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TRIHALOMETHANE PRECURSORS IN KANSAS LAKES: SOURCES AND CONTROL

PHASE II

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Prepared for
United States Geological Survey
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WATER ESSENTIAL RESOURCE

**A Research Project
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TRIHALOMETHANE PRECURSORS IN KANSAS LAKES: SOURCES AND CONTROL

Project Completion Report

by

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ABSTRACT

Trihalomethanes (THMs) are chemical compounds formed when chlorine reacts with organic matter (precursors) present in drinking water. Because THMs are suspected carcinogens, state and federal standards limit their combined concentration in public drinking water supplies to less than 100 µg/L. The primary objective of this two-year research effort was to examine the THM precursors in Kansas lakes, including those from streams, storm runoff, and wastewater effluents (allochthonous precursors) and those formed in the lakes by microbial activity and decay of vegetation (autochthonous precursors), thereby establishing a data base suitable for use in assessing the feasibility of source control of THM precursors in Kansas lakes and for characterizing the levels of precursors in raw surface water supplies in Kansas.

The research program consisted of five parts: 1) a lake study that included the use of microzone sampling techniques to identify significant sources of autochthonous THM precursors; 2) a stream study to characterize the concentrations of THM precursors in Kansas streams as well as seasonal and hydrological changes in precursor concentrations; 3) a watershed study to examine point and non-point sources of allochthonous THM precursors; 4) an experimental pond study to examine the influence of algae-control techniques on THM precursors; and 5) a laboratory study to examine the release or degradation of THM precursors from selected substrates.

Total organic carbon (TOC) and dissolved organic carbon (DOC) were found to be excellent predictors of trihalomethane formation potential (TFP) and dissolved TFP (DTFP), respectively, for samples from a particular source. The yield of THMs varied from source to source, but the variation was not great for the field samples, most of which had yields between 0.3 and 0.5 micromoles per milligram of carbon (µmol/mgC).

For the five lakes that were sampled, the average concentrations of DOC and TOC were 4.4 and 5.0 mg/L, respectively. DTFP averaged 0.39 µmol/mgC, while TFP averaged 0.42 µmol/mgC. The concentrations of THM precursors were quite similar in each lake, despite significant differences in the physical characteristics, ages, sizes, and uses of the lakes. No seasonal trends were observed, indicating that most of the precursors are allochthonous. The concentrations of precursors in top and bottom samples from stratified lakes were sometimes slightly different, but on the average they were virtually identical. Lake sediments were not a significant source of THM precursors for the lakes sampled.

Organic carbon and THM precursors were distributed quite uniformly throughout the lakes that were sampled. Elevated concentrations were observed in major inlet streams, near eroding shorelines, and in one bed of decaying weeds, but not in brush piles, sheltered coves, areas of standing timber, small sheltered inlets, or other beds of living and dead weeds. Hence, any autochthonous precursors being produced in significant amounts in microzones within the lakes that were sampled were either being produced at a slow rate relative to their rates of diffusion and dispersion or at times and places other than those of the samplings. Thick layers of gelatinous slime, observed on senescing macrophytes in the fall and on several of the substrates examined in laboratory experiments, appeared to degrade most of the material leached from senescing macrophytes before it could be released into the water.

The stream samples had an average DOC concentration of 4.5 mg/L, an average TOC concentration of 6.0 mg/L, an average DTFP yield of 0.44 µmol/mgC, and an average TFP yield of 0.47 µmol/mgC. The concentrations of organic matter and THM precursors in the streams were found to increase very substantially during periods of wet weather, indicating that mass loadings increase dramatically following storm events. The lake and stream data indicate that the lakes are net sinks for organic carbon and THM precursors.

The concentrations of organic carbon and THM formation potential were generally much higher in municipal and industrial wastewater effluents than in lakes and streams; but these sources generally contribute only a small fraction of the total stream flow. Agricultural runoff, which had extremely high concentrations of precursors is perhaps the most significant source of THM precursors in Kansas, since much of the land in Kansas is used for agricultural purposes. Runoff from non-agricultural land and urban areas also carried large quantities of precursors.

Addition of copper sulfate and simazine to experimental ponds led to algal blooms, accompanied by increased concentrations of organic matter and THM precursors. Addition of copper sulfate, simazine, and grass carp to experimental ponds infested with macrophytes caused organic matter and THM precursors to be released into the water prematurely in comparison to the control ponds, in which weeds were allowed to senesce naturally.

Organic carbon and THM precursors were found to leach in potentially significant quantities from filamentous algae, aquatic weeds, leaves, tree blossoms, wood fragments, pine needles, pine twigs, pine branches, and other substrates. Leaching from bacterial suspensions was negligible; and the organic matter in river water, secondary effluent, and soil extract did not appear to be biodegradable. Precursors released from various substrates under aerobic conditions in the laboratory were considerably more potent than those released under anaerobic conditions. Under both aerobic and anaerobic conditions, DTFP was strongly and positively correlated with DOC, UV absorbance, and color, and DTFP yield increased with an increasing ratio of UV absorbance to DOC.

Since 75-90% of the precursors in the lakes and streams were dissolved, it appears that effective source control of THMs in Kansas lakes will require a substantial reduction in soluble precursor concentrations. The majority of precursors are undoubtedly allochthonous, but attempts to control the entry of such precursors to lakes in Kansas may simply result in greater production of autochthonous precursors due to decreased turbidity. The autochthonous fraction of the precursors, though much smaller than the allochthonous fraction, may nevertheless be very significant, especially for utilities experiencing difficulty meeting the THM standard.

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INTRODUCTION

A. BACKGROUND

Trihalomethanes (THMs) are chemical compounds formed when chlorine, used to disinfect public water supplies, reacts with certain natural or synthetic organic constituents (precursors) present in the water. Because chloroform, the most abundant THM species, is a known animal carcinogen, and because the other THMs are suspected carcinogens, the Kansas Department of Health and Environment (KDHE) requires that all public water supplies in Kansas serving over 10,000 people and all new or modified water treatment plants of any size provide a water containing less than 100 µg/L of THMs. Many communities in eastern Kansas obtain their water from small water supply lakes that contain a substantial amount of organic precursor material. When chlorine is added to these supplies, it can be very difficult (or even impossible) to maintain a THM concentration below the required limit using conventional treatment methods.

There has been a very substantial amount of research done on methods of controlling THM formation during water treatment, but very little research has been done in regard to source control, i.e., minimizing the concentration of precursors in the raw water supply. While it is known that algae, bacteria, and decaying vegetation are sources of THM precursors, the relative importance of these and other sources is unknown. Also unknown is the relative amount of precursors originating from sources in the watershed (allochthonous precursors) as opposed to those formed in the lake itself (autochthonous precursors). Hence, it is not clear whether efforts to control precursor sources should be directed primarily at watersheds or lakes or both. The 1984 Revision to the Kansas Water Quality Management Plan specifically recommends that an assessment be made of the link between non-point-source pollutants and THM formation. To complicate matters further, there has been almost no research done on the effects of lake management practices (e.g., copper sulfate addition) on THM precursor concentrations, so it is not known which management practices can effectively control THM precursors and which may aggravate the situation.

B. OBJECTIVES

The specific objectives of this research effort were: 1) to identify the significant sources of THM precursors in Kansas watersheds and lakes; 2) to assess the relative importance of allochthonous and autochthonous THM precursors; 3) to evaluate management strategies for source control of THM precursors; 4) to examine the influence of several algae-control techniques on THM precursor levels; and 5) to examine the release and biodegradation of THM precursors and organic carbon from selected substrates under aerobic and anaerobic conditions.

The results of this study are intended to help decision makers to assess the relative importance of allochthonous and autochthonous THM precursors in Kansas lakes, thereby providing a rational basis for evaluating the suitability of watershed and lake management techniques for source control of THM precursors. This research is intended to complement on-going efforts by KDHE and by managers of water supply lakes to control THM formation. At the present time approximately thirty-seven surface water supplies in Kansas experience difficulty meeting the THM standard and many more are likely to be affected in the future, especially if the federal standard for THMs is substantially lowered, as has been proposed. This problem affects not only Kansas, but nearly every state, particularly those in which many communities rely on lakes as a source of potable water. Thus, the results of this research are also expected to be of interest to water supply managers in other states.

C. EXPERIMENTAL APPROACH

The research program designed to accomplish the aforementioned objectives consisted of five parts: 1) a lake study using microzone sampling techniques to identify significant sources of autochthonous THM precursors; 2) a stream study to characterize the concentrations of THM precursors in Kansas streams as well as seasonal and hydrological changes in precursor concentration; 3) a watershed study to examine point and non-point sources of allochthonous THM precursors; 4) an experimental pond study to examine the influence of algae-control techniques on THM precursors; and 5) a laboratory study to examine the release of THM precursors from selected substrates and and to observe transformations in THM precursors caused by bacterial activity.

The lake study involved seasonal sampling of selected microzones in several water-supply lakes. Microzones of interest included major inlets and outlets, side channels, anaerobic and aerobic sediments, brush piles, shoreline vegetation, and the epilimnion and hypolimnion of the main body of the lake. The data collected in this part of the study were intended to establish the distribution of THM precursors within each lake and to aid in the identification and assessment of major sources of autochthonous THM precursors. Such information is helpful in evaluating the potential impact of lake management practices (such as weed control and destratification) on THM precursor concentrations. Clinton Lake was selected for sampling because it is representative of the many (24) large federal reservoirs in Kansas. The other lakes sampled were Strowbridge Reservoir (a small water supply reservoir), Douglas Lake (a county fishing lake), Lone Star Lake (a nearby recreational lake), and Lyndon Lake (a small water supply reservoir recently stocked with grass carp to control a macrophyte problem).

During a period lasting more than one year, stream samples were collected every few weeks in an effort to determine the concentrations of stream-borne organic carbon and THM precursors typical of this region and to examine the concentrations of organic constituents as a function of rainfall, streamflow, season, etc. Another objective was to compare the precursor concentrations found in the streams with those found in the lakes, thereby providing an indication as to whether the lakes were net sources or sinks with respect to THM precursors.

For the watershed study, a sampling program was undertaken to sample a variety of natural and anthropogenic THM precursor sources, including (but not limited to) the following: municipal and industrial effluents, urban and agricultural runoff, oil-field brines and brine-contaminated groundwater, and runoff from feedlots, construction sites, and vegetated areas. Preference was given to sampling sites in the upper Wakarusa River watershed feeding Clinton Lake, since Clinton Lake was a major sampling site for the lake study and since a considerable amount of historical data is available for this watershed.

The experimental pond study was designed to evaluate the influence of several algae-control techniques on THM precursors. The study was conducted using eight identical ponds at KU's Nelson Experimental Study Area. Two ponds served as controls, two were treated with copper sulfate, two were treated with an organic herbicide (simazine), and two were stocked with herbivorous fish (grass carp). The concentrations of chlorophyll a, TOC, DOC, and total and dissolved THM precursors were monitored. From another series of six ponds, maintained at different turbidity levels to examine the influence of turbidity on pond ecology, additional data were collected to show the influence of turbidity on THM precursor production.

Laboratory studies were conducted to examine the biodegradability of THM precursors from several sources and to examine the amounts of organic carbon and THM precursor released from various substances (e.g., pine needles and aquatic weeds) under aerobic and anaerobic conditions. Since THM precursors are organic chemicals, their concentration may increase or decrease due to chemical and biochemical transformations. To assess the relative importance of various sources of THM precursors, it is helpful to know how long the precursors will persist in the environment and whether they are transformed into weaker or stronger precursors.

RELATED RESEARCH

The formation of THMs during chlorination of a water supply was first reported by Johannes Rook of the Netherlands in 1974 (Rook, 1974). Subsequent research by Rook and by scientists in the United States conclusively demonstrated that THMs are primarily a by-product of the reaction of chlorine with naturally occurring organic matter and that they are found in virtually all water supplies treated with free residual chlorine (Bellar et al., 1974; Symons et al., 1975; Rook, 1976 & 1977; Stevens et al., 1976). This research attracted considerable attention because chloroform, the most abundant species of THM identified in chlorinated water supplies, was known to be an animal carcinogen.

On November 29, 1979, after consultation with the Public Health Service, the National Cancer Institute, and the National Academy of Sciences, and after considerable public discussion and debate, the U.S. Environmental Protection Agency (EPA) promulgated an amendment to the National Interim Primary Drinking Water Regulations limiting the concentration of THMs in drinking water to 100 µg/L for supplies serving over 10,000 persons (Federal Register, 1979). The Kansas Department of Health and Environment (KDHE) decided to apply this limit not only to large supplies, but also to small supplies undergoing treatment plant modifications and to all new supplies, regardless of size.

Since 1974, great numbers of papers have been written on various aspects of the THM problem, particularly health effects, chemical reactions, regulatory control, and water treatment technology. An excellent summary of this information has been prepared by Symons et al (1981). One aspect that has received very little attention is the potential for source control of THMs, i.e., the use of management practices to reduce the level of THM precursors in the raw water supply.

Although only a very limited amount of information is available, it is clear that algae, bacteria, and decaying aquatic vegetation contribute to THM formation, since they directly produce THM precursors (Larson & Rockwell, 1979; Jacquez & Muckerman, 1979; Hoehn et al., 1980; Crane & Kovacic, 1980; Briley et al, 1980; Oliver & Shindler, 1980; Tambo & Kamei, 1981; Hoehn et al., 1984; Briley et al., 1984; and Wachter & Andelman, 1984). What has not been clearly established is the importance of these sources relative to the many other potential sources of THM precursors, whether these sources are most significant in the watershed or in the lake itself, and to what extent these and other sources can be controlled.

A comprehensive literature review (Wapora, 1984) dealing primarily with THMs and their precursors, and secondarily with the situation in Kansas, was recently completed for Region VII of the U.S. Environmental Protection Agency. A specific objective of the contracted review was to address "the sufficiency of data regarding the relative dominance of THM precursor contributions by allochthonous and autochthonous sources." The report concludes that "at present, observations concerning source dominance appear highly conjectural based upon extrapolations from indirectly related studies. Absolute answers to questions of dominance will likely require more direct, concurrent consideration of candidate sources in individual systems." Other notable and related conclusions were:

1) Source dominance will vary from reservoir to reservoir depending on site-specific factors;

2) Relative THM precursor contributions from the various sources have not been adequately quantified; and

3) The relative contributions of semi-permanent grasslands, croplands, forests, and floodplains to THM formation have not been compared.

The United States Geological Survey (USGS) is currently involved in a two-phase cooperative study with KDHE to examine water quality in water supply lakes in Kansas. In the first phase of the study, samples from 19 water supply lakes in eastern Kansas were analyzed for TOC, nutrients, metals and other constituents. Samples were taken on one or two occasions from each of 19 water supply lakes with the objective of examining the relationships between selected variables and the quality of the water. The results of this study were reported by Pope et al. (1985), who found an average TOC concentration of 6.2 mg/L in the lake samples. Statistical analysis of the data revealed that TOC concentration was significantly correlated with average maximum lake depth (negative correlation) and turbidity (positive correlation), but not with chlorophyll a, size, watershed-to-lake surface area, nutrient concentrations, or land use patterns. In a second phase of the USGS/KDHE study, samples are being taken from six lakes at more frequent intervals. Preliminary analysis of the data shows a strong correlation between total organic carbon concentration and trihalomethane formation potential (Arruda, 1985), as was found by Symons et al. (1975).

In a recent study, similar in some respects to the one described herein, Cook et al. (1984), examined sources of trihalomethane precursors in Salt Lake County, Utah. They found: 1) a linear relationship between stream discharge and TOC; 2) greatly elevated loadings and concentrations of precursors in spring runoff, with an average TOC of 3.4 mg/L; 3) potentially significant contributions from leaf litter and soil; 4) evidence that impoundment of surface water increases precursor concentrations; 5) negligible contributions from snowmelt; and 6) greater contributions from deciduous vegetation than from coniferous vegetation. Their results are quite interesting but may not be directly applicable to Kansas because most Kansas watersheds are heavily dominated by agricultural land use and gentle slopes, whereas those examined by Cook et al. tended to be mountainous, forested, steeply sloped, and used for recreation or closed to the public. Furthermore, there are significant differences in climate, soil types, and precursor concentrations between the two states. In Kansas the average TOC concentrations in streams and lakes are more than twice the maximum seasonal average reported by Cook et al. for Salt Lake County runoff; and the average THM concentration in Salt Lake County distribution systems was only 40 µg/L in 1981, well below the standard of 100 µg/L, which many Kansas utilities have difficulty meeting.

The literature contains little information regarding the concentration of organic matter in lakes as a function of depth and stratification. Biochemical oxygen demand (BOD) is known to increase in the hypolimnia of stratified lakes, but this is due, in part or in whole, to increased concentrations of iron, manganese, sulfide, and ammonia, and not necessarily to an increase in the concentration of biodegradable organic matter. Tipping and Woof (1983) reported to TOC concentrations in an anoxic hypolimnion nearly double those in the epilimnion (3.0 vs 1.5 mg/L), but the lake was a soft-water lake in England with characteristics undoubtedly much different than those of Kansas lakes. Hoehn (personal communication, 1986) found that the TOC concentration in a lake in Virginia nearly doubled (from 7 to 14 mg/L) during fall overturn and Knocke et al. (1987) presented data showing an elevated TOC concentration in the hypoliminion of a reservoir in Virginia; but these lakes are also much different than those in Kansas, having sediments containing much larger amounts of organic detritus. Thurman (1985) cites several studies showing a decrease in TOC with depth, but these were deep lakes in which most of the TOC was autochthonous; TOC decreased with depth as the dead algae settling into the hypolimnion were consumed by bacteria.

There is an immense quantity of THM data in the recent scientific literature. When organic carbon concentrations are also reported, the yield of THMs in micromoles per milligram of carbon (μmoles/mgC) can be computed. A sampling of THM yield data is presented in Table 1. Since THM formation is dependent upon chlorine dosage, pH, time, temperature, bromide concentration, and residual chlorine concentration, caution must be taken in comparing the results of one study with another.

Based upon the results shown in Table 1, the following conclusions may be drawn: 1) humic acid generally produces a higher yield of THMs than fulvic acids, but exceptions have been noted (in this case by Snoeynik & McCreary, 1980, and Oliver & Thurman, 1983); 2) the THM yields of algal cells and algal extracellular products are generally lower than for other precursors, but exceptions have been noted; 3) the THM yields produced upon chlorination of drinking water tend to be lower than those produced by humic substances and higher than those produced by algae, perhaps because the precursors in drinking water are a mixture of these and other precursors; and 4) THM yield increases with increasing molecular weight. The latter seems to be generally true (although contradictory data have been published, e.g., Oliver & Visser, 1980), but the great majority of THM precursors in most water supplies are of low molecular weight, rendering the contributions of the high-molecular-weight molecules inconsequential. Also, there is a great deal of evidence to suggest that the higher-molecular-weight molecules are much more readily removed by conventional water treatment practices. The THM yields of groundwater supplies are generally lower than those for surface water supplies, and the data of Oliver and Thurman (1983) support this. The high yields noted by Edzwald et al. (1985) are not surprising, since the waters they studied are highly colored and the organic matter in them appears to be primarily humic and fulvic acids.

TABLE 1

THM YIELDS REPORTED IN THE LITERATURE

Precursor Source	THM Yield µmoles/mgC	Conditions/Comments	Reference
Drinking water	0.23	Avg. of 80 samples taken nationwide; based on finished water TOC.	Symons *et al.* (1975)
Peat humic acid	1.20	10 mg/L Cl_2; pH = 6.5; 96 hours; 20°C yields computed from authors' graphical data.	Babcock & Singer (1979)
Peat fulvic acid	0.33		
Humic acid (Aldrich)	0.74	10 mg/L Cl_2; pH 7.0; TOC = 2.5 mg/L; 90-100 hours; yields computed from authors' graphical data.	McCreary & Snoeyink (1980)
Soil fulvic acid	0.64		
Leaf fulvic acid	0.61		
Soil humic acid	0.37		
C. pyrenoidosa	0.03-0.24	Cl_2 dosage = 50 mg/L; the highest yields were associated with the youngest cells.	Hoehn *et al.* (1980)
S. quadricauda	0.02-0.04		
A. flos-aquae	0.02-0.06		
O. tennuis	0.03-0.33		
A. oscillarioides	0.15	10 mg/L Cl_2; 20°C; 24 hours; 1 mg/L TOC; yields computed from the authors' data, assuming each material to be 40% carbon by weight.	Oliver & Shindler (1980)
A. nidulans	0.09		
S. quadricauda	0.13		
S. basiliensis	0.10		
S. capricornutum	0.09		
N. minina	0.07		
N. pelliculosa	0.11		
Fulvic acid	0.36		

TABLE 1 (cont'd)

THM YIELDS REPORTED IN THE LITERATURE

Precursor Source	THM Yield µmoles/mgC	Conditions/Comments	Reference
Anabaena cells*	1.20	8.7-23.6 mg/L Cl_2; 24 hours; pH = 6.4-7.6; 21-24°C; values computed from tabular and graphical data; upper values for day 7 of growth phase and lower values for day 21.	Briley *et al*. (1980)
Anabaena cells	0.16		
Anabaena ECP	0.15		
Anabaena ECP	0.32		
Humic acid (Aldrich)	0.80	20 mg/L Cl_2 added; TOC = 3.0 mg/L; 100 hours; pH = 7.0; 25°C.	Fleischacker & Randtke (1983)
Peat fulvic acid	0.46		
Groundwater fulvic acid	0.53		
Groundwater	0.36		
Secondary Effluent	0.28		
Algal Culture	0.54	20 mg/L Cl_2 added; TOC = 3.0 mg/L; 100 hours; pH = 7.0; 25°C; aged, mixed culture with bacteria present.	Fleischacker (1983)
Algal ECP	0.08		
Fulvic acids		10 mg/L Cl_2; 1 mg/L TOC; pH 7; 7 days; 20°C; values shown are averages of authors' data. THM formation potentially increased with increasing phenolic content, molecular weight, and color.	Oliver & Thurman (1983)
Groundwater	0.31		
Streams & Lakes	0.98		
Marshes, Bogs, Swamps	1.07		
Humic acids	0.71		
C. pyrenoidosa ECP	0.03	Cl_2 dosage = 20 mg/L; 24°C; 24 hours; pH = 7.0; ECP from early stationary growth phase.	Wachter & Andelman (1984)
A. flos-aquae ECP	0.07		
Chlorophyll	0.13		

*ECP = extracellular products

TABLE 1 (cont'd)

THM YIELDS REPORTED IN THE LITERATURE

Precursor Source	THM Yield µmoles/mgC	Conditions/Comments	Reference
Grasse River	0.65	Cl_2/TOC = 3-5; pH 7.5; 20°C; 7 days. More than 40 samples were taken from each location.	Edzwald *et al.* (1985)
Glenmore Reservoir	0.61		
Drinking Water		Cl_2/TOC = 3; pH 7.0; 20°C; 7 days. The 16 drinking water samples were raw and treated samples from 8 treatment plants. The molecular weight data were for raw and treated samples from 4 treatment plants.	Collins *et al.* (1985)
16 Samples	0.46		
MW < 500	0.45		
MW < 1,000	0.48		
MW < 5,000	0.51		
MW < 10,000	0.54		
MW < 30,000	0.54		
Groundwater	0.26	Avg. of 47 wells in Kansas; pH 8.2; 96 hours; 25°C; chlorinated in 5 mg/L Cl_2 increments to achieve a free residual.	Miller *et al.* (1986)

There is a great deal of evidence that THM concentrations vary seasonally, usually peaking during the warmer months. However, most of the data are from treatment plants in which the water temperature also varied seasonally. Hence, it is usually not possible to determine whether the elevated THM levels observed during the warmer months are due to an increase in temperature, to an increase in precursor concentration, or to a change in the chemical structure (potency) of the precursors. In a study in which chlorination conditions were controlled, Singer et al. (1982) found that THM formation potential in North Carolina streams was highest during the spring and summer; and they also noted an increase as the streams flowed from the mountains toward the coast, which they speculated might have been due to the change in the nature of the vegetation or to changes in the occurrence of humic substances. Although few such studies have been done with respect to THM precursors, there exists a very substantial body of knowledge regarding seasonal changes in the organic carbon concentrations of streams.

The export of DOC from most watersheds is seasonal (Thurman, 1985), primarily because rainfall is season, but also because vegetation is seasonal. Meyer and Tate (1983) showed that DOC export was significantly lower from a clear-cut watershed than from a similar undisturbed watershed, which they attributed to decreased DOC inputs from throughfall, leaching of fresh litter, inflow of subsurface water, and in-stream productivity.

One might expect DOC and TOC concentrations to decrease with increasing streamflow, since more water is available for dilution; but in fact, just the opposite is true. Thurman (1985) cites numerous studies showing that DOC and TOC increase with increasing stream discharge, often by 50 to 100% or more. He attributes this to the flushing action of precipitation on soil and plant organic matter and to leaching of DOC from the interstitial waters of sediments and soils; and he also notes that prairie soils are especially rich in organic matter. Antweiler and Drever measured DOC concentrations in interstitial waters (associated with the weathering of volcanic ash); DOC averaged 50 mg/L, ranging from 20 to 260 mg/L, with the highest values occurring during the spring. Increased discharge also goes hand-in-hand with increased soil erosion, which causes increased turbidity and an increase in the concentration of particulate organic carbon.

Larson (1978) found a relatively poor correlation (r = 0.36) between organic carbon concentration and mean discharge for a stream in Pennsylvania, due primarily to the wide range of concentrations observed at low discharge. However, he noted that:

> "During summer storms [DOC] concentrations increased rapidly and markedly. For example, just before one storm,...[the DOC] concentration was 6.4 mg/L. A sample taken approximately 1h after the beginning of the storm has a much higher [DOC] concentration (11.8 mg/L). A sample taken about 4h later (after the storm had largely subsided), showed 8.2 mg/L, but interestingly, had much greater visible colour. After an additional 12h, [DOC] was still 8.5 mg/L. [DOC] appeared to follow the hydrograph closely during the storm."

The scatter in the data during low discharge is presumably attributable to changes in plant growth, in-stream productivity, in-flow from groundwater, etc. These effects are apparently overwhelmed by the tremendous flushing action of a major storm.

Several investigators have reported increasing THM formation with increasing streamflow or runoff. Morris & Johnson (1976) showed that gross amounts of THM precursors were associated with agricultural runoff in Iowa; and they reported that increases in turbidity associated with agricultural runoff were a good predictor of elevated levels of organic matter, increased chlorine demand, and taste-and-odor episodes. Harms & Looyenga (1980) found a good correlation between THM formation and turbidity, which presumably increased as streamflow increased; and they also found increased concentrations of THM precursors upstream near marshes, where cattle watered, and where the river was stagnant. Cook *et al*. (1984) found a strong correlation between stream discharge and precursor concentration.

In summary, much is known about THM formation during water treatment and a number of sources of THM precursors have been identified, but there has been no study of the relative importance of specific THM precursor sources in Kansas or of the transformations that precursors might undergo in a stream or lake. Virtually no work has been reported on the effects of common reservoir management practices on THM precursor concentrations.

SAMPLING SITES AND PROCEDURES

A. LAKES

Sampling Sites

During the course of the study, samples were taken from five different lakes: Clinton Lake, Strowbridge Reservoir, Douglas County Lake, Lone Star Lake, and Lyndon Lake. Each of these is described below.

Clinton Lake

Clinton Lake is a federal reservoir constructed and operated by the U.S. Army Corps of Engineers and located in Douglas County, Kansas, near Lawrence. Construction was completed in 1977, so the lake was 9 years old in 1986. The lake is large, covering over 7,000 acres, and shallow. Weak stratification frequently occurs in the deeper channels and near the dam during the summer months. The lake is fed by local runoff, several small streams, and the Wakarusa River (see Figure 1). It is a multipurpose reservoir, providing flood control, public water supply, wildlife habitat, and recreational opportunities (fishing, boating, skiing, swimming, windsurfing, etc.) The locations of the sampling sites are shown in Figure 1 and the sites are described in Table 2.

Most of the shoreline is covered with natural vegetation, mostly trees and brush, with some grassy areas. A small amount of erosion is noticeable in a few locations. There is a considerable amount of standing timber in the lake, particularly along the submerged river channels, in coves, and along parts of the shoreline. The vegetation was left standing during construction to reduce the cost of construction and to provide good habitat for sport fish. The land in the immediate vicinity of the lake is occupied by forests, parks, a wildlife refuge, heavy brush, and a small amount of grassland. The nearest town, Clinton, is a very small community located between the two arms of the lake and a considerable distance from the shoreline. There is a small well sheltered marina located in the Bloomington Public Use Area, as well as a public beach. (The marina was recently moved to the north shore of the lake, but this occurred after the samples were collected.) A second public beach is located in a small cove in Clinton State Park.

Away from the lake, there is intensive agricultural activity. The watershed of the Wakarusa River above Clinton Lake encompasses 367 square miles. Land use consists of approximately 32% cropland, 49% grassland, 7% woodland, and 12% miscellaneous. The average annual precipitation for Topeka, located near the midpoint of the watershed, is 32.4 inches.

Strowbridge Reservoir

Strowbridge Reservoir, constructed in 1964, serves as a public water supply for the city of Carbondale and is also used for recreation (primarily fishing). According to Pope et al. (1983), the reservoir covers 284 acres,

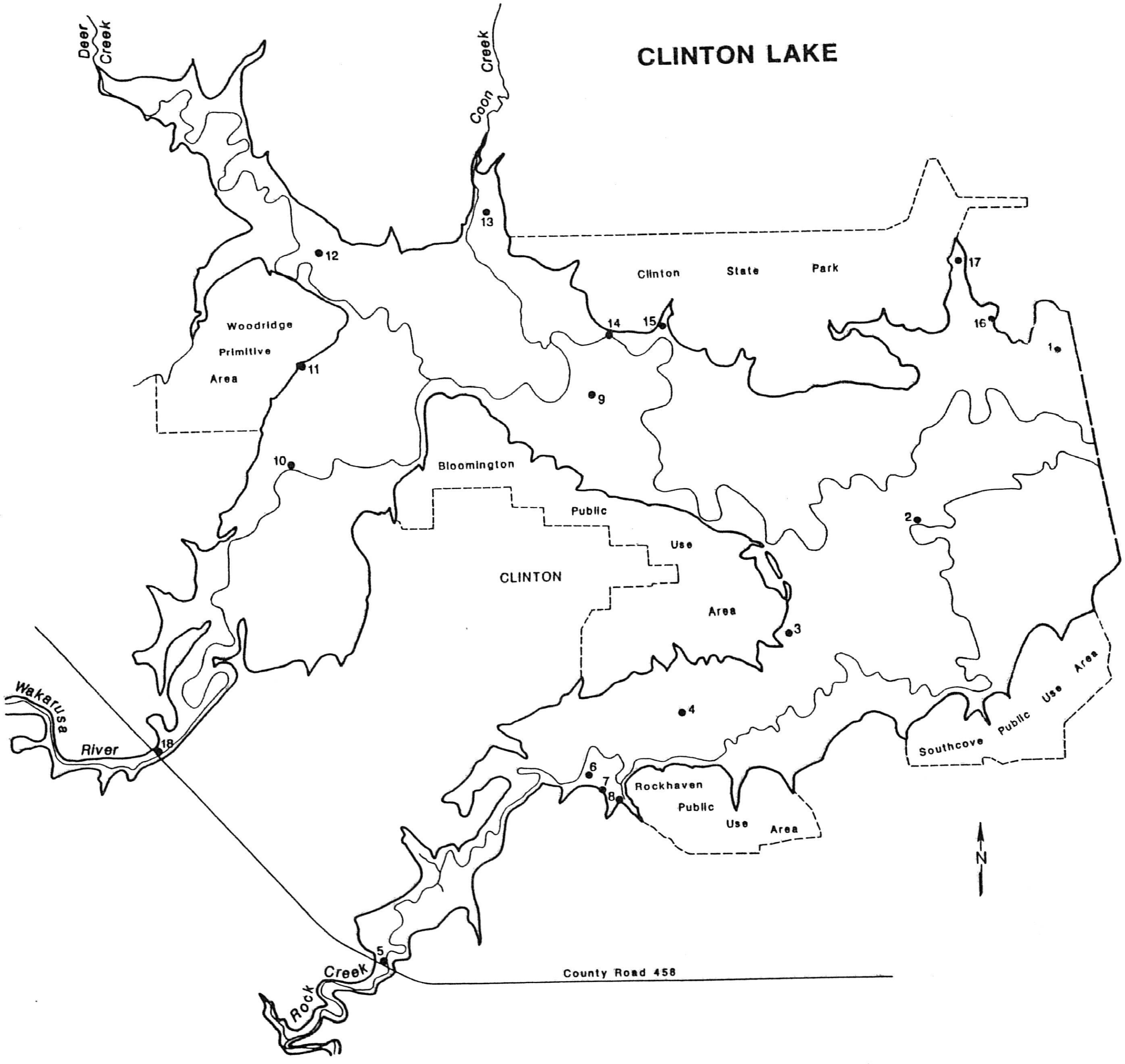

FIGURE 1: LOCATION OF SAMPLING STATIONS AT CLINTON LAKE

TABLE 2

DESCRIPTION OF SAMPLING SITES AT CLINTON LAKE

Site No.	Description
1	Near the dam; directly in front of and about 100 yards from the outlet structure (which also serves as the raw water intake for the Clinton Water Treatment Plant)
2	Center of the main body of the lake
3	Approximately 75 yards from the shore of a public beach; near the buoy directly in front of the sidewalk leading to the beach
4	Center of the south fork
5	Under the bridge over the Rock Creek inlet; in the deepest part of the channel
6	In the midst of a row of dead, partially submerged trees along the former river bank
7	Shoreline eroding at the waterline; sand and gravel on bottom near shore
8	A heavily wooded cove with an abundance of dead, partially submerged trees
9	In the center of the north fork
10	In between two rows of dead, partially submerged trees; approximately 300 yards from shore and near the raw water intake of the Tri-District Water Treatment Plant
11	A small wooded cove
12	A shallow, sheltered inlet fed by Deer Creek
13	A shallow, sheltered inlet fed by Coon Creek
14	Along the north shore in a clump of standing timber and immediately adjacent to a number of large submerged brush piles
15	At the buoy in front of the state beach
16	Eroding shoreline near a grassy knoll; very dark brown soil
17	A very sheltered and shallow cove with a heavily wooded shoreline
18	Under the bridge over the Wakarusa River inlet; in the deepest part of the channel

has an average maximum depth of 26 feet (8 meters), and has a watershed area of 3,210 acres, including 64% cropland, 17% grazed grassland, 10% ungrazed grassland, 1% forest land, and 8% other.

The locations of the sampling sites are shown in Figure 2, and the sites are further described in Table 3. The shoreline of the main body of the reservoir is somewhat rocky and forested. The arms of the reservoir were in places (near sites 6,10, and 11) separated from plowed fields by only a narrow strip of trees and brush; and in other places (near sites 4,5, and 9) plowed fields and grazed grassland sloped directly down to the shoreline. Macrophyte growths and standing timber were not observed.

Lone Star Lake

Lone Star Lake, shown in Figure 3, is a small (195-acre) recreational lake located in Douglas County, which owns and operates the lake. Construction of the dam was completed in 1939 under the WPA. The dam is located in a deep ravine, so the lake is deeper, more protected from the wind, and hence more likely to be strongly stratified than the other lakes that were sampled. The watershed is mostly forested. There are a number of small summer homes located primarily along the west side of the lake; and there is a public beach on the east side. The lake is used primarily for swimming, boating, and sport fishing. Several years ago extensive work was done to restore the lake. After it was partially drained, portions of the channels in the upper arms were dredged and a number of shoreline improvements were made. After the lake was refilled, it was stocked with grass carp in an effort to control weed growth (particularly Spanish moss).

Sampling site 1 was in the deepest part of the lake, about 50 yards from the dam. Site 2 was in a very shallow weed-infested cove adjacent to the spillway. Site 3 was directly in front (north) of the public beach.

Douglas Lake

Douglas Lake is a county fishing lake located in Douglas County north of the town of Baldwin. The lake is approximately 48 years old and is primarily used for fishing, duck hunting, and boating. The watershed, designated as a wildlife area, is largely covered with trees and brush. The lake has a normal surface area of 180 acres (250 acres at the emergency spillway level), is fairly shallow, and is relatively unprotected from wind action. Thus, it is not likely to be strongly stratified during the summer months. The normal storage capacity of the lake is 3,100 acre feet.

Douglas Lake is managed by the Kansas Fish & Game Commission. It is stocked with sport fish, and a number of brush piles have been constructed to provide better sport fish habitat. Most of the brush piles are located in small coves, some of which were formed by construction of small jetties extending out from the shoreline. The lake level is occasionally lowered to encourage growth of shoreline vegetation, which serves as habitat for fish (especially during spawning) and fowl. The locations of the sampling sites are shown in Figure 4, and the sites are further described in Table 4.

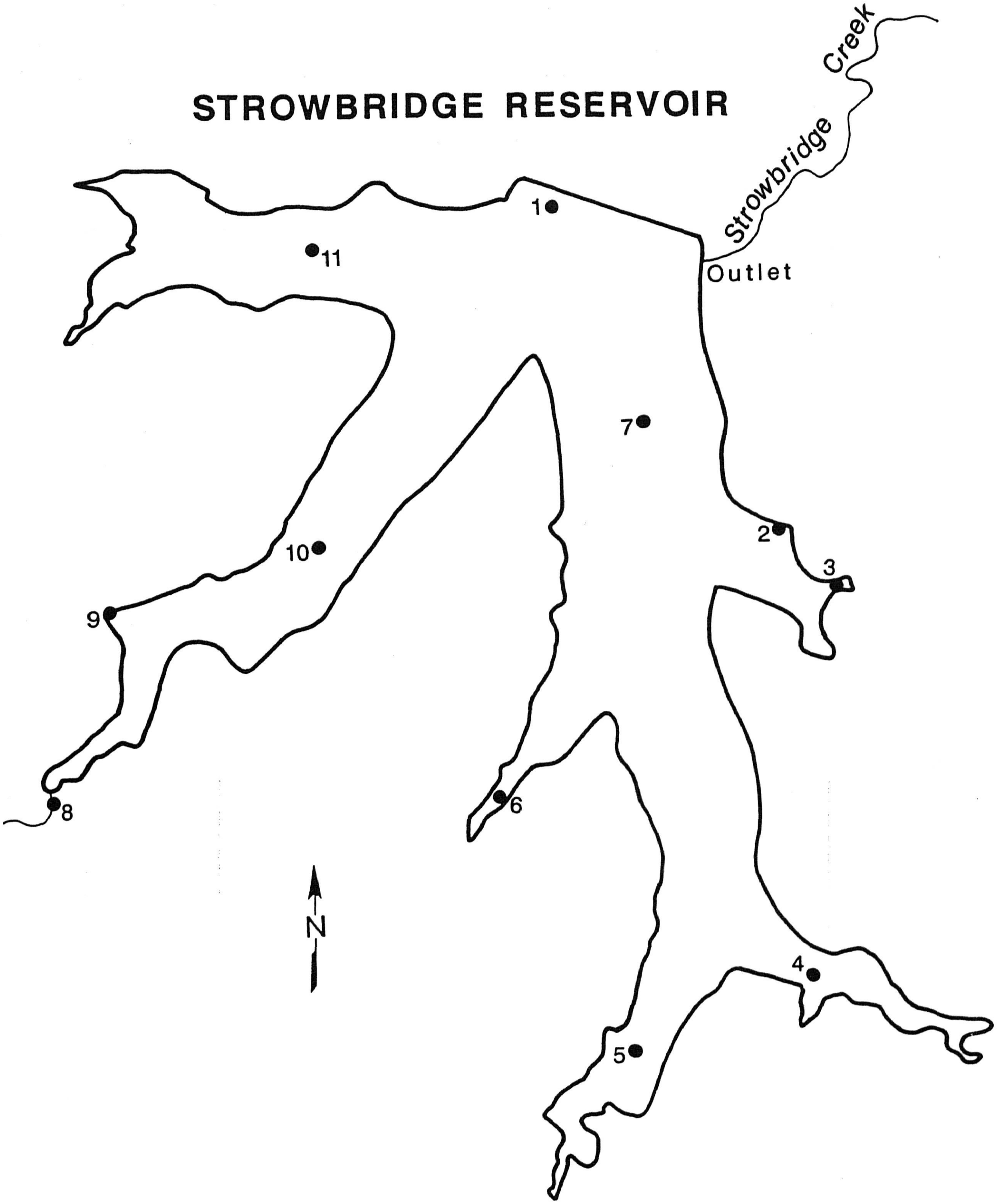

FIGURE 2: LOCATION OF SAMPLING STATIONS AT STROWBRIDGE RESERVOIR

TABLE 3

DESCRIPTION OF SAMPLING SITES AT STROWBRIDGE RESERVOIR

Site No.	Description
1	Approximately 75 feet from the dam, in front of the water treatment plant
2	A bed of cattails (*Typha* spp.) growing along the shore
3	A small open cove with no apparent inlet stream; shoreline covered with grass, brush, and a few small trees
4	A shallow branch of the south fork with a grassy shoreline; cattle were generally grazing on the south shore
5	Shallow branch of south fork; plowed field on one side and grazed grassland on the other
6	A heavily wooded cove
7	Center of south fork
8	Inlet stream; very shallow, surrounded by vegetation, rocky on east side and bottom
9	Along the shoreline near a feedlot and a farmhouse; very shallow area of the reservoir
10	Center of southwest fork
11	Center of west fork
12	Strowbridge Creek as it leaves the reservoir

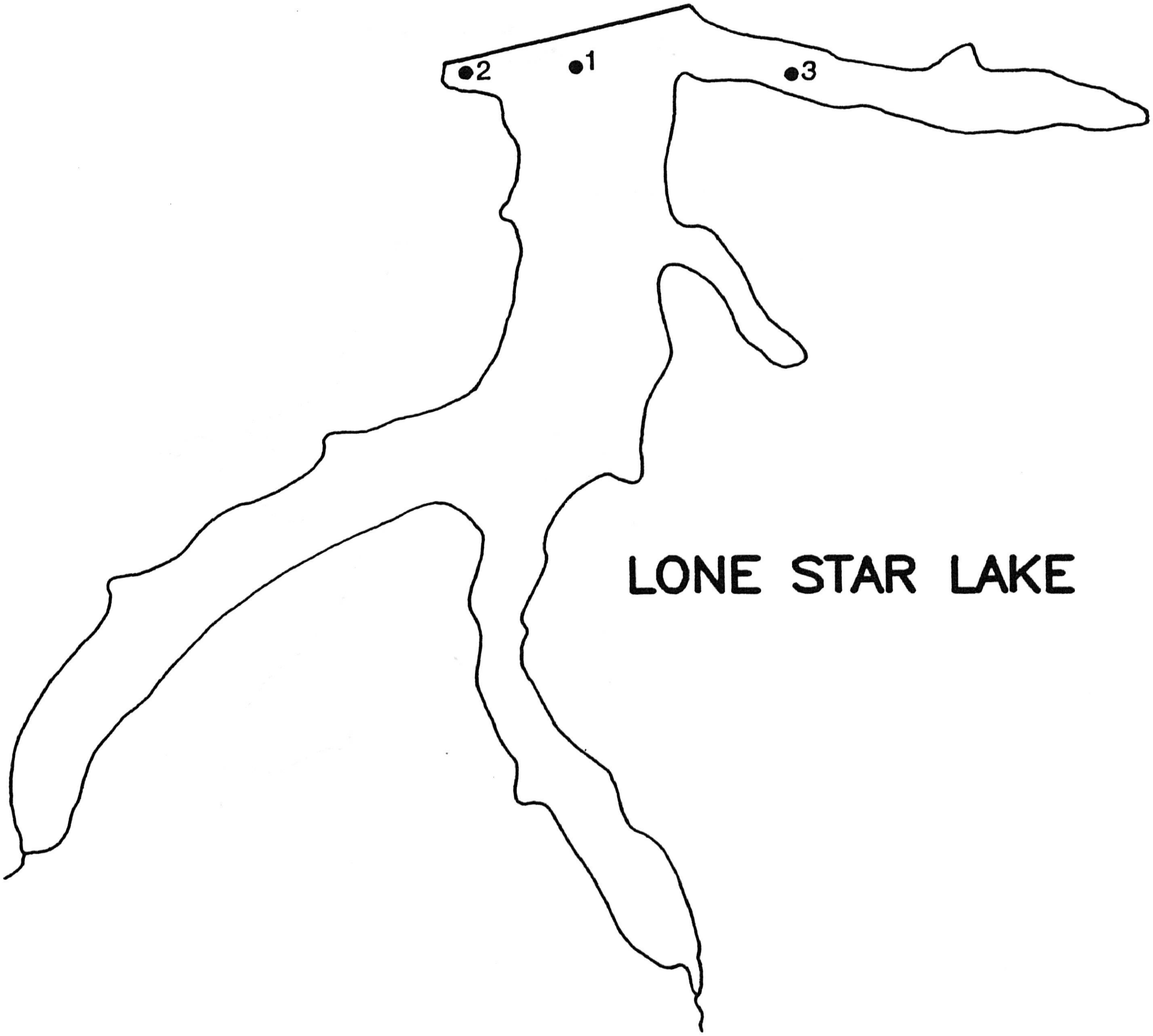

FIGURE 3: LOCATION OF SAMPLING STATIONS AT LONE STAR LAKE

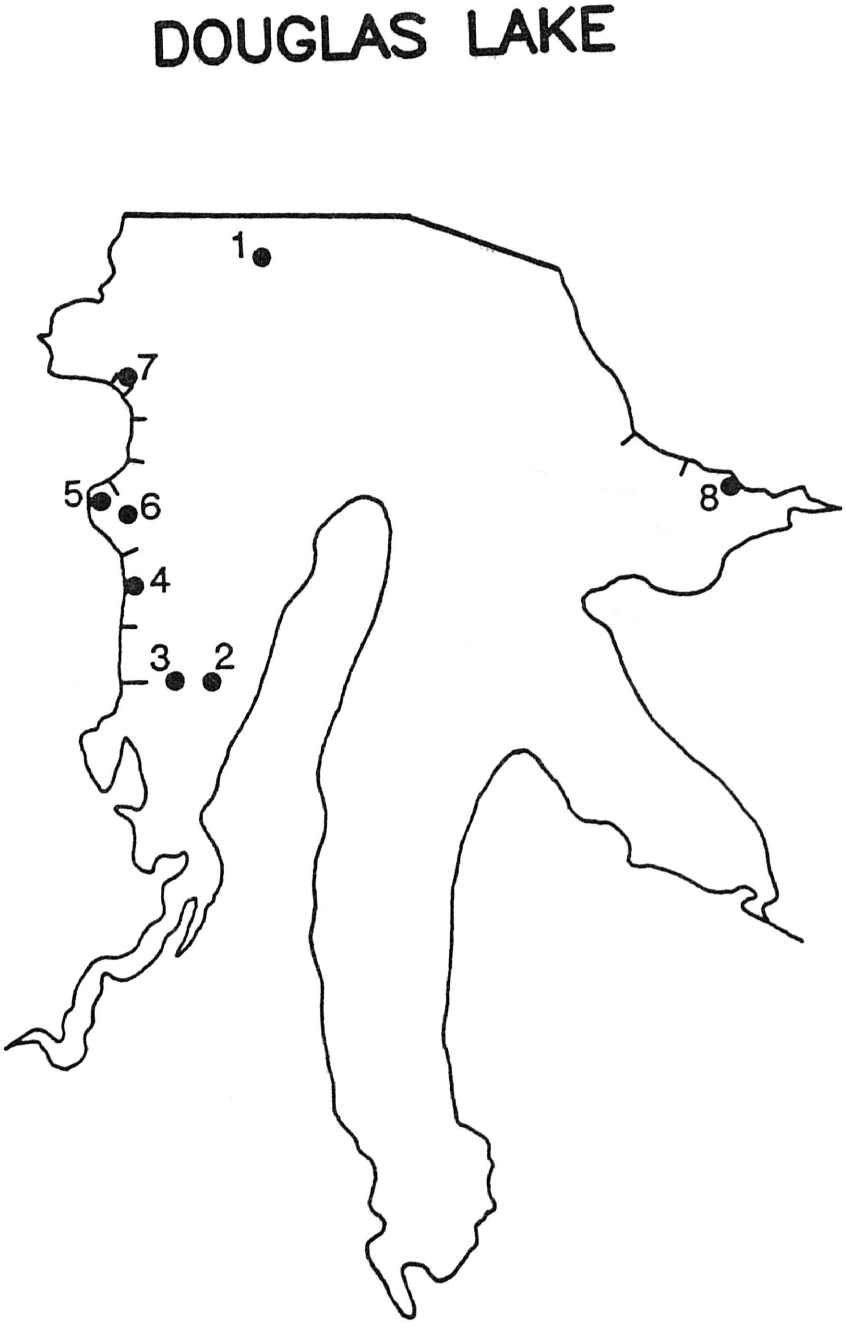

FIGURE 4: LOCATION OF SAMPLING STATIONS AT DOUGLAS LAKE

TABLE 4

DESCRIPTION OF SAMPLING SITES AT DOUGLAS LAKE

Site No.	Description
1	Approx. 50 yds from center of dam, near outlet
2	Large brush pile in center of south arm
3	Channel between site 1 and shore
4	West shore (weed bed on 9-27-85)
5	Small brushpile in shallow cove
6	Center of cove (a short distance from site 4)
7	Small brush pile near boat ramp
8	Weed bed on east side of lake

Lyndon Lake

Lyndon Lake, shown in Figure 5, was constructed in 1966 and is located in a small privately owned valley. The watershed is almost entirely grassland and pastureland; and cattle were always observed grazing in the watershed, but not near the shoreline. Except for a few very small dead trees near sampling sites 3 and 5, there was no standing timber in the lake.

