THE USE OF NATURAL WATER FLUORESCENCE TO DETERMINE TRIHALOMETHANE PRECURSOR VARIATIONS ALONG A WATER COURSE

By

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CHAPTER I

INTRODUCTION

The concept of this thesis is that in the near future EPA will be promulgating new standards for Trihalomethane (THM) content in drinking water. Presently the regulations require water from waterworks to have less than 100 ppb THM. The new regulations will require that water works have some limit between 10 and 80 ppb. Presently 25 and 50 ppb are the most commonly used limits.

Objectives and Scope

Defining specific points or areas that are producing and introducing the THM precursors into the Verdigris River is not within the scope of this research. Rather the objective of this thesis is to study the feasibility of using a fluorometer to investigate the introduction of the precursors into the Verdigris River system as shown in figure 1.

Discovering the source of the THM precursors could potentially help a waterworks reduce the formation of THM's by eliminating the sources of organic matter producing the most precursors. A fluorometer could potentially find these sources rapidly and inexpensively.

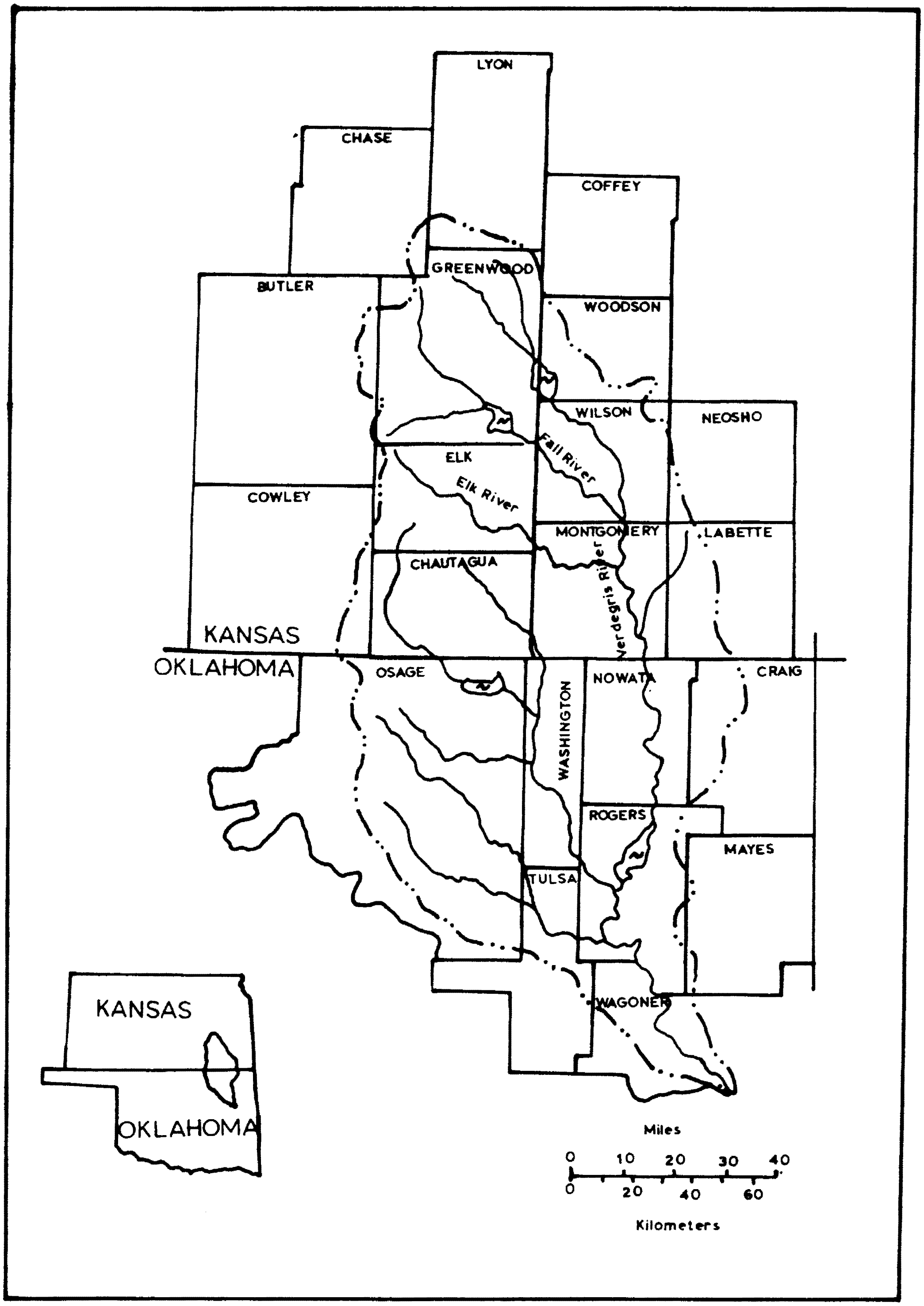


Figure 1 Location of the Verdigris River Basin in Kansas and Oklahoma (after Fader and Morton, 1975)

The proceedure used for the detection of THM's is the seven day Formation Potential Test. In this test, the water is chlorinated and allowed to sit at room temperature in an airtight, headspace-free bottle. After seven days the water is removed from the bottle and analyzed in a gas chromatograph. This method is time consuming and expensive. The formation of THM's takes place when the unsaturated bond in organic compounds is broken by chlorine, which was added for disinfectant purposes. Ultraviolet illumination of these organic compounds produces fluorescence. The source of the fluorescence is the unsaturated bond.

Trihalomethane Formation Potential (THMFP), Total Organic Carbon (TOC) and Fluorescence data were obtained from each sample and additional cation and anion data were obtained from samples at each end of the study area and at several points along the river.

The study area consists of the confines of the Verdigris River starting at the north side of Neodesha, Kansas, and ending at a bridge approximately two and a half miles south of the Oologah dam.

The sampling program entailed sampling the Verdigris River in sixteen to seventeen places and Oologah Lake at one point. Each sample point was sampled during each season and preferably before and during runoff of surface waters due to storms and spring thaw.

Sampling Points

Bridges crossing the river were used to obtain water samples because of ease of access in all types of weather conditions. Sample points were numbered north to south and identified by state. The exceptions to this numbering system are the three northern points in Kansas which were added after numbering began. These three were numbered KN-1, 2, 3 from south to north. Point K-3A was also an addition, but it followed in the general numbering system. On the August 13 collection run, point K-5 was changed from a bridge to a point that was accessible from the highway, and samples had to be dipped from the edge of the river. On the October 22 run, samples were again taken from the old point 5 and were numbered K-5A.

KN-3 is located at the north edge of the town of Neodesha, Kansas. KN-2 is located at the southeast edge of Neodesha east of the hospital. KN-1 is located where the Wilson-Montgomery county line road crosses the river at the Whitehair Bridge. K-1 is located where the Sycamore road crosses the river approximately 1.5 miles east of the town. K-2 is located approximately .75 mile east of the town of Independence. K-3 is located 3 miles east and 1.75 miles south of the town of Fruitland. The McTaggart bridge .75 mile north and 1.5 miles east of the K-3 bridge is not accessible from the west side of the river. K-3A is one mile west of the intersection of county roads 3000 and 5100 on county road 3000. K-4 is located on the north side of Coffeyville at the downstream side of the CO-OP refinery. K-5 is at the bridge on U.S. Highways 166 and 169. K-5A is at the big bend in the river on the south side of Coffeyville. K-6 is at the bridge below Coffeyville's sewage treatment plant.

OK-1 is located in Oklahoma approximately a mile south of South Coffeyville and approximately 1.5 miles east of Highway U.S. 169. OK-2 is located where State 10 crosses the river. OK-3 is located at Hancock bridge approximately a mile south of Hancock Bend. OK-4 is located approximately a mile east of Highway 169 where State 28 crosses the river. OK-5 is located approximately 4 miles west of the town of Nowata where U.S. Highway 60 crosses the river. OK-6 is located where the road to Winganon landing crosses lake Oolagah. OK-7 is located approximately 1.5 miles northwest of the community of Sageeyah and 2.5 miles due south of Oolagah Dam. Table 1 locates each sample site by river milage. The location of sample sites is shown in figure 2.

TABLE 1

LOCATION OF SAMPLE SITE BY RIVER MILES

Sample Site	River Miles	Sample Site	River Miles
KN-3	217.4	OK-1	159.4
KN-2	213.0	OK-2	144.6
KN-1	209.8	OK-3	137.0
K-1	206.3	OK-4	131.3
K-2	195.5	OK-5	121.4
K-3	188.5	OK-6	111.7
K-3a	182.6	OK-7	83.1
K-4	170.6		
K-5	169.0		
K-5a	164.6		
K-6	162.5		

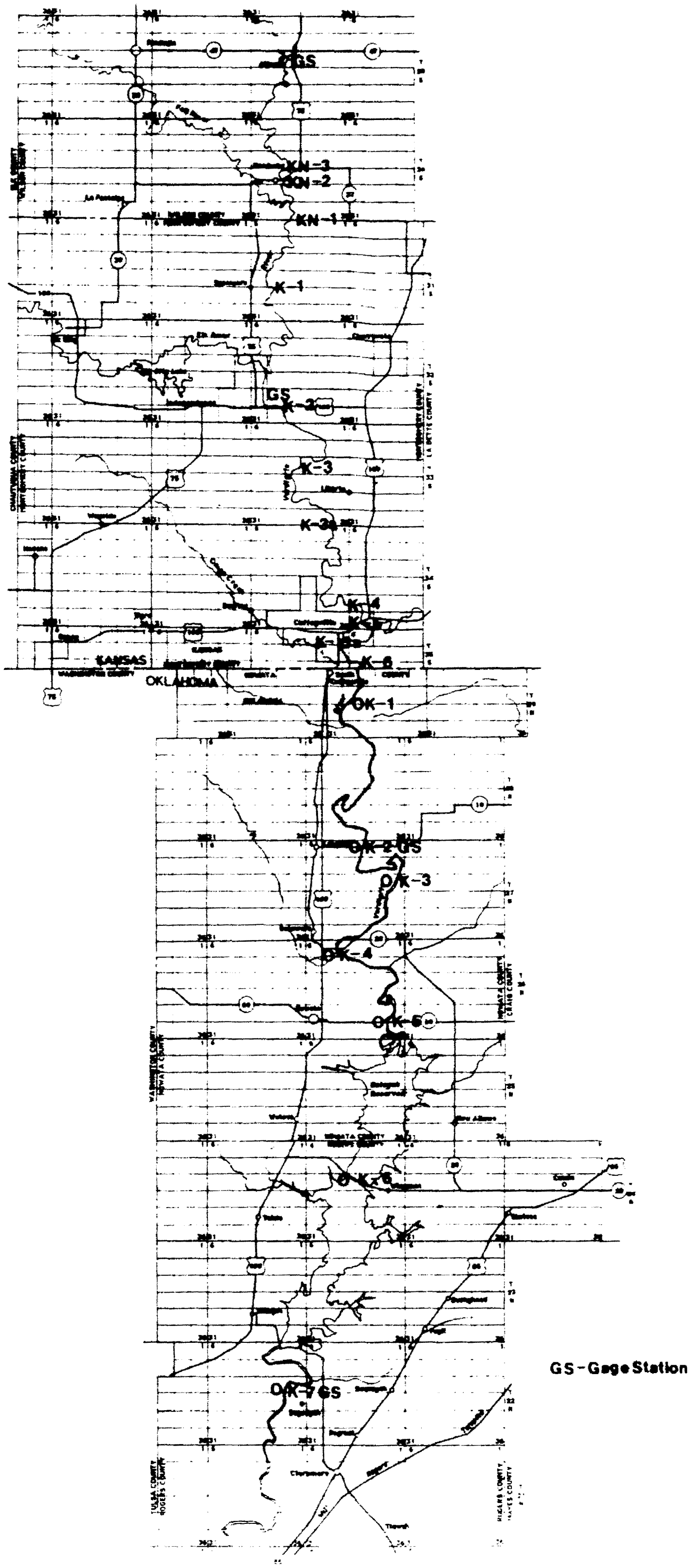


Figure 2 Sample Locations and
Gage Station Locations

Sampling Procedure

Samples were collected approximately midstream using a 1.66 inch PVC bailer on a nylon line. After the first two collection runs, the check valve was lost and samples were collected by attaching two sample bottles to the bottom of the bailer. This procedure worked well because bottom mud was not introduced to the water sample; however, sediment load was retained.

An appropriate volume of water (2000 ml) was taken and placed in plastic sample bottles. These samples were then placed on ice until transported to the laboratory. Field measurements consisted of taking temperature, pH, and TDS. Conductivity, hardness, alkalinity and fluorescence were measured in the laboratory. The first sample set was preserved with concentrated sulfuric acid. This was done before sulfate data was obtained; therefore, sulfate was not measured.

Field measurements of temperature were taken with an alcohol thermometer registering from -15 to 105 degrees C. The pH measurements were taken with an Orion pH meter model SA 210 using a gel filled combination probe. Total Dissolved Solids were obtained with a Cole Parmer dissolved solids tester that measured from 10 to 1990 ppm.

Conductivity was measured with a Hach portable conductivity meter used by the City of Tulsa. After the October 22 collection a Cole Palmer conductivity indicator based on the same design as the TDS indicator was used in the field and then checked in the laboratory.

Hardness was obtained using a handheld Hach titrator. The method of determining hardness used by the water plant is:

1) Take a 100 ml sample.
2) Add 7 drops of a hardness buffer.
3) Add 4 to 5 drops of indicator solution to the sample.
4) Titrate with EDTA until the sample turns from red to blue.
5) Multiply the amount of EDTA by 2 to get the hardness.

Alkalinity is obtained by titrating acid into a 100 ml sample until a pH of 4.5 is obtained. The bicarbonate value is also obtained from the alkalinity using the following formula:

	OH^- as $CaCO_3$	Carbonate as $CaCO_3$	Bicarbonate as $CaCO_3$
P=0	0	0	T
P<1/2 T	0	2P	T-2P
P=1/2 T	0	2P	0
P>1/2 T	2P-T	2(T-P)	0
P=T	T	0	0

P= titration of pH > 8.3 down to 8.3

T= Total alkalinity entire titration to 4.5

Fluorescence was measured on a relative scale using a fluoro-colorimeter. The meter was zeroed using a blank of Milli-Q filtered water. Then a vial containing a solution of .25 mg/l quinine sulfate was used to calibrate a 100% fluorescence. Each sample was then measured as to the relative amount of fluorescence compared to the quinine sulfate sample. This is the method used by Anderson et al. (1981) in his study using powdered activated carbon to control THM's.

The cation and silica concentrations were obtained with an atomic adsorption spectrometer. The chloride, fluoride, nitrate and sulfate were obtained using ion selective electrodes.

Trihalomethanes concentrations were obtained using gas chromatographic equipment consisting of a Hewlett Packard 5880-A with a 7673A automatic sample injector and a 60 meter glass capillary Volcal column. A liquid/liquid extraction procedure, developed by Janie M. Heard, was used to remove the trihalomethanes from the water sample.

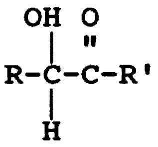
The procedure used to develop the trihalomethanes was slightly different from that used in the pilot plant study. In that study the water samples were pH adjusted to 7.5 after being chlorinated. That procedure tends to limit the amount of THM's formed and simulates what happens in the distribution system closer. The procedure that was used did not use pH adjustment. Adjustment of pH was not used because the total amount of THM's produced was of interest and not the simulation of a water distribution system.

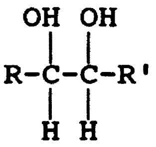
Trihalomethane Precursors

The main source of organic carbon in water supplies is the heavy organic acids. These are also the main sources of coloring in surface waters. These substances are generally found as the dark organic material in soils. According to Black and Christman (1963), Oden devised the first generally accepted method of describing the four constituents of soil organic matter in 1919. Page and duToit (1930) revised the names slightly. The four fractions are listed below using the terms as devised by Page and duToit.

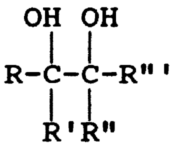
A) Soluble in alkali, not precipitated by acid.	Fulvic Acid
B) Soluble in alkali, precipitated by HCl, insoluble in alcohol.	Humic Acid
C) Soluble in alkali, precipitated by HCl, soluble in alcohol	Hymatomelanic Acid
D) Insoluble in alkali	Humin

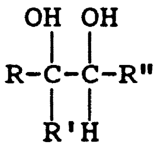
DuToit and Page (1930) studied the formation of humic matter from different plant materials. Their findings indicated that humic material formation was related to the amount of lignin in the plant rather than the cellulose, proteins, or other components making up plants. Through biologic decay, a very complex mixture of organic compounds develops. Black and Christman (1963) credit Felbeck with finding as many as sixty compounds in soil organic matter. A subsequent study by Black and Christman (1963), concentrating on the fulvic acid fraction of humic material, indicated that fulvic acid is composed of -hydroxy or an -hydroxy ketone of the following forms:

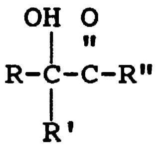

$\mathrm{R{-}\overset{OH}{\underset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}R'}$


$\mathrm{R{-}\overset{OH}{\underset{H}{C}}{-}\overset{OH}{\underset{H}{C}}{-}R'}$

Additionally compounds of the form


$\mathrm{R{-}\overset{OH}{\underset{R'}{C}}{-}\overset{OH}{\underset{R''}{C}}{-}R'''}$


$\mathrm{R{-}\overset{OH}{\underset{R'}{C}}{-}\overset{OH}{\underset{H}{C}}{-}R''}$


$\mathrm{R{-}\overset{OH}{\underset{R'}{C}}{-}\overset{O}{\overset{\|}{C}}{-}R''}$

can also be found where R and R' contain monosubstituted phenyl rings. Data from Black and Christman (1963) indicate that fulvic acids are aromatic polyhydroxy methoxy carboxylic acids.

Randnitz (1957), found that there is a humic acid substance in rhododendron leaves (and in some other unnamed leaves) that is a water soluble, surface active phosphoric ester. This is the first indication of plants forming their own form of humic acid, indicating that it may not all be produced as a by-product of decay.

CHAPTER II

AGROLOGY

Introduction

"Agrology" is used as the heading here rather than "agronomy" because of the definition found in Webster's New Collegiate Dictionary. Agrology is the branch of agriculture dealing with soils, especially in relation to crops where agronomy is the branch of agriculture that deals with field crop production and soil management.

