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THE EFFECTS OF SEASONAL CHANGE, IMPOUNDMENT,  
AND STRATIFICATION ON TRIHALOMETHANE PRECURSORS

by

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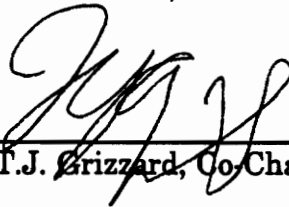
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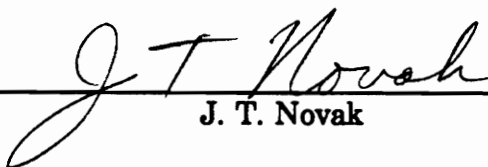
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(ABSTRACT)

The major objectives of this study were to investigate the effects of seasonal changes in Lake Manassas and its watershed (late winter to late summer), the impoundment of Broad Run, and the stratification of Lake Manassas on trihalomethane (THM)-precursors in Broad Run, upstream and downstream of the reservoir, and in Lake Manassas. An additional objective was to determine the molecular-size distributions of the dissolved organic carbon, and the THM precursors of the organic carbon pool in Lake Manassas during stratification.

Raw water samples were collected from March through August on Broad Run immediately upstream of the reservoir, at two sites in the reservoir-- one approximately 0.27 miles from the dam and the second, at a more central location, 0.73 miles from the dam, and on Broad Run 2.81 miles below the dam. During stratification two samples were collected from each lake site-- one from the epilimnion, and the second from the hypolimnion. All of the samples were size fractionated by ultrafiltration and chlorinated for determination of THMFP. The differences in THM-precursor characteristics were determined by assessing the differences in the total organic carbon (TOC) concentrations and THM-formation potentials (THMFPs) of the

various size fractions.

The TOC and THM concentrations generally increased from late winter to late summer at all stations. The concentrations in Lake Manassas and in Broad Run below the dam were consistently higher than those observed in Broad Run upstream of the lake, indicating that impoundment causes an increase in levels of THM precursors. In addition, during stratification higher THM yields were produced by the predominantly low-molecular-weight precursors ( $< 5,000$ ) in the epilimnion of Lake Manassas, while the predominantly high-molecular-weight precursors ( $> 5,000$  daltons) were low-yielding-THM precursors.

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## **I. INTRODUCTION**

### **Lake Manassas**

Lake Manassas is formed by the impoundment of Broad Run in Prince William County, Virginia, approximately sixteen miles west of the City of Manassas. The vast majority of flow to the reservoir, therefore, is contributed by Broad Run. The lake is a 706 acre, eutrophic body of water with a capacity at full pool of approximately 4.2 billion gallons (15.8 million cubic meters) (Laufer, 1986). It is presently providing 1 million gallons per day (MGD) of potable water to the City of Manassas with expectations of increasing to 8 MGD in the near future.

### **Trihalomethanes**

In 1974, Rook (1974) discovered that trihalomethanes (THMs) are produced by the chlorination of natural waters and are present in public drinking water supplies. This finding accelerated research related to various aspects of THM formation because of the potentially carcinogenic effects of THMs, particularly chloroform.

Aquatic humic substances are products of plant decomposition, which may be leached from the soil or introduced directly into the water from the decay of aquatic plants or floating leaves and debris. Humic material, algal biomass, and algal extracellular product yield THMs upon chlorination. Because of the ubiquitous nature of these and other organic THM precursors in surface waters, and due to the common

practice of chlorinating drinking water supplies, the problems associated with THM formation are widespread. Chlorine is probably the most effective oxidant used to disinfect a drinking water supply, thereby reducing the incidence of waterborne diseases. It is important, therefore, to understand the characteristics of THM formation potentials (THMFP) within the watershed to reduce the occurrence of THMs without the elimination of chlorination.

The objectives of this research were to determine, under laboratory conditions:

1. the effects of seasonal changes on THM precursors from late winter to late summer;
2. differences in THM-formation potentials (THMFPs) of water from Broad Run and Lake Manassas to determine the effects of the impoundment of Broad Run;
3. the differences in THM yields in the surface and bottom waters of Lake Manassas when the Lake was stratified;
4. the molecular-size distribution of the THM precursors in Lake Manassas during stratification.

## II. LITERATURE REVIEW

It has been demonstrated that chlorination of natural waters during water treatment results in the formation of trihalomethanes (THMs) (Rook, 1974, 1976; Bellar *et al.*, 1974). THMs are a serious public health concern because chloroform has been shown to be an animal carcinogen (Morris, 1975), and, although fewer data are available, the brominated THMs are suspected to be carcinogenic as well (Arguelló *et al.*, 1979; Schnoor *et al.*, 1979). The current research investigated the sources of THM precursor material within Lake Manassas and its major tributary, Broad Run. A necessary component of this research is to understand characteristics of THMs including aspects of their formation, the composition of precursor material, and the variations in precursors with respect to season, impoundment, and molecular size. A discussion of related research concerning these topics will be presented in this chapter.

### Trihalomethanes

In the mid-1970's, Rook (1974, 1976) and Bellar *et al.* (1974) presented data confirming the association between organic matter and THM formation in chlorinated waters. In 1974, Rook found a good correlation between THM formation and color intensity in the Meuse and the Rhine Rivers. The coloration was subsequently determined to be caused by humic substances in the raw water. Rook (1976) presented further data which demonstrated that THM production from fulvic acid was linear in

concentration up to 250 milligrams per liter (mg/L) total organic carbon (TOC). In addition, Bellar *et al.* (1974) found a direct correlation between the TOC concentration and the concentration of halogenated organics forming upon chlorination of the source water. They concluded that a chemical reaction was taking place between free chlorine and organic compounds present in the water.

In 1975 the Environmental Protection Agency (EPA) conducted an inclusive survey of the nation's drinking waters (Symons *et al.*, 1975). In general, THMs were not found in the raw waters, but some form of THM was detected in all of the finished waters sampled across the United States. The survey established that THMs were widespread in chlorinated drinking waters and resulted from chlorination.

These findings are of great significance because (1) organic matter in water supplies is ubiquitous, (2) chlorinating drinking water supplies is common place, and (3) THMs are potentially carcinogenic. The four most common trihalomethanes are chloroform ( $\text{CHCl}_3$ ) a known animal carcinogen, and dichlorobromomethane ( $\text{CHBrCl}_2$ ), dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ), and bromoform ( $\text{CHBr}_3$ ) which are suspected carcinogens (Arguello *et al.*, 1979; Schnoor *et al.*, 1979). In response to the increasing knowledge concerning THMs, the federal government has set a maximum contaminant level (MCL) of 0.10 milligrams per liter (mg/L) for any drinking water supply serving over 10,000 people. However, it is expected that the EPA will promulgate an even more stringent standard by 1991.

## Haloform Reaction

The process whereby the chlorination of water supplies containing organics produces THMs is believed to be the haloform reaction (Rook, 1976; Morris and Baum, 1978; Trussell and Umphres, 1978). It is a base-catalyzed series of halogenation and hydrolysis reactions. Several factors, including precursor concentration, chlorine dose, bromide concentration, reaction time, pH and temperature, influence this reaction and determine the amount of THMs formed.

Effect of precursor concentration. Different investigators have demonstrated that increased concentrations of THM-precursor material, upon chlorination, result in higher chloroform and total THM (TTHM) concentrations, provided that available chlorine is not limited (Stevens *et al.*, 1976; Babcock and Singer, 1979). It has been implied that the organic content of the raw water may be an indirect indication of precursor concentration and/or THM formation potential (THMFP) (Morris and Baum, 1978; Rook, 1976). However, Hoehn and Randall (1977) suggested that the more significant variables may be the particular structure and nature of the precursors.

Effects of chlorine dose. Figure 1 summarizes the three main regions where chlorine dose and THM formation maintain a consistent pattern (Trussell and Umphres, 1978). Initially, the immediate chlorine demand is exerted by inorganic material, presumably sulfide, iron (II), ammonia, and reduced manganese. In this first region trace concentrations of THMs are formed. Once the immediate chlorine demand is satisfied, the chlorine reacts with available organic material and a nearly linear relationship between chlorine dose and the THM level achieved is demonstrated



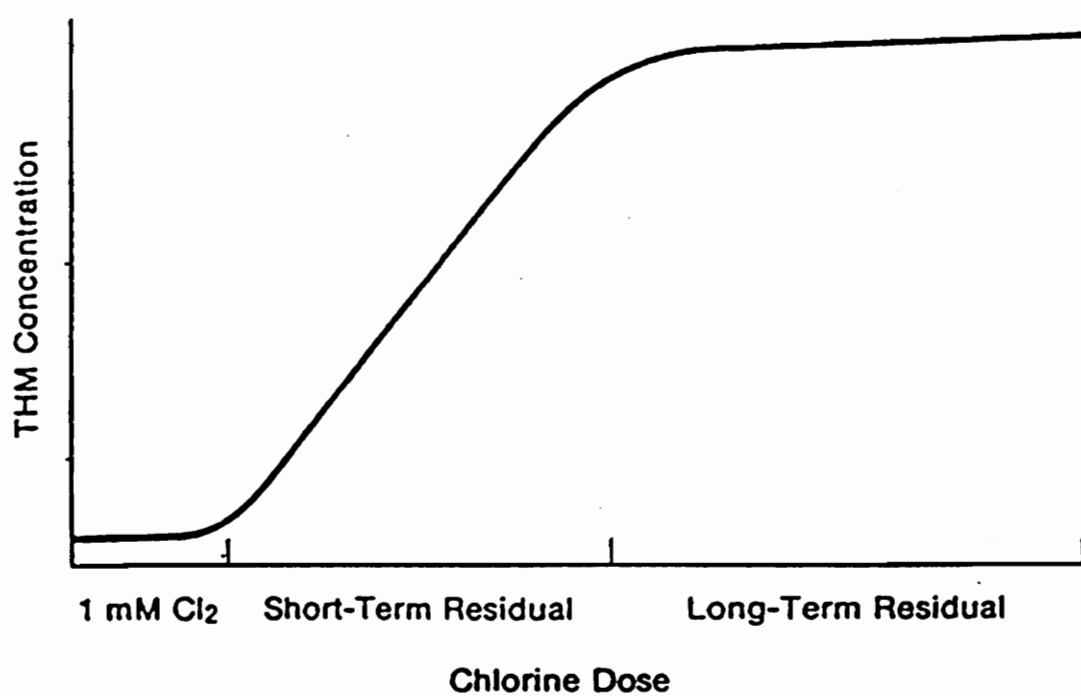


Figure 1. Influence of Chlorine Dose on THM Formation (Trussell and Umphres, 1978).

(Trussell and Umphres, 1978; Rook, 1976). Trussell and Umphres (1978) also determined that chlorinating at a dose substantially above that required to maintain a long-term residual results in minimal increases in the levels of THMs formed in the third region. Moreover, excess chlorine was more likely to cause THM speciation changes favoring the less brominated compounds.

Effects of bromide concentration. Bromide may occur naturally in waters or bromine may be a contaminant in the chlorine compound applied to the water. In the presence of chlorine, bromide is oxidized to intermediates which participate in the halogenation step of the haloform reaction much more effectively than chlorine (Trussell and Umphres, 1978). When bromide is available, there is a substantial reduction in chloroform concentrations with increasing concentrations of the brominated trihalomethanes (Bunn *et al.*, 1975). Furthermore, the presence of bromide increases the yield of TTHMs for a given chlorine dose, and increases the rate of the THM development as well (Trussell and Umphres, 1978).

Effects of pH, reaction time, and temperature. The haloform reaction is dependent on pH, such that higher THM concentrations result at alkaline pH levels. Rook (1976) found the reaction to be markedly increased at pH values from 8 to 10 but noted much less influence when it varied within one unit of pH 7. In general, the rate of formation of THMs increases with an increase in pH (Stevens *et al.*, 1976; Trussell and Umphres, 1978).

Similarly, trihalomethane concentrations have been shown to increase when the contact time between chlorine and the THM precursor material is increased (Rook, 1976; Babcock and Singer, 1979) and also when the reaction temperature is raised

(Rook, 1976; Stevens *et al.*, 1976). This temperature effect may partially explain seasonal variations in THM concentrations in finished water supplies having increased concentrations in the warmer months (Arguello *et al.*, 1979).

### Trihalomethane Precursors

Humic Substances. Humic substances are nonvolatile amorphous, hydrophilic and acidic complexes formed largely as a result of microbial activity on plants and animal material. A functional model proposed by Trussell and Umphres (1978) (Figure 2) is in agreement with other investigators' representation of the humic structure (Rook 1974; Rook citing Dragunov (1961) and Kleinhempel (1970), 1977). Basically, it is a shapeless polyhetero condensate of organic moieties with certain functional groups such as: carboxylic acids, phenolic and alcoholic hydroxyl groups, and keto functional groups extending from its surface (Thurman, 1985).

Aquatic humic substances are comprised of fulvic acids and humic acids; the latter often form aggregates and colloids with inorganic substances. It was determined by X-ray diffraction, possibly the most accurate sizing method, that fulvic acids were typically 500 to 2,000 daltons and humic acids ranged from 2,000 to 5,000 daltons (Thurman, 1985). This method, however, generates considerably lower molecular weights than ultrafiltration, which is the method used in the current research. Analysis by ultrafiltration resulted in a size range of 5,000 to 20,000 daltons for aquatic humic substances (Thurman, 1985). Amy *et al.* (1990) determined that the molecular weight distribution of aquatic humic and fulvic acids ranged from 500 to 10,000

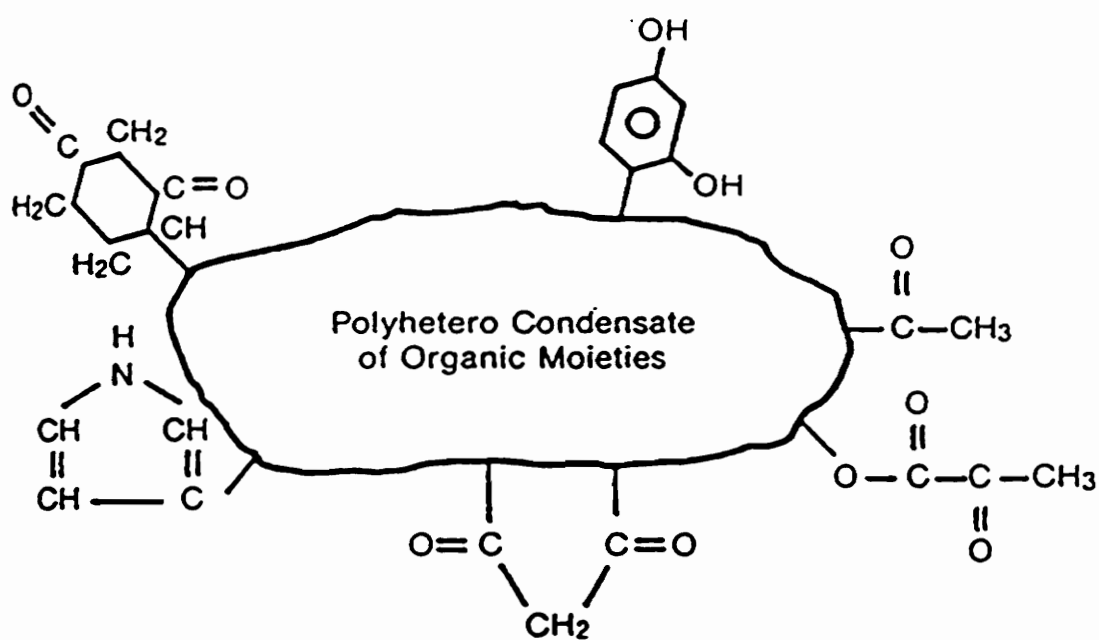


Figure 2. Model Humic Compound (Trussell and Umphres, 1978).

daltons, though, and Trussell and Umphres (1978) concluded that fulvic acids were "probably" in the 100 to 1,000 dalton range, and humic acids were likely to be 100,000 daltons or higher. The elemental composition of humic substance is approximated by 50 percent carbon, 4-5 percent hydrogen, 35-40 percent oxygen, 1-2 percent nitrogen, and less than 1 percent sulfur plus phosphorus (Thurman, 1985). Most likely no two humic molecules are exactly alike (Rook citing Dubach and Mehta (1963), 1977).

In general, humic substances originate in plant and soil systems where they are leached by interstitial water of soil into rivers and streams. Lake humics are derivatives of these allochthonous inputs but may also consist of a significant portion of autochthonous contributions via biological activity. Humic compounds are relatively resistant to microbial degradation and tend to persist in aquatic systems with long residence times (Wetzel, 1975).

Aquatic humic substances, as a whole, represent the largest fraction of natural organic matter in natural waters and comprise 40 to 60 percent of the dissolved organic carbon (Thurman, 1985). The distribution of fulvic and humic acids in a representative body of natural water is depicted in Figure 3. Thurman's approximation of the literature shows that aquatic humic substances are the dominant group of natural organic compounds in water, where fulvic acids represents 40% and humic acids accounts for 10%. Typical concentrations of humic substances in uncolored streams, rivers, and lakes range from 0.50 to 4.0 mg C/L (Thurman, 1985) and concentrations as high as 50 mg/L have been found in some colored waters (Gjessing & Samdal, 1967).

The amount of humic matter in a body of water is intrinsic evidence of the level

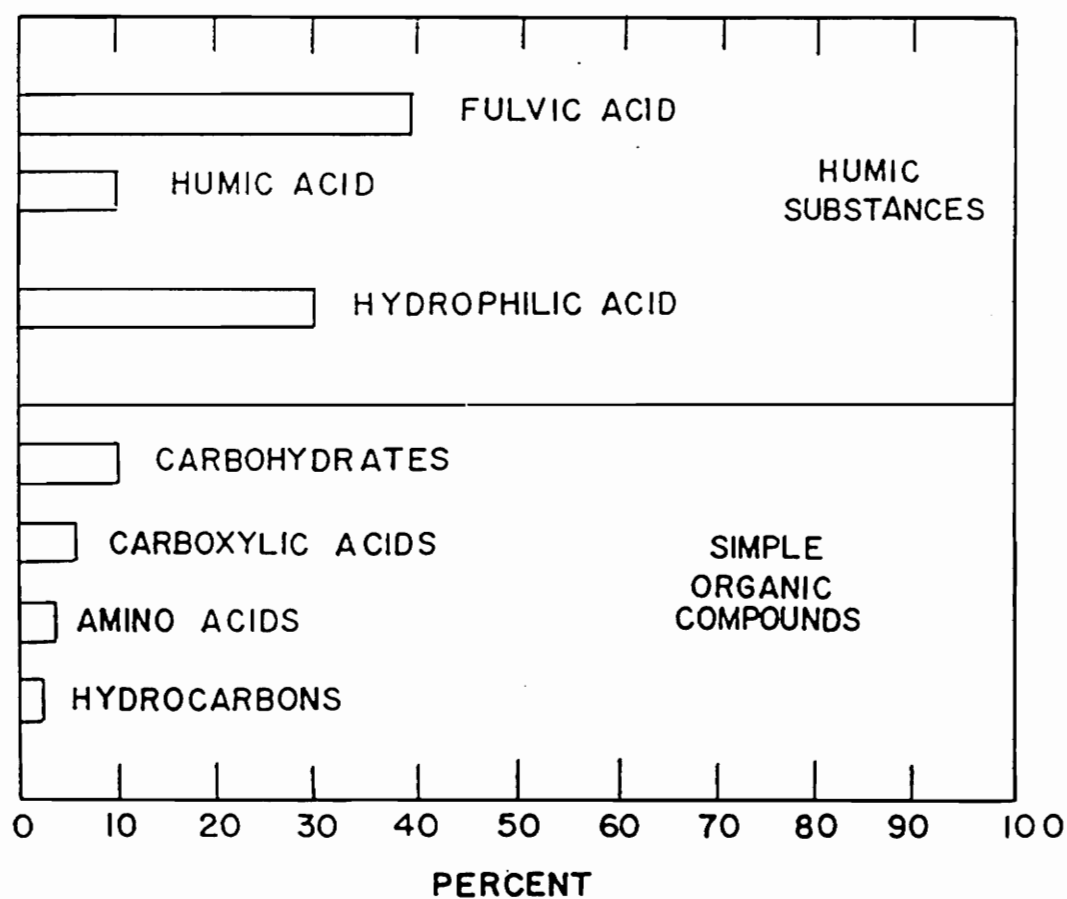


Figure 3. Dissolved Organic Carbon (DOC) Histogram for an Average River Water with a DOC Concentration of 5 mg/L (Thurman, 1985).

of water quality and is often measured as color or COD. From the points of view of aesthetics and good water treatment, humic concentrations should be kept low. Of greater significance is the correlation between the presence of humic substances and trihalomethane formation potential (THMFP) in chlorinated waters (Rook, 1976).

Algae and other sources. Algal productivity contributes considerably to aquatic organic material and may be a significant source of THM precursors. Morris and Baum (1977) were the first investigators to show that components of algae, as well as naturally occurring humic substances, can be sources of THMs in the chlorination of water supplies. After 100 hour contact with 40 mg/L aqueous chlorine, "soluble" chlorophyll at a concentration of 1.7 mg/L yielded up to 230 ug/L chloroform at pH 10. Hoehn *et al.* (1980) furthered these findings by presenting laboratory data illustrating the significance of both algal mass and algal extracellular product (ECP) as THM precursors. They determined that these autochthonous precursors, upon chlorination, can yield at least as much chloroform per unit organic carbon as has been reported from studies of humics. However, the THM yields (ug/L THM/mg/L TOC) of algal cells and algal ECP are generally lower than for other precursor material, but exceptions have been noted (Randtke *et al.*, 1987).

Limited information is available, although, it is thought that bacteria, decaying aquatic vegetation, and possibly animals and sediments are also sources of THM precursors (Randtke *et al.*, 1987; Cooke and Carlson, 1989). The relative THM-yielding capacities of individual precursor sources, however, are unknown.

## Variations in Precursors

Various factors influence THMs precursor structure and concentration; including season and stratification, impoundment, and molecular size of the precursor material.

Season and Stratification. Several investigators (Hoehn *et al.*, 1977; Arguello *et al.*, 1979; Veenstra and Schnoor, 1980) identified a general, seasonal trend toward lower THM levels during colder months over the course of a year. Veenstra and Schnoor (1980) attributed the lowest production of THMs in the Iowa River to the corresponding time of ice cover which reflects the period of minimum runoff and minimum biological activity in the river. These seasonal patterns result from the quantity and nature of the organic precursors and not from pH and temperature conditions which were controlled by the investigators. The yearly pattern for the Iowa River showed the lowest yields (ug/L THM/mg/L TOC) during the late fall and early winter months, increasing yields during late winter and early spring, with a peak yield during early summer.

Similarly, Hoehn *et al.* (1977) found the Occoquan Reservoir's THM concentrations increasing in summer, peaking in July, and declining thereafter until mid January, although there were highly variable results within any given month. They surmised that the variability could be a result of a multitude of factors such as rainfall intensity, degree of mixing in the reservoir, and extent of algal blooms. Arguello *et al.* (1980) attributed the lower THM concentrations in winter to lower precursor levels, different chemical nature of the precursors, and/or to lower water



temperature at the fourteen utilities studied.