This lake was selected for sampling during the second year of the study (1986) because it was reported to have a history of excessive macrophyte growths and relatively severe seasonal taste and odor problems. Isolated patches of leafy pondweed (*Potamogeton foliosus*) were observed at various locations in the lake, including sampling sites 2, 3, and 4 (see Figure 5). During the second sampling trip to this lake (on July 25, 1986), the investigators were informed that the lake had been stocked with approximately 200-300 grass carp in 1984 or 1985; but it was not known whether they had survived.

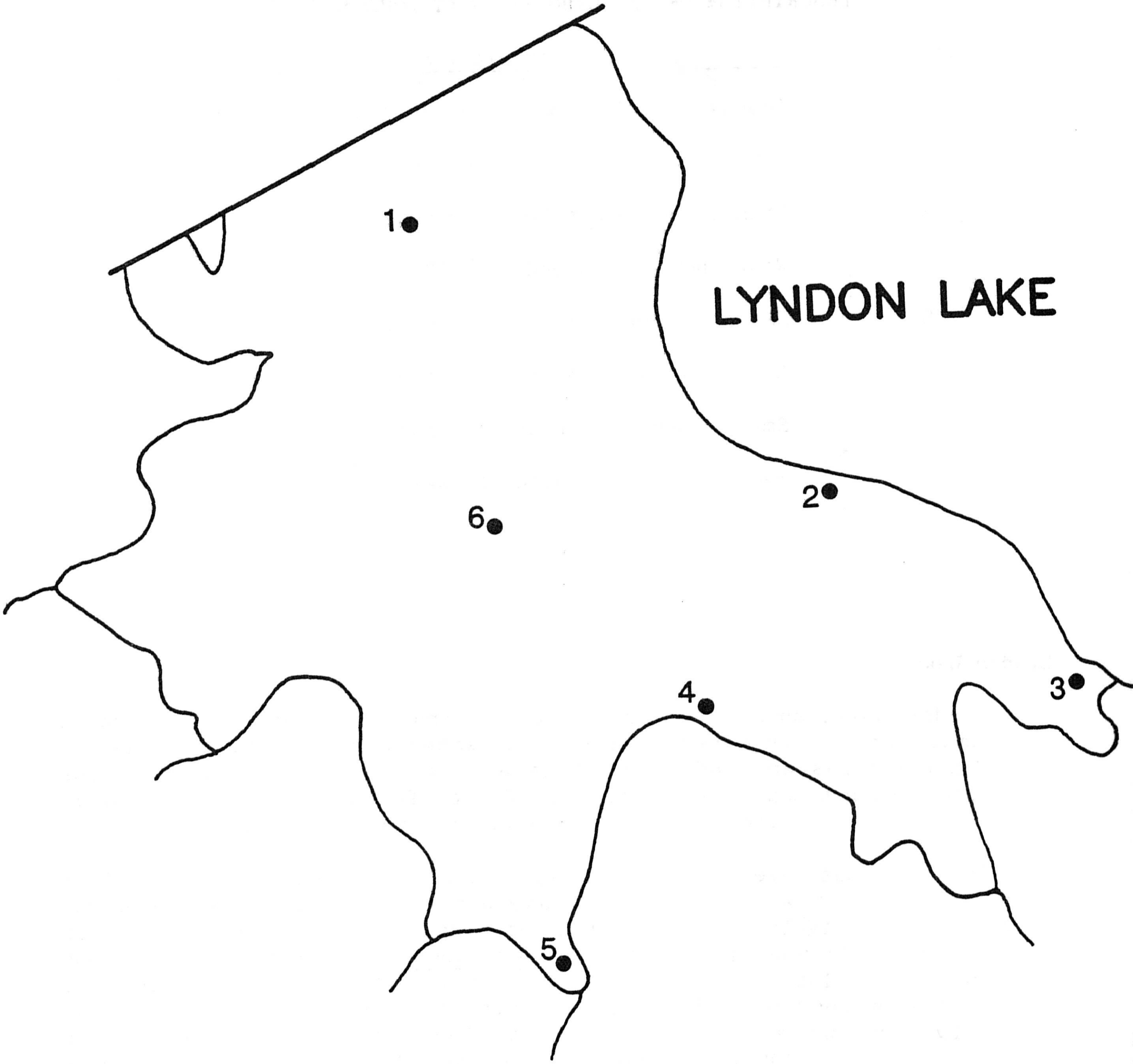

FIGURE 5: LOCATION OF SAMPLING STATIONS AT LYNDON LAKE

Sampling Procedures

Lake samples were taken using a flat-bottom motorboat. In deep water an anchor was sometimes used to prevent the boat from drifting (e.g., on windy days). When collecting a sample in shallow water, special precautions were taken to avoid disturbing the bottom sediments and littoral plants: the motor was turned off, the boat was allowed to drift into the sampling site, and the sample was taken from an undisturbed area in front of the boat.

Upon reaching a sampling site, a temperature probe on a weighted cable with meter markings was lowered into the water to measure the depth of water and the temperature of the water at various depths, including the surface and bottom. Temperature readings were taken using a YSI Model 46 TVC Telethermometer (Yellow Springs Instrument Co., Yellow Springs, Ohio). The difference between the surface and bottom temperatures, ΔT, gives an indication of the degree of stratification. On some occasions, Secchi depth readings were also taken.

At most of the sampling sites, samples were taken from a depth of one meter using a large (5-liter capacity) Van Dorn sampler (illustrated on p. 1047 of Standard Methods, APHA, 1985). In shallow water (<1.5 meters), samples were sometimes taken at a depth of less than one meter; and in very shallow water, samples were taken by lowering the sample bottle a short distance into the water and then allowing water to flow directly into the sample bottle. At some sites, bottom samples were taken one meter above the bottom sediments using the Van Dorn sampler. Each brush pile was sampled by inserting a garden hose attached to a long metal rod into the brush pile and pumping out water using a small centrifugal pump powered by a portable generator. The water was allowed to flow at several gallons per minute for several minutes to purge the hose of residues from the previous sample.

After the Van Dorn sampler was lifted into the boat, the water in the sampler was allowed to flow out through a short length of latex rubber tubing. The first sample taken was always for determination dissolved oxygen. The end of the tubing was inserted into the bottom of a 300-mL glass BOD bottle and the sample was allowed to flow gently (with minimal agitation into the bottle). After approximately two to three volumes of sample had been displaced from the BOD bottle, the tubing was slowly withdrawn and chemicals were added to "fix" the dissolved oxygen (see Analytical Methods).

The remaining water in the sampler was then used to fill a one-liter polyethylene bottle (or, on the first few sampling trips, two 300-mL glass BOD bottles). The pH of this sample was immediately measured (in the field) using a portable battery-powered pH meter (Electromate, Beckman Instruments, Inc., Fullerton, CA); and, on some sampling trips, turbidity was also measured in the field using a portable battery-powered turbidimeter (Model 16800, Hach Chemical Co., Loveland, CO). Each sample was then immediately placed in an ice chest to minimize any changes in water quality that might occur as a result of biological activity. On some sampling trips, a second one-liter polyethylene bottle was filled with sample for later measurement of chlorophyll a.

On some occasions, sediment samples were collected using a Petersen grab sampler (illustrated on p. 1117 of Standard Methods, APHA, 1985). These samples were placed in one-pint Mason jars for transport back to the laboratory.

B. STREAMS

Every few weeks, beginning 2-12-86, samples were taken from the Wakarusa River, Rock Creek, the Kansas River, and the Clinton Lake outlet (the Wakarusa River as it leaves Clinton Lake). The sampling sites for the Wakarusa River and Rock Creek were the same as those shown in Figure 1, i.e., where they enter Clinton Lake. Both rivers, where sampled, are broad, meandering, and slow moving; and much of the sediment load settles out during periods of low flow.

The Kansas River is a major river, with a watershed covering much of Northeastern Kansas. The flowrate averages 6,988 cubic feet per second (cfs), with an estimated maximum flow of 510,000 cfs and a recorded low flow of 160 cfs (USGS, 1983). Samples were taken from behind a small hydroelectric dam (Bowersock Dam) in a wide, slow moving part of the river.

At the Clinton Lake outlet, there is a large tower built into the upstream face of the dam. Water is taken into this structure through a variable-depth intake which drew water from mid-depth during the course of this study. A portion of the water is pumped to the Clinton Water Treatment Plant in Lawrence and the remainder is discharged downstream into the Wakarusa River to meet in-stream flow needs. Excess water is released through gates, usually from the bottom of the lake. Samples were sometimes taken from the tower (i.e., by lowering the sampler from the tower into the lake) and sometimes from the stilling basin at the end of the spillway, where the water discharges into the Wakarusa River. At the times when the latter samples were taken, no water was flowing through the gates, so the samples were essentially from mid-depth in the lake.

All of the samples were taken with a Kemmerer sampler (Model 1510TT, Wildlife Supply Co., Saginaw, MI), illustrated on page 1047 of Standard Methods (APHA, 1985). Samples were usually taken about one meter below the surface. No attempt was made to get a representative sample with respect to the concentration of suspended solids. All of the samples were intentionally taken near the surface in relatively quiescent areas so that heavier, rapidly settling solids (which would quickly settle to the bottom of a lake or a presedimentation basin) would be excluded. The primary purpose of the sampling program was to examine dissolved precursors.

C. WATERSHED SAMPLES

Selection of watershed sampling sites began with consideration of all potential sources of THM precursors, natural and anthropogenic, that might impact water supplies in Kansas. Those selected included a variety of runoff samples, municipal and industrial wastewater effluents, aerobically and anaerobically digested sludges, brine-contaminated groundwater samples, and oil field brines. Samples were generally limited to local urban and rural sources to minimize time and travel requirements. All of the runoff and sludge samples were collected by KU researchers. Soil samples were taken by Soil Conservation Service (SCS) personnel serving Douglas County. The domestic wastewater effluent samples were collected locally by KU researchers and the industrial effluents were provided by cooperating industries within the state. Samples of brine-contaminated groundwater and oil-field brines were taken by KDHE staff members.

Runoff Samples

All of the urban and rural runoff samples were grab samples taken on April 2, 1986 during the normal spring rains. Antecedent rainfall helped to produce good runoff conditions at most of the sampling sites. Table 5 summarizes the nature of the runoff samples taken and other information. Table 6 shows hourly precipitation data from the Clinton Lake weather station for the day the samples were collected. Each sample was collected in a one-liter polyethylene bottle, and the samples were delivered to the laboratory prior to 5:00 PM the same day they were collected. Upon arrival, the samples were well shaken and a portion of each was filtered. Filtered and homogenized portions of each sample were preserved at 4°C in scrupulously cleaned glass BOD bottles and analyzed within 24 hours.

Soil Samples

Soil erosion is a major problem in Kansas, and soil was postulated as a major source of organic carbon and THM precursors for surface water supplies in Kansas. Soil Samples were taken to represent the major soil types in Douglas County. SCS personnel identified and collected the samples as summarized in Table 7. These soils are the major soil types and constitute over 50 percent of the various soils found in Douglas County (USDA, 1977). The samples were taken from the topsoil on April 24, 1986, using a one-inch diameter core sampler.

Point-Source Samples

Several kinds of municipal and industrial wastewater effluents were sampled. Table 8 reviews the pertinent information concerning these samples. The industrial sources are not specifically identified, since the samples were requested on an anonymous basis. Samples of aerobically and anaerobically digested sludge were taken on July 16, 1985 from the Lawrence wastewater treatment plant.

TABLE 5

DESCRIPTION OF RUNOFF SAMPLES*

Sample Number	Collection Time	Description	Sample Location
1	12:45 PM	Urban-Commercial	9th & Massachusetts Lawrence, Ks.
2	1:10	Industrial Landfill (standing water)	Lawrence, KS.
3	1:25	Construction Demolition Landfill	31st & Louisiana Lawrence, Ks.
4	2:05	Terraced and Tiled Farmland	Otis Heine Farm Rural Douglas County
5	2:05	Non-terraced Farmland	Otis Heine Farm Rural Douglas County
6	2:20	Burned Bromegrass Land	Clinton W. Township Rural Douglas County
7	2:30	No-till Farmland	Homer Wulfkuhle Farm Rural Douglas County
8	2:30	Cattle Feedlot	Homer Wulfkuhle Farm Rural Douglas County
9	2:50	Tilled Farmland	Glen O'Conner Farm Rural Douglas County
10	2:55	Swine Feedlot	Lloyd Wulfkuhle Farm Rural Douglas County
11	3:00	Cattle Feedlot	Clifford Nichols Farm Rural Douglas County
12	3:10	Soybean Field	Kanawaka W Township Rural Douglas County
13	3:25	Corn Field	Kanawaka E Township Rural Douglas County
14	3:40	Corn Field	Wakarusa N Township Rural Douglas County
15	3:50	Urban-Construction	15th St., West of West Hills, Lawrence
16	3:55	Urban-Residential	Oakmont & St. Andrews Lawrence, Ks.
17	4:20	Urban-Industrial Park	Hallmark Cards Lawrence, Ks.
18	4:30	Urban Shopping Center	Northwest entrance to Hillcrest Center Lawrence, Ks.

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* The sampling date was April 2, 1986. Light to moderate rain fell during the collection of samples 1-16 and heavy rainfall occurred during sample pickups 17 and 18 (the total precipitation recorded at the Clinton Lake weather station was 0.86 inches). Sample temperatures averaged 15C and ranged from 14 to 17C.

TABLE 6

HOURLY PRECIPITATION DATA FOR CLINTON LAKE ON 4-2-86*

Time Period	Inches of Rainfall
6- 7 AM	0.06
11-12 AM	0.06
12- 1 PM	0.14
1- 2 PM	0.10
2- 3 PM	0.06
3- 4 PM	0.36
4- 5 PM	0.03
5- 6 PM	0.01
6- 7 PM	0.01
7- 8 PM	0.00
8- 9 PM	0.02
9-10 PM	0.01

* Data taken from "Hourly Precipitation Data: Kansas," National Climatic Data Center, Vol. 36, No. 4, April 1986.

TABLE 7

DOUGLAS COUNTY SOIL SAMPLES

Sample Number	Description	Soil Designation	Sample Location* Sheet No.	Sample Location* Section No.
1	Martin silty clay loam	Mc	25	13
2	Oska silty clay loam	Oe	25	14
3	Woodson silt loam	Ws	25	11
4	Vinland-Martin complex	Vm	25	3
5	Sibleyville loam	So	32	23
6	Gymer silt loam	Gm	25	11

* As identified in the mapping units of USDA (1977).

TABLE 8

POINT-SOURCE SAMPLES

No.	Sampling Date	Sample Description	Sample Location	Sampler
1	7-16-85	Secondary Effluent, Activated Sludge Plant	Lawrence POTW	KU
2	7-16-85	Effluent from the SW Stabilization Pond	Eudora POTW	KU
3	7-15-85	Domestic Stabilization Pond (non-discharging)	Clinton Lake POTW (East Pond)	KU
4	7-15-85	Domestic Stabilization Pond (non-discharging)	Clinton Lake POTW (West Pond)	KU
5	7-10-85	Sanitary Landfill, Runoff Pond	Jefferson/Douglas County Landfill Perry, Ks.	Hamm's Quarry
6	8-24-85	Refinery, Polishing Pond Effluent	-	Industry
7	7-09-85	Cellophane Manufacturing, Secondary Effluent	-	Industry
8	7-17-85	Power Plant Cooling Water (North Tower)	-	Industry
9	7-17-85	Power Plant Cooling Water (South Tower)	-	Industry
10	7-17-85	Power Plant Ash Pond Influent	-	Industry
11	7-17-85	Power Plant Ash Pond Effluent	-	Industry
12	8-26-85	Electroplating Wastewater Effluent	-	Industry
13	8-22-85	Meat Packing House, Polishing Pond Effluent	-	Industry
14	7-17-85	Fertilizer Plant, Wastewater Pond	-	KU
15	7-16-85	Aerobically Digested Sludge	Lawrence POTW	KU
16	7-16-85	Anaerobically Digested Sludge	Lawrence POTW	KU

Oil Brine and Brine-Contaminated Samples

The petroleum industry is one of the largest industries in Kansas, and the oil field brines associated with this industry can contaminate both surface and ground water supplies if improperly managed. Since oil brines come into direct contact with concentrated organic matter (oil), they could conceivably carry relatively high concentrations of organic carbon and THM precursors. Samples of groundwater contaminated with oil-field brine were collected from observation wells on August 22, 1985. Two samples of actual oil-field brine (collected on October 24, 1985, from the S & K Oil collection tank and the Gladys Unit Battery) were received on October 30, 1985. Due to concern over the accuracy of the analyses for the first two sets of samples, a second set of brine-contaminated groundwater samples was collected on April 7-8, 1986, and a second set of oil-field brine samples was collected on August 8, 1986 (received September 4, 1986). A summary of the sample designations and locations is given in Table 9. All samples were collected in one-liter polyethylene bottles.

TABLE 9

OIL-FIELD BRINE AND BRINE-CONTAMINATED GROUNDWATER SAMPLES

Sample No.	Sample Type*	Well Location	Well Designation	Depth (ft)
1	GW	Blood Orchard, Wichita	K-11A	-
2	GW	Blood Orchard, Wichita	K-11B	-
3	GW	Burton Field	EB2A	48
4	GW	Burton Field	EB2B	50
5	GW	Burton Field	EB34A	83
6	GW	Burton Field	EB34B	128
7	Brine	S & K Oil, J.H. Goering Collection Tank	26-23-4W (SW/4)	-
8	Brine	Gladys Unit Battery	28-1W	-

* GW = brine-contaminated groundwater; brine = oil-field brine.

D. EXPERIMENTAL PONDS

To examine the influence of several algae-control methods on organic carbon concentrations and THM yields, experiments were conducted at the University of Kansas Experimental Pond Facility, which is maintained as a component of the University's Experimental and Applied Ecology Program. This facility was constructed in 1977 to provide natural aquatic ecosystems that can be experimentally manipulated. The ponds are located at KU's Nelson Environmental Study Area, about 10 miles north of Lawrence, Kansas.

The pond complex consists of a large reservoir and 17 experimental ponds, all designed to prevent contamination from surface runoff. Figure 6 shows the layout of the large reservoir and 14 of the experimental ponds arranged in two rows of 7 ponds east (downslope) of the reservoir. Water for maintaining the reservoir is supplied by pumping raw water from a well which extends into the Kansas River Aquifer. The large reservoir was filled immediately after construction and a natural plankton community has developed in it. No experimental manipulation of the large reservoir is allowed. Experimental ponds or sections of divided ponds may be simultaneously filled with reservoir water such that they all contain water of the same chemical and biological quality at the beginning of an experiment.

Each of the experimental ponds is approximately 70 feet square and 9 feet deep, with side slopes of 2:1 and a volumetric capacity of about 450,000 liters. Two of the ponds, referred to as divided ponds, are subdivided by concrete walls into four equal quadrants, creating eight small ponds. Each small pond (quadrant) has a surface area of 0.006 hectares, a maximum depth of about 6 feet, and a volumetric capacity of about 63,000 liters.

The ponds were sampled using an integrated-depth sampler consisting of a length of PVC pipe with a check valve on the end. The sampler was gradually lowered into the water, taking a "core" sample of the water from the surface to approximately six inches from the bottom. At each pond, a one-liter polyethylene bottle (clear) was filled for later analysis of organic carbon and THM precursors, and a second one-liter polyethylene bottle (dark brown) was filled for later analysis of chlorophyll a. During the second year of the study, an additional sample was placed in a 125-mL glass bottle with a polyethylene-lined cap, treated with 1 mL of Lugol's iodine solution, and stored for later examination of the algal populations.

Year 1 (1985)

In the spring of 1985, the divided ponds were filled, with water from the reservoir, to a level a few feet above the top of the dividing walls. This allowed exchange of water between the quadrants so that the water in each pond would be of the same chemical and biological quality at the start

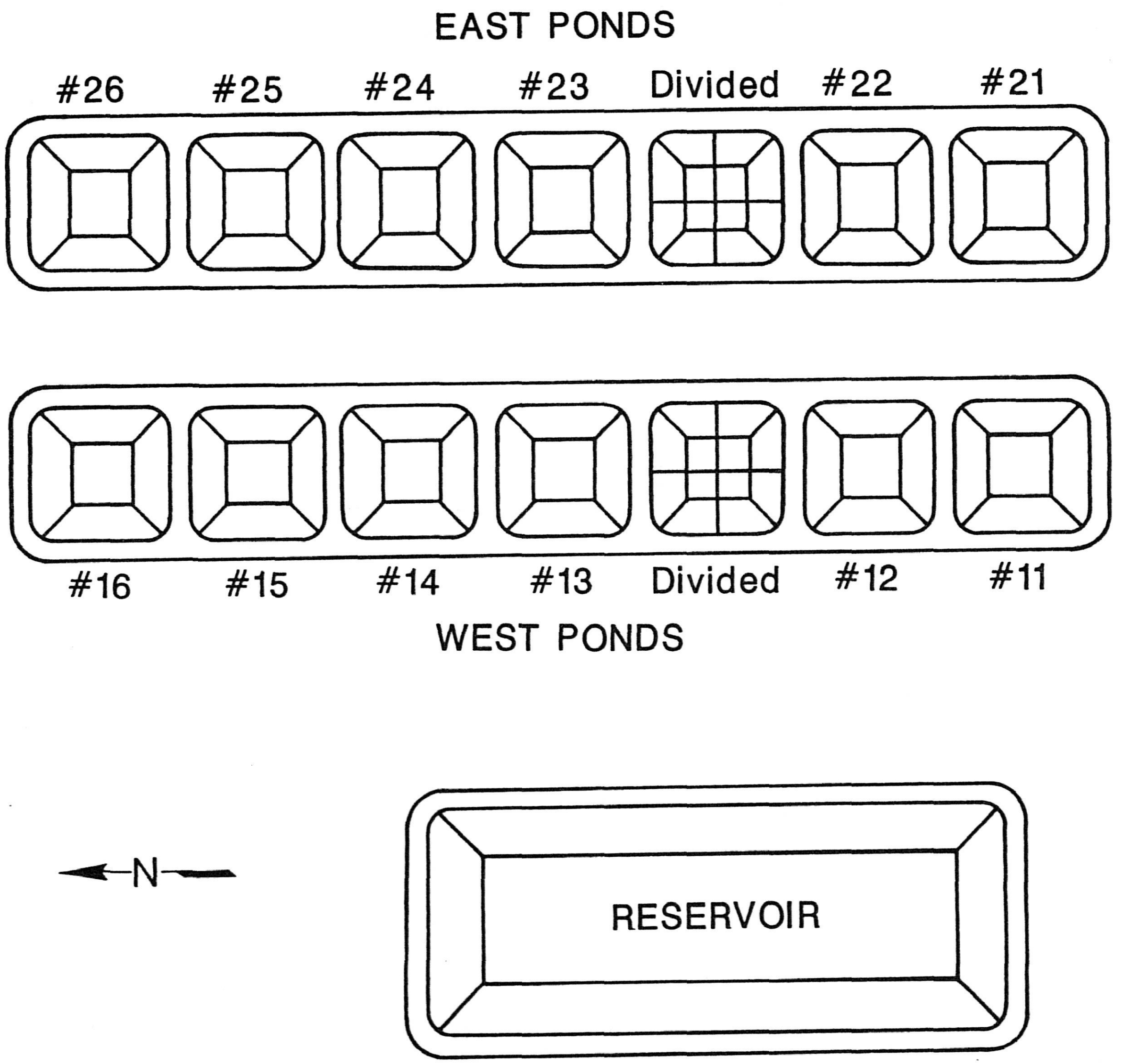

FIGURE 6: EXPERIMENTAL POND FACILITY, KU EXPERIMENTAL AND APPLIED ECOLOGY PROGRAM

of the experiment. On July 22, 1985, a composite sample was taken from each of the two divided ponds; and on July 23 the water level was lowered below the top of the dividing walls, creating eight small individual ponds. These eight ponds were then grouped into four pairs, each pair including a pond in each of the two divided ponds. Each pair of ponds was then subjected to a different algae control method.

Two ponds were designated as control ponds; two ponds were treated with 2 mg/L of copper sulfate (commercial grade, >98% pure) on July 27; and two ponds were treated with 2 mg/L of simazine (2-chloro-4,6-bis ethylamino-S-triazine) by adding 2.5 mg/L of Princep 80W (80% simazine, Ciba Geigy Corp., Greensboro, NC) on July 27. The last two ponds were stocked with grass carp (two per pond, each about 2 feet in length) on July 29. Figure 7 depicts the layout of these ponds and the pond numbering scheme.

The undivided west ponds (numbers 11-16, see Figure 6) were maintained at different turbidity levels as part of a research project sponsored by the National Science Foundation (NSF) to examine the influence of turbidity on pond ecology. Two ponds served as controls; two were treated with a small dosage of clay to create a low level of turbidity, and two were treated with a high dosage of clay to create a high level of turbidity. The clay was kept in suspension by mechanical mixing. These ponds were monitored for a wide spectrum of chemical and biological parameters as part of the NSF study. To examine the influence of turbidity on organic carbon and THM precursors, additional samples were collected and analyzed along with samples from the divided ponds.

Year 2 (1986)

During the last two weeks of May, 1986, the divided ponds were drained and cleaned, and a fence was constructed to prevent the grass carp from jumping over the wall dividing the quadrants. The ponds were then filled to a level several feet above the top of the dividing walls to allow mixing of water between quadrants. On June 9 and 10, the water level was lowered to about 6 inches below the top of the dividing walls. On June 10 (day 0), the ponds were fertilized with 0.05 mg/L phosphate (as P) and 0.20 mg/L of nitrogen (added in the form of ammonium nitrate). On June 12 (day 2), samples were taken from each pond to characterize the water quality prior to the growth of algae or macrophytes.

By the end of July, there was a heavy growth of macrophytes in each of the ponds. On July 30 (day 50), two ponds were treated with 2 mg/L of copper sulfate and two ponds were treated with 2 mg/L of simazine. The treatment scheme for year two is shown in Figure 8. On August 1 (day 52), four small (6-8 inch) grass carp were added to each of two ponds; and on August 13 (day 64), four more small grass carp were added to each of the same ponds. The ponds treated with copper sulfate were retreated on August 27 (day 78), and September 11 (day 93).

UPPER (WEST) POND

COPPER SULFATE (1-2)	SIMAZINE (1-3)
GRASS CARP (1-1)	CONTROL (1-4)

LOWER (EAST) POND

GRASS CARP (2-2)	CONTROL (2-3)
SIMAZINE (2-1)	COPPER SULFATE (2-4)

FIGURE 7: NUMBERING SCHEME FOR THE DIVIDED PONDS DURING YEAR ONE

UPPER (WEST) POND

GRASS CARP (1-2)	COPPER SULFATE (1-3)
CONTROL (1-1)	SIMAZINE (1-4)

LOWER (EAST) POND

SIMAZINE (2-2)	CONTROL (2-3)
GRASS CARP (2-1)	COPPER SULFATE (2-4)

FIGURE 8: NUMBERING SCHEME FOR THE DIVIDED PONDS DURING YEAR TWO

E. LABORATORY EXPERIMENTS

Experiments were conducted in the laboratory to assess, under both aerobic and anaerobic conditions, the release of precursors from certain substrates and the biodegradability of precursors from various sources. Two sets of experiments were conducted, hereinafter referred to as "laboratory experiment no. 1" and "laboratory experiment no. 2". The precursor sources studied in each experiment are described in Tables 10 and 11.

Solid samples were added to lake water (taken from the Clinton Lake outlet), to provide a natural microbial population and a matrix of inorganic ions representative of the study area. The weight of material used varied from substrate to substrate in the first experiment, but was held constant at 4.00 gm/L in the second experiment. The lake scum and activated sludge samples in experiment no. 1 were diluted to 1/10 strength with lake water to facilitate analysis of DOC (sample filtration). The soil extract in experiment no. 1 was seeded with 1 mL of 1/10 strength activated sludge to provide an active microbial population, and 0.1 gm KNO_3 was added to provide a source of nitrogen. The concentration of DOC in the lake water was determined initially, and in a control sample during the study, so that corrections to the DOC concentrations of diluted samples could be made if necessary. All samples were incubated in the dark in a temperature-controlled room adjusted to 25°C.

Samples to be studied under aerobic conditions were placed in 2-liter bottles, except for 2-3 samples in each experiment which were placed in 1-liter or 300-mL bottles due to the small volumes of sample available. All samples were shaken by hand once or twice each day and were at all times aerated with compressed air passed through a 4-liter bottle containing a layer of gravel and a layer of glass wool to remove impurities. The air was distributed to the bottles with a manifold system constructed of plastic tubing (Nalgene 8000, Nalge Co., Rochester, NY), fish-tank valves (bronze and plastic), and glass tubing. The tops of the bottles were covered with aluminum foil to prevent contamination of the samples with dust while still permitting the air to escape.

After three days of aeration in the first experiment, a small amount of evaporation had taken place, as evidenced by a slight drop in water level in the 300-mL bottle containing the river water sample. Therefore, a humidifier (consisting of a fritted glass tube immersed in a 2-L reservoir regularly filled with reagent-grade water) was added to the inlet line, following the filter. After fifteen days, the river water sample was noticeably diluted. This sample was on the low end of the manifold system, and water droplets (aerosols) that collected in the manifold were trickling into this sample. Therefore, a mist eliminator (a bottle containing glass wool) was added, following the saturator, to remove aerosol moisture from the air. Both the humidifer and the demister were used throughout the course of the second experiment.

Samples to be studied under anaerobic conditions were placed in one-quart Mason jars fitted with rubber stoppers (no. 13). Two holes, one small and one large, were drilled into each stopper; and a short length of glass

TABLE 10

DESCRIPTIONS OF SUBSTRATES TESTED IN LABORATORY EXPERIMENT NO. 1

Substrate	Description
Lake water	Freshly taken from Clinton Lake outlet
Pine needles	From a discarded Christmas tree (Scotch Pine)
Pine twigs (~1/8")	From a discarded Christmas tree; cut in 2" lengths
Pine branches (~1/4")	From a discarded Christmas tree; cut in 2" lengths
Pine needles	Fresh, from a live Scotch pine tree
Pine needles	Fallen, from beneath a live Scotch pine
Filamentous algae	Mat of green filamentous algae from the shoreline of a small pond
Aquatic weeds #1	Immersed, taken from site 2 near the spillway of Lone Star Lake
Aquatic weeds #2	Willow like <u>Potomogeton</u> spp. taken from Lyndon Lake
Aquatic weeds #3	Small and grasslike
Lake scum	Foamy material blown onto the shore near site 5 at Lyndon Lake; diluted to 1/10 strength
Secondary effluent	From the City of Lawrence Wastewater Treatment Plant
Activated sludge	Mixed liquor, from the City of Lawrence Wastewater Treatment Plant; diluted to 1/10 strength
Soil extract	Composite of the organic matter extracted from six Douglas-County soil samples (see "Watershed Samples")
River water	Sample taken from the Kansas River on 4-5-86 and stored at 4°C

TABLE 11

DESCRIPTIONS OF SUBSTRATES TESTED IN LABORATORY EXPERIMENT NO. 2

Substrate	Description
Fresh pine needles	Freshly picked (green) Scotch pine (*Pinus sylvesteris* L.) needles (40/gm)
Fresh pine twigs	Freshly picked Scotch pine twigs (<0.25 in.) broken into 1-inch pieces
Fallen pine needles	Brown needles collected beneath a Scotch pine during a prolonged period of dry weather (67/gm)
Fallen pine twigs	Small (<0.25 in.) twigs collected beneath a Scotch pine during a prolonged period of dry weather and broken into 1-inch pieces
Pine needles, NBS	Standard reference material 1575, National Bureau of Standards
Citrus leaves, NBS	Standard reference material 1572, National Bureau of Standards
Ash leaves	Marshall seedless ash (*Fraxinus* sp.) leaves (4/gm)*
Red oak leaves	Red oak (*Quercus borelias* maxima) leaves (4/gm)*
Cottonwood leaves	Cottonwood (*Populas deltiodes*) leaves (4/gm)*
Elm leaves	Elm (*Ulmus americana*) leaves (4/gm)*
Sycamore leaves	Sycamore (*Platanus occidentalis*) leaves (1.5/gm)*
Pagoda tree blossoms	Freshly fallen blossoms collected beneath a pagoda tree (*Saphora japonica*) during a prolonged dry spell
Aquatic weed stems	Smart weed (*Polygonum* spp.) stems collected from Douglas Lake, air dried to constant weight, and broken into one-inch pieces
Cattail head	A one-inch (4 gm) portion of the head of a cattail plant (*Typha angustafolia*) from Strowbridge Reservoir; air dried to constant weight
Hackberry wood, rotting	Rotting wood removed from the stump of a hackberry (*Celtis occidentalis* L.) tree in Clinton Lake†
Hackberry bark	Undecayed bark from a stump in Clinton Lake†
Hackberry stump	Undecayed wood from a stump in Clinton Lake†
Hackberry twigs	Small (0.25-in.) twigs from a stump in Clinton Lake†
Ground cattail head	Head of a cattail plant from Strowbridge Res.†
Ground cattail stem	Stem of a cattail plant from Strowbridge Res.†
Dried cow manure	Cow manure collected near Strowbridge Reservoir†
Periphytic algae	Periphytic algae collected from Strowbridge Res.†
Grass clippings	Fresh grass clippings from a residential fescue lawn
Lake water	Collected from the outlet of Clinton lake

* Picked after turning color in the fall and air dried to constant weight

† Air dried to constant weight and finely ground

tubing was inserted into each hole. A short length of latex rubber tubing, large enough to accept the end of a pipette for sample withdrawal, was attached to the large diameter glass tube. The smaller diameter tube was used to vent nitrogen gas through the larger opening during sampling, thereby preventing the entry of oxygen into the system. Both pieces of tubing were tightly clamped in between samplings. These (anaerobic) samples were deoxygenated using Na_2SO_3 (200 mg/L in the first experiment and 120 mg/L in the second) and seeded with (1 mL in experiment no. 1 and 0.5 mL in experiment no. 2) anaerobic digester supernatant. The jars were shaken once or twice each day to mix the contents.

Initially, the aqueous samples were analyzed for organic carbon and THM formation potential, while the solid samples were simply added to lake water to see how much organic matter would leach into the water. At regular intervals, each sample was shaken, and a 25-mL portion was withdrawn with a pipette, filtered through a 25-mm glass-fiber filter (Whatman 934AH), and analyzed for dissolved organic carbon (DOC). Samples with high concentrations of suspended solids were centrifuged prior to filtration. After 40 days of incubation, a large portion of each sample was withdrawn, filtered, and analyzed for DOC and THM formation potential, and in the second experiment for pH, UV absorbance, and color as well.

ANALYTICAL METHODS

A. SAMPLE HANDLING AND PRESERVATION

Immediately after samples were collected or received by KU researchers, they were refrigerated at 4°C. Upon arrival in the laboratory, the samples were divided into two portions; one portion was immediately filtered (for later analysis of dissolved constituents) through a glass-fiber filter (Whatman 934-AH) prewashed with reagent-grade deionized water (Milli Q, Millipore Corp., Bedford, MA). The other portion was simultaneously homogenized in a clean Waring blender. Each portion was then placed in a scrupulously cleaned 300-mL glass BOD bottle and refrigerated at 4°C. These steps were taken to reduce the possibility of biologically mediated changes in the concentrations of organic carbon and THM precursors. Analysis of the samples usually began less than 24 hours after collection.

Samples for chlorophyll a analysis were stored at 4°C; but when they could not be analyzed within 48 hours, they were frozen at -20°C until they could be analyzed. Sediment and soil samples were dried at 105°C for at least 48 hours, pulverized by grinding for 1-2 minutes in a micromill (Model A-10, Tekmar Co., Cincinnati, OH), and stored in glass vials with foil-lined caps.

B. ORGANIC CARBON

Aqueous samples were analyzed for total organic carbon (TOC) and dissolved organic carbon (DOC), and sediment and soil samples were analyzed for TOC and extractable organic carbon (EOC). Most TOC values for aqueous samples, DOC, and EOC were determined by the UV-persulfate oxidation method (505B) described in Standard Methods (APHA, 1985) for non-purgeable organic carbon, assuming that the purgeable organic carbon concentrations in the samples were negligible. A few aqueous samples, having particularly high TOC values or so much particulate matter that they could not be completely oxidized in the UV reactor, were analyzed using high temperature combustion (furnace injection). All samples were acidified to pH<2 with concentrated H_3PO_4, purged for 5 minutes at 150 cc/min/10mL at room temperature to remove CO_2, and shaken well prior to injection. The instrument used was a Dohrmann DC-80 Total Organic Carbon Analyzer (Xertex Corp., Santa Clara, CA) equipped with a sediment sampler. The precision of the analyses in the range of concentrations found was better than 2%. For unfiltered samples having high concentrations of suspended solids, the UV-persulfate method may give results that are slightly low.

On a few occasions during the study, especially during the first few months, the TOC concentration of a sample was found to be equal to or higher than the DOC concentration for the same sample. On one occasion (6-5-85) this was thought to be attributable to incomplete mixing of the samples prior to injection, so subsequent samples were very thoroughly mixed. It is also possible that the removal of bacteria from the filtered samples helped to preserve them, while the homogenized (unfiltered) samples underwent a certain amount of biodegradation. Therefore, subsamples for TOC analysis were generally taken as soon as possible and immediately acidified to prevent biodegradation of organic matter.

Sediment and Soil TOC

Since there appeared to be no well developed standard method suitable for determining TOC in the sediment and soil samples, it was necessary to develop a procedure that would be sensitive enough to detect the low concentrations of TOC present in the samples without interference from any inorganic carbon (carbonate minerals) that might be present in the samples. Beginning with a method used by Froelich (1980) to determine TOC in marine sediments, a number of variations were tested and a modified method suitable for analysis of the sediment samples was developed.

A key consideration in the development of a method for TOC in sediments was to select an acid that would be able to completely dissolve carbonate minerals without interfering with the operation of the TOC analyzer. Phosphoric acid was selected for a number of reasons: 1) it was the acid recommended for both solid and aqueous samples by the manufacturer of the TOC analyzer; 2) it was found to be free of significant quantities of impurities; 3) it does not interfere in the analysis (as does hydrochloric acid); 4) it is not as volatile as other acids (e.g., hydrochloric and nitric acids) and is therefore less likely to damage the instrument; 5) calcium phosphate precipitation should not retard dissolution of carbonate minerals to the same extent that calcium sulfate precipitation would if sulfuric acid were used; and 6) Froelich (1980) had found that it worked well for marine sediment containing substantial quantities of calcium carbonate.

In preliminary tests on several different sediment samples, phosphoric acid was found to perform satisfactorily and to give results equivalent to those obtained using nitric or hydrochloric acid. Therefore, the method was adopted for use. It was later discovered that large quantities of calcium carbonate were not completely destroyed using this method (Denne et al., 1986); but since the sediments contained little or no calcium carbonate and relatively large concentrations of TOC, the method was deemed suitable for continued use for lake sediments.

The method used to determine TOC in sediments is as follows:

1. Place approximately one gram of dried and milled sediment, weighed to the nearest 0.001 gm, into a scrupulously cleaned 50-mL Nessler tube. (The weight of sample can be adjusted, if necessary, to keep the TOC of the suspension in the proper range for the instrument.)
2. Add 25 mL of 6M phosphoric acid (407 mL of 85% H_3PO_4 per liter) prepared with reagent-grade water (Milli-Q, Millipore Corp., Bedford, Mass.) having a TOC of less than 0.05 mg/L. (Egozy, 1986, found Milli-Q water to have a TOC concentration of about 5 ppb.)

3. Allow the mixture to stand for at least 5 minutes or until evolution of carbon dioxide ceases.
4. Mix the sample thoroughly for 60 seconds using a vortex mixer (Vortex Genie Mixer, Scientific Products, McGaw Park, IL).
5. Place the test tube in a sonifier (Model B-221, Branson Cleaning Equipment Co., Shelton, CT) for 30 minutes to accelerate dissolution of carbonate minerals.
6. Determine the volume of the suspension (V) to the nearest 0.1 mL.
7. Remove any traces of dissolved carbon dioxide from the suspension by purging with 100 cc/min of nitrogen gas for 5 minutes.
8. Mix the sample for 60 seconds using a vortex mixer. While still mixing, withdraw 40 µL of the suspension using a micropipette (Eppendorf Digital Pipette 4710, Brinkman Instruments Co., Westbury, NY) and inject it into the platinum boat in the carriage inlet to the TOC analyzer.
9. Insert the platinum boat into the combustion tube, determine the TOC of the suspension, and compute the TOC of the core sample:

$$\text{TOC, mg/dry gm} = \frac{(\text{TOC of suspension} - \text{system blank}) \times (\text{V,mL})}{(\text{weight of sample, gms}) \times (1000\ \text{mL/L})}$$

Extractable Organic Carbon (EOC)

Although there are numerous procedures described in the scientific literature for extracting organic matter from soils and sediments (e.g., Stevenson, 1982), few (if any) of these procedures can be considered as "standard" procedures. In general, it has been found that strong bases extract more of the organic matter from soil than do various other extractants, and acid pretreatment often improves the extraction by stripping out multivalent cations. However, the objective of extracting the organic matter in this study was not to extract the maximum amount possible, but to estimate the amount of organic matter that could potentially be released into the water from the sediments and to examine its THM formation potential. Therefore a relatively mild extractant, sodium tripolyphosphate, was used in the following procedure:

1. Place 1.000 gm of dried and milled sample in a 50-mL polypropylene screw-cap centrifuge tube. (Portions of the soil samples were also analyzed wet, without drying or milling.)
2. Add 30.0 mL of 10 mM STP (3.6793 gm/L, prepared with reagent-grade deionized water containing less than 0.05 mg/L of TOC).
3. Mix the sample on a vortex mixer for 60 seconds.
4. Sonify the sample for 15 minutes.
5. Mix the sample on a vortex mixer for 60 seconds.
6. Centrifuge the sample for 10 minutes (at approximately 2500 rpm) or until clear.
7. Decant the supernatant (or draw it off with a pipet), taking care not to disturb the solids.

8. Inject 1.00 mL of the extract into the injection port of the TOC analyzer.

$$\text{EOC, mg/dry gm} = \frac{\text{(TOC, mg/L) (0.03 L)}}{\text{(Sample weight, gms)}}$$

C. TRIHALOMETHANE FORMATION POTENTIAL (TFP)

Although there are several very good standard analytical methods for determining the concentration of trihalomethanes in drinking water, there is presently no standard procedure for determining trihalomethane formation potential (TFP), i.e., the concentration of trihalomethanes that will be produced upon chlorination. Several years ago, scientists working for the U.S. EPA drafted a method for determination of maximum TFP (Bellar *et al.*, 1982), but the method is intended to be used for regulatory purposes rather than to compare one water sample with another. At this time the Joint Task Group on Trihalomethane Formation Potential, a committee appointed to develop a TFP method for inclusion in the next edition of *Standard Methods for the Examination of Water and Wastewater* (APHA, 1985), has begun work to develop a method; but they have not yet reached concensus, and their task is a difficult one.

Determination of TFP is complicated by the fact that the concentrations of trihalomethanes produced are dependent upon pH, time, chlorine dosage, residual chlorine concentration, bromide ion concentration, temperature, and other variables. Hence, unlike other measures that seek to quantify an intrinsic property of a sample, TFP is a function not only of the intrinsic properties of the sample but also of external conditions. Furthermore, although the external conditions can be controlled in the laboratory, not all of the key variables are independent, making complete control impractical. For example, TFP depends upon both chlorine dosage and the residual chlorine concentration. The chlorine dosage can be carefully controlled, but the residual chlorine concentration will depend upon the nature of the sample. Hence, two samples containing identical concentrations of the same organic material can be treated with the same dosage of chlorine, but differences in the residual chlorine concentration (created by other constituents in the sample, e.g., ammonium) can cause differences in the value of TFP. Or, if the two samples are treated with different dosages of chlorine such that they both end up with the same concentration of free residual chlorine, the sample receiving the higher chlorine dosage will produce a higher concentration of THMs due to the initial exposure to the higher chlorine concentration (oxidants "activate" certain precursor functional groups).

A related difficulty associated with determination of TFP is that unless the laboratory conditions are identical to those encountered in the field, the results will not accurately reflect THM formation under field conditions. Some investigators select conditions (e.g., high chlorine dosage, high pH, long contact times, etc.) designed to produce a "maximum" value of TFP; but the value is not a true maximum and the concentrations of THMs often greatly exceed those that would be produced under field conditions.

For this project, a procedure was developed that is intended to produce the maximum concentration of THMs under conditions reasonably representative of those occurring in the field, while still giving results that are somewhat comparable from one sample to another. Samples are buffered to pH 8.2, close to the pH of most of the lake and river samples, and then contacted for 4 days with enough chlorine to produce a free chlorine residual of 0.2 to 5.0 mg/L (generally 0.5 to 3.0 mg/L when organic matter is present). This procedure produces concentrations of THMs somewhat greater than would normally be encountered under typical field conditions, but the results nevertheless do provide a rough estimate of the ability of the organic matter in each sample to serve as precursor material for THM formation. The procedure is as follows:

1. Prepare the necessary reagents.
   A. Purified water: Add 3 mL of household bleach to 18 L of reagent-grade deionized water (giving about 10 mg/L of free chlorine), adjust the pH to >10.0 (by adding at least 1.8 mL of 1N sodium hydroxide), and let stand at least overnight. Immediately prior to use, reduce the chlorine residual to less than 0.1 mg/L by dropwise addition of sodium sulfite solution to the desired quantity of water. Strip the dechlorinated water for at least 30 minutes with 800 cc/min/L of high purity gas, and then adjust the pH to 8.2 with 0.1N HNO_3. A reagent blank prepared with this water and incubated for 96 hours should produce no more than 5 µg/L of THMs.
   B. Sodium sulfite solution: Add 90 gm of sodium sulfite to one liter of purified water.
   C. Chlorine solution: Prepare a concentrated chlorine solution by bubbling high purity chlorine gas into purified water and raising the pH to at least 9.5 with sodium hydroxide. Immediately prepare a working solution containing 305 mg/L of chlorine and adjust the pH of the working solution to 8.2. Store the working solution at 4°C wrapped in aluminum foil. Immediately prior to use, check the titer of the working solution and vigorously aerate it for at least 20 minutes at room temperature to remove traces of chloroform.

2. Adjust the pH of each sample to 8.2± 0.1 using 0.1N sodium hydroxide or nitric acid, and then add 50 mL to each of four serum bottles. (Smaller volumes were sometimes used for samples containing high concentrations of TOC, such as feedlot runoff.)

3. Chlorinate the samples by adding 1, 2, 3, or 4 mL of chlorine solution to each bottle (giving free chlorine dosages of 5, 10, 15, and 20 mg/L) and fill each bottle headspace free with purified water. Immediately seal the serum bottles with teflon-lined septa and aluminum seals, and then incubate them at 25°C for 96 hours (4

days). (Higher chlorine dosages were required for a few of the samples especially those containing ammonia nitrogen. When significant concentrations of ammonium ion were thought to be present, the NH_4-N concentration was determined, as described below, and the dosage of chlorine was increased stoichiometrically to remove the NH_4-N by breakpoint chlorination.)