With the understanding that the main source of the humic and fulvic acids is the decay of plant and animal matter then a close look at the soils that border the Verdigris River and the major tributaries is in order. The main problem as with geology is political boundaries. When going from county to county, names of soils change somewhat, but when going from state to state there is a significant change in names. An example of this is that the Verdigris-Osage association in Montgomery County, Kansas changes to the Radley-Wynona association in Nowata county Oklahoma. Table 2 serves two purposes. The first is to show the correlation between the associations and the second is to describe the notation on the soils map (figure 3).

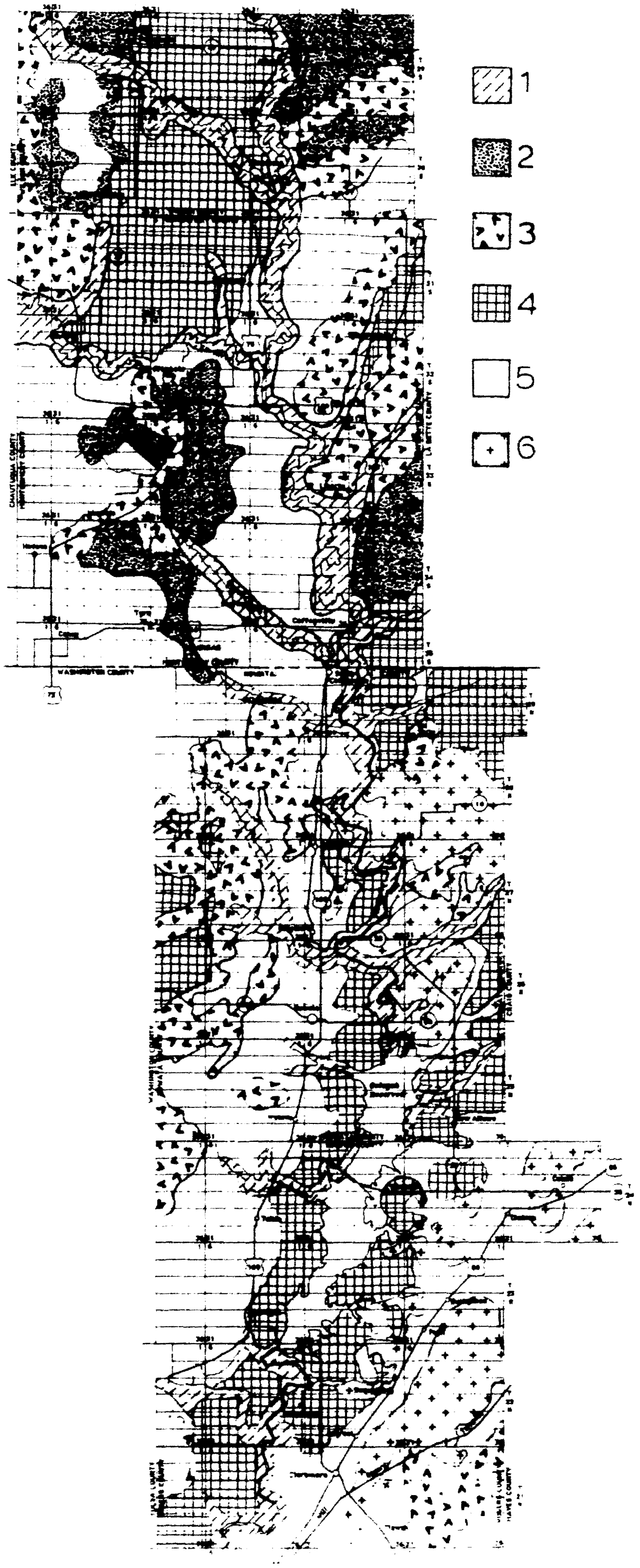


Figure 3 General Soil Map (after soil survey of Montgomery Wilson, Nowata, and Rogers counties)

TABLE 2

SOILS CORRELATION

Map	Wilson	Montgomery	Nowata	Rogers
1	Osage-Verdigris	Verdigris-Osage-Lanton	Radley-Wynoma-Mason	Verdigris-Osage
2	Woodson-Kenoma	Kenoma-Woodson-Zaar		
3	Bates-Dennis Eram & Steedman-Niotaze-Darnell	Eram-Talihina	Coweta-Bates-Eram	Collinsville-Bates
4	Catoosa-Shidler-Zaar	Catoosa-Kenoma-Zaar	Apperson-Catoosa Summit	Newtonia-Sogn-Summit
5	Bates-Collinsville-Dennis	Bates-Collinsville Dennis	Dennis Parsons Okemah	Dennis-Choteau
6			Shidler-Claremore-Kiti & Enders-Hector-Liberal	Hector-Linker

Pedons

There are approximately twenty soil types that border the Verdigris River in each of the four counties in this study. The following are modified pedon descriptions from the soil surveys of Wilson and

Montgomery Counties, Kansas; Nowata and Rogers Counties Oklahoma.

Wilson County

Dennis Series. Consists of deep, moderately well drained, slowly permeable soils on the upland. These soils formed in material weathered from shale. The typical Dennis soil contains an A horizon, very dark grayish brown silt loam, medium acid. A BA horizon is dark brown silty clay loam, medium acid. A Bt1 horizon is dark brown silty clay medium acid. A Bt2 horizon is dark brown to yellowish brown silty clay, slightly acid. A Bt3 horizon is yellowish brown silty clay that is neutral. Total depth is up to 60 inches.

Eram Series. Consists of moderately deep, moderately well drained, slowly permeable soils on the uplands derived from material weathered from shale. The A horizon is very dark grayish brown silt loam that is slightly acid. The Bt horizon is dark brown silty clay that is medium acid. The BC horizon is olive brown silty clay and is neutral. The C horizon is soft shale. Total thickness of the Eram is 32 inches.

Osage Series. Consists of deep, poorly drained, very slowly permeable soils on the flood plain and formed in clayey alluvium. The Ap horizon is black silty clay that is neutral. The A horizon is black silty clay that is mildly alkaline. The Bg1 horizon is black silty clay that is mildly alkaline. The Bg2 horizon is very dark grayish brown and is mildly alkaline. The overall thickness of the Osage series is 60 inches.

<u>Stephenville</u> <u>Series.</u> Consists of moderately deep, well drained, moderately permeable soils on the uplands that were formed from weathered sandstone. The A horizon is very dark grayish brown fine sandy loam that is medium acid. The E horizon is a dark yellowish brown fine sandy loam that is strongly acid. The Bt horizon is a reddish brown sandy clay loam that is strongly acid. The Cr horizon is a soft sandstone which gets harder with depth. Total thickness of the Stephenville series is approximately 27 inches.

<u>Verdigris</u> <u>Series.</u> Consists of deep, moderately well drained, moderately permeable soils on the flood plains that were formed in silty alluvium. The Ap and A horizons are very dark grayish brown silt loam to silty clay loam that is neutral. The AC horizon is dark brown silty clay loam that is neutral. The C1 and C2 horizons are dark brown silty clay loam that is neutral.

<u>Woodson</u> <u>Series</u>. Consists of deep, somewhat poorly drained, very slowly permeable soils on the uplands formed in old alluvial sediments. The A horizon is very dark gray silt loam that is slightly acid. The Bt horizon is very dark gray silty clay that is slightly acid. The BC horizon is gray silty clay that is

slightly acid. The C horizon is dark brown silty clay that is medium acid. The total thickness of the Woodson series is 60 inches.

Montgomery County

Bates Series. Consists of moderately deep, well drained, moderately permeable soils on the uplands. These soils are formed from material weathered from thin bedded sandstone and sandy silty shales. The typical Bates soil contains A and B horizons to a depth of approximately 27 inches. Generally described as very dark brown, very dark grayish brown, dark brown loam to clay loam. The A horizon is slightly acid; the B1 horizon is medium acid; and the B2t and B3 horizons are strongly acid.

Catoosa Series. Consists of moderately deep, well drained, moderately permeable soils on the uplands. These soils are formed from material weathered from limestone. The A1, B1, B2t horizons are all described as being dark reddish brown silt loam and silty clay loam and increasing in acidity from slightly to strongly acid. The thickness varies from 20 to 40 inches.

Collinsville Series. Consists of shallow, well drained, moderately rapidly permeable soils on the uplands. The soil is formed from material weathered from sandstone. The color is very dark grayish brown for the A1 fine sandy loam horizon and dark yellowish brown for the C fine sandy loam horizon. Thickness ranges from 4 to 20 inches and is slightly to strongly acid.

Dennis Series. Consists of deep, moderately well drained, slowly permeable soils on the uplands. These soils are formed from material weathered from shale. The A horizons are very dark brown silt loam and are medium acid. The B horizons are dark brown silty clay loam and silty clay and contain faint to distinct mottles. The B1 horizon is strongly acid; the B2 horizons are slightly acid; and the B3 horizon is mildly alkaline. The thickness is generally more than 60 inches thick.

Eram Series. Consists of moderately deep, moderately well drained, slowly permeable soils on the uplands. These soils are formed from material weathered from shale. The A horizon is very dark brown silty clay loam and slightly to medium acid; the B2t horizons are very dark to dark grayish brown silty clay and are strongly acid to neutral; the B3 horizon is grayish brown silty clay and strongly acid. The thickness is 20 to 40 inches.

Kenoma Series. Consists of deep, moderately well drained, very slowly permeable soils on the uplands. These soils are formed from old alluvium that has a high content of silt and clay. The A horizon is very dark grayish brown silt loam that is slightly to strongly acid; the B2t horizon is dark grayish brown to dark yellowish brown silty clay that is strongly acid to neutral; and the B3 horizon is dark brown silty clay that is mildly alkaline. The thickness is over 40 inches.

Lanton Series. Consists of deep, somewhat poorly drained, slowly permeable soils on flood plains along streams. They form from silty clayey alluvium. The A horizon is generally a very dark grayish brown to very dark gray silty clay loam but in some pedons is a silt loam and is strongly to slightly acidic; the C horizon is a dark gray silty clay loam or silty clay, commonly mottled red, brown and gray, and is moderately to slightly acidic. The thickness is greater than 40 inches.

Mason Series. Consists of deep, well drained, moderately slowly permeable soils on stream terraces. These soils formed from silty alluvium. The A horizon is very dark grayish brown to very dark brown dominantly silt loam but may be silty clay loam that is neutral to medium acidic; the B horizon is very dark grayish brown to very dark brown silty clay loam that is slightly to strongly acidic. The thickness ranges from 40 to over 60 inches.

Olpe Series. Consists of deep, well drained, slowly permeable soils on the upland. These soils formed in gravelly old alluvial sediments. The A horizon is brown to dark brown gravelly silt loam that is strongly to slightly acidic; the B1 horizon is dark reddish brown gravelly silty clay loam medium acidic; the B2t horizon is reddish brown to yellowish red very gravelly silty clay that is medium acid to neutral; the B3 horizon is coarsely mottled yellowish red, yellowish brown and light yellowish brown very gravelly silty clay that is neutral. It is more than 60 inches thick.

Osage Series. Consists of deep, poorly drained, very slowly permeable soils on flood plains. These soils formed in clayey alluvium. The A horizon is very dark gray to black silty clay ranging from strongly acid to neutral; the B horizon is very dark gray silty clay that is medium acid to neutral. The thickness is more than 40 inches.

Shidler Series. Consists of shallow, well drained, moderately permeable soils on the uplands formed from material weathered from limestone. The A horizon is very dark gray silt loam and is slightly acidic or neutral. The thickness ranges from 4 to 20 inches.

Talihina Series. Consists of shallow, moderately well drained, slowly permeable soils on the uplands forming in weathered shale and thinly bedded sandstones. The A horizon is very dark grayish brown silty clay loam ranging from neutral to strongly acidic; the B horizon is dark grayish brown silty clay ranging from neutral to strongly acidic; the C horizon is light olive brown silty clay with lenses of calcareous material at the base and is slightly acidic at the top to mildly alkaline at the bottom. The thickness is from 10 to 20 inches.

<u>Verdigris Series.</u> Consists of deep, moderately well drained, moderately permeable soils on flood plains that are formed from silty alluvium. The A horizon is very dark brown to dark brown silt loam to silty clay loam that is medium to slightly acidic; the C horizon is a brown silt loam to silty clay loam that is slightly acidic. The thickness ranges from 24 inches to greater than 50 inches.

<u>Zaar Series</u>. Consists of deep, somewhat poorly drained, very slowly permeable soils on the uplands formed in materials weathered from shale. The A horizon is a black silty clay to silty clay loam that is medium to slightly acidic; the B horizon is a very dark grayish brown, dark grayish brown to a light olive brown silty clay that is neutral to slightly acidic.

<u>Nowata County</u>

<u>Apperson Series.</u> Consists of deep, moderately well drained, slowly permeable soils on the uplands. These soils formed in material weathered from limestone. The A horizon is very dark gray to black silty clay loam that is slightly to medium acidic; the B1 horizon is very dark gray to black silty clay loam to silty clay and ranges from medium acidic to mildly alkaline; the B21t

horizon is very dark gray, very dark grayish brown to dark gray silty clay that is slightly acidic to mildly basic; the B22t horizon is very dark grayish brown, dark gray to dark grayish brown ranging from slightly acidic to mildly basic; the B3 horizon is dark grayish brown, yellowish brown to light olive brown and ranges from slightly acidic to moderately alkaline. The thickness ranges from 40 to 60 inches.

Catoosa Series. Consists of moderately deep, well drained, moderately permeable soils on the uplands. These soils formed from material weathered from limestone. The A horizon is very dark grayish brown, dark brown, or dark reddish brown silt loam that ranges from medium to slightly acidic; the B1 horizon is dark brown to dark reddish brown silt loam, silty clay loam or clay loam that ranges from medium to slightly acidic; the B2t horizon is dark reddish brown to dusky red silty clay loam or clay loam that ranges from strongly acidic to neutral. The thickness ranges from 20 to 40 inches.

Coweta Series. Consists of shallow, well to excessively drained, moderately permeable soils derived from material weathered from sandstone interbedded with shale. The A horizon is dark brown to very dark grayish brown loam to fine sandy loam that is slightly acid; the B2 horizon is brown, dark yellowish brown to yellowish brown fine sandy loam, loam or clay loam ranging from strongly acid to slightly acid. The thickness is from

10 to 20 inches.

Dennis Series. Consists of deep, moderately drained, slowly permeable soils on the uplands that are derived from shale or clayey sediments. The A horizon is very dark grayish brown to dark brown silt loam that is strongly to medium acidic; the B1 horizon is dark brown to brown silty clay loam to clay loam with mottles of brown, gray or red and ranging from strongly to medium acidic; the B2t horizon is brown to yellowish brown silty clay to clay mottled in shades of brown, gray or red and ranges from strongly to slightly acidic; the B3 horizon is a silty clay or clay that is coarsely mottled in shades of brown, gray or red and is medium acidic to slightly alkaline. The thickness is greater than 60 inches.

Enders Series. Consists of deep, well drained, very slightly permeable soils in the uplands derived from shales with interbedded thin sandstones. The A11 horizon is very dark grayish brown, dark brown, brown to dark grayish brown loam that is extremely to strongly acidic; the A12 horizon is brown, dark yellowish brown to yellowish brown loam that is very strongly to strongly acidic; the B1 horizon is brown to yellowish red loam that ranges from very strongly to strongly acidic; the B2t horizon is yellowish red to red clay that ranges from very strongly to strongly acidic; the B3 horizon is a very coarsely mottled clay in shades of red, brown or gray that ranges from very strongly to strongly acidic. The thickness is 32 to 60 inches.

Hector Series. Consists of shallow, well drained, moderately rapidly permeable soils on the uplands derived from materials weathered from sandstone. The A1 horizon is dark brown, brown or dark grayish brown loam or fine sandy loam ranging from strongly to slightly acidic; the A2 horizon is brown, grayish brown to dark yellowish brown loam to fine sandy loam ranging from strongly to slightly acidic; the B2 horizon is yellowish brown, brown to strongly brown loam to fine sandy loam that ranges from very strongly to strongly acidic.

Kiti Series. Consists of shallow, well drained, moderately permeable soils on the upland that are derived from materials weathered from limestone. The A horizon is very dark brown, very dark grayish brown to dark brown silty clay loam to silt loam and ranges from neutral to moderately alkaline. The thickness is 4 to 20 inches.

Liberal Series. Consists of deep, moderately well drained, slowly permeable soils on the uplands that are derived from materials weathered from shale. The A horizon is very dark grayish brown silty clay loam that is medium acidic; the B1 horizon is brown, yellowish brown to light olive brown silty clay loam that is moderately acidic; the B2t horizon is brown, yellowish brown, light olive brown, dark grayish brown to grayish brown clay, silty clay or silty clay loam ranging from strongly to medium acidic; the B3 horizon is grayish brown to dark grayish brown clay, silty clay to silty clay loam and ranging from medium acidic to neutral. The thickness is 20 to 40 inches.

Mason Series. Consists of deep, moderately well drained, moderately slowly permeable soils on flood plains that are derived from materials weathered from loamy sediment. The A horizon is very dark grayish brown to dark brown silt loam that is strongly acid to neutral; the B horizon is very dark grayish brown, dark brown, dark grayish brown, brown to dark yellowish brown silty clay loam, silt loam to clay loam ranging from strongly to medium acidic. The thickness is more than 40 inches.

Nowata Series. Consists of moderately deep, well drained, moderately slowly permeable soils on the uplands formed from materials weathered from cherty limestone. The A horizon is dark brown, very dark grayish brown to very dark brown silt loam that ranges from medium acidic to neutral; the B1 horizon is dark brown, very dark grayish brown, dark grayish brown, brown to dark reddish brown silt loam to silty clay loam and the cherty gravelly counterparts, that is medium acidic to neutral; the B2t horizon is dark brown, brown, dark reddish brown, reddish brown to yellowish red gravelly cherty silt clay loam that is medium acidic to neutral. The thickness is from 20 to 40 inches.

Okemah Series. Consists of deep, moderately well drained, slowly permeable soils on the uplands formed from material weathered from shale, clayey or loamy sediments. The A1 horizon is black, very dark brown, very dark gray to very dark grayish brown silt loam that is medium acid to neutral; the A3 or B1 horizon when present has colors that are similar to the A1 horizon and is a silt loam to silty clay loam that ranges from medium acid to neutral; the B2t horizon is very dark gray, very dark grayish brown, dark gray to dark grayish brown silty clay to clay ranging medium acidic to mildly basic; the B3 horizon is a coarsely mottled clay or silty clay in shades of gray brown or red that ranges from neutral to moderately alkaline. The thickness is greater than 60 inches.

