

PAC would be more cost effective if it were used only intermittently. Because high THM precursor concentrations often are seasonally dependent, it would be more economical to employ PAC only when the finished water THM concentration is greater than the MCL (24).

PAC is very fine with a sieve mesh size usually less than 325. Different grades of PAC have different THM precursor removal efficiencies (76). The two important physical properties of PAC are filterability and bulk density (32). PAC must be filterable by sand filters. Bulk density is important also because the mass of the carbon is proportional to its adsorptive capacity; therefore, a higher bulk density will give higher removal of adsorbate per volume of adsorbent.

For PAC to be most effective it should be used in combination with coagulation. Alum is more effective in removing THM precursors than PAC alone (23), but PAC in conjunction with polyelectrolyte coagulation was found to remove THM precursors by 50 percent while still being successful at removing tastes and odors (76). Of course, one disadvantage of using PAC with alum is that the PAC becomes enmeshed in the floc and loses efficiency.

Surrogate Parameters

The literature available on the prediction of THM levels by analysis of surrogate water quality characteristics is conflicting. There are many claims that TOC and UV absorbance are good predictors. To illustrate, a few references are discussed in the following paragraph.

Hentz et al. (23) found that UV absorbed at 254 nm (UV254) and TOC did not correlate well with the observed THM formation after PAC treatment. Reckhow and Singer (75) found that when ozone was employed, neither TOC nor UV254 were good indicators of THM precursors after preozonation and alum coagulation, yet without ozone addition, TOC and UV254 were reasonably good surrogates. Amy and Chadik (74) found that UV254 and TOC were good predictors of THM precursors after preozonation, with the UV254*TOC multiplicative product having the best surrogate relationship to THM precursors for both untreated and ozonated waters. Edzwald et al. (77) found UV254 to be an excellent surrogate for estimating raw water TOC and THM precursors in two separate waters with different characteristics.

It appears from the literature review that the successful use of a surrogate parameter to predict THM's is dependent on the particular raw water characteristics or the treatment process employed.

Harwood's Mill Reservoir

Harwood's Mill Reservoir is situated on the border of York County and Newport News, Virginia. It is a man-made reservoir that receives its water through a pumping network from the Chickahominy River and through runoff from its own watershed.

Previous studies (78, 79) conducted at the reservoir have provided valuable information for this study. Alum coagulation with 60 mg/L at a pH of 5.9 was optimum for removing maximum THM precursors (78). Sinsabaugh (79) found that the dominant precursors at Harwood's Mill Reservoir were fulvic acids and nonpolar neutral compounds. The nonpolar neutral compounds were harder to remove by coagulation, but they reacted more slowly with chlorine and produced less organohalides than fulvic acids.

Because fulvic acids are so prevalent in Harwood's Mill Reservoir, it can be assumed that if the current THM MCL is lowered, additional organic treatment options will be required.

Chapter 3

MATERIALS AND METHODS

In this chapter, the construction and operation of the activated carbon columns and the associated pilot plant facility will be described. Detailed descriptions of the sampling program and the analytical methods used to assess the GAC, BAC, and PAC performance will be included.

GAC CONTACTORS

The carbon contactors were designed to operate in the downflow mode on the basis of a 30-minute (min) empty bed contact time (EBCT) such that breakthrough would not occur for several months. The columns were constructed of 4-in (10.2 cm) inside diameter (I.D.) acrylic pipe. Polyvinyl chloride piping and 0.5-in (1.3 cm) rubber hose. The GAC bed depth was 11-ft (3.4 m) in columns 18-ft (5.5 m) long. However columns of this height could easily fall, thus it was decided to construct the GAC and BAC columns as two-stage contactors in series (Figure

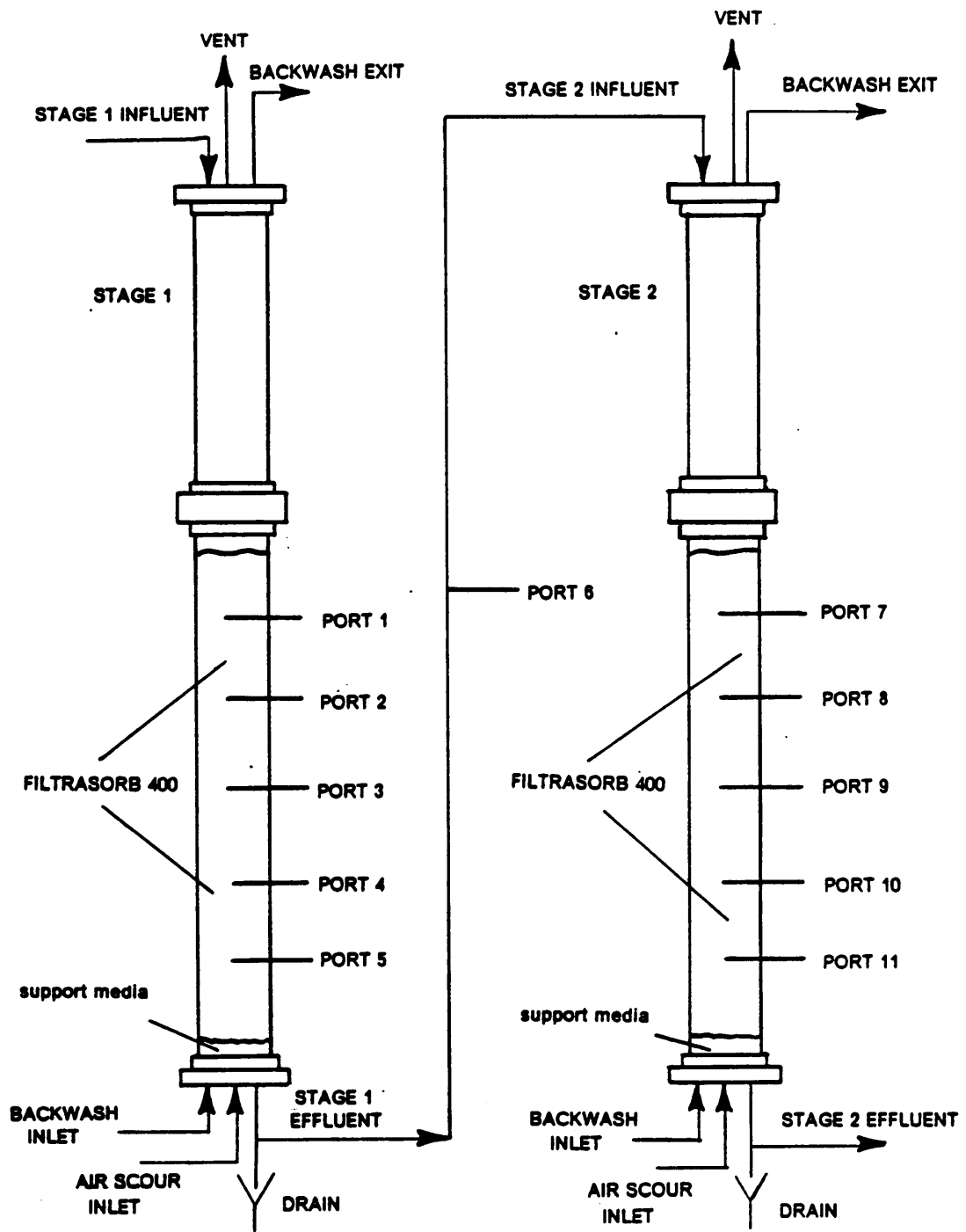


Figure 1. Schematic of the Activated Carbon Columns Used in the Pilot Plant Study at Harwood's Mill Reservoir.

1). Figure 2 illustrates the entire process train leading to the GAC and BAC contactors. Each column was 9-ft (2.7 m) high with a carbon bed depth of approximately 5.5-ft (1.7 m). The total bed depth in the GAC and BAC contactors after operation had begun was 128-in (3.25 m) and 132-in (3.4 m) respectively. Three inches (7.6 cm) of coarse garnet served as the support media for the carbon bed. Two sets of this two-stage arrangement were constructed so that parallel trains could be monitored (BAC vs. GAC). Sampling ports were installed at approximately 12-in (30.5 cm) intervals along the column so that the organic wavefront could be monitored as it passed through the carbon bed. Sampling locations also included the columns' influent and effluent.

A diffuser was placed at the base of the column to serve as an air backwash, which was incorporated into the design to prevent mudball formation. An air/water backwash was thought to be more effective than a water backwash alone for alleviating this problem when it occurred. The freeboard available during backwashing was 3.5-ft (1.1 m).

The carbon bed consisted of 11-ft (3.35 m) of Calgon's (Pittsburgh, Pennsylvania) FILTRASORB 400 (12 x 40 mesh). Table 1 provides properties and characteristics of the FILTRASORB 400 (80). GAC selection was based on the results of isotherm tests performed immediately preceding the study.

Water was supplied to the carbon columns by a 1/3 horsepower (hp) centrifugal pump and flow was controlled by rotameters and globe valves. The rotameters were calibrated periodically by timing the delivery of a fixed volume. A hydraulic loading of 2.7 gpm/ft² (110 L/min/m²) to the columns provided 30-min EBCT. The volume of water passing through the carbon beds was monitored by totalizers placed in the effluent stream from each column. The GAC was operated from August 5 through November 26, 1986 when all operations ceased. The BAC column operation also began on August 5, but was discontinued on November 8 because the ozone generating unit was returned to Infilco Degremont. There were a few minor interruptions during this period. Both the BAC and GAC columns were shut down from August

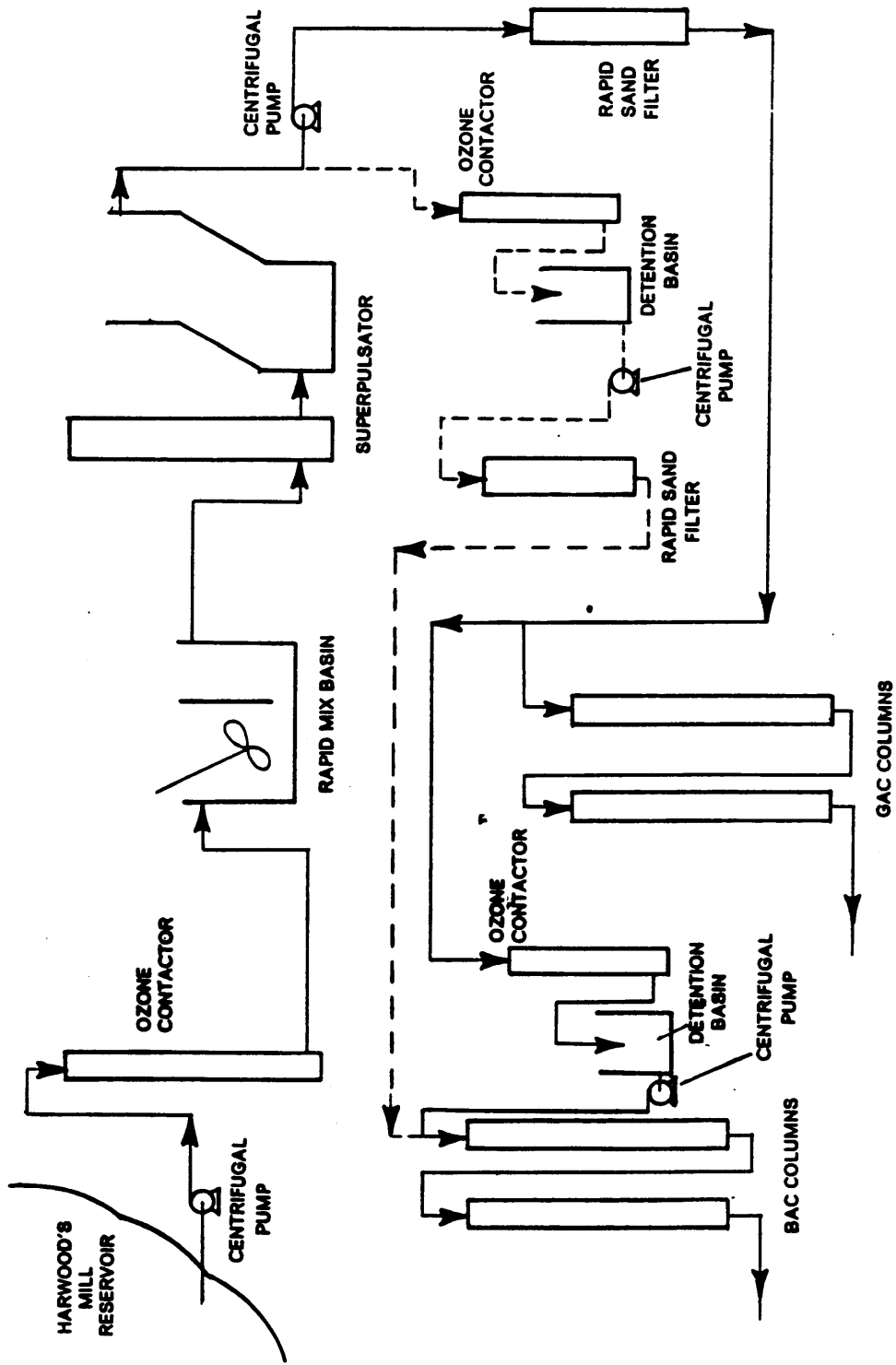


Figure 2. Schematic Diagram of the Entire Pilot Plant Process Train Used at Harwood's Mill Reservoir. (---Process stream to BAC column from August 5 through Sept. 21)

Table 1. Specifications and Properties of FILTRASORB 400 Granular Activated Carbon (80).

Characteristic	VALUE
Total Surface Area (Nitrogen BET Method, m²/g)	1050 - 1200
Bulk Density (lb/ft³)	27
Particle Density Wetted in Water (g/mL)	1.3 - 1.4
Pore Volume (mL/g)	0.94
Effective Size (mm)	0.55 - 0.75
Uniformity Coefficient	1.9 max

8 until August 10 after a flange at the base of the stage 2 BAC column failed. Supports were then placed under each stage of both column trains. From August 12 through August 20, the BAC train was operated with only one stage while a leak was repaired in the other. This resulted in an EBCT of only 15 minutes. During this time the GAC column continued operation with both stages. On August 21 the second stage of the BAC column was placed back into operation. There were no further interruptions in the operation.

Both the GAC and BAC columns were backwashed on several occasions early in the program because head losses were greater than 10-ft (3.0 m). The BAC columns were backwashed more frequently than the GAC columns until September 25, 1986, when backwashing was no longer required for either column.

Ozone Addition

The ozone added to the mixed media filter effluent before it entered the BAC column was supplied from an ozone generator which had been leased to the City by Infilco-Degremont Inc. (Richmond, Virginia). Prior to September 21, the ozone was added immediately before the mixed media filter but because the ozone addition caused soluble manganese to precipitate as manganese dioxide, the ozone application point changed to after the mixed media filter and immediately before the BAC column.

The ozone was added to the BAC influent through a diffuser at the base of a polyvinyl chloride (PVC) contact chamber which was 11-ft (3.35 m) long and 3.0-in (7.6 cm) I.D. (Figure 3). The ozone contact time was approximately 14-min at a set flow rate of 0.3 gpm (1.1 L/min). After leaving the contact chamber, the water flowed into a 40-gallon (151 L) tank to allow degasification. Degasification was necessary to prevent flow interference by air pockets that formed in the mixed media filter and BAC column.

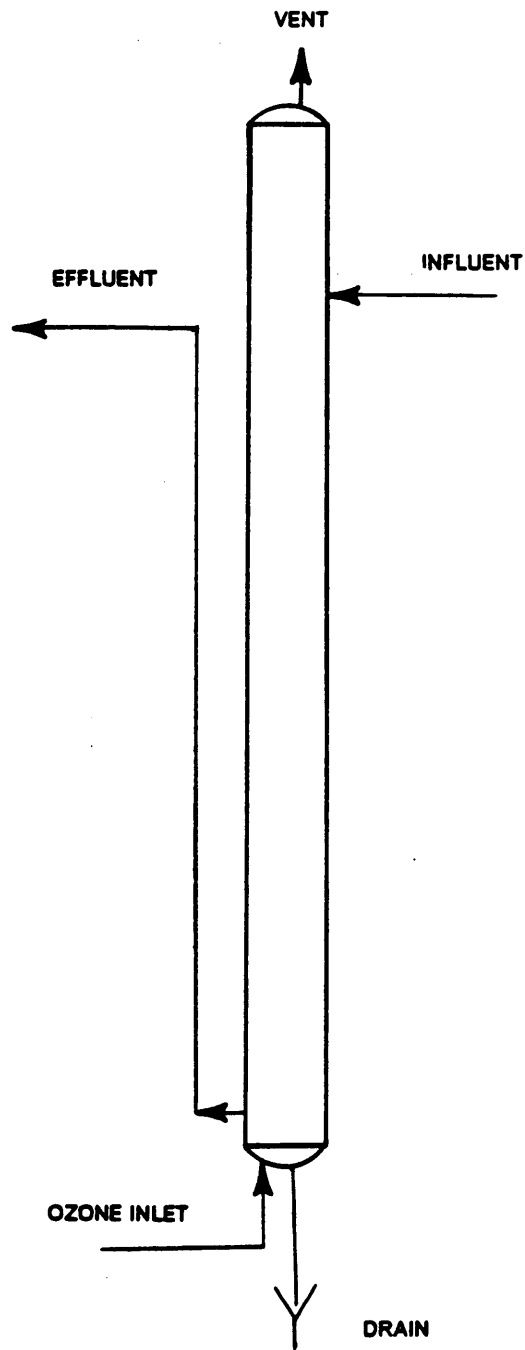


Figure 3. Schematic Diagram of the Ozone Contactor Preceding the BAC Column.

The ozone dose to the BAC influent was based on the TOC concentration. For partial oxidation of organics before entering the BAC column, an ozone dose of 0.5 to 1.0 mg ozone/mg TOC was desired (55, 56, 81, 82). The rate of ozone addition into the contactor was adjusted daily to obtain the dose within this range.

POWDERED ACTIVATED CARBON

The PAC was added to the clarifier immediately after the rapid-mix basin so that it could be incorporated directly into the floc. Westvaco's (Covington, Virginia) AQUA NUCHAR was used during June and July and NUCHAR SA was used during October. Characteristics of each carbon are presented in Table 2 (83, 84). Ozone was intermittently added to the raw water during both studies. The ozone contactor preceding the rapid-mix basin consisted of a 12-in (30.5 cm) I.D. stainless steel column 15-ft (4.6 m) in height. It provided a contact time of approximately 3.75-min. The ozone dose varied from 0.05 to 0.2 mg ozone/mg TOC, which is in the range mentioned in the literature (73, 82) as optimal for encouraging microflocculation.

Superpulsator® Operation

Innovative technology was employed for the clarification process. The Superpulsator® (Infilco Degremont Inc., Richmond, Virginia) was chosen over several other alternatives as the most cost effective and technically viable clarifier. The Superpulsator® is a unique, up-flow floc blanket clarifier. Its uniqueness lies in the facts that 1) it has no internal moving parts and 2) the sludge blanket is self-leveling. Its name is derived from the fact that water is pulsed at regular intervals into the clarifier, causing the floc blanket to expand and contract (pulse).

Table 2. Specifications and Properties of AQUA NUCHAR and NUCHAR SA Powdered Activated Carbon (83, 84).

Carbon Characteristics	AQUA NUCHAR	NUCHAR SA
Iodine Number (mg/g)	800 †	900 †
Molasses Decolorizing Index	9 †	14 †
Moisture, as packed (%)	5 ‡	10 ‡
Apparent Density (kg/m ³)	641 ‡	337 - 369
(lb/ft ³)	40 ‡	21 - 23
Sieve Analysis (mm)		
Thru 100 mesh (%)	99 ‡	95 - 100
Thru 200 mesh (%)	97 †	85 - 95
Thru 300 mesh (%)	90 †	65 - 85
Total Surface Area (Nitrogen BET method, m ² /g)	---	1400 - 1800
Total Pore Volume (cm ³ /g)	---	2.2 - 2.5

† Minimum value

‡ Maximum value

Hamann et al. (85) provides a detailed description of its operation and a brief overview of the Superpulsator® follows.

Coagulated water (alum and polymer) exited the rapid mix basin and entered a vertical column where a vacuum pump raised the water level approximately 15 inches. When a solenoid valve released, the column of water pulsed downward into the clarifier unit that contained the sludge blanket. The pulse cycle was 60 seconds and served three functions: 1) it allowed a low intensity mixing zone in the distribution duct, 2) it ensured proper mixing, and 3) it created a swirling action at the distribution pipe outlet orifices, an action that mixed the blanket uniformly, thus preventing short circuiting.

The coagulated water, upon entering the clarifier, immediately flocculated in the presence of other flocs and continued to do so as the water flowed upward. The floc blanket impinged on a series of plates near the surface at an angle of 60 degrees to the horizontal. The plate region acts as the liquid/solid separation zone. The clarified water flowed through this zone to the clarifier effluent weir and on to the mixed media filters. At a flow rate of 24 gpm (91 L/min), the detention time within the sludge blanket was approximately 48-min and 75-min for the entire Superpulsator® unit.

A sludge hopper was located approximately 5-ft (1.5 m) below the clarifier effluent weir and at the upper level of the sludge blanket. With each pulsation the sludge blanket was raised a few inches and before it settled, excess sludge spilled over a sludge weir into a hopper. By this action, the sludge level remained constant. The sludge in the hopper was wasted on a 45-min cycle. The addition of PAC added considerably to the sludge production. Approximately six pounds (lb) (2.7 kg) per day of additional sludge was wasted at a raw water flow rate of 24 gpm (91 L/min) and a PAC dose of 21 mg/L. Without PAC addition, the amount of sludge wasted per day was approximately 7.5 lb (3.4 kg).

Alum and occasionally acid were added to the influent of the rapid mix basin while polymer and PAC were added to the effluent. The PAC particles adhered to the floc formed from the alum addition and thus became part of the sludge blanket. The PAC detention time within the pulsator was approximately one day.

Alum was the chosen coagulant because it is used at the existing Harwood's Mill Water Treatment Plant. Previous studies conducted by Johnson (78) at Harwood's Mill showed that an alum dose of 60 mg/L was very effective for removing a high percentage of the THM precursors. Polymer was required because the floc in the sludge blanket is constantly subjected to shear stresses from the continuous pulsing of water entering the clarifier.

CHEMICAL FEEDS

All of the chemical feeds were by batch means. A diaphragm metering pump was used to pump all of the chemicals except acid. Acid was added by the use of a peristaltic pump. See Table 3 for complete equipment specifications.

PAC. The PAC was fed into the Superpulsator® from slurry batches prepared every other day. A drum was filled with 40-gal (151 L) of tap water into which 12 lbs (5.45 kg) of PAC was added. The contents were thoroughly mixed and then the diaphragm metering pump was activated. A special feature of this pump was an attached flushing system that purged the tubing and foot valve with a 5 second pulse of tap water every 60 seconds. AQUA NUCHAR was added to the Superpulsator® at a dose of 25 mg/L. It was the intention to add NUCHAR SA at this dose also; however, operational problems with the PAC feed pump resulted in an average dose of 16 mg/L to the Superpulsator® for a portion of the study and 21 mg/L for the remainder.

Alum. Alum was fed at the head of the rapid mix basin. Alum feed batches consisted of 40 gal (151 L) of standard industrial grade alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 14.3\text{H}_2\text{O}$) with a concentration of

Table 3. Various Equipment Specifications for Pilot Plant Operations.

Unit	Equipment Specifications
Pump to Sand Filter and GAC Columns	<i>Peerless</i> Centrifugal Pump, 1/3 hp., Series PE-B, Model # SKC37FN65X
Polymer and Alum Feed Pump	<i>Liquid Metronics, Inc.</i> , Diaphragm Metering Pump, Series B-7, Model #B711-915
PAC Feed Pump	<i>Liquid Metronics, Inc.</i> , Diaphragm Metering Pump with Auto-flush, Series B22, Model # b221 - 89
Acid Feed Pump	<i>Cole Palmer, Masterflex</i> Variable Speed Drive Peristaltic Pump, 1-100 rpm., Model # 7553-30, Pump Head # 7015, 7016, 7017, 7018
Chemical Batch Mixers	<i>Liquid Metronics, Inc.</i> , Model 10590
pH Meter	<i>Beckman</i> Model 960B Continuous Monitoring pH Meter
Turbidimeter	<i>Hach</i> Ratio Turbidimeter, Model 18900
Head Loss DP Cells	<i>Validyne</i> Model DP21542
Air Compressor	<i>Sanborn</i> , 3/4 hp., Series 44B75
Personal Computer	<i>Compaq</i> , Two disk drive, 256K memory
Programmable Controller	<i>Westinghouse, Numalogic</i> , Model PC1100-1011

approximately 480 g/L added to water in a 1:1 dilution. A dose of 60 mg/L was provided by a diaphragm metering pump. This dose was occasionally varied in response to changing raw water conditions.

Polymer. Polymer was fed to the effluent of the rapid mix basin. The feed batches consisted of 206-g (0.454 lb) of Betz (Trevose, Pennsylvania) 1160 polymer dissolved in 40-gal (151 L) of tap water. On occasion, the Betz 1165L polymer was also used. 0.2 L of 1165L polymer was mixed with 40-gal (151 L) of water. It differs from the other in that it is liquid and is slightly more resistant to degradation from preoxidants. The Betz 1165L was used during the June and July study involving PAC, while the 1160 was used during the October study. The polymer was added with a diaphragm metering pump to achieve a dose from 0.3 to 0.5 mg/l with the actual dose being dependent upon raw water conditions. No attempt was made to evaluate Superpulsator® performance as a function of polymer type. The use of one or the other was dictated totally by the treatment conditions (i.e. oxidant or no oxidant).

Acid. Sulfuric Acid was added at the head of the rapid mix to depress the pH of the raw water during the coagulation process to pH 5.8-6.0 to improve organic removal. Occasionally it was not necessary to add acid to reach this pH range and no acid was added. The acid batch was made by combining 1.0 L of 36 N sulfuric acid (H_2SO_4) to 40 gal (151 L) of tap water. It was added by a peristaltic pump rather than a diaphragm metering pump because of its potential corrosivity to the diaphragm pump head.

SAMPLING PROGRAM

GAC Studies

Samples were collected from the column influent and effluent and from five ports along the BAC and GAC columns so that the progress of the organic wavefront could be monitored. Early in the program the first five ports of the BAC and GAC columns were sampled and as the wavefront progressed, the ports lower in the carbon bed were sampled. Three measurements were employed to monitor the activated carbon columns: THMFP, TOC, and UV254. The influent and effluent TOC and UV254 analyses were conducted six days each week but only three days a week at the column ports. Influent and effluent THMFP was determined three days each week and at the column ports twice a week.

Influent and effluent streams were also analyzed for iron and manganese three times a week and a sample was taken for bacterial analysis by the standard plate count twice a week. Also, once each week 500 mL of the influent and effluent streams were filtered through a 0.45 μm filter to visually demonstrate the presence or absence of particulate matter or PAC in the water.

Powdered Activated Carbon

Measurements to evaluate the effectiveness of PAC within the sludge blanket in the Superpulsator® included the same as those used in monitoring the BAC and GAC columns. Raw water, clarifier effluent, and filter effluent streams were analyzed. Analyses of TOC and UV254 were conducted six days each week. Samples for THMFP analysis were taken three

days a week during the study conducted in June and July and five days a week during the October study. Iron and manganese measurements were made twice weekly during June and July and three times per week during October. A bacteriological sample was taken each week for standard plate count determinations. Also, samples filtered through a 0.45 μm filter were taken once a week to show the presence of particulate matter or PAC.

Total suspended solids (TSS) of the sludge blanket were determined three times each week during June and July and six times each week in October. Three of the eight ports situated at 18-in intervals were sampled to approximate the sludge TSS at the top, middle, and bottom of the blanket.

Additional Measurements

Additional sampling points included the raw water, clarifier effluent, the mixed media filter effluent, and the BAC and GAC effluent. Daily measurements were made of flowrate, pH, alkalinity, turbidity, temperature, and dissolved oxygen (DO) concentration. In addition, flowrate, totalizer readings, and chemical doses were recorded. Continuous monitoring of the influent and effluent turbidity and head loss of the carbon columns enabled precise determination of the time when head loss exceeded the allowable 10-ft (3.0 m) or when turbidity breakthrough (0.3 ntu) occurred.

Samples were collected in 120 (mL) screw cap glass bottles. UV254 samples were collected in 30 mL screw cap glass vials, while THMFP samples were collected in 40 mL glass vials with Teflon lined screw caps. Iron and manganese samples were collected in 100 mL plastic bottles and acidified to a pH less than 2 with HNO_3 . The bacteriological sample was collected and stored in a sterilized serum bottle according to *Standard Methods for the Examination of Water and Wastewater* (86). Total suspended solids were collected in 100 mL plastic bottles.

All of the glassware was washed with Alconox soap and rinsed with distilled water except where specifically described otherwise. The distilled water was provided by a Milli-RO4 and a Milli-Q water purification system (Millipore Corporation, Bedford, Massachusetts).

GENERAL PHYSICAL, CHEMICAL, AND BIOLOGICAL ANALYSES

Analysis requiring sophisticated instrumentation, and a few selected others, were performed by personnel in the Newport News Waterworks Laboratory. These analyses included iron, manganese, TOC, UV254, THMFP, TSS, and Standard Plate Counts. Samples requiring these analyses were collected by pilot plant personnel. Other routine analyses were performed at the pilot plant site. Descriptions of all analyses follow.

Iron and Manganese

Iron and manganese were analyzed by atomic absorption spectrophotometry. Specifically, a Perkin-Elmer (Norwalk, Connecticut) HGA-400 Programmer and Graphite Furnace were used in addition to the Perkin-Elmer 4000 Atomic Absorption Spectrophotometer. A Perkin-Elmer AS-40 autosampler was employed so that a large number of samples could be analyzed without continuous manual monitoring. Argon was used as the purge gas to provide an inert atmosphere for combustion.

In the graphite furnace, a sample is dispensed into a graphite tube which is heated in a stepwise fashion. The three steps toward complete atomization; which include the process

of drying, thermal decomposition of the matrix, and thermal dissociation into free atoms can be separated to provide better efficiencies. The furnace was used instead of conventional flame atomic absorption spectroscopy because the sensitivities and detection limits of most metals are from 100 to 1000 times lower than those obtained by flame analysis because the furnace allows a more complete combustion (atomization) of a sample and the atoms remain longer in the analyzing light beam (87).

Calibrations were made with a zero standard and with a standard containing the expected concentration in the sample. Each of the calibration standards contained 0.5 percent (v/v) nitric acid (HNO₃). In addition, an EPA Quality Control sample was analyzed to verify the spectrophotometer's readings. The instrument was recalibrated after every seven analyses.

The 100 mL plastic sample bottles were acid washed and rinsed with distilled water. After a sample had been collected, approximately 0.5 mL of HNO₃ (conc.) was added to preserve the sample.

Iron. Iron concentrations were determined according to method 236.2 of *EPA's Methods for Chemical Analysis for Water and Wastewater* (88). Absorbance was measured at 248.3 nanometers (nm) with an atomizing time and temperature of 10 seconds and 2700°C, respectively after the sample had been dried for 30 seconds at 125°C and thermally decomposed for 30 seconds at 1000°C. Sample volume was a 20 microliter (μL) sample. Larger or smaller volume samples would require different times and temperatures for the various stages of analysis. Each sample was analyzed in triplicate and the average was reported.

Manganese. Manganese was analyzed according to method 243.2 of *EPA's Methods for Chemical Analysis for Water and Wastewater* (88). Analyzing 20 uL samples for manganese was completed using the same heating times and temperatures as were used for the iron

analysis. The absorbance wavelength for manganese was 279.5 nm. Each sample was analyzed in duplicate with the average being reported.

Total Organic Carbon

Samples were analyzed for TOC with Sybron's (Boston, Massachusetts) PHOTOchem Organic Chemical Analyzer Model E3500 and the E3800 autosampler. This analyzer is different than other models in that it uses ultraviolet (UV) oxidation and conductivity to measure TOC ranging from 0.02 to 20,000 mg/L. It measures the change in resistivity of ultrapure distilled water caused by the ionization of carbonic acid. This is formed through the solvation of carbon dioxide produced by the photochemical oxidation of organics. It differentiates between inorganic and organic carbon in two separate analytical stages that occur during two different cycles called the dark cycle and the light cycle. The UV light remains off during the dark cycle and no oxidation of organic matter occurs. At the end of this cycle the ultraviolet lamp automatically illuminates causing the organic material to be oxidized. The difference in resistivity after the dark cycle and the light cycle is then translated into a TOC concentration for that sample (89).

Calibrations were made with a 10 mg/L standard and a blank provided by Sybron. A 4 percent (w/v) potassium persulfate ($K_2S_2O_8$) solution is injected into the analyzer with each sample. The samples were analyzed in duplicate and the average reported. The analyzer was recalibrated after each 10 analyses.

All glassware was washed and rinsed with distilled water then allowed to dry. After a sample had been collected in the 120 mL glass bottle, approximately 0.5 mL of concentrated phosphoric acid (H_3PO_4) was added for pH adjustment to less than 4.0. This was to ensure all alkalinity from the sample was removed and to prevent bacterial activity.

UV Absorbance

Sample absorbance was measured in a 10-cm cuvette at a wavelength of 254 nm against a distilled water blank. The instrument was an IBM (Danbury, Connecticut) 9410 UV-Visible Spectrophotometer. The larger pathlength permitted greater analytical sensitivity to a sample. It is important to note that all of the UV absorbance values reported in this thesis are per 10 cm and not as absorbance per cm or m as commonly reported in other literature sources.

THM and THMFP

THM Analysis

Trihalomethane concentrations were analyzed by the *Purge and Trap Method, Method 501.1*, outlined by EPA (90). The purge and trap method is applicable in determining four trihalomethanes: chloroform, bromodichloromethane, dibromochloromethane, and bromoform. Chloroform represents the largest fraction (80%) of THM's in Harwood's Mill Reservoir, with bromodichloromethane being the next highest (19%), and the other two THM's accounting for the remaining 1 percent of THM's. Concentrations of all four THM's were summed to obtain the THMFP. These percentages were comparable with concentrations found elsewhere (21).

A Tracor (Austin, Texas) Model 565 Gas Chromatograph (GC) equipped with a Tracor 700A Hall Electrolytic Conductivity Detector and a Tracor LSC-2 sample concentrator, were used to analyze the samples. A Tekmar (Cincinnati, Ohio) ALS Automatic Sampler was used for increased sampling efficiency and a Spectral Physics (Piscataway, New Jersey) SP4270

Integrator was used for plotting the chromatogram and determining the individual THM concentrations. The GC column was an 8-ft x 0.125-in (2.44 m x 3.2 mm) O.D. glass column with a packing consisting of 1 percent SP-1000 on Carbopack-B (60/80) mesh. The carrier gas was helium and hydrogen was used as the inert gas. The temperature program sequence for each sample is as follows: 45°C for 3 min, then incrementally increase temperature 8°C per min to 220°C and hold for 15 min or until all components have eluted. All samples were analyzed once though an occasional sample analysis was duplicated. The error between replicates was never greater than 3 percent. Calibrations were made daily (approximately every ten samples). The gas chromatograph was standardized with a blank and with an EPA quality control sample.

THMFP Analysis

The THMFP is the amount of THM's that form in seven days after the sample has been chlorinated. At present there is no standard method for determining the THMFP. Analytical procedures used by different investigators may vary in the amount of chlorine added, pH, or incubation time. The chlorine dose added to samples in this study was based on a 3:1 ratio of chlorine to TOC concentration. At this ratio, a chlorine residual was consistently present after seven days incubation. The chlorine solution was made up from a commercial grade of bleach which contained 5.25 percent by weight sodium hypochlorite (NaOCl). The samples were refrigerated until they were inoculated with the appropriate amount of chlorine and a phosphate buffer to stabilize the pH at 7.0, after which they were incubated in the dark at ambient room temperature for seven days. The THM formation reaction was terminated by adding a few grains of sodium thiosulfate to reduce any residual chlorine. This step followed a check of the chlorine residual with a Hach Chlorine Residual Kit that employed the colorimetric DPD method. The samples were then either analyzed immediately for THM's or were refrigerated until analysis could be performed.

The samples were collected in 40-mL screw cap glass vials with Teflon-coated liners. The vials were washed with Alconox soap, rinsed with distilled water, and heated in an oven for one hour at 103°C. Afterwards, the bottles were allowed to cool for one hour in an environment free of organics and then capped.

Total Suspended Solids

The total suspended solids (TSS) were determined by the procedure outlined in Method 160.2 of EPA's *Methods for Chemical Analysis of Water and Wastewater* (88). A 10-mL sample was filtered through a 3.2-cm diameter Whatman (Clifton, New Jersey) 934-AH glass fiber filter. The filter was dried in a Precision Scientific Model 18 drying oven at 103°C for 1 hour and then placed in a dessicator to cool for one hour before being weighed. A Mettler (Highstown, New Jersey) AE-163 balance was used to obtain the tare weight and final weight of the filter.

Standard Plate Count

The procedure for standard plate counts was performed as outlined in Method 907 of *Standard Methods for the Examination of Water and Wastewater* (86). Sample bottles were sterilized by autoclave prior to sampling.

Visible Suspended Solids

Visual suspended solids were collected for inspection by filtering approximately 500 mL of a sample through a 47-mm diameter Millipore (Bedford, Massachusetts) disc with a 0.45 µm pore size. The filters were then dried at room temperature. The amount of suspended

material collected by the filter provided visual evidence of any suspended solids in the water, particularly PAC particles.

pH

The pH was determined with a Beckman (Cedar Grove, New Jersey) 960B pH meter with a combination electrode that contained the glass and reference electrodes in a single unit. The instrument could be used for continuous monitoring of various sample streams or for individual analyses of grab samples from various points within the process train. The procedure for pH analysis is described in Method 423 of *Standard Methods for the Examination of Water and Wastewater* (86).

Turbidity

The turbidity of various process streams was measured with three Hach (Loveland, Colorado) Model 18900 Continuous Flow Ratio Turbidimeters. These turbidimeters provided continuous monitoring of the clarifier effluent, rapid sand filter effluent, and the activated carbon columns' effluents. The turbidity measurement was based on the nephelometric method as described in Method 214.A of *Standard Methods for the Examination of Water and Wastewater* (86).

Ozone Concentration

The concentration of ozone being fed into the process train was determined by modifications of the procedure outlined in Method 422 of *Standard Methods for the Examination of Water and Wastewater* (86). Ozone was fed at 0.5 to 1.0 L/min into two 500 mL traps connected in series,

each containing 400 mL of 5 percent (w/v) potassium iodide (KI) solution. As ozone was fed, the solution in the first trap turned a dark yellow to brown. The KI solution in the second trap remained clear indicating that all of the ozone had reacted with KI in the first trap. A Precision Scientific Wet Test Meter was used to determine the total amount of air-ozone that was passed through the 500 mL diffusers. After three liters of gas had passed through, the ozone flow was shut off. Then, 100 mL of the KI solution from the first trap was placed in a 250 mL Erlenmeyer beaker and 5 mL of 1 N H₂SO₄ was added to lower the pH below 2.0. The sample was then titrated with 0.00564 N phenylarsine oxide (PAO) until the color of the sample became pale yellow. A few drops of starch were then added (blue color results) as an indicator, and titration was continued until the sample became clear. The amount of titrant used was recorded. The concentration of ozone being fed can be calculated by the following equation:

$$O_3 = \frac{\alpha\beta\omega\psi \times 24}{\gamma\theta\sigma}$$

O₃ = Ozone, mg/L

α = Normality of PAO titrant

β = KI solution in diffuser, L

ω = Volume of titrant added, L

ψ = Rate ozone is added to water, L/min

γ = KI solution sample to be titrated, L

θ = Volume of air/ozone passed through KI solution, L

σ = Flowrate of water, L/min

Dissolved Oxygen

The dissolved oxygen levels at selected points in the process train were measured by a polarographic membrane electrode as outlined in Method 421.f in *Standard Methods for the Examination of Water and Wastewater* (86). The instrument used for in the analysis was a Yellow Springs Instrument (Yellow Springs, Ohio) Model 57.

Alkalinity

Samples from various points in the process train were analyzed for alkalinity by the procedure outlined in method 310.1 in *EPA's Methods for Chemical Analysis of Water and Wastewater* (88).

Color

The visual comparison method with platinum cobalt standards was employed for color analysis. This method is outlined in Method 204.A of *Standard Methods for the Examination of Water and Wastewater* (86). Samples were not filtered or centrifuged before analysis; therefore the analyses are for "apparent color" rather than "true color". A Hellige (Long Island City, New York) disc colorimeter was employed for analysis.

Chapter 4

RESULTS

The pilot plant operation was halted after five months when sufficient data had been collected to satisfy the objectives of the study. Complete breakthrough in the GAC and BAC beds had not occurred, but enough data had been collected from ports in the upper regions of the carbon bed that the time to actual breakthrough could be predicted. In addition to the treatment methods described in the Materials and Methods chapter, several other treatment options influenced the performance of the pilot plant. Potassium permanganate (KMnO_4) was added as a preoxidant for a three week period in September and two different polymers were added at various times through the study, depending on whether a preoxidant was being used or not. The specific times that these processes were being used can be found in Tables 18-21 of Appendix A. A compilation of all of the sampling results at various points in the process train can be found in Tables 18-33 of Appendix A.

RAW WATER CHARACTERISTICS

The characteristics of Harwood's Mill Reservoir water are compiled in Table 4. The wide range of values for all of the measured parameters is indicative of the variability of the raw water quality at Harwood's Mill Reservoir.

Trihalomethane Precursors

Trihalomethane formation potential (THMFP) measurements were used as indicators of THM precursor concentrations in water. This was considered practical because a large percentage of the THM-precursor material formed THM's during the seven days of chlorine contact period. Results obtained at the existing Harwood's Mill Treatment Plant indicated that actual THM concentrations after seven to eight days in the distribution system were approximately 1/2 of the THMFP value (Table 5). Hoehn (91) reported a ratio of Harwood's Mill system THM to Superpulsator® effluent THMFP ranging from 0.40 to 0.82 (av. 0.62) when the furthest point in the system was considered. A conservative THM/THMFP ratio of 2/3 was used because 1) as the Chickahominy River becomes a larger water source for Harwood's Mill reservoir, the raw water THMFP and TOC concentrations will increase and 2) the 0.5 and 0.62 ratios were obtained from data collected in the winter, spring, and fall of 1986 and not during the summer months when the THM formation rate is highest. Thus, a conservative THM/THMFP value was chosen to portray worst case situations. Some of the activated carbon analyses will also use the 0.5 THM/THMFP ratio to put the less conservative measure into perspective.

Table 4. Raw Water Characteristics for Harwood's Mill Reservoir (June 8, 1986 through November 26, 1986).