4. Add 1 scoop (approx. 0.5 gm) of sodium sulfate and 4.00 mL of solvent (THM grade pentane or 2,2,4-trimethylpentane, Burdick & Jackson, Muskegon, MI) to a 15-mL screw-cap extraction vial. Seal the vial tightly until ready for use (step 7).

5. Uncap the serum bottle that received the lowest chlorine dosage and spot test for the presence of free chlorine by placing 2 mL of sample in DPD solution. If no free chlorine is present, go on to the next sample. If chlorine is present, go on to the next step.

6. Open the extraction vial and add 2 drops of sulfite solution and then 9 mL of sample. Measure the residual chlorine concentration in the remaining 50 mL of sample using the DPD colorimetric method (APHA, 1985). If the chlorine residual is less than 0.2 mg/L, discard the sample and return to step 5. If greater than 0.2 mg/L, go on to step 7.

7. Mix the contents of the extraction vial for 30 seconds using a vortex mixer. Then, using a disposable pipet, fill a 1-mL vial with the pregnant solvent and seal the vial tightly with a teflon-lined aluminum seal. Store the vials in the dark at 4°C for THM analysis.

8. Analyze the THM concentrations in the solvent using gas chromatography. In computing the trihalomethane concentrations, take into consideration the volumes of dilution water, reagents, and solvents used.

9. For unfiltered samples, report the concentration of TFP as the sum of the individual THM species in µg/L and the yield in micromoles per mg of TOC (µmoles/mgC). For filtered samples, report the concentration of dissolved trihalomethane formation potential (DTFP) in µg/L and the yield in µmoles per mg DOC (µmoles/mgC). For organic matter extracted from soil or sediment, report the concentration of extractable trihalomethane formation potential (ETFP) in µg/L or in µmoles per mg of EOC (µmoles/mgC).

Solvent samples were analyzed for THMs using a Varian Model 2400 gas Chromatograph (Varian Corp., Palo Alto, CA) equipped with a tritium/scandium electron capture detector and a 2m x 2 mm I.D. glass column packed with 3% SP-1000 on 100/120 Supelcoport (Supelco, Inc., Bellefonte, PA). Reference standards obtained from the U.S. EPA and from an independent supplier (Supelco, Inc., Bellefonte, PA) were always within ± 3% of the in-house standards. The precision of the THM analysis is about ± 2 percent, but because of the difficulties discussed earlier, considerable caution must be exercised in comparing the TFP of one sample with another.

D. DISSOLVED OXYGEN, pH, AND AMMONIUM

Samples to be analyzed for dissolved oxygen (see Sampling Sites & Procedures) were fixed in the field by adding alkaline iodide azide and manganous sulfate from powder pillows (Hach Chemical Company, Loveland, CO) and shaking the samples well. The samples were then stored in the dark and transported back to the laboratory, where they were subsequently titrated with sodium thiosulfate to a starch endpoint (APHA, 1985).

Sample pH was determined in the field using a portable battery-powered pH meter (Electromate, Beckman Instruments, Fullerton, CA) equipped with a combination pH electrode. In the laboratory, pH was determined using a pH/ion meter (Fisher Accumet, Model 230, Fisher Scientific, St. Louis, MO). Both pH meters were equipped with combination pH electrodes (Corning No. 476182).

Ammonium nitrogen concentrations were generally determined by the ammonia-selective electrode method (417E in *Standard Methods*, APHA, 1985). The procedure was modified to use a small sample volume (10 mL), which was placed in a small test tube, adjusted to pH>11 with 10N NaOH, and mixed with a very small (0.25-inch) magnetic stirring bar while the electrode (Model 9512, Orion Research, Inc., Cambridge, Mass.) was inserted into the sample. Ammonium- and nitrate-nitrogen concentrations in the year-two (1986) pond samples were determined using automated (Alpkem continuous flow analyzer) indophenol blue and cadmium reduction methods, respectively.

E. TURBIDITY AND SUSPENDED SOLIDS

Turbidity was determined in the field using a portable battery-powered turbidimeter (Model 16800, Hach Chemical Co., Loveland, CO). Suspended solids (SS) concentrations were determined as described in *Standard Methods* (APHA, 1985) using Whatman 934AH glass-fiber filters.

F. CHLOROPHYLL

The procedure described in *Standard Methods* (APHA, 1985) for determination of chlorophyll *a* is time consuming, requires tissue grinding, and may fail to completely extract the chlorophyll for some species of algae. The standard method calls for extraction with acetone, which will not extract chlorophyll from unbroken cells; hence, tissue grinding is necessary. Recently, it has been found that DMF (N,N-dimethylformamide) is a superior extracting solvent because it extracts chlorophyll from unbroken cells, eliminating the need for tissue grinding, and extracts the chlorophyll more effectively from some species of algae than does acetone (Speziale *et al*., 1984; Hains, 1985). Therefore a modified version of the standard method, employing DMF, was used in this study. The procedure is as follows:

1. Collect each sample in a dark polyethylene bottle and immediately place it on ice. Store samples in the refrigerator for up to 48 hours at 4°C or frozen at -20°C for up to three weeks.

2. Filter 0.5 L (or as great a volume as possible) of each sample through a glass-fiber filter (Whatman 934AH).

3. Roll up each filter using tweezers and forceps and insert it into a 15-mL centrifuge tube. Place the tubes in a freezer (-20°C) for at least one hour (to help break algal cells and to keep the sample in the dark) and for up to 48 hours if the analysis cannot be completed immediately. Keep the tubes in the dark (or covered with foil) until absorbance has been read (step 7).

4. Add 10 mL of N,N-dimethylformamide (DMF) to each tube and incubate the tubes at 65°C for 15 minutes in a heated sonifier bath (Model B-221, Branson Cleaning Equipment Co., Shelton, CT).

5. Place the tubes in the freezer (-20°C) for 15 minutes to cool them.

6. Centrifuge the tubes at about 2000 rpm for 15 minutes or until clear.

7. Pipette 3 mL of DMF from each tube into a clean 1 mm cuvette and read the absorbance (against a DMF blank) at 665 mm and 750 mm. Add 0.1 mL of 0.1 N HC1, wait 90 seconds exactly, and then read the absorbance again at 665 and 750 mm. Absorbance was determined using a spectrophotometer with an adjustable slit width set to less than 2 µm (Cary 118, Varian Associates, Inc., Palo Alto, CA).

8. Compute chlorophyll a and pheophytin a:

$$\text{Chlorophyl } \underline{a} \ (\mu g/L) = \frac{28.43\ (665_o - 665_a)v}{V \times c}$$

$$\text{Pheophytin } \underline{a} \ (\mu g/L) = \frac{28.43\ (1.7 \times 665_a - 665_o)v}{V \times c}$$

Where:

665_o = initial absorbance, corrected for turbidity (750_o)

665_a = absorbance after acidification, corrected for turbidity (750_a)

v = volume of extract, mL

V = volume of sample filtered, liters

c = path length, cm

For determination of chlorophyll on the pond samples collected during the second year of the study, the adsorbances were read using a Spectronic 88 (Bausch & Lomb, Rochester, NY) with a slit width of 8 mm. Because the absorbance band for chlorophyll *a* is very sharp, use of a slit width greater than 2 mm produces low results. According to *Standard Methods* (APHA, 1985), use of a 20 mm slit width may produce results that are 40% low. Analysis of EPA check samples using the 8 mm slit width produced results that were 15% low. Therefore, concentrations of chlorophyll *a* determined using the Spectronic 88 were corrected by dividing by a factor of 0.85.

G. MOISTURE CONTENT

Each of the soil samples was also analyzed for TOC, EOC, and ETFP using an undried and unground portion of the sample. So that the concentrations of these constituents could be reported on a dry-weight basis, the moisture content of each sample was determined using the following procedure:

1. Dry an aluminum dish in the oven at 105°C for at least 4 hours, then remove the dish from the oven and place it in a dessicator containing a fresh charge of calcium sulfate. When the dish is cool, weigh it to the nearest milligram.

2. Place an accurately weighed 10 to 15 gram portion of sample in the dish and place it in the oven at 105°C for at least 24 hours.

3. Remove the dish containing the dried sample from the oven and place it in the dessicator. When the dish is cool, weigh it to the nearest milligram.

4. Compute the moisture content as the percentage of the total (wet) weight of sample comprised of water:

$$\% \text{ moisture} = \frac{(\text{wet weight} - \text{dry weight}) \times 100}{\text{wet weight}}$$

H. UV ABSORBANCE AND COLOR

UV absorbance (UVA) was determined at a wavelength of 300 mm using a Perkin-Elmer Model Lambda 3 UV/Visible Spectrophotometer and 1-cm silica cells. Color was determined by measuring the absorbance of light at a wavelength of 400 mm. Both were determined at a pH of 8.2.

I. PHYTOPLANKTON ENUMERATION

Samples were collected from the experimental ponds as described in "Sampling Sites and Procedures" and preserved by creating a 1% solution of Lugol's preservative. Organisms were concentrated in settling chambers and counted with a Wild inverted microscope.

RESULTS AND DISCUSSION

A. LAKES

Lake samples were collected on various occasions between 6-5-85 and 11-20-86. On some occasions a single lake was intensively sampled to determine the distribution of organic carbon and THM precursors within the lake. On other occasions only a few samples were collected from one or more lakes in an effort to explore seasonal changes, differences between top and bottom samples, etc. The results of the intensive samplings of Clinton Lake, Strowbridge Reservoir, Douglas Lake, and Lyndon Lake are described first. The results for the other samplings follow.

Clinton Lake

Clinton Lake was intensively sampled on 6-5-85 (late spring), on 9-5-85 (late summer), and on 7-2-86 (early summer). The organic carbon concentrations, THM formation potentials, and supporting data are presented in Tables 12 through 17. Tables 18 through 20 summarize the average organic carbon concentrations and THM yields for selected subsets of the samples collected on each date.

A cursory examination of the organic carbon data (Tables 12, 14, and 16) reveals that DOC and TOC were distributed quite uniformly throughout the lake, despite the irregular shape of the lake and differences in the microenvironments sampled. On each occasion there were no significant differences in DOC and TOC among the north arm of the lake, the south arm of the lake, and the main body of the lake, except that on 9-5-85 the DOC in the south arm of the lake was lower than in the main body of the lake (see Tables 18-20). This uniformity is rather surprising in view of the fact that each arm of the lake is fed from a different watershed. Two logical explanations for this uniformity are: 1) the lake is extremely well mixed; and 2) the organic carbon entering each arm of the lake is similar in character and concentration and there are no major sources or sinks within the lake itself.

The main body of the lake is clearly well mixed. The water temperature and dissolved oxygen data (Tables 13, 15, and 17) show that the entire lake was very much unstratified on the first two sampling dates and only weakly stratified on the third. Also, the shallow depth of the lake and its large surface area (long fetch) provide excellent conditions for mixing. Nevertheless, such mixing does not in itself entirely explain the uniformity of organic carbon concentrations (and THM yields), especially in the upper (riverine) arms of the lake and in secluded coves (e.g., site 17).

On 6-5-85, water in the upper reaches of the south arm was very turbid and light brown in color as a result of recent heavy rains (the Clinton Lake weather station reported 2.20 inches of rain on 6-4-85). The north arm was much less turbid (compare the turbidity values at sites 6 and 10, Table 13).

TABLE 12

ORGANIC CARBON AND THM FORMATION POTENTIAL IN CLINTON LAKE SAMPLES OF 6-5-85

			DTFP				TFP		
Site No.	Sample Depth m	DOC mg/L	TTHM µg/L	Yield µmoles/mgC	Res.Cl_2 mg/L	TOC[1] mg/L	TTHM µg/L	Yield µmoles/mgC	Res.Cl_2 mg/L
1	1.0	4.0	167	0.33	0.9(6)[2]	4.0	192	0.38	0.6(6)
	10.0	3.9	168	0.34	1.4(6)	3.9	192	0.39	0.6(6)
2	1.0	3.7	165	0.35	1.4(6)	4.1	176	0.34	0.4(6)
	9.5	3.9	167	0.34	1.5(6)	3.9	197	0.40	0.6(6)
3	1.0	4.3	182	0.34	1.3(6)	5.2	244	0.38	0.4(9)
4	1.0	4.2	185	0.35	1.1(6)	4.2	252	0.48	1.1(9)
5	1.0	6.8	408	0.50	0.8(6)	10.0	575	0.48	0.3(9)[3]
6	1.0	4.1	204	0.40	0.9(6)	4.1	267	0.53	0.7(9)
7	0.1	4.1	186	0.36	0.7(6)	5.2	284	0.44	1.3(12)
8	1.0	4.2	186	0.35	0.4(6)	4.3	272	0.51	0.6(9)
9	1.0	4.1	204	0.40	2.9(9)	4.1	263	0.52	0.7(9)
10	1.0	4.1	179	0.34	0.5(6)	4.5	239	0.43	0.7(9)
11	0.1	4.2	190	0.36	0.5(6)	6.0	366	0.50	1.6(9)[3]
12	1.0	4.1	193	0.38	0.6(6)	4.4	293	0.54	0.5(9)
	3.5	4.7	180	0.31	0.3(6)	4.7	253	0.43	0.6(9)
13	1.0	4.5	189	0.33	0.9(6)	4.5	246	0.44	1.2(9)
14	1.0	4.1	201	0.39	1.1(6)	4.4	260	0.48	1.6(9)
15	1.0	4.1	197	0.38	1.2(6)	4.1	245	0.47	1.6(9)
	6.2	3.9	177	0.36	1.0(6)	3.9	224	0.46	1.7(9)
16	0.1	4.0	173	0.34	0.8(6)	4.0	213	0.43	2.0(9)
17	1.0	4.0	199	0.40	0.9(6)	4.2	249	0.48	1.5(9)

[1] Some TOC values may be slightly low due to incomplete mixing during analysis or to biodegradation of TOC in the unfiltered (homogenized) samples as they were awaiting analysis. Since the TFP samples were well mixed, the yields may therefore be slightly high for some samples.

[2] Values in parentheses are chlorine dosages in mg/L.

[3] This sample was diluted by 50% prior to chlorination.

TABLE 13

SUPPORTING DATA FOR CLINTON LAKE SAMPLES OF 6-5-85

Site No.	Total Depth m	Sample Depth m	Temp. °C	ΔT* °C	DO mg/L	pH	Turbidity NTU	Secchi Depth cm
1	11.0	1.0	21.3	0.5	6.8	7.9	8.8	120
		10.0	20.8	-	4.2	7.6	26	-
2	10.5	1.0	21.3	0.1	7.4	8.0	5.3	130
		9.5	21.2	-	7.3	8.0	5.4	-
3	3.2	1.0	21.4	0.0	8.2	8.2	7.1	110
4	6.0	1.0	21.4	0.2	8.3	8.2	11	100
5	5.0	1.0	18.9	0.5	7.0	7.6	>100	5
6	2.9	1.0	21.3	0.2	8.0	8.1	53	35
7	0.5	0.1	21.2	-	-	8.2	65	-
8	2.1	1.0	21.4	0.2	9.0	8.2	27	60
9	6.5	1.0	21.8	0.2	7.8	8.1	13	70
10	3.0	1.0	21.3	0.0	7.5	7.8	24	60
11	1.0	0.1	21.0	-	-	7.9	53	65
12	4.5	1.0	21.4	2.4	7.4	8.0	28	50
		3.5	-	-	7.1	7.8	36	-
13	1.5	1.0	21.2	0.0	8.5	8.0	19	70
14	2.0	1.0	21.6	0.1	9.5	8.3	18	65
15	7.2	1.0	21.7	0.7	9.1	8.2	11	100
		6.2	21.0	-	7.3	7.8	17	-
16	0.5	0.1	21.2	-	7.5	7.9	13	-
17	2.5	1.0	20.8	3.0	8.6	8.2	13	80

* ΔT is the difference in temperature between the surface and bottom.

Note: The deep samples had NH_4-N concentrations less than 0.1 mg/L

TABLE 14

ORGANIC CARBON AND THM FORMATION POTENTIAL IN CLINTON LAKE SAMPLES OF 9-5-85

			DTFP				TFP		
Site No.	Sample Depth m	DOC mg/L	TTHM µg/L	Yield µmoles/mgC	Res.Cl_2 mg/L	TOC mg/L	TTHM µg/L	Yield µmoles/mgC	Res.Cl_2 mg/L
1	1.0	5.30†	153	0.227	0.7 (A)*	6.65†	219	0.264	2.0 (B)
	9.5	4.71	156	0.259	0.9 (A)	5.60	219	0.312	2.1 (B)
2	1.0	4.69	155	0.259	0.7 (A)	4.67	213	0.364	2.5 (B)
	8.0	4.58	149	0.256	0.7 (A)	4.86	214	0.352	2.5 (B)
3	1.0	4.13	159	0.302	0.7 (A)	4.96	226	0.365	1.7 (B)
4	1.0	4.13	156	0.297	0.7 (A)	4.88	213	0.349	2.4 (B)
	5.0	4.04	152	0.295	0.8 (A)	4.68	227	0.388	2.5 (B)
5	1.0	5.56	260	0.379	2.6 (B)	6.53	360	0.449	2.1 (C)
6	1.0	4.48	155	0.272	0.4 (A)	4.81	228	0.379	1.4 (B)
7	0.1	4.22	161	0.300	0.5 (A)	5.00	227	0.364	1.6 (B)
8	1.0	4.30	162	0.297	0.5 (A)	4.91	230	0.375	1.6 (B)
9	1.0	4.36	167	0.301	0.5 (A)	5.04	230	0.365	1.7 (B)
	3.8	4.33	160	0.290	0.5 (A)	4.56	266	0.470	8.5 (D)
10	1.0	4.62	166	0.284	0.2 (A)	5.80	267	0.371	0.8 (B)
	5.0	4.70	169	0.283	0.2 (A)	5.42	260	0.385	0.6 (A)
11	1.0	4.76	174	0.289	0.3 (A)	6.62	355	0.437	1.4 (C)
12	1.0	4.38	167	0.300	0.4 (A)	4.94	261	0.425	1.3 (B)
13	1.0	4.11	157	0.300	0.6 (A)	5.18	242	0.375	1.0 (B)
14	1.0	4.24	159	0.295	0.8 (A)	4.82	243	0.405	1.7 (B)
15	1.0	4.20	168	0.316	0.7 (A)	4.83	234	0.389	1.9 (B)
	6.0	4.07	154	0.298	0.8 (A)	4.56	230	0.404	2.0 (B)
16	0.3	3.63	154	0.333	1.0 (A)	8.40	337	0.327	1.2 (C)
17	1.0	4.13	160	0.305	0.7 (A)	4.83	254	0.423	1.3 (B)
18	1.0	5.81	295	0.409	2.1 (B)	6.82	382	0.455	1.8 (C)

* Chlorine dosages shown in parentheses; A=5 mg/L, B=10 mg/L, etc.

† Suspect data

TABLE 15

SUPPORTING DATA FOR CLINTON LAKE SAMPLES OF 9-5-85

Site No.	Total Depth m	Sample Depth m	Temp. °C	ΔT* °C	DO mg/L	pH	Turbidity NTU	Chlor. a µg/L
1	10.5	1.0	26.5	1.0	8.3	8.6	5	8.1
		9.5	25.5	-	8.3	8.6	6	8.0
2	9.0	1.0	26.0	2.1	7.3	8.6	6	7.3
		8.0	23.9	-	7.1	8.6	7	10.7
3	3.0	1.0	26.6	0.0	7.9	8.6	14	9.3
4	6.0	1.0	26.0	1.7	7.9	8.4	6	10.1
		5.0	24.3	-	6.5	8.1	9	11.1
5	-	1.0	-	-	-	7.5	33	13.5
6	4.5	1.0	26.2	0.9	6.6	8.0	12	11.2
7	0.5	0.1	27.5	0.2	7.0	8.4	15	5.7
8	4.5	1.0	26.5	2.5	6.8	8.1	13	11.3
9	4.8	1.0	27.4	1.6	7.6	8.6	11	10.2
		3.8	25.8	-	6.1	8.6	15	4.4
10	6.0	1.0	28.0	3.5	7.3	8.5	29	7.4
		5.0	24.5	-	6.0	8.4	32	7.3
11	1.0	0.5	29.1	0.2	7.2	8.4	67	17.9
12	4.0	1.0	28.6	0.8	8.4	8.6	18	12.5
13	2.0	1.0	28.5	0.0	7.4	8.6	24	11.2
14	2.5	1.0	28.0	0.3	8.4	8.6	15	-
15	7.0	1.0	27.5	3.7	8.4	8.8	10	11.7
		6.0	23.8	-	7.0	8.5	18	10.2
16	0.3	0.2	27.4	-	8.1	8.7	78	8.1
17	1.5	1.0	28.6	0.2	7.8	8.7	30	11.5
18	-	1.0	-	-	-	7.7	52	11.1

Note: The deep samples had NH_4-N concentrations less than 0.1 mg/L.

* ΔT is the temperature difference between surface and bottom.

TABLE 16

ORGANIC CARBON AND THM FORMATION POTENTIAL IN CLINTON LAKE SAMPLES OF 7-2-86

			DTFP				TFP		
Site No.	Sample Depth m	DOC mg/L	TTHM µg/L	Yield µmoles/mgC	Res.Cl_2 mg/L	TOC mg/L	TTHM µg/L	Yield µmoles/mgC	Res.Cl_2 mg/L
1	1.0	4.27	212	0.396	4.1 (B)*	5.19	229	0.352	2.5 (B)
	7.5	4.52	201	0.353	4.6 (B)	5.00	254	0.407	1.9 (B)
2	1.0	3.89	193†	0.394†	3.0	4.03	251†	0.500†	3.0
	9.0	3.90	185†	0.377†	3.0	4.28	234†	0.438†	3.0
3	1.0	3.73	183	0.386	4.5 (B)	4.38	212	0.382	1.8 (B)
4	1.0	4.04	212	0.418	4.4 (B)	4.22	256	0.488	3.3 (B)
5	1.0	6.09	289	0.388	--- (B)	11.28	463	0.339	--- (D)
9	1.0	3.85	204†	0.420†	3.0	4.56	279†	0.492†	3.0
	4.5	3.79	207†	0.433†	3.0	3.92	263†	0.540†	3.0
10	1.0	3.96	197†	0.390†	3.0	4.40	284†	0.519†	3.0
	7.0	4.28	209†	0.386†	3.0	5.01	286†	0.458†	3.0
12	1.0	3.78	207	0.435	3.6 (B)	4.40	245	0.445	1.4 (B)
	3.0	3.82	197	0.410	3.6 (B)	4.37	247	0.453	1.4 (B)
15	1.0	3.75	187†	0.395†	3.0	3.91	230†	0.469†	3.0
	7.3	3.78	186†	0.390†	3.0	3.95	232†	0.471†	3.0
18	1.0	3.85	229	0.457	--- (B)	4.74	263	0.432	--- (B)

* Chlorine dosages shown in parentheses; A=5 mg/L, B=10 mg/L, etc.

† Estimated at a free chlorine residual of 3.0 mg/L based on linear regression of three samples with different concentrations of free residual chlorine.

TABLE 17

SUPPORTING DATA FOR CLINTON LAKE SAMPLES OF 7-2-86

Site No.	Total Depth m	Sample Depth m	Temp. °C	ΔT* °C	DO mg/L	pH	Turbidity NTU
1	8.5	1.0	27.0	5.4	6.6	8.2	8
		7.5	23.6	-	4.2	7.8	10
2	10.0	1.0	27.0	5.4	6.7	8.2	8
		9.0	22.0	-	0.2	7.3	27
3	2.8	1.0	26.8	0.3	8.2	8.2	37
4	5.0	1.0	26.9	0.7	7.9	8.2	13
9	5.5	1.0	27.6	2.4	7.1	8.2	20
		4.5	25.2	-	0.6	7.4	14
10	8.0	1.0	27.6	4.1	7.4	8.2	31
		7.0	24.8	-	2.0	7.5	42
12	3.8	1.0	28.4	0.8	5.3	7.9	40
		3.0	27.6	-	4.4	7.8	42
15	8.3	1.0	27.8	3.4	6.6	8.2	8
		7.3	25.3	-	0.2	7.4	16

* ΔT is the difference in temperature between the surface and the bottom.

Note: The bottom samples from stations 2, 10, and 15 produced a yellow color upon chlorination, indicating the presence of iron and/or manganese.

TABLE 18

AVERAGE ORGANIC CARBON CONCENTRATIONS AND THM YIELDS OF CLINTON LAKE SAMPLES OF 6-5-85

Sample Group	No. of Samples	Avg. DOC (mg/L)	Avg. TOC (mg/L)	Average DTFP (µmoles/mgC)	Average TFP (µmoles/mgC)
All Samples	21	4.2 ± 0.6	4.7 ± 1.3	0.36 ± 0.04	0.45 ± 0.05
Excluding No. 5[1]	20	4.1 ± 0.2	4.4 ± 0.5	0.36 ± 0.03	0.45 ± 0.06
Excluding Nos. 5 & 9[2]	19	4.1 ± 0.2	---	0.36 ± 0.02	---
Excl. Nos. 3, 5, 7, & 11[3]	17	---	4.3 ± 0.4	---	0.45 ± 0.06
Sites 3, 7 & 11[3]	3	4.2 ± 0.1	5.5 ± 0.5	0.35 ± 0.01	0.44 ± 0.06
Main Body (Nos. 1 & 2)	4	3.9 ± 0.1	4.0 ± 0.1	0.34 ± 0.01	0.38 ± 0.03
North Arm (Nos. 9 & 10)	2	4.1 ± 0.0	4.3 ± 0.3	0.37 ± 0.04	0.48 ± 0.06
South Arm (Nos. 4 & 6)	2	4.2 ± 0.1	4.2 ± 0.1	0.38 ± 0.04	0.51 ± 0.04
Site 5[1]	1	6.8 -	10.0 -	0.50 -	0.48 -

[1] Site 5 is riverine rather than lacustrine.

[2] The filtered sample from site 9 required a higher dosage of chlorine than the other filtered samples.

[3] These sites have elevated TOC concentrations, presumably due to nearby erosion.

TABLE 19

AVERAGE ORGANIC CARBON CONCENTRATIONS AND THM YIELDS OF CLINTON LAKE SAMPLES OF 9-5-85

Sample Group	No. of Samples	Avg. DOC (mg/L)	Avg. TOC (mg/L)	Average DTFP (µmoles/mgC)	Average TFP (µmoles/mgC)
All Samples	24	4.5 ± 0.5	5.4 ± 1.0	0.30 ± 0.04	0.38 ± 0.05
Excluding Nos. 5 & 18[1]	22	4.4 ± 0.4	5.3 ± 0.9	0.29 ± 0.02	0.38 ± 0.04
Sites 11 & 16[2]	2	4.2 ± 0.8	7.5 ± 1.3	0.31 ± 0.03	0.38 ± 0.08
Main Body (Nos. 1 & 2)[3]	3	4.7 ± 0.1	5.0 ± 0.5	0.26 ± 0.00	0.34 ± 0.03
North Arm (Nos. 9 & 10)	4	4.5 ± 0.2	5.2 ± 0.5	0.29 ± 0.01	0.40 ± 0.05
South Arm (Nos 4 & 6)	3	4.2 ± 0.2	4.8 ± 0.1	0.29 ± 0.01	0.37 ± 0.02
Sites 5 & 18[1]	2	5.7 ± 0.2	6.7 ± 0.2	0.39 ± 0.02	0.45 ± 0.00

[1] Sites 5 and 18 are riverine rather than lacustrine.

[2] Elevated TOC values at sites 11 and 16 are attributed to nearby erosion.

[3] The data for the upper sample at site 1 have been excluded.

TABLE 20

AVERAGE ORGANIC CARBON CONCENTRATIONS AND THM YIELDS OF CLINTON LAKE SAMPLES OF 7-2-86

Sample Group	No. of Samples	Avg. DOC (mg/L)	Avg. TOC (mg/L)	Average DTFP (μmoles/mgC)	Average TFP (μmoles/mgC)
All Samples	16	4.1 ± 0.6	4.9 ± 1.7	0.40 ± 0.02	0.45 ± 0.05
Excluding Nos. 5 & 18[1]	14	4.0 ± 0.2	4.4 ± 0.4	0.40 ± 0.02	0.46 ± 0.05
Main Body (Nos. 1 & 2)	4	4.1 ± 0.3	4.6 ± 0.5	0.38 ± 0.02	0.42 ± 0.05
North Arm (Nos. 9 & 10)	4	4.0 ± 0.2	4.5 ± 0.4	0.41 ± 0.02	0.50 ± 0.03
South Arm (No. 4)	1	4.0	4.2	0.42	0.49
Sites 5 & 18[1]	2	5.0 ± 1.1	8.0 ± 3.3	0.42 ± 0.03	0.43 ± 0.05
Sites 2, 9, 10 & 15[2]					
Surface	4	3.9 ± 0.1	4.2 ± 0.3	0.40 ± 0.01	0.50 ± 0.02
Bottom	4	3.9 ± 0.2	4.3 ± 0.4	0.40 ± 0.02	0.48 ± 0.04

[1] Sites 5 and 18 are riverine rather than lacustrine.

[2] Stratification was observed at these sites and multiple samples were chlorinated for more accurate estimation of TFP.

Nevertheless, the respective DOC and TOC values for both arms were nearly identical. On 9-5-85 the situation was reversed: the north arm of the lake, fed by the Wakarusa River, was noticeably more turbid than the south arm. Yet once again the DOC and TOC values were quite similar in both arms of the lake.

The fact that differences in the concentration of organic carbon were small or non-existent, despite obvious differences in water quality (turbidity), water source (two different watersheds), and sample location (main body versus upper arms), suggests that the organic matter originating in each watershed is similar and that little change occurs in the lake itself. This is to some extent borne out by the stream data presented later in this section of the report (see "B. Streams"), and also by the lack of significant changes in DOC and TOC in most of the microzones that were sampled, such as sheltered coves, areas of standing timber, beaches, small inlets, etc. If organic carbon and THM precursors are being generated in significant amounts in these zones, then they are being generated at a slow rate (relative to the rate of mixing), such that no significant changes in concentrations are observed.

Examination of the data for 6-5-85 (Table 12) reveals that significantly elevated levels of organic carbon occurred at only four sites (nos. 3, 5, 7, and 11). The highest values of both DOC and TOC were found at site 5; but this site is much more riverine than lacustrine, and Rock Creek was flowing heavily on this date. Site 3 is adjacent to a public beach; but the beach was deserted at the time the samples were collected, so the increased TOC is not attributable to swimming. Perhaps a small amount of erosion was occurring along the grassy shorelines immediately north and south of the beach. At sites 7 and 11, erosion of the nearby shoreline was clearly evident and is presumed to be the cause of the higher TOC values at these sites. The measured turbidity was also higher at both sites, but the DOC concentrations were not significantly different from those elsewhere in the lake.

Examination of the organic carbon data for all three sets of samples reveals that the concentrations of DOC and TOC in four of the five riverine samples (sites 5 and 18) were higher than those of the lacustrine samples, while the concentrations in the fifth sample were similar to those in the lake. This suggests that the lake is acting as a net precursor sink, but these few data points are not adequate to support a firm conclusion. This matter is explored further in Section B ("Streams").

On 6-5-85 and 9-5-85, weak stratification was detected at only a few of the sampling sites, and no significant oxygen depletion was found in the bottom waters. On 7-2-86, however, stratification and oxygen depletion were observed at five different sampling sites within the lake. However, as shown in Table 20, there were no significant differences in the concentrations of organic carbon and THM precursors between the top and bottom samples.

Before further discussing the trihalomethane data, consideration should be given to the influence of chlorine dosage and free chlorine residual on THM formation. As shown in Table 21, higher chlorine dosages and residuals did produce slightly greater concentrations and yields of THMs for three of the Clinton Lake samples of 6-5-85. Hence, as discussed earlier (see "Analytical Methods: Trihalomethane Formation Potential"), a certain amount of caution must be exercised in interpreting THM data when different dosages of chlorine or different residual chlorine concentrations are involved.

None of the samples having elevated TOC values on 6-5-85 (sites 3, 5, 7, and 11) had TFP yields significantly different from the other samples. In examining the yields of TFP and TFP, only one value truly stands out from the others: the DTFP yield for sample 5, which is substantially higher (39% higher) than the average DTFP yield for all samples. Also, the data show that this is not due to a difference in chlorine dosage or chlorine residual. Thus, it appears that the soluble organic matter being carried in by the river was somewhat more potent, in terms of THM formation, than the soluble organic matter already present in the lake. The results from the samples taken 9-5-85 were very similar. The DTFP and TFP yields for the riverine sites (5 and 18) were both significantly higher than for the other (lacustrine) sites; but this could be an artifact due to the higher dosage of chlorine needed to maintain a free chlorine residual.

Examination of the average yields of DTFP and TFP in the main body of the lake, the major arms of the lake, and the rivers feeding the lake (see Tables 18-20) leads to the conclusion that THM yields decreased slightly as the water traveled through the lake. This is quite interesting in view of the fact that there was little or no change in DOC and TOC between the arms and main body of the lake. One reason for this might be that the more potent precursors are selectively removed by adsorption on settling solids (an extensive body of literature shows that the more potent precursors are selectively removed during water treatment). Algal growth may also replace a certain amount of the organic carbon with less potent precursors, maintaining the DOC and TOC concentrations but lowering THM yields.

As shown in Table 14, the DTFP and TFP yields were again very uniform on 9-5-85. If samples 5 and 18 are excluded, the standard deviations are only 0.02 µmoles/mgC (6.9%) and 0.04 µmoles/mgC (10.5%) for the DTFP and TFP yields, respectively, which includes true sample variability as well as the imprecision in the organic carbon and THM analyses. The 9-5-85 THM data give a good estimate of the precision of the THM formation potential analysis. If sites 5, 11, 16, and 18 (those with significantly elevated TOC concentrations) are excluded, the average DTFP average is 159.3 ± 5.78 µg/L (±3.6%) and the average TFP is 235.2 ± 17.8 µg/L (±7.6%). Since these figures include sample variation, it is reasonable to conclude that the precision (standard deviation) of the analysis was better than ± 3.6% for DTFP and ±7.6% for TFP.

Comparison of the 6-5-85 data (Table 18) with the 9-5-85 data (Table 19) reveals that, over a three month period, DOC increased 0.3 mg/L (7%), TOC increased 0.9 mg/L (20%), DTFP yield decreased 19%, and TFP yield

TABLE 21

THE INFLUENCE OF RESIDUAL CHLORINE CONCENTRATION ON THM FORMATION POTENTIAL IN CLINTON LAKE SAMPLES

Sample	TOC mg/L	Cl_2 Dosage mg/L	Res. Cl_2 mg/L	TTHM mg/L	Yield µmoles/mgC
Site 1 - 1m	4.0	6.0	0.9	167	0.33
(Filtered)		9.0	3.1	192	0.38
		12.0	5.4	200	0.40
Site 5	10.0	9.0	0.3	575	0.48
(Homogenized)		12.0	1.5	611	0.51
Site 7	5.2	9.0	<0.1	261	0.40
(Homogenized)		12.0	1.3	284	0.44

TABLE 22

STATISTICAL ANALYSIS OF CLINTON LAKE SAMPLES OF 9-5-85

Variables of Interest	No. of Samples (n)	Correlation Coefficient (r)
TOC vs Chlorophyll a*	20	0.094
(TOC-DOC) vs Chlorophyll a*	20	0.063
TFP (µg/L) vs Chlorophyll a*	20	0.126
Chlorophyll a vs Turbidity†	19	-0.030
(TOC-DOC) vs Turbidity†	20	0.241
DOC vs DTFP	24	0.752
TOC vs TFP*	21	0.796

* Excluding samples 5 and 18 and the upper sample from site 1

† Excluding samples 5, 11, 16, and 18

decreased 16% (excluding sites 5 and 18). The data of 6-5-85 and 7-2-86 (Table 20) are nearly identical. It is not clear whether the increase in organic carbon concentration between 6-5-85 and 9-5-85 was due to increased algal growth, concentration by means of evaporation, or an increase in the amount entering from the watershed. Evaporation is an unlikely explanation for two reasons: 1) rainfall probably exceeded evaporation during this time; 2) simple concentration of the organic matter should not have changed the yield of THMs. Regardless of the source of the additional organic carbon, it appears to have been a very weak precursor material, since no significant increase in the concentration of THMs occurred (1.98 μmoles/L vs 2.01 μmoles/L, excluding sites 5 and 18). Perhaps fresher organic matter produced during the growing season (whether of algal, bacterial, or terrestrial origin) is a poorer source of THM precursors than older material that is more humified and contains fewer carbohydrates. Visser (1983) found that aquatic humic substances were in a more advanced state of humification at the end of the summer than at the beginning.

The 9-5-85 data (Tables 14 and 15) were examined to see what relationships might exist among DOC, TOC, turbidity, and chlorophyll a. As shown in Table 22, TOC, particulate carbon (TOC-DOC), THM formation, and turbidity were all very poorly correlated with chlorophyll a, indicating that algae do not constitute a major fraction of the organic matter or the particles in the lake. Also, it appears that the turbidity is largely inorganic, since the correlation coefficient for particulate carbon (TOC-DOC) and turbidity was only 0.241. As expected, DTFP and TFP were strongly correlated with DOC and TOC, respectively.

Strowbridge Reservoir

Samples were taken from Strowbridge Reservoir on 6-13-85 (late spring) and again on 9-13-85 (late summer). The organic carbon concentrations, THM formation potentials, and supporting data are presented in Tables 23 through 26. Table 27 summarizes the average organic carbon concentrations and THM yields for each set of samples.

On both occasions the reservoir was unstratified; and organic carbon and THM precursor concentrations were quite uniform throughout the reservoir, except for those at site 8, a turbid inlet stream. On 6-13-85, the site 8 sample had the highest DOC and DTFP yield; but on 9-13-85, it had the highest DOC and lowest DTFP yield. On both occasions site 8 had a significantly higher TOC concentration than the other sites, but the TFP yield was similar to those of other sites.

The only other sample which clearly stands out from the rest is the sample taken 6-13-85 from site 9, a very shallow area of the lake with pasture along the shoreline and a feedlot and farmhouse nearby. On 6-13-85, the water was quite green in color and highly turbid, and cattle were standing in a small pond of water near the edge of the reservoir. The green color, the high levels of turbidity and dissolved oxygen (Table 24), and the high TOC (Table 23) at this site indicate the presence of an algal bloom.

TABLE 23

ORGANIC CARBON AND THM FORMATION POTENTIAL IN STROWBRIDGE RESERVOIR SAMPLES OF 6-13-85

			DTFP				TFP		
Site No.	Sample Depth m	DOC mg/L	TTHM µg/L	Yield µmoles/mgC	Res.Cl_2 mg/L	TOC mg/L	TTHM µg/L	Yield µmoles/mgC	Res.Cl_2 mg/L
1	1.0	5.0	270	0.42	2.8(B)*	6.8	294	0.34	0.9(B)
	5.5	4.9	222	0.35	3.0(B)	6.4	259	0.32	1.4(B)
2	0.1	5.1	246	0.38	2.7(B)	6.7	268	0.32	1.1(B)
3	1.0	4.7	259	0.43	3.1(B)	6.7	286	0.35	0.6(B)
4	1.0	5.2	254	0.38	3.4(B)	6.5	306	0.37	1.4(B)
5	1.0	5.0	267	0.42	3.0(B)	6.9	311	0.36	0.8(B)
6	1.0	4.7	263	0.44	2.7(B)	7.6	393	0.42	1.4(C)
7	1.0	4.7	245	0.41	2.9(B)	6.5	283	0.34	1.4(B)
	6.5	4.6	240	0.41	3.4(B)	6.5	294	0.36	2.0(B)
8	0.1	8.0	520	0.53	2.3(C)	15.6	713	0.37	0.5(B)
9	0.1	5.1	303	0.47	2.4(B)	9.8	383	0.31	0.6(C)
10	1.0	4.6	234	0.40	3.0(B)	7.2	317	0.35	1.0(B)
11	1.0	4.6	255	0.48	3.0(B)	6.6	311	0.37	0.9(B)
†	0.1	5.0	292	0.46	2.0(B)				

* Chlorine dosages shown in parentheses; B = 10mg/L and C = 15mg/L.

† Grab sample taken from the center of a patch of floating vegetation around the corner from site 3.

TABLE 24

SUPPORTING DATA FOR STROWBRIDGE RESERVOIR SAMPLES OF 6-13-85

Site No.	Total Depth m	Sample Depth m	Temp. °C	ΔT[1] °C	DO mg/L	pH	Turbidity NTU
1	6.5	1.0	21.3	0.8	7.9	7.7	53
		5.5	20.6	-	6.8	7.7	57
2	0.5	0.1	22.1	-	8.6	7.6	53
3	1.5	1.0	21.9	0.7	8.9	8.0	61
4[2]	2.0	1.0	21.3	2.8	8.7	7.9	61
5	2.0	1.0	20.2	1.9	8.9	7.9	68
6	1.5	1.0	20.6	0.6	8.9	8.0	60
7	7.5	1.0	21.0	0.5	7.0	7.7	50
		6.5	20.6	-	6.9	7.5	54
8	0.8	0.1	20.8	-	8.6	7.7	>100[3]
9	0.3	0.1	24.8	-	10.6	8.4	>100
10	4.8	1.0	21.0	1.8	7.1	7.7	64
11	5.0	1.0	21.4	2.5	7.5	7.7	55

[1] ΔT is the difference in temperature between the surface and the bottom.

[2] Oxygen was present at a depth of 2 meters.

[3] Very turbid, brown in color.

TABLE 25

ORGANIC CARBON AND THM FORMATION POTENTIAL IN STROWBRIDGE RESERVOIR SAMPLES OF 9-13-85

Site No.	Sample Depth m	DOC mg/L	DTFP* TTHM µg/L	DTFP* Yield µmoles/mgC	TOC mg/L	TFP* TTHM µg/L	TFP* Yield µmoles/mgC
1	1.0	4.71	207	0.34	5.13	230	0.35
	4.5	4.74	197	0.32	5.05	229	0.35
2	0.1	4.55	199	0.34	5.21	232	0.35
3	1.0	4.76	201	0.32	5.15	233	0.35
4	1.0	4.70	206	0.34	5.54	235	0.33
5	1.0	4.46	202	0.35	5.46	240	0.34
6	1.0	4.75	201	0.33	5.40	249	0.36
7	1.0	4.66	199	0.33	5.08	217	0.33
	7.0	4.59	194	0.33	5.16	235	0.36
8	0.1	7.03	264	0.29	8.63	385	0.36
9	0.1	4.70	210	0.35	5.94	266	0.35
10	1.0	4.57	206	0.35	5.30	240	0.35
	3.0	4.56	200	0.34	5.14	231	0.35
11	1.0	4.58	206	0.35	5.16	244	0.37
	4.0	4.70	204	0.34	5.13	241	0.37
12	0.1	4.56	208	0.35	6.13	276	0.36

* The DTFP and TFP results are for a free chlorine dosage of 10 mg/L, except for the TFP results for site 8, where a 15 mg/L dosage was needed to produce a free chlorine residual. In a number of the filtered samples, a 5 mg/L dosage of chlorine produced a trace of free chlorine residual; but the samples chlorinated with 10 mg/L of chlorine were analyzed so that the results would be more comparable with those of the homogenized samples.

TABLE 26

SUPPORTING DATA FOR STROWBRIDGE RESERVOIR SAMPLES OF 9-13-85

Site No.	Total Depth m	Sample Depth m	Temp. °C	ΔT* °C	DO mg/L	pH	Turbidity NTU
1	5.5	1.0	24.0	0.0	5.4	7.9	21
		4.5	24.0	-	5.3	7.9	21
2	0.3	0.1	23.4	-	6.1	8.1	19
3	2.5	1.0	22.7	0.0	6.2	8.1	--
4	2.0	1.0	22.3	0.8	6.9	8.2	24
5	1.5	1.0	22.6	0.1	7.3	8.2	24
6	1.5	1.0	23.6	0.3	6.6	8.2	20
7	8.0	1.0	24.0	0.2	5.5	8.1	23
		7.0	23.8	-	5.6	8.1	22
8	0.6	0.1	--	-	-	7.8	78
9	0.3	0.1	23.2	-	7.9	8.3	36
10	4.0	1.0	23.8	0.8	6.1	8.1	21
		3.0	23.0	-	6.2	7.9	21
11	5.0	1.0	23.7	0.2	6.1	8.0	25
		4.0	23.5	-	5.9	8.0	27
12	0.2	0.1	--	-	-	-	67
†	9.0	-	--	1.1	-	-	--

* ΔT is the difference in temperature between the surface and the bottom.

† Approximately 75-100 yards from the center of the dam (i.e., in the deepest part of the lake).

Note: The NH_4-N concentrations in the deep samples from sites 1 and 11 were 0.17 and 0.11 mg/L, respectively. The concentrations at sites 8 and 12 were both less than 0.1 mg/L.

TABLE 27

AVERAGE ORGANIC CARBON CONCENTRATIONS AND THM YIELDS OF STROWBRIDGE RESERVOIR SAMPLES

Sample Group	No. of Samples	Avg. DOC (mg/L)	Avg. TOC (mg/L)	Average DTFP (µmoles/mgC)	Average TFP (µmoles/mgC)
Samples taken 6-13-85					
All samples	14/13	5.1 ± 0.9	7.7 ± 2.5	0.43 ± 0.05	0.35 ± 0.03
Excluding No. 8*	13/12	4.9 ± 0.2	7.0 ± 0.9	0.42 ± 0.04	0.35 ± 0.03
Samples taken 9-13-85					
All samples	16	4.8 ± 0.6	5.5 ± 0.9	0.34 ± 0.02	0.35 ± 0.01
Excluding No. 8*	15	4.6 ± 0.1	5.3 ± 0.3	0.34 ± 0.01	0.35 ± 0.01

* Site 8 is a flowing stream.

Although the concentration of THMs in the chlorinated homogenized sample was quite high, the yield was lower than in any other sample. This suggests that freshly grown algae and their by-products may be less potent precursors, although they do contribute to THM formation.

Comparison of the data from the two sampling dates (Table 27) reveals that, over a period of three months, DOC decreased 0.3 mg/L, TOC decreased 1.7 mg/L, DTFP yield decreased 0.08 μmoles/mgC, and TFP yield remained unchanged (excluding site 8 in each case). Note that the chlorine dosages were nearly identical on both occasions, so this does not explain the change in DTFP. These results from Strowbridge Reservoir contrast with those for Clinton Lake, which showed an increase in organic carbon and a decrease in TFP yield, but they are nevertheless explainable.

On 6-13-85 the reservoir was very full from spring runoff and a large flow of highly turbid water was entering the reservoir at site 8. The influent water (site 8) was high in DOC and TOC; and the DTFP yield (but not the TFP yield) was elevated. Many plowed fields were visible from the watershed, but the crops were not yet established. Conditions were much different on 9-13-85: 1) the influent water at site 8 was much less turbid; 2) although the DOC and TOC concentrations at site 8 were elevated in comparison to the other sites, they were lower than the site 8 samples of 6-13-85; 3) the water in the lake was much less turbid (compare the turbidity values in Tables 24 and 26); 4) the DTFP yield for site 8 was now the lowest of any sample rather than the highest; 5) crops were growing in the fields, reducing soil loss; and 6) less water was flowing into the reservoir. It is reasonable to speculate that: 1) the decrease in TOC was due to a decrease in influent turbidity and to settling out of many of the particles carried into the reservoir by spring runoff; 2) the slight decrease in DOC was due to adsorption of soluble organic contaminants onto settling particles; 3) the decrease in DTFP was due to selective removal of the most potent soluble precursors; and 4) TFP remained constant because the particles that settled contained precursors similar to those in the particles that remained suspended.

The THM formation potential results of 9-13-85 were also examined to determine the variability of THM concentrations and yields. Excluding site 8, it was found that DTFP averaged 0.34 ± 0.0106 μmoles/mgC (±3.1%) and TFP averaged 0.351 ± 0.0119 μmoles/mgC (±3.4%). The THM concentrations averaged 203 ± 4.5 μg/L (±2.2%) for the filtered samples, indicating an analytical precision for THM formation potential of better than ±2.2% (since a portion of the variation is presumed to be due to sample variation).

Douglas Lake

Samples were taken from Douglas Lake on 9-27-85, 10-24-85, and 6-9-86. On the first occasion, only site 1 (top and bottom) was sampled; but additional sites, including three brush piles, were sampled on the other occasions. The organic carbon concentrations and THM formation potentials for these samples are shown in Table 28; supporting data are included in Table 29. Average organic carbon concentrations and THM yields for various sample subsets are shown in Table 30.