Osage Series. Consists of deep, poorly drained, very slowly permeable soils that are formed from material weathered from clayey sediments and are deposited on flood plains. The A horizon is very dark gray, black to very dark grayish brown clay ranging from medium acidic to neutral; the B2 and B3 horizons are very dark gray to dark gray clay that ranges from medium acidic to mildly basic. The thickness is greater than 40 inches.

Parsons Series. Consists of deep, somewhat poorly drained, very slowly permeable soils on the uplands that are derived from materials weathered from shale and clayey sediment. The A1 horizon is very dark grayish brown silt loam ranging from strongly to slightly acidic; the A2 horizon is dark grayish brown to grayish brown silt loam ranging from strongly to medium acidic; the B2tg horizon is very dark gray, very dark grayish brown, dark gray, dark grayish brown to grayish brown clay with mottles in shades of gray brown or red and is strongly to slightly acidic; the B3 horizon has colors that are similar to those in the B2t horizon and has mottles in shades of gray or brown and is medium acidic to mildly basic. The thickness is more than 40 inches.

Radley Series. Consists of deep, moderately well drained, moderately permeable soils on flood plains from material weathered from loamy sediment. The A horizon is dark brown to very dark grayish brown silt loam ranging from medium to slightly acidic; the B2 horizon is brown, dark grayish brown to grayish brown silt loam to silty clay loam that is medium to slightly acidic; the C horizon is brown grayish brown to dark grayish brown silt loam or silty clay loam and is medium to slightly acidic. The thickness is 45 to 60 inches.

Shidler Series. Consists of shallow, well drained, moderately permeable soils on the uplands formed from materials weathered from limestone. The A horizon is very dark brown, very dark grayish brown to dark brown silt loam to silty clay loam ranging from slightly acidic to mildly alkaline. The thickness is 4 to 20 inches.

Summit Series. Consists of deep, moderately well drained, slowly permeable soils on the uplands formed in materials weathered from loamy or clayey sediments. The A1 and B1 horizons are black, very dark brown, very dark gray to very dark grayish brown silty clay loam and ranges from medium to slightly acidic; the B21t horizon is very dark grayish brown, dark grayish brown, dark yellowish brown to olive brown silty clay that is medium acidic to neutral; the B22t and B3 horizons are brown, dark yellowish brown to olive brown silty clay that ranges from slightly acidic to mildly basic. The thickness ranges from 50 to more than 60 inches.

Wynona Series. Consists of deep, somewhat poorly drained, slowly permeable soils on the flood plain that are derived from loamy sediments. The A horizon is black, very dark brown, very dark gray to very dark grayish brown silty clay loam ranging from medium to slightly acidic; the B2g horizon has colors and reaction similar to those in the A horizon; the B3g horizon is very dark gray, dark gray to very dark grayish brown silty clay or silty clay loam that is strongly to slightly acidic. The thickness is greater than 40 inches.

Rogers County

Bates-Collinsville Complex: Bates Part. Consists of moderately deep, well drained soils on the upland formed from material weathered from sandstone and sandy and silty shales. The surface layer is very dark brown loam, and the subsoil is dark grayish brown loam in the upper part and dark yellowish brown to dark brown clay loam in the lower part. The pH ranges from 5.1 to 6.5 in both parts. Depth to bed rock is 20 to 40 inches.

Collinsville Part. Consists of very shallow to shallow, well drained to somewhat excessively drained, moderately permeable soils on the uplands derived from material weathered from sandstone. The surface layer is very dark grayish brown fine sandy loam; the next layer is brown fine sandy loam. The pH is 5.1 to 6.5 in both layers and depth to bed rock is 4 to 20 inches.

Breaks-Alluvial Land Complex: Dennis Part.

Consists of deep, moderately well drained, slowly permeable soils on the uplands. The surface layer is very dark grayish brown silt loam; the subsurface layer is dark brown silt loam; the next layer is dark brown silty clay loam; the subsoil is yellowish brown mottled clay to silty clay loam; and the underlying material is yellowish brown silty clay loam. The pH is 5.1 to 6.0 from 0 to 14 inches, 4.5 to 6.0 from 14 to 18 inches, and 5.1 to 8.4 from 18 to 62 inches. Depth to bedrock is greater than 60 inches.

Verdigris Part. Consists of deep, moderately well drained soils on the flood plain that formed in alluvium. The surface layer is very dark grayish brown silt loam; the next layer is dark brown silt loam and the sub stratum is brown silt loam. The pH is 5.6 to 7.3 in all layers and the depth to bed rock is greater than 60 inches.

Choteau Silt Loam. Consists of moderately deep, well drained, slowly permeable soils on the uplands. The surface layer is very dark grayish brown silt loam; the subsurface layer is brown silt loam; the upper subsoil layer is yellowish brown silty clay loam; the middle sub soil layer is dark yellowish brown to yellowish brown clay; and the lower subsoil layer is mottled clay. The pH is 4.5 to 6.5 from 0 to 26 inches, 4.5 to 6.0 from 26 to 32 inches and 5.1 to 7.8 from 32 to 72 inches. Depth to bed rock is greater than 60 inches.

Claremore Silt Loam. Consists of shallow, well drained, moderately permeable soils on the uplands derived from material weathered from limestone. The surface layer is dark reddish brown silt loam; and the subsoil is dark reddish brown silty clay loam. The pH is 5.6 to 6.5 from 0 to 16 inches, and 5.6 to 7.3 from 16 to 22 inches. Depth to bed rock is 10 to 20 inches.

Dennis-Bates Complex: Dennis Part. Consists of deep, moderately well drained, slowly permeable soils on the uplands. The surface layer is very dark grayish brown silt loam; the subsurface layer is dark brown silt loam; the next layer is dark brown silty clay loam; the subsoil is yellowish brown and mottled clay and silty clay loam; and the underlying material is yellowish brown silty clay loam. The pH is 5.1 to 6.0 from 0 to 14 inches, 4.5 to 6.0 from 14 to 18 inches, and 5.1 to 8.4 from 18 to 62 inches. The depth to bed rock is greater than 60 inches.

Bates Part. Consists of moderately deep, well drained soils formed from material weathered from sandstone and sandy, silty shales on the uplands. The surface layer is very dark brown loam; the subsoil is very dark grayish brown loam grading into a yellowish brown to dark brown clay loam; and the substratum is soft sandstone and silty shale. The pH ranges from 5.1 to 6.5 through the entire section. The depth to bed rock is 20 to 40 inches.

Dennis Silt Loam. Consists of deep, moderately well drained, slowly permeable soils on the uplands. The surface layer is very dark grayish brown silt loam; the next layer is dark brown silty clay loam; and the subsoil is yellowish brown and mottled clay and silty clay loam. The pH is 5.1 to 6.0 from 0 to 14 inches, 4.5 to 6.0 from 14 to 18 inches, and 5.1 to 8.4 from 18 to 6 2 inches. Depth to bed rock is greater than 60 inches.

Newtonia Silt Loam. Consists of deep, well drained, moderately permeable soils on the uplands derived from materials weathered from limestone. The surface layer is very dark grayish brown silt loam; the subsoil is dark reddish brown silty clay loam. The pH is 5.6 to 6.5 from 0 to 14 inches and 5.1 to 7.3 from 14 to 38 inches. The depth to bed rock is 40 to 60 inches.

Okemah Silty Clay Loam. Consists of deep, moderately well drained, slowly permeable soils on the uplands. The surface layer is black to very dark brown silt loam, and the subsoil is a silty clay mottled in shades of gray and brown. The pH is 5.6 to 7.3 from 0 to 18 inches, 5.6 to 7.8 from 18 to 35 inches, and 6.6 to 8.4 from 35 to 62 inches. The depth to bed rock is greater than 60 inches.

Osage Clay. Consists of deep, poorly drained soils formed in clayey alluvium on low terraces and bottom lands. The surface layer is very dark brown and black silty clay and very dark gray and dark gray silty clay subsoils. The pH is 5.1 to 7.3 from 0 to 22 inches and 5.6 to 7.8 from 22 to 60 inches. Depth to bed rock is greater than 60 inches.

Riverton Loam and Riverton Gravelly Loam. Consists of deep, well drained, moderately permeable soils on the uplands. The surface layer is dark brown gravelly loam; the upper part of the subsoil is reddish brown gravelly clay loam; the middle part is dark red or yellowish red very gravelly clay loam; and the lower part is yellowish brown very gravelly clay. The pH is 5.1 to 6.5 from 0 to 8 inches, 4.5 to 6.0 from 8 to 40 inches, and 4.5 to 5.5 from 40 to 80 inches. The depth to bed rock is greater than 60 inches.

Sogn Soils. Consists of shallow and very shallow, somewhat excessively drained soils on the upland formed from material weathered from limestone. The surface layer is very dark gray silty clay loam underlain by limestone. The pH is 6.1 to 8.4 from 0 to 8 inches. the depth to bed rock is 4 to 20 inches.

Summit Silty Clay Loam. Consist of deep, moderately well drained, slowly permeable soils on the uplands. The surface layer is black silty clay loam; the upper part of the subsoil is black silty clay; the middle part of the subsoil is very dark brown to very dark grayish brown mottled clay; and the lower part is coarsely mottled clay. The pH is 5.6 to 7.3 from 0 to 22 inches and 5.6 to 8.4 from 22 to 60 inches. The depth to bed rock is greater than 60 inches.

Taloka Silt Loams. Consist of deep, somewhat poorly drained very slowly permeable soils on uplands. The surface layer is very dark grayish brown silt loam; the subsurface layers are mottled dark grayish brown and grayish brown silt loam; the upper subsoil layer is mottled dark grayish brown silty clay; the middle subsoil is mottled brown silty clay loam; and the lower subsoil is coarsely mottled grayish and brownish silty clay loam. The pH is 5.1 to 6.0 from 0 to 22 inches and

5.1 to 8.4 from 22 to 78 inches. Depth to bed rock is greater than 60 inches.

Verdigris Silt and Clay Loams. Consist of deep, well drained soils on the flood plain that formed in alluvium. The surface layer is very dark grayish brown silt or clay loam; the next layer is dark brown silt loam; and the substratum is brown silt loam. The pH is 5.6 to 7.3 through the 60 inches to bed rock.

Woodson Soil. Consists of deep, somewhat poorly drained soils formed in silty and clayey sediments on the uplands. The surface layer is very dark gray silt loam; the subsoil is mottled very dark gray and dark gray silty clay; the substratum is mottled dark gray silty clay.

The exact soil-to-soil correlation from county to county and from state to state is not of great value in this application. What is of value is the correlation of soil associations. This correlation gives the same general soil types and their location from county to county and from state to state. These are generally easier and more accurate to correlate.

The first association, located along the river, is the Osage-Verdigris. This is the same as the Radley-Wynona-Mason association in Nowata County and is called Osage-Verdigris on the soils map. These two associations are the only north-south associations and are directly related to the river and consequently crosscut the other associations.

In Wilson County the association is described as deep, nearly level, poorly drained and moderately well drained soils that have a clayey or silty subsoil on flood plains. The association makes up about 13 percent of the county. In Montgomery County the association is described as nearly level, moderately well drained to poorly drained, silty and clayey soils on bottom land. This association makes up about 14 percent of the county. In Nowata County the correlative association is the Radley-Wynona-Mason, which is described as deep, nearly level, moderately well drained and somewhat poorly drained loamy soils that have a loamy or clayey subsoil on flood plains. The Radley-Wynona-Mason makes up about 13 percent of the county. In Rogers County this association is mostly submerged by Lake Oolagah within the study area. However, there is a small amount exposed downstream of the dam. The association is described as nearly level, deep, loamy and clayey soils on bottom lands making up approximately 11 percent of the county.

The second association is the Woodson-Kenoma. This association was correlated only in Wilson and Montgomery Counties. In Wilson County this is the Woodson-Kenoma-Dennis association covering 21 percent of the county and described as deep, nearly level to moderately sloping, somewhat poorly drained and moderately well drained soils that have a dominantly clayey subsoil located on uplands. In Montgomery County this is the Kenoma-

Woodson-Zaar association. It comprises approximately 15 percent of the county and is described as being nearly level to gently sloping, moderately well drained to somewhat poorly drained, silty and clayey soils on the uplands.

The third association is the Bates-Eram. A manifestation of this association is found in all four counties. In Wilson County this is the Bates-Dennis-Eram association and covers about 6 percent of the county. The Steedman-Niotaze-Darnell association has been grouped with the Bates-Dennis-Eram association for mapping purposes. In Montgomery County the Eram-Talihina association is the correlated series and covers approximately 20 percent of the county. In Nowata County the association is the Coweta-Bates-Eram, and it covers about 16 percent of the county. The Collinsville-Bates association is in Rogers County and covers about 10 percent of the county. These associations all are gently sloping to steeply sloping, silty to clayey soils on the uplands.

The fourth association is the Catoosa-Zaar-Summit. Generally this association strikes northeast-southwest. In Wilson County this association is the Catoosa-Shidler-Zaar and is described as deep to shallow, nearly level to moderately sloping, well drained and somewhat poorly drained soils that are silty throughout or have a clayey subsoil and located on the uplands, such as toe slopes, foot slopes, escarpments and ridge tops. It makes up about 37 percent of the county. In Montgomery County the association is the Catoosa-Kenoma-Zaar association and is described as nearly level and gently sloping, well drained to somewhat poorly drained, silty and clayey soils located on the uplands such as broad ridgetops and long side slopes. This association makes up about 15 percent of the county. In Nowata County the association is the Apperson-Catoosa-Summit. This association is described as deep and moderately deep, very gently sloping and gently sloping, moderately well drained and well drained loamy soils that have a clayey or loamy subsoil on uplands. This unit makes up approximately 18 percent of the county. Rogers County has a small amount of this unit exposed as the Newtonia-Sogn-Summit association. This association is described as gently sloping to strongly sloping loamy soils formed under prairie grass on limestone uplands and covers about 21 percent of the county.

The fifth association is being called the Bates-Dennis association. Most of this association has one of several lesser soils also associated with it. In Wilson County this is the Bates-Collinsville-Dennis association. It is described as deep to shallow, gently sloping to strongly sloping, well drained and moderately well drained soils that are loamy throughout or have a loamy, silty, or clayey subsoil on uplands such as foot slopes, side slopes and narrow ridge tops. This association makes up about 15 percent of Wilson County. In Montgomery County this is the Bates-Dennis-

Collinsville association and is described as gently sloping to moderately steep, well drained and moderately well drained, loamy and silty soils on uplands such as low hills and ridges that have short side slopes and narrow tops. This association makes up about 36 percent of the county. In Nowata County this is the Dennis-Parsons-Okemah association. It is defined as deep, nearly level to gently sloping, moderately well drained and somewhat poorly drained loamy soils that have a clayey or loamy subsoil on uplands. This unit makes up about 32 percent of the county. In Rogers County this is the Dennis-Choteau association and is described as nearly level and moderately sloping soils formed under prairie grasses on the uplands occupying nearly level to gentle sloping valleys. The soils are formed in sandstone and shale. This association comprises approximately 48 percent of the county.

The sixth association was correlated only in Nowata and Rogers Counties and is being called the Enders-Hector association. In Nowata County the Enders-Hector-Liberal association is described as being shallow to deep, sloping, well drained loamy soils that have a lomy or clayey subsoil; on the uplands. This unit makes up about 5 percent of the county. In Rogers County this is the Hector-Linker association which is described as gently sloping to very steep, well drained, loamy soils formed on the uplands. This unit occupies about 10 percent of the county. The Shidler-Claremore-Kiti association has been lumped with the Hector-Liberal association for ease of mapping.

CHAPTER III

GEOLOGY

Introduction

The Verdigris River Basin is located on the northern shelf of northeast Oklahoma and southeast Kansas. The portion of the Verdigris River basin in this study is located from the north edge of the town of Neodesha in south central Wilson County, Kansas, to a point two and a half miles south of Oolagah Dam in Rogers County Oklahoma. Elevation ranges from over 1010 feet 2.5 miles northwest of Neodesha to approximately 570 feet at the collection point below Oolagah Dam. Most of the land area next to the river is agriculturally productive, with wheat and hay being the main crops. Crude oil production throughout the area has been a major activity for many years, with coal and sand and gravel being the major mining activities for nearly as long.

