THE INFLUENCE OF ALGAL GROWTH AND RELATED ECOLOGICAL FACTORS IN RESERVOIRS ON THE PRODUCTION AND CONTROL OF TRIHALOMETHANE PRECURSORS

by

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DEDICATION

The author would like to dedicate this work to the loving memory of his mother, Sandra, whom he misses and loves dearly.

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TABLE OF CONTENTS

Chapter Page

IV. RESULTS (Continued)

LIST OF FIGURES

LIST OF TABLES

Table Page

I. INTRODUCTION

Since its first large-scale application in 1908 at the Jersey City, New Jersey water treatment plant, chlorine has become the most widely utilized agent of disinfection in the water treatment industry of this country. Its effectiveness as a disinfectant, combined with the absence of noticeable side effects to consumers of waters treated by it, served as the impetus for its widespread popularity. The role of chlorine in water treatment had never been questioned until 1974 when two independent researchers (Rook, 1974; Bellar *et al*., 1974) discovered that the chlorination of natural waters led to the formation of a class of organic compounds known as the trihalomethanes (THM's). The gravity of this discovery was realized when subsequent reports (Environmental Protection Agency, 1974; Environmental Defense Fund, 1974; Environmental Protection Agency, 1975) implicated the THM's as carcinogens.

Since that time, much research has been conducted with the intent of determining the scope, causes, effects, and treatability of the THM problem. Notable among many important discoveries was the identification of those compounds present in source waters that, when reacted with chlorine, resulted in formation of the THM's. Implicated in the role of THM precursors at the onset of research, were two components of aquatic humus, the humic and fulvic acids, and a class of low molecular weight compounds, the methylketones (e.g. acetone). Recent evidence (Morris and Baum, 1978; Hoehn *et al*., 1978), however, has suggested that the cellular components and extracellular products

(ECP) of algae are also significant THM precursors. This discovery provided the basis for the research described in this paper.

Under a grant provided by the Office of Water Research and Technology of the United States Department of the Interior, an intensive study was performed to determine the in situ role of algae in the production of compounds which serve as precursors of the THM's. Research was conducted with the following objectives:

1. to observe the successional patterns exhibited by the algal populations in a lake throughout the test period and note any influence on THM seasonal patterns.
2. to determine the existence of any relationship between algal population size and the potentials of lake water to form THM's when chlorinated.
3. to determine the influence, if any, which algal productivity and extracellular release of organic substances exert over the trihalomethane-formation potential (THMFP) of a water impoundment.
4. to determine the effectiveness of standard coagulation/sedimentation procedures upon the removal of THM precursors.

The site selected for this study was Claytor Lake near Radford, Virginia. The study began in May, 1981 and continued through November of that same year.

Several acronyms are used throughout this thesis. The most important ones, and their definitions, are as follows:

THM's: Trihalomethanes. Formed upon chlorination of water containing organic precursors.

THMFP: THM-formation potential. The THM level after seven-days contact with chlorine applied in a 5:1 ratio of Cl_2:DOC.

DOC: Dissolved Organic Carbon. That fraction of the organic content of water which passes through a 0.45 micron Whatman GF/C filter.

ECP: Extracellular Product. Soluble organic compounds liberated from algae and bacteria.

II. LITERATURE REVIEW

In 1974, Rook provided convincing evidence which implicated the chlorination process as the cause of the formation of a class of halogenated organic compounds known as the trihalomethanes (THM's). Bellar *et al*. (1974) corroborated Rook's findings. They reported the detection of chloroform and other trihalogenated methanes resulting from chlorination in several United States municipal water supplies, with the highest concentrations being found in systems where surface waters were the raw water source. The significance of this discovery was realized later that same year when a report (Environmental Protection Agency, 1974) revealed the presence of 66 organic compounds, among them the THM's, in the water supply of New Orleans. Several subsequent reports (Environmental Defense Fund, 1974; Environmental Protection Agency, 1975) established a positive correlation between the consumption of New Orleans water and the incidence of cancer.

In order to properly assess the scope of the THM problem, then-EPA Administrator Russell Train, acting under the authority dictated to him by Public Law 93-523 (The Safe Drinking Water Act), ordered the commencement of the National Organics Reconaissance Survey (NORS). The survey encompassed the testing of the water supplies of 80 U.S. cities, several in each of the EPA's ten regions, representing as wide a variety of raw water sources and treatment schemes as possible. It had as its major objectives 1) the determination of the extent of the presence of THM's, 2) the determination of what effect raw water source and treatment schemes had on the formation of these compounds, and 3) the characterization of the organic content of finished drinking water produced from raw-water sources representing the major categories in use in the U.S.

NORS (Symons _et al._, 1975) provided the following information:

1. The four THM's were widespread in chlorinated drinking water in the U.S. and result from chlorination.
2. The median concentration of the compounds found in finished waters were: chloroform: 21 μg/L, bromodichloromethane: 6 μg/L, and dibromochloromethane: 1.2 μg/L. Bromoform was undetected in 68.8 percent of the supplies surveyed.
3. The range of concentrations were: chloroform: 0.1 μg/L - 31 μg/L, bromodichloromethane: 0 - 116 μg/L, dibromochloromethane: 0 - 100 μg/L, bromoform: 0 - 92 μg/L.
4. The highest THM concentrations were associated with: a) the chlorination of surface waters, b) raw-water chlorination (prechlorination), c) water with more than 0.4 mg/L free-chlorine residual present, and d) the practice of precipitative softening.

A complement to NORS, the Region V Joint Federal/State Survey (Environmental Protection Agency, 1975) of 83 cities conducted by EPA's Chicago Regional Laboratory, produced results similar to those of NORS, reporting a median chloroform level of 19 μg/L.

In 1976, a survey of 113 municipal water supplies, the National Organics Monitoring Survey (NOMS), was undertaken to determine the occurrence and frequency of selected contaminants with the intent of establishing a data set upon which to base a Maximum Contaminant Level (MCL) and/or treatment requirements to remove the contaminants. NOMS (Environmental Protection Agency, 1978) established that organic compounds in waters were numerous but nowhere as significant as the THM's.

Numerous other studies have been completed which verify the fore-mentioned surveys as to the extent and occurrence of THM's resulting from chlorination (Saunders *et al.*, 1974; Scheimart *et al.*, 1974; Hoehn *et al.*, 1977); Arguello *et al.*, 1979; Blanck, 1979; Nelson and Khalifa, 1980).

Health Effects and Resultant MCL's

After publication of reports establishing the probable link between the organically contaminated waters of New Orleans and the incidence of cancer among its consumers (Environmental Defense Fund, 1974; Environmental Protection Agency, 1975), several studies were undertaken to assess the extent of the problem. On April 30, 1975, EPA published a report that concluded "although some organic contaminants have carcinogenic potential, the cancer risk is judged to be minor because of their low concentration and/or infrequent occurrence in drinking water." Somewhat contradictory to this, the National Cancer Institute (1976) issued a report that indicated chloroform was carcinogenic to male rats. Further, a report by Page _et al_. (1976) on regression studies performed with Louisiana data, indicated "...there is a link between carcinogens in drinking water and cancer mortality." Numerous other studies (Environmental Protection Agency, 1977; Taithill and Moore, 1980; Theiss _et al_., 1977; Simmon and Tardiff, 1978; Loper _et al_., 1978; Alavanja _et al_., 1978), both pro and con, have since been published. Perhaps the most influential with respect to enactment of an MCL were two studies: 1) that conducted by Tardiff (1977), which established that the risk of cancer incidence lay between no risk of kidneys and liver and a maximum risk of 1.6 per million population/year, and 2) that conducted by the National Academy of Sciences (1976), which stated that cancer risk is probably a cumulative phenomenon and thus it would be desirable to reduce human exposure to proven or suspected carcinogens whenever possible. In response to this, the EPA published on November 28, 1979, in final form, an MCL of 0.10 mg/L and associated monitoring and reporting requirements for total trihalomethanes (TTHM's) (Environmental Protection Agency, 1979).

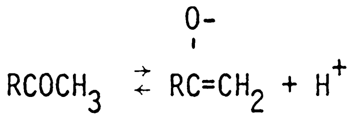
Specific Characteristics of the Trihalomethanes

The ubiquitous nature of the trihalomethanes required formulation of cost-effective means to efficiently reduce their concentration in finished waters. Prior to initiation of treatment modifications, however, it was necessary to ascertain fully the chemical properties of the haloforms. The results of this analytical research follow.

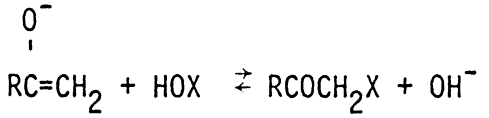
The Mechanism of THM Formation

It became apparent in the early stages of research that a reaction was taking place between free-chlorine and organic compounds present in water (Rook, 1974; Bellar et al., 1974). Because of the chemical nature of the THM's, it was hypothesized that the classical haloform formation mechanism was the most likely pathway leading to the production of THM's in finished waters (Rook, 1976; Stevens et al, 1976; Trussel and Umphres, 1978).

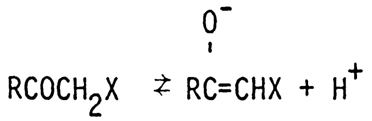
Evidence for this was proposed by Rook (1976) who determined that precursors for the haloform reaction had to be substances with extremely low vapor pressure and strongly recalcitrant properties. The molecules which Rook suspected to be the most significant precursors, the humic and fulvic acids, fulfilled these requirements. Further, the tendency of the reaction to proceed more effectively at a high pH (i.e., pH 11) coincided convincingly with the fact that the initial enolization step of the haloform reaction is significantly more efficient at elevated pH's. Following is a skeletal diagram and brief description of the haloform reaction (Morris and Boyd, 1975; Morris, 1975):



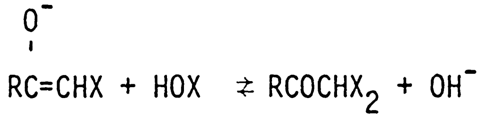
$$RCOCH_3 \rightleftarrows R\overset{\overset{O-}{|}}{C}=CH_2 + H^+ \qquad [1]$$



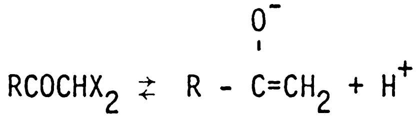
$$R\overset{O^-}{\overset{|}{C}}=CH_2 + HOX \rightleftarrows RCOCH_2X + OH^- \qquad [2]$$



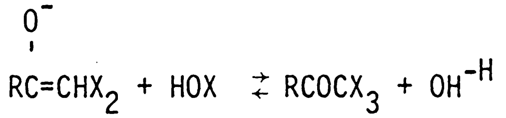
$$RCOCH_2X \rightleftarrows R\overset{O^-}{\overset{|}{C}}=CHX + H^+ \qquad [3]$$



$$R\overset{O^-}{\overset{|}{C}}=CHX + HOX \rightleftarrows RCOCHX_2 + OH^- \qquad [4]$$



$$RCOCHX_2 \rightleftarrows R - \overset{O^-}{\overset{|}{C}}=CH_2 + H^+ \qquad [5]$$



$$R\overset{O^-}{\overset{|}{C}}=CHX_2 + HOX \rightleftarrows RCOCX_3 + OH^{-H} \qquad [6]$$

$$RCOCX_3 + OH^- \rightleftarrows RCOOH + CX_3^- \qquad [7]$$

$$CX_3^- + H^+ \rightleftarrows CHX_3 \qquad [8]$$

The initial step (the rate-limiting step) is the enolization of the keto-enol through base catalysis. Subsequent halogenation of the enolate is a rapid reaction involving an electrophic halogen addition to the carbon-carbon double bond. The positive halogen end of the halogenated dipole attacks the α-carbon and the negative moiety is released. Electrophilic addition to the halogenated methyl group continues until all hydrogens are replaced. The final step, nucleophilic attack on the carbonyl carbon, results in the cleavage of the triply-halogenated methyl group from the molecule.

Because hypochlorous acid (HOCl) is the reagent most often utilized for disinfective purposes, chloroform ($CHCl_3$) is the predominant species produced by the above-described reaction. The brominated analogs, bromodichloromethane ($CHCL_2Br$), dichlorobromomethane ($CHCl_2Br$), and bromoform ($CHBr_3$), come about through the oxidation of bromide ions (by chlorine) to hypobromous acid (HOBr) which then participates in the halogenation step of the THM reaction sequence, in the same manner as hypochlorous acid.

Precursors

This section is presented in three segments, each offering a brief explanation of a specific class of compounds that, when chlorinated, result in the formation of THM's.

1. Aquatic humus. Rook (1974) provided the initial evidence which implicated humic substances as THM precursors. Subsequent work by this same researcher (1976) confirmed this fact.

The humics, often referred to as the color-causing compounds of water, comprise the largest fraction (approximately 85 percent) of the total organic content of water. They result from the decay of vegetative material of both autochthonous and allochthonous origin (Cole, 1979).

The humic substances consist of three categories of organic acids: the fulvic acids, the hymatomelanic acids, and the humic acids. Table 1 details the characteristics of each group (Kavanaugh, 1978).

Fulvic acids, when chlorinated, yield less than half as much chloroform as the humic acids and consume less chlorine (Babcock and Singer, 1979). This would seem to indicate that humic acids are of

Table 1. Characteristics of Organics of Natural Origin in Water Supplies (Kavanaugh, 1978).

	Humic Substances		
Characteristic	Fulvic Acids	Hymatomelanic Acids	Humic Acids
Occurrence	Most prevalent	Intermediate	Least prevalent
Molecular Weight, Size	Low molecular weight (200-1000)	Increasing size	High molecular weight (to 200,000)
Equivalent Weight	Low equivalent weight	Intermediate	High equivalent weight
Charge Density	High charge density	Intermediate	Low charge density
Light Scattering	Low	Intermediate	High

greater significance in THM production, however, in natural waters, the opposite appears to be true (Trussel and Umphres, 1978). There are two possible explanations for this. One is that the fraction of aquatic humus present as humic acid is so small it is essentially insignificant. The other involves the reactive sites on the humic molecules (Rook, 1976). These sites, known as the meta-dihydroxy aromatic compounds, are well-suited for the haloform reaction by way of enolization. It is postulated that minute amounts of these structures are present in humic acid molecules (as opposed to large numbers on fulvic acid molecules), thus resulting in their lower THM-yielding potential.

2. Low-molecular-weight compounds. Rook (1976) first proposed that methylketones, especially acetone, may play a role as precursors in the production of THM's but was unable to substantiate this hypothesis due to a lack of measurable quantities of these compounds in Rotterdam waters. Stevens et al. (1976) found acetone to be an insignificant precursor at near-neutral pH's due to its low concentration in source waters, but at elevated pH's, compounds containing the acetyl moiety contributed significantly to TTHM production. Further, they stated that the determination of true precursor identity is complicated because a mixture of compounds with differing reactivities at varying pH values is involved.

The work of Oliver and Lawrence (1979) contradicted the above-described findings of Stevens et al. Oliver and Lawrence found virtually no difference in the THM production of chlorinated samples of water containing volatile compounds (with acetyl moiety) and chlorinated samples of water without volatile compounds (no acetyl moiety) at pH's of 7 and 11, thus indicating that possession of acetyl moiety properties has little, if any, bearing on THM production.

To date, there is no definite answer as to the actual role of the low molecular weight compounds in THM formation. This is an area which will require further substantive research.

3. Algal biomass and ECP. Morris and Baum (1978) demonstrated that chlorination of algal components could produce chloroform. Hoehn *et al*. (1978, 1980) verified this with detailed field and laboratory studies. Due to the relevance of this particular finding to the work reported in this thesis, the role of algal components as THM precursors will be discussed in detail later in this review.

Water Source Influence

Bellar *et al*. (1974) found a significant correlation between finished water THM concentrations and the nature of the source water. Finished waters with the highest concentrations of THM's were derived from surface-water sources, while those with the lowest concentrations were groundwaters. NORS (1975) corroborated this finding in reporting that groundwater sources yielded lower average TTHM concentrations than surface waters. This phenomenon is likely due to the concentration of organics within a particular source water, specifically groundwaters typically display low organic content, while surface waters usually have a significantly higher organic concentration. This statement is of course, a generalization and does not apply to coastal regions, but on the whole, surface waters can be expected to yield greater THM concentrations than groundwaters because of their higher organic content.

Treatment Influence

NORS (1975) reported that certain treatment schemes resulted in high finished-water THM concentrations. Specifically implicated were systems that employed raw-water chlorination, precipitative softening procedures, and the maintenance of high free-chlorine residuals. In contrast to this, locations which utilized powdered activated carbon (PAC) had average TTHM concentrations lower than those locations not using PAC.

Precursor Concentration Influence

Numerous researchers (Symons *et al*., 1975; Environmental Protection Agency, 1975; Rook, 1976; Stevens *et al*., 1979) have reported that THM concentrations were directly influenced by the organic content of the water, provided that sufficient chlorine was added to create a chlorine residual. Rook (1976) determined that the relationship of chloroform production from organic material (fulvic acid) is linear in concentrations up to 250 mg/L. The work of Stevens *et al*. (1976) and Babcock and Singer (1979) achieved the same result. It must be noted, however, that this relationship was determined with synthetically produced organic compounds. In natural waters, researchers (Hoehn *et* al., 1978; Young and Singer, 1979) have shown that there is a poor correlation between raw water Total Organic Carbon (TOC) levels and chloroform formation. Two explanations for this phenomenon have been offered. The first (Young and Singer, 1979) states that TOC is a collective measure of all organic constituents, only a fraction of which are precursors of chloroform. The other (Hoehn *et al.*, 1977; Hoehn *et al.*, 1978) hypothesizes that the seasonal change in the nature of organic compounds in the raw-water causes variations in the THM-formation potentials of the organic substances.

Chlorine Dose and Residual

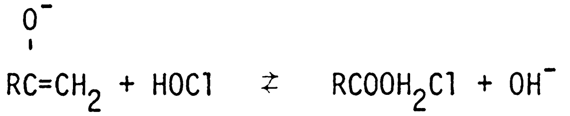
The relationship between THM production and chlorine dose is well documented (Symons *et al.*, 1975, Hoehn *et al.*, 1977; Rook, 1976; Trussell and Umphres, 1978; Oliver and Lawrence, 1979; Siemak *et al.*, 1979; Young and Singer, 1979). Trussell and Umphres (1978) outlined the three, main, chlorine-dose regions affecting THM formation. The first region is that where immediate chlorine demand is exerted by inorganic materials such as sulfide, iron (II), and ammonia, resulting in trace formation of THM's. Once the demand is satisfied, the remaining chlorine begins to react with the available organic material. Within this region there is a near-linear relationship between chlorine dose and the THM level achieved. Once the organic chlorine demand is satisfied, a long-term chlorine residual is obtained and any further increases in THM formation with chlorine dosage are rather modest.

Trussel and Umphres (1978) also stated that chlorine doses substantially greater than those required to maintain a long-term residual will result in modest increases in the levels of THM's. On the other hand, reducing chlorine dosage to the level at which long-term residuals aren't maintained will reduce THM formation substantially. Young and Singer (1979) achieved virtually identical results.

Hoehn et al. (1977) noted an interesting relationship between the TTHM concentration in a water supply and chlorine demand. Such a correlation deserves merit as a future research area.

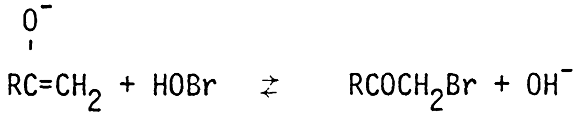
Bromide

The brominated THM's ($CHCl_2Br$, $CHClBr$, and $CHBr_3$) are the result of the oxidation of bromide ions which, in the presence of chlorine, participate in the haloform reaction described in a previous section. The amount of compounds formed depends on the relative rates of the following reactions.



$$R\overset{O^-}{C}=CH_2 + HOCl \rightleftarrows RCOOH_2Cl + OH^-$$

[1a]



$$R\overset{O^-}{C}=CH_2 + HOBr \rightleftarrows RCOCH_2Br + OH^-$$

[1b]

The sources of the various bromide forms are thought to be bromine impurities contained in the applied chlorine (Bellar et al., 1974), the presence of bromide in underground water supplies, mainly from chalk wells (Rook, 1974), and the low levels usually found in most water supplies (Siemak et al., 1979). Dramatic increases in raw-water bromide levels can occur as a result of saltwater intrusion, usually in estuarine regions during drought conditions (Siemah et al., 1979); Nelson and Khalifu, 1980), the effect of which is a shift towards increased bromination of the THM compounds formed during treatment.

Trussel and Umphres (1978) found that bromine participated in the THM reaction sequence much more efficiently than chlorine and, as a result, increased the yield of THM's for a given chlorine dose. It was also noted that bromine may increase the rate of THM development.

Arguello et al. (1979) reported that the ratio of brominated THM's to chloroform is directly linked to the concentration of bromine in raw water.

Reaction Time

Several researchers (Bellar et al., 1974; Rook, 1976; Oliver and Lawrence, 1979; Hoehn et al., 1978; Young and Singer, 1979) have demonstrated the effect of chlorine contact time upon THM levels, although no two have reported similar results in the reaction time frame. Times required for completion of the reaction vary from four to 96 hours.

Young and Singer (1979) noted that reaction time is critical in the formation of THM's for raw-water samples that are chlorinated whereas the production of chloroform in coagulated waters is not as sensitive to reaction time.

pH

NORS (Symons *et al.*, 1975) revealed that the average TTHM concentrations in finished waters from the 17 precipitative softening plants included in the survey were almost twice as high as the average concentrations in the finished waters of the 80 cities surveyed. According to Rook (1976), this follows the expected trend for the pH-dependent enolization step of the haloform reaction. Significant increases in the rate of the reaction occur in the pH range of 8 to 10 through optimization of the enolization step. Stevens *et al.* (1976) expressed the possibility that precursor methylketone compounds, such as acetone, don't contribute significantly to the overall reaction until elevated pH's are achieved. Due to the controversy surrounding the true role of acetyl precursors, such a possibility is purely speculative.

Numerous other researchers (Trussel and Umphres, 1978; Siemak *et al.*, 1979; Harms and Looyenga, 1977) have reported the effect of elevated pH's increasing finished water THM concentrations.

Temperature

The effect of temperature on THM formation has been documented by a number of researchers, most notably Hoehn *et al.* (1977), Stevens *et al.*(1976), and Young and Singer (1979). Young and Singer reported that over a temperature range of 5.6°C in January to 28°Cin July, the concentration of chloroform in the finished water more than doubled. It must be stated, however, that a number of factors working in concert may account for this increase, not simply the rise in temperature.

Kinetically, low temperatures would serve to slow the THM reaction rate but should not alter the THMFP of a given water.

Control of the THM Problem

Treatment options by which the THM problem can be controlled are as follows: 1) modification of treatment schemes, 2) removal of THM's, 3) utilization of alternate disinfectants, and 4) removal of precursor compounds. Each option will be reviewed to emphasize its advantages, disadvantages, and limitations.

Treatment Modifications

Alteration of the point of prechlorine application. Numerous studies (Blanck, 1979; Babcock and Singer, 1979; Siemak *et al.*, 1979; Young and Singer, 1979; Harms and Looyenga, 1977) have been performed in which the point of chlorination was shifted from the point of entry into the pumping system or the treatment plant to a later stage in the treatment scheme, typically following clarification. Success in reducing THM concentrations has been mixed, with some plants reporting substantial reductions of up to 76 percent (Blanck, 1979; Young and Singer, 1979; Harms and Looyenga, 1977) and another reporting only "nominal" reductions (Siemak *et al.*, 1979).

A second advantage in shifting the chlorination point is that there is a marked reduction in the amount of chlorine required to achieve a residual (Blanck, 1979; Babcock and Singer, 1979; Siemak *et al.*, 1979; Harms and Looyenga, 1977). This is due to the lower chlorine demand of the water which results from the decrease in organic content brought about by the coagulation/sedimentation procedures. Because of the expense of chlorine, this modification provides for a substantial cost savings.

A possible drawback to this alteration is the significant reduction in chlorine contact time and the resultant lowering of disinfective capacity (Hoehn _et al._, 1978; Siemak _et al._, 1979). Also, the introduction of chlorine following clarification eliminates the algicidal and slime removal action of chlorine in the clarifiers, thus allowing for slime growth and the possibility of a loss in clarification efficiency. Extensive research should be initiated to investigate the biological ramifications of this particular treatment modification.

Sand filtration prior to chlorination. McBride (1978) found that dual media sand filtration, with the intent of removing precursor materials prior to chlorination, resulted in a nearly 50 percent reduction of THM concentrations (levels were reduced from 19 mg/L without filtration to 10 mg/L following filtration). Unfortunately, McBride's article gave very few details as to the cost of filtration and the necessary frequency and efficiency of maintenance (i.e. filter washings, replacements, etc.), both items which are critical in determining the cost effectiveness of a modification of this type. Also, there remains the question of how effective this option would be when dealing with a raw-water of high organic content.

Removal of THM's

Aeration stripping. Rook (1976) proposed the use of aeration stripping for removal of the volatile THM's and achieved results that were labelled "promising." No details concerning operational parameters, percent removals, or maintenance and operational costs were provided.

Siemak *et al*. (1979) reported that aeration following chlorination removed 90 percent of the chloroform formed during water treatment. Like Rook, these authors made no mention of operational parameters and costs.

Ozonation. Siemak *et al*. (1979) reported that effective reduction of THM's by ozonation required such large doses of ozone, its application would be extremely cost-prohibitive.

Powdered activated carbon. Siemak *et al*. (1979) reported results with PAC that were similar to those of ozonation, with the large dosages required for effective THM removal posing the problem of prohibitively high costs.

Granular activated carbon (GAC). Several researchers (Blanck, 1979; Rook, 1977; Siemak *et al*., 1979) have utilized GAC, each with disappointing results due to the inability of the GAC columns to remove significant levels of THM's for periods of time longer than three to four weeks. Utilization of GAC is far too expensive for such short-term benefits.

Alternative disinfectants. The topic of alternative disinfectants is not only tentative but controversial due to the questions which remain about their disinfective capacities and effect upon the health of consumers. Each has advantages, disadvantages, and limitations, and while there is no intent to minimize the importance of this topic, it is beyond the scope of this literature review to sufficiently explore the characteristics of each. With this in mind, it must be stated that a tremendous amount of research is now being conducted on alternative disinfectants and the interested reader will find many readily available sources of information concerning the status and findings of this research in periodicals such as the Journal of the American Water Works Association.

Removal of THM precursors.

Generally speaking, the easiest way to avoid a problem is to stop it at its source. The THM's are no exception and the majority of researchers feel that the solution to the haloform problem is the effective removal of THM precursors. Achievement of this goal has been attempted through two treatment modes: the use of GAC and modified coagulation procedures. Discussion of research results in each area follow.

Granular activated carbon. Removal of precursors by adsorption onto GAC to date, has met with only marginal success (Blanck, 1979; Stevens *et al.*, 1976) and its effectiveness appears to be limited to just a few weeks, thus requiring frequent reactivation or replacement cycles, both of which are cost-prohibitive. This form of treatment has not been widely researched, however, and in time, may prove to be an effective means of precursor removal.

Modified coagulation procedures. As stated earlier in this review, prior to attempted alleviation of a water-related problem, the specifics of the problem must be known so as to effect optimal and cost-effective treatment. Researchers (Stevens *et al*., 1976; Kavanaugh, 1978; Babcock and Singer, 1979; Oliver and Lawrence, 1979; Young and Singer, 1979; Brett and Calverly, 1979) in the area of precursor removal via coagulation/sedimentation procedures have discovered several vital characteristics of the THM precursors and have demonstrated that utilization of this knowledge to achieve optimal treatment conditions can result in extremely effective precursor removal (60 - 80 percent of humic materials). Removals of this magnitude can lower the THM-formation potential of finished waters by as much as 70 percent. Following is a summarization of the important parameters detected by recent research and the results achievable by modified coagulation procedures.

Stevens *et al*. (1976) determined by selective filtration experiments that the important THM precursors were either particulates or substances strongly sorbed onto particulate matter, such as clay particles. Thus, if conventional coagulation/sedimentation procedures could be modified to optimize the removal of particulates, ultimate THM concentrations well below the MCL could be achieved.

Kavanaugh (1978) explored and defined the necessary parameters to achieve modified coagulation. Basically, this involved three procedural modifications:

1. Utilization of coagulant doses proportional to the fulvic acid concentration. Fulvics were chosen because these compounds were found to be more difficult to remove than the humics and thus required approximately twice the dosage necessary for humic acid removals.
2. Dependent upon the coagulant utilized, the optimal pH range must be adhered to strictly. For alum, this range is between 5 and 6.5 and for ferric sulfate the range is between 3 and 5.
3. Polymers (anionic organic polyelectrolytes) at doses of 1 to 10 mg/L supplement the action of the coagulant and aid in providing optimum humic removal.

Inherent in this discussion is the fact that modified coagulation parameters are site-specific and must be determined on a case-by-case basis.

Research utilizing the modified coagulation procedures mentioned above has yielded the following results:

1. Chloroform-formation potentials in finished waters were reduced by 60-70 percent (Kavanaugh, 1978; Babcock and Singer, 1979; Oliver and Lawrence, 1979; Young and Singer, 1979).
2. Because removals of TOC by alum were significantly lower than the corresponding reductions in THMFP, it appears that alum

selectively removes THM precursors from the Dissolved Organic Carbon Dissolved Organic Carbon (DOC) pool. Iron coagulants don't exhibit this quality (Kavanaugh, 1978; Babcock and Singer, 1979; Oliver and Lawrence, 1979; Young and Singer, 1979; Brett and Calverly, 1979).

3. Prechlorination should follow coagulation, thus allowing for removal of precursors and the lowering of finished water THM levels (Kavanaugh, 1978; Babcock and Singer, 1979; Young and Singer, 1979).
4. Optimization of coagulation appears to be the least expensive and simplest means by which to reduce or possibly solve the THM problem (Kavanaugh, 1978; Babcock and Singer, 1979).

Special Topics

Since the 1974 discovery of THM's in finished waters, the majority of research on the topic has been directed towards defining the chemical properties of these compounds with the intent of effecting their removal from potable waters. Studies outside of these areas have been limited in number but have produced results that have the potential to highlight aspects of the THM dilemma that may be of extreme importance. These areas of special study are: 1)THM increases in distribution systems, 2) Seasonal variations in THM concentrations and 3) The relationship between algae and THM's. Following is a brief review of the literature concerning each topic.

THM Increases in Distribution Systems

Harms and Looyenga (1977) first reported that the concentration of chloroform fluctuated in the distribution system and was greater at the consumer's household than at the plant. Other researchers (Arguello *et al.*, 1979; Hoehn *et al.*, 1978) have verified this fact, and a study by Brett and Calverly (1979) that was specifically designed to monitor this phenomenon for one year, showed significant increases within the distribution system where finished waters contained a chlorine residual. These increases were as high as 75 percent over the concentration in the plant effluent.

Obviously this presents a serious problem to the water treatment industry because the THM concentration reaching the consumer is what determines the ultimate potability of the water and the resulting health of the community.

Seasonal Variations in THM Concentrations

A number of researchers (Hoehn *et al.*, 1977; Arguello *et al.*, 1979; Veenstra and Schooner, 1980; Otson *et al.*, 1981) have reported a distinct seasonal pattern of THM concentrations in finished waters, with maximum concentrations generally occurring in the early-to-mid summer and the lowest concentrations occurring in the late fall to early winter. Several explanations have been offered to interpret these seasonal trends, the most plausible of which are: 1) variations in raw-water precursor concentrations, 2) variations in the chemical nature of raw-water precursors, 3) quantities of chlorine applied, 4) variations in raw-water temperatures, 5) rainfall influence, 6) degree of mixing of water strata, and 7) extent of algal blooms.

Veenstra and Schooner (1980), utilizing apparent molecular weight fractionation by means of gel-permeation chromatography, determined that these patterns result from the seasonal variation in the nature of the precursors and not from environmental conditions such as pH or temperature, both of which were monitored very carefully.