Characteristic	MEAN	RANGE
Trihalomethane Formation Potential ($\mu\text{g/L}$)	362	184 - 651
Total Organic Carbon (mg/L)	6.38	4.40 - 7.76
UV absorbance at 254 nm (O.D./10 cm)	1.770	1.440 - 2.750
Iron (mg/L)	0.400	0.113 - 0.834
Manganese (mg/L)	0.121	0.057 - 0.604
Turbidity (ntu)	6.2	2.8 - 24.0
pH	7.0	6.5 - 7.6
Alkalinity (mg/L as CaCO_3)	54.6	42 - 86
Temperature ($^{\circ}\text{C}$)	23	10 - 30
Dissolved Oxygen (mg/L)‡	7.4	3.0 - 9.9
Color (color units)	48	20 - 110

‡ Measured from August 5 through November 26, 1986 only.

Table 5. Determination of THM/THMFP Ratio for Harwood's Mill Reservoir Distribution System (September 10, 1986 through December 15, 1986).

THMFP of Filter Effluent Before Leaving Harwood's Mill Treatment Plant (µg/L)	THM After Approximately Seven Days in the Distribution System (µg/L)	THM/THMFP
200	158	0.79
240	139	0.56
238	177	0.74
246	116	0.47
235	71	0.30
209	98	0.47
212	109	0.51
242	91	0.38
198	93	0.47
240	77	0.32
		<hr style="width: 10%; margin-left: auto; margin-right: 0;"/> AVERAGE = 0.50

CARBON COLUMN OPERATIONS

The GAC and BAC columns were constructed identically and differed in operation in that ozone was added before the BAC column. An important fact to remember while analyzing the data is that until September 20, 1986, one and a half months into the study, the influent to the BAC and GAC columns were from two separate mixed media filters. When the BAC ozone-contact chamber was moved on September 20, so that it followed the mixed media filter, the influent to the BAC and GAC originated from the same mixed media filter.

The GAC column operation was discontinued on November 26, 1986 after 113 days (107 days with an EBCT of 30 min) of operation. The BAC column was operated for 95 days (83 days with an EBCT of 30 min), terminating on November 8, 1986 eight days after ozone addition was stopped. The discrepancy between the actual days of operation and the days of operation with an EBCT of 30 min is because the GAC and BAC columns were shut down for five days early in the program and the BAC column operated with an EBCT of only 15 minutes for 9 days. Approximately 5,100 bed volumes of water passed through the GAC columns and 4,000 through the BAC columns. It was expected that the organic wavefront would not have progressed as far in the BAC columns as it had in the GAC column because the applied organic loading to the BAC columns was lower.

The GAC and BAC performance data are expressed in terms of bed volumes rather than operating times because time of operation is a function of flow rate and does not provide an adequate interpretation of the bed life when flows vary. However for purposes of general comparison with the expected operations of the new Harwood's Mill Water Treatment Plant, 48 bed volumes correspond to 1 day of operation with an EBCT of 30-min.

Variability of Organics in the Influent

THMFP. Figures 4 and 5 show the influent and effluent THMFP concentrations of the GAC and BAC columns respectively. The influent THMFP was significantly lower during the month of October than at any other time in the study. This can be attributed to the use of PAC in the Superpulsator® which reduced the THMFP concentration in the clarifier effluent. If this period is excluded, the mean GAC and BAC influent THMFP concentration were 153 and 145 µg/L respectively. The influent values during the period of PAC addition were not taken into account since in actual practice PAC and GAC would not be used simultaneously.

TOC. The TOC varied similarly in the GAC and BAC influent as did the THMFP (Figures 6 and 7). The average TOC concentration for the GAC and BAC influent excluding the period of PAC use was 3.46 and 3.31 mg/L, respectively.

GAC and BAC Effluent Quality

The water quality exiting the two sets of columns was excellent. The turbidity never was greater than 0.1 NTU, and the concentrations of THMFP and TOC in the effluent never increased significantly. Figures 4 and 5 show that the GAC and BAC effluent were continuously below 20 and 25 µg/L THMFP respectively, indicating that the wavefront did not break through the 11-ft (132-in) (3.4 m) of carbon during the 16 week study period. During this time, the GAC and BAC columns removed greater than 80 percent of the THM precursors present in the influent.

Figures 6 and 7 show the effluent TOC for the GAC and BAC was below 1.0 mg/L throughout the study. Both columns consistently removed greater than 70 percent of the TOC. A complete listing of the GAC and BAC effluent qualities can be found in Table 6.

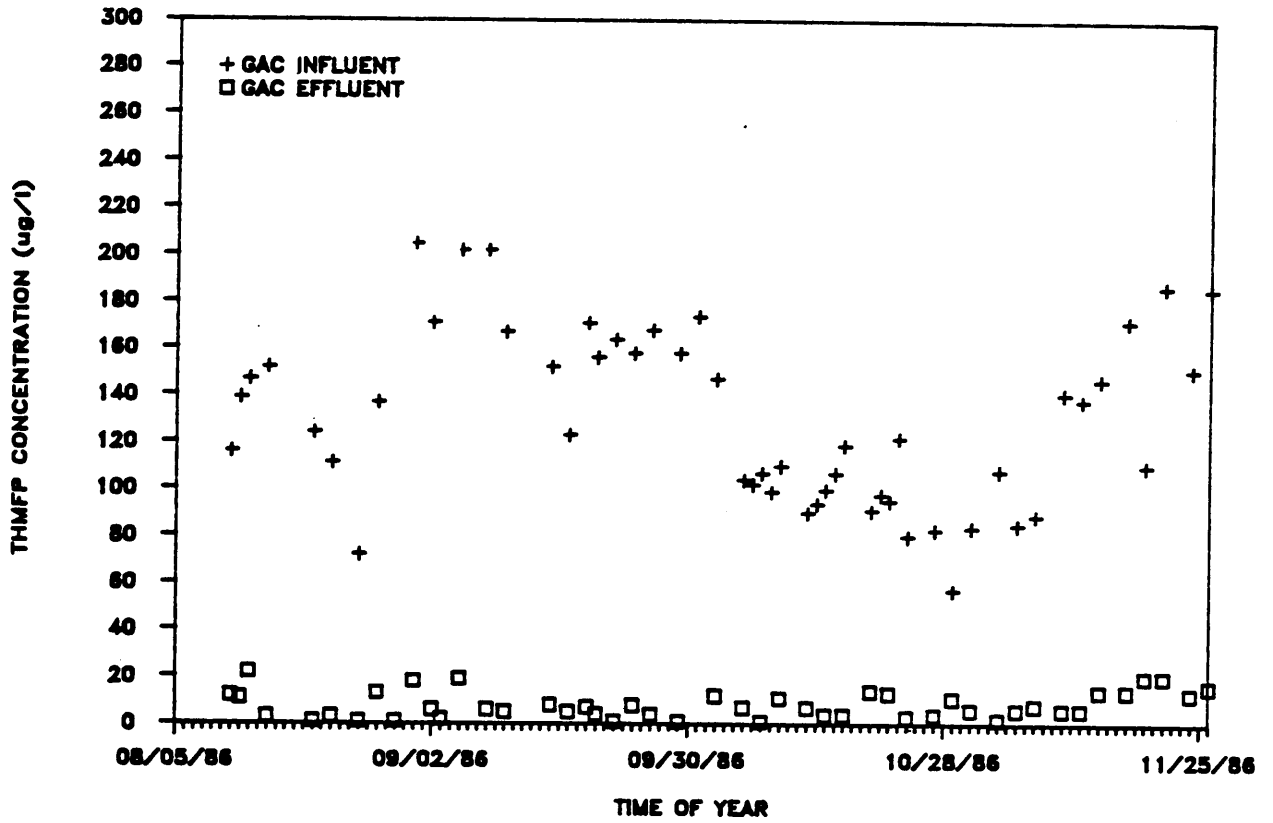


Figure 4. Variation of the THMFP Concentration in the GAC Influent and Effluent From August 5 through November 26, 1986.

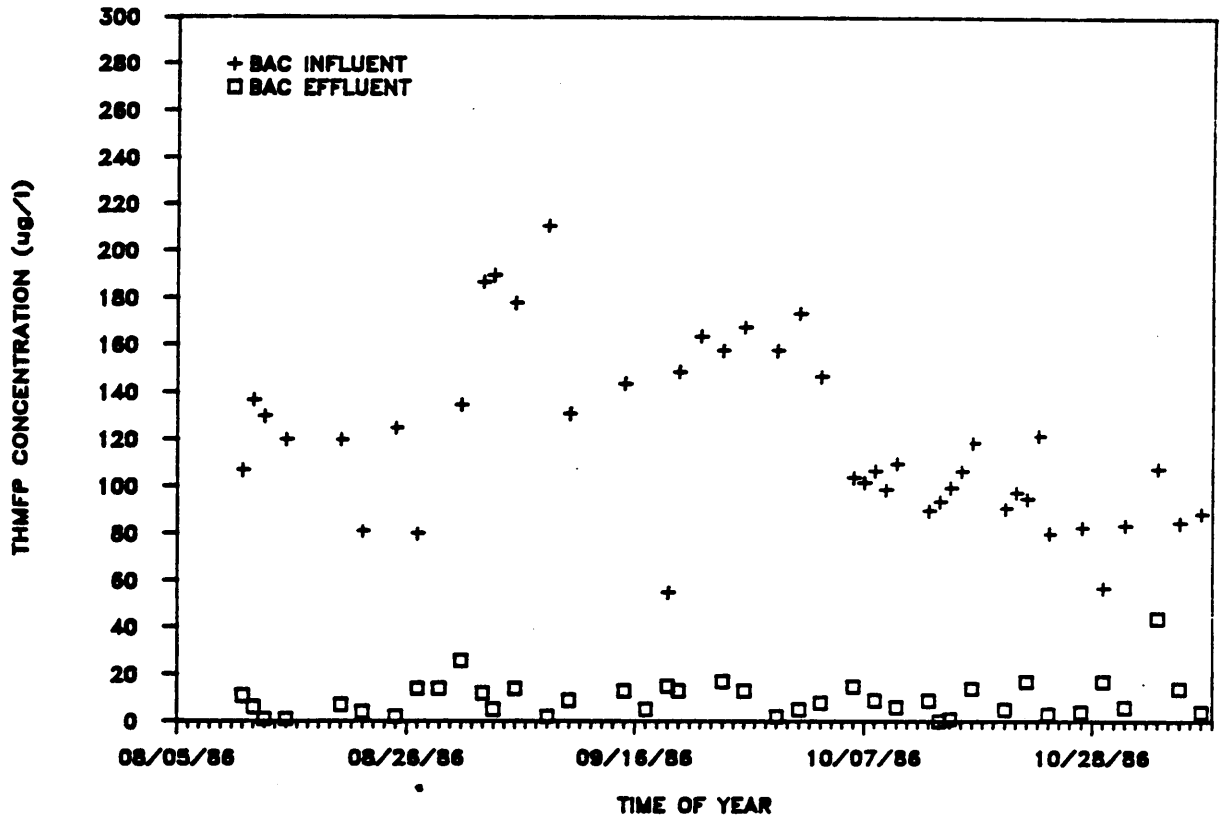


Figure 5. Variation of the THMFP Concentration in the BAC Influent and Effluent From August 5 through November 8, 1986.

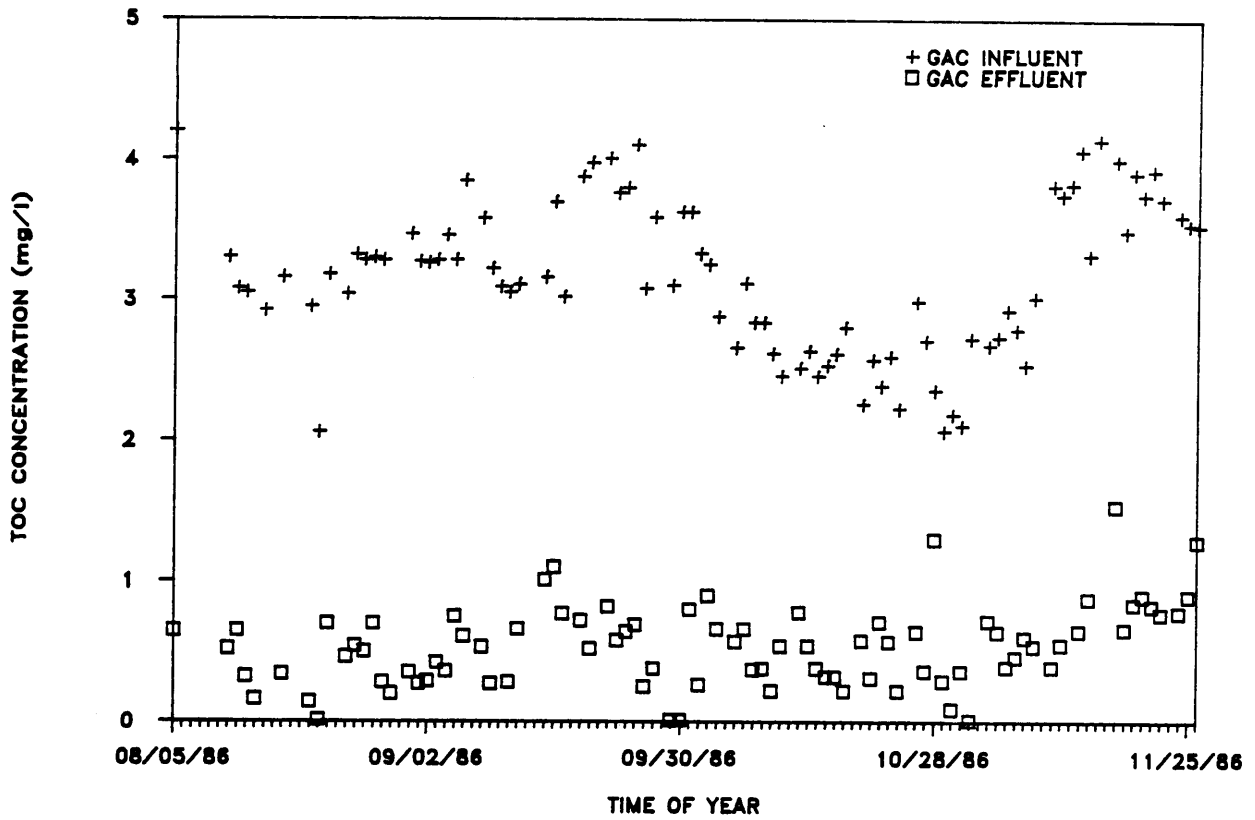


Figure 6. Variation of the TOC Concentration in the GAC Influent and Effluent From August 5 through November 26, 1986.

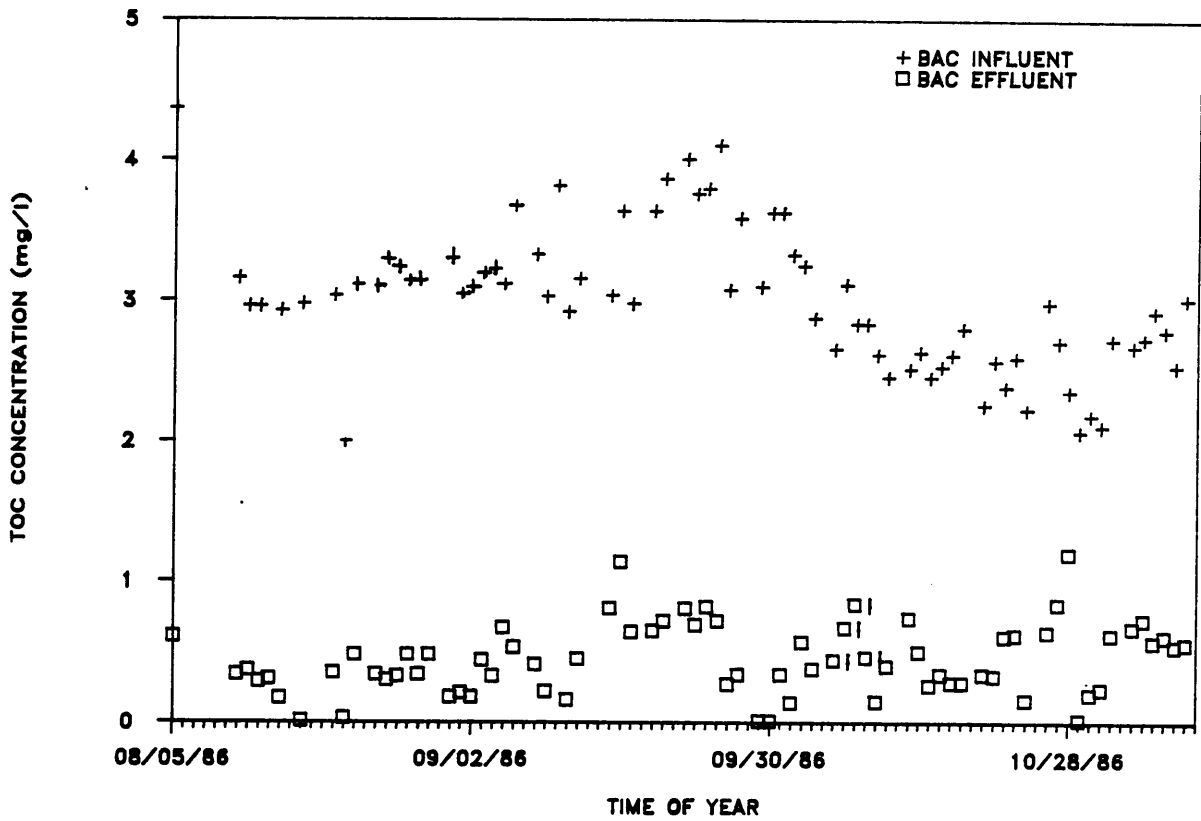


Figure 7. Variation of the TOC Concentration in the BAC Influent and Effluent From August 5 through November 8, 1986.

Table 6. Summary of the GAC and BAC Effluent Characteristics with an EBCT of 30 min and 2.7 gpm/ft² Loading (August 5, 1986 through November 26, 1986).

	GAC		BAC	
	Mean	Range	Mean	Range
THMFP (µg/L)	8	1 - 22	10	1 - 44
TOC (mg/L)	0.54	0.01 - 1.54	0.45	0.01 - 1.20
UV Absorbance (254 nm)†	0.016	0.001 - 0.134	0.037	0.001 - 0.319
Dissolved Oxygen (mg/L)	6.6	2.7 - 9.8	5.8	2.9 - 8.7
Turbidity (ntu)	0.09	0.04 - 0.40	0.18	0.05 - 2.0
Iron (mg/L)	0.017	0.000 - 0.116	0.068	0.000 - 0.491
Manganese (mg/L)	0.063	0.003 - 0.163	0.039	0.002 - 0.114
pH	5.9	5.1 - 6.7	6.0	5.5 - 6.8
Alkalinity (mg/L as CaCO ₃)	17	2 - 48	15	3 - 27
Temperature (°C)	21	8 - 30	22	15 - 30
Standard Plate Count (#/mL)	1420	200 - 10,000	3560	100 - 30,000

† UV absorbance reported as per 10 cm.

THMFP and TOC Breakthrough Within The Carbon Bed

A wavefront can be better defined when considering only pure substances that pass an adsorbent. In this study, TOC, being widely varied in chemical nature, passes as a "front" rather than as a "band" of TOC. The wavefront is not a narrow band as it moves through the carbon bed. Due to the different adsorption activities of the various TOC components the TOC concentration is dispersed throughout the bed and does not uniformly progress through the carbon bed. The THM precursors move through the bed similarly; however, their movement is not as dispersed as the TOC.

Figures 8 and 9 describe the THM precursor concentration at varying bed depths of the GAC and BAC beds during the study. The ratio, C_e/C_o , is representative of the fraction of THMFP passing through the bed (i.e. ratio of the column effluent concentration to the mean influent concentration). Different times are represented by the number of bed volumes of water that has passed through the entire column. Figure 8 shows that after 1100 bed volumes (period of 25 days) of water had passed through the GAC column little THMFP had penetrated the GAC bed. However, by the time 5,000 bed volumes (104 days) had passed, the THMFP had penetrated to a greater depth (e.g. only about 30 percent THMFP removal at the 60-in depth). In contrast, Figure 9 shows that the THMFP had not penetrated very deep into the BAC bed (e.g. 80 percent THMFP removal at the 60-in depth) even after 4,000 bed volumes (83 days) had passed through the bed.

Figures 10 and 11 represent breakthrough curves for the GAC columns from varying depths within the carbon bed. THMFP concentrations, reported as C_e/C_o (fraction passing), at depths of 20, 44, 64, and 84-in (51, 112, 163, 213 cm) (ports 2, 4, 6, and 8) are shown as they vary with increasing bed volumes. The ratio C_e/C_o normalizes the variations of the influent concentration that occurred during this study. It is apparent that the wavefront passed the ports located deeper in the carbon bed at higher bed volumes as would be expected.

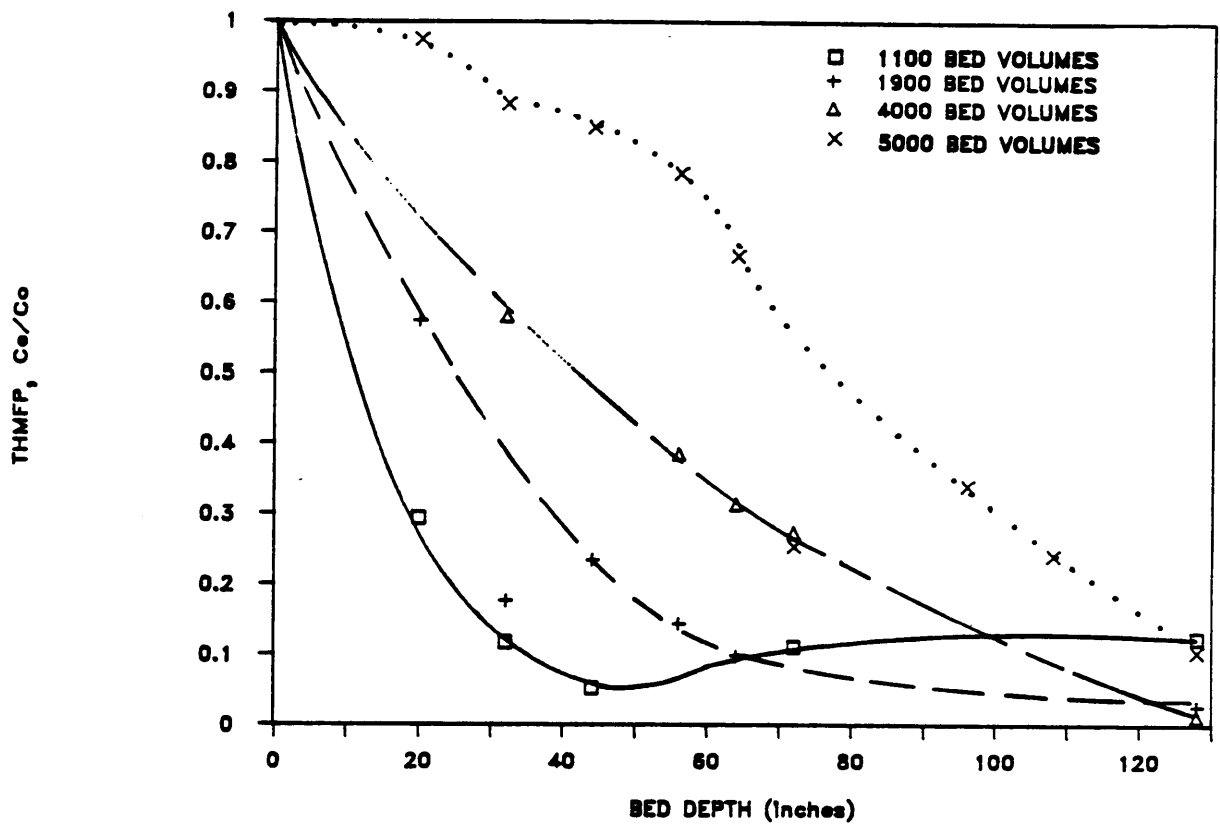


Figure 8. THM Precursor Concentrations at Varying Depths of the GAC Bed at Various Times of the Study.

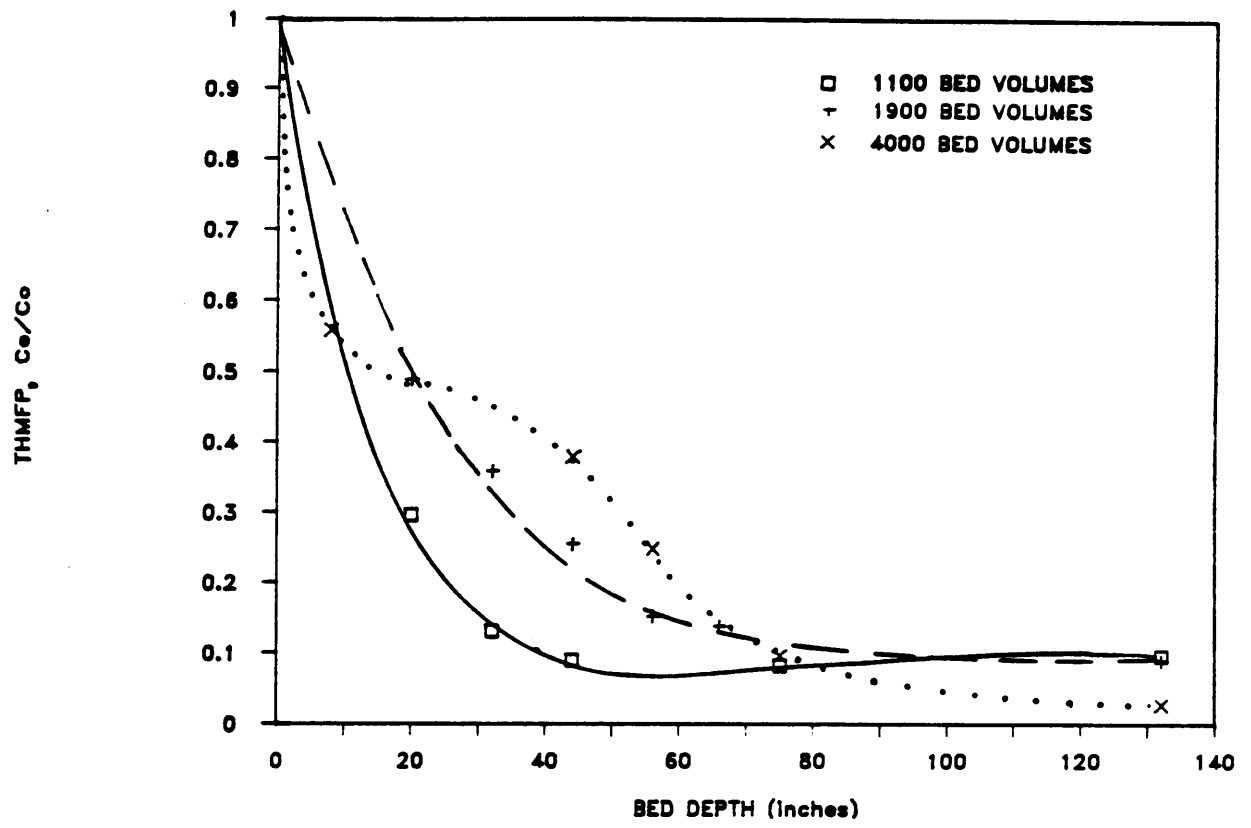


Figure 9. THM Precursor Concentrations at Varying Depths of the BAC Bed at Various Times of the Study.

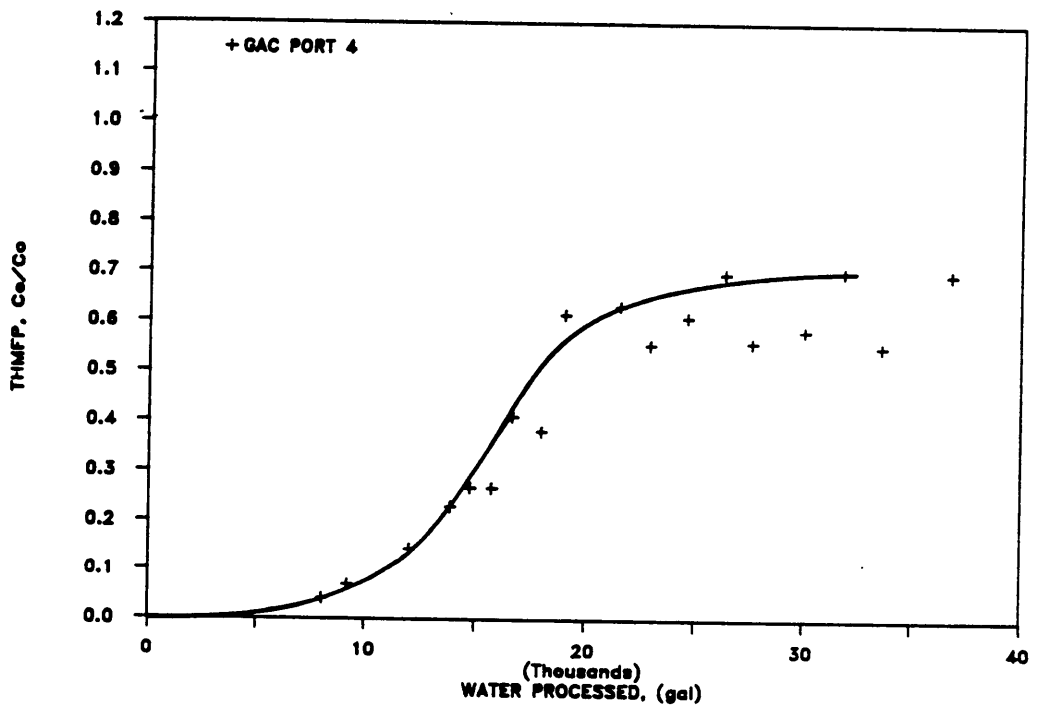
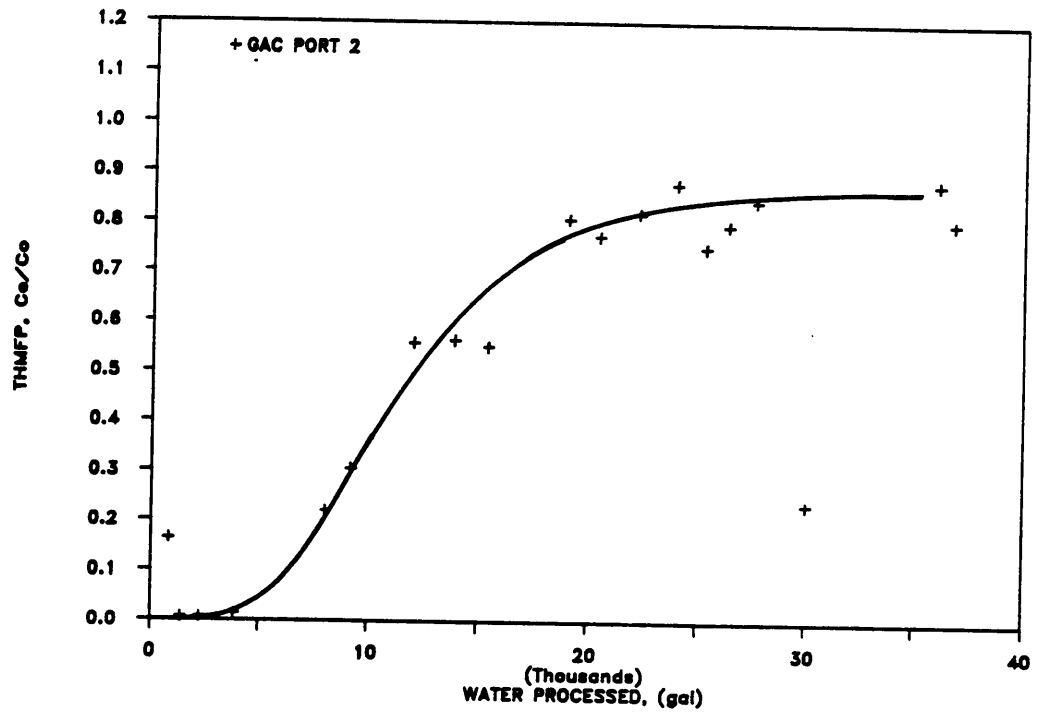


Figure 10. THMFP Breakthrough Curves in the GAC Bed at Ports 2 and 4 (20 and 44-in) During Pilot Plant Study.

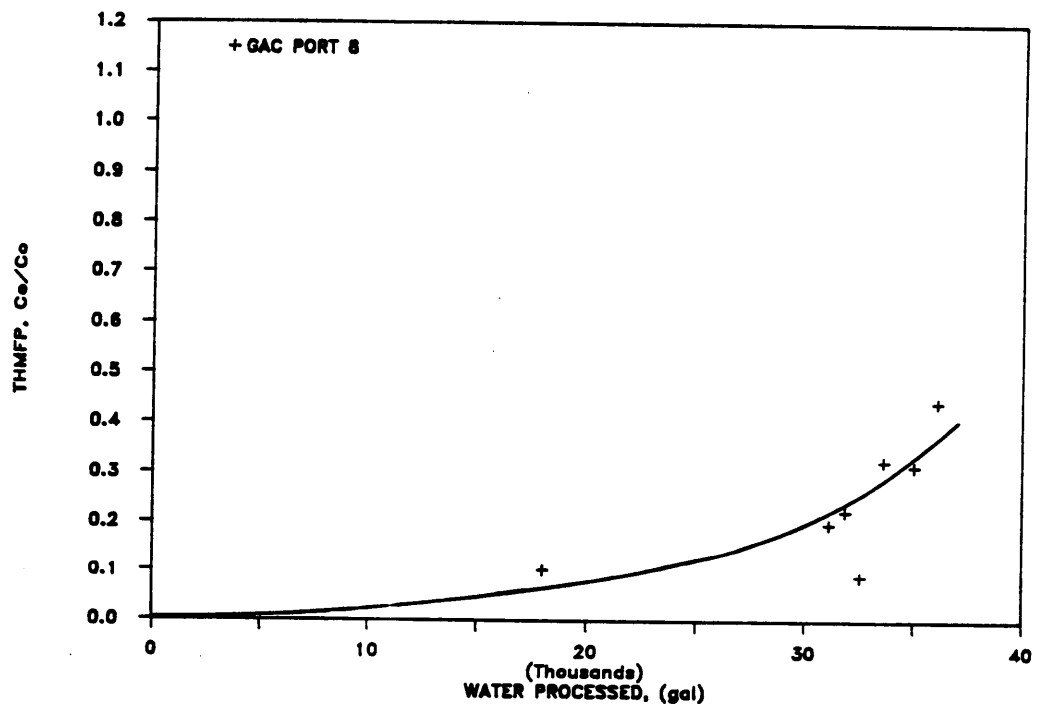
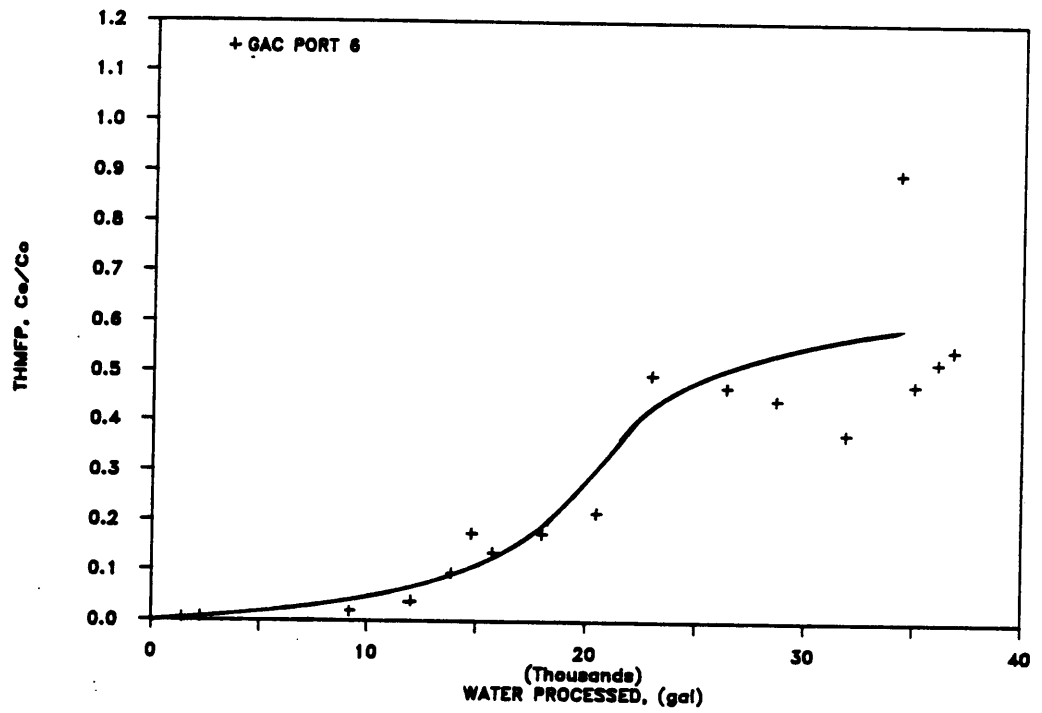


Figure 11. THMFP Breakthrough Curves in the GAC Bed at Ports 6 and 8 (64 and 84-in) During Pilot Plant Study.

Corresponding breakthrough curves for the BAC column can be found in Figures 12 and 13. These plots describe the wavefront breakthrough for ports 2, 4, and 6 which corresponds to carbon bed depths of 20, 44, and 64-in (51, 112, and 163 cm) respectively. Port 8 of the BAC column was not included because the wavefront had not progressed to that depth. It is apparent that the wavefront proceeded more slowly through the BAC bed than through the GAC bed.

Predicted THMFP Breakthrough for the GAC and BAC Effluent

System THM goals of 25 $\mu\text{g/L}$, 50 $\mu\text{g/L}$, and 75 $\mu\text{g/L}$ were chosen as the basis for analysis of the carbon columns. Using the THM/THMFP ratio of 2/3 discussed earlier, these values correspond to THMFP values of 37.5 $\mu\text{g/L}$, 75 $\mu\text{g/L}$, and 112.5 $\mu\text{g/L}$ respectively. Using the THM/THMFP ratio of 0.5, the THM values correspond to 50 $\mu\text{g/L}$, 100 $\mu\text{g/L}$, and 150 $\mu\text{g/L}$ THMFP. Table 7 shows the corresponding C_e/C_o value for each specified THM goal. Calculations used to arrive at these values can be found in Appendix H.

Predictions can be made as to when the THM precursor concentration will exceed the specified treatment goals in the effluent stream by sampling at the ports within the 11 feet of carbon bed. Assuming the entire carbon bed will adsorb THM precursors uniformly, then the number of bed volumes required for breakthrough to occur at a given port can be used to extrapolate the approximate total number of bed volumes that will pass through the entire column before the THM treatment goals are exceeded in the effluent. This number is important in sizing the columns and performing a cost analysis.

Figure 14 shows the breakthrough curves at ports 2 and 4 (bed depths of 20 and 44-in) of the GAC column. This figure is similar to Figure 10 except that the x-axis has been altered. Instead of showing the actual number of bed volumes that has passed through the entire

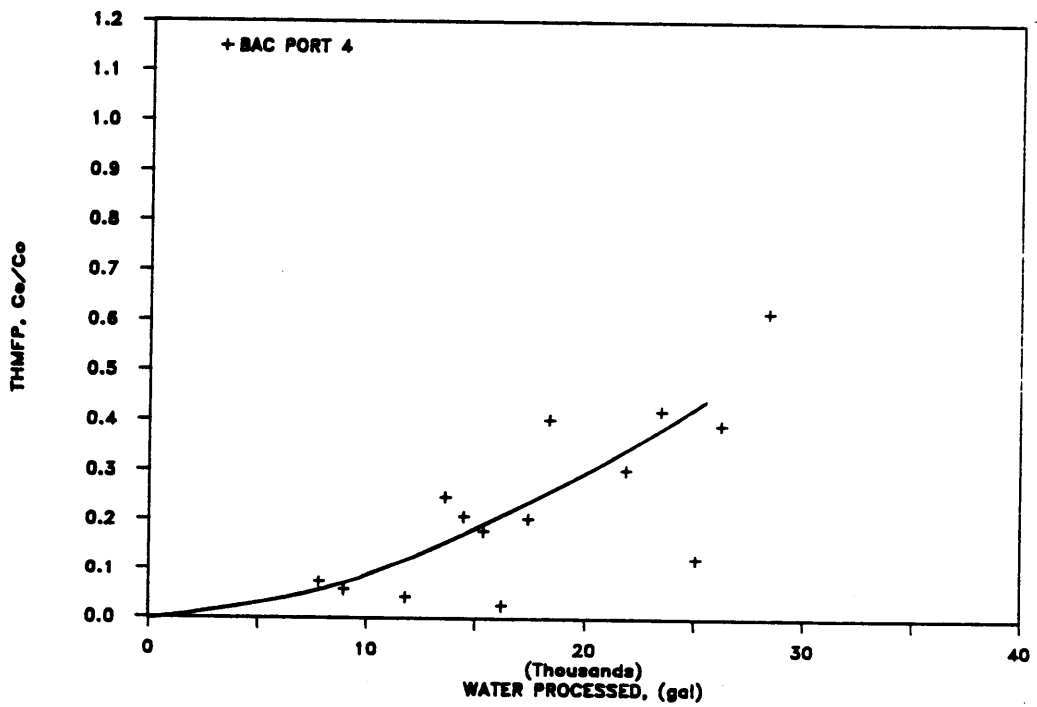
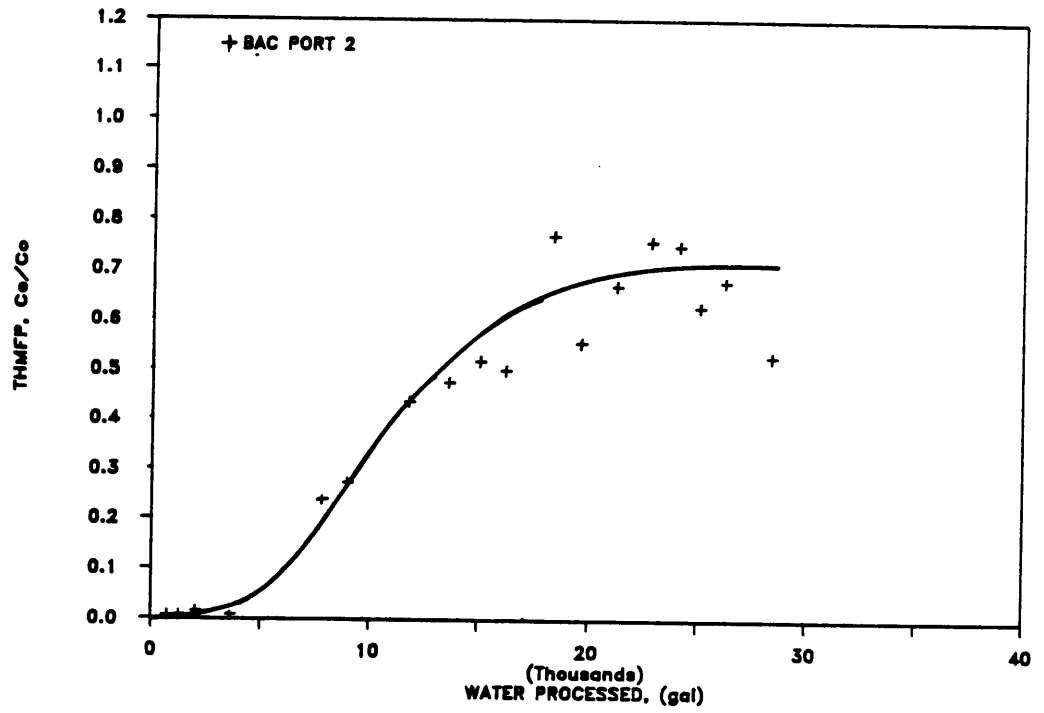


Figure 12. THMFP Breakthrough Curves in the BAC Bed at Ports 2 and 4 (20 and 44-in) During Pilot Plant Study.