The geology of this area has been thoroughly studied for many years. Eramus Haworth made the first published attempt to correlate the exposed formations along the Verdigris River in the thesis area of Kansas that was found. Many others have since looked at the structure and the stratigraphy in their search for petroleum,

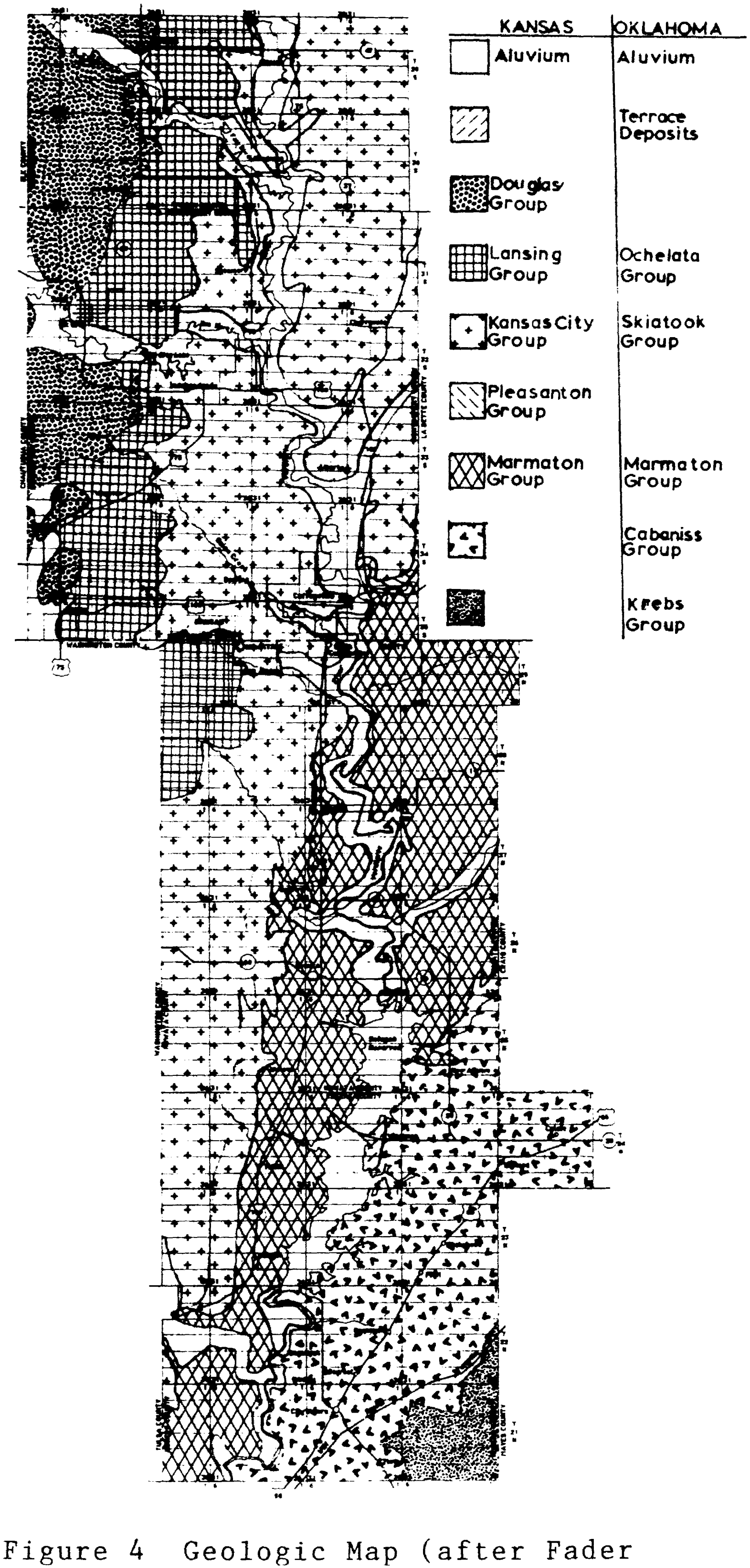


Figure 4 Geologic Map (after Fader and Morton, 1975)

coal, sand, and gravel.

Exposed Sections

Most of the outcrop sections in the thesis area are middle to upper Pennsylvanian in age. These units are composed of limestone and shale with significant amounts of sandstone interlayered with the shale. The whole generally strikes slightly east of north and dips gently to the west. The exposed units that are not Pennsylvanian in age are Recent alluvium or terrace deposits. The following is a description of the outcrop sections modified from O'Connor and Marcher and Bingham.

Alluvial and Terrace Deposits. Composed of gravel to clay sized particles on the flood plain of the river. The bottom 0 to 14 feet are sand and gravel. As an aquifer these deposits yield small to moderate amounts of fair to good quality water.

Wann-Vilas Shale to Lane Shale. Shale with thin sandstones and the Plattsburg limestone. These are poor aquifers yielding small volumes of fair to poor quality water.

Iola Fm-Iola Limestone. Limestone and shale. This formation generally consists of two limestones separated by a black fissile shale containing phosphatic concretions. As an aquifer it yields only small amounts of fair to poor quality water.

Chanute Fm-Chanute Shale. A gray shale and fine grained sandstone. The Noxie sandstone member exists extensively in the bottom portion of the formation. The Thayer coal bed is in the middle section of the formation. The Noxie sand yields moderate amounts of fair to good quality water from as deep as 400 feet. The upper portion yields only small amounts of fair to poor quality water.

Dewey Fm-Drum Limestone. This is a gray to light gray crossbedded highly fossiliferous oolitic limestone. This unit yields only small amounts of fair to poor quality water.

Nellie Bly Fm-Cherryvale shale. Chiefly a shale with flags at the top that increase in abundance in a southerly direction. Water yields are small and of fair to poor quality.

Hogshooter Fm-Dennis limestone. Limestone locally sandy or oolitic in the upper part with a gray to black fissile shale in the middle and lower part and having a limestone bed at the base locally. This formation yields only small amounts of fair to poor quality water.

Coffeyville Fm-Coffeyville Fm. Chiefly a shale and siltstone formation with the upper part containing abundant fine grained sandstone and several thin coal beds. The lower section contains darker colored shale with 1 to 6 feet of limestone near the middle. Yields only small amounts of fair to poor quality water.

Checkerboard Fm-Checkerboard Fm. Consists of two limestone layers separated by a shale. The lower limestone weathers to a brownish color and is a crossbedded coquina. Yields small amounts of fair to poor quality water.

Seminole Fm-Seminole Fm. This formation is chiefly shale with sandstone interbedded and a few thin coal seams. It yields only small amounts of fair to poor quality water.

Lenapah Fm-Holdenville shale and Lenapah limestone. The overlaying Holdenville shale is a gray to bluish green fossilferous shale, and the underlaying Lenapah limestone is massive in the upper portion and nodular in the lower portion with a thin shale separating them. This formation yields small amounts of fair to poor quality water.

Nowata Fm-Nowata shale and Altamont limestone. The Nowata shale consists chiefly of shale with some fine grained sandstone. The underlaying Altamont limestone has an upper and lower member separated with a thin dark fissile shale. These units yield only very small amounts of fair to poor quality water. Figure 5 is a generalized geologic section after Fader and Morton (1975).

System	Series		Group		Formation	Thickness		Lithology	
	Ks	Ok	Ks	Ok		Ks	Ok	Ks	Ok
	Pleistocene Holocene	Pleistocene Holocene			Alluvium	50 to 60	30 to 35	silt, clay, sand and gravel	fine sand, silt and clay
					Terrace Deposits		10		clay, silt and sand slightly Indurated
Pennsylvanian	Upper Pennsylvanian	Missouri	Shawnee	Ochelata		50	150	shale, sandy shale, and limestone	sandstone, shales, limestone and small amount of conglomerate
			Douglas			120 to 300		shale, sandy shale, sandstone and limestone	
			Lansing	Skiatook		80	400 to 500	shale and sandy shale with limestone	Mostly shale silty shale sandstone and limestone
			Kansas City			350		shale, sandy shale, sandstone and limestone	
			Pleasanton			250		limestone and shale	
	Middle Pennsylvanian	Des Moines	Marmaton	Marmaton		250	500	shale, sandy shale, sandstone, limestone and siltstone	Mostly shale with smaller amounts of limestone and sandstone
				Cabaniss			300		Predominately dark gray to black shale interbedded with sandstone, limestone, and slight amount of coal
				Krebs			400		shale interbedded with thinner units of sandstone and limestone

Figure 5 Generalized section of geologic units (after Fader and Morton, 1975)

Chapter IV

HYDROLOGY

Introduction

The Verdigris River basin is located in southeast Kansas and northeast Oklahoma. The area's present main industrial activity is agricultural, but recently oil and gas and coal mining have been large industrial activities in the area. Petroleum production is still a significant industrial activity in the area.

The drainage area above Oolagah Dam is 4339 square miles. This is the approximate drainage area of the thesis area. A small area below the dam is not included in the above total.

Climate

Average annual rainfall over the basin varies. Pettyjohn et al (1983) indicated that the rain varied from 36 to 41 inches from the west to the east side of the basin. The soil survey of Rogers County confirms this with an average annual rainfall of 38.08 inches for the thirty-year span of 1931 to 1960.

Two climatological stations along the Verdigris river had rainfall data, Nowata and Independence. Two additional climatological stations along major tributaries had data also, Fall River Lake and Elk City

Lake. The May collection date followed four days of rain totaling 1.29 inches at Nowata, 2.22 inches at Fall River Lake, and .75 inch at Elk City Lake. This May date was two days after four days of rain totaling 1.46 inches. The July collection data had not been preceded by rain within five days at any of the climatological stations. The August collection date was three days after a 1 inch rain and a day after a trace amount at Nowata. Independence was in the middle of a three-day rain with .13 inch the preceding day and 1.23 inches the day of collection. Elk City Lake had .14 inch the day of collection, which did not allow enough time to affect the water at K-2 sampling location. Fall River Lake recorded a trace of precipitation three days before the collection date and .24 inch five days preceding that. Therefore, KN-1 had no influence from rain in August.

The October collection date found Nowata during a dry period and Independence, being essentially dry, having only a trace the day of collection, .02 inch three days before collection, and a trace amount two days before that. Elk City Lake had .06 inch three days before the collection date, and Fall River Lake had .19 inch three days before the collection date and a trace the day before that. The January collection date had .25 inch and .06 inch at Nowata and Elk City Lake respectively. Independence had .20 inch the day before the collection date, and Fall River Lake had a trace three days before the collection date. The April collection date had no precipitation five days before the collection date.

Precipitation hydrographs for each of the climatological stations are shown in figures 6 through 9. It should be noted at this point that the United States Environmental Protection Agency considers any precipitation event under .10 inch as being non-measurable.

The average annual temperature varies from 72.2 degrees in Rogers County to 69.7 degrees in Montgomery County for a maximum and 48.5 degrees in Rogers County to 45.3 degrees in Wilson County.

As C. D. Race (1985) stated, most of the previous investigations have been compilations of available data, including ground water levels, precipitation hydrographs, ground water and surface water chemical analysis and stream discharge hydrographs. These compilations have been performed by State Geological Surveys and the U.S. Geological Survey and other participating entities.

Aquifers

Fader and Morton (1975) classified ground water quality into three classes. The good class is described as having dissolved solids of less than 500 mg/l or less than 250 mg/l chloride and sulfate. The fair class contained between 500 to 1000 mg/l dissolved solids or between 250 to 500 mg/l chloride and sulfate. The poor

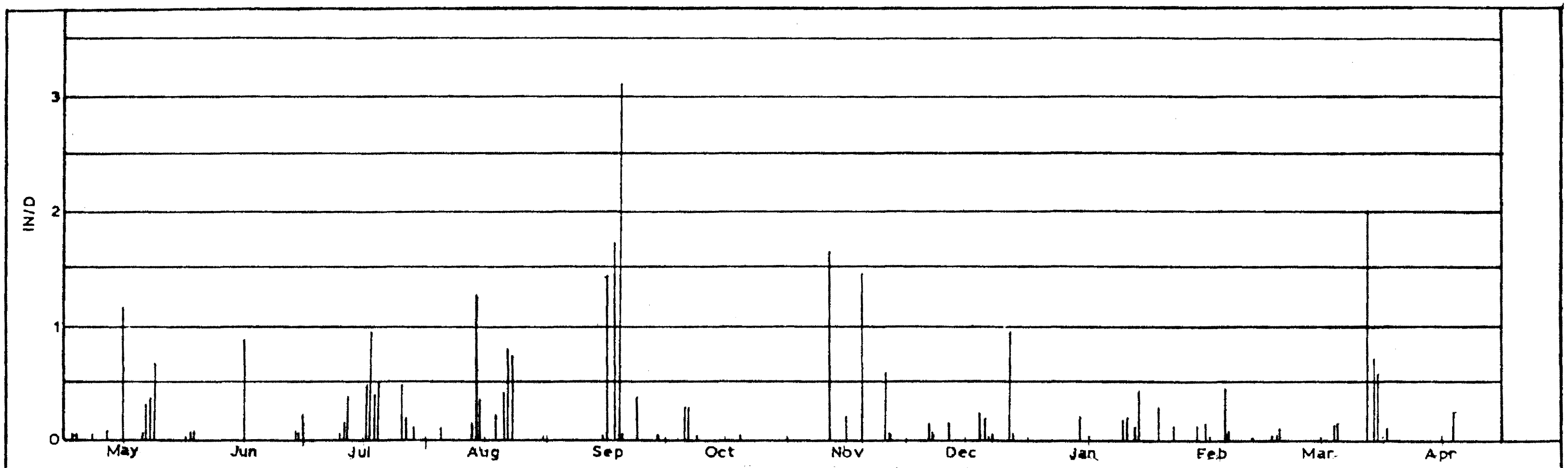


Figure 6 Rain Hydrograph at Independence, Kansas

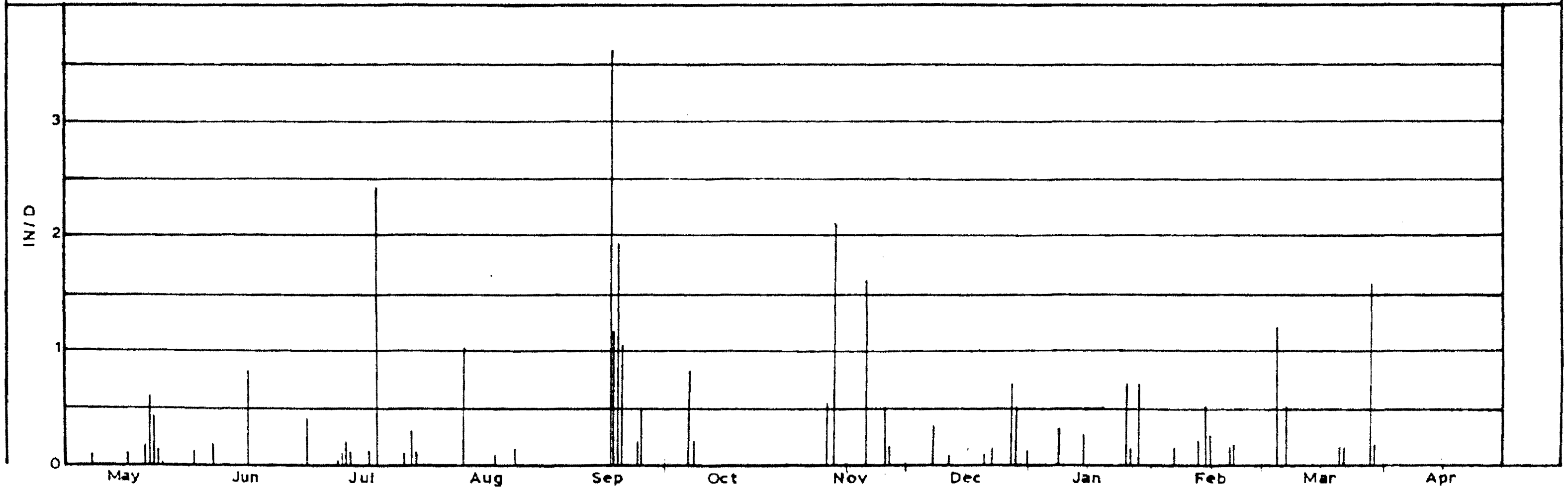


Figure 7 Rain Hydrograph at Nowata, Oklahoma

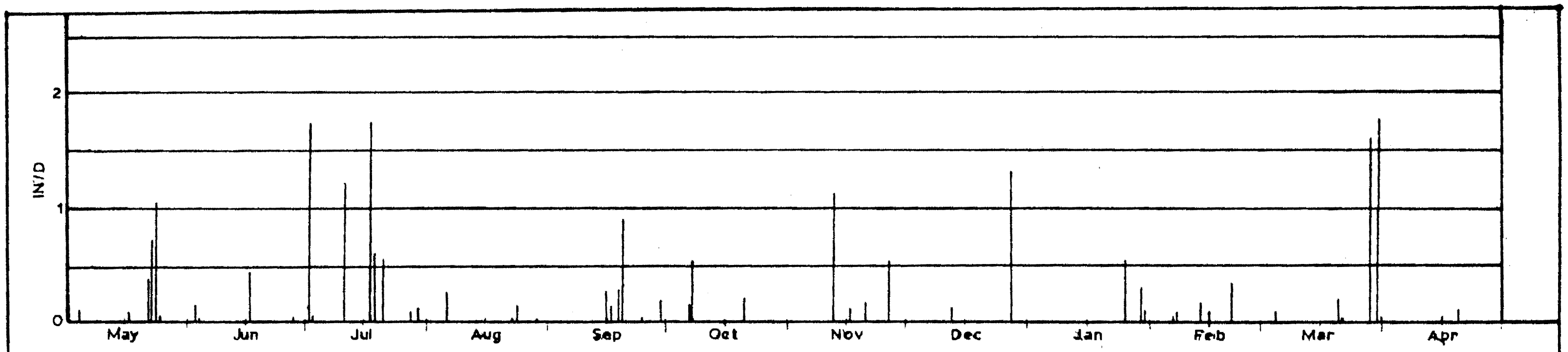


Figure 8 Rain Hydrograph at Fall River Lake

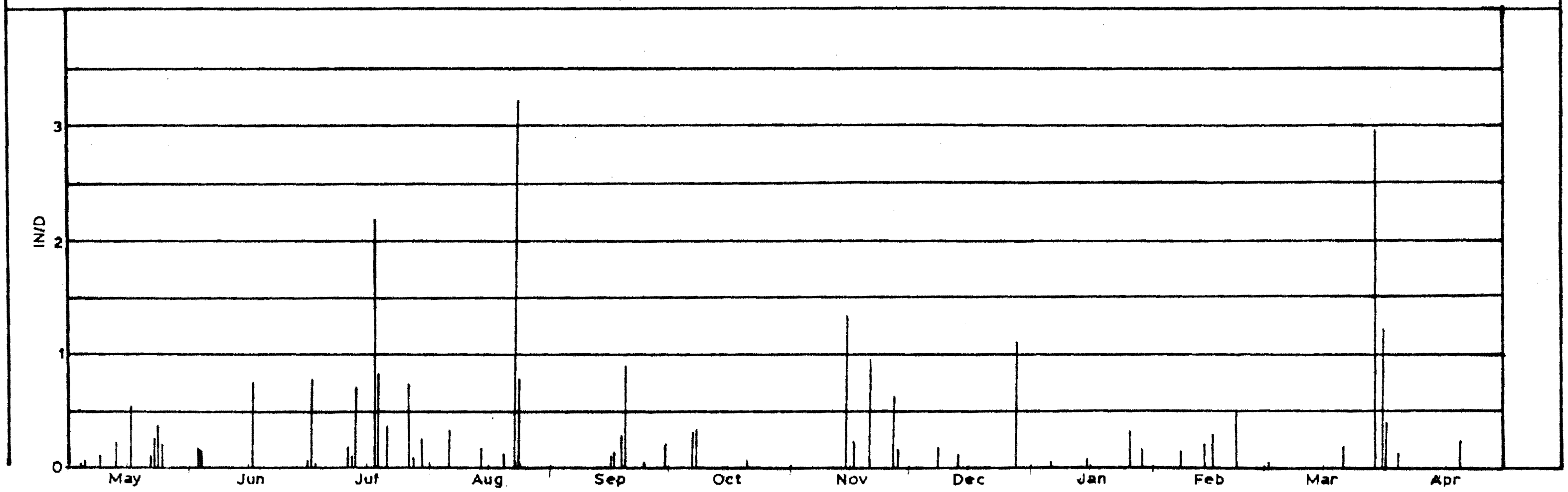


Figure 9 Rain hydrograph at Elk City Lake

class contained more than 1000 mg/l dissolved solids or more than 500 mg/l chloride and sulfate.