Seasonal variation was also noted in the brominated THM's by the same researchers, and the highest concentrations occurred during late fall and early winter, which was the period when the bromide ion concentration was at its highest.

The Relationship Between Algae and THM's

Hoehn *et al*. (1980) established that the finished-water THM concentrations, in water taken from the Occoquan Reservoir, corresponded closely to the concentrations of chlorophyll-a from June through November of 1975. This relationship prompted laboratory culture work which produced the following results:

1) Algal biomass and extracellular products (ECP), when chlorinated, often yielded THM levels greater than those from proportional concentrations of humic and fulvic acids, and
2) The THM yields were extremely high when the algal cultures were in the late exponential phase of growth.

They hypothesized that, while the humic materials provide background precursor levels in reservoirs when algal growth is at a minimum, the algae provide added precursors during the warmer and highly productive summer months. The implication of this finding is that THM control strategies which are effective during the cooler months of nominal algal activity, may not be effective during the algal growing season.

It is the intent of this paper to further qualify the role of algae in the production of THM's in freshwater impoundments.

Algal Extracellular Products

This review will be limited to those areas of the subject that are directly involved in the formation and presence of THM's. With this in mind, a brief review will be provided on the topics of 1) background information on ECP, 2) the role which photosynthesis and photorespiration play in ECP production, with special emphasis on environmental factors and the enzyme system, Ribulose 1,5-bisphosphate carboxylase/oxygenase, referred to as ribulose diphosphate in many references, and 3) a discussion on the specific extracellular product, glycollate.

Background Information

Extracellular products, which may be defined as soluble organic substances liberated from healthy algae (Fogg, 1966), are of considerable importance, not only to the aquatic community of a particular body of water but to the water treatment industry as a whole.

Fogg (1966) grouped ECP into two categories, Type I and Type II. Type I products are low molecular weight metabolic intermediates; such as simple sugars, amino acids, and, perhaps most importantly, glycollic acid. These substances are released chiefly by diffusion through the cell wall with the rate of release being dependent upon the concentration gradient of the substance across the membrane and the permeability constant of the membrane for the substances (Hellebust, 1974; Stadelmann, 1962; Stadelmann, 1969). Type II substances are high molecular weight end products of metabolism; such as polysaccharides, proteins, and polyphenolic compounds (Fogg, 1969). These molecules are excreted by complex processes usually involving the fusion of intracellular vesicles containing the macromolecules, with the cell wall (Hellebust, 1974; McCalla, 1968; Wholey _et al_., 1972). Kinetic studies revealed that Type I products are liberated in relatively greater amounts than Type II products from natural populations (Fogg, 1966).

Tables 2 - 4 provide a comprehensive listing of the major forms of ECP of the various phyla of algae along with literature references for each division.

Fogg (1958, 1963, 1964, 1965), in a number of investigations, has found that between seven and 50 percent of the total carbon fixed by algae in the photic zone of the water column was released as ECP, and

Table 2. Extracellular Nitrogenous Substances (After Hellebust, 1974)

Family or Group	Genera	Nitrogenous Substances
Cyanophyceae	Anabaena, Calothrix, Chlorogloea, Coccochloris, Lyngbya, Microcystis, Nostoc, Oscillatoria, Westiellopsis	amino acids, peptides proteins
Chlorophyceae*	Scenedesmus	glucosamine
	Chlamydomonas	nicotinic acid
	Chlamydomonas, Chlorella, Scenedesmus, Dunaliella, Pyramimonas	amino acids, peptides
	Chlamydomonas, Volvox	proteins
Euglenophyceae	Euglena	amino acids glycoproteins protoporphyrin
Chrysophyceae	Ochromonas	amino acids, nucleic acids, proteins
Dinophyceae	Exuviella, Gymnodinium, Peridinium	amino acids, peptides, protein
Zooxanthellae		nucleoside-polyphosphates
Bacillariophyceae	Chaetoceros, Cyclotella, Skeletonema, Stephanodiscus Synedra, Rhizosolenia, Thalassiosira	amino acids, peptides
Rhodophyceae	Porphyridium, Chondrus, Polysiphonia	complex nitrogenous (protein) materials
Phaeophyceae	Ectocarpus Ascophyllum, Fucus, Laminaria	complex nitrogenous (protein) materials

*Including Prasinophyceae

Table 3. Algal Extracellular Carbohydrates
(After Hellebust, 1974).

Family or Group	Genera	Carbohydrate
Cyanophyceae	Anabaena, Nostoc	polysaccharides
	Anabaena, Nostoc, Calothrix, Scytonema (lichen symbionts)	simple sugars
Chlorophyceae*	Chlamydomonas, Scenedesmus, Platymonas, Palmella, Oocystis, Dunaliella, Pyramimonas	polysaccharides
	Chlorella, Scenedesmus	simple sugars
	Zoochlorellae	simple sugars
	Chlorella, Chlorococcum, Pyramimonas, Dunaliella. Trebouxia and other lichen symbionts	sugar alcohols
Bacillariophyceae	Nitzschia, Synedra, Stephanodiscus, Skeletonema, Thalassiosira	polysaccharides
Dinophyceae	Katodinium, Gymnodinium	polysaccharides
Zooxanthellae		glycerol
Xanthophyceae	Olisthodiscus	mannitol
Phaeophyceae	Fucus, Ascophyllum, Laminaria	polysaccharides heteropolysaccharides
Rhodophyceae	Porphyridium, Chondrus	polysaccharides heteropolysaccharides

*Including Prasinophyceae

Table 4. Extracellular Organic Acids (After Hellebust, 1974).

Family or Group	Genera	Organic Acids
Cyanophyceae	Coccochloris, Anacystis, Oscillatoria	glycollate
Chlorophyceae*	Chlorella, Chlorococcum, Dunaliella, Pyramimonas, Hormotila, Ankistrodesmus, Chlamydomonas, Scenedesmus	glycollate
	Zoochlorellae	glycollate
	Chlorella, Scenedesmus	formate, acetate lactate
	Chlamydomonas, Chlorella	keto acids
	Ankistrodesmus	mesotartrate isocitrate acid semialdehyde
Xantophyceae	Olisthodiscus	glycollate
Chrysophyceae	Monochrysis	glycollate
Haptophyceae	Coccolithus, Cricosphaera, Isochrysis	glycollate
Dinophyceae	Exuviaella, Amphidinium, Peridinium, Gymnodinium	glycollate
Bacillariophyceae	Chaetoceros, Skeletonema, Cyclotella, Thalassiosira, Rhizosolenia, Stephanodiscus	glycollate

*Including Prasinophyceae

release was proportional to the amount of carbon fixed in the algal cell.

Ecologically, ECP constitutes a major source of carbon and energy for aquatic life, because these substances are readily assimilated by heterotrophic organisms (Fogg, 1966). Of even greater importance to this study, however, is the fact that ECP can have a very high THM-formation potential (Hoehn *et al.*, 1980).

Carbon Dioxide Fixation, Ribulose-1,5-Bisphosphate, and Glycollate Production

Carbon dioxide is the carbon source utilized by algae for photoautotrophic growth. In this process, light energy is absorbed and converted into the chemical energy forms of adenosine triphosphate (ATP) and reduced nicotinamide dinucleotide phosphate ($NADPH_2$), the most important functions of which are to convert the source - CO_2 into reduced carbon compounds (Raven, 1974).

The pathway of autotrophic CO_2 fixation in algae is the photosynthetic carbon reduction cycle or the Calvin Cycle (illustrated in Figure 1). The cycle is initiated, catalyzed, and regulated by the enzyme Ribulose-1,5-bisphosphate (RuBP), the CO_2 acceptor, which is active primarily in the chloroplasts of algae where it occurs as interthylakoidal crystals (McFadden and Purohit, 1978). RuBP, a five-carbon, sugar-phosphate continually produced in the cell, catalyze the fixed CO_2 and Mg^{2+} to yield two molecules of 3-phosphoglycerate

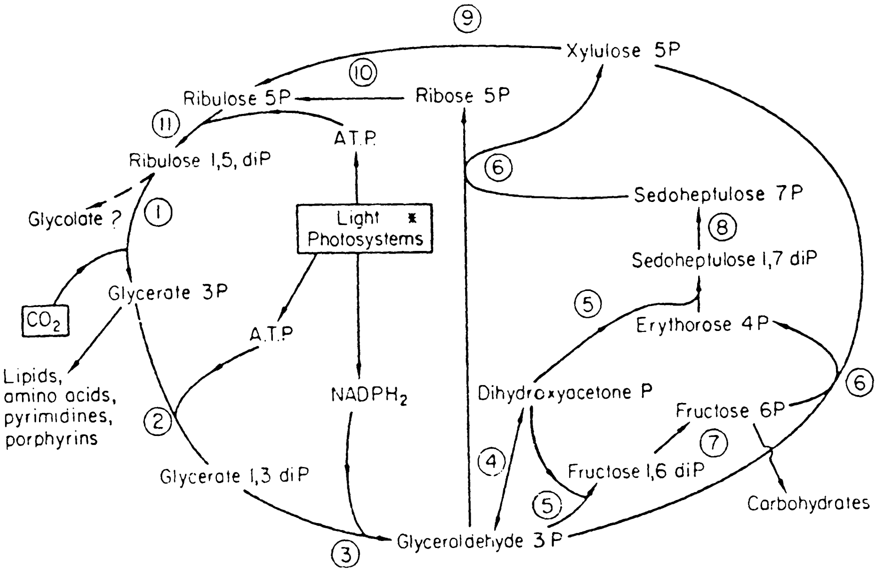


Figure 1. The photosynthetic carbon reduction cycle (Calvin-Benson Cycle). From Hellebust, 1974.

(PGA). (In this manner RuBP acts as a carboxylase.) These molecules are reduced (utilizing the energy of ATP and NADPH, mentioned previously) to form phosphoglyceraldehyde which combines with dihydroxyacetone phosphate (another reduced form of PGA) to form a six-carbon, sugar-phosphate, fructose diphosphate. A fraction of this compound is used to regenerate the RuBP pool which, in turn, accepts more CO_2, while the remaining fraction forms the carbohydrates, glucose, sucrose, and starch (Weier _et al._, 1974).

The action of RuBP, thus the degree of CO_2 fixation and ultimately photosynthesis, is influenced by a number of external factors, including CO_2 concentration, pH, light intensity, and oxygen concentration (Raven, 1974). Specifically, light intensities of approximately 1500 lux, pH's below 9, and CO_2 concentrations above 0.1 percent (in atmospheres), stimulate the carboxylase action of RuBP (Weier _et al._, 1974). The CO_2 influence appears to be a simple quantity effect, meaning the greater the available concentration of CO_2, the more RuBP is required to fix the CO_2 (Pritchard _et al._, 1962).

While RuBP acts in a carboxylase capacity, photosynthesis occurs along with the liberation of Type II ECP (Fogg, 1966). Hoehn _et al._, (1980) have shown that certain of these compounds have a very high THM-formation potential. Thus, the RuBP enzyme system and the THMFP of Type II ECP appear to be linked in an important manner.

The alternate function of RuBP is that of an oxygenase. This manifests itself when the CO_2 concentration is below 0.1 percent (in atmosphere), light intensity is significantly greater than 1500 lux, pH's are equal to or greater than 9, and high Dissolved Oxygen (DO) concentrations cause exertion of the Warburg Effect, the oxygen inhibition of photosynthesis (Fogg, 1966; Fogg and Nalewajko, 1964; Pritchard, 1962). This alternate state is known as photorespiration, the most significant function of which (to this study) is the biosynthesis and liberation of the extracellular product, glycollate (Fogg, 1966; Fogg and Nalewajko, 1964; Pritchard et al., 1962; Talbert, 1974).

Glycollate is produced along the metabolic glycollitic pathway (illustrated in Figure 2). This would indicate that RuBP is the precursor to glycollate (Fogg, 1966; Fogg and Nalewajko, 1964; Pritchard et al., 1962; Talbert, 1974). Apparently, the quantity effect mentioned earlier is important in the mode also, meaning the concentration of RuBP is far greater than that of the CO_2 to be fixed, the RuBP avails itself to the influences of the glycollytic pathway (Pritchard et al., 1962). Once this pathway is initiated, the liberation of glycollate can be significant. Tolbert and Zill (1966) found that up to 90 percent of the carbon fixed during photosynthesis was excreted by algal cells after the cells entered the physiological state of photorespiration.

Hoehn et al., (1980) have shown that glycollate has a low THMFP. Again, this situation is worthy of emphasis, for the RuBP enzyme system and the THMFP of Type I ECP (glycollate), appear to be linked in a very important manner.

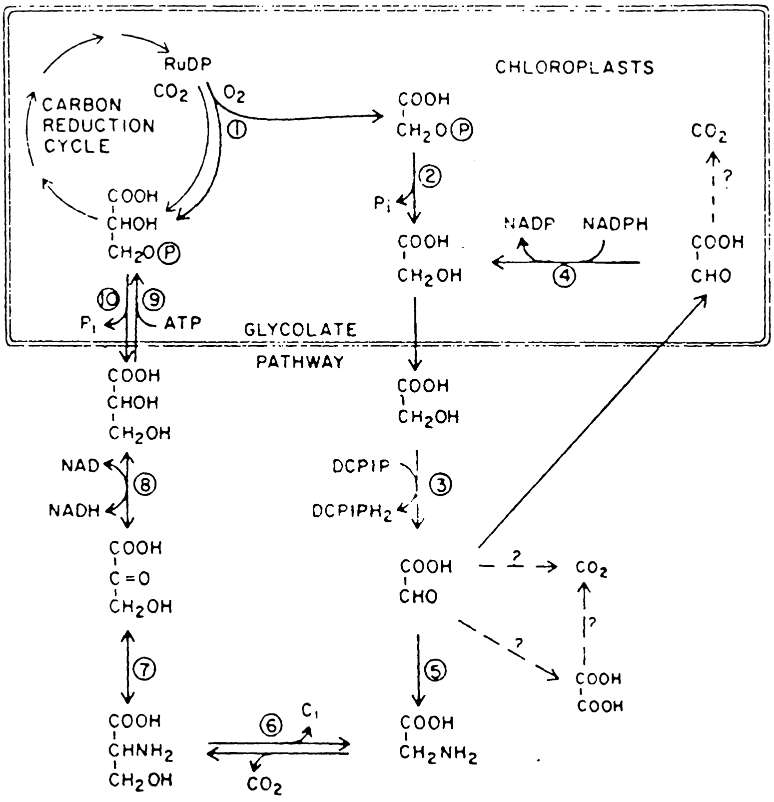


Figure 2. The glycollate pathway in algae. From Tolbert, 1974.

III. MATERIALS AND METHODS

In order to fully assess the extent to which planktonic algae, and possibly bacteria, contributed to the THM problem, weekly testing was conducted on water from two sampling sites on Claytor Lake during the period from May through November, 1981. This interval of time allowed for analyses to be conducted under diverse seasonal and meteorlogical conditions.

A variety of tests were performed on the water to provide the necessary information concerning the physical, chemical, and biological character of Claytor Lake. Specific tests conducted were:

1. physical: Secchi disk-transparency and temperature
2. chemical: pH, dissolved oxygen (DO), carbon dioxide (CO_2), alkalinity, dissolved organic carbon (DOC), trihalomethane formation potential (TTHMP), total phosphorus, and orthophosphate
3. biological: algal and bacterial enumeration, algal identifications to genera, ^{14}carbon-uptake primary productivity.
4. treatability: standard coagulation/sedimentation jar tests, followed by tests to evaluate the removal of DOC and THMFP.

Following is a detailed description of the procedures utilized during the research period, prefaced by a brief characterization of the study area and sampling sites.

Description of Study Area

Claytor Lake is a large, hydroelectric-power reservoir located on the New River in Pulaski County, Virginia. The reservoir was built by the Appalachian Power Company (APCO) during 1934-1940 and has the following characteristics (Environmental Protection Agency, 1976):

surface area: 18.19 square kilometers
mean depth: 29 meters
maximum depth (near dam): 35 meters
volume: 527 cubic meters
length: 34,923 meters
mean hydraulic retention time: 63 days

Generally speaking, Claytor Lake is a phosphorus-limited, eutrophic ecosystem that receives an annual total phosphorus loading of 10.07 grams per square meter per year (g/m^2/year) (Environmental Protection Agency, 1976), placing it in the "dangerous eutrophic rate" classification, as proposed by Vollenweider (1968).

Several researchers (Bellar *et al.*, 1974; Symons *et al.*, 1975) have determined that the source of a water supply significantly affects its THM-formation potential. In order to evaluate the extent of this source-related phenomenon, sampling sites of contrasting character, with particular emphasis on phytoplankton populations and eutrophic state, were selected within Claytor Lake. A brief description of each follows:

Station 1: Peak Creek Arm

This sampling site, located in a small cove on Peak Creek approximately three miles below the Pulaski Sewage Treatment Plant outfall, was chosen because of its close proximity to the sewage treatment plant, the relative shallowness of the creek (approximately nine meters), its lentic velocity (two cubic meters per second, m^3/sec), and its highly nutrient-enriched (eutrophic) waters that cause prolific growths of phytoplankton.

Peak Creek contributes ten percent of the total phosphorus input to Claytor Lake, six percent of which originates from the treatment plant effluent, and four percent from non-point sources (Environmental Protection Agency, 1976).

Station 2: Claytor Lake Dam

This sampling site, located approximately 100 meters above the APCO dam, is of contrasting physical character to the Peak Creek site. Turbulent waters of considerable depth (greater than 35 meters) typify this area. Because the dam's penstock openings are located 13 meters below the water's surface, the water which is discharged is cool, oxygen deficient, and nutrient-rich. As a result, this part of the lake develops an expansive epilimnion of approximately 14 meters during summer stratification.

As might be expected, phosphorus concentrations and phytoplankton populations are generally significantly lower than those at the Peak Creek site.

Overview of Field and Laboratory Procedures

In May 1981, *in situ* studies were performed on Claytor Lake with the objective of determining the influence which biological activity (algal and bacterial) exerted over the THM-formation potential of the lake water. Additionally, an evaluation of the effectiveness of alum coagulation in the removal of THM precursors was performed.

Field testing was conducted at two sites of contrasting physical and chemical character and included measurement of transparency, pH, dissolved oxygen, temperature, carbon dioxide, and alkalinity. Laboratory testing involved determination of dissolved organic carbon concentrations, THM-formation potential, and algal and bacterial population densities, along with bench-scale coagulation/sedimentation procedures. Additional primary productivity studies based on the ^{14}C-uptake method were performed on four occasions over periods of 12 to 24 hours to assess the relationship between algal productivity, ECP release, and the THMFP of the lake water on a diurnal basis.

The sequence of activities was as follows: The boat was launched from the Claytor Lake State Park public dock at approximately 11:30 a.m. Testing at the dam site began at approximately 12:00 noon and involved measurements of transparency (Secchi disk), temperature, and dissolved oxygen in the water column profile, pH, free available carbon dioxide, and alkalinity (by titration). Samples were then collected and put on ice for subsequent laboratory analysis. Sampling at the Peak Creek site commenced at approximately 1:15 p.m.

Upon arrival in the laboratory (approximately 3:00 p.m.) the samples designated for algal enumeration were fixed with Lugol's solution. Pond-water agar and dilution blanks (for bacterial enumeration) were made up, autoclave sterilized, appropriate serial dilutions were made and one-ml aliquots of lake water were plated out and incubated for five days at the temperature of the lake water. All other samples were refrigerated at 4°C.

The following day, jar tests were performed, and the settled samples were processed (pH measured, water filtered through Whatman GF/C filter, and filtrate refrigerated). Total phosphorus and orthophosphate concentrations of the raw-water samples were then determined.

The second day after sample collection was devoted to analyses of DOC in both the raw and finished water samples. Chlorination of the samples that were designated for THM analysis after a seven-day reaction time followed. Gas chromatographic determination of the previous week's THM samples began on the second day after sampling and continued the following day.

Preparation and standardization of test reagents, along with glassware preparation, were the tasks for the fourth day after sampling, and, finally, on the fifth day algal and bacterial population densities were enumerated.

Preparatory Measures for Field Work

Glassware Preparation

All glassware was washed with an organic-free detergent, rinsed three times with tap water, rinsed three times more with distilled, deionized water, and dried for one hour at 105°C. Flasks and beakers were covered with aluminum foil until use.

Reagent Preparation

0.02 normal sodium hydroxide (NaOH), used in the carbon-dioxide titrmetric determination procedure, was prepared and standardized according to instructions outlined in Method 402.3, *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association *et al*., 1980) (hereafter referred to simply as *Standard Methods*).

Sulfuric acid (H_2SO_4), 0.02 normal, for use in the alkalinity determinations, was prepared and standardized according to Method 403 in *Standard Methods*.

Field Procedures

Secchi Disk Transparency Measurement

Secchi disk measurements were performed from a point on the boat which allowed for the sun (if not behind cloud cover) to be positioned over the observer's right shoulder and far enough away from the boat to prevent the disk from entering the shaded area caused by the boat.

The disk was lowered into the water until it disappeared. The depth at which this occurred was recorded. The disk was then raised until the alternating black and white markings could be clearly distinguished and this depth was noted. The transparency value was the mean of the two recorded depths.

Temperature and Dissolved Oxygen Profiles

Temperature and dissolved oxygen (DO) concentrations were determined with a Yellow Springs Instrument Company (Yellow Springs, Maryland) Model 51B Oxygen Meter. Readings were taken at the water's surface, at 0.5 meters, and at one-meter intervals to fifteen meters depth at the dam sampling station and to six meters at the Peak Creek sampling station.

pH

The pH of the water was determined with the use of Fisher-Scientific (Raleigh, N.C.) Accumet-Portable Model 150 pH Meter. Values were determined only at depths of the highest DO concentrations.

Free Carbon Dioxide

The free carbon dioxide (CO_2) concentration of the water depth exhibiting the highest DO concentration was determined by the Titrimetric Method described in Section 406B of *Standard Methods*.

Alkalinity

Alkalinity determintions were made utilizing the field titrametric method described in Section 403.4 of Standard Methods.

Sample Collection and Storage

Samples designated for later laboratory analysis were collected with a two-liter Van Dorn sampler and were transfered immediately to BOD bottles. Samples were collected for: (a) DOC analysis, (b) Phosphorus analysis, (c) Algal enumeration, (d) Bacterial enumeration, (e) THM analysis, and (f) Bench-Scale coagulation/sedimentation experiments (Jar tests).

Samples were collected only at the depth where the highest DO was observed. Because algal photosynthesis liberates significant quantities of oxygen, it was believed that DO concentrations could be used as an indicator of the depth at which the algal population density would be the greatest.

Immediately following collection, the samples were put on ice and upon arrival at the laboratory, were placed in a refrigeration unit maintained at a constant 4°C. Care was taken to ensure that the samples were exposed to as little light as possible.

Laboratory Procedures

Sample Processing

Because sample age was often a critical factor for ensuring the validity of the analytical results, certain sample analyses were given a higher priority. A listing and description of processing priority and need is as follows:

(1) fixation of algal samples: performed immediately

(2) plating of bacterial samples: performed immediately

(3) determination of phosphorus concentrations: samples could be stored for several days at 4°C.

(4) analysis for DOC: samples could be stored for several days at 4°C.

(5) jar-testing: samples could be stored for several days at 4°C.

(6) chlorination of samples for subsequent THM analysis: samples could be stored for several days at 4°C.

Algal Enumeration

Immediately upon arrival at the laboratory, the algal samples were fixed with Lugol's solution (made up of 10 gm of pure iodine, 20 gm of potassium iodide, 200 ml distilled water, and 20 gm glacial acetic acid) at a ratio of one ml lugol's to 100 ml sample. A unique feature of Lugol's solution is that it allows for a sample storage time of several months if samples are kept in the dark.

Enumeration of the algal population was performed with the use of a Sedgwick-Rafter (S-R) counting chamber. The counting technique chosen was "field counting" due to the high density of algal cells. Statistically, 30 randomly counted fields would ensure an accurate cross-sectional analysis of the algal population, but personal conversation with an algal specialist (Parker, 1981) revealed that 60 counted fields provided highly-reproducible and accurate results. Thus, the decision was made to count 60 fields.

The specific method for utilization of the S-R cell was that described in Method 1002F, Section d, of Standard Methods. Algae were identified to genera.

Bacterial Enumeration

Enumeration of the bacterial population was performed by spread-plating appropriate dilutions of lake water onto a pond-water-agar medium (PWA), which was prepared in the following manner: 500 ml of Claytor Lake water was filtered through a Whatman GF/C filter and mixed with 500 ml distilled water. The following ingredients were then dissolved in the water: 1.0 g proteose peptone, 0.1 g yeast extract, and 15 g agar. The medium was autoclave sterilized for 15 minutes at 121°C, poured into Petri plates, and allowed to gel.

Serial dilutions were made in autoclave sterilized, distilled water and 0.1 ml aliquots of 1:10, 1:100, and 1:1000 were dispersed onto the surface of the agar. The sample was then spread over the agar surface with a bent, glass rod that was flame sterilized prior to each spreading operation. Triplicates of each dilution were prepared. The plates were incubated five days at the temperature of the lake water at the time of sample collection. Following incubation, the bacterial colonies were counted and the final population number was arrived at through incorporation of the dilution multiplication factor.

Primary Productivity Determinations

Primary productivity in the Peak Creek arm was determined by a modification of the technique described by Strickland and Parsons (1968). Samples from 0.5 m were collected at one-or-two-hour intervals, spiked with 5 μCi of $Na_2\,^{14}CO_3$ and incubated in the lake at 0.5 m, for a period of four hours. Following incubation, samples were removed from the lake, fixed with 1 ml of formalin, and returned to the laboratory on ice in the dark. The samples were first filtered through Whatman glass microfiber filters (934-AH). The filtrates were then acidified in the scintillation vials with one drop of concentrated hydrochloric acid (HCl) and left exposed to the atmosphere in a fume hood for 24 hours before scintillation counts were obtained (Th filterable fraction will be referred to hereafter as "algal ECP"). The filters were dried in a dessicator containing HCl to destroy any residual carbonate and placed in scintillation vials with 15 ml Scintiprep (Fisher Scientific, Pittsburgh) and then counted in a scintillation counter (Backman Model LSC-2) for five minutes with an error setting of two percent at a gain of 350. Instrument efficiency was determined by comparison of counts obtained to standards.

Phosphorus

Analysis of the lakewater was performed to determine the total phosphorus concentration and the orthophosphate concentrations. Total phosphorus was determined by the Persulfate Digestion Method, Section 424CIII, with the Ascorbic Acid Method, Section 424F outlined in Standard Methods. The orthophosphate concentration was determined by the Ascorbic Acid Method, Section 424F in Standard Methods.

Dissolved Organic Carbon

Dissolved organic carbon (DOC) was measured utilizing a Dohrman-Envirotech (Santa Clara, CA) DC-54 Ultra-Low Level Total Organic Carbon Analyzer. Samples, prior to injection into the analyzer, were filtered through 0.45 micron Whatman GF/C filters to remove particulate matter and then mixed with a phosphoric acid/potassium persulfate solution. Replicate samples were analyzed to obtain values that fell within two percent of one another. Values were then averaged.

Bench-Scale Coagulation/Sedimentation Procedures

One-liter samples of lake water were placed in each of six jars and dosed with varying concentrations of alum. The stock solution contained 2.469 g $Al_2(SO_4)_3 \cdot 18 H_2O$ in 100 ml so that one milliliter was equivalent to 2.0 mg Al^{3+}. Usually, the applied alum dosages were 1, 2, 3, 4, 6, and 8 mg/L as Al^{3+}.

As the alum was added, the samples were rapidly mixed for 60 seconds, allowed to flocculate at a slow paddle speed for 20 min, and settling was permitted for 30 min. A standard six-place laboratory jar-test apparatus was used in these studies.

Settled water was withdrawn from each jar and the pH was measured. Then, a portion was filtered through a Whatman GF/C filter and the DOC concentration was determined by analysis of a portion of the filtrate. Another portion of the filtrate was placed in a 30-ml vial, chlorinated, then sealed for incubation and development of THM's.

Determination of Trihalomethane Formation Potential (THMFP)

Samples of raw lakewater and alum-treated lakewater were chlorinated for THM analysis by a gas chromatographic purge-and-trap technique. The protocol was as follows: Each sample was transferred to a 30 ml sample vial (Pierce No. 13075 Pierce Company; Rockford, Illinois) containing 0.3 ml 1.0 M NaH_2PO_4/0.1 M Na_2SO_4 buffer solution (to provide a pH of 6.6 - 6.8). The vial was filled to three-quarters capacity, allowing for mixing of the sample and buffer. Next, 0.5 mL of stock calcium hypochlorite solution (2000 mg/L available chlorine) was pipetted into each vial, the vial quickly filled to capacity, and sealed with a Pierce No. 12722 Teflon septum inside a screw cap, with care being taken to prevent the formation of any headspace in the vial.

After a seven-day, ambient room temperature incubation period, THM concentrations were determined with a Tracor 560 Gas Chromatograph (Tracor Company, Austin, Texas), equipped with a Tekmar LSC-2 concentrator (Tekmar Company, Cincinnati, Ohio), by the purge-and-trap method developed by the Environmental Protection Agency (Environmental Protection Agency, 1979).

Preparation of the stock calcium hypochlorite solution was performed by the addition of 4 g calcium hypochlorite into one liter distilled water, giving an available chlorine concentration of 2 g/L. The solution was standardized with an Amperometric Titrator.

IV. RESULTS

Field Results

Figures 3 and 4 depict key meteorological and physical/chemical limnological characteristics measured in the field at the Peak Creek and dam sites, respectively, during the study period. The actual field data appear in tabular form in Appendix A. Important features of these data are emphasized in the following paragraphs.

Rainfall

Rainfall was sporadic throughout the 23 week test period, with the greatest amounts of precipitation falling between July 12 and August 15.

Air Temperature

The average summer-early autumn (May 31 - September 6) air temperature was 28.6°C, while the mean late fall (September 9 - November 23) temperature was 15.7°C.

Secchi Disk Transparency

Figure 3 reveals that Peak Creek Secchi disk transparency readings displayed a distinctly seasonal pattern. The late-spring to early-autumn interval (May 31 - October 3) was characterized by low transparency [mean, 1.03 meters (m)], while the late-autumn period of October 11 to November 14 exhibited markedly higher transparency values (mean, 1.95 m).

