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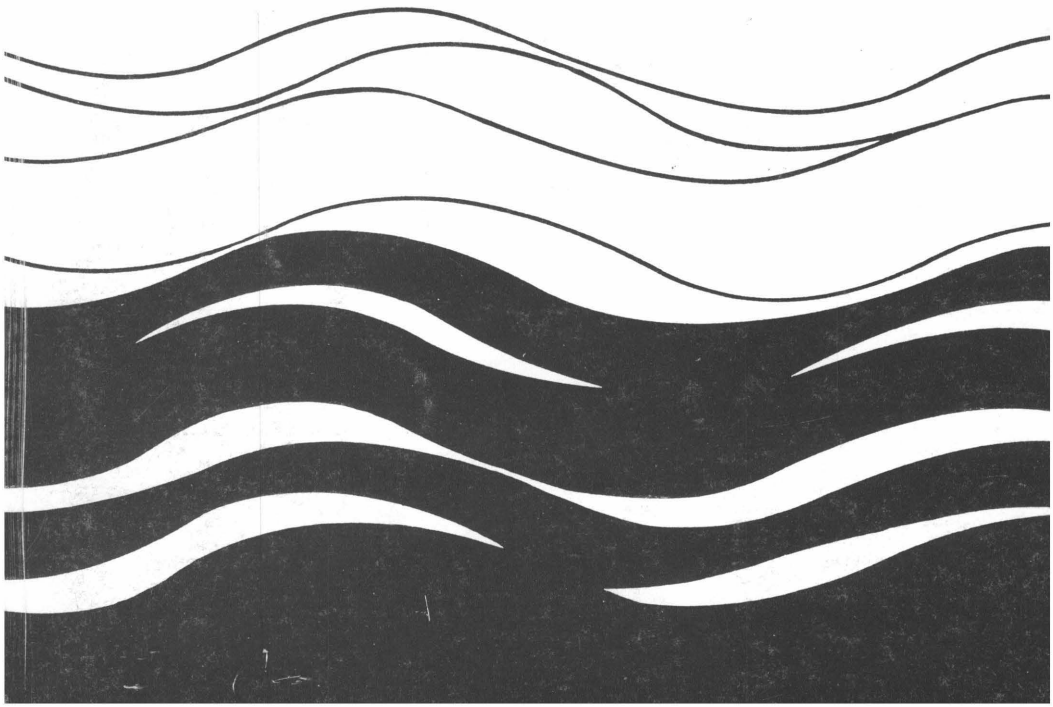

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Seasonal Variations in the Nature and Removability of Reservoir THM Precursors

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ABSTRACT

A major objective of this study was the assessment of the importance of biological activity in a reservoir in altering the nature of dissolved organic carbon (DOC) content, especially that portion of DOC that serves as precursors for trihalomethanes (THMs). The study also evaluated the effectiveness of alum coagulation for removing THM precursors during summer and fall.

Lake water and incubated lake-water samples were fractionated into hydrophilic and hydrophobic solubility classes and analyzed for DOC content and THM-formation potential (THMFP). Algal productivity and extracellular product (ECP) production during a 6-hr period were determined by in situ studies. Diurnal studies were made to relate primary productivity (P) and ECP production to daily variations in lake DOC concentrations and THMFP.

Results showed that the majority of lake-water DOC and THM precursors were hydrophobic in nature, as were the ECPs after a 6-hr incubation. The diurnal studies provided the strongest evidence to date that both algal and heterotrophic populations are involved in the production of THM precursors. No consistent relationships existed between algal or bacterial population densities and the 7-day THMFP of lake water collected as grab samples. Aluminum sulfate proved to be moderately effective for removing THM precursors from lake water.

Key Words: Trihalomethanes, Drinking Water Treatment, Algae, Trihalomethane Precursors, Lake-Water Organics

LIST OF ABBREVIATIONS

DOC	Dissolved organic carbon; that fraction of the total organic carbon in water that passes a 0.45 micrometer filter
DOM	Dissolved organic matter
ECPs	Extracellular products; soluble organic compounds liberated from algae and bacteria
EPA	Environmental Protection Agency
GAC	Granular activated carbon
MCL	Maximum contaminant level
P	Primary productivity
THMs	Trihalomethanes; compounds, such as chloroform, that form upon the chlorination of natural waters that contain certain kinds of organic compounds
THMFP	Trihalomethane-formation potential; the THM concentration that will develop in seven days in the presence of excess chlorine
TOC	Total organic carbon
TTHMs	Total trihalomethanes, including chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$)

INTRODUCTION

I. The Problem

In the mid-1970s, two independent researchers [Rook, 1974; Bellar, Lichtenberg, and Kroner, 1974] reported finding chloroform, a trihalomethane (THM), in drinking water that had been disinfected by chlorination. This finding took on added significance because of a series of events that followed. In 1975 an Environmental Protection Agency (EPA) study [1975a] revealed the presence of THMs and more than 50 other organic chemicals in the drinking water supply of New Orleans. The following year, an epidemiological study [Page, Harris, and Epstein, 1976] demonstrated a correlation between water supply and cancer mortality among white males, and the National Cancer Institute [1976] published a report that showed chloroform to be carcinogenic to rats and mice. Meanwhile, EPA Administrator Russell Train, acting under authority granted him by the Safe Drinking Water Act of 1974 (P.L. 93-523), ordered a national survey of drinking water supplies to assess the extent of the THM problem. The ensuing "80-city" survey [Symons et al., 1975] showed the problem to be widespread, with the worst cases found in localities where water was supplied by surface sources, such as rivers or reservoirs, and where prechlorination was practiced. Another survey [Brass et al., 1977], this time of 113 municipal water suppliers, found numerous organic compounds in finished waters, but none were as significant in concentration as the THMs.

In 1979 EPA [1979a] published a proposed interim maximum contaminant level (MCL) for total trihalomethanes (TTHMs) of 0.10 mg/L. The THMs of importance, in order of decreasing abundance in most water supplies, were chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$). After a period for public comment, the interim MCL and specific monitoring requirements for utilities were published on November 28, 1979 [EPA, 1979b]. These regulations require that water utilities serving more than 10,000 customers be in compliance by November 1983.

Rook [1974] was the first to postulate that naturally occurring humates in surface water are the major precursors of THMs that appear in drinking water. These humates, substances derived from the structural components of living and decaying plants, account for the yellow-brown coloration of water supplies [Black and Christman, 1963]. They are com-

prised of three classes of compounds—humic acids, fulvic acids, and hymatomelanic acids—which appear in varying amounts depending on the nature of the raw water source.

Numerous studies have verified Rook's postulate, but since 1977 attention also has been given to other naturally occurring organic compounds (or sources of organic compounds) that can react with halogens such as chlorine to produce THMs. Hoehn et al. [1978] reported that summertime variations in THM concentrations in a Northern Virginia water supply were related in part to the chlorophyll-a concentrations in the reservoir, a relationship that indicated that algae may play an important role in the formation of THM precursors. Morris and Baum [1978] found that acetogenins, a class of compounds common in plant pigments, yielded $CHCl_3$ when chlorinated. Chlorophyll itself also served as a $CHCl_3$ precursor. Laboratory studies [Barnes, 1978; Thompson, 1978] have shown conclusively that algal extracellular products (ECPs) can serve as precursors for THMs.

II. The Objectives

Before this study was initiated, no investigations with the major purpose of demonstrating in situ the actual significance of algae as contributors to the precursor pool had been published, although studies have since emerged [Briley et al., 1979; Crane, Erickson, and Hawkins, 1980; Oliver and Shindler, 1980]. Recognizing the need for information in this area, the authors undertook the present study. It was postulated that biological activity within a reservoir could account, at least in part, for seasonal variations in finished water THM concentrations that had been observed in earlier studies [Hoehn and Randall, 1979; Hoehn et al., 1980]. The investigators speculated that the presence of algal metabolites and/or their decomposition products would alter the efficiency of THM-precursor removal by routinely used drinking-water treatment processes. The study reported herein was devised to test these hypotheses.

The specific objectives of this study included the following:

1. To relate THM-formation potential (THMFP) of reservoir water to algal activity within that reservoir at intervals during one active growing season;

2. To determine whether any observed seasonal variations in selected

gross characteristics of organic solutes in the reservoir water, as well as other chemical and biological characteristics of the water, could be related to algal growth;

3. To establish by in situ techniques whether algal productivity could increase the THM-formation potential of reservoir water; and

4. To determine whether seasonal variations affect the removability of THM precursors and dissolved organic carbon (DOC) by routine water treatment processes (coagulation, flocculation, and sedimentation) and, if so, to determine whether these variations correspond to increased algal or bacterial growth within the reservoir.

BACKGROUND INFORMATION

This section summarizes work from published studies that provides background information relative to this study. Topics of discussion include the haloform reaction; trihalomethane (haloform) precursors, including humates and algal metabolites, in natural waters; algal ECPs; and water treatment processes for removing THM precursors.

I. The Haloform Reaction

The haloform reaction, which likely accounts for much of the THM formation that occurs during the disinfection of drinking water with chlorine, occurs between hypochlorous acid (the predominant form of chlorine in water at near-neutral pH) and various organic compounds. Under alkaline conditions, chlorination of organic compounds containing an acetyl group ($CH_3-\overset{\overset{O}{\|}}{C}-$) or a structure that, under the proper conditions, can be oxidized to the acetyl group will produce chloroform and a carboxylic acid. Morris [1975] described the process through the following overall reactions:

$$CH_3COR + 3HOCl \rightarrow CCl_3COR + 3H_2O \quad (1)$$

$$CCl_3COR + H_2O \rightarrow CHCl_3 + RCOOH \quad (2)$$

Morris also described the mechanisms of the reaction as a dissociation of hydrogen ion forming a carbanion which then adds positive halogen. Further dissociations and halogen addition take place until the carbon is fully halogenated. The series of reactions occur as illustrated below:

$$\underset{\text{ketone}}{RCOCH_3} \rightarrow \underset{\text{enolate ion}}{RC(O^-)=CH_2} + H^+ \quad (3)$$

$$RC(O^-)=CH_2 + HOCl \rightarrow RCOCH_2Cl + OH^- \quad (4)$$

$$RCOCH_2Cl \rightarrow RC(O^-)=CHCl + H^+ \quad (5)$$

$$RC(O^-)=CHCl + HOCl \rightarrow RC(=O)CHCl_2 + OH^- \quad (6)$$

$$RCOCHCl_2 \rightarrow RC(O^-)=CCl_2 + H^+ \quad (7)$$

$$RC(O^-)=CCl_2 + HOCl \rightarrow RCOCCl_3 + OH^- \quad (8)$$

$$RCOCCl_3 + OH^- \rightarrow RCOOH + CCl_3^- \quad (9)$$

$$CCl_3^- + H^+ \rightarrow CHCl_3 \quad (10)$$

The rate-limiting step in the above series of reactions occurs during the initial reaction (3). Therefore, once the reaction has begun, it will proceed at the same rate.

Stevens et al. [1976] investigated the influence of pH and temperature upon THM formation. It is believed that these factors influence reaction (3) involving the enolization of a ketone.

A reaction similar to the haloform reaction occurs when the halogen is a bromine compound. When a combination of hypobromous and hypochlorous acids is present, the relative amounts of chloroform, bromoform, or one of the chlorobromomethane compounds that are produced depend on the relative rates of the following reactions:

$$RC(O^-)=CH_2 + HOCl \rightarrow RCOOH_2Cl + OH^- \quad (11a)$$

$$RC(O^-)=CH_2 + HOBr \rightarrow RCOCH_2Br + OH^- \quad (11b)$$

The initial rate-determining step for this situation is also reaction (3).

In finished drinking water, chloroform is, by far, the most prevalent THM. When the chlorine dosage was sufficient, several investigators [Stevens et al., 1976; Babcock and Singer, 1979] discovered a definite link between total organic carbon (TOC) and THM formation. As TOC increases, THM formation will increase as long as a chlorine residual is maintained. Babcock and Singer [1979] determined that a dose of chlorine 5 times greater than the TOC concentration is sufficient to ensure a chlorine residual after 7 days.

II. Trihalomethane Precursors

A. Sources of Organic Compounds

In a surface water supply, thousands of organic compounds, which have the potential for reacting with chlorine to form THMs, may exist in varying concentrations at various times of the year. A discussion, then, of THM precursors should include an identification of the various sources of organic compounds in a surface supply.

Organic compounds originate from man-made or natural sources. Man-made sources include recreational activities (i.e., boating), runoff from urban and industrial sites, and effluent discharges from industrial and municipal waste treatment plants. Man-made sources such as these can contribute an infinite array of organic compounds to surface waters and significantly alter the natural organic pool.

Natural sources of organic compounds are also numerous and contribute a variety of THM precursors. A major natural source is the watershed of a surface supply. Such factors as the type and amount of soil, vegetation, and precipitation in a watershed influence the organic loading. Another natural source, which is under investigation in this study, is the active biological community in surface waters. Organic compounds that originate as a result of daily functions of aquatic life, such as algae, bacteria, and fish, can contribute significantly to the organic pool.

B. Known THM Precursors

While the types of organic compounds in a surface supply are numerous, not all produce significant amounts of THMs upon chlorination. There-

fore, much research has been undertaken to identify which organic compounds act as THM precursors. This information is useful for treatment facilities where THM formation is prevalent. A discussion of identified THM precursors follows.

Humic and Fulvic Acids: Humic and fulvic acids are classes of compounds often found in abundance in surface water supplies. Humic acids, first identified by Rook [1974] as THM precursors, have shown great potential in THM production. Humic acids are large-molecular-weight organic compounds derived from the decomposition of plant and animal matter. The mineralization of algae also produces humic acids [Young and Singer, 1977]. Because humic acids are a complex and varied mixture of compounds, their potential as THM precursors is dependent on the types of compounds present at any one time.

The class of humics known as fulvic acids is also composed of a variety of compounds. Black and Christman [1963] defined fulvic acids as the acid-soluble fraction of aquatic humus. Approximately 85 percent of the organic loading in a natural environment is fulvic acids. Jewitt and O'Brien [1979] confirmed the fact that fulvics are a mixture of compounds that generally lead to the formation of THMs when chlorinated. They noted, however, that the yield of THMs is dependent on the particular fractions of the fulvic acids that are present.

Algal Extracellular Products: Nalewajko [1977] defined extracellular releases as "the liberation of soluble organic compounds by living organisms." These compounds are generally low-molecular-weight organic acids and some higher-molecular-weight compounds. Algae excrete considerable amounts of organic compounds that, as a group, have been shown to form THMs upon chlorination. Fogg [1962] determined that algal ECPs are a significant part of the organic pool. He hypothesized that excretion may (1) take place until an equilibrium is attained, (2) be a by-product as a result of metabolism, or (3) be a result of hydrolysis of capsular material. Lefevre [1964] recognized substances that algae produce as *active substances* that aid in increased cell division and growth. The extent of liberation, according to Lefevre, is determined by the type of algae, pH, and amount of light.

The composition of algal ECPs is varied and is dependent on many factors, both internal and environmental. However, many researchers have identified the organic compounds released by specific algae under various

conditions. A wide array of algal ECPs can contribute to the organic pool of a surface supply. Some of the more common ECPs include glycollate, polysaccharides, amino acids, peptides, amide nitrogen, organic phosphorus compounds, vitamins, lipids, phenolic and volatile substances, and various enzymes [Lewin, 1956; Hellebrust, 1974; Watt and Fogg, 1966; Watt, 1969; Jüttner and Matuschek, 1978; Jüttner, 1981].

Several researchers have quantified the ECPs of specific algal species. Watt [1969] found that the diatom *Stephanodiscus* sp. released glycollate, polysaccharide, and amino acids, while *Synedra* sp. released polysaccharide and amino acids but no glycollate. Lewin [1956] determined that 25 percent of the TOC produced from green alga *Chlamydomonas* sp. was polysaccharide composed mainly of galactose and arabinose. Jüttner and Matuschek [1978] found that 58 percent of the total, low-molecular-weight excretion was comprised of sugars and oligosaccharides. Glycolic acid made up 20.5 percent, with various amino acids making up 12 percent.

Chrost and Faust [1980] fractionated dissolved organic matter (DOM) released by phytoplankton according to molecular weight (mw). Of the fractions, two groups dominated the algal ECPs. The dominant fractions consisted or organic compounds $<$1,000 mw and 10,000-30,000 mw. The researchers determined that DOM from algae can range from 1-70 percent of the total carbon fixed during photosynthesis. The organic matter analyzed ranged from simple compounds to high-molecular-weight products.

While it has been shown both in the laboratory and in situ that algae produce an array of organic compounds, the true gross amount of ECPs may not be completely accounted for because of bacterial utilization of algal ECPs. According to Nalewajko [1977], bacteria utilize a variety of low-molecular-weight compounds whose uptake is almost simultaneous with release. A close coupling has been observed by Nalewajko, Lee, and Fay [1980] between algae and bacteria, with bacterial growth confined to daylight hours. Bacterial growth occurred at the expense of glycollate, a major ECP of algae. Radioactive carbon release-rates appeared much lower in mixed, algae-bacteria cultures than in axenic algal cultures. Nalewajko, Lee, and Fay also indicated that 80 percent of algal ECPs may be used up in 7-8 hr; however, ^{14}C products are often consumed after a lag time of approximately 2 hr. Therefore, a 2-hr ^{14}C study may be a close estimation of the gross amount of dissolved organic carbon

(DOC) released by algae. This information leads to the hypothesis that algal ECPs may contribute more significantly to the organic pool during those times when bacterial communities are not well established, e.g., during spring when algal blooms are first established and during times of algal species dominance shifts.

The levels of ECPs produced, in general, are dependent on various environmental factors. Researchers [Nalewajko, 1966; Fogg, 1965] have shown that any factor inhibiting cell multiplication but still permitting photosynthesis to occur causes the production of large amounts of ECPs. These factors include high light intensities and low CO_2 at high pHs. Jones and Stewart [1969] stated that any rapid environmental change can cause high ECPs.

Because algal ECPs can constitute a large array of organic compounds in the algal environment, laboratory studies have been conducted to determine what role, if any, they may play in THM formation. Several researchers [Hoehn et al., 1980; Briley et al., 1979; Crane, Erickson, and Hawkins, 1980] have shown that blue-green and green algal ECPs produce, upon chlorination, chloroform levels comparable to humics and fulvics. Hoehn et al. [1980] showed that the ECPs produced more THMs than did the actual macerated biomass, and they determined that the highest THM levels were produced when chlorination took place during the late exponential phase of growth.

Oliver and Shindler [1980] also concluded that algae contribute to the THM-precursor pool; however, they found the extent of THM formation to be dependent on chlorine dosage and reaction pH. A fractionization of algal components was used to determine if any single compound or cell component led to the major portion of THM. These researchers found no such component or compound; however, they were dealing mainly with algal biomass components, such as chlorophyll-a, and not algal ECPs.

III. THM Seasonal Variation

The impetus for the study reported in this bulletin was derived from reports of THM-level variations occurring on a seasonal cycle. Several researchers [Arguello et al., 1979; Veenstra and Schnoor, 1980; Hoehn et al., 1977] have demonstrated that a definite seasonal variation does exist. Arguello et al. [1979] found that higher THM levels occurred during

warmer months while lower concentrations occurred in colder months. They postulated that the decrease in concentration in colder months could be a result of decreased concentrations of THM precursors or a result of lower temperatures but did not mention the possibility that the lower THM-precursor concentration may also be a result of decreased algal activity during colder months.

Veenstra and Schnoor [1980] fractionated a surface supply water according to the molecular-weight characteristics of organic compounds. They observed two major peaks, possibly representing fulvic acids, in TOC in the ranges of 1,000-2,300 atomic mass units (amu) and >40,000 amu. The researchers found that 87 percent of the TTHMs were formed in the range of <3,000 amu, with 33 percent being in the <1,000 amu. Their study revealed that higher-molecular-weight compounds do not contribute as much as lower-molecular-weight compounds in THM production.

IV. The Role of Ribulose-1,2-Bisphosphate in Algal ECP Production

A factor that plays a decided role in determining THM-formation potential of algal ECPs appears to be the physiological state of algae when ECPs are liberated. This factor has been studied in considerable detail, primarily in the laboratory. Another key factor is the destruction and alteration of algal ECPs by the heterotrophic community. The following discussion provides the basis for interpreting diurnal studies of variations in algal productivity, ECP production, and lake-water THM-formation potentials observed in the fall of 1981.

Extracellular products released from photorespiring algae are low-molecular-weight metabolic intermediates that diffuse through the algal cell wall. They include simple sugars, amino acids, organic phosphates, and, most notably, glycollate. These intermediates are referred to as *Type I* substances [Fogg, 1966]. Hoehn et al. [1980] have shown that glycollate and other Type I intermediates have low THM-formation potentials.

Compounds released during active photosynthesis are high-molecular-weight metabolic end-products known as *Type II* substances. They are represented by carbohydrates, peptides, aldehydes, ketones, enzymes, and various growth-promoting and growth-inhibiting substances [Fogg, 1966]. Compounds of this nature have been shown to possess high THM-formation potential [Hoehn et al., 1980].

It is a well-established fact that the physiological state of algae is determined by an interplay of environmental factors such as light intensity, available free CO_2 concentration, temperature, pH, and dissolved oxygen concentration. It is logical, then, that as these conditions and the physiological state of the algae vary, the THM-formation potentials of algal ECPs will differ, perhaps radically. A discussion of the roles that these various environmental factors play follows.

A. The Effect of CO_2

Photoautotrophic growth is predicated on the incorporation of a carbon source, usually CO_2, into the biochemical pathways of a cell where it can be transformed into reduced carbon compounds by the converted light-energy forms ATP and $NADPH_2$ [Raven, 1974]. The CO_2-fixation mechanism in the phytoplankton follows the Calvin-Benson cycle. Initiation and regulation of the cycle are performed by the enzyme ribulose-1,5-biphosphate (RuBP), which is the actual CO_2 acceptor [McFadden and Purohit, 1978]. Once fixed, CO_2 is introduced into the cycle by RuBP and is catalyzed to yield two molecules of 3-phosphoglycerate (PGA). RuBP plays the role of a carboxylase. The energy that is liberated by ATP and $NADPH_2$ is used to reduce PGA to phosphoglyceraldehyde, which, when combined with dehydroxyacetone phosphate (also a reduced form of PGA), forms the six-carbon sugar-phosphate known as *fructose disphosphate.* A fraction of this compound is chemically converted to RuBP, while the remainder forms the carbohydrates glucose, sucrose, and starch [Weier et al., 1974]. This complex set of processes, when simplified, is expressed by the familiar overall equation describing photosynthesis:

$$6\,CO_2 + 12\,H_2O \xrightarrow[\text{RuBP}]{\text{light}} C_6H_{12}O_6 + 6\,H_2O + 6\,O_2$$

It is clear from the equation that the level of CO_2 fixation is ultimately determined by the degree of activity of RuBP.

Depending upon the conditions, RuBP functions either as a carboxylase or an oxygenase. The specific conditions under which it acts as a carboxylase include high CO_2 concentrations (above 0.1 percent in atmospheres), low-to-saturating light intensities (approximately 15,000 lux), pH $\leqslant$7.8, temperatures of 15-20° C, and low dissolved oxygen concentra-

tions [Raven, 1974]. When the CO_2 concentration becomes limiting and light intensity and dissolved oxygen concentrations reach prohibitive levels, the RuBP alternates its role and begins to function as an oxygenase. In doing so, it actively takes up oxygen and releases CO_2. This occurrence signals the onset of a process known as *photorespiration.*

The true function of photorespiration is, as yet, unknown to phycologists, although a number of hypotheses have been advanced. The importance of photorespiration to this study is that it results in the liberation of ECPs which have a significantly lower THM-formation potential than do photosynthetically produced ECPs.

Of particular note is the ECP glycollate, which is by far the most abundant and significant photorespiratory product. Glycollate is produced by the glycollate pathway. Its initiation is apparently the result of a quantity effect. This means that once the concentration of RuBP, while it is acting as a carboxylase, is greater than that of the free CO_2 available for fixation by photosynthesis, the excess RuBP becomes subject to the influences of the glycollate pathway. In this respect, RuBP can be characterized as the precursor to glycollate. Once the glycollate pathway is initiated, the liberation of glycollate can be quite significant. Estimates as high as 90 percent of the total carbon fixed during photosynthesis have been made for the carbon being released as glycollate [Tolbert and Zill, 1956]. For emphasis, it should be restated that glycollate is not a high-yielding THM precursor.

B. The Influence of Light Intensity

Algal growth and photosynthetic rates are directly influenced by light intensity. However, a given intensity will elicit highly diverse responses from the many algal species because of great differences in their adaptability to light [Wetzel, 1975]. Thus, generalizations concerning quantitative responses are subject to error. With this in mind, the relationship between photosynthetic rates and light intensity can be described only in the broadest of terms, such as *proportional to.* The vital relationship that exists between increasing intensity and photosynthetic rate breaks down when the intensity reaches a level that induces photo-oxidative destruction of enzymes involved in the photosynthetic process. This phenomenon, known as *photoinhibition,* is quite common near the water's surface and results in a distinct depression in the epilimnetic photosynthetic rate. For this reason, the inhibitory effect of high light inten-

sity can be considered a significant factor in the overall physiological state of algae during periods of photorespiration.

C. The Effect of Temperature

Great diversity exists in tolerance to temperature variations among algae. However, it is an acknowledged fact that water temperatures of 15-20° C are optimal for the majority of phytoplankton [Wetzel, 1975]. Thus, one would expect ECP production, as well as other metabolic functions, to increase during the warmer months of the year.

V. Separation and Classification of Organics in Aqueous Mixtures

The separation and identification of organic compounds in an aqueous solution are necessary in order to test and analyze compounds for their potential THM production upon chlorination. In the past, however, the problem has been to find a comprehensive fractionation scheme that separates compounds with a high degree of recovery but with a low degree of alteration. A technique was needed that could satisfactorily separate compounds of similar characteristics for further analyses. A number of methods were considered:

1. Baker and Malo [1967] discussed the need for separation and identification techniques and considered the use of carbon filter, freeze concentration, distillation, spectroscopy, glass-liquid chromatography, paper chromatography, thin-layer chromatography, and carbon analysis for these purposes. They concluded that spectrographic and chromatographic procedures provide the most promising techniques.

2. Goldberg, Delong, and Kahn [1971] used a continuous, liquid-solvent extractor to concentrate organic compounds with little alteration or biodegradation.

3. Two research teams [Junk et al., 1974; Burnham et al., 1973] investigated the usefulness of macroreticular resins such as XAD. The technique used in these studies involved the sorption of organic compounds onto resins contained in small chromatography columns followed by their elution with diethyl ether.

Leenheer and Huffman [1976] identified several problems with techniques for classifiying organics in natural aquatic environments:

1. The number of organic compounds possible,

2. The smaller concentration of organic compounds compared to inorganic compounds,

3. The limits of present analytical techniques, and

4. The lack of a comprehensive analytical scheme.

They developed an analytical scheme that used macroreticular resins for the classification of organic solutes into hydrophobic-hydrophilic acid, base, and neutral compounds. While this scheme, by their own admission, is not perfect, satisfactory results can be obtained for several applications of this technique to natural aquatic environments. For this reason, the Leenheer-Huffman scheme was used in the research for this study. (Leenheer [1981] later developed a refined procedure that recovered >90 percent of the DOC from resin absorbents.)

VI. Water-Treatment Processes for Removing THM Precursors

Generally speaking, the easiest way to avoid the formation of large concentrations of THMs in drinking water is to remove the precursor organics before chlorine for disinfection is introduced. Perhaps the easiest method to accomplish THM-precursor removal is to delay chlorination for as long as possible in the treatment scheme so that coagulation with metal salts, such as aluminum sulfate (alum) or ferric sulfate, can be accomplished. After the coagulant is added in a water treatment plant, there is a brief period of rapid mixing followed by a longer period (20-30 min) for flocculation to occur. During this time, a floc forms and grows while the water is gently agitated. This floc enmeshes other floc and suspended particles within the water column. Organic precursors can also be enmeshed and adsorbed to the floc surfaces. A period of quiescent settling (about 2-4 hr) allows the removal of as much floc as possible before filtration.

Researchers in the area of precursor removal by treatment involving coag-

ulation/flocculation/sedimentation have discovered several characteristics of THM precursors and their reduction in finished water:

1. The important THM precursors are particulates or substances that strongly adsorb to particulates such as clay particles [Stevens et al., 1976].

2. THM-formation potentials in finished waters can be reduced by as much as 60-70 percent by coagulation [Babcock and Singer, 1979; Kavanaugh, 1978; Oliver and Lawrence, 1979; Young and Singer, 1979].

