TRIHALOMETHANE FORMATION POTENTIAL OF SIX OHIO WATER SERVICE RESERVOIRS

by

Richard J. Ciotola Y-10-4

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James R. Toepfer for Lauren Schroeder 8/23/94
Advisor Date

8/26/94
Dean of the Graduate School Date

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Thesis Approval Form

Thesis Title: Trihalomethane Formation Potential of Six Ohio Water Service Reservoirs.

Author: Richard James Ciotola

Degree: Master of Science in Biological Sciences

Advisor: Dr. Lauren Schroeder

Committee Members:	Accept	Reject
David B. MacLean	✓	
	✓	
James E. Tepfer	✓	

Date: 8/23/94

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Trihalomethane Formation Potential of Six Ohio Water Service Reservoirs

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Richard Curtola 8/23/94
Student Date

Approvals:

James R. Taylor for Lauren Schroeder 8/23/94
Thesis Advisor Date

David B. MacLean 8/23/94
Committee Member Date

Daryl W. Mincey 8/23/94
Committee Member Date

Peter J Kasvinsky 8/26/94
Dean of Graduate Studies Date

ABSTRACT

TRIHALOMETHANE FORMATION POTENTIAL
OF SIX OHIO WATER SERVICE RESERVOIRS

Richard J. Ciotola
Master of Science
Youngstown State University, 1994

Trihalomethane formation potential of six reservoirs was investigated along with related water parameters (TOC, SOC, TSI, HA and COND). This was done to better understand the relationship between constituents of potable water and levels of chlorinated organics in the finished water.

Trihalomethane formation potential (THMFP) was variable with season and between lakes. The greatest THMFP occured in Lake Girard, and the least was in Lake Evans. Lakes Mckelvey and Evans had similar levels of organic carbon, but the THMFP was greater in McKelvey. The percentage of the organic carbon in the form of dissolved humic and fulvic acids was greatest for Lake McKelvey.

Although dissolved humic substances were greater in the inflow and hypolimnion than the epilimnion and outflow, no significicant differences in THMFP were detected between any of the different sampling locations.

There was no correlation between THMFP and organic carbon content, and only weak correlation between THMFP and lake trophic state. Humic acid was correlated with THMFP, but not well enough to use as a reliable surrogate parameter.

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Trihalomethane formation potential (ug/L)	THMFP
Trophic state index (chlorophyll a)	TSICHL
Trophic state index (total phosphorous)	TSITP
Trophic state index (Sechii disk)	TSISD
Total organic carbon (mg/L)	TOC
Soluble organic carbon (mg/L)	SOC
Soluble humic and fulvic acids (mg/L)	HA
Absorbance at 254 nm	A254
Absorbance at 340 nm	A340
Absorbance at 400 nm	A400
Conductivity (umhos)	COND
Ratio of HA to TOC	HATOC
Ratio of HA to SOC	HASOC
Accumulated rainfall three days prior to sampling	RAIN3

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INTRODUCTION

Surface waters used as a source of potable water are subjected to a variety of treatment procedures. This is done to improve taste and odor, and to prevent the outbreak of waterborne diseases. Typical treatment steps include flocculation, sedimentation, filtration and disinfection. Several effective methods of disinfection are available, of which the most commonly used is chlorination (Montgomery, 1985).

Chlorination of surface water may result in the formation of halogenated organic byproducts. Trihalomethanes (THMs) are trihalogen substituted methanes that may be present in finished drinking water (Rook, 1974). Bunn, et.al. (1975) found the following five THMs in chlorine treated water: chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), bromoform ($CHBr_3$), and dichloriodomethane ($CHCl_2I$). Laboratory chlorination experiments produced an additional five THMs. Trihalomethanes containing fluorine were not detected by these authors (Bunn, et.al. 1975).

Trihalomethanes containing bromine are thought to occur, because chlorine is capable of oxidizing naturally occurring inorganic bromides to Br_2. In this form, bromine is capable of entering into halogenating reactions (Rook, 1974). Chlorine is also able to oxidize inorganic iodide in a similar manner. Due to the greater nonmetallic character of fluoride, chlorine will not oxidize fluoride to fluorine (Nebergal. et.al. 1980). This could account for the presence of iodine in some THMS, but not fluorine.

The presence of THMs in drinking water is of concern because of health risks associated with their contact. Chloroform has been shown to cause tumors in laboratory rats (Reuber, 1979). Valema (1987) reviewed research on the health effects of consuming chlorinated water. Many of these studies showed an increase in cancer risk for populations that used chlorinated water. In 1979, the United States Environmental Protection Agency set a maximum allowable contaminate level of 100 ug/liter (ppb) total THMs in finished drinking water (Federal Register, 1979).

Trihalomethanes were first detected in chlorinated drinking water by Rook (1974). He found chlorinated Rhine River water contained 54.0 ppb $CHCl_3$, 20.0 ppb $CHCl_2Br$, 13.3 ppb $CHClBr_2$, and 2.0 ppb $CHBr_3$. Subsequent filtration and aeration was able to reduce the THM levels significantly (Rook, 1974). Arruda and Fromm (1989), found THM levels as high as 354 ppb in one sample of Kansas drinking water. Raw water from this source (Howard City Lake) produced more than 700 ppb THMs upon chlorination.

Several studies (Rook, 1974, Oliver and Lawrence, 1979 and Bunn et.al. 1975) have shown chloroform to be the most abundant THM formed. Others (El-Dib and Ali, 1992) found greater percentages of the brominated THMs than chloroform. At one site in the Al-Giza waterworks (Cairo, Egypt), THM levels were $CHCl_3$ 30.3 ppb, $CHClBr_2$ 78.7 ppb, $CHCl_2Br$ 2.3 ppb, and $CHBr_3$ 1.0 ppb. The levels of these four THMs varied at different steps in the treatment process. No THMs containing iodine were found in this study (El-Dib and Ali, 1992).

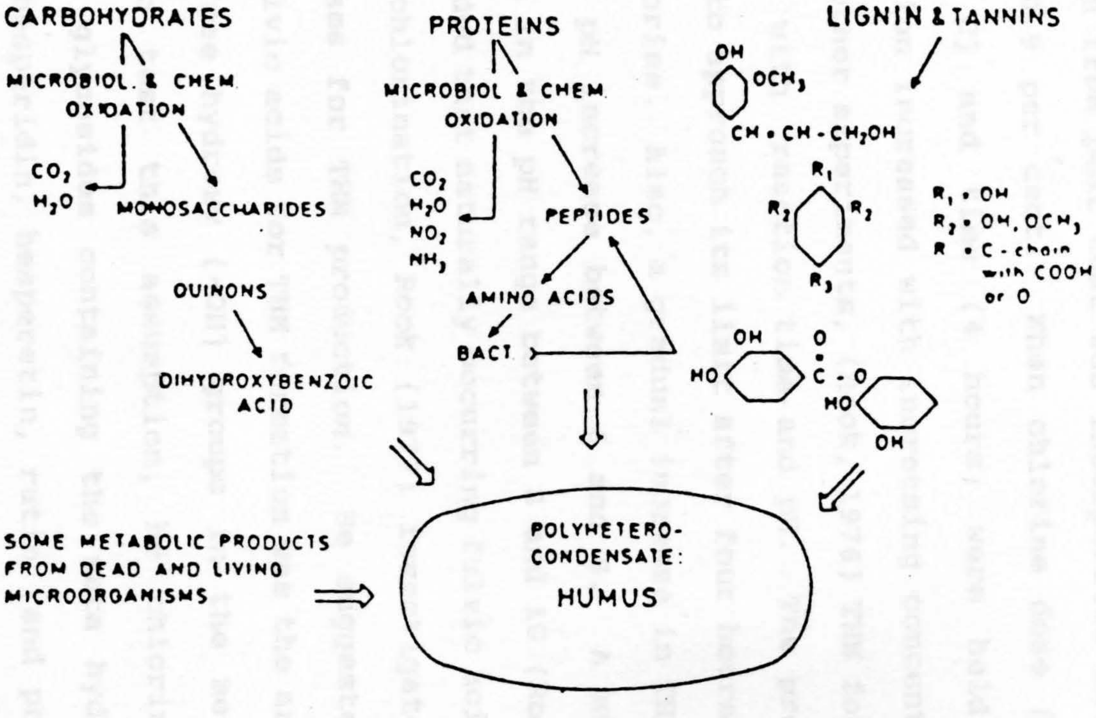
Trihalomethanes are formed from the reaction of chlorine with naturally occurring organic precursors (Rook, 1974). Organic compounds in lake water are either produced within the lake (autochthonous) or transported in by runoff from the watershed (allochthonous). They are classified as either dissolved organic carbon (DOC) or particulate organic carbon (POC). Dissolved organic carbon is defined as particle size less than 0.5 *u*m. The ratio, DOC/POC is typically 6/1 to 10/1 (Wetzel, 1983). Particulate organic carbon is either living or dead, although the former is generally found in much smaller concentrations (Wetzel, 1983).

Organic carbon in lakes can also be classified as either humic or non-humic. The non-humic organics include such labile molecules as carbohydrates, proteins, peptide, amino acids and pigments (Wetzel, 1983). Humic materials are formed primarily from the degradation of terrestrial plants and are transported into the lake via surface runoff (Gjessing, 1976). This process is illustrated in Figure 1. These large, refractory compounds are divided into three classes: the water insoluble humin, the base soluble humic acids and the water soluble fulvic acids (Wetzel, 1983).

In addition to solubility, there are other differences between humic and fulvic acids. The humic fraction tends to contain larger molecules with a greater percentage of aromatic carbon, while the fulvic acids are smaller with a larger aliphatic content and greater number of oxygen containing functional groups (Reckhow, et.al. 1990).

Although organic carbon is found in many forms in lake water, not all of them appear to be suitable precursors for THM formation

Fig. 1. Natural formation of humic material (Redrawn from Gjessing, 1975).


CARBOHYDRATES
MICROBIOL. & CHEM. OXIDATION
CO2
H2O
MONOSACCHARIDES
OUINONS
DIHYDROXYBENZOIC ACID
PROTEINS
MICROBIOL. & CHEM. OXIDATION
CO2
H2O
NO2
NH3
PEPTIDES
AMINO ACIDS
BACT.
LIGNIN & TANNINS
OH
OCH3
CH = CH - CH2OH
R1
R2
R2
R3
R1 = OH
R2 = OH, OCH3
R = C - chain with COOH or O
OH
HO
O
C - O
HO
OH
SOME METABOLIC PRODUCTS FROM DEAD AND LIVING MICROORGANISMS
POLYHETERO-CONDENSATE:
HUMUS

(Rook, 1974). Rook (1976) investigated aquatic fulvic acids as a possible THM precursor. He found that chlorination of fulvic acid solutions extracted from peat produced variable amounts of chloroform depending on the reaction conditions. The amount of fulvic acid carbon from peat that was incorporated into THMs was between 0.3 and 0.9 per cent. When chlorine dose (885 mg/L), temperature (10° C) and time (4 hours) were held constant, chloroform formation increased with increasing concentrations of fulvic acid. In other experiments, (Rook, 1976) THM formation was shown to increase with reaction time and pH. The production of chloroform began to approach its limit after four hours of contact with 500 mg/L chlorine. Also, a gradual increase in THM formation was observed for pH increase between 6 and 8. A much greater increase occurred in the pH range between 8 and 10 (Rook, 1976).

Having concluded that naturally occurring fulvic acids produced chloroform upon chlorination, Rook (1977) investigated possible reaction mechanisms for THM production. He suggested that the active site in fulvic acids for THM formation was the aromatic ring that contained free hydroxy (-OH) groups in the meta position (Figure 2). To test this assumption, he chlorinated lower molecular weight glycosides containing the meta hydroxy group. Chlorination of hesperidin, hesperetin, rutin and phlorizin all produced chloroform yields ranging from 30 to 90 molar percent (Rook, 1977). The proposed mechanism for this reaction involves chlorine addition to the carbon between the two meta -OH groups (Figure 3). Subsequent separation from the ring produces the free haloforms (Rook, 1977). This mechanism differs from the haloform

Fig. 2. Proposed structure of humic acid molecule. (Redrawn from Gjessing, 1975). Free hydroxy groups in the meta position are indicated by and "*".

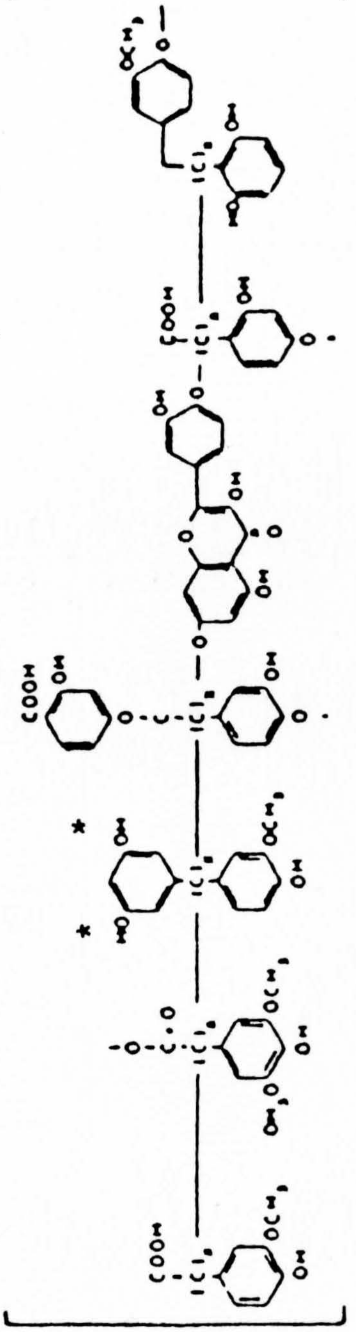


Fig. 3. Proposed mechanism of THM formation from aromatic compound containing a carbon between two meta-hydroxy groups (Redrawn from Rook, 1976).

reaction (Figure 4), in which haloforms are produced from the reaction of chlorine with the methyl ketone group (Fessenden and Fessenden, 1982).

Oliver and Thurman (1983) found that the phenolic content of humic materials did not correlate well with THMFP, and suggested that "THM precursors are more likely to be highly conjugated chromophoric systems rather than hydroxylated aromatic structures." Reckhow et al. (1990) noted that the presence of resorcinol in humic acids has not been conclusively established, and mentioned syringaldehyde as a possible fulvic acid monomer that could produced chlorinated byproducts.

Other potential THM precursors have also been investigated. Oliver and Schindler (1980) studied haloform production from the chlorination of aquatic algae. Trihalomethane formation was measured for seven species of cultured algae, including blue-greens, greens, and diatoms. Chloroform yields varied from approximately 4 to 40 ug/mg dry weight of algal material. Depending on species, and chlorine concentration, chloroform formation was as much as ten times greater at pH 11 than pH 7. This is in contrast to humic materials, which show on average only a doubling of THM formation over the same range of pH increase (Rook, 1976). Also, the formation of $CHCl_3$ from algal material was linear with time, while $CHCl_3$ production from humic materials is rapid in the first fifteen minutes and then levels off with time. This suggests a different reaction mechanism for algal products than for humic and fulvic acids (Oliver and Schindler 1980).