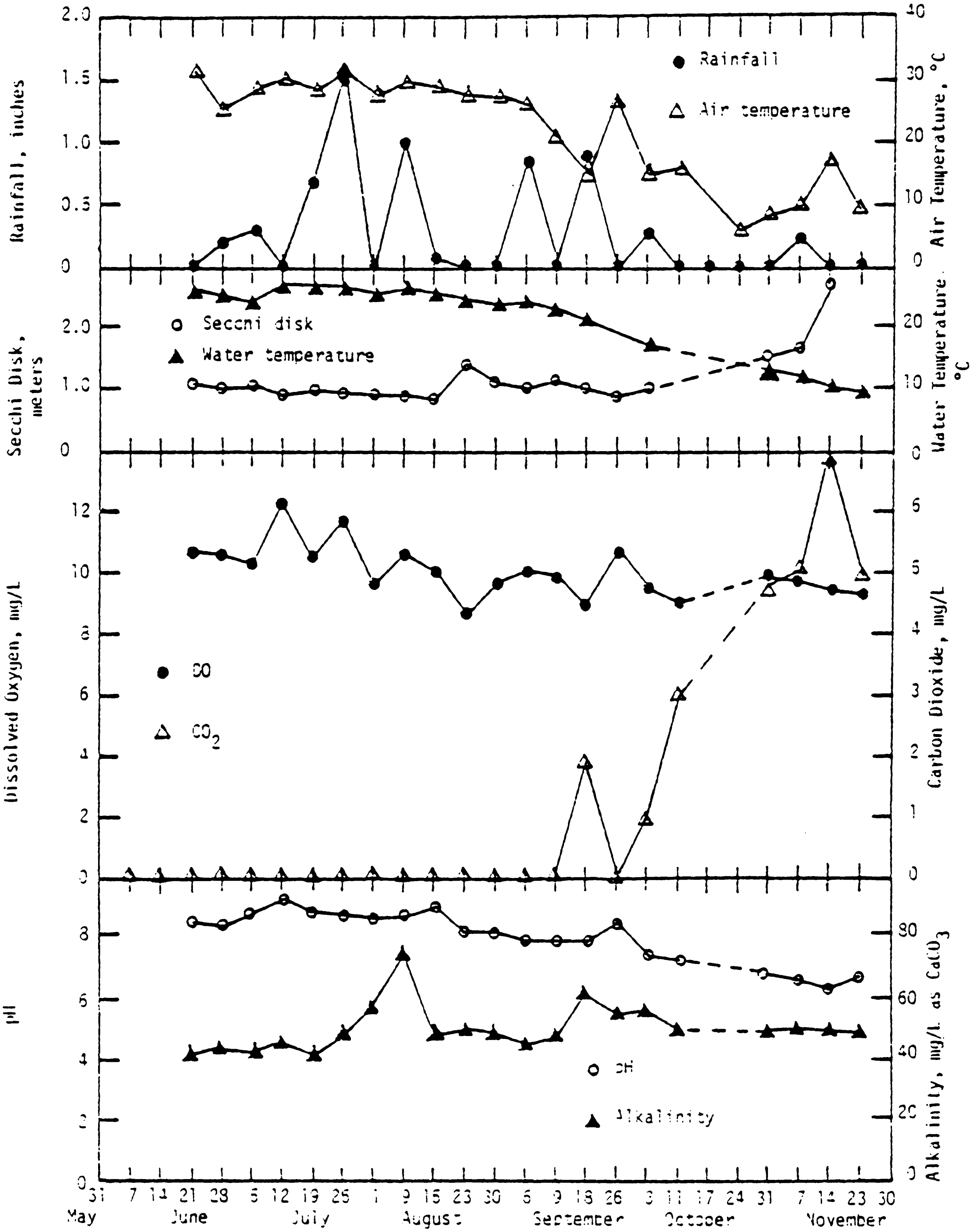


Figure 3. Seasonal variations in physical and chemical field parameters, Peak Creek arm of Claytor Lake, 1981.

Figure 4 shows that the typical summer phenomenon of low transparency was of much shorter duration at the dam than at Peak Creek, with low values occurring for just five weeks (June 21 - July 19). Mean transparency during this interval was 1.37 m as compared to the 2.29 m mean value for the subsequent nine week period.

Transparency at the dam was significantly greater than at Peak Creek during the study, as evidenced by the respective mean values of 1.96 m and 1.17 m.

Table 5 reveals the seasonality of transparency along with the marked variance in transparency between Peak Creek and dam waters.

Dissolved Oxygen

In analyzing dissolved oxygen results, two aspects are worthy of note: the seasonal trend in concentrations at a depth of 0.5 m and the depth profiles.

Seasonally, DO concentrations at Peak Creek were highest during the interval from June 21 to August 15 with values ranging from 9.6 mg/L to 12.2 mg/L (Figure 3), while the period from August 23 to November 23 was characterized by markedly lower concentrations that ranged from 8.6 mg/L to 10.7 mg/L. Mean concentrations during each interval were 10.7 mg/L and 9.6 mg/L, respectively.

Seasonal trends at the dam were similar to those at Peak Creek, with the notable difference of markedly lower DO concentrations in waters near the dam. DO concentrations were highest during the period from June 21 to July 19, with values ranging from 8.4 mg/L to 10.2 mg/L,

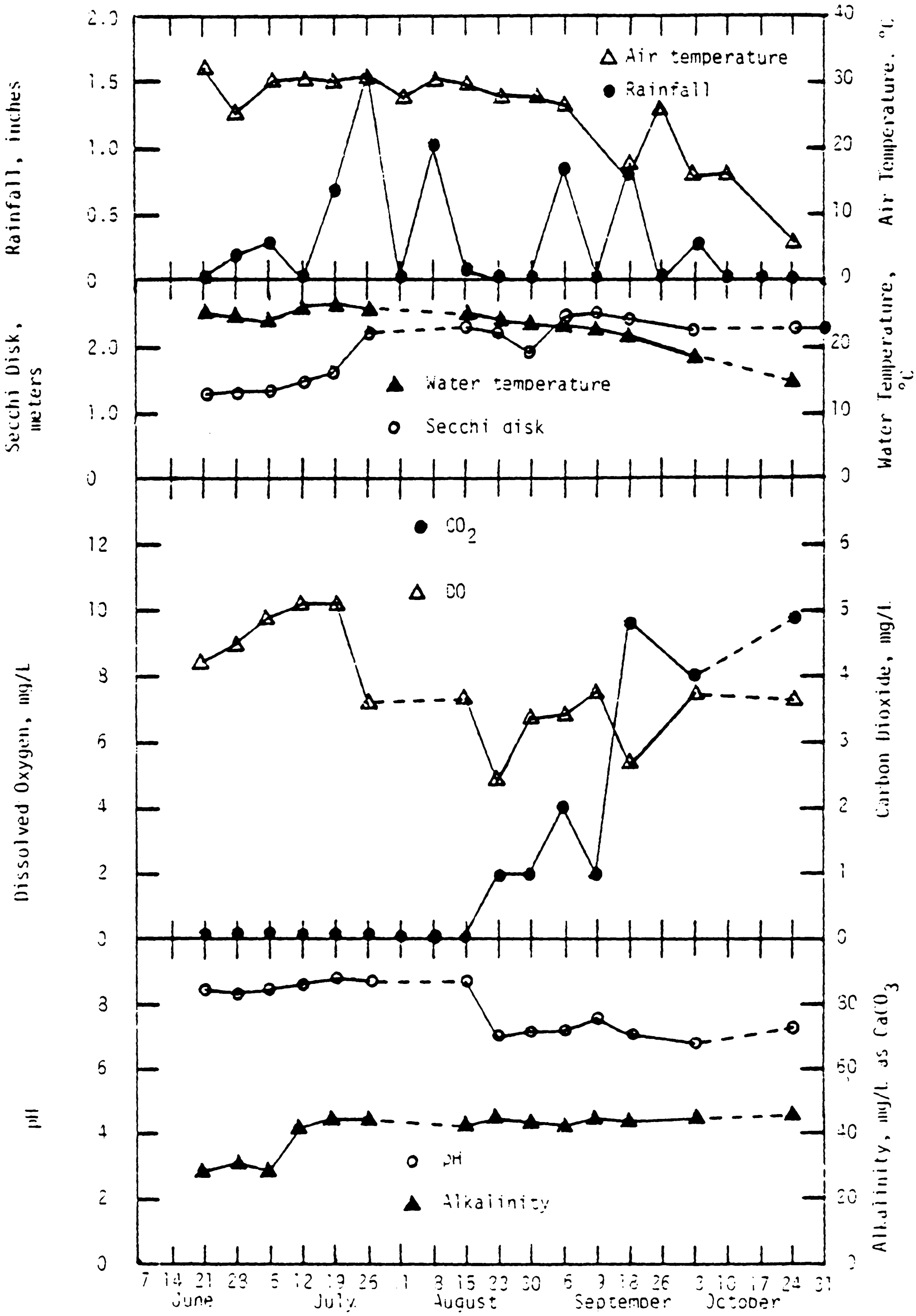


Figure 4. Seasonal variations in physical and chemical field parameters, Claytor Lake dam site, 1981.

Table 5. Comparison of Monthly Secchi Disk Transparency Values Received from the Peak Creek Arm and the Claytor Lake Dam Sites.

Station	Month, 1981	Mean Transparency m	Minimum Transparency m	Maximum Transparency m	No.*
Peak Creek	June	1.06	1.03	1.09	2
	July	0.97	0.90	1.05	4
	August	1.03	0.83	1.43	5
	September	1.04	0.94	1.15	4
	October	1.25	0.98	1.52	2
Dam	June	1.28	1.25	1.31	2
	July	1.64	1.28	2.23	4
	August	2.12	1.88	2.31	3
	September	2.46	2.43	2.52	3
	October	2.29	2.25	2.33	2

*No. = Number of measurements

while the remainder of the test period exhibited a markedly lower range of 4.8 mg/L to 7.6 mg/L (Figure 4). Mean concentrations during each interval were 9.5 mg/L and 6.7 mg/L, respectively.

These trends indicate that at both sites, DO was present in greatest quantity during the early-to-mid-summer months and decreased significantly thereafter.

Peak Creek DO profiles revealed a near-anaerobic hypolimnion from May 31 to September 9, after which time, increased circulation resulted in a hypolimnion of high DO content. Figure 5 illustrates the various DO profiles encountered at Peak Creek. Epilimnetic DO concentrations mirrored the seasonal trends described previously.

DO profiles at the dam revealed a hypolimnion that was moderately oxygenated for the first five weeks of the test period and which underwent a marked decrease in DO until near-anaerobiosis resulted during the interval from July 26 to September 6. The autumn overturn was signalled by a dramatic increase in hypolimnetic DO levels on approximately September 9 and the remainder of the test period was characterized by a well-oxygenated hypolimnion. Figure 6 illustrates the various DO profiles encountered near the dam.

Epilimnetic DO concentrations mirrored the seasonal trends described earlier.

Water Temperature

Like DO, the water temperatures at 0.5 m and the temperature profiles are best analyzed on a seasonal basis. Seasonally, surface

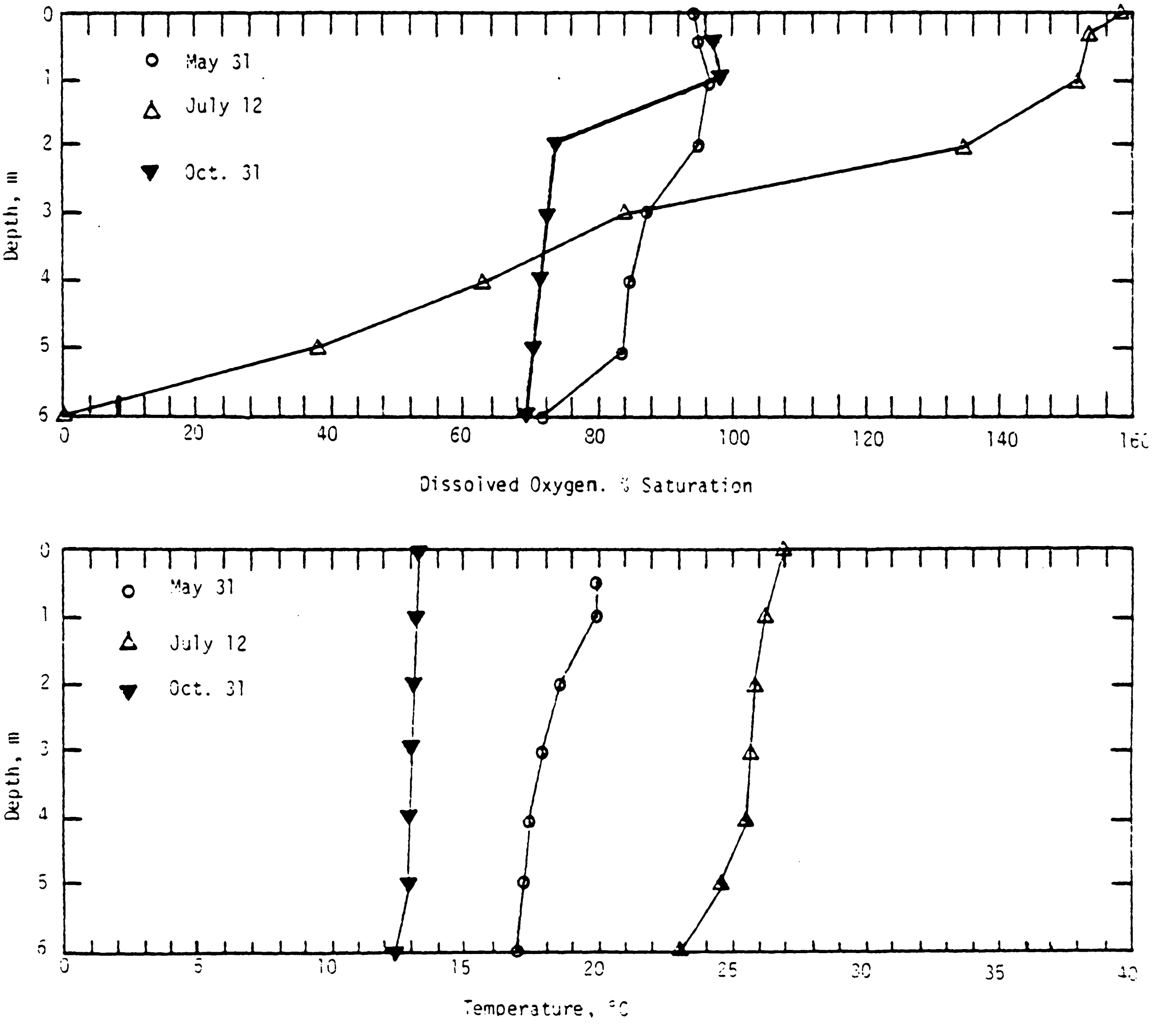


Figure 5. Profiles of dissolved oxygen and temperature on selected dates, Peak Creek arm.

water temperatures at Peak Creek fluctuated little during the period from June 21 to September 6, ranging from 23.9°C to 26.8°C. Subsequent temperatures decreased markedly from 24.2°C to 9.5° by November 23 (Figure 3). Mean temperatures during these intervals were 25.6°C and 18.8°C, respectively.

Temperatures near the dam remained fairly constant through mid-September, ranging from 21.8°C to 26.7°C, followed by a significant decrease to 14.8°C by October 24 (Figure 4).

On the whole, the Peak Creek temperature profiles mirrored the seasonal trends just described. Figure 5 illustrates the temperature profiles on several dates during the test period. Note that the lake at the Peak Creek site never thermally stratified to any great degree, most probably because of its relatively shallow depth and the instability induced by the current of the flowing waters.

The temperature profiles of the lake at the dam revealed some interesting developments, the most important of which are illustrated in Figure 6. On June 21, a temperature difference of 8.8°C existed from the water's surface to 15 m's, indicating strong thermal stratification. By September 6, however, temperatures were uniform throughout the upper 15 m, signaling the potential for overturn and circulation of the entire water column. The remainder of the season was characterized by temperature profiles similar to that of September 6.

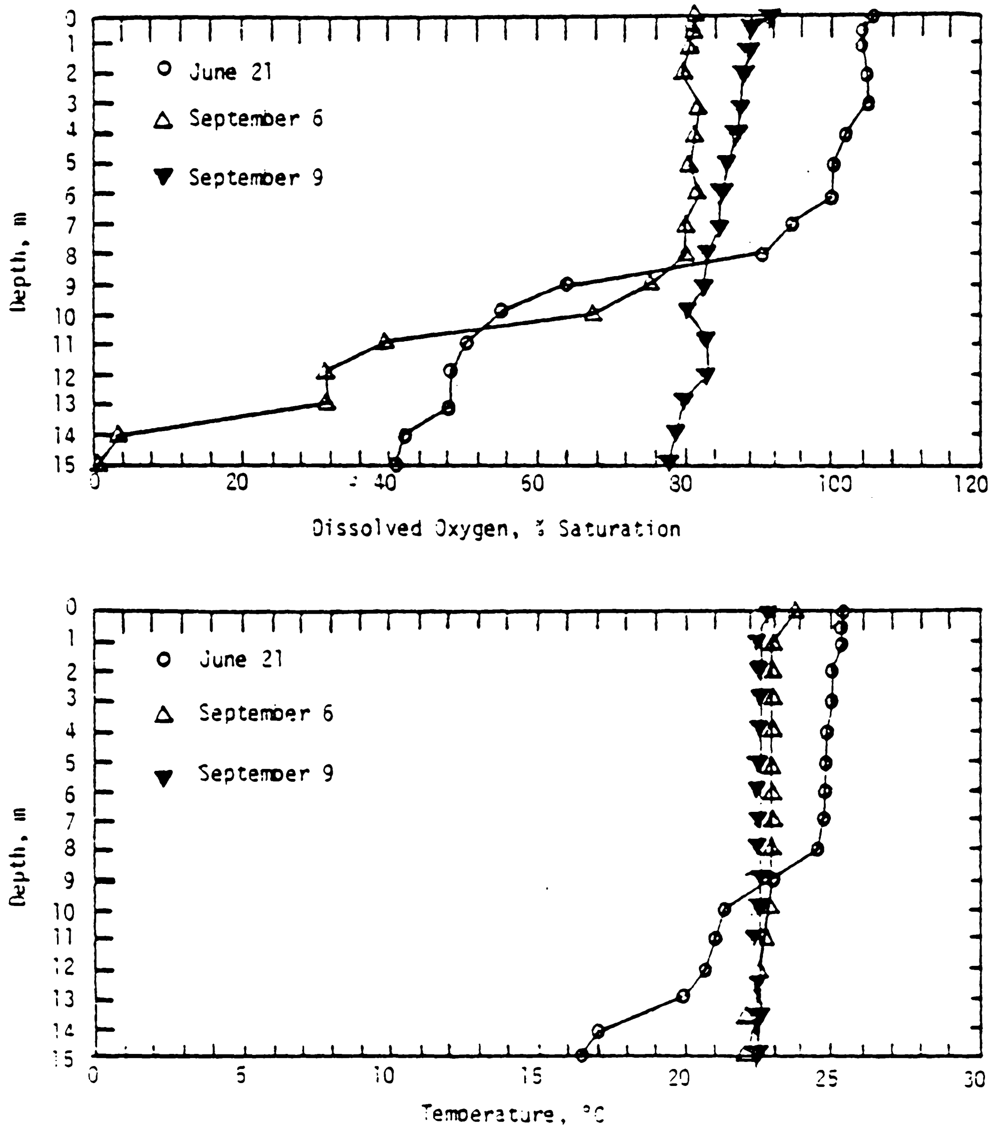


Figure 6. Profiles of dissolved oxygen and temperature on selected dates, dam site.

Free Carbon Dioxide

Figure 3 reveals that day-time free carbon dioxide levels in Peak Creek waters exhibited definite seasonal trends. Prior to the onset of summer, the available CO_2 concentration at 0.5 m was 5 mg/L (May 31). With the establishment of typical summer conditions (e.g. warm air and water temperatures and prolific algal activity) free CO_2 concentrations decreased to undetectable levels and remained undetectable for 15 weeks, the approximate duration of the summer season. With the onset of cooler weather, free CO_2 concentrations became detectable once again and reached a level of 7 mg/L by November 14.

Similar patterns occurred at the dam, as is evident from Figure 4, with undetectable levels prevailing for the initial seven weeks (June 21 - August 15), followed by steady increases throughout the remainder of the study. The maximum level of five mg/L was recorded on October 24.

pH

At both sampling sites, pH levels followed the same general pattern of seasonality exhibited by several other lake characteristics. At Peak Creek, the mean pH during the period from June 21 to August 30 was 8.8 compared to a mean pH of 7.4 for the remainder of the test period (September 6 - November 23).

A similar trend was evident at the dam where the average pH during the mid-summer months (June 21 - August 15) was 8.6, while the mean during the late summer-early autumn interval (August 23 - October 24) was 7.2.

Alkalinity

The outstanding characteristic of Peak Creek alkalinity levels, evident from Figure 3, was the lack of any discernible, seasonal pattern, while concentrations at the dam (Figure 4) steadily increased from July 12 through October 24. Mean values at the Peak Creek and dam sites during the entire period of study, were 50 mg/L and 41 mg/L, respectively.

Laboratory Results

Biological and chemical features of Claytor Lake that required laboratory analyses are presented in this section. In addition, the results of jar tests, which were intended to demonstrate the removability of DOC and reduction of THMFP by chemical coagulation, will be presented. Actual laboratory data appear in tabular form in Appendix B.

Bacterial Populations

Figure 7 demonstrates that the Peak Creek bacterial population, determined by the spread-plate technique, increased generally throughout the 14 week period (June 21 - September 18) from 4,200 colony-forming units per ml (CFU/ml) to 37,000 CFU/ml. The remainder of the test period was characterized by marked decreases in the population to a level of 3,300 CFU/ml, by the end of the study.

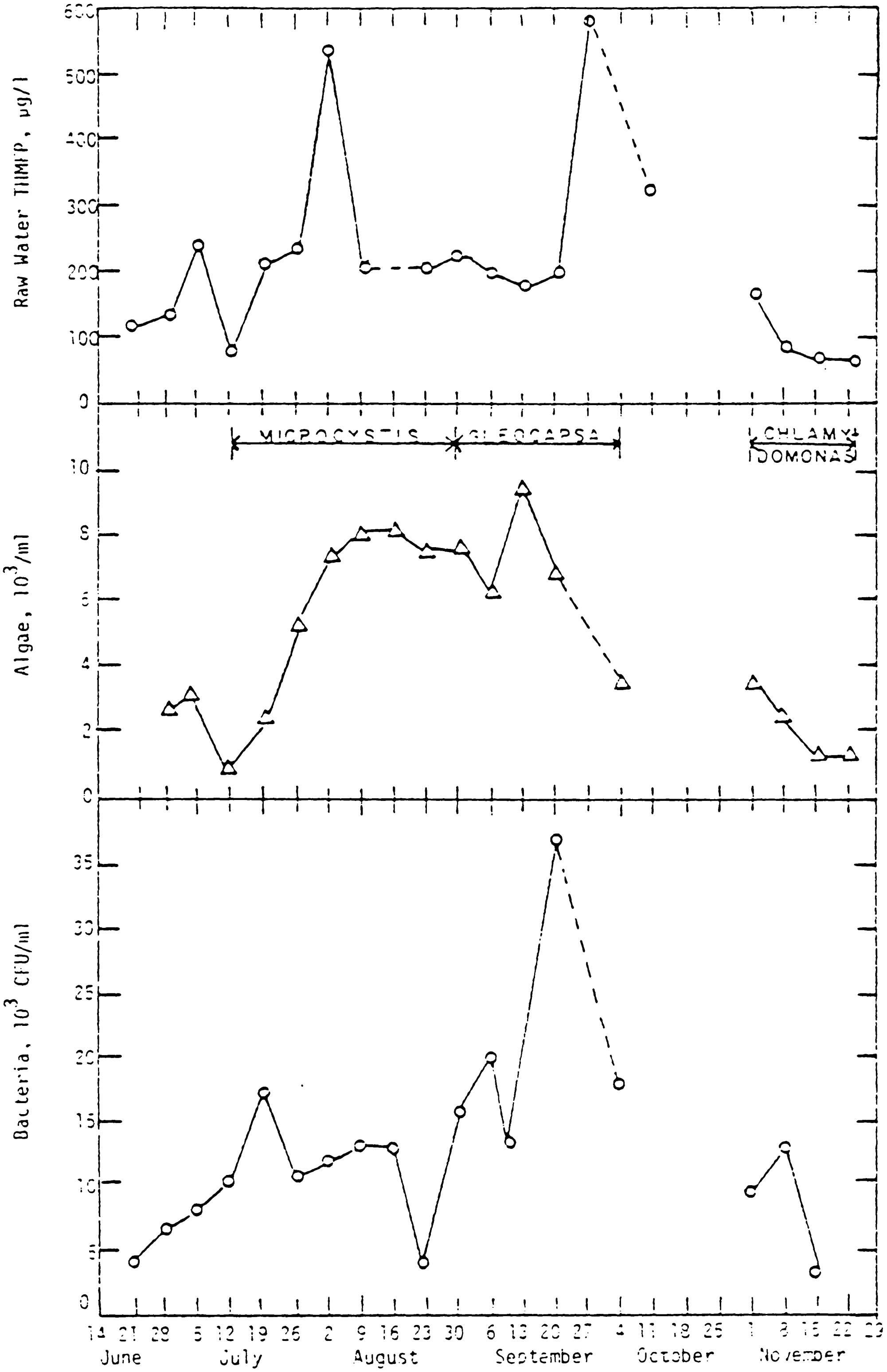


Figure 7. Variations in THM-formation potentials of Claytor Lake water at the Peak Creek site shown in relationship to observed fluctuations in the algal and bacterial population densities, 1981.

The bacterial population at the dam (Figure 8), unlike that at Peak Creek, exhibited no discernible growth patterns or trends. Highly variable population numbers were detected throughout the test period, ranging from 1,900 CFU/ml (June 21-28) to 19,300 CFU/ml (September 6). The overall mean population of 7,390 CFU/ml was significantly lower than the 12,778 CFU/ml mean population of Peak Creek.

Algal Populations and Taxa

In order to achieve a complete understanding of the trends experienced by the phytoplankton community, analysis of the algal enumeration results has taken several forms, including total population size, population size of each Division, emphasis of dominance at the divisional and generic level, and extent of diversity.

Peak Creek Site. The Peak Creek algal community (Figure 7) exhibited a number of important trends in population size during the course of the test period. Initially, the population was characterized by an interval of growth (June 28 - August 15), exhibiting a seven-fold increase from 1,195 organisms/ml to 8,110/ml. This was followed by a three week period of moderate decline to a level of 6,240 ml. The largest population density, 9,480 ml, was observed the following week (September 9) and from that point on, community density decreased markedly to a low of 1,300/ml by November 23.

Of the 18 weeks that algal population density size was measured, 13 were dominated by the Division, Cyanophyta, the blue-green algae. On occasion, the blue-greens constituted 99.3 percent of the algae present.

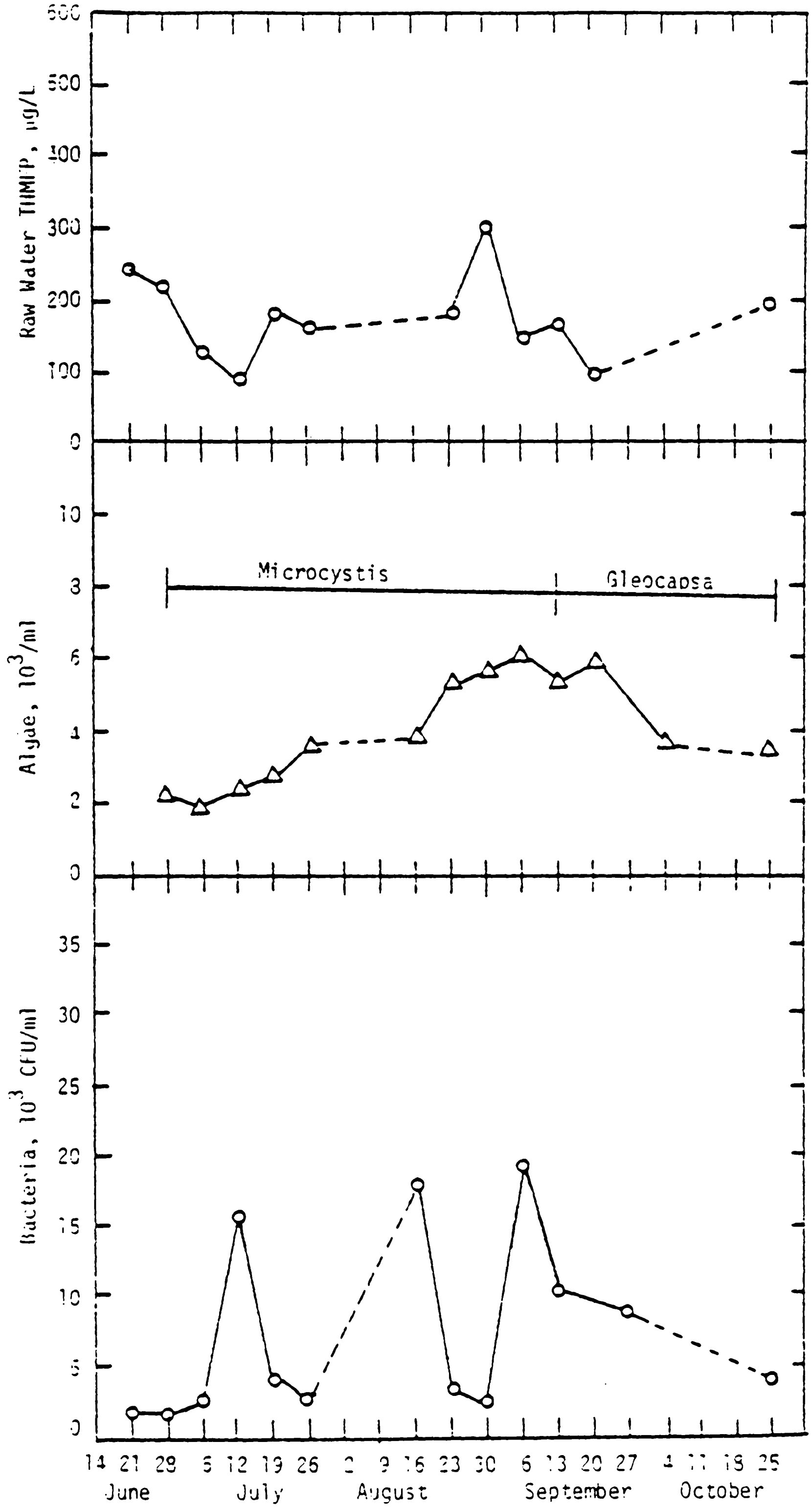


Figure 8. Variations in THM-formation potentials of Claytor Lake water at the dam site shown in relationship to observed fluctuations in the algal and bacterial population densities, 1981.

They comprised an average 68.2 percent of the total population during the 18 week study period and 90 percent during the 13 week period of prolific growth, thus illustrating the extent to which the so-called "nuisance algae" dominated in the Peak Creek arm. Cyanophytan population densities ranged from less than one per ml on November 23 to 9,320/ml on September 9. The mean population density was 4,097/ml.

Closer analysis reveals that in the 13 week period during which the blue-greens were most abundant, *Microcystis aeruginosa* dominated for eight weeks, *Gleocapsa* for four, and *Anabaena* for one. A typical sample of Peak Creek water contained the blue-green algae *Microcystis*, *Oscillatoria*, *Coelsphaerium*, *Gleocapsa*, *Aphanocapsa*, *Anabaena*, *Chroococcus*, and *Aphanizomenon* (Appendix B). In all, ten species of blue-greens were detected. Note that at the beginning of the test period it was not unusual for a grab sample to contain representatives of all these genera, but by mid-summer, only three or four genera (*Microcystis*, *Anabaena*, *Oscillatoria*, and *Coelsphaerium*) were represented. Thus, not only did the most dominant forms become numerous, but they did so almost to the exclusion of all other blue-green species.

The green algal Division, Chlorophyta, was represented throughout the entire test period, with population sizes ranging from 50/ml to 3,180/ml, and averaging 730/ml. Through the first 13 weeks, the greens never attained significant proportions, averaging a rather low 302/ml because of the dominance of the blue-green algae. Once the blue-green population waned, however, the green algae grew prolifically and dominated during the final four weeks of testing, averaging 1,973 organisms/ml and constituting up to 98 percent of the total population. *Chlamydomonas* became the most prevalent genus during this period.

The Chlorophyta community exhibited significant diversity, and a typical grab sample included *Gleocystis*, *Scenedesmus*, *Kirchneriella*, *Staurastrum*, *Mougeotia*, *Zygnema*, *Selenastrum*, *Pediastrum*, *Microspora*, *Cosmarium*, *Ankistrodesmus*, *Coelastrum*, and *Crucigenia* (Appendix B). In the earliest test dates, as many as eleven different genera were found in a sample of Peak Creek water. As expected, the prolific growth of blue-greens reduced chlorophyta diversity, on occasion limiting it to only two species. Recovery in late autumn did occur, although not to the degree experienced in the early summer months.

The Bacillariophta (diatom) remained depressed throughout the entire test period, never exceeding a level of 228 organisms/ml. On two occasions none were found. The average number of diatoms/ml was a mere 69.1 and never constituted more than 15.1 percent of the total algal community. The Bacillariophton community was dominated by such genera as *Cyclotella*, *Coscinodiscus*, *Fragilaria*, *Tabellaria*, and *Stephanodiscus*, the most prevalent being *Coscinodiscus*.

Dam Site. The algal community at the dam (Figure 8) displayed a distinctly seasonal trend of increasing populations during the warm summer-early autumn months, followed by a marked decline with the onset of cooler weather.