Aluvial and Terrace

These deposits range in thickness from 60 feet in Wilson County to 30 feet in Rogers County. These deposits consist of clay to gravel size material, and wells will yield up to 100 gallons per minute. Water quality tends to be good to fair; however, some samples by O'Conner (1974) have been shown to contain 1250 mg/l of dissolved solids and 450 mg/l sulfate and 65 mg/l of chlorides. Fader and Morton have estimated the Hydraulic Conductivity as being between 70 and 700 feet per day in Wilson and Montgomery Counties, 10 to 100 ft/d in Nowata County, and 0 to 10 ft/d in Rogers County. Annual recharge to the unconsolidated aquifers was estimated by Fader and Morton to be in the order of 166,000 acre-feet annually.

Consolidated Rocks

The consolidated rocks that yield water in this area are sandstones, siltstones, limestones, and shales. These units vary in thickness from 0 to 500 feet in Nowata and Rogers Counties. In Wilson and Montgomery Counties these units vary from 0 to 350 feet.

O'Conner states that in general the water that comes from the consolidated aquifers is of fair to poor quality and is inadequate in volume except for domestic use or for livestock. Fader and Morton indicate that water from shallow wells tends to be of good to fair quality with quality deteriorating with depth. Additionally, water quality has a tendency to deteriorate with extended dry weather periods. Fader and Morton also state that yields of 10 gpm or less from outcrop sections can be expected. Yields may be increased significantly with deeper penetration of the aquifer, but as stated earlier quality degrades rapidly. Hydraulic Conductivity has not been estimated for the consolidated aquifers by either O'Conner or Fader and Morton.

CHAPTER V

DISCUSSION

Graphs

Two types of graphs are used in this paper. The first involves a plot of a parameter versus the location of the sample. This gives a view of the change of the parameter as one moves along the stream on a particular date. Thus a change in water composition entering the river may be observed or a source of THM precursors may be narrowed. Additionally, with the plotting of only one parameter, features on the graph would not be masked by an overly large or small scale that may result in plotting several parameters together.

The second type of graph uses plots of THM and Fluorescence versus TOC. This type of graph shows the relationship between the three parameters. The main problem with this type of graph is that the difference in scale between THM and Fluorescence has a tendency to mask ticks in the Fluorescence graph. A reduction of THM by a factor of 10 has been used, thus retaining the fluctuations in both parameters.

The three sets of location graphs are Fluorescence, TOC and THM. Generally speaking, each of the three sets of graphs shows that something is happening between the

K-3 and K-5 sample points.

The Location versus Fluorescence series of graphs in general indicate that in the early summer a high fluorescence can be found in the northern range of sample points and at approximately K-3 the fluorescence levels out. In the mid and late summer months fluorescence has a tendency to attain a constant level throughout the entire length of stream that was sampled. However, the individual sample points have a tendency to vary widely. There is still a major fluctuation at K-3A. The winter and early spring sample periods indicate that fluorescence is relatively low in the northern reach, and at approximately K-3A or K-4 fluorescence increases dramatically.

The Location versus TOC series of graphs have a tendency to follow the Location versus Fluorescence series of graphs. The main difference is that the Location versus TOC series, in general, have lower TOC values in the northern portion of the sample range, and approximately at K-4 a significant increase in the amount of TOC in the sample is found. There additionally appears to be a low set of values starting at about OK-3 and ending at OK-6.

The Location versus THM series of graphs indicate that there is more of a seasonal variation than shown by the TOC series of graphs but not quite as strongly as the fluorescence series. With the THM series the late spring and early summer periods have a tendency to average fairly flat. The late summer periods have a tendency to average out to a slightly positive slope. The fall and winter periods tend to average to a slightly stronger positive slope. A point to note is that in almost every sample trip there is a very strong dip at sample point OK-1 or OK-2. This series of graphs also has a tendency to fluctuate widely from one end to the other of the reach of stream that was sampled.

The indication of higher values in the late summer and fall seasons reinforces the idea that the growing season increases the amount of plant material that is available to decay, and this decay introduces a larger amount of humic and fulvic acids in the soil that may be available for introduction into the stream system.

The obvious points of inflection that are shown on the graphs such as the OK-3 and the K-3A points indicate that something is influencing the quality of water in the stream. There is a real probability that this is a gaining stream segment and groundwater would have the effect of leaching out the humic and fulvic acids in the bottom sediments. During investigations in the spring of 1991, it was noticed that there was an inflow of water between sample points K-3 and K-3A. At sample point K-3A, clear water had not mixed completely with the murkier water in the river. This is most likely groundwater being introduced to the river.

The six graphs showing the relationship of the three parameters are displayed in the time mode, as were the parameter/location graphs. These graphs are displayed with the THM graph shown at a tenth scale. This scale helps to show the relationship between Fluorescence and THM.

The first noticeable feature is the exaggerated variations of the fluorescence scale. This wide variation was noted in the Fluorescence verses Location series of graphs. There may be several reasons for this variation:

1) The analog meter on the fluorometer may not have been as accurate as required. The meter on the fluorometer has been used to obtain much lower concentrations of fluorocene dye, so this is most likely not the cause.

2) Operator error may have been the cause by not allowing the meter to stabilize or not obtaining a true zero of the fluorometer. Obtaining a true zero also is likely not to be the cause of the wild fluctuations because the fluorometer was zeroed previous to each set of samples that were examined. This error would also only affect the base line and not the fluctuations. Insufficient time for fluorometer stabilization is a very possible cause of the fluctuations. With a change in humic or fulvic acid composition there may be a change in the fluorescence spectra that was not picked up because there was no spectral analysis done on the Verdigris River water over the year. Originally because relative fluorescence was sought and not qualitative

fluorescence, a composition change in the organic matter may have changed the spectrum, resulting in a higher or lower fluorescence than anticipated. If this is the case, then a spectral analysis has to be completed on every sample which is opposite of what D. B. Van Dongen (1977) stated and may reflect some of the concerns of M. Ewald et al. (1984).

3) The third possibility is that fluctuations observed are real.

The May 1988 graph indicates that there is an overall increase in both THM and Fluorescence with an increase in TOC. This increase is accompanied by an overall direct relationship between THM and Fluorescence. There also appear to be two inflection points at approximately 5.0 mg/l and 5.2 mg/l. Direct inflection points can be interpreted as being direct or nearly direct reactions between THM and Fluorescence with a change in the organic carbon in the water course. The indirect or inverse inflection points indicate that the THM and Fluorescence do not follow each other during changes. The inflection points at 5.0 mg/l and 5.2 mg/l are thought to show a change in the chemical composition of the organic carbon in the water at this concentration.

The July 1988 graph shows only a very slight increase in both THM and Fluorescence with an increase in TOC. There is also a split in the relationship of the two curves; a general inverse relationship exists before approximately 5.1 mg/l and a direct relationship after 5.1 mg/l. This change in relationship indicates that the more soluble organic carbon has a change in chemical composition that changes the relationship between the THM and Fluorescence. Two inflection points appear at approximately 5.1 mg/l and 5.8 mg/l. These inflection points show a change in the chemical composition of the organic carbon in the water.

The August 1988 graph also has a very slight increase in THM and Fluorescence in relation to the increase of TOC. There is an overall inverse relationship between the two curves. This inverse relationship shows that the chemical composition of the organic carbon entering the stream through its entire length has stabilized and is not changing in the water column overall. At approximately 4.6 mg/l an inflection is shown. This inflection point probably indicates a slight change in chemical composition of the organic carbon in the water such that it changes the way the carbon fluoresces and forms THM's.

The October 1988 graph shows an overall increase in THM and Fluorescence with respect to an increase in TOC. There is also a general inverse relationship between the two curves. This inverse relationship continues to show the stability of the composition of the organic compounds entering the water system. Two inflection points at approximately 4.4 mg/l and 5.3 mg/l are shown. These inflection points are most likely the result of slight changes in chemical composition of the organic carbon in the water. These chemical changes form compounds of a weight that change the way Fluorescence occurs and THM's develop.

The January 1989 graph shows a slight increase in THM and Fluorescence with an increase in TOC. There also appears to be a general inverse relationship between the two curves. Two inflection points at approximately 4.8 mg/l and 5.7 mg/l can be envisioned. The inverse relationship of the two curves and the inflection points continues the suggestion of stability of composition of compounds entering the water system and slight changes in composition of organic compounds causing variations in Fluorescence and THM production potential.

The April 1989 graph shows a strong increase in THM and Fluorescence with an increase in TOC. There is also a direct relationship between the two curves. The change to a direct relationship indicates that a major change in chemical composition has occurred within the organic carbon compounds. This is most likely due to the scouring of the bottom sediments and the infusion into the stream of the contained organic compounds. These bottom sediments have stored different organic compounds giving rise to the change in the relationship between the Fluorescence and THM production potential. There is a relatively strong inflection point at approximately 5.4 mg/l and a weaker one at approximately

5.0 mg/l. These inflection points show changes in the Fluorescence and THM production potential of the organic compounds at these particular concentrations.

It should be noted that the preceding conjectures concerning the changes in organic compounds are just conjectures. A detailed fraction of the organic carbon compounds needs to be performed to establish the conjectures as fact.

Several observations concerning the THM and Fluorescence verses TOC series of graphs have been made. During the winter and spring there is generally a direct relationship between the THM and Fluorescence curves shown, whereas the summer and fall show an inverse relationship between the THM and Fluorescence curves. This could be due to possible changes in the molecular structure of the organic compounds as they are buried in the bottom sediments over a period of time, mainly late fall and early spring. The summer and fall period could be showing that the organic compounds are fresher and probably more diverse. This quite possibly is corroborated by the smaller overall increase in THM and Fluorescence with a corresponding increase in TOC during the summer and fall as compared to the winter and fall. Additionally, the fluctuations that are observed are found to be more severe and over a longer range of TOC in the summer and fall than in the winter and spring. This indicates that the organics during the winter and spring are changed or at least sorted to a more uniform and consistent series of compounds. During the summer and fall, while production of THM precursors is large, the series of organic compounds is more varied, thus there are higher fluctuations and smaller overall increases in the parameters as the TOC increases.

Water Chemistry

Miller et al. (1990) studied Kansas groundwater supplies for THM precursors. Their study indicated higher levels of TOC coming from alluvial aquifers than from consolidated aquifers. They also found that iron, manganese, and ammonia were associated with higher levels of TOC. They also related chlorine demand with higher THMFP, which is related to TOC, ammonia, iron, and manganese. The following formula was used to calculate chlorine demand: $\text{Demand} = 5.91 * NH4 + 0.63 * Fe + 1.29 * Mn + 8.34 * H2S + TOC$. All units are mg/l. These findings may be of some use in determining the source of THM precursors in surface waters, especially during periods of dry weather and low stream flow.

The analysis of the analytical data using WATEVAL program has indicated that there was not a major water chemistry deviation. The only odd occurrence that arose was in January. A relatively high potassium content was observed. This is thought to be due to the use of salt on the highways. A subsequent inquiry to the Kansas highway department indicated that they had not used a special salt mixture. This does not preclude the possibility of obtaining a high potassium salt in the delivery that was used on that stretch of road. There is another possibility. Groundwater may be relatively high in potassium. This could subsequently be reduced by the plant life in the river during the growing season. During the dormant season a smaller volume of the potassium is used, and thus it becomes evident in the water chemistry.

In general, a look at the relationship of fluorescence and the constituents of the water shows a flat graph with numerous spikes. Thus the indication is given that most constituents of the water do not influence the fluorescence. The calcium ion, however, had a slight negative slope. That is to say that as fluorescence increased, calcium decreased. Conductivity showed the same characteristic, and this is quite possibly due to the decrease in the calcium ion.

Statistics

A rather quick look at the water data from a statistical point of view was provided by Darlene Sherrod with Wiley and Associates in Englewood, Colorado. She suggested that there is a relationship between TOC and THM or Fluorescence. A quick look at a linear regression shows that late winter and early to mid spring have the best fit. Late spring, summer and fall tend to show the lowest correlation according to the data. This may be due to a larger variety of precursors during the growing season, and during the winter and spring the old precursors are washed out by the spring melt. This may indicate that the time to look for precursor sources should be during the winter and spring.

WATEVAL and FACTOR are two computer programs developed by Dr. Hounslow to determine sources of ground water and the extent of mixing. These two programs were used to evaluate the amount of ground water mixing. Additionally the mixing of surface run off and tributary contribution could be evaluated with the Factor program. The only strange occurrence that appeared was during the January collection trip, and as stated previously potassium was anomalously high.

CHAPTER VI

SUMMARY AND CONCLUSIONS

Summary

In summary it appears that graphing the different parameters may be a method of narrowing the potential areas of THM precursors but the graphs still do not pinpoint the exact area of entry to the stream. The purpose of this work was to attempt to use a relatively inexpensive, rapid and easy method to potentially discover the source of the precursors.

The statistical methods were not in the scope of this paper. Statistically, though, this may be the best and most accurate method once it is developed.

The water chemistry did not show a relationship to the precursors. Water chemistry has been proven to be a contributing factor by Miller et al, (1990). The particular parameters that were shown to be a factor by Miller in Kansas groundwaters were not tested for in this study because at the time of sample collection and analysis it was not realized that the parameters of iron, manganese, and ammonia might be related to THM's. Expanded and or more focused parameters should be used in any future studies.

The soils either contacting the river or in close proximity to the river are generally very fertile and have a relatively high organic content. In Wilson and Montgomery Counties these soils contain from 1 to 4 percent organic matter. The soil surveys for Nowata and Rogers Counties do not list a specific percentage of organic matter but do classify them as being naturally fertile. This indicates that the soils along the river from Neodesha, Kansas, to the vicinity of Oolagah, Oklahoma, are generally of the same quality and would produce approximately the same amount of THM precursors at any agricultural spot within the Thesis area. This is brought out when the THM analyses are viewed. Generally, no one sample point tended to produce more THM's. The general tendency was for a slight decrease going down stream possibly due to settling of the heavy organic compounds. Periods of high stream flow had a tendency to increase THM's quite possibly due to bottom scour.

Conclusions

1. Because the precursors are primarily derived from decaying plant material point, source areas are essentially masked by the decaying vegetation both upstream and downstream of the point source.

2. To be able to detect the very small fluctuations in the florescence at a point, a very large number of samples (weekly or biweekly) must be taken

over a long time (several years) to be able to get a good least squares plot of the changes in THMFP versus fluorescence. Only at this point can there be a determination that the fluorescence is within or outside the limits of the least squares curve that has been generated.

3. Because of such biological phenomena as algae blooms and changes in vegetation, which are essentially uncontrollable, relatively large fluctuations in the precursor volume take place over relatively short spans of time. Fluorescence may be used as an initial indicator of increasing precursors at a waterworks plant. This may help the plant reduce trihalomethanes in its distribution system. Additionally, the monitoring of wastewater plant effluent with fluorescence may be able to catch a release of precursors in time to remove them from the system.

4. There does not appear to be a relationship between the dissolved mineral content and the organic content. This was determined by useing the FACTOR program.

5. Most of the observations were taken at periods of low flow. Due to the restrictions that the city of Tulsa placed on the project, because of their high workload and the expense of the analysis being run, samples were taken only during each season, not taking into account stream flow. However, two sample times, May 1988 and April 1989 had relatively high flows. The

sample in May was during a time at the end of the high spring flow that was relatively constant for a couple of weeks. The April sample was several days after the ebb of a spring storm flow.

6. Peaks found in the time-quantity plots at times when the total organic carbon or the THMFP should be decreasing are due to rainfall variations, the amount of plant growth that had taken place, and the amount of decay that had been incurred.