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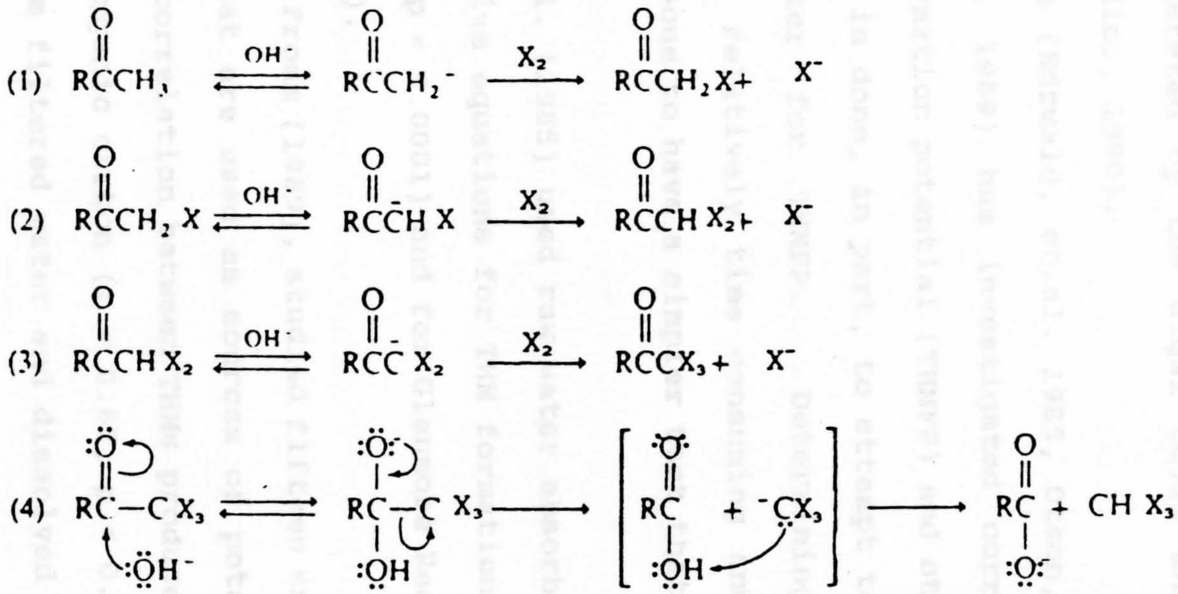
Fig. 4. The haloform reaction. Formation of THMs from the methyl ketone group (Redrawn from Fessenden and Fessenden, 1982). X = Cl, Br, or I.



$$\text{(1)}\quad R\overset{\overset{O}{\|}}{C}CH_3 \underset{}{\overset{OH^-}{\rightleftharpoons}} R\overset{\overset{O}{\|}}{C}CH_2^- \xrightarrow{X_2} R\overset{\overset{O}{\|}}{C}CH_2X + X^-$$

$$\text{(2)}\quad R\overset{\overset{O}{\|}}{C}CH_2X \overset{OH^-}{\rightleftharpoons} R\overset{\overset{O}{\|}}{C}\bar{C}HX \xrightarrow{X_2} R\overset{\overset{O}{\|}}{C}CHX_2 + X^-$$

$$\text{(3)}\quad R\overset{\overset{O}{\|}}{C}CHX_2 \overset{OH^-}{\rightleftharpoons} R\overset{\overset{O}{\|}}{C}\bar{C}X_2 \xrightarrow{X_2} R\overset{\overset{O}{\|}}{C}CX_3 + X^-$$

$$\text{(4)}\quad R\overset{\overset{:\ddot{O}}{\|}}{C}-CX_3 + :\ddot{O}H^- \rightleftharpoons R\overset{\overset{:\ddot{O}:^-}{|}}{\underset{\underset{:\ddot{O}H}{|}}{C}}-CX_3 \longrightarrow \left[R\overset{\overset{:\ddot{O}}{\|}}{\underset{\underset{:\ddot{O}H}{|}}{C}} + {}^-:CX_3 \right] \longrightarrow R\overset{\overset{O}{\|}}{\underset{\underset{:\ddot{O}:^-}{|}}{C}} + CHX_3$$

In order to determine which fraction of the aquatic algae was responsible for THM production, cells were processed with sonication and solvent extraction. Soluble material accounted for only about twenty per cent of the total chloroform yield. The remainder was generated by the algal cells and cell fragments (Oliver and Schindler, 1980).

Other research (Edzwald, et.al. 1985, Otson, et.al. 1981 and Arruda and Fromm, 1989) has investigated correlations between trihalomethane formation potential (THMFP) and other water quality parameters. This is done, in part, to attempt to find a suitable surrogate parameter for THMFP. Determining THMFP by gas chromatography is relatively time consuming and expensive. It would be advantageous to have a simpler test that could adequately predict THMFP.

Edzwald, et.al. (1985) used raw water absorbance at 254 nm to construct predictive equations for THM formation for Grasse River water, ($r^2 = 0.92$ $p = 0.0001$) and for Glenmore Reservoir water, ($r^2 = 0.82$ $p = 0.0001$).

Arruda and Fromm (1989), studied fifteen small reservoirs in eastern Kansas that are used as sources of potable water. They found a positive correlation between THMs produced from unfiltered water and total organic carbon ($r = 0.87$, $p < 0.0001$) and between THMs produced from filtered water and dissolved organic carbon ($r = 0.92$, $p < 0.0001$). They also found THMs from unfiltered water to correlate with trophic state index (TSICHL) calculated from chlorophyll a data ($r = 0.73$, $p = 0.007$). Correlation of TSICHL with THMs from filtered water was significant at the 0.1 level (r

= 0.54, p = 0.07). Three of the most turbid lakes had greater THMFP than would be expected based on TOC or TSI.

A 1990 water quality survey of six, small reservoirs (Schroeder and Ciotola, unpublished) showed an apparent exception to the correlation between THMFP and organic carbon and between THMFP and lake trophic state. Lake McKelvey had a greater than expected THMFP based on carbon content or trophic state. Pine Lake had a greater average trophic state than McKelvey but approximately the same THMFP. Lake Evans, with a similar trophic state to McKelvey also had less THM formation. Lake Girard followed the predicted relationship between THMFP organic carbon and lake trophic state.

The purpose of this research was to investigate further the relationship between raw water quality and THMFP. The influence of rainfall, season and watershed on THMFP was also considered. Other water quality parameters were evaluated as potential surrogates for THMFP.

It is likely that there are significant differences in water quality between the epilimnia of different reservoirs. This hypothesis was tested separately for the following parameters THMFP, TOC, SOC, TSICHL, TSITP, TSISD, HA and COND.

The percentage of organic carbon that is a suitable THM precursor may vary among lakes. Differences in this percentage could help explain why THMFP does not always correlate with organic carbon. The percentage of carbon in the form of suitable THM precursors was estimated by the following ratios: HA/TOC and HA/SOC. Mean epilimnion values were used to test this hypothesis.

Trihalomethane formation potential may also vary within a lake. The primary source of the principle THM precursor (HA) is allocthonous organic matter. As this material enters the lake it will be physically and chemically modified by changes in water quality parameters (Gjessing, 1974). Since the different fractions of humic material produce variable amounts of $CHCl_3$ (Oliver and Visser, 1980), it is likely that THMFP will change as water moves through a reservoir. Differences in THMFP and HA between the inflow, epilimnion and hypolimnion were tested for all lakes. Differences between sites would indicate whether any one location was more or less important in influencing the overall THMFP of a lake.

Differences in the mean THMFP of each lake inflow was tested to see if the nature of the primary inflow; wetland, strip mine, forest or outflow from another lake had any influence on THMFP. Also, correlation between THMFP in the inflows, and rainfall was investigated to see if precipitation influences THMFP. Seasonal changes in THMFP and HA during the course of this study were also studied.

Correlations between THMFP and other water quality parameters were tested to search for a suitable surrogate. Arruda and Fromm (1989), showed correlations between raw water organic carbon, lake trophic state and THMFP. These correlations were tested for the OWS reservoirs at all sites, the epilimnion, the inflow and the hypolimnion.

Correlations between THMFP and humic indicators (HA, A254, A340, A400) were tested for all sites, the inflow, the epilimnion and the hypolimnion. Rook (1977) suggested aquatic fulvic acids as a potential source of THMs. UV absorbance at 254 nm was shown to be related to THMFP (Edzwald et.al., 1985). This relationship was tested as were correlations with absorbance at 340 nm and 400 nm. The excitation wavelength of dissolved humic materials is 340 nm (Susic and Boto 1990). Reckhow et.al. (1990) measured humic material UV-absorbance at 400 nm.

Salts of calcium and magnesium are capable of precipitating humic acids (Susic and Boto, 1990). This phenomena could affect THMFP in lakes with large concentration of Ca++ and Mg++ such as Lake Evans and Lake Hamilton. Correlations between THMFP and conductivity, a measure of dissolved ions, was determined for all sites, the epilimnion, the hypolimnion and the inflow.

STUDY SITES

Field sites were six small reservoirs owned by the Ohio Water Service Company (OWS). These six reservoirs, Pine, Evans, Liberty, Girard, Hamilton, and McKelvey provide a range of productivity, hardness, pH, stratification and watershed properties to study the relationship of THMFP and water quality variables. These reservoirs are all located in the vicinity of the city of Youngstown, in Northeast Ohio. With the exception of Lake McKelvey, the reservoirs are used for recreational fishing and boating. Lake Evans is also used as the potable water supply for the Poland village and Poland township, Ohio. Water is also taken from Girard and Hamilton for domestic use. The following descriptions of each reservoir were summarized from research reports (Schroeder, and Farran, 1987 unpublished, and Schroeder and Ciotola, 1990 unpublished), and from United States geological survey topographical maps.

Pine Lake

Pine Lake is located in southern Mahoning County, just north of the Columbiana County line. The primary inflow is Yellow Creek. A shallow inflow bay exists just prior to the main body of the lake. During the summer, this area is dominated by rooted macrophytes, particularly water lilies.

The length is 3.05 km and the breadth is 1.10 km. The maximum depth is 3 m with a mean depth of 0.91 m. The surface area is 191 x 10^4 m^2 with a shoreline length of 9.21 km and a shoreline development of 1.88. The basin volume is 174 x 10^4 m^3.

Pine Lake is subject to thermal stratification. The shallow depth and relatively large surface area allow the stratification to be easily disrupted by wind motion. The mean trophic state index calculated from chlorophyll a was 65.5 ± 9.7 for the three summer months from 1986 to 1990 (Table 1).

Evans Lake

Evans Lake is located approximately 3 km north of Pine Lake. These two reservoirs are connected via Yellow Creek. Between Pine and Evans, Yellow Creek flows through an area of coal strip mining. Runoff and leaching from the strip mine area greatly increases the non-carbonate hardness of Evans Lake.

The length is 3.6 km and the breadth is 1.39 km. Maximum depth is 12.5 m with a mean depth of 5.03 m. The surface area is 264 x 10^4 m^2 with a shoreline length of 14.6 km and a shoreline development of 2.53. The basin volume is 1330 x 10^4 m^3.

Summer stratification of Lake Evans is stronger than in Pine, although weaker than the other reservoirs. Epilimnion depth has been recorded in excess of 5 m. For the months of June, July and August, average TSICHL was 50.7 ± 10.6 during the period 1986-1990 (Table 1).

Lake Hamilton

Lake Hamilton is located between Poland village and the city of Struthers, Ohio. It is part of the Yellow Creek watershed. Yellow Creek forms the primary inflow of Lake Hamilton. Between the outflow of Evans and the inflow of Hamilton, Yellow Creek flows

Table 1: Morphometric and productivity data for Ohio Water Service reservoirs. Trophic state indecies were averaged for June, July and August from 1986 to 1990. (Schroeder and Farran, 1987. unpublished. and Schroeder and Ciotola, 1990. unpublished).

Lake	Pine	Evans	Liberty	Girard	Hamilton	McKelvey
l (km)	3.05	3.60	1.34	1.93	1.14	-
b (km)	1.10	1.39	0.62	1.28	0.67	-
A	191	264	41.9	101	39.7	-
V	174	1330	194	482	274	-
Zm (m)	3.0	12.5	14	15	17	-
Z (m)	0.91	5.03	4.62	4.77	7.08	-
D	1.88	2.53	2.79	3.06	3.7	-
TSICHL	65.5 ± 9.7	50.8 ± 10.6	59.8 ± 10.7	60.7 ± 10.4	56.0 ± 11.4	48.7 ±

Maximum length (l). The maximum distance on the lake surface where wind can interact without land interference.

Maximum breadth (b). The maximum distance perpendicular to the l axis where wind can interact without land interference.

Area (A). The surface area of the lake given in $m^2 \times 10^4$.

Voume (V). Units are in $m^3 \times 10^4$.

Maximum depth (Zm). The deepest location in the lake.

Mean depth (Z). Z = V/A.

Shoreline developmnent (D). The ratio of the length of shore to the length of shore for a circular lake of equal area.

through the Poland Forest. This area is a predominately mixed hardwood stand, with a few areas of conifers. The Poland Forest is drained by a small creek (Drake Run) which flows into Yellow Creek prior to Lake Hamilton.

The length is 1.14 km and the breadth is 0.67 km. The maximum depth is 17 m with a mean depth of 7.08 m. m. The surface area is 39.7 x 10^4 m^2 with a shoreline length of 4.13 km and a shoreline development of 3.7. The basin volume os 274 x 10^4 m^3.

Lake Hamilton generally develops a strong, stable thermal stratification during the summer. The typical epilimnion depth is 4 m. The average summer epilimnion TSICHL for the years 1986-1990 was 56.0 ± 11.4 (Table 1).

Girard Lake

Girard Lake is located in Trumbal County, adjacent to route 11. The primary inflow is Squaw Creek, a tributary of Crab Creek. An additional inflow is located along Oriel Rodgers road. A small wetland area is located just prior to the beginning of the lake at this inflow.

The length is 1.93 km and the breadth is 1.28 km. The maximum depth is 15 m with a mean depth of 4.77 m. The surface area is 101 x 10^4 m^2 with a shoreline length of 10.9 km and a shoreline development of 3.06. The basin volume is 482 x 10^4 m^2.

Lake Girard typically develops a strong, stable summer stratification. The epilimnion depth at this time is generally around 4 m. The mean summer TSICHL for the epilimnion was 60.8 ± 10.4 for the period 1986-1990 (Table 1).

Liberty Lake

Liberty Lake is connected to Lake Girard via Squaw Creek. The outflow of Girard forms the primary inflow to Liberty. In addition, a small wooded are is adjacent to the inflow bay of Liberty.

The length is 1.34 km and the breadth is 0.62 km. The maximum depth is 14 m with a mean depth of 3.88 m. The surface area is 41.9 x 10^4 m^2 with a shoreline length of 6.40 km and a shoreline development of 2.79. The basin volume is 194 x 10^4 m^3.

Liberty Lake typically does not stratify as strongly as does Lake Girard. The epilimnion depth has been recorded in excess of 5 m. Mean epilimnion TSICHL was 59.8 ± 10.7 for summer months June, July and August during the years 1986-1990 (Table 1).

Lake McKelvey

Lake McKelvey is located east of Youngstown, Ohio. The primary inflow is Dry Run Creek. A floodplain exists along the banks of the inflow creek. During periods of heavy rain, this area turns into a relatively large inflow bay, with subsequent submergence of the plants along the bank.

Morphometric data were not available for Lake Mckelvey. Lake Mckelvey has a dendritic shoreline, and thus a relatively large shoreline development. The maximum depth is in excess of 15 m (personal observation). Lake McKelvey is capable of strong, stable thermal stratification, with a typical epilimnion depth of 4 m. Mckelvey is generally less productive than the other five reservoirs. The mean summer TSICHL for 1986 to 1990 was 48.7 ± 8.0 (Table 1).

MATERIALS AND METHODS

Sampling Procedure

Six sampling trips were made during the spring and summer of 1992 . Samples were drawn at approximately monthly intervals from March to September, a time period that covers spring turnover and summer stratification. One additional sampling trip was made during the first week of September, 1993 (Table 2).

Samples were collected in one liter bottles from the primary inflow (site 0) and the outflow (site 5). Outflow samples were collected only when water was flowing over the spillway. Surface samples were also collected from the upper middle and lower reaches of the reservoir (sites 1, 2, 3 and 6) and the hypolimnion (site 4). Sampling locations are illustrated in Figure 5. The Squaw Creek primary inflow to Girard Lake was not readily accessible either by boat or land. Therefore, site 0 was taken at the Oriel Rogers road inflow. Hypolimnion samples (site 4) were taken from all lakes except Pine. Hypolimnion samples were collected about one meter from the sediment surface with a VanDorn water bottle. In addition, a surface sample was taken from the secondary inflow bays (site 6) in lakes McKelvey, Liberty and Girard. Site 6 in Lake Girard is near the Squaw Creek inflow.