3. Reduction in THM-formation potential may be a selective process when alum is used but not when iron salts are the coagulant [Babcock and Singer, 1979; Brett and Calvery, 1979; Kavanaugh, 1978; Oliver and Lawrence, 1979].

4. Chlorination should follow, rather than precede, other water treatment processes for maximum THM-precursor removal [Babcock and Singer, 1979; Kavanaugh, 1978; Young and Singer, 1979].

Kavanaugh [1978] defined several important factors in achieving effective coagulation:

1. The optimum coagulant dose is determined by the concentration of fulvic acids. (Fulvic acids were chosen because this class of humates is more difficult to remove than are humic acids [Amy and King, 1981; Kavanaugh, 1978; Babcock and Singer, 1979; Young and Singer, 1979]).

2. The optimal pH range is between 5 and 6 when alum is used and between 3 and 5 when ferric sulfate is used.

3. Polymers (anionic organic polyelectrolytes) at doses of 1-10 mg/L can enhance the removal of humic materials by metal salts.

However, each of these treatment variations must be optimized on a plant-by-plant basis because of inherent differences in water supplies.

Studies have also been undertaken to assess the effectiveness of granular activated carbon (GAC) removal of THM precursors by adsorption. To

date, GAC as a viable treatment alternative has not gained wide acceptance because the carbon must be reactivated or replaced after just a few weeks of use. Thus, it is quite costly [Blanck, 1979; Stevens et al., 1976]. Research is continuing, however, and this treatment option may someday prove to be more feasible.

OVERVIEW OF THE STUDY

Beginning in March 1981, in situ studies of primary productivity (P) and ECP production were begun in Claytor Lake near Pulaski, Virginia, to determine the significance of algae in contributing to the THM precursor pool. Samples were collected in a highly eutrophic arm of the lake, spiked with a small amount of labeled sodium carbonate ($Na^{14}CO_3$), and incubated 4-6 hr in the lake at the depth from which they were collected. The ^{14}C-uptake method used was basically that developed by Strickland and Parsons [1968]. Other samples were collected from the same depth and placed on ice for transport to the laboratory, where they were evaluated for changes in THM-formation potentials, DOC concentrations, and gross characteristics of the DOC according to their solubility class. This phase of the work continued into early August.

At the end of the incubation period, the samples were fixed, returned to the laboratory, and filtered. The radioactivities of the filtered material and the filtrates were determined, and the ensuing data were used to calculate P and ECPs, respectively. The filtrates were subjected to a gross fractionation procedure (Leenheer and Huffman, 1976] to determine the relative abundance of the hydrophobic and hydrophilic acid, base, and neutral components before and after the ^{14}C-uptake incubation period. It was anticipated that there would be a detectable change in the relative abundance of these fractions as algal activity in the lake became more pronounced.

Nonradioactive samples were fractionated by the same procedures used for radioactive samples but with a different set of ion-exchange columns. The fractions were spiked with enough chlorine to provide a free-chlorine residual after seven days in order to determine the THM-formation potential of the organic components of the lake water. These data, it was hoped, would reveal whether one or more fractions of the lake DOC pool was more productive of THMs and whether there were shifts in time as the lake became more biologically active.

Another aspect of this study was begun in early June 1981 and continued until late November when algal growth and other microbiological activity had vastly diminished. This part of the study was designed to provide additional data that could be examined for their significance in relation to the THM-formation potential of the lake water. Tests were conducted to determine levels of pH, dissolved oxygen, carbon dioxide, alkalinity,

dissolved organic carbon (DOC), and THM-formation potential (THMFP). Algal and bacterial population densities also were determined. In addition, a series of primary productivity studies by the ^{14}C-uptake method were performed on three occasions during one day to assess the relationships between algal productivity and THMFP of the lake water.

Laboratory studies (jar tests) were conducted to determine the removability by alum coagulation of total DOC and, in particular, that fraction of DOC that served as THM precursors. This aspect of the study was conducted to assess the impact of biological activity on the THM-formation potential of the lake water itself and on lake water treated for human consumption.

THE STUDY AREA

Claytor Lake is a large reservoir in Pulaski County, Virginia, that was formed when Appalachian Power Company (APCO) built a dam on New River in the 1930s to provide a source of hydroelectric power. The surface area of the lake is 18.2 km^2 and mean depth is 29 m. Maximum depth is slightly greater than 35 m. The mean hydraulic retention time is 63 days. An estimate of the annual total phosphorus loading is about 10.1 g/m^2 [EPA, 1975b].

Two sampling stations at the lake were selected for this study, one in the upper reaches and one near the dam. Descriptions of these sites follow.

I. Peak Creek Arm

One sampling site was located in a small cove in the Peak Creek arm of the reservoir approximately 3 mi below the effluent outfall from the Pulaski, Virginia, sewage treatment plant. This site was selected because of its high level of algal productivity. Peak Creek has been estimated to contribute about 10 percent—6 percent coming from the sewage treatment plant and 4 percent from nonpoint sources—of the total phosphorus load in Claytor Lake[EPA, 1975b]. The high phosphorus content of the water, its relative shallowness (about 9 m), and its relative low flow rate (2 m^3/sec) contributed to the high algal productivity.

II. Dam Site

The second sampling site was approximately 100 m above the APCO dam. The characteristics of this area are markedly different from those of the Peak Creek site. Turbulent waters of considerable depth (>35 m) typify the area. Because the dam penstocks are located 13 m below the surface, water released from the lake is cool, oxygen deficient in the summer, and usually nutrient rich. Thus, the lake develops an expansive epilimnion approximately 14 m deep during periods of summer stratification. In general, phosphorus concentrations and algal productivity are lower here than in the Peak Creek arm, but algal population densities are still quite high. It should be noted that this site was not included in the studies designed to define chemical characteristics of dissolved organic matter in the reservoir water.

MATERIALS AND METHODS

The information in this section describes the field and laboratory procedures used to characterize the lake and analyze its chemical constituents, enumerate the algal and bacterial populations and evaluate algal productivity, separate lake-water organic constituents into hydrophobic and hydrophilic components, and evaluate the effects of alum coagulation on levels of THM precursors and DOC in the lake water.

I. Glassware Preparation

All glassware was washed with an organic-free, laboratory detergent; rinsed with tap and distilled water and, in special instances, with 20 percent hydrochloric acid (HCl); dried at 103° C; cooled; and covered with aluminum foil until its use.

II. Chemical Analyses

Samples for chemical analyses were collected from the lake with a 2-L Van Dorn sampler. Some samples were returned to the laboratory for analysis, while others were analyzed in the field. Those returned to the laboratory were stored on wet ice until they could be refrigerated at 4° C. Chemical analyses were performed to measure pH, alkalinity, free carbon dioxide, and dissolved organic carbon.

A. pH

A Fisher Scientific (Raleigh, North Carolina) Accumet portable pH meter, Model 150, was used in the field to determine the pH of samples immediately upon collection.

B. Alkalinity

Not only is a determination of water alkalinity required in the calculation of algal productivity, but it is also used to describe the buffering capacity of the water. Alkalinity was determined in the field by a titrimetric procedure outlined in *Standard Methods for the Examination of Water and Waste Water,* Section 403.4 [American Public Health Association et al., 1980].

C. Free Carbon Dioxide

The free carbon dioxide (CO_2) concentration of lake-water samples was determined in the field by the tritrimetric method described in Section 406B of *Standard Methods* [American Public Health Association et al., 1980]. The analysis was performed only on samples collected at a depth exhibiting the highest dissolved oxygen concentration. Care was taken to avoid mixing the sample with air during transfer from the Van Dorn sampler to the test bottle.

D. Dissolved Organic Carbon

Samples from the field were filtered in the laboratory through 0.45 micrometer (μm) Whatman GF/C glass-fiber filters to remove all particulate matter, then analyzed with a Dohrmann-Envirotech (Santa Clara, California) DC-54 Ultra-Low Total Organic Carbon Analyzer. Replicate samples were analyzed to obtain values that were within 2 percent of one another. (Values outside that range were discarded.) These values were then averaged.

III. Biological Analyses

Bacterial and algal populations in Claytor Lake were monitored at the Peak Creek and dam sites beginning in June and continuing through November 1981. Descriptions of the procedures used to enumerate algal and bacterial populations follow.

A. Algal Enumeration

Samples returned to the laboratory from the field (stored on ice in the dark) were fixed with Lugol's solution (1 mL per 100 mL sample). Enumerations were performed with a Sedgwick-Rafter counting chamber. Because cell densities were generally quite high, the researchers selected a field-counting procedure in which the algae in 60 microscope fields were counted. Method 1002F, Section d, in *Standard Methods* [American Public Health Association et al., 1980] was used. Algae were identified to genera.

B. Bacterial Enumeration

Bacteria were grown on a pond-water agar (PWA) medium by the spread-plating technique. The PWA was prepared as follows:

1. Five hundred mL of Claytor Lake water was filtered through a Whatman GF/C filter and mixed with 500 mL of distilled water;

2. One-g proteose peptone, 0.1-g yeast extract, and 15-g agar were dissolved in the water; and

3. The medium was autoclave-sterilized for 15 min at 121° C, poured into Petri plates, and allowed to harden.

Serial dilutions were made in sterile, distilled water; and 0.1-mL aliquots of 1:10, 1:100, and 1:1000 were dispersed onto the surface of the agar. Triplicates of each were prepared. Each sample was then spread over the surface of the agar with a bent glass rod that was flame-sterilized after each spreading operation. The plates were incubated for 5 days at the temperature of the lake water at the time of collection. The colonies were then enumerated.

IV. Primary Productivity Determinations

Primary productivity within the lake was determined by a modification of the technique described by Strickland and Parsons [1968]. In one phase of the study, four 300-mL BOD bottles were filled with lake water from a depth of 0.5 m at the Peak Creek Station. (No evaluations were made at the dam site.) A control bottle was fixed with 1-mL formalin. All bottles were then spiked with 5 microcuries (μCi) of $NaH^{14}CO_3$, suspended in the lake at a depth of 0.5 m, and incubated for 1, 2, 4, or 6 hr. The control was also incubated for 6 hr. As the bottles were retrieved after their respective incubation times, they were fixed with 1 mL of formalin and were put on ice until they were returned to the laboratory. P was determined by calculations (*Table A4*) that involved alkalinity and pH of the lake water [Saunders, Trans, and Bachmann, 1962].

Late in the summer of 1981, additional ^{14}C-uptake studies were conducted in the Peak Creek arm during an entire day to record the relation between hourly changes in THM-formation potential and variations in P and ECP production. At 1-hr intervals, lake-water samples were collected

from 0.5 m and returned to the lab on ice to be evaluated for THM-formation potential and DOC concentration. Other samples from 0.5 m were collected at 1- or 2-hr intervals during the day, spiked with 5 μCi of $Na_2{}^{14}CO_3$, and incubated in the lake at 0.5 m. An incubation period of 4 hr was allowed for these tests. Samples were removed from the lake after incubation, fixed as previously described (see above), and returned to the laboratory on ice in the dark.

In order to drive off any ^{14}C remaining in the inorganic form, each BOD bottle harvested during the productivity studies was acidified with nitric acid (HNO_3) to an approximate pH of 2 and purged with nitrogen gas for 10 min. Samples were then filtered through Whatman glass microfiber filters (934-AH), dried at 103° C for 24 hr, placed in scintillation vials with 15 mL of Scintiprep (Fisher Scientific, Pittsburgh, Pennsylvania) made up as 1:24 Scintiprep in toluene, and counted in a scintillation counter (Beckman Model LSC-2) for 5 min with an error setting of 2 percent at a gain of 350. Instrument efficiency was determined by comparison of counts obtained to standards.

A modification of the sample-handling procedure was used for samples collected during the day-long P studies conducted in the fall. This modified procedure involved delaying the acidification step and treating the filtrates and filters in a different manner. Thus, the filtrates were acidified in the scintillation vials (1 drop of concentrated hydrochloric acid [HCl]) and left exposed to the atmosphere in a fume hood for 24 hr before counts were obtained. Filters were dried in a dessicator containing HCl to destroy any residual carbonate.

The filtrate containing the algal ECPs was stored in Erlenmeyer flasks covered with aluminum foil and was refrigerated until the organic compounds could be separated into their solubility classes.

V. Determination of Trihalomethane Formation Potential

Samples of untreated lake water, lake water treated by alum coagulation (see "Jar Test Procedures" [p. 28]), and lake-water fractions produced by a resin adsorption/elution procedure (see "Organic Fractionation Scheme" [p. 26]) were chlorinated with excess chlorine and allowed to react at 20° C for 7 days before analysis with a gas chromatographic purge-and-trap procedure for THMs. The protocol included several steps.

Each sample to be evaluated was placed in 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. The vial was filled ¾-full and mixed with the buffer. Next, 0.5 mL of a stock calcium hypochlorite solution (2,000 mg/L available chlorine) was added to each vial; the vial was then quickly filled to capacity and sealed with a Pierce No. 12722 Teflon septum inside a screw cap. Care was taken to prevent the formation of any headspace in the vial. After the 7-day incubation period, THMs were determined with a Tracor 560 Gas Chromatograph equipped with an LSC-2 concentrator (Tracor Company, Austin Texas) by the purge-and-trap method developed by EPA [1979b]. Specifications for the analysis are given in *Table 1.*

VI. Organic Fractionation Scheme

A fractionation scheme was used to separate organic compounds in both radioactive and nonradioactive lake-water samples according to their hydrophobic-hydrophilic acid, base, and neutral characteristics. Two separate sets of columns were used to avoid contamination of nonradioactive samples.

The fractionation scheme used in this study was basically that developed by Leenheer and Huffman [1976] but with a few minor changes. The flow-train consisted of a series of three ion-exchange columns with an inner diameter of 9 mm and an outer diameter of 25 cm. These columns, ChromatoFlo series B obtained from Pierce (Rockford, Illinois), were acid-washed (20 percent HCl) and packed with macroreticular resins.

Column I was packed with XAD-2 resin on the bottom half and XAD-8 resin on the top. The two resins were separated with glass wool. Before the columns were packed, the resins were purified by sequential 24-hr Soxhlet extractions using ether, acetonitrile, and methanol. Once packed, each column was flushed with distilled water until DOC concentrations comparable to those of distilled water were obtained.

Column II was packed with Bio-RAD AG MP-50 cation-exchange (H-form) resin. Before this column was packed, the resin was purified by a 24-hr Soxhlet extraction using methanol. Flushing with distilled water was again carried out until a low DOC concentration was obtained.

Column III was packed with Bio-RAD AG MP-1 anion-exchange (OH-

form) resin. Before it was packed, the resin was extracted with methanol for 24 hr. A distilled water flush followed.

Figure 1 illustrates the separation procedure, which included the following steps:

1. The filtered sample (approximately 700 mL) was adjusted to a pH of 6-8 when necessary.

2. One hundred mL of lake water was collected for DOC determination, chlorination, and subsequent THM determination. This sample of unfractionated lake water was labeled DOC I and THM I.

3. The remaining 600-mL volume was pumped through column I at a flow rate of 4 mL/min to adsorb the hydrophobic bases and neutrals.

4. The effluent (step 3) sample was collected and set aside.

5. Column I was then back-flushed with 50 mL of 0.1 N nitric acid (HNO_3) at a flow rate of 2 mL/min. This process desorbed the hydrophobic bases, denoted as DOC II and THM II. (Note: Leenheer and Huffman's original fractionation scheme used HCl in place of HNO_3. Nitric acid was used in this study because of its better compatibility with the DOC analyzer.)

6. All three columns were then connected in a series.

7. The effluent sample from step 4 was adjusted to a pH of 2 with 1 N HNO_3 and pumped through the series of columns at a flow rate of 4 mL/min.

8. DOC samples IV, V, and VI were collected as indicated in step c of *Figure 1.* DOC VI was collected first from column III, which was then disconnected from the series. DOC V was collected from column II, which was then disconnected, allowing for the collection of DOC IV from column I. (A sample was also collected at these three points for THM IV, V, and VI.)

9. All columns were disconnected, and column I was back-flushed

with 50 mL of 0.1 N sodium hydroxide (NaOH). This sample, designated DOC and THM III, contained the hydrophobic acids.

10. At all collection sites for DOC samples I-VI, 100 mL of sample was obtained. Approximately 60 mL was analyzed for DOC, and the remainder was chlorinated and analyzed for THMs 7 days later.

11. Hydrophobic-hydrophilic acid, base, and neutral concentrations were calculated by the method described in *Table A1.*

Radioactive samples (those that contained ^{14}C-labeled organic compounds produced by algae during the incubation period that was allowed for P evaluations) were treated somewhat differently during the fractionation procedure. A second set of columns, prepared in the same manner as those used for separating the other lake-water samples, was used. Only 150 mL of sample was pumped through the columns. One L of sample was collected from the DOC analysis sample site and added to 9 mL of Scintiverse (Fisher Scientific, Pittsburgh, Pennsylvania) for later counting in the scintillation counter. (This mixture will hereafter be termed *algal ECPs.*)

A small volume of sample was allowed to pass through each of the columns to permit uniform distribution and was discarded before samples to be analyzed were collected. After each separation was completed, all columns were flushed with distilled water, and the column effluents were then analyzed to ensure that the columns were free of residual organic carbon and radioactivity.

VII. Jar Test Procedures

Throughout the summer and fall, samples from the two study areas were returned to the laboratory and treated by alum coagulation/flocculation/sedimentation processes to determine the effectiveness of routine water treatment processes in removing dissolved organic carbon and THM precursors. Samples of 500 mL each were placed in battery jars and dosed with varying amounts of an aluminum sulfate [$Al_2(SO_4)_3 \cdot 18\ H_2O$] solution. The stock solution was prepared on each test date by adding 2.468 g of $Al_2(SO_4)_3 \cdot 18\ H_2O$ to 100 mL water. The samples were dosed with 0.5, 1.0, 1.5, 2.0, 3.0, and 4.0 mL stock solution to provide dosages, respectively, of 1, 2, 3, 4, 6, and 8 mg/L as Al^{3+}.

After coagulant addition and a flash-mixing period of 60 sec, flocculation was allowed to proceed for 20 min. The flocculent material (floc) was allowed to settle for 30 min. This entire treatment was carried out on a Phipps and Bird 6-place jar-testing apparatus. After settled water was siphoned off, a four-step procedure was followed:

1. pH was measured,

2. Samples were filtered through Whatman GF/C filters to remove any residual floc,

3. DOC concentrations were measured, and

4. Samples were chlorinated to evaluate THM-formation potential.

RESULTS

The results of this study illustrate the following:

1. Changes from early spring to late summer 1981 in the solubility-class structure of the pool of organic compounds within Claytor Lake and the influence of algal growth on these changes;

2. Changes from early summer to late fall 1981 in algal and bacterial population densities in relation to variations in the THM-formation potential of the lake water;

3. The relationships determined by diurnal in situ studies between P and the THM-formation potential of the lake; and

4. Variations from late spring to late fall 1981 in the effectiveness of alum coagulation for removing DOC and THM precursor from the lake water.

I. Variations in Algal Productivity and Solubility-Class Structure of ECPs

Figure 2 shows the patterns observed in P and ECP production in the Peak Creek arm of Claytor Lake from early March through early August 1981. The values were obtained from analyses of samples that were incubated for 6 hr. The ECP has been expressed in terms of actual counts/min/mL of sample rather than as carbon fixed during the incubation period. It should be noted that peak ECP production was observed in May, whereas P increased gradually until it was maximal in late July.

It can be seen in *Figure 3* that the organic components of lake-water filtrates containing algal ECPs were predominantly (54-77 percent) hydrophobic compounds, especially during June and July before the peak primary productivity was observed. These hydrophobic compounds were predominantly comprised of neutral components, ranging from 43 to 55 percent, except in early May when acid components were dominant and in early August when the base fraction predominated (*Figure 4*). The composition of the hydrophilic fraction (*Figure 5*) varied during the sampling period. The hydrophilic bases were predominant (69-83 percent) during the first half of the study, but acidic compounds were predominant (53-62 percent) during the last half. *Table A2* shows the

observed changes in ECP concentration, represented by increases in filtrate radioactivity, during each of the incubation intervals of 1, 2, 4, and 6 hr. Later in the study, only two intervals—4 and 6 hr—were used. Note that the same fractions were consistently dominant throughout any given 6-hr incubation period. *Tables A1-A5* contain all the methods and laboratory data used in calculating algal ECPs and productivity values appearing in *Figures 3-5.*

II. Comparisons of ECP, DOC, and THM-Precursor Solubility Classes

The distributions among solubility classes of total DOC and THM precursors present in lake water at the beginning of each 6-hr incubation period are shown, along with the ECP distribution, in *Table 2.* Note that all organic compounds in the lake, and especially those that were precursors for THMs, were in the same classes as the ECPs present in the lake water after the 6-hr incubation period in BOD bottles.

III. Changes in DOC and THM Precursors during Incubation

Twice during the study, a set of bottles containing lake water from 0.5-m depth, but without the radioisotopic carbonate, was incubated alongside the set used for determining P and ECPs. These bottles were taken to the laboratory for fractionation and analyses of DOC and THM-formation potentials. The residuals of these studies, shown in *Table 3,* were similar in a few respects but different in several. In the August study, there was a considerable increase (70 percent) in the DOC concentration in the whole-lake sample (unfractionated, *Table 3*) but a small increase (10 percent) in THM-formation potential. During the second study (September 18), an increase of only 19 percent in DOC was observed, but THM-formation potential increased 35 percent. Hydrophilic compounds comprised the majority of DOC produced during the 6-hr incubation period in both studies, but the predominant solubility-class of THM precursors was the hydrophilic class in the August study and the hydrophobic class in the September study. A considerable number of anomalies were noted in the data (*Table 3*) in the individual components of the two major solubility classes. In most instances these anomalies could be attributed to the fact that more material was found in the acid and base elutriates from the columns than was present in either of the solubility-class fractions. The cause of this problem was not identified.

IV. Chloroform Yields Per Unit DOC in Solubility Class Fractions Compared to ECP

Yields of $CHCl_3$ from the DOC (μg $CHCl_3$/mg DOC) in each of the solubility-class fractions have been plotted in *Figures 6-11* along with the ECP concentrations (counts per minute per milliliter [cpm]/mL) determined from each of the P studies. The $CHCl_3$/DOC ratio gives one an idea of how organic compounds in the lake react with chlorine to produce THMs and how these compounds can be used to indicate a change in the nature of DOC in a body of water. Patterns of fluctuation in ECPs and the $CHCl_3$/DOC ratio were similar in the fractionated sample as well as in the various solubility-class fractions. The highest ratios (mean of 56 g/mg, neglecting the one extremely high value) were for Fraction III (hydrophobic acids) and the lowest (mean of 3.3 μg/mg) for Fraction VI (hydrophilic neutrals). The average ratio in unfractionated samples was 75 μg/mg for April 4-August 4, 1981. These data are summarized in *Table A6.*

V. Variations in Solubility-Class Structure of Total DOC Pool and THM-Precursor Pool

Lake-water samples collected at the beginning of each primary productivity study were returned to the laboratory, fractionated into various solubility classes, and analyzed for DOC concentrations and THM-formation potentials. (A summary of the data [*Table 2*] was presented in "Comparisons of ECP, DOC, and THM-Precursor Solubility Classes" [p. 31].) This section of the report gives a detailed discussion of distributions observed among various solubility classes. It should be emphasized that the data presented in this section describe components of the lake at several times throughout the spring and summer of 1981. These components included organic compounds in the lake from a variety of allochthonous and autochthonous sources.

A. DOC Solubility Classes

The solubility-class structures of the DOC throughout the study period can be seen in *Figures 12-14.* As noted in *Table 2,* 53-82 percent of the DOC was comprised of hydrophobic compounds (*Figure 12*). In that class, neutral compounds were dominant in approximately half of the samples, and acid compounds were dominant in the remainder (*Figure 4*). However, no pattern was observed. Of the hydrophilic compounds,

which comprised the smaller proportion of the total (18-47 percent), the basic compounds dominated throughout the sampling period, comprising 53-79 percent of the total hydrophilic fraction. *Tables A7-A9* contain the data used to produce *Figures 12-14. Table A8* shows the distribution of DOC among various fractions produced by the separation scheme. It can be seen that recoveries were in the range of 69-111 percent, except for the last sample analysis when recovery was only 47 percent.

B. THM-Precursor Solubility Classes

The most prevalent THM formed in the chlorinated samples was $CHCl_3$. *Figures 15-17* illustrate the observed variations in distributions of THM-precursors among various solubility classes of DOC in Claytor Lake throughout the sampling period. The hydrophobic fractions consistently produced the majority (63-90 percent) of chloroform (*Figure 15*). Of the hydrophobic compounds (*Figure 16*), neutrals dominated for most of the sampling period (40-98 percent), except in early July when acid compounds dominated. Of the hydrophilic compounds (*Figure 17*), bases were the most prevalent during most of the sampling period (67-98 percent), except in early July when acids dominated (81 percent). Data used in constructing these figures appear in *Tables A10-A12.*

VI. Relationships between DOC, ECP, and THM Production

Variations with time in DOC and chloroform-formation potentials and relationships between the two can be seen in *Figures 18-23.* The data were obtained by analyses of the fractions collected during organic fractionation procedures. In most fractions there appears to have been some correlation between DOC and subsequent chloroform yields; that is, the two followed similar patterns of variation throughout the study period.

Regression analyses were performed to determine if any correlations could be demonstrated among DOC, $CHCl_3$ formation, and ECPs in various solubility-class fractions. Only a few were evident. *Figure 24* shows a negative correlation (apparently forced by one value at the high end of the ECP scale) between the DOC of the lake water and ECPs produced during the 6-hr incubation period, whereas *Figure 25* illustrates a weak positive correlation between the $CHCl_3$-formation potential of those samples and the ECPs. *Figures 26* and *27* show the same relationships

for Fraction II, the hydrophobic bases. This fraction constituted only a small fraction of the total hydrophobic class (*Figure 16*).

VII. Variations in Lake THM-Formation Potentials and Populations of Algae and Bacteria

The observed relationships between THM-formation potential and populations of algae and bacteria at the Peak Creek and dam stations, respectively, are plotted in *Figures 28* and *29.* In the Peak Creek arm, average THM-formation potential ranged between 200 and 300 μg/L for much of the summer with the exception of one day in early August when it exceeded 500 μg/L. This occurrence was recorded again in late September. As can be seen from *Figure 28,* the algal population—predominantly the blue-green algae *Microcystis* and *Gleocapsa*—increased steadily during the summer. The composition of the algal population in the Peak Creek arm on each sampling date is shown in *Table 4.* Bacterial populations generally increased throughout the summer and began to decline in the fall when algae also began to wane. By October 3, the surface temperature of the water was 17.5° C, with a steady decrease to 9.5° C by November 23. A similar picture was evident at the dam site (*Figure 29*), although algal populations—still dominated by the blue-greens—generally were slightly less dense (*Table 5*).

VIII. Diurnal Variations in THM-Formation Potentials

A. Diurnal Study 1

On August 1, 1981, a 12-hr study was conducted at the Peak Creek site to assess hourly variations in THM-formation potential and to relate these variations to indicators of algal activity (increased DO concentrations and pH and declining CO_2 concentrations). *Figure 30* summarizes the data obtained from this diurnal study. Several facts uncovered during the study should be noted:

1. THMFP was greatest at 0800 hours (military time is used in this report) when it peaked at 670 μg/L but decreased steadily thereafter;
2. DOC concentrations increased slightly to 3.45 mg/L at 1700 hours;
3. DO, reflecting algal activity, peaked at 1700 hours at 10.7 mg/L;

4. CO_2 became unavailable by 1000 hours; and

5. pH increased to 9.2, coinciding with the precipitous decline in alkalinity from 52 mg/L to 49 mg/L.

The results of the 12-hr 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 P and ECP determinations (soluble, ^{14}C-labeled organic compounds) included as part of the testing protocol. The incubation period was 4 hr.

B. Diurnal Study 2

Figure 31 summarizes the data obtained from the second diurnal study conducted on September 25 and 26, 1981, in the Peak Creek arm of Claytor Lake. A significant increase was noted in THMFP throughout the nighttime and early morning hours, culminating in the peak formation potential of 729 mg/L by 0900 hours on September 26. This peak coincided with the peak of ECP liberation (314.5 mgC/m^3). After peaking, both THMFP and ECP output 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 nighttime and early morning hours of September 26, then decreased 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 (as a result of lower respiration) and a significant diel increase (because of photosynthesis) to 12.8 mg/L by 1700 hours on September 26. The pattern of pH fluctuations mirrored that of the DO, peaking at 10.2 by 1600 hours on September 26, when it decreased precipitously from 55 mg/L to 50 mg/L.