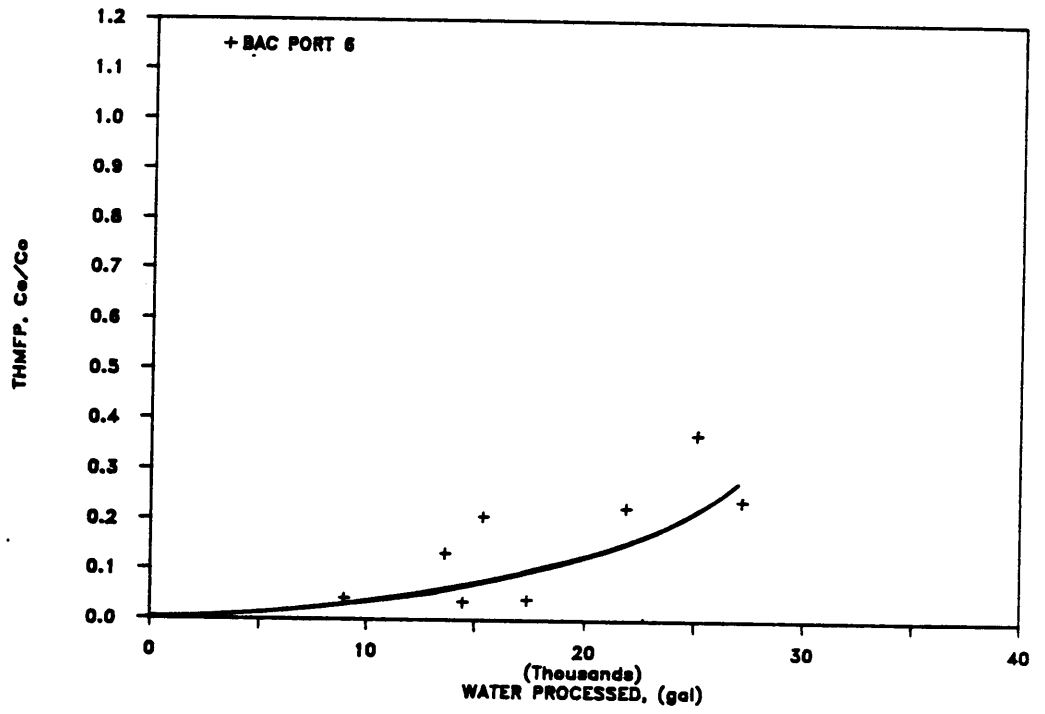


Figure 13. THMFP Breakthrough Curves in the BAC Bed at Port 6 (64-in) During Pilot Plant Study.

Table 7. THMFP and Ce/Co Ratio for Each Specified THM Treatment Goal Using 0.66 and 0.5 THM/THMFP Ratios.

		Ce/Co				
THM Treatment Goal (µg/L)	THMFP Treatment Goal (µg/L)		BAC C ₀ = 146 µg/L		GAC C ₀ = 153 µg/L	
	0.66	0.50	0.66	0.5	0.66	0.5
25	37.5	50	0.26	0.35	0.25	0.33
50	75	100	0.52	0.70	0.49	0.65
75	112.5	150	0.79	1.05	0.74	0.98

carbon bed (as does Figure 10), the x-axis of Figure 14 shows the number of bed volumes that has passed through ports 2 and 4 respectively. Notice that the range of the x-axis is different for each plot. Because the term bed volume is inversely based on the volume of carbon, more bed volumes will pass port 2 than port 4 because the volume of carbon is less above port 2. Drawing a horizontal line at the C_e/C_o value (0.25 found in Table 7) that corresponds to a system THM concentration of 25 $\mu\text{g/L}$ and a THM/THMFP ratio of 0.66 (Table 7) results in the intersection of the breakthrough curve and the C_e/C_o line. Drawing a vertical line at this intersection to the x-axis produces the number of bed volumes that this column could operate if the remaining carbon adsorbed identically to the carbon above port 2 or 4. This is the predicted bed life of the carbon bed. Ports 2 and 4 have a predicted bed life of 8,250 and 6,000 for the 25 $\mu\text{g/L}$ THM treatment goal.

Repeating this procedure at each port for each THM treatment goal in the GAC and BAC column results in relatively accurate predictions of bed life. Tables 8 and 9 summarize the number of bed volumes that the GAC and BAC column could operate before the carbon bed was exhausted for each THM/THMFP ratio (0.5 and 0.66). These values were obtained from Figures 30 - 35 and 36 - 41 in Appendices B and C.

Assuming the THM/THMFP ratio of 0.66, Table 8 shows that the THMFP wavefront had progressed through port 8 (84 inches) for the treatment goals of 25 $\mu\text{g/L}$ and 50 $\mu\text{g/L}$. For the treatment goal of 75 $\mu\text{g/L}$, the wavefront had progressed only to port 4.

Tables 8 and 9 show that assuming a THM/THMFP ratio of 0.5 the number of bed volumes passing through the carbon bed is greater than when assuming a ratio of 0.66. Thus, a longer bed life is expected when assuming the smaller ratio. It is doubtful that the 75 $\mu\text{g/L}$ THM treatment limit will ever be reached using the 0.5 ratio because the column effluent THMFP would have to reach 150 $\mu\text{g/L}$ which is the same as the influent concentration. Tables 8 and 9 indicate that a THM/THMFP ratio of 0.65 would enable the GAC column to meet the 25 $\mu\text{g/L}$ THM treatment option for 6,875 bed volumes (143 days). In addition, it can meet the 50 $\mu\text{g/L}$

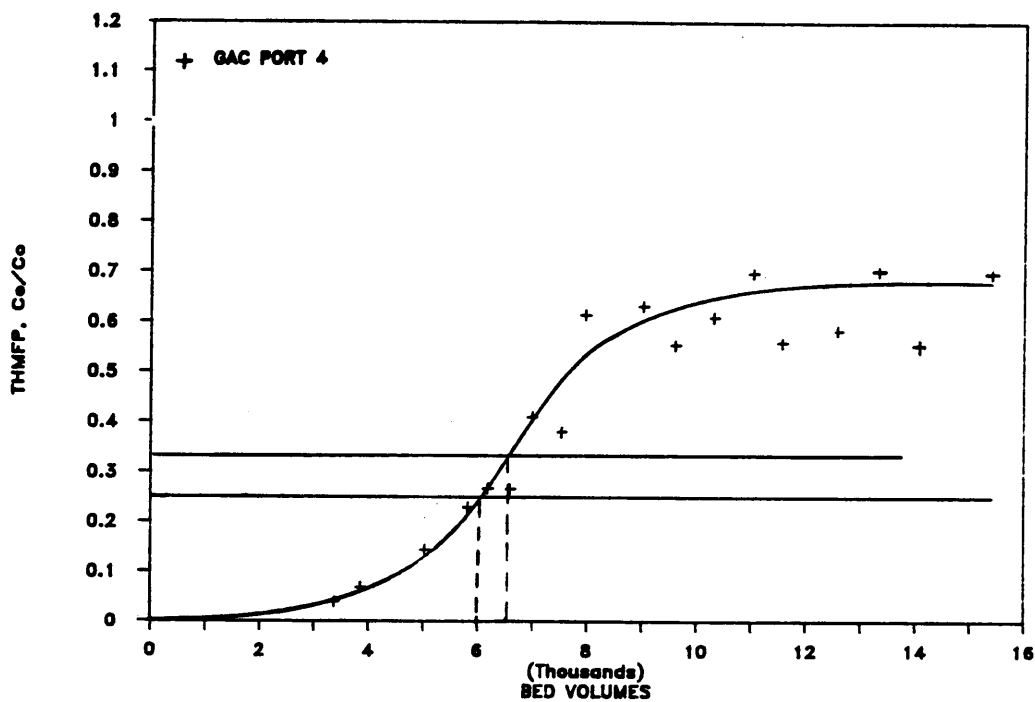
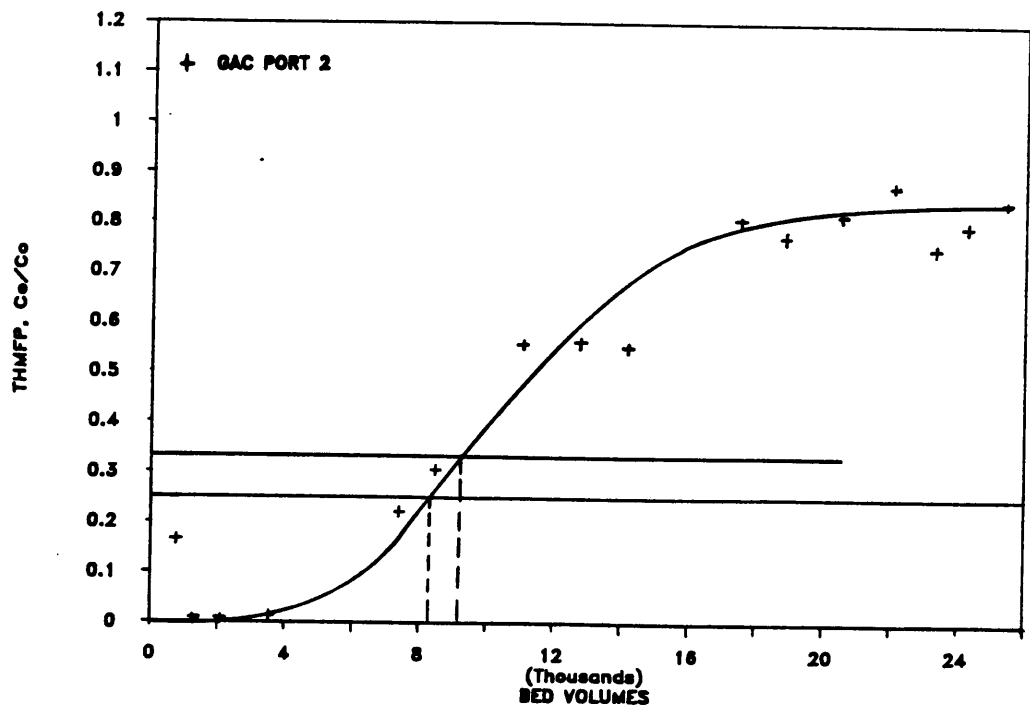


Figure 14. THMFP Breakthrough Curves for GAC Ports 2 and 4 as a Function of the Bed Volume Throughput for Carbon Above Ports 2 and 4 Respectively.

Table 8. Bed Volumes Passed through the GAC Bed as Predicted by THMFP Collected at Various Ports Within the Carbon Bed Using 0.66 and 0.5 as THM/THMFP Ratios (EBCT of 30 min and 2.7 gpm/ft² Loading).

		Predicted Bed Volume Throughput of the GAC Bed For Each THM Treatment Goal					
Port #	Depth (in)	THM/THMFP = 0.66			THM/THMFP = 0.5		
		25 µg/L	50 µg/L	75 µg/L	25 µg/L	50 µg/L	75 µg/L
2	20	8,250	11,500	14,500	9,000	13,000	----
4	44	6,000	7,500	13,000	6,500	10,750	----
6	64	5,750	7,500	----	6,250	10,500	----
8	84	7,500	8,200	----	8,000	----	----
10	108	----	----	----	----	----	----
Average		6,875	8,675	13,750	7,450	11,400	----

— THMFP concentration had not reached specified limit at these ports.

Table 9. Bed Volumes Passed through the BAC Bed as Predicted by THMFP Collected at Various Ports Within the Carbon Bed Using 0.66 and 0.5 as THM/THMFP Ratios (EBCT of 30 min and 2.7 gpm/ft² Loading).

		Predicted Bed Volume Throughput of the BAC Bed For Each THM Treatment Goal					
Port #	Depth (in)	THM/THMFP = 0.66			THM/THMFP = 0.5		
		25 µg/L	50 µg/L	75 µg/L	25 µg/L	50 µg/L	75 µg/L
2	20	8,000	12,000	19,000	9,500	16,000	----
4	44	7,800	10,500	----	8,800	12,000	----
6	64	6,800	----	----	7,250	----	----
8	84	----	----	----	----	----	----
10	108	----	----	----	----	----	----
Average		7,500	11,250	----	8,500	14,000	----

---- THMFP concentration had not reached specified limit at these ports.

and 75 µg/L THM option for 8,675 and 13,750 bed volumes (188 and 270 days) respectively. Assuming a THM/THMFP ratio of 0.5, the GAC column can meet the 25 µg/L and 50 µg/L THM treatment options for 7,450 and 11,400 bed volumes (155 and 237 days) respectively.

The predicted breakthrough of THM precursors in the BAC effluent can be found from Figures 36 - 41 of Appendix C. These show that the THMFP wavefront had passed port 6 for the THM treatment goal of 25 µg/L and port 4 for the treatment goal of 50 µg/L. However for the THM treatment goal of 75 µg/L, the wavefront had only passed port 2.

Assuming a THM/THMFP ratio of 0.66, the BAC column can meet the THM treatment goals of 25 µg/L and 50 µg/L for approximately 7,500 and 11,250 bed volumes (156 and 234 days) respectively. Column operation was suspended before breakthrough of 75 µg/L occurred. Analyzing the BAC column assuming a THM/THMFP ratio of 0.5, the expected carbon bed life at THM treatment goals of 25 and 50 µg/L was 8,500 and 14,000 bed volumes (177 and 292 days) respectively. Unless the influent THMFP concentration increased, the 75 µg/L THM treatment limit will probably not be reached.

GAC Requirements For Meeting Different Treatment Goals

Determining the GAC requirements to meet a specified THM treatment goal required additional analysis which involved calculating the specific THMFP removal of the carbon. Figure 15 shows the specific THMFP removal as a function of the number of bed volumes required to surpass a specified THM treatment goal. The specific THMFP removal for a particular port is found by finding the intersection of the curve in Figure 15 and a vertical line from the x-axis. The vertical line corresponds to the predicted number of bed volumes that would surpass a specified treatment goal. These predicted bed volumes are obtained from Tables 8 and 9. For example, data from GAC port 2 predicted a total carbon bed life of 8,250

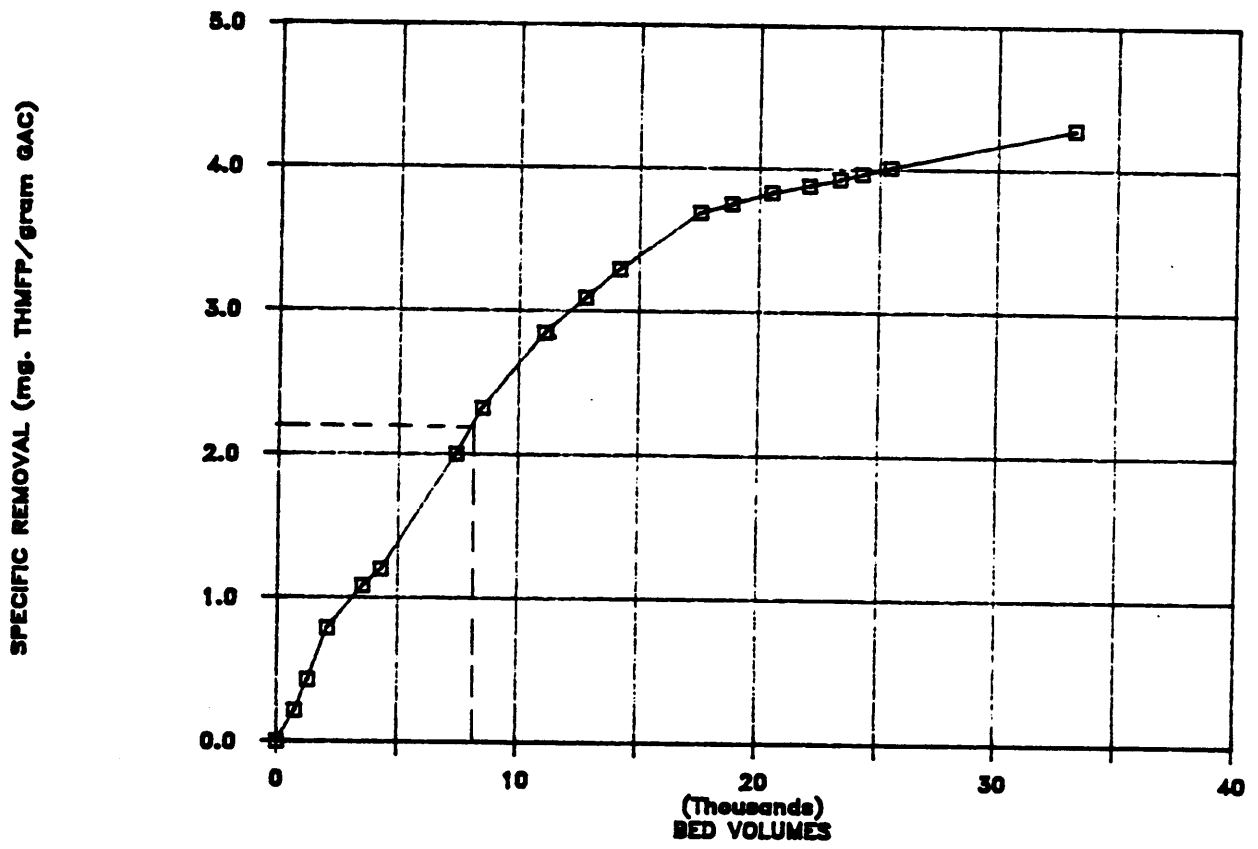


Figure 15. Specific THMFP Removal Measured at GAC Port 2.

bed volumes to meet the 25 µg/L THM treatment goal using a THM/THMFP ratio of 0.66 (Table 8). A vertical line drawn at 8,250 bed volumes on Figure 15 intersects the curve at a specific removal of 2.2 mg THMFP/g GAC. THMFP data from GAC ports 4, 6, and 8 (Table 8) predicted a carbon bed life of 6000, 5750, and 7500 bed volumes to meet the 25 µg/L THM treatment goal. Referring to Figures 16, 17, and 18 (GAC ports 2, 4, and 6) the specific THMFP removals for each of the respective predicted bed volumes are 1.3, 1.8, and 2.0 mg THMFP/gram GAC. Averaging all four specific removals results in an average specific removal of 1.8 mg THMFP/g GAC. Assuming the average THMFP concentration in the influent is 150 µg/L, the amount of GAC that would be required to meet the 25 µg/L THM treatment goal would be 83 mg GAC/L of water treated (0.70 lb GAC/1000 gal). Sample calculations for determining the GAC requirement for the GAC and BAC processes can be found in Appendix I.

Similarly, the GAC requirements for the BAC column can be found from Figures 19, 20, and 21 which represent BAC ports 2, 4, and 6. Also, the amount of carbon needed to meet the other THM treatment goals at THM/THMFP ratios of 0.66 and 0.5 can be found by applying this method. Tables 10 and 11 summarize all of the GAC requirements for meeting each THM treatment goal. As noted in these tables, the amount of carbon to meet the 25 µg/L THM treatment goal is considerably higher than that needed to meet the 50 µg/L and the 75 µg/L treatment goal. The BAC requires less carbon to achieve the same level of treatment and a longer bed life. This method shows again that the BAC column is superior to the GAC column in terms of THM precursor removal.

TOC Breakthrough Curves for the GAC and BAC Columns

The TOC breakthrough curves for both the GAC and BAC columns can be found in Appendix D. These plots are included to give the reader an idea of how well the GAC and BAC also adsorb TOC. By comparing the TOC and the THMFP breakthrough curves taken from each

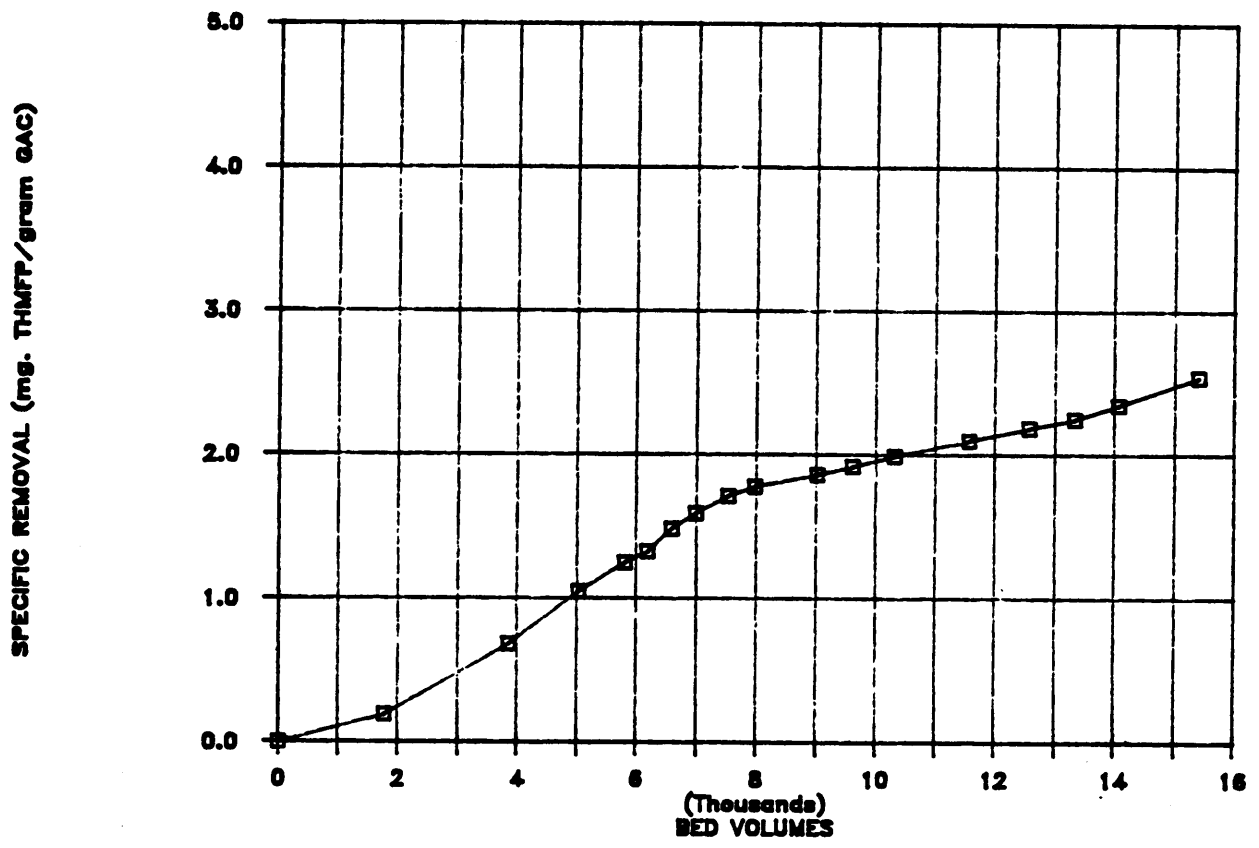


Figure 16. Specific THMFP Removal Measured at GAC Port 4.

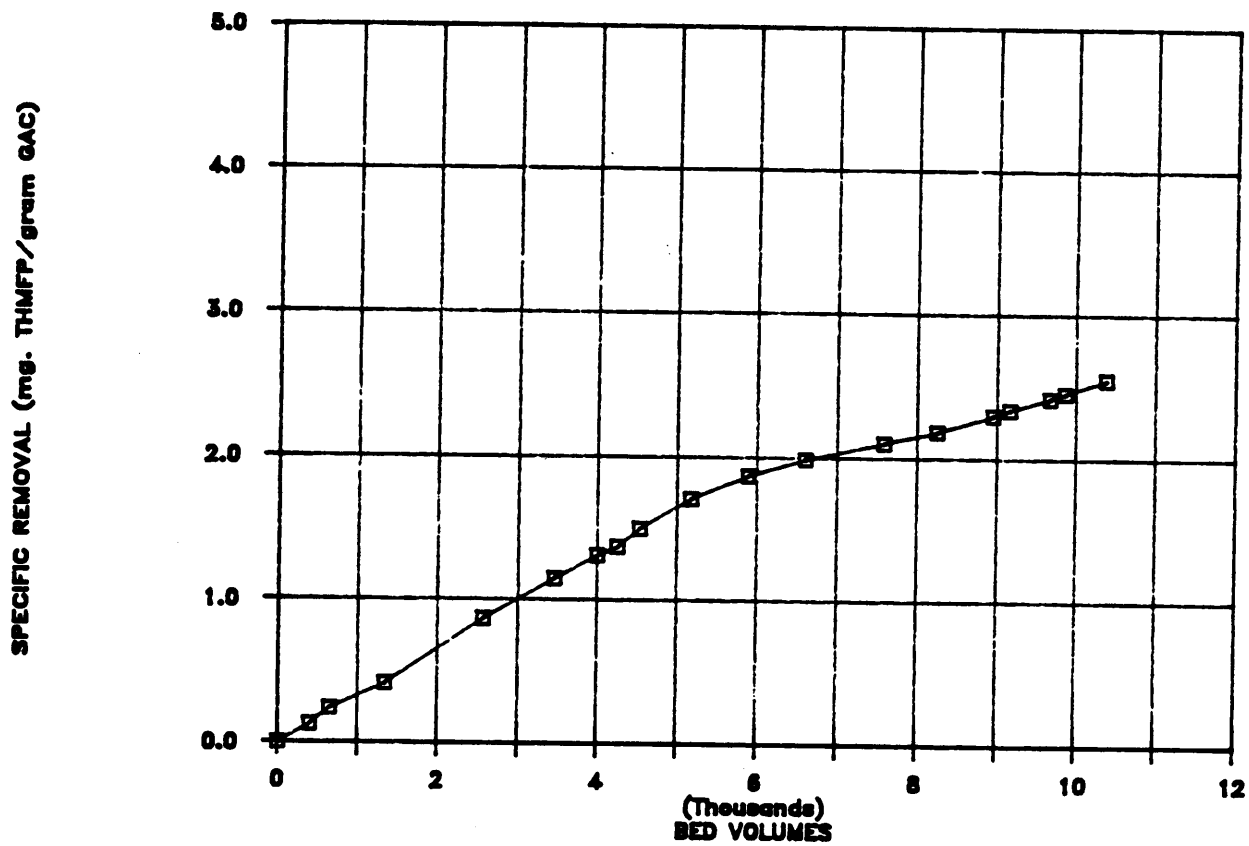


Figure 17. Specific THMFP Removal Measured at GAC Port 6.

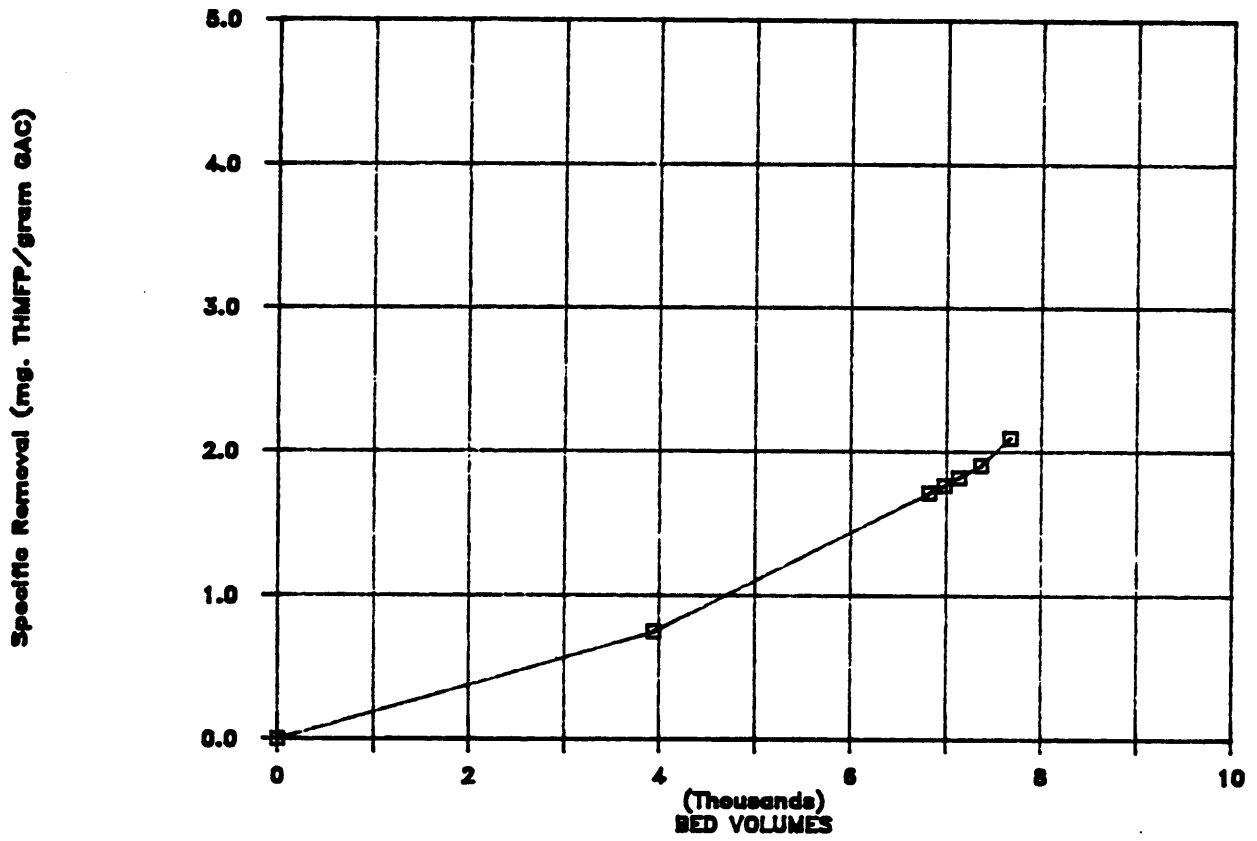


Figure 18. Specific THMFP Removal Measured at GAC Port 8.

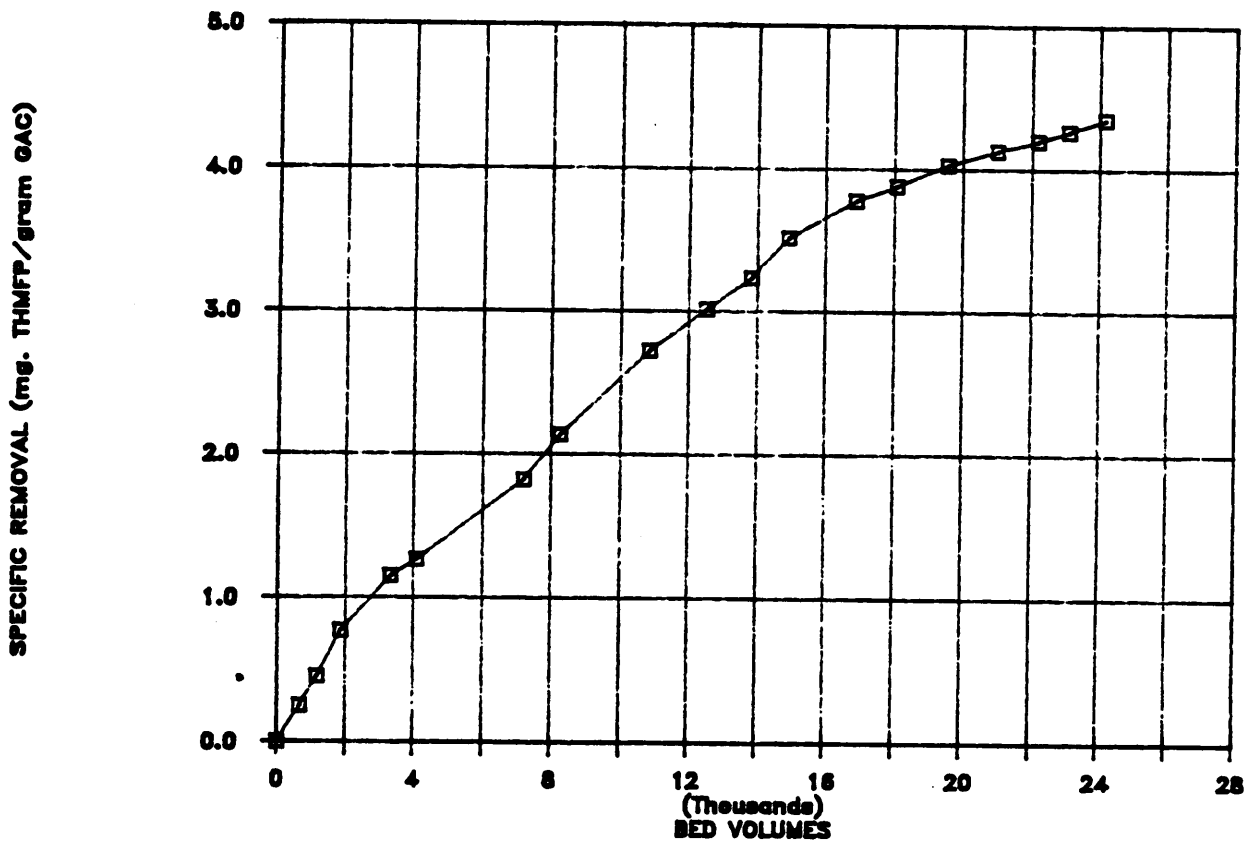


Figure 19. Specific THMFP Removal Measured at BAC Port 2.

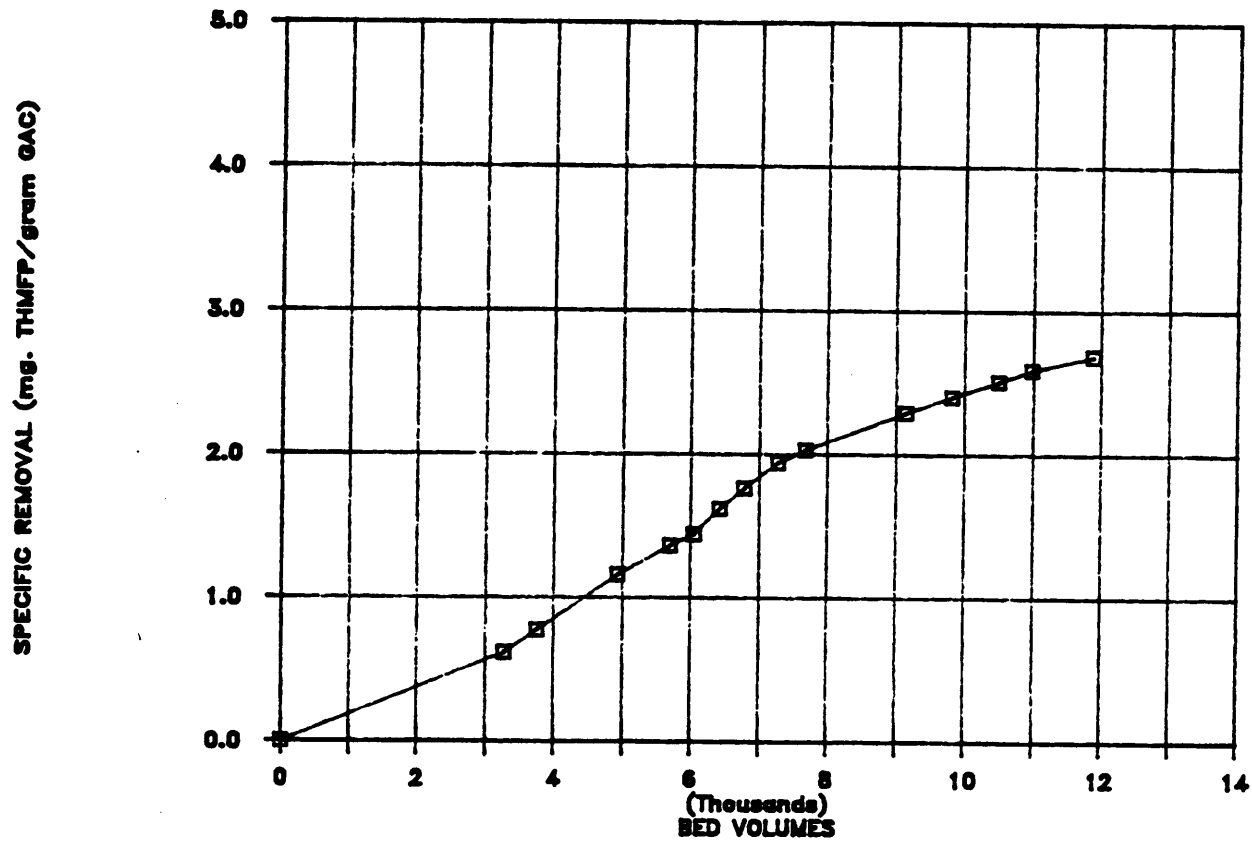


Figure 20. Specific THMFP Removal Measured at BAC Port 4.

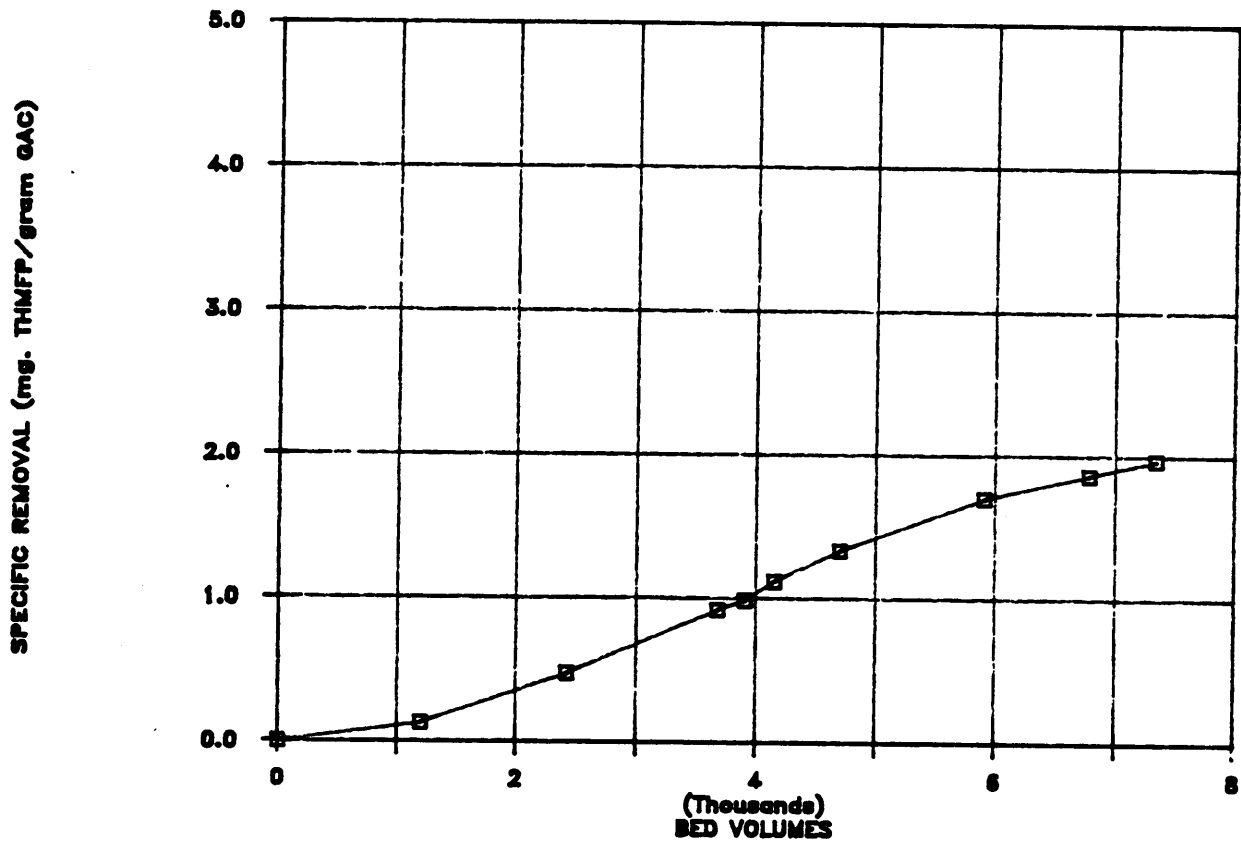


Figure 21. Specific THMFP Removal Measured at BAC Port 6.

Table 10. FILTRASORB 400 Requirements in the BAC and GAC Columns to Meet the Specified THM Treatment Goals Using the THM/THMFP Ratio of 0.66 (EBCT of 30 min and 2.7 gpm/ft²).

THM Treatment Goal (µg/L)	Port #	Predicted Bed Volumes To Meet THM Treatment Goal		Specific Removal		Carbon Requirements	
		BAC	GAC	mg THMFP/gram BAC	GAC	BAC	lb/1000 gal (mg/L) GAC
25	2	8,000	8,250	2.1	2.2		
	4	7,800	6,000	2.1	1.3		
	6	6,800	5,750	1.9	1.8		
	8	-----	7,500	---	2.0		
				$\bar{X} = 2.0$		$\bar{X} = 1.8$	0.62 (75)
50	2	12,000	11,500	2.9	2.9		
	4	10,500	7,500	2.5	1.7		
	6	-----	7,500	---	2.1		
	8	-----	8,200	---	2.2		
				$\bar{X} = 2.7$		$\bar{X} = 2.2$	0.46 (56)
75	2	19,000	14,500	4.0	3.3		
	4	-----	13,000	---	2.2		
	6	-----	-----	---	---		
	8	-----	-----	---	---		
						$\bar{X} = 2.75$	0.46 (55)

Table 11. FILTRASORB 400 Requirements in the BAC and GAC Columns to Meet the Specified THM Treatment Goals Using the THM/THMFP Ratio of 0.5 (EBCT of 30 min and 2.7 gpm/ft³).

THM Treatment Goal (µg/L)	Port #	Predicted Bed Volumes To Meet THM Treatment Goal		Specific Removal		Carbon Requirements	
		BAC	GAC	mg THMFP/gram BAC	gram GAC	BAC lb/1000 gal	GAC (mg/L)
25	2	9,500	9,000	2.4	2.5		
	4	8,800	6,500	2.2	1.4		
	6	7,250	6,250	1.9	1.9		
	8	-----	8,000	-----	2.2		
					$\bar{x} = 2.2$	$\bar{x} = 2.0$	0.57 (68)
50	2	16,000	13,000	3.6	3.1		
	4	12,000	10,750	2.7	2.8		
	6	-----	10,500	-----	2.8		
	8	-----	-----	-----	-----		
					$\bar{x} = 3.2$	$\bar{x} = 2.9$	0.40 (48)

respective port, one notices that the fraction of TOC adsorbed onto the carbon is less than that of the THMFP.