TABLE 28

ORGANIC CARBON AND THM FORMATION POTENTIAL IN SAMPLES TAKEN FROM DOUGLAS LAKE

Site No.	Sample Depth m	DOC mg/L	DTFP* TTHM µg/L	DTFP* Yield µmoles/mgC	TOC mg/L	TFP* TTHM µg/L	TFP* Yield µmoles/mgC
Samples taken 9-27-85							
1	1.0	5.50	205	0.30	6.02	255	0.34
	6.0	4.78	212	0.35	5.98	284	0.38
Samples taken 10-24-85							
1	1.0	5.82	252	0.35	5.94	291	0.40
2	1.2	5.60	256	0.37	6.79	309	0.37
3	1.0	5.47	253	0.38	5.54	281	0.41
4	0.1	7.24	306	0.35	9.01	487	0.45
5	0.8	6.12	265	0.35	6.85	336	0.40
6	0.8	5.75	261	0.37	6.60	295	0.36
7	0.5	5.55	260	0.38	6.97	310	0.36
Samples taken 6-9-86							
1	1.0	4.03	282	0.56	4.29	306	0.58
	7.5	4.33	261	0.49	4.77	297	0.51
2	1.0	3.80	271	0.57	4.68	325	0.56
3	1.0	3.92	275	0.56	4.40	326	0.60
	4.0	4.43	264	0.48	4.48	296	0.53
4	0.2	4.00	285	0.57	4.84	335	0.56
5	1.0	4.01	265	0.53	4.29	332	0.63
6	1.0	4.20	266	0.51	4.39	311	0.57
7	1.0	3.96	278	0.56	4.27	328	0.62
8	0.2	4.45	264	0.48	4.95	310	0.51

* All samples were chlorinated with 10 mg/L CL_2 (enough to maintain a free residual), except the TFP sample for site 4, which required a 20 mg/L chlorine dosage.

TABLE 29

SUPPORTING DATA FOR SAMPLES TAKEN FROM DOUGLAS LAKE

Site No.	Total Depth m	Sample Depth m	Temp. °C	ΔT* °C	DO mg/L	pH	Turbidity NTU
Samples taken 9-27-85							
1	7.0	1.0	-	-	8.9	-	-
		6.0	-	-	8.6	-	-
Samples taken 10-24-85							
1	7.0	1.0	16.0	2.0	-	8.2	23
2	1.5	1.2	16.3	0.0	-	8.2	25
3	4.0	1.0	16.3	0.0	-	8.1	23
4	0.3	0.1	16.4	-	-	8.3	82
5	1.5	0.8	16.3	0.1	-	8.2	43
6	2.5	0.8	16.2	0.4	-	8.2	27
7	0.8	0.5	16.6	0.1	-	8.2	43
Samples taken 6-9-86							
1	8.5	1.0	26.4	8.0	8.2	-	9
		7.5	18.4		1.1	-	73
2	2.0	1.0	-	-	7.2	-	41
3	4.5	1.0	26.9	5.4	7.6	-	16
		4.0	21.5	-	1.3	-	42
4	0.5	0.2	-	-	-		85
5	1.5	1.0	26.8	0.0	8.0	-	20
6	2.0	1.0	-	-	8.0	-	11
7	1.5	1.0	26.9	-	8.0	-	32
8	0.4	0.2	-	-	-	-	14

* ΔT is the difference in temperature between the surface and the bottom.

TABLE 30

AVERAGE ORGANIC CARBON CONCENTRATIONS AND THM YIELDS OF DOUGLAS LAKE SAMPLES

Sample Group	No. of Samples	Avg. DOC (mg/L)	Avg. TOC (mg/L)	Average DTFP (µmoles/mgC)	Average TFP (µmoles/mgC)
Samples taken 9-27-85					
Both Samples	2	5.1 ± 0.5	6.0 ± 0.0	0.33 ± 0.04	0.36 ± 0.03
Samples taken 10-24-85					
All Samples	7	5.9 ± 0.6	6.8 ± 1.1	0.36 ± 0.01	0.39 ± 0.03
Open Water (1, 3 & 6)	3	5.7 ± 0.2	6.0 ± 0.5	0.37 ± 0.02	0.39 ± 0.03
Brush Piles (2, 5 & 7)	3	5.8 ± 0.3	6.9 ± 0.1	0.37 ± 0.02	0.38 ± 0.02
Weeded Shoreline (4)	1	7.2 -	9.0 -	0.35 -	0.45 -
Samples taken 6-9-86					
All Samples	10	4.1 ± 0.2	4.5 ± 0.2	0.53 ± 0.04	0.57 ± 0.04
Open Water (1, 3 & 6)	5	4.2 ± 0.2	4.5 ± 0.2	0.52 ± 0.03	0.56 ± 0.03
Brush Piles (2, 5 & 7)	3	3.9 ± 0.1	4.4 ± 0.2	0.55 ± 0.02	0.60 ± 0.03
Weeded Shoreline (4 & 8)	2	4.2 ± 0.2	4.9 ± 0.1	0.53 ± 0.05	0.54 ± 0.03

On 9-27-85, Douglas Lake was unstratified. Because the lake is relatively shallow and unprotected from the wind, it was not expected to stratify strongly; and antecedent cool and windy conditions were sufficient to break up any stratification that might have been present earlier in the summer. The organic carbon concentrations and THM yields in the top and bottom samples were quite similar.

On 10-24-85, the lake was noticeably drawn down and submerged brush piles could be easily seen from the boat. Along the shoreline, weeds that had been green in September were dead and decaying. Compared to the samples of 9-27-85, the open-water samples of 10-24-85 had slightly higher DOC concentrations, similar TOC concentrations, and very slightly (perhaps insignificantly) higher THM yields.

On 10-24-85 the branches in the brush piles were covered with a thick layer of slime, apparently composed of a mix of bacteria and periphytic algae. Water samples withdrawn from three of the brush piles (sites 2, 5, and 7) had DOC concentrations and THM yields virtually identical to those of the open-water samples. However, the brush-pile samples had significantly higher TOC concentrations, perhaps due to particles dislodged from the branches during sampling or perhaps due to a naturally higher concentration of microorganisms living in the brush pile. In any event, if the brush piles were producing THM precursors, they were producing them at a slow rate relative to their rate of diffusion (dispersion) away from the brush piles.

Among the samples taken 10-24-85, the one sample that really stands out from the others is the one taken from the shoreline (site 4) in a patch of small dead and decomposing macrophytes. The water at this site was visibly more turbid than the water elsewhere in the lake, and it had a very noticeable yellow-brown color. The DOC and TOC concentrations and TFP yield of this sample were all higher than those of the other samples. Although a high concentration of THMs was formed upon chlorination, the DTFP yield was similar to the values for the other samples. Since there was no evidence of shoreline erosion, it appears that the increase in organic carbon was associated with macrophyte decay. The fact that higher concentrations of THM formation potential were found at site 4 is significant, since the precursors were being generated at a rapid enough rate to be easily detected. These data, though extremely limited, suggest that decaying macrophytes may be a very significant source of THM precursors.

Douglas Lake was resampled on 6-9-86 for two reasons: 1) to see if any release of organic carbon and THM precursors from brushpiles could be detected earlier in the year (when the microorganisms associated with the brushpiles might be more active); and 2) to determine whether increased concentrations of organic carbon and THM precursors would be found in the weed-infested areas while the macrophytes were actively growing. The data, shown in Tables 28 and 29 and summarized in Table 30, demonstrate that there were no significant differences between the open-water samples and those from weed-infested areas.

On 6-9-86 the lake was found to be strongly stratified near the dam and at site 3, as evidenced by strong temparature gradients and oxygen depletion in the bottom samples (Table 29). The concentrations of DOC and TOC were very slightly higher in the bottom samples, which were also much more turbid than the surface samples. However, the concentrations of DTFP and TFP were very slightly lower. Though some of these differences appear to be real, they are not substantial, and it can be concluded that the concentrations of organic carbon and THM precursors in the top and bottom samples were very similar.

Lyndon Lake

Lyndon Lake was selected for sampling because it serves as a source of public water supply and has a history of weed (macrophyte) infestations and severe seasonal taste and odor problems. The lake was first sampled on 6-12-86. On this day, the water in the lake was clearer than the water in the other lakes sampled, perhaps as a consequence of the small grass-covered watershed; and the lake was mildy stratified. The results are shown in Tables 31 and 32.

The concentrations of organic carbon and THM precursors in the samples taken from patches of macrophytes (Potamogeton foliosus, at sites 2, 3, and 4) were very slightly higher than those in the surface samples from sites 1 and 6, which were free of weeds. However, the differences are relatively insignificant.

The concentrations of DOC and TOC were quite similar in the top and bottom samples at sites 1 and 6, but TFP concentrations were significantly lower in the bottom samples. However, both the top and bottom samples received the same dosage of chlorine. Although a 5 mg/L dosage of chlorine produced a free chlorine residual in both the top and the bottom samples, the residual concentration was probably much lower in the bottom samples due to the presence of iron, manganese, or ammonium. To examine this matter more closely, additional samples were collected later in the summer (see "Seasonal Samples", below), and their TFP concentrations were determined as a function of the concentration of free residual chlorine.

At site 5, a layer of floating "scum" had accumulated along the shoreline as a result of wind action. A sample of this "scum" was found to have a very high TOC concentration (257.5 mg/L), most of which is attributable to particulate organic matter (since the DOC concentration was only 6.6 mg/L). The DTFP and TFP yields for this sample were typical, but the TFP concentration was extremely high. Although floating "scum" is not likely to enter a well designed water supply intake, it would be interesting to know more regarding the nature of this material and the mechanism whereby it was concentrated.

Several additional samples were collected from Lyndon Lake on 7-25-86 and 8-28-86. The results are included in the section "Seasonal Samples" below. Since the macrophyte beds did not appear to be expanding during the summer, and since the quality of the water was similar on each occasion during the summer, the lake was not intensively sampled again. However, an

TABLE 31

ORGANIC CARBON AND THM FORMATION POTENTIAL IN LYNDON LAKE SAMPLES OF 6-12-86

Site No.	Sample Depth m	DOC mg/L	DTFP TTHM µg/L	DTFP Yield µmoles/mgC	TOC mg/L	TFP TTHM µg/L	TFP Yield µmoles/mgC
1	1.0	3.05	131	0.34(A)[1]	4.14	155	0.30(A)
	7.5	3.18	93	0.23(A)[2]	3.30	96	0.23(A)[2]
2	0.2	3.74	139	0.29(A)	3.91	170	0.35(A)
3	0.2	3.31	142	0.34(A)	4.18	171	0.33(A)
4	0.2	3.50	139	0.31(A)	3.64	150	0.33(A)
5	<0.1	6.60	313	0.39(C)	257.5	8530	0.28(C)[3]
6	1.0	3.27	130	0.31(A)	3.60	145	0.32(A)
	5.0	3.46	112	0.25(A)	3.65	144	0.31(A)
Averages							
All (excl. no. 5)		3.36	127	0.30	3.77	147	0.31
Sites 2, 3, & 4		3.52	140	0.31	3.91	164	0.34
Sites 1 & 6, Top		3.16	131	0.33	3.87	150	0.31
Sites 1 & 6, Bottom		3.32	103	0.24	3.48	120	0.27

[1] Chlorine dosages shown in parentheses; A = 5 mg/L and C = 15 mg/L.

[2] A dark yellow color after chlorination indicated the presence of iron and/or manganese.

[3] Diluted more than 30-fold prior to chlorination.

TABLE 32

SUPPORTING DATA FOR LYNDON LAKE SAMPLES OF 6-12-86

Site No.	Depth m	Sample Depth m	Temp. °C	ΔT[1] °C	DO mg/L	pH
1	8.8	1.0	24.0	4.5	7.4	8.3
		7.5	19.5		0.6	7.6
2	0.7	0.2	-	-	-	8.5
3	<1.0	0.2	-	-	-	8.4
4	<1.0	0.2	-	-	-	8.4
5	<0.1	<0.1	-	-	-	8.4
6	6.0	1.0	24.8	4.4	7.6	8.4
		5.0	20.4		3.1	7.8

[1] ΔT is the difference in temperature between the surface and the bottom.

algal bloom, accompanied by a severe taste and odor problem, occurred in the fall, forcing the city of Lyndon to switch to another source of supply (Donald Gilliland, KDHE, personal communication; John White, Mid-Kansas Engineering Consultants, personal communication, 1986). Presumably, the relative clarity of the water, activities in the watershed, and the fall overturn combined to cause the algal bloom. Unfortunatley, another sampling trip could not be arranged, so it was not possible to determine the effect of the algal bloom on THM precursors.

Seasonal Samples

In each of the four seasons, samples were collected from several of the lakes, often just a top and bottom sample from the main body of the lake. This was done for several purposes: 1) to see if there were significant seasonal changes in the concentrations of organic carbon and THM precursors; 2) to provide additional information regarding the effects of stratification; and 3) to gather additional data on the effect of weed senescence on THM precursor concentrations. The samples collected during the winter are discussed first, followed by those collected during the other seasons.

Wintertime Samples

Top and bottom samples were taken from each of four lakes on 3-7-86, late in the winter, when organic carbon and THM precursor concentrations were expected to be at a minimum. The organic carbon and THM formation potential data are shown in Table 33, and supporting data are shown in Table 34. Although the ice had melted by this time, the temperature data show that water was still very cold. Also, a significant amount of spring rain had not yet fallen (rainfall data are included in Appendix A). The water in the lakes was relatively clear, as evidenced by the fact that three of the lakes had turbidity values significantly lower than the values measured during 1985. The fourth, Clinton Lake, had low turbidity values about equal to those during 1985 at the same site.

The DOC values in the lakes were nearly the same, ranging from 4.08 to 4.87 mg/L, despite the large differences in the sizes, ages, and characteristics of the lakes. The TOC values were also quite similar, ranging from 4.64 to 6.58 mg/L. The higher TOC values in Strowbridge Reservoir are associated with higher turbidity (Table 34) and are attributable to the large amount of agricultural activity in close proximity to the reservoir.

The DTFP and TFP yields were quite similar for all of the lakes, but tended to be on the high end of the range of yields found in the intensive samplings conducted in the spring, summer, and fall. Higher yields might be expected to occur in the wintertime samples due to decomposition of the more biodegradable precursors during the summer and fall, leaving more resistant (and more potent) precursors in the lake during the winter and early spring.

TABLE 33

ORGANIC CARBON AND THM FORMATION POTENTIAL IN WINTERTIME LAKE SAMPLES OF 3-7-86

		DTFP			TFP	
Sample Depth m	DOC mg/L	TTHM μg/L	Yield μmoles/mgC	TOC mg/L	TTHM μg/L	Yield μmoles/mgC
Strowbridge Res.						
1.0	4.82	260	0.43	6.58	351	0.43
8.0	4.54	264	0.46	6.51	339	0.42
Douglas Lake						
1.0	4.69	239	0.41	4.77	267	0.45
6.0	4.56	233	0.41	4.64	261	0.45
Lone Star Lake						
1.0	4.53	268	0.48	5.61	323	0.47
10.0	4.87	270	0.45	4.95	304	0.50
Clinton Lake						
1.0	4.08	228	0.45	5.28	280	0.43
10.0	4.28	245	0.46	4.86	280	0.46
Average	4.55	251	0.44	5.40	301	0.45
Std. Dev.	0.26	17	0.03	0.77	34	0.03

Note: 1. DOC and TOC values could be slightly high due to sparger malfunction (low flowrate); if so, the DTFP and TFP yields are slightly low.

2. All DTFP and TFP results are for a free chlorine dosage of 10 mg/L, which was sufficient to maintain a free chlorine residual in all samples.

TABLE 34

SUPPORTING DATA FOR WINTERTIME LAKE SAMPLES OF 3-7-86

Lake	Sample Depth m	Temp. °C	ΔT* °C	DO mg/L	pH	Turbidity NTU
Strowbridge	1.0	5.6	0.0	12.6	8.1	17
	8.0	5.6	-	10.1	8.1	22
Douglas	1.0	5.5	0.2	11.3	7.6	16
	6.0	5.3	-	11.4	7.6	16
Lone Star	1.0	5.0	0.0	13.2	8.1	2
	10.0	5.0	-	13.4	8.1	2
Clinton	1.0	4.0	0.0	11.5	7.7	5
	10.0	4.0	-	11.7	7.7	5

* ΔT is the difference in temperature between the surface and the bottom.

It is also conceivable that the water flowing into the lakes during the winter carries more potent of THM precursors; this hypothesis is examined below (see B. Streams).

Lone Star Lake

Lone Star Lake was sampled repeatedly (six times) between 9-20-85 and 11-20-86, primarily for two reasons: 1) among the lakes being sampled, this lake was considered to be the one most likely to strongly stratify, and more data were needed to assess the influence of stratification on THM precursors; and 2) the very large patch of aquatic weeds in the shallow sheltered cove at sampling site 2 afforded an ideal location to examine, under field conditions, the release of THM precursors from living and senescing aquatic weeds. The data are shown in Tables 35 and 36.

Inspection of the data for the surface water at site 1, in the main body of the lake, reveals that the concentrations of DOC and TOC were relatively constant over time. The greatest change in the concentrations of DOC and TOC occurred between June 9 and July 25, 1986, and was accompanied by a drop in the yield of DTFP and TFP. This increase may have been caused by an algal bloom or by an influx of precursors from the watershed (a large amount of rain fell early in July), but no significant change was observed during the remainder of the year. The DTFP and TFP concentrations were quite consistent, except for those of the samples taken 9-20-85, which were lower than the others for reasons unknown.

The lake was found to be stratified on three different occasions: June, July, and August of 1986. Although the stratification weakened over the course of the summer, the level of anoxia increased, as expected, and by August the hypolimnetic water had a strong sulfide odor. On each occasion, the concentrations of DOC, TOC, DTFP, and TFP in the water near the surface were very similar to those of the hypolimnetic water. On two occasions, 7-25-86 and 8-28-86, samples receiving different dosages of chlorine were analyzed so that the concentrations of DTFP and TFP could be examined as a function of the free residual chlorine concentration. The results, shown in Table 5, indicate that THM formation was approximately 10-15% higher in the bottom samples, which also had very slightly higher concentrations of organic carbon.

On four occasions, a sample was taken from the large patch of aquatic weeds in the shallow cove at site 2. The results for these samples were very similar to those of the open water samples taken at site 1, indicating that the release of THM precursors was either too small or too slow (relative to the rate of diffusion or dispersion) to be readily detected. The first official freeze of 1986 occurred on 11-8-86. On 11-20-86 the weeds were clearly senescing and were covered with a thick layer of gelatinous slime. However, the concentrations of DOC and TOC were similar to those found at site 1. It is reasonable to hypothesize that most of the degradable organic material in the senescing weeds is decomposed by bacteria in the slime layer, while much of the nonbiodegradable materials remains in the stubble. Small amounts of THM precursors may diffuse through the slime, but at a slow rate, such that the concentration does not increase significantly in the immediate vicinity of the plants.

TABLE 35

ORGANIC CARBON AND THM FORMATION POTENTIAL IN SEASONAL LONE STAR LAKE SAMPLES

			DTFP			TFP	
Site No.	Sample Depth m	DOC mg/L	TTHM µg/L	Yield µmoles/mgC	TOC mg/L	TTHM µg/L	Yield µmoles/mgC
Samples taken 9-20-85							
1	1.0	4.32	200	0.37(B)[1]	4.42	206	0.38(B)
	8.0	4.63	204	0.35(B)	4.71	237	0.41(B)
Samples taken 3-7-86							
1	1.0	4.53	268	0.48(B)	5.61	323	0.47(B)
	10.0	4.87	270	0.45(B)	4.95	304	0.50(B)
Samples taken 6-9-86							
1	1.0	4.15	252	0.49(B)	4.29	288	0.55(B)
	11.0	4.04	249	0.50(B)	4.14	288	0.57(B)
2	0.1	4.51	251	0.45(B)	5.12	283	0.45(B)
Samples taken 7-25-86							
1	1.0	5.05	224[2]	0.36[2]	5.46	278[2]	0.42[2]
	11.0	5.21	260[2]	0.41[2]	5.62	323[2]	0.47[2]
2	0.1	4.64	224	0.39(B)	5.42	275	0.41(B)
3	1.0	4.54	221	0.39(B)	5.53	255	0.38(B)
Samples taken 8-28-86							
1	1.0	5.26	250[2]	0.38[2]	5.55	293[2]	0.43[2]
	11.0	5.48	273[2]	0.41[2]	5.58	343[2]	0.50[2]
2	0.1	5.07	270	0.43(B)	--[3]	--[3]	--[3]
Samples taken 11-20-86							
1	1.0	5.23	--	--	5.49	--	--
2	0.1	5.12	--	--	5.35	--	--

[1] Chlorine dosages shown in parentheses; A = 5 mg/L, B = 10 mg/L, and C = 15 mg/L.

[2] Estimated by data regression for a free residual chlorine concentration of 3.0 mg/L.

[3] Not analyzed due to the presence of detritus in the sample.

TABLE 36

SUPPORTING DATA FOR SEASONAL LONE STAR LAKE SAMPLES

Site No.	Total Depth m	Sample Depth m	Temp. °C	ΔT[1] °C	DO mg/L	pH	Turbidity NTU
Samples taken 9-20-85							
1	9.0	1.0	22.8	0.0	7.0	7.4	5
		8.0	22.8		7.0	7.4	6
Samples taken 3-7-86							
1	11.0	1.0	5.0	0.0	13.2	8.1	2
		10.0	5.0		13.4	8.1	2
Samples taken 6-9-86							
1	12.0	1.0	26.5	8.6	8.6	-	12
		11.0	17.9		0.3	-	13
2	0.5	0.1	-	-	-	-	6
Samples taken 7-25-86							
1	12.0	1.0	28.8	6.3	9.0	8.6	11
		11.0[2]	22.5		0.4	7.5	75
2	0.5	0.1	-	-	-	-	13
3	2.0	1.0	30.5	-	-	-	10
Samples taken 8-28-86							
1	12.0	1.0	25.0	3.4	7.5	7.6	6
		11.0[3]	21.6		0.1	7.1	15
2	0.5	0.1	-	-	-	-	-
Samples taken 11-20-86							
1	12.0	1.0	7.0	0.0	-	-	-
2	0.5	0.1	7.0	-	-	-	-

[1] ΔT is the difference in temperature between surface and bottom.

[2] The bottom sample contained 0.23 mg/L of ammonium.

[3] The bottom sampled had a strong sulfide odor.

On 7-25-86, a sample was taken directly in front of the public beach (site 3) while a typical number of individuals were swimming. There was no observable difference in the concentrations of DOC, TOC, DTFP, and TFP in comarison to the samples from the other sites.

Other Seasonal Samples

Results for a variety of additional lake samples are presented in Tables 37 and 38. Several of the lakes were strongly stratified when sampled, including Clinton Lake and Strowbridge Reservoir on 6-9-86 and Lyndon Lake on 7-25-86. However, in each case, the concentrations of DOC, TOC, DTFP, and TFP were nearly identical in the top and bottom samples.

A sample taken on 7-25-86 from a patch of weeds (Potamogeton foliosus) in Lyndon Lake had concentrations of DOC, DTFP, and TFP similar to those of the open water, but slightly higher concentrations of TOC and turbidity. A sample taken on 11-20-86 from a large patch of senescing smartweed (Polygonum ssp.) in Douglas Lake had DOC and TOC concentrations nearly identical to those in the main body of the lake. Interestingly, these and other senescing weeds in the lake were covered with a thick layer of gelatinous slime, similar to that observed on the weeds at Lone Star Lake on 11-20-86 (cf. ea.).

Lake Sediments

Many sediment samples were taken from the lakes during the spring and summer of 1985, and several more samples were taken during 1986. All of the samples were analyzed for TOC; and the results are displayed in Tables 39 and 40.

The amount of organic carbon in the sediments ranged from 3.68 mg/dgm (0.37%) to 39.38 mg/dgm (3.94%) and averaged between 15 and 21 mg/dgm (1.5-2%) at each of the lakes sampled. These values are very low compared to the values of 20-30% and higher often associated with natural glacial lakes that are more fertile and less turbid; but they are quite reasonable for midwestern lakes that receive enormous loads of inorganic solids carried in by turbid streams, and they are very typical values for stream-borne sediments (Thurman, 1985). This accounts in part for the general lack of correlation between TOC and turbidity in the lake samples, since many of the suspended particles in the lakes are probably similar in composition to the sediments (largely inorganic). Most of the sediment organic carbon is probably quite old (tens of years old or more), resistant to biodegradation, and relatively insoluble. Therefore, these lake sediments are clearly not a significant source of THM precursors.

As can be seen by examining the data in Tables 39 and 40, the organic carbon content of the sediments did not change significantly during the period of late spring to late summer, nor was there any noticeable increase in TOC in the sediment sample taken from Lone Star Lake on 8-28-86 following a long period of stratification. However, it should be noted that the sediment sampler took the top several inches of sediment, more than is likely to accumulate over a three-month period at most of the sampling

TABLE 37

ORGANIC CARBON AND THM FORMATION POTENTIAL IN VARIOUS SEASONAL LAKE SAMPLES

Site No.	Sample Depth m	DOC mg/L	DTFP TTHM µg/L	DTFP Yield µmoles/mgC	TOC mg/L	TFP TTHM µg/L	TFP Yield µmoles/mgC
Clinton Lake, 6-9-86							
1	1.0	4.11	244	0.48(B)[1]	4.35	296	0.55(B)
	10.0	3.52	235	0.54(B)	4.00	277	0.56(B)
2	1.0	3.78	255	0.54(B)	4.05	305	0.61(B)
	9.0	4.00	231	0.46(B)	4.42	267	0.49(B)
Strowbridge Reservoir, 6-9-86							
1	1.0	4.82	278	0.46(B)	5.31	322	0.48(B)
	5.0	4.14	268	0.52(B)	4.17	305	0.58(B)
Strowbridge Reservoir, 7-25-86							
1	1.0	4.56	209	0.36(B)	5.79	254	0.35(B)
	6.0	4.69	203	0.34(B)	5.40	253	0.37(B)
Lyndon Lake, 7-25-86							
1	1.0	3.30	130[2]	0.31[2]	4.02	157[2]	0.31[2]
	7.0	3.45	122[2]	0.28[2]	3.66	152[2]	0.33[2]
4	0.2	3.47	137	0.31(B)	4.93	202	0.33(B)
Lyndon Lake, 8-28-86							
1	1.0	3.56	NA[3]	NA	4.42	NA	NA
	7.0	3.54	NA	NA	4.41	NA	NA
Douglas Lake, 11-20-86							
1	1.0	4.59	NA	NA	5.25	NA	NA
8	0.1	4.51	NA	NA	5.37	NA	NA

[1] Chlorine dosage shown in parentheses; A = 5 mg/L, B = 10 mg/L, etc.

[2] Estimated by data regression for a free residual chlorine concentration of 3.0 mg/L.

[3] NA = not analyzed.

TABLE 38

SUPPORTING DATA FOR VARIOUS SEASONAL LAKE SAMPLES

Site No.	Total Depth m	Sample Depth m	Temp. °C	ΔT[1] °C	DO mg/L	pH	Turbidity NTU
Clinton Lake, 6-9-86							
1	12.0	1.0	24.8	6.1	10.3	-	8
		10.0	18.7		0.4	-	35
2	10.0	1.0					
		9.0					
Strowbridge Reservoir, 6-9-86							
1	7.0	1.0	24.7	5.2	7.2	7.0?	17
		5.0	19.5		0.8	7.0?	67
Strowbridge Reservoir, 7-25-86							
1	7.0	1.0	27.9	1.3	6.2	8.2	27
		6.0	26.6		5.0	7.9	48
Lyndon Lake, 7-25-86							
1	8.0	1.0	27.6	7.4	7.4	8.2	13
		7.0	20.2		0.9	7.4	15
4	0.5	0.2	-	-	-	8.2	71
Lyndon Lake, 8-28-86							
1	8.3	1.0	24.7	3.3	7.0	8.2	9
		7.0	21.4		0.1	7.3	12
Douglas Lake, 11-20-86							
1	-	1.0	6.0	0.0	-	-	-
8	0.3	0.1	6.0		-	-	-

[1] ΔT is the difference in temperature between surface and bottom.

TABLE 39

ORGANIC CARBON, EXTRACTABLE ORGANIC CARBON, AND EXTRACTABLE TFP IN SEDIMENT AND SOIL SAMPLES TAKEN FROM CLINTON LAKE IN 1985

		Samples taken 6-5-85				Samples of 9-5-85
Site	Sample	TOC mg/dgm	EOC mg/dgm	EOC %	ETFP µmoles/mgC	TOC, mg/dgm
1	Sediment	10.59 ± 0.10*	0.46	4.3	0.30	7.38 ± 0.15
2	Sediment	19.38 ± 0.33	1.03	5.3	0.29	20.60 ± 0.28
3	Sediment	11.41 ± 0.51	0.52	4.5	0.31	11.22 ± 0.13
4	Sediment	23.60 ± 0.37	1.19	5.0	0.32	26.06 ± 0.79
5	Sediment	17.82 ± 0.17	1.13	6.3	0.25	12.64 ± 0.08
6	Sediment	18.90 ± 0.40	0.95	5.0	0.31	39.38 ± 0.18
7	Sediment	3.68 ± 0.06	0.15	4.1	0.24	3.92 ± 0.04
8	Sediment	---	--	-	--	13.08 ± 0.06
9	Sediment	5.46 ± 0.62	0.79	14.5	0.32	10.26 ± 0.12
10	Sediment	10.24 ± 0.06	0.46	4.5	0.28	20.50 ± 0.28
12	Sediment	24.40 ± 0.06	1.22	5.0	0.31	24.24 ± 0.35
13	Sediment	18.32 ± 0.03	0.94	5.1	0.25	21.80 ± 0.46
15	Sediment	18.90 ± 0.04	0.95	5.0	0.38	18.18 ± 0.59
18	Sediment	---	--	-	--	14.85 ± 0.35
7	Shoreline Soil	---	--	-	--	8.02 ± 0.15
16	Shoreline Soil	---	--	-	--	31.16 ± 0.76
	Average	15.23	0.82	5.7	0.30	17.71
	Std. Dev.	6.77	0.34	2.8	0.04	9.45

* Standard deviations shown for samples analyzed in duplicate.

TABLE 40

ORGANIC CARBON CONTENT OF VARIOUS LAKE SEDIMENT SAMPLES

Lake	Station	TOC, mg/dgm	
Strowbridge Res.		6-13-85	9-13-85
	1	8.50 ± 0.54*	25.12 ± 1.06
	2	10.55 ± 0.13	16.94 ± 0.32
	3	19.69 ± 0.18	16.78 ± 0.37
	4	18.84 ± 0.51	22.14 ± 0.54
	5	20.97 ± 0.32	23.32 ± 0.04
	6	12.63 ± 0.30	18.04 ± 0.22
	7	31.85 ± 0.04	22.51
	8 (center)	24.66 ± 0.47	-
	8 (edge)	36.70 ± 1.30	-
	9	21.91 ± 0.86	-
	10	25.44 ± 0.37	23.79
	11	11.32 ± 0.11	21.70
	Avg.	20.26 ± 8.67	21.15 ± 3.10
Lone Star Lake			
9-20-85	1	20.97	
7-25-86	1	26.74	
7-25-86	3	22.69	
8-28-86	1	24.46	
	Avg.	23.72 ± 2.47	
Douglas Lake			
9-27-85	1	14.67	
Clinton Lake			
7-2-86	2	21.54	
	4	23.42	
	9	14.81	
	12	24.16	
	15	19.58	
	Avg.	20.70 ± 3.74	
Lyndon Lake			
7-25-86	1	19.82	

* Standard deviations shown for samples analyzed in duplicate.

sites. The average values were similar for all of the lakes sampled, suggesting that these values are typical of those elsewhere in the region.

There was a considerable amount of variation in the organic carbon content (TOC) of the samples taken from Clinton Lake. Although the samples from some locations had a similar TOC concentrations on both occasions, samples from other sites did not. While the latter may have been due to real changes in the organic carbon content of the sediments at these locations, it is more likely attributable to variations in sampling. The variations between sites are probably due both to sampling imprecision and to real variations in sediment quality. The low TOC values for site 7, for example, are quite reasonable, since the samples from this site contained mostly sand and gravel, unlike the other samples, which were more muck-like in character.

The first sediment samples taken from Clinton Lake (on 6-5-85) were also analyzed for extractable organic carbon (EOC) and extractable TFP (ETFP). The results are shown in Table 39. These sediment samples contained very little EOC, and only a small and relatively constant fraction (about 6%, on the average) of the TOC was extractable. Even this small amount may be largely atttributable to DOC that remained in the pore water as the samples were dried. The yields of THMs produced upon chlorination of the extracted organic matter averaged 0.30 µmoles/mgC, very similar to the yields for the soil samples (see "Watershed Samples") and for many of the aqueous lake samples.

Summary of Lake Data

Table 41 summarizes the lake sample data. The organic carbon concentrations and THM yields show remarkably little variation considering the differences in the sizes, ages, uses, and other characteristics of the lakes. Lyndon Lake, which has the least erodable watershed, had the lowest DOC and TOC concentrations as well as the lowest THM yields. The low yields may be due to the fact that only one spring and two summer samples were taken, since the THM yields tended to be lower in the summer months, as discussed below. Clinton Lake, the youngest and largest lake sampled, also had relatively low concentrations of DOC and TOC, but not much lower than those of the other (older and smaller) lakes. Thus lake size and age do not appear to exert a major influence on organic carbon concentrations. Strowbridge Reservoir, Douglas Lake, and Lone Star Lake had the highest TOC concentrations, as would be expected on the basis of their small size, shallow depth, age, and watershed characteristics.

Seasonal averages are also included in Table 41. No average is given for the fall, since three of the four fall samples were from the same lake and since three of the four did not include TFP data. Also, it should be noted that the data are somewhat biased due to differences in the number of times the lakes were sampled during each season. Nevertheless, it does not appear that there were any seasonal trends in the DOC and TOC concentrations, which strongly supports the hypothesis that most of the organic matter is allochthonous (since autochthonous precursors should

TABLE 41

SUMMARY OF LAKE SAMPLE DATA

Sample Description	No. of Samps.	Avg. DOC (mg/L)	Avg. TOC (mg/L)	Avg. DTFP (μmol/mgC)	Avg. TFP (μmol/mgC)
Clinton Lake					
6-5-85 (excl. no. 5)	20	4.1	4.4	0.36	0.45
9-5-85 (excl. 5 & 18)	22	4.4	5.3	0.29	0.38
3-7-86	2	4.2	5.1	0.46	0.45
6-9-86	4	3.9	4.2	0.51	0.55
7-2-86 (excl. 5 & 18)	14	4.0	4.4	0.40	0.46
	Average	4.1	4.7	0.40	0.46
Strowbridge Reservoir					
6-13-85 (excl. no. 8)	12	4.9	7.0	0.42	0.35
9-13-85 (excl. no. 8)	15	4.6	5.3	0.34	0.35
3-7-86	2	4.6	6.5	0.44	0.43
6-9-86	2	4.5	4.7	0.49	0.53
7-25-86	2	4.6	5.6	0.35	0.36
	Average	4.6	5.8	0.41	0.40
Douglas Lake					
9-27-85	2	5.1	6.0	0.33	0.36
10-24-85 (Sites 1,3, & 6)	3	5.7	6.0	0.37	0.39
3-7-86	2	4.6	4.7	0.41	0.45
6-9-86 (Sites 1,3, & 6)	5	4.2	4.5	0.52	0.56
11-20-86	2	6.0	-	-	-
	Average	5.1	5.3	0.41	0.44
Lone Star Lake					
9-20-85	2	4.5	4.6	0.36	0.40
3-7-86	2	4.7	5.3	0.47	0.49
6-9-86	3	4.2	4.5	0.48	0.52
7-25-86	4	4.9	5.5	0.39	0.42
8-28-86	2	5.4	5.6	0.40	0.47
11-20-86	2	5.2	5.4	-	-
	Average	4.8	5.2	0.42	0.46
Lyndon Lake					
6-12-86 (excl. no. 5)	7	3.4	3.8	0.30	0.31
7-25-86	3	3.4	4.2	0.30	0.32
8-28-86	2	3.6	4.4	-	-
	Average	3.5	4.2	0.30	0.32
Avg. of all lakes	(5)	4.4	5.0	0.39	0.42
Winter Average	(4)	4.5	5.4	0.45	0.46
Spring Average	(7)	4.2	4.7	0.44	0.47
Summer Average	(9)	4.4	5.0	0.35	0.40

markedly increase during the warmer months). The average TFP yields were noticeably lower during the summer, which could be due to a change in the characteristics of the organic matter. Visser (1983) has reported that the aquatic humic substances in lakes are more humified at the end of the summer; and it is likely that fresher, less humidified organic matter accumulated in the lakes during the spring and summer.

The average concentrations of DOC and TOC, 4.4 and 5.0 mg/L, respectively, are typical for the climate of the region, and the average TOC concentration is similar to the 6.2 mg/L average found by Pope et al. (1985). Approximately 88% of the TOC was soluble rather than particulate, so efforts to control THMs at the source would have to address soluble precursors to have much impact. The DTFP and TFP yields are approximately equal, and the slightly higher TFP yields are perhaps due to the slightly higher dosages of chlorine sometimes needed to produce a free chlorine residual in the unfiltered samples.

Table 42 summarizes the data for the top and bottom samples collected from lakes that were strongly stratified at the time of sampling, i.e., those having a top to bottom temperature gradient of at least 3°C and a hypolimnetic oxygen concentration of no more than 2.0 mg/L. As shown in the table, there were sometimes small but significant differences between the top and bottom samples, which could have been due to photosynthetic activity in the epilimnion or to accumulation of detritus in the hypolimnion. In fact, the hypolimnetic samples were often much more turbid than those taken from the epilimnion. However, on the average, the results for the top and bottom samples were virtually identical. In practice, the cooler temperature of the hypolimnetic water would retard THM formation, but increased concentrations of iron, manganese, and ammonium would be expected to increase the demand for chlorine and to increase the cost and difficulty of water treatment.

TABLE 42
SUMMARY OF SAMPLES TAKEN FROM STRATIFIED LAKES

		DTFP			TFP	
Lake and Date	DOC mg/L	TTHM µg/L	Yield µmoles/mgC	TOC mg/L	TTHM µg/L	Yield µmoles/mgC
Clinton Lake (6-9-86)						
Top	4.1	244	0.48	4.4	296	0.55
Bottom	3.5	235	0.54	4.0	277	0.56
Clinton Lake (7-2-86; avg. of 4 sites)						
Top	3.9	195*	0.40*	4.2	261*	0.50*
Bottom	3.9	197*	0.40*	4.3	254*	0.48*
Strowbridge Reservoir (6-9-86)						
Top	4.8	278	0.46	5.3	322	0.48
Bottom	4.1	268	0.52	4.2	305	0.58
Douglas Lake (6-9-86; avg. of 2 sites)						
Top	4.0	279	0.56	4.3	316	0.59
Bottom	4.2	263	0.49	4.6	297	0.52
Lone Star Lake (6-9-86)						
Top	4.2	252	0.49	4.3	288	0.55
Bottom	4.0	249	0.50	4.1	288	0.57
Lone Star Lake (7-25-86)						
Top	5.1	224*	0.36*	5.5	278*	0.42*
Bottom	5.2	260*	0.41*	5.6	323*	0.47*
Lone Star Lake (8-28-86)						
Top	5.3	250*	0.38*	5.6	293*	0.43*
Bottom	5.5	273*	0.41*	5.6	343*	0.50*
Lyndon Lake (6-12-86)						
Top	3.1	131	0.34	4.1	155	0.30
Bottom	3.2	93	0.23	3.3	96	0.23
Lyndon Lake (7-25-86)						
Top	3.3	130*	0.31*	4.0	157*	0.31*
Bottom	3.5	122*	0.28*	3.7	152*	0.33*
Lyndon Lake (8-28-86)						
Top	3.6	-	-	5.3	-	-
Bottom	3.5	-	-	5.4	-	-
Average Top	4.1	220	0.42	4.7	241	0.46
Average Bottom	4.1	218	0.42	4.5	259	0.47

* Estimated at a free residual chlorine concentration of 3 mg/L by regression of multiple data points

B. STREAM SAMPLES

The analytical results for the stream samples are shown in Tables 43-46, and a statistical summary of the data is given in Table 47. The DOC and TOC concentrations are presented graphically in Figures 9 and 10, and temporal variations in TOC and rainfall are shown in Figures 11-13 for three of the streams.

The average concentrations of DOC and DTFP (Table 47) were quite similar in each of the four streams, but were slightly lower for the Clinton Outlet (the Wakarusa River downstream from Clinton Lake) than for the other streams. The similarity of the results for the Kansas River, Rock Creek, and the Wakarusa River suggests that the size (average discharge) of a stream has little influence on DOC and DTFP concentrations in this area.

The average concentrations of TOC and TFP were highest in the Kansas River (the largest river sampled), lower in Rock Creek and the Wakarusa River (which had nearly identical average concentrations), and lowest in the Clinton Outlet samples, reflecting the pattern of the average suspended solids concentrations as well as the average ratio of DOC to TOC. Hence, as expected, streams carrying higher levels of suspended solids had higher concentrations of TOC and TFP even though the majority of each was dissolved.

The DTFP and TFP yields were quite similar at each location. The TFP yields were slightly higher than the DTFP yields, but this is probably due to the higher chlorine dosages needed to maintain a free residual, or to a slight underestimation of TOC, and not to a real difference in precursor characteristics. The similarity in yields among streams presumably reflects the strong similarities in watershed characteristics.

The relationships between organic carbon, THM formation, and suspended solids (SS) were examined using linear regression, and the correlation coefficients are shown in Table 47. DOC and TOC were strongly correlated, reflecting the fact that a major fraction of the TOC was comprised of DOC. DTFP and TFP were strongly correlated with DOC and TOC, respectively, as had been expected on the basis of many previous studies. (The correlation coefficients for DTFP vs DOC and TFP vs TOC for the Clinton Outlet are lower than for the other streams because the concentrations of all these constituents in the Clinton Outlet samples were relatively constant over time.) The yields of DTFP and TFP were very weakly correlated with DOC and TOC, respectively; and all but one of the correlations were negative, suggesting that THM precursors become slightly less potent as their concentration increases.

TOC and TFP were strongly correlated with SS, except for the Clinton Outlet samples (which had very low concentrations of SS and little particulate carbon). This was expected, since the SS are partially comprised of organic matter. Interestingly, DOC was also correlated with SS, with the correlation coefficients for three of the streams (all but

TABLE 43

ORGANIC CARBON AND THM FORMATION POTENTIAL IN SAMPLES FROM THE KANSAS RIVER

	DOC	DTFP		TOC	TFP		SS
Date	mg/L	µg/L	µmoles/mgC	mg/L	µg/L	µmoles/mgC	mg/L
02-12-86	5.14	254	0.39	5.45	271	0.39	62
02-26-86	3.49	203	0.43(B)[1]	5.11	242	0.36(B)	19
03-19-86	3.49	188	0.41(A)	4.22	317	0.59(B)	60
04-02-86	3.26	180	0.40(A)	6.02	313	0.40(B)	47
04-05-86	7.33	372	0.42(A)	48.0	1,573	0.27(A)[2]	4,272
04-17-86	3.79	223	0.45(A)	5.41	339	0.50(B)	---
04-30-86	4.13	249	0.47(B)	6.91	440	0.51(C)	123
05-14-86	4.21	294	0.55(B)	7.02	405	0.46(C)	322
05-29-86	4.77	259	0.43(B)	6.03	349	0.47(B)	340
06-11-86	3.23	222	0.52(A)	5.61	422	0.60(C)	142
07-02-86	4.47	252	0.45(B)	20.0	701	0.29(G)[3]	1,912
07-07-86	5.23	204	0.31(B)	10.1	572	0.47(E)	---
08-07-86	4.22	267	0.49(B)	7.77	419	0.43(C)	---
08-28-86	5.25	305	0.46(B)	8.10	488	0.49(B)[3]	246
09-16-86	5.96	294	0.39(B)	15.0	580	0.31(B)[2]	882
10-07-86	7.45	341	0.37(B)	10.2	664	0.53(B)[2]	432
10-31-86	6.38	319	0.41(A)[2]	10.4	549	0.43(B)[2]	158
11-18-86	4.66	319	0.54(B)	6.00	470	0.63(B)[2]	52
12-09-86	5.26	324	0.49(B)	7.85	517	0.53(B)[2]	175
01-07-87	4.12	296	0.55(B)	4.94	334	0.52(B)	22
02-24-87	3.29	209	0.47(A)	4.70	285	0.46(B)	27

[1] Chlorine dosages shown in parentheses; A = 5 mg/L, B = 10 mg/L, etc.

[2] This sample was diluted prior to chlorination.

[3] No free chlorine residual remained after 96 hours.

TABLE 44

ORGANIC CARBON AND THM FORMATION POTENTIAL IN SAMPLES FROM ROCK CREEK

	DOC	DTFP		TOC	TFP		SS
Date	mg/L	µg/L	µmoles/mgC	mg/L	µg/L	µmoles/mgC	mg/L
02-12-86	(frozen over)						
02-26-86	2.58	119	0.36(B)	2.92	146	0.40(B)	17
03-19-86	2.34	113	0.37(A)	2.86	133	0.36(A)	34
04-02-86	2.71	155	0.45(A)	3.20	178	0.44(A)	36
04-05-86	5.68	312	0.45(B)	6.19	433	0.58(C)	52
04-17-86	4.04	235	0.47(A)	4.22	347	0.67(B)	--
04-30-86	3.04	159	0.42(B)	4.12	245	0.48(B)	24
05-14-86	6.25	419	0.56(C)	13.84	609	0.37(B)[2]	322
05-29-86	4.86	271	0.46(B)	4.93	370	0.61(C)	23
06-11-86	4.56	183	0.32(A)	5.10	313	0.49(B)	42
07-02-86	6.09	289	0.39(B)	11.3	463	0.34(D)	296
07-07-86	6.26	277	0.36(B)	8.78	442	0.42(D)	--
08-07-86	4.29	256	0.47(B)	5.89	302	0.41(B)	--
08-28-86	4.95	259	0.42(B)	5.26	359	0.55(C)	42
09-16-86	5.17	211	0.32(A)	7.01	321	0.37(B)	27
10-07-86	7.23	429	0.49(B)	8.29	546	0.54(C)	25
10-31-86	5.17	375	0.59(B)	5.66	396	0.57(B)	79
11-18-86	2.76	209	0.59(B)	3.49	239	0.54(B)	9
12-09-86	4.05	340	0.68(B)	4.65	387	0.68(B)	32
01-07-87	2.86	149	0.41(A)	3.22	253	0.63(B)	15
02-24-87	3.81	208	0.44(A)	3.93	161[3]	0.33(A)[3]	16

[1] Chlorine dosages shown in parentheses; A = 5 mg/L, B = 10 mg/L, etc.

[2] This sample was diluted prior to chlorination.

[3] Suspect data.

TABLE 45

ORGANIC CARBON AND THM FORMATION POTENTIAL IN SAMPLES FROM THE WAKARUSA RIVER

Date	DOC mg/L	DTFP µg/L	DTFP µmoles/mgC	TOC mg/L	TFP µg/L	TFP µmoles/mgC	SS mg/L
02-12-86	(frozen over)						
02-26-86	3.74	156	0.32(B)[1]	4.39	204	0.37(B)	14
03-19-86	2.90	136	0.35(A)	2.98	154	0.40(A)	43
04-02-86	3.38	174	0.40(A)	3.60	176	0.38(A)	38
04-05-86	6.16	361	0.48(B)	6.53	460	0.58(C)	102
04-17-86	4.18	230	0.44(A)	4.74	290	0.49(B)	--
04-30-86	3.85	187	0.38(A)	4.54	267	0.47(B)	23
05-14-86	7.77	346	0.37(B)	11.56	535	0.38(B)[2]	248
05-29-86	5.07	287	0.46(B)	7.00	395	0.46(C)	73
06-11-86	4.41	179	0.32(A)	4.88	333	0.55(B)	49
07-02-86	3.85	229	0.46(B)	4.74	263	0.43(B)	16
07-07-86	7.01	354	0.41(B)	10.8	511	0.39(D)	--
08-07-86	5.13	290	0.45(B)	6.86	401	0.47(C)	--
08-28-86	4.60	--	--	5.78	346	0.48(C)	38
09-16-86	5.44	288	0.42(B)	6.96	341	0.40(B)	59
10-07-86	8.48	392	0.38(B)	9.30	422	0.37(B)	37
10-31-86	5.84	374	0.52(B)	5.90	461	0.63(C)	43
11-18-86	4.44	275	0.49(B)	4.66	348	0.59(B)	11
12-09-86	2.78	213	0.59(A)	3.39	222	0.51(A)	18
01-07-87	4.04	286	0.56(B)	5.16	376	0.58(C)	24
02-24-87	2.96	189	0.49(A)	3.39	204	0.47(A)	21

[1] Chlorine dosages shown in parentheses; A = 5 mg/L, B = 10 mg/L, etc.