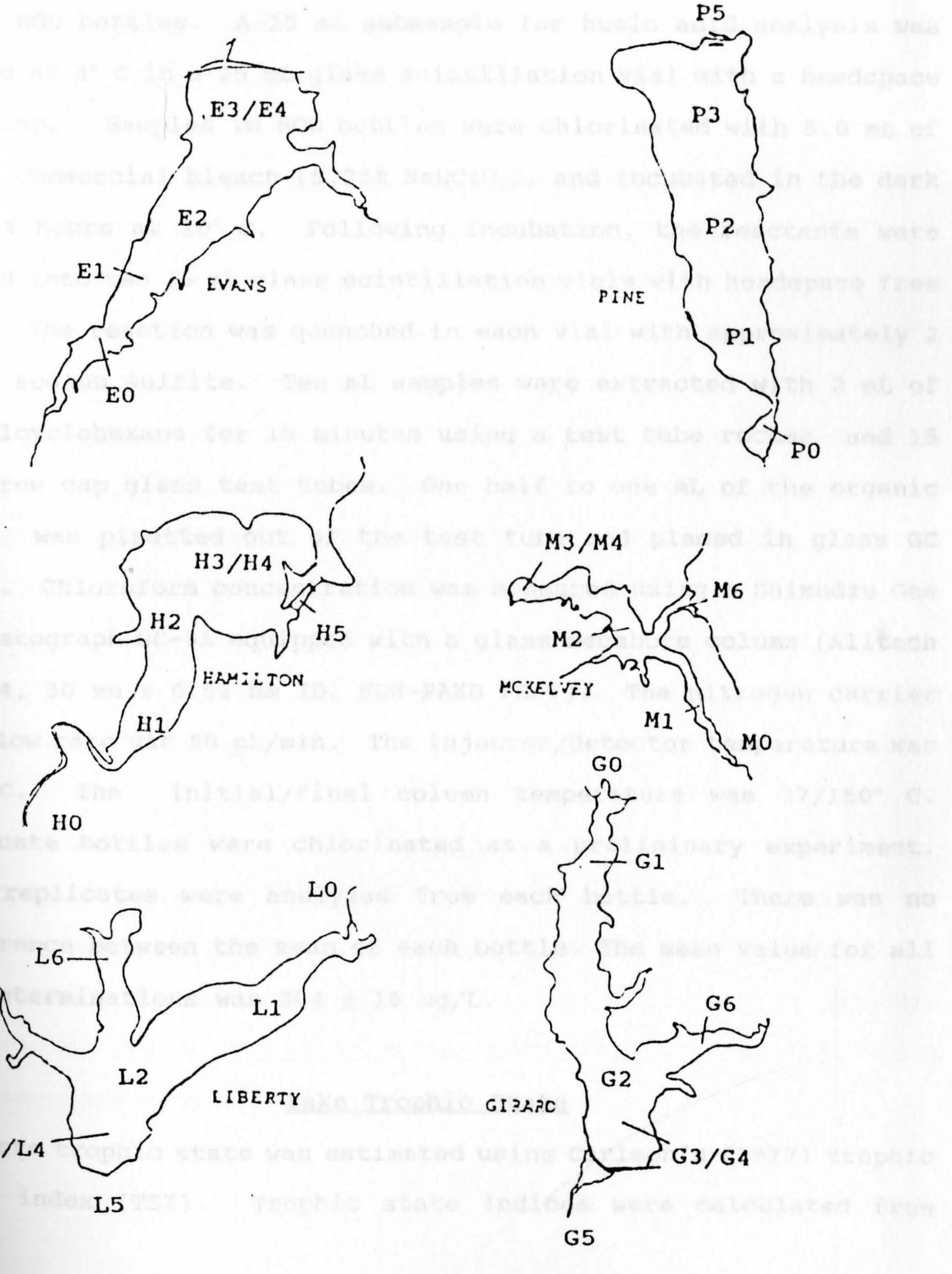
Trihalomethane Formation Potential

Trihalomethane formation potential (THMFP) was determined by chlorination of filtered and buffered lake water. Raw water was filtered with a Whatman filter apparatus, using 34 mm diameter,

Table 2: Sampling dates for OWS reservoirs.

	Sample Sequence						
Lake	1	2	3	4	5	6	7
Pine	3/17/92	4/7/92	4/30/92	5/26/92	7/29/92	8/21/92	9/4/93
Evans	3/17/92	4/7/92	4/30/92	5/26/92	7/29/92	8/21/92	9/4/93
Hamilton	3/18/92	4/7/92	4/29/92	5/27/92	7/30/92	8/23/92	9/6/93
McKelevy	3/18/92	4/8/92	4/29/92	5/27/92	7/30/92	8/23/92	9/6/92
Liberty	3/19/92	4/8/92	4/28/92	5/28/92	7/30/92	8/22/92	9/5/93
Girard	3/19/92	4/8/92	4/28/92	5/28/92	7/30/92	8/22/92	9/5/93

Fig. 5. Sampling locations in OWS reservoris. Maps are not drawn to scale.


E3/E4
E2
E1
EVANS
E0
P5
P3
P2
PINE
P1
P0
H3/H4
H2
H5
HAMILTON
H1
H0
M3/M4
M6
M2
MCKELVEY
M1
M0
G0
G1
L0
L6
L1
L2
LIBERTY
L3/L4
L5
G6
G2
GIRARD
G3/G4
G5

0.45 *u*m pore glass fiber filters. Three hundred fifty mL of filtered water was buffered with 10.0 mL of pH 7.8 borate buffer (2 ml 0.05 M $Na_2B_4O_7$ $10H_2O$ + 8 ml 0.2 m H_3BO_3) and used to fill 304 mL glass BOD bottles. A 25 mL subsample for humic acid analysis was stored at 4° C in a 25 mL glass scintillation vial with a headspace free cap. Samples in BOD bottles were chlorinated with 5.0 mL of fresh commercial bleach (5.25% $NaHClO_3$), and incubated in the dark for 24 hours at 20° C. Following incubation, the reactants were poured into two 25 mL glass scintillation vials with headspace free caps. The reaction was quenched in each vial with approximately 2 mg of sodium sulfite. Ten mL samples were extracted with 2 mL of methylcyclohexane for 15 minutes using a test tube rocker and 15 mL screw cap glass test tubes. One half to one mL of the organic phase was pipetted out of the test tube and placed in glass GC vials. Chloroform concentration was measured using a Shimadzu Gas Chromatograph GC-9A equipped with a glass megabore column (Alltech AT-624, 30 mm x 0.53 mm ID. NON-PAKD FSOT). The nitrogen carrier gas flow rate was 50 mL/min. The injector/detector temperature was 200° C. The initial/final column temperature was 37/150° C. Replicate bottles were chlorinated as a preliminary experiment. Five replicates were analyzed from each bottle. There was no difference between the mean of each bottle. The mean value for all ten determinations was 304 ± 16 *u*g/L.

Lake Trophic State

Lake trophic state was estimated using Carlson's (1977) trophic state index (TSI). Trophic state indices were calculated from total phosphorous (TP), chlorophyll a (CHL) and Sechii disk transparency (SD) data. The formulas for calculating these parameters are as follows:

$$TSITP = 10\ (6 - \ln\ (48/TP)/\ln 2)$$

$$TSICHL = 10\ (6 - (2.04 - 0.68\ \ln CHL)/\ln 2)$$

$$TSISD = 10\ (6 - \ln\ SD/2)$$

Where: TP = total phosphorous concentration in ppb.
CHL = chlorophyll a concentration in ppb.
SD = Sechii disk transparency in cm.

Total Phosphorous

Total phosphorous (TP) was determined based on the molybdate method (Lind, 1985). Sample size was reduced from 50.0 mL to 10.0 mL with a proportional reduction in reagent volumes. Sample pH was not adjusted. Absorbance was measured at 880 nm in a 1 cm sipper cell and a slit width of 2 nm, using a Shimadzu UV- Visible Recording Spectrophotometer UV-260. The instrument was calibrated with an external standard.

Chlorophyll a

Chlorophyll a, in the presence of phaeophytin was estimated by the acetone extraction method (Lind, 1985). Absorbance of the pigment extracts was measured at 750, 665, 645, and 630 nm with the Shimadzu UV-260 in the multi lambda mode. The cell and slit width were the same as for TP.

Transparency

Sechii disk transparency was measured at sites 1, 2 and 3 in all lakes, and also at site 6 in lakes Liberty, Girard, and Mckelvey.

Organic Carbon

Total organic carbon (TOC) and soluble organic carbon (SOC) were measured with a Shimadzu Total Organic Carbon Analyzer TOC-500. Unfiltered water was used for TOC analysis. Samples for determination of soluble organic carbon were filtered through Whatman 34 mm diameter, 0.45 um pore glass fiber filters. The instrument was calibrated via an external standard (potassium phthalate ($KHC_8H_4O_4$) + Na_2CO_3 + $NaHCO_3$). Organic carbon was calculated as the difference between total carbon and inorganic carbon. The instrument was run in the TOC mode at the x 3 sensitivity range and carrier gas flow (O_2) of 150 mL/min.

Humic Acid

Humic acid (HA) was measured by direct florescence of filtered and buffered lake water using a Spectrovision FD-300 Dual Monochromator Fluorescence Detector fluorometer. At the wavelength settings, excitation 340 nm and emission 440 nm, humic and fulvic acids have similar fluorescence (Susic and Boto 1990). Parts per million soluble humic and fulvic acids was estimated by comparing lake water fluorescence to a humic acid standard (humic acid, sodium salt, technical purchased from Aldrich Chemical Company Inc.).

Absorbance

Absorbance was measured for filtered and buffered samples at 400, 340, and 254 nm. Analysis was performed with the Shimadzu UV-260 in the multi lambda mode.

pH and Conductivity

pH was measured on unfiltered water samples with an Orion Research Inc. Digital Ion Analyzer 501, calibrated to pH 7, and set for automatic temperature correction. Conductivity was measured on the same samples with a Corning Portable Conductivity Probe. Both parameters were measured in the laboratory within five hours of collection. Sample temperature was within five degrees of room temperature (20° C) at the time of analysis.

Rainfall

Rainfall data were taken from the published reports of the National Oceanic and Atmospheric Administration. Daily rainfall was measured at the National Weather Service Office located at the Youngstown Municipal Airport. Accumulated rainfall was calculated for the three days prior to each sampling trip. Rainfall data from the airport is likely to differ from the actual amount over each reservoir.

Statistics

Analysis of variance, correlation and multiple regression analyses were performed with SPSS statistical software. The multiple range test for all ANOVAS was the Student-Newman-Keuls test with significance level 0.05. Pearson's correlation coefficients were also considered significant at the 0.05 level.

RESULTS

Mean Values for Sample Sites

Mean values for each sampling location in each lake were calculated for the seven trips (Appendix A). Mean THMFP did not exceed 800 ppb for any location during this period, although individual samples were sometimes greater than 1000 ppb. Values at or around 1000 ppb were typically found during the summer in lakes, Girard, Liberty and McKelvey (Appendix B).

Average TOC ranged from 4.3 ± 3 ppm at McKelvey site 4 to 12.0 ± 7 at Pine site 5. Average SOC at each location was between 2.4 ± 3 ppm at McKelvey site 3 and 8.8 ± 6 ppm at Girard site 0.

The mean TSICHL was between 44.7 ± 10.7 at Mckelvey site 3 and 67.2 ± 9.5 at Girard site 1. For epilimnion sites, the range of mean TSITP values was between 46.7 ± 4.8 at Mckelvey site 3 and 65.3 ± 1.9 at Pine site 1. The mean TSISD was between 44.0 ± 4.0 at Evans site 3 to 70.0 ± 5.6 at Pine site 1.

Mean values for each site were calculated for humic acid (HA) and absorbance at 254 nm (A254), 340 nm (A340) and 400 nm (A400). Mean HA ranged from 2.6 ± 0.6 ppm at Evans site 2 to 11.3 ± 6 ppm at Girard site 0. Average A254 absorbance was between 0.0650 ± 0.03 at Evans site 2 and 0.1970 ± 0.14 at Girard site 0. Mean A340 absorbance ranged from 0.0121 ± 0.0072 at Evans site 2 to 0.0672 ± 0.0035 in the hypolimnion of Girard. Mean A400 absorbance was between 0.0048 ± 0.0035 at Evans site 2 and 0.0247 ± 0.213 at Girard site 0.

Overall, the OWS reservoirs tended to be basic. The mean pH for the entire population was 8.2 ± 0.6 (n = 189). The average of all hypolimnion sites was 7.5 ± 0.4. Mean Ph values ranged from 7.1 ± 0.2 in the Pine inflow to 8.7 ± 0.6 at Liberty site 1. There was a wide range of conductivity observed, from 290 ± 56 *u*ohms at McKelvey site 3 to 1007 ± 43 *u*ohms in the hypolimnion of Evans.

Oneway ANOVAs

Oneway analysis of variance was performed on mean values for epilimnion sites 1, 2 and 3. Multiple comparisons were not always successful in grouping lake means. Uncertainty of placement is indicated by overlapping lines in the following diagrams. Lake name represents mean epilimnion values and are listed from smallest to largest. Mean THMFP was significantly different among lakes (Oneway ANOVA, F = 5.58, p = 0.003, n = 95). The mean epilimnion THMFP was greater in Girard than in Evans (S-N-K, p = 0.05):

Evans Pine Liberty McKelvey Hamilton Girard

Mean epilimnion TOC was significantly different among lakes. (Oneway ANOVA, F = 8.52, $p \leq 0.005$, n = 79). The means for Evans and McKelvey were not significantly different from one another, but were significantly less than those from Liberty, Girard, Hamilton and Pine:

Evans McKelvey Liberty Girard Hamilton Pine

Significant differences in the mean SOC content of epilimnion water were detected (Oneway ANOVA, F = 6.96, p = 0.0001, n = 55). Lake McKelvey had the least amount of soluble carbon. All other reservoirs were not significantly different form one another:

McKelvey Evans Liberty Pine Girard Hamilton

Average TSISD was significantly different among the reservoirs (ANOVA, F = 4.63, p = 0.0009, n = 85). Multiple comparisons could not conclusively separate mean values of TSISD:

McKelvey Evans Liberty Hamilton Girard Pine

The average TSITP was significantly different among the reservoirs (Oneway ANOVA, F = 8.71, $p \leq 0.00005$, n = 98). Multiple comparisons could not conclusively separate mean values of TSITP for lakes Hamilton, Liberty and Girard:

Evans McKelvey Hamilton Liberty Girard Pine

Average TSICHL was significantly different among the reservoirs (Oneway ANOVA, F = 5.02, $p \leq 0.005$, n = 85), but differences could not be isolated by multiple comparison:

McKelvey Evans Hamilton Liberty Girard Pine

Mean humic acid content was significantly different among the epilimnion of OWS reservoirs (Oneway ANOVA, $F = 33.60$, $p \leq 0.00005$, $n = 99$). Average epilimnion humic acid content was greatest in Lake Hamilton. Lake Girard was greater than all remaining lakes. Liberty and McKelvey were greater than both Pine and Evans. Pine Lake had significantly greater mean, epilimnion humic acid levels than Lake Evans:

Evans Pine McKelvey Liberty Girard Hamilton

Epilimnion conductivity values were significantly different among the of the reservoirs (Oneway ANOVA, $F = 262.65$, $p \leq 0.00005$, $n = 99$). The greatest conductivity was in Evans. Hamilton had greater average conductivity than any of the remaining lakes. Liberty and Girard had greater average conductivity than Pine or McKelvey:

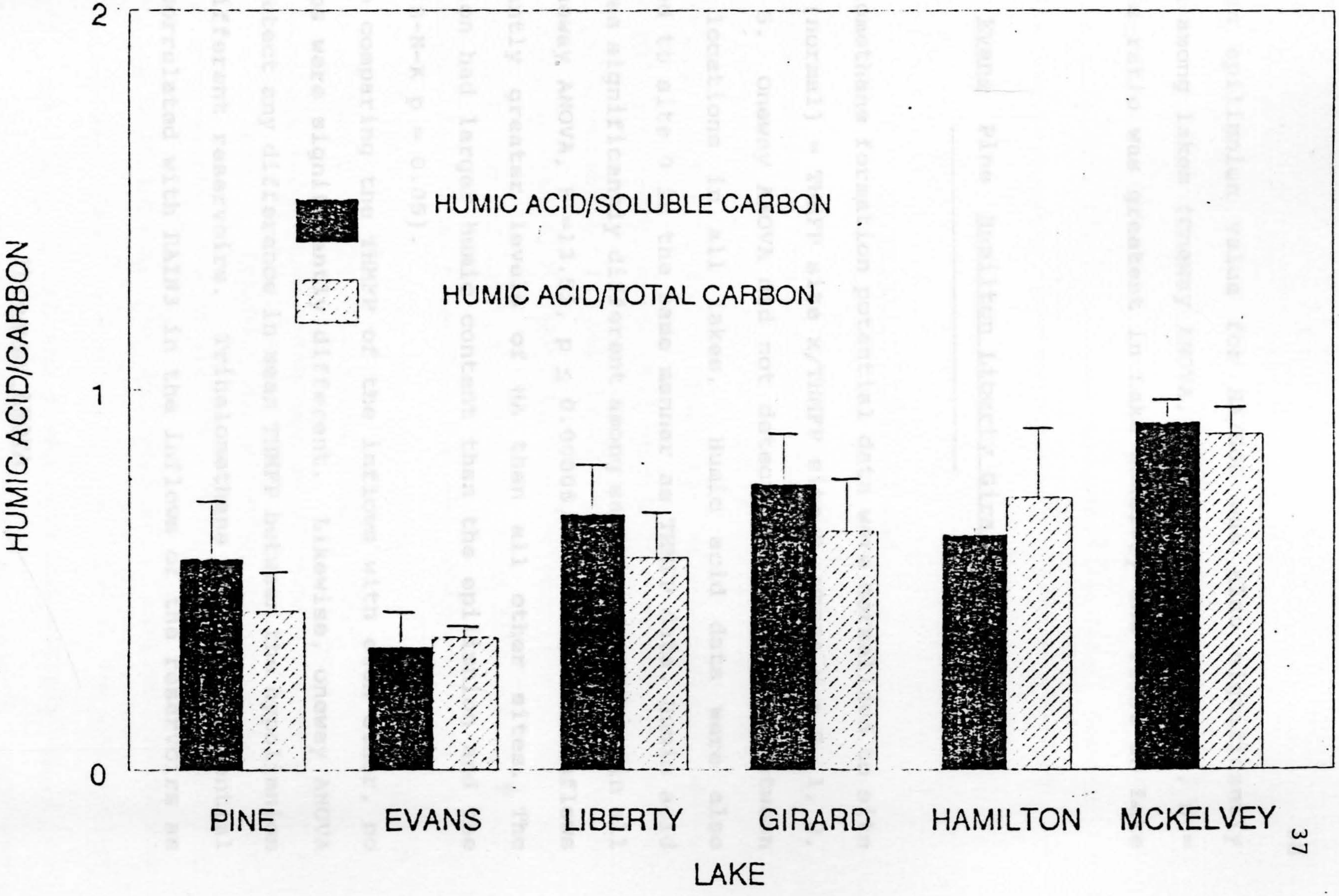
McKelvey Pine Girard Liberty Hamilton Evans

The ratios: HA/TOC and HA/SOC were averaged for epilimnion sites 1, 2 and 3 for each lake (Figure 6). The mean HA/TOC was significantly different among lakes (Oneway ANOVA, $F = 33.14$, $p \leq 0.00005$, $n = 79$). This ratio was greatest in Lake McKelvey and least in Pine and Evans:

Evans Pine Liberty Girard Hamilton McKelvey

Fig. 6. Humic acid to carbon ratios. Mean values of all samples from sites 1, 2 and 3 (epilimnion) ± SD.

HUMIC ACID TO CARBON RATIOS



The mean epilimnion value for HA/SOC was also significantly different among lakes (Oneway ANOVA, $F = 30.17$, $p \leq 0.00005$, $n = 54$). This ratio was greatest in Lake McKelvey and least in Lake Evans:

Evans Pine Hamilton Liberty Girard McKelvey

Trihalomethane formation potential data were normalized to site 0. THMFP (normal) = THMFP site x/THMFP site 0, where $x = 0, 1, 2, 3, 4,$ or 5. Oneway ANOVA did not detect any difference between sampling locations in all lakes. Humic acid data were also normalized to site 0 in the same manner as THMFP data. Humic acid content was significantly different among sampling locations in all lakes (Oneway ANOVA, $F = 13.53$, $p \leq 0.00005$, $n = 185$). The inflows significantly greater levels of HA than all other sites. The hypolimnion had larger humic content than the epilimnion and the outflow (S-N-K $p = 0.05$).

When comparing the THMFP of the inflows with each other, no two groups were significantly different. Likewise, oneway ANOVA did not detect any difference in mean THMFP between the hypolimnion of the different reservoirs. Trihalomethane formation potential was not correlated with RAIN3 in the inflows of the reservoirs as a group.

Threeway ANOVA

The effect of lake, sample location and sampling date on water quality parameters using a threeway ANOVA. Results of three way

ANOVA are given in Table 3. Trihalomethane formation potential was significant for lake and sampling date , but not for site. Mean HA was significant for site, lake, and sampling date. Average TSISD was significant for site, lake and sampling date. Mean TSITP was by lake and by season. Average TSICHL was variable by lake and sampling date.

Correlation Coefficients

Trihalomethane formation potential was not correlated with either TOC ($r = 0.095$, $p = 0.698$) or SOC ($r = 0.157$, $p = 0.101$) for all sites sampled (Table 4a). There was no correlation between THMFP and TOC ($r = 0.033$, $p = 0.782$) or SOC ($r = -0.005$, $p = 0.971$) for epilimnion sites 1, 2, and 3 (Table 4b). Soluble organic carbon was correlated with THMFP in the inflows ($r = 0.394$, $p = 0.047$) but TOC was not ($r = 0.229$, $p = 0.207$) (Table 4c). Trihalomethane formation potential did not correlate with either TOC ($r = 0.223$, $p = 0.358$) or SOC ($r = 0.058$, $p = 0.857$) in the hypolimnia of the five dimictic lakes (Table 5d).

For all locations, THMFP was not correlated with TSITP ($r = 0.078$, $p = 0.289$). Trophic state index chlorophyll a did correlate with THMFP ($r = 0.219$, $p = 0.019$) for all locations excluding the hypolimnion. For all epilimnion samples, TSISD was not correlated with THMFP ($r = -0.102$, $p = 0.330$). For epilimnion sites 1, 2, and 3 only, TSISD and THMFP were not correlated ($r = -0.038$, $p = 0.735$). For epilimnion sites 1, 2 and 3 THMFP was correlated with TSICHL ($r = 0.276$, $p = 0.027$) but not TSITP (r =

Table 3: Results of three way ANOVA. THMFP and related parameters were tested by lake (LCN), site (SC) sampling trip (SMP).

THMFP

Source of Variation	Sum of Squares	DF	Mean Square	F	Sig of F
Main Effects	4893181.018	16	305823.814	10.523	.000
LCN	1459347.617	5	291869.523	10.043	.000
SC	185710.369	5	37142.074	1.278	.277
SMP	3401447.006	6	566907.834	19.507	.000
Explained	4893181.018	16	305823.814	10.523	.000
Residual	3778012.873	130	29061.637		
Total	8671193.891	146	59391.739		

HA

Source of Variation	Sum of Squares	DF	Mean Square	F	Sig of F
Main Effects	538.961	16	33.685	19.575	.000
LCN	400.942	5	80.188	46.598	.000
SC	33.134	5	6.627	3.851	.003
SMP	103.017	6	17.169	9.977	.000
Explained	538.961	16	33.685	19.575	.000
Residual	221.990	129	1.721		
Total	760.951	145	5.248		

Table 3: Continued.

TSISD

Source of Variation	Sum of Squares	DF	Mean Square	F	Sig of F
Main Effects	6689.178	14	477.798	10.906	.000
LCN	2854.990	5	570.998	13.033	.000
SC	412.083	3	137.361	3.135	.030
SMP	4017.359	6	669.560	15.283	.000
Explained	6689.178	14	477.798	10.906	.000
Residual	3373.375	77	43.810		
Total	10062.553	91	110.578		

TSITP

Source of Variation	Sum of Squares	DF	Mean Square	F	Sig of F
Main Effects	5802.588	16	362.662	4.924	.000
LCN	2496.064	5	499.213	6.778	.000
SC	614.753	5	122.951	1.669	.147
SMP	2436.060	6	406.010	5.513	.000
Explained	5802.588	16	362.662	4.924	.000
Residual	9427.074	128	73.649		
Total	15229.662	144	105.762		

TSICHL

Source of Variation	Sum of Squares	DF	Mean Square	F	Sig of F
Main Effects	7778.680	14	555.620	20.144	.000
LCN	2616.664	5	523.333	18.973	.000
SC	91.221	4	22.805	.827	.513
SMP	4908.194	5	981.639	35.589	.000
Explained	7778.680	14	555.620	20.144	.000
Residual	1903.207	69	27.583		
Total	9681.887	83	116.649		

Table 4a: Correlation coefficients for all sites sampled. Table gives r, n and p. Probabilities listed as .000 are ≤ .0005.

Analyte

THMFP	TOC	SOC	TSICHL	TSITP	TSISD	HA	COND	PH	A254	A340	A400
r	.0949	.1574	.2193	.0779	-.1015	.3242	-.2809	.1341	.3658	.3676	.3301
n	150	110	115	187	94	189	190	189	174	174	174
p	.248	.101	.019	.289	.330	.000	.000	.066	.000	.000	.000

Table 4b: Correlation coefficients for epilimnion sites 1, 2, and 3.

THMFP	TOC	SOC	TSICHL	TSITP	TSISD	HA	COND	PH	A254	A340	A400
r	.0326	-.0052	.2759	.0398	-.0377	.4072	-.3372	.2236	.5309	.4889	.3908
n	75	53	64	93	83	94	95	95	47	47	47
p	.782	.971	.027	.703	.735	.000	.001	.029	.000	.000	.000

Table 4c: Correlation coefficients for inflow sites.

THMFP	TOC	SOC	TSICHL	TSITP	TSISD	HA	COND	PH	A254	A340	A400
r	.2293	.3937	.1387	.1792		.3146	-.3350	.0942	.2691	.3675	.3421
n	32	26	30	40		41	41	41	35	35	35
p	.207	.047	.465	.268		.045	.032	.558	.118	.030	.044

Table 4d: Correlation coefficients for hypolimnion sites. Includes all lakes except Pine.

THMFP	TOC	SOC	TSICHL	TSITP	TSISD	HA	COND	PH	A254	A340	A400
r	.2232	.0585		.0145		.1421	-.0716	.1230	.2381	.2459	.2071
n	19	12		22		23	23	23	23	23	23
p	.358	.857		.949		.518	.746	.567	.274	.258	.343

0.040, $p = 0.703$). For the inflows, THMFP did not correlate with either TSICHL ($r = 0.139$, $p = 0.465$) or TSITP ($r = 0.179$, $p = 0.268$).

For all the locations sampled, THMFP was positively correlated with HA ($r = 0.324$, $p \leq 0.0005$), A254 ($r = 0.366$, $p \leq 0.005$), A340 ($r = 0.368$, $p \leq 0.005$) and A400 ($r = 0.330$, $p \leq 0.005$). When only epilimnion sites 1, 2 and 3 are tested THMFP again was correlated with all four parameters: HA ($r = 0.407$, $p \leq 0.005$), A254 ($r = 0.531$, $p \leq 0.005$), A340 ($r = 0.489$, $p \leq 0.005$) and A400 ($r = 0.391$, $p \leq 0.005$). For all lake inflows, THMFP did not correlate with A254 ($r = 0.2691$, $p = 0.118$) but did for A340 ($r = 0.3675$, $p = 0.03$), A400 ($r = 0.342$, $p = 0.044$) and HA ($r = 0.315$, $p = 0.045$). In the hypolimnion of the dimictic lakes, THMFP did not correlate with any of the humic material indicators: HA ($r = 0.142$, $p = 0.518$), A254 ($r = 0.238$, $p = 0.274$), A340 ($r = 0.246$, $p = 0.258$) and A400 ($r = 0.207$, $p = 0.343$).

For all locations, THMFP was negatively correlated with conductivity ($r = -0.281$, $p \leq 0.0005$). Trihalomethane formation potential was negatively correlated with conductivity in the epilimnion ($r = -0.337$, $p = 0.001$) and inflow ($r = -0.335$, $p = 0.032$), but not in the hypolimnion ($r = -0.072$, 0.746). Multiple regression analysis with THMFP as the dependent variable and the remaining variables as the independents had an r^2 of only 0.187.

DISCUSSION

For THMFP and related water quality parameters, Lake Girard and Lake Evans tended to be the most different. Mean THMFP and TOC was greater in the epilimnion of Girard than Evans. This was consistent with the predicted correlation between THMFP and TOC (Arruda and Fromm, 1989). Deviations from this relationship were seen in Lake McKelvey. The average TOC of the epilimnion was the same as Evans but the mean THMFP was almost twice as great. Because statistical analyses grouped Pine with both McKelvey and Evans for mean THMFP, the significant difference between the later two could not be entirely confirmed. Liberty Lake and Lake Hamilton were similar to Girard with respect to THMFP and organic carbon. Pine lake grouped with Girard for TOC and SOC, but the THMFP appeared to be closer to Evans.

The TSITP was greater in Pine Lake than in Lake Evans or Lake McKelvey. Other than that, multiple comparisons of one way ANOVA results for trophic state indices were generally inconclusive. Based on TSITP, the THMFP of Evans and McKelvey should be similar, but this was not the case. For OWS reservoirs, organic carbon content and trophic state indices were not always good indicators of THMFP.

For mean humic and fulvic acid content (HA), all lakes were significantly different except Mckelvey was the same as Liberty. The smallest average HA was observed in Lake Evans. This corresponds well with the lesser THMFP organic carbon and TSI of this reservoir. The greatest mean HA was found in Lake Hamilton.

this is likely due to contributions of humic material from the Poland Woods. Although greater in humic content, than Girard, McKelvey or Liberty, Lake Hamilton was not greater in THMFP than any of these three. Lake Liberty had lower average humic content than Girard. This is consistent with the findings of Rasmussen, et.al. (1989), who showed that lakes tended to be less colored when they received significant inflow from the outflow of another lake.

Differences existed between lakes in the ratios HA/TOC and HA/SOC. For both these ratios, Lake McKelvey is greater than the other five. This is possibly the reason that Lake Mckelvey has a greater than expected THMFP based on organic carbon of trophic state alone. Differences in these ratios could also explain why Pine Lake had smaller than expected THMFP based on TOC and TSI. These ratios alone were not sufficient too explain all differences in THMFP. They were greater in McKelvey than Liberty, but the THMFP was the same.

For all lakes, THMFP was not significantly greater in the primary inflow, nor was it correlated with the amount of rainfall. It is possible that the contribution to the total THMFP varied between particular inflows on specific occasions. For sample sequence 5, heavy rains increased the humic content in the primary inflows of both McKelvey and Hamilton (Appendix B). A corresponding increase in the THMFP was seen in the McKelvey inflow, but not in the Hamilton inflow. The lack of significant differences between inflows could have been due to a large variation during the course of the year. The McKelvey inflow ranged from 293 pbb $CHCl_3$ in March to 1282 ppb $CHCl_3$ in August.

Nykvist (1963), found that different types of leaf litter leached different quantities and types of organic substances. It is possible that humic materials leached from the Poland Forest were less suitable THM precursors than what was produced in the McKelvey inflow flood plain.

Trihalomethane formation potential does not show significant correlation with either TOC or SOC for the epilimnion of the OWS reservoirs, and would not make a suitable surrogate parameter to index THMFP in the epilimnia of the OWS reservoirs. Trihalomethane formation potential was correlated with SOC in the inflows of all lakes. The SOC of any water sample is a combination of a variety of compounds. Since it is likely that the percentage of the different classes of compounds can vary, it can be assumed that the per cent made up of suitable THM precursors could also vary. The correlation between THMFP and SOC in the lake inflows could be due to a greater percentage of THM precursors than in the epilimnion. Allocthonous THM precursors can mix with non-precursor SOC already present in the epilimnion, thus altering the percentage of SOC that is able to form THMs.

Rook (1977) implicated humic materials as likely THM precursors in lake water. For the epilimnion of OWS reservoirs, there was positive correlation between THMFP and humic acids. While HA would likely be a better surrogate parameter than TOC or SOC, the r^2 is still relatively low overall.