C. Diurnal Study 3

Data obtained from a diurnal study conducted on October 10 and 11, 1981, in the Peak Creek arm is summarized in *Figure 32.* Two features worthy of note are the similarity of results to two previous studies and the diminishing of peak levels of productivity, ECP output, THMFP, pH, and DO, all symptoms of decreased algal activity with the onset of cooler autumn days.

In this third study, ECP output, P, and THMFP peaked at noon on October 11. Observed concentrations were 125 mg C/m^3, 119 mg C/m^3, and 339 μg/L, respectively; levels far below those detected during earlier diurnal studies. The DO concentration peaked at a much lower level of 9.0 mg/L on October 11, as did pH, which peaked at 7.4. However, CO_2 concentrations were notably higher than in the previous studies (due, no doubt, to the limited algal activity), reaching a maximum level of 6 mg/L by 0500 hours on October 11 and never falling below 1 mg/L.

D. Diurnal Study 4

Figure 33 summarizes data obtained from the fourth diurnal study conducted on November 23, 1981, in the Peak Creek arm. The cold, short days of late autumn exerted much influence on the lake's ecosystem, evident in the significantly decreased peak levels of this study as compared to those of the September 25-26 study. Productivity decreased by 84.6 percent (to 87 mg C/m^3), ECP liberation by 84.1 percent (to 50 mg C/m^3), and THMFP by 90.4 percent (to 70 μg/L). Carbon dioxide was prevalent, with concentrations ranging from 5-9 mg/L, while DO peaked at 9.5 mg/L. DOC concentrations fluctuated randomly between 1.92 mg/L and 1.41 mg/L. Alkalinity concentrations remained constant at 49 mg/L, and pH peaked at 6.9.

IX. Effectiveness of Alum Coagulation for Reducing DOC Concentrations and THM-Formation Potentials

Table 6 summarizes the results of coagulation tests designed to evaluate the effectiveness of aluminum sulfate in removing THM precursors and DOC from the lake water. *Figures 34* and *35* show residual DOC and THM-formation potentials of water samples treated with alum in concentrations of 2, 3, and 4 mg/L as Al^{+3}. Selection of data for the *Figures* was based on the constraint that the final pH of the treated water had to fall within a pH range of 5.0-6.5, the optimum range of aluminum hydroxide insolubility. (The dosages of 6 and 8 mg/L as Al^{+3} produced finished waters with pHs outside this range.)

The 2 mg/L Al^{+3} dose proved to be quite effective in reducing THMFP of the water from both sampling sites. The mean reduction in Peak Creek THMFP was 42.9 percent, while the mean reduction at the dam site was 50.5 percent; the mean finished-water THMFP concentrations were 82 μg/L and 76 μg/L, respectively. The average removal of DOC was signif-

icantly 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 3 mg/L Al^{+3} dose was also quite effective. The mean reduction in Peak Creek THMFP was 44.8 percent, while the corresponding reduction in water from the dam site was 50.6 percent; the resultant mean residual TTHM concentrations were 85 μg/L and 95 μg/L, respectively. DOC removals from Peak Creek waters averaged 42.8 pecent, and removals from waters taken near the dam averaged 47.5 percent. Mean residual DOC concentrations were 1.31 mg/L and 1.11 mg/L, respectively, for the Peak Creek and dam sites. Finished-water DOC levels fluctuated weekly and exhibited no discernible trends.

A dose of 4 mg/L Al^{+3} proved to be effective with waters from both sampling sites. Peak Creek finished-water THMFP and DOC removals were identical (43.6 percent). 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 for THMFP and 45 percent for DOC. No discernible trends were found in finished-water DOC levels.

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

DISCUSSION

I. Limitations of the Organic Fractionation Scheme

As is true of any organic analysis involving concentration and recovery procedures, the characterization of lake organic matter and ECPs according to solubility classes and the variations in these classes with time were affected by inadequacies in the particular analytical scheme selected for this study. Leenheer and Huffman [1976] found the procedure to give more reliable results when DOC concentrations were between 5 and 25 mg/L; during this study, it never exceeded 5 mg/L. As noted earlier (see "DOC Solubility Classes" [p. 32]), total recoveries ranged from 69 to 111 percent (*Table A8*), but apportionment among various solubility classes was limited by (1) the efficiency of adsorption onto the resins and (2) the efficiency of elution with the acid and base.

Problems arise in converting concentrations to mass units to obtain a mass balance for the system, especially when determination of the quantity of one class involves subtracting values (which might be too high or too low depending on the recovery efficiency that particular day) obtained for one or two other classes. It seems likely, then, that the largest errors could occur in quantifying and apportioning various components of the hydrophobic compound class (see *Table A1* and *Figure 1*).

The adsorption efficiency (or lack thereof) on the XAD resins could account to a large extent for the relative abundance of the hydrophobic and hydrophilic compounds. It should be recalled that the hydrophobic substances were dominant throughout the study (*Figures 3, 12,* and *15*). If the recoveries were low when the XAD column was backwashed with acid and later with base, the hydrophobic neutral fraction proportion would be inflated. However, that fraction did not predominate during the entire study.

The hydrophilic fraction was obtained by direct analysis of a column effluent (Fraction IV, *Figure 1*). Therefore, if the adsorption steps had been inefficient (i.e., removing the hydrophobic bases and neutrals, then the hydrophobic acids), the hydrophilic-class proportion would have tended to have been inflated. On occasion the total hydrophilic class did comprise nearly half of the total DOC pool (*Figure 12*) and the algal ECPs (*Figure 3*). The most obvious problem that might be caused by inefficient adsorption would be to overestimate the hydrophilic neutral

proportion. That fraction was obtained by direct analyses of the last column effluent (*Figure 1*). However, the hydrophilic fraction of DOC (*Figure 14*) was predominant only once (in March) and never accounted for a significant proportion of ECPs (*Figure 5*).

II. Solubility Class Structure of DOC and ECPs

An interpretation of the solubility-class data obtained during this study can be facilitated by a review of naturally occurring organic substances in surface waters. Humic and fulvic acids, which usually are contributed to surface supplies by runoff, can comprise a large percentage of the total organic pool in surface waters. Humic acids are very large, complex molecules that most likely will be hydrophobic in nature because of their molecular size. Therefore, they logically should be included in the hydrophobic acid category. In this study, the hydrophobic acid fraction contained high concentrations of DOC during April and May (*Figure 13*), a finding attributed to considerable rainfall—nearly 4.5 in.—washing humic substances from the watershed into the lake. Fulvic acids, defined as a complex mixture of acid-soluble aquatic humus [Black and Christman, 1963], are comprised of both hydrophobic and hydrophilic compounds that may be recovered from natural waters [Leenheer and Huffman, 1976]. The hydrophobic base fraction of the DOC pool was never dominant during this study (*Figure 13*), but the hydrophilic base fraction was the dominant fraction of the total hydrophilic DOC throughout the entire sampling period with the exception of March (*Figure 14*).

Algal ECPs are also comprised of a large number of compounds. For example, a healthy algal bloom generally will excrete various organic acids and an array of sugars. Since the most common organic acids are of relatively small molecular weight, they logically should fall within the hydrophilic acid group. As is shown in *Table 2* and *Figure 5,* this group dominated the ECPs in this study for part of the summer. It was also during the same period that productivity (*Figure 2*) was greatest, an indication that algae were fixing carbon. In early July, the THM yield from the hydrophilic acid fraction was higher than that from any other fraction (*Table 2*), thus supporting the hypothesis that there is a definite link between algal ECPs and THM-formation potential. The sugars produced by algae would be expected to appear in the hydrophilic neutral fraction of the ECPs [Leenheer and Huffman, 1976]. However, that fraction was small throughout the study. It is possible that bacterial utilization of these common algal products could account for the low propor-

tion of this fraction [Nalewajko, 1977]. Since bacteria rapidly use low-molecular-weight sugars and organic acids for growth and metabolism, the other classes of hydrophilic compounds that dominated the ECPs (*Figure 5*) most likely were those used much more slowly by the bacterial population. The hydrophobic acid portion of ECPs may have consisted of certain amino acids and nucleic acids, and it is likely that lipid material produced by algae would fall into the hydrophobic neutral solubility class. The hydrophilic base portion can consist of compounds with characteristics similar to amino sugars [Leenheer and Huffman, 1976].

In addition to algal compounds and humic and fulvic acids, other organic compounds were entering the Peak Creek arm of Claytor Lake from various sources. The principal source was a domestic wastewater treatment facility upstream on Peak Creek, but organic compounds were also contributed by the gasoline-powered engines of boats on the lake. (Components of oil and gasoline and the hydrocarbons arising from their combustion are classified as hydrophobic neutrals.) Organic compounds of several varieties also can originate from the decay of dead fish and other aquatic organisms and from active planktonic bacteria that produce extracellular products [Nalewajko, 1977].

Hydrophobic compounds, especially the neutral fraction, most often comprised the majority of both the total lake water DOC (*Figure 13*) and ECPs (*Figure 4*) present after a 6-hr incubation of lake-water samples. Although the actual percentages attributed to acid, base, and neutral components may be in error because of recovery-efficiency problems, the neutral component was shown to be the highest $CHCl_3$-yielding fraction of the lake-water DOC (*Figure 16*). In early July, the ECP peak occurred along with an increase in the $CHCl_3$/DOC ratios in the hydrophobic fractions (*Figures 7* and *8, Table A6*), which suggests that the increased ECP production, while not greatly altering the DOC concentration of the lake, did contribute to increases noted in the $CHCl_3$ concentration and hence in the $CHCl_3$/DOC ratio for the lake water (*Figure 6*).

A definite shift, primarily from basic compounds early in the study to acidic ones later (*Figure 5*), occurred in the predominance of the hydrophilic components of algal ECPs. However, the majority of the lake-water DOC was comprised of basic compounds from April through August (*Figure 14*). The hydrophilic bases within the total DOC pool were the highest THM-yielding fraction for most of the year, except during that

one sampling period in July when the dominant hydrophilic class within the ECPs shifted from basic to acidic. Hydrophilic acids dominated the DOC at that time as well, which could be interpreted to mean that algal ECPs contributed to the THM-precursor pool without necessarily changing the *total* DOC within the lake, but rather contributing to a change in the *nature* of the DOC.

III. ECPs and Productivity

As is evident in *Figure 2,* algal ECP production appears to have peaked early in the year, long before cellular fixation of carbon by algae (P in *Figure 2*) was maximal. It can be seen in *Figure 28* that an increase in the bacterial population in the Peak Creek arm occurred from June through September, except for a brief period in August. Nalewajko [1977] has discussed the role of bacteria in altering algal ECPs, and it is likely that this factor greatly influenced the observed relationship between ECP production and cellular fixation of carbon by algae. Another factor is that ECP production is variable during the day and is dependent on a variety of environmental conditions. Since ECP determinations shown in *Figure 2* were made only once on each of the indicated dates, different relationships between P and ECPs could have emerged if more daily studies were performed. This factor will be discussed in more detail in "Variations in Productivity and THM-Formation Potentials of Lake Water" [p. 45].

IV. Relationships between DOC, THM-Formation Potentials, and ECPs

The THMFP of the lake water did not always vary in direct response to changes in DOC concentrations observed during this study. An examination of the fluctuations in the $CHCl_3$-to-DOC ratios in all six fractions obtained from the organic-fractionation scheme (*Figures 6-11*) generally reveals similar patterns of fluctuation of both the $CHCl_3$/DOC ratio and ECP production, especially in unfractionated lake water (*Figure 6*), in Fraction IV (total hydrophilic fraction, *Figure 9*), and in Fraction V (hydrophilic acids and bases, *Figure 10*). The greatest yields of $CHCl_3$ from DOC (highest ratios) were observed in unfractionated lake water and in hydrophilic fractions. This relationship may be significant because it indicates that the activity of algae (and likely that of bacteria as well) can influence the possible overall THM production upon chlorination of surface waters without a noticeable alteration of the DOC concentration.

It cannot be determined from data shown in *Figures 18-23* whether any one of the DOC fractions in the lake water consistently contributed more to the THM-precursor pool than any other. While some similarities in certain patterns of DOC concentrations and $CHCl_3$ yields upon chlorination exist, for the most part the variations generally seem to be random.

Figures 24-27 illustrate certain relationships observed between ECP solubility classes and corresponding DOC and THMFP levels. The negative slope of the regression line in *Figure 24* seems to indicate that ECPs in unfractionated lake water were not a function of DOC. Although the relationship is weak, the positive slope of the regression (shown in *Figure 25*) could be interpreted to mean that THMFP is a function of ECP production. *Figures 26* and *27* illustrate these same two relationships for the hydrophobic base fraction. The variations in ECPs in the other fractions were entirely random with respect to variations in DOC and THMFP. Thus, even though hydrophobic bases usually accounted for the smallest percentages of total DOC and THMFP, the relationship between them and the hydrophobic base portion of the ECPs was more consistent. Perhaps the most significant fact revealed by regression analyses is that no strong statistically significant correlations existed between measured ECP levels and either the DOC or THMFP of the lake water before incubation.

V. Variations in DOC and THMFP during Incubation

Table 3 illustrates the observed changes in DOC and THMFP (expressed in terms of $CHCl_3$ only) of various solubility-class fractions that occurred upon incubation of samples in situ at the depth from which the water was taken. A notable change occurred in the DOC of unfractionated lake-water samples during the first study (2.54-4.32 mg/L), but THMFP changed only slightly (198-217 μg/L). During the second study six weeks later, there was a smaller increase in DOC (2.05-2.43 mg/L) but a larger increase in THMFP (142-192 μg/L). The increase in DOCs and THMFP of the total hydrophilic component was the most pronounced change during both studies, though DOC yielded virtually no haloforms upon chlorination in the second study. Problems existed with recovery in the second study, but, overall, the results indicate that the water on the two dates was vastly different with respect to the solubility-class structure of the organic pool and with respect to the changes brought about by algae or the algal/bacterial system in the lake. A shift in the predominant algae (*Microcystis* and *Gleocapsa*) occurred between the two sampling dates, though blue-green algae still accounted for 98 percent of the total

population (*Table 4*). In addition, the bacterial population density increased by approximately three and one-half times.

Two major facts are suggested by the studies of DOC and THMFP:

1. Algal activity during a 6-hr period is capable of increasing both THM-formation potential and DOC levels of lake water, and

1. The particular composition of the DOC pool will differ depending on the particular biotic composition of the water.

In addition to the utilization of algal ECPs by heterotrophic microbiota for maintenance and growth, bacterial and fungal ECP production is also well documented. Thus, a portion of the ^{14}C-labeled ECPs may have been heterotrophic metabolites of algal products. These factors combine to produce a vastly complex array of dissolved chemicals, colloids, and particulate matter that could be expected to be highly variable with time [Nalewajko, 1977]. Much more study is needed to isolate the variables that lead to increased THM-precursor production in natural waters. Studies are also needed to evaluate directly changes in the organic solubility class structure that are brought about by autotrophic/heterotrophic systems in lakes. A concentration of lake water prior to its fractionation would eliminate many of the problems encountered in this study.

VI. Seasonal Changes in Microbiotic Populations and THM-Formation Potentials

A. Relationships between Seasonal Population Densities and THMFP

If algal ECPs provide THM precursors, one would expect that the more ECPs present in water, the higher the potential of the water to form THMs. Thus, the highest raw-water THMFP could be expected to occur during periods of peak algal growth when the output of ECPs should be at its greatest, unless the ECPs were modified in some way or removed from the water column. The converse situation of smaller algal excretions of ECPs imparting a lower THMFP to the water should also hold true. *Figure 28* reveals this situation generally to be the case at the Peak Creek site. Broadly speaking, as algal populations increased, so did THMFP, and as populations waned, THMFP decreased markedly. This pattern did not occur at the dam site, however (*Figure 29*).

General impressions about the relationship between algal population size and THMFP can be derived from analyses of the proportion of THMs to DOC in relation to population densities (*Figures 36* and *37*). In general, it was found at both sites that as algal populations increased, the yields of chloroform per unit DOC in the water also increased. This increase 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 THMs. The DOC pool was quite stable at both the dam and Peak Creek stations, averaging 2.3 and 2.6 mg/L, respectively, with standard deviations of only 0.4 and 0.6 mg/L, respectively.

Unfortunately, the THM/DOC ratio did not vary in direct proportion to the algal population density. A possible reason may be that both THMFP and DOC concentrations were determined by 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 because a single grab sample simply cannot provide data representative of the complex array of interactions occurring in the water column. In order to assess properly the dynamic forces that exert control over the algal and bacterial role in THM formation and to provide a much more complete picture of what is actually occurring in the complex aquatic ecosystem, diurnal studies incorporating a broad spectrum of water chemistry and biological determinations should be performed as often as possible.

Of considerable interest is the observation that bacterial populations increased markedly in both raw and alum-treated waters on two occasions at each site (July 12 and August 15 at Peak Creek, *Figure 36,* and July 19 and September 18 at the dam, *Figure 37*) immediately before a marked increase in the THM-to-DOC ratio. It is possible that bacteria may have altered the organic carbon pool in some manner so that a larger fraction of its produced THMs upon chlorination. It is also possible that bacterial ECPs served as THM-precursor materials. It is well documented that bacteria, like algae, generate significant quantities of ECPs [Nalewajko, Lee, and Fay, 1980].

It was not until after an analysis of these data was complete that the potentially significant role of heterotrophic organisms in the 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 lake-water measurements in the data base in order to define better the relationship between variations in algal biomass and THMFP of the lake water during the year. Cell numbers alone are inadequate for this purpose.

B. Algal Succession and Its Influence on THMFPs

Figures 28 and *29* show that algal succession occurred at both sampling sites and was especially pronounced at Peak Creek. At this site, the expected shift from small populations of green algae to extremely dense growths of blue-green algae occurred during the summer months, followed by the re-emergence of green algae during mid-to-late autumn. The immediate impression one gets from an analysis of *Figures 28* and *29* is that successional shifts in the dominant genera and species of algae had little effect on the THMFP of the water. The fact that ECPs 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 green algae in mid-to-late autumn may have been the result of decreased output of ECPs excreted by dwindling algal populations rather than a 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 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 autumn 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. Additional research is needed to define more accurately this aspect of the problem.

VII. Variations in Productivity and THM-Formation Potentials of Lake Water

Figures 30-33 illustrate an important fact; namely, that the production of ECPs—especially those products which affect THM-formation potentials—is highly variable during any given 24-hr period. The complexities are many. Both heterotrophs and algae are involved in this process, and no one knows for sure which biotic component exerts the greater influence. The diurnal studies do illustrate the complex nature of the system

and help explain why grab-sampling, when used as a basis for studying time-variable phenomena in relation to the THM-formation potential of a lake, can lead to conflicting interpretations. Most water treatment plants withdraw water from their sources continually, and any changes in finished-water THM concentrations over any given time period represent some type of composite that reflects changes in the source water during the same period. Thus, the assumption that relationships between algae, or an algal/bacterial system, and the THMFP of a natural body of water can be understood by sporadic grab-sampling and analyses of source water over several months appears to be fallacious. A more concentrated effort under different environmental conditions of temperature, biotic composition, light intensity, etc., is needed. The three additional diurnal studies, depicted in *Figures 31-33,* were prompted by the first study (*Figure 30*), in which no productivity measurements were made, and were attempts to understand more fully the complexity of changes that take place during any given day. Unfortunately, the main thrust of these studies was directed at the algal component, so the role of heterotrophic organisms can only be inferred from chemical data such as CO_2 and DO concentrations. These three studies are discussed in detail in the following sections.

A. Second Diurnal Study

The results of the September 25-26 diurnal study (*Figure 31*) strongly implicate both algae and heterotrophs as important agents in the processes that account for diurnal fluctuation in THMFP. Of considerable interest is the observation that the THMFP increased steadily during the night (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. In addition, the CO_2 concentration increased from 0 mg/L at 2100 hours on September 25 to 3.0 mg/L by 0500 hours on September 26. These data strongly suggest that the heterotrophic population plays an important role in creating THM precursors either by modifying the structure of the organic compounds already present (algal ECPs) so that they are more reactive with chlorine in the THM-producing reactions or by releasing ECPs that have a high THMFP.

The algal contribution to diurnal fluctuations in THMFP appears to have been significant. Observed increases in productivity and ECP production coincided with steady increases in THMFP, probably as a result of increased algal density at the sampling depth or the algal excretion of ECPs

with a high THMFP (as shown in studies conducted by Hoehn et al. [1980]). Unfortunately, chlorophyll-a and algal volume were not determined. 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 on September 26 could have been caused by a number of ecological factors, such as:

1. The possible liberation of algal ECPs 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 pHs) characteristic of the late morning-afternoon hours forced the algae into a photorespiratory state, a condition typified by the extracellular release of glycollate. From 1000-1400 hours, when both ECP production and THMFP were declining, there was a decrease in the THM-to-DOC ratio from a high of 385 μg/mg, which, incidentally, was more than double the maximum ever observed in grab samples (*Figures 36* and *37*), to 155 μg/mg. This observation seems to suggest that ECPs liberated beyond 1000 hours included low THM-yielding substances such as glycollate;

2. A possible downward migration of the algae as midday light intensities became prohibitive [Moss, 1969] resulted in the release of THM precursors at a depth below that from which the samples for THMFP analyses were drawn;

3. The possible oxygen inhibition of bacteria [Kuenen, 1979] resulted in the lowering of their capability to produce THM precursors and/or to alter the structure of already existing algal ECPs; and

4. Heterotrophs destroyed low-molecular-weight and hydrolyzed high-molecular-weight Type II algal ECPs [Nalewajko, 1977].

A number of abiotic processes also could account for the reduction in THMFP. Nalewajko [1977] mentioned two:

1. The binding of low-molecular-weight ECPs to colloids, which removes them from solution, and

2. The binding of high-molecular-weight molecules to one another and to colloids or detritus and their subsequent removal from the water column by sedimentation.

Another possibility is that precursors were removed by sedimentation on marl (calcium carbonate) that apparently formed at approximately 1400 hours when pH was quite high. The precipitous decreases in alkalinity beginning at that time can be seen in *Figure 31.*

B. Third Diurnal Study

The third diurnal study (*Figure 32*) began at 1400 hours on October 11 and continued until 1300 hours the next day. Since water turns colder (16.8° C) during autumn, the P and ECP levels were much lower than during the September study. Throughout the night, CO_2 levels continually increased, attaining concentrations of 6.0 mg/L by 1700 hours. After sunrise (about 1800 hours), the production of ECPs and cellular fixation of CO_2 (P) began and steadily increased until the study was terminated. Skies varied from sunny to partly cloudy throughout the day.

The results of this study corroborated findings of the first and second diurnal studies, again implicating algae and bacteria as important agents in the diurnal fluctuation of THMFP. Similar to the September 25-26 study, THMFP increased steadily during the nighttime hours. The corresponding increase in CO_2 and relatively stable concentrations of DOC offer evidence that heterotrophs either played a role in alterating algal ECPs or released ECPs themselves. This study accentuated the influence of algae since the daytime peak in THMFP coincided with the peak of ECP release.

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 by 60 percent, and THMFP by 53 percent. These reductions were thought to reflect the retardation of algal and bacterial metabolic activity by cooler temperatures and, thus, a reduction in the capacity of algae and bacteria to alter ECP type or concentration, thereby decreasing the extent of diurnal fluctuation in THMFP. Despite the dampening ef-

fect that cooler temperatures exerted on the biota, the data in *Figure 32* suggest that the biological community significantly altered the potential of the water to form THMs.

C. Fourth Diurnal Study

The final diurnal study (*Figure 33*) vividly demonstrated the impact of environmental factors upon the capacity of biota to predispose a lake water to form THMs. A November water temperature of 9.6° C and an effective daylight duration of 10 hours contributed to reductions in P, ECP output, and THMFP of 85, 86, and 90 percent, respectively, of the levels recorded during the second diurnal study two months earlier. With biotic activity retarded, the diurnal fluctuation in THMFP and DOC was nominal, as can be seen from the *Figure.*

In conclusion, it is evident from the results of the diurnal studies that biological activity, whether it be algal alone or algal and bacterial combined, exerts a tremendous influence over the potential of a lake water to form THMs.

VIII. Reductions in DOC and THMFP by Alum Treatment

A. The Effect of Dose

Alum treatment in jar tests proved to be moderately effective in reducing both DOC and THMFP from Claytor Lake water, although it was generally more effective in treating water taken from the dam site than the Peak Creek site (*Figures 34* and *35*). The average removals cited in *Table 6* are similar to those reported by others [Kavanaugh, 1978; Babcock and Singer, 1979; Oliver and Lawrence, 1979; Young and Singer, 1979; Brett and Calverly, 1979]. Alum appeared selectively to remove THM precursors from the DOC pool. This preferential removal also 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].

On seven occasions the most efficient reductions in THMFP from water at both sites were obtained by treatment with alum dosages of 6 and 8 mg/L as Al^{+3}. The pH of finished waters treated by such large dosages of alum was below 4.5. If the application of high dosages of coagulant was considered by water-treatment plant managers as a potential THM

control measure, the added costs of coagulant, of lime to neutralize the excessive acid resulting from the addition of higher coagulant dosages, and of handling the excess sludge that would be produced would all have to be considered.

On 10 of the 14 dates when Peak Creek waters were treated and on 5 of 9 test dates when waters taken from near the dam were treated, the best removals were achieved with alum dosages of 2, 3, and 4 mg/L as Al^{+3}. The finished-water pHs were in the range of 5.0-6.5. Treatment with these levels of alum would not be inordinately costly either in terms of actual chemical costs or for sludge handling, though lime costs may increase somewhat. Clearly, marked reductions in the THMFP of Claytor Lake water could be brought about solely by coagulation with alum.

B. Influence of Biological Activity

Figures 38 and *39* demonstrate the observed patterns in THMFP fluctuation and removability by alum treatment and those of algal and bacterial population densities at the dam and Peak Creek sites, respectively. No similarity in pattern was observed at the dam site. In the Peak Creek arm of the reservoir, however, the lowest THMFP levels and the greatest effectiveness of alum for reducing THMFP generally were observed when algal population density was at its greatest. If indeed some cause-and-effect relationship existed, it was unexpected. Although any explanation can only be highly speculative, two are suggested:

1. Bacteria, stimulated to grow by high ECP concentrations during times of peak algal growth, degraded ECPs (as has been demonstrated by Bell and Sakshaug [1980]) that were THM precursors and produced other products that were easily removed by alum coagulation; or

2. Algae, in some way, enhanced the removability of THM precursors by alum, perhaps by producing polymer-like substances (as part of their ECPs) that acted as effective coagulant aids.

However, as emphasized earlier, different patterns of treatment effectiveness and of THMFP levels probably would have been observed if the sampling and analyses had been more frequent than weekly. Algal successional patterns seemed to exert little, if any, influence on treatability.

Observed variations in algal and bacterial population densities in relation both to DOC concentrations before and after treatment and to removal-efficiency curves at the dam and Peak Creek sites, respectively, are illustrated by *Figures 40* and *41.* It can be seen from these *Figures* that finished-water concentrations were routinely between 1.0-2.0 mg/L, but removal efficiencies were somewhat erratic. Neither population density nor successional patterns appeared to influence DOC concentration.

An analysis of temporal variations in the THM-to-DOC ratio (*Figures 36* and *37*) enables one to identify periods when the nature of the DOC pool was altered in some manner, resulting in the production of more THMs. At both sites, the raw-water THM-to-DOC ratio fluctuated widely, but the largest values were observed when algae were prolific. Because DOC varied by no more than 2 mg/L at each site, indicating a generally stable level of DOC, variations in the THMFP of available organic carbon can best be explained by changes in the nature of DOC that were probably induced by biotic activity. At a minimum, one can safely conclude from the data that Claytor Lake waters had a much greater potential to form THMs during the productive months, a potential not reflected by DOC variability.

Fluctuations in the THM-to-DOC ratio in treated waters were similar to those in raw waters taken from both sites (*Figures 36* and *37*). If algae were indeed responsible for these fluctuations and if similar influences of algae on the THMFP of potable water will be manifested when algal growth is prolific, a dimension can be added to existing concerns over excess eutrophication in reservoirs. Not only will algae cause problems such as filter clogging and offensive tastes and odors in finished water, but they will also make it more difficult for a water treatment plant to meet the existing THM standard. If the average removal of THM precursors can only reach about 50 percent, as in these studies, then the influence of reservoir ecology on the production of a potable water that meets current THM standards cannot be ignored!