[2] This sample was diluted prior to chlorination.

TABLE 46

ORGANIC CARBON AND THM FORMATION POTENTIAL IN SAMPLES FROM CLINTON OUTLET

	DOC	DTFP		TOC	TFP		SS
Date	mg/L	µg/L	µmoles/mgC	mg/L	µg/L	µmoles/mgC	mg/L
02-12-86	3.89	173	0.42	4.74	204	0.40	3
02-26-86	3.96	207	0.42(B)	4.34	228	0.42(B)	4
03-19-86	3.46	172	0.39(A)	3.78	188	0.40(A)	10
04-02-86	3.50	183	0.41(A)	3.56	218	0.49(A)	9
04-05-86	3.61	181	0.40(A)	3.75	226	0.48(B)	10
04-17-86	3.68	205	0.44(A)	3.75	---	----	--
04-30-86	3.66	167	0.36(A)	4.02	226	0.45(A)	10
05-14-86	3.54	170	0.38(A)	3.76	232	0.49(B)	6
05-29-86	3.92	184	0.37(B)	4.27	242	0.46(B)	5
06-11-86	3.79	195	0.41(A)	4.16	218	0.42(A)	12
07-02-86	4.27	212	0.40(B)	5.19	229	0.35(B)	--
08-07-86	3.95	233	0.47(B)	4.72	287	0.49(B)	--
08-28-86	5.02	226	0.36(B)	5.29	273	0.42(B)	10
09-16-86	4.56	191	0.33(A)	5.50	255	0.37(B)	16
10-07-86	4.89	216	0.35(A)	5.44	266	0.39(B)	18
10-31-86	5.09	228	0.36(A)	6.84	307	0.36(B)	3
11-18-86	4.34	263	0.48(B)	4.89	271	0.44(B)	10
12-09-86	4.05	240	0.47(A)	5.09	335	0.53(B)	7
01-07-87	4.45	287	0.52(B)	5.12	361	0.57(B)	7
02-24-87	3.88	187	0.37(A)	3.92	268	0.54(B)	5

[1] Chlorine dosages shown in parentheses; A= 5 mg/L, and B=10 mg/L.

TABLE 47

STREAM SAMPLE STATISTICS

	Kansas River	Rock Creek	Wakarusa River	Clinton Outlet
Average DOC, mg/L	4.72	4.44	4.80	4.08
Average TOC, mg/L	7.84[1]	5.74	5.86	4.61
Ratio of DOC to TOC	0.60	0.77	0.82	0.89
Average DTFP, µg/L	265	248	260	206
Average TFP, µg/L	433[1]	332	335	254
Average SS, mg/L	295[1]	64	50	9
Average DTFP, µmoles/mgC	0.45	0.45	0.44	0.41
Average TFP, µmoles/mgC	0.46	0.49	0.47	0.45
Corr. Coef., DOC vs TOC	0.61	0.83	0.93	0.91
Corr. Coef., DTFP conc. vs DOC	0.80	0.83	0.88	0.59
Corr. Coef., TFP conc. vs TOC	0.84[1]	0.85	0.87	0.59
Corr. Coef., DTFP yield vs DOC	-0.41	0.05	-0.19	-0.18
Corr. Coef., TFP yield vs TOC	-0.59[1]	-0.33	-0.29	-0.44
Corr. Coef., DOC vs SS	0.53	0.51	0.61	0.21
Corr. Coef., TOC vs SS	0.93[1]	0.88	0.77	0.05
Corr. Coef., TFP Conc. vs SS	0.70[1]	0.62	0.64	-0.09
Corr. Coef., TFP yield vs SS	-0.57[1]	-0.40	-0.20	-0.29

[1] Excluding the data of 4-5-86

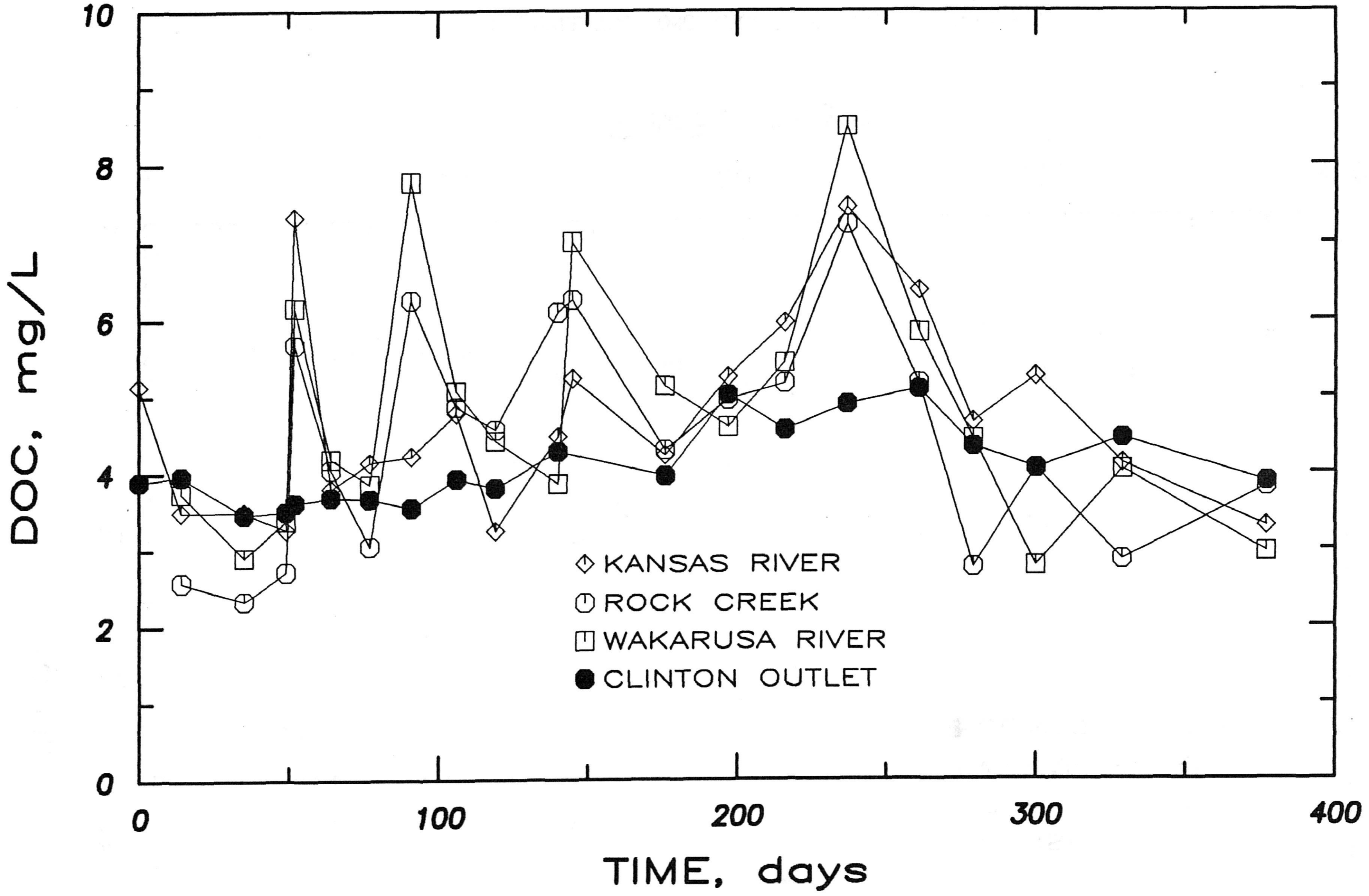

FIGURE 9: STREAM SAMPLE DOC CONCENTRATIONS (DAY 0 = 2-12-86)

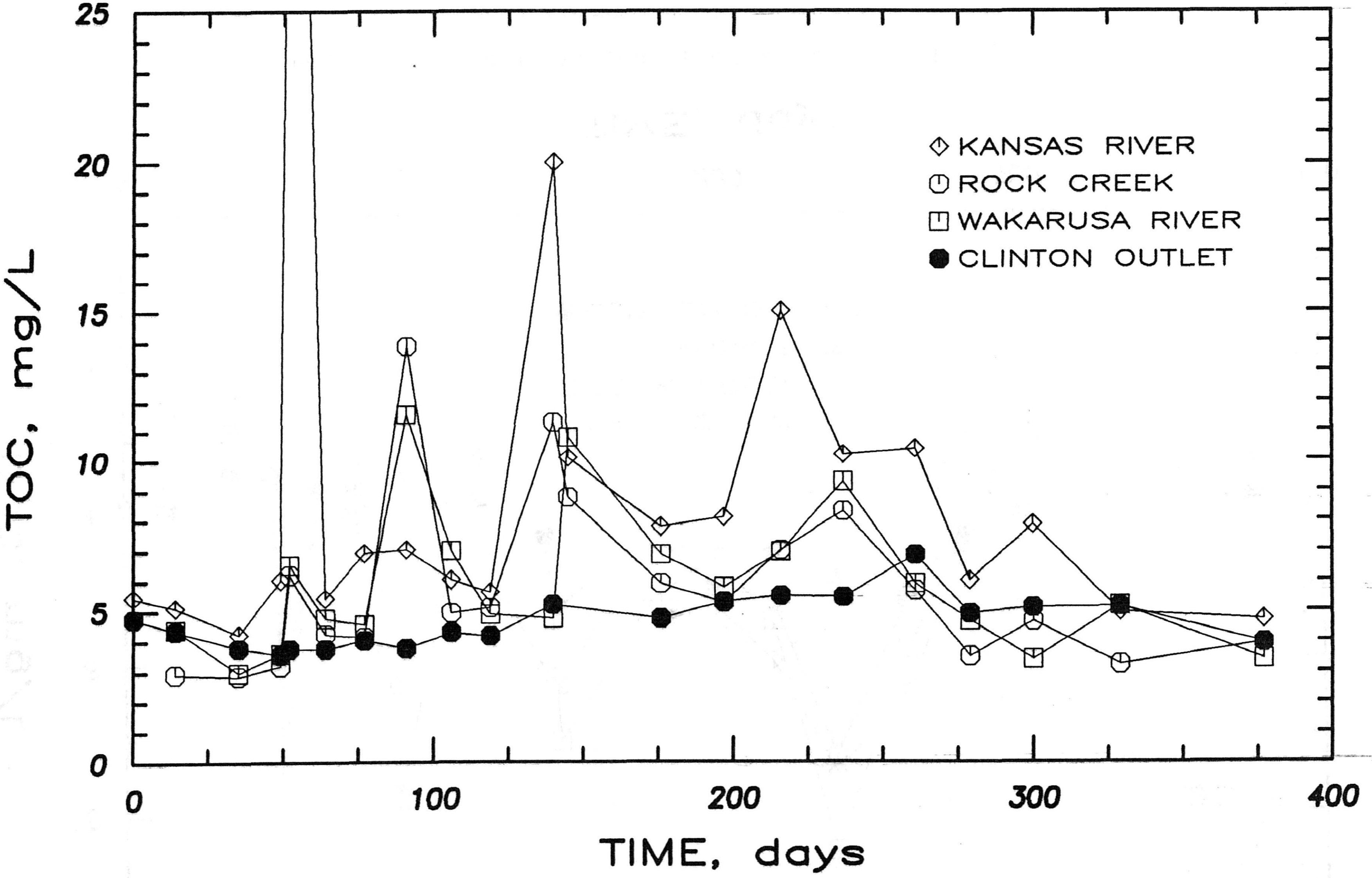

FIGURE 10: STREAM SAMPLE TOC CONCENTRATIONS (DAY 0 = 2-12-86)

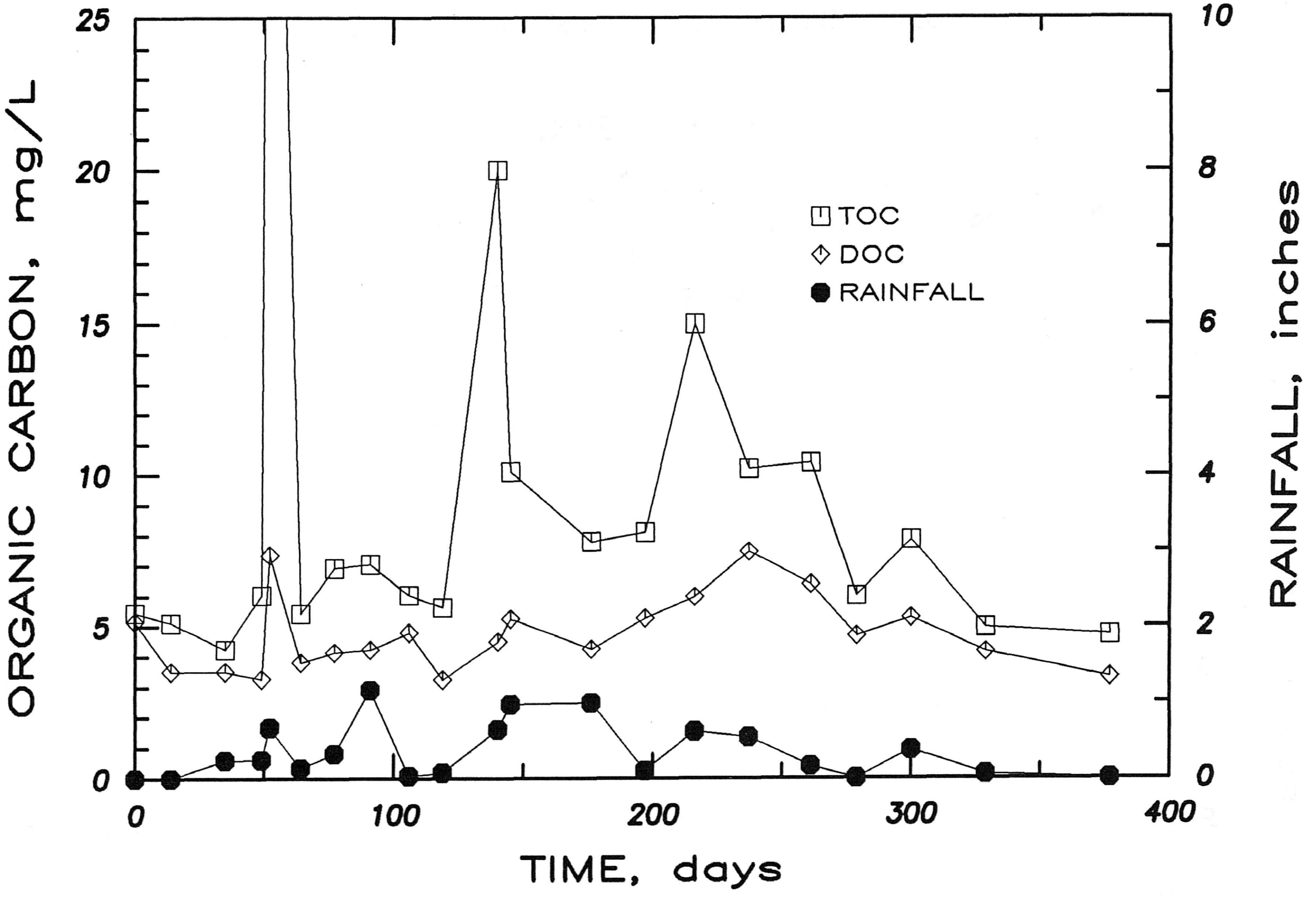

FIGURE 11: ORGANIC CARBON CONCENTRATIONS VS RAINFALL FOR THE KANSAS RIVER

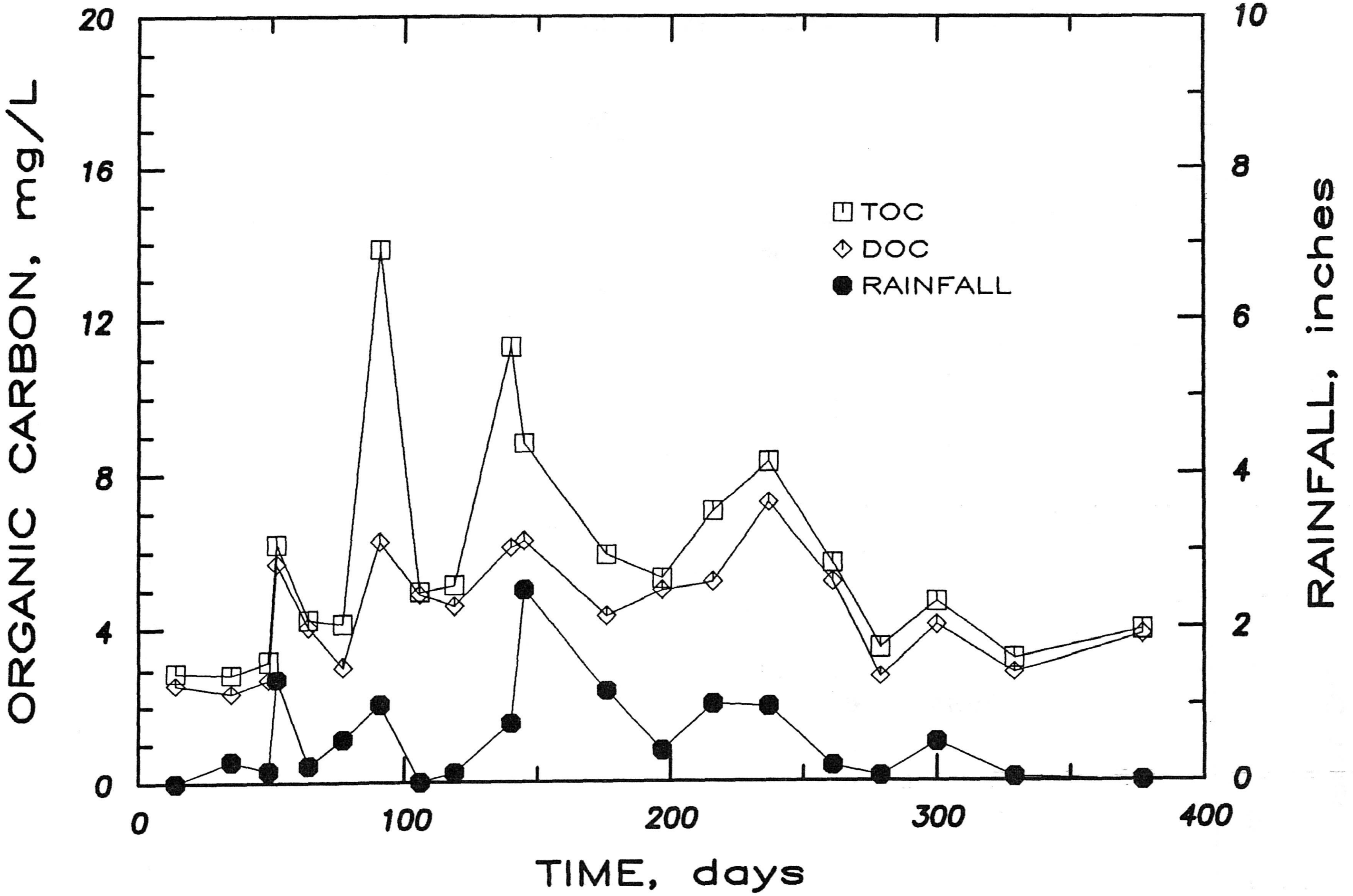

FIGURE 12: ORGANIC CARBON CONCENTRATIONS VS RAINFALL FOR ROCK CREEK

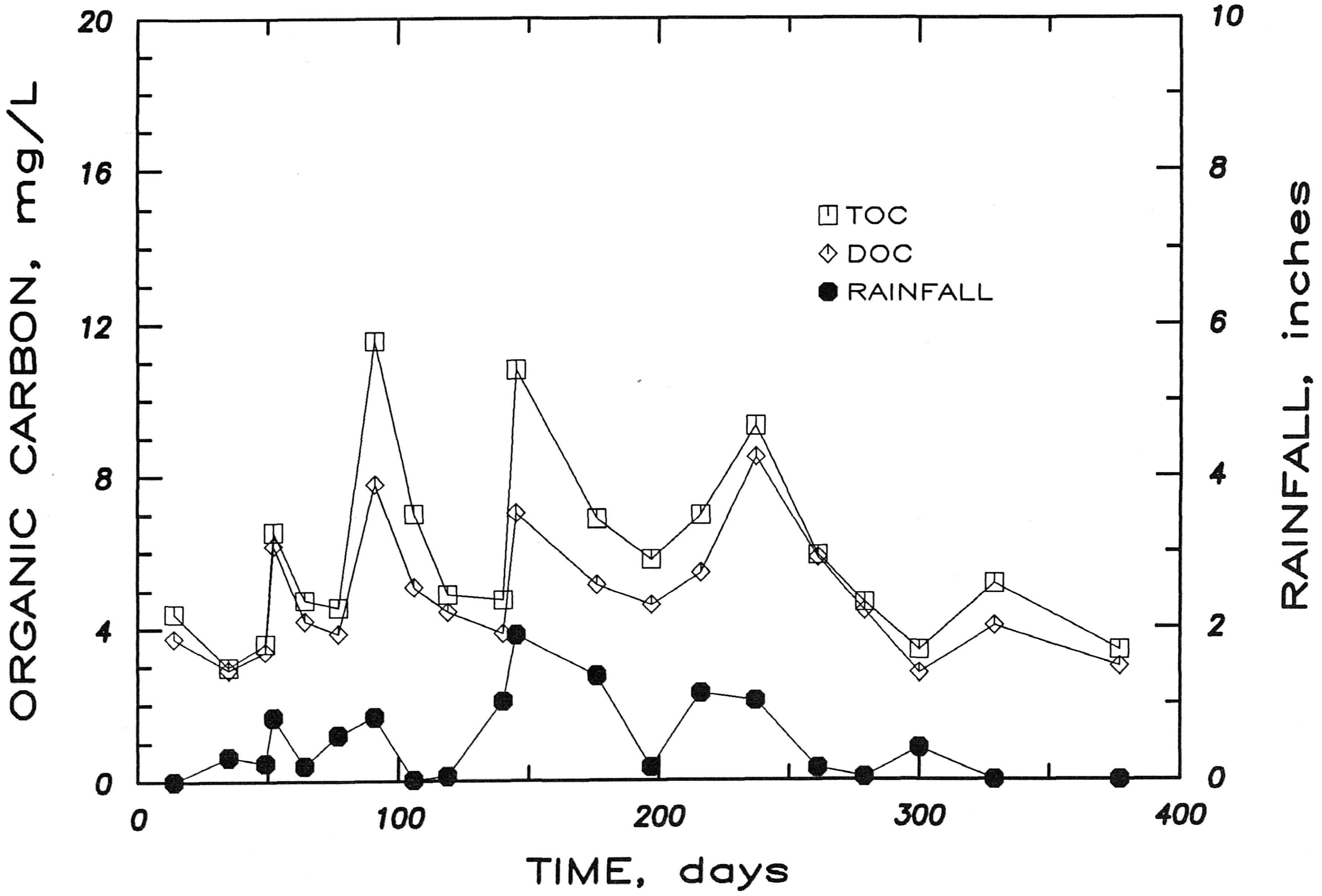

FIGURE 13: ORGANIC CARBON CONCENTRATIONS VS RAINFALL FOR THE WAKARUSA RIVER

Clinton Outlet) being significant at the 95% level of confidence. Since SS concentrations are generally expected to increase with increasing runoff (stream discharge), these correlations suggest a relationship between organic carbon concentrations and rainfall.

The yield of TFP was negatively correlated with SS for each of the four streams, although the correlations were quite weak. This suggests that the precursors in erodible soil are somewhat weaker than those present during dry weather, which is borne out by the low yields associated with the organic matter that was extracted from soil samples (see C. Watershed Samples).

Figures 9 and 10 illustrate the temporal variations in DOC and TOC, respectively, for each of the four streams. The concentrations of DOC and TOC tended to be lower in the late fall and winter (days 0-35 and 279-377) and, except for Clinton Outlet, to be quite variable during the warmer months.

The DOC and TOC concentrations in the Clinton Outlet samples were much less variable and generally lower than those in the other stream samples. Although the data are insufficient to permit construction of an accurate mass balance for Clinton Lake, it is clearly apparent based on a simple visual inspection of the data for Rock Creek, the Wakarusa River, and the Clinton Outlet that the lake acts as a net "sink" for THM precursors, especially particulate precursors. Indeed, a comparison of the average DOC and TOC values in the lake samples (cf. ea.) and the stream samples strongly suggests that most of the precursors in the lakes that were sampled are allochthonous, but a significant contribution of autochthonous precursors to several of the lakes can not be ruled out.

The average THM yields (Table 47) were lower in the Clinton Outlet sample than in those from Rock Creek and the Wakarusa River, the major tributaries to Clinton Lake. This could be due to the production of weaker THM precursors in the lake (by microorganisms), but it could just as likely be the result of coagulation and settling of a fraction of the more potent precursors.

The highest TOC value observed, 48 mg/L in the Kansas River on 4-5-85, was found in a sample taken just after the first major runoff event of the season. Other elevated concentrations of DOC and TOC also seemed to follow storm events; and the variability of the data in Figures 9 and 10, as well as the positive correlations of DOC and TOC with SS, suggested that storm runoff might cause an increase in THM precursors rather than diluting them. Indeed, other investigators have observed that DOC export increases with stream discharge (see "Related Research").

Since stream discharge data were either unavailable (Rock Creek and Wakarusa River) or not applicable (the discharges of Clinton Outlet and the Kansas River are artificially controlled), an attempt was made to correlate DOC and TOC concentrations with rainfall. For each sampling date, the data in Appendix A were used to determine the amount (inches) of rain that had fallen over the past six days plus the amount that fell on the day of sampling. Data from the Topeka weather station were used for the Kansas River, while data from the Auburn and Clinton Lake weather stations were used for the Wakarusa River and Rock Creek, respecitely. The results, shown in Figures 11-13, clearly show that DOC and TOC concentrations tend to increase during periods of wet weather. Hence mass loadings (concentration times discharge) of organic matter and THM precursors to lakes can be expected to rise very sharply following storm events.

C. WATERSHED SAMPLES

Runoff Samples

Runoff samples were collected during a spring rainstorm on April 2, 1986. The soil was nearly saturated with moisture due to antecedent rainfall earlier in the day and the day before. Since total precipitation earlier in the year had only been 2.19 inches, much of which was snow, this runoff represented the first major flush of the year. Organic carbon concentrations, THM formation potentials, and other data for these samples are presented in Table 48. All of the samples were quite turbid, and only one (grassland runoff) had a suspended solids (SS) concentration below 100 mg/L. Only one sample (#2) contained more than 1.5 mg/L of ammonia nitrogen; and all of the samples had a pH in the range of 7.3-8.3.

The runoff samples contained substantial amounts of organic carbon and THM precursors. Average concentrations of DOC, TOC, DTFP, and TFP for various subsets of samples are shown in Table 49. Approximately 26% of the organic carbon was soluble, ranging from 21% to 31% for the various sample subsets. As might be anticipated, DOC and TOC concentrations were higher in agricultural runoff than urban runoff and higher in feedlot runoff than farmland runoff. DTFP and TFP yields were typical of the yields exhibited by precursors from other sources. Yields were higher for agricultural sources than urban sources and higher for farmland sources than feedlot sources.

The two samples producing the highest concentrations of DTFP and TFP were both taken from cattle feedlots. As shown in Table 49, the average concentrations of DOC and TOC in the three feedlot samples were substantially higher than those in the other groups of samples. THM yields were slightly lower for the feedlot samples than for the farmland samples, which might be due to the presence of fresher, more cellulosic organic matter in the feedlot runoff (versus more humified material in the farmland runoff). However, it should be noted that the TOC values for two of the feedlot samples were obtained using the furnace injection method, which could also explain the lower yields (see Analytical Methods: Organic Carbon).

Sample number 2 contained a very high concentration of DOC, but the yield of DTFP was extremely low. This sample was taken from standing water at an industrial landfill operated by a manufacturer of farm chemicals (fertilizers). The ammonia concentration was 1,300 mg/L, so a very large dosage of chlorine was required to produce a free chlorine residual. The sample presumably contained some organic compound (or compounds) of low molecular weight (perhaps urea or alcohol). The DTFP and TFP yields of this sample were so low that the sample is obviously atypical, and it has therefore been excluded from most of the data summaries in Table 49.

The average DOC concentration of the urban runoff samples (6.6 mg/L) is typical of that generally found in streams and lakes in the area. However, the average DOC and TOC concentrations in the samples of agricultural runoff (19.3 and 75.9 mg/L, respectively) are very high and demonstrate that

TABLE 48

ORGANIC CARBON AND THM FORMATION POTENTIAL IN RUNOFF SAMPLES

Site No.	Site Description	DOC mg/L	DTFP		TOC mg/L	TFP		SS mg/L	NH_4^+-N mg/L	pH
			µg/L	µmoles/mgC		µg/L	µmoles/mgC			
1	Urban-Commercial	17.8	461	0.214	67.0*	1,152	0.143	460	0.5	7.3
2	Industrial Landfill	257.0	1,205	0.039	337.0*	1,555	0.038	528	1,300	7.9
3	Construction Landfill	6.06	230	0.304	19.9	967	0.403	644	0.5	8.0
4	Terraced/Tiled Farmland	4.52	129	0.234	203.4*	4,329	0.178	8,056	0.3	7.8
5	Non-terraced Farmland	4.92	230	0.374	7.55	400	0.431	130	0.7	7.4
6	Burned Bromegrass Land	6.39	325	0.418	7.93	409	0.425	13	<0.1	7.4
7	No-till Farmland	4.72	168	0.276	7.09	482	0.549	152	0.1	7.3
8	Cattle Feedlot	64.1*	1,682	0.216	382.7*	13,482	0.302	2,196	1.5	7.3
9	Tilled Farmland	16.7	1,104	0.553	29.6	1,651	0.465	352	<0.1	7.6
10	Swine Feedlot	13.0	757	0.477	26.5	1,383	0.429	272	0.1	7.3
11	Cattle Feedlot	71.1	2,834	0.330	122.5*	4,747	0.322	416	0.5	7.3
12	Soybean Field	9.92	483	0.400	13.6	710	0.432	136	<0.1	7.5
13	Corn Field	3.74	149	0.322	17.2	591	0.284	2,876	1.5	7.3
14	Corn Field	13.4	541	0.331	17.3	1,008	0.481	432	<0.1	7.4
15	Urban Construction	3.03	107	0.262	22.7*	1,486	0.542	176	<0.1	7.3
16	Urban Residential	5.12	348	0.566	6.99	395	0.471	260	0.1	7.8
17	Industrial Park	4.48	98	0.181	6.72	274	0.343	218	0.2	8.3
18	Shopping Center	3.09	97	0.262	5.22	268	0.428	186	<0.1	8.3

* Furnace injection method used instead of UV-persulfate method

TABLE 49

AVERAGE ORGANIC CARBON CONCENTRATIONS AND THM YIELDS OF RUNOFF SAMPLES

Sample Group	No. of Samples	Avg. DOC (mg/L)	Avg. TOC (mg/L)	Average DTFP (μmoles/mgC)	Average TFP (μmoles/mgC)
All samples	18	---	---	0.320 ± 0.13	0.370 ± 0.14
All samples except #2	17	14.8 ± 20.5	56.7 ± 98.8	0.336 ± 0.12	0.390 ± 0.11
Urban runoff (except #2)	6	6.60 ± 5.61	21.4 ± 23.5	0.298 ± 0.14	0.388 ± 0.14
Agricultural runoff	11	19.3 ± 24.3	75.9 ± 119	0.357 ± 0.10	0.391 ± 0.11
Feedlot runoff	3	49.4 ± 31.7	177 ± 184	0.341 ± 0.13	0.351 ± 0.07
Farmland runoff	8	8.04 ± 4.81	38.0 ± 67.3	0.364 ± 0.10	0.406 ± 0.12
Furnace Inj. (except #2)	5	---	160 ± 142	---	0.297 ± 0.16
UV-Persulfate Method	12	---	13.8 ± 8.32	---	0.428 ± 0.07

agricultural runoff is a major source of organic carbon and THM precursors for Kansas lakes and streams.

Half of the unfiltered runoff samples produced THM concentration in excess of 1,000 µg/L, a very high concentration when compared to the primary drinking water standard of 100 µg/L. Such concentrations are rarely observed in finished drinking water because: 1) most surface water treatment plants are either designed with presedimentation basins or withdraw water from a lake; 2) chlorination practice at most water treatment plants has been modified to reduce THM concentrations; and 3) few water supplies contain such a high concentration of precursors. Nevertheless, very high concentrations of THMs have been observed in the finished water of surface water treatment plants practicing prechlorination.

Glaze and Rawley (1979) observed THM concentrations in excess of 900 µg/L in the finished water of two surface water supplies in East Texas. On several occasions in April of 1980, Walls (1985) observed THM concentrations in excess of 1,000 µg/L at the Iola water treatment plant in Kansas. This plant withdraws water from the Neosho River 30 miles downstream from the John Redmond Reservoir. The watershed is 43% cropland and 52% pasture. After a dry winter, heavy spring rains led to the release of 9000 cubic feet per second of water from the reservoir during a two week period in April. During this time, the river approached flood stage, and THM concentrations averaged 973 µg/L. After the releases were lowered and the flow subsided, THM concentrations dropped substantially, to the 130-150 µg/L range.

Soil Samples

After their arrival at the laboratory, the one-inch diameter soil samples were broken up and mixed with a spatula so that more homogeneous subsamples could be obtained. A 10-15 gm subsample was analyzed for moisture content and a one-gram subsample was extracted with 10 mM STP. The extract was analyzed for organic carbon (EOC) and THM formation potential (ETFP), and the results are reported on a dry-weight basis, mg/dry gram (mg/dgm). The remainder of each sample was dried, ground to a fine powder, and analyzed for TOC. A one-gram subsample of the dried powder was also analyzed for EOC.

The analytical results are presented in Table 50. The TOC concentrations in the soils were all relatively low and quite similar, ranging from 12.06 to 29.84 mg/dgm (1.2 to 3.0%). An average of 32% of the TOC was extracted from the wet samples and 37% from the dry samples, typical values for soils extracted under mild conditions (slightly alkaline pH without acid pretreatment). A higher percentage of the TOC was extracted from the dried and ground samples than from the wet samples (37% vs 32%), but the difference is smaller (37% vs 34%) if the anomalous sample 4 is excluded. The EOC concentrations are very similar to the DOC concentrations found in the stream and lake samples.

The ETFP values were surprisingly low compared to the values for other sources of precursors (especially agricultural runoff), averaging only 0.207 µmoles/mgC, with a high value of 0.311. Since the organic matter in soils

TABLE 50

EXTRACTABLE ORGANIC CARBON (EOC) AND EXTRACTABLE THM FORMATION POTENTIAL (ETFP) IN SOIL SAMPLES

Sample No.	Moisture (%)	TOC mg/dgm	EOC Wet Sample mg/dgm	EOC Wet Sample %	EOC Dry Sample mg/dgm	EOC Dry Sample %	ETFP µmoles/mgC
1	18.97	12.82	5.16	40	4.84	38	0.172
2	16.44	20.17	5.20	26	6.41	32	0.229
3	17.55	13.27	5.47	41	5.34	40	0.175
4	23.55	29.84	6.75	23	11.21	38	0.311
5	15.78	12.06	3.72	31	4.60	38	0.191
6	17.69	16.06	5.18	32	5.83	36	0.166
Average	18.33	17.37	5.25	32	6.37	37	0.207
Std. Dev.	2.78	6.79	0.96	7	2.46	3	0.056

is largely comprised of humic substances, and since humic substances are well known for their ability to form THMs upon chlorination, higher yields had been expected. Possible explanations include: 1) a more potent fraction of precursors had already been leached out of the soil and into runoff or deeper into the ground; 2) organic matter extracted from the topsoil (in this case the top few inches of topsoil) contains a larger fraction of complex carbohydrates (poor precursors) than the organic matter found deeper in the soil; and 3) the humic substances that leach naturally from the soil are better precursors than those extracted with 10 mM STP. It is also quite possible that organic matter extracted from additional samples of these or other soils would yield greater amounts of ETFP, comparable to the yields of DTFP and TFP for the samples of agricultural runoff.

Point-Source Samples

Samples of a variety of municipal and industrial effluents, power plant cooling water and ash pond water, and aerobically and anaerobically digested sludges were analyzed for organic carbon, THM formation potential, and ammonia nitrogen (Table 51). All of the samples had measurable amounts of THM precursors, yielding an average DTFP of 0.259 μmoles/mgC and an average TFP of 0.257 μmoles/mgC (Table 52). Hence, the precursors in these samples were similar in yield to those from other sources.

The highest THM yields were produced by the industrial secondary effluents and the power plant samples (Table 52), but the yields were comparable to those of natural precursors in lakes, streams, and agricultural runoff. The precursors in the power plant samples almost certainly originated in the raw water source and are therefore natural. The ash pond influent was lower in DOC and TOC than the cooling water, perhaps due to adsorption of natural humic materials onto the ash. The ash pond effluent is slightly higher in DOC and TOC than the influent, perhaps due to growths of bacteria and algae in the pond.

The lowest THM yields were produced by samples of municipal secondary effluent, algae laden samples, and aerobically digested sludge. While it is known that bacteria and algae produce precursors, relatively little is known regarding the yields of THMs produced by these precursors and the factors influencing yield. Since the precursors in these particular samples can be assumed to be almost entirely produced by bacteria and algae, one might conclude that such precursors are relatively weaker than those from other sources. However, two points should be noted in this regard:

1. The data base presented herein is extremely small. The two stabilization pond samples (from Clinton Lake), which were anomalously low in DTFP and TFP, represent one third of the algae laden samples and one half of the municipal secondary effluent samples. Furthermore, only one sample of aerobically digested sludge was analyzed. It is quite conceivable that additional samples from such sources would exhibit higher (more typical) yields.

TABLE 51

ORGANIC CARBON AND THM FORMATION POTENTIAL IN POINT-SOURCE SAMPLES

Site No.	Site Description	DOC mg/L	DTFP		TOC mg/L	TFP		NH$_4$-N mg/L
			µg/L	µmoles/mgC		µg/L	µmoles/mgC	
1	Municipal Secondary Eff. (Act. Sl.)	9.15	279	0.233(0.9)†	9.57	304	0.242(0.4)†	<0.1
2	Municipal Secondary Eff. (Stab. Pond)	16.4	453	0.220(1.4)	41.4*	1,093	0.210(0.6)	2.4
3	Municipal Secondary Eff. (Stab. Pond)	32.7	661	0.167(1.4)	55.3*	926	0.137(0.3)	9.6
4	Municipal Secondary Eff. (Stab. Pond)	28.4	573	0.166(0.7)	54.2*	1,027	0.156(1.5)	4.5
5	Sanitary Landfill Runoff Pond	3.0	151	0.375(1.7)	3.6	154	0.318(1.4)	<0.1
6	Refinery Effluent	26.9	1,494	0.370(3.2)	42.0	2,071	0.359(2.5)	<0.1
7	Cellophane Manufacturing Effluent	5.4	236	0.312(4.3)	8.3	272	0.241(0.7)	<0.1
8	Power Plant Cooling Water	7.0	322	0.327(1.3)	8.4	315	0.267(0.3)	<0.1
9	Power Plant Cooling Water	7.0	336	0.342(1.6)	7.8	340	0.310(0.4)	<0.1
10	Power Plant Ash Pond Influent	3.7	120	0.227(1.9)	3.9	151	0.275(0.9)	<0.1
11	Power Plant Ash Pond Effluent	4.7	237	0.364(2.1)	6.1	421	0.535(1.0)	<0.1
12	Electroplating Plant Effluent	9.4	126	0.106(1.1)	10.7	156	0.118(1.5)	2.6
13	Meat Packing House Effluent	16.1	568	0.273(0.9)	20.8	819	0.313(1.8)	<0.1
14	Fertilizer Plant Wastewater Pond	11.2	214	0.150(2.6)	16.2*	242	0.120(<0.1)	<0.1
15	Aerobically Digested Sludge	20.7	287	0.110(0.5)	1,120*	15,890	0.120(0.2)	14.5
16	Anaerobically Digested Sludge	94.7	3,397	0.301(<0.1)	6,090*	202,841	0.280(8.8)	350

* Furnace injection method

† Residual chlorine concentrations for trihalomethane formation potentials are shown in parentheses.

TABLE 52

AVERAGE ORGANIC CARBON CONCENTRATIONS AND THM YIELDS OF POINT-SOURCE SAMPLES

Sample Group	No. of Samples	Average DOC (mg/L)	Average TOC (mg/L)	Average DTFP (µmoles/mgC)	Average TFP (µmoles/mgC)
All Samples (except sludges)	14	12.9 ± 9.8	20.5 ± 19.0	0.259 ± 0.091	0.257 ± 0.112
All Industrial Effluents	6	12.3 ± 8.3	17.4 ± 13.2	0.263 ± 0.111	0.281 ± 0.159
Industrial Secondary Effluents	3	16.1 ± 10.8	23.7 ± 17.0	0.318 ± 0.049	0.304 ± 0.059
Municipal Secondary Effluents	4	21.7 ± 10.8	40.1 ± 21.3	0.197 ± 0.035	0.186 ± 0.048
Power Plant Samples	4	5.6 ± 1.7	6.6 ± 2.0	0.315 ± 0.060	0.347 ± 0.127
Algae Laden Samples*	6	22.0 ± 8.5	38.3 ± 16.5	0.224 ± 0.085	0.216 ± 0.099
Sludge Samples	2	--	--	0.206 ± 0.135	0.200 ± 0.113

* Those having a very green color (samples 2,3,4,6,13, and 14)

2. Although many natural precursors are undoubtedly of microbial origin, they are on the average much older and more humified than the precursors in municipal wastewaters effluents, and they may also have undergone photochemical reactions. It would not be surprising to find that freshly formed algal and bacterial byproducts are less potent precursors than the humic substances naturally present in the environment.

It is interesting to compare the results for the secondary effluent and sludge samples (nos. 1, 15, and 16 in Table 51), all taken on the same day from the Lawrence Wastewater Treatment Plant. The anaerobically digested sludge produced the highest yields of DTFP and TFP, while the aerobically digested sludge produced the lowest yields. Thus, it may be hypothesized that anaerobic environments may be more conducive to the production of THM precursors than aerobic environments. If so, this might be significant for a water supply lake subject to seasonal stratification (producing anaerobic conditions in the hypolimnion). Data collected on samples from anaerobic hypolimnia in this study contradict this hypothesis, but the organic matter in Kansas lakes is largely non-biodegradable, and different results might have been obtained if different types of lakes had been studied.

On the basis of these results it is reasonable to conclude that point sources of precursors are generally insignificant in Kansas. The yields produced by precursors from these sources are similar to those produced by other precursors, and most point sources are substantially diluted either upon discharge into the environment or prior to withdrawal by downstream water users. The potential impact of any given discharge on a downstream water supply can be estimated (generally within ± 50%) by multiplying the TOC or DOC of the wastewater by 0.26 μmoles THM/mgC, taking dilution into account, and neglecting losses of precursors in transit.

Oil Brines and Brine-Contaminated Groundwater

The samples of oil brine and brine-contaminated groundwater (see Sampling Sites and Procedures) were particularly difficult to analyze for several reasons: 1) the high levels of chloride sometimes interfered with TOC and DOC analysis; 2) some of the unfiltered samples contained a considerable amount of particulate matter that interfered with the UV-persulfate oxidation method for TOC; 3) organic matter in the first sets of samples adsorbed to the sides of the sample containers (1 liter polyethylene bottles); and 4) constituents in the brine, probably iodide and bromide, interfered with measurement of residual chlorine. Despite these difficulties, meaningful results were obtained.

The first set of brine-contaminated groundwater samples was collected August 22, 1985. Since the laboratory was already inundated with samples and these samples were not likely to contain biodegradable organic matter, they were stored for several weeks prior to analysis (contrary to the usual practice). On September 19, 1985 and September 20, 1985, these samples (numbers 1 through 6) were analyzed for TOC and DOC, respectively (see Table 53). The TOC values were very high, but the DOC values were surprisingly

TABLE 53

DOC AND TOC CONCENTRATIONS OF BRINE-CONTAMINATED GROUNDWATER SAMPLES COLLECTED 8-22-85 AND OIL-FIELD BRINE SAMPLES RECEIVED 10-30-85*

Site No.	Sample Designation	TOC on 9-19-85	DOC on 9-20-85	DOC on 4-2-86	TOC on 4-2-86	TOC after Sonification on 4-5-86
1	K-11A	73.9	2.71	2.40	4.12	32.5†
2	K-11B	94.3	1.75	1.66	65.0†	78.6†
3	EB-2A	46.7	3.70	3.32	6.72	8.19
4	EB-2B	43.7	1.36	1.26	1.84	2.37
5	EB-34A	50.9	1.30	0.87	1.15	1.78
6	EB-34B	44.5	1.38	1.16	1.21	4.16
7	S&K Oil	-	-	1.02	0.17	NR
8	Gladys	-	-	11.37	35.0†	45.9†

* All DOC and TOC values are in mg/L

† These values were measured using the furnace injection method

NR = Not Reproducible

low, indicating that little or no organic matter had dissolved into the water. These DOC values are typical of shallow groundwater (such as that found in alluvial aquifers) and could be due in large part or in whole to naturally occurring organic material (humic substances). Except in the case of the sample from site 2 (K-11B), the TOC analyzer produced unusually sharp peaks, indicative of the presence of soluble and easily oxidized organic matter.

Samples from sites 1 and 2 (K-11A and B) were very turbid, containing light and dark brown particles, respectively. The others were considerably less turbid, containing yellow or orange colored particles. The filtered samples were all very clear and colorless. None of the samples had any noticeable odor, all were very saline, and all had NH_3-N concentrations below 0.1 mg/L. Due to difficulties with the gas chromatograph and the urgency of completing other tasks, these samples were stored until April 2, 1986 before further analysis.

The first set of oil-brine samples (sites 7 and 8) was received October 30, 1985 and immediately analyzed. However, due to the very high concentration of chloride in these samples, accurate and reproducible results could not be obtained using the standard UV-persulfate method for TOC and DOC. These samples had a very strong petrochemical odor, but the odor could not be detected in the acidified and aerated samples prepared for organic carbon analysis. Also, there appeared to be substantial amounts of oily material adhering to the sides of the sample containers. The filtered samples were clear, but still gave off a petrochemical odor. These samples were also stored at 4°C until April 2, 1985 for further analysis.

On April 2, 1986, both sets of samples were removed from storage for TFP and DTFP analysis. The samples appeared to be unchanged; but since they had been stored a long time, the TOC and DOC values were rechecked (this time using a persulfate reagent specifically designed for high-salt samples). As shown in Table 53, most of the TOC was no longer in solution, while DOC values were only slightly lower. The UV-persulfate method gave unacceptable TOC results for two of the samples (sites 2 and 8), so the high-temperature combustion method was used for these two samples.

Close examination of the sample containers revealed that many fine particles had strongly adsorbed to the walls of the containers, forming an oily layer, and had not been dislodged when the samples were shaken prior to analysis. To see if this could explain the loss of TOC, each container was placed in a heated sonifier bath (Model B-221, Branson Cleaning Equipment Co., Shelton, Conn.) for five minutes on April 5, 1986. The TOC values following sonification (see Table 53) were higher for all samples, demonstrating that adsorption to the sample container did account for at least a portion (if not all) of the TOC loss. However, not all of the adsorbed material could be dislodged by sonification.

Filtered and unfiltered portions of each sample were then analyzed for DTFP and TFP (see Table 54, first set of samples). The average yield of DTFP was 0.40 ± 0.06 μmoles/mgC, typical of the values observed for other sources of precursors. The average yield of TFP was 0.32 ± 0.14 μmoles/mgC,

TABLE 54

ORGANIC CARBON AND TRIHALOMETHANE FORMATION POTENTIAL IN BRINE-CONTAMINATED GROUNDWATER SAMPLES

Site	DOC	DTFP			TOC	TFP		
Number	mg/L	µg/L	µM	µmoles/mgC	mg/L	µg/L	µM	µmoles/mgC
First Set								
1	1.26	107	0.430	0.342(A)*	32.5	1887	8.074	0.248(D)
2	2.40	282	1.128	0.470(B)	78.6	2470	16.111	0.205(B)
3	3.32	345	1.401	0.422(A)	8.19	348	1.413	0.172(A)
4	1.66	184	0.763	0.459(A)	2.37	261	1.046	0.441(A)
5	1.16	103	0.412	0.355(A)	1.78	232	0.942	0.531(A)
6	0.87	76.7	0.320	0.368(A)	4.16	332	1.327	0.319(A)
Second Set†								
1	2.38	245	0.977	0.410	2.38	245	0.976	0.410
2	2.18	169	0.700	0.322	2.88	277	1.144	0.397
3	2.52	330	1.323	0.524	14.04	643	2.611	0.186
4	1.13	126	0.512	0.455	1.45	191	0.761	0.526
5	1.21	146	0.586	0.483	4.88	184	0.736	0.151
6	1.24	96.2	0.384	0.310	1.79	129	0.516	0.288

* Chlorine dosage yielding a free residual greater than 0.2 mg/L; A=5 mg/L, B=10 mg/L, etc.