Oliver and Visser (1980), however, determined that in a specific molecular weight fraction, seasonal variations and changing aqueous environment had little effect on chloroform concentrations. Furthermore, Randtke (1987) found higher winter (March 7, 1986) THM yields in four Kansas lakes due to the "decomposition of the more biodegradable precursors during the summer and fall, leaving the more resistant (and more potent) precursors in the lake during the winter and early spring." It could also be possible that the runoff into the lakes in the winter carried higher-yielding THM precursors.

One might expect stratification to have an effect on THM formation potential due to decreased temperatures in the hypolimnion retarding the rate of THM formation, the influence of reduced substances (iron, manganese, sulfide, and ammonia) on chlorine demand, and the influence of eventual turnover events on algal population growth. Characteristically, the epilimnion is well mixed and remains aerobic during stratification. However, the hypolimnion turns anoxic or anaerobic; therefore, substances from the sediment are reduced. Randtke *et al.* (1987) determined that the dissolved THM formation potential is strongly and positively correlated with the dissolved organic carbon (DOC) concentration and color for both aerobic and anaerobic conditions in the laboratory. Interestingly, the aerobic samples had lower DOC but more color, and produced higher THM yields than the anaerobic samples. Randtke *et al.* gave two possible reasons for this: One, some of the organic matter in the anaerobic samples may have been non-colored, biodegradable material (carbohydrate-like) which was poor precursor material that was degraded in the aerobic

samples, and, two, the aerobic samples seemed to have "browning" reactions which may have resulted in structural changes producing compounds more conducive to THM formation. The data suggest that the precursors released from organic matter under aerobic conditions yield appreciably more THMs than those released under anaerobic conditions. Regardless of these findings, Randtke *et al.* determined that even when the Kansas lakes were strongly stratified (top to bottom temperature gradients of at least 3 degrees Celsius and hypolimnetic oxygen concentrations of no more than 2.0 mg/L), the concentrations of DOC, TOC, and THMFP were nearly identical in the top and bottom samples.

Impoundment. Gjessing and Samdal (1967) demonstrated that within the watercourse of Trehorningen, Norway, a series of stream connected lakes, there is a decrease in color (correlated with humus) downstream. In the lakes, the decrease was attributed primarily to biological processes and appeared to be correlated with the time of storage. In an indirectly related study, Randtke (1987) showed that average THM precursor concentrations were higher in streams feeding the Kansas lakes than in the outlet streams, indicting that the lakes were net sinks for precursors. He also discovered that the average TOC and THM yields in all of the stream samples were slightly higher than those of the lake samples.

Contrary to these findings, Rook (1974) claimed that the humic substances of the Meuse and Rhine Rivers were very resistant to biological decay and did not appreciably diminish in concentration during impoundment. In addition, Cook found evidence that in Salt Lake County, Utah, impoundment of surface water actually increased THM-precursor concentrations (Randtke, 1987 citing Cook *et al.*. 1984).

Schnoor *et al.* (1984) discovered a slight tendency for greater THM yields downstream from the Coralville Reservoir in eastern Iowa. This effect could have been due to biological degradation and sedimentation of the higher-molecular-weight compounds, which were found in this study to be less reactive with chlorine.

Molecular Size. Molecular sizes are often expressed in atomic mass units or daltons although some methods (ultrafiltration and gel permeation chromatography) actually measure the size, not the weight, of the molecules. The extrapolation of molecular size data to molecular weight data is not exact due to different molecular geometries, however, the current research will assume the two are interchangeable. Some amount of precision may be forfeited as a result; nevertheless, useful data may be generated, and valuable comparisons can be made between studies using molecular-sizing methods.

The effect of molecular weight (MW) of trihalomethane precursor material on THM formation also seems to be site specific. In a broad analysis of related research, however, Randtke *et al.* (1987) made these generalizations:

1. Humic acids generally produce a higher yield of THMs than fulvic acids (lower MW), but exceptions have been noted;
2. THM yields increase with increasing MW.

(The majority of THM precursors in most water supplies, however, are of low MW, rendering the contributions of the high MW molecules inconsequential. Also, the high MW fraction is more readily removed during treatment.)

Research by Joyce *et al.* (1984), which involved humic samples from three regions in Massachusetts with dissimilar geographic and geomorphic natures,

demonstrated that the higher MW fractions are more reactive toward chlorine per unit carbon. Using molecular weight exclusion groups of >50,000; >10,000; >5000; >1000; and >700; the investigators showed that the MW fractions of 5000 to 10,000 contributed most to chloroform formation, whereas the fraction of <1000 MW contributed the least. The different formation potentials for the various MW fractions within each sample may be attributable to structural differences existing among the fractions with respect to functional group content (Joyce *et al.*, 1984).

In contradiction, Schnoor *et al.* (1979) found that 75 percent of THMs formed upon chlorination of Iowa River water were derived from organics less than MW 3000 and 20 percent on the average were derived from compounds of less than MW 1000. In general, THMs (TTHM) were formed in the MW ranges where the greatest concentration of TOC was detected, but yields were larger for the organics less than molecular weight 1700.

From the previous discussion, it is obvious that caution must be utilized in comparing and/or extrapolating results from one study to another. Since THM formation is dependent upon chlorine dosage, pH, time, temperature, bromide concentration, as well as site specific environmental factors, THM research may require individual, regionalized solutions.

### Molecular Size Determinations

#### Comparison of gel permeation chromatography, ultrafiltration, and XAD resin.

Both gel permeation chromatography (GPC) and ultrafiltration are laboratory

techniques that define apparent molecular weight (AMW). In a comparison of the two methods, Amy *et al.* (1985) found that both provided comparable trends in the relative molecular weight distribution of dissolved organic matter. However, GPC generally indicated somewhat higher molecular weights than ultrafiltration and was affected more by pH conditions. Although neither GPC nor ultrafiltration can provide absolute values of molecular weight, they do provide an "index" of AMW that can be used for relative comparisons (Collins *et al.*, 1986).

Gel permeation chromatography separates by the size of the molecule. In principle, smaller molecules penetrate into the pores of the gel and take a longer time to come out of the column; however, in practice, this is not always the case. A large molecule, which is too big to penetrate the pores, may adsorb onto the gel thus increasing its retention time which would indicate a smaller molecule. On the other hand, ion exclusion may give a false indication of a larger molecule. Aquatic humic substances are negatively charged molecules, and the gels also have some negative charge. This creates a potential for mutual repulsion where a small molecule is excluded from the gel, resulting in a shorter retention time. These complications may be lessened or altered with pH buffering (Thurman, 1985).

Like GPC, ultrafiltration actually measures size rather than molecular weight. Ultrafiltration concentrates and fractionates humic substances with porous membranes. The major drawback with this method is the potential for adsorption of solutes onto the membranes. Sinsabaugh (1985) provided a good evaluation of ultrafiltration performance and found that the replicability of the results was good.

When nonionic XAD resins are used for fractionating organic matter, the

mechanism of adsorption involves weak, physical forces, and the solutes desorb quantitatively. In general, the literature suggests that the resins adsorb and desorb efficiently, although care must be taken to keep them clean to minimize dissolved organic carbon (DOC) bleed (Thurman, 1985). In general, fractionation with XAD resins is considered to be the best method for determining molecular-size distributions.

For this research project, the ultrafiltration method was utilized because of past proven performance, availability, and for economic reasons.

### III. METHODS AND MATERIALS

#### Overview

This chapter describes Lake Manassas and its watershed, the experimental design, and the analytical methods used for the characterization of organics distribution in the lake and Broad Run. Samples were collected from the surface and bottom strata of the reservoir when it was stratified, and only from the surface when it was not. Samples were collected also from Broad Run at the sites of inflow and outflow to the reservoir. The organic matter in these samples was fractionated by ultrafiltration, and the fractions were subsequently chlorinated and analyzed for trihalomethane formation potential (THMFP).

#### Lake Manassas

The following information has been obtained from Laufer's masters thesis, Nutrient Dynamics in the Lake Manassas (Virginia) Watershed (1986).

Lake Manassas is located in Prince William County, Virginia, approximately 16 miles west of the City of Manassas. The lake is a 706 acre public water supply for Manassas, formed by the damming of Broad Run. Its watershed drains approximately 46,500 acres of rural land (either forested, pastureland, or used for agricultural purposes) that is expected to undergo rapid development in the next twenty five years. Currently, 803 acres of Lake Manassas waterfront is being transformed into a planned

community and resort complete with several golf courses and a convention center. The impact of this development on the lake with respect to eutrophication and algal growth is yet to be seen.

Laufer's data from October, 1984 through April, 1986 indicated that Lake Manassas is eutrophic with average raw water turbidity of 2.5 to 3.5 NTU. In the same study, however, lake productivity (determined by chlorophyll a concentrations and Secchi disk transparency) as a whole was not very high. Algal blooms have previously occurred in the reservoir, although, none were evident during Laufer's two-year study.

Some significant morphometric parameters of Lake Manassas defined by Laufer are listed in Table 1. The shoreline development index is defined to be "the ratio of the length of the shoreline to the length of the circumference of a circle of area equal to that of the lake" (Wetzel, 1975). The shoreline development index is indicative of the potential for greater development of littoral communities in relation to the volume of the lake (Wetzel, 1975).

### Experimental Design

Figure 4 shows the locations of the individual sampling sites in Lake Manassas and its major tributary, Broad Run. (Site ST 30 is not in Figure 4; it is 2.81 miles below the Lake Manassas Dam.) Two sites within Lake Manassas, one 0.27 miles from the dam (LM 01) and the other at a more central location 0.73 miles from the dam (LM 04), were chosen based on comparability and stratification potential. The surface waters of both sites were sampled four times during the study period from March to



Table 1. Morphometric Features of Lake Manassas (Laufer, 1986)

Parameter	Metric Units	U.S. Customary Units
Area	2.86x10 <sup>6</sup> m <sup>2</sup>	706 acres
Volume	1.58x10 <sup>7</sup> m <sup>3</sup>	4.2x10 <sup>9</sup> gal
Mean Depth	7.7 m	25 ft
Maximum Depth	16.8 m	55 ft
Shore Line	26.5 km	42.6 mi
Length	3.7 km	2.3 mi
Shoreline Development Index SDI = $\frac{\text{Shore Length}}{2(\pi \text{ Area})}^*$	4.4	4.4
----- Hydraulic Retention Time (Volume/Rate of Outflow) = 123 days*		

\* Assumed inflow = outflow.

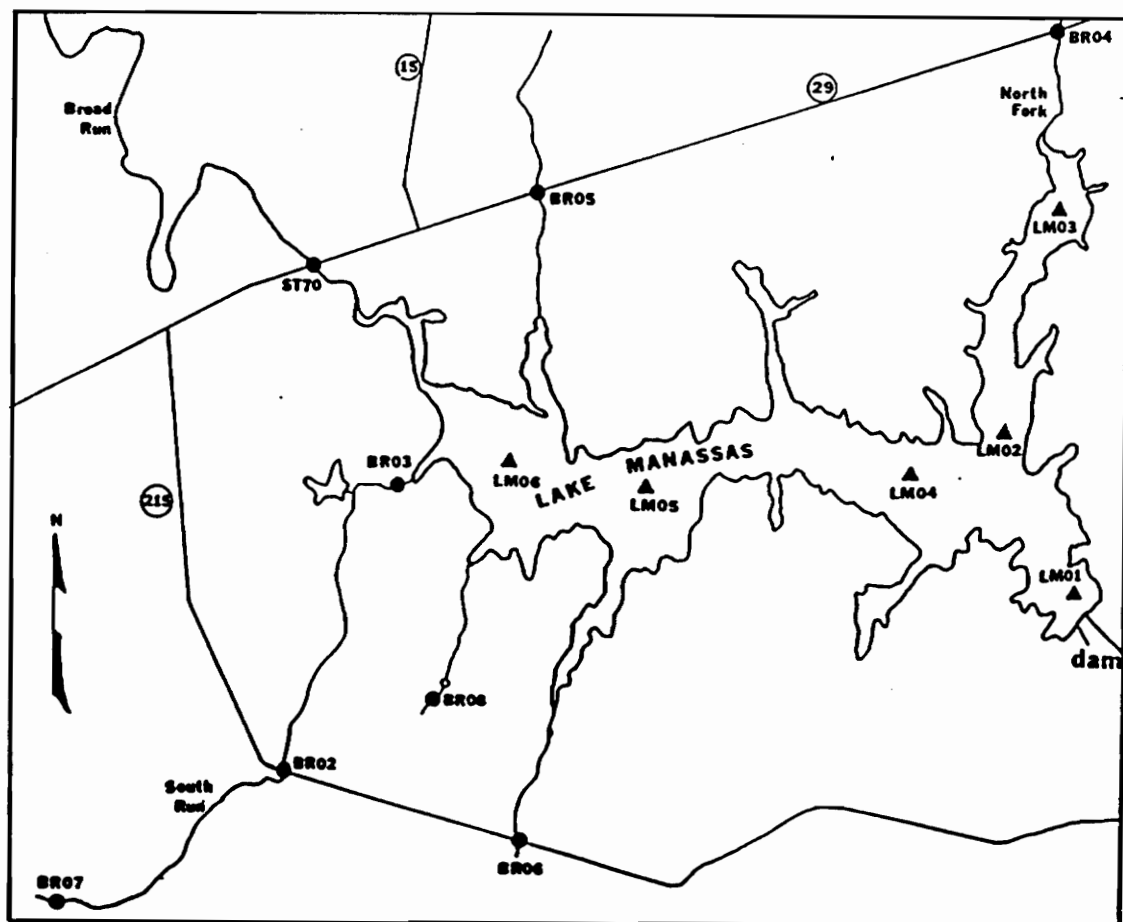


Figure 4. Sampling Sites on Lake Manassas and Its Tributaries (Laufer, 1986).  
(Sampling Sites are Designated by the Occoquan Watershed Monitoring Laboratory.)

August 1989, and the hypolimnetic waters were sampled twice following summer stratification. Prior to stratification the reservoir was well-mixed; therefore, it was conjectured that there would be no notable differences between the epilimnetic and hypolimnetic waters. The two additional sampling sites on Broad Run, ST 70 (3.3 miles from the dam at Buckland) and ST 30 (near Bristow), were sampled four times in conjunction with the lake surface water sampling.

All samples were collected during dry weather periods to eliminate the influences of runoff. The Occoquan Watershed Monitoring Laboratory (OWML) staff was responsible for raw-water sample collection and transport to the Environmental Laboratories at Virginia Tech in Blacksburg, Virginia, where the analyses were conducted.

The samples were shipped in one-quart, plastic containers. All samples were subsequently filtered through pre-combusted Gelman glass-fiber filters (type A/E) within two days of collection. Filtering separated particulate and dissolved matter and helped prevent agglomerations of organic matter in the samples. The filtrate was either processed immediately or refrigerated in acid-washed, glass containers with Teflon seals.

The filtered samples were fractionated according to molecular size by the ultrafiltration method. Each size fraction and each raw sample were analyzed for total organic carbon (TOC) concentrations, then buffered to pH 7 and dosed with chlorine. The THM concentration were determined after seven days.

## Sample Analysis

Glassware Preparation. All glassware used was acid washed in chromic acid, rinsed thoroughly with carbon-free water, and dried in an oven at 105° C. The glass vials were capped immediately following their removal from the oven.

Size Fractionation. Filtrate from the glass-fiber filters was passed through four, Amicon (Danvers, Massachusetts) series YM and one series YC ultrafilters. Table 2 summarizes the ultrafilters specification data.

Prior to use, the ultrafilters were soaked for one hour in carbon-free water which was changed every 20 minutes. After this initial period of soaking (during which contaminating organic matter was leached), the filters were mounted on the ultrafiltration units and flushed several times with carbon-free water. Flushing continued until the TOC concentrations of the filtered carbon-free water was approximately the same (to within 0.05 mg/L) as that of the unfiltered carbon-free water. The sample water (200 ml) was then placed in the ultrafiltration cells, and 40 mL was wasted prior to collection for analysis. Cleaned filters, when not being utilized, were stored in sodium azide solution (1 g/L) to prevent bacterial growth on them.

Ultrafiltration of the water samples was performed in stirred, 200 mL Amicon ultrafiltration cells under a pressure of 2.8 kg/cm<sup>2</sup> nitrogen at room temperature (approximately 25° Celsius). The fractionated samples were collected in 30 mL vials and analyzed with a Dohrmann/Envirotech Model DC-54 Ultralow Level Organic Carbon Analyzer (replicates to within five percent) on the day of fractionation.

Table 2. Pore Size and Nominal Molecular Weight Exclusion Limits of Ultrafilters (Carlson, 1988)

Membrane	Approximate Pore Size (nm)	Nominal Molecular Weight Exclusion Limit (daltons)
YC05	1.1	500
YM2	1.4	1,000
YM5	1.5	5,000
YM10	1.6	10,000
YM30	2.1	30,000
YM100	5.1	100,000

Duplicate samples were collected in amber-colored, glass bottles with Teflon seals and refrigerated for subsequent THMFP analysis.

THMFP Determinations. The duplicate water samples, including raw water samples and glass-fiber-filtered samples, were chlorinated at a chlorine:TOC weight ratio of 3:1, and buffered to pH 7 with a pH 7 phosphate buffer solution. The samples were sealed headspace-free with Teflon septa and screw caps in 40-mL, amber vials and incubated in the dark at room temperature for seven days. At the end of the incubation period, sodium sulfite was added to halt the haloform reaction. In addition, nitric acid was added to reduce the pH, thus preventing the hydrolysis of THMs from organic halide intermediates. These samples were refrigerated until the gas chromatographic analyses could be performed (within 30 days).

The THMFP analysis was performed using the purge-and-trap method described in Part 514 Standard Methods, 15th Edition. A Tracor (Austin, Texas) Model 560 gas chromatograph with Tracor LSC-2 purge-and-trap module and a Hall electronic conductivity detector was used to determine THM concentrations. Duplicate samples were analyzed to ensure reproducibility, but if the duplicate analyses were not within 10 percent of one another, a third analysis was performed. In addition, organic-free water blanks were used to monitor for any background THM contributions.

#### IV. RESULTS AND DISCUSSION

In this section, the data accumulated during the study period from March through August, 1989, will be presented and discussed. The specific sampling dates before the lake stratified were March 15 and April 26, 1989, and during stratification, samples were collected on June 28 and August 9, 1989. During March and April, the lake was assumed to be completely mixed, and, therefore, of uniform quality from top to bottom. Thus, only a surface sample was collected at each lake site (LM 04, LM 01). Once Lake Manassas stratified (indicated by near-zero hypolimnetic dissolved oxygen concentrations), two samples were collected from each lake site-- one from the epilimnion and the other from the hypolimnion. The dissolved oxygen and temperature profiles at sites LM 04 and LM 01 during the study period are presented in Figures 5-8. Figures 6 A and 8 A show that by June 28, 1989, the dissolved oxygen in the hypolimnion (15 feet and deeper) was depleted, and the lake was completely stratified.

Grab samples were collected from Broad Run, the major tributary to the lake, at the influent and discharge points of the lake (ST 70 and ST 30, respectively) on all four sampling days. (The sampling site locations were illustrated previously in Figure 4.) The ensuing evaluation of the data is intended to identify seasonal trends, effects caused by impoundment, variations due to stratification, and the distributions of molecular weight fractions, for both TOC and THMFP concentrations in the Lake Manassas/Broad Run system.

The concentrations of the individual THMs and total THM yields can be found

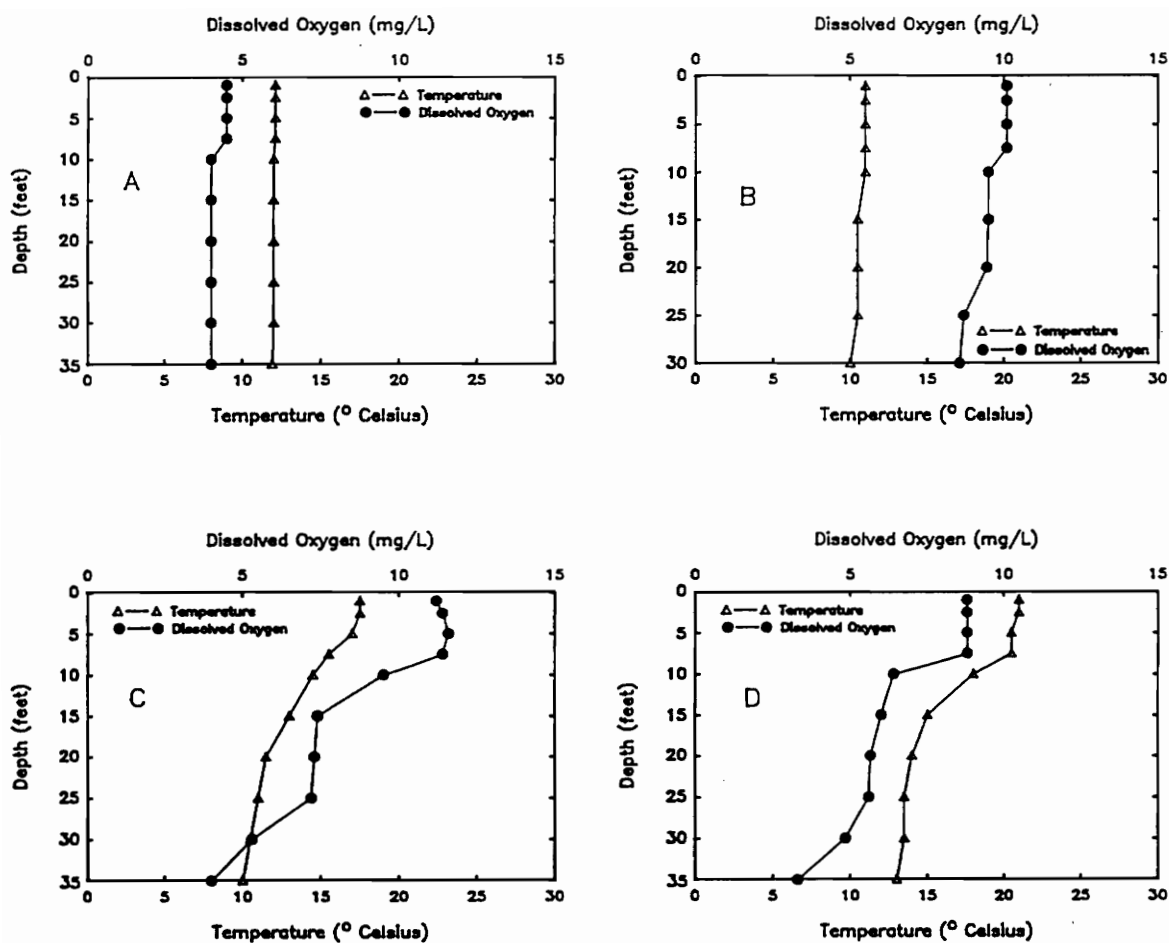


Figure 5. Dissolved Oxygen and Temperature Profiles in Lake Manassas at LM 04 on March 15, 1989 (A), April 12, 1989 (B), April 26, 1989 (C), and May 24, 1989 (D).