THM Precursor Adsorption Onto Carbon

It is apparent that the fraction of TOC that is passing through the carbon bed is higher than that of the THMFP. Thus a larger fraction of the TOC is composed of nonadsorbable components. To evaluate the selectivity of the carbon for THM precursors and the effectiveness of TOC as a predictor of THMFP breakthrough, plots were made of the ratio THMFP/TOC versus time. Variations in the THMFP/TOC ratio indicate whether the THM precursors vary in their adsorption characteristics. Low column effluent THMFP/TOC values would indicate that the majority of the THM precursors were part of the adsorbable TOC fraction. Larger values of the ratio would indicate that THM precursors comprise a greater percentage of the non-adsorbable fraction of TOC. Figure 22 shows the THMFP/TOC ratio of the raw water over the study period. As can be seen, the values ranged between 40 and 70.

Figures 23 and 24 show the THMFP/TOC ratio in the GAC influent, GAC effluent, and GAC port 6 and Figure 25 shows the ratio in the BAC influent and effluent. Figures 23 and 25 show that there is a large amount of fluctuation for the ratio in the GAC and BAC effluent. However, the majority of the data is below 25 $\mu\text{g}/\text{mg}$ which indicates that a relatively large portion of the THM precursors are adsorbable. Figures 23 and 25 show that the GAC and BAC influent ratio fluctuated early in the study but remained fairly constant afterwards at approximately 40 $\mu\text{g}/\text{mg}$. Thus, the BAC and GAC columns reduced the THMFP/TOC ratio by one-half. The THMFP/TOC ratio at port 6 (Figure 24) of the GAC column steadily increased over time from 10 $\mu\text{g}/\text{mg}$ to 35 $\mu\text{g}/\text{mg}$. This increase is very similar to the breakthrough curve shown in the analysis of the activated carbon columns. A similar increase was not observed in the BAC column at port 6.

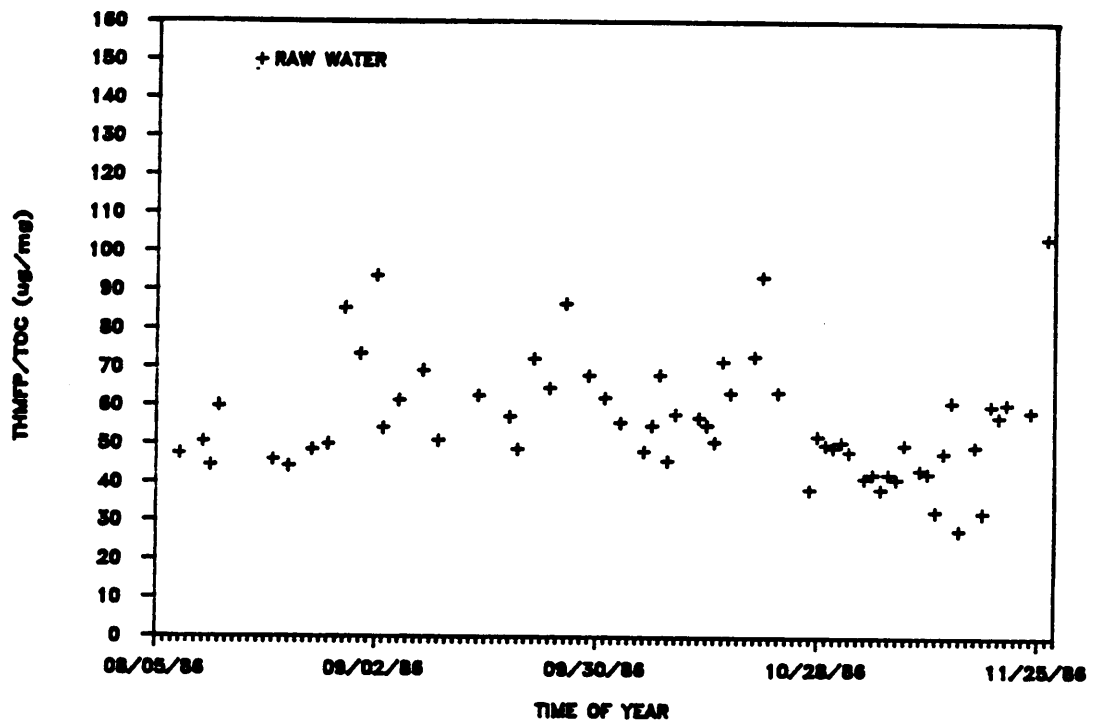


Figure 22. Raw Water THMFP/TOC Ratio in Harwood's Mill Reservoir.

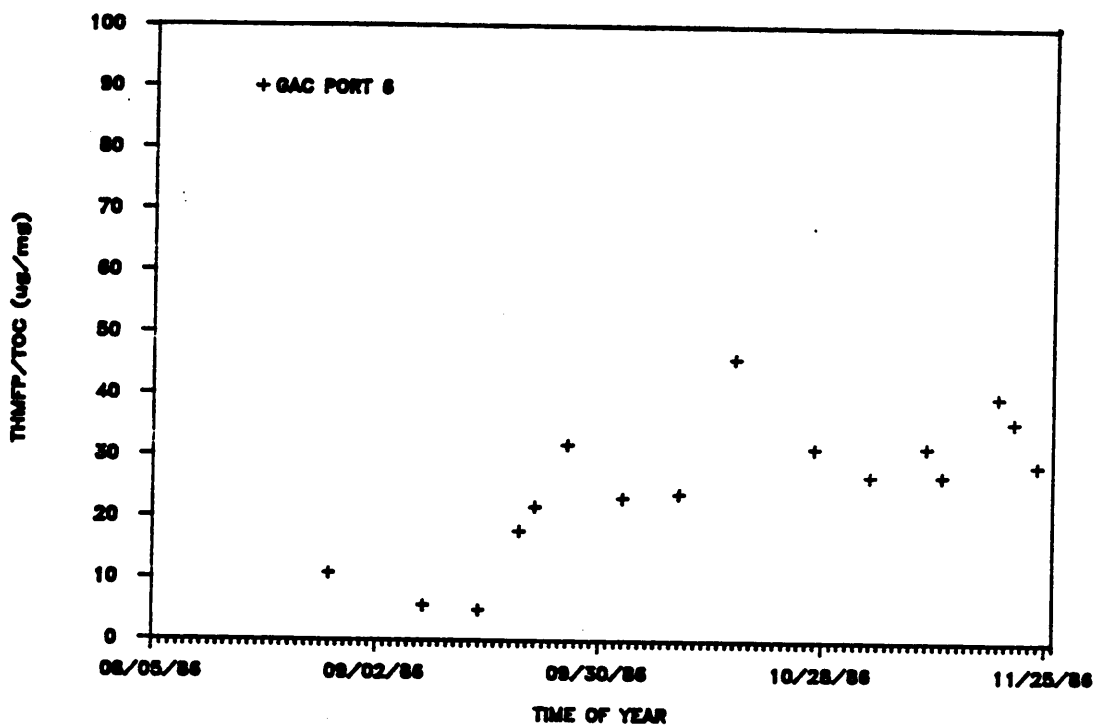


Figure 24. THMFP/TOC Ratio in Port 6 of the GAC Column.

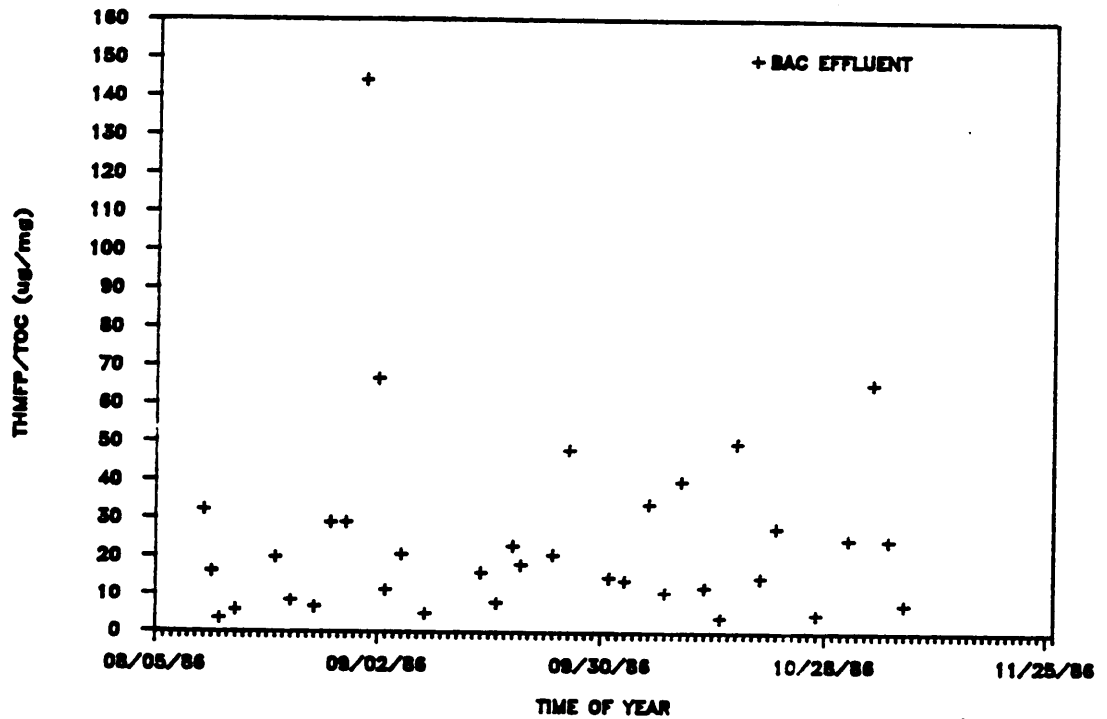
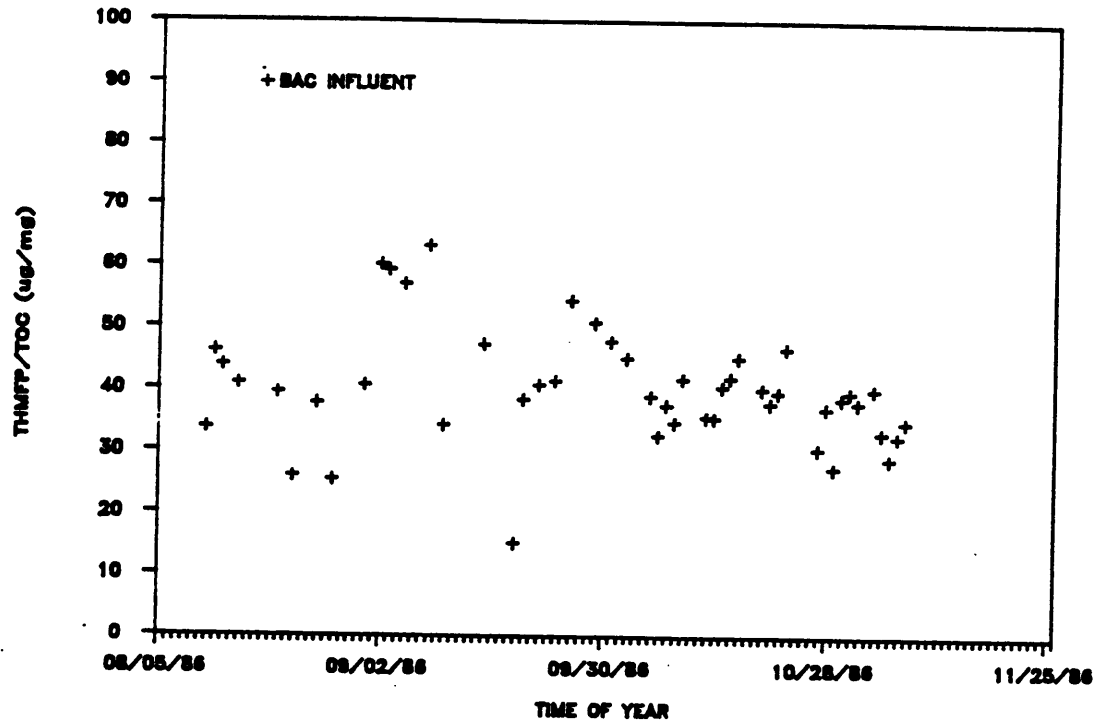


Figure 25. THMFP/TOC Ratio in the BAC Influent and Effluent.

Biological Growth in the Activated Carbon Columns

Tables 22 - 24 in Appendix A show that the standard plate count (SPC) indicated significant growth was present on the BAC columns in late August and September, 1986. The SPC decreased dramatically from roughly 6000 colonies/mL to 1000 colonies/mL approximately the same time PAC was started in the pulsator. These lower values continued until the end of the testing period. Generally the BAC effluent had higher SPC values than the GAC effluent.

Figure 26 provides indirect evidence that biological growth in the BAC columns was slightly greater than in the GAC columns. The cumulative dissolved oxygen uptake in the BAC column was somewhat greater than in the GAC columns, thus indicating indirectly that a higher degree of biological growth was present in the BAC.

Inorganic Removal by Activated Carbon

Although activated carbon is designed primarily to remove organic material, Tables 22- 24 in Appendix A indicate that manganese and iron were also removed in the BAC and GAC process trains with the BAC generally achieving greater removal than the GAC. Manganese and iron concentrations in the effluent were many times reduced to negligible levels.

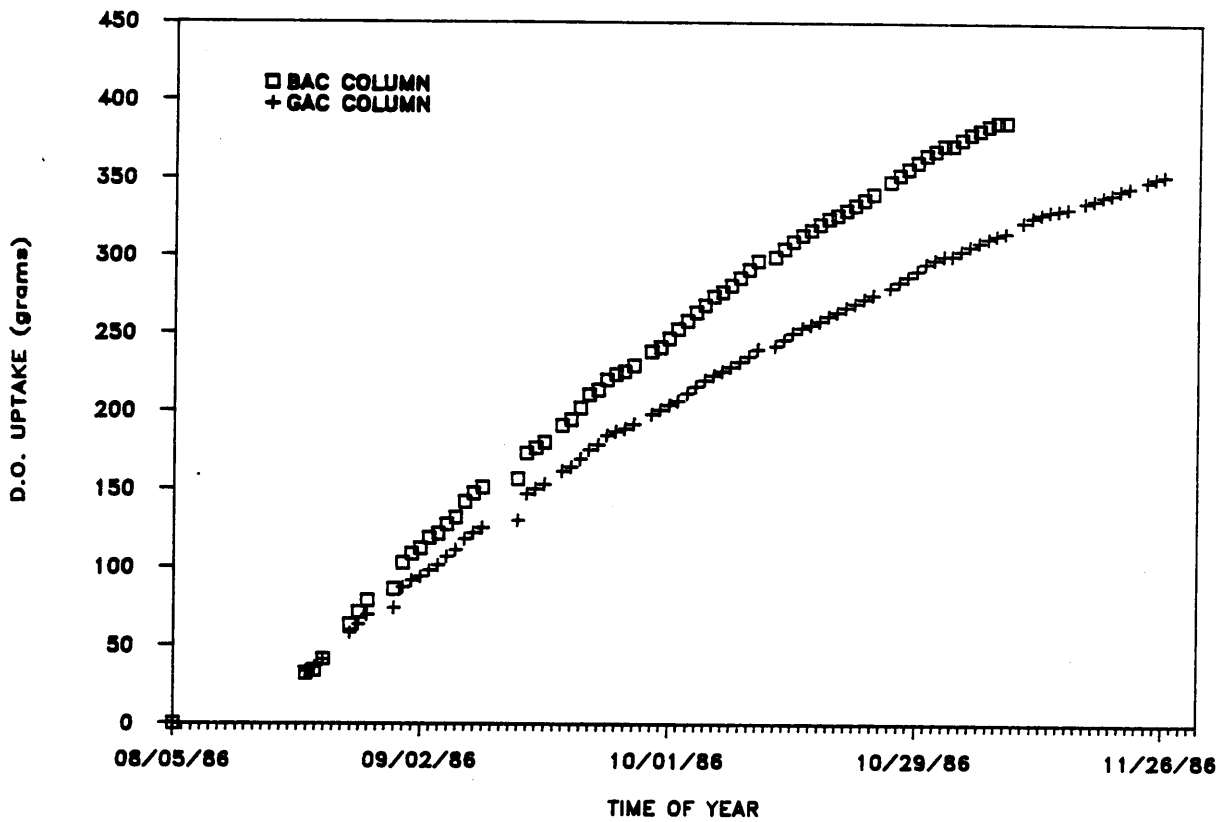


Figure 26. Cumulative Dissolved Oxygen Uptake in the BAC and GAC Column, August 5 Through November 26, 1986 (EBCT of 30 min and 2.7 gpm/ft² Loading).

PAC TREATMENT

Two types of PAC were used in this study. AQUA NUCHAR (PAC1) carbon was used during the months of June and July and NUCHAR SA (PAC2) was used in the month of October with the latter being regarded as the superior carbon.

Variation in Raw Water THMFP and TOC Values

Figure 27 depicts the variations in the raw water and clarifier effluent THMFP concentrations during the study. As can be seen, the day to day variation was often extreme with large increases usually occurring after heavy precipitation. The clarifier effluent THMFP concentration remained fairly constant except during parts of July and October when it was considerably lower (approximately 100 µg/L rather than 150 µg/L). This corresponded to periods of PAC addition to the Superpulsator®. Immediately after PAC addition was halted (July 28 and November 8, 1986), the clarifier effluent levels increased.

During early portions of the NUCHAR SA study in October, the PAC feed unit was not working properly resulting in a lower dose (16 mg/L) than desired. After this unit was repaired, a NUCHAR SA dose of 21 mg/L was provided to the Superpulsator®. Even though the dose was increased by 40 percent, the THMFP removal did not increase significantly.

Figure 28 indicates that the raw water and clarifier effluent TOC concentrations did not vary quite as much as the THMFP. The raw water concentration varied between 5 and 7 mg/L. The clarifier effluent TOC concentration was similar to the THMFP concentration in that lower concentrations occurred when PAC was added to the Superpulsator®.

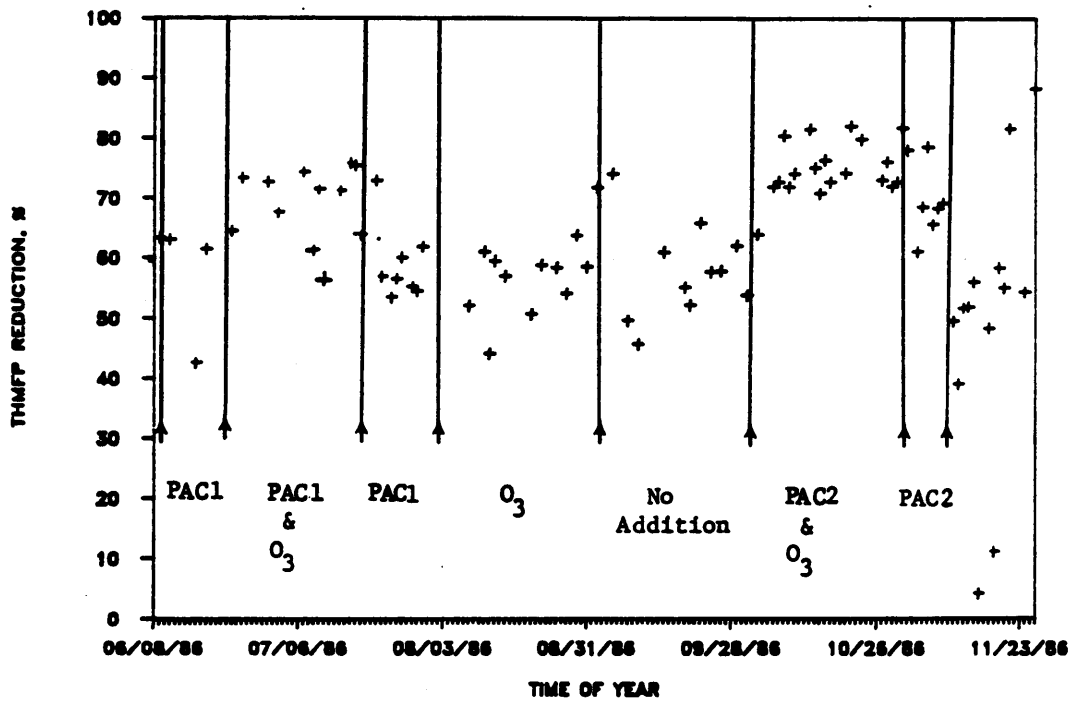
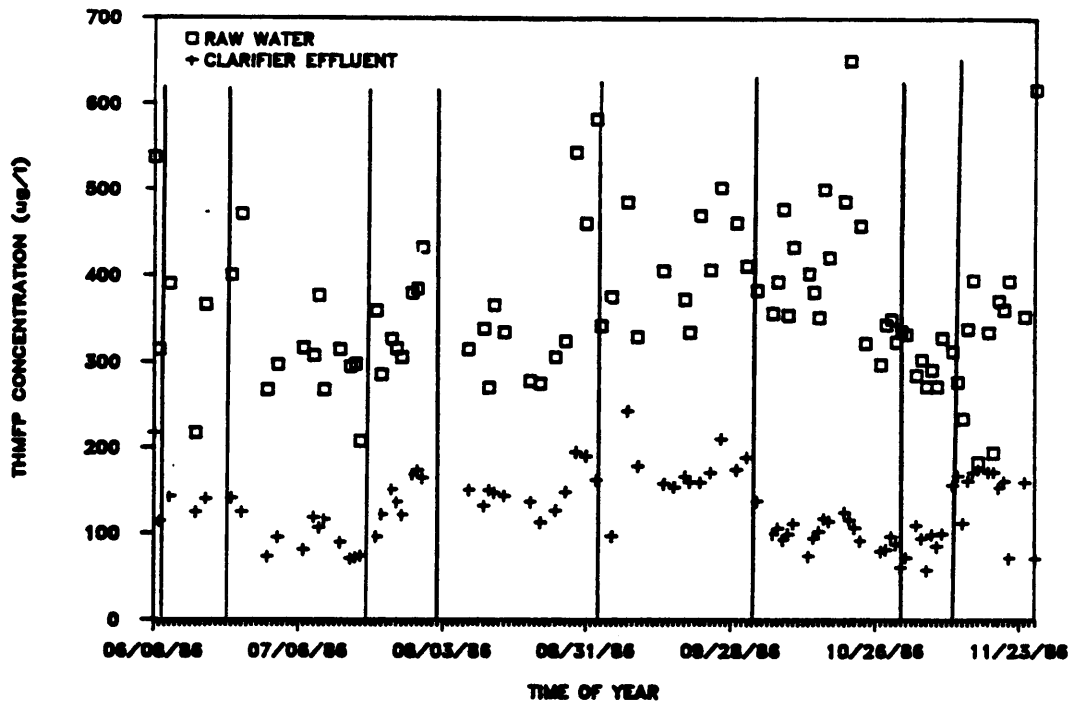


Figure 27. THMFP Concentrations in the Raw Water and Clarifier Effluent and the THMFP Percent Removal Across the Superpulsator®, June 8 through November 26, 1986.

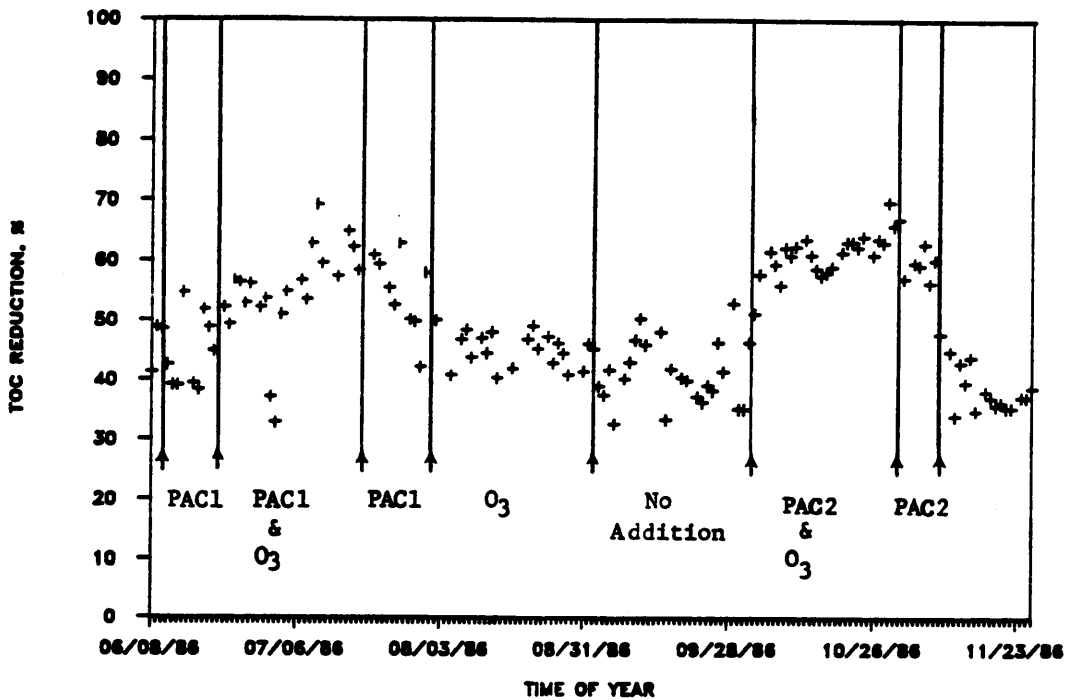
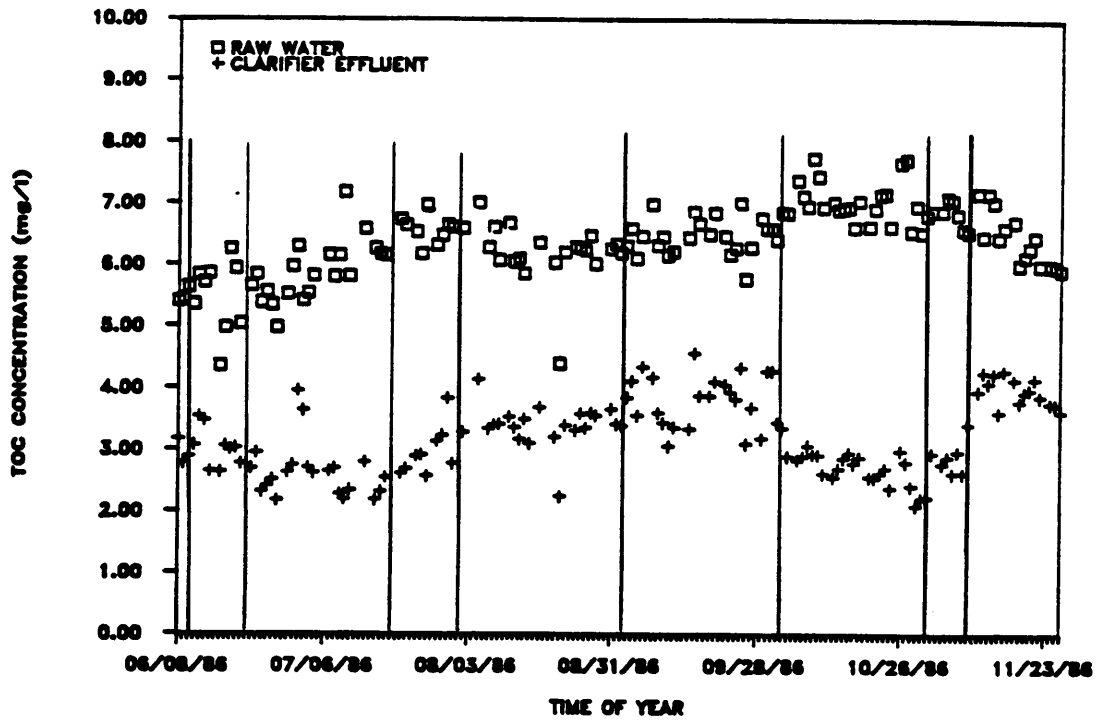


Figure 28. TOC Concentrations in the Raw Water and Clarifier Effluent and the TOC Percent Removal Across the Superpulsator®, June 8 through November 26, 1986.

THMFP and TOC Removal by Ozone/PAC and PAC Alone

Ozone was used as a preoxidant for both PAC studies. It was discontinued for a brief period each time PAC was added so that the performance of PAC alone could be evaluated. Tables 12 and 13 summarize the Superpulsator® performance when PAC and ozone were used singly and in combination. Figure 27 shows the percentage THMFP removal during the period. The peak percentage removals in July and October correspond to the time both ozone and PAC were being added to the process train. The NUCHAR SA carbon consistently removed a higher percentage of THMFP than the AQUA NUCHAR, even though both carbons consistently reduced THMFP concentrations below 100 µg/L. The NUCHAR SA achieved greater than 80 percent removal on several occasions. Similarly, Figure 28 indicates the use of NUCHAR SA carbon consistently resulted in higher TOC removals than when AQUA NUCHAR was used. Once ozone addition was stopped, the THMFP and TOC removals began to decrease (Figures 27 and 28) regardless of the carbon being used; however, the increase was more dramatic with AQUA NUCHAR than with NUCHAR SA.

Tables 12 and 13 indicate that treatment with NUCHAR SA and AQUA NUCHAR in combination with ozone produced approximately the same quality of water. However NUCHAR SA treatment provided a higher removal efficiency of THMFP and TOC at a lower dose than treatment with AQUA NUCHAR. Treatment with both carbons in conjunction with ozone removed significantly more THMFP than when PAC was not added to the Superpulsator®. Treatment with NUCHAR SA and AQUA NUCHAR and ozone increased the THMFP removal by 21 and 14 percent, respectively, over coagulation alone, but treatment with these two carbons in the absence of ozone increased the removals by only 15 and 3 percent, respectively. This suggests that ozone with PAC provides slightly better organic removals than PAC alone, especially when AQUA NUCHAR was used. The Duncan's Multiple Range Test (95 percent confidence level) was used to determine if there were statistical differences in the removal efficiency of PAC alone and PAC with ozone. The test showed that there was

Table 12. THMFP Removal Across Pulsator and Concentration in the Clarifier Effluent.

Process Description	Number of Samples	Mean ($\mu\text{g/L}$)	Range ($\mu\text{g/L}$)	Average Removal Across Pulsator (%)
Coagulation (No PAC) (8/3/86 - 10/2/86) (11/9/86 - 11/26/86)	37	156	71 - 244	55
AQUA NUCHAR (PAC1) 25 mg/L With Ozone (6/21/86 - 7/18/86)	13	97	71 - 142	69
AQUA NUCHAR (PAC1) 25 mg/L Without Ozone (6/10/86 - 6/20/86) (7/19/86 - 7/31/86)	13	141	97 - 175	58
NUCHAR SA (PAC2) 16 mg/L With Ozone (10/3/86 - 10/15/86)	9	102	74 - 138	74
NUCHAR SA (PAC2) 21 mg/L With Ozone (10/16/86 - 10/31/86)	11	98	61 - 125	76
NUCHAR SA (PAC2) 21 mg/L Without Ozone (11/1/86 - 11/8/86)	7	89	58 - 111	70

Table 13. TOC Removal Across Pulsator and Concentration in the Clarifier Effluent.

Process Description	Number of Samples	Mean (mg/L)	Range (mg/L)	Average Removal Across Pulsator (%)
Coagulation (No PAC) (8/3/86 - 10/2/86) (11/9/86 - 11/26/86)	60	3.71	2.24 - 4.58	42
AQUA NUCHAR (PAC1) 25 mg/L With Ozone (6/21/86 - 7/18/86)	21	2.64	2.18 - 3.96	55
AQUA NUCHAR (PAC1) 25 mg/L Without Ozone (6/10/86 - 6/20/86) (7/19/86 - 7/31/86)	19	3.00	2.58 - 3.85	49
NUCHAR SA (PAC2) 16 mg/L With Ozone (10/3/86 - 10/15/86)	11	2.87	2.56 - 3.36	60
NUCHAR SA (PAC2) 21 mg/L With Ozone (10/16/86 - 10/31/86)	14	2.59	2.10 - 3.00	63
NUCHAR SA (PAC2) 21 mg/L Without Ozone (11/1/86 - 11/8/86)	7	2.90	2.63 - 3.43	58

no statistical difference in the THMFP removal efficiency between PAC alone and PAC with ozone.

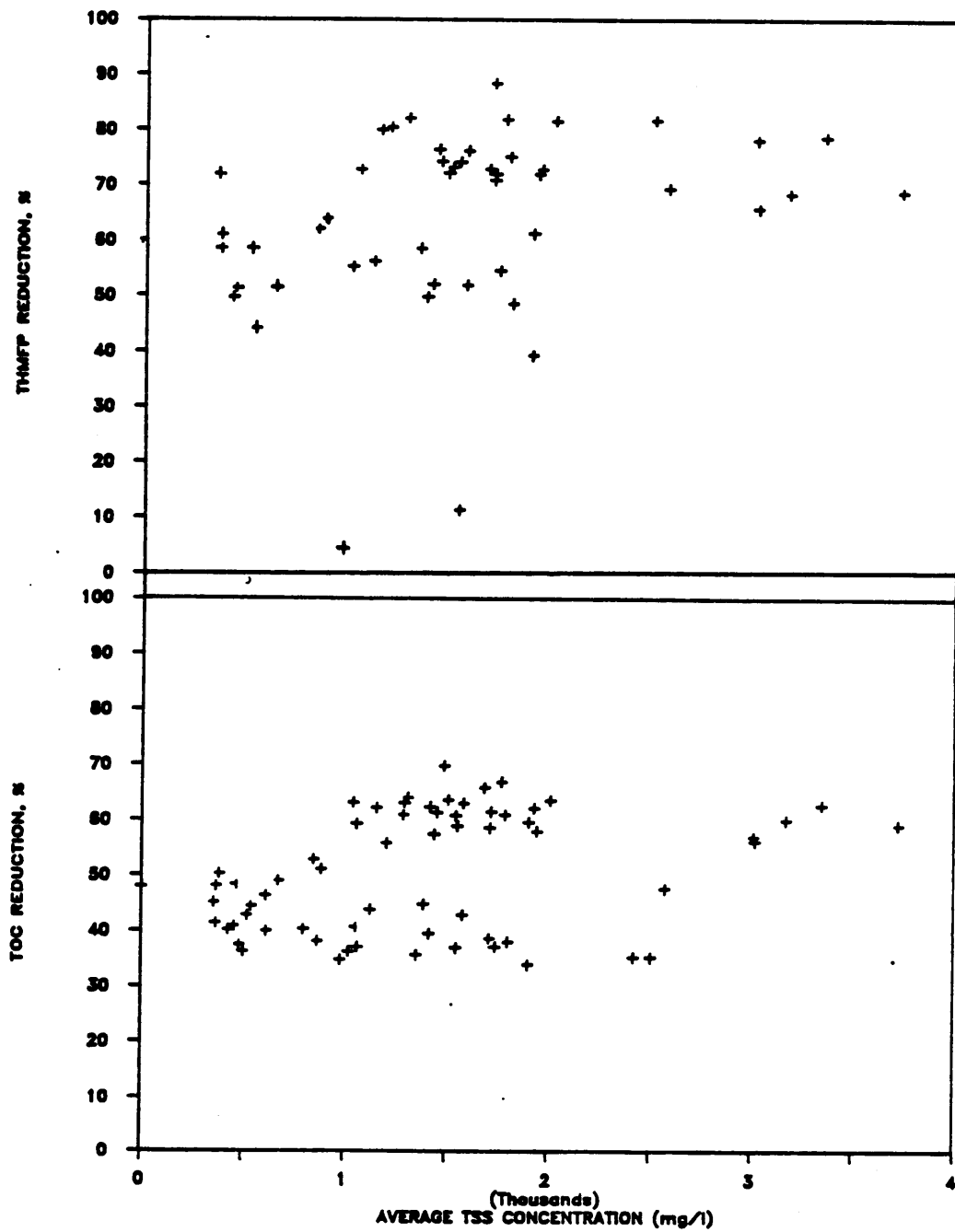
Although NUCHAR SA without ozone produced a lower mean THM precursor concentration in the clarifier effluent than PAC with ozone, one should not consider this to be the superior process. Referring to the THMFP percent removal in Table 12, it is evident that NUCHAR SA without ozone is somewhat less effective at removal than when it is added with ozone. Improved raw water conditions contributed to the lower THMFP concentrations in the clarifier effluent during NUCHAR SA additions without ozone.

TSS Correlation With TOC and THMFP Removal

There was some belief that a correlation existed between the TSS of the sludge blanket and THMFP removal. Therefore, the sludge blanket solids were increased as much as possible by increasing polymer dose and optimizing the sludge wastage rate. Figure 29 relates TSS with THMFP and TOC percent removal. As can be seen there is no definitive correlation between these parameters.

SURROGATE PARAMETERS

The measurement for THMFP is a time consuming process. Therefore, the relationships between THMFP and two other water quality parameters (TOC and UV254) were examined to determine if any relationship existed. In addition to testing the surrogates relationship with THMFP in the carbon columns, samples were taken from the raw water and clarifier effluent to determine if UV254 and TOC could be surrogates for THMFP around the Superpulsator®



While this effort did not constitute a major part of the study, the results are summarized here and presented in Appendix G. Figures 55 and 56 show that neither UV254 nor the multiplicative factor UV*TOC had very high correlation coefficients when compared with THMFP. Figure 54 showed that TOC correlated slightly better with THMFP, and thus, TOC may be used to obtain very general predictions of THMFP in the clarifier effluent.

TOC and UV254 as Surrogates for THMFP in the GAC and BAC Columns

TOC. In contrast to the raw water and clarifier effluent data, the correlations between THMFP and TOC in the activated carbon columns were much better. Table 14 shows that the correlations between THMFP and TOC concentrations in water treated by the GAC beds were quite good with the minimum correlation coefficient being 0.75. In contrast, the correlations between THMFP and TOC in water treated by the BAC process were not as good especially deeper in the bed. The TOC and THMFP relationships can be found in Appendix F (Figures 50 - 53).

UV Absorbance. UV absorbance measured at 254 nm predicted THMFP extremely well in the GAC column. As shown in Table 15, it had stronger correlations as a predictor of THMFP from various ports within the carbon bed than the TOC. The minimum correlation coefficient was 0.80, and this was in port 8.

In contrast, the UV absorbance was not an accurate predictor of the THMFP concentration in the BAC column. No reliable correlation could be made in any of the ports measured. The UV254 and THMFP relationships can be found in Appendix E (Figures 46 - 49).

Table 14. Linear Relationships Between THMFP and TOC Measured at Various Ports in the GAC and BAC Bed.

	PORT NUMBER			
	2	4	6	8
GAC				
slope (m)	36.4	37.9	43.5	29.5
y-intercept (b)	-2.7	-11.1	-21.2	1.1
correlation coefficient (r^2)	0.90	0.77	0.92	0.75
BAC				
slope (m)	31.0	24.2	3.9	---
y-intercept (b)	4.3	-0.2	14.8	---
correlation coefficient (r^2)	0.83	0.58	0.12	---

Table 15. Linear Relationships Between THMFP and UV254† Measured at Various Ports in the GAC and BAC Bed.				
	PORT NUMBER			
	2	4	6	8
GAC				
slope (m)	278	253	309	384
y-intercept (b)	15.2	15.8	8.2	2.0
correlation coefficient (r ²)	0.94	0.84	0.93	0.80
BAC				
slope (m)	213	15.0	37.3	---
y-intercept (b)	25.0	26.9	16.4	---
correlation coefficient (r ²)	0.67	0.09	0.19	---

† UV absorbance reported as per 10 cm.

Chapter 5

DISCUSSION

Preliminary Remarks

It is important to remember that inherent to this study were many limitations which hampered the analysis of the GAC and BAC column performance. The study of these processes was only part of the overall testing program employed at Harwood's Mill. Other tests involving various preoxidants, polymers, and PAC were conducted simultaneously with the GAC columns because commitments were made to test several treatment options within a specified time frame. Changing these processes made analysis of the data from the carbon columns difficult at times.

The best example of these difficulties is the addition of PAC to the Superpulsator® during October 1986. Normally, PAC would not be used in conjunction with GAC except in extreme cases. The use of PAC resulted in a significant reduction of the THM precursor loading onto the BAC and GAC contactors. Thus, the data projections predict a slightly longer bed life for the GAC than if PAC were not used. Because PAC was added for a relatively short period, its

effect on the results were probably minimal; nevertheless, the predictions of carbon bed life stated in this study are greater because PAC was added at least a portion of the time. To partially account for this, the analysis of the carbon beds was based on some conservative factors which will be mentioned later.

Because the analyses of the activated carbon beds were based in large part on graphical techniques, some discrepancies may be found if comparing this study to others. Great care was taken to accurately determine the predicted time (water throughput) that the column effluent would exceed the specified THM Limit; however, small variations in these values can change the GAC requirements for each carbon process. Thus, it should be remembered that the values reported in the results and discussion are approximate values and could be subject to small variations depending on the interpretation of data.

Variations in Raw Water Quality

Large variations seen in Table 4 that describe raw water quality can be explained by several factors. During the first three months of this study, a severe drought plagued the area. As a result, the water quality in the reservoir improved because there was less runoff into its tributaries and the Chichahominy River. However, frequent algal blooms in the reservoir during the late summer months caused wide fluctuations in the raw water quality. Copper sulfate was frequently applied to the reservoir to control the algae growth. In addition, rainfall during the final three months of the study was above normal which resulted in poorer water quality.

Another cause for variations in the raw water quality was that the reservoir level was reduced by ten feet while a raw water pump station for the new treatment plant was being installed. During this time the raw water quality was highly influenced by a tributary entering the

reservoir adjacent to the pilot plant intake. Runoff from upstream commercial business areas during heavy rains resulted in the creek being heavily polluted at times.

Variations in the Clarifier Effluent

Variations in THMFP levels in the clarifier effluent during the pilot plant study can be attributed to a number of factors, including alterations in alum and polymer dose, changes in the process operations of the Superpulsator®, the use of different preoxidants, and the addition of PAC.

System THM Precursors

The projections of GAC bed life in this thesis were based on the assumption that the THM level in the Harwood's Mill distribution system would be approximately two-thirds of the measured THMFP of the activated carbon effluent. This fraction, more than likely, is conservative because the actual average ratio between the THMFP of the treated Harwood's Mill Reservoir water (at the existing water treatment plant) and the THM level measured at a distant point in the distribution system (Haywood Forest) was 0.5 during September through November, 1986 (Table 5). That ratio, however, was developed from data collected during the fall rather than the summer when the water temperature would be higher and, likely, the system THM level would also be greater. The two-thirds ratio was chosen simply because it was more conservative, and could account for factors (e.g. PAC use during column analysis and good raw water quality) that could provide an overly optimistic analysis of the carbon columns. One should remember that while analyzing the data that the actual GAC column bed life may be longer than estimated. Some comparative data using the THM/THMFP ratio of 0.5 are given in Tables 8, 9, 11, and 17 to put the less conservative ratio into perspective.