† A chlorine dosage of 5 mg/L produced a free chlorine residual greater than 0.2 mg/L in all samples; the homogenized portion of sample 3 was diluted prior to chlorination.

slightly lower and more variable than the DTFP yield. Also, the samples with the highest TOC concentrations had the lowest TFP yields, suggesting that the organic constituents associated with the brine were relatively poor precursors.

The oil brine samples were also dosed with chlorine (up to 25 mg/L). No THMs were detected, but there did not appear to be any free residual chlorine present in the samples following incubation. Something in the samples seemed to interfere with the residual chlorine analysis. Upon addition of DPD a very faint pink color could be seen in some samples, but the amount of color did not increase with chlorine dosage. Addition of iodide produced a yellow color (iodine?) rather than the red color associated with combined chlorine.

Because of the changes that had occurred in the samples during storage and the analytical difficulties experienced, a second set of samples was collected. The second set of brine-contaminated groundwater samples was collected on April 7, 1986 and April 8, 1986 and analyzed May 6, 1986. These samples were much less turbid than those in the first set, and there were no visible deposits on the walls of the containers. The turbidity that was present appeared to be due to fine particles of clay.

The results of the analyses for the second set of brine-contaminated groundwater samples are also shown in Table 54. The DOC values were again very low, all below 3 mg/L, and the average DTFP yield was 0.45 ± 0.10 µmoles/mgC, very similar to the results for the first set of samples (0.40 ± 0.06). The TOC values were lower than for the first set of samples; but the TFP yields averaged 0.33 ± 0.14 µmoles/mgC, nearly identical to the earlier results (0.32 ± 0.14). Once again, the highest TOC concentrations produced the lowest TFP yields. In all cases except one (the unfiltered portion of the sample from site 2 in the first set of samples), THM formation was strongly dominated by bromoform, as would be expected because of the relatively high concentration of bromide in oil brines.

A second set of oil-field brine samples was collected on 8-8-85, two samples from site 7 and two from site 8. The samples from site 7 contained a large quantity of separable oil; they were combined, mixed, and settled, and the oil was then decanted. The samples from both sites were extremely salty and contained high concentrations of ammonium. The pH values of the samples ranged from 5.9 to 6.8. Large dosages of chlorine, in 10 mg/L increments, were used in the TFP analyses, and the free residual chlorine concentrations were titrated to a yellow (rather than colorless) endpoint. The results are shown in Table 55. The organic carbon concentrations for sample 7 were surprisingly low, and the TFP yields for all of the samples were low in comparison to the yields for the lake and stream samples.

On the basis of these results, it is reasonable to conclude that contamination of groundwater or surface water by small quantities of oil brine will not result in a significant increase in THM formation. It is not clear whether the organic carbon present in the samples was originally in the groundwater prior to brine contamination, leached from the sediments by the brine, or transported into the groundwater along with the brine.

Nevertheless, the concentrations of precursors in these samples are quite low, especially in view of the fact that only very minute quantities of brine could be tolerated in a potable water supply due to its extremely high salt content.

TABLE 55

ORGANIC CARBON AND THM FORMATION POTENTIAL IN OIL-FIELD BRINE SAMPLES COLLECTED 8-8-86

			DTFP				TFP		
Site No.	NH_4-N mg/L	DOC mg/L	TTHM µg/L	Yield µmoles/mgC	Res.Cl_2 mg/L	TOC mg/L	TTHM µg/L	Yield µmoles/mgC	Res.Cl_2 mg/L
7	26.5	5.54	368	0.28	7.5	11.27	498	0.18	6.4
8A	24.3	3.54	213	0.25	8.7	6.61	389	0.24	10.0
8B	23.9	3.28	209	0.27	3.8	9.36	427	0.19	3.7

D. EXPERIMENTAL PONDS

Year 1 (1985)

Composite samples were taken from the divided ponds on 7-22-85, the day before the water levels were lowered below the tops of the dividing walls. The concentrations of organic carbon and THM precursors were quite high (Table 56), but the THM yields were moderate. Since the TOC concentration in the well water feeding the main reservoir is about 0.5 mg/L, and since the ponds are constructed in such a way that surface runoff cannot enter them (except for runoff directly from the sides of the ponds above the waterline), it is reasonable to conclude that most of the organic matter in the pond water is of plant or microbial origin, with perhaps some contribution from rainfall and airborne particles.

The divided ponds were treated during the last week of July (cf. ea.) and both the divided ponds and the turbidity ponds were sampled on 8-7-85. As shown in Table 57, the organic carbon and THM precursor concentrations were nearly the same for all the ponds in each group.

Among the divided ponds, only the two treated with copper sulfate stand out: both were high in chlorophyll and noticeably greener in color than the other ponds. The lower (east) copper-sulfate-treated pond was very green and had a TOC concentration significantly greater than that of the other samples. Thus, the copper sulfate seems to have actually caused an algal bloom to occur. Perhaps by killing the natural phytoplankton assemblage, releasing the nutrients within the algal cells, and then rapidly precipitating out, the copper sulfate created an excellent opportunity for rapid growth of one or more resistant or newly introduced species of algae. It is also quite possible that the copper sulfate retarded the growth of macrophytes and filamentous algae, thereby providing an opportunity for the planktonic algae to become better established.

Although copper sulfate is a very good algicide, its effects are very temporary (as these data nicely illustrate), and frequent application may be required, creating a situation analogous to drug dependency. The THM yields for the samples from the copper-sulfate-treated ponds are also somewhat elevated, suggesting that the precursors associated with algal blooms can be potent. However, it is not known whether the increases in TOC and THM yield are directly due to algae and algal byproducts or to bacteria feeding on them.

The organic carbon concentrations in the 8-7-85 samples were substantially lower than those measured on 7-22-86, and the reasons for the decrease are unclear. Possible explanations include: 1) growth of benthic plants and periphyton, resulting in adsorption of organic matter; 2) dilution by rainfall (3.15 inches over a 4-day period, accounting for perhaps as much as a 10% decrease); and 3) increased respiration relative to photosynthesis as a result of increased cloud cover.

TABLE 56

ORGANIC CARBON AND THM FORMATION POTENTIAL IN THE DIVIDED POND SAMPLES OF 7-22-85

Sample	DOC mg/L	DTFP TTHM µg/L	DTFP Yield µmoles/mgC	DTFP Res.Cl_2 mg/L	TOC mg/L	TFP TTHM µg/L	TFP Yield µmoles/mgC	TFP Res.Cl_2 mg/L
Composite of upper (west) ponds	9.17	293	0.25	0.9(B)*	10.37	319	0.25	1.2(C)
Composite of lower (east) ponds	9.44	280	0.24	0.9(B)	10.17†	398	0.31	1.6(C)

* Chlorine dosages shown in parentheses; B = 10mg/L and C = 15mg/L.
† Suspect data

TABLE 57

ORGANIC CARBON AND THM FORMATION POTENTIAL IN THE EXPERIMENTAL POND SAMPLES OF 8-7-85

Pond Sample	DOC mg/L	DTFP TTHM µg/L	DTFP Yield µmoles/mgC	TOC mg/L	TFP TTHM µg/L	TFP Yield µmoles/mgC	Chlor. a µg/L
Divided Ponds							
Control (1-4)	7.1	259	0.29(B)*	7.2	253	0.28(B)	2.24
Control (2-3)	8.1	305	0.30(B)	7.5	308	0.33(B)	2.37
$CuSO_4$ (1-2)	7.1	276	0.31(B)	7.2	303	0.34(B)	16.7
$CuSO_4$ (2-4)	7.5	365	0.39(B)	9.5	513	0.44(D)	19.9
Simazine (1-3)	6.8	230	0.27(B)	7.6	295	0.31(C)	2.18
Simazine (2-1)	7.6	269	0.28(B)	7.6	280	0.29(B)	2.24
Grass Carp (1-1)	7.2	261	0.29(B)	6.9	241	0.28(B)	4.17
Grass Carp (2-2)	7.0	282	0.32(B)	7.1	303	0.34(B)	3.79
Turbidity Ponds							
Control (13)	10.0	322	0.26(B)	10.4	360	0.28(B)	8.53
Control (15)	9.9	343	0.28(B)	10.8	360	0.27(B)	6.98
Low Turb. (12)	9.5	302	0.26(B)	9.6	340	0.29(B)	6.60
Low Turb. (16)	9.0	314	0.28(B)	9.4	347	0.30(B)	6.94
High Turb. (11)	8.6	295	0.28(B)	9.3	309	0.27(B)	4.93
High Turb. (14)	9.0	307	0.27(B)	9.4	324	0.28(B)	7.39

* Chlorine dosages shown in parentheses; B = 5 mg/L, C = 10 mg/L, D = 10 mg/L.

Note: The divided ponds were all quite clear (low in turbidity). Algal blooms were observed in both copper sulfate ponds; pond 1-2 was slightly green in color, while pond 2-4 was very green.

The lower (east) divided ponds tended to have slightly higher organic carbon concentrations throughout the study. This is attributed to increased fertility resulting from fertilization of the lower ponds during a previous experiment (Dean Kettle, personal communication, 1986).

In the turbidity ponds, there was a slight but clearly distinguishable trend of decreasing concentrations of organic carbon and THM precursors with increasing turbidity. Whether this was caused by decreased photosynthesis or removal of organic matter by adsorption onto clay and settling is not known. Although there is quite a bit of scatter in the chlorophyll a data, algal growth does appear to have been hindered by the clay, supporting the former explanation; but a substantial amount of clay settled to the bottom of the ponds (despite the mixing), supporting the latter explanation. Since the THM yields were remarkably consistent, there is no hint of a change in the characteristics of the THM precursors.

A second set of samples from the divided ponds was taken on 8-27-85 (Table 58). The organic carbon concentrations continued their downward trend, and the THM yields remained unchanged. The organic carbon concentrations in the lower copper-sulfate-treated pond were still significantly elevated, indicating that the algal bloom observed on 8-7-85 was still influencing water quality even after the bloom had ended. The DOC concentrations were quite similar in each of the ponds, but the TOC concentrations appeared to be suppressed in the simazine-treated ponds and slightly elevated in the ponds with grass carp.

The divided ponds were sampled once more on 9-19-85. The organic carbon concentrations (Table 59) were very similar to those measured three weeks earlier on 8-27-85, so the samples were not chlorinated. The DOC and TOC concentrations were, with one exception, lower in the respective control ponds than in the treated ponds, but the differences were quite small.

The turbidity ponds were resampled again on 8-27-85 and 9-19-85. The organic carbon concentrations (Table 60) were very similar to those measured earlier (Table 57); and there was again a trend of decreasing organic carbon with increasing turbidity.

Under normal weather conditions, algal blooms would be expected to occur in these ponds, which are relatively fertile. However, during August and September of 1985, the weather was unusually cool and wet (see Tables A1 and A5 in Appendix A), with rainfall in August 5.83 inches above normal. Since algal blooms did not occur in the control ponds, the effectiveness of the algae-control measures tested cannot be evaluated, except that copper sulfate appeared to cause a bloom to occur. However, it can be concluded that the algae-control measures had a small to negligible impact on organic carbon and THM precursors in the absence of an algal bloom.

TABLE 58

ORGANIC CARBON AND THM FORMATION POTENTIAL IN THE EXPERIMENTAL POND SAMPLES OF 8-27-85

		DTFP			TFP		
Pond Sample	DOC mg/L	TTHM μg/L	Yield μmoles/mgC	TOC mg/L	TTHM μg/L	Yield μmoles/mgC	Chlor. a μg/L
Control (1-4)†	5.93	246	0.33 (B)*	7.37	400	0.44 (C)	1.65
Control (2-3)	6.20	252	0.32 (B)	6.75	280	0.33 (B)	1.22
$CuSO_4$ (1-2)	6.05	223	0.29 (B)	7.32	267	0.29 (B)	1.42
$CuSO_4$ (2-4)	7.30	259	0.28 (B)	8.22	299	0.29 (B)	1.85
Simazine (1-3)	6.22	231	0.30 (B)	6.62	257	0.31 (B)	2.25
Simazine (2-1)	6.73	247	0.29 (B)	6.84	301	0.35 (B)	1.54
Grass Carp (1-1)	6.47	246	0.30 (B)	8.16	299	0.30 (C)	3.30
Grass Carp (2-2)	6.24	242	0.31 (B)	7.25	265	0.29 (B)	1.25

† The sample from control pond 1-4 had a very distinct brownish yellow color, which is presumed to have been caused by disturbance of the bottom sediments during sampling.

* Chlorine dosages shown in parentheses; B = 5 mg/L, C = 10 mg/L.

TABLE 59

ORGANIC CARBON CONCENTRATIONS IN THE DIVIDED POND SAMPLES OF 9-19-85

Pond Sample	DOC mg/L	TOC mg/L	Chlor. a μg/L
Control (1-4)	5.95	6.19	2.56
Control (2-3)	6.63	6.90	4.72
$CuSO_4$ (1-2)	6.27	6.47	2.79
$CuSO_4$ (2-4)	7.04	7.73	1.99
Simazine (1-3)	6.82	6.80	2.56
Simazine (2-1)	7.27	7.85	1.38
Grass Carp (1-1)	6.42	6.52	3.98
Crass Carp (2-2)	6.58	7.17	1.82

TABLE 60

ORGANIC CARBON AND CHLOROPHYLL CONCENTRATIONS IN THE TURBIDITY POND SAMPLES OF 8-27-85 AND 9-19-85

	8-27-85			9-19-85	
Pond	DOC mg/L	TOC mg/L	Chlor. a µg/L	DOC mg/L	TOC mg/L
Control (13)	9.05	10.02	4.35	9.42	9.97
Control (15)	10.32	10.81	4.04	10.22	10.55
Low Turb. (12)	-	-	-	-	-
Low Turb. (16)	9.53	10.31	2.84	9.92	10.40
High Turb. (11)	-	-	-	-	-
High Turb. (14)	8.13	10.74	3.81	8.39	9.61

Year 2 (1986)

In the spring of 1986, the divided ponds were prepared as described in "Sampling Sites and Procedures E. Experimental Ponds". The ponds were fertilized with nitrogen and phosphorus (intended to stimulate algal growth) on 6-10-86; and samples were taken from each of the ponds on 6-12-86 (day 0). The results of the first sampling (Table 61), as well as visual field observations, indicate that the ponds were initially very similar, although the lower ponds were observed to be slightly more turbid than the upper ponds.

One month later, on 7-14-86 (day 34), the ponds were again sampled. The analytical results, presented in Table 62, show that all of the ponds still had similar concentrations of organic carbon and TFP, although both had decreased slightly in comparison to the concentrations measured on 6-12-86. By this date, it was obvious that macrophytes were outcompeting algae for the available nutrients. Thick growths of submerged macrophytes were present in each of the ponds, and the pond water remained relatively clear. There appeared to be little likelihood of algal blooms occurring under these conditions. Therefore, it was decided to proceed with the treatment of the ponds rather than waiting for algal blooms to occur.

On 7-30-86 (day 50) the simazine and copper sulfate treatments were applied, and on 8-1-86 grass carp were added to two of the ponds. By 8-7-86 (day 58) changes were clearly evident in the treated ponds; those treated with copper sulfate and simazine had become darker in color, and algal blooms appeared to be occurring in the lower ponds. The grass carp appeared to have eaten some of the macrophytes, while the control ponds were relatively unchanged in appearance.

The analytical results for samples taken on 8-7-86 (day 58) are shown in Table 63. The concentrations of DOC and TOC were clearly elevated in the lower ponds treated with copper sulfate and simazine, and the lower simazine-treated pond had substantially elevated levels of DTFP and TFP. The chlorophyll data confirmed visual observations that algal blooms had occurred in the lower simazine- and copper-sulfate-treated ponds.

On 8-13-86 (day 64) the ponds were visually examined. Three of the four ponds treated with simazine or copper sulfate were noticeably improved, while a fourth remained green in color. The grass carp had not consumed much of the macrophyte population, so four additional 6-8 inch grass carp were added to each pond.

By 8-26-86 (day 77), the grass carp had consumed virtually all of the macrophytes, leaving the ponds clean but more turbid than the control ponds, which appeared unchanged. The upper copper-sulfate-treated pond was nearly identical to the control pond in appearance. The lower copper-sulfate-treated pond and the simazine-treated ponds were so turbid that it could not be determined whether all of the macrophytes had been eliminated, and algal blooms were clearly evident in the simazine-treated ponds. The analytical results for samples taken 8-26-86 (day 77) are shown in Table 64. The concentrations of organic carbon and THM precursors in the treated ponds were greater than those in the control ponds, except for DOC and DTFP in the

TABLE 61

ANALYTICAL RESULTS FOR THE EXPERIMENTAL POND SAMPLES OF 6-12-86 (Day 0)

	DTFP*			TFP*		
Pond Sample	DOC mg/L	TTHM µg/L	Yield µmoles/mgC	TOC mg/L	TTHM µg/L	Yield µmoles/mgC
Control (1-1)	6.1	274	0.36	6.1	319	0.42
Control (2-3)	6.0	300	0.40	6.4	382	0.49
$CuSO_4$ (1-3)	6.2	278	0.36	6.3	310	0.40
$CuSO_4$ (2-4)	6.0	296	0.40	6.3	375	0.48
Simazine (1-4)	6.3	292	0.37	6.3	307	0.39
Simazine ()	6.1	313	0.41	6.5	374	0.47(B)
Grass Carp (1-2)	6.0	277	0.37	6.2	322	0.42
Grass Carp (2-1)	6.4	302	0.38	6.5	377	0.48

* All of the samples received a free chlorine dosage of 10 mg/L, which was sufficient to produce a free chlorine residual.

TABLE 62

ANALYTICAL RESULTS FOR THE EXPERIMENTAL POND SAMPLES OF 7-14-86 (Day 34)

	DTFP*			TFP*		
Pond Sample	DOC mg/L	TTHM µg/L	Yield µmoles/mgC	TOC mg/L	TTHM µg/L	Yield µmoles/mgC
Control (1-1)	5.3	181	0.27	5.3	214	0.32
Control (2-3)	5.6	199	0.28	6.0	217	0.29
$CuSO_4$ (1-3)	5.8	175	0.24	5.9	197	0.27
$CuSO_4$ (2-4)	5.9	207	0.28	6.7	243	0.29
Simazine (1-4)	5.3	185	0.28	5.4	210	0.31
Simazine ()	5.9	207	0.28(B)	6.4	240	0.30(B)
Grass Carp (1-2)	5.5	196	0.28(B)	5.6	226	0.32
Grass Carp (2-1)	5.9	205	0.28(B)	5.8	219	0.30

* All of the samples received a free chlorine dosage of 10 mg/L, which was sufficient to produce a free chlorine residual.

TABLE 63

ANALYTICAL RESULTS FOR THE EXPERIMENTAL POND SAMPLES OF 8-7-86 (Day 58)

Pond Sample	DOC mg/L	DTFP TTHM µg/L	DTFP Yield µmoles/mgC	TOC mg/L	TFP TTHM µg/L	TFP Yield µmoles/mgC	Chlor. a µg/L
Control (1-1)	7.7	258	0.27(B)*	7.9	352	0.36(C)	6.7
Control (2-3)	6.5	247	0.30(B)	7.0	360	0.41(C)	19.4
$CuSO_4$ (1-3)	7.1	279	0.31(B)	7.1	324	0.37(C)	31.2
$CuSO_4$ (2-4)	8.7	294	0.27(B)	9.4	336	0.29(C)	128.8
Simazine (1-4)	7.0	243	0.27(B)	8.2	315	0.31(C)	0.0
Simazine (2-2)	9.3	478	0.42(D)	14.5	772	0.44(D)	184.0
Grass Carp (1-2)	7.8	270	0.28(B)	8.1	352	0.35(C)	14.0
Grass Carp (2-1)	7.3	291	0.32(B)	7.6	380	0.40(C)	16.0

* Chlorine dosage shown in parentheses; A = 5 mg/L, B = 10 mg/L, C = 15 mg/L, D = 20 mg/L.

TABLE 64

ANALYTICAL RESULTS FOR THE EXPERIMENTAL POND SAMPLES OF 8-26-86 (Day 77)

Pond Sample	DOC mg/L	DTFP TTHM µg/L	DTFP Yield µmoles/mgC	TOC mg/L	TFP TTHM µg/L	TFP Yield µmoles/mgC	Algae cells/mL
Control (1-1)	8.4	299	0.29(B)*	8.4	371	0.36(B)	--
Control (2-3)	8.2	317	0.31(B)	8.4	402	0.39(B)	3,332
$CuSO_4$ (1-3)	9.0	385	0.35(B)	9.0	447	0.40(B)	--
$CuSO_4$ (2-4)	10.1	354	0.29(B)	10.1	419	0.34(B)	11,564
Simazine (1-4)	8.0	275	0.28(B)	10.4	526	0.41(C)	--
Simazine (2-2)	11.1	391	0.29(B)	13.5	571	0.35(C)	47,628
Grass Carp (1-2)	9.6	351	0.29(B)	9.3	406	0.35(B)	--
Grass Carp (2-1)	9.9	439	0.36(B)	10.3	447	0.35(B)	2,940

* Chlorine dosage shown in parentheses; A = 5 mg/L, B = 10 mg/L, C = 15 mg/L.

upper simazine-treated pond. Evidently, destruction of the macrophytes was resulting in the release of small but significant amounts of organic matter into the water. Algal counts for the lower pond samples supported the visual observation that an algal bloom had occurred in the lower simazine-treated pond, and high numbers of algal cells were also present in the lower copper-sulfate-treated pond. Bacteria were extremely abundant in the lower control pond. On 8-27-86 (day 78), the copper-sulfate treatments were repeated, since macrophytes were still abundant in the upper copper-sulfate-treated pond.

To more closely examine the THM precursors present in the ponds on 8-26-86 (day 77), the THM concentrations in samples chlorinated at two different dosages were determined. The results are shown in Figures 14-17. As shown in Figures 14 and 15, TFP and DTFP concentrations in the treated ponds were clearly higher than those in the control ponds, with the exception of the DTFP concentration in the upper simazine-treated pond. TFP yields, however, were elevated only in the upper copper-sulfate-treated and simazine-treated ponds (Figures 16 and 17), while DTFP yields were elevated only in the upper coper-sulfate-treated pond and the lower grass-carp pond. Hence, TFP yields remained relatively constant despite the changes in TFP concentrations, indicating that DOC and TOC remained good predictors of DTFP and TFP, respectively.

The ponds were once again examined on 9-4-86 (day 86). There were still very heavy growths of macrophytes in the control ponds, and upon close observation it was determined that the leaves of the macrophytes were covered with a green layer of slime, presumably composed of algae and bacteria. No macrophytes were visible in the grass-carp ponds, but the water was turbid (dark). The upper copper-sulfate-treated pond was still very similar to the control pond in appearance. No macrophytes were observed in the lower copper-sulfate-treated pond or in the simazine-treated ponds, but all of these were quite turbid, and the simazine-treated ponds had a greenish tint indicative of an algal bloom.

Analytical results for samples taken from the ponds on 9-4-86 (day 86) are presented in Table 65. The upper grass-carp pond and all of the lower treated ponds had DOC and TOC concentrations higher than those of the control ponds. This was especially true of the lower simazine-treated and grass-carp ponds. Interestingly, all of the treated ponds had elevated concentrations of ammonium, indicating that macrophyte decomposition was also releasing nutrients into the water.

The ponds were visually examined again on 9-11-86 (day 93). Heavy growths of macrophytes were still present in the control ponds, but they appeared to be slightly decreasing in abundance. The upper copper-sulfate-treated pond was still very similar in appearance to the control ponds. No macrophytes were visible in the other treated ponds, but they were all quite turbid. The grass-carp ponds were very dark in color, while the simazine-treated ponds and the lower copper-sulfate-treated pond had a light green color. The copper-sulfate treatments were repeated once again.

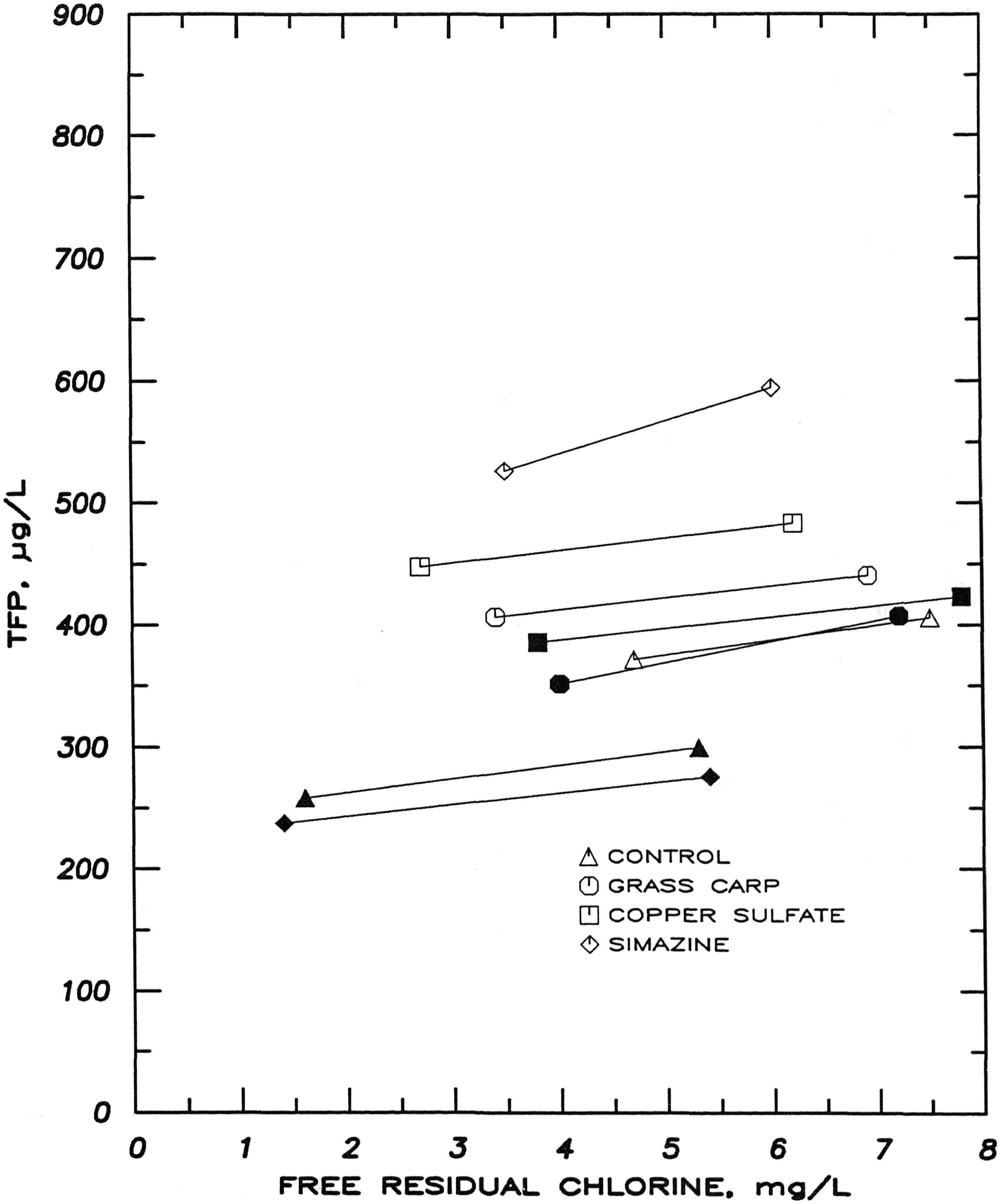

FIGURE 14: TFP CONCENTRATIONS IN THE UPPER PONDS ON 8-26-86
(Solid symbols represent DTFP)

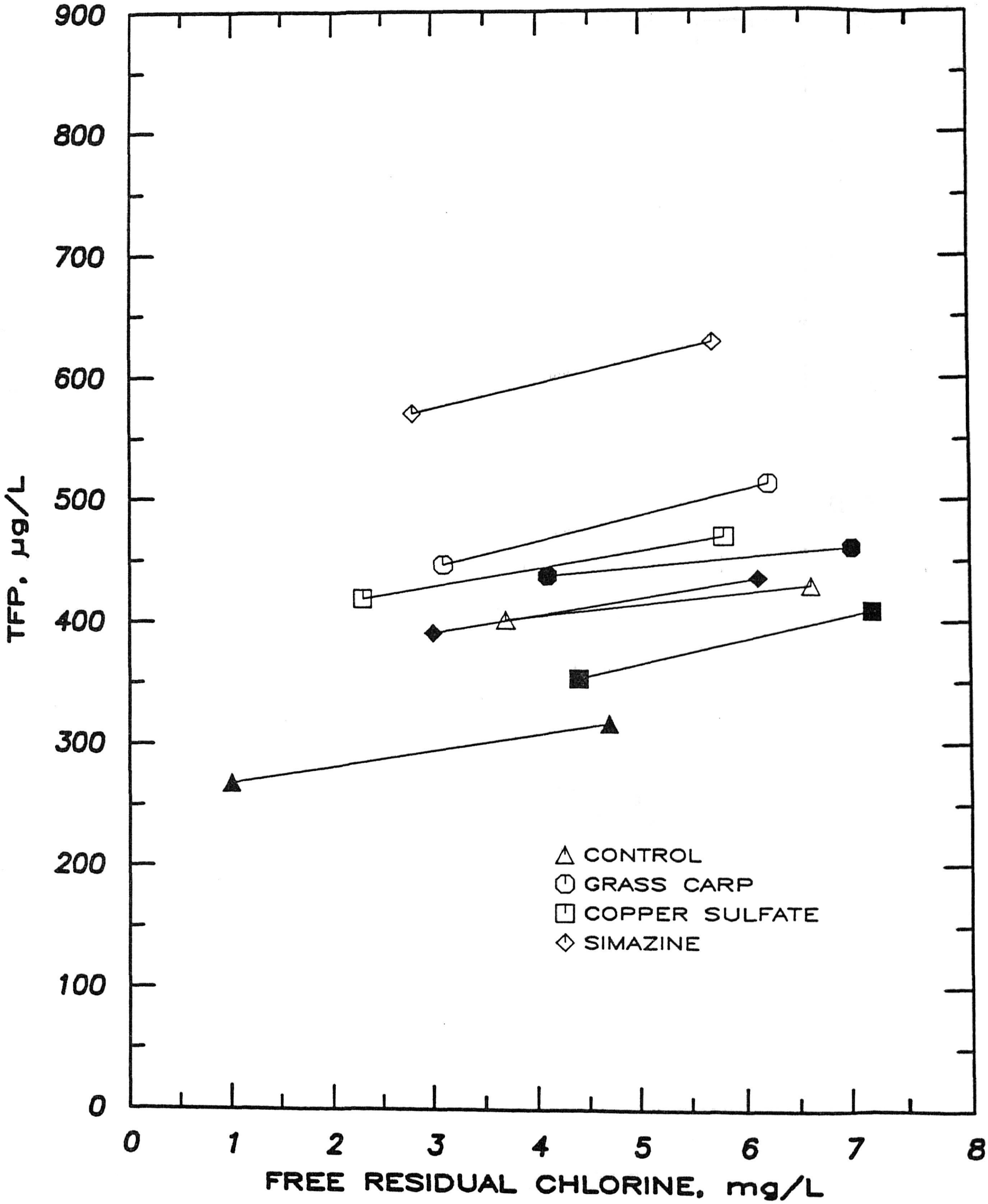

FIGURE 15: TFP CONCENTRATIONS IN THE LOWER PONDS ON 8-26-86
(Solid symbols represent DTFP)

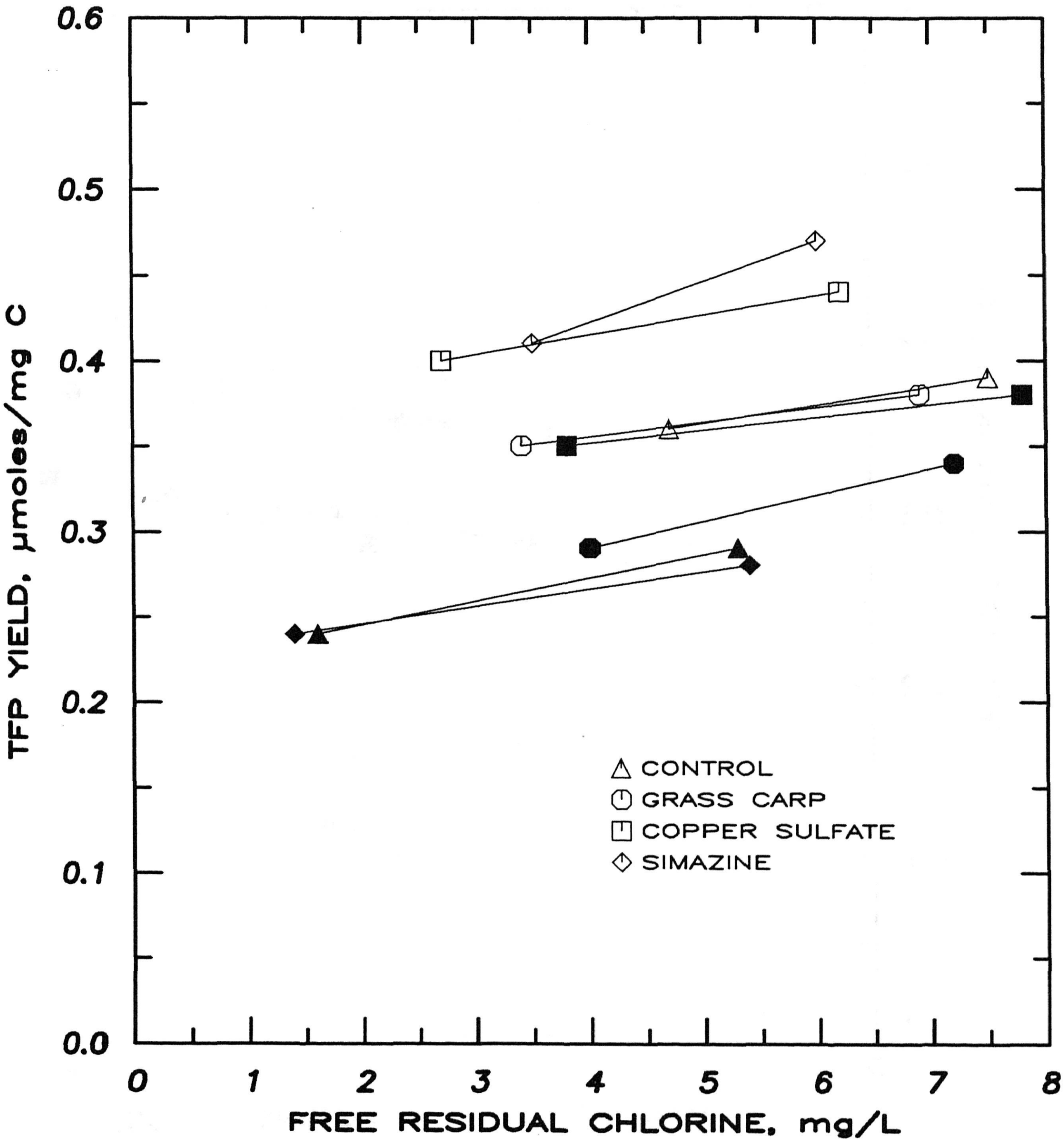

FIGURE 16: TFP YIELDS IN THE UPPER PONDS ON 8-26-86
(Solid symbols represent DTFP)

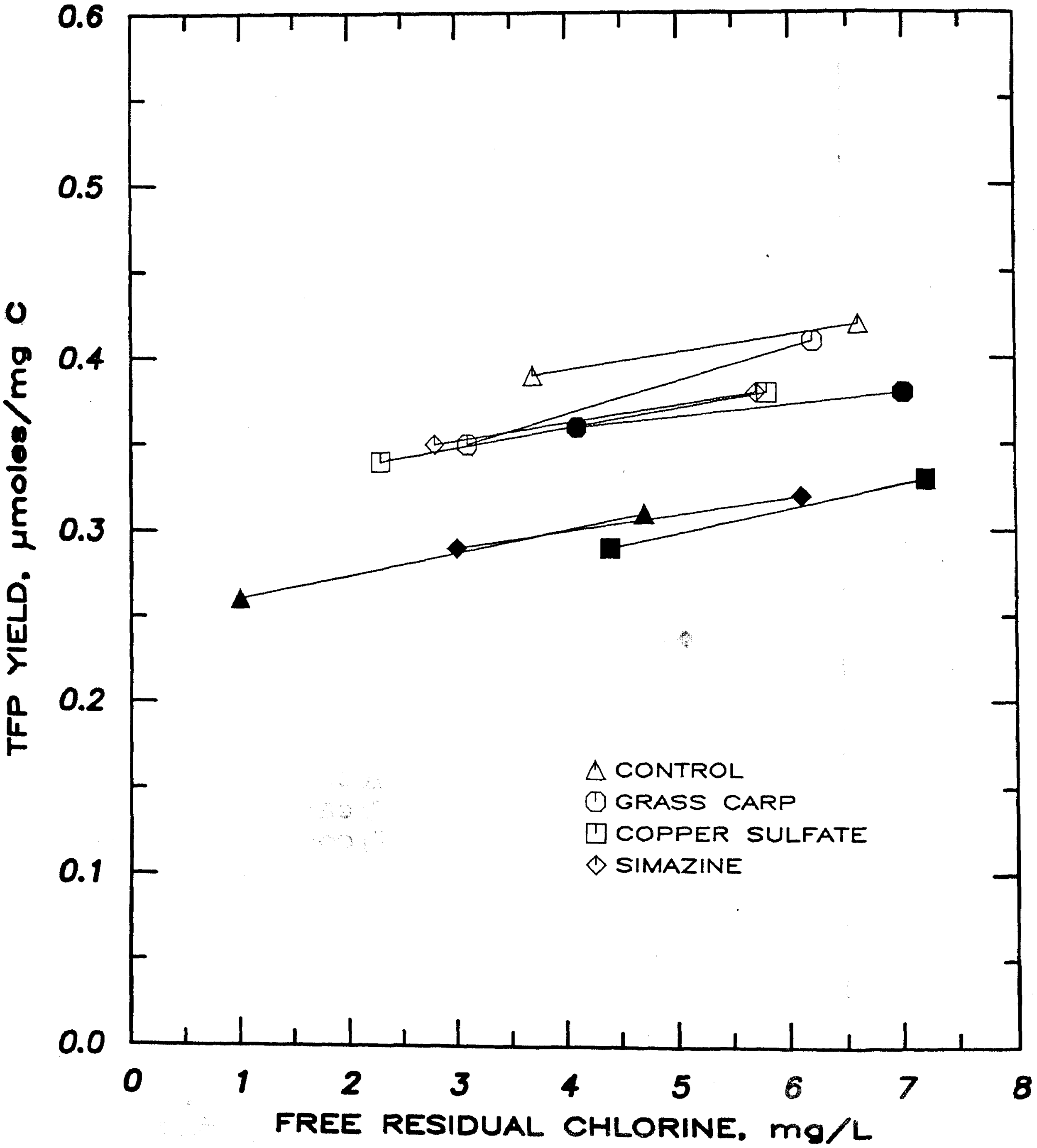

FIGURE 17: TFP YIELDS IN THE LOWER PONDS ON 8-26-86
(Solid symbols represent DTFP)

TABLE 65

ANALYTICAL RESULTS FOR THE EXPERIMENTAL POND SAMPLES OF 9-4-86 (Day 86)

Pond Sample	DOC mg/L	TOC mg/L	Nitrate-N µg/L	Ammonium-N mg/L
Control (1-1)	8.9	9.4	0.00	0.01
Control (2-3)	8.0	8.7	0.06	0.01
$CuSO_4$ (1-3)	8.5	9.6	0.00	0.03
$CuSO_4$ (2-4)	9.4	10.6	0.00	0.05
Simazine (1-4)	8.4	9.2	0.00	0.20
Simazine (2-2)	12.0	13.5	0.00	0.10
Grass Carp (1-2)	9.7	10.4	0.00	0.27
Grass Carp (2-1)	10.9	12.3	0.00	0.13

Note: A sample taken from the control pond after gentle shaking of some macrophytes near the point of sampling was found to contain 147 µg/L of chlorophyll and 330 µg/L of pheophytin a.

On 9-18-86 (day 100), it was evident that the macrophyte population in each of the control ponds was clearly declining. The upper control pond was very turbid, and macrophytes were visible only in the shallow areas of the pond. Filamentous algae were very abundant in the lower control pond. The upper copper-sulfate-treated pond was also very turbid, similar to the upper control pond; and although no macrophytes were visible (due to the turbidity), hand inspection revealed that they were still abundant. The remaining ponds were also turbid, most having a slight green color. The grass-carp ponds were darker than the others, while the lower copper-sulfate-treated pond had a brownish color.

The analtyical results for the samples taken on 9-18-86 (day 100) are shown in Table 66. Among the upper ponds, the control pond had the highest DOC concentration and the second highest TOC concentration, presumably due to the release of organic matter associated with macrophyte senescence; but the control pond had the lowest concentration of DTFP and the second lowest concentration of TFP. Hence, the organic materials released into the control pond were relatively poor THM precursors. Among the lower ponds, the control pond had the highest concentrations of TOC and TFP, the lowest concentration of DTFP, and the second lowest concentration of DOC. Macrophyte senescence in the control ponds and the copper-sulfate-treated ponds appeared to have stimulated the algal blooms evidenced by the very high concentrations of chlorophyll a in the ponds. Elevated concentrations of ammonium-N were found in the grass-carp ponds and the lower simazine-treated pond.

The algal populations were examined only in the samples from the lower ponds. The cell counts are shown in Table 66. A massive bloom of very small edible algae was clearly evident in the sample from the lower copper-sulfate treated pond. The other ponds all had relatively low numbers of planktonic algae. The very high concentration of chlorophyll a in the lower control pond is attributable to the filamentous algae visually observed to be present in the sample analyzed for chlorophyll a. The filamentous algae were apparently clumped, since none were found in the sample preserved for counting. The number of bacteria present in the lower control pond was much higher than in the other ponds. A comparison of the samples of 8-26-86 with those of 9-18-86 shows: 1) a major species shift in the copper-sulfate-treated and simazine-treated ponds, due in the latter case to a great decline in the populations of three species dominant on 8-26-86; 2) a major increase in the population of small edible algae in the copper-sulfate-treated pond; 3) a substantial decline in the population of algae in the simazine-treated pond; and 4) no significant changes in the control pond or the grass-carp pond.

The THM precursors present in the ponds on 9-18-86 were more closely examined by determining the THM concentrations in samples having two different concentrations of free residual chlorine. The results are shown in Figures 18-21. Among the upper ponds, the grass-carp pond and the copper-sulfate-treated pond had elevated DTFP and TFP concentrations relative to the control pond and the simazine-treated pond (Figure 18). Among the lower ponds, the control pond had the lowest concentration of DTFP

TABLE 66

ANALYTICAL RESULTS FOR THE EXPERIMENTAL POND SAMPLES OF 9-18-86 (Day 100)

Pond Sample	DOC mg/L	DTFP TTHM µg/L	DTFP Yield µmoles/mgC	TOC mg/L	TFP TTHM µg/L	TFP Yield µmoles/mgC	Chlor. a µg/L
Control (1-1)	9.3	318	0.27(B)*	9.2	407	0.36(C)	166.1
Control (2-3)	8.7	327	0.30(B)	14.7	777	0.44(D)**	346.6
$CuSO_4$ (1-3)	7.7	388	0.41(C)	10.4	485	0.38(D)	126.2
$CuSO_4$ (2-4)	7.3	374	0.41(C)	9.7	474	0.40(C)	83.1
Simazine (1-4)	6.8	331	0.39(C)	7.7	372	0.39(C)	20.1
Simazine (2-2)	10.3	368	0.29(C)	10.9	456	0.34(D)	23.8
Grass Carp (1-2)	9.0	400	0.36(C)	8.5	445	0.43(C)	52.6
Grass Carp (2-1)	8.9	399	0.37(C)	9.4	407	0.36(C)	9.2

* Chlorine dosage shown in parentheses following yield; A = 5 mg/L, B = 10 mg/L, etc.