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APPENDIX A

WATER CHEMISTRY TABLE

WATER CHEMISTRY TABLE

Date	7/88	8/88	10/88	1/89	4/89
Temp C	26	23	13	3	11
pH	7.63	7.80	7.92	8.20	8.23
TDS	170	230	130	150	260
Hard	134	162	148	228	194
Alkaln	118	150	130	196	161
Fluor	132	84	55	19	28
Conduc	300	405	340	540	450
Ca	42.22	54.90	49.67	79.68	64.45
Mg	6.00	10.88	6.05	8.30	9.71
Na	15.00	21.70	14.09	19.03	20.09
K	9.30	4.60	4.03	12.43	2.65
Cl	37.0	53.8	27.6	44.3	30.8
F	0.232	0.23	0.21	0.16	0.17
Nitrate	2.70	1.35	1.00	1.74	4.33
Sulfate	<1	30.8	48.3	29.6	13.0
Silica	5.27	9.18	6.21	4.06	3.21
HCO_3	118	150	130	196	161
TOC	5.78	3.96	4.52	4.17	4.56
THM ug/l	310	339	260	316	446

KN-3

Date	7/88	8/88	10/88	1/89	4/89
Temp C	26	28	13	2	11
pH	7.52	8.05	7.80	8.10	8.26
TDS	160	240	130	140	160
Hard	126	172	144	236	191
Alkaln	111	149	123	240	162
Fluor	122	63	67	15	30
Conduc	290	405	305	520	460
HCO_3	111	149	123	240	162
TOC	5.89	3.93	4.45	3.84	4.69
THM ug/l	278	250	168	312	430

KN-2

Date	7/88	8/88	10/88	1/89	4/89
Temp C	30	29	14	3	12
pH	7.84	8.29	7.92	8.20	8.19
TDS	240	250	140	170	160
Hard	178	170	157	261	188
Alkaln	173	154	145	228	160
Fluor	67	58	58	12	16
Conduc	400	405	385	600	450
HCO_3	173	154	145	228	160
TOC	4.44	3.98	4.28	4.03	4.99
THM ug/l	195	379	264	332	486

KN-1

Date	5/88	7/88	8/88	10/88	1/89	4/89
Temp C	24	28	31	14	3	12
TDS	300	210	260	130	170	160
Hard	250	150	178	148	267	188
Alkaln		150	164	128	229	162
Fluor	65	73	55	67	12	18
Conduc		375	475	340	600	450
Ca	45.38	54.40	58.39	45.67	86.63	62.21
Mg	3.70	8.06	10.51	5.63	12.52	8.85
Na	9.37	15.00	23.20	14.52	32.06	18.78
K	26.36	13.70	7.90	4.19	18.29	2.85
Cl	42.0	33.0	49.6	20.4	62.2	36.5
F	0.18	0.24	0.24	0.22	0.22	0.21
Nitrate		4.0	1.2	1.3	2.2	3.65
Sulfate		17	25	2	45	13
Silica	1.88	4.42	5.18	7.00	2.69	4.03
HCO$_3$		150	164	128	227	162
TOC	4.87	4.86	4.12	4.30	4.18	5.03
THM ug/l	238	224	345	221	294	455

K-1

Date	5/88	7/88	8/88	10/88	1/89	4/89
Temp C	23	30	32	15	3	13
pH	8.17	8.13	8.16	8.2	8.3	8.26
TDS	240	210	250	150	150	160
Hard	220	140	160	151	227	187
Alkaln		142	145	132	198	154
Fluor	91	78	51	58	19	20
Conduc		320	410	380	500	430
HCO$_3$		142	145	132	194	154
TOC	5.12	4.95	4.89	4.37	4.57	5.13
THM ug/l	309	242	258	224	344	412

K-2

Date	5/88	7/88	8/88	10/88	1/89	4/89
Temp C	23	31	33	15	2	13
pH	8.27	8.2	8.42	8.08	8.2	8.17
TDS	270	240	260	150	140	150
Hard	244	156	192	156	232	180
Alkaln		160	149	140	195	152
Fluor	77	55	52	45	18	21
Conduc		395	375	385	500	430
HCO$_3$		160	149	140	195	152
TOC	5.51	4.45	5.56	4.02	4.71	5.42
THM ug/l	420	215	323	194	238	450

K-3

Date	7/88	8/88	10/88	1/89	4/89
Temp C	30	33	16	3	14
pH	8.41	8.70	8.16	8.0	8.13
TDS	280	260	160	140	150
Hard	184	164	170	219	180
Alkaln	169	148	149	181	145
Fluor	28	42	36	15	48
Conduc	410	400	400	510	420
Ca			52.88	72.99	59.99
Mg			6.81	10.34	8.08
Na			18.4	23.13	16.06
K			3.21	15.78	3.18
Cl			27.1	45.3	39.9
F			0.24	0.22	0.20
Nitrate			1.10	2.14	3.51
Sulfate			38.3	47.8	21.0
Silica			4.00	3.72	4.72
HCO_3	169	130	149	181	145
TOC	4.88	4.26	4.21	5.29	5.09
THM ug/l	324	408	288	312	412

K-3A

Date	5/88	7/88	8/88	10/88	1/89	4/89
Temp C	23	31	31	16	3	13
pH	8.11	8.26	8.25	8.11	8.3	7.99
TDS	270	300	250	150	150	110
Hard	236	210	144	157	231	132
Alkaln		197	144	134	201	111
Fluor	69	28	86	46	11	39
Conduc	510	390	385	530	310	
HCO_3		197	144	134	193	111
TOC	5.06	4.29		4.24	5.05	6.11
THM ug/l	326	283	283	277	374	4.37

K-4

Date	5/88	7/88	10/88	1/89	4/89
Temp C	23	30	17	2	13
pH	8.14	8.35	7.92	8.2	7.99
TDS	260	350	190	170	110
Hard	232	192	168	240	133
Alkaln		200	131	192	109
Fluor	64	44	63	19	39
Conduc		605	475	580	330
HCO_3		200	131	184	109
TOC	4.55	6.60	5.50	5.82	6.00
THM ug/l	312	328	189	374	474

K-5

Date	8/88	10/88	1/89	4/89
Temp C	31	17	3	12
pH	7.90	7.85	8.20	7.99
TDS	230	180	150	120
Hard	126	174	226	136
Alkaln	126	125	183	111
Fluor	99	59	24	38
Conduc	375	415	540	330
HCO_3	102	125	179	111
TOC	4.73	6.31	5.97	6.27
THM	413	273	426	491

K-5A

Date	8/88	10/88	1/89	4/89
Temp C	31	18	4	13
pH	7.96	7.92	8.20	7.98
TDS	260	210	170	120
Hard	156	178	231	135
Alkaln	128	131	181	112
Fluor	91	54	29	88
Conduc	425	490	580	340
HCO_3	128	131	181	112
TOC	5.85	5.87	5.88	6.35
THM ug/l	371	251	339	504

K-6

Date	5/88	7/88	8/88	10/88	1/89	4/89
Temp C	22	32	28	18	3	13
pH	9.50	8.78	8.24	8.10	8.20	7.99
TDS	220	320	230	190	150	130
Hard	194	210	128	174	225	140
Alkaln	180	103	136	175	114	
Fluor	73	38	99	48	29	41
Conduc		560	330	425	560	340
Ca		61.06	44.82	57.79	73.20	48.62
Mg		12.38	8.16	7.58	10.86	7.18
Na		32.50	23.70	25.26	35.04	14.90
K		4.90	5.90	5.37	16.29	3.74
Cl		58.0	52.4	42.2	66.5	23.0
F		0.50	0.67	0.64	0.59	0.28
Nitrate		5.9	1.81	1.60	3.85	2.98
Sulfate		46.0	39.5	11.6	64.9	23.0
Silica		0.72	6.97	3.71	3.82	9.42
HCO_3		180	103	136	175	114
TOC	4.59	6.20	5.34	5.59	5.94	6.43
THM ug/l	303	287	310	405	437	303

OK-1

Date	5/88	7/88	8/88	10/88	1/89	4/89
Temp C	22	30	30	18	4	13
pH	8.46	8.41	8.41	8.89	8.4	8.08
TDS	240	290	250	180	140	120
Hard	206	214	166	173	215	144
Alkaln		197	141	132	167	118
Fluor	47	34	64	45	18	40
Conduc		530	400	405	510	350
HCO_3		197	141	122	161	118
TOC	5.20	5.58	5.03	5.26	5.13	6.30
THM ug/l	247	235	343	455	490	395

OK-2

Date	5/88	7/88	8/88	10/88	1/89	4/89
Temp C	23	31	30	17	4	12
pH	8.37	8.41	8.20	8.15	8.40	8.02
TDS	250	310	240	170	140	120
Hard	218	212	156	164	206	137
Alkaln		178	135	137	167	114
Fluor	49	32	63	46	17	39
Conduc		510	405	400	480	330
HCO_3		177	134	137	161	114
TOC	5.08	5.07	4.46	4.60	5.05	6.07
THM ug/l	304	302	347	357	348	453

OK-3

Date	5/88	7/88	8/88	10/88	1/89	4/89
Temp C	27	34	29	17	4	13
pH	8.58	8.57	8.30	8.16	8.50	8.00
TDS	250	340	240	170	130	110
Hard	212	204	162	158	199	128
Alkalin		172	141	133	163	107
Fluor	59	34	50	44	19	36
Conduc		600	410	395	440	310
HCO_3		172	141	133	157	107
TOC	5.32	6.66	4.66	4.37	4.86	5.91
THM ug/l	414	276	347	347	418	572

OK-4

Date	5/88	7/88	8/88	10/88	1/89	4/89
Temp C	24	29	29	17	4	13
pH	8.16	8.94	8.21	7.70	7.90	7.93
TDS	270	270	210	130	110	120
Hard	216	180	140	128	160	134
Alkaln	193	162	127	103	129	110
Fluor	43	24	46	86	34	38
Conduc		490	335	300	380	310
Ca	54.84	56.03	45.92	39.88	57.63	44.43
Mg		10.78	8.36	4.86	7.04	6.07
Na	13.17	27.40	24.40	12.50	17.69	11.58
K	27.90	1.80	6.20	3.54	10.58	3.02
Cl	53.0	56.0	43.4	23.3	32.8	18.8
F	0.20	0.30	0.30	0.29	0.20	0.17
Nitrate	2.86	7.90	1.25	1.40	2.02	2.81
Sulfate		17.0	25.0	33.0	38.0	12.0
Silica	1.18	1.48	3.72	8.85	5.86	8.93
HCO_3	193	162	127	103	129	110
TOC	4.20	5.70	4.52	4.61	5.88	6.22
THM ug/l	264	384	298	348	392	351

OK-5

Date	7/88	8/88	10/88	1/89	4/89
Temp C	28	27	18	4	11
pH	9.18	8.34	8.28	8.20	8.16
TDS	190	210	130	120	140
Hard	150	166	168	178	167
Alkaln	106	128	130	122	110
Fluor	46	72	38	18	37
Conduc	350	380	130	122	410
HCO_3	106	128	130	122	110
TOC	4.73	4.14	4.05	4.03	6.40
THM ug/l	301	340	249	305	488

OK-6

Date	7/88	8/88	10/88	1/89	4/89
Temp C	28	28	18	4	10
pH	8.91	8.37	8.30	8.00	8.46
TDS	270	380	380	200	150
Hard	212	288	402	322	190
Alkaln		112	130	166	126
Fluor	43	56	40	18	7
Conduc	500	575	900	670	440
Ca	69.10	94.97	123.69	73.77	58.69
Mg	11.18	16.94	12.89	10.30	12.53
Na	18.30	24.80	39.23	26.24	16.46
K	1.40	7.50	5.28	19.82	2.75
Cl	34.0	50.6	55.2	26.9	26.3
F	0.25	0.33	0.40	0.27	0.19
Nitrate	5.10	1.12	1.00	3.23	2.16
Sulfate	72.0	221.0	86.6	200.0	79.0
Silica	6.38	8.56	3.04	4.34	0.35
HCO_3	122	112	130	166	124
TOC	4.67	5.96	5.79	4.19	4.21
THM ug/l	327	406	330	295	290