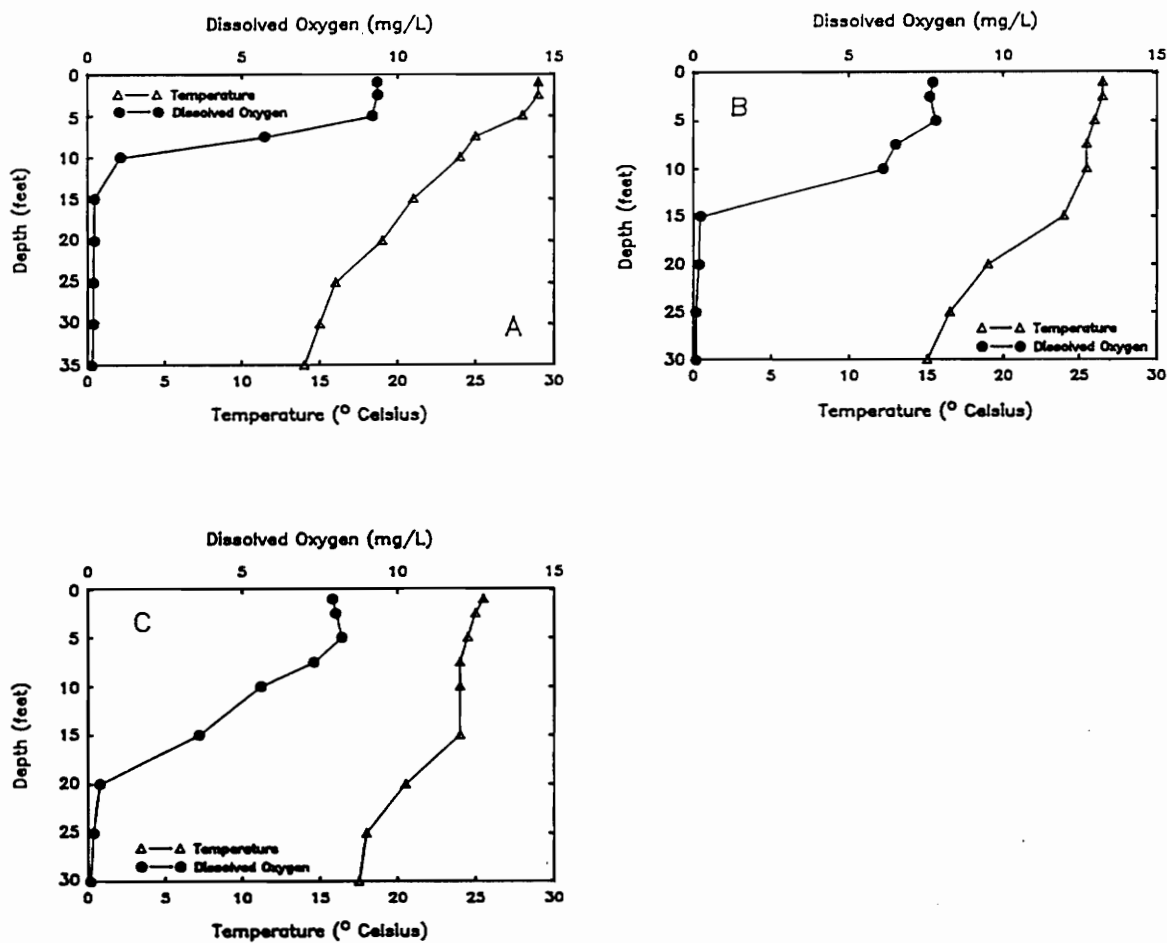


Figure 6. Dissolved Oxygen and Temperature Profiles in Lake Manassas at LM 04 on June 28, 1989 (A), July 19, 1989 (B), and August 16, 1989 (C).

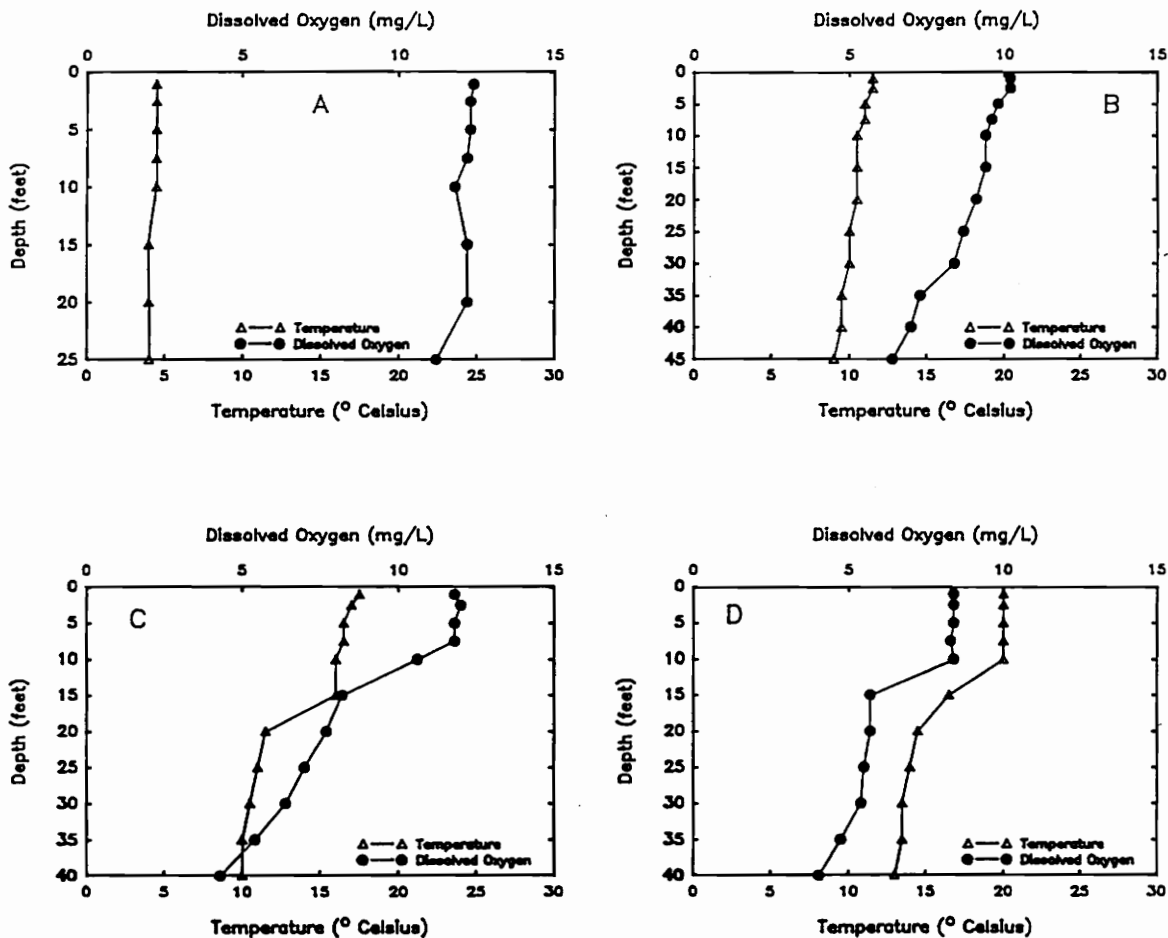


Figure 7. Dissolved Oxygen and Temperature Profiles in Lake Manassas at LM 01 on March 15, 1989 (A), April 12, 1989 (B), April 26, 1989 (C), and May 24, 1989 (D).

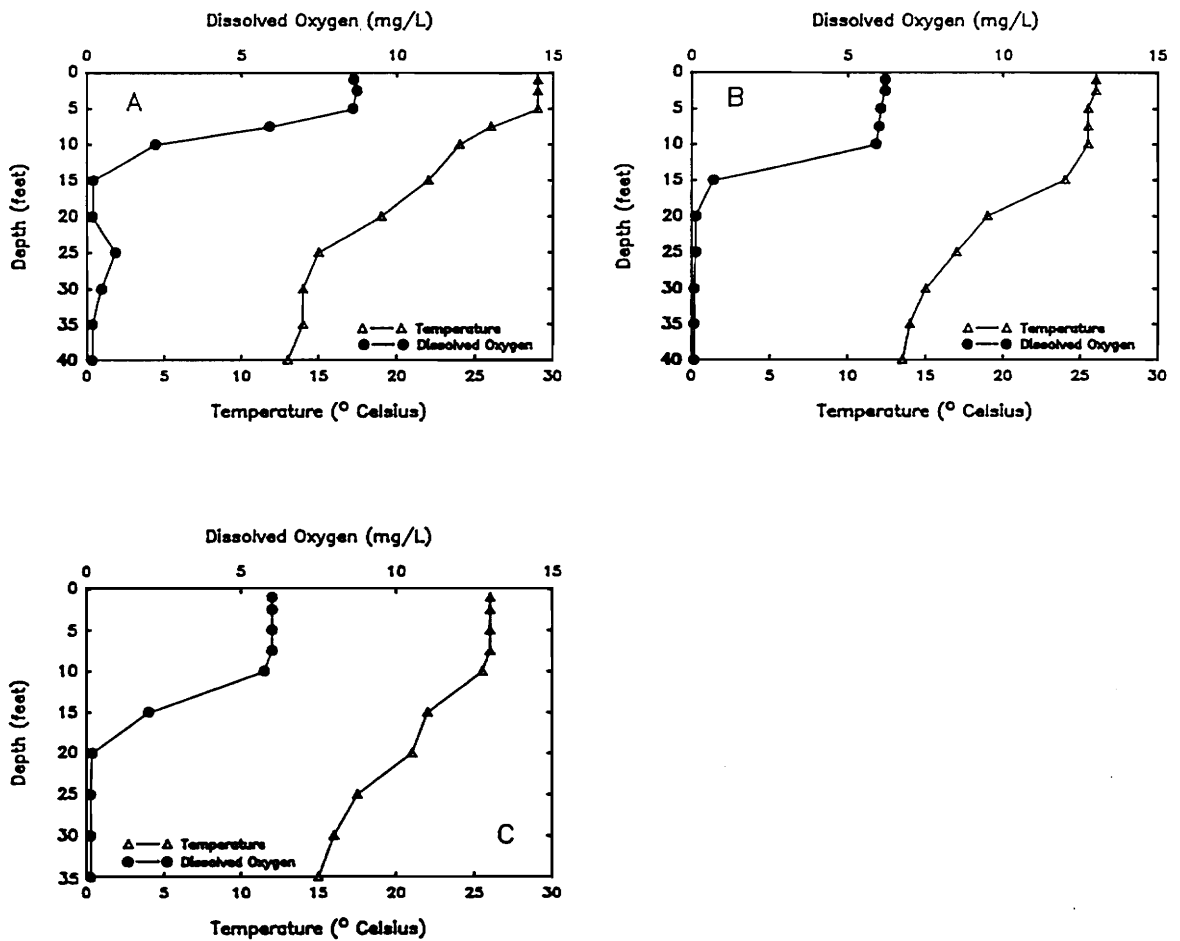


Figure 8. Dissolved Oxygen and Temperature Profiles in Lake Manassas at LM 01 on June 28, 1989 (A), July 19, 1989 (B), and August 2, 1989 (C).

in Appendix A. Dissolved oxygen, temperature, nutrient concentrations (phosphorus and nitrogen), Secchi disc transparency, and chlorophyll a data for Lake Manassas can be found in Appendix B. These data were obtained by the Occoquan Watershed Monitoring Laboratory as part of the routine monitoring of Lake Manassas.

### Seasonal Changes in Raw Water TOC and THMFP

The raw-water TOC concentrations and THMFPs of samples collected during March through August, 1989, are presented in Figures 9 and 10. The dominant trend in each of these graphs is the increase in raw water TOC and THMFP concentrations from late winter through the end of summer. The lowest recorded, raw-water THMFP concentration was at sample site ST 70 in March (115 ug/L), and the highest was the hypolimnetic sample at station LM 04 in June (420 ug/L).

Throughout the investigation, chloroform and bromodichloromethane were the only THMs formed upon chlorination of the samples. The more-highly-brominated THM compounds, dibromochloromethane and bromoform, were never produced. Hoehn *et al.* (1977) identified comparable characteristics in Bull Run and the Occoquan Reservoir, which, like Broad Run and Lake Manassas, are located within the Occoquan Watershed in Northern Virginia. In that study, "chloroform accounted for 90 percent or more of the TTHM on all occasions; CHBrCl<sub>2</sub> constituted the majority of the remainder, and CHBr<sub>3</sub> and CHBr<sub>2</sub>Cl were seldom detected." Hence, the THMFP concentrations generated in the current research represent the combined concentrations of chloroform and bromodichloromethane.

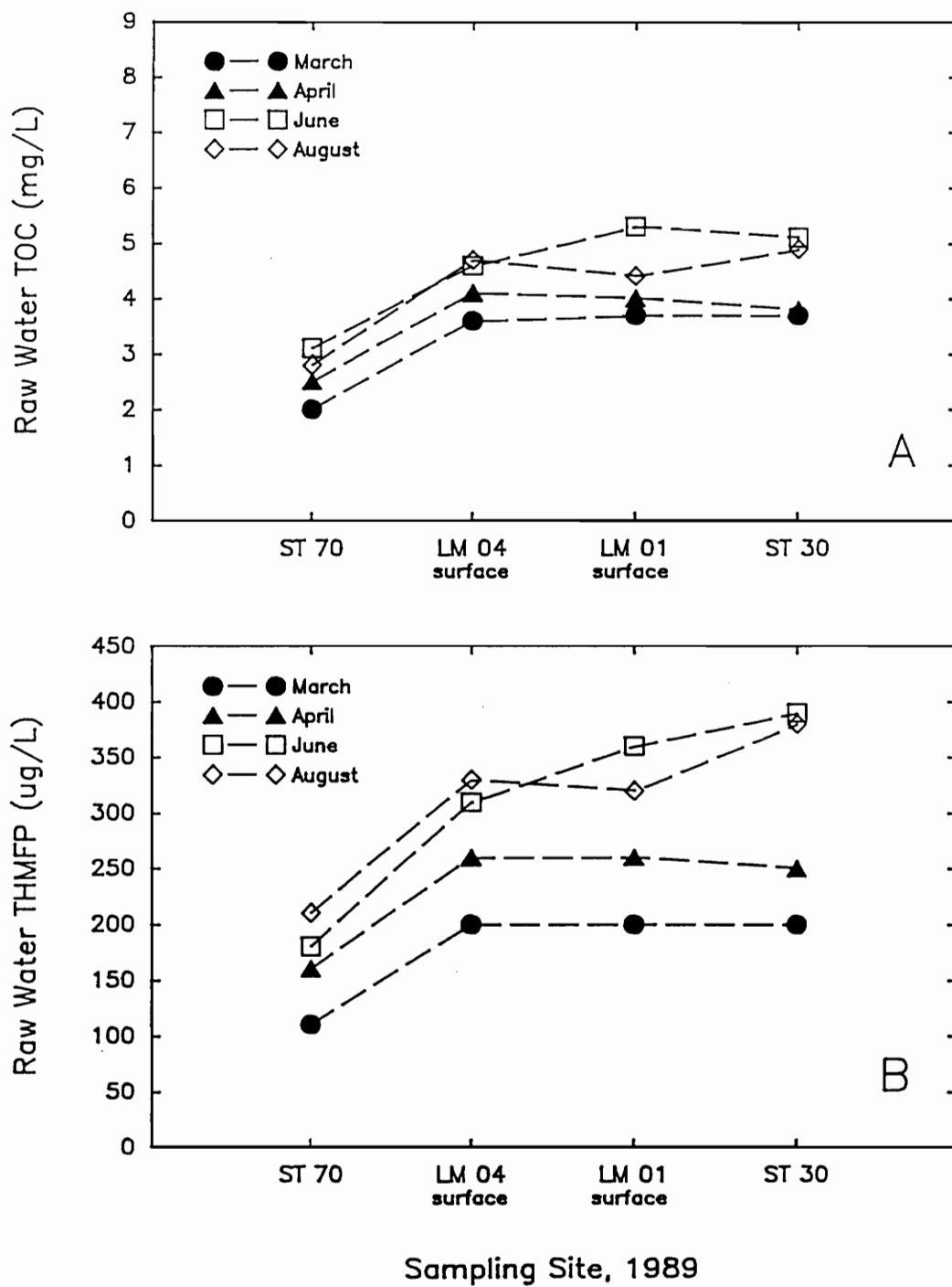


Figure 9. Raw Water TOC (A) and THMFP (B) Concentrations at ST 70, LM 04 (surface), LM 01 (surface), and ST 30 on the Sampling Dates in March, April, June, and August.

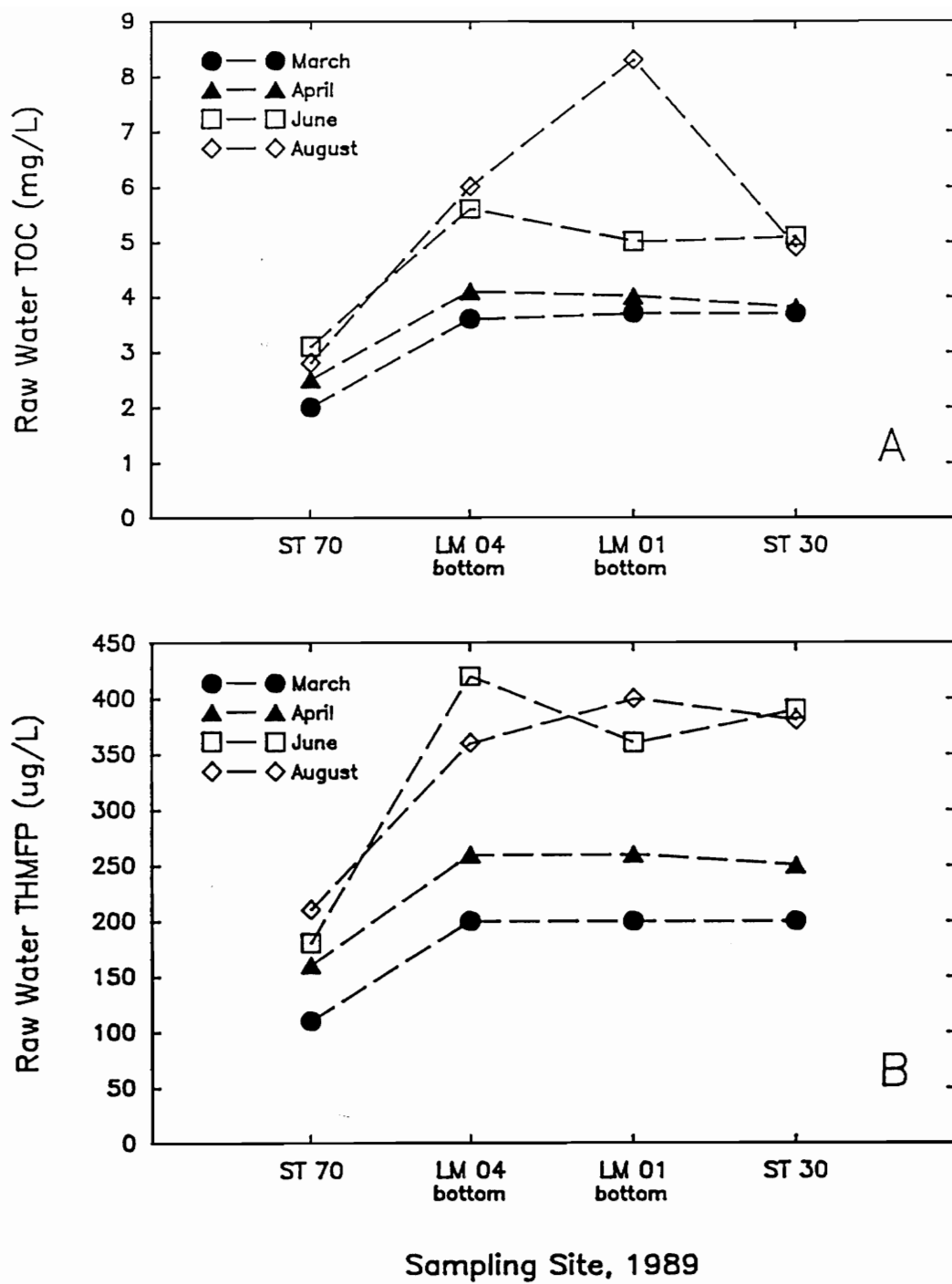


Figure 10. Raw Water TOC (A) and THMFP (B) Concentrations at ST 70, LM 04 (bottom), LM 01 (bottom), and ST 30 on the Sampling Dates in March, April, June, and August.

TOC and THMFP concentrations. Figures 9 and 10, show seasonal variations in raw-water TOC and THMFP concentrations at the four sampling stations. Figure 9 depicts the concentrations in the epilimnetic samples, and Figure 10 depicts those in the hypolimnetic samples. (The values for ST 70 and ST 30 are identical in Figures 9 and 10.) The seasonal variations are readily apparent. The TOC concentrations and levels of THMFP at all sites were lowest in March and higher or equal concentrations (as in Broad Run) were observed in April. The concentrations observed in the warmer months of June and August were consistently higher than those detected in the late winter/early spring (March and April).

Chlorophyll a is an indicator of the trophic conditions of a lake as well as an indicator of phytoplankton biomass concentrations. Table 3 presents commonly used trophic level indicators developed by Sakamoto, the National Academy of Sciences, Dobson, and EPA's National Eutrophication Survey. Generally, in the present study, Chlorophyll a increased in concentration from March to May but, after consecutive applications of copper sulfate on May 30 and 31, 1989 (2200 and 3000 lbs., respectively) they decreased through July (Figure 11). During August, however, the chlorophyll a concentrations began to increase again at both LM 04 and LM 01. At this time of year, late summer to early fall, blue-green algal blooms occur, contributing additional organic matter to the water column (Cooke and Carlson, 1989).

Supersaturation of oxygen near the surface of a water body indicates extensive algal productivity, which is associated with biological functionings such as excretion and secretion, death and decay. On the days of sampling during April and June, dissolved oxygen concentrations were greater than 100 percent saturation in the

Table 3. Trophic States Determined by Chlorophyll a Concentrations (Laufer, 1986 citing Reckhow, 1979).