** This sample was diluted 50% prior to chlorination.

Pond Sample	NH_4-N mg/L	NO_3-N mg/L	Algae cells/mL
Control (1-1)	<0.02	0.03	--
Control (2-3)	<0.02	<0.01	4,900
$CuSO_4$ (1-3)	<0.02	<0.01	--
$CuSO_4$ (2-4)	<0.02	<0.01	194,922
Simazine (1-4)	<0.02	0.08	--
Simazine (2-2)	0.25	<0.01	5,242
Grass Carp (1-2)	0.15	<0.01	--
Grass Carp (2-1)	0.14	0.03	4,900

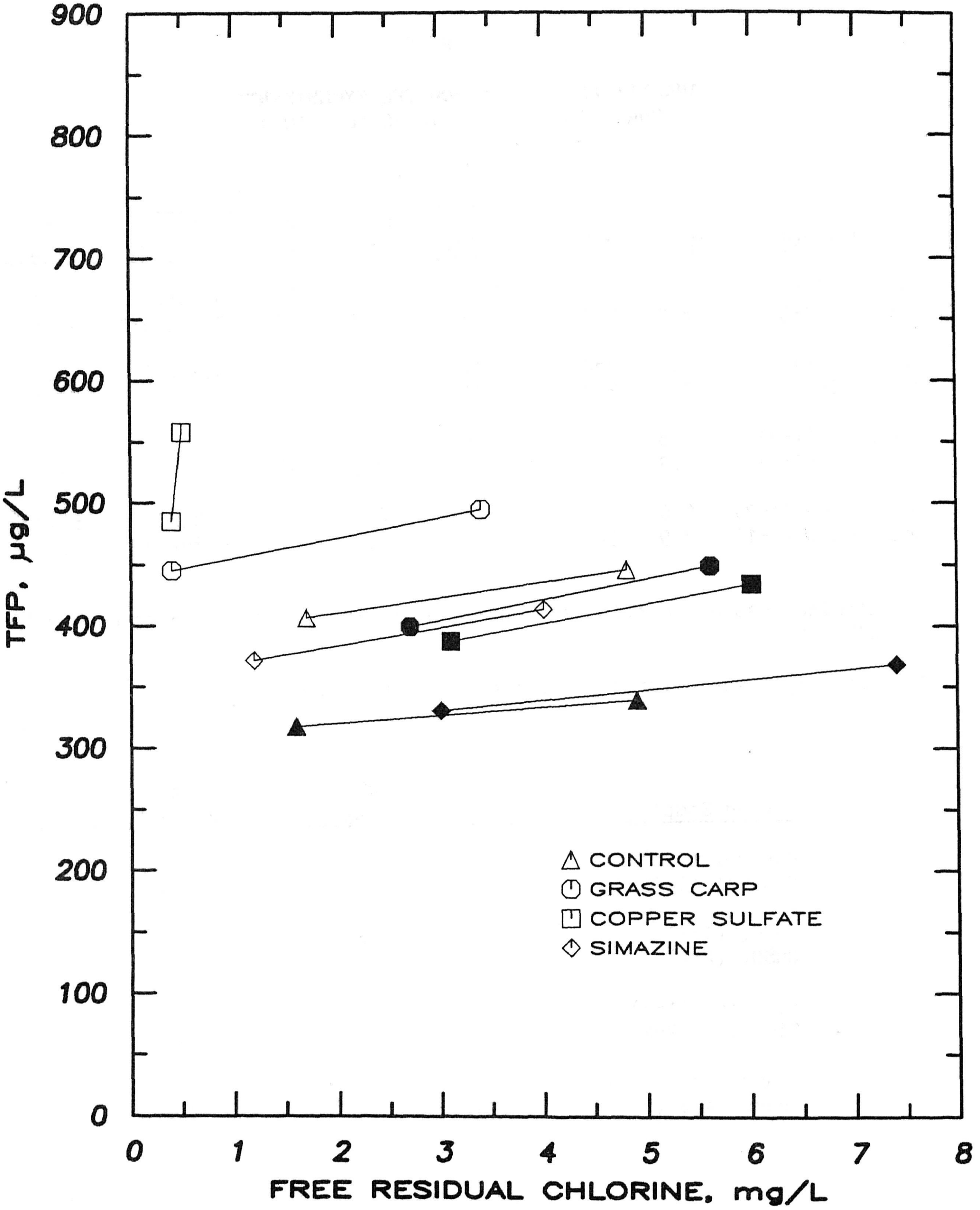

FIGURE 18: TFP CONCENTRATIONS IN THE UPPER PONDS ON 9-18-86
(Solid symbols represent DTFP)

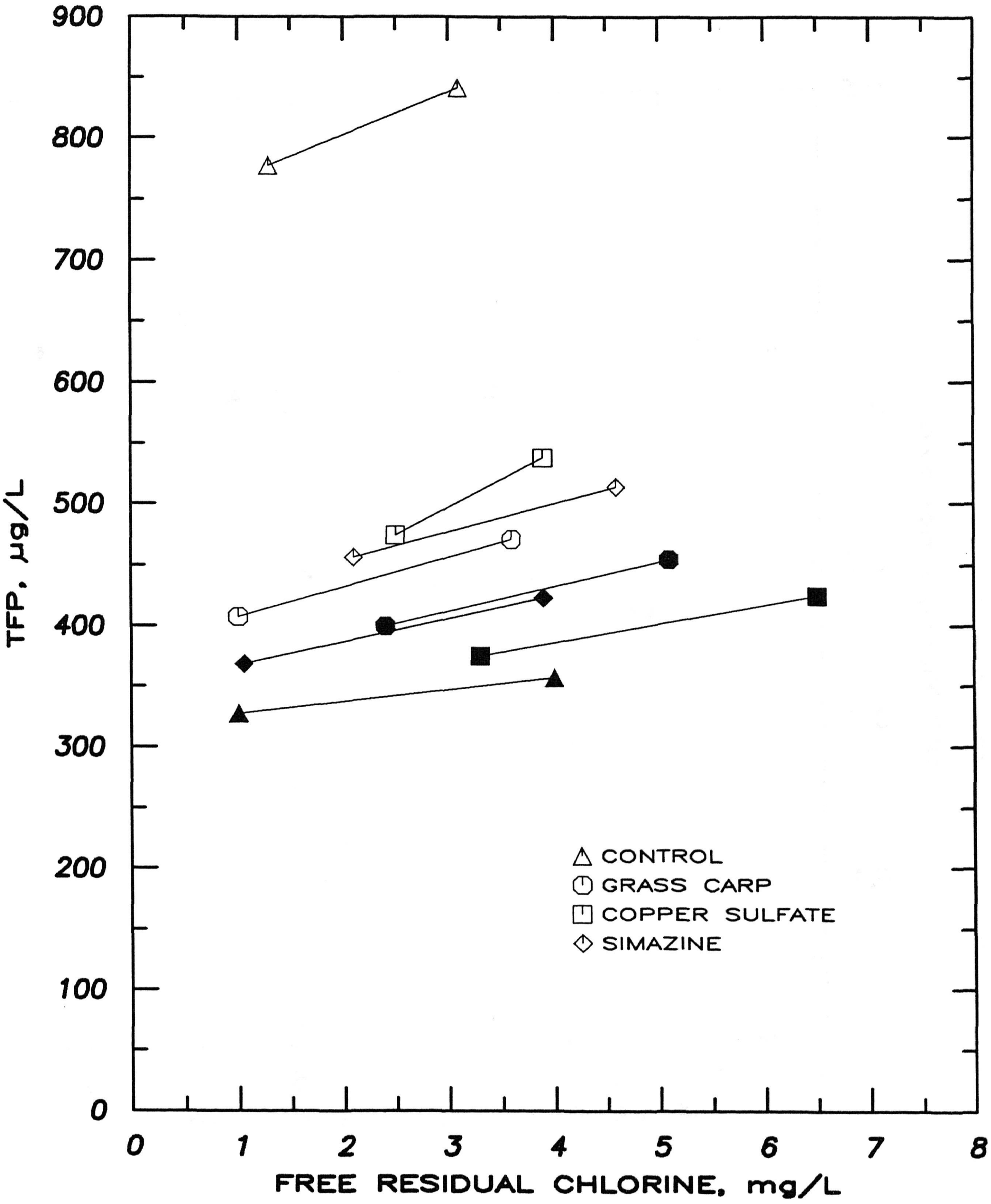

FIGURE 19: TFP CONCENTRATIONS IN THE LOWER PONDS ON 9-18-86
(Solid symbols represent DTFP)

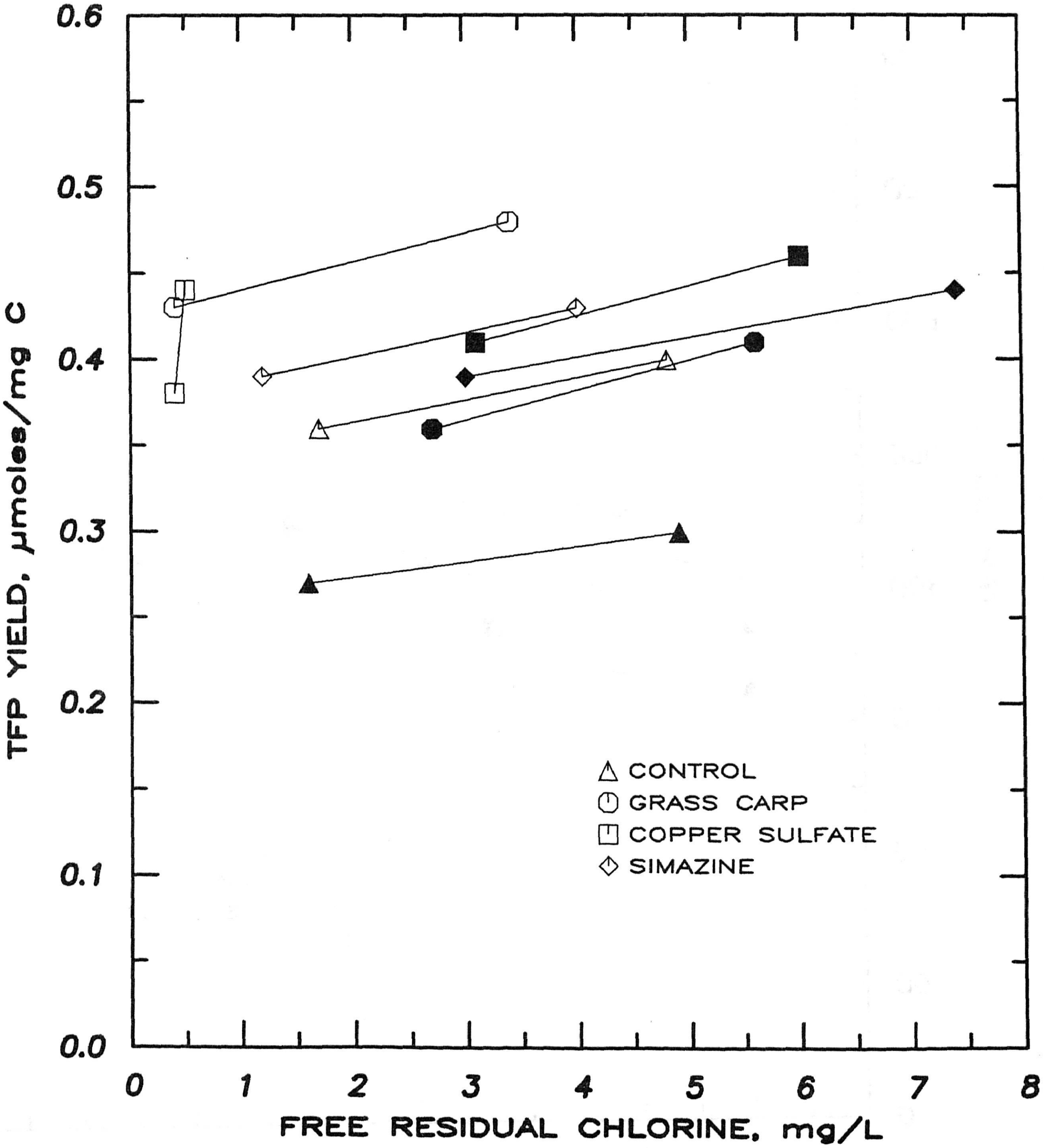

FIGURE 20: TFP YIELDS IN THE UPPER PONDS ON 9-18-86
(Solid symbols represent DTFP)

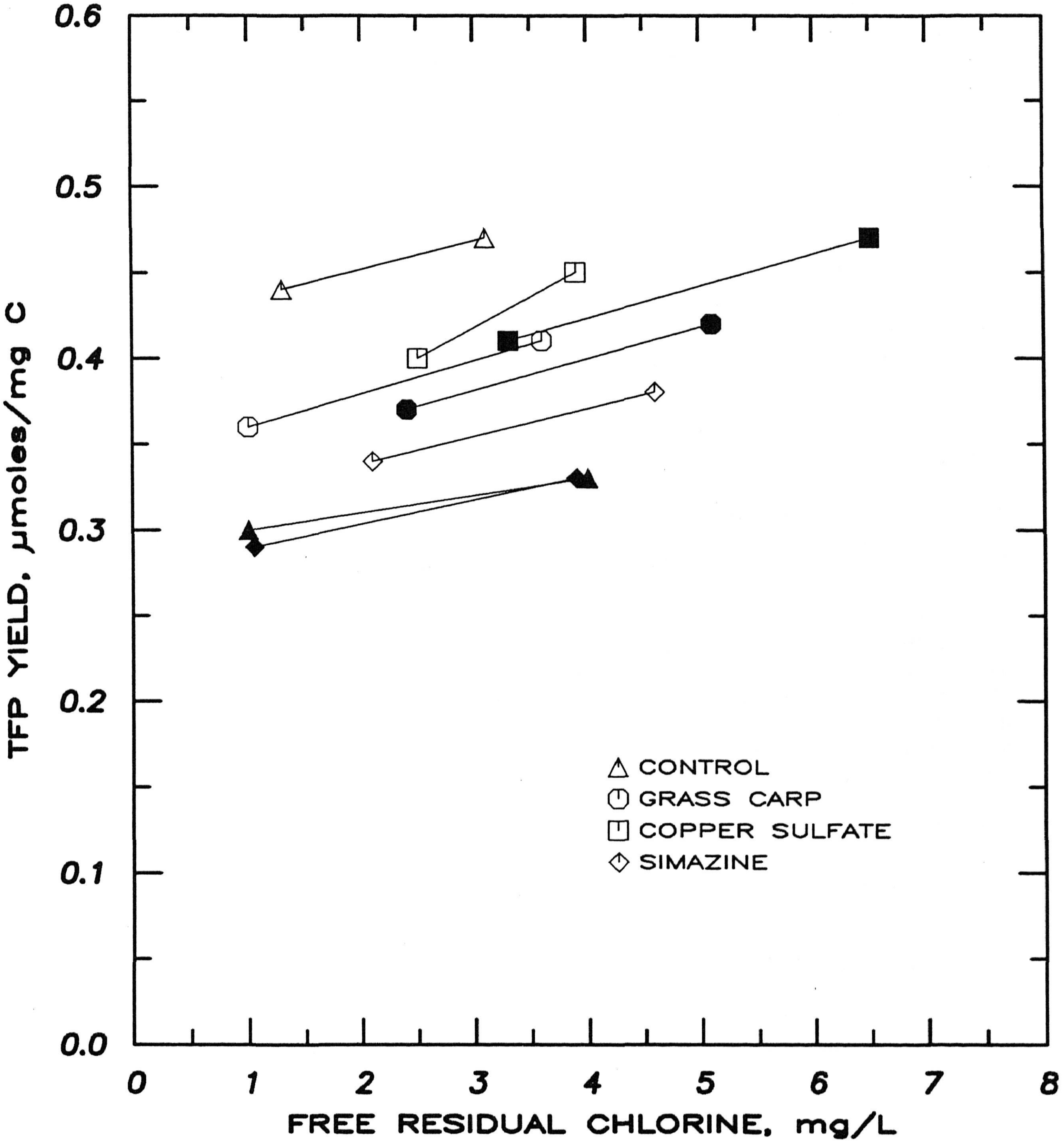

FIGURE 21: TFP YIELDS IN THE LOWER PONDS ON 9-18-86
(Solid symbols represent DTFP)

and the highest concentration of TFP (Figure 19). The TFP concentration in the lower control pond sample was much greater than in any of the other samples, perhaps due to the presence of the filamentous algae. Samples from the upper treated ponds produced higher yields of DTFP and TFP than the upper control pond (Figure 20), while samples from the lower treated ponds produced lower concentrations of TFP than the control pond. However, the DTFP yield was very low in the lower control pond, so it appears that the filamentous algae in the lower control pond sample may be responsible for the anomalous TFP results.

Heavy rains fell on September 19, 23, 24, 27, 29, and 30, as well as on October 1, 3 and 12, of 1986 (see Appendix A). Total rainfall in Lawrence for the month of September was 12.29 inches, 8.35 inches above normal. On 10-9-86 (day 121), the water level in the ponds was found to be about 4 inches over the top of the dividing walls. By 10-16-86 (day 128), the water had dropped below the top of the dividing walls in the lower ponds but not in the upper ponds. The ponds were noticeably clearer than on 8-26-86. A few dead stems could be seen on the bottoms of the control ponds and the copper-sulfate-treated ponds, but the other ponds were all very clean. Samples were taken from the lower ponds, and the analytical results are shown in Table 67. The DOC and TOC concentrations had decreased slightly, perhaps due to dilution by rainfall, and the control pond had the lowest level of chlorophyll a. Thus the bloom of filamentous algae observed in the lower control pond on 9-18-86 appears to have been quite transient.

By 10-20-86, the water level had also dropped below the top of the dividing walls in the upper ponds. On 10-30-86 (day 142) the ponds were visually inspected and found to be relatively clean and clear, except for the grass-carp ponds, which were turbid (especially the upper one). Dead weed stems were still visible in the upper copper-sulfate-treated pond. Analytical results for samples taken 10-30-86 are shown in Table 68. The results were very similar for all of the ponds, except that the upper treated ponds had slightly higher concentrations of TOC than the upper control pond.

Figures 22-25 illustrate the temporal variations in DOC and TOC in the ponds over the course of the experiment. The upper ponds exhibited remarkably similar trends in the concentrations of DOC and TOC (Figures 22 and 23), although the concentration of DOC in the control pond reached its peak later than in the treated ponds. There were more pronounced differences in the lower ponds (Figures 24 and 25), where increases in DOC and TOC in the control pond clearly lagged behind those in the other ponds. It appears that the treatments caused a premature release of organic matter that would eventually have been released as the weeds senesced.

Despite the many differences among the ponds during the course of the experiment they were, by the end of the experiment, all remarkably similar in regard to their appearance and water quality. The grass-carp ponds were slightly more turbid; and the control ponds generally had slightly lower concentrations of TFP and DTFP, perhaps due to the relatively rapid macrophyte senescence at the end of the season. Perhaps the most important

TABLE 67

ANALYTICAL RESULTS FOR THE EXPERIMENTAL POND SAMPLES OF 10-16-86 (Day 128)

Pond Sample	DOC mg/L	TOC mg/L	Chlorophyll a μg/L	Pheophytin a μg/L
Control (2-3)	7.4	7.9	3.1	0.7
$CuSO_4$ (2-4)	7.3	9.7	14.5	34.0
Simazine (2-2)	7.4	8.9	9.5	23.1
Grass Carp (2-1)	7.4	9.4	6.1	8.8

TABLE 68

ANALYTICAL RESULTS FOR THE EXPERIMENTAL POND SAMPLES OF 10-30-86 (Day 142)

Pond Sample	DOC mg/L	TOC mg/L	Nitrate-N μg/L	Ammonium-N mg/L	Chlor. a μg/L
Control (1-1)	6.7	6.9	0.00	0.10	0.0
Control (2-3)	7.2	8.6	0.00	0.01	11.6
$CuSO_4$ (1-3)	7.4	7.5	0.00	0.11	0.0
$CuSO_4$ (2-4)	7.6	8.5	0.00	0.05	3.6
Simazine (1-4)	6.5	8.0	0.00	0.07	2.7
Simazine (2-2)	7.4	8.1	0.03	0.06	0.0
Grass Carp (1-2)	6.5	9.1	0.08	0.08	1.4
Grass Carp (2-1)	7.6	8.2	0.00	0.03	1.1

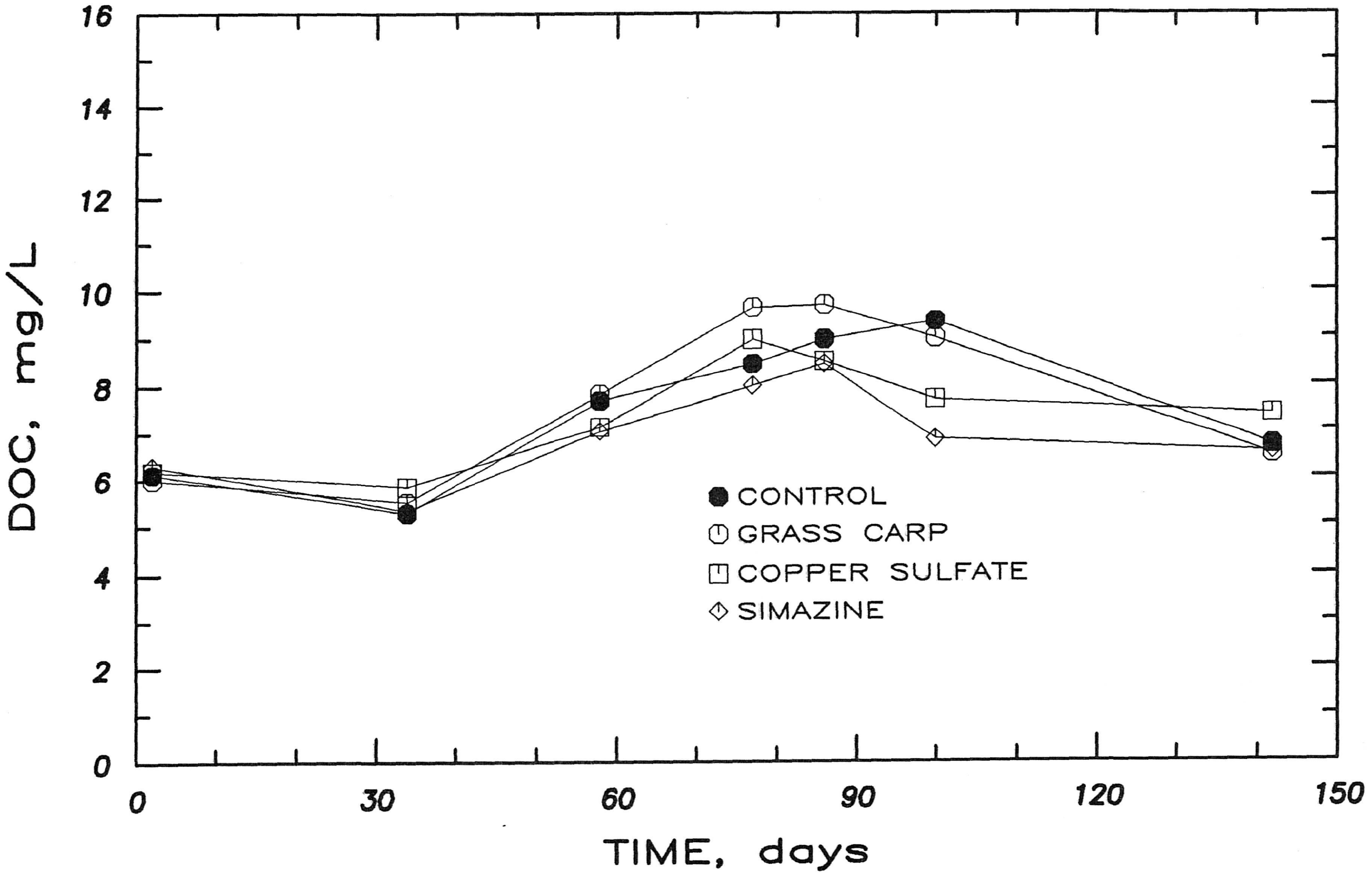

FIGURE 22: TEMPORAL VARIATIONS IN DOC IN THE UPPER PONDS

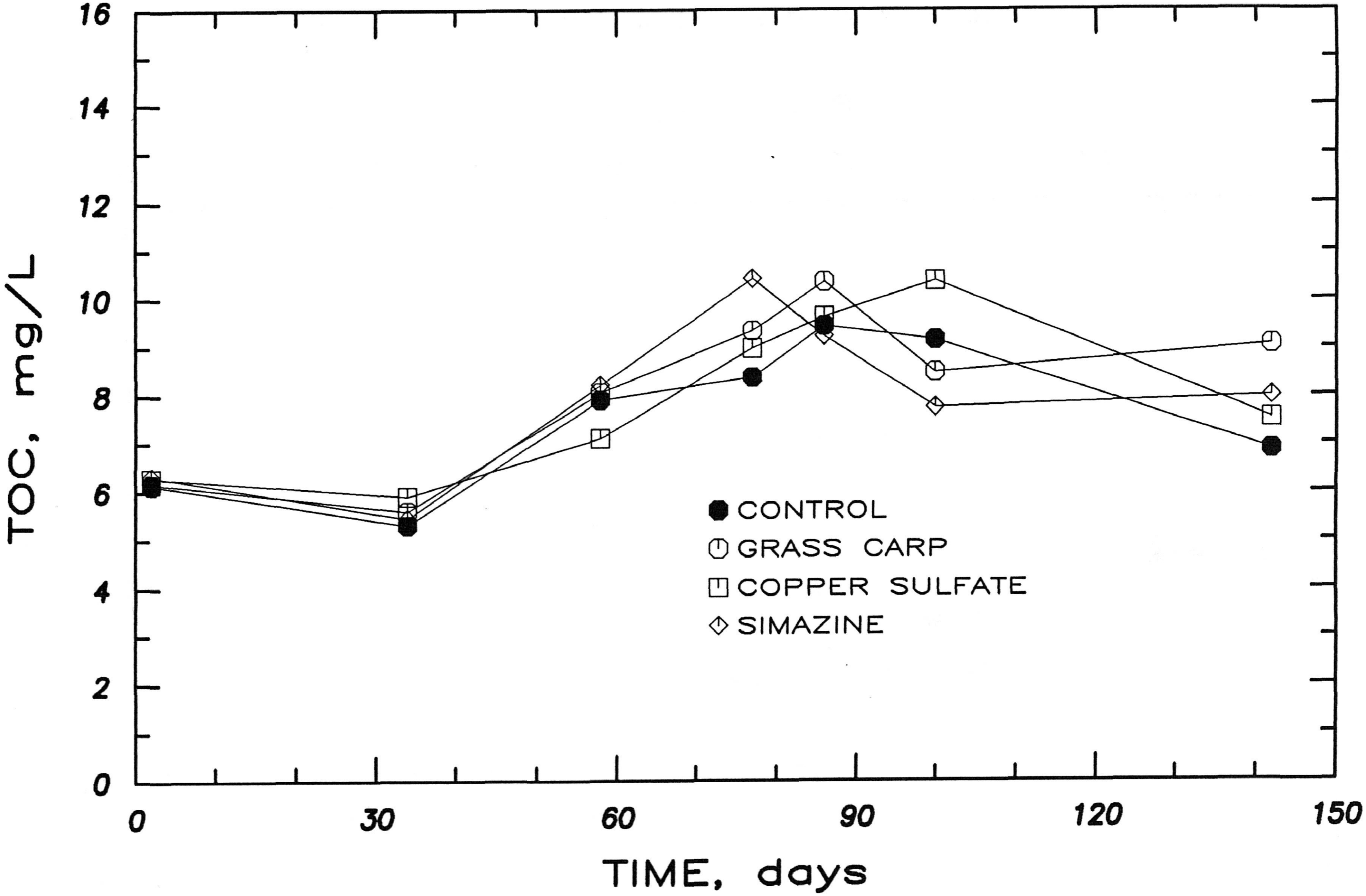

FIGURE 23: TEMPORAL VARIATIONS IN TOC IN THE UPPER PONDS

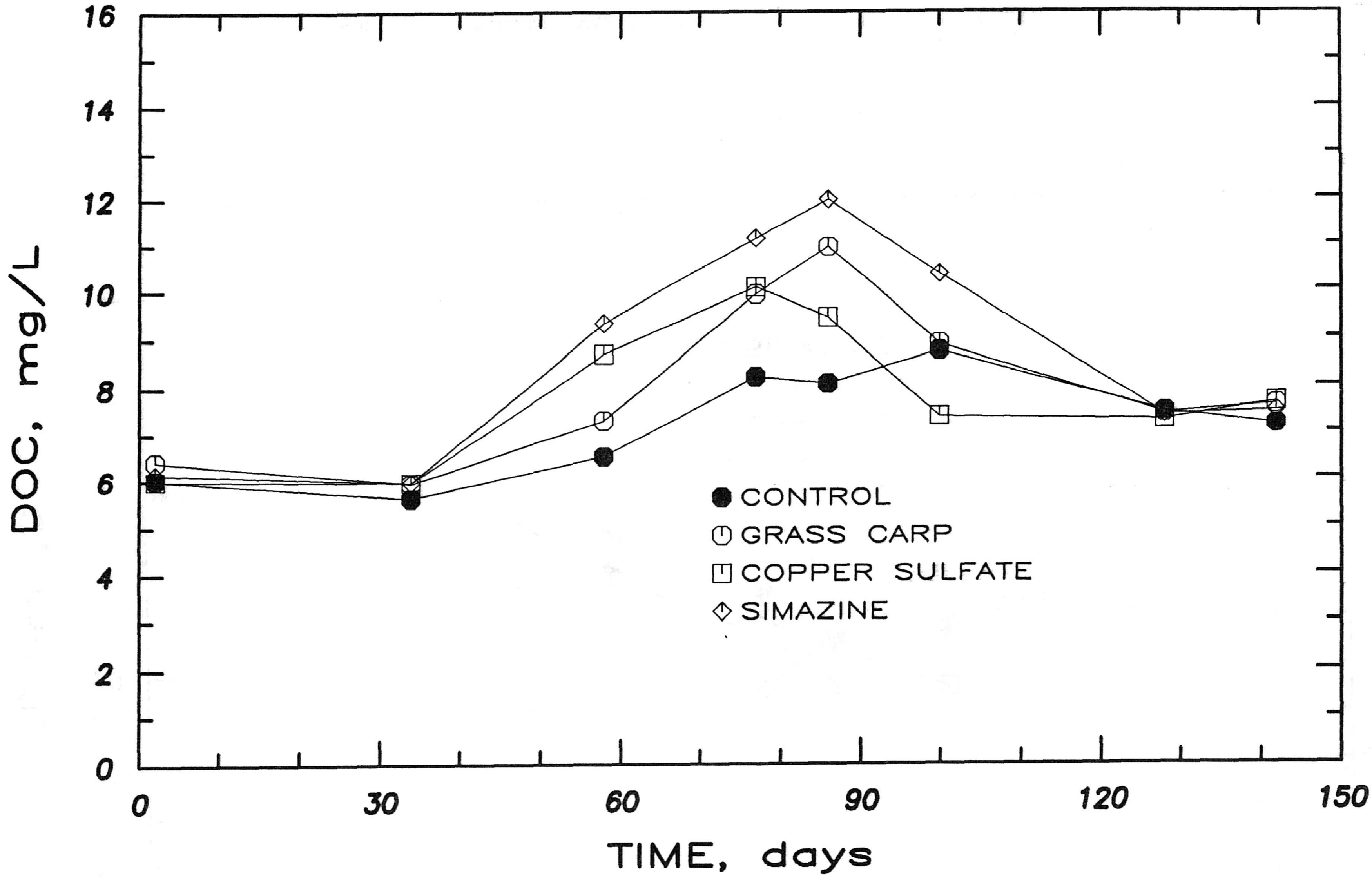

FIGURE 24: TEMPORAL VARIATIONS IN DOC IN THE LOWER PONDS

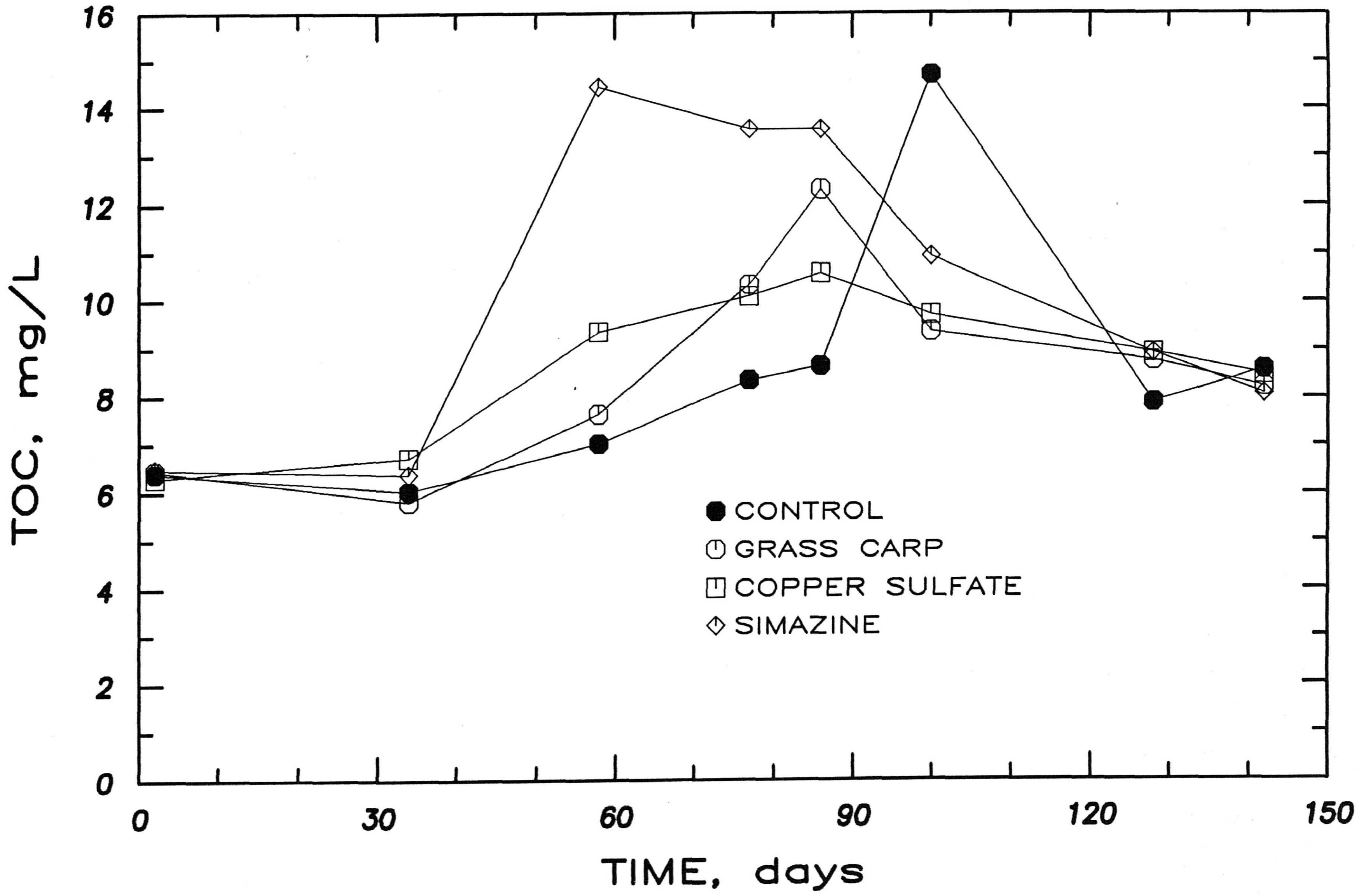

FIGURE 25: TEMPORAL VARIATIONS IN TOC IN THE LOWER PONDS

conclusion to be drawn from this data is that the treatments in the lower ponds did influence organic carbon and THM precursor concentrations. Thus it may be possible to exert a significant degree of control over the concentrations of THM precursors in lakes infested with macrophytes or algae. Further research is needed in this area.

E. LABORATORY EXPERIMENTS

Two sets of laboratory experiments were conducted to assess the release of THM precursors and organic carbon from selected substrates under aerobic and anaerobic conditions, and also to assess the biodegradability of precursors from several sources. The experimental procedures are described in Sampling Sites and Procedures (E. Laboratory Experiments), and the results of each set of experiments (designated no. 1 and no. 2) are discussed separately below.

Laboratory Experiment No. 1

The data for the first experiment are presented in Tables 69 and 70. Under aerobic conditions, the DOC of the lake water rose slightly, with fluctuations in concentration. Whether this was due to contamination (dirty air, leaching of organic matter from the tubing, etc.) or to biological activity is not known. Although nothing can be concluded from these data regarding the biodegradability of the THM precursors in the lake water, it can be concluded from these data and from the data for other samples (soil extract, secondary effluent, river water) that gross contamination did not occur and that the large DOC concentrations in other sample bottles were truly leached from the materials added.

The pine needles, twigs, and branches leached substantial amounts of DOC and color into the water, and a thick gelatinous slime, similar to that observed on the weeds in several of the lakes during the fall (see A. Lakes), formed on them. The concentrations of DOC fluctuated, perhaps as a result of bacterial population dynamics. The aquatic weeds and filamentous algae released less DOC than the pine substrates; but the DOC concentrations were still rising after 40 days, and these materials appeared to remain alive for a long period of time (despite being kept in the dark).

A small amount of DOC was released from the activated sludge (Table 69), but the concentration was low and variable. The DOC of the secondary effluent varied somewhat, but appeared to increase slightly over the last 30 days of the experiment, perhaps due to the occurrence of nitrification. The DOC of the soil extract was increased slightly by addition of the bacterial seed, but then remained unchanged for 10 days. The DOC of the river water also appeared to remain unchanged, but sample evaporation and possibly contamination occurred. Although the data for these samples are somewhat in question, it would appear that the precursors in these samples were not readily biodegradable.

Under anaerobic conditions (Table 70), the pine needles, filamentous algae, and aquatic weeds released large amounts of DOC, more than under aerobic conditions; and the DOC concentration for the pine needles was still increasing after 40 days. The DOC concentration of the lake water (control) remained low, but increased slightly, perhaps due to leaching of a small amount of TOC from the rubber stopper or latex tubing.

TABLE 69

DOC AND DTFP DATA FOR THE AEROBIC SAMPLES IN LABORATORY EXPERIMENT NO. 1

	Day 0				DOC, mg/L					DTFP[1], Day 40	
	TOC	DTFP		DOC							
Sample Description	mg/L	µg/L	µmol/mgC	mg/L	Day 3	Day 10	Day 20	Day 30	Day 40	µg/L	µmol/mgC
Lake water	5.0	219	0.39	4.5	5.0	4.5	6.1	5.8	7.3	--	--
Christmas tree											
Pine needles(25 gm/L)[2]	-	-	-	4.5	169	207	274	343	315	9,877	0.24
Pine twigs(25 gm/L)	-	-	-	4.5	228	170	176	166	171	7,890	0.30
Pine branches(25 gm/L)	-	-	-	4.5	127	152	186	176	138	3,788	0.20
Fresh pine needles(25 gm/L)	-	-	-	4.5	258	313	279	228	216	22,523	0.70
Fallen pine needles(25 gm/L)	-	-	-	4.5	67.6	95.4	146	156	111	5,964	0.38
Filtamentous algae(75 gm/L)	-	-	-	4.5	9.0	11.6	18.5	27.6	40.6	5,662	0.99
Aquatic Weeds #1(34 gm/L)	-	-	-	4.5	20.9	13.9	17.2	17.1	19.2	1,299	0.59
Aquatic Weeds #2(62 gm/L)	-	-	-	4.5	8.7	19.3	27.3	24.3	34.1	3,306	0.61
Aquatic Weeds #3(16 gm/L)	-	-	-	4.5	5.7	6.2	10.0	13.3	21.1	1,993	0.67
Lake scum (10%)	25.8	139	0.50	2.3	2.9	2.8	3.7	2.8	3.3	--	--
Secondary Effluent	8.8	287	0.28	8.2	8.6	7.7	9.0	9.4	10.9	--	--
Activated sludge (10%)	114	74.3	0.36	1.7	18.9	4.0	5.9	6.2	7.1	--[3]	--[3]
Soil extract	-	447	0.27	14.0	15.6[4]	15.6	-[6]	-	-	--	--
River water	48.0	372	0.42	7.3	8.5[5]	7.3	-[6]	-	-	--	--

[1] Estimated by linear regression for a free residual chlorine concentration of 3.0 mg/L.

[2] The weights shown are for wet/undried material.

[3] No free chlorine remained, presumably due to an excess of ammonium released during decomposition.

[4] The increase since day zero is presumed to be due to the DOC of the seed.

[5] The increase since day zero was due to evaporation; the sample was subsequently diluted to raise the water level to the correct position.

[6] These smaller samples were lost due to freezing caused by malfunction of the controller on Day 11.

TABLE 70

DOC DATA FOR THE ANAEROBIC SAMPLES IN LABORATORY EXPERIMENT NO. 1

Sample Description	Concentration	DOC, mg/L					
		Day 0	Day 3	Day 10	Day 20	Day 30	Day 40
Lake water (control)	100%	4.49	5.95	6.16	6.55	7.10	7.10
Pine needles(Christmas tree)	32 gm/L	-	278	490	740	891	1008
Filamentous algae	110 gm/L	-	97.0	248	442	488	283
Aquatic weeds #1	53 gm/L	-	282	462	588	613	476
Aquatic weeds #2	84 gm/L	-	488	942	1261	1233	675
Aquatic weeds #3	26 gm/L	-	67.7	163	234	297	264
Secondary effluent	100%	8.17	8.17	8.91	9.22	10.1	9.7
Activated sludge	10%	1.68	15.6	19.0	14.5	10.9	12.5

How much of the DOC from the pine substances, algae and weeds was biodegradable is not known; and it is conceivable that natural biocides were also leached into the water, suppressing biological growth. The residual solids were not weighed, but visual observations indicated very little loss of material. Therefore, these substances may have continued to release precursors for a long period of time.

The DTFP yields of several of these samples were determined after they had incubated for 40 days. DTFP concentrations were not determined for the samples lost by freezing; and no free chlorine remained in some of the samples (including several of the anaerobic samples), presumably due to the presence of high concentrations of ammonium. The partial results in Table 69 indicate that the organic matter released from several of the substrates was a good source of THM precursors, with some of the yields exceeding those typically found in natural water samples. These results were interesting enough that it was decided to run a second experiment (discussed below).

Laboratory Experiment No. 2

The second experiment focused on the release of DOC and DTFP from dried vegetation upon its immersion in lake water under aerobic and anaerobic conditions. The same concentration, 4.00 gm/L, of each substrate was added in each case, so that the results would be more comparable among the different substrates. The analytical data are shown in Tables 71 and 72.

By day 7, the water in contact with all of the substrates was visibly darker in color and all of the anaerobic samples had a strong sulfide odor except sample 5, which still had a noticeable pine odor. The samples all became darker in color with time, but the aerobic samples became much darker in color than the anaerobic samples. Throughout the incubation period the anaerobic samples contained few solids and were relatively easy to filter, while a number of the aerobic samples were extremely difficult to filter (especially samples 5, 6, 12, 15, and 23) and some foamed excessively during filtration. The pH values of the aerobic samples remained relatively unchanged, while those of the anaerobic samples decreased to the range of 5-6.

By day 28, the DOC concentrations were reasonably stable, although still decreasing slightly in a number of aerobic samples and increasing slightly in some of the anaerobic samples. The opposing trend is readily explained by the fact that anaerobic bacteria grow more slowly than aerobic bacteria and are unable to reduce substrate concentrations as low due to the decreased amount of energy available to them. On day 28, the incubation period was ended, and the samples were analyzed for DOC, DTFP, pH, UV absorbance (UVA), and color (absorbance at 400 mm). To reduce the chlorine demand of the anaerobic samples, they were acidified to pH 2.5 with concentrated H_3PO_4, purged to remove H_2S, and then adjusted to a pH of 8.2 for DTFP analysis. Surprisingly, the substrates removed from the water on day 28 appeared to have remained almost entirely intact, showing little or no sign of decay. Hence, the DOC concentrations may have increased a great deal more had the substrates been left to incubate for an extended period of time.

TABLE 71

ANALYTICAL DATA FOR THE AEROBIC SAMPLES IN LABORATORY EXPERIMENT NO. 2

Samp. No.	Sample Description	DOC, mg/L				Day 28			DTFP[1] on Day 28	
		Day 7	Day 14	Day 21	Day 28	pH	UVA	Color	µg/L	µmol/mg C
1	Fresh pine needles	65.4	24.0	13.8	11.8	8.3	0.217	0.069	797	0.56
2	Fresh pine twigs	22.7	15.2	14.1	15.4	8.3	0.264	0.082	1,170	0.63
3	Fallen pine needles	40.0	28.8	31.2	35.8	8.2	0.487	0.129	2,216	0.52
4	Fallen pine twigs	37.5	25.6	23.6	24.0	8.4	0.365	0.089	1,583	0.55
5	Pine needles, NBS	421	235	219	206	7.9	3.095	1.150	11,158	0.45
6	Citrus leaves, NBS	464	137	113	86.6	8.8	2.005	0.595	3,939	0.38
7	Ash leaves	388	230	183	142	8.2	2.665	0.935	9,548	0.56
8	Red oak leaves	202	101	85.9	84.5	8.2	1.825	0.800	8,337	0.83
9	Cottonwood leaves	109	71.6	51.3	47.2	8.5	1.405	0.435	4,511	0.80
10	Elm leaves	390	118	85.4	63.2	8.7	1.865	0.715	6,564	0.87
11	Sycamore leaves	291	156	143	140	8.2	3.605	1.960	18,357	1.10
12	Pagoda tree blossoms	560	239	185	157	8.5	3.615	3.295	12,987	0.69
13	Aquatic weed stems	46.7	33.4	26.6	23.0	8.3	0.810	0.300	3,747	1.36
14	Cattail head	22.4	24.3	24.0	26.7	8.5	0.685	0.175	2,294	0.71
15	Hackberry wood[2]	206	203	211	201	8.5	3.535	0.750	14,571	0.61
16	Hackberry bark	27.1	26.5	28.8	30.1	8.7	0.712	0.171	2,606	0.72
17	Hackberry stump	90.7	73.2	64.8	54.5	8.5	0.950	0.178	10,394	1.60
18	Hackberry twigs	31.2	25.9	23.6	23.1	8.5	0.800	0.218	4,658	1.68
19	Ground cattail head	115	50.4	37.2	32.0	8.3	0.764	0.205	3,055	0.79
20	Ground cattail stem	184	106	94.6	92.8	8.5	2.080	0.595	8,233	0.74
21	Dried cow manure	80.7	85.4	69.1	62.6	8.6	1.695	0.554	5,145	0.69
22	Periphytic algae	28.2	17.7	12.6	11.6	8.5	0.211	0.048	618	0.43
23	Grass clippings	167	75.2	57.6	57.9	8.2	1.775	0.485	4,570	0.66
24	Lake water[3]	3.4	3.4	3.3	3.3	8.4	0.034	0.005	200	0.48

[1] Estimated at a free residual chlorine concentration of 3.0 mg/L.

[2] Taken from a rotting area of a hackberry stump.

[3] DOC = 3.6 mg/L on day 0; used as dilution water for the other samples.

TABLE 72

ANALYTICAL DATA FOR THE ANAEROBIC SAMPLES IN LABORATORY EXPERIMENT NO. 2

Samp.		DOC, mg/L				Day 28			DTFP[1] on Day 28	
No.	Sample Description	Day 7	Day 14	Day 21	Day 28	pH	UVA	Color	µg/L	µmol/mg C
1	Fresh pine needles	57.1	76.8	60.2	60.1	6.6	0.179	0.026	1,829	0.25
2	Fresh pine twigs	55.1	74.0	80.2	72.5	6.6	0.402	0.066	3,626	0.42
3	Fallen pine needles	65.7	98.8	107	116	6.4	0.318	0.068	3,333	0.24
4	Fallen pine twigs	47.5	60.2	60.9	64.0	6.6	0.333	0.052	1,924	0.25
5	Pine needles, NBS	440	434	431	433	5.6	1.700	0.417	13,829	0.27
6	Citrus leaves, NBS	553	569	573	630	5.3	1.700	0.370	10,525	0.14
7	Red oak leaves	181	206	214	234	5.9	1.920	0.530	7,789	0.28
8	Cottonwood leaves	149	198	215	230	6.4	1.010	0.261	5,195	0.19
9	Lake water (control)	3.9	3.6	3.9	4.7	7.2	0.054	0.011	193	0.33

[1] Estimated at a free residual chlorine concentration of 3.0 mg/L.

So that the DTFP concentrations would be more directly comparable, a series of samples for each substrate was chlorinated. The chlorine dosages ranged from 5 to 40 mg/L in 5 mg/L increments, and the three samples having the lowest free chlorine residuals greater than 0.2 mg/L were extracted. The data, included in Appendix B, were then used to estimate the DTFP concentration at a free residual chlorine concentration of 3.0 mg/L. This was done using a reciprocal regression model or a linear regression model, depending upon which gave the best fit for each data set.

Even as the samples were being analyzed, it was clearly evident that the aerobic samples, despite having lower DOC concentrations than the anaerobic samples, had more color, adsorbed more UV light, and produced a higher yield of THMs. This is borne out by the averages presented in Table 73, especially for those substrates incubated under both anaerobic and anaerobic conditions. These data indicate that although DOC concentrations tend to be higher under anaerobic conditions, TFP yields are higher under aerobic conditions. Two possible reasons for this are: 1) some of the organic matter in the anaerobic samples may have been carbohydrate-like material (non-colored, biodegradable) that was a very poor precursor material and that was degraded in the aerobic samples; and 2) the presence of oxygen in the aerobic samples appear to have promoted "browning" reactions which may have resulted in structural changes more conducive to THM formation.

Although the very high DTFP concentrations stand out in comparison to those for the lake and stream samples, the DOC concentrations are also quite high. However, the yields of TFP for the aerobic samples were, on the average, much higher than those of the lake, stream, pond, soil, runoff, and point-source samples, and higher than most yields reported in the literature (see "Related Research"). These high yields clearly identify aerobic decomposition of both aquatic and terrestrial plant matter as an important source of relatively potent THM precursors. Interestingly, the three samples having the highest DTFP yields were the hackberry twigs, hackberry stump, and aquatic weed stems, all of which were taken from aquatic environments. The cattail head and ground cattail head and stems also produced high yields in comparison to other samples, including lake water and dried periphytic algae. The yield for the lake water sample was slightly higher than normal, but entirely reasonable for a fall (September) sample.

The linear regression correlation coefficients for various correlations examined are shown in Table 74. As expected based on previous research, the concentration of DTFP was strongly correlated with DOC for both the aerobic and the anaerobic samples; but the correlation for all samples combined was weaker due to the much lower THM yield of the anaerobic samples. Hence, DOC was a good predictor of DTFP for samples from similar environments.