OK-7

APPENDIX B

FLUORESCENCE AND THM VS TOC GRAPHS

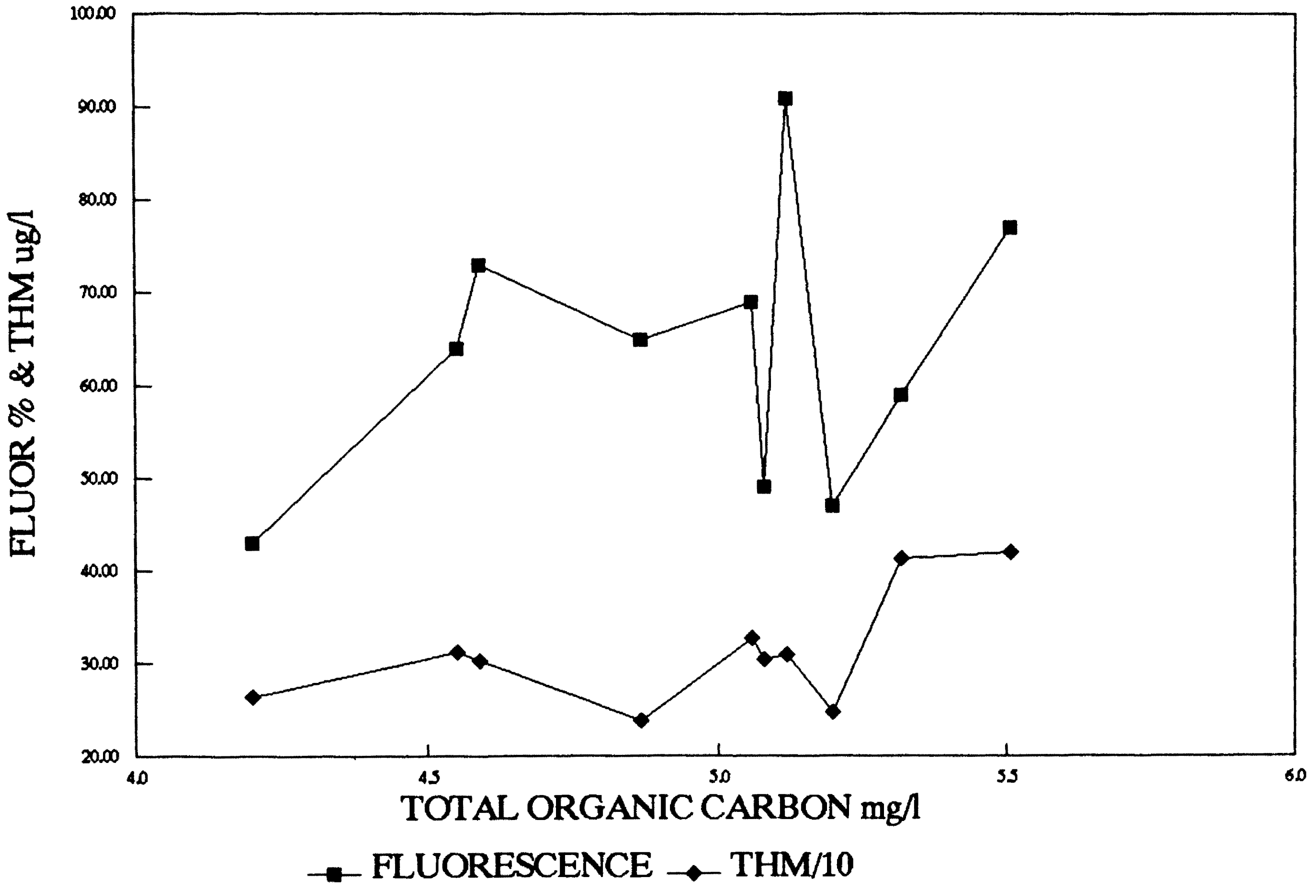

Figure 10 Fluorescence and THM vs TOC May 1988

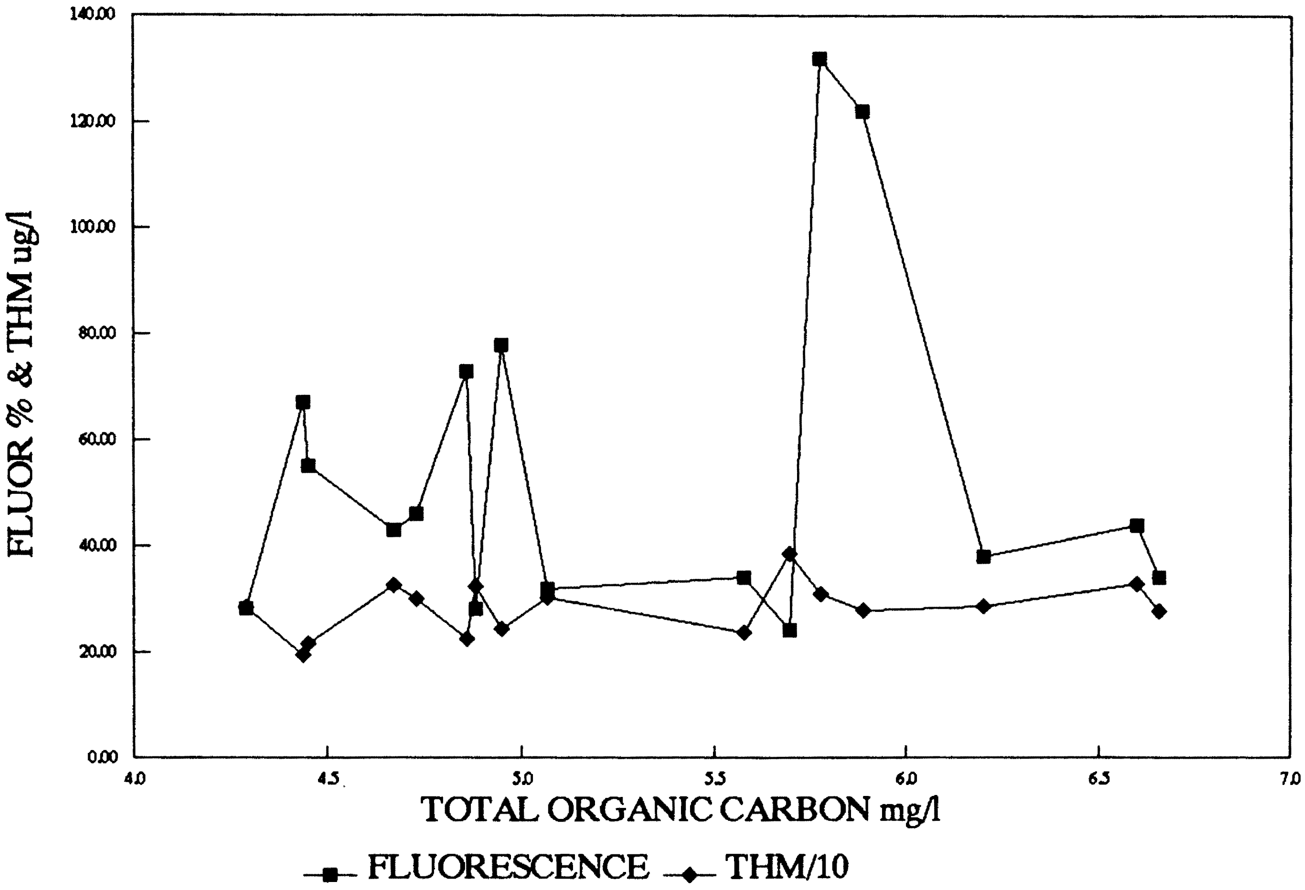

Figure 11 Fluorescence and THM vs TOC July 1988

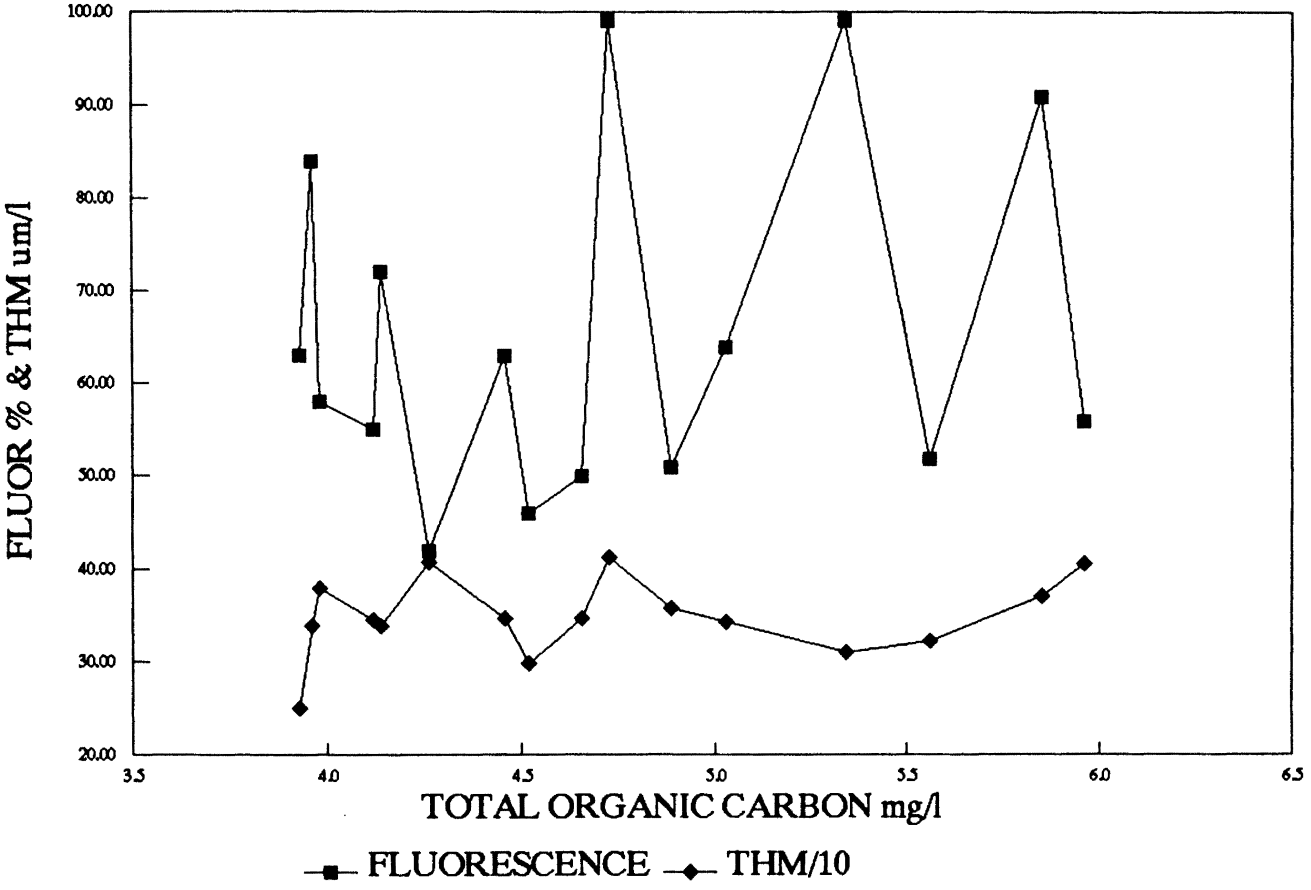

Figure 12 Fluorescence and THM vs TOC August 1988

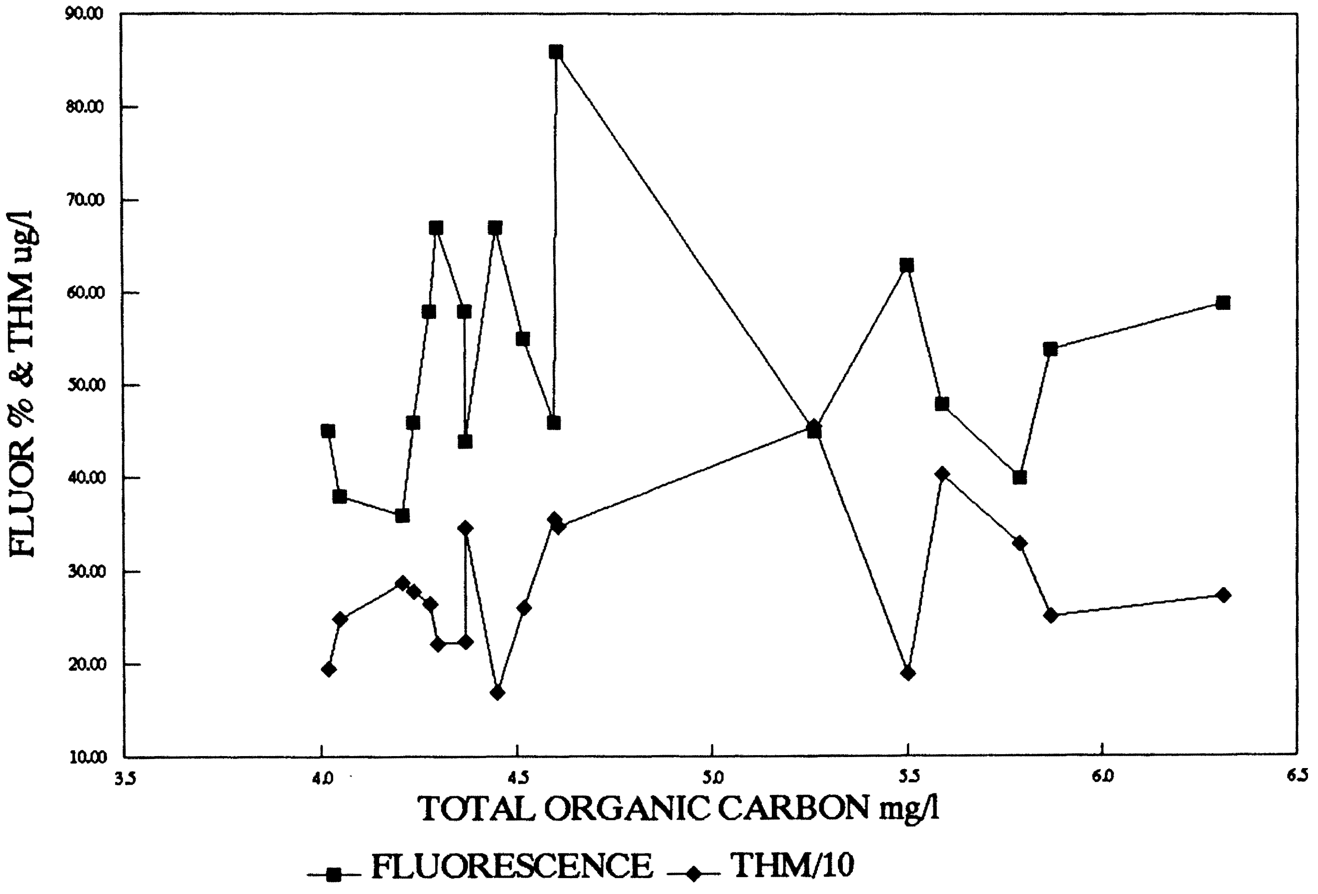

Figure 13 Fluorescence and THM vs TOC October 1988

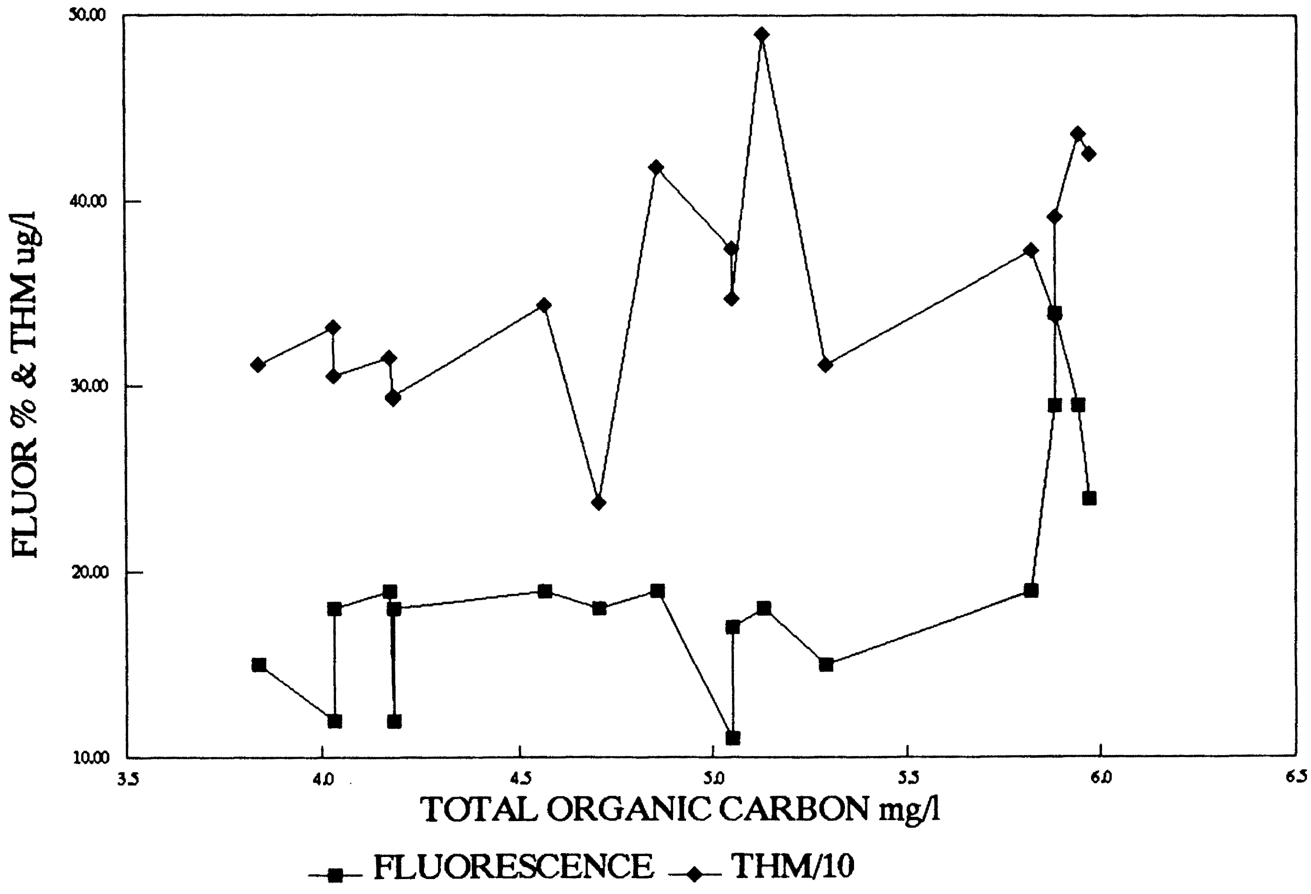

Figure 14 Fluorescence and THM vs TOC January 1989

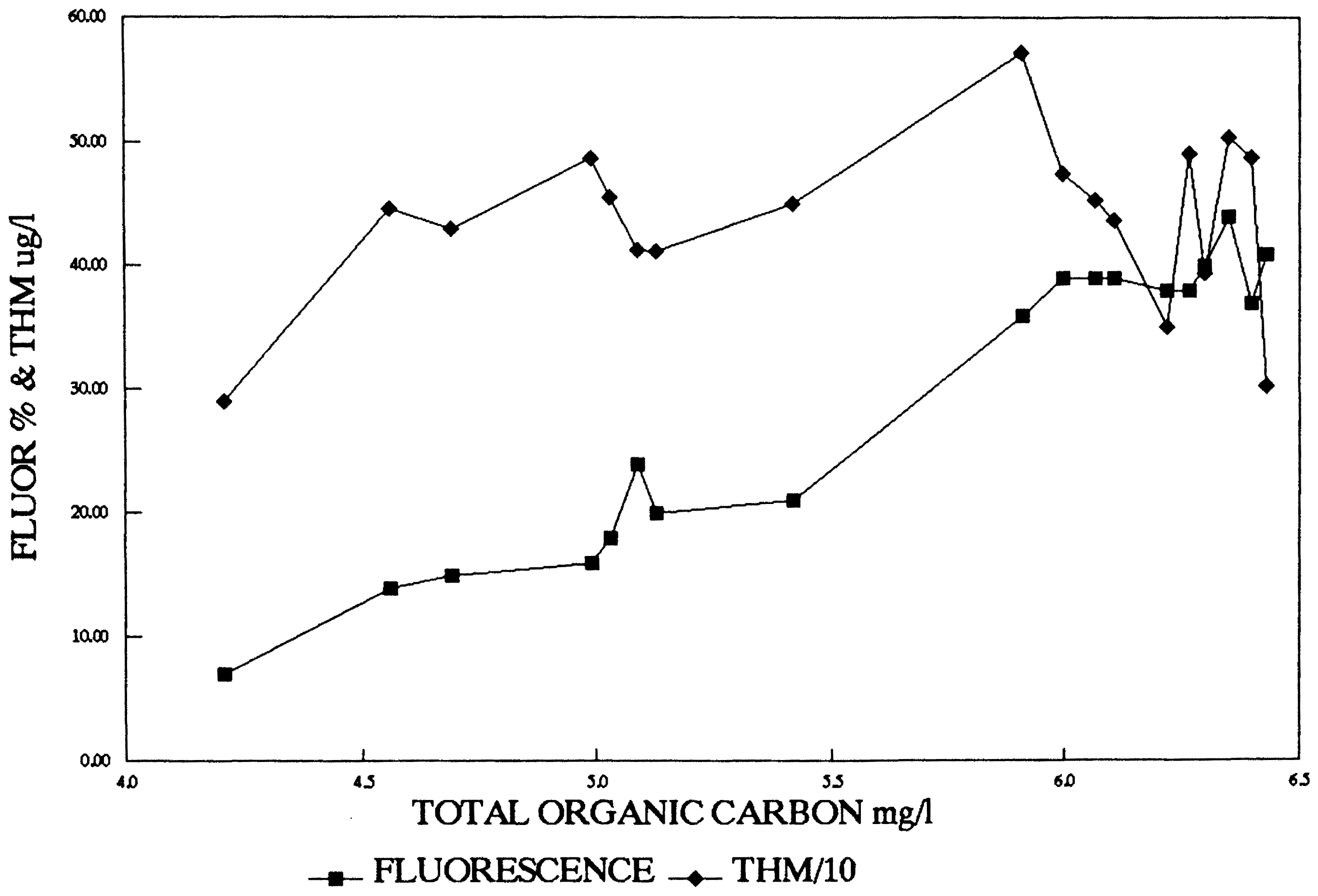

Figure 15 Fluorescence and THM vs TOC April 1989