The interval from July 5 through September 9 was characterized by a three-fold increase in the algal density, from 1,950 organisms/ml to 6,000/ml. The ensuing seven week period resulted in a marked decline in population density to a level of 3,230/ml by October 24. Comparatively speaking, an average Peak Creek algal population numbered 4,896/ml, while an average dam algal population numbered 3,975/ml.

The Division Cyanophyta, dominated the dam algal community on all 13 test dates, at times constituting up to 99.7 percent of the total algal population present. The blue-greens were so prevalent that they comprised an average of 88.6 percent of the total algal community.

On nine of the 13 weeks in which algal densities were determined, _Microcystis aeruginosa_ was the dominant species and during the other four weeks, _Gleocapsa_ dominated. Typical samples of lake water from the dam site were composed of cyanophytan forms such as _Microcystis_, _Gleocapsa_, _Oscillatoria_, _Coelsphaerium_, _Anabaena_, _Aphanocapsa_, _Nostoc_, _Chroococcus_, _Oocystis_, and _Coelastrum_, a diverse population of eleven genera. As was observed at the Peak Creek site, the blue-green forms of _Microcystis_, _Gleocapsa_, _Oscillatoria_, and _Anabaena_ became dominant, almost to the exclusion of all other species, during the last eight weeks of the season, again pointedly demonstrating the dominant role which the blue-greens played in the Claytor Lake algal community.

The Chlorophyta population declined markedly throughout the test period, decreasing from a level of 650 organisms/ml on June 28 to less than one/ml by November 3.

The green algae rarely constituted a major portion of the algal community, averaging a low of 9.7 percent of the total population present. Typically, the genera observed were *Kirchneriella*, *Scenedesmus*, *Cosmarium*, *Pediastrum*, *Closterium*, *Zygnema*, *Selenestrum*, *Gleocystis*, *Mougeotia*, *Staurastrum*, *Microspora*, *Ankistrodesmus*, and *Tetrastrum*, in all a diverse representation of the Chlorophytan division, with 14 genera being present. As the blue-greens became dominant, chlorophytan diversity declined markedly, decreasing to two or three genera, principally *Kirchneriella*, *Microspora*, and *Ankistrodesmus*.

The Bacillariophytan community was observed on only seven occasions, never numbering greater than 170 organisms/ml and never constituting more than 7.6 percent of the total algal population. In fact, the average Bacillariophytan percentage of total algae was a mere 1.6 percent.

When the diatoms were observed, the following genera were represented: *Coscinodiscus*, *Ankistrodesmus*, *Stephanodiscus*, *Tabellaria*, *Fragilaria*, and *Cyclotella*. *Coscinodiscus* was the most prevalent form observed.

In summary, both sampling sites supported large algal populations that were dominated by the blue-green algae. Early in the season, diversity was high among all phyla, but as the blue-greens began to grow prolifically, diversity was much reduced, and on occasion, the only algae observable were the most dominant genera of the blue-greens, *Microcystis*, *Gleocapsa*, and *Oscillatoria*.

Phosphorus

On all test dates, the orthophosphate and total phosphorus concentrations were below the ascorbic acid method detection limit of 0.15 mg/L (1 cm path length). This finding is consistent with the EPA determination that Claytor Lake is a phosphorus-limited aquatic ecosystem (EPA, 1979).

Raw-Water Dissolved Organic Carbon

The raw-water DOC concentration at Peak Creek (Figure 9) fluctuated moderately throughout the test period, ranging from 1.92 mg/L (November 23) to 4.38 mg/L (August 15). The mean DOC concentration was 2.65 mg/L.

DOC levels at the dam site also fluctuated moderately with a range of 1.76 mg/L (August 23) to 3.064 mg/L (July 12). The mean DOC concentration was 2.38 mg/L (Figure 10).

Raw-Water THM-Formation Potential

Figure 9 shows that the THM-formation potential (THMFP) of Peak Creek waters varied greatly during the test period, fluctuating from 68 μg/L (November 23) to 589 μg/L (September 26). The mean THMFP was 207 μg/L.

Figure 10 shows that the THMFP of waters near the dam fluctuated markedly less than those at Peak Creek, with values ranging from 93 μg/L (September 18) to 300 μg/L (August 30). The mean THMFP of 169 μg/L was also significantly lower than that of Peak Creek waters.

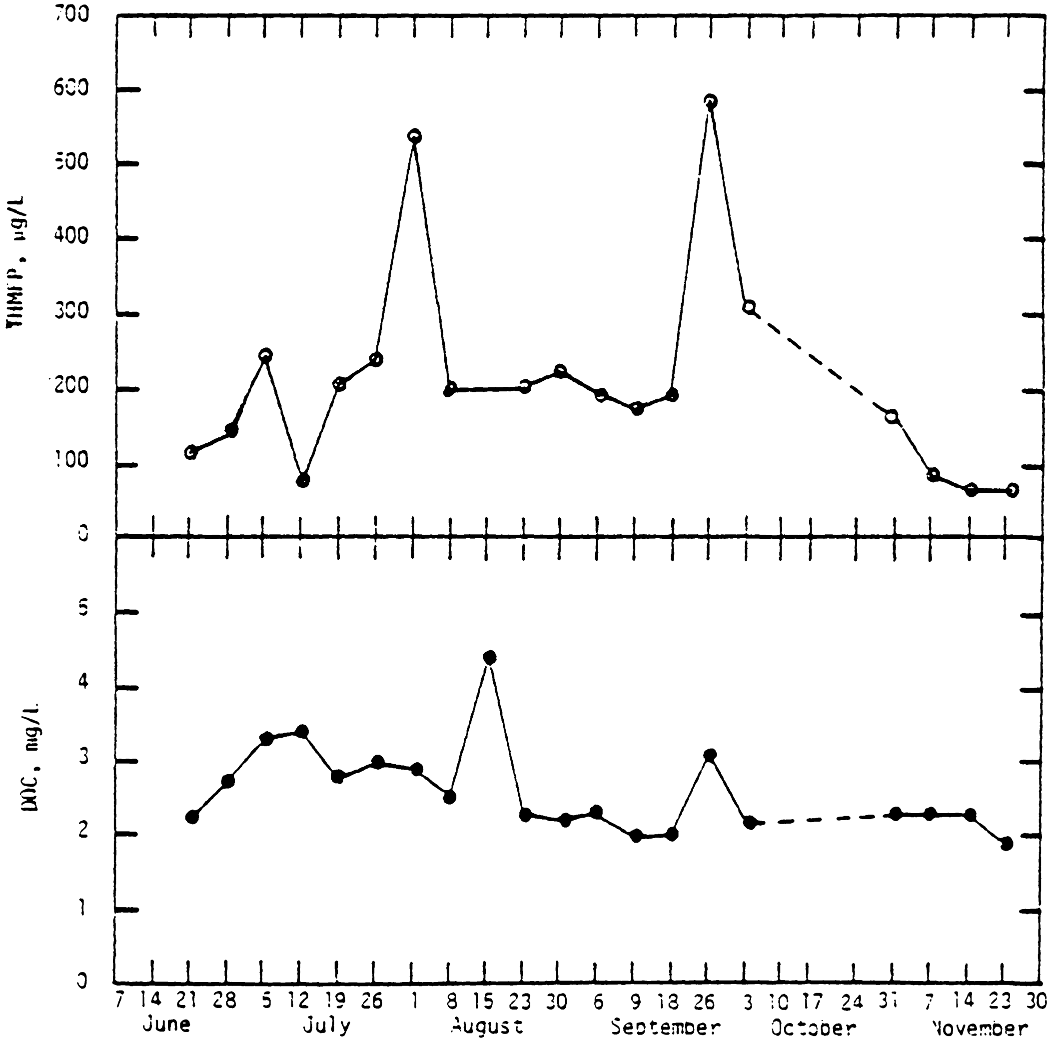


Figure 9. Variations in THM-formation potentials (THMFP) of Claytor Lake water at the Peak Creek site in relationship to observed fluctuations in dissolved organic carbon (DOC) levels, 1981.

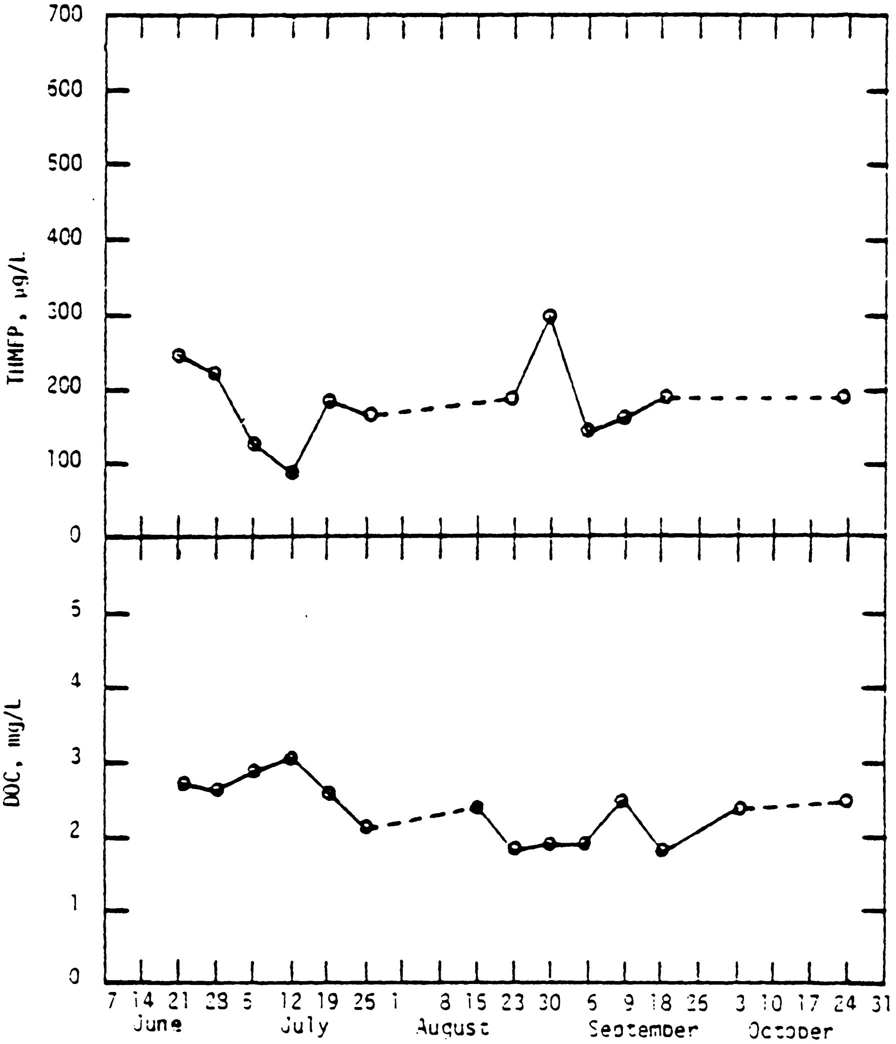


Figure 10. Variations in THM-formation potentials (THMFP) of Claytor Lake water at the dam site in relationship to observed fluctuations in dissolved organic carbon (DOC) levels, 1981.

Jar Tests

Table 6 summarizes the results of the coagulation tests designed to evaluate the effectiveness of aluminum sulfate for the removal of THM-precursors and DOC from the lake water. Figures 11 and 12 show residual DOC and THM-formation potentials of the water samples treated with alum in concentrations of 2, 3, and 4 mg/L as Al^{+3}. The selection of these particular data for the figures was based upon the constraint that the final pH of the treated water had to fall within the pH range of 5.0 to 6.5, the optimum range of aluminum hydroxide solubility. (The dosages of 6 and 8 mg/L as Al^{+3} produced finished waters with pH's outside of this range.)

2 mg/L Al^{+3} proved to be quite effective in reducing the THMFP of the water from both sampling sites. The mean reduction in Peak Creek THMFP was 42.9 percent, while at the dam the mean reduction was 50.5 percent. The mean residual, finished-water THM concentrations were 82 μg/L and 76 μg/L, respectively. The average removal of DOC was significantly less than the average reduction in THMFP. Mean DOC removals by 2 mg/L Al^{+3} were 35.9 percent from Peak Creek water and 43.3 percent from dam water, while the average residual concentrations were 1.45 mg/L and 1.18 mg/L, respectively. Finished water DOC levels fluctuated weekly and exhibited no discernible seasonal trends.

The treatability of the lake water utilizing 3 mg/L Al^{+3} was significant. The mean reduction in Peak Creek THMFP was 44.8 percent while the corresponding reduction in dam water was 50.6 percent. The

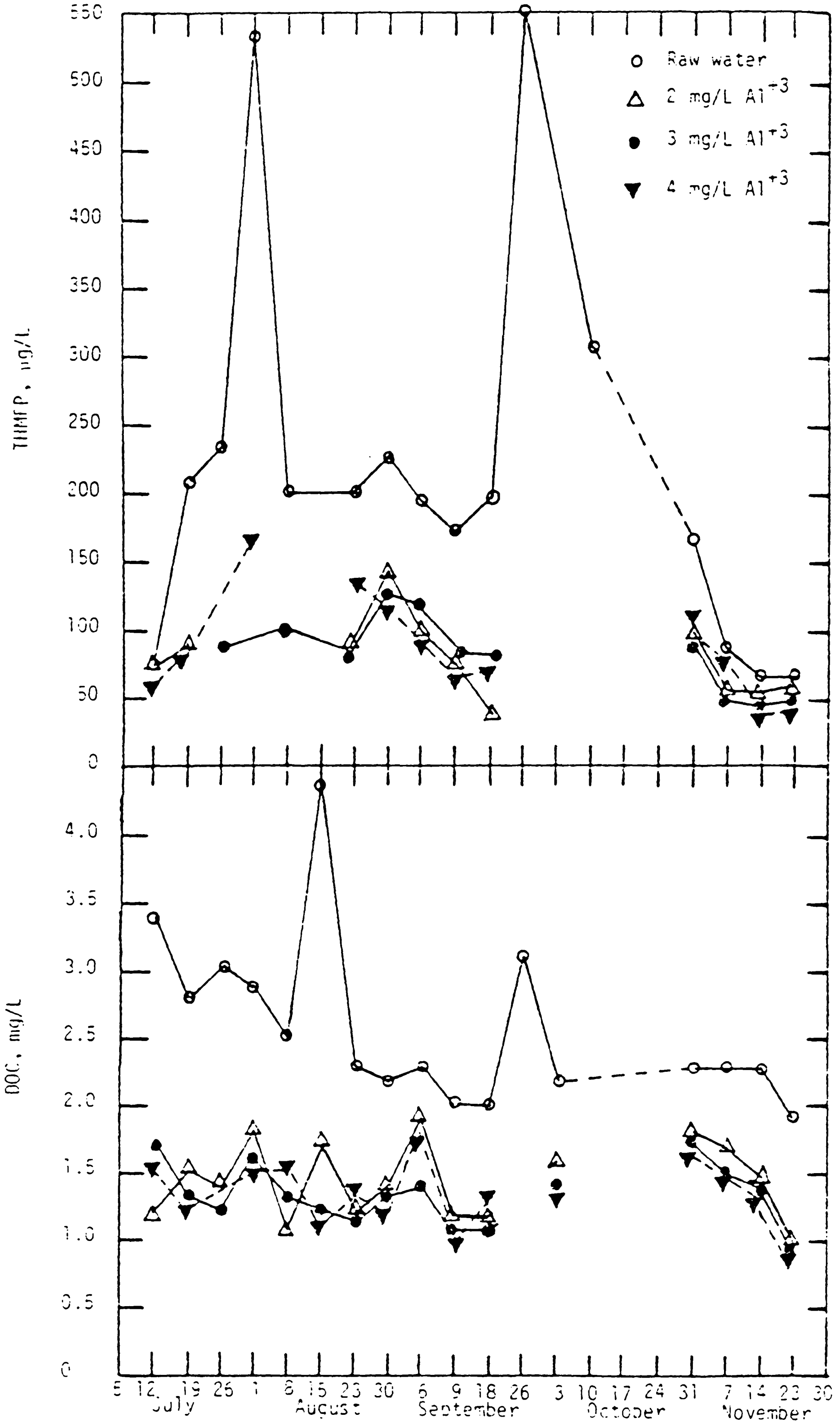


Figure 11. Variations of raw and alum-coagulated waters from the Peak Creek arm of Claytor Lake, 1981.

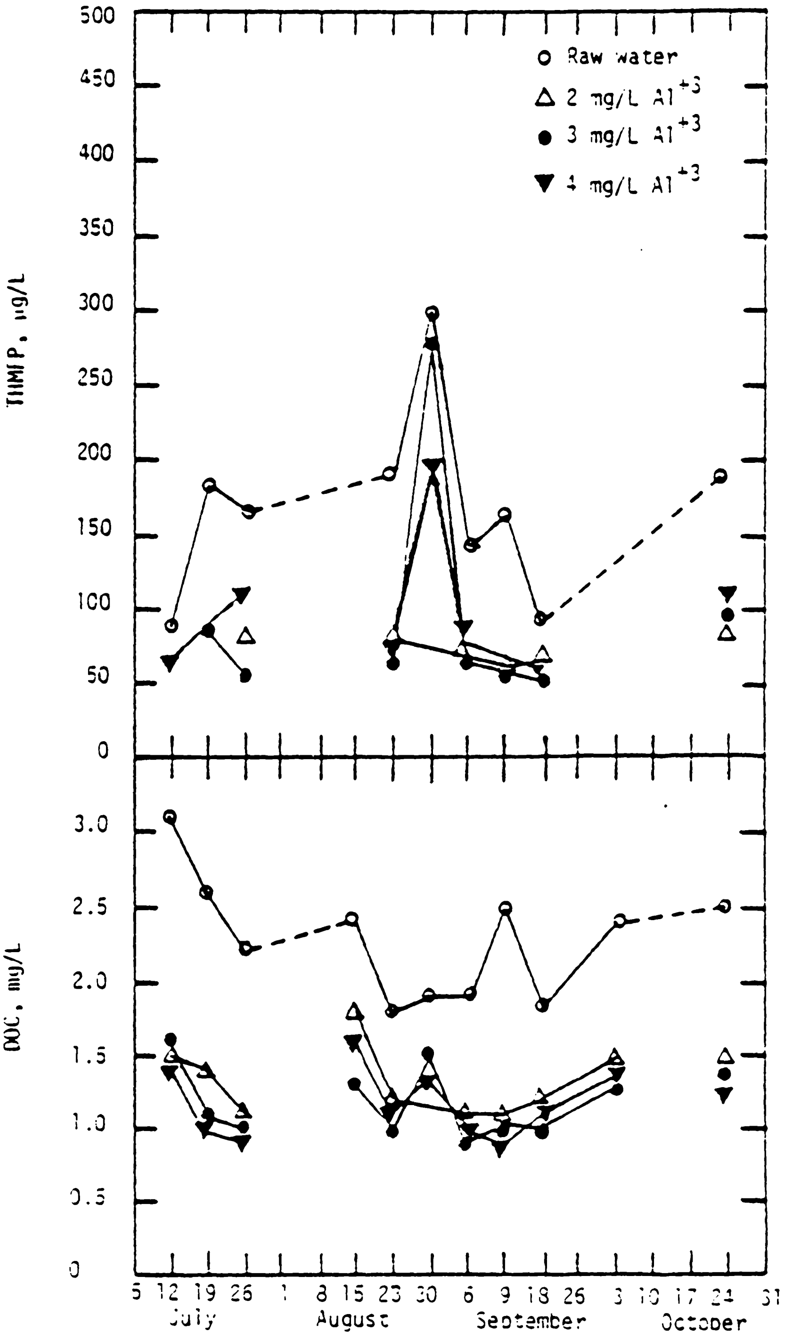


Figure 12. Variations in the THM-formation potentials (THMFP) and the dissolved organic carbon concentrations (DOC) of raw and alum-coagulated waters from the Claytor Lake dam site, 1981.

resultant mean residual TTHM concentrations were 85 μg/L and 95 μg/L, respectively. DOC removals averaged 42.8 percent with Peak Creek waters and 47.5 percent with dam waters. Mean residual concentrations were 1.31 mg/L and 1.11 mg/L, respectively. Finished water DOC levels fluctuated weekly and exhibited no discernible trends.

Utilization of 4 mg/L Al^{+3} proved to be effective with waters from both sampling sites. Peak Creek finished-water THMFP and DOC removal were identical, with reductions of 43.6 percent being achieved. Respective residual concentrations were 89 μg/L and 1.34 mg/L. Reductions achieved upon treatment of water from the dam site were 45.2 percent and 45 percent for THMFP and DOC, respectively. Residual concentrations were 92 μg/L and 1.23 mg/L DOC. There were no discernible trends in finished water DOC levels.

In summary, the coagulation tests with dosages of 2, 3, and 4 mg/L Al^{+3} resulted in the efficient reductions in THMFP and removal of DOC from waters from both sampling sites. In all cases, these reductions were more complete with lake water drawn from near the dam than those achieved with water from the Peak Creek arm.

Diurnal Studies

The following paragraphs briefly describe the results of the four diurnal studies of the variations in algal productivity and selected chemical characteristics of waters at the Peak Creek site on Claytor Lake. The data have been tabulated in Appendix C and appear in Figures

13-16.

Diurnal Study #1

Figure 13 summarizes the data obtained from the diurnal study conducted on August 1, 1981, in the Peak Creek arm of Claytor Lake. Note that the THMFP of the water was greatest early in the day (0800 hours), peaking at 670 g/L, and decreasing steadily thereafter. Also note that 1) DOC concentrations increased slighly to 3.45 mg/L at 1700 hours, 2) DO, reflecting algal activity, peaked at 1700 hours at 10.7 mg/L, 3) CO_2 became unavailable by 1000 hours, and 4) the pH increased to 9.2, coinciding with the precipitous decline in alkalinity from 52 mg/L to 49 mg/L.

The results of this study indicated a possible link between algal activity and the formation of THM precursors. In order to determine the validity of this hypothesis, three subsequent studies were performed, each with primary productivity and ECP determinations included as part of the testing protocol.

Diurnal Study #2

Figure 14 summarizes the data obtained from the diurnal study conducted on September 25 and 26, 1981, in the Peak Creek arm of Claytor Lake. Note the significant increase in THMFP throughout the nighttime and early morning hours, culminating in the peak formation potential of 714 mg/L by 0900 hours (September 26). Also note that this coincided with the peak of ECP liberation (314.5 mgC/m^3). After peaking, both the

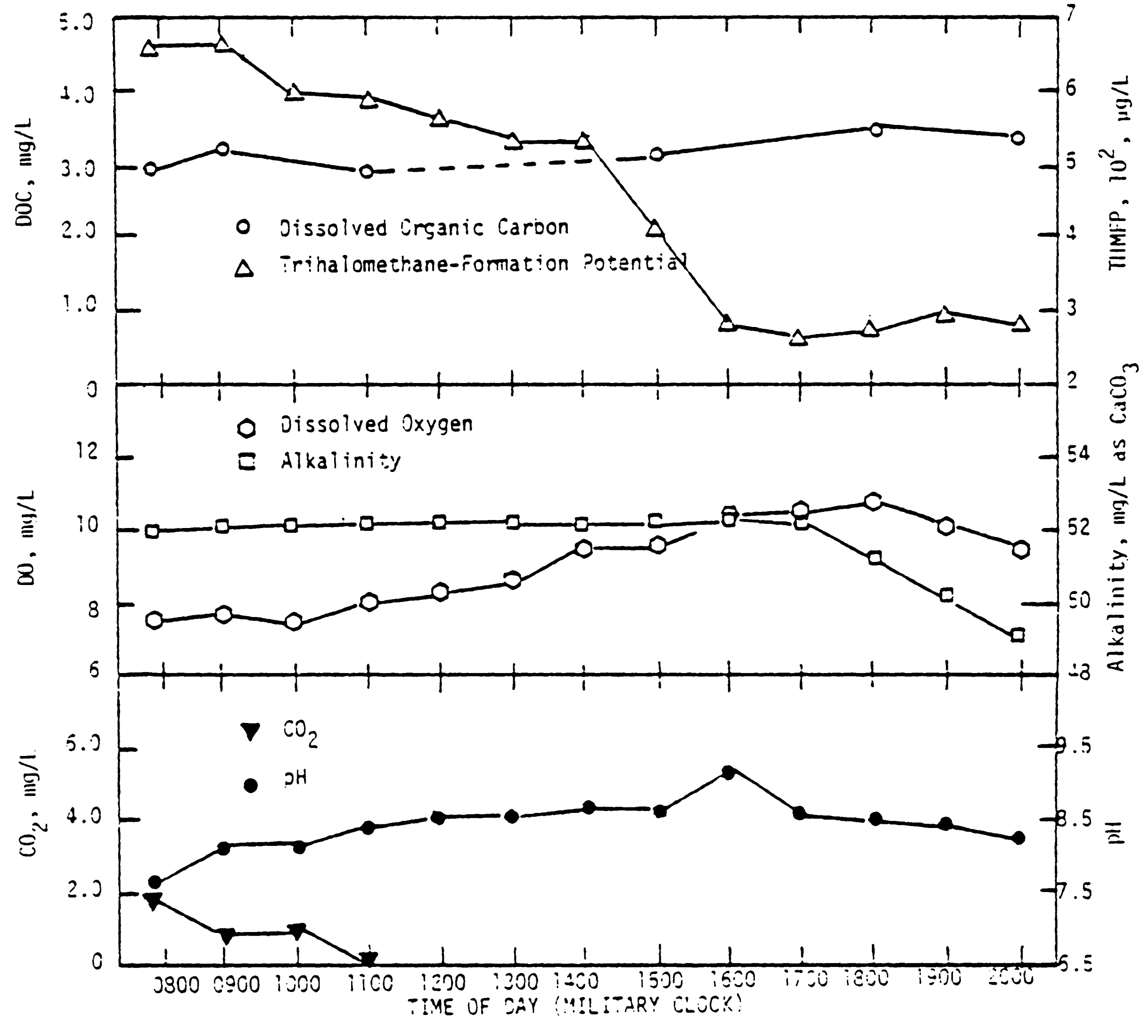


Figure 13. Diurnal variations in chemical indicators of algal activity compared to those of dissolved organic carbon (DOC) and trihalomethane-formation potentials (THMFP) at the Peak Creek site in Claytor Lake, August 1, 1981.

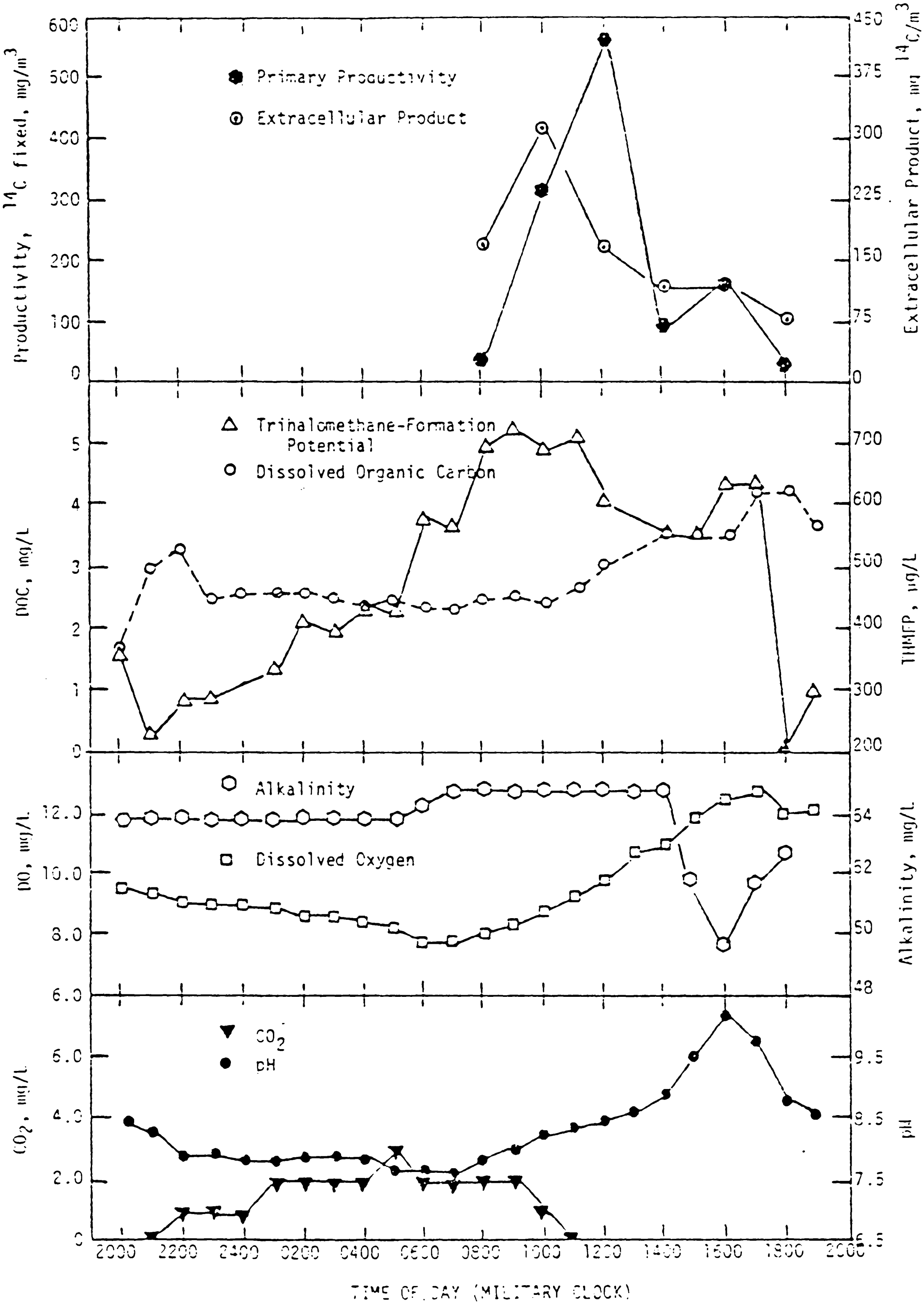


Figure 14. Diurnal fluctuations in algal activity (Peak Creek site, 9/25-26/81) shown in relation to variations in THMFP, DOC, and other selected chemical characteristics.

THMFP and output of ECP declined proportionally and steadily throughout the day. On the whole, productivity levels mirrored the patterns of ECP output and THMFP levels.

Concentrations of DOC fluctuated during the nightime and early morning hours of September 26, then increased steadily throughout the day, reaching a maximum of 4.31 mg/L by 1700 hours. The DO concentration followed the expected trend of a decline at night due to respiration and a significant diel increase due to photosynthesis to 12.8 mg/L by 1700 hours on September 26. The pattern of pH fluctuations of the water mirrored that of the DO, peaking at 10.2 by 1600 hours on September 26, while the alkalinity concentration remained relatively constant throughout the day until 1600 hours on September 26, when it decreased precipitously from 55 mg/L to 50 mg/L.

Diurnal Study #3

Figure 15 summarizes the data obtained from the diurnal study conducted on October 10 and 11, 1981 in the Peak Creek arm of Claytor Lake. Two features worthy of note are the similarity of the results to the two previous studies and the diminishing of peak levels of productivity, ECP output, THMFP, pH and DO, all symptoms of decreased algal activity and the onset of cooler autumn days.