GRANULAR ACTIVATED CARBON

The placement of the ozone contactor before the BAC columns came under considerable discussion a month into the operation. This placement was causing considerable operational problems. The mixed media filter-run times were lower than expected with turbidity breaking through the filter after only 10 to 15 hours. This was especially a problem when potassium permanganate (KMnO_4), a preoxidant, was added to the pulsator. The pH was low (5.9 - 6.1) while KMnO_4 was being added and low pH generally does not favor rapid oxidation of manganese and iron. Ozone oxidized the manganese and produced solid manganese dioxide which was trapped by the filters, resulting in even lower mixed media filter run times and increasing the rate of head loss buildup on the BAC carbon.

After the ozone contact chamber was moved to a position between the mixed media filter and the activated carbon columns, the mixed media filter run times increased, and fewer turbidity problems were experienced for the remainder of the study. This was due in part to the potassium permanganate addition being discontinued and the mixed media filter removing additional particulate and organic material before the water entered the ozone contactor.

The ozone contactor was originally placed before the mixed media filter because of ozone's ability to oxidize many materials and cause subsequent precipitation. Rice (43) recommended that a filter be placed after the ozone contactor to prevent high loading of precipitated solids onto the carbon. This would reduce the rate of head loss on the carbon bed and the number of backwashings required. However, in full-scale operations, the ozone contactor is usually placed between the GAC and the mixed media filter (48, 64, 92). From the experiences gained at the pilot plant, a full scale operation should be designed such that the mixed media filter precedes the ozone contactor.

Analysis of the Wavefront Progression in the BAC and GAC Columns.

To reduce the large amount of data collected on the carbon columns, only ports 2, 4, 6, and 8 (20, 44, 64, and 84-in depths) were used in the analyses. These were representative of the data collected in the other ports of the carbon columns.

THMFP. Appendices B and C contain plots that show the predicted THM precursor breakthrough for the GAC and BAC columns. Total bed life estimates based on the analyses of water collected at ports in the upper reaches of the carbon beds were larger than estimates based on water quality at the lower ports. This occurs because initially the THMFP wavefront was quite broad, with the majority of the THM precursors being adsorbed. The ports located in the upper regions of the bed predicted a longer bed life, since the majority of the THMFP is being adsorbed there. As time passed, the wavefront dispersed with the less adsorbable THMFP extending deeper into the bed before being adsorbed. At ports located deeper in the carbon bed, the predictions generally decrease but do not follow a uniform pattern (Tables 8 and 9). The predicted bed life was based on the average of the predictions made from data taken at each port. The bed life of the BAC and GAC column predicted from data taken at port 4 (44-in) (112 cm) and below were fairly uniform.

Although the total water throughput was less through the BAC columns, enough had passed through so that accurate predictions of bed life could be made. A summary of the predicted water throughput and time of operation to meet a specified THM treatment goal for the BAC and GAC columns is given in Table 16. This shows that the BAC's bed life is 10 to 15 percent longer than the GAC in meeting the 25 µg/L THM treatment limit and 24 percent longer in meeting the 50 µg/L limit. If the 0.5 THM/THMFP ratio is valid, then an increase in bed life of 9 to 24 percent could be expected for the carbon columns.

Table 16. Predicted Bed Life for the GAC and BAC Beds For Specified Treatment Goals Assuming a THM/THMFP Ratio of 0.5 and 0.66.

		THM/THMFP = 0.66				THM/THMFP = 0.5			
THM Treatment Goal (µg/L)	GAC		BAC		GAC		BAC		
	Bed Volumes	Bed Life (Days)	Bed Volumes	Bed Life (Days)	Bed Volumes	Bed Life (Days)	Bed Volumes	Bed Life (Days)	
25	6,875	143	7,500	156	7,450	155	8,500	177	
50	8,675	188	11,250	234	11,400	237	14,000	292	
75	13,750	270	—	—	—	—	—	—	

In a full-scale facility, a number of GAC contactors are usually employed and their effluent streams are blended in a clear well. Thus, it is possible that one column can operate beyond its THM treatment limit concentration as long as the average THM concentration from all of the effluents is below that limit. By blending the effluents, the bed life of the carbon column can be extended significantly.

TOC. The fraction of TOC passing through the carbon bed was much higher than that of THMFP because the TOC contains more poorly adsorbing organics than THMFP. As a result, the TOC concentration in the column effluent is high, approximately one-third of the influent value. The TOC that passes through composes the nonadsorbable fraction.

GAC Requirements for Meeting Different Treatment Goals

To more accurately define the carbon requirements for the BAC and GAC, calculations were made to determine the total amount of THM precursors (THMFP) adsorbed onto the carbon. Plotting the specific THMFP removal per gram of GAC as a function of the predicted number of bed volumes (bed life) provides a method of determining the amount of carbon that will be needed to meet a specified treatment goal. Tables 10 and 11 summarized the amount of carbon that will be needed to meet each specified THM treatment goal.

As seen in Tables 10 and 11, the GAC requirements varied in both the BAC and GAC columns. Each THM treatment goal required a different amount of GAC to treat a unit amount of water. The lowest THM treatment goal ($\mu\text{g/L}$) required the largest amount of GAC. Meeting the 25 $\mu\text{g/L}$ limit would require 20 to 40 percent more carbon for either column than if the limit were 50 $\mu\text{g/L}$. Using the 0.5 THM/THMFP ratio rather than 0.66 for column analysis resulted in savings of 9 to 26 percent in the amount of GAC required. Thus, accurately knowing the actual THM/THMFP ratio for the Harwood's Mill distribution system is crucial in determining the

amount of GAC that would be required to meet a treatment goal. In addition, if the 0.5 ratio is accurate, then no further treatment beyond alum coagulation, flocculation, and filtration will be required to meet the 75 $\mu\text{g/L}$ goal because the mixed media filter effluent during the study was approximately 150 $\mu\text{g/L}$ THMFP.

The BAC process would require 10 to 15 percent less carbon than the GAC for meeting each treatment goal. The BAC column removed significantly more THMFP per gram of carbon than the GAC at each port examined and for each THM treatment goal. This was expected since more THM precursors were being removed in the BAC column than in the GAC column. These results are important because it underscores two important advantages that the BAC process has over GAC: 1) BAC has increased bed life and 2) BAC requires less carbon to meet a specified THM treatment goal. A detailed economic study will be required to determine if the savings in the carbon requirements would offset the increased costs of ozone addition.

Adsorption Characteristics of THM Precursors

The THMFP/TOC ratio can be an extremely effective indicator of whether the GAC is selective in adsorbing the THM precursor fraction of the TOC. It can also indicate whether the THM precursors are part of the adsorbable fraction or the nonadsorbable fraction of the TOC. Figures 23 - 25 showed that the average value for the ratio in the BAC and GAC influent was approximately 40 $\mu\text{g/mg}$. After GAC and BAC treatment, the values of the ratio were consistently below the 25 to 30 $\mu\text{g/mg}$ range, indicating that the THM precursors are indeed readily adsorbable by FILTRASORB 400 (Figures 23 and 25). It is interesting to note that the THMFP/TOC ratios in the GAC effluent were consistently lower and had less variation than the ratios in the BAC effluent. A likely explanation is that the ozone associated with the operation of the BAC column was converting part of the nonadsorbable fraction of TOC into an

adsorbable fraction; therefore, a larger amount of TOC was adsorbed in the BAC than the GAC and, as a result, the THMFP/TOC ratio in the BAC effluent would be larger than in the GAC effluent. It appears that the ozone enables the BAC process to be more efficient in the adsorption of both TOC and the THM precursor fraction of the TOC.

Benefits Provided by BAC

In this study, BAC was established as the superior organic removal process. This finding is in agreement with what is generally reported in the literature (47, 57, 59, 61, 63, 64). The difference between BAC and GAC, as mentioned earlier, is that ozone is added ahead of the activated carbon column. Theory holds that ozone oxidizes the large THM precursor molecules, thus making them more susceptible to biological degradation or adsorption onto the carbon. There is considerable debate as to which of the two processes the increased organic removal can be attributed to.

In this study, changes in dissolved oxygen concentration across both the GAC and the BAC columns were measured. Figure 26 showed that the dissolved oxygen uptake in the BAC column was greater than in the GAC column, thus providing indirect evidence that microbial growth was occurring on the carbon. It does not indicate whether the biota were actively degrading the precursors or were respiring endogenously. The standard plate counts of the BAC and GAC effluents were inconclusive because results varied widely.

Ozone can produce small molecular weight THM-precursor molecules from larger ones. Lee (39) found that the adsorption capacity of and rate of uptake by activated carbon increased as the molecular weight of the organic matter decreased. Because these smaller molecules can penetrate further into the carbon's microporous structure, the adsorption kinetics are improved; therefore, a higher percentage of the carbon would be utilized for adsorption and

would provide a longer bed life. Peel and Benedek (54) have proposed a theory that suggests adsorption continues over a long period with small organic molecules penetrating deep into the microporous structure (slow adsorption kinetics). This increased adsorption would improve the GAC bed life. Whether biological degradation or slow adsorption kinetics predominates is a matter for speculation because none of the available data strongly supports either theory. A safe assumption would be that a combination of slow adsorption kinetics and biological degradation contributed to the higher THM precursor removal in the BAC.

Inorganic Removal by Activated Carbon

Iron and manganese removals occurred in both the GAC and BAC columns. This result can be attributed to the filterability of activated carbon and not adsorption. Manganese removals were greater on the BAC because ozone tended to oxidize soluble manganese (Mn II) to manganese dioxide. This precipitate was then removed by the carbon filter. In both columns, especially the BAC, dark brown deposits could be seen in the top two inches of the carbon. The deposits were indicative of insoluble manganese and were especially prevalent when potassium permanganate was added in the Superpulsator®. Iron removal was also slightly better in the BAC column. At various times the manganese concentration was higher in the column effluents than in the influent, most likely because particulate Mn (IV) was passing through the bed.

POWDERED ACTIVATED CARBON

As was noted in the Results chapter, both types of PAC provided significantly higher organic removals when added with ozone than alum coagulation alone. Activated carbons that have

a large surface area are capable of more efficient adsorption (31, 32). NUCHAR SA has more surface area than AQUA NUCHAR and, as expected, the NUCHAR SA carbon was superior in organic removal. Although the AQUA NUCHAR was added at a higher dosage than the NUCHAR SA, the NUCHAR SA consistently removed a higher percentage of THM precursors than the AQUA NUCHAR. Both carbons increased THMFP removal by 14 to 21 percent and TOC removal by 13 to 19 percent (Tables 12 and 13) when a preoxidant (ozone) was used. PAC alone increased THMFP removal by 3 to 15 percent and TOC removal by 7 to 16 percent. AQUA NUCHAR represents the lower range of the THMFP and TOC percent removals and NUCHAR SA represents the higher removals.

Ozone Enhancement of PAC

Ozone addition in conjunction with PAC decreased the THMFP and TOC concentrations in the clarifier effluent for both carbons. AQUA NUCHAR produced the most significant improvement when ozone was added by decreasing the average THMFP level in the clarifier effluent from 141 to 97 µg/L. In contrast, the effluent THM precursor concentrations were greater when ozone and NUCHAR SA were added than when ozone was added alone, even though the combined treatment produced a higher percentage of THM precursor removal. This was most likely the result of lower THM precursor concentrations in the raw water and not because of some action by ozone itself. Both types of PAC provided better THM precursor and TOC removals than alum coagulation alone.

Table 12 showed that an increase in dose of NUCHAR SA did not proportionally increase the THM precursor removal. A slight improvement was noticed in the average concentration and the average efficiency of removal, but it was small. A statistical analysis using the Duncan Multiple Range Test (95 percent confidence level) showed there was no significant difference between the removal efficiencies of either process. This may be attributed in part to the fact

that the raw water THMFP was decreasing at the same time the PAC dose was being increased. The data also suggest that increasing the NUCHAR SA dose beyond 15 to 20 mg/L may not be economically feasible because it may not provide comparable reductions in the effluent THMFP concentration.

Estimates of the THM's in the Harwood's Mill distribution system based on the THM/THMFP ratio can be made from the mean clarifier effluent concentrations for each PAC process (Table 12). Table 17 summarizes these estimates and show that PAC with or without ozone can provide THM levels at Haywood Forest (seven days in distribution system) between 44 and 93 µg/L depending on which process is employed and which THM/THMFP ratio is used. When reviewing Table 17, remember that these effluent levels are not representative of the efficiency of the process, therefore processes with the lowest clarifier effluent levels may not be the most efficient (see Table 12).

Early in the study, there was some hope that the THMFP and TOC removal efficiencies were related to the total suspended solids (TSS) in the Superpulsator®. It was believed that a denser sludge blanket would contain more PAC and, therefore, be more effective at removing organic matter from the flocculating water. However as seen in Figure 29, no relationship was evident. This phenomenon was not fully explored, however, because the sludge-wasting rate was not carefully regulated during the entire study, and no studies were conducted to determine if increasing the PAC feed rate would increase the TSS of the sludge blanket. More work on this aspect of the problem is required.

Table 17. Predicted THM's in the Harwood Mill Distribution System at Haywood Forest after PAC Treatment Using 0.66 and 0.5 as the THM/THMFP Ratio.

Process Description	Predicted THM's at Haywood Forest ($\mu\text{g/L}$)	
	THM/THMFP RATIO	
	0.66	0.5
Coagulation (No PAC) (8/3/86 - 10/2/86) (11/9/86 - 11/26/86)	103	78
AQUA NUCHAR (25 mg/l) with Ozone (6/21/86 - 7/18/86) sk.	64	49
AQUA NUCHAR (25 mg/l) without Ozone (6/10/86 - 6/20/86) (7/19/86 - 7/31/86)	93	71
NUCHAR SA (16 mg/l) with Ozone (10/3/86 - 10/15/86)	67	51
NUCHAR SA (21 mg/l) with Ozone (10/16/86 - 10/31/86)	65	49
NUCHAR SA (21 mg/l) without Ozone (11/1/86 - 11/8/86)	59	45

SURROGATE PARAMETERS

Raw Water and Clarifier Effluent

One objective of this study was to determine if TOC or UV absorbance could serve as surrogate parameters for the THM precursor (THMFP) concentration in the carbon columns. As outlined in the results, the TOC and UV absorbance do not appear to be a good predictor for THMFP when considering the raw water and clarifier effluent values together. A linear regression analysis performed on the data showed that only TOC had a high enough correlation for it to qualify as a surrogate for THMFP. This correlation was not high (0.68); however, and TOC should only be used to make general predictions of THMFP in the clarifier effluent.

GAC and BAC Columns

Tables 14, 15 and Appendices E and F show THMFP as a function of UV254 and TOC in each carbon column and these indicate that the surrogate parameters could predict THMFP much more accurately in the GAC column than in the raw water or clarifier effluent. There was a strong correlation between TOC and THMFP in the GAC column. Table 14 showed that the minimum correlation coefficient between THMFP and TOC in the GAC column was 0.75. In addition, the THMFP/TOC data representing conditions in the effluent of port 6 in the GAC column (Figure 24) resembled a typical breakthrough curve with the values approaching the influent values over time. This would indicate that the adsorbability of THMFP and TOC are proportional with time, and TOC would be a fairly accurate surrogate for predicting THMFP. UV absorbance exhibited an even stronger relationship with THMFP at all ports measured in

the GAC column. Table 15 showed the minimum correlation coefficient between THMFP and UV254 was 0.80.

In contrast, the TOC was a poor indicator of THMFP in the BAC columns. Only sampling ports located in the BAC carbon bed where the wavefront had completely passed was the correlation between TOC and THMFP fairly good. At ports deeper in the carbon bed this was not true. This may have been due in part to lower THMFP values since the THMFP wavefront had not progressed as deep into the carbon bed as it had in the GAC column. UV254 was a poorer surrogate than TOC for THMFP. It was poor at almost every port sampled.

The poor predictions of THMFP by UV254 in the BAC column effluent may have been caused by ozone addition. Ozone has been shown to affect the ability of UV absorbance to predict THMFP (59, 62, 73, 75) by destroying UV absorbing substances while not effectively reducing the THM precursor concentrations. It appears that the value of UV absorbance as an indicator of THMFP is dependent upon the natural raw water source and the THM precursors it contains.

In summary, UV absorbance measured at 254 nm and TOC were excellent predictors of THMFP in the GAC column. TOC possibly could be used in the BAC as an indicator for THMFP but it could not be totally relied upon. UV absorbance should not be used as a surrogate because of interferences created by ozonation.

Chapter 6

SUMMARY AND CONCLUSIONS

The primary objectives of this study were focused on organic control options that would significantly reduce the amount of THM's that are found in the Harwood's Mill water distribution system. Four processes involving activated carbon were employed: GAC, ozone-GAC (BAC), PAC, and ozone-PAC. A comparison of the four processes was performed to determine each carbon's ability to remove THM-precursors. Two GAC contactors, one incorporating ozone in the influent (BAC) and the other as a control, were run in parallel with an EBCT of 30 minutes and a loading rate of 2.7 gpm/ft² to determine the efficiency of GAC to remove THMFP. Two types of PAC (NUCHAR SA and AQUA NUCCHAR) were added to coagulated water entering the Superpulsator® and their efficiency at removing THMFP and TOC were measured. During PAC addition, ozone was used as a preoxidant intermittently to determine if it helped improve organic removal.

Both the GAC and BAC processes remove organics equally well; however, the BAC would be more efficient. It was found that the BAC column could operate for 156 to 177 days while providing THM levels under 25 µg/L at the most distant point in the Harwood's Mill distribution system. It could operate for 234 to 292 days while providing THM levels under 50 µg/L. The

GAC column could operate for 143 to 155 days while meeting the 25 µg/L limit and for 188 to 237 days while meeting the 50 µg/L. The BAC process would require approximately 10 to 15 percent less carbon than the GAC process and would have a longer bed life. It should be remembered that these results were based on the performance of a single contactor. Typical carbon column designs incorporate multiple contactors and their effluents are blended. Blending the column effluents will usually significantly increase the bed life.

Both PAC's, with or without ozone, improved THM precursor and TOC removals over alum coagulation alone. NUCHAR SA could provide as high as 76 percent THMFP removal in the Superpulsator®. Either PAC could provide between 58 and 76 percent THMFP removal and 49 to 63 percent TOC removal. This confirms previous findings that THM-precursors are preferentially removed from the TOC pool by activated carbon and coagulation. NUCHAR SA provided the lowest THM-precursor concentrations in the clarifier effluent ranging between 89 and 102 µg/L THMFP (45 to 68 µg/L THM at Haywood Forest); however, the level of treatment attained by either PAC is not as high as that for the GAC processes.

The significant conclusions that may be drawn from this research are:

1. The BAC process provided longer bed life and required less carbon to achieve a desired THM treatment level than the GAC process.
2. The BAC and GAC columns consistently produced water with a THMFP and TOC concentration under 25 µg/L and 1.0 mg/L respectively throughout the study. There appeared to be no difference between the GAC and BAC processes when considering the level of treatment obtained.
3. The granular activated carbon processes, as expected, were far superior to PAC for organics removal.

4. The addition of 16 to 25 mg/L of PAC to the Superpulsator® improved the TOC and THMFP removal over what could be achieved by alum coagulation alone. The PAC was readily retained by the sludge blanket.

5. The effects of 0.05 to 0.2 mg ozone/mg TOC on organic removal by PAC were variable. Significant improvement upon ozone addition was evident on one occasion when raw-water conditions were highly variable, but later studies showed little improvement when raw water conditions were stable.

6. TOC and UV254 proved to be very good surrogate parameters for THMFP in the GAC process but not in the BAC process.

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Appendix A
Data Summary of All Sample Points in the
Process Train

Table 20. Raw Data for the Newport News Pilot Plant.

DATE	INFLUENT RATE (mg/sec-ft)				CHEM FEED BASE (mg/l)				DOSE (mg/l)				BAC MICRO (mg/l)				BAC MICRO (mg/l)				TEMPERATURE (C)				PH				ALKALINITY (mg/l as CaCO ₃)				TURBIDITY (NTU)				THROUGHPUT VOLUME (bed vol's)			
	CLR	F	B1	F	ALUM	POLY	HYDRA	PAC	OCI	BAC	MICRO	BAC	MICRO	RAW	BEFF	RAW	BEFF	RAW	BEFF	RAW	BEFF	RAW	BEFF	RAW	BEFF	RAW	BEFF	RAW	BEFF	RAW	BEFF	RAW	BEFF	RAW	BEFF	RAW	BEFF			
09/19/86	1.5	2.7	2.7	2.7	71	0.31			11.6	0.0	0.6	0.00	23	25	16.7	5.6	5.6	5.6	5.6	53	12	9	10	5.6	0.2	0.09	0.00	0.11	0.05	1770	1815	1654	1893							
09/20/86	1.5	2.7	2.7	2.7	50	0.31	0.7		12.4	0.0	0.8	0.00	23	24	16.7	5.6	5.6	5.6	5.6	50	16	10	11	6.1	0.9	0.11	0.09	0.07	0.06	1810	1855	1896	1935							
09/21/86	1.5	2.7	2.7	2.7	50	0.33	1.0		13.1	0.0			23	23	16.5	5.8	6.0	6.0	6.0	48	17	15	17	6.2	0.4	0.15	0.27	0.10	0.00	1869	1907	1949	1989							
09/22/86	1.5	6.0	6.0	2.7	55	0.33	1.1		12.0	0.0	0.5	0.00	23	23	16.5	5.8	6.0	6.0	6.0	49	16	17	17	6.4	0.2	0.14	0.28	0.13		1930	1974	2013	2059							
09/23/86	1.5	6.0	6.0	2.7	55	0.33	1.1		12.2	0.0	0.6	0.00	25	27	16.5	5.8	6.0	6.0	6.0	50	16	20	17	4.4	0.2	0.11	0.13	0.60	0.00	2007	2059	2093	2140							
09/24/86	1.5	6.0	6.0	2.7	55	0.33	1.2		16.9	0.0	1.7	0.00	24	25	16.6	6.0	6.2	6.0	6.0	48	17	20	18	4.6	0.2	0.12	0.11	2.00	0.09	2030	2091	2126	2181							
09/25/86	1.5	6.0	6.0	2.7	55	0.33	1.1		12.2	0.0	1.7	0.00	24	28	16.6	5.8	6.2	5.6	5.6	17	23	11	11	4.6	0.2	0.11	0.11	1.33	0.29	2052	2105	2140	2196							
09/27/86	1.5	6.0	6.0	2.7	50	0.33	1.0		13.9	0.0	1.1	0.00	24	25	16.6	6.0	6.2	5.9	4.7	16	15	15	15	4.9	0.1	0.14	0.14	1.05	0.09	2086	2142	2176	2234							
09/28/86	1.5	6.0	6.0	2.7	50	0.33	1.1		12.0	0.0	0.9	0.00	24	29	16.6	5.7	6.2	6.0	4.5	15	18	16	16	4.5	0.3	0.09	0.10	0.46	0.00	2128	2189	2220	2283							
09/29/86	1.5	6.0	6.0	2.7	50	0.33	1.1		13.0	0.0	1.0	0.00	24	25	16.0	5.8	6.2	6.0	4.6	15	14	14	14	4.0	0.6	0.14	0.13	0.43	0.09	2164	2231	2259	2327							
09/30/86	1.5	6.0	6.0	2.7	50	0.33	1.2		14.2	0.0	1.2	0.00	25	25	16.0	5.9	6.2	5.9	4.6	15	13	15	15	3.9	0.5	0.13	0.13	0.07	0.00	2192	2264	2286	2361							
10/01/86	1.5	6.0	6.0	2.7	55	0.33		19.0	17.7	0.0	2.3	0.00	25	25	16.6	5.8	6.1	5.8	4.7	15	16	15	16	4.2	0.3	0.14	0.13	0.14	0.07	2279	2351	2377	2452							
10/02/86	1.5	6.0	6.0	2.7	50	0.40		19.0	14.4	0.0	1.5	0.11	26	26	16.6	5.6	6.0	5.8	4.7	14	18	16	16	5.2	0.3	0.10	0.11	0.05	0.05	2324	2405	2424	2500							
10/03/86	1.5	6.0	6.0	2.7	50	0.40		19.0	12.5	0.0			26	26	17.2	5.8	5.8	6.0	4.5	13	11	13	13	3.3	0.3	0.13	0.12	0.05	0.05	2369	2454	2471	2560							
10/04/86	1.5	6.0	6.0	2.7	50	0.45		17.0	13.7	1.1	1.2	0.13	23	23	17.0	6.1	6.2	6.0	4.7	16	16	16	16	3.5	0.4	0.17	0.18	0.09	0.05	2406	2497	2509	2604							
10/05/86	1.5	6.0	6.0	2.7	50	0.45		14.9	13.0	0.9	1.1	0.13	23	23	17.0	6.1	6.2	6.0	4.7	16	16	16	16	3.7	1.1	0.06	0.06	0.05	0.04	2493	2594	2600	2706							
10/06/86	1.5	6.0	6.0	2.7	50	0.45		13.5	14.8	1.0	1.7	0.13	23	23	17.0	6.1	6.2	6.0	4.6	16	17	16	16	2.8	0.9	0.07	0.07	0.06	0.04	2537	2642	2644	2756							
10/07/86	1.5	6.0	6.0	2.7	50	0.40		13.5	14.2	0.9	1.6	0.12	22	19	17.1	6.0	6.3	6.0	4.8	18	16	17	17	3.2	1.0	0.07	0.08	0.05	0.05	2452	2546	2557	2655							
10/08/86	1.5	6.0	6.0	2.7	50	0.45		14.9	14.0	0.9	1.6	0.13	22	20	17.0	6.0	6.3	6.1	4.8	18	16	17	17	3.7	1.1	0.06	0.06	0.05	0.04	2493	2594	2600	2706							
10/09/86	1.5	6.0	6.0	2.7	50	0.45		12.4	12.7	0.9			20	20	17.0	6.0	6.3	6.1	5.0	19	17	17	17	2.8	0.9	0.07	0.07	0.06	0.04	2570	2680	2689	2804							
10/10/86	1.5	6.0	6.0	2.7	50	0.40		12.4	12.3	0.7	1.1	0.10	20	21	17.0	6.1	6.2	6.1	4.7	18	19	18	18	4.5	0.2	0.09	0.15	0.09	0.09	2794	2930	2914	3058							
10/11/86	1.5	6.0	6.0	2.7	50	0.40		12.4	13.7	1.1	1.5	0.15	20	18	17.0	6.0	6.2	6.1	4.7	18	17	17	17	6.0	0.6	0.07	0.08	0.05	0.05	2838	2978	2940	3106							
10/12/86	1.5	6.0	6.0	2.7	50	0.40		19.3	13.5	1.1	1.4	0.16	19	17	17.0	5.8	6.0	5.9	4.4	17	16	15	15	8.0	0.9	0.07	0.07	0.05	0.05	2879	3024	3003	3154							
10/13/86	1.5	6.0	6.0	2.7	50	0.40		19.3	13.5	1.1	1.3	0.17	19	16	16.8	5.9	6.0	5.9	4.8	18	18	16	16	4.6	0.3	0.07	0.07	0.06	0.05	2920	3048	3046	3200							
10/14/86	1.5	6.0	6.0	2.7	50	0.40		20.4	13.2	1.0			17	15	17.0	5.8	6.0	5.9					3.9	0.5	0.07	0.08	0.06	0.05	2968	3118	3096	3252								
10/15/86	1.5	6.0	6.0	2.7	50	0.40		20.4	12.9	1.0	1.3	0.15	17	16	17.1	6.2	6.3	6.1	4.6	15	17	16	16	4.4	0.6	0.07	0.09	0.06	0.05	3009	3162	3138	3298							
10/16/86	1.5	6.0	6.0	2.7	61	0.40		20.4	14.1	1.3	1.6	0.19	17	15	16.7	1.6	6.5	6.3	4.7	17	17	17	17	4.6	0.5	0.06	0.07	0.06	0.04	3049	3205	3180	3343							
10/17/86	1.5	6.0	6.0	2.7	50	0.40		17.1	12.3	1.0	1.0	0.13	17	17	17.2	6.2	6.3	6.2	4.7	17	16	16	16	3.7	0.3	0.08	0.08	0.08	0.05	3095	3253	3220	3393							
10/18/86	1.5	6.0	6.0	2.7	50	0.40		24.8	0.5	12.2	0.9	0.8	0.13	17	19	17.2	6.2	6.2	6.0	5.0	19	15	16	4.1	0.4	0.07	0.09	0.14	0.13	3178	3340	3315	3484							
10/19/86	1.5	6.0	6.0	2.7	61	0.50		24.8	0.5	12.0	0.9	0.9	0.14	17	19	17.2	6.1	6.4	6.2	4.9	20	18	19	6.2	0.3	0.08	0.09	0.08	0.06	3221	3388	3360	3534							
10/20/86	1.5	6.0	6.0	2.7	50	0.50		24.8	12.3	1.0	0.8	0.13	17	17	17.0	6.1	6.3	6.1	4.8	18	18	14	14	8.0	0.2	0.09	0.08	0.07	0.05	3310	3477	3452	3627							
10/21/86	1.5	6.0	6.0	2.7	50	0.55		19.7	0.5	12.1	0.9	0.8	0.12	17	20	16.9	6.2	6.2	6.1	4.9	18	18	17	7.8	0.3	0.09	0.10	0.08	0.06	3353	3524	3497	3676							
10/22/86	1.5	6.0	6.0	2.7	50	0.50		24.8	0.5	12.3	1.0	1.0	0.15	18	19	17.0	6.1	6.2	6.1	4.7	18	18	18	5.3	0.3	0.09	0.09	0.06	0.05	3395	3570	3541	3724							
10/23/86	1.5	6.0	6.0	2.7	50	0.50		18.6	12.5	0.9	1.1	0.14	17	18	17.1	6.1	6.3	6.2	5.1	19	20	20	20	4.8	0.2	0.09	0.09	0.06	0.05	3437	3618	3585	3774							
10/24/86	1.5	6.0	6.0	2.7	50	0.55		18.6	12.5	0.9	1.1	0.14	17	18	17.1	6.1	6.2	6.1	5.1	19	20	20	20	4.8	0.2	0.09	0.09	0.06	0.05	3481	3665	3631	3823							
10/25/86	1.5	6.0	6.0	2.7	50	0.50		18.6	0.5	13.0	1.1	1.4	0.17	17	17	17.1	6.1	6.2	6.1	5.1	19	18	18	6.2	0.2	0.09	0.09	0.06	0.05	3508	3695	3659	3854							

LEGEND: RAW - RAW WATER, CLR - CLARIFIER EFFLUENT, F01 - FILTER EFFLUENT (GAC INFLUENT)
 F 02 - FILTER EFFLUENT (BAC INFLUENT), MICRO - MICROFLOCCULATION, ND - NOT DETECTABLE
 BACS - BAC PORT B6 (HALF WAY THROUGH BAC COLUMN), BEFF - BAC EFFLUENT
 GACS - GAC PORT B6 (HALF WAY THROUGH GAC COLUMN), GEFF - GAC EFFLUENT

Table 21. Raw Data for the Newport News Pilot Plant.

DATE	WTP LOADING RATE (gpm/54-ft)			CHEM FEED RATE (mg/l)			IRONING RATE: IRONING RATE (mg/mg)			pH			ALKALINITY (mg/l as CaCO ₃)			TURBIDITY (ntu)			THROUGHPUT VOLUME (cc-ft)													
	CLR	F	R2	BAC	GAC	ALUM	POLY	EMDIA	PAC	GCL	BAC	MICRO	BAC	CLR	BEFF	GEFF	IRAN	CLR	BEFF	GEFF	IRAN	CLR	F	R2	BEFF	GEFF	BAC	GAC	BAC	GAC		
11/01/86	1.5	6.0	6.0	2.7	2.7	50	0.50	22.6	0.5	10.0	0.0	17	20	19	17.1	6.2	6.2	6.2	53	24	22	21	5.9	0.1	0.11	0.11	0.00	0.00	3544	3737	3696	3898
11/02/86	1.5	6.0	6.0	2.7	2.7	44	0.50	22.6	0.5	10.0	0.0	17	16	16	17.1	6.2	6.4	6.4	49	20	23	25	4.8	0.1	0.14	0.12	0.09	0.07	3587	3784	3741	3947
11/03/86	1.5	6.0	6.0	2.7	2.7	50	0.50	20.4	10.0	0.0	0.0	17	16	16	17.0	6.2	6.4	6.2	52	23	25	23	5.0	0.1	0.15	0.17	0.09	0.09	3630	3833	3786	3998
11/04/86	1.5	6.0	6.0	2.7	2.7	55	0.50	20.4	10.0	0.0	0.0	17	10	10	17.0	6.2	6.3	6.2	53	24	24	23	6.6	0.3	0.15	0.13	0.09	0.09	3672	3880	3830	4047
11/05/86	1.5	6.0	6.0	2.7	2.7	41	0.50	20.8	0.5	10.0	0.0	16	17	16	16.8	6.2	6.3	6.2	50	27	25	26	6.7	0.3	0.15	0.14	0.09	0.09	3713	3926	3873	4095
11/06/86	1.5	6.0	6.0	2.7	2.7	50	0.50	20.8	0.5	10.0	0.0	16	16	17	16.8	6.2	6.2	6.2	53	25	26	26	6.0	0.3	0.14	0.09	0.09	0.09	3756	3973	3918	4144
11/07/86	1.5	6.0	6.0	2.7	2.7	50	0.50	20.0	0.5	10.0	0.0	16	10	19	16.6	6.2	6.1	6.1	57	25	27	26	7.5	0.3	0.16	0.17	0.12	0.11	3797	4013	3960	4188
11/08/86	1.5	6.0	6.0	2.7	2.7	41	0.35	1.0	1.0	1.0	1.0	10	17	16.8	6.3	6.3	6.3	62	28	28	28	6.2	0.3	0.16	0.16	0.19	0.19	4160	4339	4339	4339	
11/09/86	1.5	6.0	6.0	2.7	2.7	50	0.35	1.0	1.0	1.0	1.0	17	17	16.6	6.3	6.2	6.2	56	29	30	30	9.1	0.3	0.13	0.13	0.07	0.07	4210	4391	4391	4391	
11/10/86	1.5	6.0	6.0	2.7	2.7	50	0.35	1.0	1.0	1.0	1.0	15	14	16.8	6.3	6.4	6.4	50	29	29	29	9.4	0.5	0.13	0.13	0.06	0.06	4260	4443	4443	4443	
11/11/86	1.5	6.0	6.0	2.7	2.7	50	0.35	1.0	1.0	1.0	1.0	14	14	16.8	6.2	6.2	6.2	49	25	25	25	115.0	0.3	0.13	0.13	0.07	0.07	4305	4490	4490	4490	
11/12/86	1.5	6.0	6.0	2.7	2.7	55	0.35	1.0	1.0	1.0	1.0	11	8	16.8	6.3	6.2	6.2	49	25	24	24	111.3	0.3	0.12	0.12	0.06	0.06	4352	4539	4539	4539	
11/13/86	1.5	6.0	6.0	2.7	2.7	41	0.35	1.0	1.0	1.0	1.0	10	10	16.7	6.3	6.3	6.3	50	26	26	26	113.1	0.3	0.13	0.13	0.07	0.07	4396	4585	4585	4585	
11/14/86	1.5	6.0	6.0	2.7	2.7	50	0.35	1.0	1.0	1.0	1.0	12	12	17.0	6.5	6.3	6.3	40	27	26	26	120.0	0.3	0.12	0.12	0.07	0.07	4448	4639	4639	4639	
11/15/86	1.5	6.0	6.0	2.7	2.7	50	0.35	1.0	1.0	1.0	1.0	12	13	16.9	6.5	6.3	6.3	54	30	30	30	112.0	0.3	0.12	0.13	0.07	0.07	4495	4688	4688	4688	
11/16/86	1.5	6.0	6.0	2.7	2.7	55	0.35	1.0	1.0	1.0	1.0	12	12	16.8	6.4	6.4	6.4	55	26	27	27	120.0	0.4	0.13	0.13	0.05	0.05	4542	4737	4737	4737	
11/17/86	1.5	6.0	6.0	2.7	2.7	50	0.35	2.0	2.0	2.0	2.0	10	11	16.8	6.4	6.4	6.4	56	29	29	29	114.2	0.4	0.13	0.13	0.05	0.05	4584	4781	4781	4781	
11/18/86	1.5	6.0	6.0	2.7	2.7	50	0.35	2.0	2.0	2.0	2.0	11	12	16.8	6.5	6.5	6.5	53	28	30	30	124.0	0.3	0.11	0.09	0.05	0.05	4636	4835	4835	4835	
11/19/86	1.5	6.0	6.0	2.7	2.7	50	0.35	2.0	2.0	2.0	2.0	10	11	16.8	6.5	6.5	6.5	53	28	29	29	112.0	0.3	0.11	0.11	0.05	0.05	4681	4882	4882	4882	
11/20/86	1.5	6.0	6.0	2.7	2.7	50	0.35	2.0	2.0	2.0	2.0	10	10	16.8	6.3	6.5	6.5	53	27	29	29	114.0	0.3	0.12	0.12	0.05	0.05	4731	4934	4934	4934	
11/21/86	1.5	6.0	6.0	2.7	2.7	50	0.35	2.0	2.0	2.0	2.0	11	13	17.0	6.4	6.3	6.3	54	31	29	29	9.9	0.3	0.11	0.12	0.05	0.05	4761	4966	4966	4966	
11/22/86	1.5	6.0	6.0	2.7	2.7	50	0.35	2.0	2.0	2.0	2.0	11	11	17.0	6.4	6.4	6.4	53	30	20	20	7.1	0.3	0.13	0.12	0.05	0.05	4824	5031	5031	5031	
11/23/86	1.5	6.0	6.0	2.7	2.7	44	0.40	2.0	2.0	2.0	2.0	11	15	16.9	6.3	6.3	6.3	55	26	27	27	6.9	0.5	0.12	0.09	0.05	0.05	4876	5086	5086	5086	
11/24/86	1.5	6.0	6.0	2.7	2.7	44	0.40	2.0	2.0	2.0	2.0	11	15	16.9	6.3	6.3	6.3	55	26	27	27	6.9	0.5	0.12	0.09	0.05	0.05	4922	5134	5134	5134	

LEGEND: RAW - RAW WATER, CLR - CLARIFIER EFFLUENT, F01 - FILTER EFFLUENT (GAC INFLUENT)
 F R2 - FILTER EFFLUENT (BAC INFLUENT), MICRO - MICROFLOCCULATION, NO - NOT DETECTABLE
 BACS - BAC PORT B6 (HALF WAY THROUGH BAC COLUMN), BEFF - BAC EFFLUENT
 GACS - GAC PORT B6 (HALF WAY THROUGH GAC COLUMN), GEFF - GAC EFFLUENT

Table 24. Raw Data for the Newport News Pilot Plant.

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DATE	DISSOLVED OXYGEN (mg/l)										IRON (mg/l)										MANGANESE (mg/l)										SURFACED SOLIDS (mg/l)										S OIL SLUDGE VOL (ml)										METEORITIC PLATE COUNT BACTERIA (1/ml)									
	RAW	CLR	F	B1	F	B2	BAGS	BEFF	CAGS	BEFF	RAW	CLR	F	B1	F	B2	BEFF	GEFF	RAW	CLR	F	B1	F	B2	BEFF	GEFF	P	B2	P	B4	P	B4	P	B6	P	B2	P	B4	P	B4	P	B6	RAW	CLR	F	B1	F	B2	BEFF	GEFF										
	19.5	10.2	10.0	9.0	8.0	6.2	8.5	7.0	0.000	0.000	0.000	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	10.040	0.020	0.023	0.023	0.023	0.023	0.023	0.023	3255	2650	3120	800	800	910	790	780	860	1045	1045	2020	720	710	780	500	300	7500	700	1000													
11/01/86	19.5	10.2	10.0	9.0	8.0	6.2	8.5	7.0	0.000	0.000	0.000	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	10.040	0.020	0.023	0.023	0.023	0.023	0.023	0.023	3255	2650	3120	800	800	910	790	780	860	1045	1045	2020	720	710	780	500	300	7500	700	1000													
11/02/86	18.4	9.9	9.0	9.0	8.0	6.0	9.3	7.4	0.000	0.000	0.000	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	10.040	0.020	0.023	0.023	0.023	0.023	0.023	0.023	3255	2650	3120	800	800	910	790	780	860	1045	1045	2020	720	710	780	500	300	7500	700	1000													
11/03/86	18.4	9.9	9.0	9.0	8.0	6.0	9.3	7.4	0.000	0.000	0.000	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	10.040	0.020	0.023	0.023	0.023	0.023	0.023	0.023	3255	2650	3120	800	800	910	790	780	860	1045	1045	2020	720	710	780	500	300	7500	700	1000													
11/04/86	19.4	10.0	9.9	9.0	9.3	6.0	8.4	7.7	0.000	0.000	0.000	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	10.040	0.020	0.023	0.023	0.023	0.023	0.023	0.023	3255	2650	3120	800	800	910	790	780	860	1045	1045	2020	720	710	780	500	300	7500	700	1000													
11/05/86	18.2	9.5	9.4	9.5	8.2	7.2	8.4	7.4	0.000	0.000	0.000	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	10.040	0.020	0.023	0.023	0.023	0.023	0.023	0.023	3255	2650	3120	800	800	910	790	780	860	1045	1045	2020	720	710	780	500	300	7500	700	1000													
11/06/86	18.1	9.5	9.5	9.5	7.8	7.4	8.2	7.6	0.000	0.000	0.000	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	10.040	0.020	0.023	0.023	0.023	0.023	0.023	0.023	3255	2650	3120	800	800	910	790	780	860	1045	1045	2020	720	710	780	500	300	7500	700	1000													
11/07/86	17.9	9.7	9.7	9.7	8.1	7.6	8.3	8.0	0.000	0.000	0.000	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	10.040	0.020	0.023	0.023	0.023	0.023	0.023	0.023	3255	2650	3120	800	800	910	790	780	860	1045	1045	2020	720	710	780	500	300	7500	700	1000													
11/08/86	17.4	8.9	8.0	6.7	7.6	6.7	7.8	7.6	0.000	0.000	0.000	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	10.040	0.020	0.023	0.023	0.023	0.023	0.023	0.023	3255	2650	3120	800	800	910	790	780	860	1045	1045	2020	720	710	780	500	300	7500	700	1000													
11/09/86	19.2	10.0	9.9	7.4	10.192	0.009	0.000	7.4	10.192	0.009	0.000	0.000	0.000	0.000	0.030	0.030	0.030	0.030	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000																						
11/10/86	18.3	9.8	9.6	7.3	7.3	7.3	7.3	7.3	7.3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000																					
11/11/86	17.4	9.0	9.0	7.6	10.386	0.025	0.000	7.6	10.386	0.025	0.000	0.016	0.132	0.065	0.056	0.056	0.056	0.056	0.056	0.016	0.132	0.065	0.056	0.056	0.056	0.056	0.056	0.016	0.132	0.065	0.056	0.056	0.056	0.056	0.056	0.016	0.132	0.065	0.056	0.056	0.056	0.056	0.056	0.056	0.056															
11/12/86	17.3	9.4	9.3	7.9	7.9	7.9	7.9	7.9	7.9	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000																				
11/13/86	18.2	10.5	10.5	9.8	10.517	0.052	0.031	9.8	10.517	0.052	0.031	0.000	0.145	0.099	0.063	0.063	0.063	0.063	0.063	0.000	0.145	0.099	0.063	0.063	0.063	0.063	0.063	0.000	0.145	0.099	0.063	0.063	0.063	0.063	0.063	0.000	0.145	0.099	0.063	0.063	0.063	0.063	0.063	0.063	0.063	0.063														
11/14/86	18.0	9.9	9.8	8.5	10.382	0.042	0.025	8.5	10.382	0.042	0.025	0.000	0.143	0.135	0.128	0.128	0.128	0.128	0.128	0.000	0.143	0.135	0.128	0.128	0.128	0.128	0.128	0.000	0.143	0.135	0.128	0.128	0.128	0.128	0.128	0.000	0.143	0.135	0.128	0.128	0.128	0.128	0.128	0.128	0.128	0.128														
11/15/86	17.5	9.7	9.5	8.2	8.2	8.2	8.2	8.2	8.2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000																			
11/16/86	18.2	10.2	10.2	8.3	10.643	0.000	0.000	8.3	10.643	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000																				
11/17/86	19.0	10.8	10.8	9.6	9.6	9.6	9.6	9.6	9.6	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000																			
11/18/86	18.5	10.1	9.7	9.3	9.3	9.3	9.3	9.3	9.3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000																			
11/19/86	18.5	10.1	9.7	9.3	9.3	9.3	9.3	9.3	9.3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000																			
11/20/86	18.5	10.1	9.7	9.3	9.3	9.3	9.3	9.3	9.3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000																			
11/21/86	19.7	10.8	10.7	9.3	9.3	9.3	9.3	9.3	9.3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000																			
11/22/86	19.6	10.9	10.8	9.3	9.3	9.3	9.3	9.3	9.3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000																			
11/23/86	19.6	10.9	10.8	9.3	9.3	9.3	9.3	9.3	9.3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000																			
11/24/86	19.6	10.9	10.8	9.3	9.3	9.3	9.3	9.3	9.3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000																			
11/25/86	19.8	10.8	10.7	9.1	9.1	9.1	9.1	9.1	9.1	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000																			
11/26/86	19.9	10.7	10.6	9.6	9.6	9.6	9.6	9.6	9.6	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000																			

LEGEND: RAW - RAW WATER, CLR - CLARIFIER EFFLUENT, F, B1 - FILTER EFFLUENT (GAC INFL

Table 25. Raw Data for the Newport News Pilot Plant.