Applicability of findings of biological influence to plant-scale operations should be made with caution for several reasons:

1. Even though the quality of finished waters in this study was about equal to that of finished waters at an actual water treatment plant, chlorination was delayed until all other treatment steps were completed and a number of the THM precursors had been removed. In

many treatment plants, chlorination cannot always be delayed that long because chlorine is used for slime control in the plant and because the raw-water quality is such that prechlorination is required for effective disinfection. Nevertheless, *delayed chlorination,* a technique that allows for the removal of THM precursors by clarification processes, is proving to be an effective and economical means for reducing THMs to acceptable levels in many treatment facilities in the United States today.

2. The maximum contaminant level (MCL) for THMs (0.10 mg/L) is based on concentration at the tap (*instantaneous* concentration), not on the 7-day THMFP as was reported throughout this report. Obviously, the chlorine-contact time will influence the degree to which higher THMFP levels, made possible by biological activity in the reservoir, will pose difficulties in meeting the MCL for THMs.

3. Because a water treatment plant treats water continuously, the finished-water THM concentration would represent some composite average of the effectiveness of alum coagulation at times when algae were either highly active or inactive. Too, diurnal variations in raw-water THMFP (and, hence, finished-water THMFP) would be dampened by storage reservoirs normally used in most treatment systems.

The value of the treatability studies of Claytor Lake waters lies in the fact that the results corroborate those of many earlier researchers [Babcock and Singer, 1979; Brett and Calverly, 1979; Hoehn et al., 1980; Kavanaugh, 1978; Oliver and Lawrence, 1979; Young and Singer, 1979]. It is evident from the results of these studies that optimization of standard alum treatment offers a means to achieve significant reductions in THM concentrations of potable waters. Additional studies are now underway at Virginia Tech, and results should be available by late 1983.

One aspect of THM formation not included in this study was an evaluation of the *rate of change* of THM formation over several hours or days and the effect of algal growth in the reservoir on it. If algal ECPs, whether altered by bacterial activity or not, are responsible for introducing fast-reacting THM precursors into a water treatment plant, THM levels after just a few hours could be a significant fraction of the 7-day THMFP. This aspect of the overall problem should be studied carefully.

SUMMARY AND CONCLUSIONS

Results of the solubility-class fractionation studies showed that hydrophobic compounds consistently comprised the highest percentages of (1) the algal extra-cellular products (ECPs) present in lake-water samples after a 6-hr incubation period, (2) the lake water itself (collected on a grab-sampling basis), and (3) the trihalomethane (THM)-formation potential (THMFP) of the lake water after a 7-day contact with excess chlorine. The range of percentages of hydrophobic compounds for these three systems, respectively, were 54-77 percent, 52-82 percent, and 70-90 percent. In addition, the dominant solubility class of algal ECPs among the hydrophilic fraction shifted from bases to acids midway through the sampling period (early July). The role of bacteria in altering algal ECPs was not assessed, but population densities were approximately 8,000/mL by this time.

The greatest concentrations of THMs formed after chlorination of hydrophilic components were in the base portion, with a brief shift to the acid portion at a time that corresponded to a shift in the predominant ECP group from bases to acids. Problems with efficient recovery of acidic and basic hydrophobic compounds complicated attempts to assign accurate percentages of the total hydrophobic fraction to acid, base, and neutral components.

The apparent relationship between algal population densities and successional patterns and the 7-day THMFP of Claytor Lake water collected on a grab-sampling basis from June through November 1981 was general at best. Prevailing meteorological conditions appeared directly to affect the THMFP of a water by influencing the physiological state of algal and bacterial communities.

Aluminum sulfate proved to be a moderately effective agent for removing THM precursors from the water, probably by enmeshment or adsorption to the *sweep floc* (aluminum hydroxide). The mean removals of DOC (28-47 percent) and mean reductions 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 in reservoirs most likely can significantly affect the ability of a water treatment plant to meet the THM standard, especially if the average re-

moval efficiency of THM precursors can be expected to be only 50 percent. Therefore, the impact of reservoir ecology on treatment capacity is a factor that cannot be ignored.

The diurnal studies provided the strongest evidence to date that both algal and heterotrophic populations are extremely important in producing THM precursors. Algal ECPs themselves, no doubt, are THM precursors, but the role of 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. Heterotrophic activity may result either in the production of bacterial ECPs that are THM precursors or in the modification of the algal ECPs in such a way that the altered chemicals are more likely to form THMs upon chlorination. In either case, fluctuations in THMFP observed during this study undoubtedly resulted from biological activity, again suggesting that 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 must be determined by analyses of samples collected at several times during the year (in different seasons) and on a diurnal basis.

The following significant conclusions were derived from this study:

1. The lake-water pool of organic compounds (including those that were THM precursors), as well as the algal ECPs produced after a 6-hr incubation in situ, was comprised primarily of hydrophobic compounds throughout the study. The hydrophobic neutral components, the largest group, yielded high levels of THMs per unit DOC upon chlorination.

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

3. Because the types of ECPs liberated by algae and bacteria could have such a profound effect on the THMFP of lake water and because the liberation of various types of algal ECPs appears to be a distinctly diurnal phenomenon, future studies of algal-bacterial/

THM relationships should be conducted over a 24-hr period. In this manner, a more complete assessment of the role of algae and bacteria in altering the THMFP of reservoir water can be made.

4. No consistent relationship existed between algal or bacterial population densities and the 7-day THMFP of lake water when collection of the water was made on a grab-sample basis, although yields of THM per unit DOC were generally highest when algal population densities were greatest and seemed to lag pronounced increases in bacterial populations by a short time. This conclusion emphasizes the need for either composite or discreet, sequential sampling of a body of water during a 24-hr period.

5. Alum coagulation followed by clarification reduced THM precursors in Claytor Lake by about 50 percent, and the effectiveness of the treatment did not appear to be reduced either by increases in algal population density or by the succession of algae from one type to another in the water supply. The diurnal effectiveness of alum treatment was not evaluated, however.

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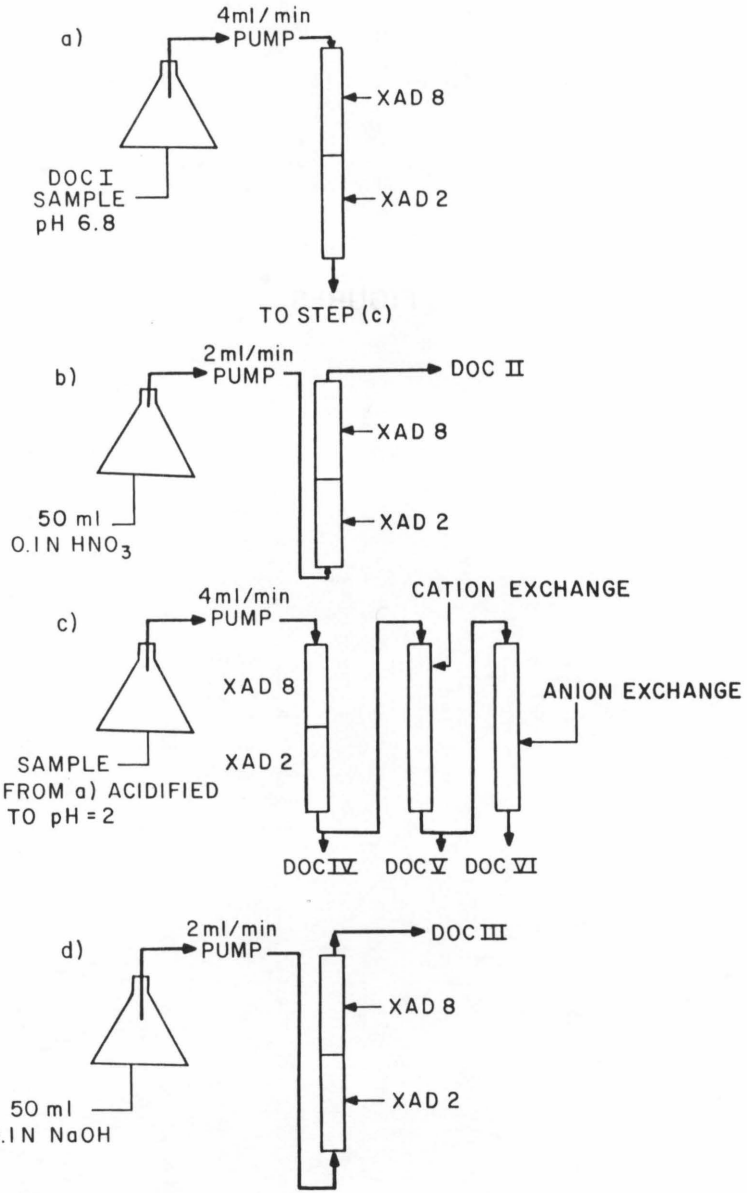
FIGURES

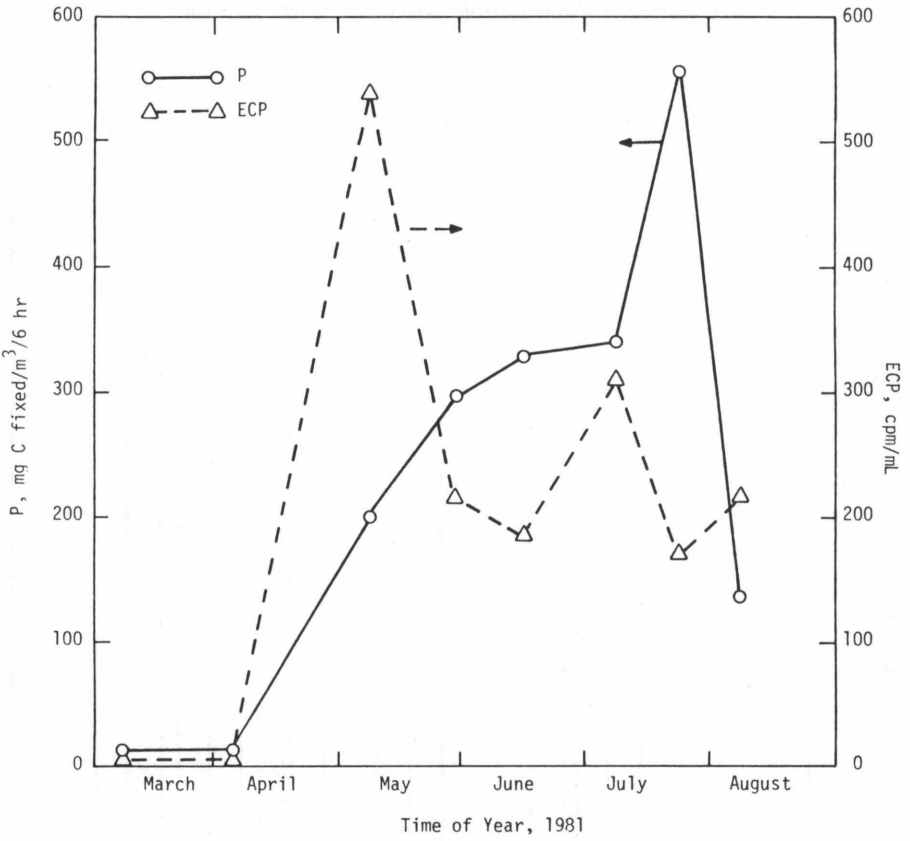
FIGURE 1

Schematic of Fractionization Procedure Used to Separate Lake-Water Organic Components According to Solubility Classes*



*From Leenheer and Huffman, 1976.

FIGURE 2
Variations in P and ECP Production in Claytor Lake*



*Data obtained from samples incubated in situ for 6 hr.

FIGURE 3

Variations in Relative Quantities of Hydrophilic and Hydrophobic Components of Algal ECP after 6-Hr Incubation In Situ in Peak Creek Arm of Claytor Lake

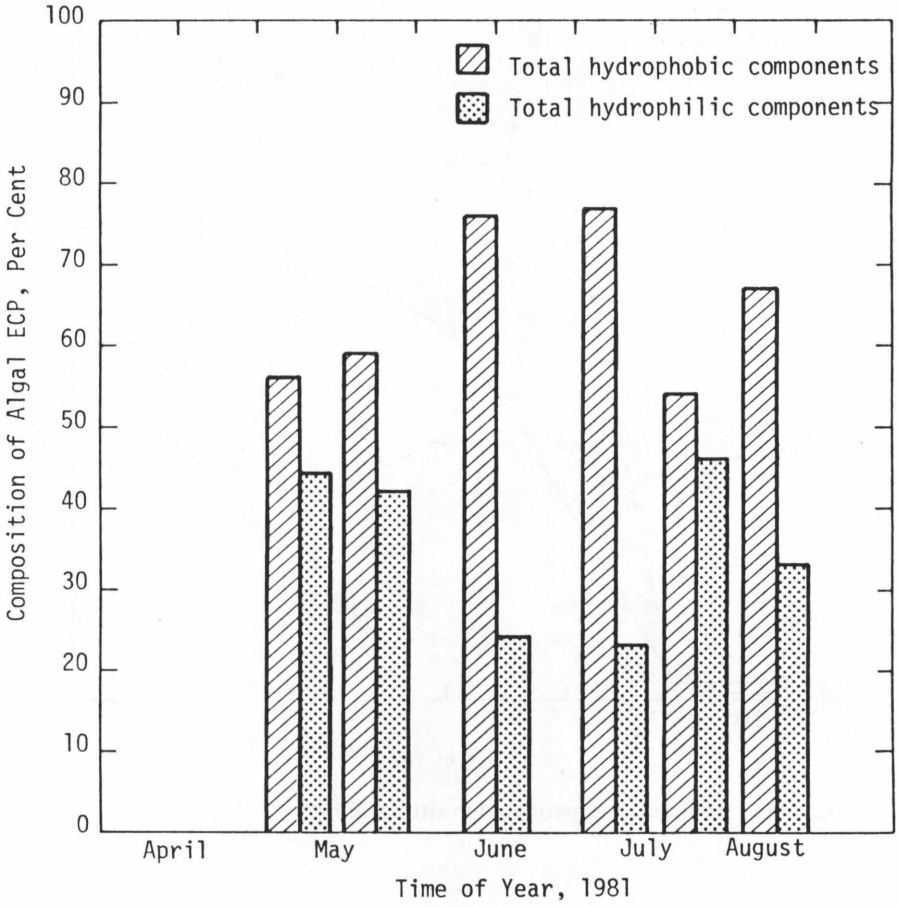


FIGURE 4

Variations in Relative Abundance of Acid, Base, and Neutral Hydrophobic Components of ECP Produced after 6-Hr Incubation In Situ in Peak Creek Arm of Claytor Lake

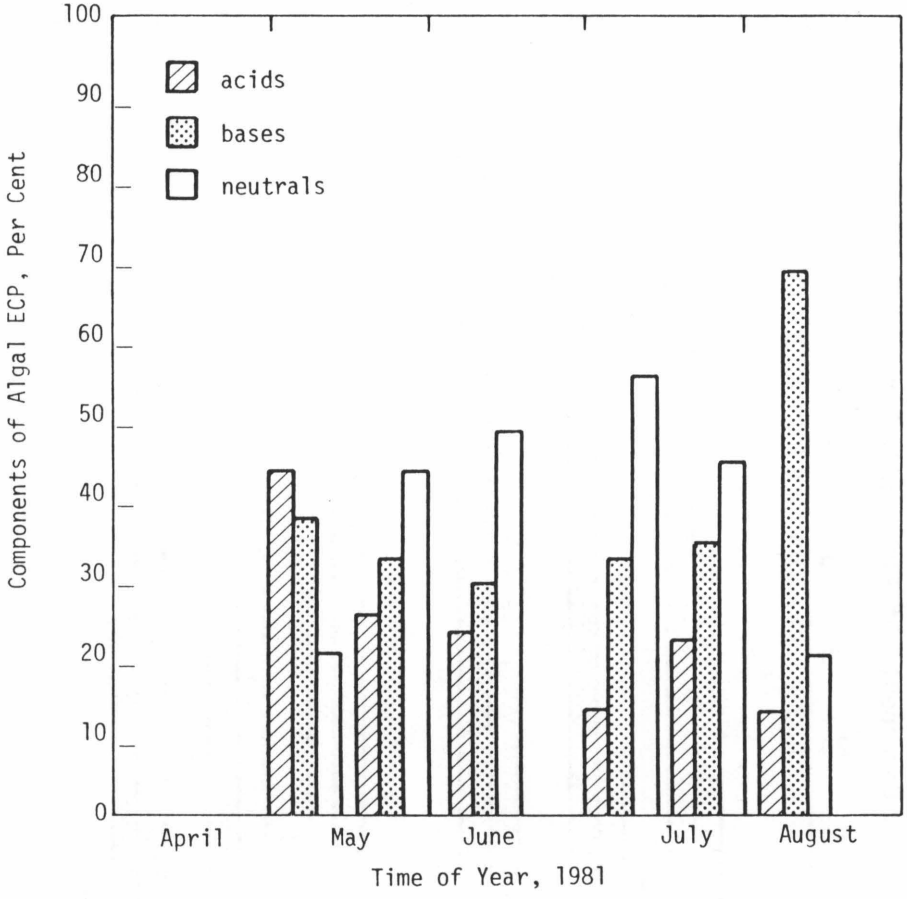


FIGURE 5

Variations in Relative Abundance of Acid, Base, and Neutral Hydrophilic Components of ECP Produced after 6-Hr Incubation In Situ in Peak Creek Arm of Claytor Lake

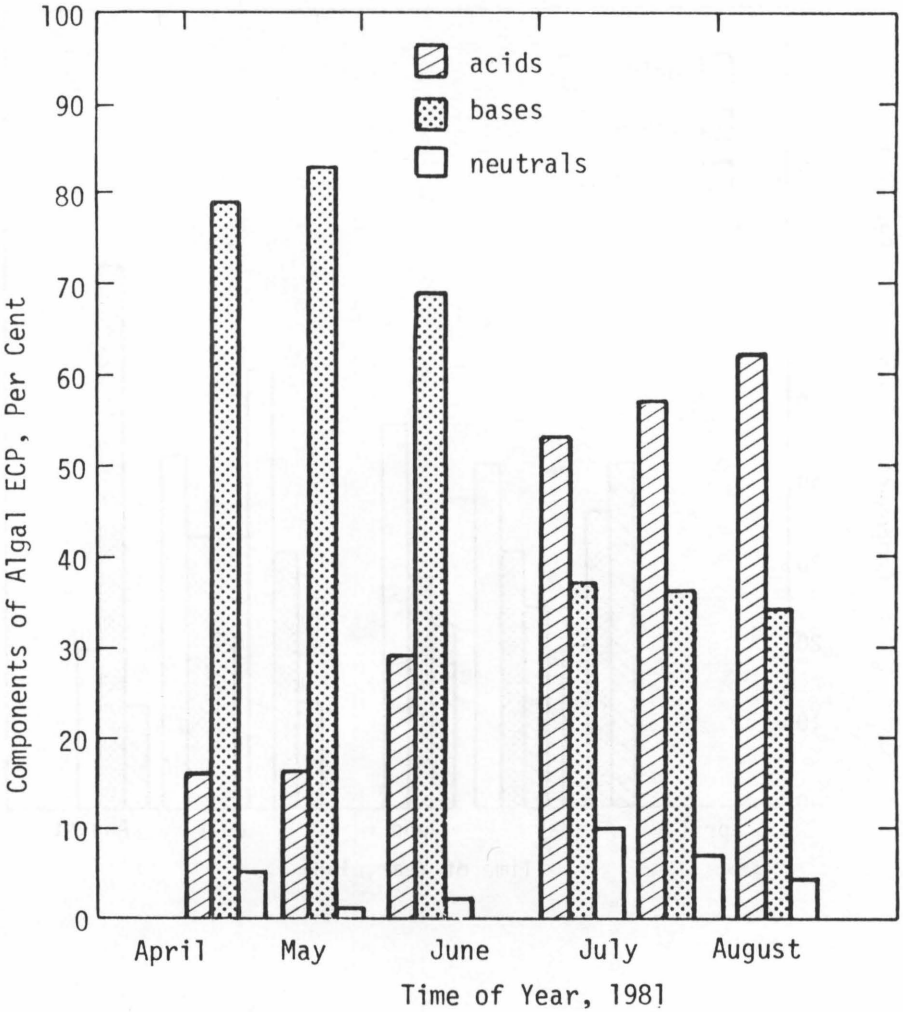


FIGURE 6

Variations in Yields of $CHCl_3$ from DOC in Unincubated, Unfractionated Lake Water Compared to ECP Present after 6-Hr Incubation In Situ

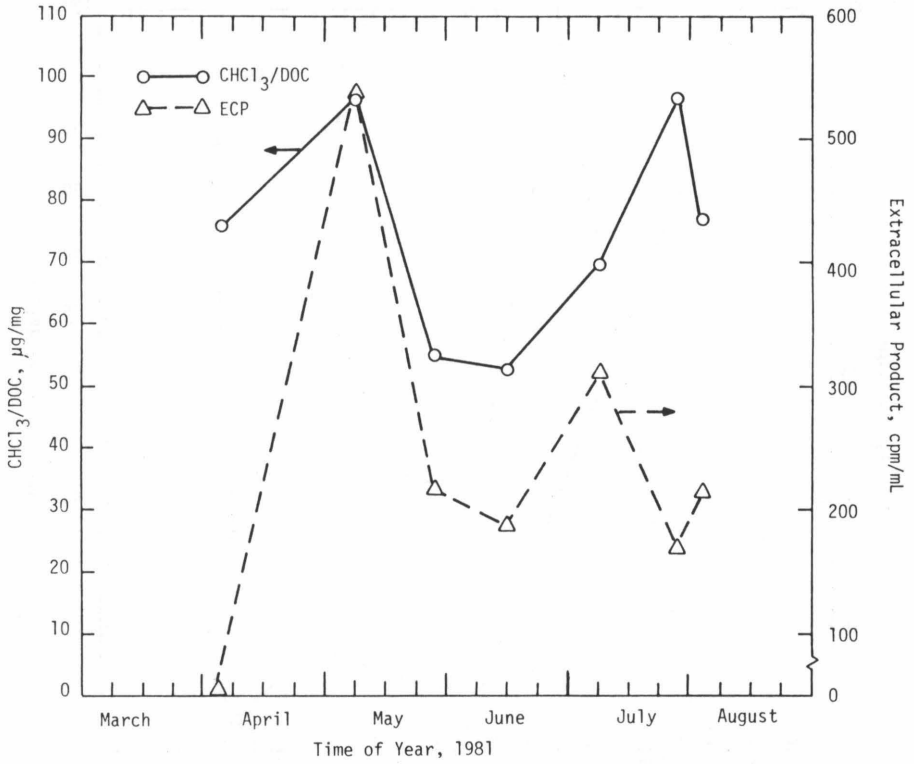


FIGURE 7
Variations in $CHCl_3$ Yields from DOC in Fraction II of Unincubated Lake Water Compared to ECP Present in Fraction II after 6-Hr Incubation In Situ

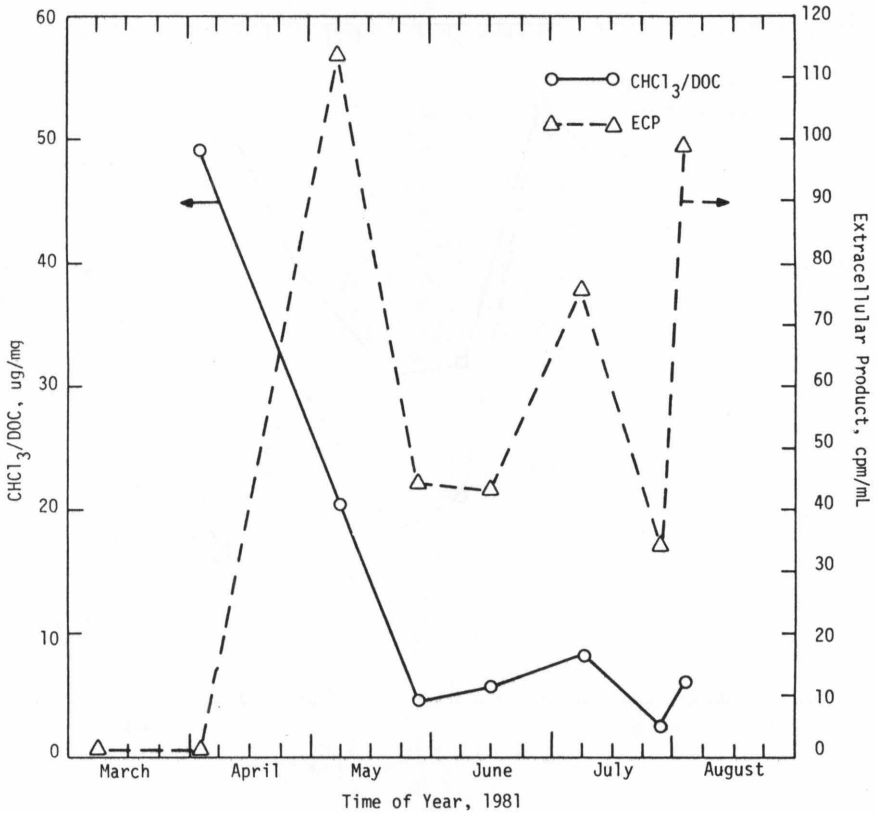


FIGURE 8

Variations in $CHCl_3$ Yields from DOC in Fraction III of Unincubated Lake Water Compared to ECP Present in Fraction III after 6-Hr Incubation In Situ

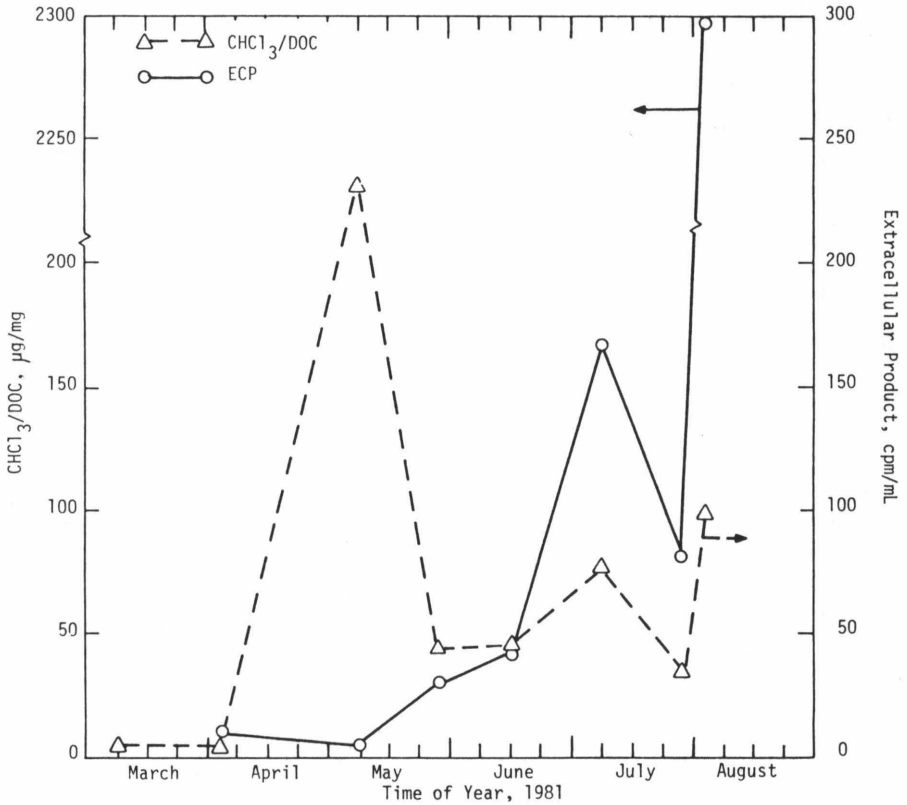


FIGURE 9

Variations in $CHCl_3$ Yields from DOC in Fraction IV of Unincubated Lake Water Compared to ECP Present in Fraction IV after 6-Hr Incubation In Situ