Specifically, ECP output, primary productivity, and THMFP peaked at noon on October 11. The observed concentrations were 124.8 mg C/m^3, and 339 μg/L, respectively; levels far below those detected during the previous diurnal studies. The DO concentration peaked at a much lower

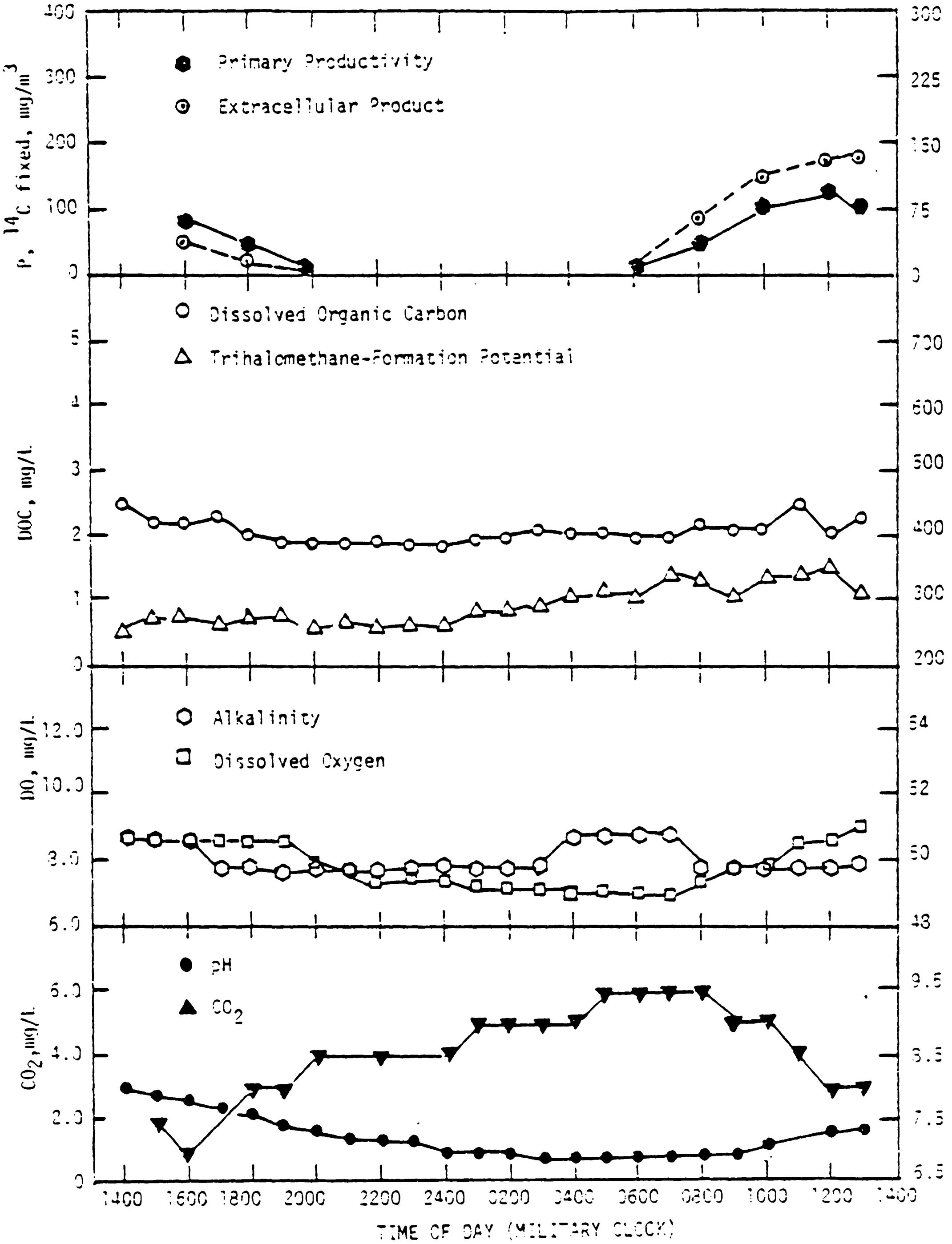


Figure 15. Diurnal variations in the chemical indicators of algal activity compared to those of dissolved organic carbon (DOC) and trihalomethane formation potentials (THMFP) and shown in relation to primary productivity (P) and extracellular product (ECP) production at the Peak Creek site in Claytor Lake, Oct. 10, 1981.

level of 9.0 mg/L on October 11, as did pH, which peaked at 7.4. Finally, CO_2 concentrations were notably higher than in the previous studies, reaching a maximum level of 6 mg/L by 0500 hours (October 11) and never falling below 1 mg/L.

Diurnal Study #4

Figure 16 summarizes the data obtained from the diurnal study conducted on November 23, 1981 in the Peak Creek arm of Claytor Lake. Note the influence which the cold, short days of late autumn exerted upon the lake's ecosystem, in that the peak levels of this study, compared to those of the second dirunal study of September 25-26 were significantly decreased. Productivity decreased by 84.6 percent (87 mg C/m^3), ECP liberation decreased by 84.1 percent (50 mg C/m^3), and THMFP decreased by 90.4 percent (70 μg/L). Carbon dioxide was prevalent, with concentrations ranging from 5 to 9 mg/L, while the DO peaked at 9.5 mg/L. The DOC concentrations fluctuated randomly between 1.92 mg/L and 2.41 mg/L. Alkalinity concentrations remained constant at 49 mg/L, and pH peaked at 6.9.

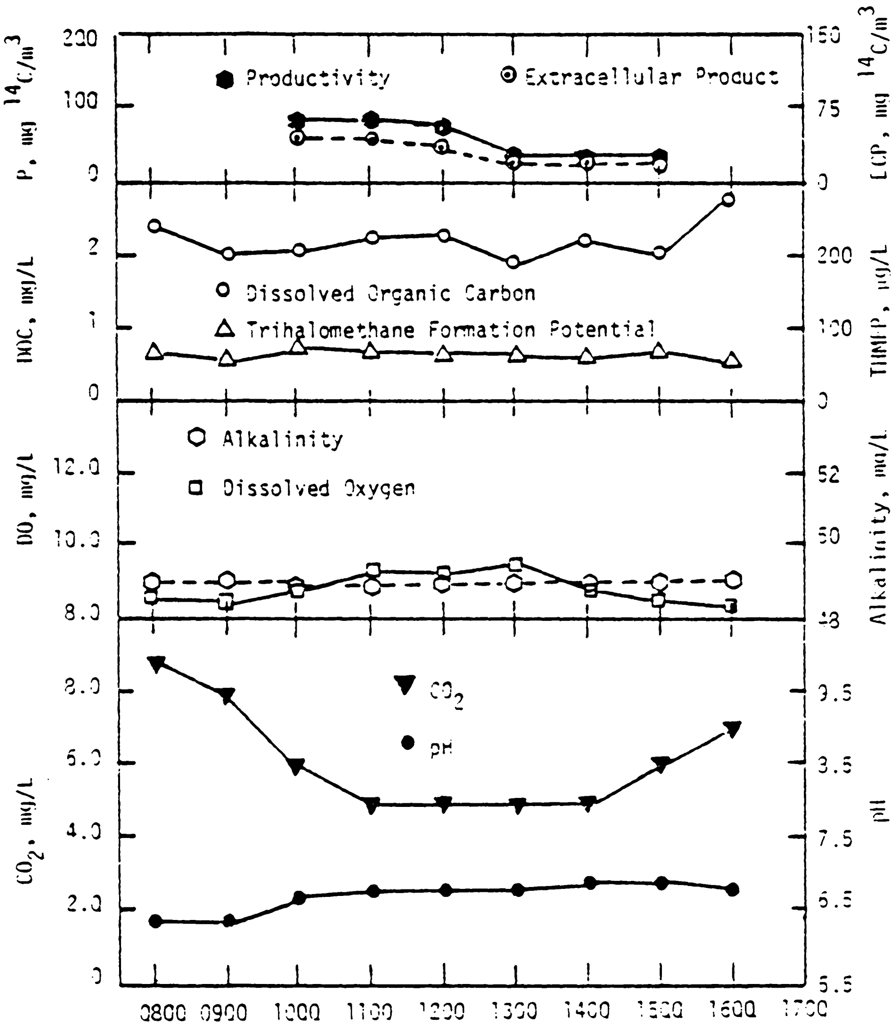


Figure 16. Diurnal variations in the chemical indicators of algal activity compared to those of dissolved organic carbon (DOC) and trihalomethane formation potentials (THMFP) and shown in relation to primary productivity (P) and extracellular product (ECP) production at the Peak Creek site in Claytor Lake, Nov. 23, 1981.

V. DISCUSSION

The Trophic Status of Claytor Lake

The data obtained during this study indicated that Claytor Lake was eutrophic, as previously stated by the Environmental Protection Agency (1976). Evidence for this determination included the following:

1. The low Secchi disk transparency values received from both sampling sites (Figures 3 and 4).
2. The fluctuations (seasonal and diurnal) in the free carbon dioxide concentrations (Figures 3, 4, 13-16),
3. The fluctuations (seasonal and diurnal) in surface pH and dissolved oxygen concentrations (Figures 3, 4, 13-16),
4. The establishment of a clinograde dissolved oxygen profile during summer stratification (Figures 5 and 6),
5. The condition of anaerobiosis in the hypolimnetic layers of water during summer stratification (Figures 5 and 6),
6. The presence and predominance of a dense, non-diverse blue-green algal population (Appendix B, Tables 3 and 4), and
7. The high levels of primary productivity measured at the Peak Creek site (Figures 14-16).

The importance of these data is that they demonstrated Claytor Lake to be an ideal site for a study of the interrelationships that may exist between algae and THM-formation potentials. An oligotrophic or mesotrophic body of water may not have been as suitable for a study of this type.

Aspects of Algal and Bacterial Growth and Their Relationship to THM-Formation Potentials of Lake Water

Determination of the role which algae and bacteria play in affecting a particular water's potential to form THM's must be performed in a manner which incorporates and takes into account the behavioral patterns exhibited by an algal community. With this in mind, discussion and evaluations will be made based upon the following:

1) the effect which algal population size exerts upon raw water THM concentrations.
2) the effect which algal successional patterns exert upon raw-water THM concentrations.

Algal Population Size and THM-Formation Potential

If algal ECP provides THM precursors, one would expect that the more ECP present in water, the higher the water's potential to form THM's. Thus, the highest raw-water THMFP could be expected to occur during the period of peak algal growth when the output of ECP should be at its greatest, unless the ECP were in some way modified or removed from the water column. The converse situation of smaller algal excretions of ECP imparting a lower THMFP to the water should also hold true. Figures 7 and 8 revealed this generally to be the case. In broad terms, as algal populations increased so too did the THMFP and as populations waned, THMFP decreased markedly. There was, however, a rather significant degree of variability from the expected pattern, particularly in the data gathered from the dam site. This was not due to the lack of a relationship between algal activity and the formation of THM's but rather, in all probability, was attributable to the flaws inherent in characterizing the lake on the basis of information derived from analyses of grab samples. By its very nature, a single grab sample simply cannot provide data representative of the complex array of interactions occurring in the water column. In order to properly assess the dynamic forces which exert control over the algal and bacterial role in THM formation, diurnal studies incorporating a broad spectrum of water chemistry and biological deteminations should be performed as often as possible, for they provide a much more complete picture of what is actually occurring in the complex aquatic ecosystem.

General impressions about the relationship between algal population size and THMFP can also be derived from analysis of the proportion of THM's to DOC in relation to population densities (Figure 17 and 18). In general, as the algal populations increased, the yields of chloroform per unit DOC in the water also increased at both sites. This took place despite the relative stability in DOC levels, implying that prolific algal growth can significantly alter the potential of the DOC pool to form THM's.

Unfortunately, the THM/DOC ratio, did not vary in direct proportion to the algal population density. A possible reason may be, as was just discussed, that both the THMFP and DOC concentrations were determined by

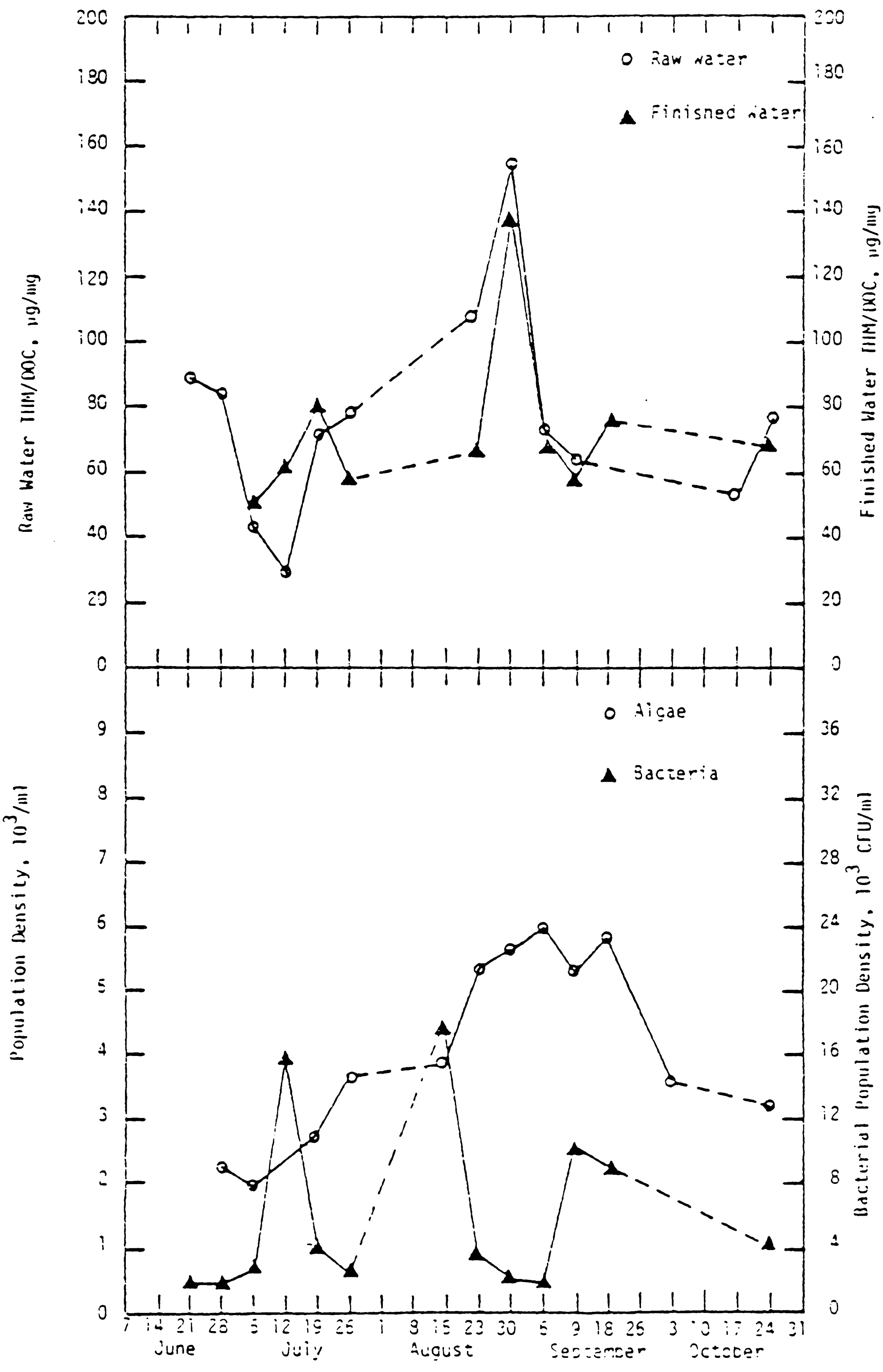


Figure 17. Variations in the THM/DOC ratio in comparison to fluctuations in algal and bacterial population densities in the Peak Creek arm of Claytor Lake, 1981.

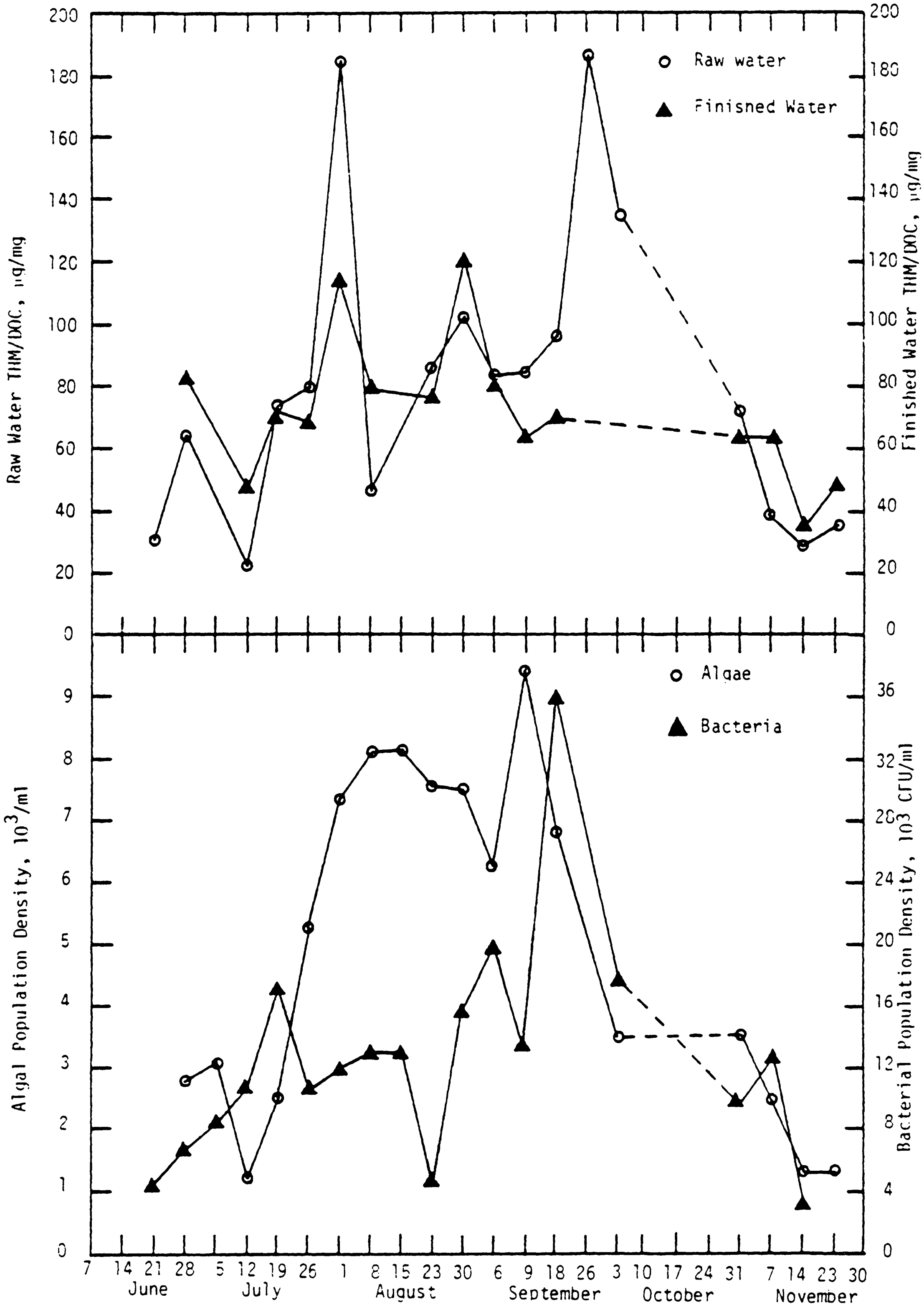


Figure 18. Variations in the THM/DOC ratio in comparison to fluctuations in algal and population densities at the Claytor Lake dam site, 1981.

analyses of grab samples. While these data might suggest that a causative relationship existed between the extent of algal growth and the THM-formation potential of Claytor Lake water, they were by no means conclusive.

Of considerable interest is the observation that bacterial populations increased markedly on two occasions (July 12 and August 15 at Peak Creek, Figure 17, and July 19 and September 18 at the dam, Figure 18) immediately prior to a marked increase in the ratio of THM-to-DOC, in both the raw and alum-treated waters. It is possible that the bacteria may have, in some manner, altered the organic carbon pool so that a larger fraction of it produced THM's upon chlorination. It is also possible that bacterial ECP itself served as THM precursor materials. It is well-documented that bacteria, like algae, generate significant quantities of ECP (Nalewajko _et al_., 1980).

As noted earlier, fluctuations in lakewater THMFP did not correspond well to fluctuations in algal population densities at either sampling site, though both decreased markedly in October when the water temperature had decreased to below 20°C. (Figures 19 and 20). These data provide additional evidence that the THM precursors are more abundant when conditions are more favorable for biological activity, both autotrophic and heterotrophic.

It was not until after an anlysis of these data was complete that the potentially significant role of heterotrophic organisms in the

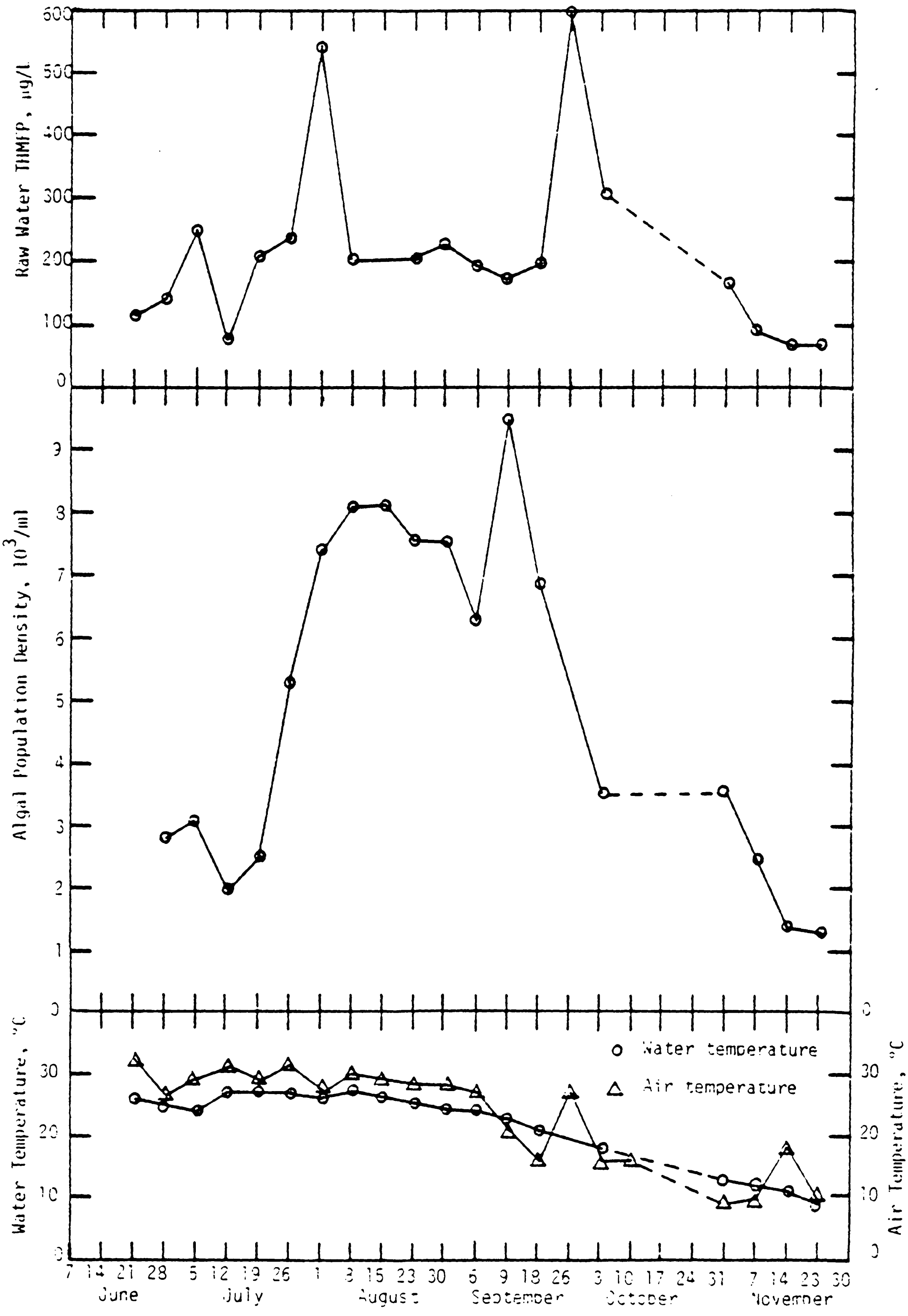


Figure 19. Variations in the THM-formation potentials and algal population densities in relationship to fluctuations in air and water temperatures at the Peak Creek arm.

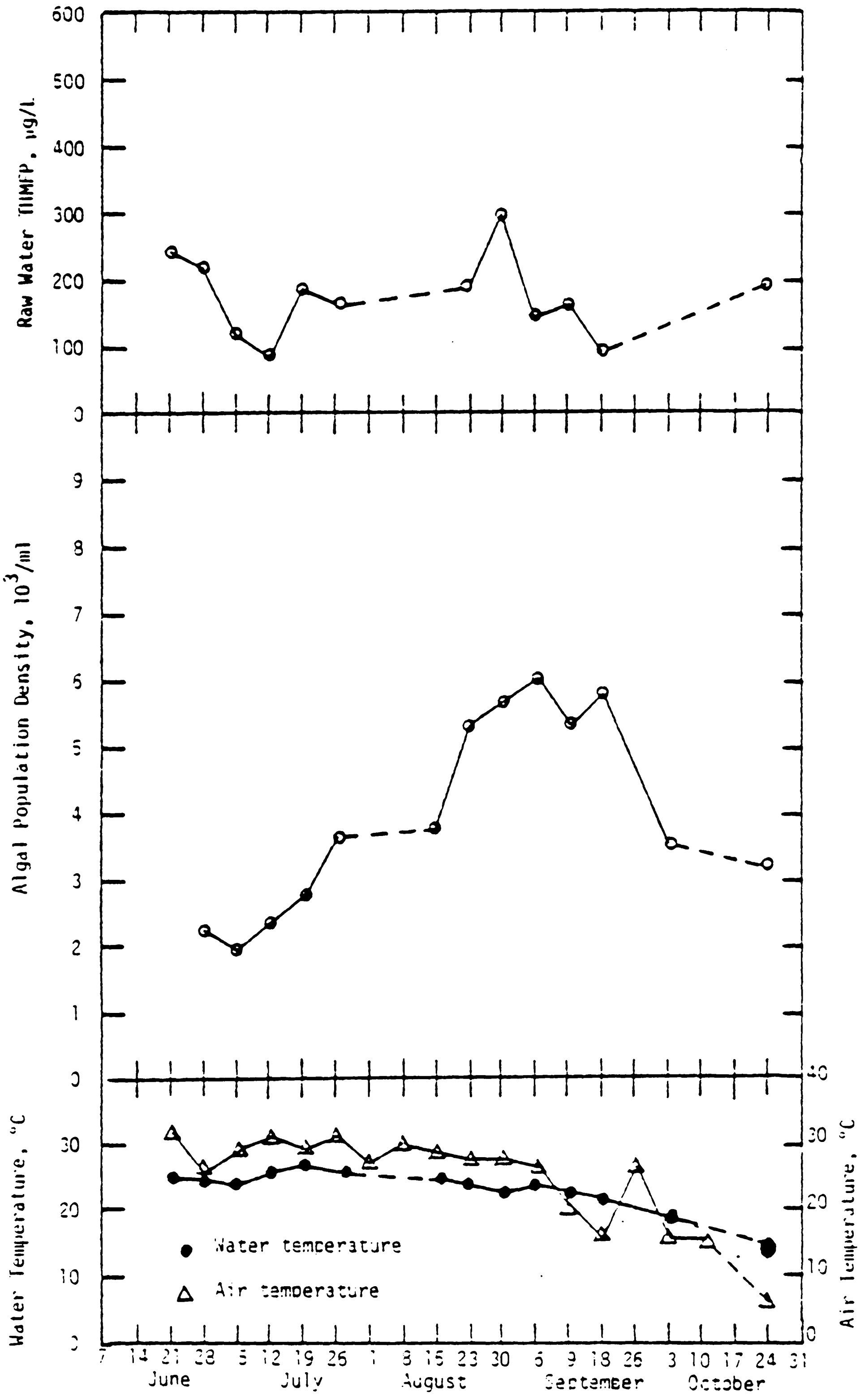


Figure 20. Variations in the THM-formation potentials and algal population densities in relationship to fluctuations in air and water temperatures at the Claytor Lake dam.

formation of THM precursors was realized. Had it been recognized earlier, more effort would have been given to better-defining their role.

Also in retrospect, it would have been better to have included chlorophyll-a and/or algal volume per unit volume of lakewater measurements in the data base in order to better define the relationship between variations in algal biomass and THMFP of the lake water during the year. Cell numbers alone are inadequate for this purpose.

Algal Succession and Its Influence on THM-Formation Potentials

Figures 7 and 8 show that the phenomenon of algal succession was evident at both sampling sites and was especially pronounced at Peak Creek. In these waters, the expected shift from small populations of green algae to extremely dense growths of blue-green algae was observed during the summer months. This was followed by the reemergence of the green algae during mid-to-late autumn.

The immediate impression one gets from analysis of Figures 7 and 8 is that successional shifts in the dominant genera and species of algae had little effect on the THMFP of the water. The fact that the ECP of the vast majority of algae are ubiquitous in nature (Tables 2-4) could account for this. The decreased formation potential of Peak Creek water with the emergence of the green algae in the mid-to-late autumn time frame may have been the result of the decreased output of ECP excreted by the dwindling algal populations rather than the shift in the dominant phytoplankton species. It is possible, however, that a relationship between the predominant species and THMFP may have been masked by the way in which the population densities were estimated. Microcystis aeruginosa and Gleocapsa cells were quite small in comparison to the much larger Chlamydomonas cells. Therefore, on a volume basis, the mass of green algae present in the fall may have been as large as the mass of blue-green algae that predominated earlier. If this were the case, a link between succession and THMFP could possibly have existed and blue-green algae would then be suspect as the major contributor of THM precursors to the organic carbon pool in Claytor Lake. More research is needed to better define this aspect of the problem.

The Effectiveness of Alum Coagulation in the Removal of DOC and Reduction of THMFP

Aluminum sulfate proved to be an effective agent for reducing raw water DOC concentrations and THM-formation potentials in bench-scale coagulation/sedimentation tests (Table 6). Mean DOC removal percentages from Peak Creek waters utilizing alum in dosages of 2, 3, amd 4 mg/L (as Al^{+3}) were 35.9 percent, 42.8 percent, and 43.6 percent, respectively, while the corresponding mean percentage reductions in THMFP were 42.9 percent, 44.8 percent, and 43.6 percent. From waters near the dam, mean DOC removal percentages resulting from utilization of the same alum dosages were 43.3 percent, 47.5 percent, and 45 percent, respectively, while the corresponding mean percentage reductions in THMFP were 50.5

Table 6. Effectiveness of Varying Alum Doses on the Reduction of Organic Carbon Concentrations and Trihalomethane Formation Potentials of Claytor Lake in the Peak Creek Arm, and at the Dam.

Station	Alum Dose, mg/L	pH Ave.	pH Range	pH No.	DOC, mg/L Ave.	DOC, mg/L Range	DOC, mg/L No.	DOC, Removal,% Ave.	DOC, Removal,% Range	THMFP, μg/L Ave.	THMFP, μg/L Range	THMFP, μg/L No.	THMFP Removal,% Ave.	THMFP Removal,% Range
Peak Creek	0	7.9	6.4-9.1	18	2.6	1.9-4.4	18	-	-	221	68-259	18	-	-
	1	6.6	6.2-7.3	14	1.7	1.2-2.3	14	24.2	3-38.7	90	42-144	8	44.3	32.1-75.9
	2	6.4	5.9-7.2	16	1.5	1.0-1.9	16	35.9	19.3-48.0	81	41-144	11	42.9	7.9-79.3
	3	6.1	5.6-6.8	16	1.3	1.0-1.7	16	42.8	27.3-55.8	85	50-127	12	44.8	19.2-63.9
	4	5.5	4.7-6.4	16	1.3	0.9-1.8	16	43.6	21.5-57.2	89	43-170	12	43.6	11.5-68.3
	6	4.2	3.8-4.7	16	1.4	1.0-1.8	16	42.2	24.8-59.0	105	55-190	12	33.9	0.9-66.9
	8	4.1	3.6-4.5	16	1.4	1.1-1.5	16	43.1	33.5-55.7	94	53-153	12	47.4	18.8-71.4
Dam	0	7.6	6.8-8.8	11	2.3	1.7-3.0	11	-	-	169	93-300	9	-	-
	1	6.4	6.1-6.8	11	1.4	1.3-2.4	11	30.9	18.1-48.8	112	68-269	6	39.4	10.5-57.1
	2	6.1	5.7-6.5	10	1.2	1.1-1.5	10	43.3	33.2-48.7	76	64-91	6	50.5	28.8-60.7
	3	5.9	5.2-6.6	11	1.1	0.9-1.5	11	47.5	23.4-58.2	95	53-277	8	50.4	7.7-66.7
	4	4.9	4.2-5.6	11	1.2	1.0-1.5	11	45.0	28.4-61.2	92	58-195	8	45.2	25.3-64.6
	6	4.1	3.6-4.3	11	1.2	1.0-1.4	11	47.7	28.9-59.6	86	34-179	8	45.7	4.9-79.5
	8	4.0	3.5-4.1	11	1.3	1.0-1.6	11	40.9	18.1-52.8	92	3-266	6	51.3	11.4-97.1

percent, 50.6 percent, and 45.2 percent. Treatment was generally more effective for dam waters than for those from Peak Creek. These removal efficiency values are similar to the reported findings of other researchers (Kavanaugh, 1978; Babcock and Singer, 1979; Oliver and Lawrence, 1979; Young and Singer, 1979; Brett and Calverly, 1979). Worthy of note is the finding that alum selectively removed THM precursors from the DOC pool. This preferential removal has been observed and explained by a number of earlier researchers (Kavanaugh, 1978; Babcock and Singer, 1979; Oliver and Lawrence, 1979; Young and Singer, 1979; Brett and Calverly, 1979).