Determining HA by direct fluorescence is more time consuming and expensive than measuring light absorbance at wavelengths 254, 340, and 400 nm. Even though fluorescence is likely to be more specific than uv-absorbance, the correlations with THMFP are no greater. UV-absorbance is equally as effective for predicting THMFP as HA.

There was a lack of correlation between THMFP and HA, A254, A340, A400 in the hypolimnion of the five dimictic lakes. A significant increase in HA concentration occurred between sites 3 and 4 but with no corresponding increase in the THMFP. Gjessing (1975) reported that changes in water quality could produce both qualitative and quantitative changes in humic materials. Not all humic acid fractions produce an equal amount of THMs upon chlorination. Oliver and Visser (1980), found that the 30,000-50,000 molecular weight fraction tended to produce the greatest amount of chloroform. Humic acids could settle out of the epilimnion adsorbed to particulates. As humics accumulate in the hypolimnion, differences in the amount of light, oxygen and temperature could induce changes in the humic acids so as to convert them to less suitable forms.

A positive, correlation exists between THMFP and TSICHL. This indicates that primary productivity has some influence on the THMFP of the OWS reservoirs. Trophic state indices calculated from Sechii disk and total phosphorous data do not show any correlation with THMFP. This could be due to the fact that TSICHL tends to be the most accurate estimate of a lake's trophic state (Carlson, 1977). Total phosphorous indicates only the potential for algal growth, not the actual amount. Sechii disk transparency can be biased by turbidity, particularly near the inflow.

The watershed of a lake can have an influence on the THMFP.

This can be accomplished by increasing the calcium and magnesium ions in the lake, which then is able to precipitate out humic acids. This effect was noted by the significant negative correlation between conductivity and THMFP.

No single water quality parameter, or combination of parameters tested was sufficient to use as a surrogate parameter for THMFP. The quantity of THMs produced by a particular lake are a result of both internal and external factors. The influence of the different factors is likely to vary between lakes. To understand the causes of THMs in a lake, and thus how most efficiently to manage it for a potable water source, a variety of factors should be looked at. These would include amount and types of algae present, the amount of humic material, and the conditions of the watershed. Watershed factors that could lower THMFP would be anything that increased the loading of Ca^{++} and Mg^{++} such as a strip mining. The presence of forested or wetland inflows may increase the concentration of THM precursors depending on the types of vegetation present of the amount of rainfall. Other factors to consider would be the reservoirs shoreline development and whether or not a reservoir was fed by outflow form another reservoir.

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APPENDIX A

Mean values for water quality parameters. Results are averaged for each location sampled, and expressed as mean ± standard deviation.

Trhalomethane formation potential (THMFP). ug/L $CHCl_3$ formed.

Site	Pine	Evans	Liberty	Girard	Hamilton	McKelvey
0	564 ± 158	565 ± 323	628 ± 268	869 ± 334	538 ± 103	717 ± 365
1	535 ± 156	389 ± 129	676 ± 386	879 ± 439	673 ± 240	616 ± 193
2	510 ± 111	365 ± 149	532 ± 146	781 ± 444	644 ± 276	570 ± 220
3	458 ± 152	346 ± 82	521 ± 217	682 ± 297	590 ± 121	667 ± 186
4	-	495 ± 196	524 ± 133	597 ± 127	521 ± 114	438 ± 94
5	487 ± 119	-	531 ± 217	579 ± 372	663 ± 298	-
6	-	-	551 ± 150	663 ± 288	-	772 ± 430

Total organic carbon (TOC). mg/L.

0	13.5 ± 3.2	10.3 ± 3.3	11.5 ± 5.0	12.8 ± 4.4	12.7 ± 4.0	12.4 ± 7.5
1	12.2 ± 2.0	8.4 ± 3.0	12.4 ± 4.8	10.7 ± 1.7	12.9 ± 1.8	7.2 ± 0.6
2	12.6 ± 2.2	10.1 ± 2.2	11.4 ± 4.0	10.1 ± 1.3	11.3 ± 0.8	6.6 ± 0.5
3	10.4 ± 1.9	8.0 ± 3.1	10.1 ± 2.2	11.6 ± 5.2	11.5 ± 1.2	6.5 ± 0.7
4	-	10.9 ± 1.1	11.2 ± 2.5	12.7 ± 4.0	11.3 ± 2.7	5.7 ± 1.0
5	15.0 ± 1.7	-	9.3 ± 1.4	9.6 ± 1.6	11.5 ± 1.9	-
6	-	-	11.3 ± 2.8	13.5 ± 6.8	-	7.1 ± 0.4

Soluble organic carbon (SOC). mg/L.

0	10.0 ± 2.2	9.2 ± 2.0	10.8 ± 2.6	12.7 ± 3.5	9.1 ± 1.8	7.7 ± 2.0
1	8.6 ± 0.9	8.2 ± 2.1	9.0 ± 1.7	9.2 ± 1.4	10.4	6.5 ± 0.5
2	9.7 ± 1.1	9.2 ± 1.7	8.9 ± 1.4	8.9 ± 1.0	10.2 ± 0.1	6.2 ± 0.6
3	8.8 ± 0.8	7.0 ± 2.6	7.9 ± 0.6	9.5 ± 1.9	9.2 ± 1.0	6.1 ± 0.0
4	-	9.7 ± 0.4	9.1 ± 1.4	10.0 ± 0.7	10.2 ± 0.5	5.3 ± 0.4
5	10.4 ± 1.1	-	8.2 ± 1.2	8.2 ± 1.2	8.4 ± 2.8	-
6	-	-	9.0 ± 1.7	10.3 ± 2.1	-	6.7 ± 0.4

Trophic state index calculated from chlorophyll a data (TSICHL).

Site	Pine	Evans	Liberty	Girard	Hamilton	McKelvey
0	58.9 ± 7.1	56.8 ± 5.3	56.9 ± 10.1	49.0 ± 20.3	51.8 ± 14.8	53.0 ± 16.4
1	67.2 ± 9.5	51.8 ± 6.4	52.4 ± 16.1	60.2 ± 20.8	44.5	53.7 ± 12.6
2	64.4 ± 8.4	48.0 ± 8.1	47.0 ± 7.0	59.5 ± 10.3	55.9 ± 10.0	49.0 ± 8.6
3	65.5 ± 14.0	48.6 ± 3.0	57.1 ± 16.0	58.8 ± 10.2	54.9 ± 12.2	44.7 ± 10.7
4	-	-	-	-	-	-
5	63.1 ± 4.4	-	51.9 ± 2.2	56.7 ± 3.0	64.2 ± 6.7	-
6	-	-	56.5 ± 13.8	54.3	-	55.2 ± 13.0

Trophic state index calculated from total phosphorous data (TSITP).

0	68.0 ± 9.5	60.7 ± 5.8	58.4 ± 6.0	68.2 ± 6.1	60.5 ± 13.4	63.4 ± 12.6
1	65.3 ± 1.9	53.4 ± 1.0	57.4 ± 6.2	64.9 ± 5.5	63.0 ± 17.4	53.6 ± 4.2
2	64.5 ± 3.3	51.8 ± 10.3	55.2 ± 7.3	57.9 ± 3.6	53.5 ± 14.7	51.2 ± 6.2
3	63.5 ± 2.9	45.7 ± 4.3	56.2 ± 2.8	58.8 ± 3.1	49.9 ± 16.7	46.7 ± 4.8
4	-	54.7 ± 2.3	59.2 ± 6.1	58.7 ± 27.7	54.4 ± 16.3	55.5 ± 12.7
5	61.9 ± 7.2	-	54.2 ± 6.6	60.2 ± 3.9	60.7 ± 11.2	-
6	-	-	62.1 ± 7.5	65.2 ± 12.6	-	52.3 ± 5.7

Trophic state index calculated from Sechii disk transparencey data (TSISD).

0	-	-	-	-	-	-
1	64.0 ± 5.6	55.1 ± 2.8	57.0 ± 13.8	64.7 ± 6.7	60.8 ± 13.4	52.8 ± 5.6
2	61.1 ± 6.0	47.9 ± 5.7	53.5 ± 14.3	57.7 ± 11.7	56.3 ± 13.9	46.5 ± 4.9
3	59.3 ± 4.6	44.0 ± 4.0	54.2 ± 13.2	57.6 ± 10.9	54.2 ± 13.3	45.6 ± 4.9
4	-	-	-	-	-	-
5	-	-	-	-	-	-
6	-	-	58.9 ± 13.4	59.5 ± 12.1	-	49.4 ± 7.4

Soluble humic and fulvic acids (HA). mg/L.

Site	Pine	Evans	Liberty	Girard	Hamilton	McKelvey
0	9.2 ± 4.4	4.2 ± 1.2	6.6 ± 0.9	11.8 ± 6.0	10.1 ± 4.2	9.6 ± 3.8
1	5.0 ± 1.1	2.9 ± 0.8	6.4 ± 1.0	8.1 ± 1.4	9.5 ± 4.4	6.3 ± 0.6
2	4.6 ± 1.1	2.7 ± 0.6	5.6 ± 0.5	6.8 ± 0.7	8.0 ± 2.4	6.0 ± 0.7
3	4.8 ± 1.3	2.6 ± 0.7	5.9 ± 0.9	6.8 ± 0.8	7.6 ± 1.9	6.2 ± 0.8
4	-	3.3 ± 0.9	7.8 ± 2.3	9.6 ± 3.3	6.8 ± 1.0	7.0 ± 2.2
5	4.3 ± 0.9	-	6.1 ± 0.8	6.7 ± 0.6	7.7 ± 2.5	-
6	-	-	6.5 ± 0.8	7.5 ± 1.2	-	6.6 ± 0.9

Conductivity (COND). umhos.

0	312 ± 10	835 ± 150	387 ± 49	373 ± 67	860 ± 267	342 ± 117
1	316 ± 23	979 ± 61	365 ± 37	352 ± 38	574 ± 173	289 ± 54
2	313 ± 20	999 ± 70	386 ± 52	379 ± 55	642 ± 149	321 ± 72
3	317 ± 34	987 ± 67	375 ± 49	368 ± 55	640 ± 107	290 ± 56
4	-	1007 ± 43	424 ± 38	418 ± 38	819 ± 11	387 ± 48
5	330 ± 13	-	416 ± 35	402 ± 37	664 ± 155	-
6	-	-	359 ± 47	361 ± 34	-	284 ± 59

pH

0	7.1 ± 0.2	8.1 ± 0.2	8.4 ± 0.5	8.2 ± 0.6	7.9 ± 0.5	7.9 ± 0.7
1	8.1 ± 0.6	8.1 ± 0.3	8.7 ± 0.6	8.7 ± 0.8	8.2 ± 0.6	8.3 ± 0.6
2	8.2 ± 0.4	8.1 ± 0.2	8.4 ± 0.6	8.5 ± 0.9	8.4 ± 0.5	8.1 ± 0.5
3	8.4 ± 0.5	8.2 ± 0.1	8.6 ± 0.6	8.6 ± 0.7	8.6 ± 0.4	8.1 ± 0.4
4	-	8.0 ± 0.1	7.4 ± 0.2	7.4 ± 0.2	7.8 ± 0.5	7.2 ± 0.2
5	8.3 ± 0.2	-	8.1 ± 0.5	8.2 ± 0.6	8.4 ± 0.3	-
6	-	-	8.7 ± 0.6	8.6 ± 0.6	-	8.2 ± 0.5

Absorbance at 254 nm x 10^4 (A254).

Site	Pine	Evans	Liberty	Girard	Hamilton	McKelvey
0	1672 ± 682	870 ± 146	1428 ± 310	2523 ± 1294	1615 ± 889	1899 ± 1251
1	1274 ± 201	864 ± 172	1552 ± 264	1821 ± 270	1883 ± 769	1598 ± 198
2	1136 ± 238	764 ± 229	1394 ± 54	1629 ± 307	1670 ± 378	1391 ± 360
3	1234 ± 203	790 ± 116	1365 ± 296	1520 ± 364	1458 ± 429	1494 ± 208
4	-	813 ± 322	1446 ± 519	1878 ± 771	1004 ± 137	1202 ± 319
5	1144 ± 333	-	1212 ± 309	1308 ± 318	1383 ± 443	-
6	-	-	1491 ± 231	1577 ± 155	-	1577 ± 141

Absorbance at 340 nm x 10^4 (A340).

0	489 ± 225	193 ± 50	347 ± 99	787 ± 519	508 ± 387	708 ± 371
1	272 ± 65	168 ± 37	364 ± 37	461 ± 73	552 ± 376	400 ± 72
2	237 ± 83	132 ± 53	344 ± 35	390 ± 65	449 ± 158	320 ± 136
3	258 ± 66	158 ± 33	323 ± 85	360 ± 103	352 ± 114	358 ± 71
4	-	128 ± 66	401 ± 207	672 ± 352	243 ± 57	342 ± 173
5	216 ± 90	-	282 ± 106	302 ± 106	372 ± 178	-
6	-	-	371 ± 47	407 ± 39	-	414 ± 44

Absorbance at 400 nm x 10^4 (A400).

0	214 ± 113	76 ± 32	134 ± 56	324 ± 200	215 ± 176	290 ± 161
1	115 ± 29	72 ± 20	147 ± 16	187 ± 46	223 ± 190	156 ± 34
2	96 ± 47	50 ± 31	143 ± 27	147 ± 24	178 ± 83	126 ± 48
3	103 ± 38	65 ± 18	124 ± 46	135 ± 57	128 ± 49	134 ± 33
4	-	46 ± 33	150 ± 88	242 ± 155	87 ± 36	150 ± 90
5	82 ± 51	-	96 ± 58	102 ± 62	152 ± 79	-
6	-	-	152 ± 28	166 ± 32	-	162 ± 15

APPENDIX B

Fig. 1. Accumulated rainfall three days prior to sampling.