DATE	TOC (mg/l)																				
	RAW	CLR	F 01	FR2	BASELINE	BAC1	BAC2	BAC3	BAC4	BAC5	BAC6	BAC7	BAC8	BAC9	BAC10	BAC11	BEFF	0.41	0.45		
08/05/86	7.01	4.15	4.21	4.37																	
08/06/86		6.28	3.34																		
08/08/86		6.61	3.41																		
08/09/86		6.08	3.42																		
08/10/86																					
08/11/86		6.68	3.54	3.30	3.16																
08/12/86		6.05	3.36	3.08	2.96	0.33	0.24	0.20	0.26												
08/13/86		6.18	3.17	3.05	2.96	0.55	0.36	0.28													
08/14/86		5.86	3.50																		
08/15/86		3.10	2.92	2.93		0.21	0.08	0.07	0.12												
08/16/86										0.06											
08/17/86		6.36	3.69	3.16	2.98																
08/18/86																					
08/19/86																					
08/20/86		6.04	3.21	2.95	3.04	0.77	0.53	0.48		0.38											
08/21/86		4.40	2.24	2.06	2.00	1.71	0.51	0.40		0.55											
08/22/86		6.20	3.40	3.18	3.12																
08/23/86																					
08/24/86		6.38	3.32	3.04	3.10	1.76	0.82	0.70		0.73											
08/25/86		6.28	3.59	3.32	3.30																
08/26/86		6.24	3.36	3.28	3.24																
08/27/86		6.48	3.60	3.30	3.15	1.82	0.70	0.54		0.52											
08/28/86		6.02	3.56	3.28	3.15	1.97	0.90	0.57	0.50	0.47											
08/29/86		6.35	3.57																		
08/30/86																					
08/31/86		6.27	3.67	3.47	3.31																
09/01/86		6.35	3.42	3.27	3.06																
09/02/86		6.20	3.40	3.26	3.10	0.86	0.48	0.35		0.25											
09/03/86		6.32	3.86	3.28	3.20																
09/04/86		6.60	4.13	3.46	3.23																
09/05/86		6.11	3.56	3.28	3.12	1.92	0.86	1.00	0.96	0.76											
09/06/86		6.47	4.36	3.85	3.68																
09/07/86																					
09/08/86		6.99	4.18	3.58	3.33	1.48	0.80	0.55		0.71											
09/09/86		6.32	3.60	3.22	3.03																
09/10/86		6.46	3.44	3.09	3.82																
09/11/86		6.16	3.06	3.05	2.92																
09/12/86		6.22	3.37	3.11	3.16																
09/13/86																					
09/14/86																					
09/15/86		6.45	3.35	3.16	3.04	1.88	1.22	0.95		0.84											
09/16/86		6.87	4.58	3.70	3.64																
09/17/86		6.68	3.88	3.02	2.98	2.54	1.86	1.42	1.13	0.79											
09/18/86																					

LEGEND: RAW - RAW WATER, CLR - CLARIFIER EFFLUENT, FR1 - FILTER EFFLUENT (GAC INFLUENT)
 F 02 - FILTER EFFLUENT (BAC INFLUENT), MICRO - MICROFLOCCULATION, ND - NOT DETECTABLE
 BAC5 - BAC PORT 06 (HALF WAY THROUGH BAC COLUMN), BEFF - BAC EFFLUENT
 GAC5 - GAC PORT 06 (HALF WAY THROUGH GAC COLUMN), GEFF - GAC EFFLUENT

Table 31. Raw Data for the Newport News Pilot Plant.

DATE	RAW	CLR	F #1	F#2	BAC1	BAC2	BAC3	BAC4	BAC5	BAC6	BAC7	BAC8	BAC9	BAC10	BAC11	BEFF	GAC1	GAC2	GAC3	GAC4	GAC5	GAC6	GAC7	GAC8	GAC9	GAC10	GAC11	BEFF		
08/05/86	1.722	0.525	0.533	0.382												0.078														0.134
08/06/86	1.654	0.500	0.496	0.306	0.090											0.069	0.060	0.052	0.038	0.038	0.007	0.047	0.024							
08/07/86	1.574	0.442														0.007	0.006	0.002	0.003	0.006	0.007	0.004	0.004						0.023	
08/08/86	1.916	0.421														0.010	0.025	0.016	0.016	0.023	0.025	0.023							0.022	
08/09/86	1.786	0.247														0.054	0.043	0.037	0.031	0.040	0.003	0.017							0.028	
08/10/86																0.024	0.026	0.012	0.013	0.016	0.003	0.014							0.016	
08/11/86	1.612	0.280	0.106	0.022	0.006											0.009	0.023	0.009											0.003	
08/12/86	2.358	0.442	0.400	0.236	0.004	0.003	0.002									0.027	0.031	0.013	0.015	0.010	0.025	0.008							0.013	
08/13/86	2.580	0.458	0.390	0.230	0.002	0.001	0.002									0.024	0.029	0.017	0.005	0.014	0.005	0.016							0.008	
08/14/86	1.671	0.343														0.019	0.134	0.012	0.016		0.012	0.025							0.017	
08/15/86	1.740	0.395	0.370	0.224	0.039	0.038	0.014	0.108	0.029							0.019	0.136	0.024	0.025	0.018	0.018	0.010							0.011	
08/16/86																0.011	0.155	0.031	0.011	0.021	0.005	0.003							0.012	
08/17/86	1.501	0.411	0.356	0.218	0.009	0.002										0.014	0.158	0.019	0.001	0.001	0.001	0.002							0.010	
08/18/86																0.012	0.157	0.023	0.001	0.001	0.001	0.001							0.004	
08/19/86																0.003	0.143	0.027	0.012	0.003	0.003	0.001							0.009	
08/20/86	1.672	0.423	0.234	0.299	0.041	0.028	0.018	0.016	0.020							0.047	0.088	0.055	0.054	0.045	0.045	0.003							0.050	
08/21/86	1.723	0.371	0.352	0.192	0.025	0.028	0.013	0.018	0.017							0.010	0.187	0.053	0.008	0.009	0.005	0.003							0.014	
08/22/86	1.712	0.374	0.360	0.183	0.045	0.021	0.019			0.026						0.008	0.029	0.006	0.010	0.003	0.003								0.014	
08/23/86																0.003	0.044	0.001	0.006	0.001	0.001								0.001	
08/24/86	1.438	0.388	0.345	0.223	0.048	0.048	0.015			0.021						0.045	0.103	0.049	0.052	0.041	0.042	0.043							0.024	
08/25/86	1.597	0.372	0.346	0.170	0.069	0.023	0.012	0.013		0.015						0.050	0.331	0.131	0.056	0.043	0.039	0.026	0.031						0.041	
08/26/86	1.513	0.385	0.372	0.203	0.063	0.015	0.011			0.003						0.045	0.323	0.135	0.055	0.071	0.031	0.032							0.041	
08/27/86	1.570	0.382	0.349	0.187	0.091	0.018	0.004	0.004		0.003						0.045	0.323	0.135	0.055	0.071	0.031	0.032							0.041	
08/28/86	1.692	0.423	0.352	0.195	0.101	0.023	0.015			0.014						0.045	0.323	0.135	0.055	0.071	0.031	0.032							0.041	
08/29/86																0.047	0.088	0.055	0.054	0.045	0.045	0.003							0.050	
08/30/86	1.699	0.380	0.693	0.719	0.147	0.069	0.058	0.054		0.057						0.010	0.187	0.053	0.008	0.009	0.005	0.003							0.014	
09/01/86	1.633	0.394	0.344	0.274	0.081	0.025	0.010	0.044		0.012						0.003	0.029	0.006	0.010	0.003	0.003								0.014	
09/02/86	1.538	0.375	0.338	0.188	0.028	0.002	0.013			0.010						0.003	0.044	0.001	0.006	0.001	0.001								0.001	
09/03/86	1.552	0.368	0.330	0.162	0.033	0.009	0.028			0.002						0.045	0.103	0.049	0.052	0.041	0.042	0.043							0.024	
09/04/86	1.673	0.530	0.482	0.200	0.058	0.040	0.031	0.040	0.036	0.048						0.050	0.331	0.131	0.056	0.043	0.039	0.026	0.031						0.041	
09/05/86	1.686	0.580	0.489	0.233	0.180	0.103	0.070	0.053		0.048						0.045	0.323	0.135	0.055	0.071	0.031	0.032							0.041	
09/06/86	1.817	0.529	0.468	0.216	0.215	0.090	0.059	0.043		0.043						0.017	0.172	0.071	0.017	0.016	0.010	0.002							0.015	
09/07/86																0.016	0.172	0.071	0.017	0.016	0.010	0.002							0.015	
09/08/86	1.682	0.607	0.468	0.201	0.179	0.080	0.054			0.014						0.038	0.175	0.093	0.019	0.023	0.009	0.007							0.034	
09/09/86	1.872	0.512	0.449	0.170	0.068	0.032	0.017	0.020	0.036							0.007	0.153	0.068	0.016	0.009	0.004	0.002							0.005	
09/10/86	1.741	0.584	0.429	0.183	0.053	0.028	0.017	0.011		0.011						0.017	0.187	0.087	0.045	0.033	0.031	0.002							0.005	
09/11/86	1.889	0.445	0.410	0.283	0.072	0.037	0.041	0.028	0.031							0.017	0.187	0.087	0.045	0.033	0.031	0.002							0.005	
09/12/86	1.901	0.644	0.490	0.265												0.017	0.187	0.087	0.045	0.033	0.031	0.002							0.005	
09/13/86																0.017	0.187	0.087	0.045	0.033	0.031	0.002							0.005	
09/14/86																2.910	0.207	0.104	0.041	0.021	0.001	0.001							0.001	
09/15/86	1.923	0.493	0.466	0.284	0.078	0.029	0.001	0.023	0.015	0.018						0.241	0.242	0.128	0.069	0.030	0.025	0.014							0.002	
09/16/86	1.953	0.756	0.484	0.292	0.127	0.078	0.050	0.044	0.038	0.044						0.005	0.378	0.244	0.120	0.059	0.024	0.012							0.006	
09/17/86	1.890	0.799	0.416	0.239	0.101	0.011	0.051	0.030	0.017	0.008						0.005	0.378	0.244	0.120	0.059	0.024	0.012							0.006	
09/18/86																0.005	0.378	0.244	0.120	0.059	0.024	0.012							0.006	

ALL MEASUREMENTS MADE WITH A 10 cm PATHLENGTH
 LEGEND: RAW - RAW WATER, CLR - CLARIFIER EFFLUENT, F#1 - FILTER EFFLUENT (GAC INFILTRANT), F#2 - FILTER EFFLUENT (GAC INFILTRANT), MICRO - MICROFLOCCULATION, ND - NOT DETECTABLE
 BAC6 - BAC POINT #6 (HALF WAY THROUGH BAC COLUMN), BEFF - BAC EFFLUENT

Appendix B
THMFP Breakthrough Curves for GAC at Each
THM Treatment Level

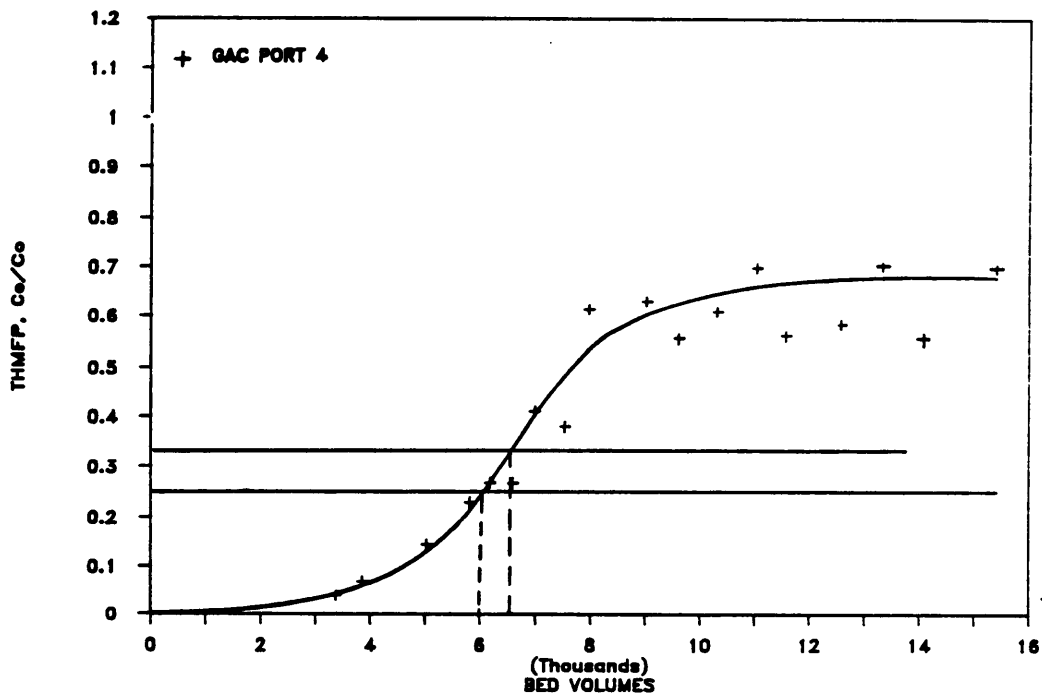
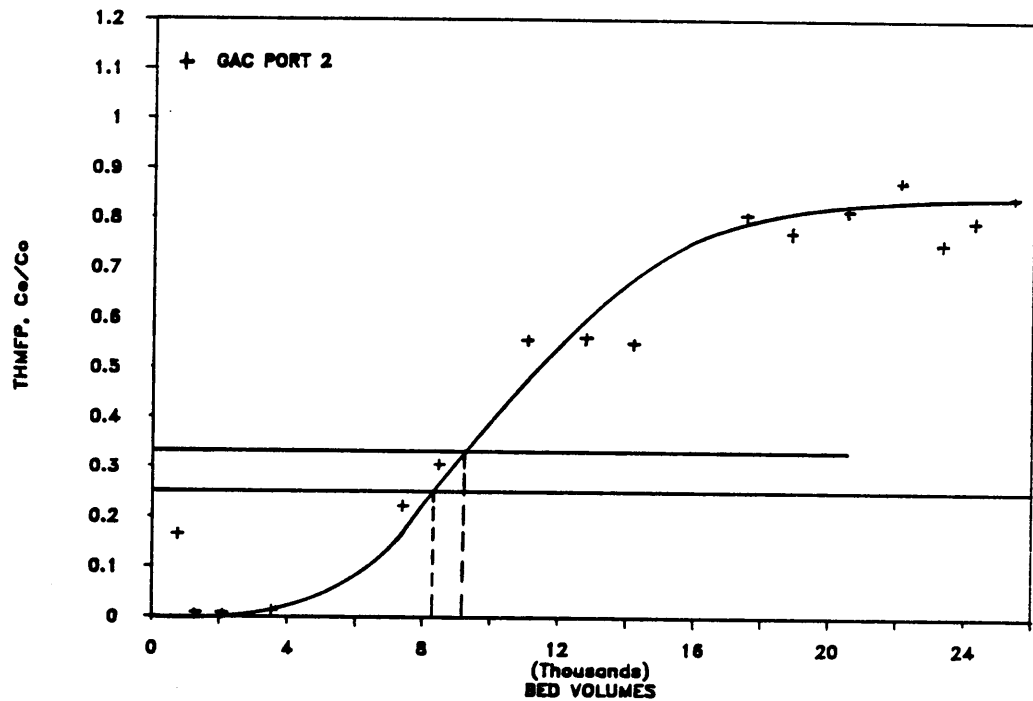


Figure 30. THMFP Breakthrough Curves for GAC ports 2 and 4 (20 and 44-in depth) for 25 $\mu\text{g/L}$ system THM Treatment Level.

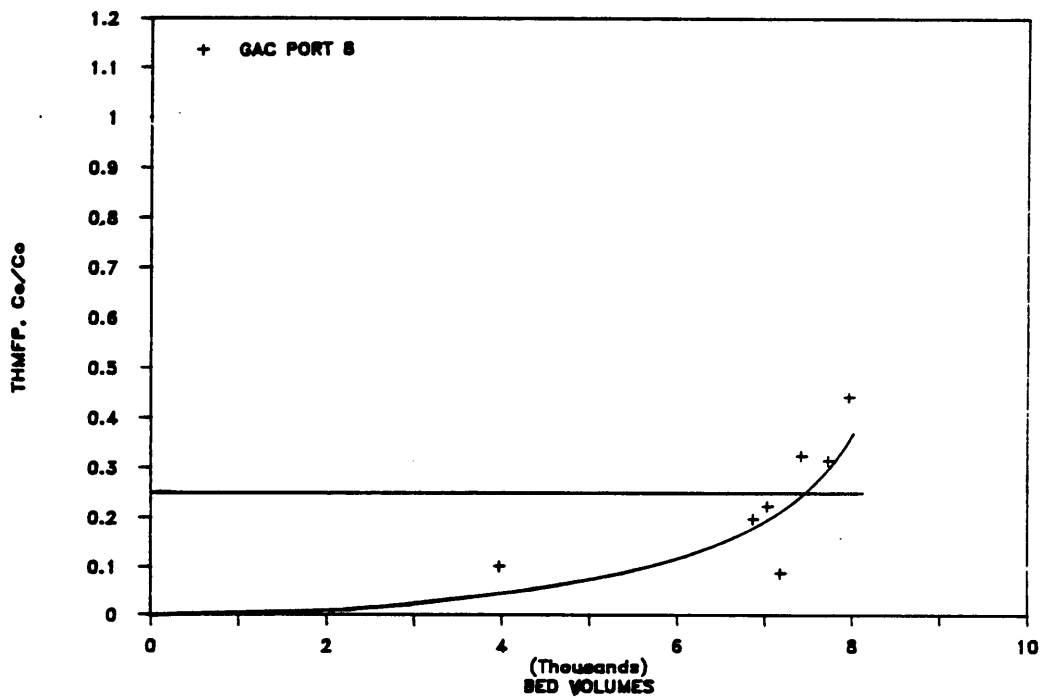
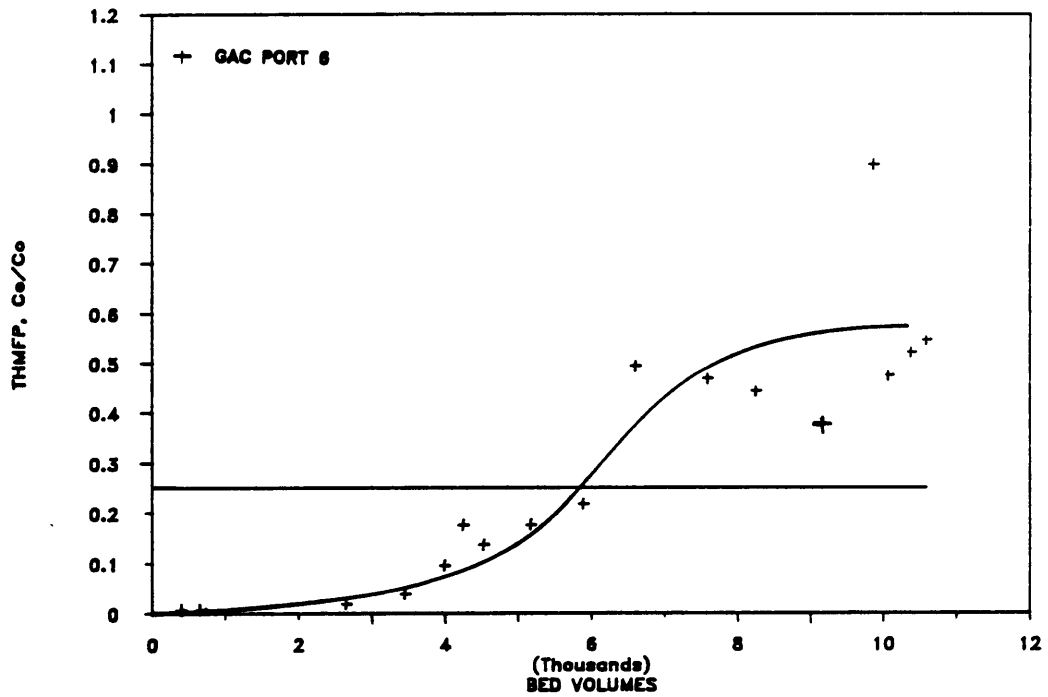


Figure 31. THMFP Breakthrough Curves for GAC ports 6 and 8 (64 and 84-in depth) for 25 $\mu\text{g/L}$ system THM Treatment Level.

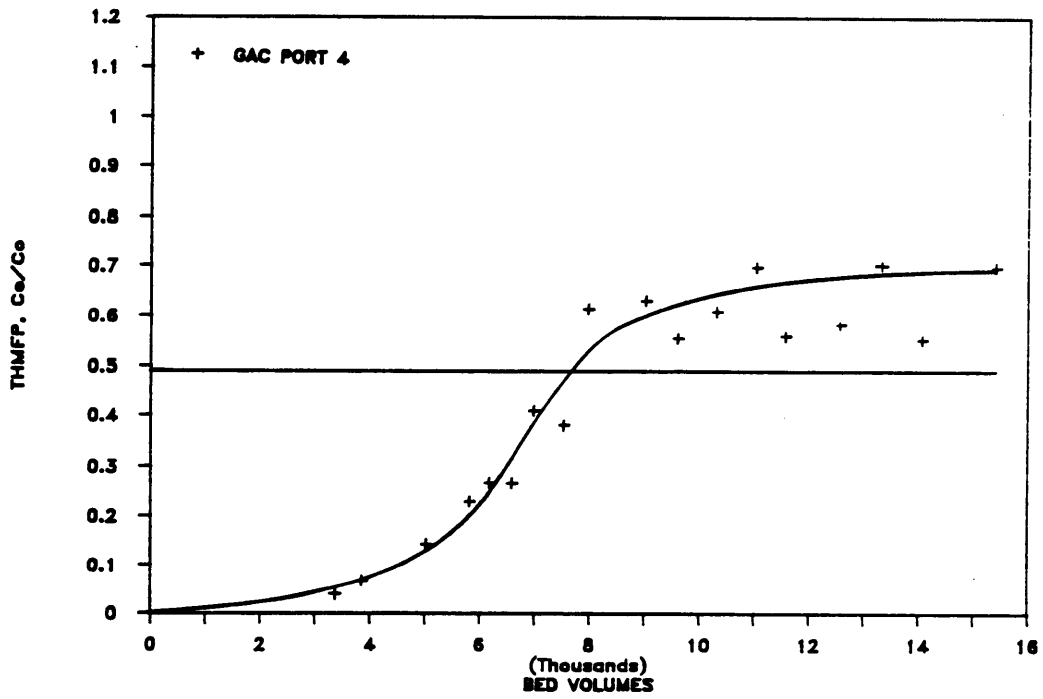
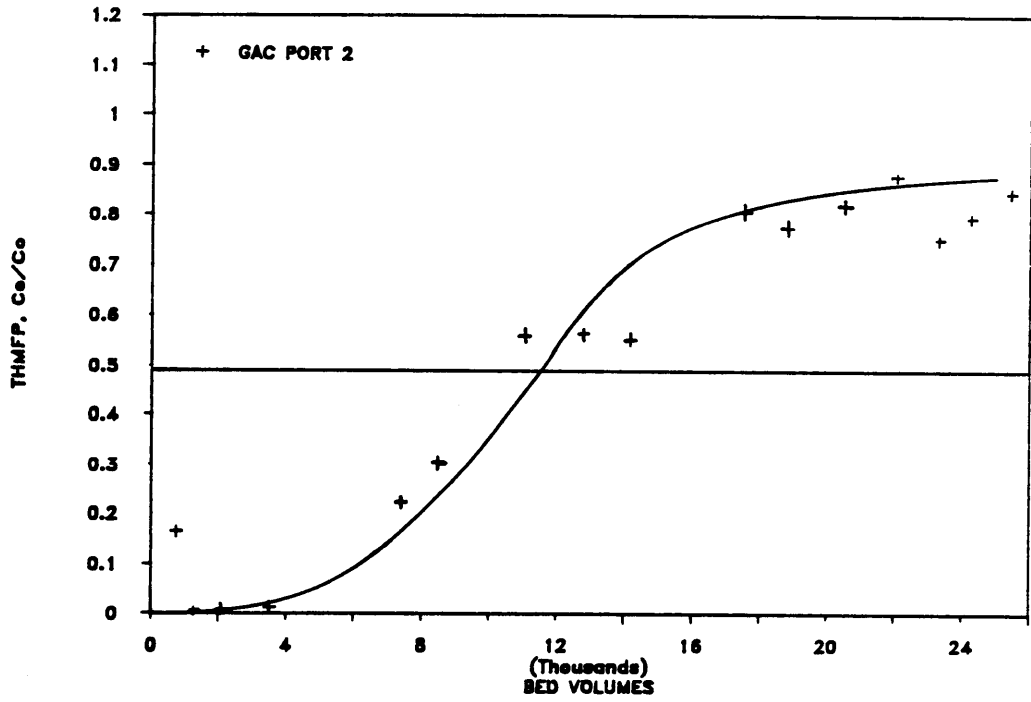


Figure 32. THMFP Breakthrough Curves for GAC ports 2 and 4 (20 and 44-in depth) for 50 µg/L system THM Treatment Level.

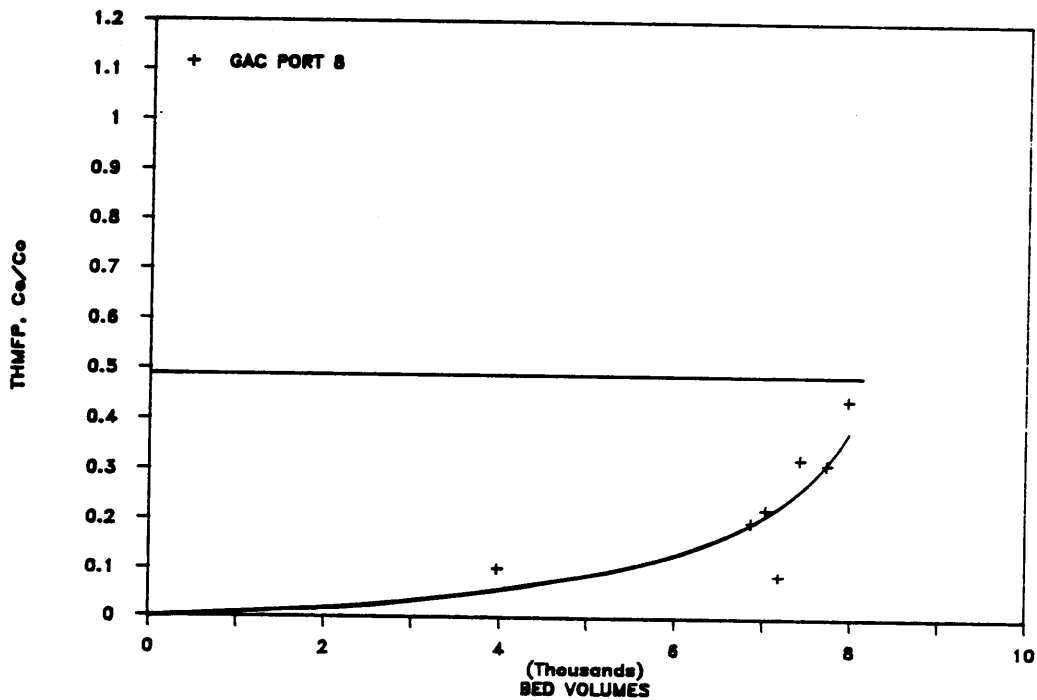
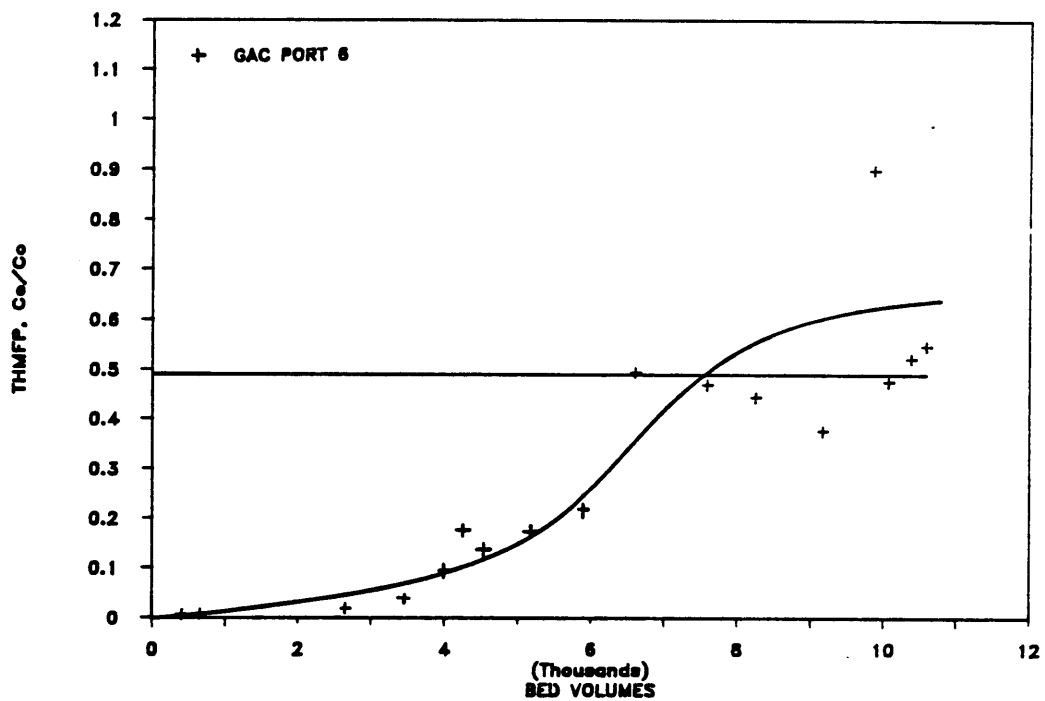


Figure 33. THMFP Breakthrough Curves for GAC ports 6 and 8 (64 and 84-in depth) for 50 µg/L system THM Treatment Level.

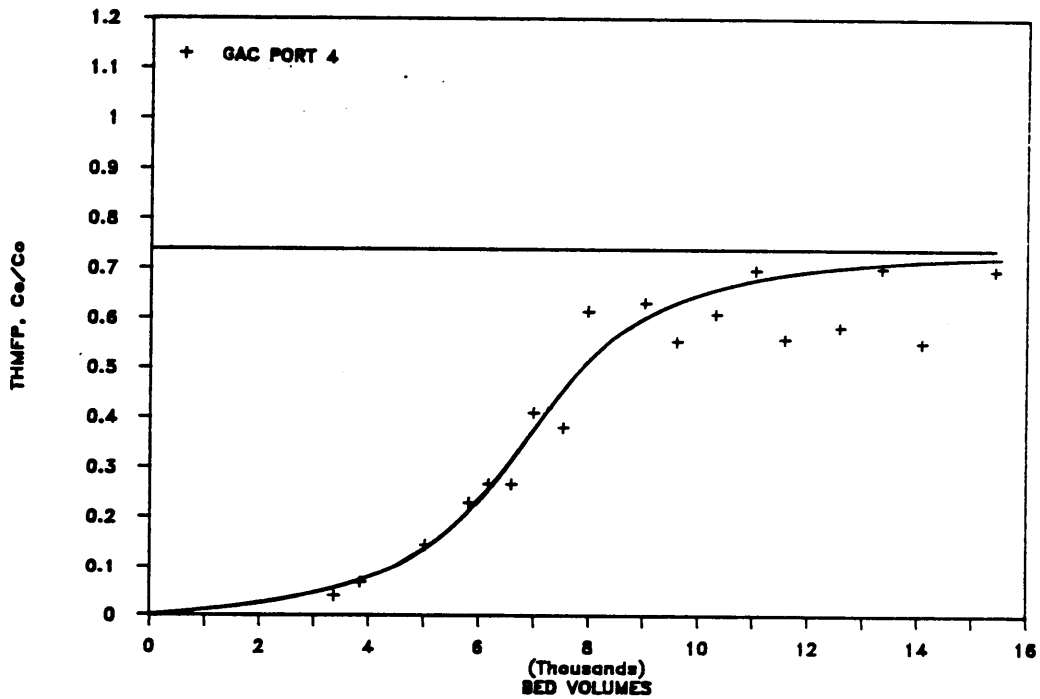
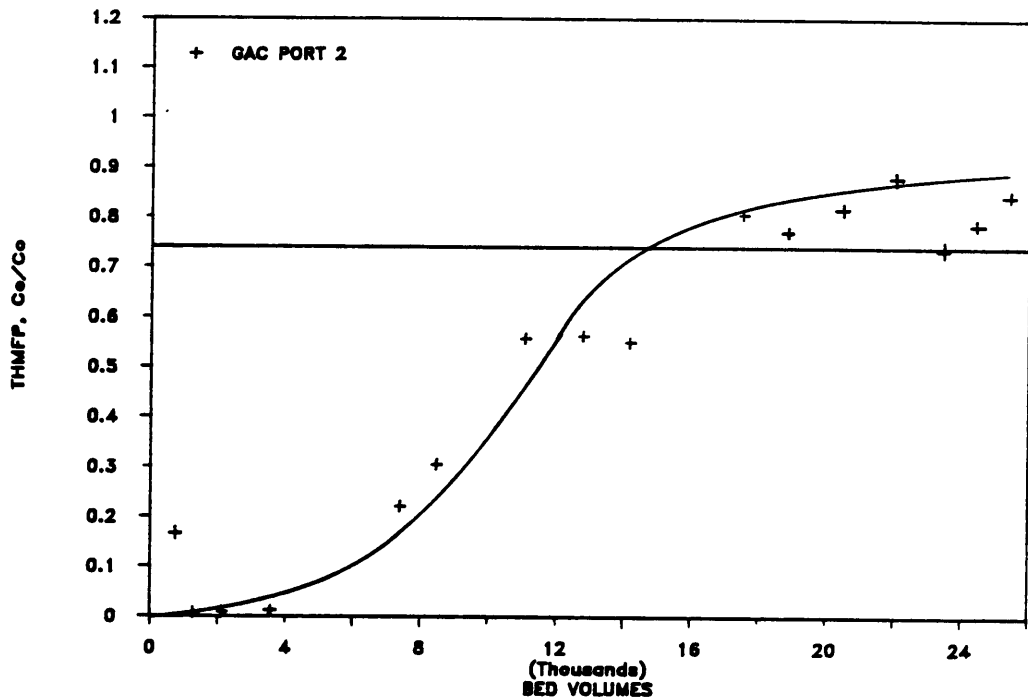


Figure 34. THMFP Breakthrough Curves for GAC ports 2 and 4 (20 and 44-in depth) for 75 $\mu\text{g/L}$ system THM Treatment Level.

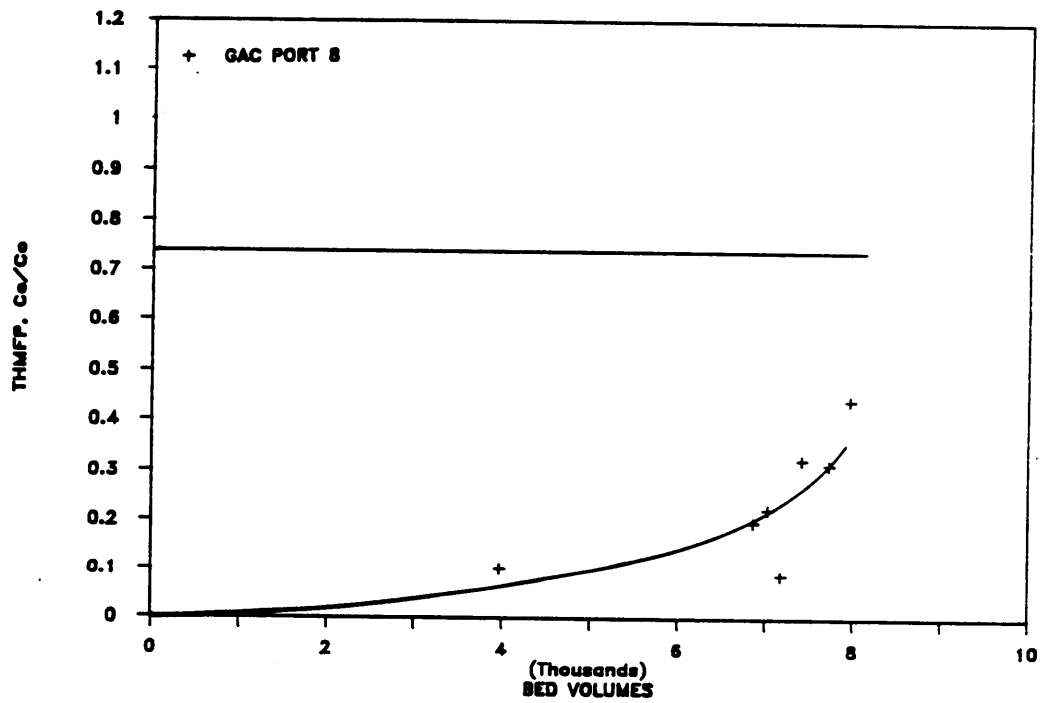
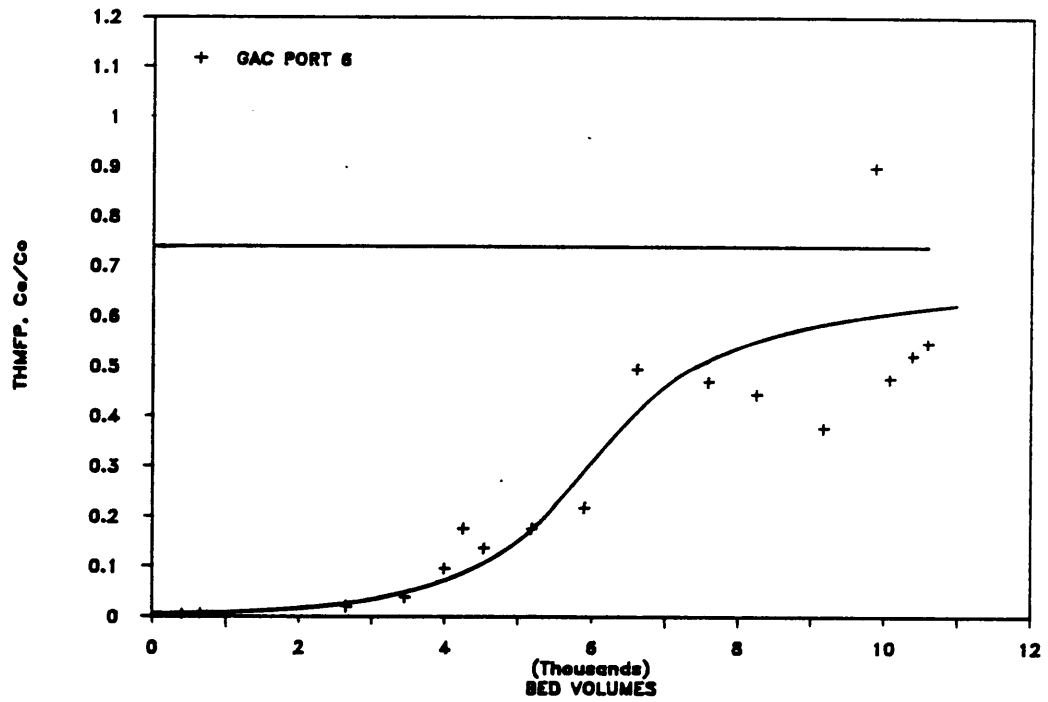


Figure 35. THMFP Breakthrough Curves for GAC ports 6 and 8 (64 and 84-in depth) for 75 µg/L system THM Treatment Level.