Trophic Condition	Chlorophyll a (ug/L)			
	Sakamoto	Academy	Dobson	EPA-NES
Oligotrophic	0.3-2.5	0-4	0-4.3	<7
Mesotrophic	1-15	4-10	4.3-8.8	7-12
Eutrophic	5-140	> 10	>8.8	> 12



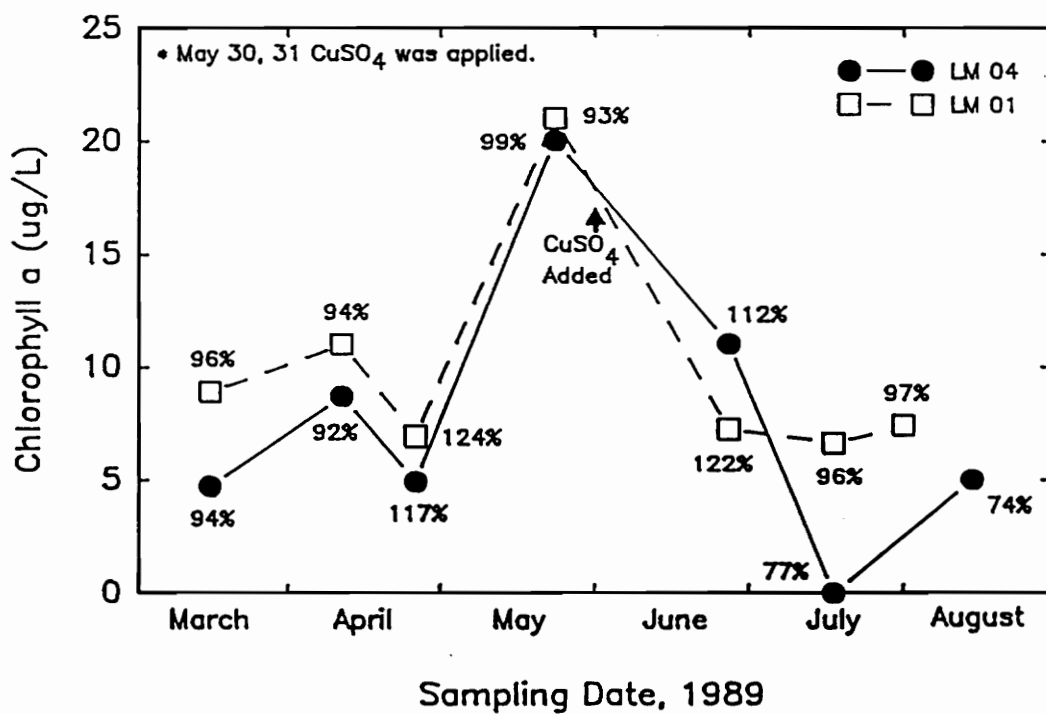


Figure 11. Chlorophyll a Concentrations and Corresponding Dissolved Oxygen Saturation Percentages in Lake Manassas at Sites LM 04 and LM 01 during the Study Period.

surface waters at sites LM 04 and LM 01 (Figure 11). From the surface to depths to 5-10 feet, the oxygen concentrations exceeded those of saturation (See Tables B-1 and B-3).

The increases in the biological activities of algae and bacteria during the warmer weather can likely account for some of the observed THMFP increases through the study period. Hoehn *et al.* (1980) established that both algal mass and algal extracellular product (ECP) may be significant sources of THM precursors. Bacterial activity, in addition, may alter algal cells, secretions and excretions, making them more amenable to reaction with chlorine to form THMs (Hoehn *et al.*, 1980).

Correspondingly, the existence of a seasonal trend with respect to THM production is strong evidence that the THM-precursor material is autochthonous. The data presented in Figures 9 and 10 support this theory. On all sampling dates, the TOC and THMFP concentrations were considerably higher in the lake (LM 04 and LM 01, surface and bottom waters) than those observed in the headwaters of the reservoir (ST 70).

Many investigators (Randtke *et al.*, 1987 citing Morris and Johnson, 1976; Harms and Looyenga, 1980; Cook *et al.*, 1984) have reported strong positive correlations between stream discharge and precursor concentrations/THM formation. Throughout the current study, the samples were collected during base flow conditions with the exception of the March 15th sample. (See Appendix C for discharge and rainfall data.) In March, the mean daily discharges at ST 70 and ST 30 were higher than the baseflows, and higher than the discharges on any other sampling date. The TOC and THMFP levels, however, were the lowest of all the sampling dates at every

site. Since the TOC and THMFP mass loadings at ST 70 were equal or higher in April and June (not August) than March, it is conceivable that the THM-precursor pool in Broad Run upstream of the reservoir was so depleted (or was comprised of predominantly low-yielding THM precursors), due to the relatively low biological activity in March, that despite the high flows, the TOC and THM concentrations were low. At ST 30, however, the mass loadings of TOC and THMFP were highest in March, therefore the low TOC and THMFP concentrations were due to dilution created by a high discharge from the dam. The cause of the higher mass loadings could be settled organic matter stored in the hypolimnion/sediment being displaced by the force of the released water.

Key features of Figures 9 and 10. At sites LM 01 (surface and bottom) and ST 30, the TOC concentrations in March were almost identical to those observed in April. The THMFP values, however, were very different; the April samples generated approximately 25 percent more THMs than were produced from the raw water in March (Figures 9 and 10). As the warmer months advance and water temperature increases, aquatic biological activity is expected to increase. Correspondingly, as previously stated, the surface waters at LM 01 were supersaturated with oxygen on April 26th (but not on March 15th), indicating extensive algal productivity, which could contribute significantly to the THM-precursor pool (Figure 11). The nature of the constituents in the TOC pool will affect the concentrations of THMFP produced. The precursors derived from the April algal activity may have been higher-THM-yielding precursors than those available in March.

Likewise, seasonal influences, such as increased temperature and biological

productivity, could impact the hypolimnetic TOC pool at LM 01 directly, either by increased microbiological activity in the sediments, or through sedimentation of higher-yielding THM precursors, which would have higher THMFP. On April 26, a portion of the discharge from the reservoir went over the spillway and another portion went through the sluice gates below. The flow at ST 30, therefore, was comprised of hypolimnetic and epilimnetic waters of the reservoir and had THM-precursor characteristics similar to those in the lake at the surface and bottom.

In addition, examination of the hypolimnetic concentrations of TOC and THMFP at site LM 04 reveals that the TOC concentration was higher in August than in June, despite a higher THMFP in June than August (Figure 10). The sediments of Lake Manassas are very loose and could easily be incorporated into the hypolimnetic water sample. If the sediments were high in organic carbon which was not largely THM-precursor material, this would explain this particular characteristic of the data.

TOC and THMFP correlation. Additional TOC and THMFP trends in Figures 9 and 10 are also noteworthy. It is evident from these figures that, despite individual discrepancies, the characteristic shapes of the TOC and THMFP plots for the same raw-water sample are similar. Trihalomethane formation potential (THMFP) concentrations increased and decreased in phase with similar changes in TOC concentrations on each sampling date. Least squares linear regression analyses showed, however, that the correlation coefficient ( $r^2$ ) value for the raw water TOC and THMFP concentrations for all sites and sampling dates was 0.78 (Figure 12), while the  $r^2$  values for individual sites ranged from 0.76 to 0.99 (Figures 13-15).

The data suggest that, at individual sites, the TOC concentration may be a

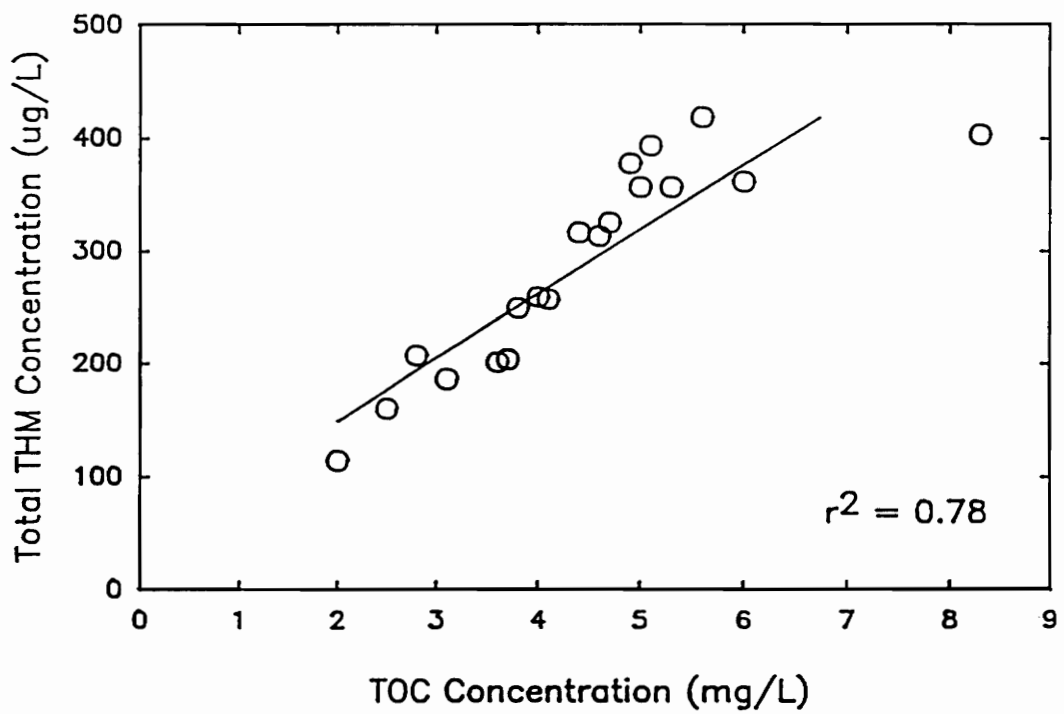


Figure 12. Raw Water TOC and TTHMFP Correlation for All Sites on All Sampling Dates.

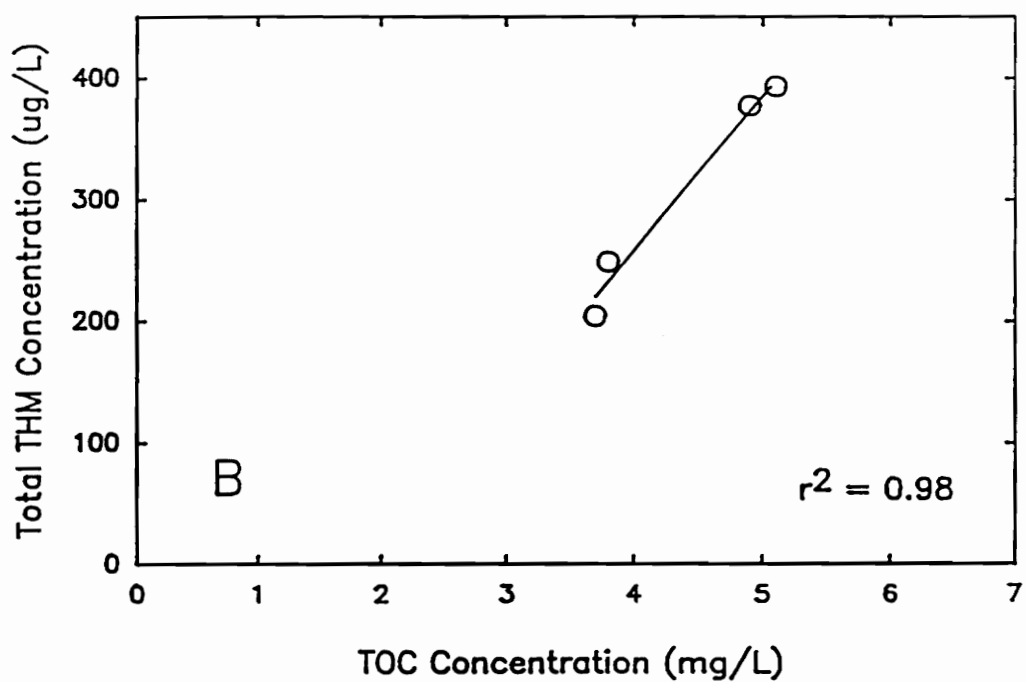
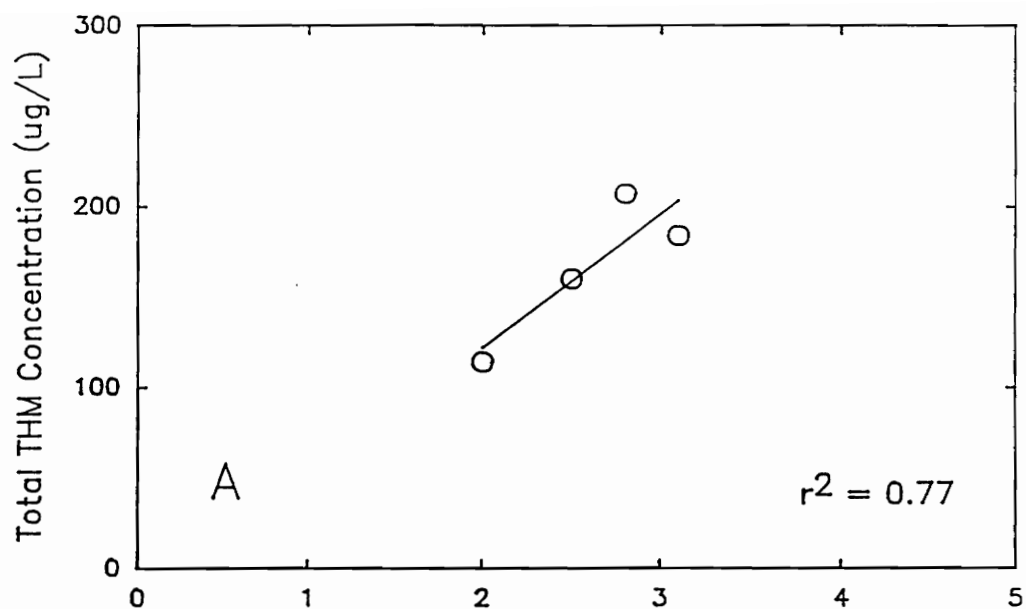


Figure 13. Raw Water TOC and TTHMFP Correlations at Sites ST 70 (A) and ST 30 (B).

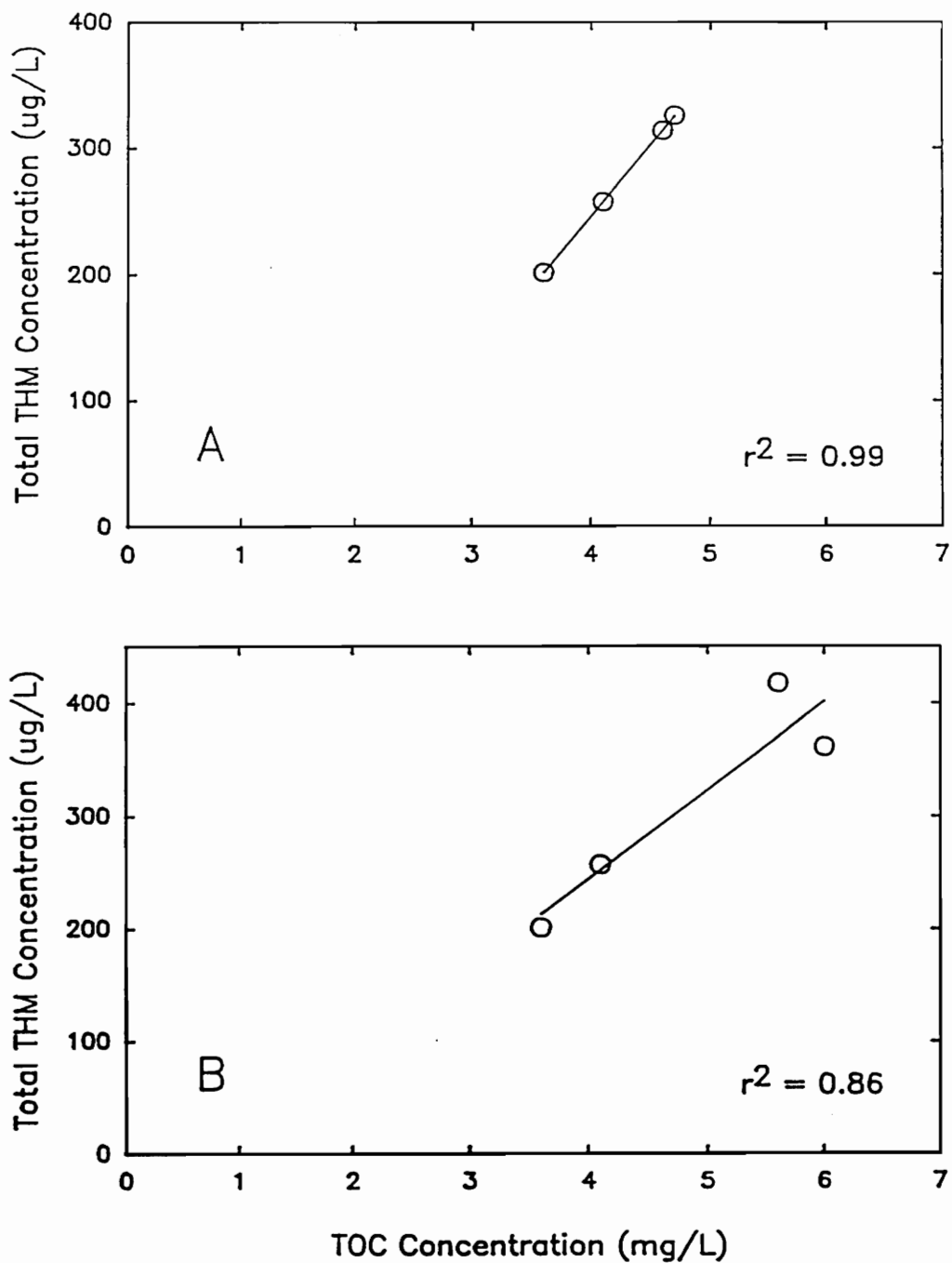


Figure 14. Raw Water TOC and TTHMFP Correlations at Sites LM 04, Surface (A) and LM 04, Bottom (B).

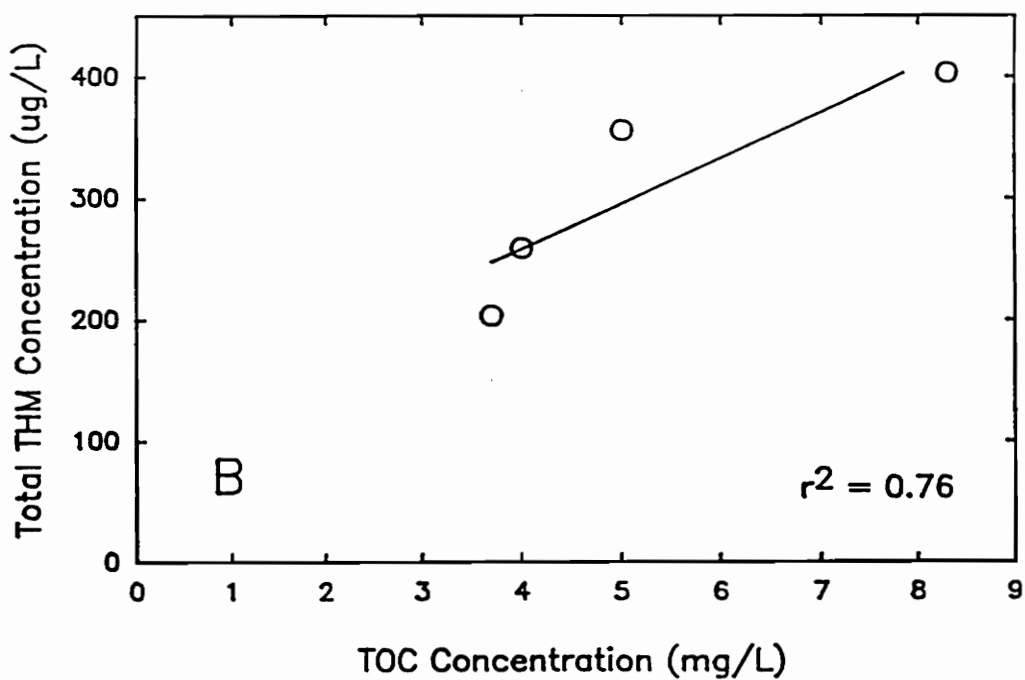
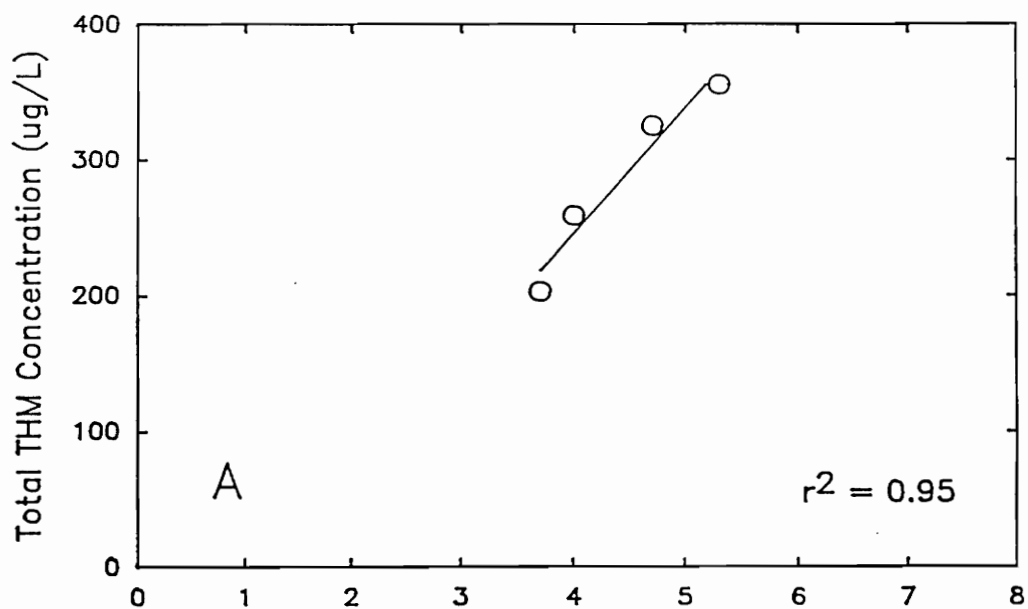


Figure 15. Raw Water TOC and TTHMFP Correlations at Sites LM 01, Surface (A) and LM 01, Bottom (B).



reliable indicator of the THMFP produced. There exists a different relationship, however, between TOC and THMFP by location. The slope of the individual regression lines, which represents the THM yield (mass of THM per mass of TOC), therefore, are different.

The correlations for the bottom water samples at LM 04 and LM 01 were the lowest (along with site ST 70), which may be attributed to the loose sediment in Lake Manassas. This sediment could easily be included in the water sample, and may be rich in organics which are not THM-precursor material, or are lower-THM-yielding precursors. Their respective correlations, therefore, will be affected by the amount of sediment included in the sample. Cooke and Carlson, (1989), furthermore, determined from preliminary experiments by Martin (1988), Palmstrom (1987), and Randtke *et al.* (1987) that sediments may be a minor source of THM precursors.

#### Effects of Impoundment on TOC and THMFP Concentrations

It is also evident from Figures 9 and 10 that TOC and THMFP concentrations generally increased along the length of the reservoir from the input to the lake to the outflow. On the four sampling dates, the lowest concentrations were always associated with Broad Run upstream of Lake Manassas (ST 70). A sharp increase in concentrations from this station to LM 04 was noted.