Figures 21 and 22 show that on seven occasions, the most efficient reductions in THMFP (from both Peak Creek and dam waters) were obtained with the use of the higher alum dosages of 6 and 8 mg/L as Al^{+3}. The pH's of finished waters treated by such large dosages of alum were below 4.5. While the removal efficiencies achieved by these dosages are significant, usage on a plant-scale would be impractical due to the prohibitively low pH's which would result, the expense of the increased quantity of alum, and the added costs of handling the excess sludge that would be generated. Further, on ten of the fourteen dates when Peak Creek waters (Figure 21) were treated and on five of nine test dates when waters taken from near the dam were treated, (Figure 22), the best removals were achieved with alum dosages of 2, 3, and 4 mg/L as Al^{+3}; dosages that would produce waters with a pH in the range of 5.0 - 6.5

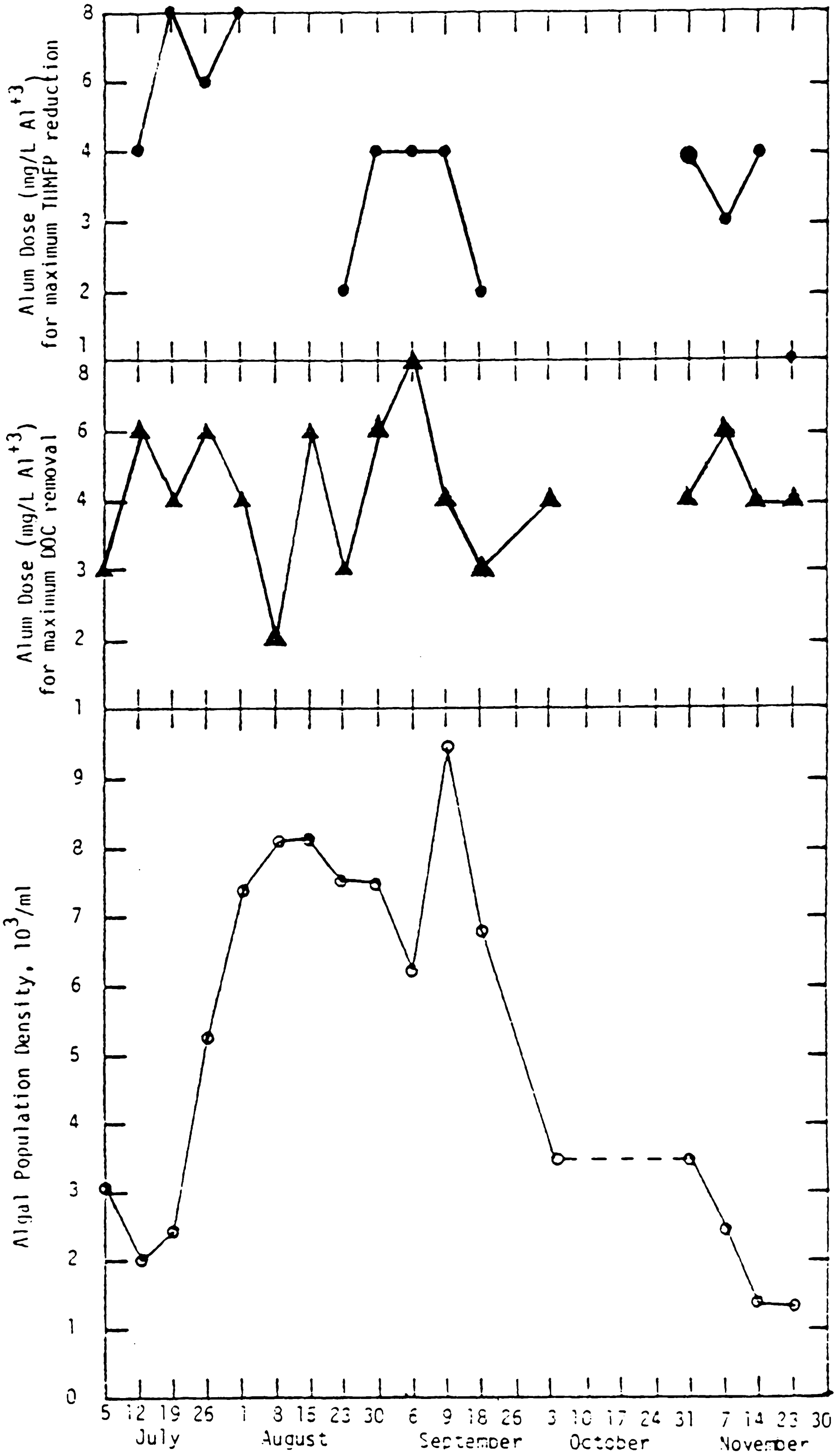


Figure 21. Variations in alum required for maximum DOC removal and THMFP reduction in comparison to fluctuations in algal population densities, Peak Creek arm.

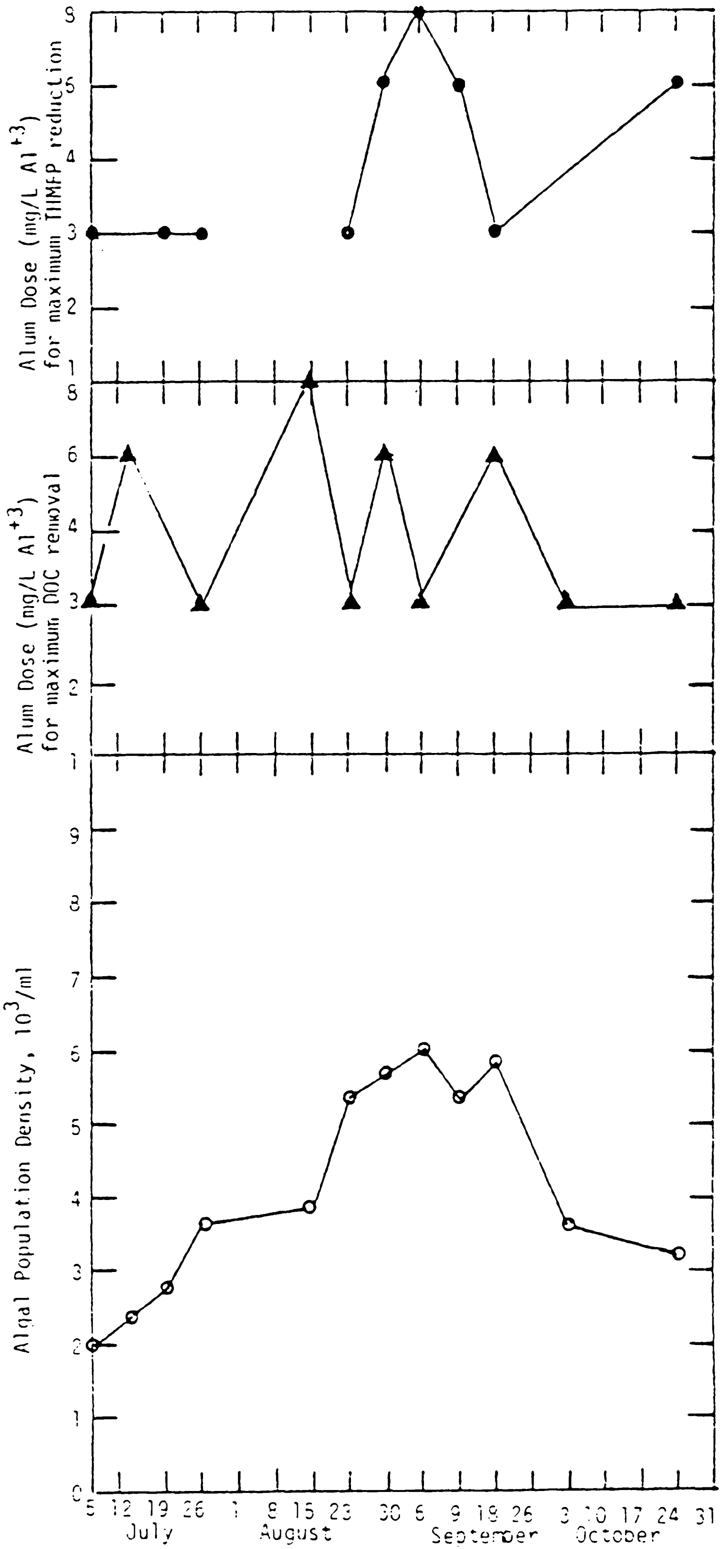


Figure 22. Variations in alum required for maximum DOC removal and THMFP reduction in comparison to fluctuations in algal population densities, Claytor Lake dam site.

and that would not be inordinately costly, either in terms of actual chemical costs for alum and lime or for handling of the sludge.

Clearly, marked reductions in the THMFP of Claytor Lake water could be brought about solely by coagulation with alum if Claytor Lake were to be used as a drinking water source and if chlorination could be delayed until after clarification were completed.

Figures 23-25 show that the treatability of the waters near the dam with respect to reduction in THMFP did not appear to be influenced by the density of the algal population nor by the form of algae which was dominant at a particular time. Percent removal curves showed a wide fluctuation in values during the entire test period.

Treatability (reduction of THMFP) of Peak Creek waters, on the other hand, appeared to be closely linked to algal population density, as can be seen in Figures 26-28, with the most significant reductions in THMFP coinciding with periods of pronounced algal growth. This trend ran contrary to initial expectations, and the exact cause of it cannot be ascertained from the limited amount of data available. It can be postulated, however, that bacterial degradation of the algal ECP, which served as the THM precursor, might have been responsible for the instances of most efficient treatability corresponding with periods of peak algal growth. Bell and Sakshaug (1980) have shown that algal blooms stimulate the _in situ_ activity of bacterial consumption of ECP. If this were the case at Peak Creek, those periods of high algal density would stimulate large-scale bacterial degradation of the ECP excreted by

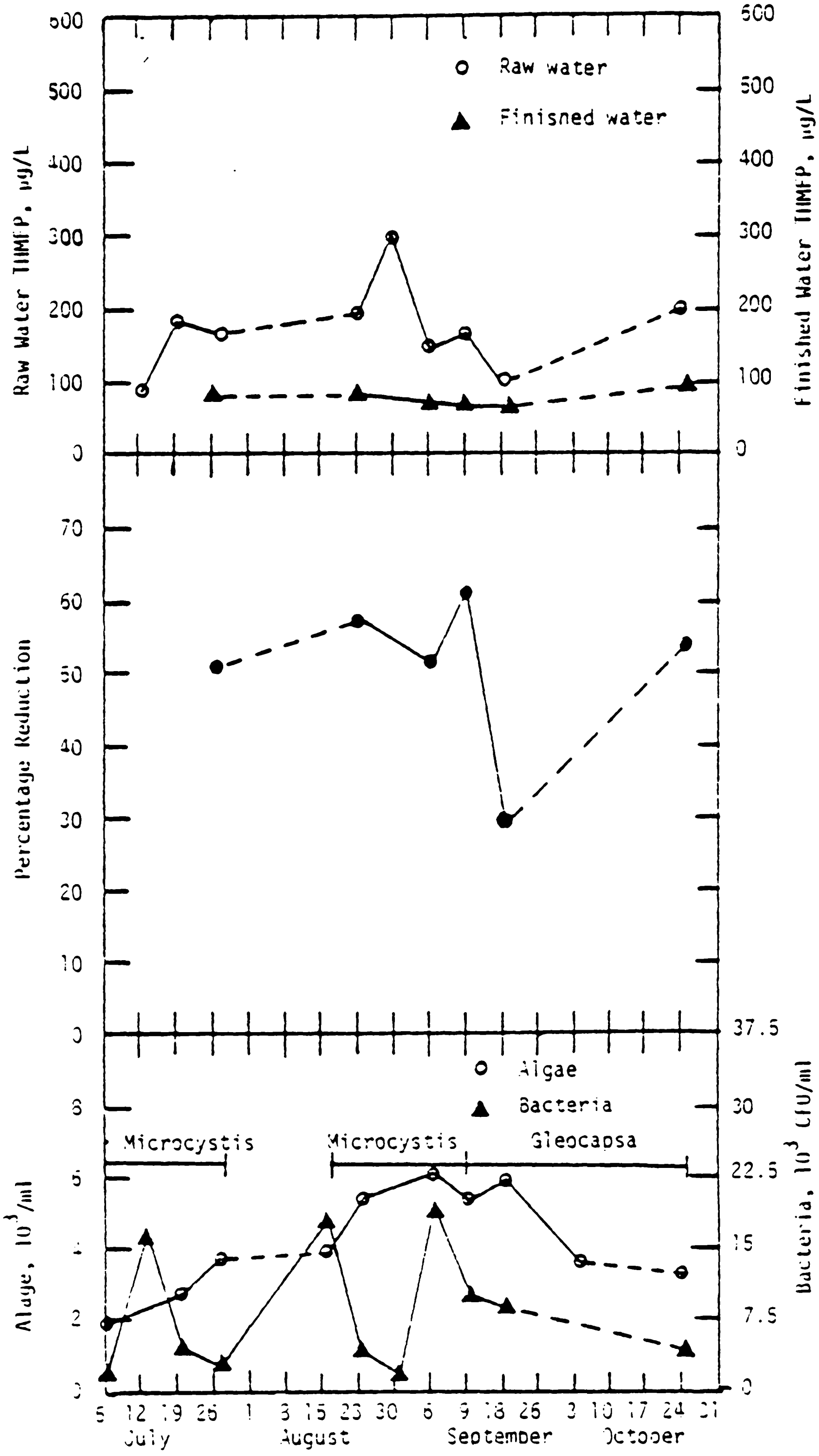


Figure 23. Reductions in the THM-formation potentials of Claytor Lake water (dam site) by alum coagulation with 2 mg/L Al^{+3} shown in comparison to fluctuations in algal and bacterial population densities, 1981.

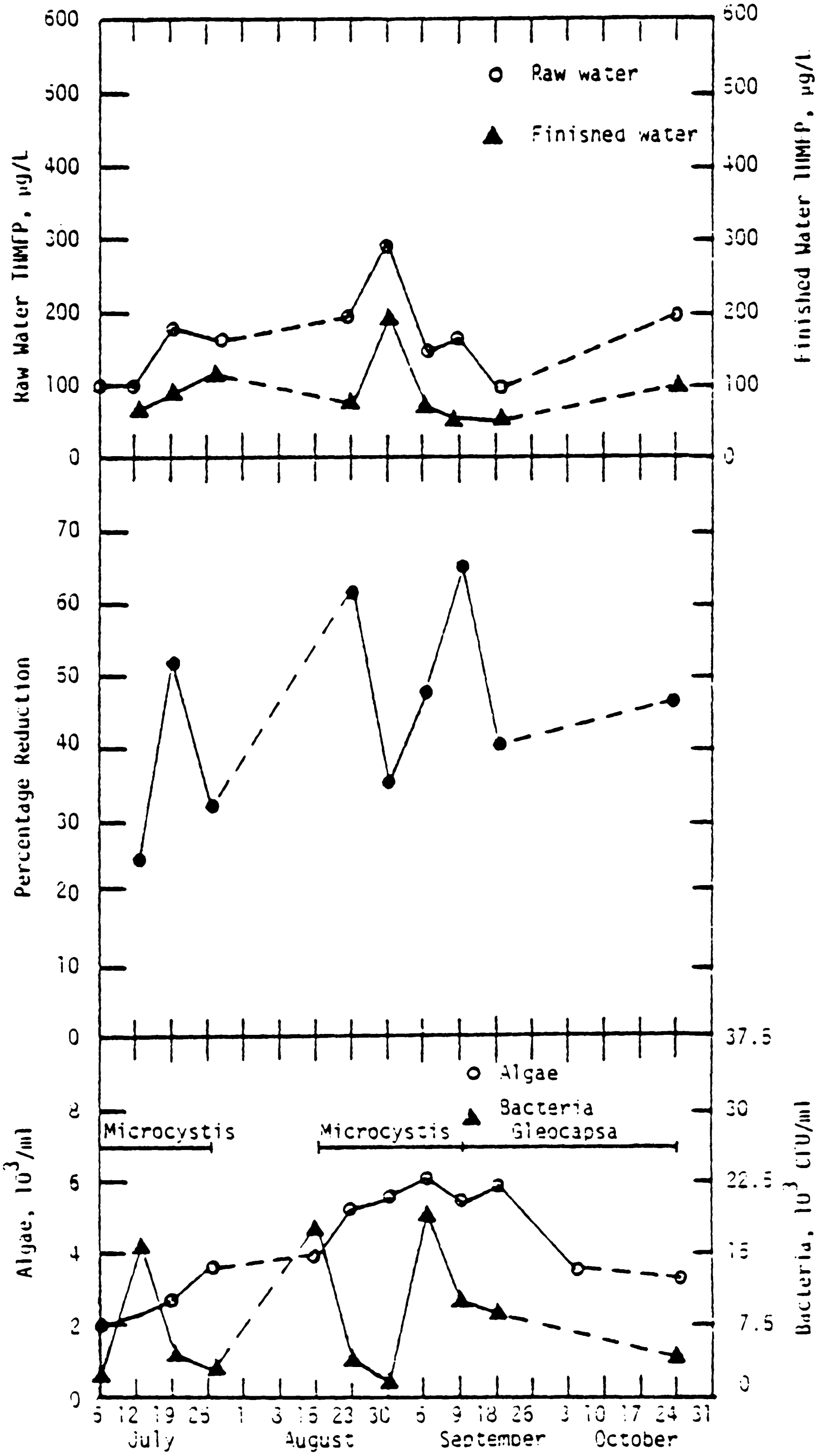


Figure 24. Reductions in the THM-formation potentials of Claytor Lake water (dam site) by alum coagulation with 3 mg/L Al^{+3} shown in comparison to fluctuations in algal and bacterial population densities, 1981.

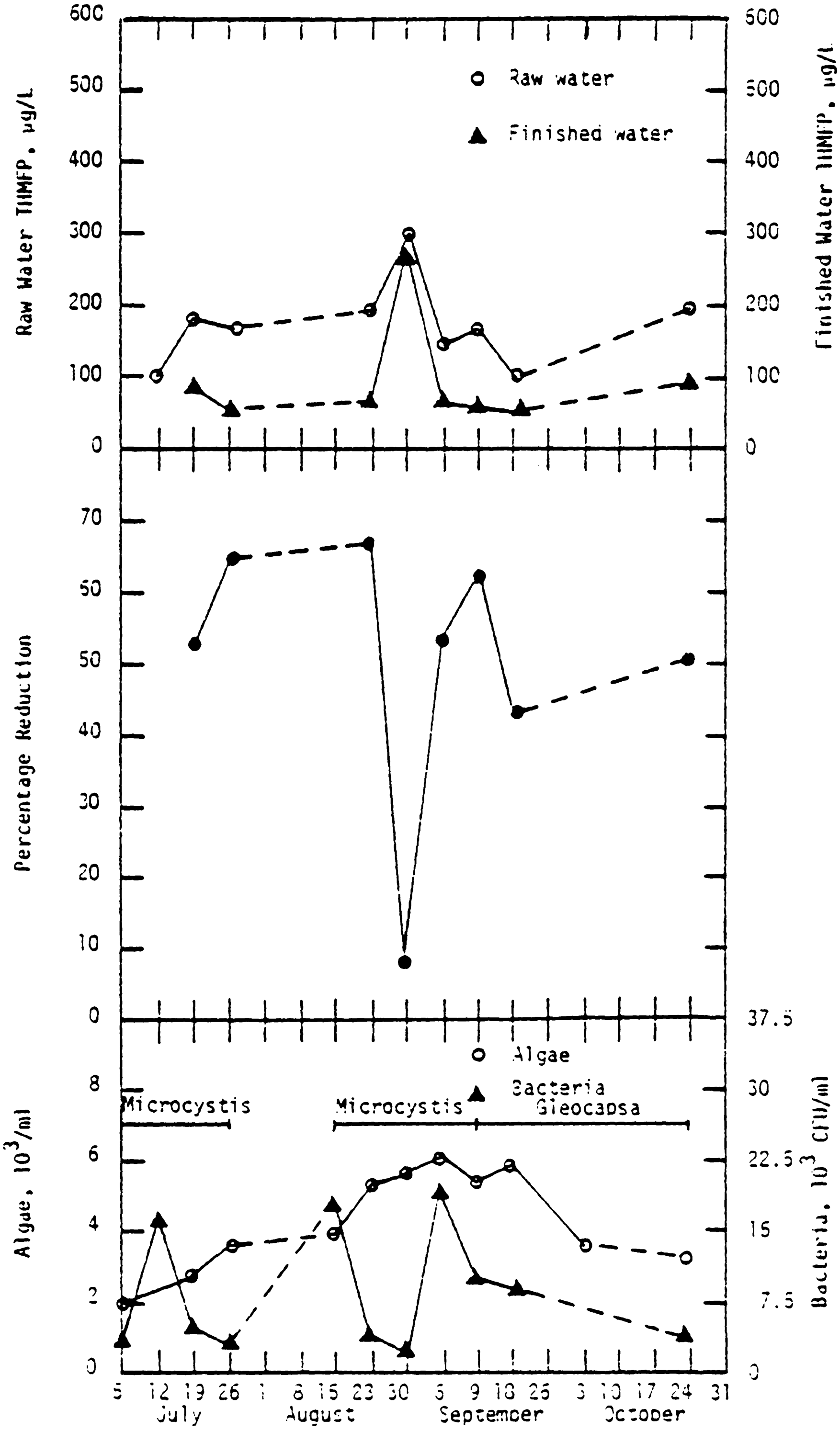


Figure 25. Reductions in the THM-formation potentials of Claytor Lake water (dam site) by alum coagulation with 4 mg/L Al^{+3} shown in comparison to fluctuations in algal and bacterial population densities, 1981.

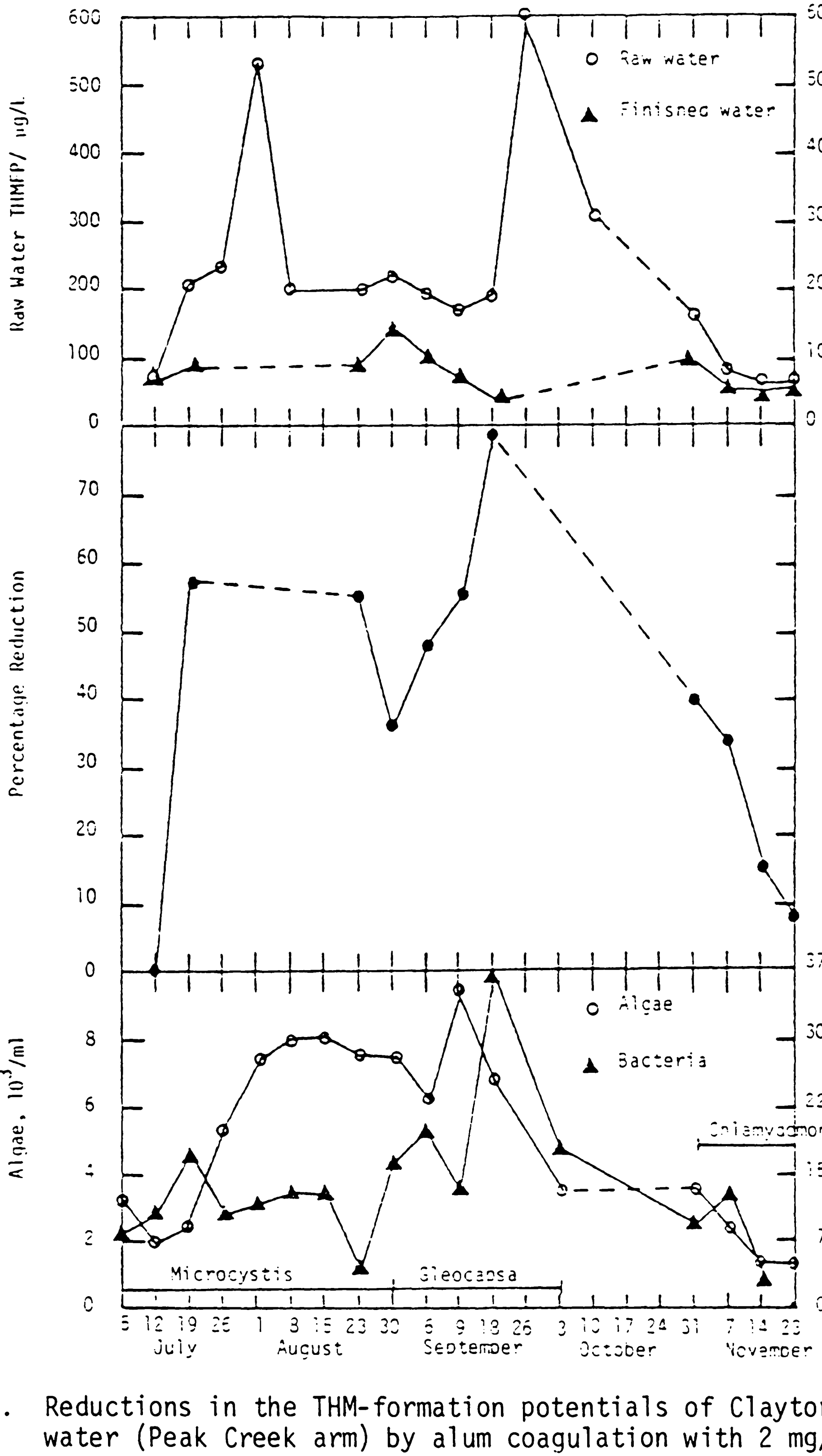


Figure 26. Reductions in the THM-formation potentials of Claytor Lake water (Peak Creek arm) by alum coagulation with 2 mg/L Al^{+3} shown in comparison to fluctuations in algal and bacterial population densities, 1981.

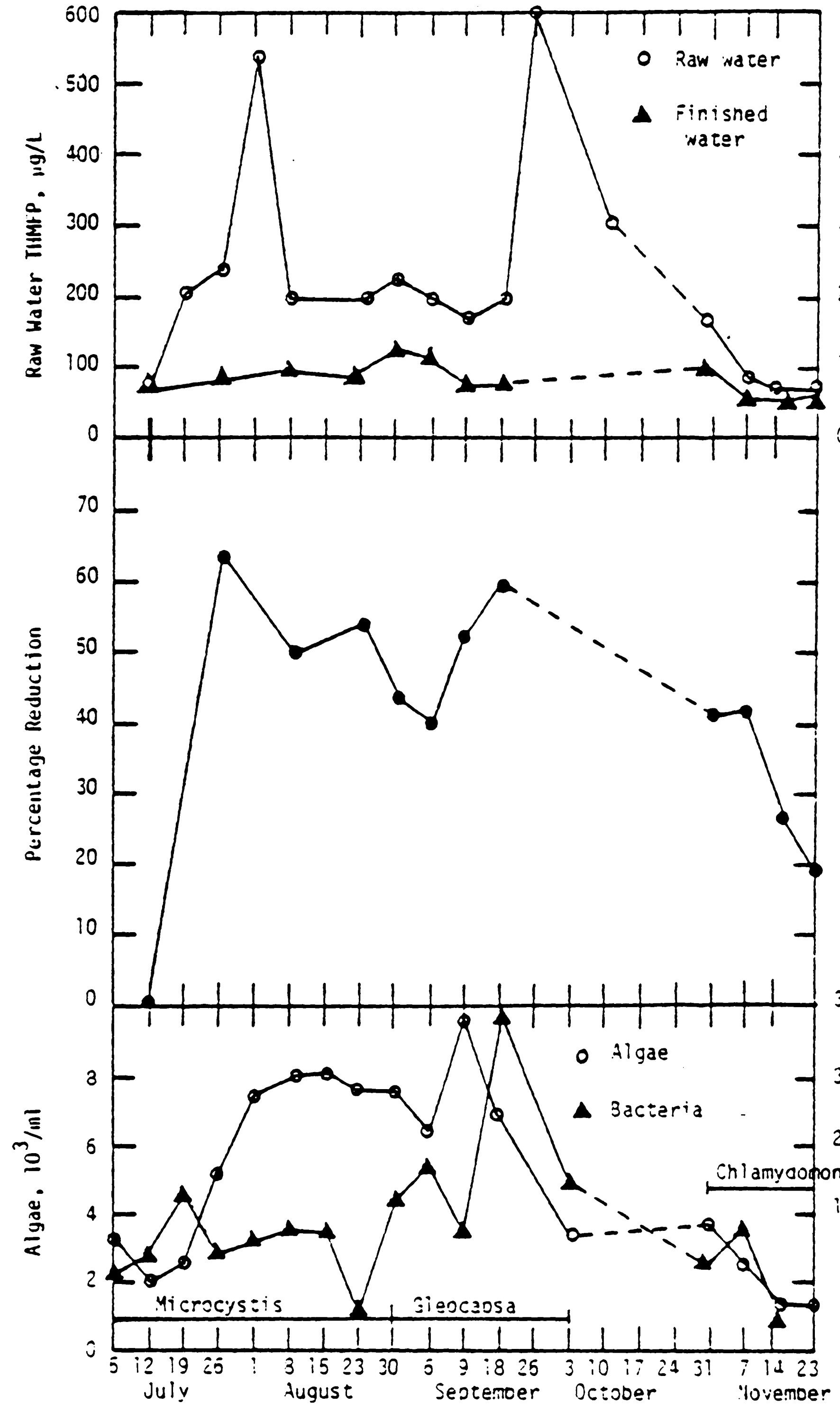


Figure 27. Reductions in the THM-formation potentials of Claytor Lake water (Peak Creek arm) by alum coagulation with 3 mg/L Al+3 shown in comparison to fluctuations in algal and bacterial population densities, 1981.