Appendix C
THMFP Breakthrough Curves for BAC at Each
THM Treatment Level

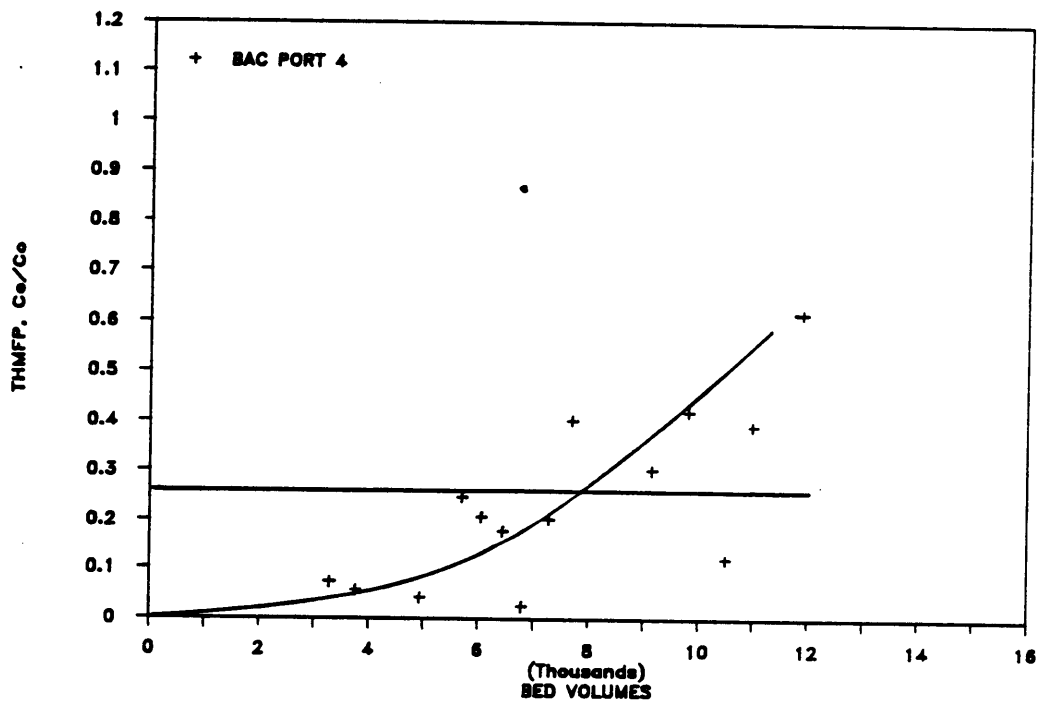
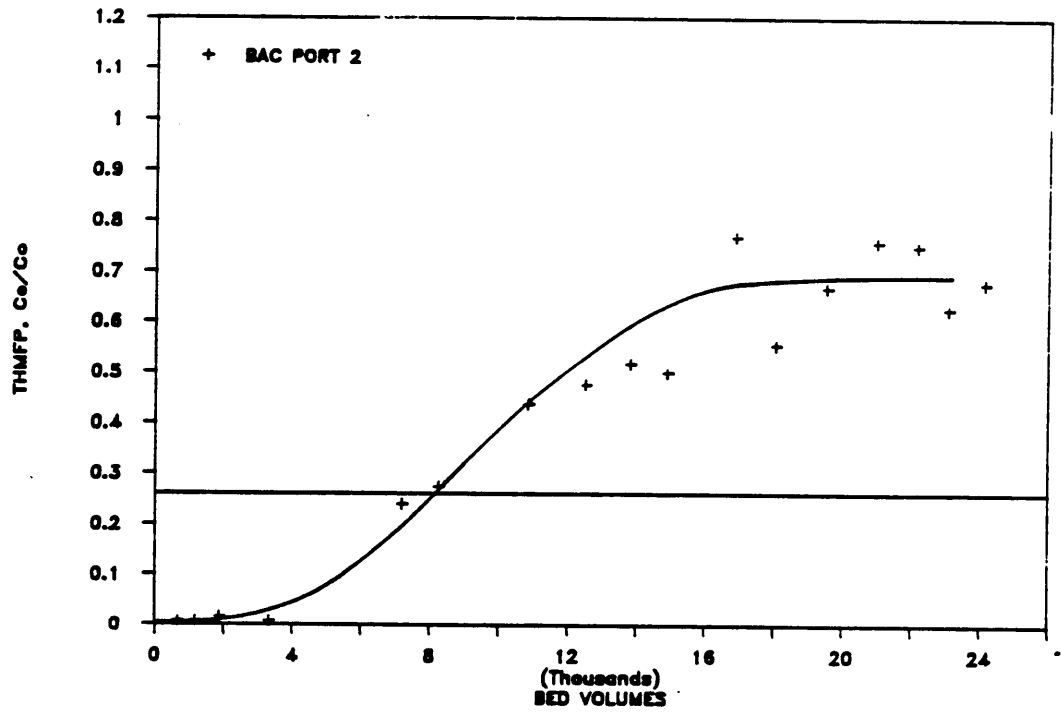


Figure 36. THMFP Breakthrough Curves for BAC ports 2 and 4 (20 and 44-in depth) for 25 $\mu\text{g/L}$ system THM Treatment Level.

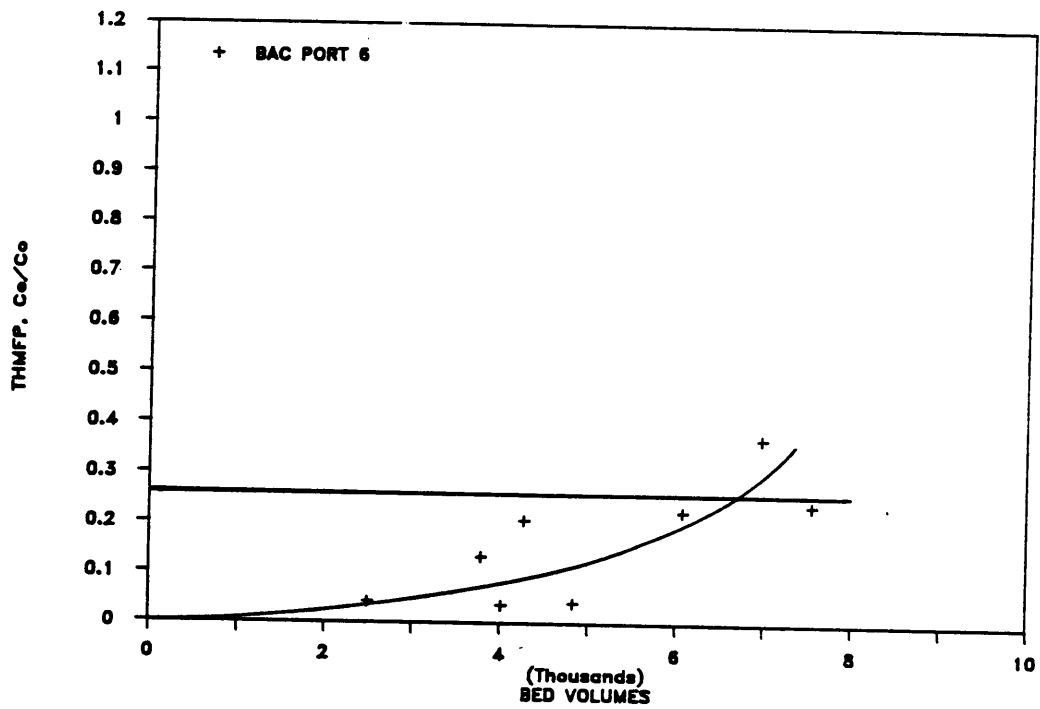


Figure 37. THMFP Breakthrough Curve for BAC port 6 (64-in depth) for 25 $\mu\text{g/L}$ system THM Treatment Level.

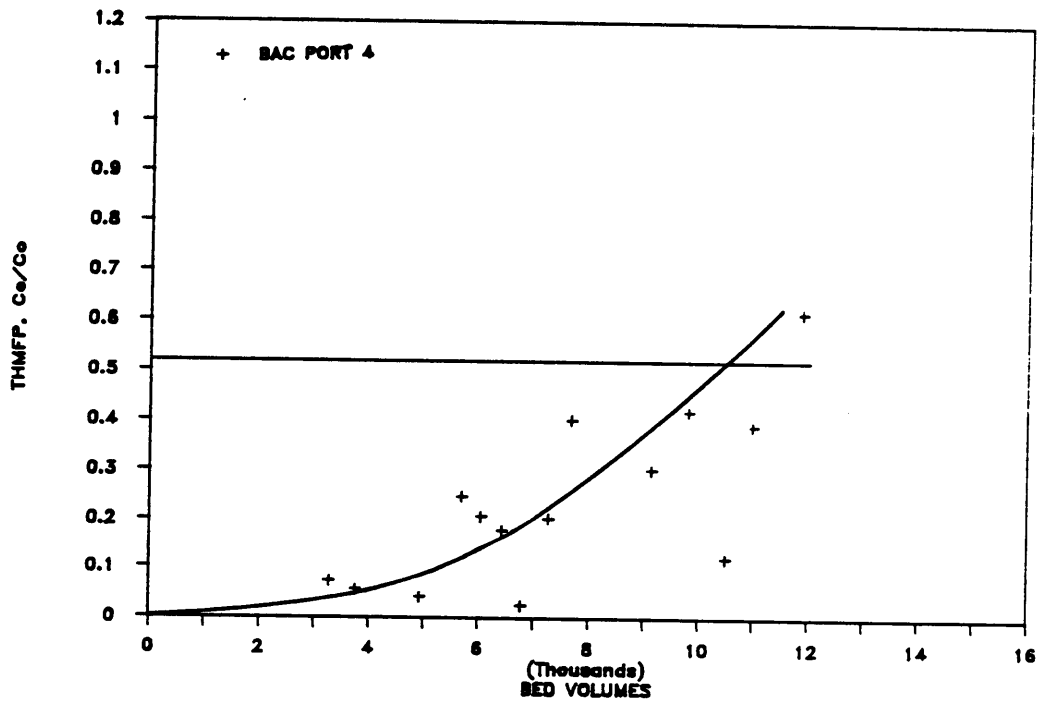
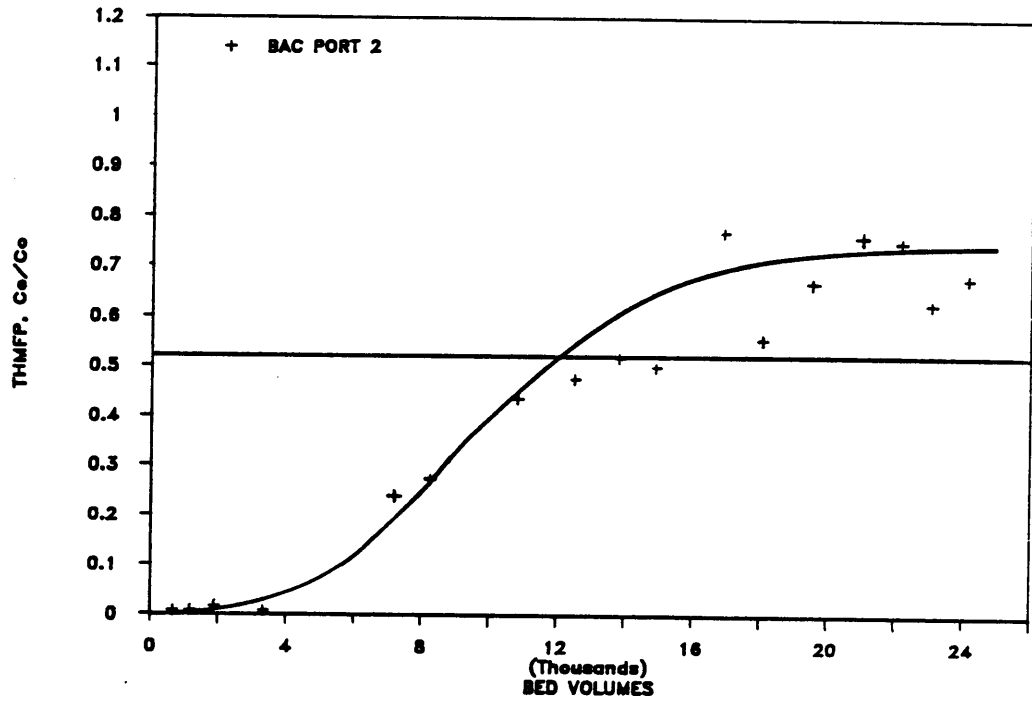


Figure 38. THMFP Breakthrough Curves for BAC ports 2 and 4 (20 and 44-in depth) for 50 µg/L system THM Treatment Level.

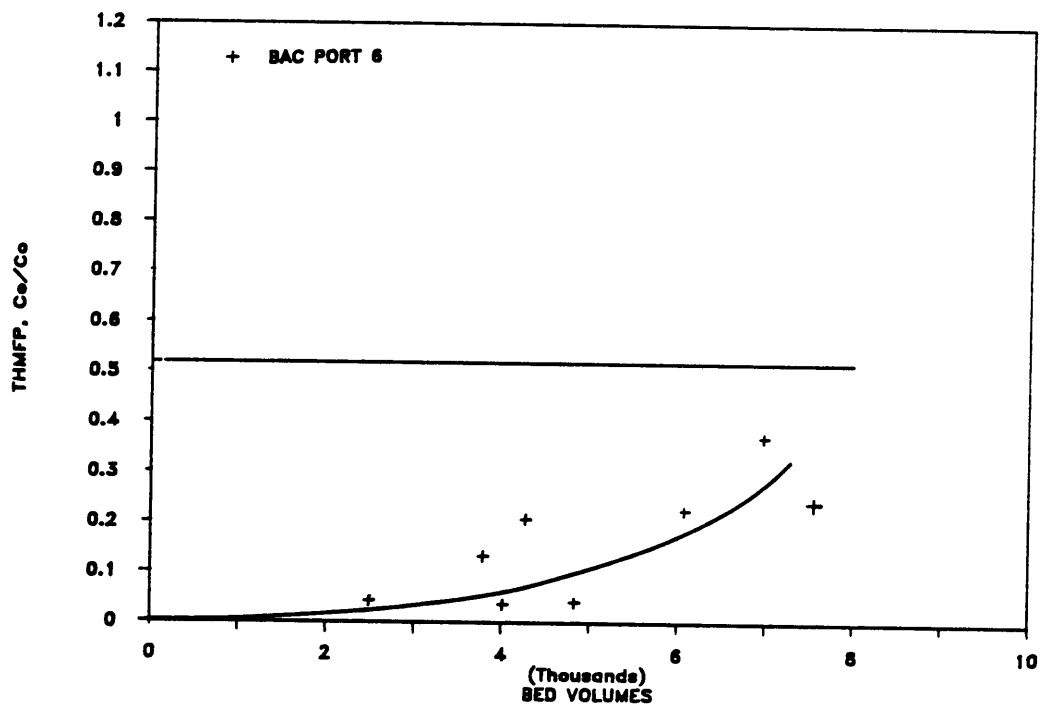


Figure 39. THMFP Breakthrough Curve for BAC port 6 (64-in depth) for 50 $\mu\text{g/L}$ system THM Treatment Level.

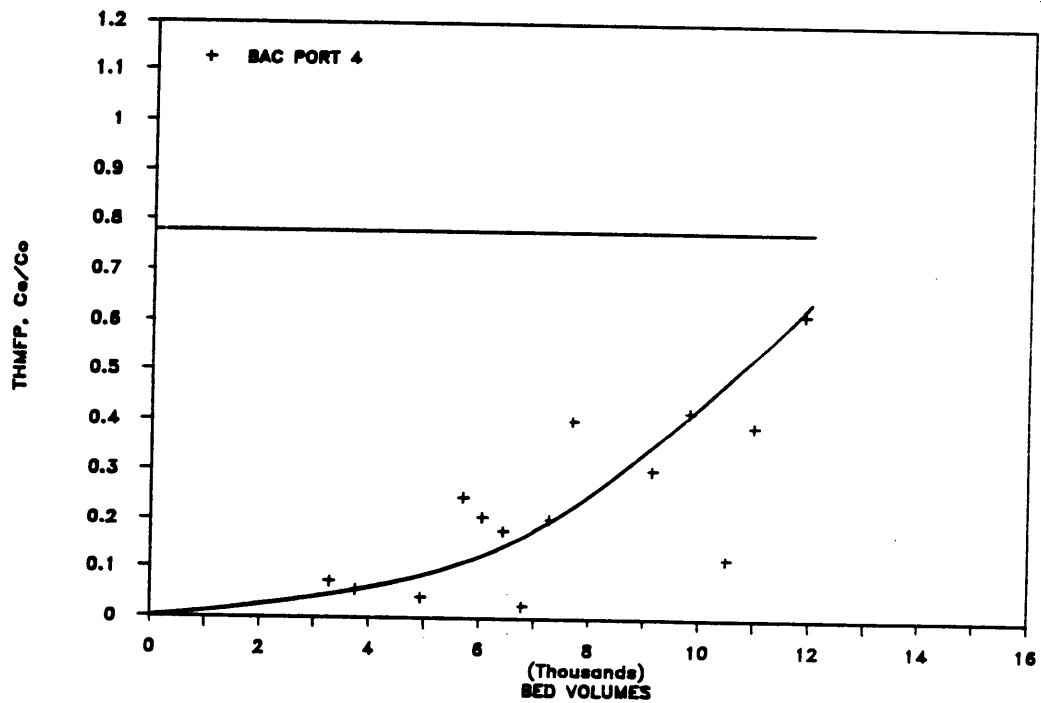
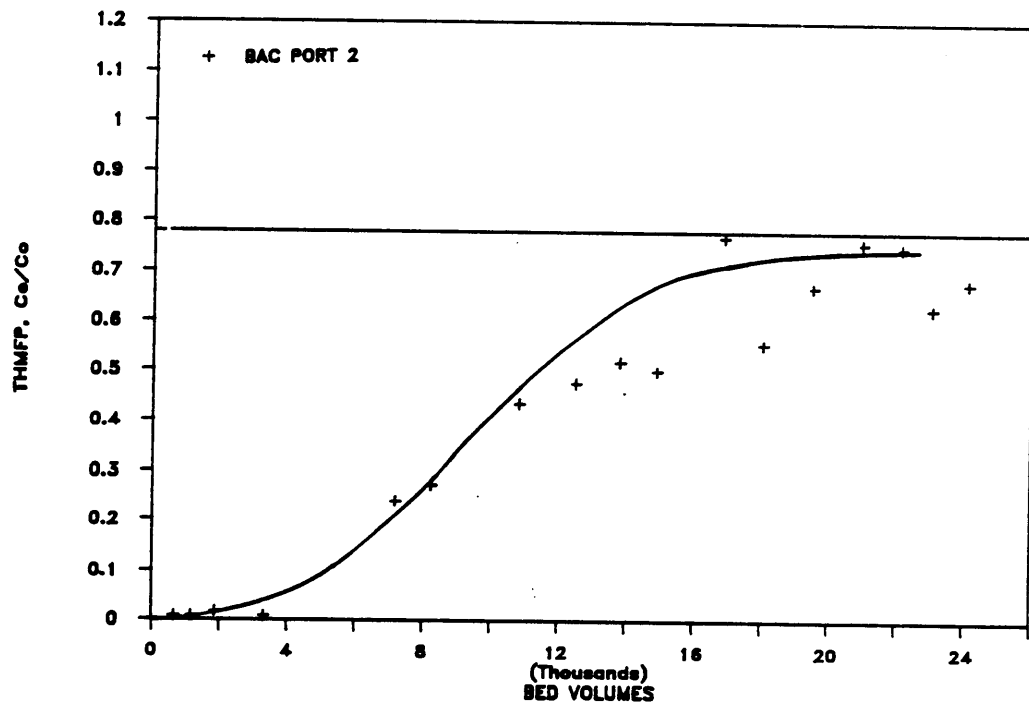


Figure 40. THMFP Breakthrough Curves for BAC ports 2 and 4 (20 and 44-in depth) for 75 µg/L system THM Treatment Level.

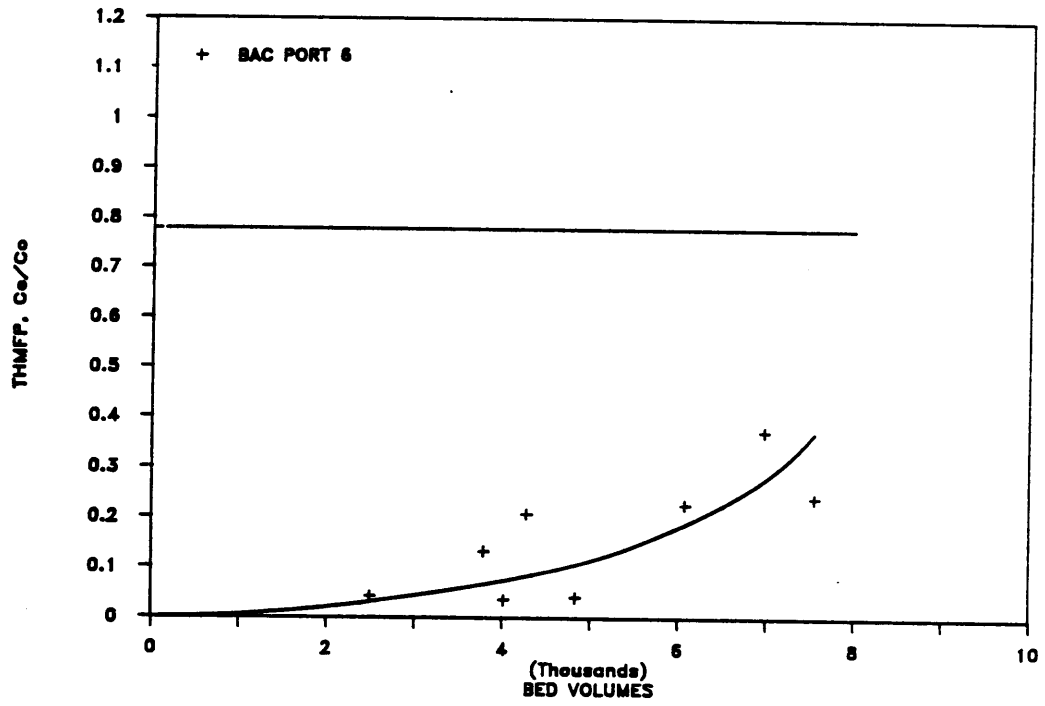


Figure 41. THMFP Breakthrough Curve for BAC port 6 (64-in depth) for 75 $\mu\text{g/L}$ system THM Treatment Level.

Appendix D
TOC Breakthrough Curves for the GAC and
BAC Columns

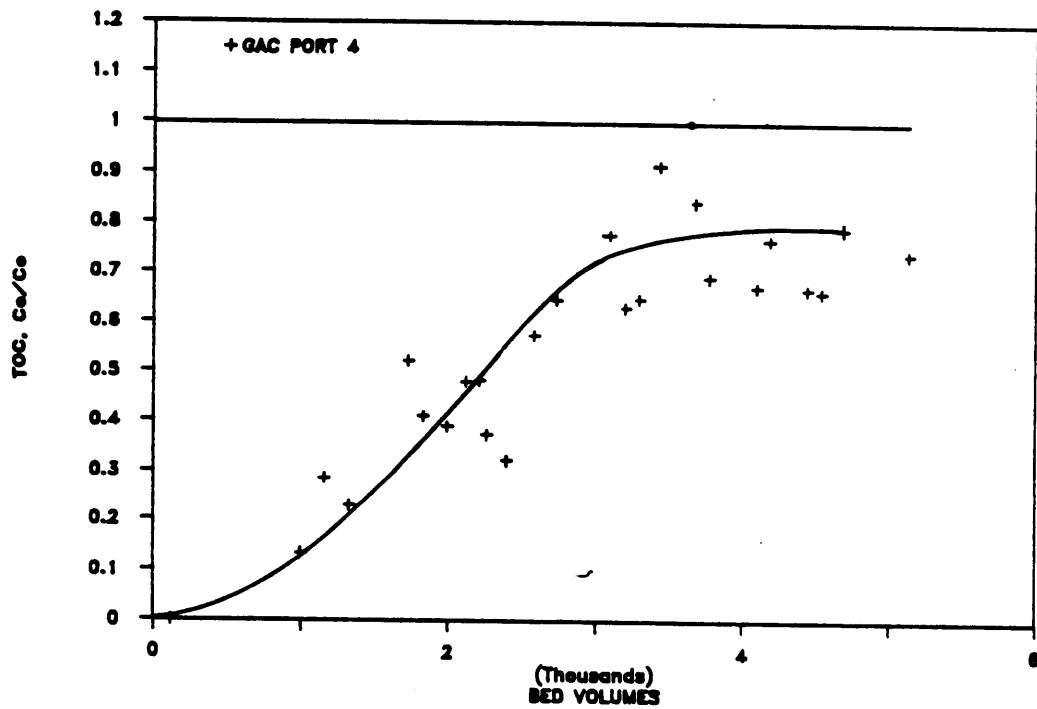
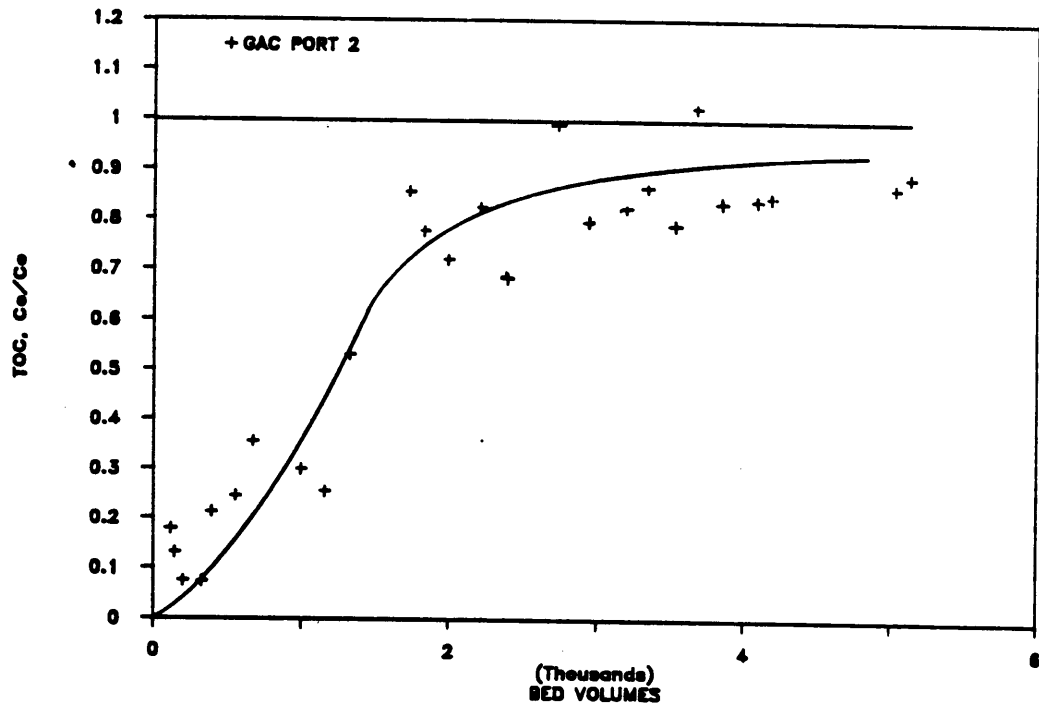


Figure 42. TOC Breakthrough Curves for GAC ports 2 and 4 (20 and 44-in depth).

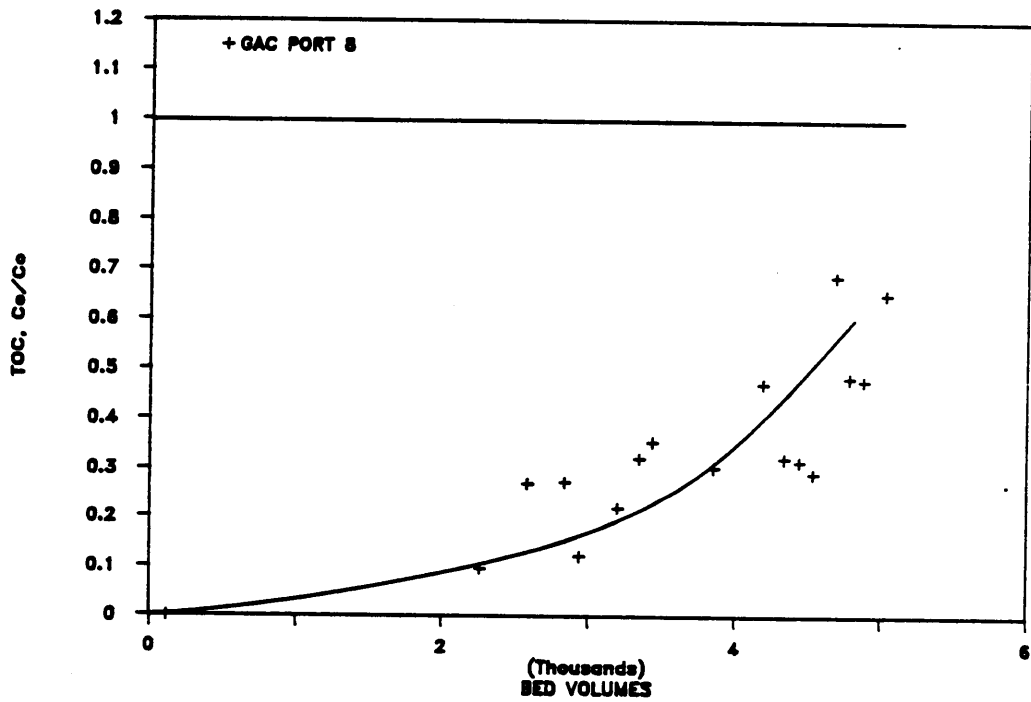
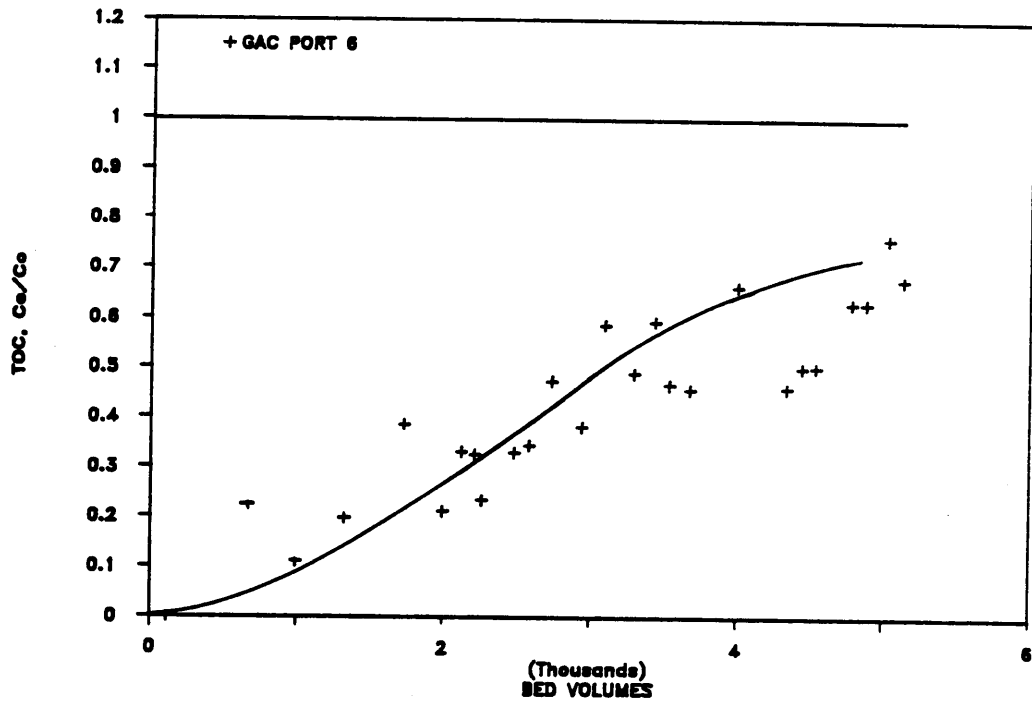


Figure 43. TOC Breakthrough Curves for GAC ports 6 and 8 (64 and 84-in depth).

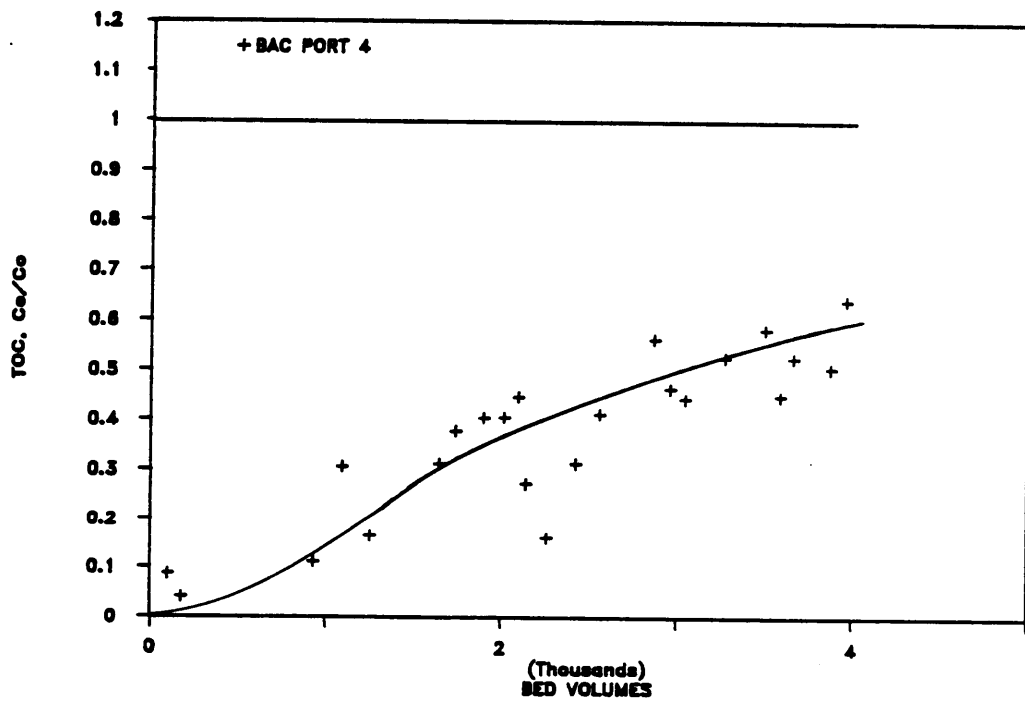
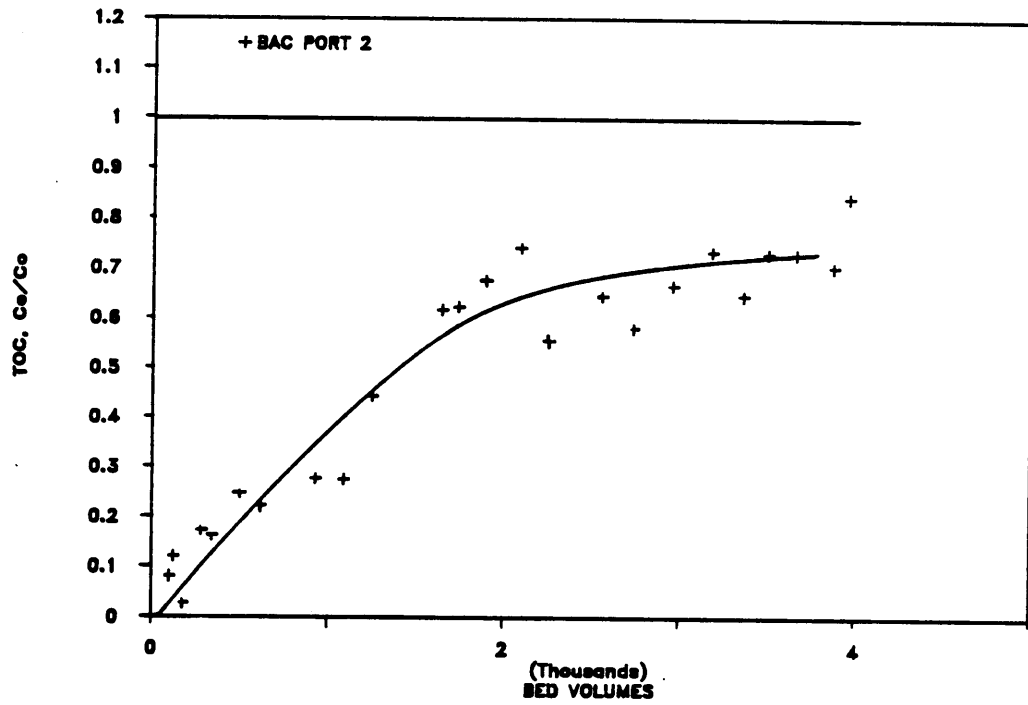


Figure 44. TOC Breakthrough Curves for BAC ports 2 and 4 (20 and 44-in depth).

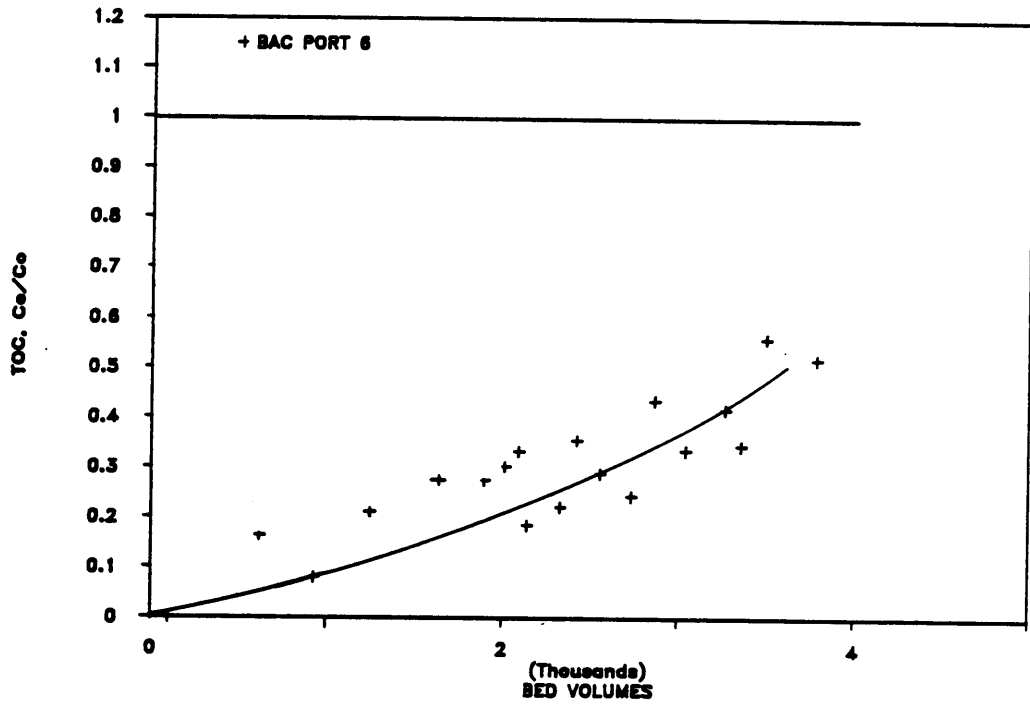


Figure 45. TOC Breakthrough Curve for BAC port 6 (64-in depth).

Appendix E
UV254 as a Surrogate for THMFP in the BAC
and GAC Column

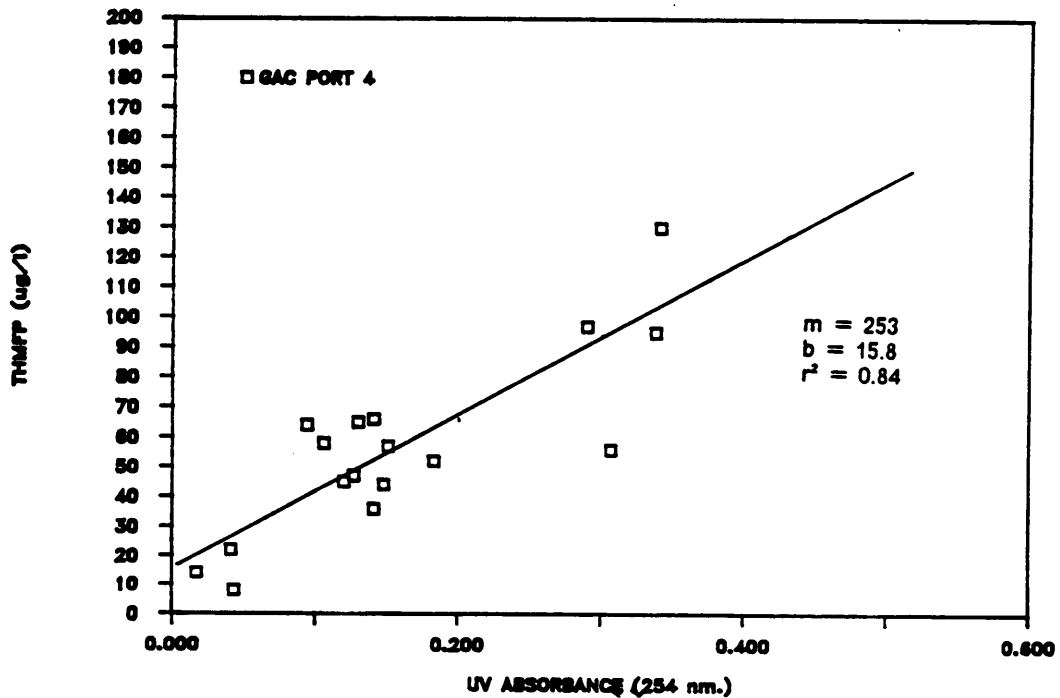
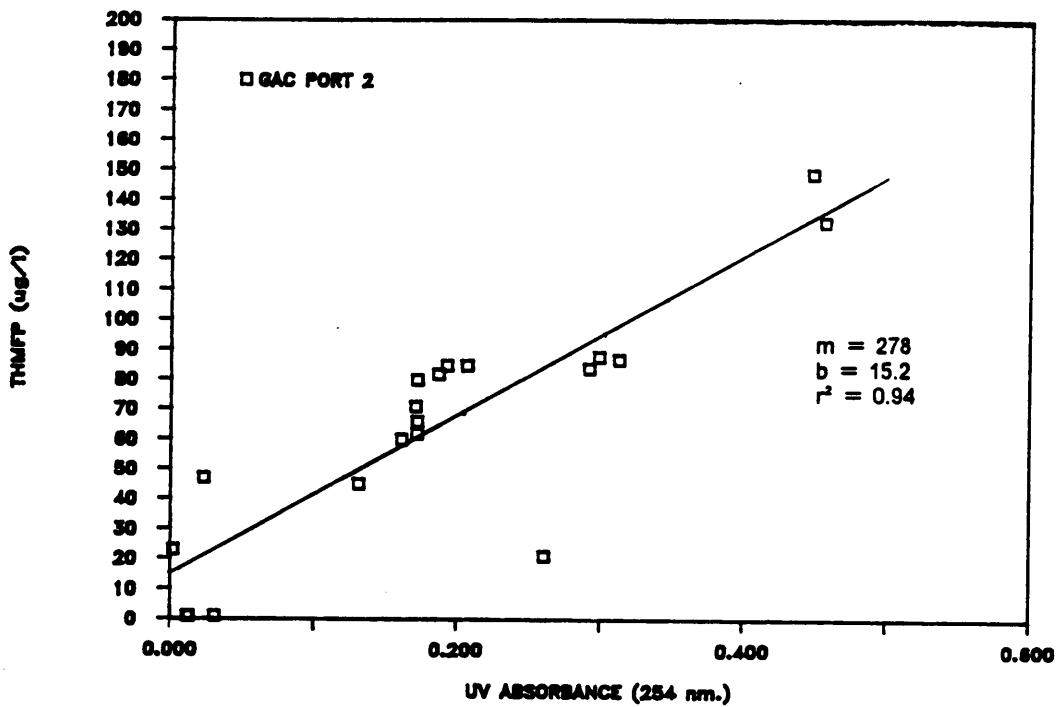


Figure 46. UV Absorbance (measured at 254 nm using a 10 cm cell) as a Surrogate Parameter for THMFP in GAC ports 2 and 4.