RAINFALL THREE DAYS PRIOR TO SAMPLING

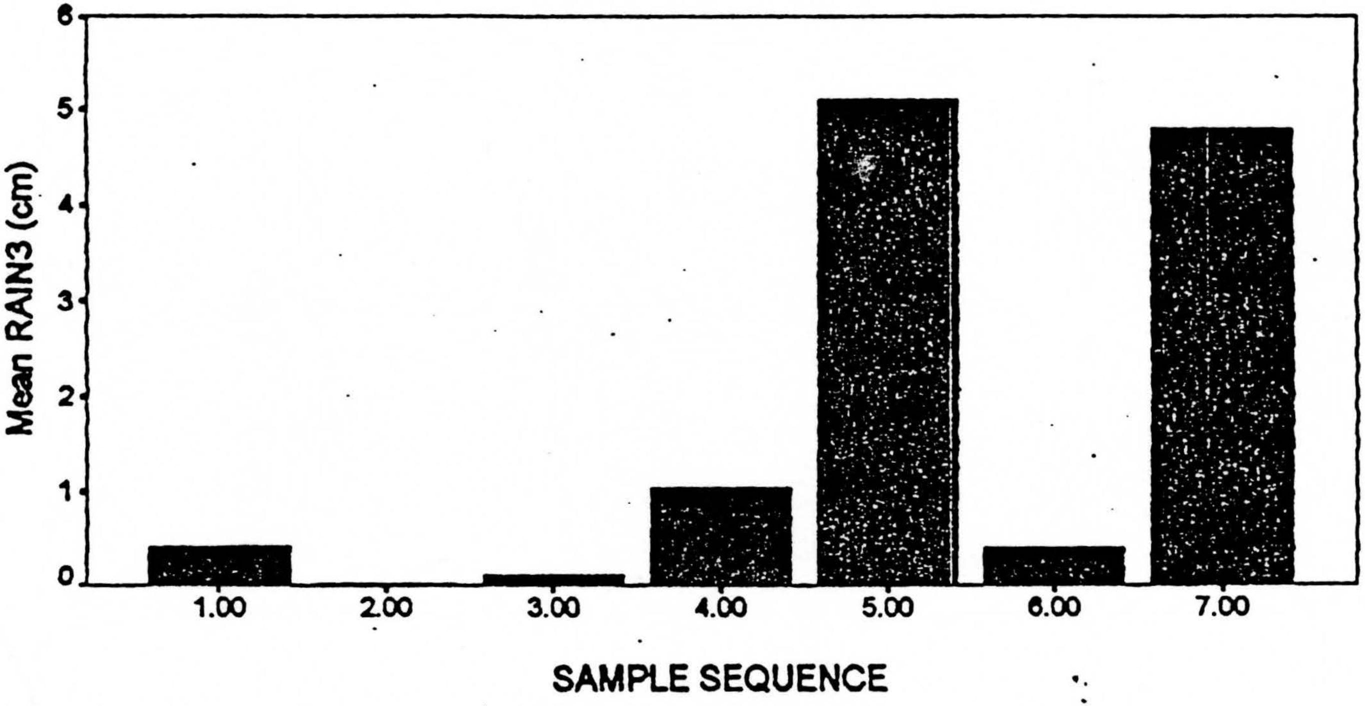
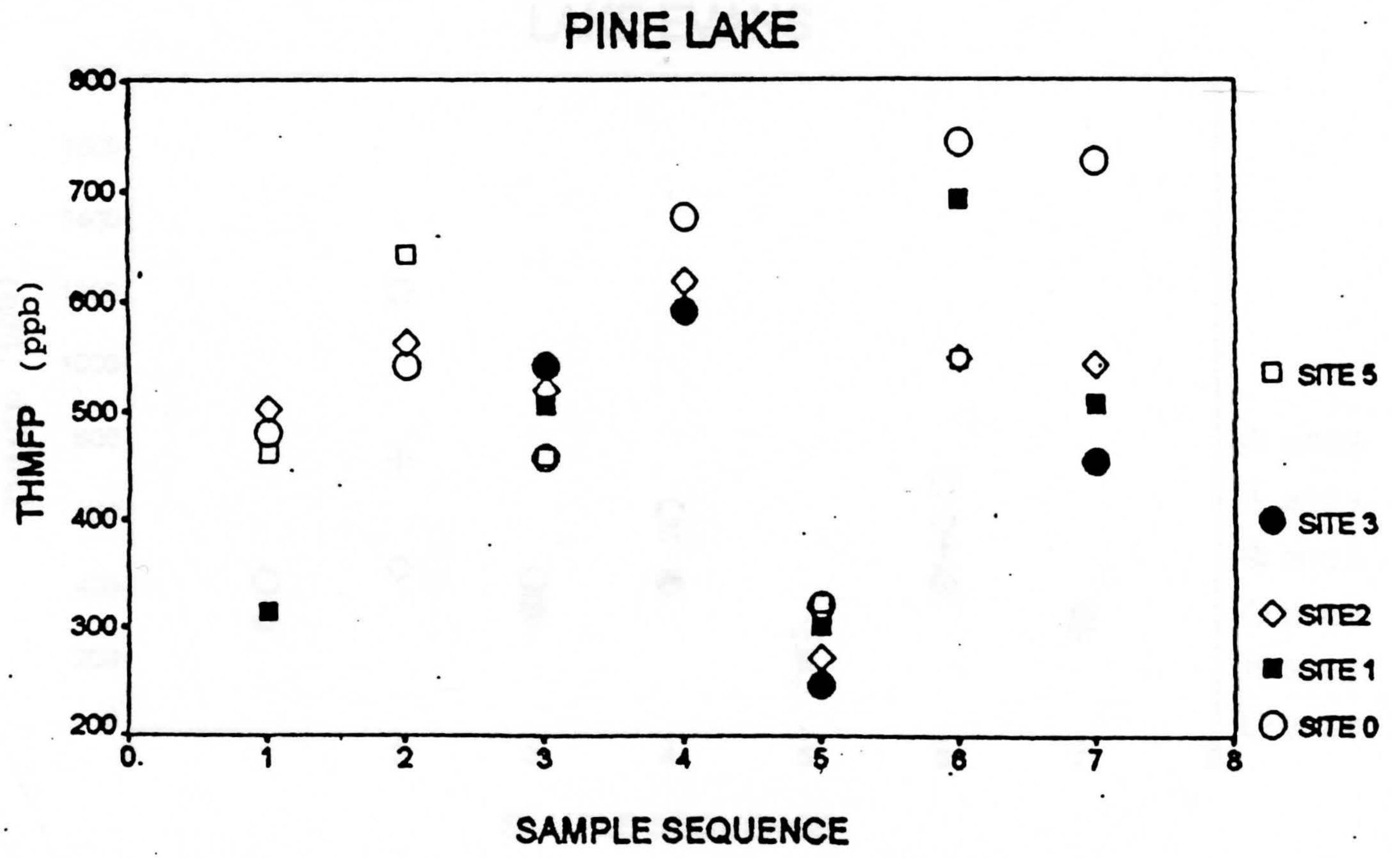
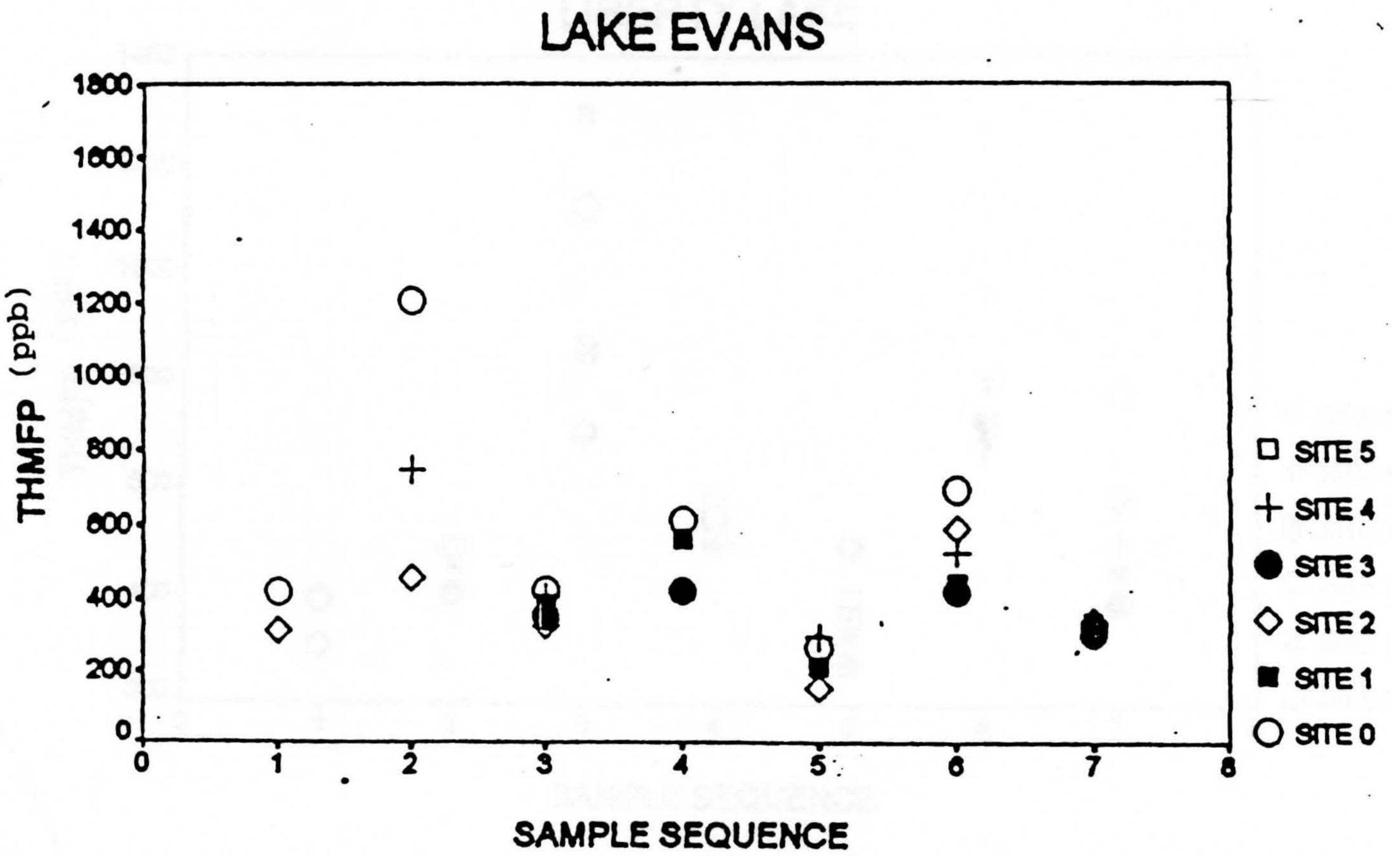
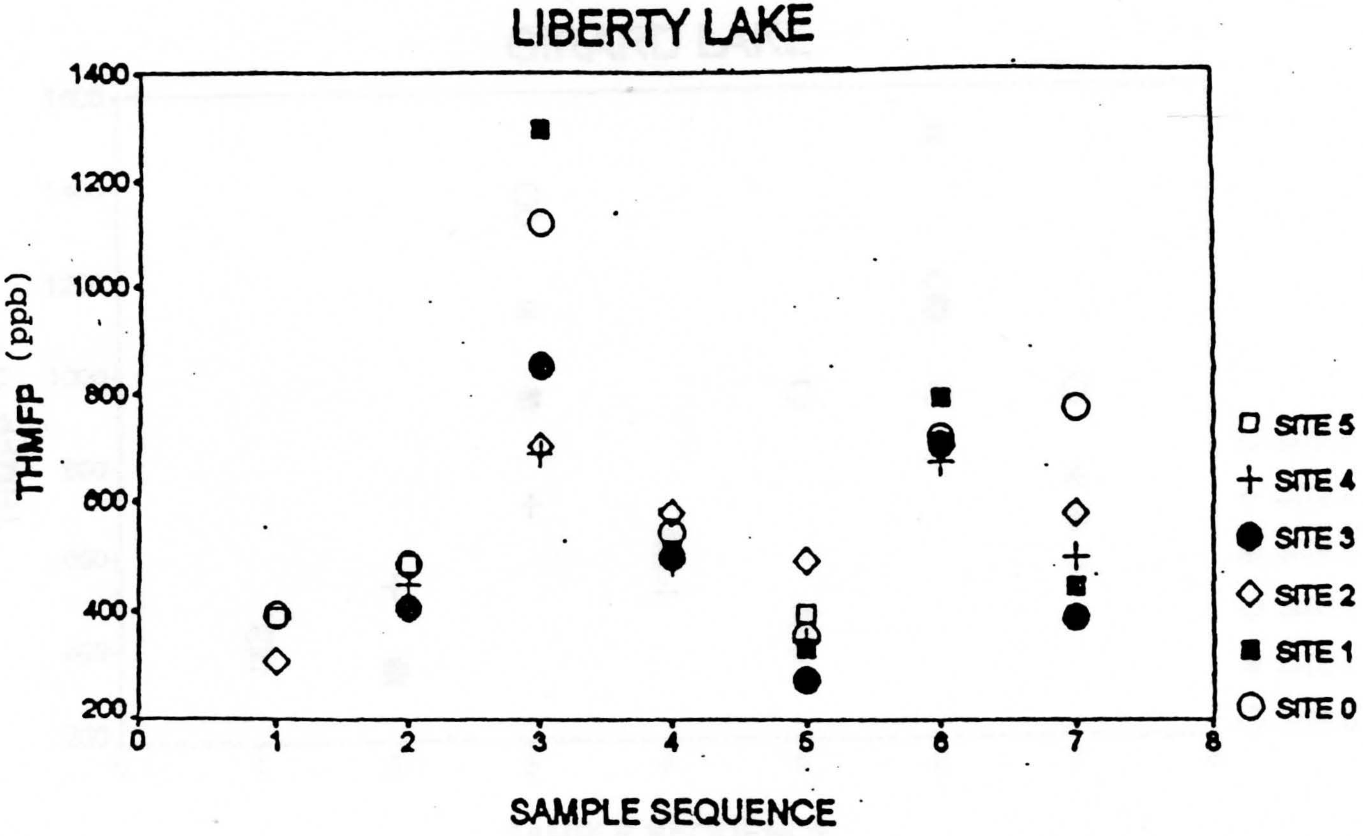
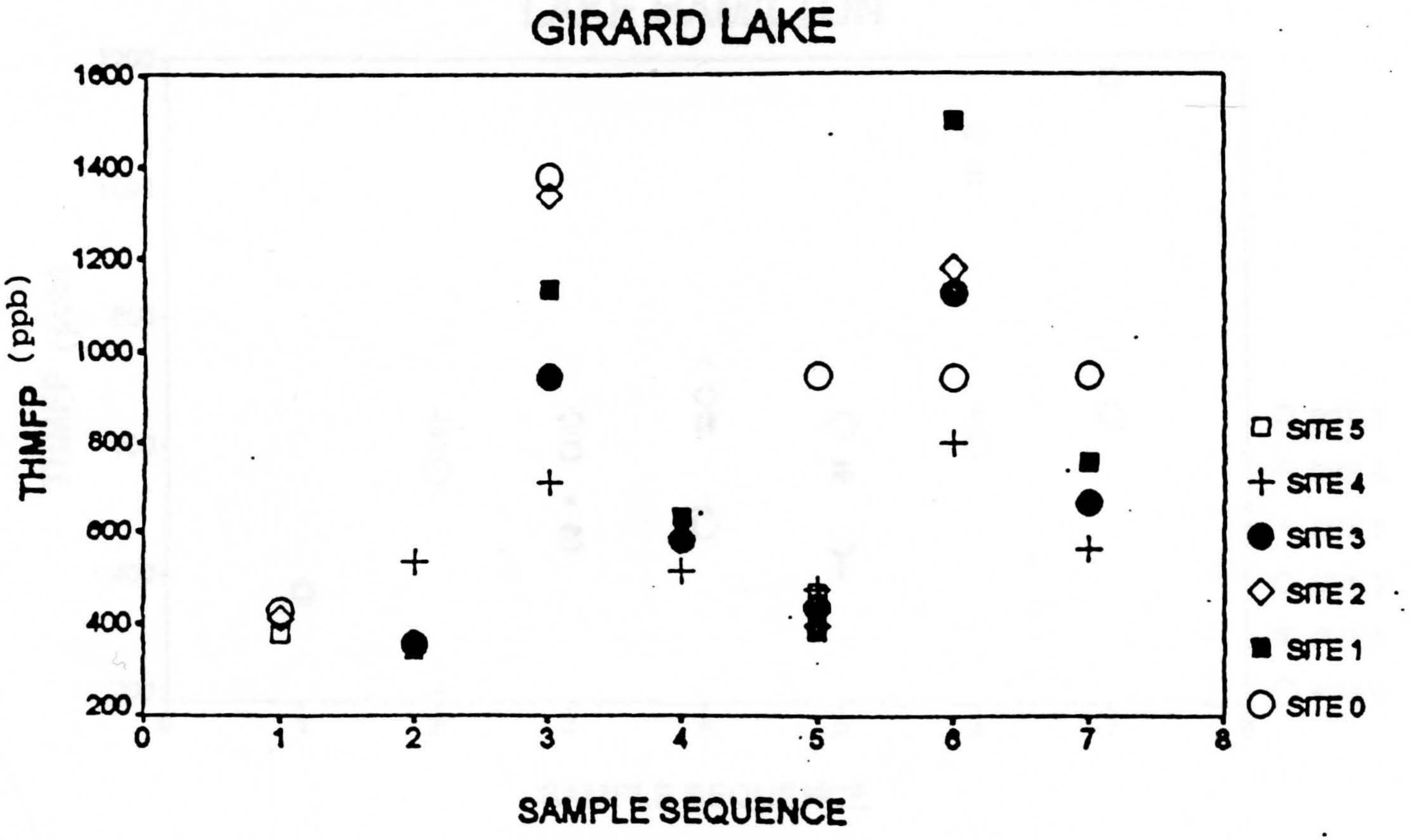