Accordingly, the differences between the inflow and outflow TOC and THMFP concentrations were quite evident. In Figure 16, the raw water TOC and THMFP concentrations at the Broad Run stations upstream of Lake Manassas (ST 70) and

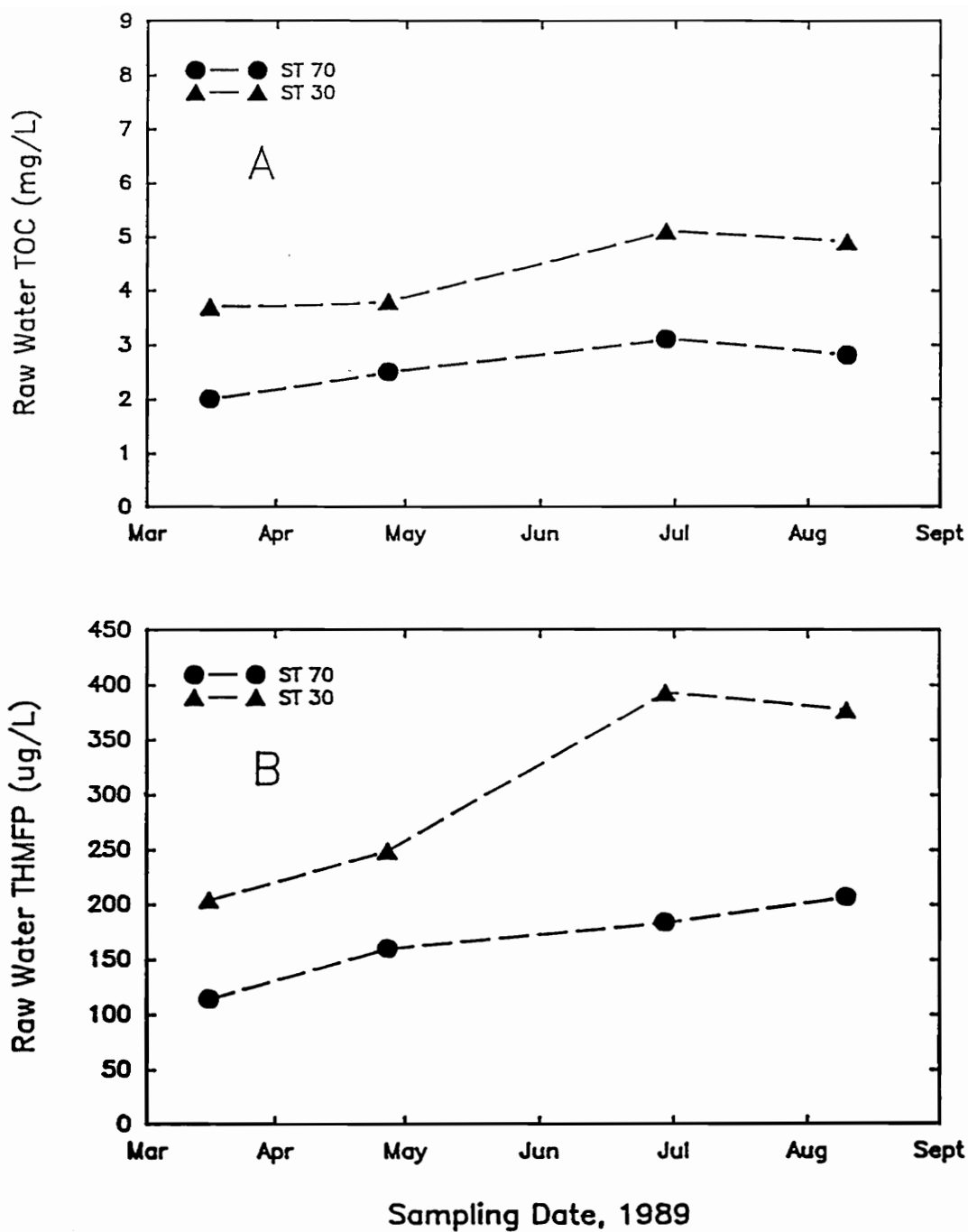


Figure 16. Raw Water TOC (A) and THMFP (B) Concentrations at Sites ST 70 and ST 30.

downstream from the lake (ST 30) have been plotted with respect to the corresponding dates of collection. The TOC and THMFP concentrations at ST 30 were greater than those at ST 70 on all sampling dates. There was a net increase of 56 percent in April to 111 percent in June in raw water TOC and THMFP concentrations between the reservoir's input (ST 70) and output (ST 30).

The results show clearly that impoundment resulted in an increase in levels of THM precursors. A considerable amount of the THM-precursor material in Lake Manassas, therefore, is likely autochthonous. The major internal source is likely the phytoplankton that flourish and die each year, producing extracellular products that are THM precursors while living, and decay products after their death that also are THM precursors. Of course, organic matter from the watershed that is trapped in the reservoir and decays is also a significant source of the THM precursors.

During the colder months of March and April, TOC concentrations and levels of THMFP in the lake were relatively constant from the headwaters to the dam. In June, however, the concentrations increased from the headwaters to the dam, corresponding to the dissolved oxygen saturation values at sites LM 04 and LM 01. On June 28, 1989, the percent saturation of dissolved oxygen at LM 04 was 112 compared with 122 at LM 01 (Figure 11) which indicated that phytoplankton activity was higher down-reservoir on that date. Contributions to the THM-precursor pool and THMFP concentrations would most likely be higher, therefore, at LM 01. In August, no in-reservoir increases in TOC and THMFP concentrations were noted, and, likewise, the waters at sites LM 04 and LM 01 were not supersaturated with oxygen, nor were there indications of substantial changes in algal biomass concentrations according to the

chlorophyll a data (Figure 11).

The THMFP of Broad Run 2.81 miles below the dam (ST 30), however, was always greater than the surface water THMFP in the reservoir during stratification. For three of the four sampling dates, the pool levels were higher than the dam crest level of 87 m (285 ft) above mean sea level (MSL), which indicates that on those three occasions, a portion of the discharge was over the spillway (from the epilimnion) instead of through the sluice gates below. Only on August 9 was the lake level lower than the crest of the dam. On that date, the discharge was solely from the hypolimnion through the sluice gates. Since the hypolimnetic THMFP concentrations were higher than the epilimnetic concentrations in August, it would be expected that the waters at ST 30 had higher THMFP than the surface waters.

In June, however, the THMFP concentrations at LM 01 (approximately 75 yards from the dam) were the same in the surface and bottom waters, yet the raw-water THMFP concentration was higher at ST 30. Since the discharge and rainfall influences were minimal on June 28th (Appendix C) and the TOC concentrations were similar, continued biological activity, such as bacterial alteration of the THM-precursor material, from LM 01 to ST 30 was likely the reason for the higher THMFP concentrations.

Furthermore, there was a distinct increase in the TOC and THMFP concentrations from March through August. However, a slight decrease was noted from June to August (except for the THMFP concentration at ST 70 which continued to increase.) This occurrence was presented previously in the section titled "Seasonal Trends in TOC and THMFP."

## Differences in TOC and THMFP Concentrations due to Stratification

The raw-water TOC and THMFP concentrations in the epilimnion and hypolimnion (surface and bottom waters) during the months of June and August are presented in Figure 17. The TOC concentrations and THMFP, despite lower THM yields, were generally higher in the bottom samples than those in the surface waters. The THMFP of the hypolimnetic waters, therefore, may have been higher simply because the mass of TOC available to react with chlorine was greater. Knocke *et al.* (1987) also observed higher TOC concentrations in the hypolimnion than the epilimnion during stratification of the Harwood's Mill Reservoir, Virginia. In the current study, though, exceptions were noted. For example, at site LM 01 in June the epilimnetic TOC concentration was slightly higher than that in the hypolimnion, and the surface and bottom THMFP concentrations were equal. The corresponding dissolved oxygen saturation levels, however, were the highest on this date at LM 01 during stratification. The increased algal productivity and the characteristics of the ECP associated with the supersaturation of oxygen may account for the high TOC and THMFP concentrations in the epilimnion.

Another notable feature of Figure 17 is that the differences between the epilimnetic and hypolimnetic TOC concentrations were consistently greater in August than in June, but the corresponding THMFP differences were not. During June, both the chlorophyll *a* levels and the oxygen saturation values were higher than during August. The nature of the TOC pool was likely very different, and, during June, the

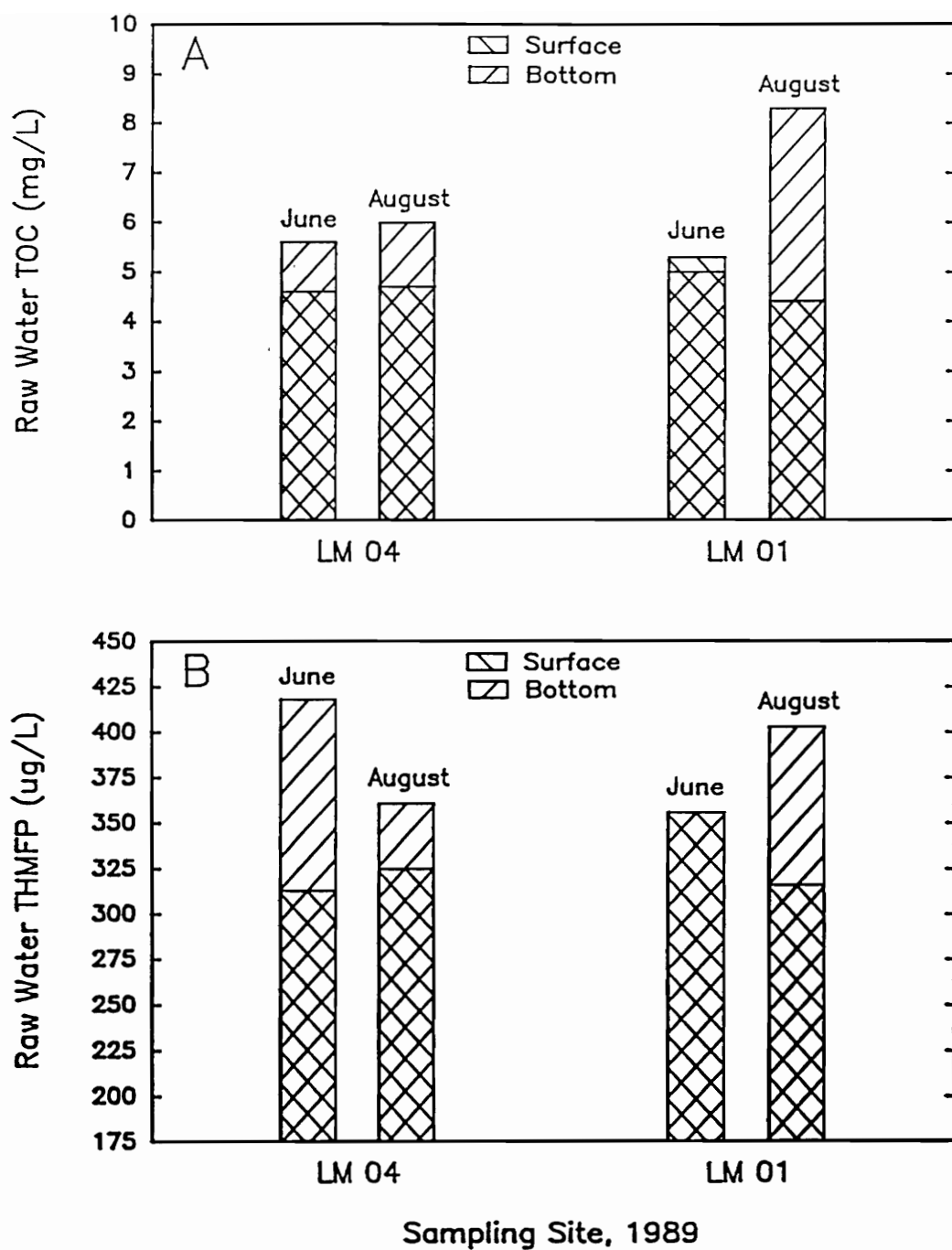


Figure 17. Raw Water TOC (A) and THMFP (B) Concentrations Observed in the Epilimnion and Hypolimnion at Sites LM 04 and LM 01.

TOC was higher-yielding-THM precursors that possibly included algal biomass and ECP.

### Molecular Weight Distributions of TOC and THMFP

Figures 18-23 present the molecular-weight distributions of the TOC and THMFP precursors in samples from ST 70, ST 30, and the epilimnetic and hypolimnetic samples from sites LM 04 and LM 01. As can be seen from these figures, the percentage of TOC was more evenly distributed among the various molecular-weight fractions than the percentage of THMFP. However, the largest proportions of both TOC and THMFP were in the 1,000 to 5,000 dalton range. Amy *et al.* also determined that the predominant molecular weight range was 1,000-5,000 daltons for river and lake samples from Northern California.

Molecular Weight distributions of THM precursors at sampling sites. Figures 24-26 show the percentages of TOC and THMFP contributed by the low-molecular-weight organics (less than 5,000 daltons) at all sites. In Figures 25 and 26, the March and April data are the same for the surface and bottom waters at LM 04 and LM 01, since the lake was assumed to be uniformly mixed.

On three of the four sampling dates at ST 70 and ST 30, more than 50 percent of the THMFP was in the molecular-size ranges less than 5,000 daltons (Figures 24 A and B). Likewise, the TOC and THMFP percentages corresponding to the surface waters of Lake Manassas (Figures 25 A and 26 A, respectively) indicate that higher proportions of the total THMFP generally were produced from organics in the smaller

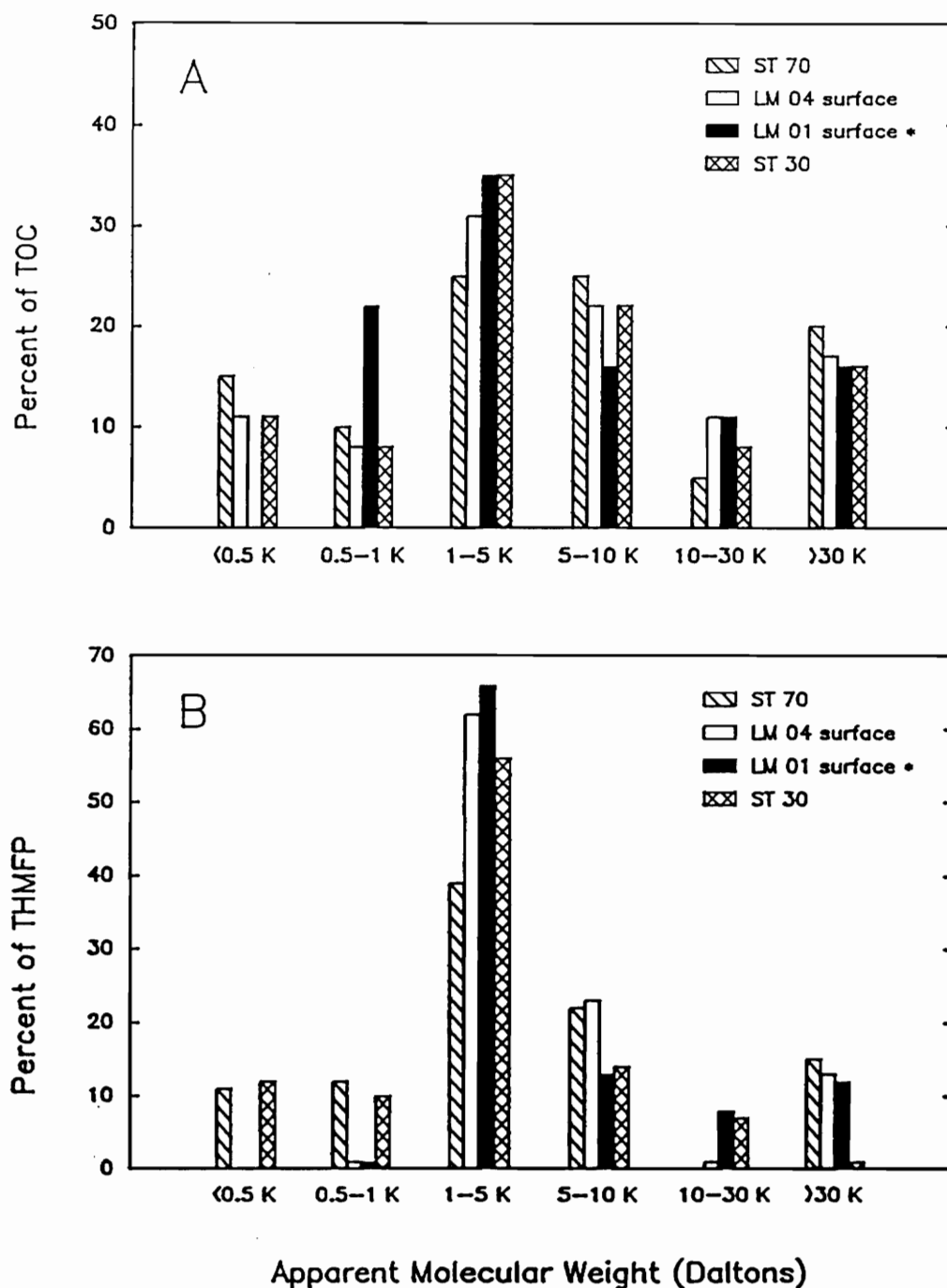


Figure 18. The Molecular Weight Distributions of TOC (A) and THMFP (B) at All Sites in March.

\* No Data for <0.5 K at LM 01 surface.



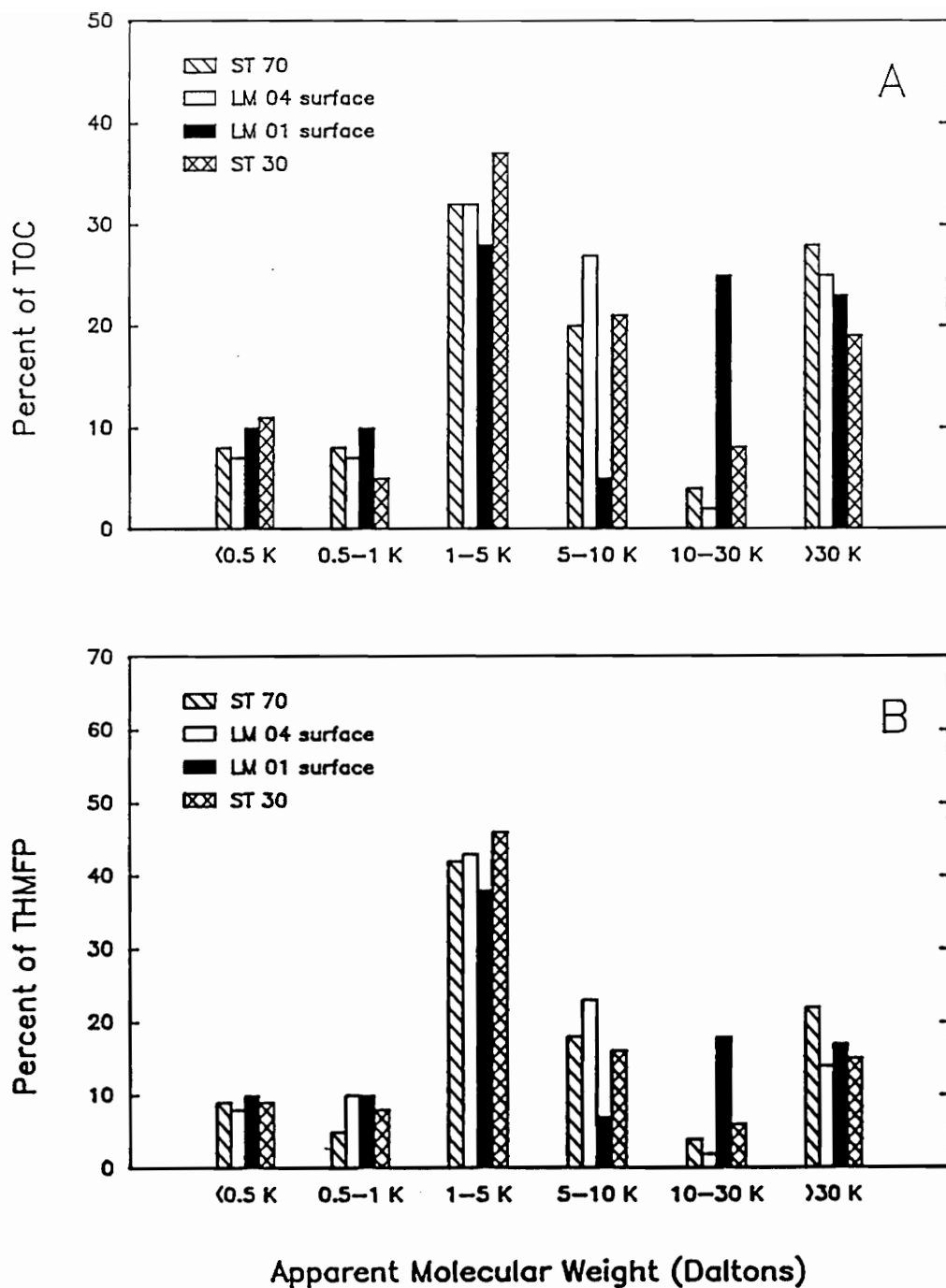


Figure 19. The Molecular Weight Distributions of TOC (A) and THMFP (B) at All Sites in April.

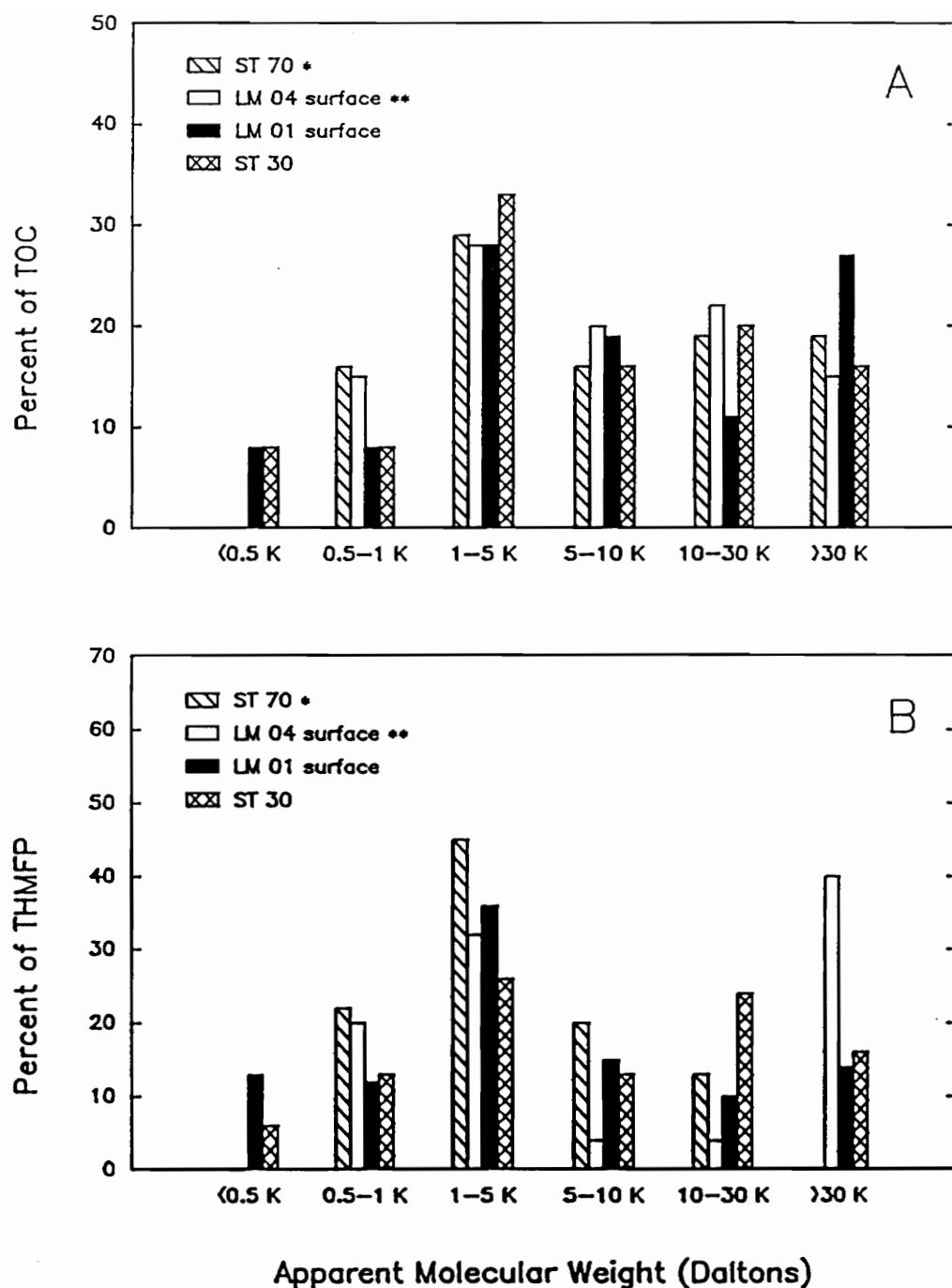


Figure 20. The Molecular Weight Distributions of TOC (A) and THMFP (B) at Sites ST 70, the Epilimnion at LM 04 and LM 01, and ST 30 in June.