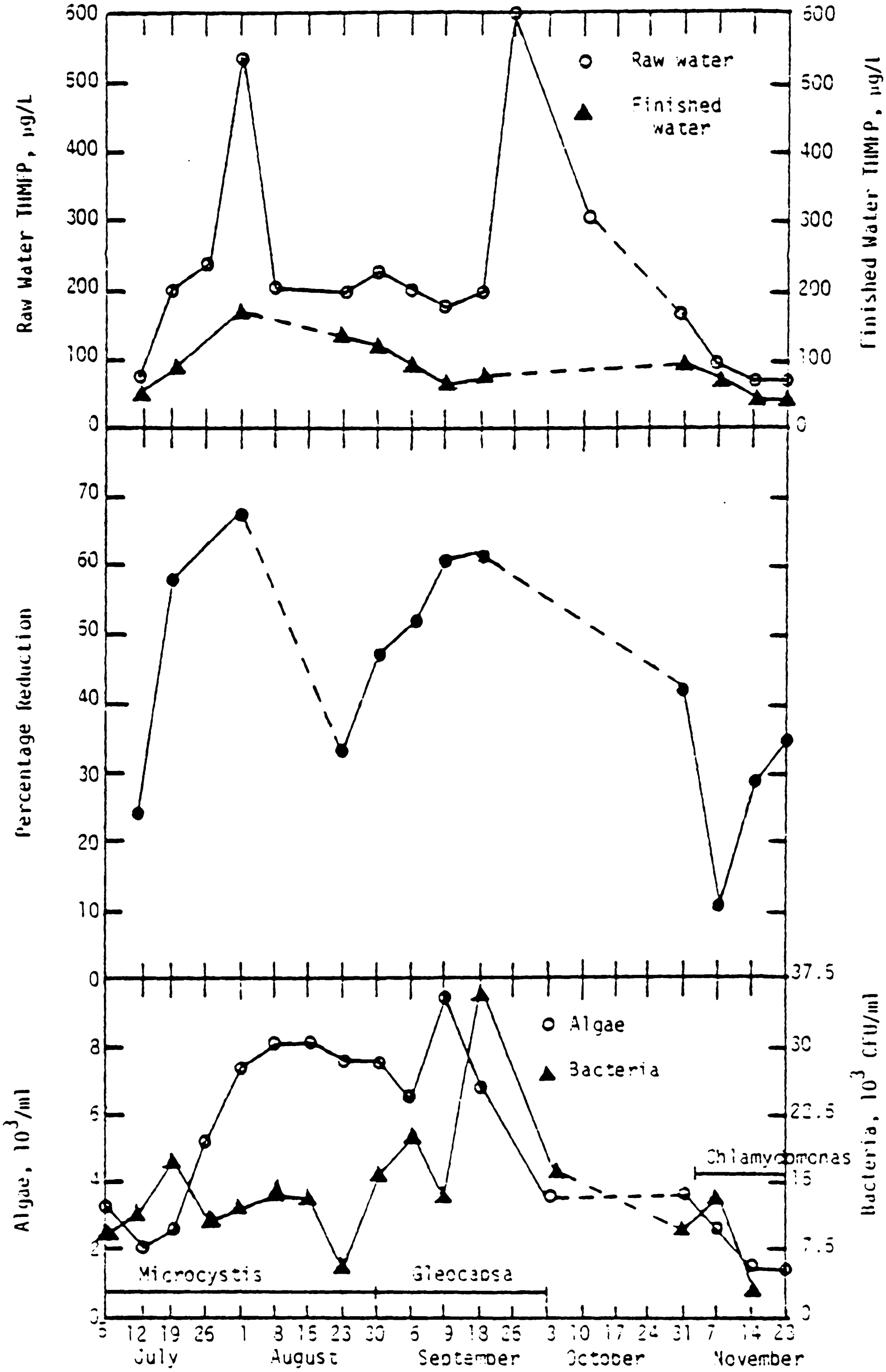


Figure 28. Reductions in the THM-formation potentials of Claytor Lake water (Peak Creek arm) by alum coagulation with 4 mg/L Al^{+3} shown in comparison to fluctuations in algal and bacterial population densities, 1981.

the bloom, thus lowering the water's potential to form THM's and, possibly, producing substances as by-products that are more amenable to alum treatment. At this point in time, the true bacterial role is purely speculative. It is also possible that the algal presence in some way enhanced the removability, perhaps by the production of polymers that aid coagulation.

Similar to the situation encountered with waters taken from near the dam, successional patterns at Peak Creek seemed to exert little, if any, influence over treatability, with similar percent removal values being detected during shifts in dominance by the various algal species present.

With respect to DOC removal (Figures 29-34), the widely fluctuating weekly concentrations produced after treatment of water from both sampling sites, indicate that the treatability achieved by the utilization of alum was irrespective of algal population density and successional patterns.

A revealing application of test data is the ratio of THM/DOC because it allows for the detection of general changes in the nature of the DOC pool. At both sites (Figures 17 and 18) the raw water THM/DOC ratio exhibited significant degrees of fluctuation on a weekly basis, with the highest values being obtained during periods of prolific algal growth. Because DOC levels varied by no more than 2 mg/L at either site (indicating a generally stable DOC level in the waters), the variance in the THMFP of the DOC can be explained only by a change in the

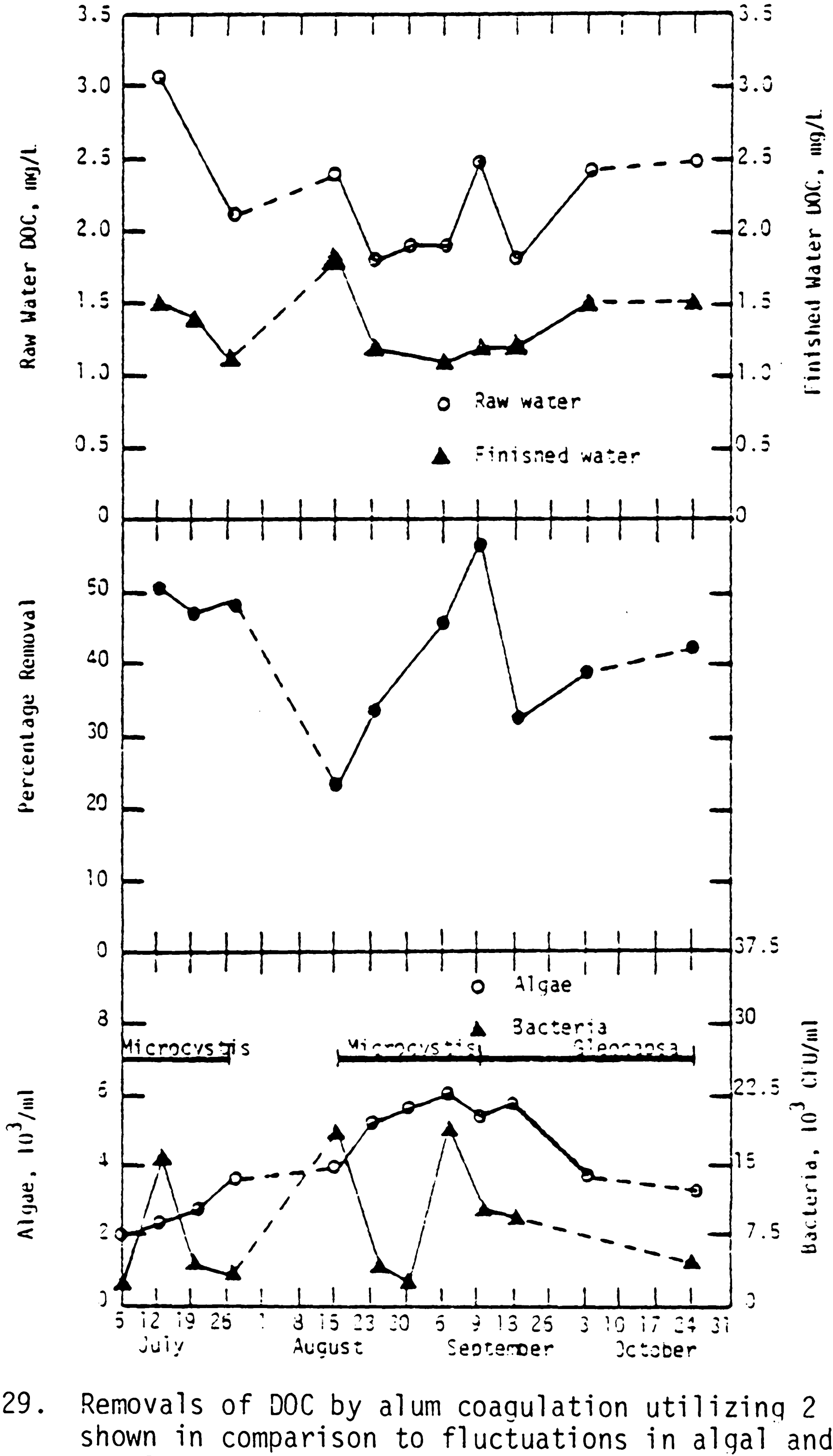


Figure 29. Removals of DOC by alum coagulation utilizing 2 mg/L Al^{+3} shown in comparison to fluctuations in algal and bacterial population densities at the Claytor Lake dam site.

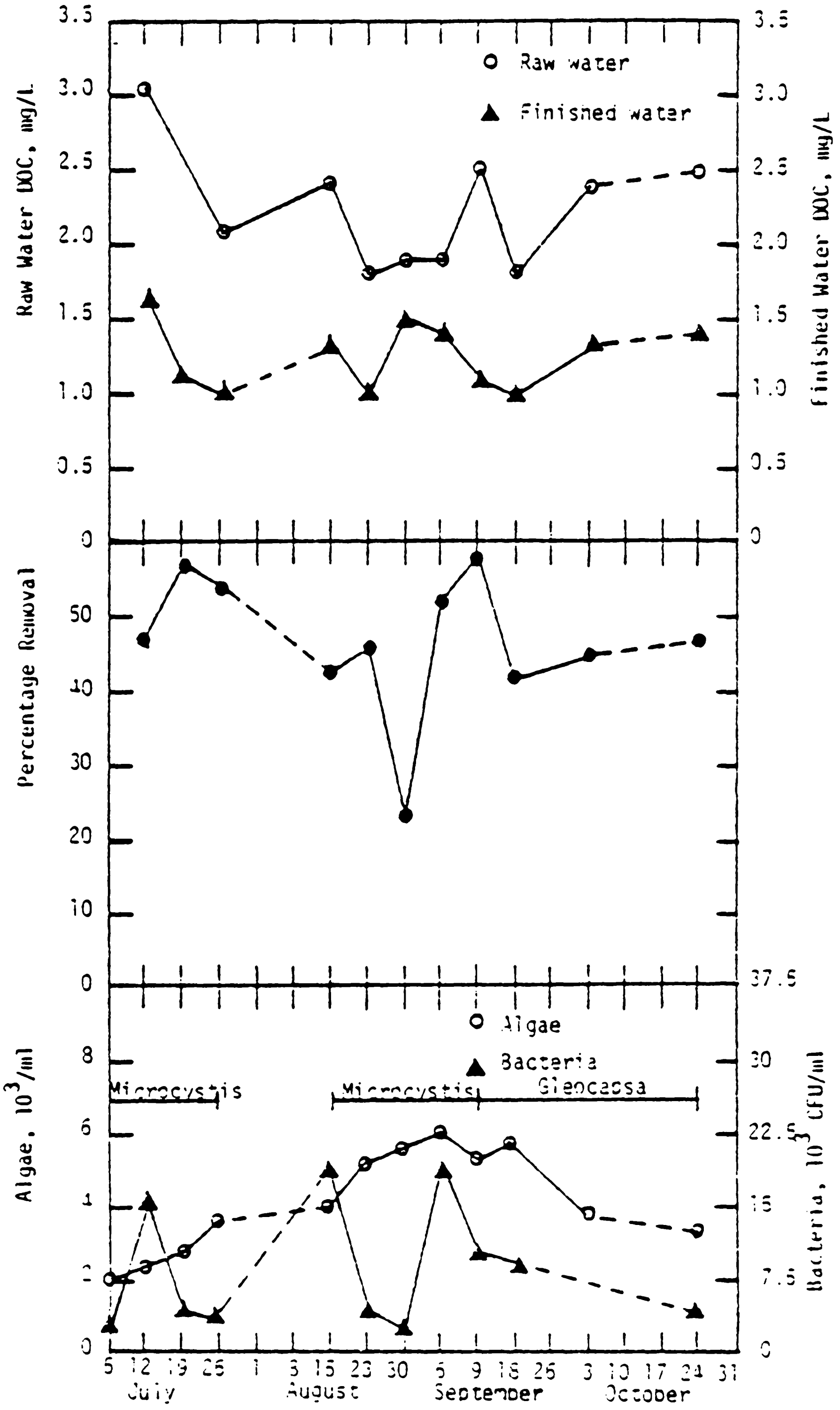


Figure 30. Removals of DOC by alum coagulation utilizing 3 mg/L Al^{+3} shown in comparison to fluctuations in algal and bacterial population densities at the Claytor Lake dam site.

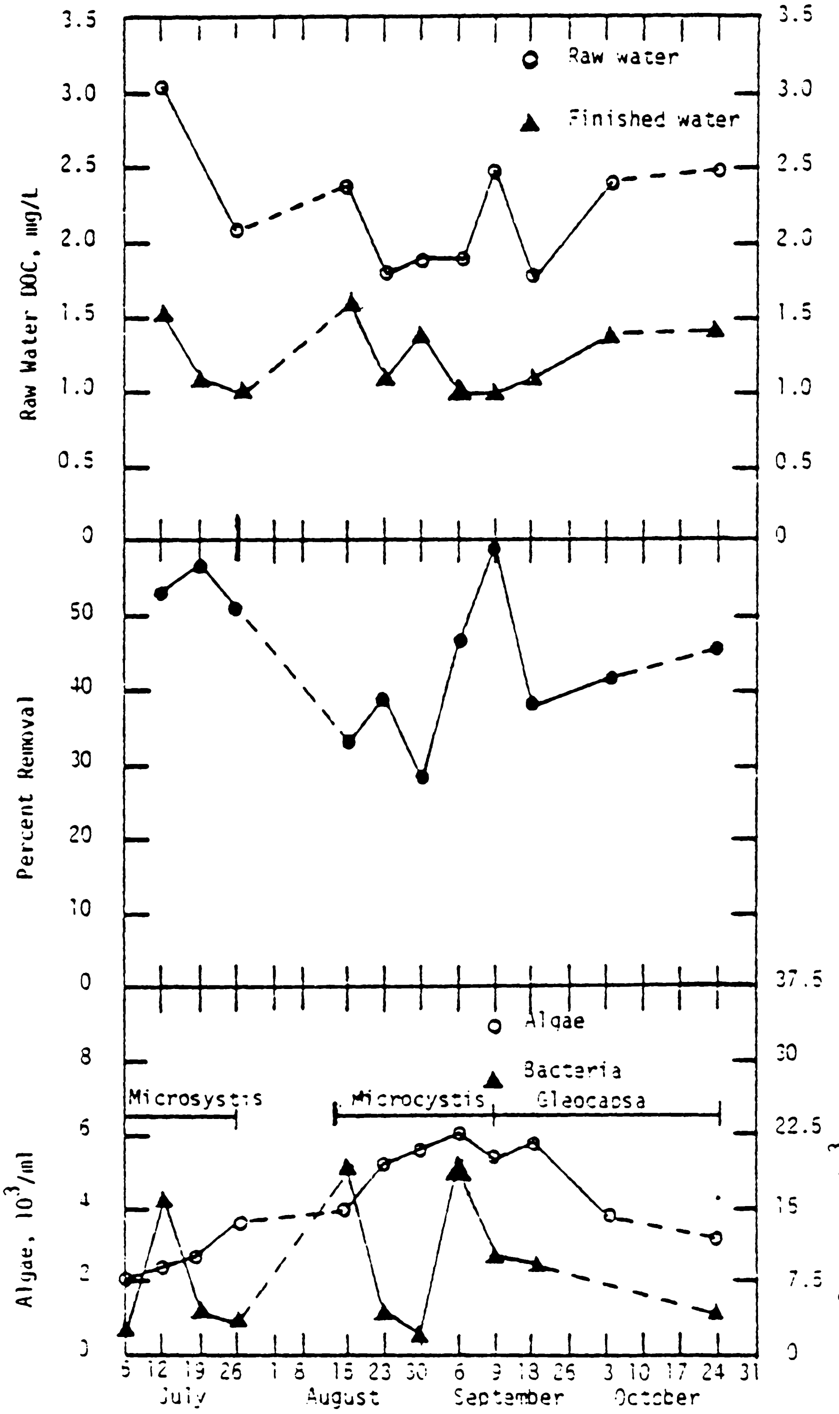


Figure 31. Removals of DOC by alum coagulation utilizing 4 mg/L Al^{+3} shown in comparison to fluctuations in algal and bacterial population densities at the Claytor Lake dam site.

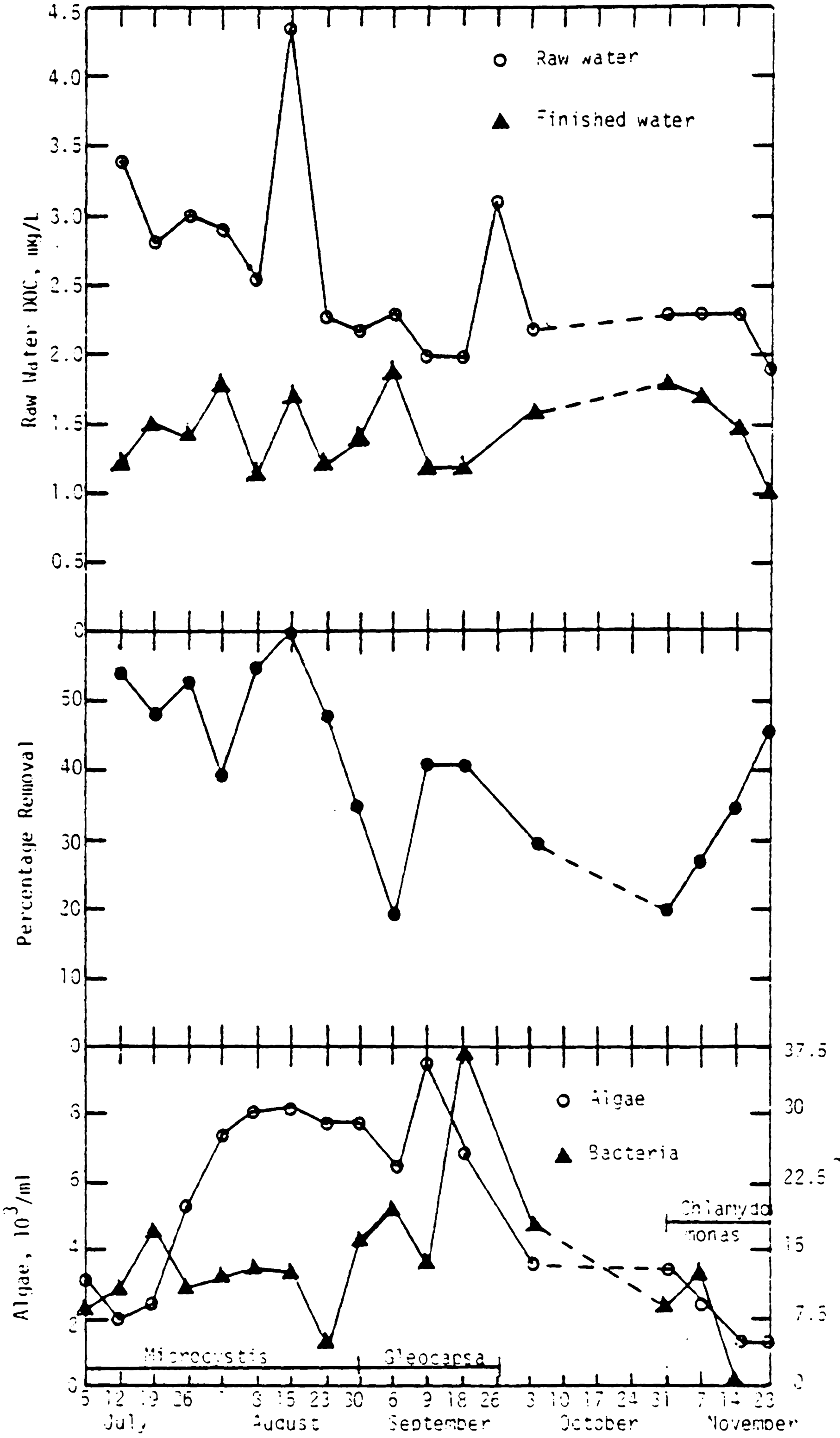


Figure 32. Removals of DOC by alum coagulation utilizing 2 mg/L Al^{+3} shown in comparison to fluctuations in algal and bacterial population densities at the Peak Creek arm site.

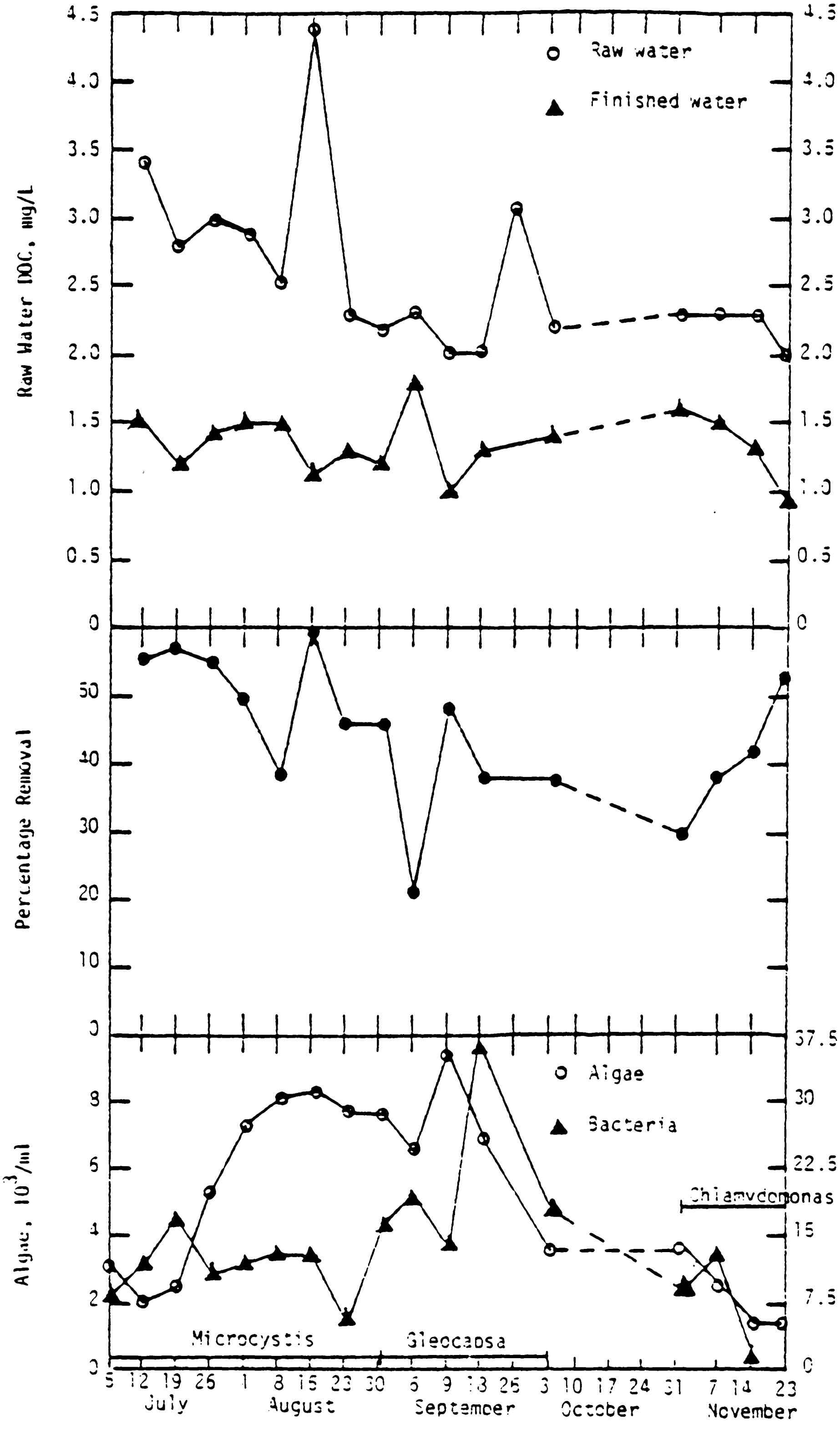


Figure 33. Removals of DOC by alum coagulation utilizing 3 mg/L Al^{+3} shown in comparison to fluctuations in algal and bacterial population densities at the Peak Creek arm site.

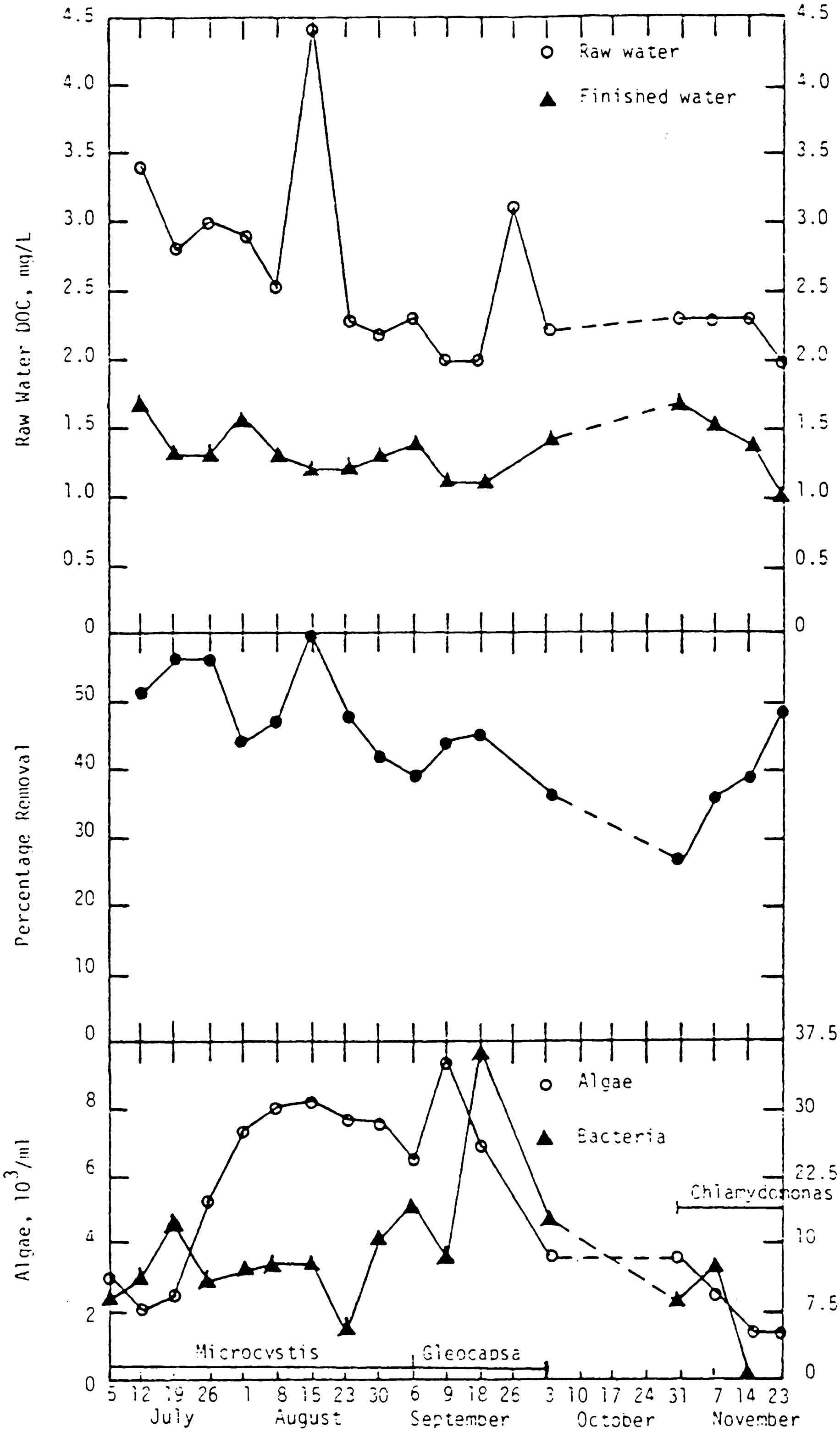


Figure 34. Removals of DOC by alum coagulation utilizing 4 mg/L Al^{+3} shown in comparison to fluctuations in algal and bacterial population densities at the Peak Creek arm site.

composition of the DOC pool (probably due to algal and bacterial influences) which made it more amenable to THM formation. This is important to note, for it is clear that Claytor Lake waters had a much greater potential to form THM's during the productive months, despite relatively stable DOC levels.

The THM/DOC ratio of the finished waters from both sites mirrored the patterns exhibited by the raw-water THM/DOC ratios. This finding is a matter of some concern insofar as a water treatment plant's capacity to produce a water safe (healthy) for human consumption is concerned; for if prolific growth of algae can significantly influence a finished-water's THMFP, as Figures 17 and 18 indicate, the algae will play a definite role in determining the safety of the water, with respect to the health of those who consume it. Also, if there are biologically-induced increases in the THM-formation potentials of lake water, as the data suggest to be true, and if the average removal efficiency of THM precursors can be expected to be only 50 percent, then the impact of reservoir ecology on the ability of a water treatment plant to meet the THM standard cannot be ignored. Clearly, these are areas which warrant much more intensive study and research.

Finally, application of the findings of the coagulation studies to plant-scale operations should be made with caution for the following reasons:

1. The quality of the finished waters, for which values have been reported here, would be about equal to that of finished waters from a

treatment plant. Chlorination of these samples was performed only after all treatment steps were completed. In a treatment plant, chlorination cannot always be delayed until after the completion of all other treatment. At best, chlorination can only be delayed until after sedimentation, if there is to be effective slime control and disinfection.

2. The Maximum Contaminant Level (MCL) for THM's (0.10 mg/L) in potable water is based upon the "instantaneous" THM concentration at the tap, not on the seven-day THMFP as was reported here. The instantaneous values obviously would have been much lower than the THMFP values. (The seven-day THMFP was utilized in order to standardize test conditions thereby enabling the direct comparison of all results.)

3. The effect of diurnal variability of the THMFP would be diluted out at the water treatment plant, through utilization of holding tanks which would serve to equalize and mix the waters with high THMFP's with those possessing low THMFP's.

Despite these factors, the merits of this study cannot be overlooked, for they corroborate the work of many earlier researchers (Hoehn et al, 1980; Kavanaugh, 1978; Babcock and Singer, 1979; Oliver and Lawrence, 1979; Young and Singer, 1979; Brett and Calverly, 1979) of the THM phenomenon. It is evident to this researcher, that optimization of standard alum treatment processes offers a significant means by which the THM problem can be controlled to achieve compliance with the EPA-mandated MCL of 0.10 mg/L TTHM.

Diurnal Studies

The diurnal studies conducted on four dates in 1981 (August 1, September 25-26, October 10-11, and November 23) provided comprehensive data on which to base an analysis of the potential roles of algae and bacteria in altering the THMFP of lake water. Because the main thrust of testing was directed at measuring algal activity, the role of the heterotrophs (bacteria and fungi) will have to be inferred from the carbon dioxide and dissolved oxygen concentrations that were monitored during each study.

The first diurnal study (Figure 13) showed a dramatic fluctuation in the THMFP of the lake water over the course of the day (from 670 μg/L at 0800 hours to 285 μg/L at 1900 hours), while the DOC concentration remained relatively constant (3-4 mg/L). It is obvious that even though DOC concentrations are expressed in mg/L and THMFP is expressed as μg/L, the DOC concentration was increasing while the THMFP was decreasing. The increases in DO concentrations and pH during the day and the patterns in DOC and THMFP were of sufficient interest to prompt further and more detailed investigations of these diurnal phenomena.

The results of the September 25-26 diurnal study (Figure 14) strongly implicate both algae and heterotrophs as important agents in the processes that account for the diurnal fluctuation in THMFP.

Of considerable interest is the observation that the THMFP of the water increased steadily during the nighttime hours (from 229 μg/L at

2100 hours on September 25 to 581 μg/L at 0600 hours on September 26) while the corresponding DOC concentration remained relatively unchanged. Too, the CO_2 concentration increased from 0 mg/L at 2100 hours (September 25) to 3.0 mg/L by 0500 hours (September 26). These data strongly suggest that the heterotrophic population plays an important role in creating THM precursors, as was suggested earlier, either by modifying the structure of the organic compounds already present (algal ECP) so that they are more reactive with chlorine in the THM-producing reactions or by their releasing of ECP that has a high THMFP.