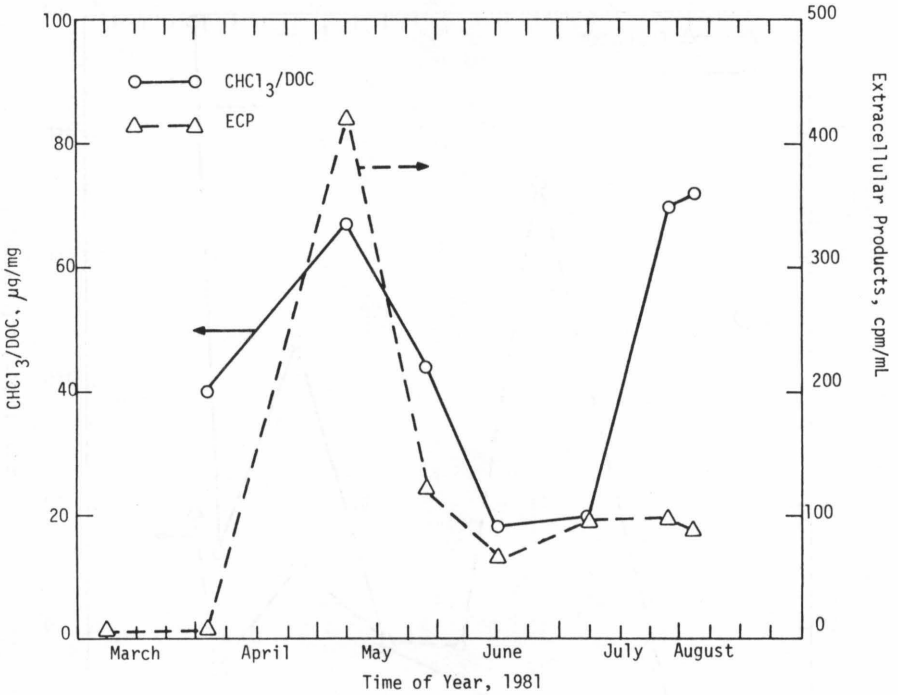


FIGURE 10

Variations in $CHCl_3$ Yields from DOC in Fraction V of Unincubated Lake Water Compared to ECP Present in Fraction V after 6-Hr Incubation In Situ

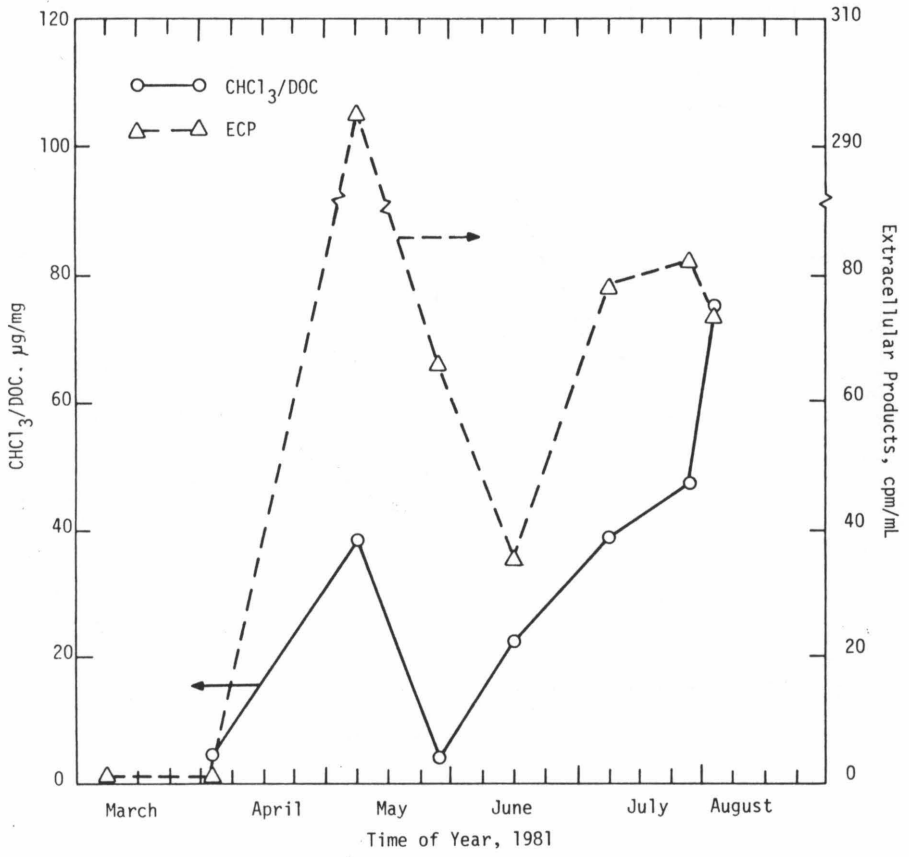


FIGURE 11

Variations in $CHCl_3$ Yields from DOC in Fraction VI of Unincubated Lake Water Compared to ECP Present in Fraction VI after 6-Hr Incubation In Situ

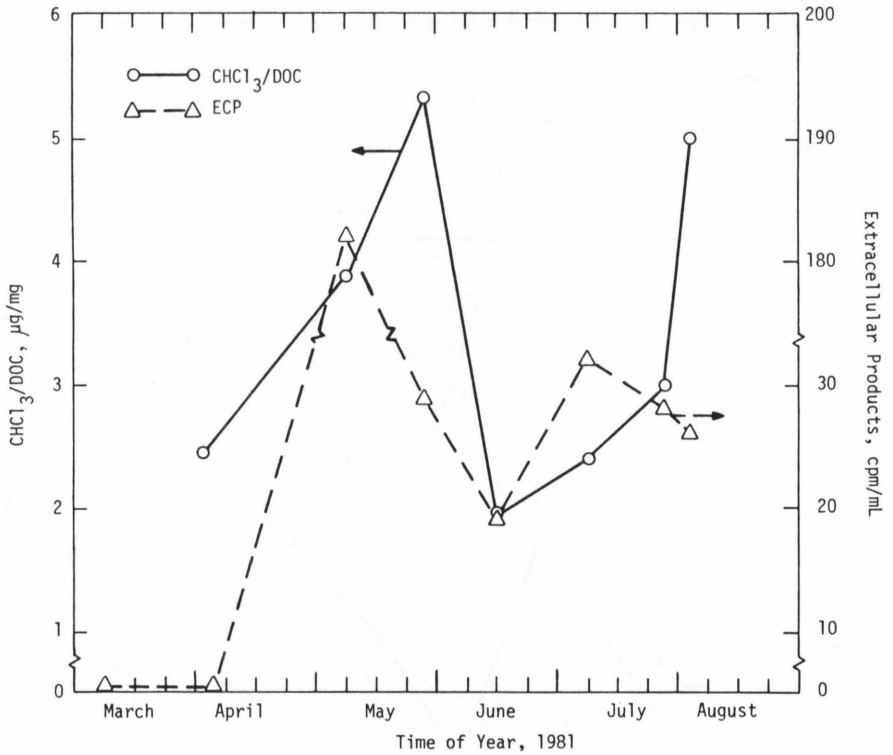


FIGURE 12

Distribution of DOC among Hydrophilic and Hydrophobic Solubility Classes in Peak Creek Arm

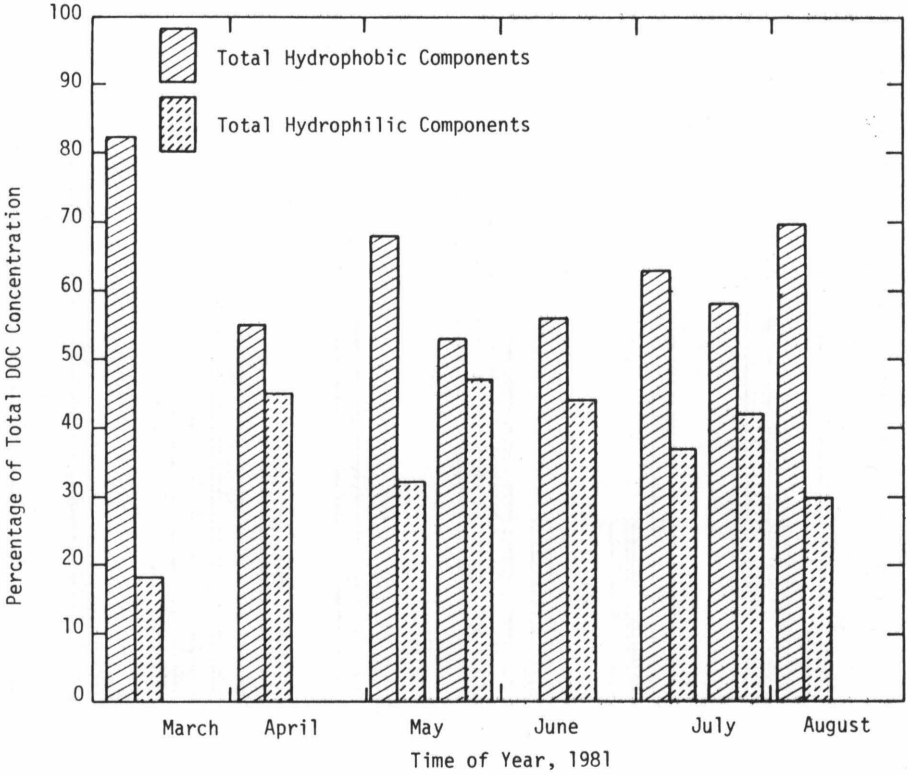


FIGURE 13

Distribution of Hydrophobic Fraction of DOC among Acid, Base, and Neutral Components in Peak Creek Arm

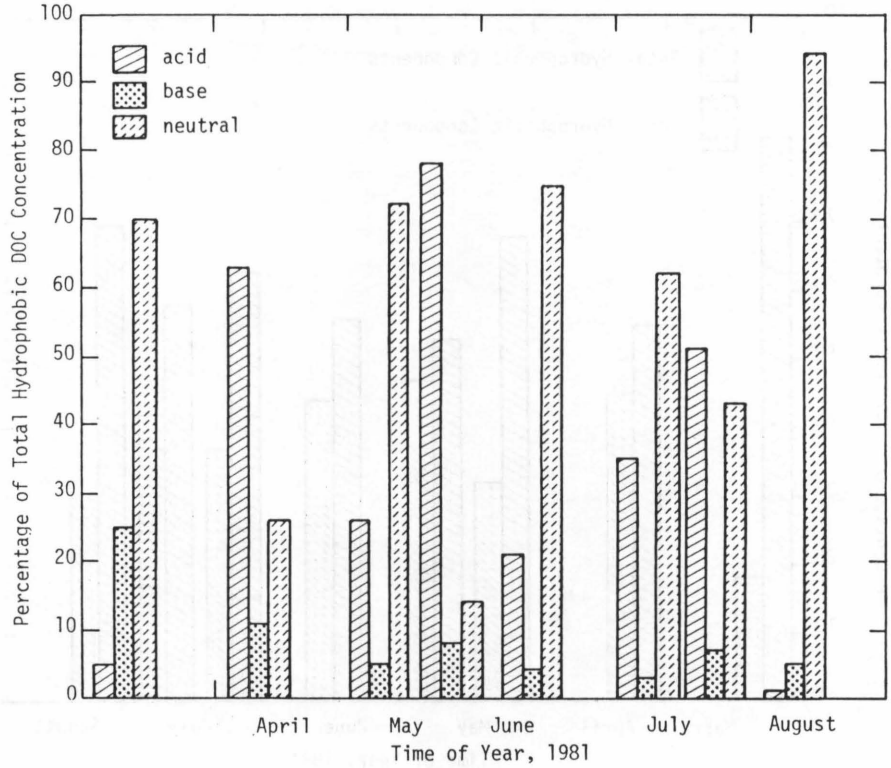


FIGURE 14

Distribution of Hydrophilic Fraction of DOC among Acid, Base, and Neutral Components in Peak Creek Arm

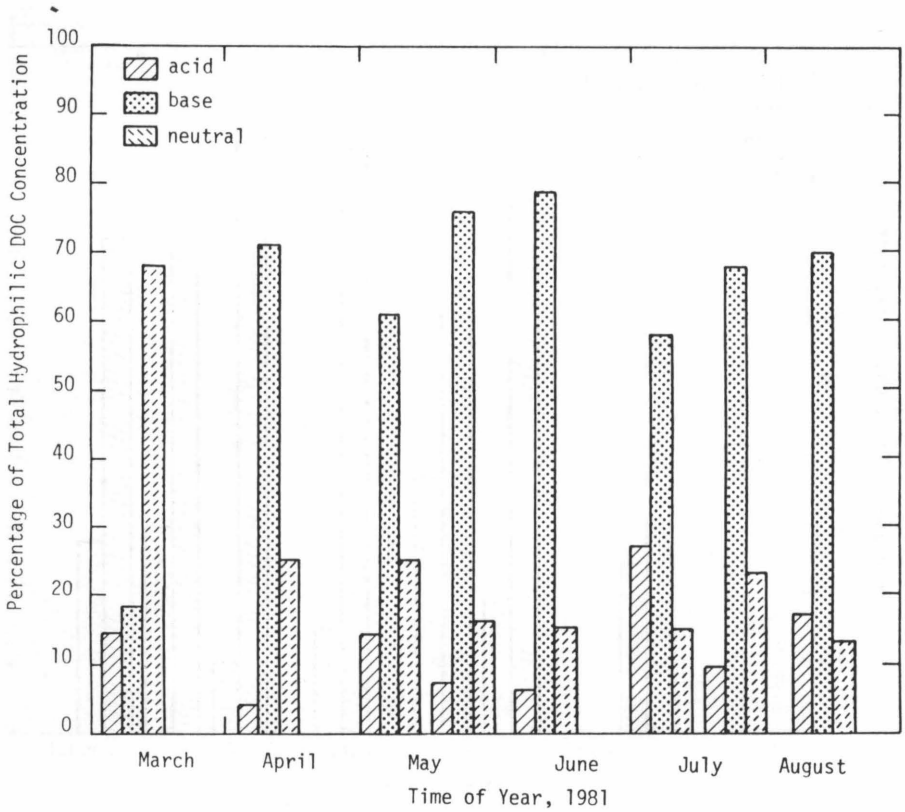


FIGURE 15

Variations in Distribution of Chloroform Precursor between Hydrophobic and Hydrophilic Components of DOC in Peak Creek Arm

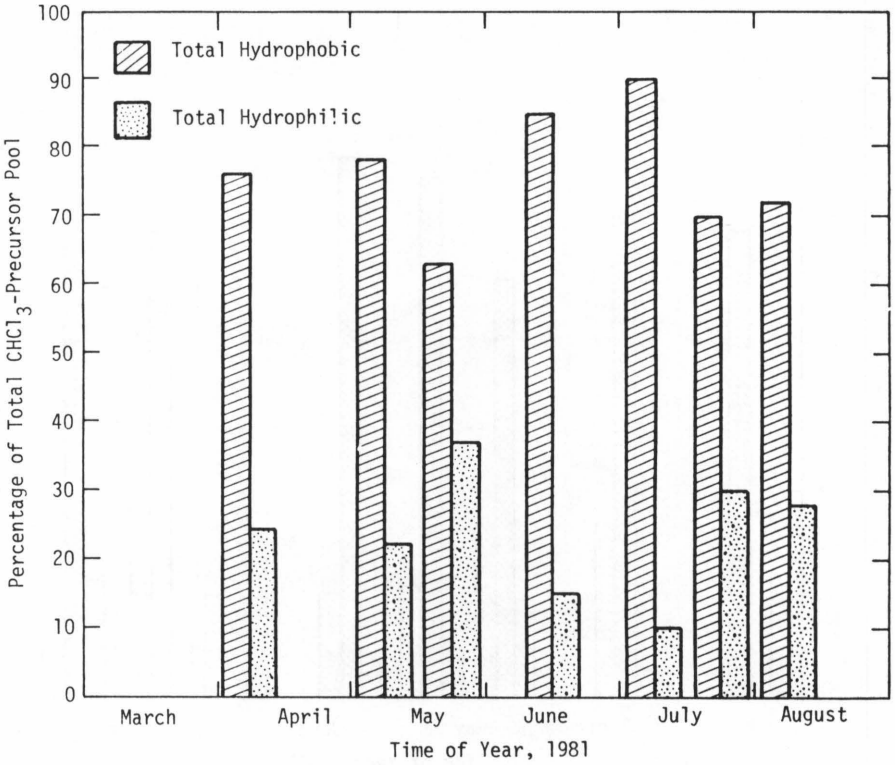


FIGURE 16

Variations in Distribution of Chloroform Precursors among Hydrophobic Acids, Bases, and Neutral Components of DOC in Peak Creek Arm

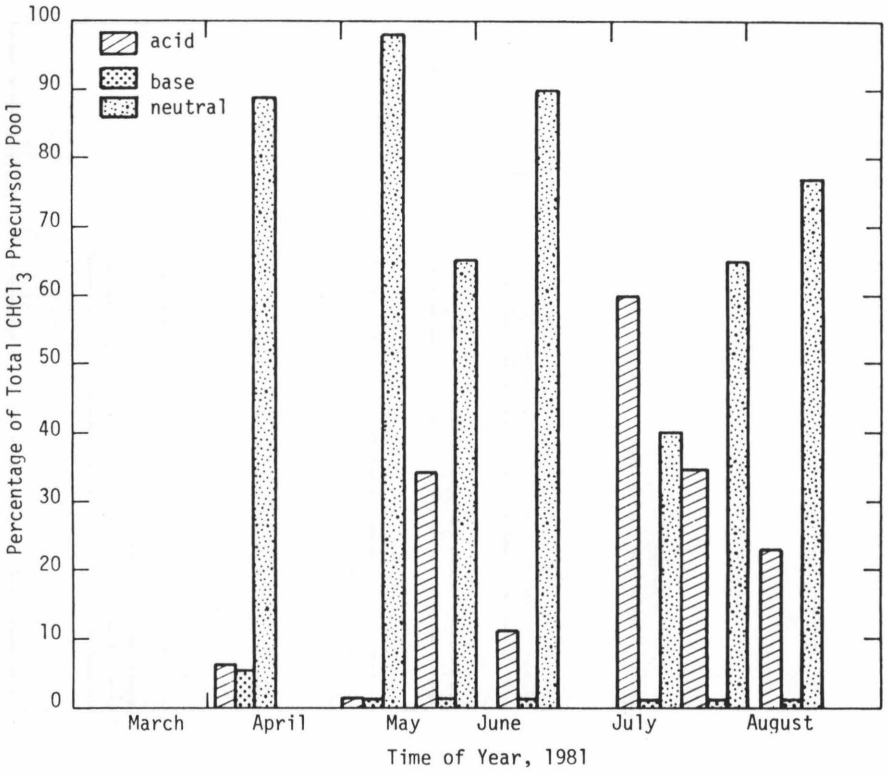


FIGURE 17

Variations in Distribution of Chloroform-Precursor Pool among Hydrophilic Acid, Base, and Neutral Components of DOC in Peak Creek Arm

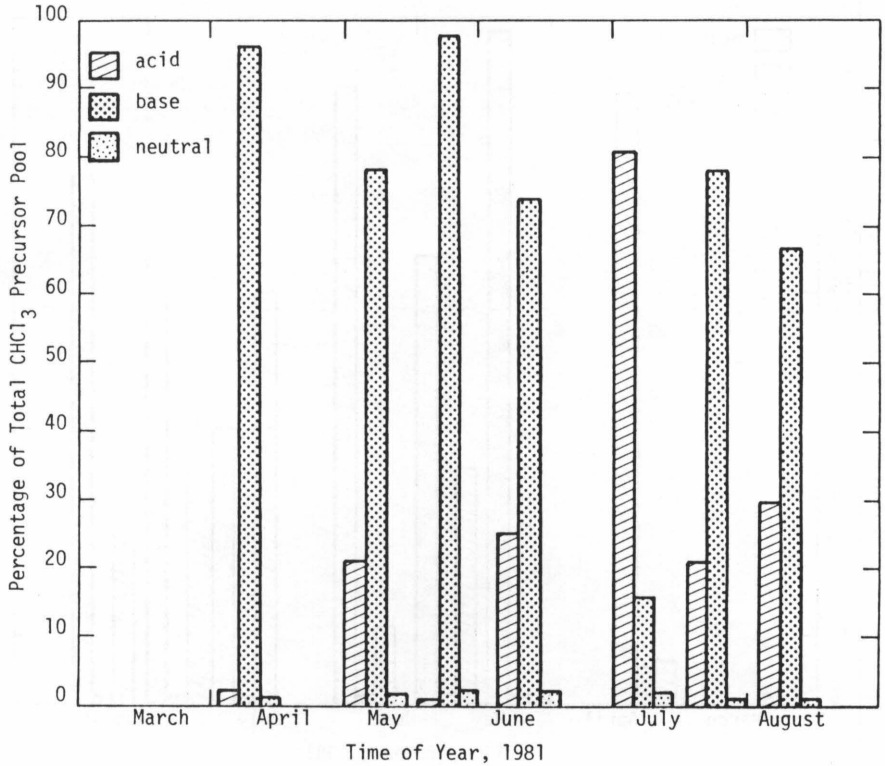


FIGURE 18

DOC and Chloroform-Yield Variations in Unfractionated Claytor Lake Water, Peak Creek Arm

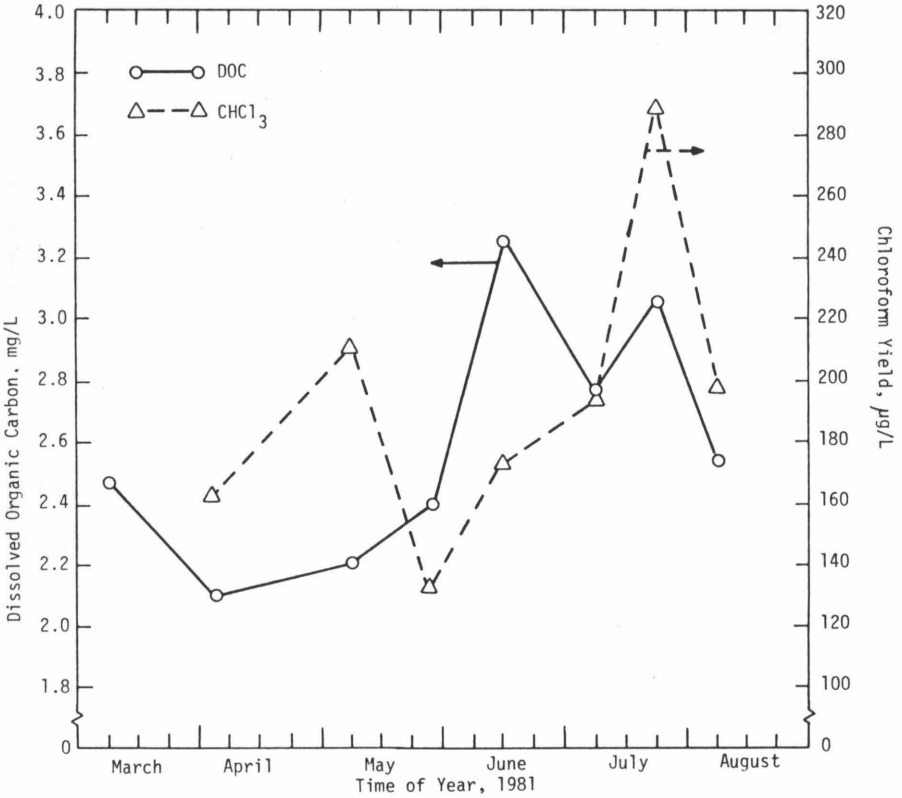


FIGURE 19

Variations in DOC and Chloroform Yields from Fraction II Obtained from Fractionation of Claytor Lake Water, Peak Creek Arm

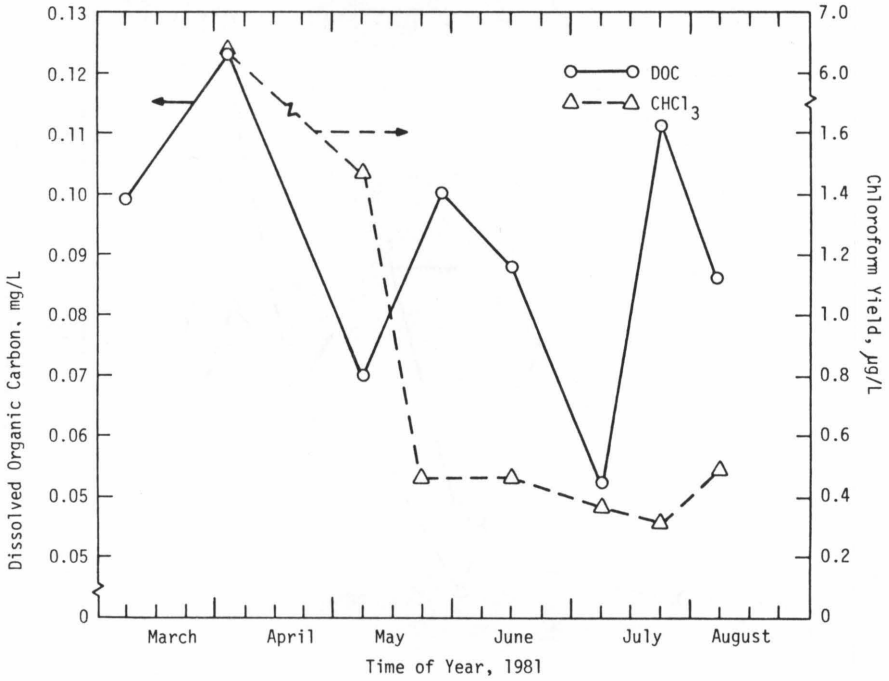


FIGURE 20

Variations in DOC and Chloroform Yields from Fraction III Obtained from Fractionation of Claytor Lake Water, Peak Creek Arm

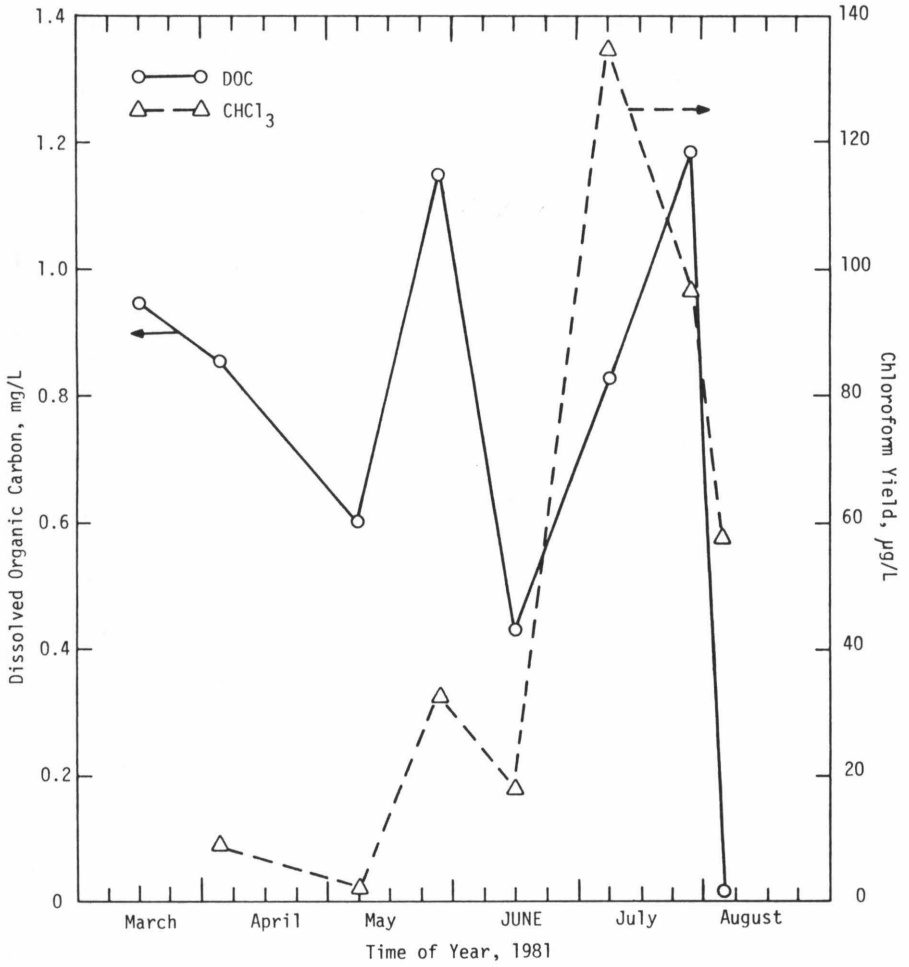


FIGURE 21

Variations in DOC and Chloroform Yields from Fraction IV Obtained from Fractionation of Claytor Lake Water, Peak Creek Arm