\* No Data for <0.5 K at ST 70.

\*\* No Data for <0.5 K at LM 04 surface.

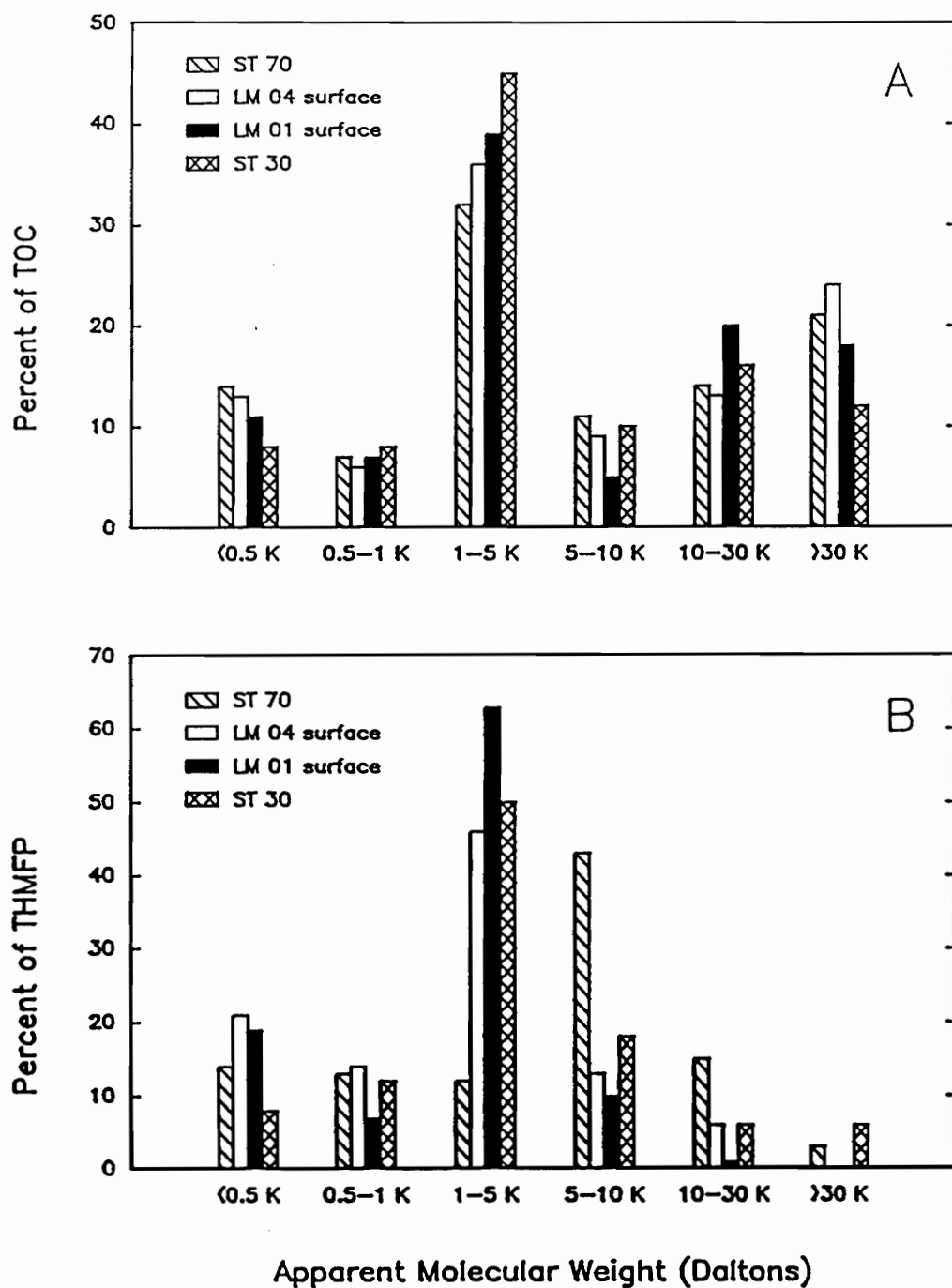


Figure 21. The Molecular Weight Distributions of TOC (A) and THMFP (B) at Sites ST 70, the Epilimnion at LM 04 and LM 01, and ST 30 in August.

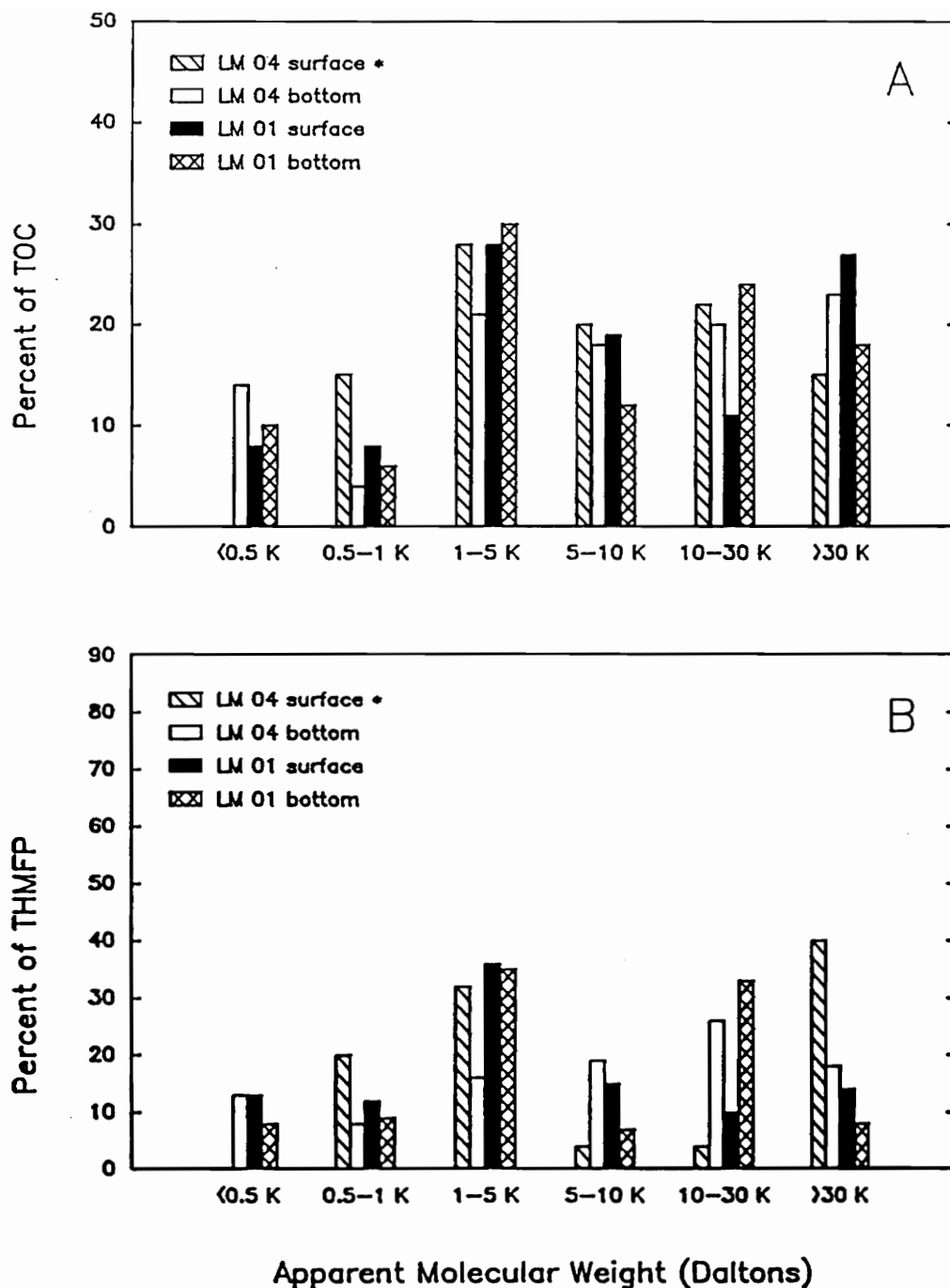
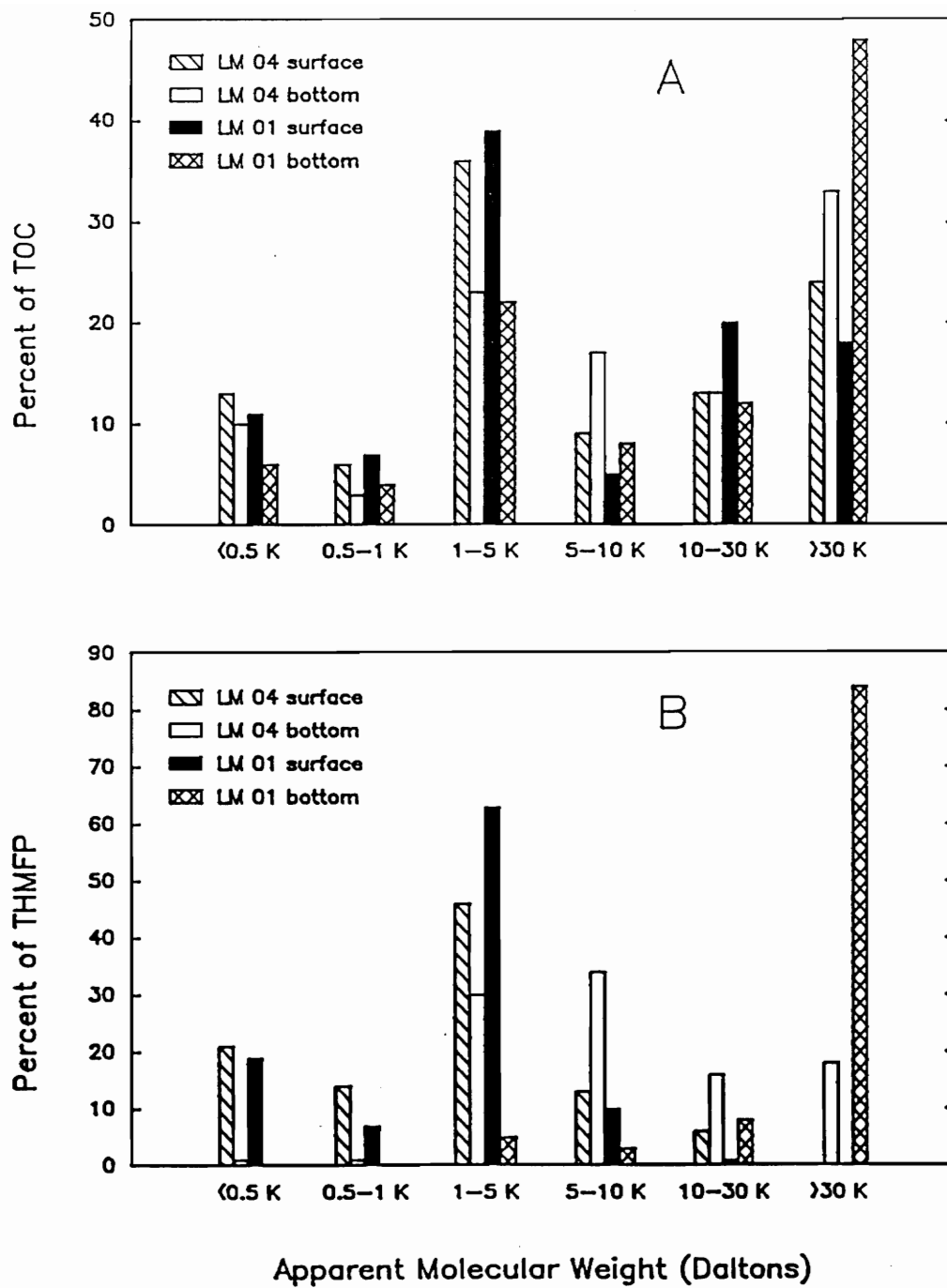


Figure 22. The Molecular Weight Distributions of TOC (A) and THMFP (B) at the Surface and Bottom Waters of LM 04 and LM 01 in June.

\* No Data for <0.5 K at LM 04 surface.



**Figure 23. The Molecular Weight Distributions of TOC (A) and THMFP (B) at the Surface and Bottom Waters of LM 04 and LM 01 in August.**

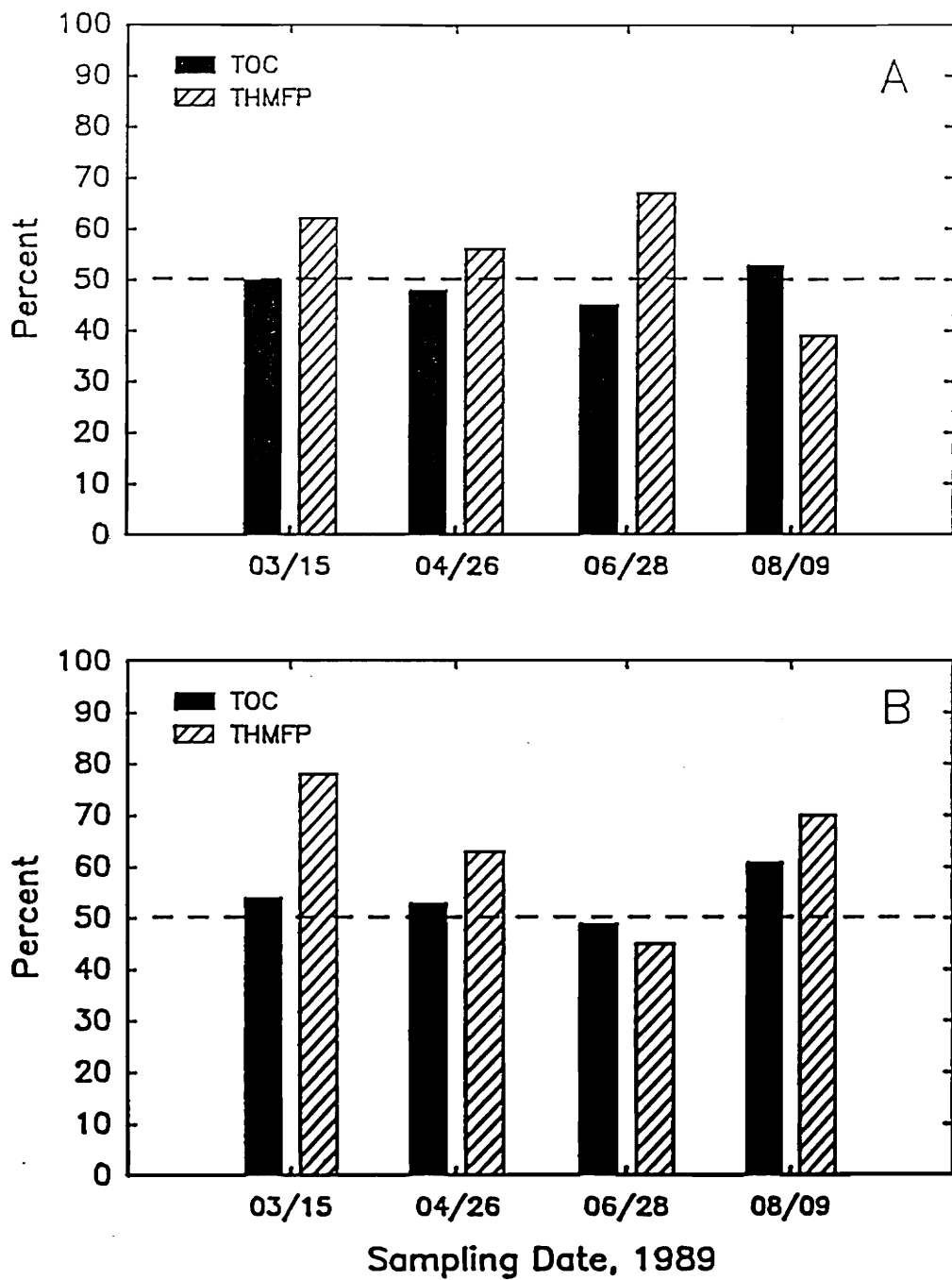


Figure 24. Percent of Raw Water TOC and THMFP Concentrations Observed in the Less Than 5,000 Molecular Weight Ranges at Sites ST 70 (A) and ST 30 (B).

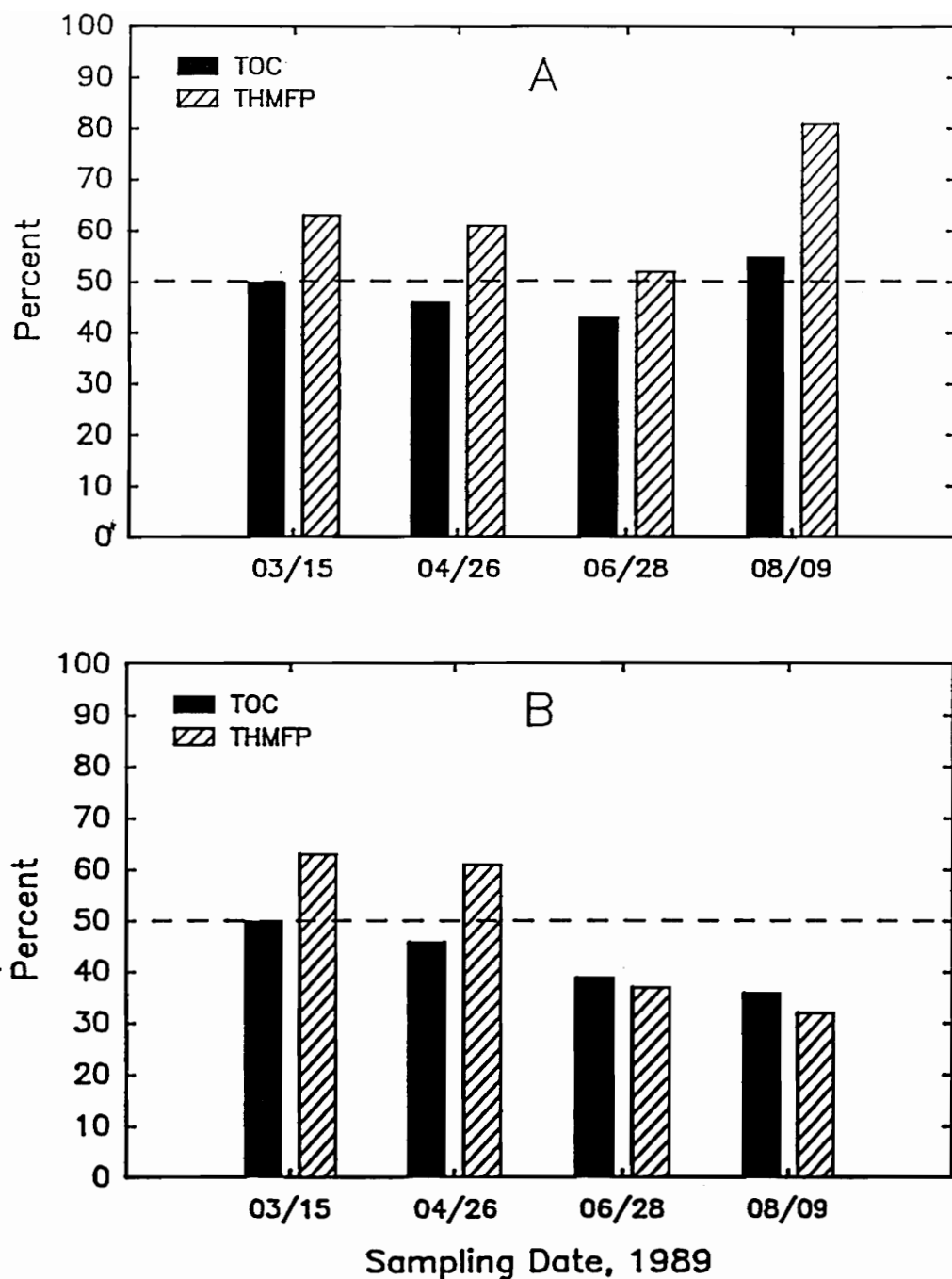


Figure 25. Percent of Raw Water TOC and THMFP Concentrations Observed in the Less Than 5,000 Molecular Weight Ranges at Sites LM 04, Surface (A) and LM 04, Bottom (B).

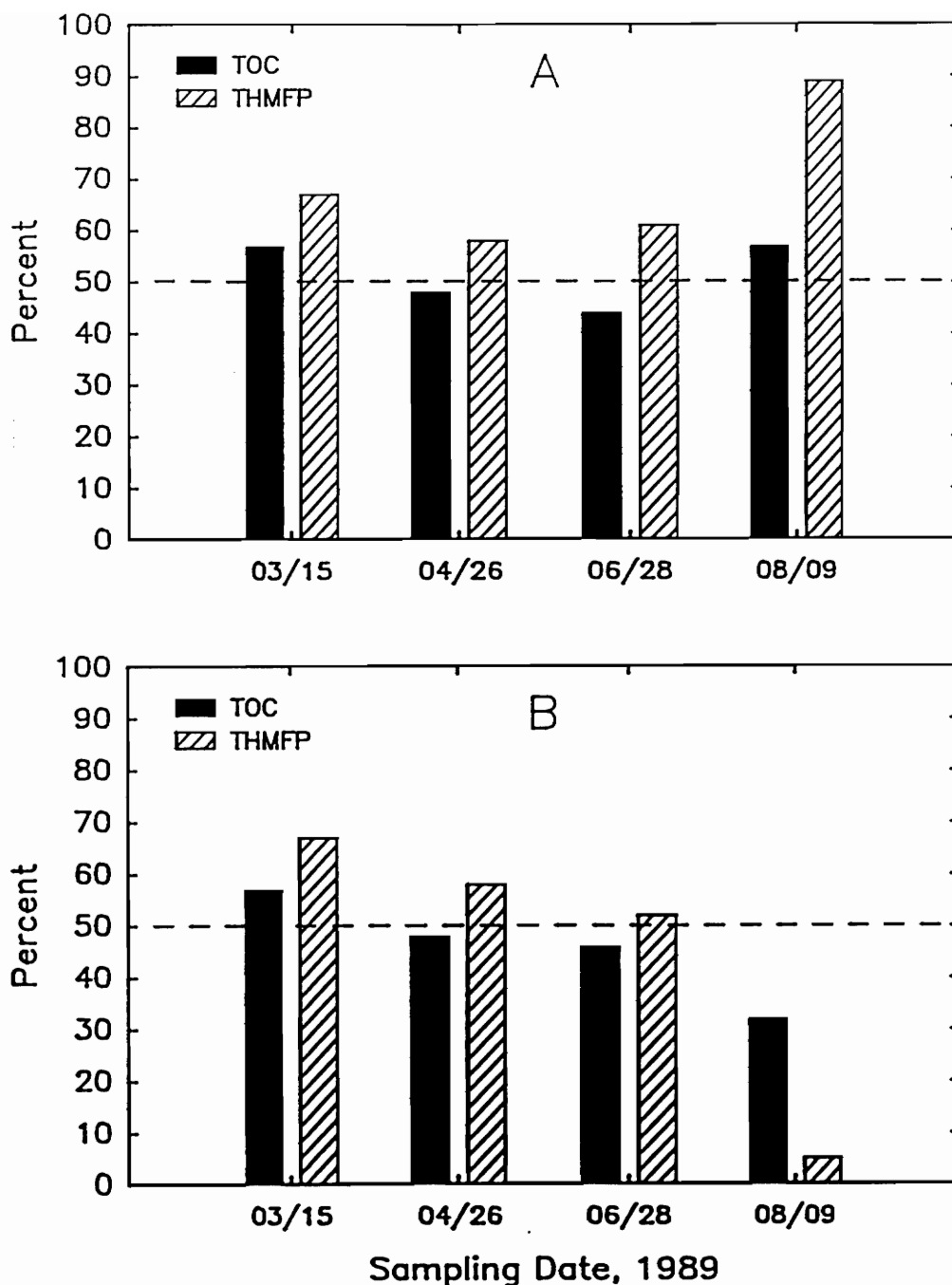


Figure 26. Percent of Raw Water TOC and THMFP Concentrations Observed in the Less Than 5,000 Molecular Weight Ranges at Sites LM 01, Surface (A) and LM 01, Bottom (B).



molecular-size fractions (< 5,000 daltons) rather than those in the > 5,000 molecular-size ranges. Amy *et al.* (1990) also noted that the three molecular-size ranges with the greatest proportion of THM-precursors in river and lake waters were 1,000-5,000; 500-1,000; and < 500 daltons.