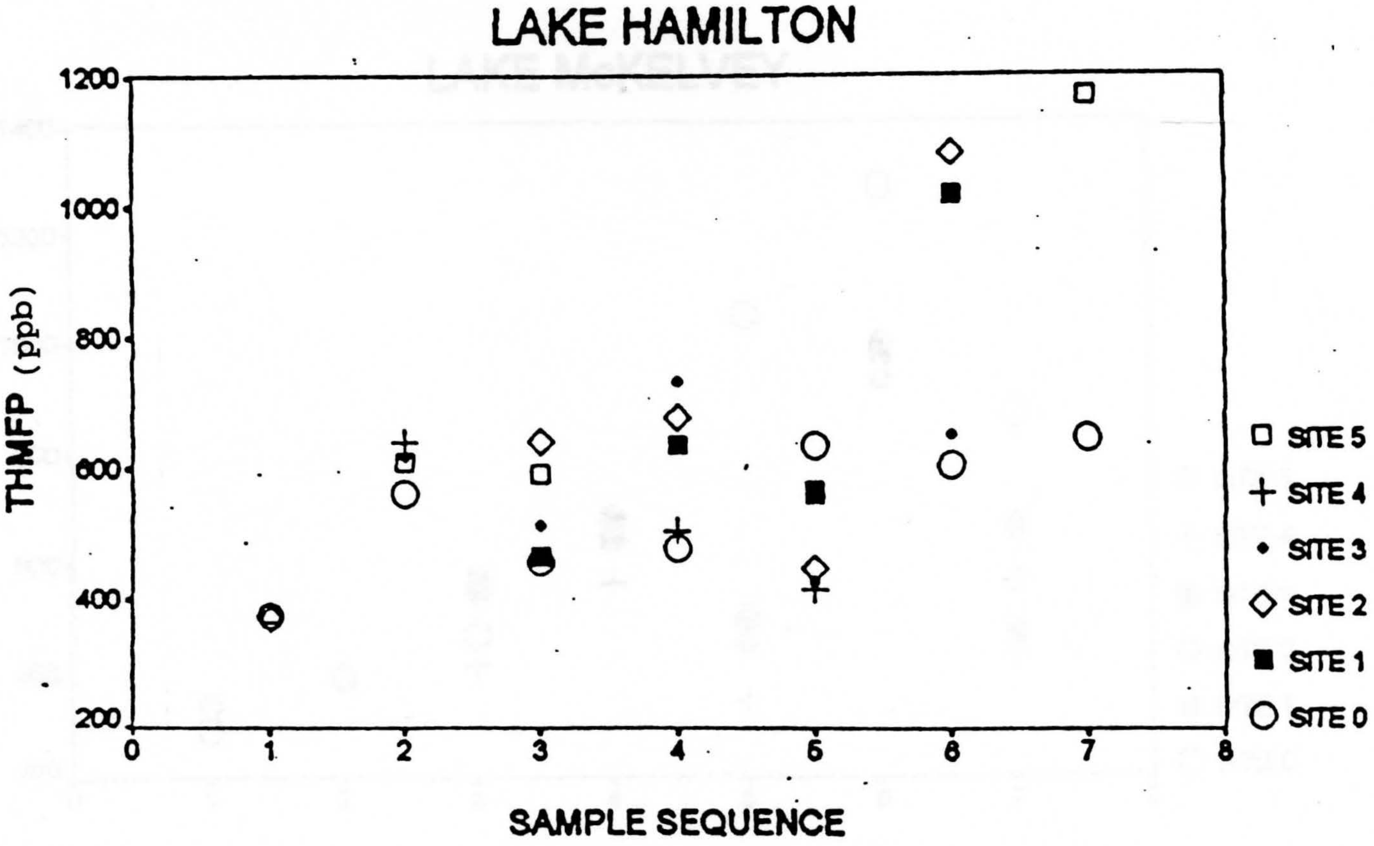
Fig. 2 (a-f). Seasonal variation of THMFP in OWS reservoirs.

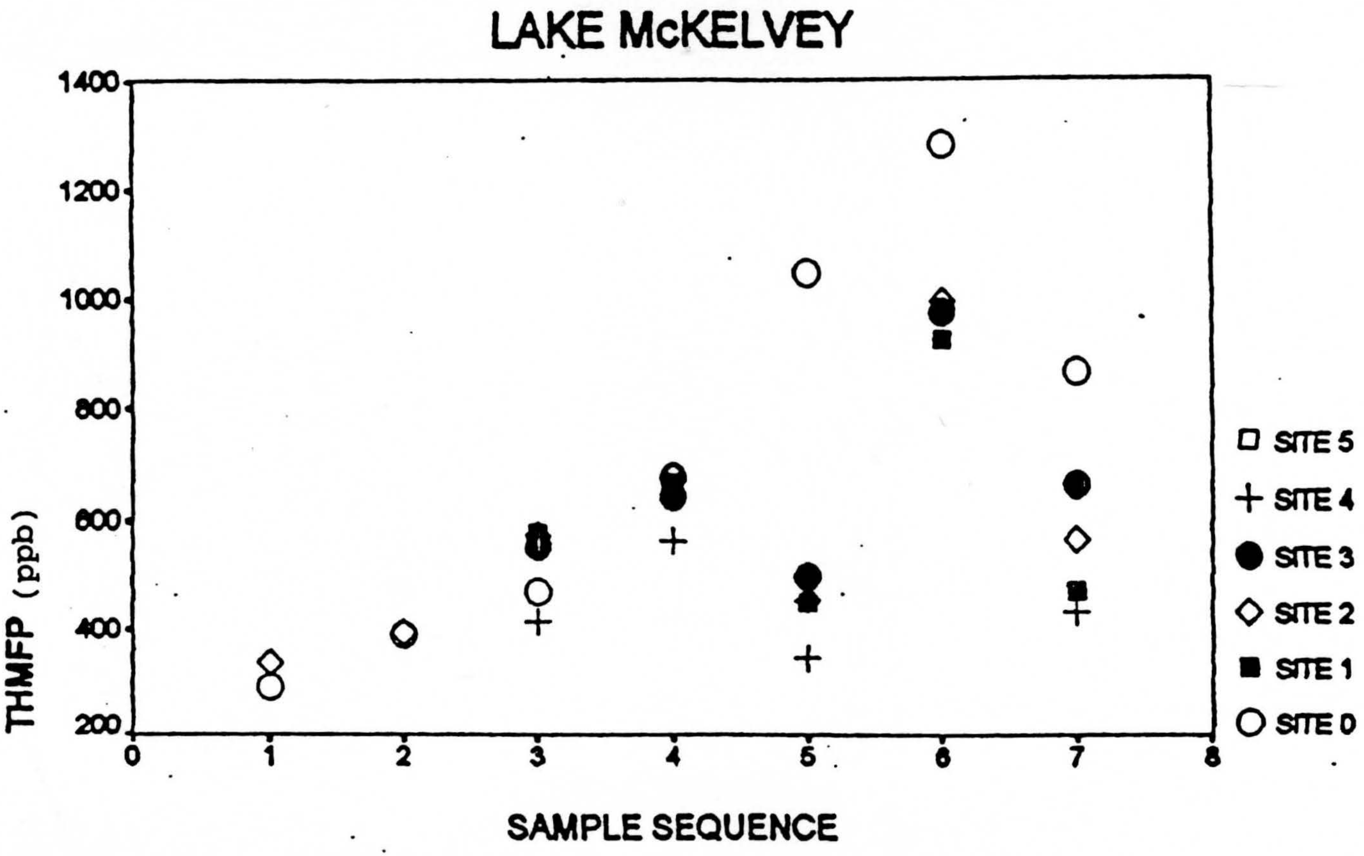

PINE LAKE
THMFP (ppb)
800
700
600
500
400
300
200
0.
1
2
3
4
5
6
7
8
SAMPLE SEQUENCE
□ SITE 5
● SITE 3
◇ SITE2
■ SITE 1
○ SITE 0


LAKE EVANS
THMFP (ppb)
1800
1600
1400
1200
1000
800
600
400
200
0
0
1
2
3
4
5
6
7
8
SAMPLE SEQUENCE
□ SITE 5
+ SITE 4
● SITE 3
◇ SITE 2
■ SITE 1
○ SITE 0

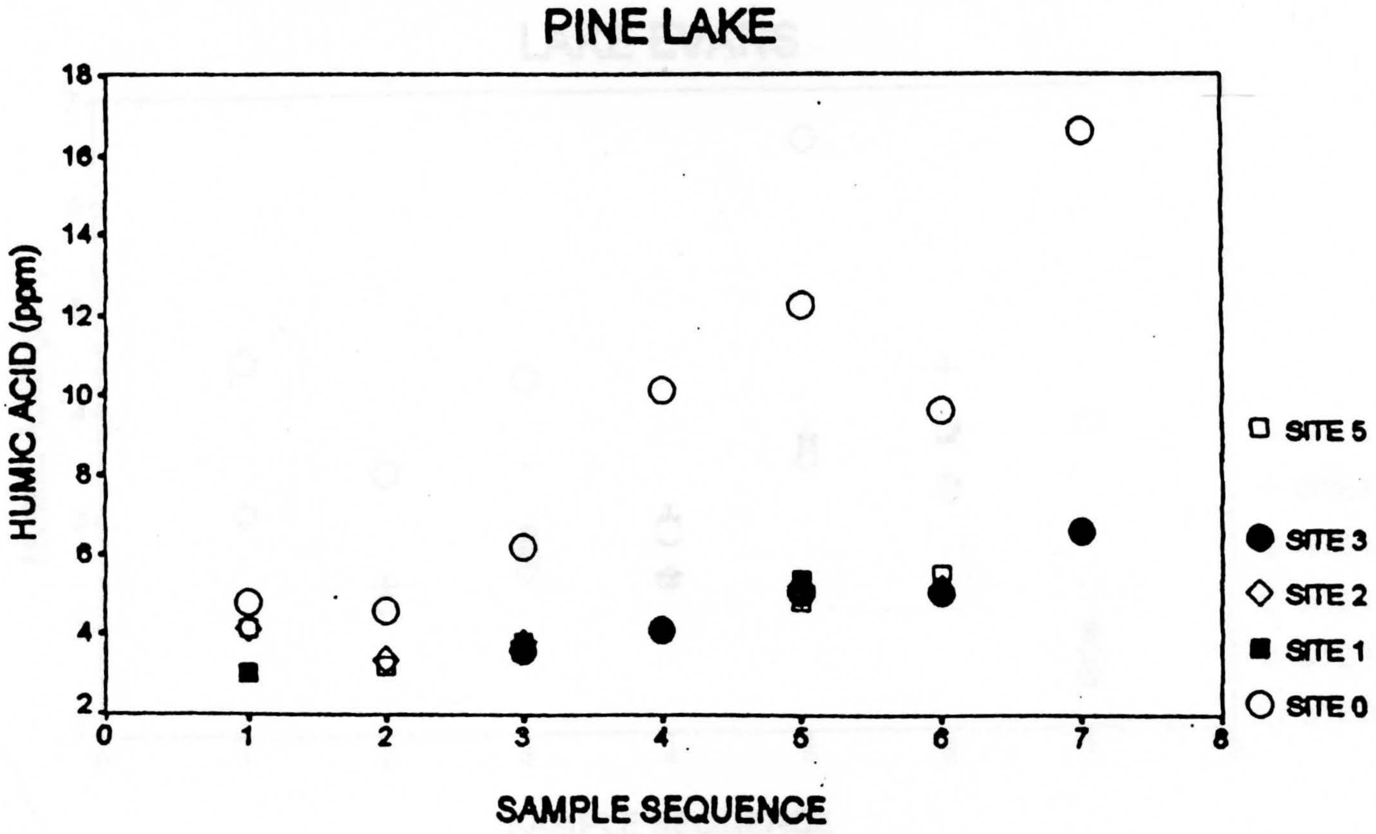

LIBERTY LAKE
THMFP (ppb)
1400
1200
1000
800
600
400
200
0
1
2
3
4
5
6
7
8
SAMPLE SEQUENCE
□ SITE 5
+ SITE 4
● SITE 3
◇ SITE 2
■ SITE 1
○ SITE 0


GIRARD LAKE
THMFP (ppb)
1600
1400
1200
1000
800
600
400
200
0
1
2
3
4
5
6
7
8
SAMPLE SEQUENCE
□ SITE 5
+ SITE 4
● SITE 3
◇ SITE 2
■ SITE 1
○ SITE 0


LAKE HAMILTON
THMFP (ppb)
1200
1000
800
600
400
200
0
1
2
3
4
5
6
7
8
SAMPLE SEQUENCE
□ SITE 5
+ SITE 4
• SITE 3
◇ SITE 2
■ SITE 1
○ SITE 0


LAKE McKELVEY
THMFP (ppb)
1400
1200
1000
800
600
400
200
0
1
2
3
4
5
6
7
8
SAMPLE SEQUENCE
□ SITE 5
+ SITE 4
● SITE 3
◇ SITE 2
■ SITE 1
○ SITE 0

Figs. 3 (a-f). Seasonal variation of humic acid content of OWS reservoirs.