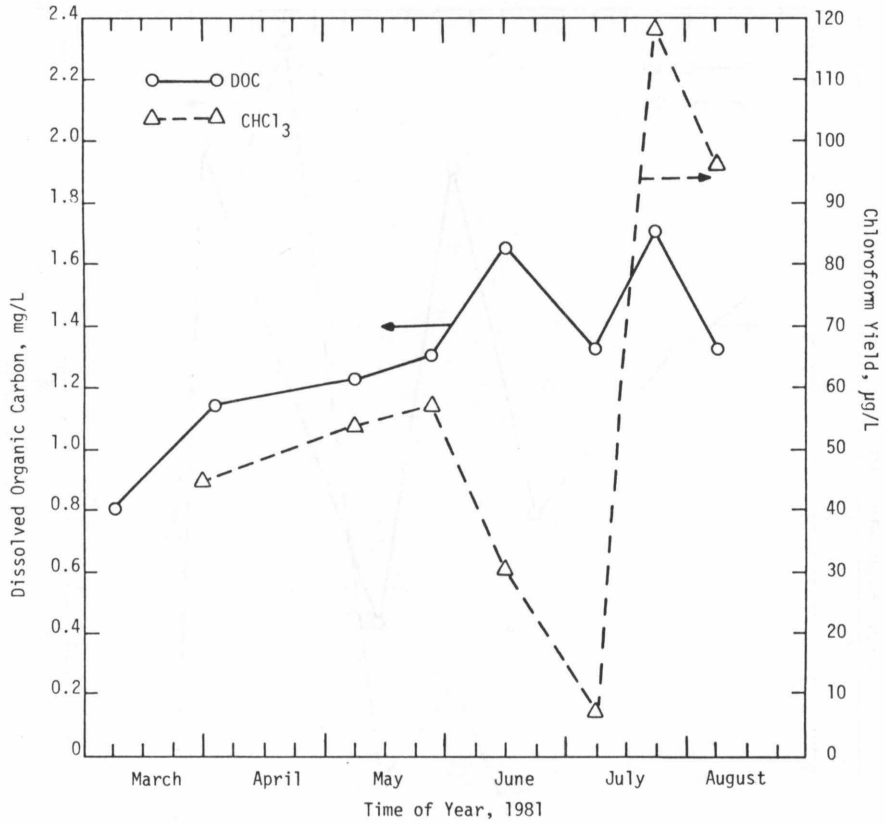


FIGURE 22

Variations in DOC and Chloroform Yields from Fraction V Obtained from Fractionation of Claytor Lake Water, Peak Creek Arm

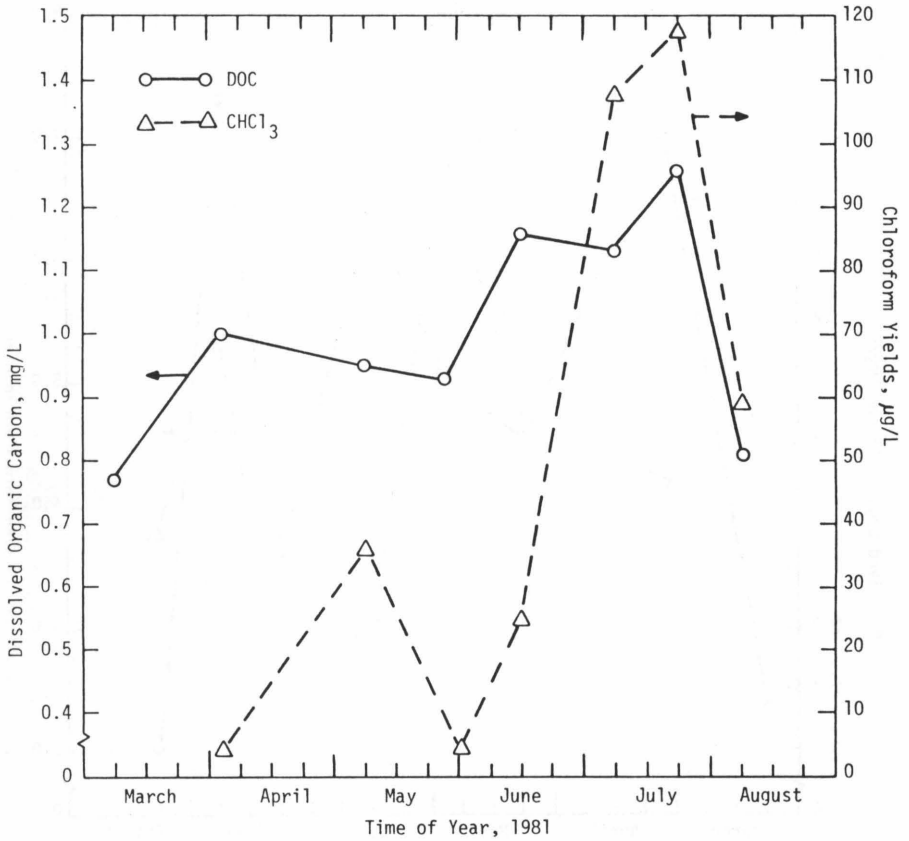


FIGURE 23

Variations in DOC and Chloroform Yields from Fraction VI Obtained from Fractionation of Claytor Lake Water, Peak Creek Arm

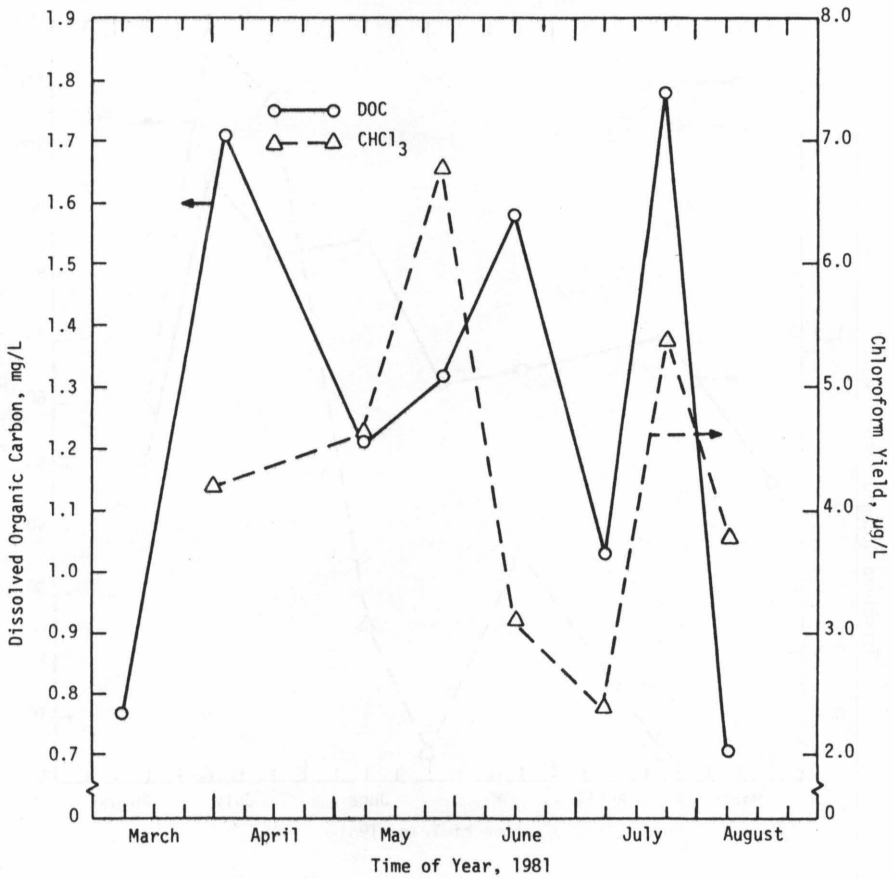


FIGURE 24

Regression Relationship between DOC and ECP in Peak Creek Arm

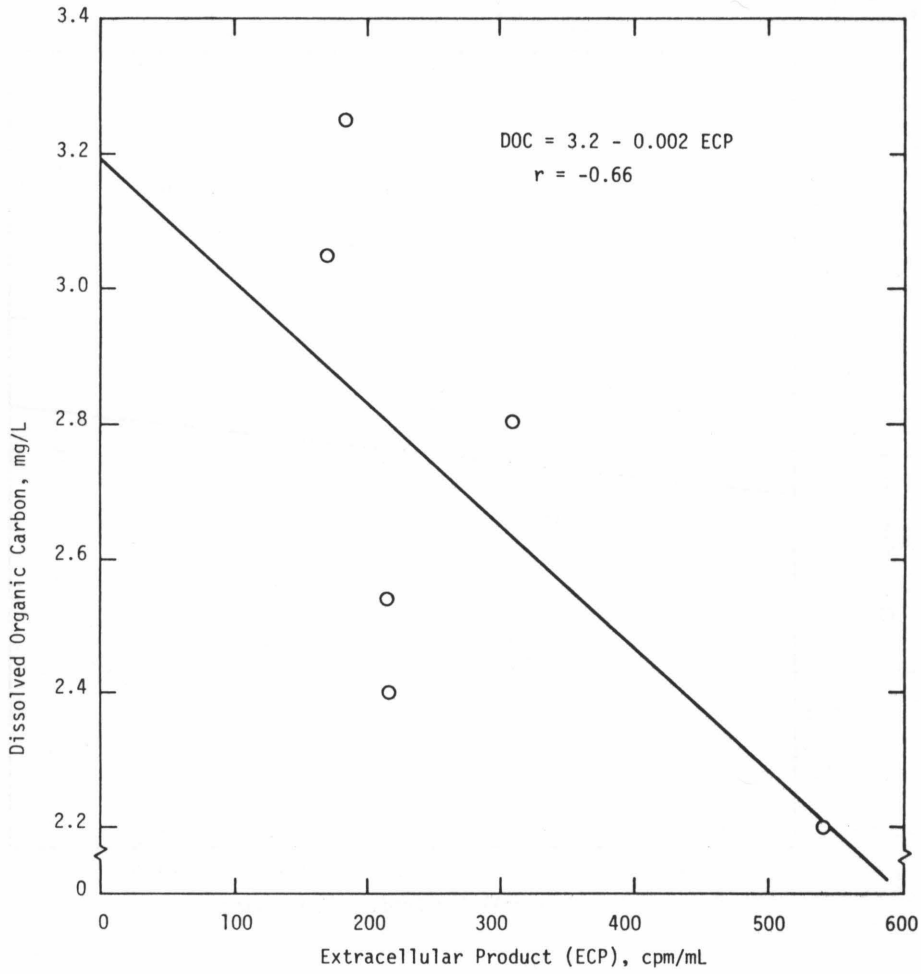


FIGURE 25

Regression Relationship between Chloroform Yields and ECP Present after 6-Hr Incubation In Situ at Peak Creek Site

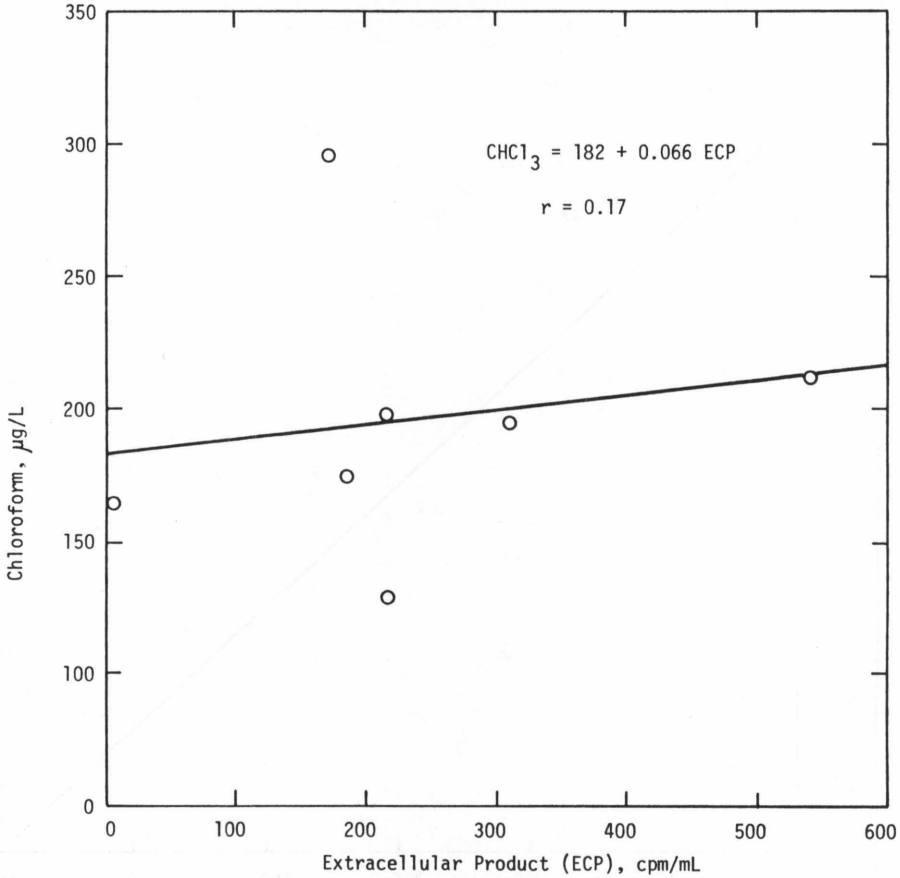


FIGURE 26

Regression Relationship between DOC in Fraction II and ECP Appearing in Fraction II after 6-Hr Incubation In Situ at Peak Creek Site

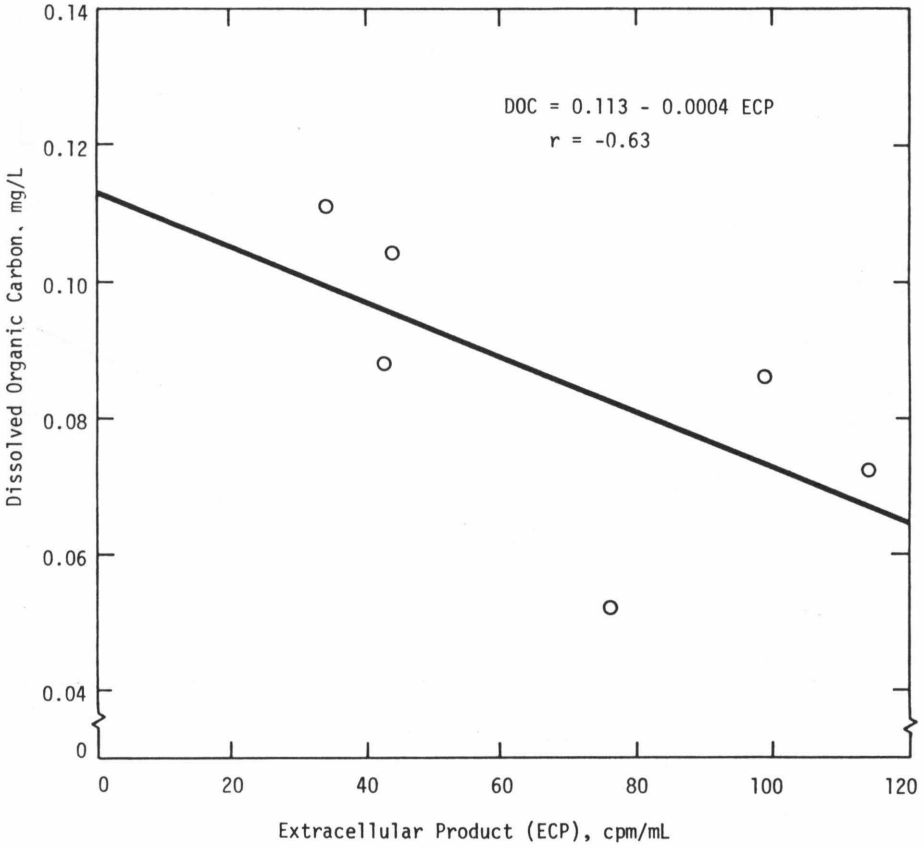


FIGURE 27

Regression Relationship between Chloroform Yields from Fraction II and ECP Appearing in Fraction II after 6-Hr Incubation In Situ at Peak Creek Site

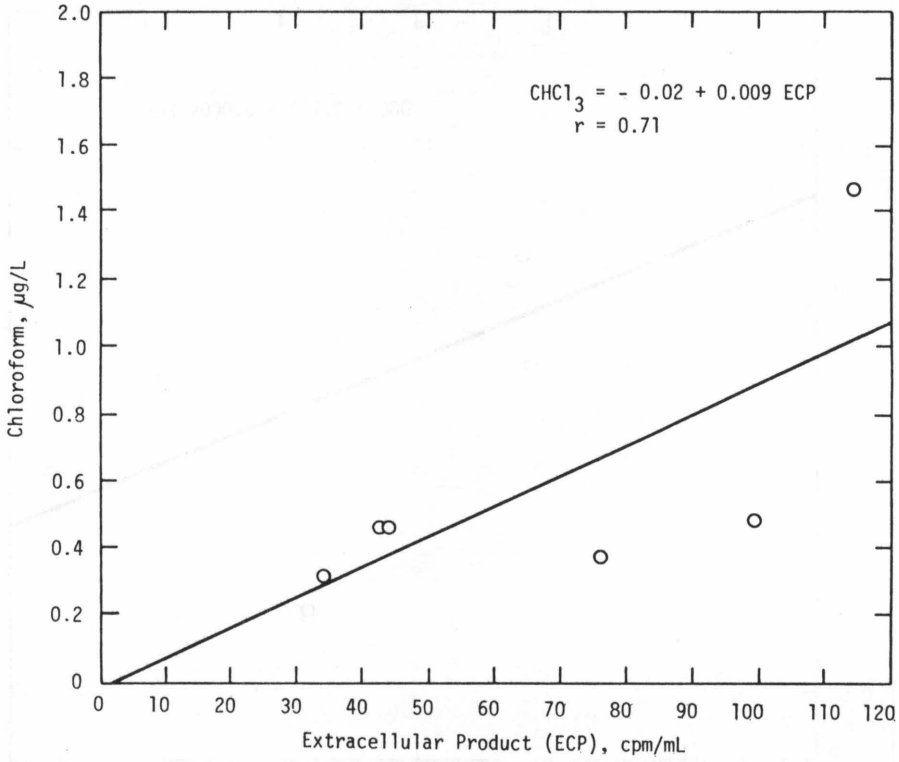


FIGURE 28

Variations in THM-Formation Potentials in Relation to Observed Fluctuations in Algal and Bacterial Population Densities, Peak Creek Site

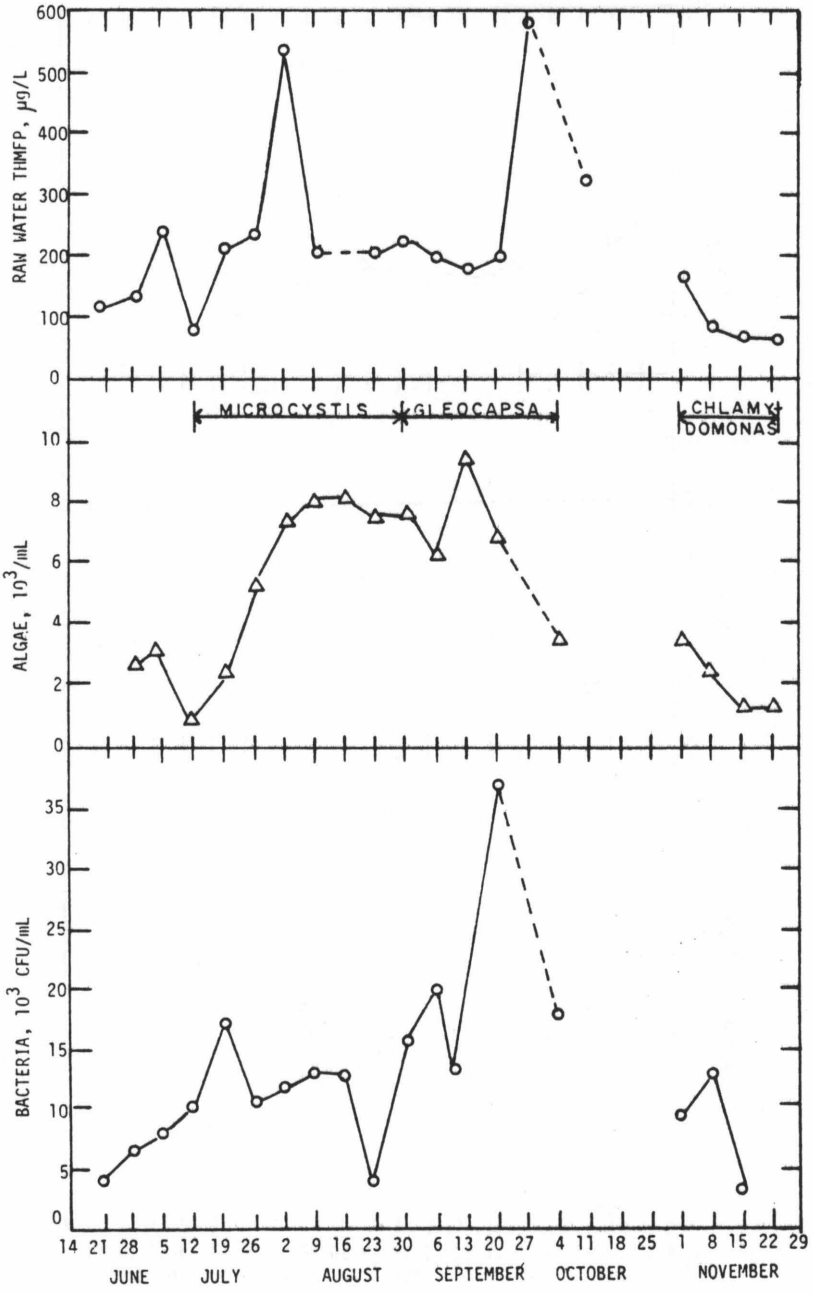


FIGURE 29

Variations in THM-Formation Potentials in Relation to Observed Fluctuations in Algal and Bacterial Population Densities at Dam Site

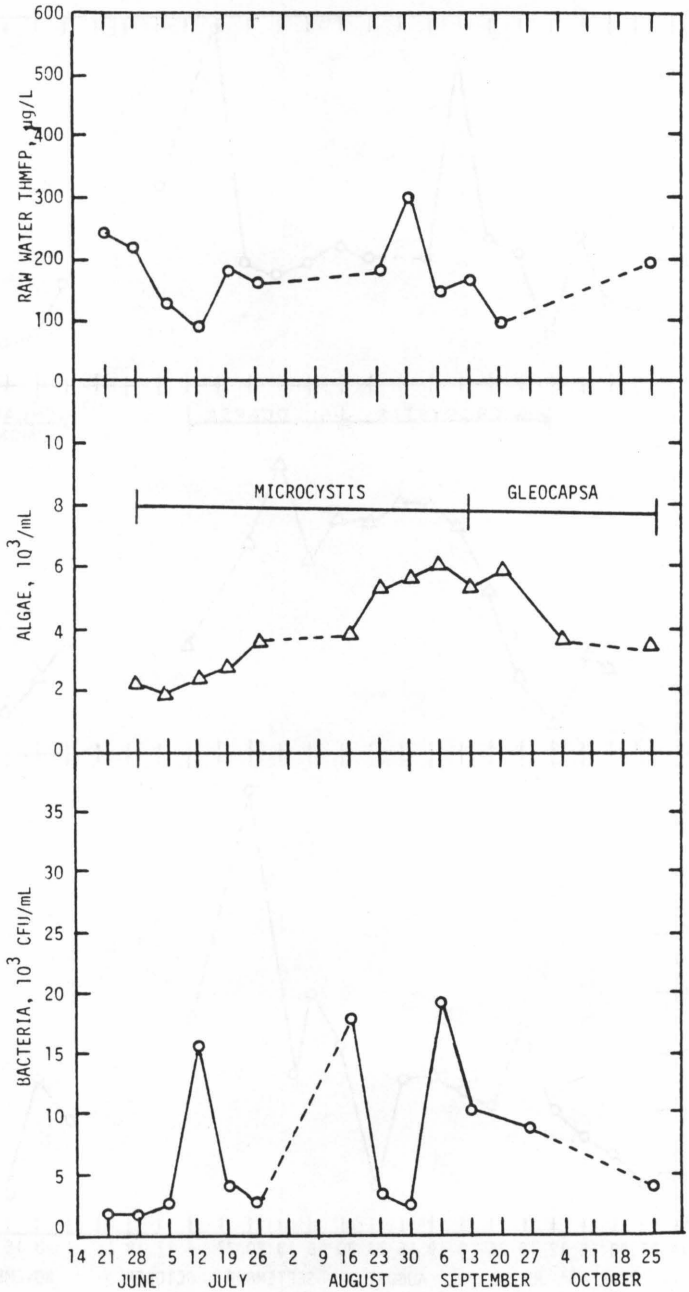


FIGURE 30

Diurnal Variations in Chemical Indicators of Algal Activity Compared to Those of DOC and THMFP at Peak Creek Site on August 1, 1981

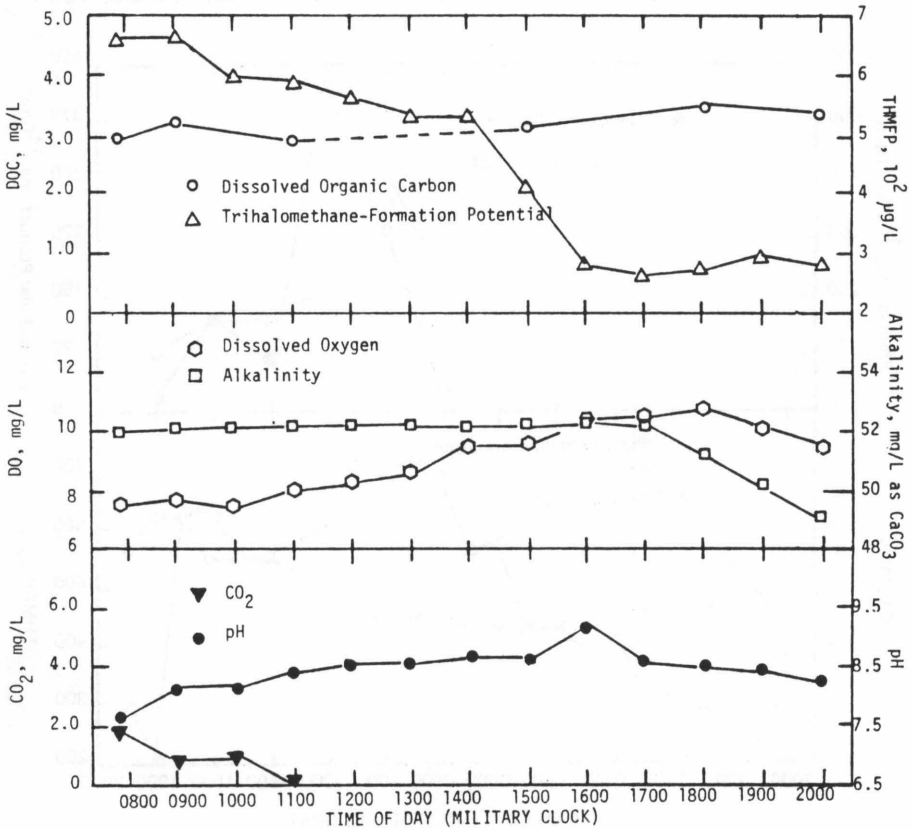
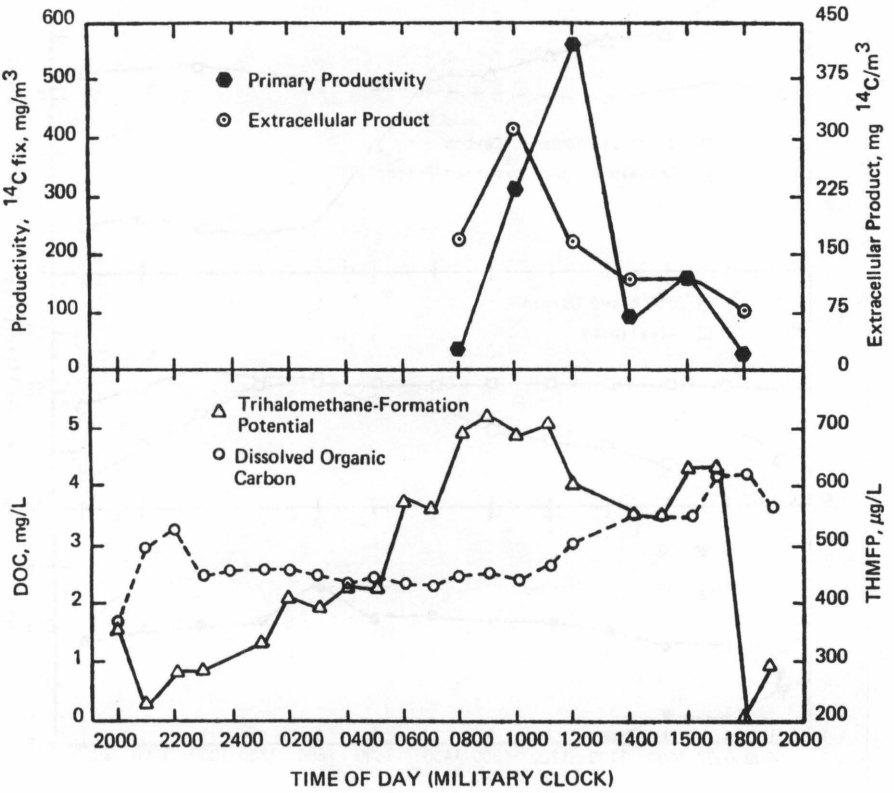