Interestingly, DTFP concentration correlated more strongly with UVA than with DOC (Table 74). A plot of DTFP vs UVA (Figure 26) shows some scatter about the regression line, but considering the diversity of the samples the fit is noteworthy. The outliers farthest above the regression line correspond to the hackberry stump, the aerobic sycamore leaves, and the

TABLE 73

SUMMARY OF AVERAGES FOR CONSTITUENTS DETERMINED IN LABORATORY EXPERIMENT NO. 2

Parameter	Aerobic Samples	Anaerobic Samples	Aerobic Samples Corresponding to the Anaerobic Samples
DOC, mg/L	68.0	204.9	57.2
DTFP, μg/L	5886	5360	3768
DTFP, μmoles/mgC	0.767	0.263	0.578
UVA	1.478	0.846	1.077
Color	0.581	0.200	0.373
UVA/DOC	0.0224	0.0052	0.0182
Color/DOC	0.0075	0.0011	0.0057

TABLE 74

DATA CORRELATIONS FOR LABORATORY EXPERIMENT NO. 2

Correlation	Linear Regression Correlation Coefficient All Samples	Aerobic Samples	Anaerobic Samples
DTFP vs DOC	0.608	0.865	0.892
Yield vs DOC	-0.388	-0.150	-0.612
DOC vs UVA	0.432	0.945	0.834
DTFP Conc. vs UVA	0.879	0.908	0.903
DTFP Yield vs UVA	0.118	-0.042	-0.340
Color vs UVA	0.827	0.822	0.990
DOC vs Color	0.228	0.712	0.756
DTFP Conc. vs Color	0.702	0.751	0.858
DTFP Yield vs Color	0.148	-0.011	-0.355
DTFP Conc. vs UVA/DOC	0.046	0.060	-0.347
DTFP Yield vs UVA/DOC	0.752	0.557	0.521
DTFP Conc. vs Color/DOC	0.334	0.451	-0.105
DTFP Yield vs Color DOC	0.570	0.302	0.345

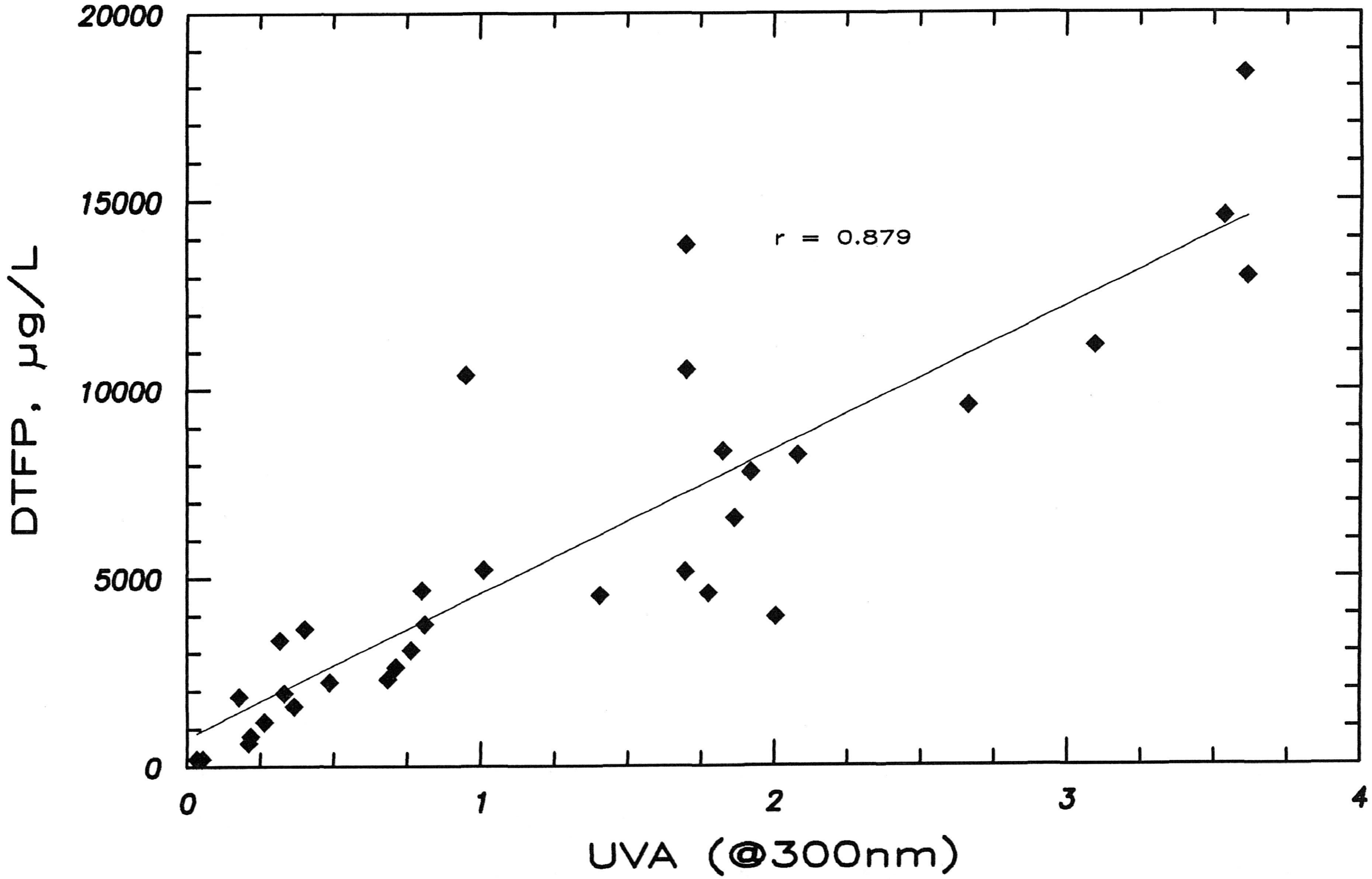

FIGURE 26: DTFP VS UVA FOR AEROBIC AND ANAEROBIC SAMPLES

anaerobic pine needles and citrus leaves; the outlier farthest below the regression line corresponds to the aerobic citrus-leaf sample. The strong correlation between DOC and UVA for the aerobic samples (Table 74 and Figure 27), in addition to the strong correlation between DTFP and UVA, indicates that UVA might be a useful surrogate for examining the release of THM precursors by vegetation.

DTFP and DOC also correlated quite well with color, although not as well as they did as with UVA. Figure 28 shows the relationship between DTFP and color for the aerobic samples. The two outliers farthest above the regression line corresponds to the hackberry stump and rotting hackberry wood, while the outlier farthest below the regression line corresponds to the pagoda tree blossoms, which were bright yellow in color and imparted a great deal more color to the water, relative to DOC, than the other samples.

As reported by Edzwald et al. (1985), waters having a high proportion of humic materials exhibit a higher ratio of UVA to DOC. Since increased humification has also been found, at least by some investigators, to be associated with increased THM yields, this suggests that THM yields might increase as the ratio of UVA to DOC increases. This was indeed the case in this experiment, as shown in Table 74 and Figure 29. The correlation is not particularly strong ($r = 0.752$); but it is considerably improved (to $r = 0.854$) by exclusion of the highest outlier, the hackberry stump sample, and the trend of the data is clear.

The average amount of DOC released from the substrates under aerobic conditions, 68 mg/L, represents 1.7% of the initial substrate mass (about 3.5% of the initial mass of carbon), while 5% of the substrate mass was released as DOC under anaerobic conditions. While these percentages are small, the amounts of organic carbon and THM precursors released are indeed very substantial.

If 2% of the mass of a precursor material is converted to DOC, and if the DTFP yield of the released material is assumed to be only 0.42 µmoles/mgC, then adding 0.05 gm of solid precursor material to a liter of water will increase the DTFP concentration by 50 µg/L, a very significant amount relative to the current standard of 100 µg/L and the lower standards being considered.

For Douglas Lake, 0.05 gm/L represents only about one ton per acre, assuming that the lake is an average of 15 feet deep. One ton per acre is roughly equal to the mass of weeds that might grow annually in a typical lake of moderate turbidity. It is also similar in magnitude to the mass of timber and brush that might be left standing in a lake to improve fish habitat or the mass of trees that might be used to construct fish attractors in a small lake. Hence, materials releasing as much organic matter as was released from the pine substrates in this study could cause a significant increase in the concentration of THM precursors in a lake. While lakes are flowing systems, and some amount of dilution will therefore occur, continued release of precursors is also expected to occur, since these materials decompose very slowly.

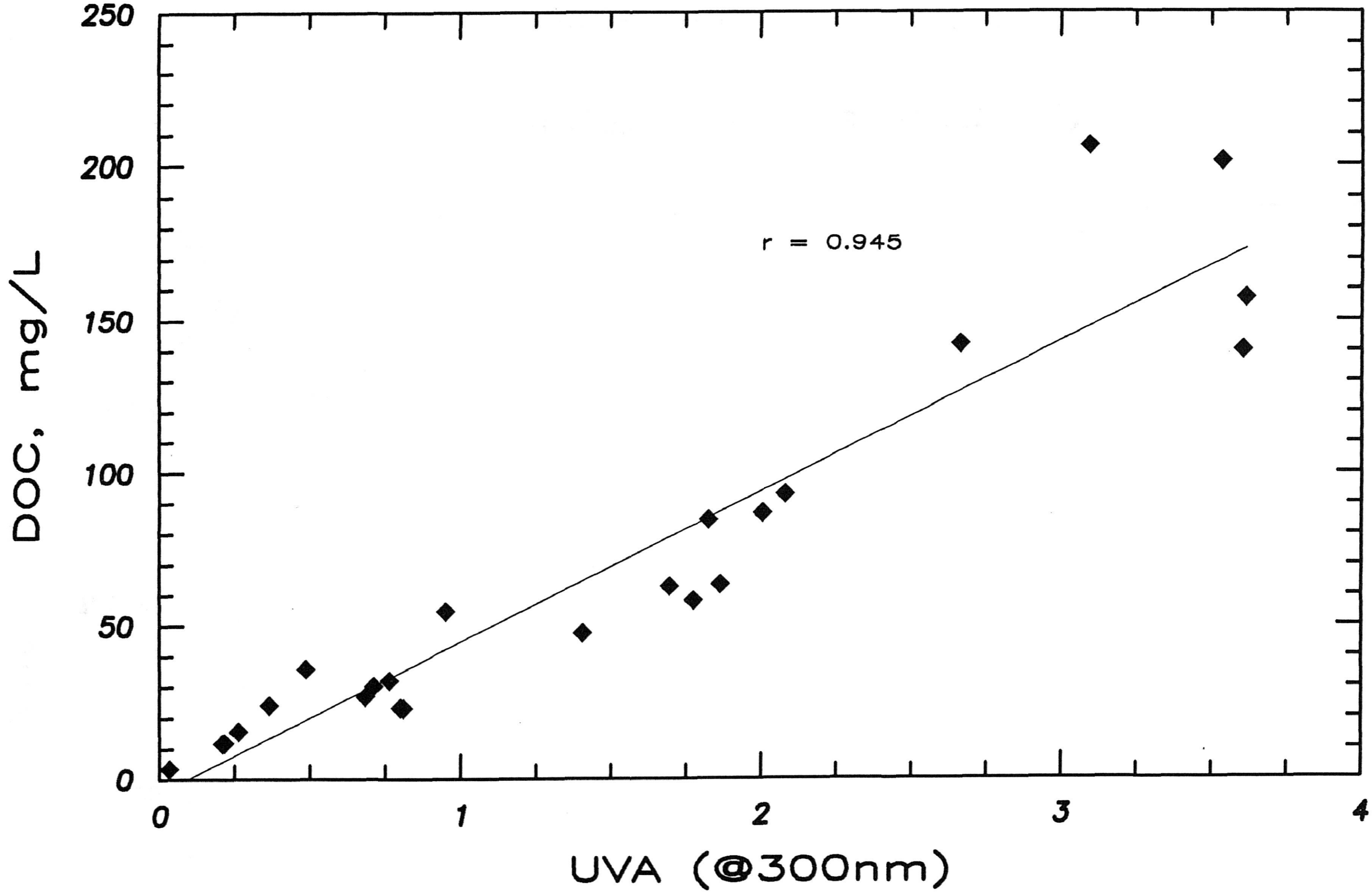

FIGURE 27: DOC VS UVA FOR THE AEROBIC SAMPLES

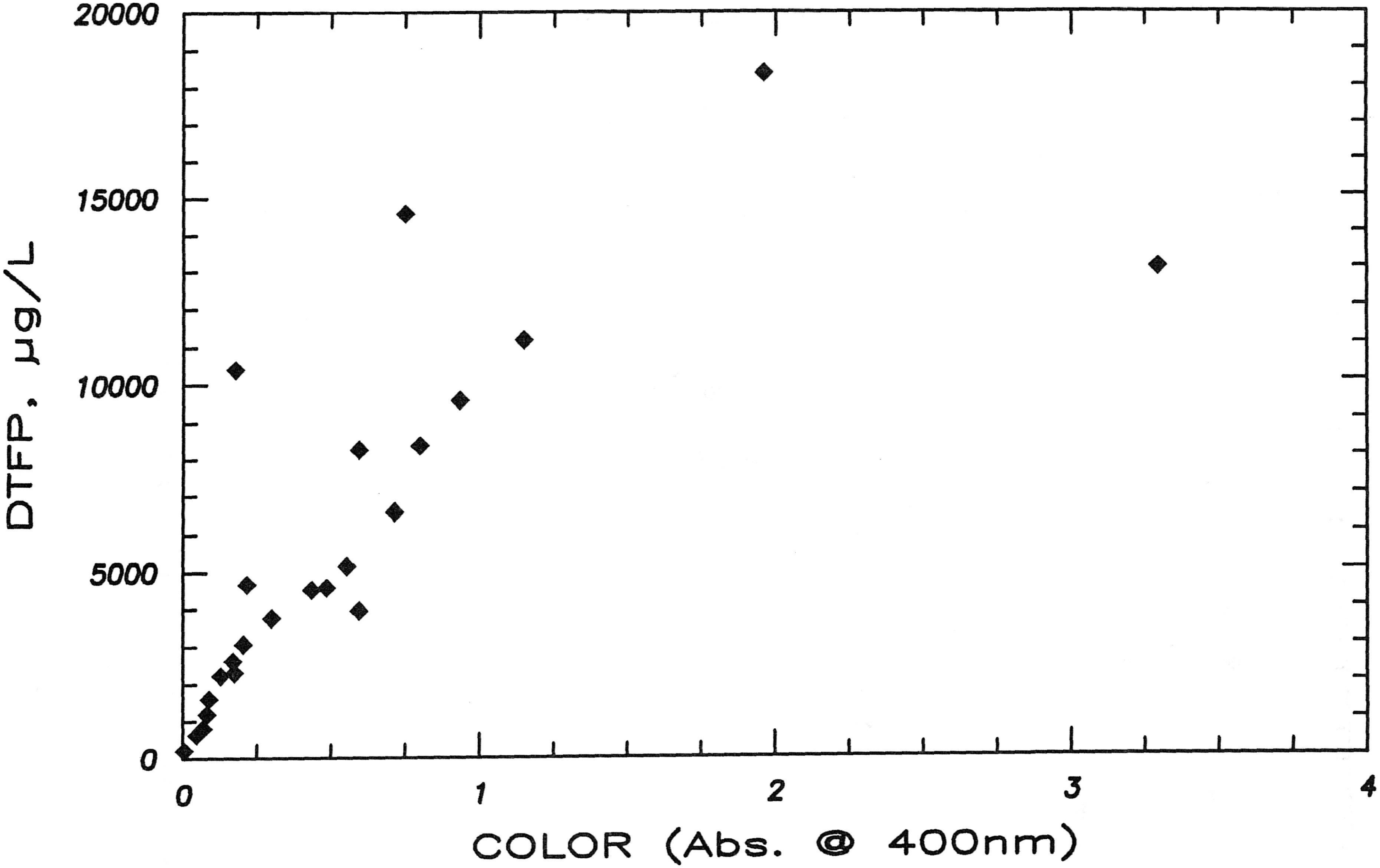

FIGURE 28: DTFP VS COLOR FOR THE AEROBIC SAMPLES

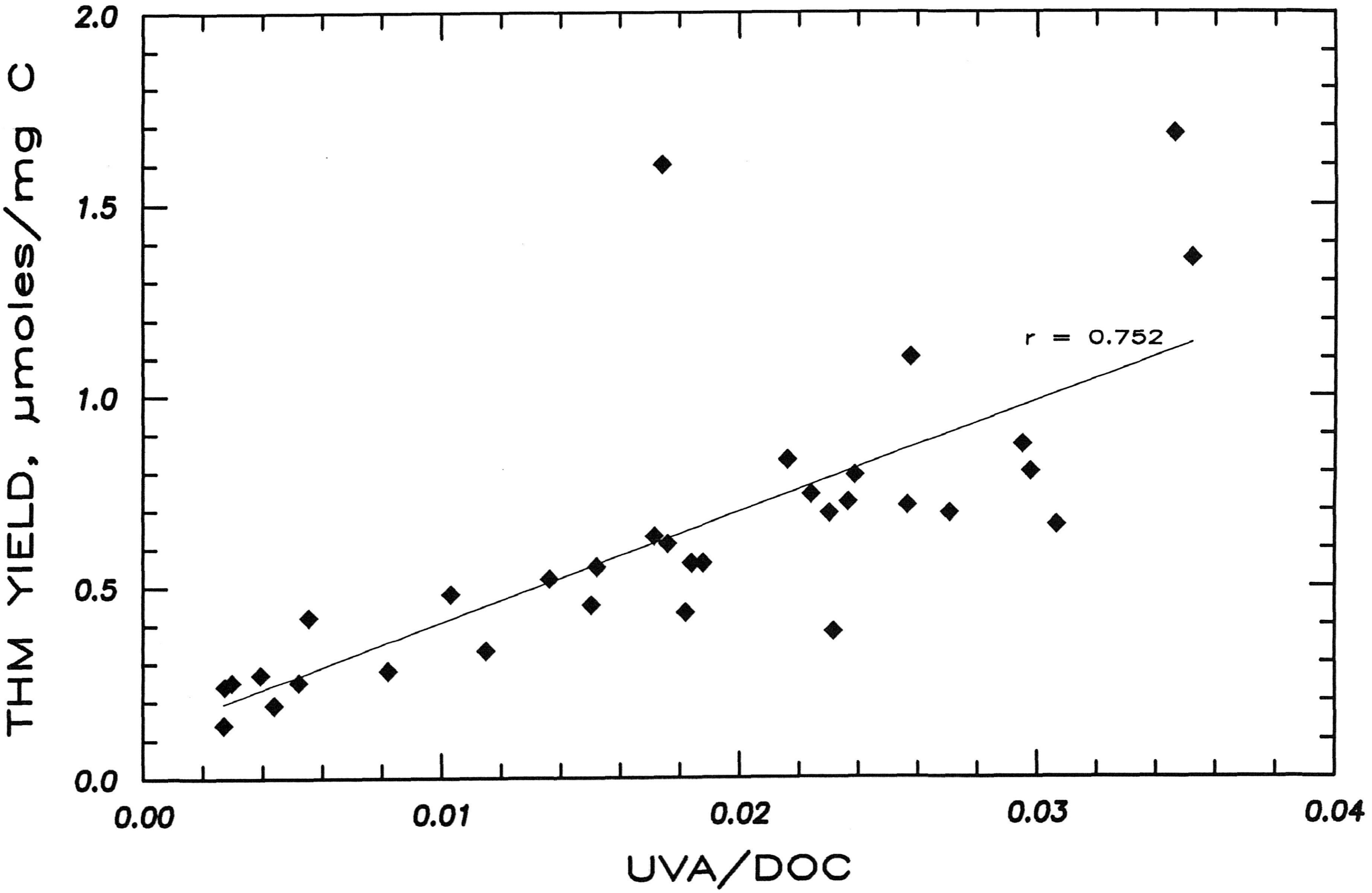

FIGURE 29: DTFP YIELD VS THE RATIO OF UVA TO DOC FOR AEROBIC AND ANAEROBIC SAMPLES

F. SUMMARY AND EVALUATION OF FIELD DATA

A summary of the organic carbon concentrations and THM yields for the field samples is presented in Table 75. Although the organic carbon concentrations varied widely from one source to another (and often within a given source), the average THM yields were remarkably similar for all sources, ranging from 0.19 to 0.47 µmoles/mgC.

DOC represented 88% of TOC for the lakes sampled and 75% of TOC for the streams sampled, somewhat lower than the 90% typical of most lakes and streams (Thurman, 1985), but not surprising considering the high turbidity of lakes and streams in Kansas. A much smaller fraction of the organic carbon in the other samples was soluble. Clearly, effective source control of THM precursors can be achieved only with a substantial reduction in the concentration of soluble precursors.

The streams and lakes had lower average DOC and TOC concentrations than the average runoff and point-source samples. Stream and runoff samples collected during periods of elevated discharge showed significantly higher concentrations of DOC, TOC, and THM precursors, in agreement with the findings of other investigators (see Related Research). Hence, the average volume-weighted DOC and TOC concentrations would be much greater than the values reported in Table 75 for the streams. Furthermore, the average TOC concentrations of the stream samples taken upstream from Clinton Lake were significantly greater than the average TOC concentration in Clinton Lake, and the same was true for the few samples of the stream feeding into Strowbridge Reservoir. These data clearly indicate that the lakes that were sampled are net sinks for THM precursors.

The data are not sufficient to permit calculation of the percentage of organic carbon in the lakes that is autochthonous. However, several pieces of information suggest that the percentage is quite low. First, as discussed in the previous paragraph, the lakes appear to be net sinks for THM precursors, so any production of autochthonous precursors must be offset by an equal or greater loss of allochthonous precursors; and the latter are expected to be much less biodegradable than autochthonous organic matter. Secondly, as was shown in Table 47, the THM yields upstream and downstream of Clinton Lake were very similar, suggesting that no major change in precursor composition occurred. Third, rapidly flushed lakes (reservoirs) generally receive large quantities of allochthonous organic matter, which they are unable to efficiently retain and process (Groeger & Kimmel, 1984). Thurman (1985) estimates that the percentage of autochthonous carbon in lakes ranges from 30% for riverine lakes with high flushing rates to 100% for eutrophic groundwater-fed lakes. Even 30% may be too high for Kansas lakes.

Another piece of information suggesting that most of the organic matter in Kansas lakes in autochthonous is the low ratio of chlorophyll a to TOC. Chlorophyll a constitutes approximately 1-2% of the dry weight of planktonic algae (APHA, 1985). Pope et al. (1985), in a survey of 19 water-supply

TABLE 75

SUMMARY OF AVERAGE ORGANIC CARBON AND THM FORMATION POTENTIAL DATA FOR THE FIELD SAMPLES*

Sample Source	DOC mg/L	DTFP µmoles/mgC	TOC mg/L	TFP µmoles/mgC
Lakes	4.4	0.39	5.0	0.42
Streams	4.5	0.44	6.0	0.47
Runoff	14.8	0.34	56.7	0.39
Urban Runoff	6.6	0.30	21.4	0.39
Agricultural Runoff	19.3	0.36	75.9	0.39
Point Sources	12.9	0.26	20.5	0.26
Industrial	12.3	0.26	17.4	0.28
Municipal	21.7	0.20	40.1	0.19
Algae-Laden	22.0	0.22	38.3	0.22
Soils	-	0.21†	-	-
Brine-Contaminated Groundwater	1.8	0.41	12.9	0.32
Oil-Field Brines	4.5	0.27	10.2	0.20

* Averages of the average concentrations found in the five lakes and four streams sampled and average of the samples analyzed for the other sources of samples.

† ETFP yield.

lakes in Kansas, found an average chlorophyll concentration of 11 µg/L and a TOC of 6.2 mg/L. Assuming that the chlorophyll represented 1.5% of algal biomass, the algae would account for only 11.8% of the TOC. Of course, a fraction of the algal extracellular products might persist long after the algal cells had died, but the algal biomass would be highly biodegradable and THM precursors of algal origin have generally been found to be quite weak (see Related Research). Furthermore, much of the chlorophyll a may itself be allochthonous (for the Clinton Lake samples of 9-5-85 the highest chlorophyll a concentrations were found in Rock Creek and near an eroding shoreline); and the high turbidity in Kansas lakes retards the decay of chlorophyll a by sunlight.

The average DOC and TOC concentrations of the point-source samples were substantially higher than those of the lakes and streams (Table 75), but their THM yields were relatively low. Since the flowrates associated with such sources is generally so low in comparison to streamflow, their contributions to the mass loading of THM precursors should generally be negligible. However, streams or lakes receiving heavy contributions of flow from such sources may indeed experience an increase in the concentration of THM precursors.

Agricultural runoff is a particularly significant source of precursors in Kansas, since so much of the land in the state is used for agricultural purposes. As shown in Table 75, the organic carbon concentrations in agricultural runoff were very high, and the THM yields were, interestingly, very similar to those of the lake samples. Hence, agricultural runoff appears to be a prime target for source control of THM precursors, and it appears to be the only source of allochthonous precursors for which effective source control would be likely to result in a significant reduction in THM precursors entering downstream lakes.

Source control of the THM precursors associated with agricultural runoff might be accomplished by use of stormwater retention ponds, establishment of vegetated strips of land along streambanks, terracing, changes in cultivation practices, etc. These methods are also useful for soil conservation, preservation of wildlife habitat, and other purposes; but they are unlikely to be economically justifiable solely for the purpose of THM control, except perhaps for very small watersheds. One possible drawback to these methods, in terms of THM control, is that they will also reduce turbidity. The productivity of many Kansas lakes is light limited, so any decrease in turbidity will likely result in an increase in the production of autochthonous precursors. The experimental ponds, which received no runoff and were therefore clear, had elevated TOC and DOC concentrations compared to the lakes and streams. Also, decreased TOC was observed in the ponds to which clay was added to increase turbidity.

Although the majority of the THM precursors in most Kansas lakes are probably allochthonous, autochthonous precursors could also be quite significant, since even a modest increase in the concentration of autochthonous precursors could cause a violation of the THM standard. Also, autochthonous organic matter is likely to be less removable by water treatment and more biodegradable than allochthonous organic matter (and therefore more likely to stimulate the growth of bacteria in the distribution system). Hoehn *et al*. (1984) found that the THM yields of the precursors remaining after coagulation were generally greater when biological activity in the reservoir was high. The data from the experimental ponds show the significant effect that autochthonous precursors can have on THM formation. The laboratory experiments demonstrate that aquatic plants are potential sources of autochthonous precursors; and, if the growth of such plants is not controlled, either naturally or artificially, increased THM formation may result. Randtke *et al*. (1985) have discussed at length the potential impacts of a variety of lake management practices on autochthonous organic carbon and THM precursors, but more research on this topic is clearly needed.

CONCLUSIONS

1. DOC and TOC were found to be excellent predictors of DTFP and TFP, respectively, for samples from a particular source.

2. The yield of THMs varied from source to source, but the variation was not great for the field samples, most of which had yields between 0.3 and 0.5 µmoles/mg C.

3. For the five lakes that were sampled, the average concentrations of DOC and TOC were 4.4 and 5.0 mg/L, respectively, ranging from 3.5 to 5.1 and 4.2 to 5.8 mg/L, respectively. DTFP averaged 0.39 µmoles/mg C, while TFP averaged 0.42 µmoles/mg C. The concentrations of organic matter and THM precursors were quite similar in each lake, despite significant differences in the physical characteristics, ages, sizes, and uses of the lakes.

4. No seasonal trends in the concentrations of organic matter and THM precursors in the lakes were observed, indicating that most of the organic matter and precursors are allochthonous.

5. Organic carbon and THM precursors were distributed quite uniformly throughout the lakes that were sampled. Elevated concentrations of organic carbon and THM precursors were observed in major inlet streams, near eroding shorelines, and in one bed of decaying weeds, but not in brush piles, sheltered coves, areas of standing timber, small sheltered inlets, or other beds of living and dead weeds. Hence, any autochthonous precursors being produced in significant amounts in microzones within the lakes that were sampled were either being produced at a slow rate relative to their rates of diffusion and dispersion or at times and places other than those of the samplings.

6. Thick layers of a gelatinous slime were observed on senescing macrophytes in the fall, and on several of the substrates examined in laboratory experiments. Thus, it appears that biodegradable material leached from senescing macrophytes may be largely consumed before it is released into the water.

7. The concentrations of organic matter and THM precursors in the top and bottom samples from stratified lakes sometimes exhibited very small differences. However, the overall average concentrations in top and bottom samples taken on 10 different occasions were virtually identical. Thus, stratification did not significantly influence the concentration of THM precursors. (However, stratification can influence THM formation in practice due to the influence of temperature on the rate of THM formation, the influence of reduced substances on chlorine demand, and the influence of turnover events on algal growth.)

8. Lake sediment samples contained only 1.5 to 2.0% organic carbon (dry weight basis) of which only about 6%, on the average, was extractable; and the average THM yield of the extracted organic matter was 0.30

µmoles/mg C. Therefore, the sediments are not a significant source of THM precursors in the lakes that were sampled.

9. The stream samples had an average DOC concentration of 4.5 mg/L, an average TOC concentration of 6.0 mg/L, an average DTFP yield of 0.44 µmoles/mg C, and an average TFP yield of 0.47 µmoles/mg C. These averages are just slightly higher than those of the lake samples.

10. The concentrations of organic matter and THM precursors in streams were found to increase very substantially during periods of wet weather, indicating that mass loadings increase dramatically following storm events. Hence, the flow-weighted average concentrations of organic carbon and THM precursors in the streams are expected to be substantially higher than the sample averages reported in conclusion 9.

11. The streams feeding Clinton Lake had higher average concentrations of organic carbon and THM precursors than the outlet stream, indicating that Clinton Lake is a net sink for precursors. The lake and stream data suggest that this is generally true of all of the lakes sampled.

12. The concentrations of organic carbon and THM formation potential were generally much higher in municipal and industrial wastewater effluents than in lakes and streams; but these sources should be insignificant in most cases, since they generally contribute only a small fraction of the total stream flow.

13. Agricultural runoff is perhaps the most significant source of THM precursors in Kansas. Agricultural runoff had extremely high concentrations of organic carbon and THM precursors, and much of the land in Kansas is used for agricultural purposes. Runoff from non-agricultural land and urban areas also carried large quantities of THM precursors.

14. Oil-field brines were not a significant source of organic carbon or THM precursors. The small concentrations of precursors found in oil-field brines and in brine-contaminated groundwater samples may have been naturally occurring humic substances unrelated to the presence of oil.

15. Organic matter extracted from soil produced relatively low yields of THMs, yet humic substances of terrestrial origin have generally been found to be strong precursors. The most likely explanation for the low yields that were observed is that the humic materials that leach naturally from the soil are more potent precursors than those that were extracted in the laboratory procedure that was used.

16. Addition of copper sulfate and simazine to experimental ponds led to the development of algal blooms, accompanied by increased concentrations of organic matter and THM precursors. Whether such increases were directly related to algae and their extracellular byproducts or to bacteria feeding on them was not determined.

17. Addition of copper sulfate, simazine, and grass carp to experimental ponds infested with macrophytes caused organic matter and THM

precursors to be released into the water prematurely in comparison to the control ponds, in which weeds were allowed to senesce naturally. By fall, all of the ponds once again had similar concentrations of organic carbon and were quite similar in appearance, although the grass carp ponds were more turbid than the others.

18. In laboratory experiments, organic carbon and THM precursors were found to leach in potentially significant quantities from filamentous algae, aquatic weeds, leaves, tree blossoms, wood fragments (from standing timber in Clinton Lake), pine needles, pine twigs, pine branches, and other substrates, especially under anaerobic conditions. Leaching from bacterial suspensions (activated sludge mixed liquor and lake scum) was negligible; and the organic matter in river water, secondary effluent, and soil extract did not appear to be biodegradable.

19. Precursors released from various substrates under aerobic conditions in the laboratory were considerably more potent than those released under anaerobic conditions. For substrates incubated under both aerobic and anaerobic conditions, DTFP was strongly and positively correlated with DOC, UV absorbance, and color, and DTFP yield increased with an increasing ratio of UV absorbance to DOC.

20. Since 75-90% of the precursors in the lakes and streams were soluble, it appears that effective source control of THMs in Kansas lakes will require a substantial reduction in soluble precursor concentrations. The majority of precursors are undoubtedly allochthonous, but attempts to control the entry of such precursors to lakes in Kansas may simply result in greater production of autochthonous precursors due to decreased turbidity. The autochthonous fraction of the precursors, though much smaller than the allochthonous fraction, may nevertheless be very significant, especially for utilities experiencing difficulty meeting the THM standard. Additional research is needed to examine both the short-term and long-term effects of lake management practices on autochthonous precursors.

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APPENDIX A

PRECIPITATION AND TEMPERATURE DATA

TABLE A1

MONTHLY PRECIPITATION DATA FOR THE STUDY AREA DURING 1985*

Month	Clinton Lake	Lawrence	Topeka	Auburn	Lyndon
January	1.58	2.33	0.70	1.28	1.31
February	2.20	2.20	2.02	1.85	2.02
March	2.05	2.22	2.38	1.82	2.56
April	4.59	2.99	3.60	2.93	2.61
May	5.77	5.42	3.79	4.18	4.88
June	6.93	7.11	5.15	8.94	8.17
July	1.96	2.49	2.90	2.53	3.97
August	9.95	9.77	7.97	6.27	9.28
September	8.84	7.89	8.16	8.65	6.18
October	6.60	6.95	5.20	4.56	7.32
November	2.44	2.18	2.02	2.01	2.99
December	1.14	1.70	0.71	1.08	1.00
Total	54.05	53.25	44.60	46.10	52.29

* The Lawrence weather station is located at Kansas University; it is approximately 10 miles south of the experimental ponds but it is the closest weather station from which data were available. Topeka is located on the Kansas River, about 25 miles west of Lawrence. Auburn is located in the Wakarusa River watershed upstream from Clinton Lake. Lyndon Lake was sampled during the second year of the study. The data were taken from "Climatological Data: Kansas", National Climatic Data Center, Volume 99 (1985).

TABLE A2

MONTHLY PRECIPITATION DATA FOR THE STUDY AREA DURING 1986*

Month	Clinton Lake	Lawrence	Topeka	Auburn	Lyndon
January	0.00	0.00	0.00	0.00	0.00
February	0.86	0.77	1.55	1.35	1.45
March	1.20	1.76	1.35	1.18	1.89
April	5.53	5.33	3.15	3.98	4.49
May	5.45	6.35	7.35	4.89	4.81
June	2.21	2.88	2.51	1.54	2.01
July	8.14	9.13	4.21	7.99	7.55
August	4.72	5.63	5.50	5.52	4.25
September	9.21	12.29	6.21	4.70	8.74
October	3.78	4.30	3.30	3.96	4.50
November	0.93	1.13	0.87	0.95	0.95
December	1.03	1.88	1.20	0.88	1.51
Total					

* Data taken from "Climatological Data: Kansas", National Climatic Data Center, Volume 100 (1986).

TABLE A3

MONTHLY PRECIPITATION DATA FOR THE STUDY AREA DURING 1987*

Month	Clinton Lake	Lawrence	Topeka	Auburn	Lyndon
January	0.97	1.03	1.09	0.62	0.95
February	1.64	1.51	2.71	1.67	1.79

* Data taken from "Climatological Data: Kansas", National Climatic Data Center, Volume 101 (1987).

TABLE A4

SELECTED DAILY PRECIPITATION DATA FOR THE STUDY AREA[1]

Month and Year	Day[2]	Auburn	Clinton Lake	Lawrence	Topeka
January, 1986	-	-	-	-	-
February, 1986	3	0.46	0.38	0.37	0.57
	4	0.71	0.26	0.33	0.84
	5	0.08	0.10	-	T
	14	0.08	0.05	0.01	0.04
March, 1986	9	-	-	-	0.07
	10	0.34	0.55	0.72	0.39
	11	T	T	0.13	0.02
	12	0.17	0.17	0.10	0.26
	13	0.20	0.20	0.08	-
	17	T	T	T	0.25
	18	0.44	0.35	0.50	0.09
	26	0.03	0.15	0.21	0.17
April, 1986	1	0.47	0.25[3]	0.31	0.22
	2	T	0.05[3]	0.08	0.39
	3	0.38	0.90[3]	0.97	1.05
	4	0.81	1.48[3]	1.40	-
	7	0.47	0.06	0.02	0.04
	8	0.08	0.95	0.58	-
	13	-	-	-	0.30
	14	0.34	0.40	0.28	-
	17	0.05	0.04	0.02	0.02
	18	0.26	0.28	0.28	0.32
	27	0.29	0.41	0.05	0.81
	28	0.80	0.71	1.34	T

[1] Data taken from "Climatogical Data: Kansas," National Climatic Data Center, Volumes 100 (1986) and 101 (1987).

[2] No more than 0.05 inches of precipitation were recorded at any of the four sites on the days omitted.

[3] Hourly precipitation data from the National Climatic Data Center (Volume 36, No. 4, April 1986) shows 0.13 on 4-1-86, 0.86 in. on 4-2-86, 1.25 in. on 4-3-85, and 0.00 in. on 4-4-86.

TABLE A4 (cont'd)

SELECTED DAILY PRECIPITATION DATA
FOR THE STUDY AREA

Month and Year	Day	Auburn	Clinton Lake	Lawrence	Topeka
May, 1986	3	0.32	0.71	0.72	0.55
	4	0.03	-	0.20	-
	5	-	-	-	1.06
	6	0.35	0.65	0.98	0.57
	7	0.22	0.30	0.31	0.42
	8	-	-	-	0.29
	9	0.82	0.13	0.06	0.77
	10	0.57	0.90	1.30	0.95
	11	0.16	0.06	0.13	-
	12	-	-	-	0.63
	13	0.11	0.95	0.64	0.25
	14	T	T	0.23	T
	15	0.39	0.08	0.09	0.21
	16	T	T	0.04	1.02
	17	1.54	1.60	1.45	0.73
	18	0.08	0.07	0.20	-
	29	0.02	-	-	0.07
	30	0.28	T	-	T
June, 1986	4	-	-	-	0.26
	5	0.12	0.16	0.30	0.08
	6	-	0.08	0.28	T
	9	-	-	-	0.10
	15	0.30	-	T	-
	16	0.02	0.50	-	-
	19	-	0.10	-	-
	21	-	-	-	1.35
	22	-	1.15	0.73	0.17
	23	-	0.04	1.04	0.02
	24	0.18	T	-	-
	27	0.44	-	-	0.02
	28	-	0.55	0.48	-
	29	-	-	-	-
	30	0.48	0.10	0.04	0.48

TABLE A4 (cont'd)

SELECTED DAILY PRECIPITATION DATA FOR THE STUDY AREA

Month and Year	Day	Auburn	Clinton Lake	Lawrence	Topeka
July, 1986	1	1.13	0.55	1.07	1.10
	2	0.02	0.33	0.49	-
	3	0.27	0.12	-	-
	6	-	0.25	0.06	1.15
	7	2.39	3.72	4.10	0.16
	8	0.34	0.11	0.02	0.01
	10	-	-	-	0.24
	11	1.93	1.20	1.51	0.33
	12	1.33	1.28	0.69	0.85
	13	0.37	0.06	0.36	-
	24	-	0.10	0.03	0.15
	25	-	0.01	0.08	T
	26	0.18	0.33	0.34	0.20
	27	T	0.06	0.33	-
August, 1986	1	-	-	-	
	2	0.12	0.09	0.17	0.20
	5	0.47	0.34	0.39	1.04
	6	0.17	0.15	0.11	-
	7	1.97	1.80	2.12	1.22
	8	0.09	-	-	-
	9	-	-	-	1.75
	10	1.09	0.48	0.85	-
	11	T	-	-	-
	12	0.47	T	T	0.54
	13	-	0.45	0.51	0.06
	14	0.08	0.04	0.02	T
	15	0.03	0.45	0.53	0.19
	16	-	0.07	0.11	-
	18	-	-	-	0.19
	19	0.66	0.05	0.07	-
	23	0.12	0.01	T	T
	26	-	-	-	0.24
	27	0.22	0.79	0.71	-

TABLE A4 (cont'd)

SELECTED DAILY PRECIPITATION DATA
FOR THE STUDY AREA

Month and Year	Day	Auburn	Clinton Lake	Lawrence	Topeka
September, 1986	7	0.05	0.06	0.08	0.08
	11	2.28	1.90	1.93	1.45
	15	--	0.12	0.28	0.07
	16	T	T	--	T
	17	T	0.31	0.15	T
	18	0.12	0.07	0.51	0.35
	19	--	0.53	0.82	T
	22	--	--	--	1.17
	23	--	3.08	3.56	0.52
	24	0.17	0.70	0.87	--
	25	--	--	--	--
	26	--	--	--	0.52
	27	0.63	0.39	1.77	--
	28	--	T	0.06	0.40
	29	0.20	0.72	0.46	1.03
	30	1.25	1.33	1.75	0.27
October, 1986	1	0.08	0.76	0.61	T
	2	0.37	0.30	0.21	1.29
	3	1.27	0.82	0.98	0.06
	4	0.35	0.08	0.08	T
	9	0.07	0.02	T	0.14
	10	T	0.04	0.01	--
	11	0.12	0.07	0.04	1.00
	12	0.72	0.90	1.17	--
	13	T	0.02	0.02	0.09
	14	--	0.05	0.22	T
	18	0.12	--	--	--
	19	0.20	--	--	--
	22	--	0.17	--	0.32
	23	0.12	0.14	0.33	--
	24	0.32	0.02	0.87	T
	25	--	0.19	0.55	0.40
	26	0.22	0.20	0.08	T
	27	0.09	--	--	--

TABLE A4 (cont'd)

SELECTED DAILY PRECIPITATION DATA FOR THE STUDY AREA

Month and Year	Day	Auburn	Clinton Lake	Lawrence	Topeka
November, 1986	3	0.02	--	0.01	0.41
	4	0.44	0.27	0.15	0.15
	5	0.22	0.39	0.51	0.04
	7	--	T	T	0.07
	8	--	0.11	0.12	--
	9	--	--	--	--
	10	0.14	--	--	0.11
	11	--	--	0.17	--
	12	--	0.13	0.03	T
	17	0.08	--	--	--
	26	0.03	--	0.09	--
December, 1986	1	T	0.01	0.22	0.28
	2	0.05	0.01	0.23	T
	6	--	--	--	0.12
	7	--	0.16	0.83	0.61
	8	0.56	0.60	0.32	0.15
	9	0.27	0.25	0.28	0.04
January, 1987	3	T	0.09	0.11	0.12
	9	0.28	0.33	0.36	0.56
	10	--	0.10	0.13	T
	16	0.30	0.04	0.01	0.25
	17	--	0.30	0.23	0.18
	18	--	0.11	0.17	0.03
February, 1987	4	--	--	--	0.08
	5	0.52	0.41	0.27	0.34
	6	--	0.04	0.21	--
	15	0.72	1.02	0.36	0.38
	16	--	--	0.01	0.08
	27	0.18	0.14	0.19	0.08
	28	0.20	--	0.40	1.65

TABLE A5

MONTHLY PRECIPITATION AND TEMPERATURE IN LAWRENCE[1]

Month	Average Temperature (°F)	Departure from Normal	Total Precipitation (inches)	Departure from Normal
1985				
January	22.6	-5.8	2.33	1.22
February	29.1	-5.3	2.20	0.95
March	50.0	6.3	2.22	-0.28
April	60.3	3.4	2.99	-0.28
May	67.9	1.6	5.42	1.20
June	71.9	-3.2	7.11	1.62
July	80.3	0.2	2.49	-1.96
August	75.0	-3.4	9.77	5.83
September	69.7	-0.6	7.89	3.95
October	59.2	-0.4	6.95	3.73
November	39.8	-5.1	2.18	0.20
December	2.74	-6.8	1.70	0.26
1986				
January	40.0	11.6	T	-0.11
February	35.4	1.0	0.77	-0.48
March	52.7	9.0	1.76	-0.74
April	60.8	3.9	5.33	2.06
May	67.9	1.6	6.35	2.13
June	78.4	3.3	2.88	-2.61
July	81.8	1.8	9.13	4.68
August	73.6	-4.8	5.63	1.69
September	73.2	2.9	12.29	8.35
October	58.8	-0.8	4.30	1.08
November	41.0	-3.9	1.13	-0.85
December	36.5	2.3	1.88	0.44
1987				
January	31.7	3.3	1.03	-0.08
February	42.4	8.0	1.51	0.26

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[1] Data taken from "Climatogical Data: Kansas," National Climatic Data Center, Volumes 99 (1985), 100 (1986), and 101 (1987).

APPENDIX B

TFP DATA FOR LABORATORY EXPERIMENT NO. 2

TABLE B1

TFP DATA FOR LABORATORY EXPERIMENT NO. 2

Sample	DOC	Res. Cl_2	TFP		
No.	mg/L	mg/L	μg/L	μM	μmoles/mg C
Aerobic Samples					
1	11.8	0.2	700	5.78	0.490
		3.1	782	6.47	0.549
		6.8	950	7.88	0.667
2	15.4	1.0	1,030	8.55	0.555
		4.3	1,180	9.79	0.636
		8.4	1,239	10.29	0.668
3	35.8	0.7	1,888	15.72	0.439
		4.6	2,476	20.65	0.577
		8.1	2,870	23.95	0.669
4	24.0	2.7	1,546	12.86	0.536
		6.6	1,791	14.90	0.621
		10.4	1,831	15.24	0.635
5	206	0.2	8,181	68.47	0.332
		4.4	10,785	90.27	0.438
		8.6	11,856	99.23	0.482
6	86.8	1.9	3,864	30.81	0.356
		4.6	4,303	36.00	0.416
		7.8	5,144	43.03	0.497
7	142	2.2	9,229	77.12	0.543
		6.6	10,118	84.55	0.595
		10.4	10,166	84.95	0.598
8	84.5	2.0	8,322	69.60	0.824
		6.2	8,410	70.34	0.832
		10.8	8,632	72.19	0.854
9	47.2	1.1	4,461	37.30	0.790
		4.8	4,539	37.95	0.804
		9.0	4,754	39.75	0.842
10	63.2	2.3	6,572	54.84	0.868
		6.2	6,714	56.02	0.886
		10.4	7,279	60.75	0.961
11	140	0.7	18,354	153.24	1.095
		4.5	18,360	153.64	1.097
		9.4	18,365	153.70	1.098

TABLE B1 (CONT'D)

TFP DATA FOR LABORATORY EXPERIMENT NO. 2

Sample No.	DOC mg/L	Res. Cl_2 mg/L	TFP		
			µg/L	µM	µmoles/mg C
Aerobic Samples (Cont'd)					
12	157	1.7	12,751	106.77	0.680
		5.8	13,496	113.01	0.720
13	23.0	2.6	3,762	31.36	1.363
		6.6	3,780	31.52	1.371
		11.2	3,944	32.89	1.430
14	26.7	0.3	2,288	18.93	0.709
		3.0	2,276	18.82	0.705
		6.8	2,326	19.23	0.720
15	201	0.6	13,563	113.52	0.565
		4.8	15,516	129.87	0.646
		9.2	16,624	139.15	0.692
16	30.1	0.4	2,290	19.11	0.635
		4.8	2,640	22.03	0.732
		8.8	2,631	21.95	0.729
17	54.5	3.5	10,398	87.01	1.596
		8.2	10,440	87.36	1.603
18	23.1	3.6	4,743	39.62	1.715
		7.8	4,952	41.37	1.791
		12.6	5,066	42.33	1.832
19	32.0	2.3	3,056	25.39	0.793
		6.8	3,106	25.80	0.806
		10.6	3,250	27.01	0.844
20	92.8	0.7	8,068	66.94	0.721
		3.8	8,233	68.26	0.736
		7.8	8,274	68.65	0.740
21	62.6	2.5	5,155	43.05	0.688
		7.0	5,222	43.61	0.697
		9.6	5,460	45.60	0.728
22	11.6	1.1	569	4.62	0.398
		4.8	670	5.46	0.470
		9.0	746	6.09	0.525

TABLE B1 (CONT'D)

TFP DATA FOR LABORATORY EXPERIMENT NO. 2

Sample	DOC	Res. Cl_2	TFP		
No.	mg/L	mg/L	µg/L	µM	µmoles/mg C
Aerobic Samples (Cont'd)					
23	57.9	0.5	4,003	33.21	0.574
		3.4	4,554	37.82	0.653
		6.8	4,673	38.80	0.670
24	3.3	1.6	179	1.40	0.425
		4.5	205	1.61	0.488
		9.8	224	1.78	0.539
Anaerobic Samples					
1	60.1	3.6	1,883	15.63	0.260
		8.1	2,057	17.15	0.285
		12.6	2,104	17.54	0.292
2	72.5	2.7	3,551	29.66	0.409
		7.2	4,081	34.10	0.470
		11.3	4,141	34.60	0.477
3	116	4.4	3,798	31.74	0.274
		8.6	4,491	37.54	0.324
		13.4	4,750	39.71	0.342
4	64.0	3.2	1,940	16.19	0.253
		7.6	2,342	19.55	0.306
		11.2	2,659	22.21	0.347
5	433	0.6	11,751	98.34	0.227
		5.1	14,482	121.21	0.280
		10.1	13,905	116.40	0.269
6	630	3.8	10,742	88.92	0.141
		7.7	11,672	97.67	0.155
		11.8	12,753	106.00	0.168
7	234	4.0	8,041	67.27	0.287
		8.4	8,552	71.56	0.306
		13.2	8,623	72.16	0.308
8	230	1.4	5,143	43.04	0.187
		5.6	5,252	43.93	0.191
		10.4	6,026	50.40	0.219
9	4.7	0.7	176	1.39	0.295
		4.5	205	1.63	0.346
		8.6	234	1.88	0.399