PINE LAKE
HUMIC ACID (ppm)
18
16
14
12
10
8
6
4
2
0
1
2
3
4
5
6
7
8
SAMPLE SEQUENCE
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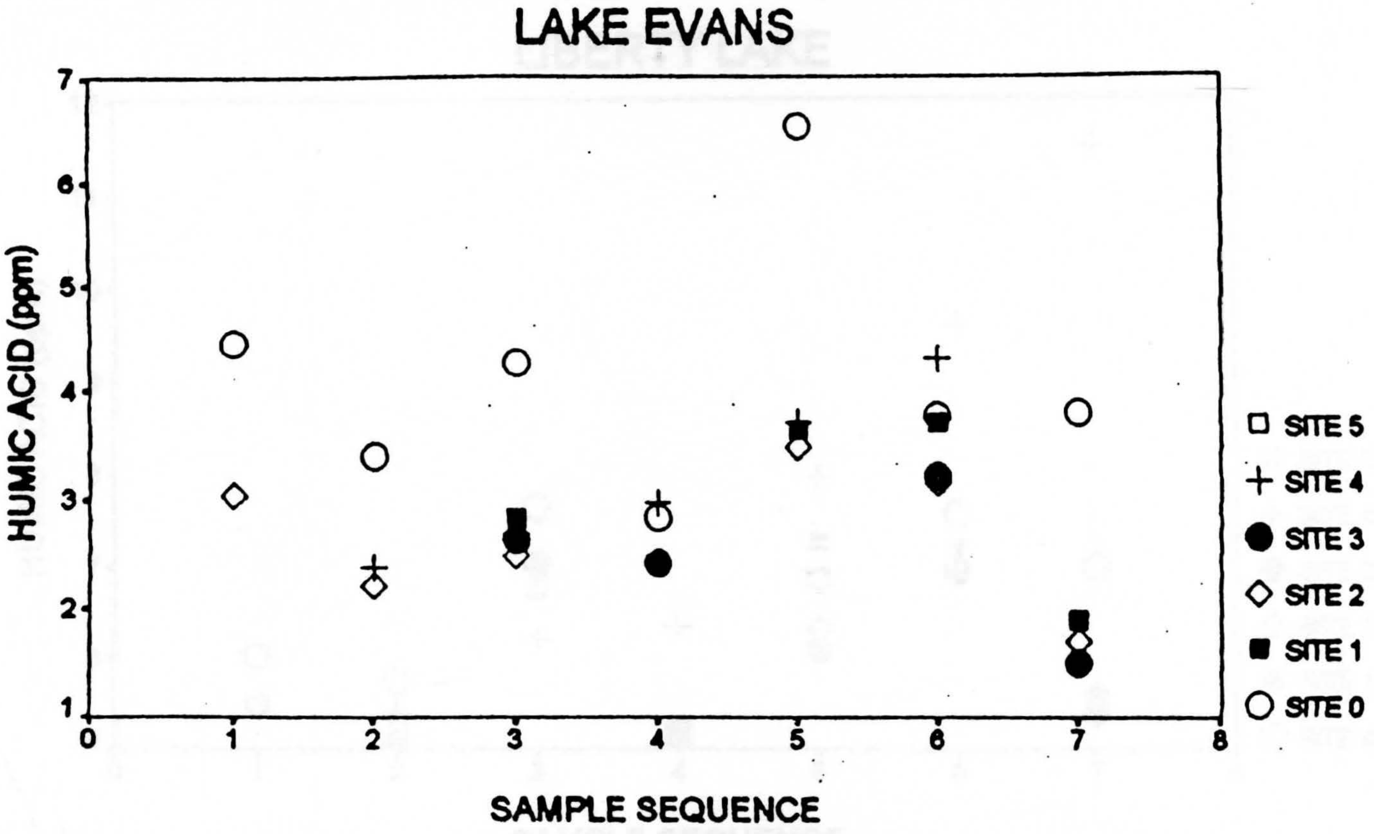
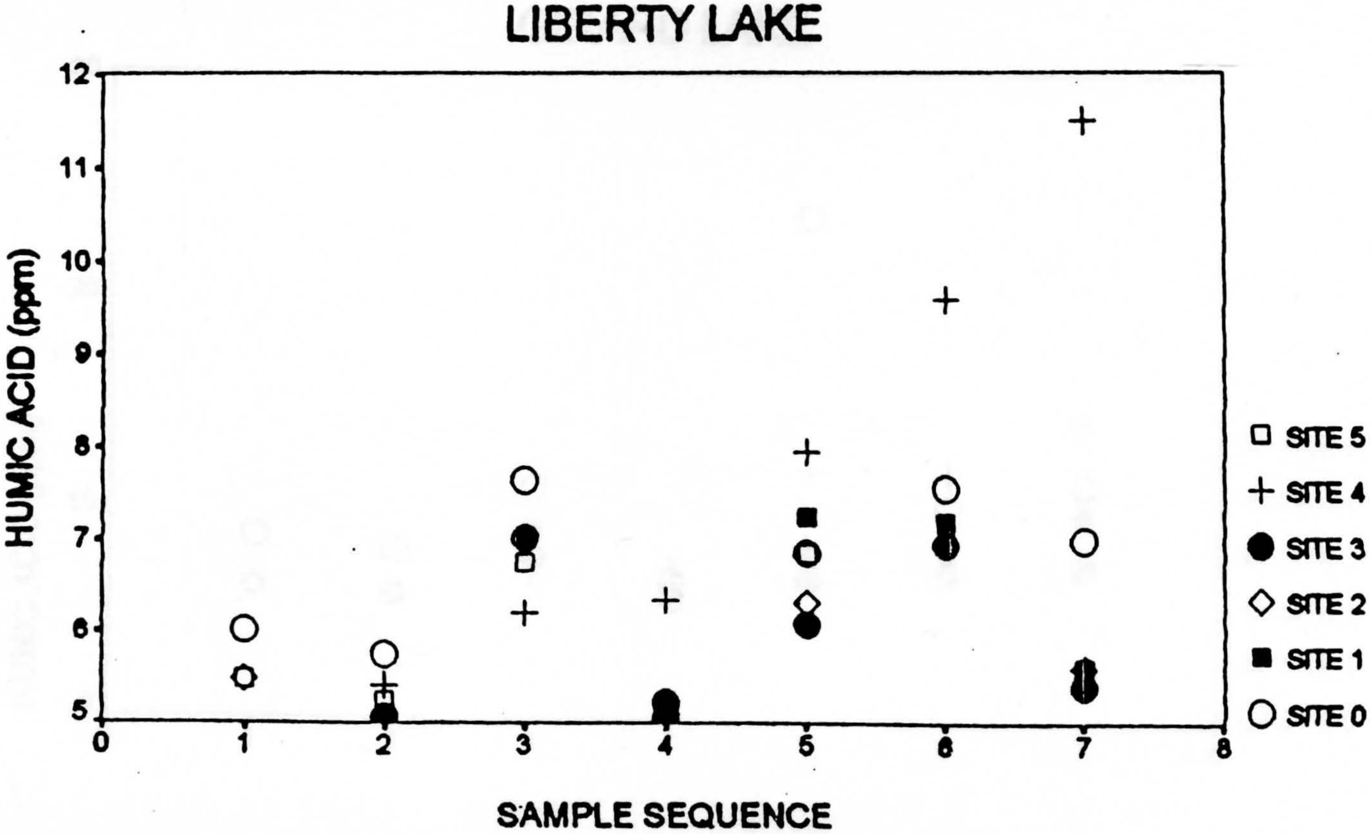
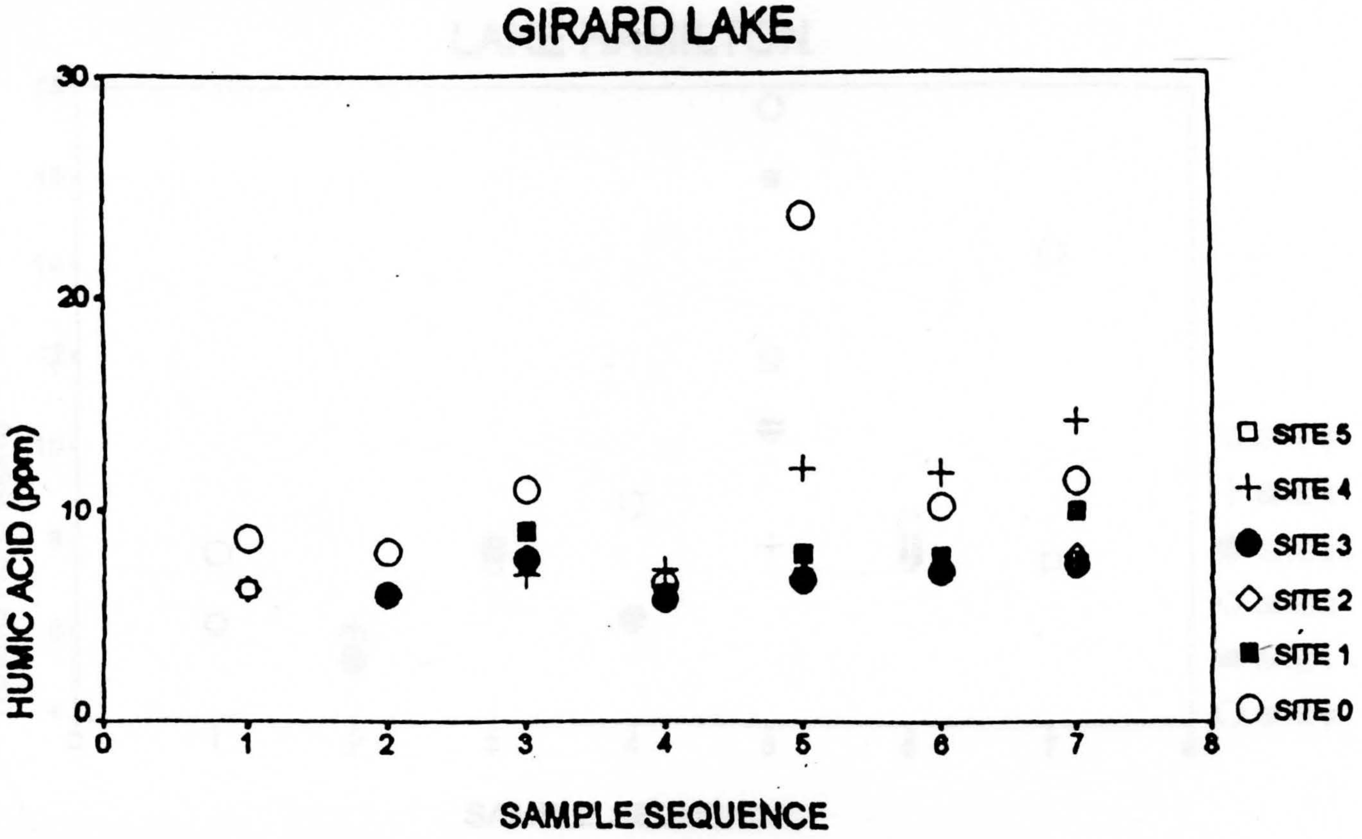
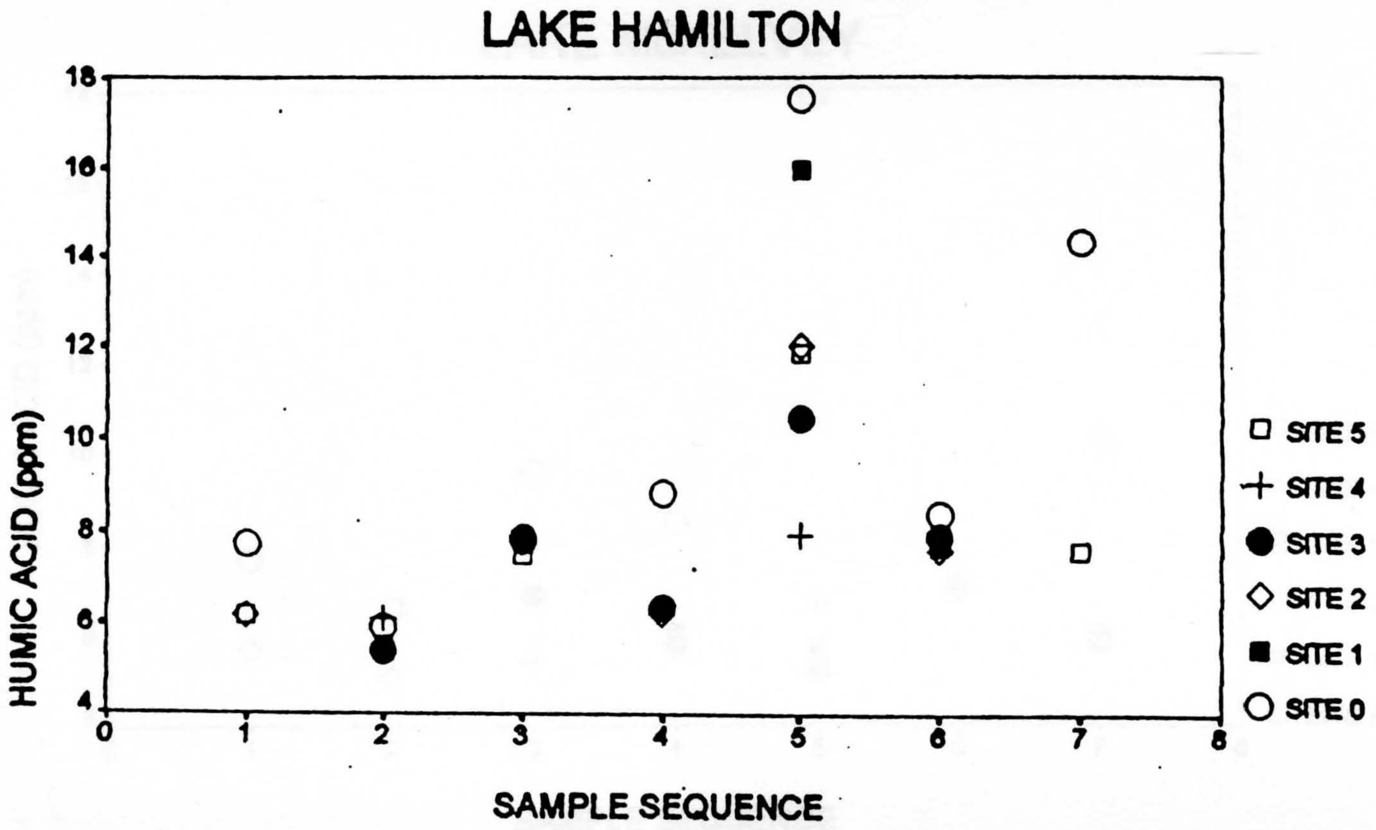
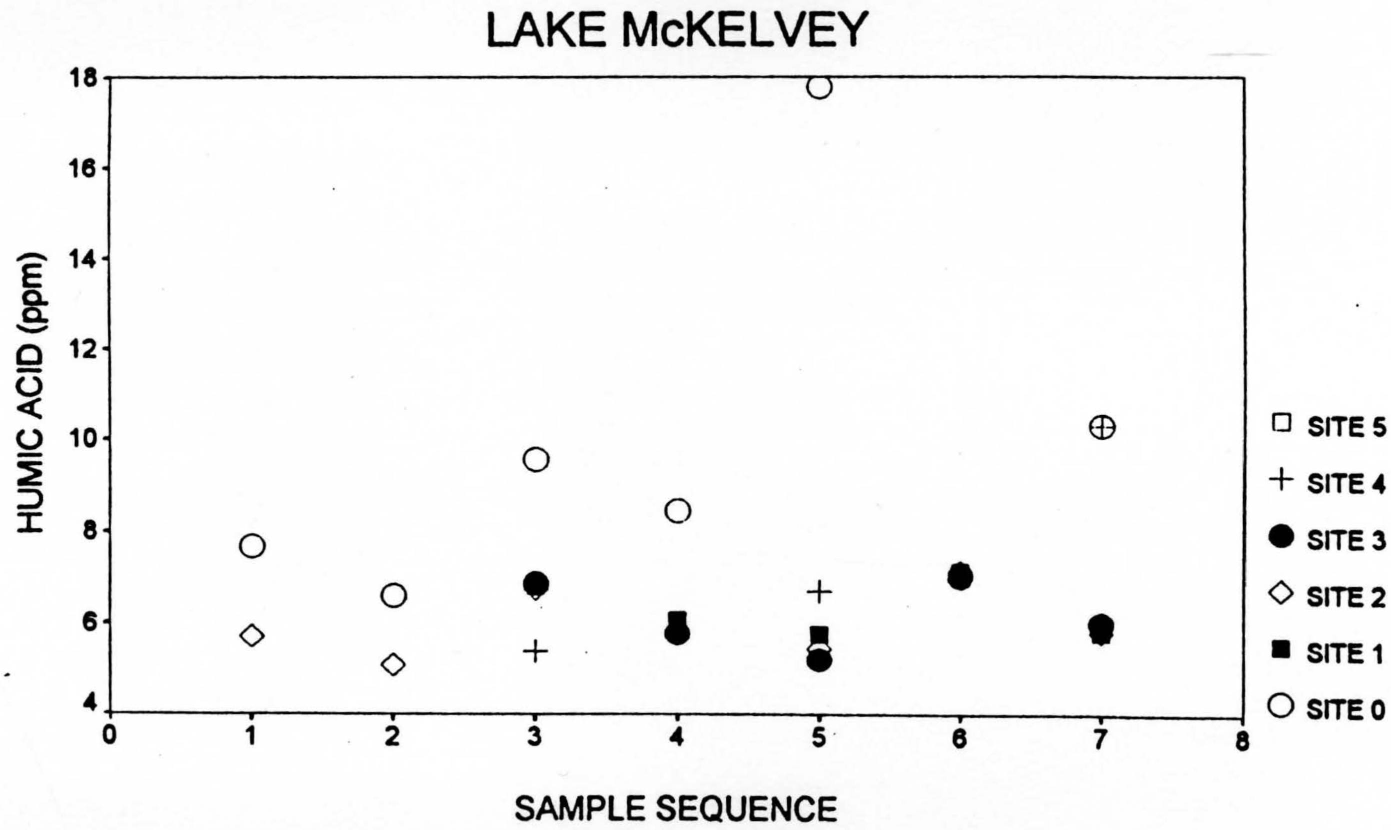
● SITE 3
◇ SITE 2
■ SITE 1
○ SITE 0


LAKE EVANS
HUMIC ACID (ppm)
1
2
3
4
5
6
7
0
1
2
3
4
5
6
7
8
SAMPLE SEQUENCE
□ SITE 5
+ SITE 4
● SITE 3
◇ SITE 2
■ SITE 1
○ SITE 0


LIBERTY LAKE
HUMIC ACID (ppm)
12
11
10
9
8
7
6
5
0
1
2
3
4
5
6
7
8
SAMPLE SEQUENCE
□ SITE 5
+ SITE 4
● SITE 3
◇ SITE 2
■ SITE 1
○ SITE 0


GIRARD LAKE
HUMIC ACID (ppm)
0
10
20
30
SAMPLE SEQUENCE
0
1
2
3
4
5
6
7
8
□ SITE 5
+ SITE 4
● SITE 3
◇ SITE 2
■ SITE 1
○ SITE 0


LAKE HAMILTON
HUMIC ACID (ppm)
18
16
14
12
10
8
6
4
0
1
2
3
4
5
6
7
8
SAMPLE SEQUENCE
□ SITE 5
+ SITE 4
● SITE 3
◇ SITE 2
■ SITE 1
○ SITE 0


LAKE McKELVEY
HUMIC ACID (ppm)
18
16
14
12
10
8
6
4
0
1
2
3
4
5
6
7
8
SAMPLE SEQUENCE
□ SITE 5
+ SITE 4
● SITE 3
◇ SITE 2
■ SITE 1
○ SITE 0