FIGURE 31

Diurnal Variations in Chemical Indicators of Algal Activity Compared to Those of DOC and THMFP and Shown in Relation to P and ECP Production at Peak Creek Site on September 25-26, 1981



(continued)

FIGURE 31 (continued)

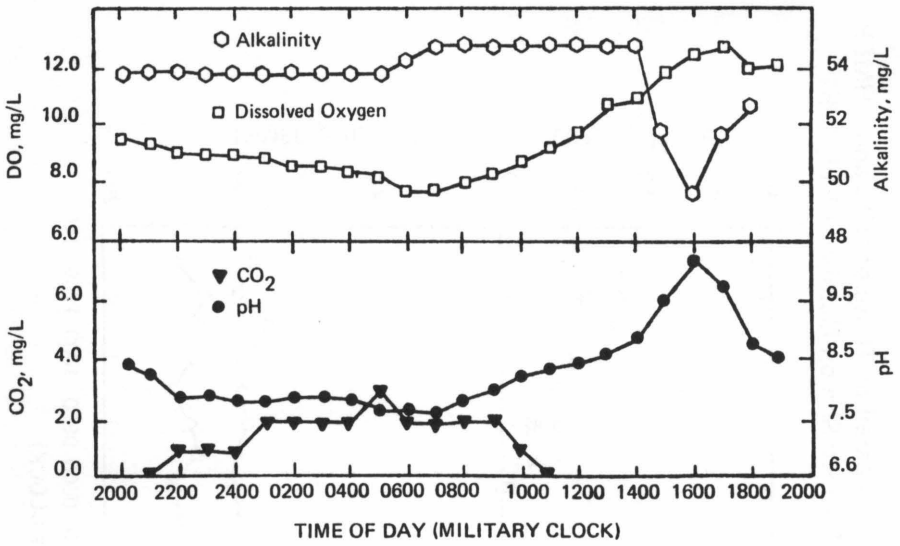
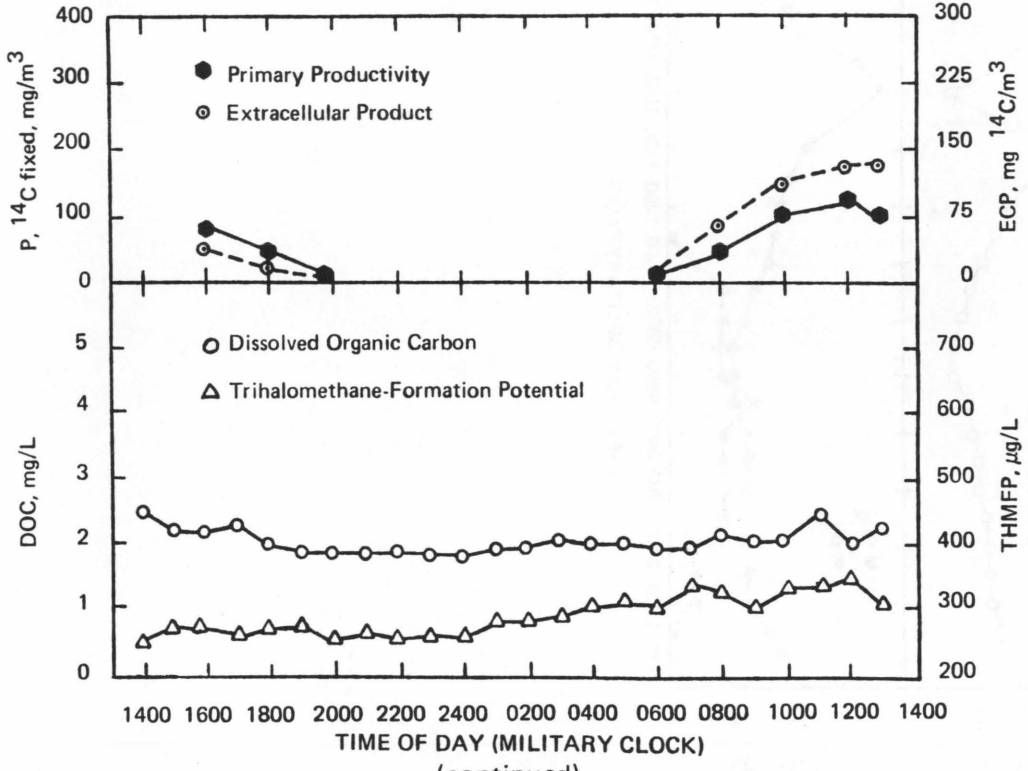


FIGURE 32

Diurnal Variations in Chemical Indicators of Algal Activity Compared to Those of DOC and THMFP and Shown in Relation to P and ECP Production at Peak Creek Site on October 10-11, 1981



(continued)

FIGURE 32 (continued)

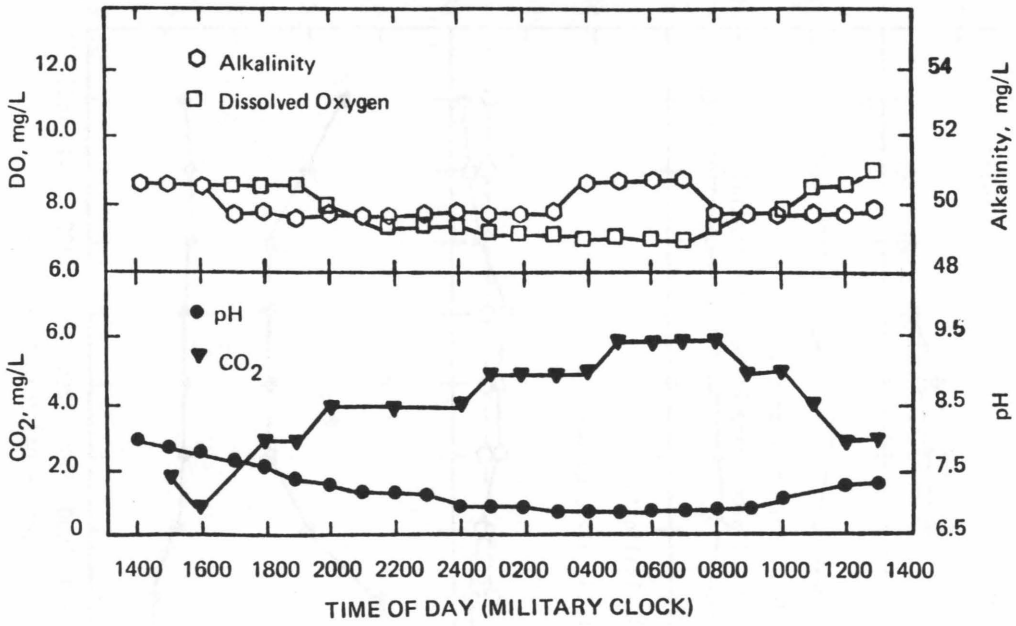


FIGURE 33

Diurnal Variations in Chemical Indicators of Algal Activity Compared to Those of DOC and THMFP and Shown in Relation to P and ECP Production at Peak Creek Site on November 23, 1981

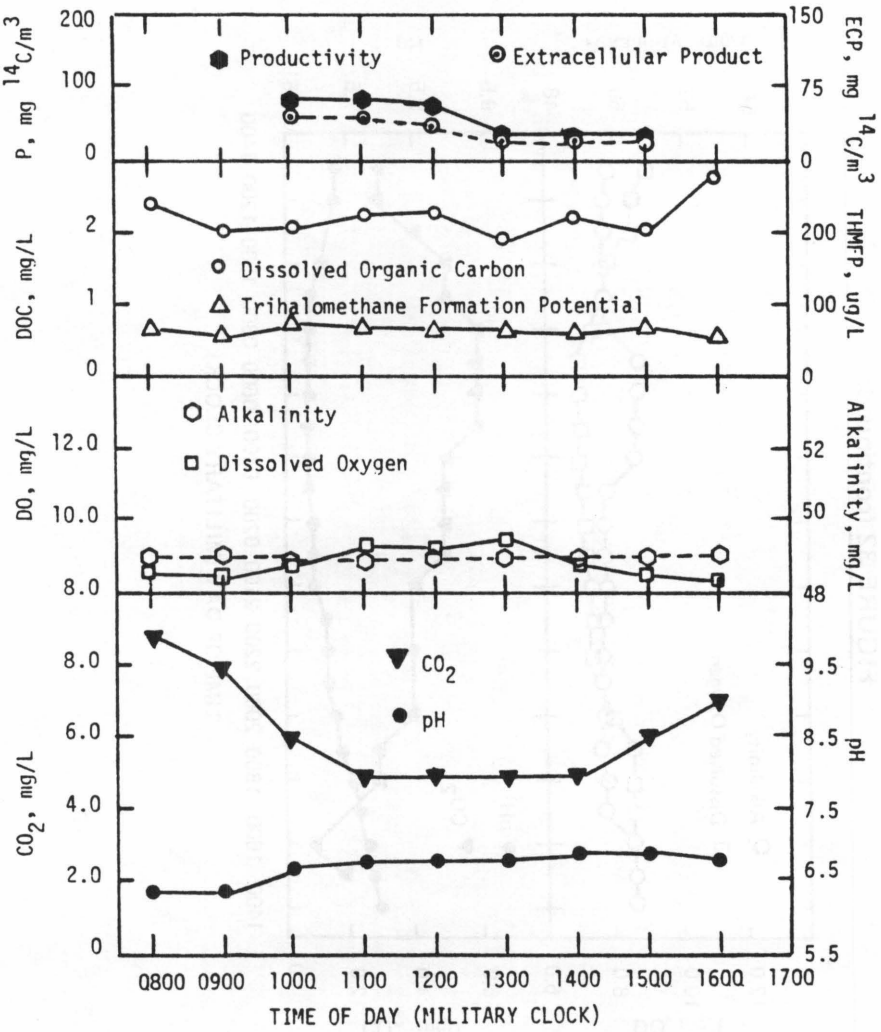
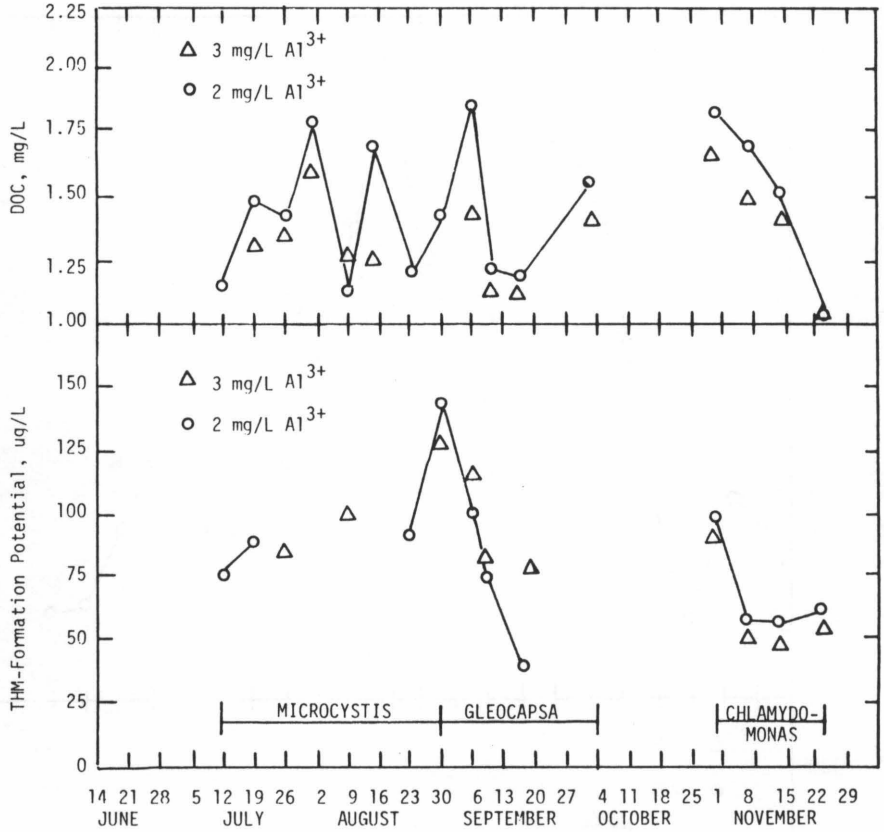


FIGURE 34

Variations in DOC Concentrations and THMFP at Peak Creek Site after Treatment by Alum Coagulation, Flocculation, Sedimentation, and Filtration*



*Dominant algae indicated on lines at base of *Figure.*

FIGURE 35

Maximum Reductions in THMFP and DOC by Alum Coagulation Compared to Fluctuations in Algal Population Densities at Peak Creek Site

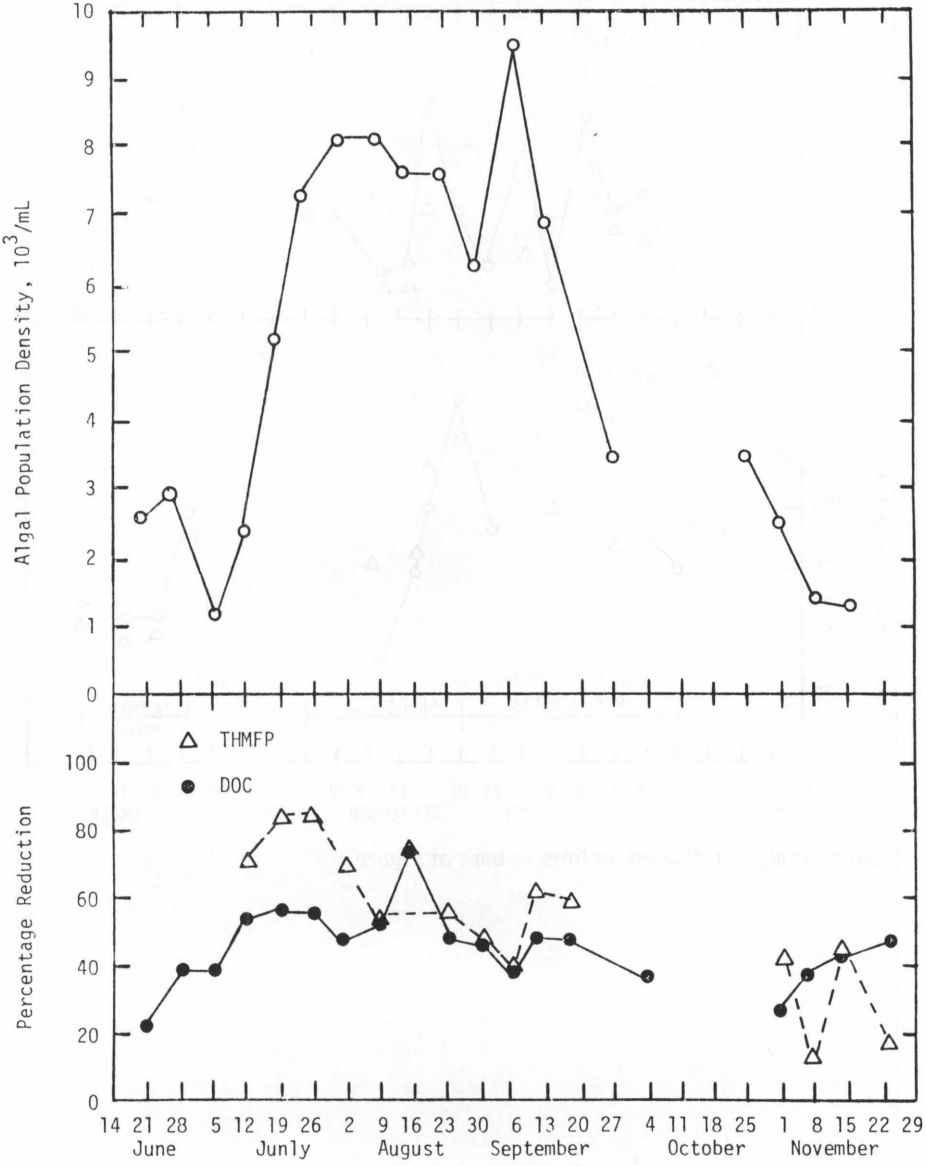


FIGURE 36

Variations in THM-to-DOC Ratio Compared to Fluctuations in Algal and Bacterial Population Densities at Peak Creek Site

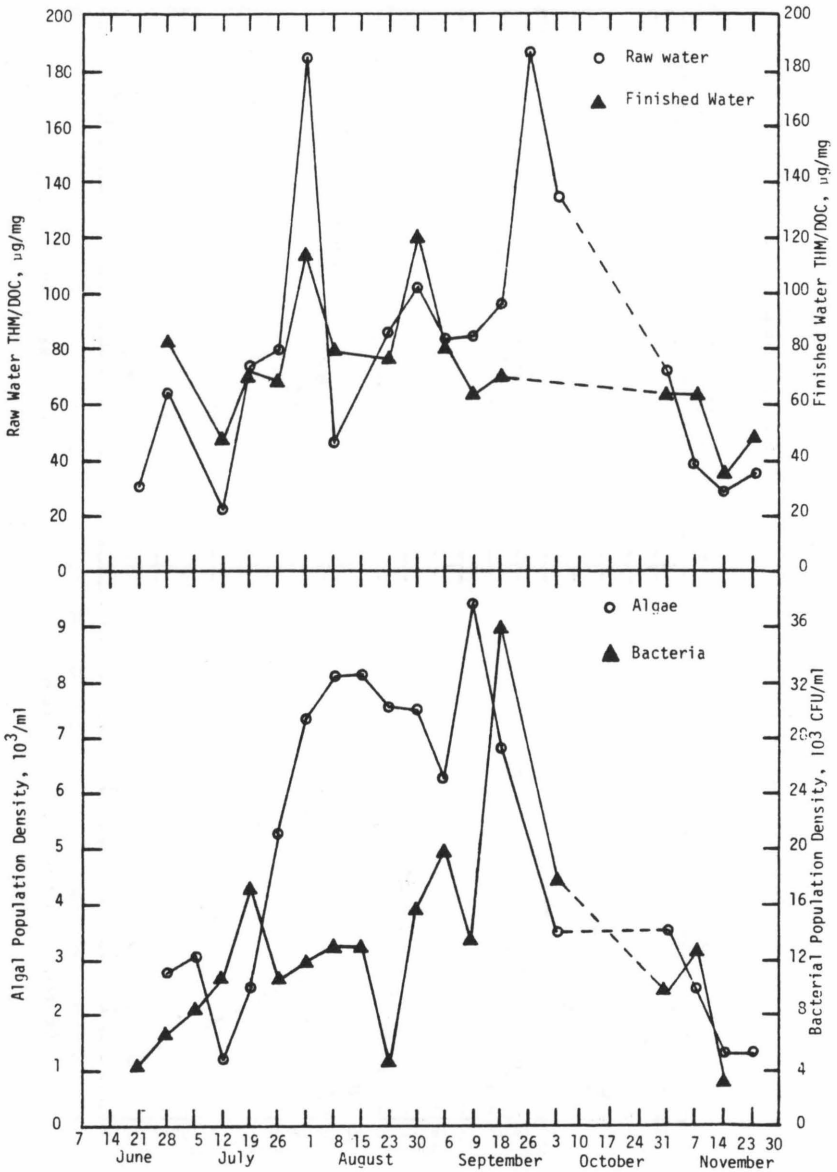


FIGURE 37
Variations in THM-to-DOC Ratio Compared to Algal and Bacterial Population at Dam Site

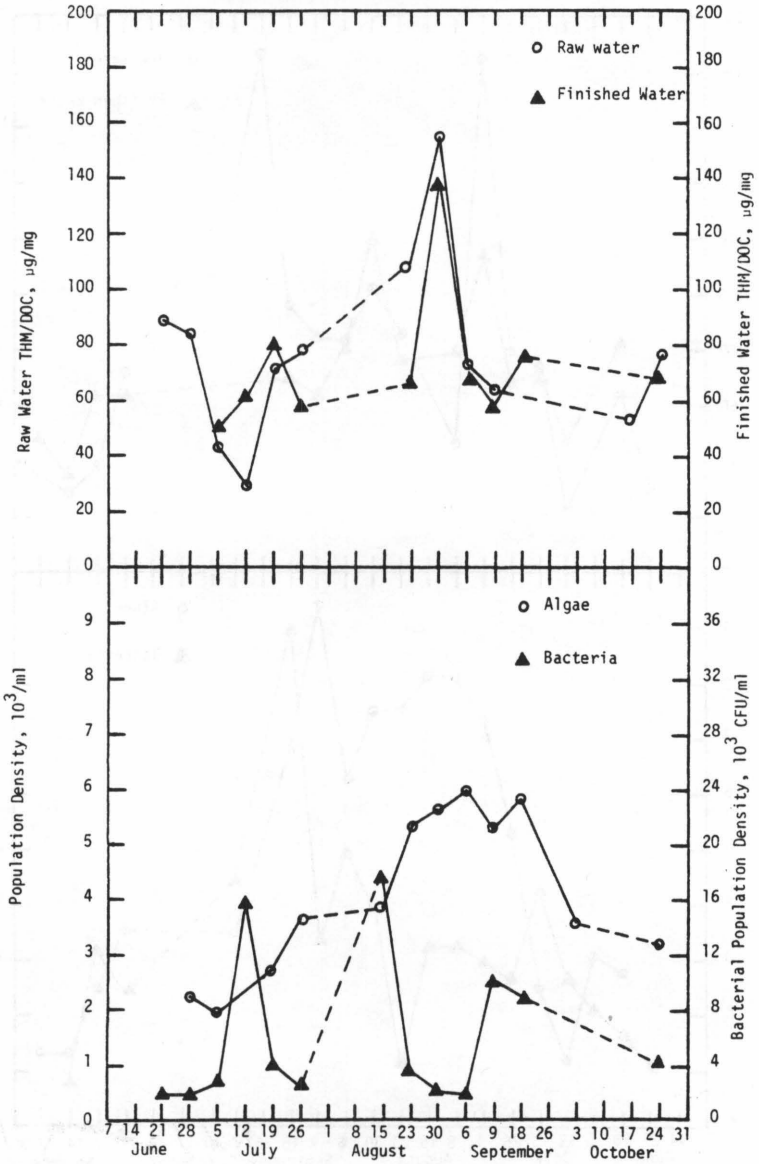


FIGURE 38

Reductions in THMFP by Alum Coagulation Compared to Algal and Bacterial Population Densities at Dam Site

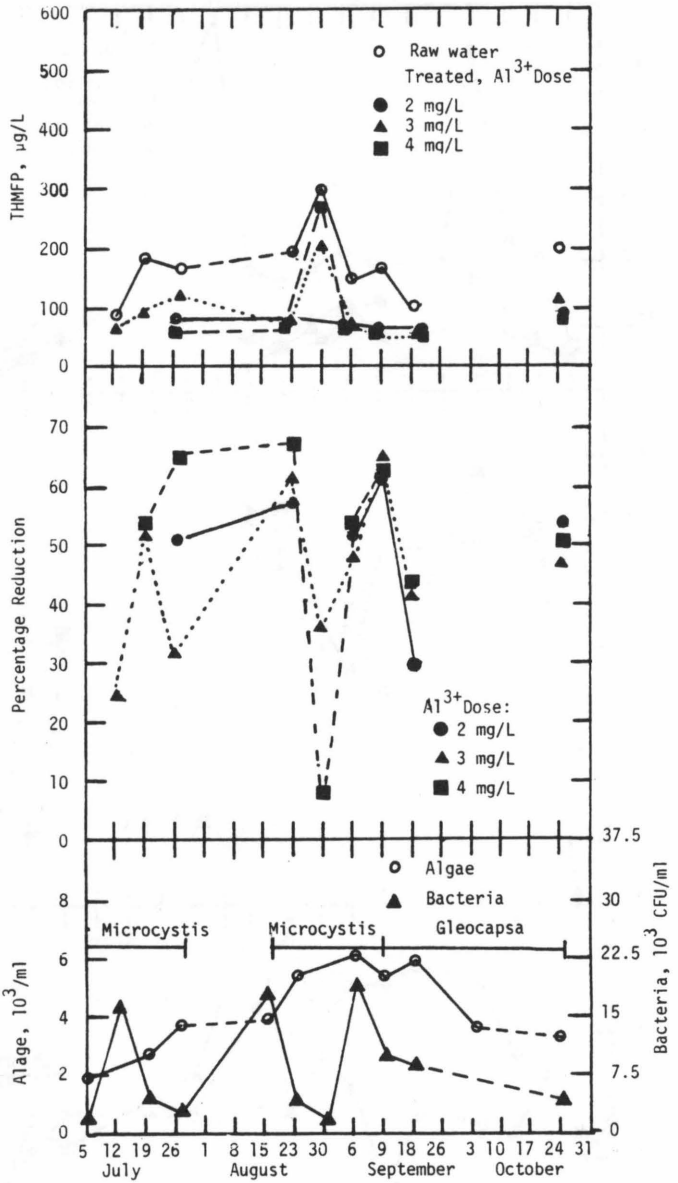


FIGURE 39

Reductions in THMFP by Alum Coagulation Compared to Algal and Bacterial Population Densities at Peak Creek Site

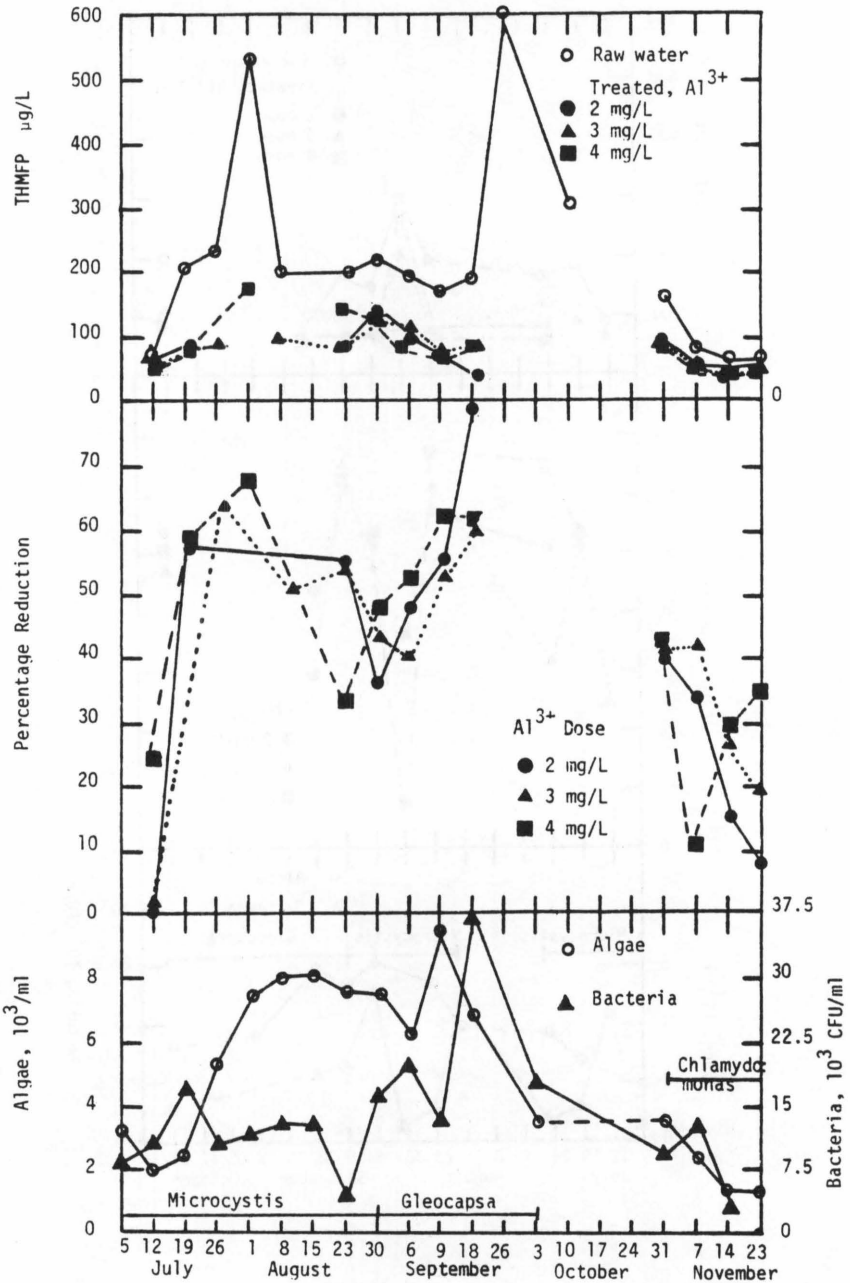


FIGURE 40

The Relationship between DOC Removals by Alum Coagulation and Population Densities of Algae and Bacteria at Peak Creek Site