Organics in the < 5,000 molecular-weight range could include a considerable amount of algal ECP such as glycolate, organic acids nitrogenous compounds, carbohydrates, lipids, enzymes, nucleic acids, phosphorus compounds, and vitamins (Barnes, 1978 citing Tolbert and Zill (1956); Hellebust (1965); Watt (1966); Hellebust (1974); Kuenzler (1970); and Aaronson, *et al.* (1971)), as well as a fraction of the humic acid component and most or all of the fulvic acids in the samples. The chlorophyll a and oxygen saturation data (Figure 11) support the hypothesis that algae contributed the low-molecular-weight precursors (< 5,000 daltons) in the surface waters of Lake Manassas, particularly in the photolytic zone. (The Secchi disk transparency measurements ranged from 36 to 75 inches during the study period (Appendix B).)

Readily apparent from Figures 25 B and 26 B is the tendency for the hypolimnetic TOC and THMFP concentrations to originate from the larger-molecular-size fractions (> 5,000 daltons) relative to the surface waters. The more humic-acid like compounds (> 5,000 daltons) are in the bottom waters during decay of these organics, while the smaller molecular weight substances may include fulvic acids, algal ECP and bacterial ECP which are more likely to be observed in the surface waters, particularly in the photolytic zone. The greater than 5,000 molecular size range may incorporate much of the humic substances present in the water course. Humic substances are major sources of THM-precursor material, and their presence in the

bottom waters would support higher TOC and THM concentrations in the hypolimnion relative to the epilimnion.

The TOC concentrations were approximately evenly distributed between the molecular size ranges greater than and less than 5,000 daltons at sites ST 70, ST 30, and the surface waters at LM 04 and LM 01 (Figures 24, 25 A, and 26 A), although the precursors < 5,000 daltons produced greater concentrations of THMFPs. The lower-molecular-weight organics (possibly algal ECP), therefore, were higher-yielding precursors than those greater than 5,000 daltons. The hypolimnetic TOC concentrations (Figures 25 B and 26 B) however, clearly indicate that the majority of the TOC is within the molecular size ranges greater than 5,000 daltons.

### THM Yields

Organic substances may be characterized by their ability to form THMs upon chlorination. The term "yield" is used to describe this tendency, and is expressed as mass of THM per mass of C.

The THM yields in this study ranged from 0 to 1.01  $\mu$  moles THM/mg C (0-125  $\mu$ g THM/mg C) (Figures 27-29). In comparison, the THM yields reported in the literature from a wide variety of precursor sources ranged from 0.07 to 1.20  $\mu$  moles/mg C (10-150  $\mu$ g THM/mg C). The highest reported yields (1.20  $\mu$  moles/mg C) have been produced from the chlorination of algal cells and peat humic acid (Randtke *et al.*, 1987).

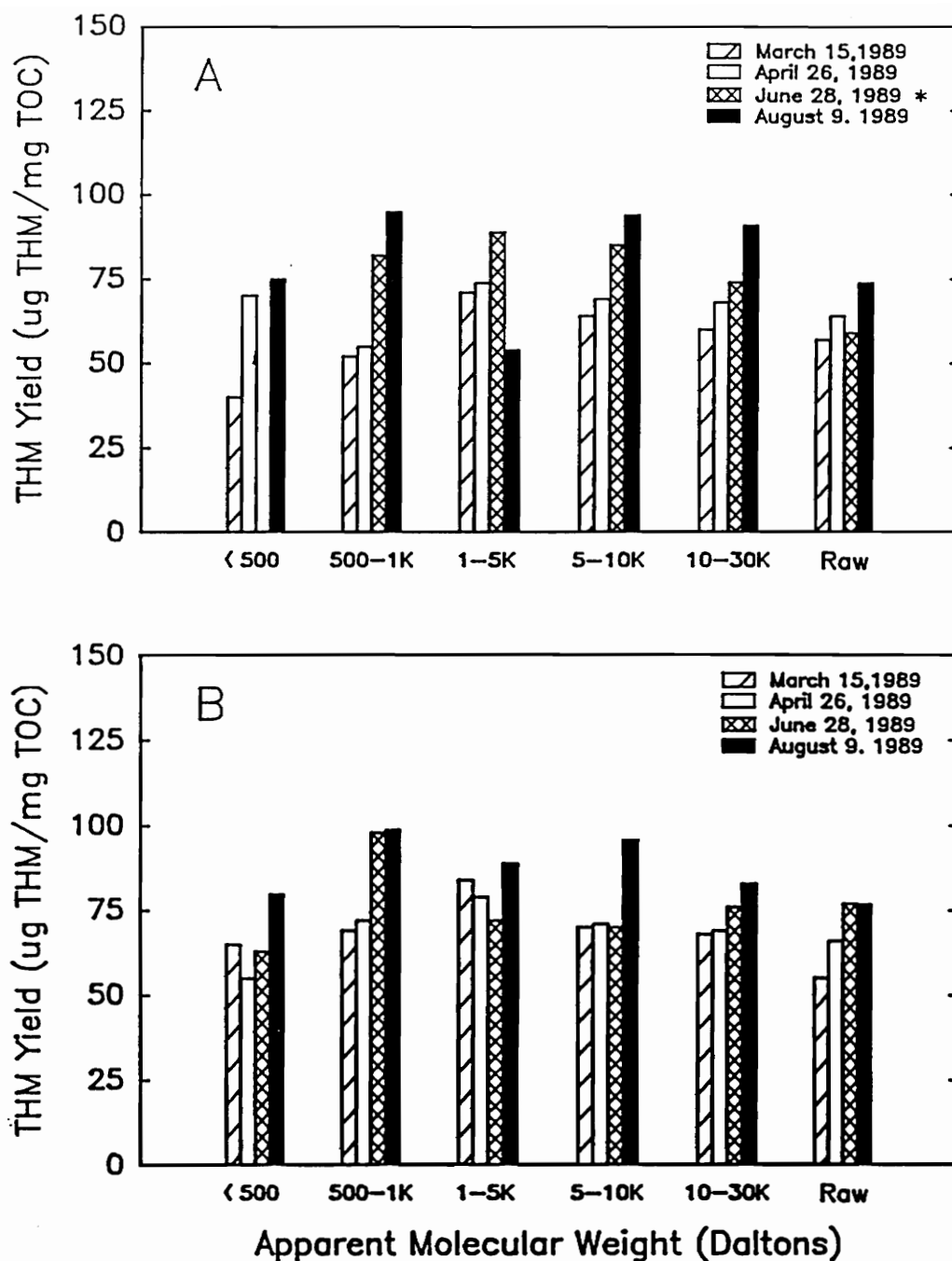


Figure 27. Molecular Weight Distributions of THM Yields at Sites ST 70 (A) and ST 30 (B).

\* No Data for <0.5 K at ST 70 in June.

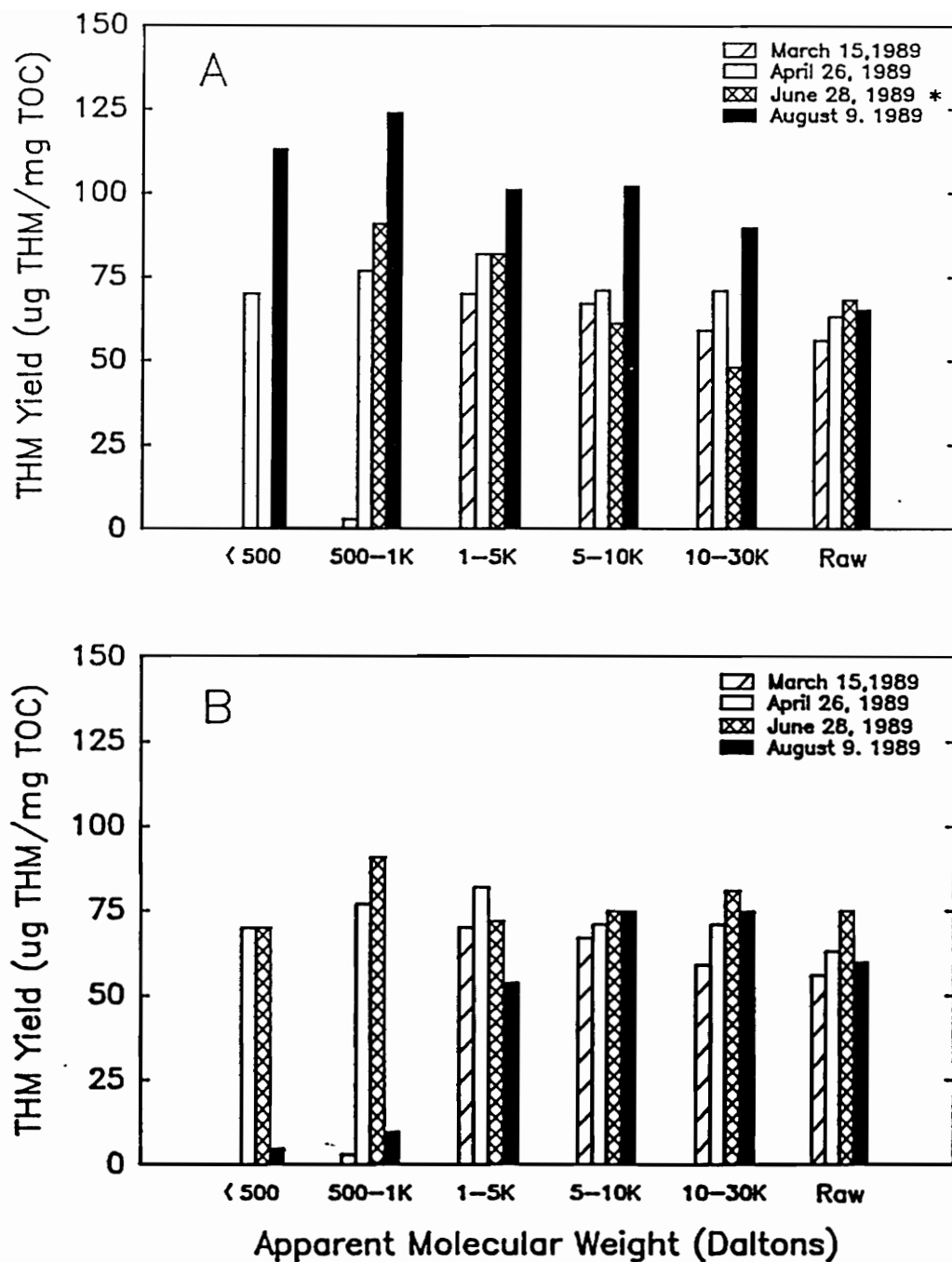


Figure 28. Molecular Weight Distributions of THM Yields at Sites LM 04, Surface (A) and LM 04, Bottom (B).

\* No Data for <0.5 K at LM 04 surface in June.

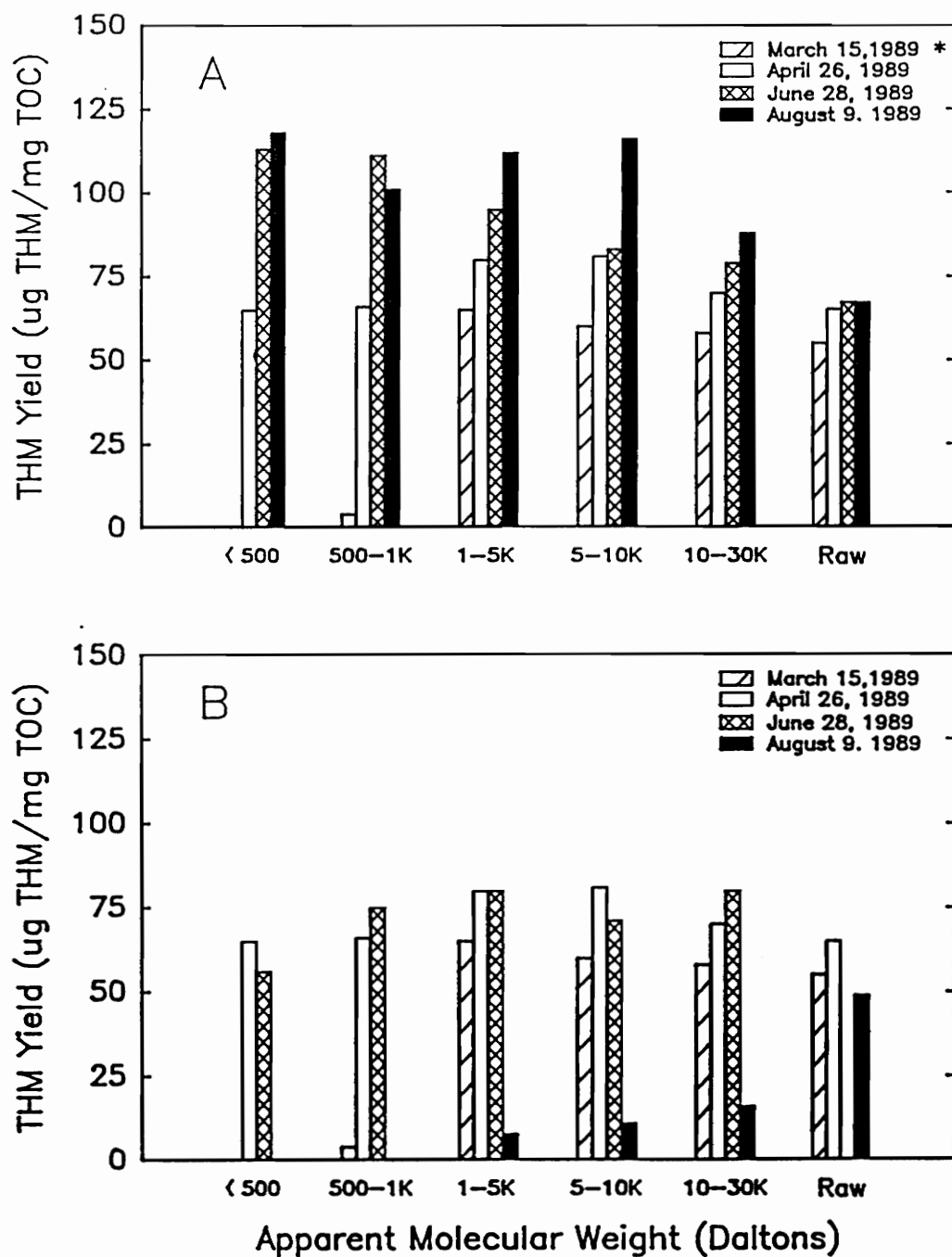


Figure 29. Molecular Weight Distributions of THM Yields at Sites LM 01, Surface (A) and LM 01, Bottom (B).

In the present study, the yields were highest within the low-molecular-weight ranges of the epilimnetic samples (LM 04 and LM 01) during August. The lowest yields, however, were produced by low-molecular-weight precursors in the hypolimnion in the same month, and by the low-molecular-weight precursors in the epilimnion during March.

Seasonal trends. Generally, increasingly higher yields were produced at all sites as the investigation approached late summer. As Broad Run, Lake Manassas, and their respective watersheds became more biologically active in the warmer months, higher-THM-yielding precursors were observed.

The decreased yields from the hypolimnetic water from June to August may be attributable to the loose sediment of Lake Manassas possibly being included in the water sample collected. The sediments may not be THM-precursor material or may be low-THM-yielding organics which, if included in a sample, would decrease the

\* No Data for <0.5 K at LM 01 surface in March.

overall yield of that sample.

Effects of impoundment. No distinct trends were obvious among the sampling sites on a particular sampling date with respect to variations in THM yields.

Effects of stratification. Generally, the higher yields for the epilimnetic samples were grouped in the lower molecular-weight ranges less than 5,000 daltons (Figures 28 and 29). Greater THM yields, however, were demonstrated in the lower molecular size ranges during June and August than before stratification at the epilimnetic lake sites. This increase may be attributed to the elevated biological functioning, particularly algal activity end-products such as secretions, excretions, and

increased viable or dead cells, which is a potentially rich source of THM precursors.

The highest yields at the hypolimnetic sites were observed in the larger molecular-weight ranges, but these were the lowest yields relative to the other sites in all molecular-weight fractions during stratification. The explanation may be partially attributed to the fact that anoxic conditions in the reservoir will produce organics that are not high-THM yielding. Randtke *et al.* (1987) determined that "precursors released from various substrates under aerobic conditions in the laboratory were considerably more potent than those released under anaerobic conditions."

Molecular weight distributions. Generally, relatively high THM yields were observed in the 1,000 to 5,000 dalton range. The highest yields were primarily in the molecular weight ranges less than 5,000 daltons, however, the highest yields in the hypolimnion were observed in the larger molecular weight ranges (> 5,000 daltons).

## V. CONCLUSIONS

1. Seasonal changes in the watershed, from late winter to late summer, caused increased concentrations of THM precursors and THM-formation potentials (THMFPs) in both Broad Run and Lake Manassas, and, in the surface waters, higher-yielding-THM precursors during the summer than in March and April. These trends were likely due to increased biological activity in the watershed and, particularly at the lake surface, algal metabolism in the warmer months.
2. Impoundment of Broad Run increased the THMFP of the water, likely by increasing the opportunity for algal activity and microbiological decay of allochthonous and autochthonous TOC, both of which increase THMFP.
3. Stratification of Lake Manassas resulted in higher THM yields from the available organic material in the epilimnion than the hypolimnion, probably caused by 1. anoxic conditions in the bottom waters producing organics that are lower-yielding-THM precursors; 2. higher concentrations of low-molecular-weight precursors ( $<5,000$  daltons), which were higher-yielding-THM precursors than those  $>5,000$  daltons, in the epilimnion than in the hypolimnion.
4. There was an apparent difference in organics in the epilimnion and hypolimnion with respect to size and THM formation potential. Higher percentages of the total THMFP were produced in the smaller-molecular-size



fractions ( $< 5,000$  daltons) at the surface of Lake Manassas, whereas a greater proportion of the total THMFP in the hypolimnion originated from the larger-molecular-size fractions ( $> 5,000$  daltons). Most of the THM precursors were in the 1,000-5,000 dalton size range.

**APPENDIX A**  
**TOC AND THM CONCENTRATIONS, THM YIELDS**

Table A-1. ST 70 Fractionation Data - TOC, CHCl<sub>3</sub> and CHCl<sub>2</sub>Br Formation, TTHM, THM Yield.

Filter Size Daltons	TOC mg/L	CHCl <sub>3</sub> ug/L	CHCl <sub>2</sub> Br ug/L	TTHM ug/L	THM Yield u moles/mg C
<u>March 15, 1989</u>					
Raw	2.0	103	11	114	0.47
0.45 um	2.0	98	11	109	0.44
30 K	1.6	85	11	96	0.49
10 K	1.5	86	10	96	0.52
5 K	1.0	61	10	71	0.57
1 K	0.5	19	7	26	0.40
500	0.3	7	5	12	0.30
<u>April 26, 1989</u>					
Raw	2.5	148	12	160	0.53
0.45 um	2.2	136	12	148	0.55
30 K	1.8	112	11	123	0.56
10 K	1.7	106	11	117	0.56
5 K	1.2	79	10	89	0.60
1 K	0.4	16	6	22	0.43
500	0.2	9	5	14	0.53

Table A-1 (cont'd).

Filter Size Daltons	TOC mg/L	CHCl <sub>3</sub> ug/L	CHCl <sub>2</sub> Br ug/L	TTHM ug/L	THM Yield u moles/mg C
<u>June 28, 1989</u>					
Raw	3.1	169	15	184	0.49
0.45 um	3.1	182	16	198	0.52
30 K	2.5	171	15	186	0.61
10 K	1.9	147	15	162	0.70
5 K	1.4	112	13	125	0.73
1 K	0.5	33	8	41	0.65
500	ND	ND	ND	ND	ND
<u>August 9, 1989</u>					
Raw	2.8	192	15	207	0.61
0.45 um	2.6	169	13	182	0.58
30 K	2.2	186	15	201	0.75
10 K	1.8	156	14	170	0.77
5 K	1.5	69	12	81	0.43
1 K	0.6	49	8	57	0.77
500	0.4	25	5	30	0.60

ND - No Data.

Table A-2. LM 04 (surface) Fractionation Data - TOC, CHCl<sub>3</sub> and CHCl<sub>2</sub>Br Formation, TTHM, THM Yield.

Filter Size Daltons	TOC mg/L	CHCl <sub>3</sub> ug/L	CHCl <sub>2</sub> Br ug/L	TTHM ug/L	THM Yield u moles/mg C
<u>March 15, 1989</u>					
Raw	3.6	185	16	201	0.46
0.45 um	3.6	174	16	190	0.43
30 K	3.0	160	16	176	0.48
10 K	2.6	157	16	173	0.54
5 K	1.8	111	15	126	0.53
1 K	0.7	2	0	2	0.03
500	0.4	0	0	0	0
<u>April 26, 1989</u>					
Raw	4.1	242	15	257	0.52
0.45 um	3.9	237	16	253	0.53
30 K	3.1	203	16	219	0.58
10 K	3.0	198	16	214	0.59
5 K	1.9	142	14	156	0.67
1 K	0.6	35	11	46	0.60
500	0.3	13	8	21	0.53

Table A-2 (cont'd).