The algal contribution to the diurnal fluctuation in THMFP appears to have been significant. The observed increases in productivity and ECP production coincided with steady increases in the THMFP, probably as the result of increased algal density at the sampling depth or the algal excretion of ECP with a high THMFP, as shown in studies conducted by Hoehn *et al*. (1977, 1980). Unfortunately, chlorophyll-a and algal volume measurements were not performed and because *Microcystis aeruginosa* (the dominant alga at the time) are known to migrate upward through the water column during the early morning hours, the possibility exists that the daytime increase in THMFP (during the morning hours of 0600 and 1100) was caused simply by a mass effect; that is, there were more algae present at the sampling depth during the morning hours to produce a greater abundance of precursors than at any other time of the day.

The decrease in THMFP observed after 1200 hours (September 26) could have been caused by a number of ecological factors, including:

1) the possible liberation of algal ECP with a relatively-low THMFP (such as glycollate) as stress-causing environmental conditions (high DO tensions, an exhausted supply of CO_2, prohibitive light intensities, and elevated pH's) characteristic of the late morning-afternoon hours forced the algae into a photorespiratory state; a condition typified by the extracellular release of glycollate.

2) a possible downward migration of the algae as mid-day light intensities became prohibitive (Moss, 1969), resulting in the release of THM precursors at a depth below that from which the samples for THMFP analyses were drawn, and

3) the possible oxygen inhibition of bacteria (Kuenen, 1979) resulting in the lowering of their capability to produce THM precursors and/or to alter the structure of already-existing algal ECP.

Because these factors were not quantified, their true role in the aquatic ecosystem remains speculative.

Finally, the striking decrease in THMFP beginning at about 1200 hours (Figure 14) could also be explained by the possible adsorption of THM precursors onto a marl complex which could have formed and precipitated from solution at the elevated pH of the water. Note that there was a precipitous decrease in the alkalinity beginning at 1400 hours.

The third diurnal study (Figure 15) corroborated the findings of the earlier studies, again implicating the algae and bacteria in the role of important agents in the diurnal fluctuation of THMFP. Similar to the September 25-26 study, THMFP increased steadily during the nighttime hours. The corresponding rise in CO_2 concentration and relatively stable concentrations of DOC offer evidence of the bacterial role in the alteration of algal ECP or of the direct release of ECP from bacterial cells.

Algal influence was accentuated in this study as the daytime peak in THMFP coincided with the peak of ECP release.

Of considerable interest was the observation that the peak levels of productivity, ECP release, and THMFP were markedly lower than the corresponding peak values obtained during the September 25-26 diurnal study. (Productivity was decreased by 79 percent, ECP output was decreased by 60 percent, and THMFP was decreased by 53 percent.) This is thought to be the result of cooler water temperatures retarding algal and bacterial metabolic activity and impeding their capacity to alter ECP type or concentration, thereby decreasing the degree of diurnal fluctuations in THMFP.

Despite the dampening effect which the cooler temperatures exerted over the biota, the evidence presented here suggests that the biological community significantly altered the potential of the water to form THM's.

The final diurnal study (Figure 16) provided a vivid demonstration of the impact that environmental factors had upon the capacity of the biota to predispose a lake water to form THM's. With a water temperature of only 9.6°C and an effective daylight duration of only 10 hours, peak productivity was reduced by 85 percent, ECP output was decreased by 86 percent, and THMFP was decreased by 90 percent, as compared to the September 25-26 study when the water temperature was 20.6°C and the effective daylight duration was 14 hours. With biotic activity being so retarded in the November study, the diurnal fluctuation in THMFP and DOC was nominal, as can be seen in Figure 16.

It is evident from all the data that the degree of biological activity, whether it be algal alone or algal and bacterial, exerts a tremendous influence over the potential of a lake water to form THM's.

VI. SUMMARY AND CONCLUSIONS

A summary of the data derived from each segment of this project is given in the following paragraphs before statement of the conclusions of the study.

Results of the field testing conducted at both sampling sites showed that Claytor Lake was a highly eutrophic water system. Evidence of this condition was 1) the limited transparency of the water, 2) the occurrence of a clinograde oxygen profile with an anaerobic hypolimnion during summer stratification, 3) the absence of free carbon dioxide during periods of prolific algal growth and productivity, and most importantly 4) the presence of a dense, non-diverse blue-green algal population throughout the summer and early-autumn months.

The apparent relationship between algal population densities and successional patterns and the seven-day trihalomethane-formation potentials (THMFP) of Claytor Lake water collected on a grab-sampling basis from June through November, 1981, were general at best. The prevailing meteorological conditions appeared to directly affect the THMFP of a water by their influence over the physiological state of the algal and bacterial communities.

Aluminum sulfate proved to be an effective agent for removing THM precursors from the water, probably by enmeshment or adsorption to the "sweep floc" of aluminum hydroxide. The mean removals of DOC (28-47 percent) and mean reduction in THMFP (34-51 percent) were similar to values reported in the literature. Reductions that could be achieved by alum treatment did not appear to be directly related to bacterial or algal population densities or to algal successional patterns. However, biologically induced increases in THM precursor concentration can significantly affect the ability of a water treatment plant to meet the THM standard, especially if the average removal efficiency of THM precursors can be expected to be only 50 percent. Therefore, the impact of reservoir ecology on treatment capacity is a factor which cannot be ignored.

The diurnal studies provided the strongest evidence to date that both the algal and heterotrophic populations are extremely important in producing THM precursors. Algal ECP no doubt are THM precursors themselves, but the role of the algae also may be one of providing organic nutrients for heterotrophic metabolism, which may be more pronounced in the dark when algae are not producing supersaturated DO conditions. The heterotrophic activity may result either in the production of bacterial ECP that are THM precursors or in the modification of the algal ECP in such a way that it is more likely to form THM's upon chlorination. In either case, the fluctuations in THMFP observed during this study no doubt were the result of biological activity. Thus, the biological state of a reservoir cannot be discounted when one makes predictions about the potability of a potential water source. Furthermore, the extent to which a potential THM problem may exist in any given body of water cannot be based on analyses of grab samples but, instead, must be determined by an analysis of samples collected at several times during the year (in different seasons) and on a diurnal basis.

The significant conclusions derived from this study are:

1. Claytor Lake is a eutrophic water impoundment displaying symptoms classically attributed to a culturally-enriched water system.

2. Algal metabolic activity in a lake has a significant effect in altering the THMFP of the lake water. Algal metabolites, and perhaps products resulting from heterotrophic utilization of these metabolites or bacterial ECP itself, yield extremely high levels of THM per unit of DOC.

3. Because the types of ECP being liberated by algae and bacteria could have such a profound effect on the THMFP of lake water and because the liberation of the various types of algal ECP appears to be a distinctly diurnal phenomenon, it is suggested that future studies of algal-bacterial/THM relationships should be conducted over a 24-hour period. In this manner, a more complete assessment of the role of algae in the altering of THMFP can be made.

4. There was no consistent relationship between algal or bacterial population densities and the seven-day THMFP of lake water when collection of the lake water was made on a grab-sample basis, although the yields of THM per unit DOC were generally highest when algal population densities were greatest and seemed to lag by a short time, pronounced increases in bacterial populations. This conclusion

emphasizes the need for composite or discreet, sequential sampling of a body of water during a 24-hour period.

5. Alum coagulation followed by clarification reduced the THM precursors in Claytor Lake by about 50 percent, and the effectiveness of the treatment was not reduced either by increases in the algal population density or by the succession of algae from one type to another.

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APPENDIX A

Table A1. Raw Field Data Collected from Peak Creek Arm, Claytor Lake 1981

Date, 1981	Secchi Disk Transparency, m	Carbon Dioxide, mg/L	pH	Dissolved Oxygen, mg/L	Alkalinity, mg/L $CaCO_3$	Air Temperature, °C	Water Temperature, °C	Rainfall, inches
May 31	1.21	5.0	6.9	8.6	44	26	20.5	0
June 21	1.09	0	8.6	10.7	42	32	26.0	0
28	1.03	0	8.5	10.6	44	36	25.2	0.18
July 5	1.05	0	8.9	10.3	43	29	24.2	0.28
12	0.90	0	9.4	12.2	46	31	26.8	0
19	0.98	0	8.9	10.5	42	29	26.8	0.68
26	0.96	0	8.8	11.7	48	31	26.5	1.56
Aug. 1	0.89	0	8.7	9.6	58	27	25.6	0
9	0.87	0	8.8	10.7	75	30	26.6	1.00
15	0.83	0	9.1	10.1	49	29	25.5	0.05
23	1.43	0	8.3	8.6	51	28	24.7	0
30	1.13	0	8.3	9.6	49	28	23.9	0
Sept. 6	1.03	0	8.0	10.0	45	27	24.2	0.85
9	1.15	0	8.0	9.9	48	21	23.2	0.04
18	1.03	2.0	8.0	9.0	62	16	21.1	0.88
26	0.94	0	8.6	10.7	55	27	-	0
Oct. 3	0.98	1.0	7.5	9.5	57	16	17.5	0.27
11	-	3.0	7.4	9.0	50	16	-	0
31	1.52	5.0	6.9	9.9	50	9	13.4	0
Nov. 7	1.65	5.0	6.7	9.8	51	10	12.3	0.21
14	2.69	7.0	6.4	9.5	50	18	10.6	0
23	-	5.0	6.8	9.3	49	9	9.5	0

Table A2. Raw Field Data Collected from Claytor Lake Dam, 1981

Date, 1981	Secchi Disk Transparency, m	Carbon Dioxide, mg/L	pH	Dissolved Oxygen, mg/L	Alkalinity, mg/L $CaCO_3$	Air Temperature, °C	Water Temperature, °C	Rainfall, inches
June 21	1.25	0	8.5	8.4	30	32	25.3	0
28	1.31	0	8.4	9.0	33	26	24.8	0.18
July 5	1.28	0	8.5	9.8	30	29	24.0	0.28
12	1.45	0	8.7	10.2	42	31	26.0	0
19	1.58	0	8.8	10.2	45	29	26.7	0.68
26	2.23	0	8.7	7.2	45	31	25.9	1.56
Aug. 15	2.31	0	8.7	7.3	42	29	25.1	0.08
23	2.18	1.0	7.0	4.8	45	28	24.0	0
30	1.18	1.0	7.2	6.7	44	28	23.5	0
Sept. 6	2.43	2.0	7.2	6.8	43	27	23.6	0.85
9	2.52	1.0	7.6	7.6	45	21	22.8	0.04
18	2.44	5.0	7.1	5.2	44	16	21.8	0.88
Oct. 3	2.25	4.0	6.8	7.4	45	15.6	18.8	0.27
24	2.33	5.0	7.3	7.3	46	6	14.8	0

Table A3. Raw Field Data Collected from Peak Creek - Dissolved Oxygen Profile

Depth, m	DO, mg/L on Date Shown																					
	May	June		July				August					September				October			November		
	31	21	28	5	12	19	26	1	9	15	23	30	6	9	18	26	3	11	31	7	14	23
Surface	-	10.0	10.2	9.8	12.4	10.0	10.5	9.4	10.1	10.3	8.7	9.7	9.9	10.0	9.2	10.7	9.7	9.0	9.8	9.9	9.4	9.2
0.5	8.6	10.7	10.6	10.3	12.2	10.5	11.7	9.6	10.7	10.1	8.6	9.6	10.0	9.9	9.0	10.7	9.5	9.0	9.9	9.8	9.5	9.3
1.0	8.8	11.0	10.8	10.1	12.1	10.5	11.1	8.9	11.0	9.8	8.4	9.5	10.3	9.8	8.8	10.3	9.4	-	10.1	9.8	9.3	-
2.0	6.8	8.1	9.0	8.1	10.7	8.5	9.9	7.7	10.3	8.3	8.2	9.1	9.2	9.4	8.7	9.7	8.9	-	9.9	9.6	9.0	-
3.0	6.8	7.3	8.4	7.4	6.7	7.2	7.9	7.5	8.1	7.5	7.3	7.8	7.9	8.7	7.9	8.4	8.7	-	9.1	9.8	8.9	-
4.0	6.7	7.0	7.8	6.5	5.1	6.9	7.3	7.4	7.7	7.4	7.0	7.8	7.8	8.2	7.8	8.4	7.7	-	8.9	9.4	8.9	-
5.0	6.7	6.7	6.9	5.9	3.1	5.9	6.9	6.5	7.9	7.3	6.4	7.0	7.0	7.4	7.2	8.9	7.2	-	8.8	9.5	8.8	-
6.0	6.6	0.2	0.1	4.3	0	2.2	2.3	6.0	6.3	6.5	5.5	6.7	6.0	6.5	7.3	0.4	7.3	-	7.5	9.5	6.3	-
6.5	-	0	0	1.6	0	0.4	-	0.5	6.1	4.5	0.4	0.4	0.1	4.2	6.4	-	5.1	-	-	3.5	6.3	-

Table A4. Raw Field Data Collected from Claytor Lake Dam - Dissolved Oxygen Profile

Depth, m	DO, mg/L on Date Shown														
	June		July				August			September			October	
	21	28	5	12	19	26	15	23	30	6	9	18	3	24
Surface	8.5	9.0	9.3	10.2	10.0	7.4	7.4	4.4	6.8	6.8	7.7	5.3	7.5	7.4
0.5	8.4	9.0	9.8	10.1	10.2	7.2	7.3	4.8	6.7	6.8	7.6	5.2	7.4	7.3
1	8.4	9.1	8.9	10.2	10.4	7.0	7.4	4.8	6.7	6.9	7.6	5.2	7.3	7.3
2	8.6	9.2	8.9	10.1	10.1	6.9	7.4	4.7	6.6	6.8	7.5	5.2	7.3	7.1
3	8.6	9.2	8.6	8.0	9.8	6.9	7.2	4.9	6.3	7.0	7.5	5.3	7.3	7.0
4	8.4	9.0	8.5	7.9	9.4	6.5	7.1	4.6	6.0	6.9	7.5	5.2	7.3	7.0
5	8.2	8.9	7.3	6.1	8.5	6.3	6.8	4.5	5.9	6.9	7.4	5.2	7.3	7.0
6	8.2	8.8	7.5	4.6	7.7	6.2	6.7	4.4	5.8	7.0	7.3	5.2	7.3	6.9
7	7.7	8.8	6.3	4.1	7.7	5.8	6.6	4.4	5.7	6.8	7.3	5.3	7.2	6.8
8	7.5	4.7	6.3	4.0	5.4	5.3	6.2	4.3	5.5	6.8	7.1	5.1	7.2	6.8
9	5.4	4	6.0	3.2	3.8	4.3	5.7	4.3	5.5	6.5	7.1	5.2	7.2	6.8
10	4.8	4	5.9	2.4	3.5	3.1	4.8	4.3	5.5	5.7	7.0	5.1	7.2	6.7
11	4.4	3.9	2.8	2.8	2.9	2.6	2.1	4.3	5.5	3.3	7.1	5.1	7.2	6.7
12	4.3	3.9	2.5	2.9	3.2	2.2	0.4	4.4	5.3	2.7	7.1	5.2	7.1	6.7
13	4.3	3.7	3.0	2.4	2.9	1.3	0.2	4.3	5.3	2.7	6.9	5.3	7.1	6.7
14	4.0	3.1	3.4	1.8	1.6	0.7	0.1	4.4	0.8	0.3	6.8	5.3	7.2	6.8
15	4.0	3.1	3.5	1.6	1.2	0.2	0.1	4.2	0.3	0.1	6.7	5.4	7.2	6.8

Table A6. Raw Field Data Collected from Claytor Lake Dam - Temperature Profiles

Depth,	Temperature, (°C), on Date Shown													
	June		July				August			September			October	
m	21	28	5	12	19	26	15	23	30	6	9	18	3	24
Surface	25.3	25.0	24.0	26.0	26.9	26.1	25.1	24.0	23.5	23.8	22.9	21.8	18.8	14.8
0.5	25.3	24.8	24.0	26.0	26.7	25.9	25.1	24.0	23.5	23.6	22.8	21.8	18.8	14.8
1	25.3	24.5	24.0	26.0	26.5	25.5	25.1	24.0	23.4	23.0	22.8	21.8	18.8	14.9
2	25.0	24.5	24.0	25.8	26.2	25.2	25.1	23.9	23.3	23.0	22.8	21.8	18.8	14.9
3	25.0	24.4	24.0	25.6	26.1	25.1	25.1	23.8	23.2	23.0	22.7	21.8	18.8	14.9
4	24.9	24.1	24.0	24.4	26.0	25.1	25.0	23.6	23.1	23.0	22.6	21.8	18.8	14.9
5	24.8	23.6	23.7	23.8	25.5	25.1	25.0	23.4	23.1	23.0	22.6	21.8	18.8	14.9
6	24.8	23.2	23.3	23.5	25.5	25.1	25.0	23.3	23.1	23.0	22.6	21.8	18.8	14.9
7	24.8	23.0	23.2	23.2	25.4	25.1	25.0	23.3	23.1	23.0	22.6	21.8	18.8	15.0
8	24.5	22.8	23.2	23.0	25.1	25.0	25.0	23.2	23.0	23.0	22.6	21.8	18.8	15.0
9	23.0	22.5	23.2	22.9	24.1	24.9	25.0	23.2	23.0	23.0	22.6	21.8	18.5	15.0
10	21.5	22.4	23.1	22.8	23.8	24.6	24.9	23.2	23.0	22.9	22.6	21.8	18.5	15.0
11	21.0	21.5	22.7	22.5	23.2	24.3	24.8	23.2	23.0	22.8	22.6	21.8	18.5	15.0
12	20.8	21.3	22.5	22.4	23.1	24.8	24.8	23.2	23.0	22.6	22.6	21.8	18.5	15.0
13	20.0	21.3	22.1	22.2	23.1	23.4	24.7	23.2	23.0	22.5	22.6	21.8	18.5	15.0
14	17.1	21.3	21.5	21.9	23.0	23.0	24.6	23.1	22.8	22.3	22.5	21.8	18.5	15.0
15	16.5	21.3	21.0	21.8	22.8	22.8	24.5	23.1	22.6	22.2	22.5	21.7	18.5	15.0

APPENDIX B

Table 1B. Total Population Numbers of Algae and Bacteria from Peak Creek Arm, 1981

Date, 1981	Algae, per ml	Bacteria, CFU/ml
June 21	-	4200
28	2760	6600
July 5	3060	8300
12	1195	10700
19	2450	17300
26	5274	10600
Aug. 1	7380	12000
9	8075	13200
15	8110	13000
23	7560	4200
30	7510	16000
Sept. 6	6240	20100
9	9480	13200
18	6810	37000
Oct. 3	3510	18000
31	3540	9600
Nov. 7	2480	12700
14	1370	3300
23	1330	-

Table 2B. Total Population Numbers of Algae and Bacteria from Claytor Lake Dam, 1981

Date, 1981	Algae, per ml	Bacteria, CFU/ml
June 21	-	1900
28	2230	1900
July 5	1950	2800
12	2350	15800
19	2755	4200
26	3630	2640
Aug. 15	3830	18000
23	5330	3800
30	5630	2230
Sept. 6	6000	19300
9	5310	10200
18	5840	8900
Oct. 3	3600	-
24	3230	4400
Nov. 7	2480	12700
14	1370	3300
23	1330	-

Table 3B. Composition of the Algal Population in the Peak Creek Arm of Claytor Lake, 1981.

Date, 1981	Percent of Total Count			Total Count (per ml)	Dominant Algae	
	Cyanophyta	Chlorophyta	Chrysophyta		Alga	Percent
June 28	46	48	6	2760	Microcystis	34
July 5	76	20	4	3060	Microcystis	58
12	62	35	3	1195	Trichodesmium	33
19	74	25	1	2450	Microcystis	40
26	83	13	4	5274	Microcystis	67
Aug. 1	94	6	1	7380	Microcystis	83
9	97	3	1	8075	Microcystis	86
15	98	2	1	8110	Microcystis	91
23	96	4	1	7270	Microcystis	96
30	97	2	1	7510	Microcystis	52
Sept. 6	98	2	1	6130	Gleocapsa	51
9	98	2	1	9320	Gleocapsa	63
18	99	1	0	6760	Gleocapsa	59
Oct. 3	97	1.5	1.5	3510	Gleocapsa	65
31	10	90	1	3540	Chlamydomonas	78
Nov. 7	1	98	1	2480	Chlamydomonas	52
14	2	83	15	1370	Chlamydomonas	53
23	0	85	15	1330	Chlamydomonas	44

Table 4B. Composition of the Algal Population in Claytor Lake, 1981.

	Percent of Total Count			Total Count (per ml)	Dominant Algae	
Date, 1981	Cyanophyta	Chlorophyta	Chrysophyta		Alga	Percent
June 28	63	29	8	2230	Microcystis	39
July 5	70	27	3	1370	Microcystis	59
12	72	24	4	2350	Microcystis	54
19	73	24	3	2725	Microcystis	43
26	89	8	3	3630	Microcystis	76
Aug. 15	92	8	0	3830	Microcystis	86
23	98	2	0	5330	Microcystis	90
30	99	1	0	5630	Microcystis	87
Sept. 6	99	1	0	6000	Microcystis	61
9	99	1	0	5310	Gleocapsa	51
18	99	1	1	5840	Gleocapsa	65
Oct. 3	100	0	1	3690	Gleocapsa	48
24	100	1	0	3230	Gleocapsa	64

Table 5B. Dissolved Organic Carbon Concentrations and the Trihalomethane-Formation Potentials of Claytor Lake Water from the Peak Creek Site Before and After Treatment by Alum Coagulation, Flocculation, Sedimentation, and Filtration.

		Dissolved Organic Carbon, mg/L After Dosage of Alum, mg/L Al^{+3}							THM-Formation Potential, µg/L After Dosage of Alum, mg/L Al^{+3}					
Date, 1981	Raw-Water	1	2	3	4	6	8	Raw-Water	1	2	3	4	6	8
July 12	3.4	2.7	1.2	1.7	1.5	1.5	1.8	74	-	76	-	56	69	-
19	2.8	2.3	1.5	1.3	1.2	1.3	1.3	208	-	89	-	88	-	82
26	3.0	1.9	1.4	1.3	1.4	1.2	1.3	238	-	-	86	-	84	92
Aug. 1	2.9	2.2	1.8	1.6	1.5	1.5	1.5	535	-	-	-	170	177	153
9	2.5	1.7	1.1	1.3	1.5	1.8	1.9	202	-	-	101	-	190	-
15	4.4	1.6	1.7	1.2	1.1	1.1	1.1	-	-	-	-	-	-	-
23	2.3	1.8	1.2	1.2	1.3	1.4	1.4	203	114	91	92	136	126	117
30	2.2	2.1	1.4	1.3	1.2	1.2	1.2	226	144	144	127	120	140	125
Sept. 6	2.3	1.6	1.9	1.4	1.8	1.8	1.5	195	119	102	117	92	101	100
9	2.0	1.4	1.2	1.1	1.0	1.1	1.1	172	99	76	82	67	75	77
18	2.0	1.3	1.2	1.1	1.3	1.3	1.3	197	47	41	80	74	73	79
26	3.1	-	-	-	-	-	-	589	-	-	-	-	-	-
Oct. 3	2.2	-	1.6	1.4	1.4	1.4	1.5	-	-	-	-	-	-	-
10	2.3	-	-	-	-	-	-	311	-	-	-	-	-	-
31	2.3	1.7	1.9	1.7	1.6	1.6	1.4	165	98	99	97	97	114	88
Nov. 7	2.3	2.3	1.7	1.5	1.5	1.4	1.4	88	60	58	51	78	87	71
14	-	-	1.5	1.4	1.3	1.4	1.5	68	-	57	50	48	55	54
23	1.9	1.2	1.0	1.0	1.0	1.0	1.0	68	42	62	55	43	66	-

Table 6B. Dissolved Organic Carbon Concentrations and the Trihalomethane-Formation Potentials of Claytor Lake Water from the Dam Site Before and After Treatment by Alum Coagulation, Flocculation, Sedimentation, and Filtration.

		Dissolved Organic Carbon, mg/L After Dosage of Alum, mg/L Al^{+3}							THM-Formation Potential, μg/L After Dosage of Alum, mg/L Al^{+3}					
Date, 1981	Raw-Water	1	2	3	4	6	8	Raw-Water	1	2	3	4	6	8
July 12	3.1	2.0	1.5	1.6	1.5	1.4	1.4	88	-	-	-	66	84	3
19	2.6	2.4	1.4	1.1	1.1	1.2	1.4	183	-	-	86	88	89	-
26	2.1	1.5	1.1	1.0	1.0	1.1	1.3	165	-	81	57	112	-	-
Aug. 15	2.4	1.9	1.8	1.3	1.6	1.3	1.3	-	-	-	-	-	-	-
23	1.8	1.2	1.2	1.0	1.1	1.0	1.0	191	88	82	63	73	70	73
30	1.9	1.6	-	1.5	1.4	1.4	1.6	300	269	-	277	195	179	266
Sept. 6	1.9	1.2	1.1	0.9	1.0	1.0	1.0	144	77	70	68	75	65	44
9	2.5	1.3	1.1	1.1	1.0	1.0	1.1	164	68	64	61	58	34	-
18	1.8	1.3	1.2	1.0	1.1	1.0	1.0	93	81	66	53	54	77	79
Nov. 3	2.4	1.6	1.5	1.3	1.4	1.4	1.4	-	-	-	-	-	-	-
24	2.5	2.0	1.5	1.4	1.4	1.4	1.4	194	96	91	95	104	88	91

APPENDIX C

Table 1C. Raw Data Obtained from the Diurnal Study Conducted on August 1, 1981.

Time Military Clock	pH	Dissolved Oxygen, mg/L	Carbon Dioxide, mg/L	Alkalinity, mg/L $CaCO_3$	Dissolved Organic Carbon, mg/L	THMFP, µg/L
0700	7.7	7.6	2.0	52	3.0	665
0800	8.2	7.7	1.0	52	3.2	670
0900	8.2	7.5	1.0	52	-	597
1000	8.5	8.0	0	52	2.9	596
1100	8.6	8.3	0	52	-	564
1200	8.6	8.6	0	52	-	534
1300	8.7	9.6	0	52	-	535
1400	8.7	9.6	0	52	3.1	412
1500	9.2	10.4	0	52	-	287
1600	8.7	10.6	0	51	-	265
1700	8.6	10.7	0	50	3.4	274
1800	8.5	10.1	0	49	-	301
1900	8.3	9.5	0	49	3.3	285

Table 2C. Raw Data Obtained from the Diurnal Study Conducted on September 25-26, 1981.

Time Military Clock	pH	Dissolved Oxygen, mg/L	Carbon Dioxide, mg/L	Alkalinity, mg/L $CaCO_3$	Dissolved Organic Carbon, mg/L	THMFP, µg/L	Primary Productivity mg C/m^3	Extracellular Products, mg C/m^3
2000	8.5	9.6	0	54	4.1	371	-	-
2100	8.3	9.3	0	54	3.0	229	-	-
2200	7.9	9.1	1.0	54	3.3	283	-	-
2300	7.9	9.0	1.0	54	2.5	289	-	-
0000	7.8	9.0	1.0	54	2.6	-	-	-
0100	7.8	8.9	2.0	54	2.6	332	-	-
0200	7.9	8.6	2.0	54	2.6	418	-	-
0300	7.9	8.6	2.0	54	2.5	399	-	-
0400	7.8	8.5	2.0	54	2.4	437	-	-
0500	7.7	8.3	3.0	54	2.5	425	-	-
0600	7.6	7.8	2.0	-	2.3	581	-	-
0700	7.6	7.8	2.0	55	2.3	561		
0800	7.8	8.1	2.0	55	2.5	698	44.6	172.5
0900	8.0	8.3	2.0	55	2.5	729	-	-
1000	8.3	8.8	1.0	55	2.4	700	319.4	314.5
1100	8.3	9.3	0	55	2.7	711	-	-
1200	8.5	9.8	0	55	3.1	611	566.7	170.1
1300	8.6	10.7	0	55	3.1	589	-	-
1400	8.9	11.0	0	55	3.5	561	93.0	121.7
1500	9.6	11.8	0	52	3.6	553	-	-
1600	10.2	12.5	0	50	3.5	636	171.7	121.9
1700	9.8	12.8	0	52	4.3	635	-	-
1800	8.8	12.1	0	53	4.3	211	35.7	80.3
1900	8.6	12.1	0	-	3.7	311	-	-

Table 3C. Raw Data Obtained from the Diurnal Study Conducted on October 10-11, 1981.

Time Military Clock	pH	Dissolved Oxygen, mg/L	Carbon Dioxide, mg/L	Alkalinity, mg/L $CaCO_3$	Dissolved Organic Carbon, mg/L	THMFP, µg/L
1400	8.0	-	-	51	2.5	260
1500	7.9	8.8	2.0	51	2.2	280
1600	7.9	8.8	1.0	51	2.2	267
1700	7.7	8.6	2.0	50	2.4	257
1800	7.6	8.6	3.0	50	2.0	271
1900	7.4	8.6	3.0	50	1.9	276
2000	7.3	8.0	4.0	50	1.9	259
2100	7.2	7.7	4.0	50	1.9	264
2200	7.2	7.4	4.0	50	1.9	257
2300	7.2	7.4	4.0	50	1.8	261
0000	7.0	7.4	4.0	50	1.8	255
0100	7.0	7.2	5.0	50	1.9	279
0200	7.0	7.1	5.0	50	1.8	283
0300	6.9	7.1	5.0	50	2.1	289
0400	6.9	7.0	5.0	51	2.0	308
0500	6.9	7.0	6.0	51	2.0	312
0600	6.9	6.9	6.0	51	1.9	297
0700	6.9	6.9	6.0	51	1.9	337
0800	6.9	7.3	6.0	50	2.2	329
0900	7.0	7.7	5.0	50	2.1	302
1000	7.2	7.7	5.0	50	2.0	333
1100	7.2	8.5	4.0	50	2.5	335
1200	7.3	8.6	3.0	50	2.0	339
1300	7.4	9.0	3.0	50	2.3	311

Table 4C. Raw Data Obtained from the Diurnal Study Conducted on November 23, 1981.

Time Military Clock	pH	Dissolved Oxygen, mg/L	Carbon Dioxide, mg/L	Alkalinity, mg/L $CaCO_3$	Dissolved Organic Carbon, mg/L	THMFP, µg/L	Primary Productivity, mg C/m^3	Extracellular Products, mg C/m^3
0800	6.4	8.5	9.0	49	2.4	67	-	-
0900	6.4	8.6	8.0	49	2.0	53	-	-
1000	6.7	8.6	6.0	49	2.1	70	87.1	45.3
1100	6.8	8.8	5.0	49	2.3	70	83.2	50.3
1200	6.8	9.3	5.0	49	2.3	68	77.0	38.4
1300	6.8	9.3	5.0	49	1.9	68	38.9	20.6
1400	6.9	9.5	5.0	49	2.3	61	23.5	24.8
1500	6.9	8.9	6.0	49	2.1	69	24.3	21.0
1600	6.8	8.5	7.0	49	2.9	54	-	-

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THE INFLUENCE OF ALGAL GROWTH AND RELATED ECOLOGICAL FACTORS IN RESERVOIRS ON THE PRODUCTION AND CONTROL OF TRIHALOMETHANE PRECURSORS

by

Kevin L. Dixon

(ABSTRACT)

The study reported in this thesis was conducted on Claytor Lake (Virginia) during the late spring, summer, and fall of 1981 and had as its objectives: 1) to assess the role of algae and bacteria in altering the pool of organic compounds, especially those that form trihalomethanes upon chlorination and 2) to evaluate the effectiveness of alum coagulation, followed by clarification, for removing THM precursors from lake water.

The weekly grab samples provided evidence of a general relationship between algal population densities and the THMFP of the lake water. Successional shifts in the dominant genera and species of algae had little discernible effect on the THMFP of the water.

Diurnal analysis clearly showed that the biota of a water impoundment can have a profound effect on the water's potential to form THM's. Alteration of the THMFP may be brought about by liberation of various types of algal ECP (known THM precursors), bacterial ECP, or modification of algal ECP by bacterial agents.

Alum coagulation was effective for the removal of DOC and THM precursors throughout the course of the study, despite shifts in bacterial and algal density and algal community structure. Average removals of DOC and THM-precursors were approximately 24-48 percent and 34-51 percent, respectively.