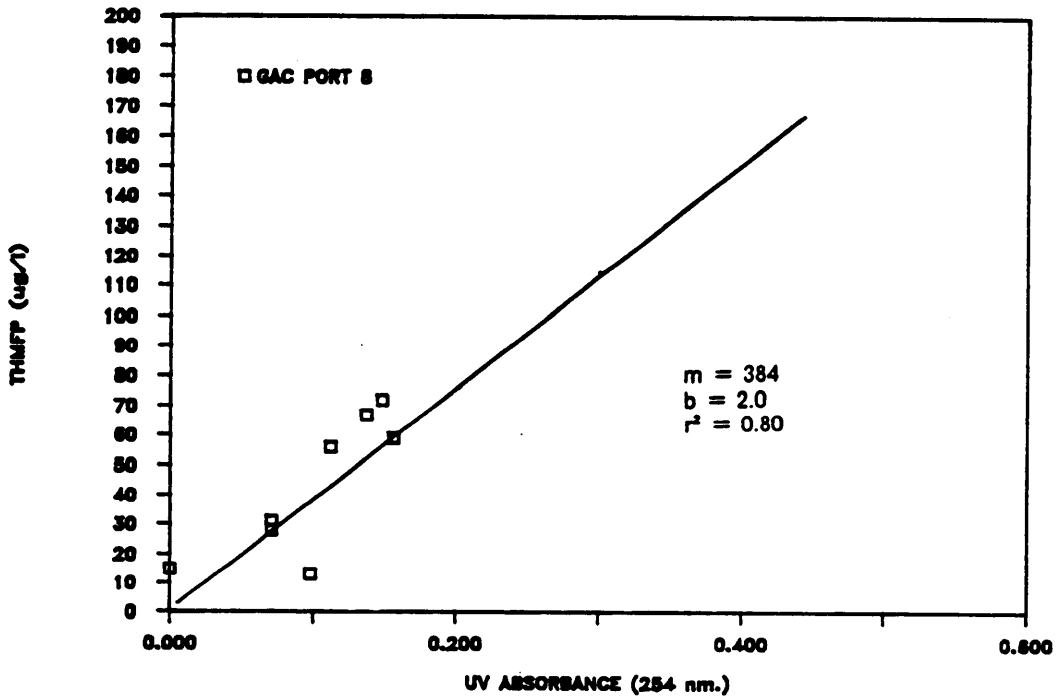
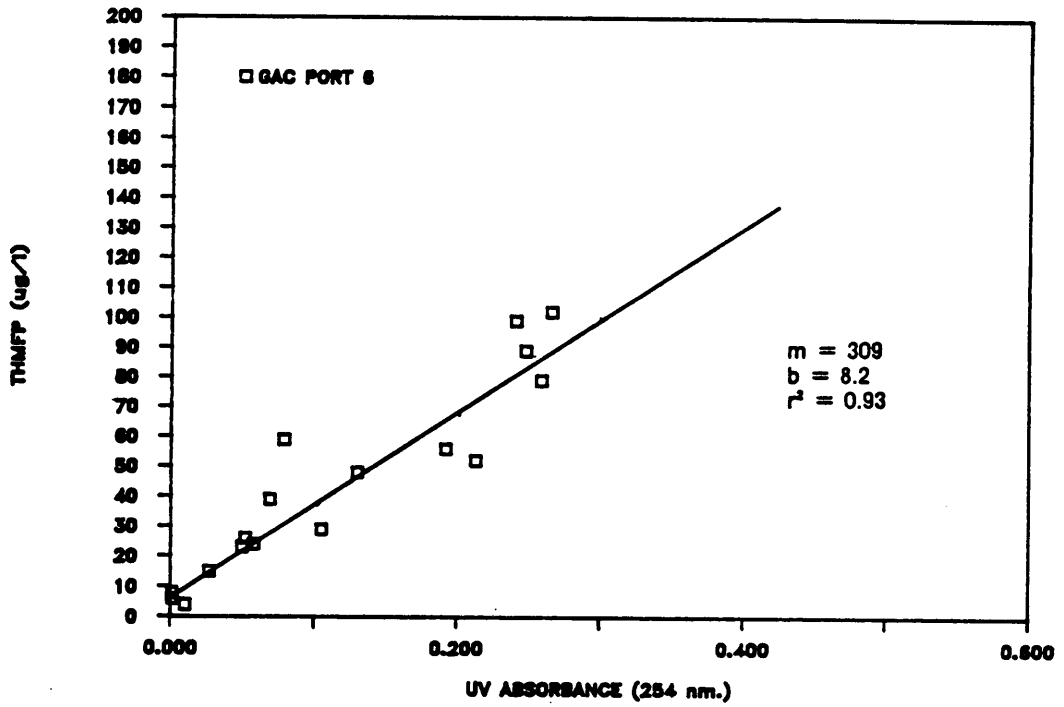


Figure 47. UV Absorbance (measured at 254 nm using a 10 cm cell) as a Surrogate Parameter for THMFP in GAC ports 6 and 8.

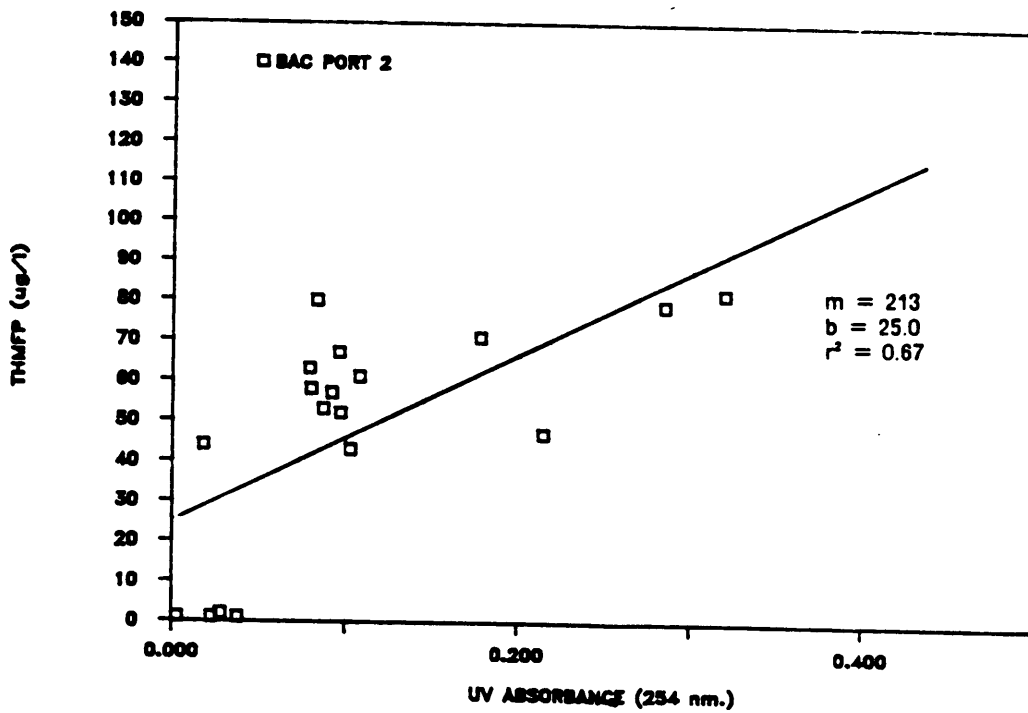


Figure 48. UV Absorbance (measured at 254 nm using a 10 cm cell) as a Surrogate Parameter for THMFP in BAC port 2.

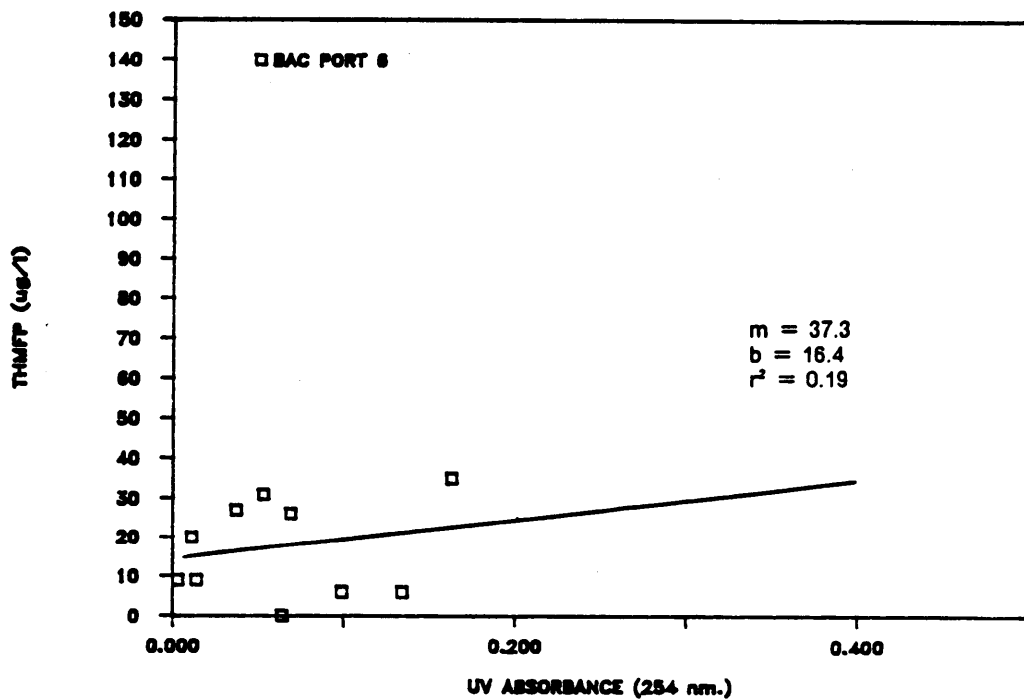
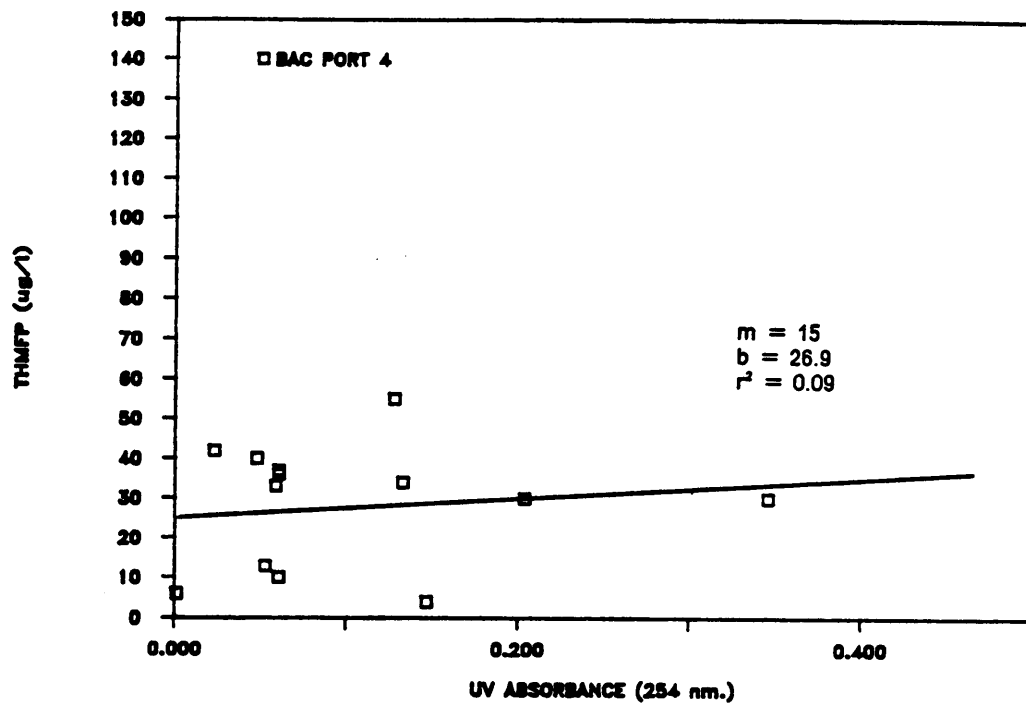


Figure 49. UV Absorbance (measured at 254 nm using a 10 cm cell) as a Surrogate Parameter for THMFP in BAC ports 4 and 6.

Appendix F
TOC as a Surrogate for THMFP in the GAC
and BAC Column

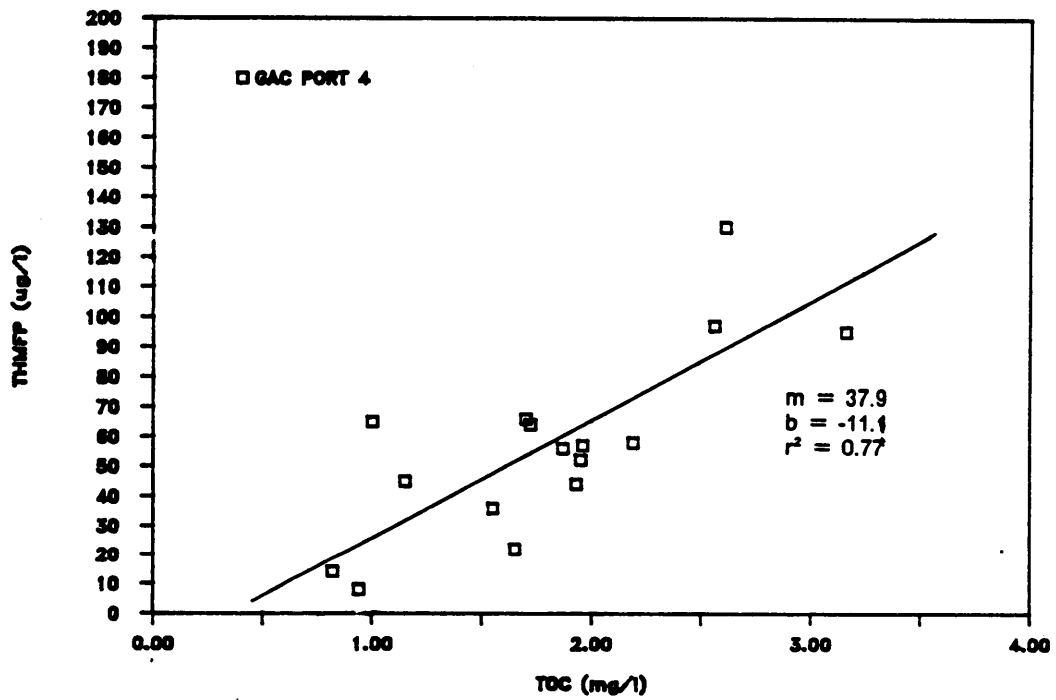
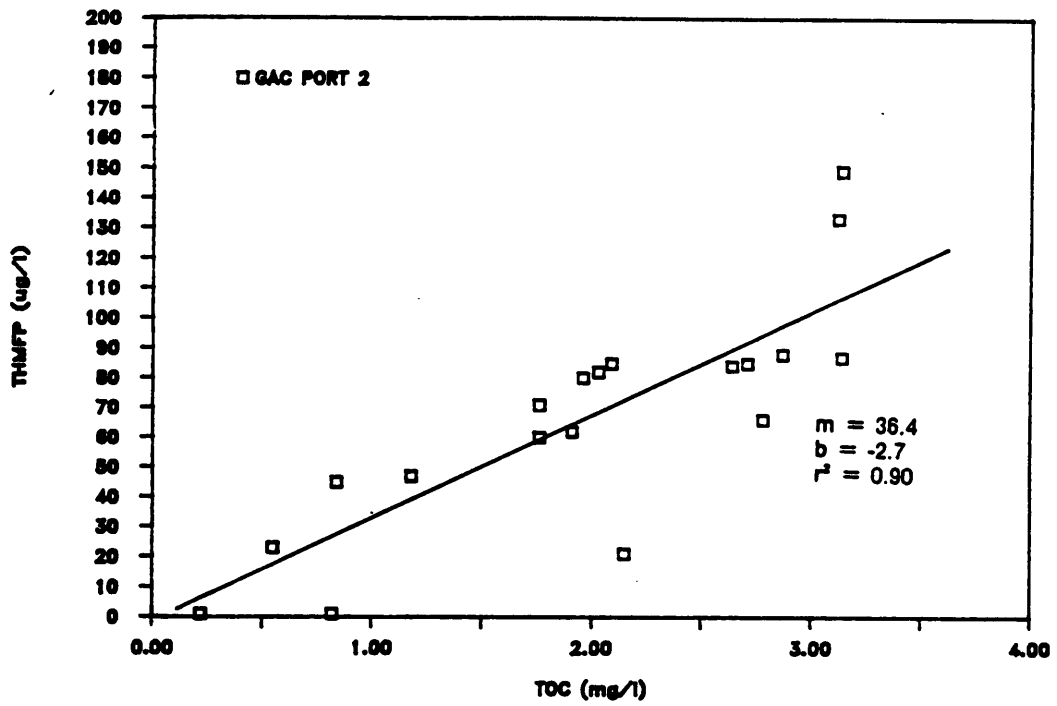


Figure 50. TOC as a Surrogate Parameter for THMFP in GAC ports 2 and 4.

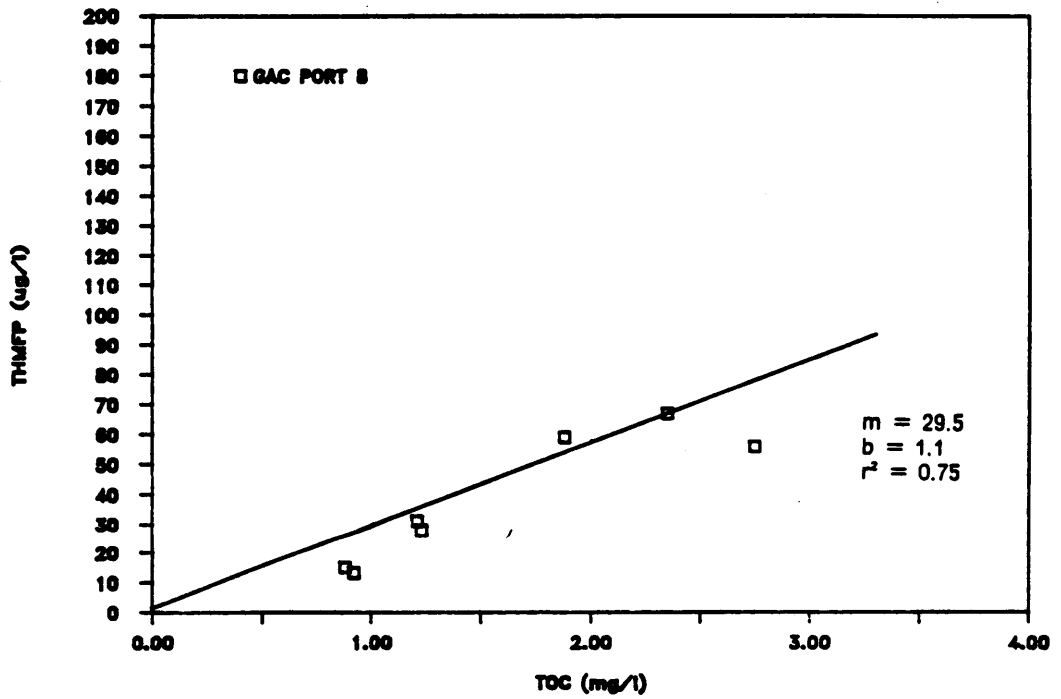
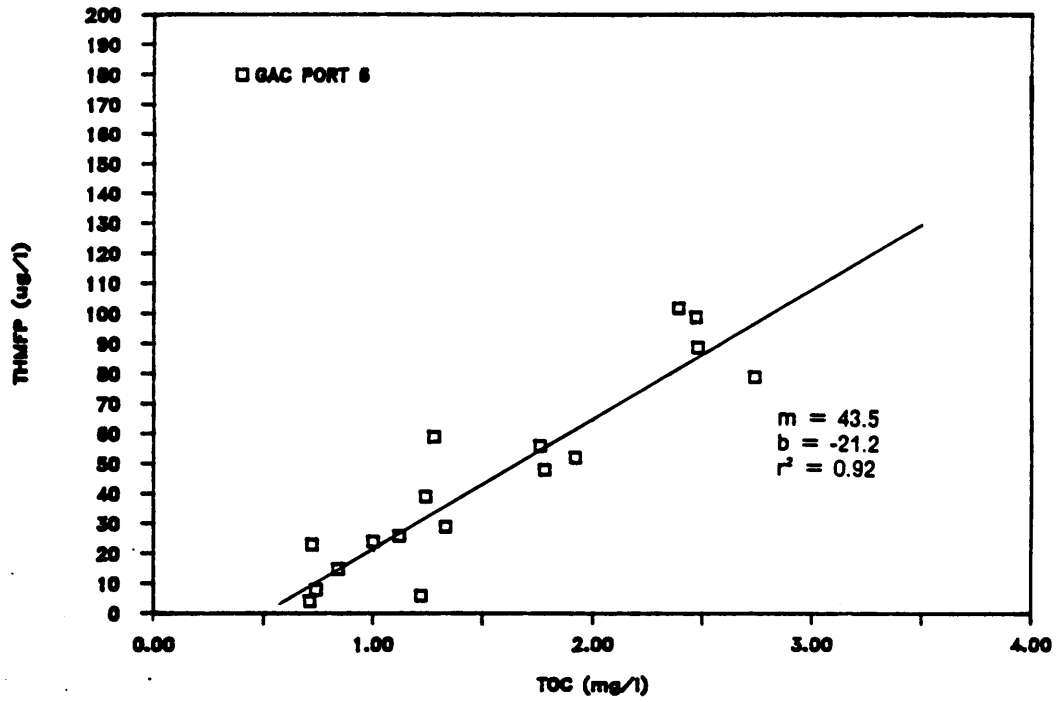


Figure 51. TOC as a Surrogate Parameter for THMFP in GAC ports 6 and 8.

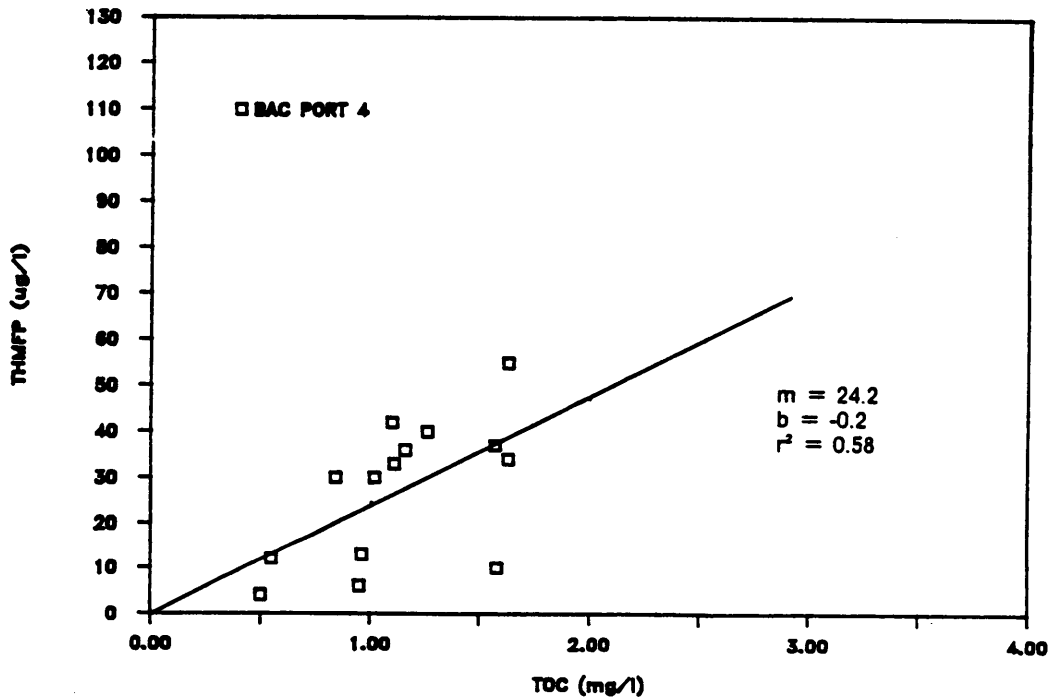
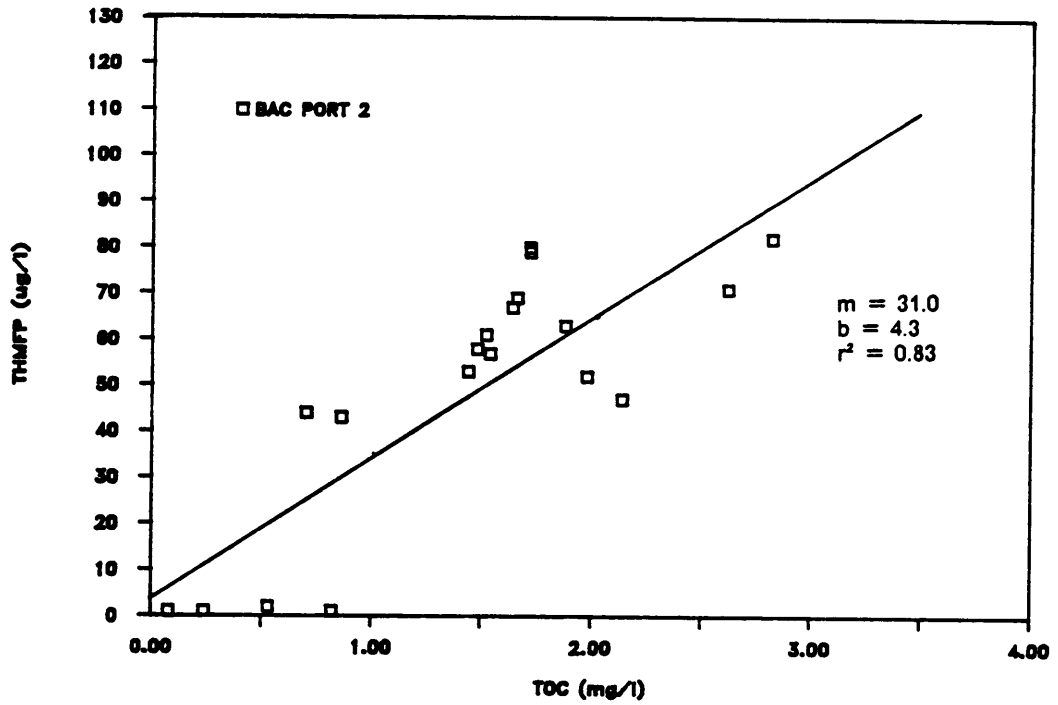


Figure 52. TOC as a Surrogate Parameter for THMFP in BAC ports 2 and 4.

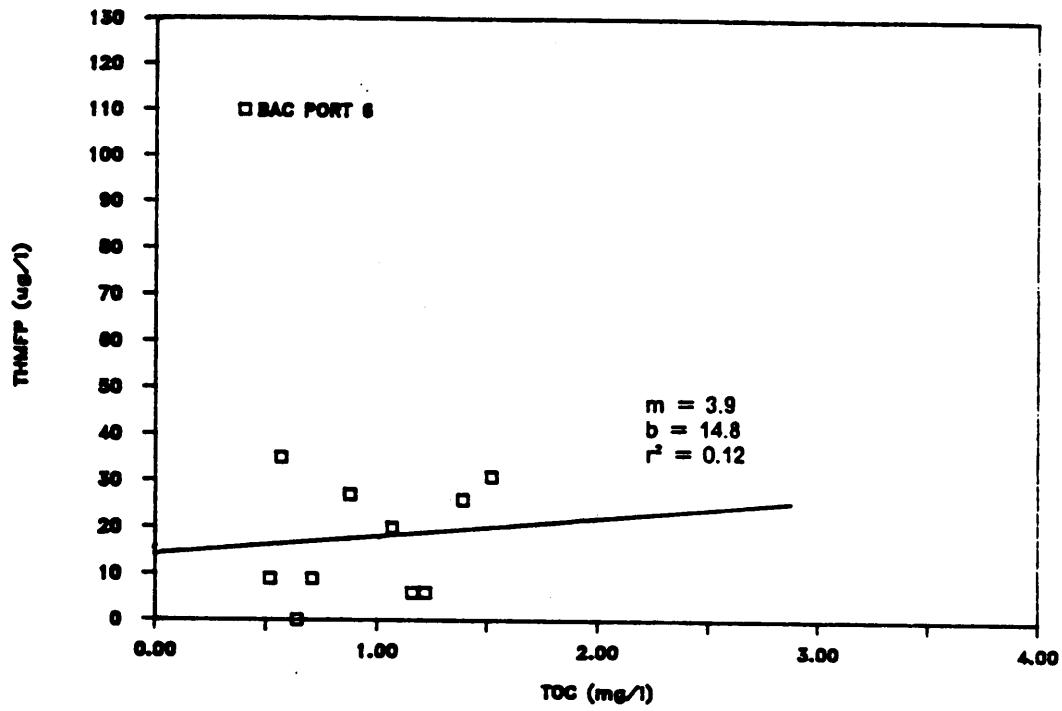


Figure 53. TOC as a Surrogate Parameter for THMFP in BAC port 6.

Appendix G
TOC and UV254 as a Surrogate for THMFP in
the Raw Water and Clarifier Effluent

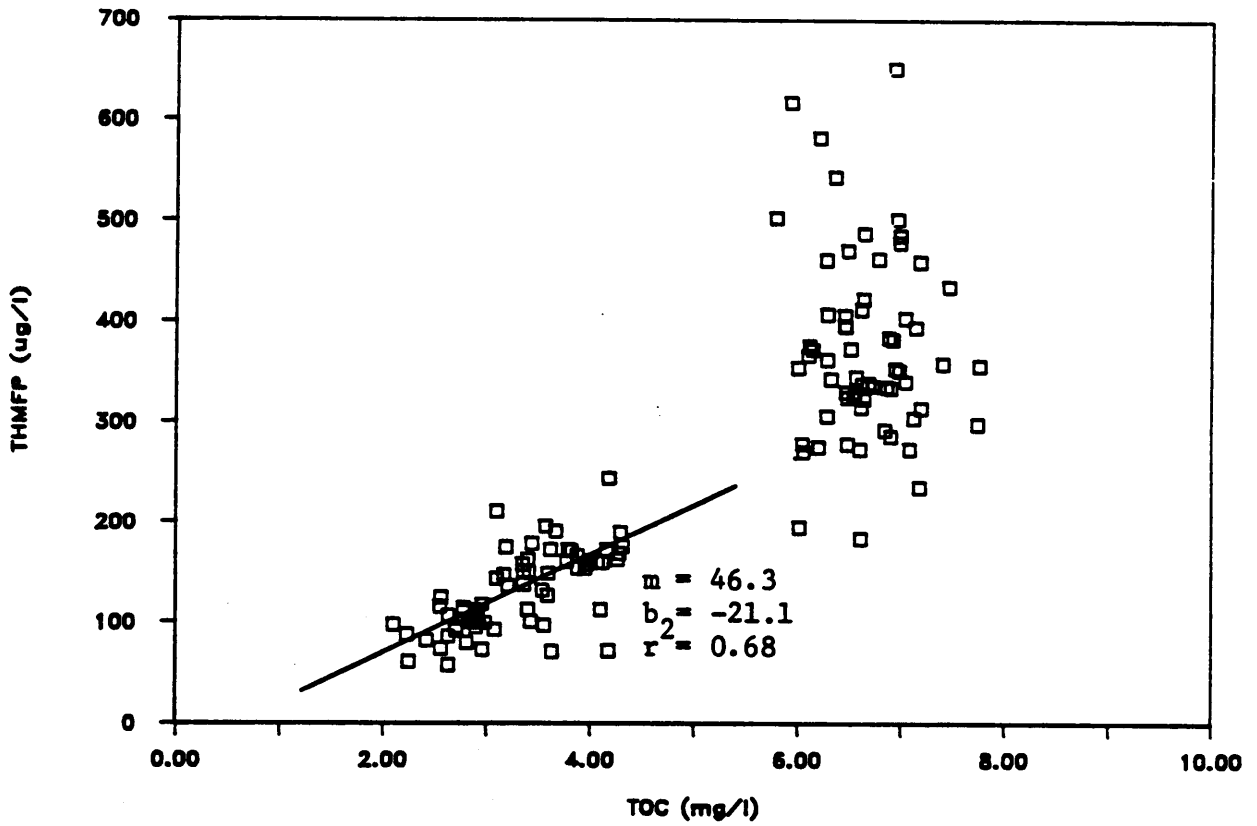


Figure 54. TOC as a Predictor for THMFP in the Raw Water and Clarifier Effluent.

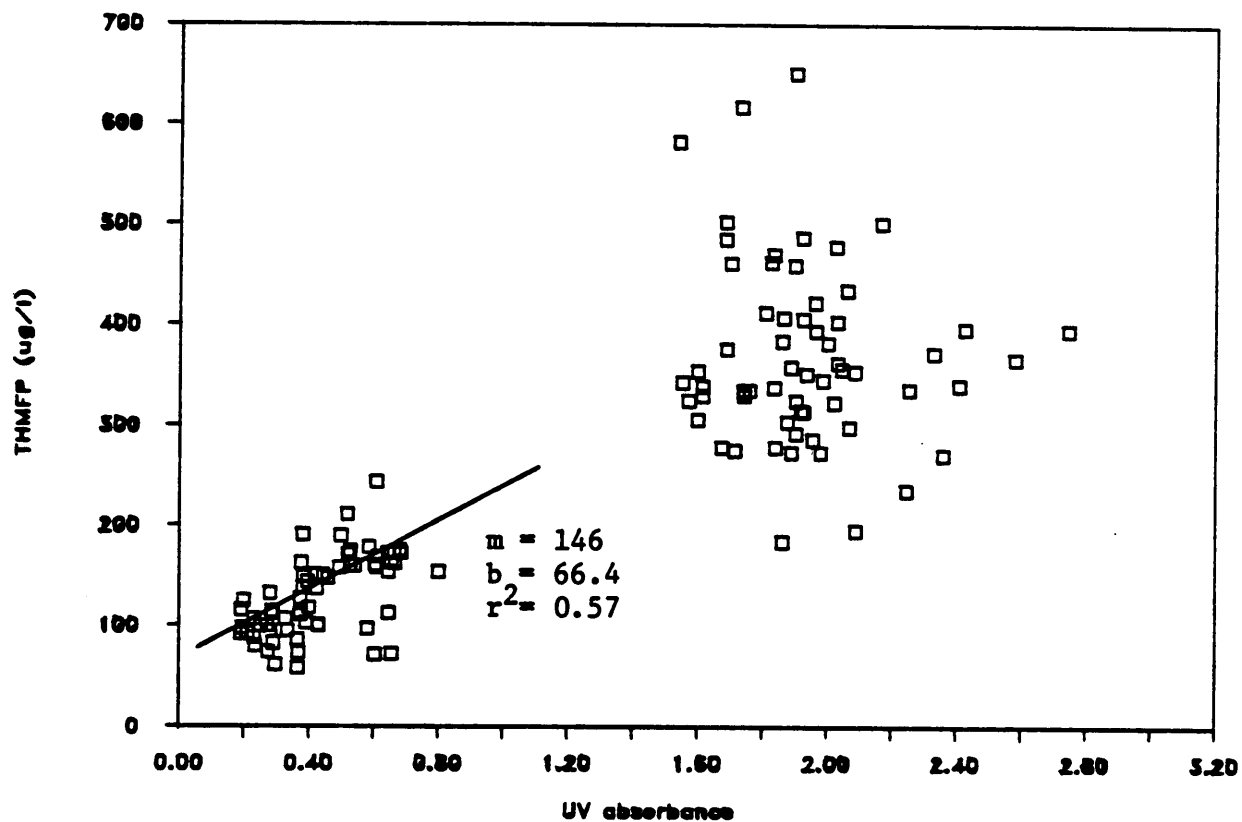


Figure 55. UV Absorbance (Measured at 254 nm in a 10-cm cell) as a Predictor for THMFP in the Raw Water and Clarifier Effluent.

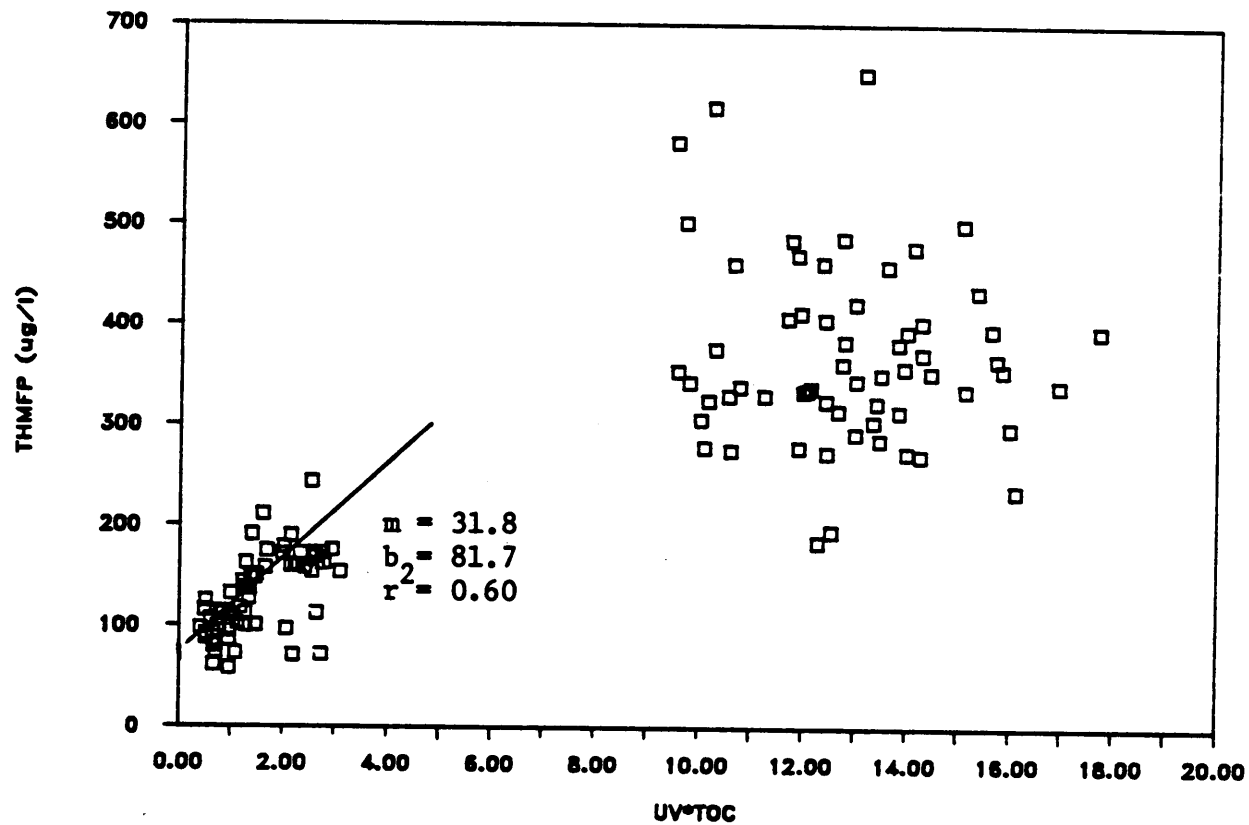


Figure 56. UV*TOC as a Predictor for THMFP in the Raw Water and Clarifier Effluent.

Appendix H

Sample Calculations for Fraction Passing (Ce/Co) Carbon Column for Each THM Treatment Level

Calculating the value of Ce/Co for each THM treatment level required the mean THMFP influent concentration for the GAC and BAC column in addition to the THM/THMFP ratio for the Harwood's Mill Distribution system. The three THM treatment levels that the analysis of the carbon columns was based are 25 µg/L, 50 µg/L, and 75 µg/L. Two different THM/THMFP ratios were used, 0.66 and 0.5.

Employing the 0.66 ratio, a 25 µg/L THM concentration corresponds to:

$$\frac{25}{0.66} = 37.5 \text{ } \mu\text{g/L THMFP}$$

For the GAC column, the mean THMFP influent concentration (Co) was 153 µg/L. Therefore, Ce/Co for the 25 µg/L THM treatment level is:

$$\frac{Ce}{Co} = \frac{37.5}{153} = 0.25$$

For the BAC column, Co = 145 µg/L:

$$\frac{Ce}{Co} = \frac{37.5}{145} = 0.26$$

Similarly, the Ce/Co ratios for 50 and 75 µg/L THM treatment level for each THM/THMFP ratio can be found. At the point the THMFP (Ce/Co) became greater than one of these calculated values, breakthrough at that sampling point had occurred.

Appendix I

Sample Calculations for Determining the Carbon Usage Rate for the GAC and BAC Processes

Determining the amount of carbon that would be required in the GAC and BAC columns to meet a THM treatment level initially requires a graphical analysis as described in the results. From Table 10, it was found that to maintain the column effluent below a maximum of 25 µg/L system THM's (THM/THMFP ratio of 0.66) resulted in the BAC and GAC column having average specific removals of 2.0 and 1.8 mg THMFP/gm GAC, respectively. The carbon requirements to treat a unit amount of water with these specific removals are as follows.

Assuming the mean influent THMFP concentration (Co) for BAC and GAC to be 0.15 mg/L, the carbon requirements for the BAC column would be:

$$\frac{0.15 \text{ mg/L}}{2.0 \text{ mg THMFP/gm GAC}} \left(\frac{1000 \text{ mg}}{1 \text{ gm}} \right) = 75 \frac{\text{mg GAC}}{\text{L water treated}}$$

$$75 \frac{\text{mg GAC}}{\text{L}} \left(\frac{3.785 \text{ L}}{1 \text{ gal}} \right) \left(\frac{1 \text{ lb}}{453596 \text{ mg}} \right)$$

$$= 0.00062 \frac{\text{lb GAC}}{\text{gal water treated}} = 0.62 \frac{\text{lb GAC}}{1000 \text{ gal treated}}$$

Similarly for the GAC column:

$$\frac{0.15 \text{ mg/L}}{1.8 \text{ mg THMFP/gm GAC}} \left(\frac{1000 \text{ mg}}{1 \text{ gm}} \right) = 83 \frac{\text{mg GAC}}{\text{L water treated}}$$

$$83 \frac{\text{mg GAC}}{\text{L}} \left(\frac{3.785 \text{ L}}{1 \text{ gal}} \right) \left(\frac{1 \text{ lb}}{453596 \text{ mg}} \right)$$

$$= 0.00070 \frac{\text{lb GAC}}{\text{gal water treated}} = 0.70 \frac{\text{lb GAC}}{1000 \text{ gal treated}}$$

Repeating these calculations for the other specific removals, the amount of GAC required to produce water under each THM treatment goal can be found.

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