Filter Size Daltons	TOC mg/L	CHCl <sub>3</sub> ug/L	CHCl <sub>3</sub> Br ug/L	TTHM ug/L	THM Yield u moles/mg C
<u>June 28, 1989</u>					
Raw	4.6	302	11	313	0.56
0.45 um	4.6	298	11	309	0.56
30 K	3.9	176	12	188	0.40
10 K	2.9	167	10	177	0.50
5 K	2.0	154	10	164	0.68
1 K	0.7	55	9	64	0.74
500	ND	ND	ND	ND	ND
<u>August 9, 1989</u>					
Raw	4.7	291	13	304	0.54
0.45 um	4.2	271	13	284	0.56
30 K	3.6	311	14	325	0.75
10 K	3.0	291	14	305	0.84
5 K	2.6	249	13	262	0.83
1 K	0.9	101	11	112	1.01
500	0.6	57	11	68	0.91

ND - No Data.

Table A-3. LM 04 (bottom) Fractionation Data - TOC, CHCl<sub>3</sub> and CHCl<sub>2</sub>Br Formation, TTHM, THM Yield.

Filter Size Daltons	TOC mg/L	CHCl <sub>3</sub> ug/L	CHCl <sub>2</sub> Br ug/L	TTHM ug/L	THM Yield u moles/mg C
<u>June 28, 1989</u>					
Raw	5.6	407	11	418	0.62
0.45 um	ND	ND	ND	ND	ND
30 K	4.3	339	11	350	0.68
10 K	3.2	229	11	240	0.62
5 K	2.2	150	9	159	0.60
1 K	1.0	81	10	91	0.74
500	0.8	47	9	56	0.56
<u>August 9, 1989</u>					
Raw	6.0	352	9	361	0.50
0.45 um	5.2	284	8	292	0.47
30 K	4.0	289	9	298	0.62
10 K	3.2	232	8	240	0.62
5 K	2.2	111	7	118	0.44
1 K	0.8	8	0	8	0.08
500	0.6	3	0	3	0.04

ND - No Data.

Table A-4. LM 01 (surface) Fractionation Data - TOC, CHCl<sub>3</sub> and CHCl<sub>2</sub>Br Formation, TTHM, THM Yield.

Filter Size Daltons	TOC mg/L	CHCl <sub>3</sub> ug/L	CHCl <sub>2</sub> Br ug/L	TTHM ug/L	THM Yield u moles/mg C
<u>March 15, 1989</u>					
Raw	3.7	187	16	203	0.45
0.45 um	3.5	178	16	194	0.45
30 K	3.1	163	16	179	0.47
10 K	2.7	146	16	162	0.49
5 K	2.1	121	15	136	0.53
1 K	0.8	3	0	3	0.03
500	ND	ND	ND	ND	ND
<u>April 26, 1989</u>					
Raw	4.0	244	15	259	0.53
0.45 um	3.7	219	15	234	0.52
30 K	3.1	203	15	218	0.58
10 K	2.1	156	15	171	0.67
5 K	1.9	137	15	152	0.65
1 K	0.8	42	11	53	0.52
500	0.4	17	9	26	0.49



Table A-4 (cont'd).

Filter Size Daltons	TOC mg/L	CHCl <sub>3</sub> ug/L	CHCl <sub>2</sub> Br ug/L	TTHM ug/L	THM Yield u moles/mg C
<u>June 28, 1989</u>					
Raw	5.3	344	12	356	0.56
0.45 um	5.0	340	12	352	0.58
30 K	3.9	299	11	310	0.66
10 K	3.3	262	11	273	0.69
5 K	2.3	206	12	218	0.78
1 K	0.8	79	10	89	0.90
500	0.4	36	9	45	0.89
<u>August 9, 1989</u>					
Raw	4.4	283	12	295	0.56
0.45 um	4.3	276	13	289	0.56
30 K	3.6	303	13	316	0.73
10 K	2.7	299	13	312	0.96
5 K	2.5	268	13	281	0.93
1 K	0.8	71	10	81	0.82
500	0.5	46	13	59	0.93

ND - No Data.

Table A-5. LM 01 (bottom) Fractionation Data - TOC, CHCl<sub>3</sub> and CHCl<sub>2</sub>Br Formation, TTHM, THM Yield.

Filter Size Daltons	TOC mg/L	CHCl <sub>3</sub> ug/L	CHCl <sub>2</sub> Br ug/L	TTHM ug/L	THM Yield u moles/mg C
<u>June 28, 1989</u>					
Raw	ND	ND	ND	ND	ND
0.45 um	4.9	347	9	356	0.60
30 K	4.1	316	10	326	0.66
10 K	2.9	198	9	207	0.59
5 K	2.3	174	9	183	0.66
1 K	0.8	53	7	60	0.61
500	0.5	23	5	28	0.45
<u>August 9, 1989</u>					
Raw	8.3	393	10	403	0.40
0.45 um	6.3	248	8	256	0.34
30 K	4.3	68	0	68	0.13
10 K	3.3	35	0	35	0.09
5 K	2.6	21	0	21	0.07
1 K	0.8	0	0	0	0
500	0.5	0	0	0	0

ND - No Data.

Table A-6. ST 30 Fractionation Data - TOC, CHCl<sub>3</sub> and CHCl<sub>2</sub>Br Formation, TTHM, THM Yield.

Filter Size Daltons	TOC mg/L	CHCl <sub>3</sub> ug/L	CHCl <sub>2</sub> Br ug/L	TTHM ug/L	THM Yield u moles/mg C
<u>March 15, 1989</u>					
Raw	3.7	188	16	204	0.45
0.45 um	3.4	178	17	195	0.47
30 K	3.1	194	17	211	0.56
10 K	2.8	180	17	197	0.58
5 K	2.0	151	16	167	0.68
1 K	0.7	37	11	48	0.54
500	0.4	17	9	26	0.49
<u>April 26, 1989</u>					
Raw	3.8	232	17	249	0.54
0.45 um	3.7	220	17	237	0.53
30 K	3.1	196	18	214	0.57
10 K	2.8	181	17	198	0.58
5 K	2.0	141	16	157	0.64
1 K	0.6	32	11	43	0.56
500	0.4	14	8	22	0.42

Table A-6 (cont'd).

Filter Size Daltons	TOC mg/L	CHCl <sub>3</sub> ug/L	CHCl <sub>2</sub> Br ug/L	TTHM ug/L	THM Yield u moles/mg C
<u>June 28, 1989</u>					
Raw	5.1	378	15	393	0.64
0.45 um	5.0	358	14	372	0.62
30 K	4.3	312	15	327	0.63
10 K	3.3	218	13	231	0.58
5 K	2.5	166	13	179	0.59
1 K	0.8	67	11	78	0.79
500	0.4	18	7	25	0.48
<u>August 9, 1989</u>					
Raw	4.9	363	14	377	0.64
0.45 um	4.8	358	14	372	0.64
30 K	4.3	344	14	358	0.69
10 K	3.5	323	13	336	0.80
5 K	3.0	253	14	267	0.73
1 K	0.8	69	10	79	0.80
500	0.4	24	8	32	0.62

**APPENDIX B**  
**LAKE MANASSAS DATA**

Table B-1. Lake Manassas Limnological Data Derived from the Surface Waters at Site LM 04. (Provided by the Occoquan Watershed Monitoring Laboratory.)

Parameter	03/15	04/12	04/26	05/24	06/28	07/19	08/16
D.O. (mg/L)	12.10	10.10	11.20	8.80	9.33	7.70	7.90
D.O. % Sat.	94	92	117	99	122	96	97
Temp. (°C)	4.5	11.0	17.5	21.0	29.0	26.5	25.5
Secchi (in)	39	41	51	36	45	63	54
Chl-a (ug/L)	4.7	8.7	4.9	20	11	-1.0	5.8
TKN (mg/L)	0.42	0.44	0.32	0.39	0.45	0.37	0.32
TP (mg/L)	0.02	0.03	+0.01	0.04	0.02	0.02	0.01

D.O. - Dissolved Oxygen

% Sat. - Percent Saturation

Temp. - Temperature

Secchi - Secchi Depth

Chl-a - Chlorophyll-a Trichromatic

TKN - Total Kjeldahl Nitrogen

TP - Total Phosphorus

Table B-2. Lake Manassas Limnological Data Derived from the Bottom Waters at Site LM 04. (Provided by the Occoquan Watershed Monitoring Laboratory.)

Parameter	03/15	04/12	04/26	05/24	06/28	07/19	08/16
D.O. (mg/L)	11.90	8.55	4.00	3.30	0.15	0.10	0.01
D.O. % Sat.	91	76	35	31	1	1	<1
Temp. (°C)	4.0	10.0	10.0	13.0	14.0	15.0	17.5
TKN (mg/L)	0.35	0.41	0.55	0.57	0.52	1.55	1.15
TP (mg/L)	0.03	0.06	+0.02	0.09	0.07	0.28	0.12

D.O. - Dissolved Oxygen  
 % Sat. - Percent Saturation  
 Temp. - Temperature  
 TKN - Total Kjeldahl Nitrogen  
 TP - Total Phosphorus

Table B-3. Lake Manassas Limnological Data Derived from the Surface Waters at Site LM 01. (Provided by the Occoquan Watershed Monitoring Laboratory.)

Parameter	03/15	04/12	04/26	05/24	06/28	07/19	08/02
D.O. (mg/L)	12.40	10.20	11.80	8.40	8.61	6.20	6.0
D.O. % Sat.	96	94	124	93	112	77	74
Temp. (°C)	4.5	11.5	17.5	20.0	29.0	26.0	26.0
Secchi (in)	41	39	43	40	58	68	64
Chl-a (ug/L)	8.9	11	6.9	21	7.2	6.6	7.4
TKN (mg/L)	0.39	0.40	0.42	0.54	0.49	0.43	0.20
TP (mg/L)	0.01	0.03	0.01	0.04	0.01	+0.01	+0.01

D.O. - Dissolved Oxygen

% Sat. - Percent Saturation

Temp. - Temperature

Secchi - Secchi Depth

Chl-a - Chlorophyll-a Trichromatic

TKN - Total Kjeldahl Nitrogen

TP - Total Phosphorus



Table B-4. Lake Manassas Limnological Data Derived from the Bottom Waters at Site LM 01. (Provided by the Occoquan Watershed Monitoring Laboratory.)

Parameter	03/15	04/12	04/26	05/24	06/28	07/19	08/02
D.O. (mg/L)	11.80	6.40	4.30	4.05	0.18	0.10	0.15
D.O. % Sat.	91	55	38	38	2	1	1
Temp. (°C)	4.5	9.0	10.0	13.0	13.0	13.5	15.0
TKN (mg/L)	0.45	0.54	0.71	1.00	0.82	0.95	0.44
TP (mg/L)	0.02	0.05	0.06	0.20	0.06	0.05	+0.02

D.O. - Dissolved Oxygen  
 % Sat. - Percent Saturation  
 Temp. - Temperature  
 TKN - Total Kjeldahl Nitrogen  
 TP - Total Phosphorus

**APPENDIX C**  
**DISCHARGE AND RAINFALL DATA**

Mean Daily Discharge (cubic feet per second)  
Broad Run at Buckland  
1989

	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.
1	9.86	12.6	22.4	71.9	144	25.3	11.1	32.6	2.40	7.83	27.6	18.6
2	11.1	12.1	20.7	48.6	433	22.3	8.91	19.6	2.48	100	22.9	17.9
3	11.7*	11.6	19.9	42.9	143	19.8	8.49	14.7	2.35	50.0	23.3	18.0
4		21.0	19.4	39.6	86.2	19.3	11.3	10.6	2.02	25.5	23.4	18.2
5		18.5	22.6	40.3	421	15.9	62.7	8.36	1.92	19.2	22.1	16.3
6		15.7	156	70.6	1533	28.4	86.4	6.48	1.75	16.2	21.3	16.6
7		14.1	122	50.5	429	150	42.8	5.36	1.60	14.8	19.5	17.3*
8		13.8	61.1	56.3	201	54.0	25.2	6.18	1.58	15.3	21.2	
9	56.4*	11.8	46.5	49.5	153	107	17.9	5.61	1.59	16.7	36.0	
10	43.6	10.4	45.3	41.2	246	131	16.3	4.57	1.60	12.9	34.7	
11	35.8	10.0	39.4	36.7	174	54.4	13.9	4.87	1.48	9.29	26.4	
12	50.4	10.5	36.0	33.5	137	37.8	9.05	5.86	2.29	8.95	22.6	16.3
13	57.1	10.5	30.0	30.8	107	38.3	9.03	6.27	3.67	6.81	19.2	17.9*
14	36.7	14.8	28.3	26.0	89.5	125	14.8	6.48	2.84	6.74	17.7	
15	77.7	18.9	27.3	29.6	91.7	88.3	10.7	7.11	2.59	6.69	18.0	
16	57.8	22.9	23.8	37.6		59.1	75.4	6.51*	5.14	7.38	67.4	
17	38.9	22.2	19.4	28.2		47.0	37.7	5.53	11.6	23.0	44.7	
18	31.1	19.9	18.7	27.4	148	36.2	22.5	5.01	5.84	23.8	27.7	15.6*
19	26.3	18.6	20.3	115	117	27.3	17.2	5.21	4.51	240	23.5	
20	22.7	17.5	16.7	71.1	94.8	38.0	123	5.26	4.49	238	21.3	
21	19.8	24.9	30.7	48.8	79.8	38.0	67.8	5.05	5.68	121	19.7	
22	15.1	74.1	26.9	39.9	63.9	29.8	37.2	5.71	15.5	63.8	16.8*	9.87
23	15.2	70.1	21.6	33.2	66.1	44.7	25.2	5.45	8.41	41.5	19.2*	8.17
24	15.8	43.0	337	28.4	70.5	42.7	20.6	4.22	7.58	31.8	18.9*	8.98
25	16.1	31.2	199	24.8	51.4	45.1	16.9	3.51	4.58	25.8	18.9*	8.91
26	15.0	28.8	104	23.2	43.8	28.5	13.0	3.05	36.6	22.7	24.2*	10.7
27	13.8	26.0	70.0	21.0	41.1	21.2	12.4	2.91	21.2	20.5	29.9*	11.5
28	13.6	23.1	52.2	18.7	36.5	17.6	10.9	2.92	11.7	18.7	27.0	12.3
29	12.7		43.6	24.4	32.9	17.3	9.38	2.88	9.62	17.8		13.4
30	12.5		39.9	25.1	27.6	14.1	6.93	2.90	8.81	17.6	18.7*	14.6
31	12.5		82.9		25.6		8.67	2.48		19.6		29.8
Monthly Avg.	28.05	22.45	58.18	41.16	182.32	47.45	27.53	6.88	6.45	40.32	25.30	15.05

NOTES: \* Period of 12 hours or more missing during baseflow conditions.  
\*\* Period of 4 hours or more missing during stormflow conditions.

Mean Daily Discharge (cubic feet per second)  
Broad Run near Bristow  
1989

	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.
1	3.42	5.89	11.1	16.2	245	2.25	1.84	1.74	5.09	3.59	28.5	2.02
2	4.06	5.69	11.5	17.6	1026	2.23	1.84	17.6	5.60	29.1	35.8	1.28
3	4.60	8.40	10.7	58.9	430	2.62	2.26	4.82	5.74	5.62	32.2	1.49
4	7.13	18.4	12.1	50.0	245	2.53	3.33	1.75	5.79	1.82	51.5	84.4
5	6.51	13.8	18.2	15.6	377	2.44	6.82	3.12	2.90	1.44	2.85	2.44
6	4.75	11.4	397	146	3687	2.81	101	2.15	0.71	1.58	1.81	1.31
7	5.40	10.6	426	141	1199	821	133	1.41	0.81	2.58	4.99	1.28
8	11.8	9.18	131	120	389	222	26.3	2.11	10.8	4.05	14.1	73.4
9	57.5	7.98	191	68.9	275	194	3.47	2.06	1.63	5.12	30.3	18.8
10	48.8	6.41	51.7	28.3	399	253	5.79	1.54	0.90	23.3	23.7	1.31
11	27.7	6.05	76.8	41.4	277	88.5	45.1	1.53	0.96	2.18	23.4	1.04
12	71.2	5.75	35.9	24.4	107	46.2	44.2	1.57	1.15	1.22	22.4	1.05
13	69.9	5.05	27.0	8.26	72.4	34.5	1.33	1.70	1.31	1.98	25.9	1.21
14	26.9	8.64	66.3	4.69	35.3	60.4	0.89	1.93	1.31	3.53	140	116
15	169*	14.7	57.9	27.4	182	239	0.99	1.99	1.33	5.01	265	169
16	47.4*	21.2	35.9	23.9	498	86.3	3.27	1.99	1.97	11.9	374	17.4
17	25.2*	22.9	2.34	16.8	641	38.3	75.3	2.29	3.41	31.1	97.1	35.9
18	11.7	15.3	2.04	49.6	418	30.3	4.90	2.52	4.29	10.4	12.0	89.1
19	10.4	13.2	3.99	225	238	24.1	9.64	2.60	1.84	180	4.08	38.5
20	7.27	11.5	4.00	132	33.2	73.3	422	2.68	1.47	118	2.83	8.34
21	6.97	61.1	95.7	44.5	18.2	77.3	96.4	3.53	126	133	16.2	9.92
22	4.29	133	191	30.1	113	52.7	5.20	4.42	84.1	77.0	42.9	95.9
23	3.27	52.1	76.1	4.39	198	8.17	7.04	4.37	2.04	77.9	8.19	10.7
24	2.78	33.1	798	18.8	167	12.5	21.1	4.12	1.31	96.5	1.70	1.65
25	4.54	27.9	820	11.5	50.4	78.9	9.42	4.44	1.28	191	1.48	1.07
26	3.97	12.4	262	8.56	20.7	67.3	2.00	5.39	5.94	2.87	2.23	1.04
27	3.47	42.5	56.0	5.39	35.3	14.0	3.13	3.81	2.70	2.59	3.24	1.06
28	2.76	33.2	55.4	3.59	9.78	7.39	4.35	1.10	1.54	7.49	2.60	0.85
29	2.73		24.2	75.5	7.43	2.32	4.63	1.95	1.69	8.79	7.81	0.70
30	4.30		55.0	23.3	25.3	2.25	1.33	3.20	3.07	11.5	14.1	0.70
31	5.91		82.6		9.05		0.88	4.36		14.1		2.28

Monthly Avg.	21.47	22.05	131.89	46.05	368.65	84.95	33.83	3.22	9.62	34.40	43.10	25.52
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NOTES: \* Period of 12 hours or more missing during baseflow conditions.

\*\* Period of 4 hours or more missing during stormflow conditions.

DATE1	OWML Rain
-------	--------------

03/15/89	0.00
03/16/89	0.00
03/17/89	0.00
03/18/89	0.10
03/19/89	0.00
03/20/89	0.10
03/21/89	0.14
03/22/89	0.00
03/23/89	0.34
03/24/89	0.85
03/25/89	0.00
03/26/89	0.00
03/27/89	0.00
03/28/89	0.00
03/29/89	0.00
03/30/89	0.36
03/31/89	0.16
04/01/89	0.16
04/02/89	0.00
04/03/89	0.08
04/04/89	0.01
04/05/89	0.57
04/06/89	0.00
04/07/89	0.26
04/08/89	0.00
04/09/89	0.02
04/10/89	0.00
04/11/89	0.00
04/12/89	0.00
04/13/89	0.00
04/14/89	0.00
04/15/89	0.45
04/16/89	0.00
04/17/89	0.00
04/18/89	0.43
04/19/89	0.15
04/20/89	0.00
04/21/89	0.00
04/22/89	0.00
04/23/89	0.00
04/24/89	0.00
04/25/89	0.00
04/26/89	0.00
04/27/89	0.00
04/28/89	0.00
04/29/89	0.56
04/30/89	0.00
05/01/89	0.26
05/02/89	0.00
05/03/89	0.00

DATE1	OWML Rain
-------	--------------

05/04/89	0.00
05/05/89	3.21
05/06/89	0.43
05/07/89	0.00
05/08/89	0.00
05/09/89	0.43
05/10/89	0.07
05/11/89	0.02
05/12/89	0.01
05/13/89	0.00
05/14/89	0.00
05/15/89	0.88
05/16/89	0.63
05/17/89	0.00
05/18/89	0.00
05/19/89	0.00
05/20/89	0.00
05/21/89	0.00
05/22/89	0.00
05/23/89	1.25
05/24/89	0.00
05/25/89	0.00
05/26/89	0.00
05/27/89	0.15
05/28/89	0.00
05/29/89	0.00
05/30/89	0.00
05/31/89	0.00
06/01/89	0.00
06/02/89	0.00
06/03/89	0.00
06/04/89	0.00
06/05/89	0.35
06/06/89	0.87
06/07/89	1.06
06/08/89	0.00
06/09/89	0.98
06/10/89	0.00
06/11/89	0.00
06/12/89	0.01
06/13/89	0.09
06/14/89	0.33
06/15/89	0.65
06/16/89	0.47
06/17/89	0.00
06/18/89	0.00
06/19/89	0.00
06/20/89	0.53
06/21/89	0.00
06/22/89	0.02

DATE1	OWML Rain
-------	--------------

06/23/89	0.01
06/24/89	0.14
06/25/89	0.00
06/26/89	0.00
06/27/89	0.00
06/28/89	0.00
06/29/89	0.00
06/30/89	0.00
07/01/89	0.00
07/02/89	0.00
07/03/89	0.00
07/04/89	0.64
07/05/89	0.12
07/06/89	0.30
07/07/89	0.01
07/08/89	0.00
07/09/89	0.00
07/10/89	0.00
07/11/89	0.00
07/12/89	0.00
07/13/89	0.34
07/14/89	0.00
07/15/89	0.00
07/16/89	1.49
07/17/89	0.01
07/18/89	0.00
07/19/89	0.00
07/20/89	1.45
07/21/89	0.00
07/22/89	0.00
07/23/89	0.00
07/24/89	0.00
07/25/89	0.00
07/26/89	0.00
07/27/89	0.00
07/28/89	0.00
07/29/89	0.00
07/30/89	0.00
07/31/89	0.10
08/01/89	0.48
08/02/89	0.22
08/03/89	0.01
08/04/89	0.00
08/05/89	0.00
08/06/89	0.00
08/07/89	0.00
08/08/89	0.00
08/09/89	0.00
08/10/89	0.06
08/11/89	0.01

DATE1	QWML Rain
08/12/89	0.02
08/13/89	0.00
08/14/89	0.00
08/15/89	0.00
08/16/89	0.00
08/17/89	0.08
08/18/89	0.04
08/19/89	0.00
08/20/89	0.00
08/21/89	0.28
08/22/89	0.00
08/23/89	0.00
08/24/89	0.00
08/25/89	0.00
08/26/89	0.00
08/27/89	0.00
08/28/89	0.00
08/29/89	0.00
08/30/89	0.00
08/31/89	0.00
09/01/89	0.00
09/02/89	0.00
09/03/89	0.00
09/04/89	0.00
09/05/89	0.00
09/06/89	0.00
09/07/89	0.00
09/08/89	0.00
09/09/89	0.00



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## VITA

Anne M. Aiken was born on December 31, 1963-- the last child of seven born to William E. and Margaret G. Aiken in Syracuse, New York.

A handwritten signature in cursive script that reads "Anne M. Aiken". The signature is written in a dark ink and is positioned centrally on the page.