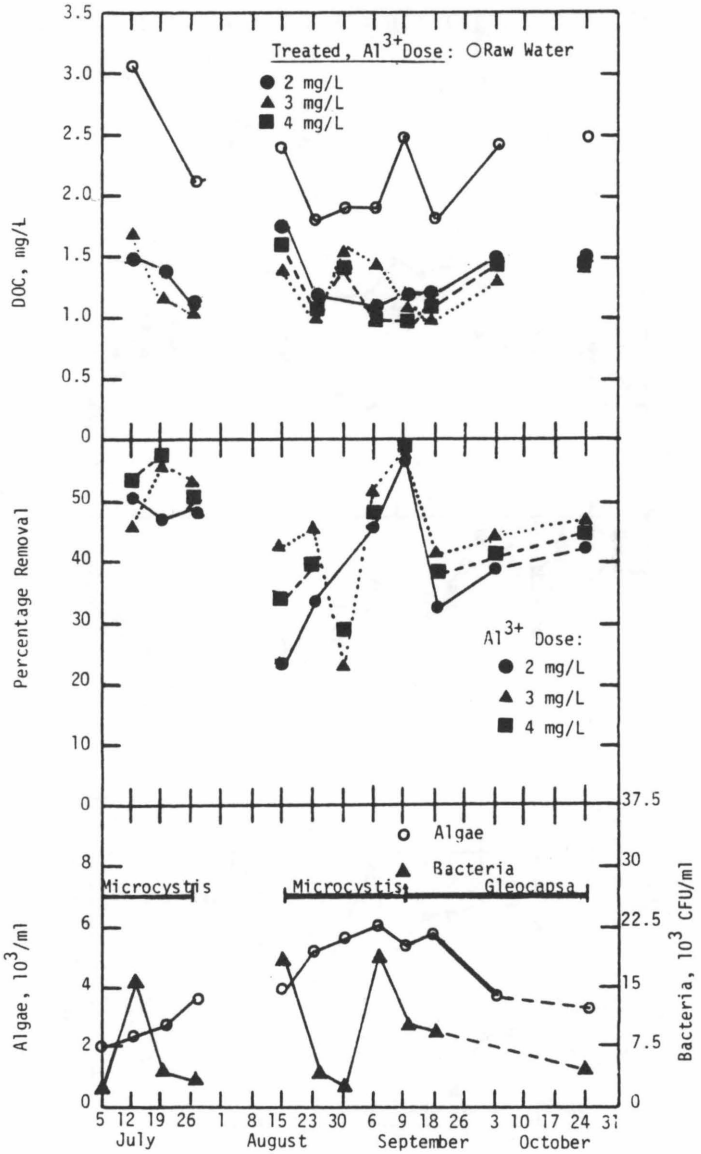
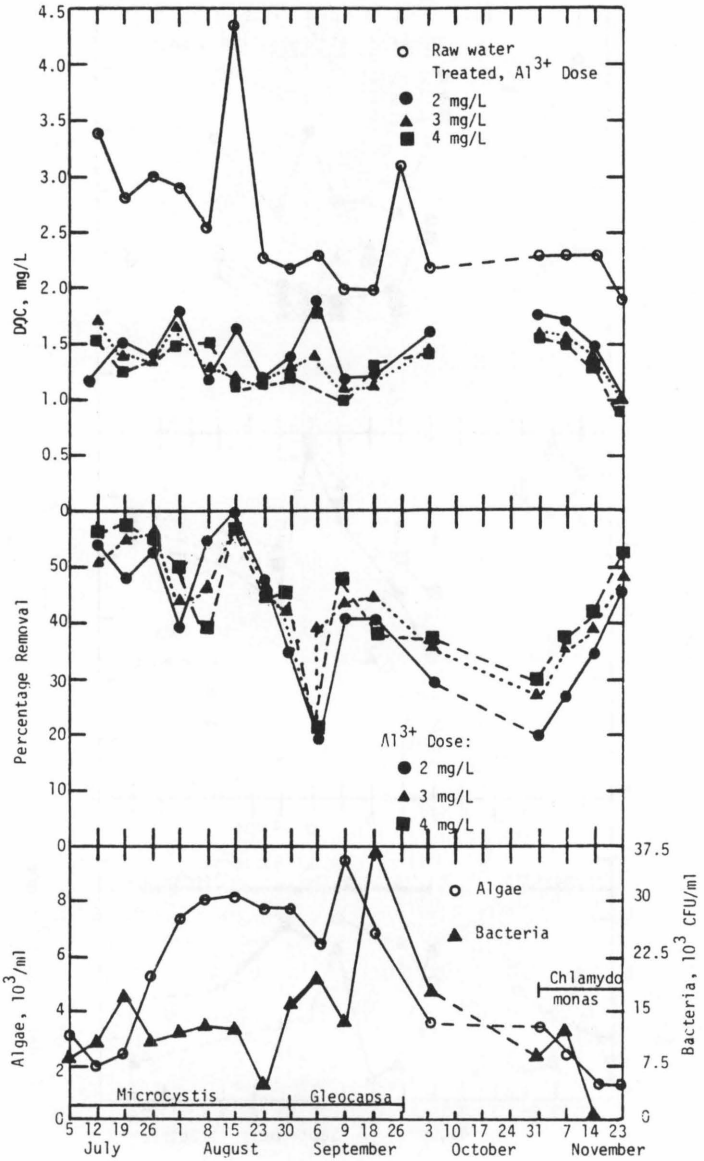


FIGURE 41

The Relationship between DOC Removals by Alum Coagulation and Population Densities of Algae and Bacteria at Dam Site



TABLES

TABLE 1
Analytical Conditions for THM Analyses by the Purge-and-Trap Method*

Parameter	Specifications
Purge Volume:	5 mL
Purge Gas:	Helium at 50 mL/min
Column Parameters:	8 ft long . 0.1 in. ID glass tubing. Packed with 1 percent SP-1000 on Carbopack-B (60/80) mesh.
Temperature Program Sequence:	45° C isothermal for 3 min, program at 8° C/min to 220° C then hold for 15 min.

*EPA, 1979.

TABLE 2
Distribution of ECP, DOC, and THM-Formation Potential among Various Solubility Groups of Organic Compounds

	Organic Component		
Solubility Class	**ECPs***	**DOC†**	**THM Formation†**
Hydrophobic	54-77%‡	53-82%	70-90%
Acid	Dominant in early May	Dominant in parts of April and May	Dominant in early July
Base	Dominant in August		
Neutral	Dominant most of sampling period	Dominant most of sampling period	Dominant most of sampling period
Hydrophilic	23-46%	18-47%	10-37%
Acid	Dominant in second half of sampling period		Dominant in early July
Base	Dominant in first half of sampling period	Dominant most of sampling period	Dominant most of sampling period
Neutral		Dominant in March	

*Extracellular products in lake water after 6-hr incubation at 0.5 m.

†Before incubation.

‡All percentages are percentages of the total hydrophobic and hydrophilic classes.

TABLE 3

Changes in Solubility-Class Structure of DOC and THM-Precursor Pools in Claytor Lake Water after 6-Hr Incubation In Situ

Solubility Fraction	August 4, 1981 DOC (mg/L) Initial	6 Hr	THM (μg/L) Initial	6 Hr	September 18, 1981 DOC (mg/L) Initial	6 Hr	THM (μg/L) Initial	6 Hr
Unfractionated	2.54	4.32	198	217	2.05	2.43	142	192
Total Hydrophobic	1.22*	1.15	102	55	0.40	0.29	135	189
Base	0.09	0.31	<1	<1	1.22	0.77	133	161
Acid	0.02	0.02	58	126	1.20	1.60	29	23
Neutral	1.12	0.82	44	†	†	†	†	†
Total Hydrophilic	1.32	3.17	96	162	1.65	2.15	7	3
Base	0.51	0.73	36	118	0.26	0.35	1	<1
Acid	0.10	1.09	56	39	0.57	0.40	<1	<1
Neutral	0.71	1.35	4	5	0.82	1.40	6	5

*Totals will not always equal sum of components because of imprecision in the analytical method.

†Could not be calculated. Value <0 obtained.

TABLE 4
Composition of the Algal Population in the Peak Creek Arm of Claytor Lake

Date	Percent of Total Count			Total Count (per mL)	Dominant Algae	
	Cyanophyta	Chlorophyta	Chrysophyta		Alga*	Percent
6/28/81	46	48	6	2760	Mi	34
					UG	22
7/5/81	76	20	4	3060	Mi	58
7/12/81	62	35	3	1195	Tr	33
7/19/81	74	25	1	2450	Mi	40
7/26/81	83	13	4	5274	Mi	67
8/1/81	94	6	< 1	7380	Mi	83
8/9/81	97	3	< 1	8075	Mi	86
8/15/81	98	2	< 1	8110	Mi	91
8/23/81	96	4	< 1	7270	Mi	96
8/30/81	97	2	1	7510	Mi	52
					Gl	43
9/6/81	98	2	< 1	6130	Gl	51
					Mi	44
9/9/81	98	2	< 1	9320	Gl	63
					Mi	33
9/18/81	99	1	0	6760	Gl	59
					Mi	38
10/3/81	97	1.5	1.5	3510	Gl	65
					Mi	24
10/31/81	10	90	< 1	3540	Ch	78
11/7/81	1	98	1	2480	Ch	52
					Co	29
11/14/81	2	83	15	1370	Ch	53
					Co	22
11/23/81	0	85	15	1330	Ch	44
					Co	32

*Microcystis (Mi), Unidentified Green (UG), Trichodesmium (Tr), Gleocapsa (Gl), Chlamydomonas (Ch), Coleocystis (Co).

TABLE 5
Composition of the Algal Population near Claytor Lake Dam

Date	Percent of Total Count			Total Count (per mL)	Dominant Algae	
	Cyanophyta	Chlorophyta	Chrysophyta		Alga*	Percent
6/28/81	63	29	8	2230	Mi	39
7/5/81	70	27	3	1370	Mi	59
7/12/81	72	24	4	2350	Mi	54
7/19/81	73	24	3	2725	Mi	43
7/26/81	89	8	3	3630	Mi	76
8/15/81	92	8	0	3830	Mi	86
8/23/81	98	2	0	5330	Mi	90
8/30/81	99	1	0	5630	Mi	87
9/6/81	99	1	0	6000	Mi	61
					Gl	35
9/9/81	99	1	0	5310	Gl	51
					Mi	45
9/18/81	99	< 1	< 1	5840	Gl	65
					Mi	34
10/3/81	100	0	< 1	3690	Gl	48
					Mi	46
10/24/81	100	< 1	0	3230	Gl	64
					Mi	30

*Microcystis (Mi), Gleocapsa (Gl).

TABLE 6

Effectiveness of Alum Doses on the Reduction of Organic Carbon Concentrations and THM-Formation Potentials in Claytor Lake

Alum Dose (mg/L)	pH			DOC (mg/L)			DOC Removal (%)		THMFP (μg/L)			THMFP Removal (%)	
	Average	Range	No.	Average	Range	No.	Average	Range	Average	Range	No.	Average	Range
						Peak Creek Site							
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
						Claytor Dam Site							
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

APPENDIX

TABLE A1

Procedure for Calculation of Hydrophobic and Hydrophilic Acid, Base, and Neutral Compounds

Compound	Calculation
Total Hydrophobic	Fractions I-IV*
Total Hydrophilic	Fraction IV
Hydrophobic Base	Fraction II†
Hydrophobic Acid	Fraction III†
Hydrophobic Neutral	A-C-D
Hydrophilic Base	Fractions IV-V
Hydrophilic Acid	Fractions V-VI
Hydrophilic Neutral	Fraction VI

*These calculations are applicable to DOC I-VI, THM I-VI, and ^{14}C-labeled fractions. Values must be in mass, such as mg, or as cpm, in order to use these calculations.

†Sample calculation for Fractions II and III:

$$\frac{(\text{Fraction II, mg/L})(0.05\ \text{L})}{\text{Total sample filtered, L}}$$

$$\frac{(\text{Fraction III, mg/L})(0.05\ \text{L})}{\text{Total sample filtered, L}}$$

TABLE A2

Raw Data Collected from Primary Productivity Studies*

Sample	Fraction Number	5/9/81	5/30/81	6/14/81	7/8/81	7/23/81	8/4/81
Background		19	25	16	12	14	18
Control		19	40	16	12	14	18
1 Hr†	1	90	85	100	116	79	73
	2	26	23				
	3	20	21				
	4	53	47				
	5	23	44				
	6	19	42				
2 Hr	1	155	94	228	181	117	109
	2	28	20	23	41	20	28
	3	41	27	45	41	22	21
	4	100	62	72	98	91	67
	5	66	55	38	73	66	58
	6	22	23	18	34	29	31
4 Hr	1	312	155	173	253	145	175
	2	98	44				
	3	44	40				
	4	147	115				
	5	111	32				
	6	49	24				

(continued)

TABLE A2 (continued)

Sample	Fraction Number	5/9/81	5/30/81	6/14/81	7/8/81	7/23/81	8/4/81
6 Hr	1	542(175)‡	216(150)	186(150)	310(150)	170(150)	215(150)
	2	114 (50)	44 (50)	43 (50)	76 (50)	34 (50)	99 (50)
	3	232 (50)	44 (50)	42 (50)	41 (50)	28 (50)	23 (50)
	4	420(100)	121(125)	65(125)	95(125)	99(125)	87(125)
	5	295 (30)	66(100)	35(100)	78(100)	82(100)	73(100)
	6	182 (20)	29 (50)	19 (50)	32 (50)	28 (50)	26 (50)

*Figures given in cpm/mL.

†Incubation times.

‡Sample volumes in mL shown in parentheses. These volumes were necessary in mass-balance calculations.

TABLE A3
Raw Data Collected from Primary Productivity Studies*

Sample	Fraction Number	5/9/81	5/30/81	6/14/81	7/8/81	7/23/81	8/4/81
Control		Bg†	Bg	Bg	Bg	Bg	Bg
1 Hr	1	12,425	9,000	12,630	15,570	9,750	8,250
	2	3,010	1,810				
	3	1,520	1,700				
	4	3,420	2,625				
	5	114	970				
	6	0	430				
2 Hr	1	23,800	10,320	31,770	25,410	15,450	13,650
	2	3,310	1,300	2,460	4,500	1,590	3,450
	3	5,160	2,790	6,360	4,540	2,260	1,800
	4	8,080	4,575	7,050	10,775	9,650	7,350
	5	1,422	1,490	2,220	6,100	5,160	5,000
	6	60	0	110	1,100	760	650
4 Hr	1	51,250	19,440	23,550	36,090	19,620	23,550
	2	13,150	4,260				
	3	6,660	3,390				
	4	12,760	11,225				
	5	2,766	370				
	6	596	0				
6 Hr	1	91,542	28,680	25,470	44,700	23,340	31,050
	2	19,080	5,320	5,690	10,830	4,340	14,000
	3	22,270	4,200	4,400	4,460	2,800	2,600
	4	40,080	12,000	6,150	10,425	10,675	10,350
	5	8,274	2,040	1,890	6,560	6,780	6,875
	6	1,984	110	130	1,010	700	400

*Measurements in cpm. Cpm = (cpm/mL - background) x sample volume (mL).

†Bg = Background.

TABLE A4

Raw Data and Primary Productivity in Claytor Lake*

Sample	5/9/81 (Cpm/300 mL)	5/30/81 (Cpm/150 mL)	6/14/81 (Cpm/150 mL)	7/8/81 (Cpm/150 mL)	7/23/81 (Cpm/150 mL)	8/4/81 (Cpm/150 mL)
Control	86	49	42	62	119	171
1 Hr	10,433	32,526	21,975	30,241	18,479	10,455
2 Hr	32,930	46,439	31,018	47,131	52,000	33,190
4 Hr	58,650	74,936	52,260	106,910	46,350	60,500
6 Hr	126,266	82,160	105,266	125,825	146,500	119,300
	96†	137†	151†	156†	256†	65†

*Method of calculation from Saunders et al. [1962].

†Productivity, (P), mg - c/m^3, calculated as follows:

$P = (r/R)(C)(f)$

where:

P = C-fixation, mg/m^3

$r - \frac{\text{cpm} \div \text{counting efficiency of scintillation counter}}{\text{fraction of total volume filtered}} = \text{dpm}$

R = total ^{14}C in system (5μCi)

C = concentration of ^{12}C from alkalinity, mg/m^3

f = factor to correct for increased use of ^{14}C over ^{12}C = 1.06.

TABLE A5

Distribution of P among Various Hydrophobic and Hydrophilic Organic Compounds in Peak Creek Water

Organic Compounds	5/9/81 (cpm)	(%)	5/30/81 (cpm)	(%)	6/14/81 (cpm)	(%)	7/8/81 (cpm)	(%)	7/23/81 (cpm)	(%)	8/4/81 (cpm)	(%)
Total Hydrophobic*	51,462	56	16,680	58	19,320	76	34,275	77	12,665	54	20,700	67
Total Hydrophilic*	40,080	44	12,000	42	6,150	24	10,425	23	10,675	46	10,350	33
Hydrophobic†												
Acid	22,270	43	4,200	25	4,400	23	4,460	13	2,800	22	2,600	13
Base	19,080	37	5,320	32	5,690	29	10,830	32	4,340	34	14,000	68
Neutral	10,112	20	7,160	43	9,230	48	18,985	55	5,525	44	4,100	20
Hydrophilic†												
Acid	6,290	16	1,930	16	1,760	29	5,550	53	6,080	57	6,475	63
Base	31,806	79	9,960	83	4,260	69	3,865	37	3,895	36	3,475	34
Neutral	1,984	5	110	1	130	2	1,010	10	700	7	400	4

*Percentages expressed as percentage of total.

†Percentages expressed as percentage of either total hydrophobic or total hydrophilic numbers, not as percentage of total organic pool.

TABLE A6

$CHCl_3$/DOC Ratios* Obtained from Chlorination of Peak Creek Samples

Fraction	4/4/81	5/9/81	5/30/81	6/14/81	7/8/81	7/23/81	8/4/81
I	76	97	55	54	70	97	77
II	49	21	5	6	8	3	6
III	10	4	29	42	167	82	2300
IV	40	66	44	18	20	69	72
V	5	38	4	22	39	48	75
VI	2	4	5	2	2	3	5
Total Hydrophobic	106	111	65	81	100	117	80
Total Hydrophilic	40	66	44	18	20	69	73
Hydrophobic Acid	10	4	29	42	170	82	2309
Hydrophobic Base	49	21	5	6	8	3	7
Hydrophobic Neutral	368	19	289	97	64	174	65
Hydrophilic Acid	18	97	3	69	59	162	129
Hydrophilic Base	55	84	56	17	6	80	72
Hydrophilic Neutral	2	4	5	2	2	3	50

*μg/DOC (mg).

TABLE A7

Observed Variation in Concentration* of DOC in the Fractionation of Peak Creek

Fraction	DOC	Sample Volume	DOC	Sample Volume	DOC	Sample Volume	DOC	Sample Volume
	3/9/81		4/4/81		5/9/81		5/30/81	
I	2.45	1.30	2.14	0.70	2.20	0.70	2.40	0.70
II	2.58	0.05	1.72	0.05	1.01	0.05	1.46	0.05
III	13.29	0.05	10.31	0.05	4.83	0.05	13.86	0.05
IV	0.80	0.70	1.14	0.60	1.23	0.40	1.32	0.60
V	0.78	0.60	1.00	0.20	0.95	0.20	0.93	0.20
VI	0.77	0.50	1.71	0.10	1.21	0.10	1.32	0.10
	6/4/81		7/8/81		7/23/81		8/4/81	
I	3.25	0.75	2.78	0.65	3.05	0.70	2.54	0.70
II	1.24	0.05	0.68	0.05	1.33	0.05	1.20	0.05
III	5.61	0.05	8.03	0.05	10.58	0.05	0.19	0.05
IV	1.67	0.65	1.33	0.50	1.71	0.45	1.32	0.40
V	1.64	0.20	1.37	0.25	1.26	0.20	0.81	0.20
VI	1.58	0.10	1.03	0.10	1.78	0.10	0.71	0.10

*Concentration of DOC expressed in mg/L.

†All sample volumes expressed in L.

TABLE A8

DOC Expressed as Mass* and Percent of Fractions Obtained at Peak Creek

Fraction	3/9/81 (mg)	(%)	4/4/81 (mg)	(%)	5/9/81 (mg)	(%)	5/30/81 (mg)	(%)	6/14/81 (mg)	(%)	7/8/81 (mg)	(%)	7/23/81 (mg)	(%)	8/4/81 (mg)	(%)
I	3.19		1.50		1.54		1.68		2.44		1.81		1.83		1.78	
II	0.13	4	0.09	6	0.05	3	0.07	4	0.06	3	0.03	2	0.07	4	0.06	3
III	0.66	21	0.52	35	0.24	16	0.69	41	0.28	11	0.40	22	0.53	30	0.01	<1
IV	0.56	18	0.68	45	0.49	32	0.79	47	1.08	44	0.67	37	0.77	42	0.53	30
V	0.46	14	0.20	13	0.19	12	0.19	11	0.23	9	0.28	15	0.25	14	0.16	9
VI	0.38	12	0.17	11	0.12	8	0.13	8	0.16	7	0.10	6	0.18	10	0.07	4
		69		110		71		111		74		82		100		47

*DOC mass (mg) = DOC (mg/L) x sample volume (L).

TABLE A9

Distribution of DOC among Various Hydrophobic and Hydrophilic Organic Compounds in Peak Creek Water

Fraction	3/9/81 (mg)	(%)	4/4/81 (mg)	(%)	5/9/81 (mg)	(%)	5/30/81 (mg)	(%)	6/14/81 (mg)	(%)	7/8/81 (mg)	(%)	7/23/81 (mg)	(%)	8/4/81 (mg)	(%)
Total Hydrophobic	2.63*	82	0.82	55	1.05	68	0.89	53	1.36	56	1.14	63	1.06	58	1.25	70
Total Hydrophilic	0.56	18	0.68	45	0.49	32	0.79	47	1.08	44	0.67	37	0.77	42	0.53	30
Hydrophobic Acid	0.13	5	0.52	63	0.24	23	0.69	78	0.28	21	0.40	35	0.53	50	0.01	1
Hydrophobic Base	0.66	25	0.09	11	0.05	5	0.07	8	0.06	4	0.03	3	0.07	7	0.06	5
Hydrophobic Neutral	1.84	70	0.21	62	0.76	72	0.13	14	1.02	75	0.71	62	0.46	43	1.18	94
Hydrophilic Acid	0.08	14	0.03	04.4	0.07	14	0.06	8	0.07	6	0.18	27	0.07	9	0.09	17
Hydrophilic Base	0.10	18	0.48	71	0.30	61	0.60	76	0.85	79	0.39	58	0.52	68	0.37	70
Hydrophilic Neutral	0.38	68	0.17	25	0.12	25	0.13	16	0.16	15	0.10	15	0.18	23	0.07	13

*Totals will not always equal sum of components because of imprecision in the analytical method.

TABLE A10

Raw THM Data from Chlorination of Samples Obtained from Peak Creek*

Fraction (THM)	4/4/81		5/9/81		5/30/81		6/14/81	
	$CHCl_3$	$CHCl_2Br$	$CHCl_3$	$CHCl_2Br$	$CHCl_3$	$CHCl_2Br$	$CHCl_3$	$CHCl_2Br$
I	163	12	213	6	133	6	174	4
II	6	†	7	†	<1‡	<1	<1	<1
III	9	†	3	†	34	<1	18	<1
IV	45	5	54	3	58	4	30	2
V	5	†	36	5	4	†	26	2
VI	4	†	5	†	7	†	3	†

Fraction (THM)	7/8/81				7/23/81				8/4/81	
	$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	$CHCl_3$	$CHCl_2Br$
I	195	4	†	†	295	6	†	†	198	5
II	<1	†	<1	<1	<1	<1	<1	†	<1	†
III	104	<1	<1	2	97	<1	†	†	58	2
IV	7	†	†	3	119	4	†	2	96	3
V	109	<1	3	<1	59	4	†	2	60	3
VI	2	†	2	3	5	2	†	†	4	-

*Measurements in μg/L (7-day contact, x mg/L chlorine dose).

†No peaks observed.

‡Peak observed but value obtained less than 1.

TABLE A11

THM Data Obtained from Chlorination of Peak Creek Fractions*

Fraction (THM)	4/4/81 $CHCl_3$ (μg)†	4/4/81 $CHCl_3$ (%)	4/4/81 $CHCl_2Br$ (μg)	5/9/81 $CHCl_3$ (μg)	5/9/81 $CHCl_3$ (%)	5/9/81 $CHCl_2Br$ (μg)	5/30/81 $CHCl_3$ (μg)	5/30/81 $CHCl_3$ (%)	5/30/81 $CHCl_2Br$ (μg)	6/14/81 $CHCl_3$ (μg)	6/14/81 $CHCl_3$ (%)	6/14/81 $CHCl_2Br$ (μg)
I	114		9	149		<1‡	93		4	131		3
II	4	4	§	<1	<1	§	<1	<1	<1	<1	<1	<1
III	5	5	§	<1	<1	§	20	22	<1	12	9	<1
IV	27	24	3	33	22	2	35	38	3	20	15	2
V	<1	<1	§	8	5	<1	<1	<1	§	5	4	<1
VI	<1	§	§	<1	§	§	<1	<1	§	<1	<1	§

Fraction (THM)	7/8/81 $CHCl_3$ (μg)	7/8/81 $CHCl_3$ (%)	7/8/81 $CHCl_2Br$ (μg)	7/8/81 $CHBr_2Cl$ (μg)	7/8/81 $CHBr_3$ (μg)	7/23/81 $CHCl_3$ (μg)	7/23/81 $CHCl_3$ (%)	7/23/81 $CHCl_2Br$ (μg)	7/23/81 $CHBr_2Cl$ (μg)	7/23/81 $CHBr_3$ (μg)	8/5/81 $CHCl_3$ (μg)	8/5/81 $CHCl_3$ (%)	8/5/81 $CHCl_2Br$ (μg)
I	127		2	§	§	177		4	§	§	139		4
II	<1	<1	§	§	<1	<1	<1	<1	<1	§	<1	<1	§
III	68	54	<1	<1	<1	44	25	<1	§	§	23	16	<1
IV	13	10	<1	<1	2	53	30	2	§	<1	38	27	<1
V	11	9	<1	<1	<1	12	7	<1	§	<1	12	9	<1
VI	§	§	§	<1	<1	<1	<1	<1	§	§	<1	<1	§

*7-day Cl_2 contact, 30 mg/L dose.

†All percentages express fraction of total of THM-formation potential of unfractionated water.

‡Peak observed but value obtained less than 1.

§No peaks observed.

TABLE A12

$CHCl_3$ Yields from Various Fractions of Peak Creek Water

Fraction	4/4/81		5/9/81		5/30/81		6/14/81		7/8/81		7/23/81		8/4/81	
	(μg)	(%)*	(μg)	(%)	(μg)	(%)	(μg)	(%)	(μg)	(%)	(μg)	(%)	(μg)	(%)
Total Hydrophobic	87	76	116	78	58	62	111	85	114	90	124	70	100	72
Total Hydrophilic	27	24	33	22	35	38	20	15	13	10	53	30	38	28
Hydrophobic Base	4	4	<1	<1	0.3	0.6	0.4	0.3	0.2	0.2	0.2	0.1	0.3	0.3
Hydrophobic Acid	5	6	<1	<1	20	35	12	11	68	60	44	35	23	23
Hydrophobic Neutral	78	90	114	98	38	65	99	89	45	40	80	65	77	77
Hydrophilic Base	0.5	2	7	21	0.2	1	5	25	11	85	11	21	12	32
Hydrophilic Acid	26	96	25	76	34	97	15	75	2	15	42	79	26	68
Hydrophilic Neutral	0.4	2	0.5	2	0.7	2	0.3	1	0.2	1	0.5	1	0.4	1

*All percentages express fraction of total THM-formation potential of unfractionated water.

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