APPENDIX C

FLUORESCENCE VS LOCATION GRAPHS

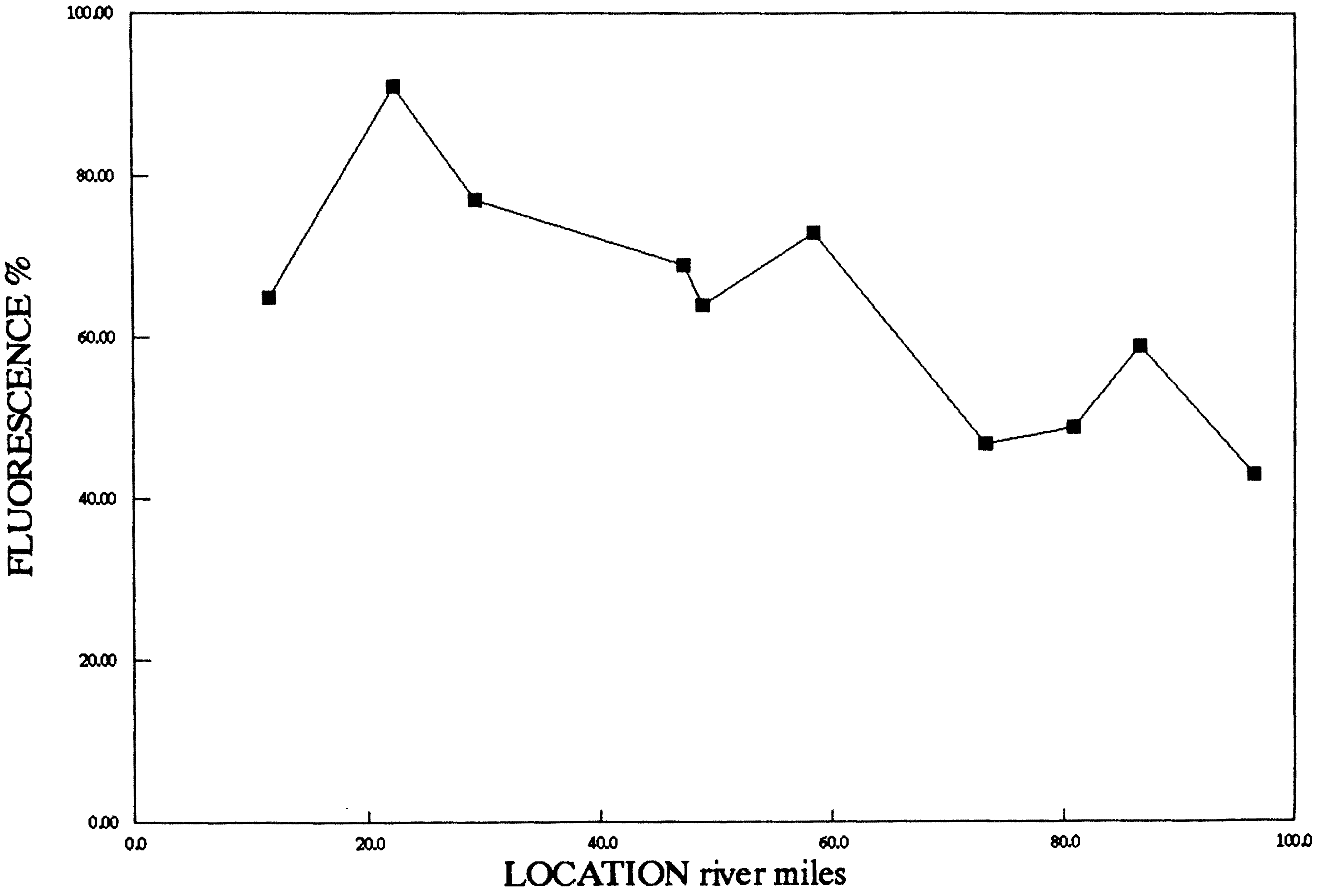

Figure 16 Fluorescence vs Location May 1988

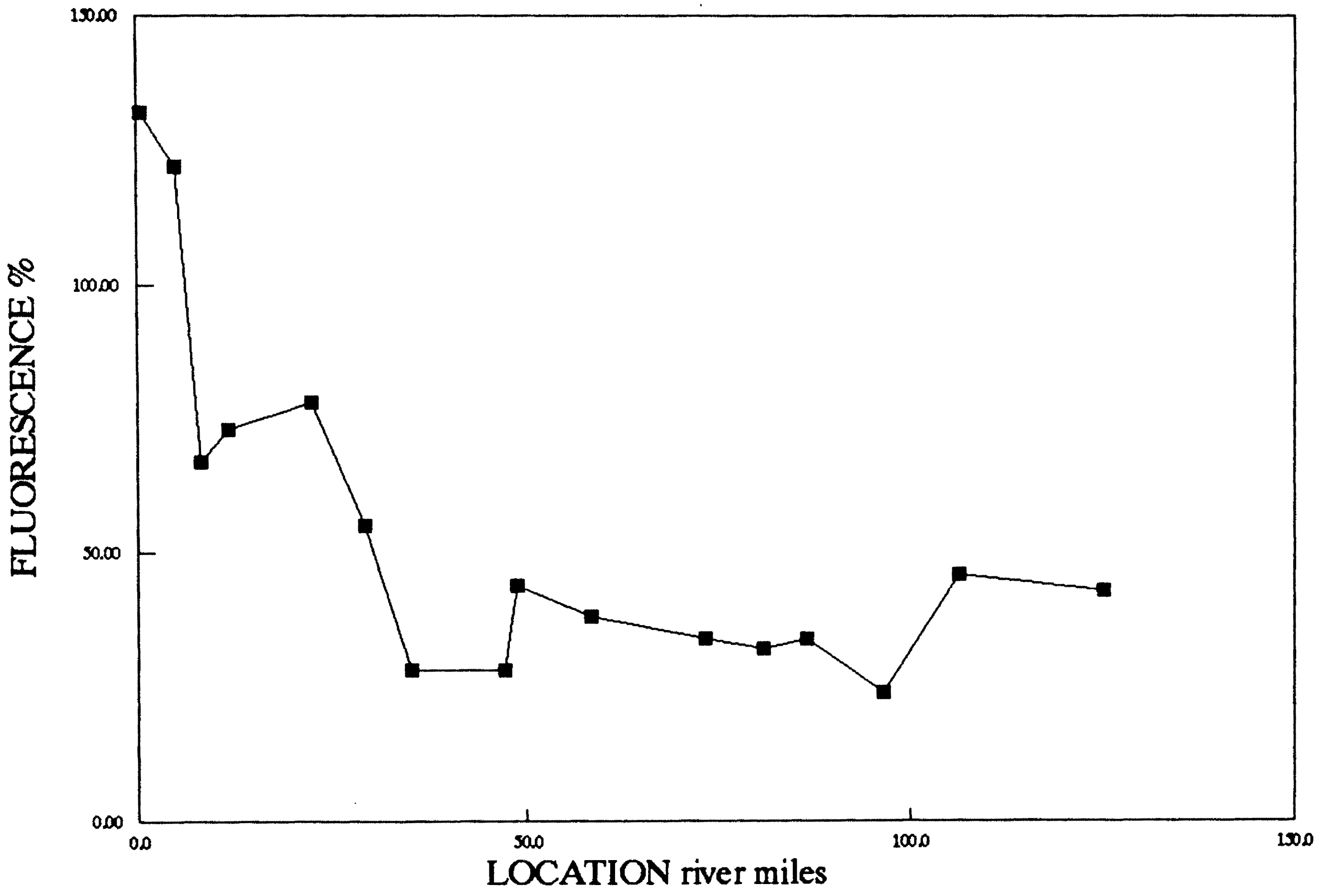

Figure 17 Fluorescence vs Location July 1988

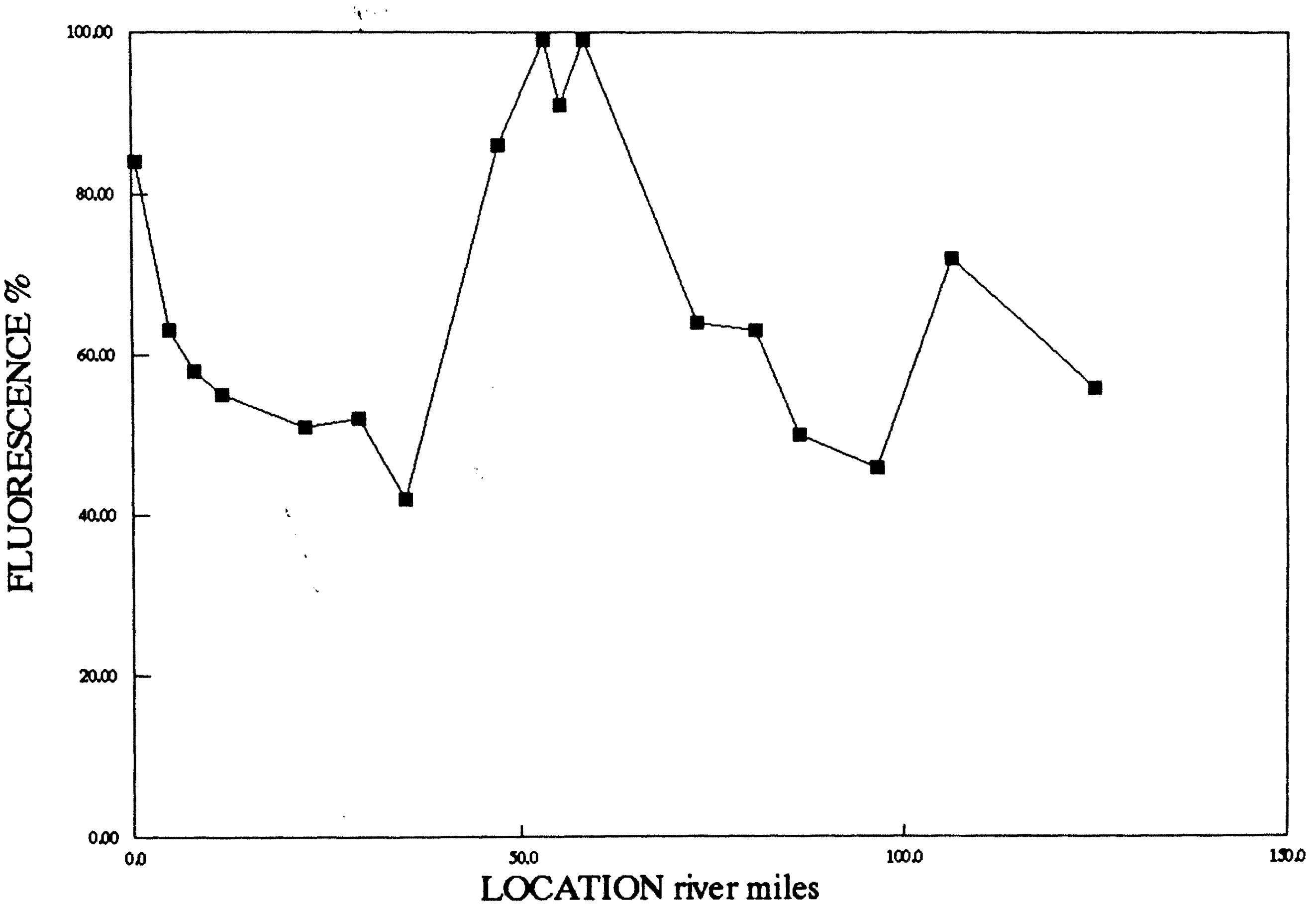

Figure 18 Fluorescence vs Location August 1988

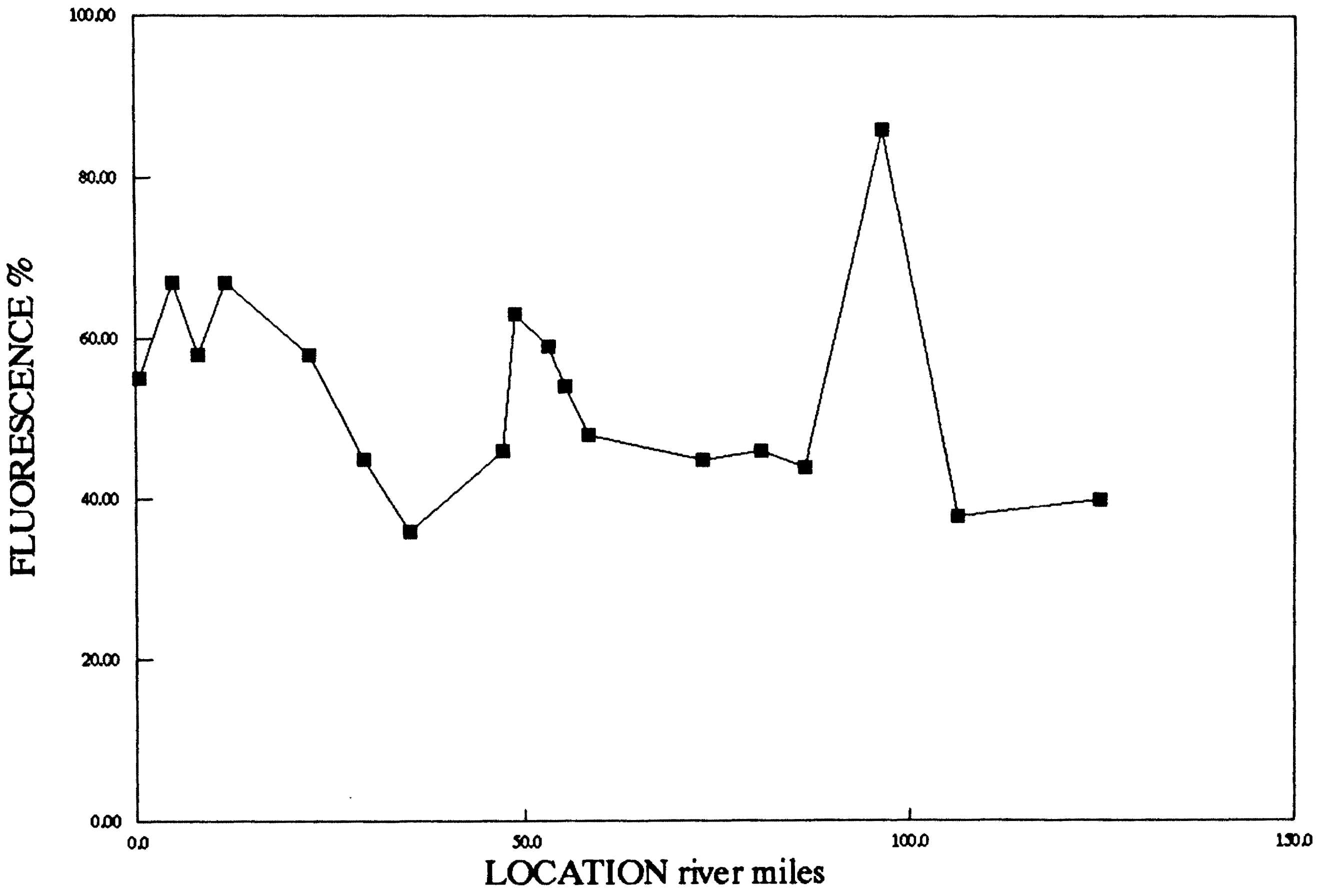

Figure 19 Fluorescence vs Location October 1988

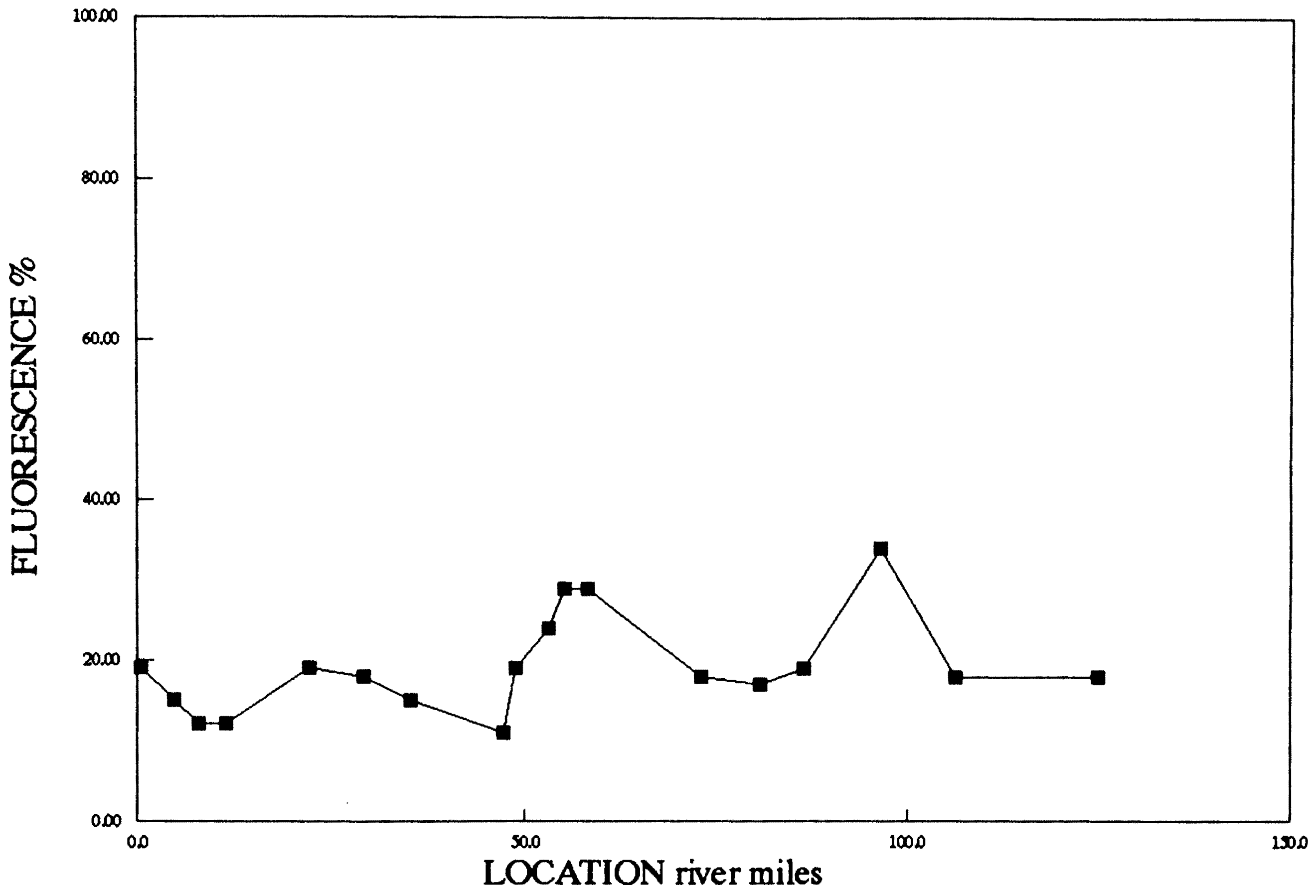

Figure 20 Fluorescence vs Location January 1989

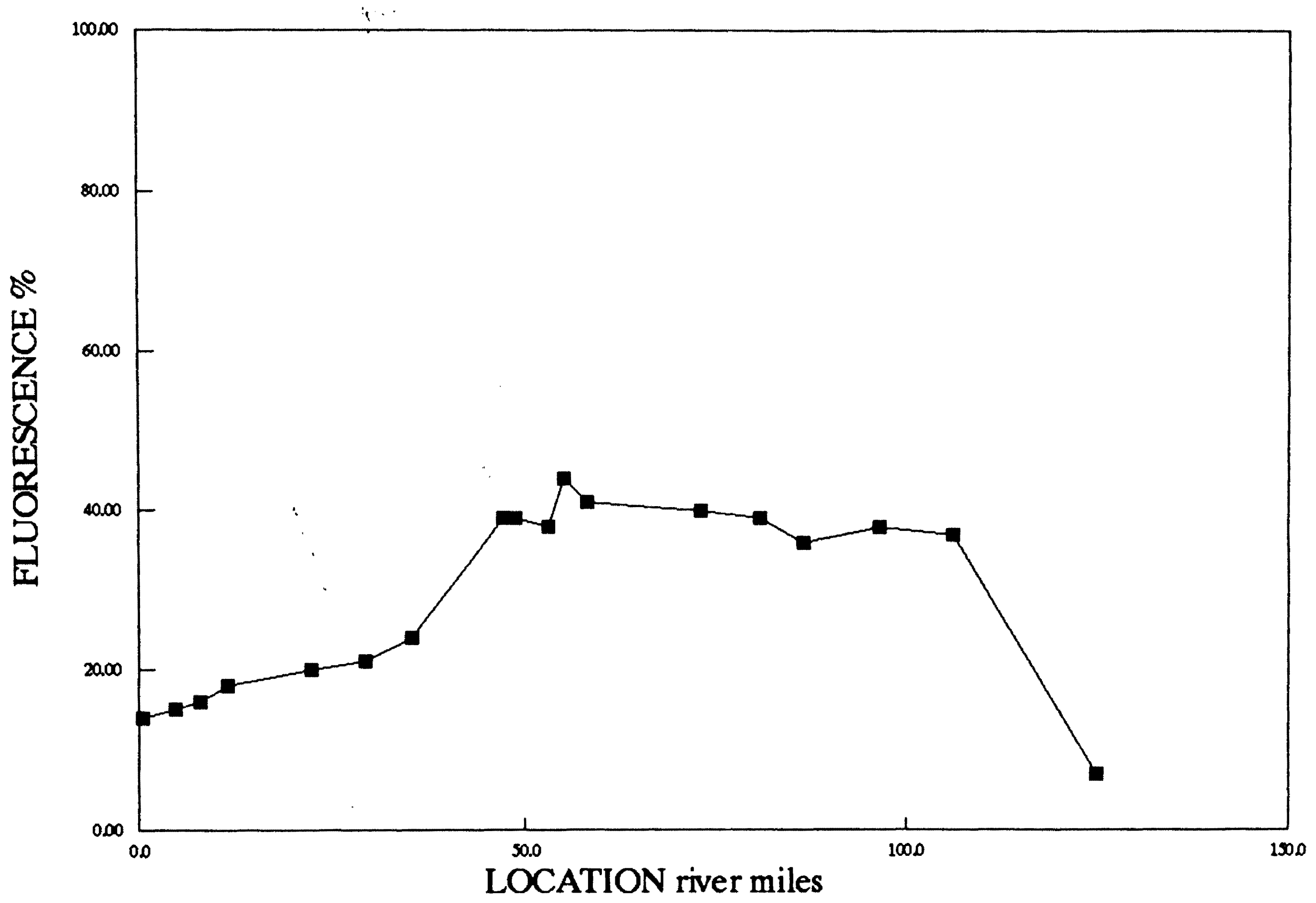

Figure 21 Fluorescence vs Location April 1989

APPENDIX D

THM VS LOCATION GRAPHS

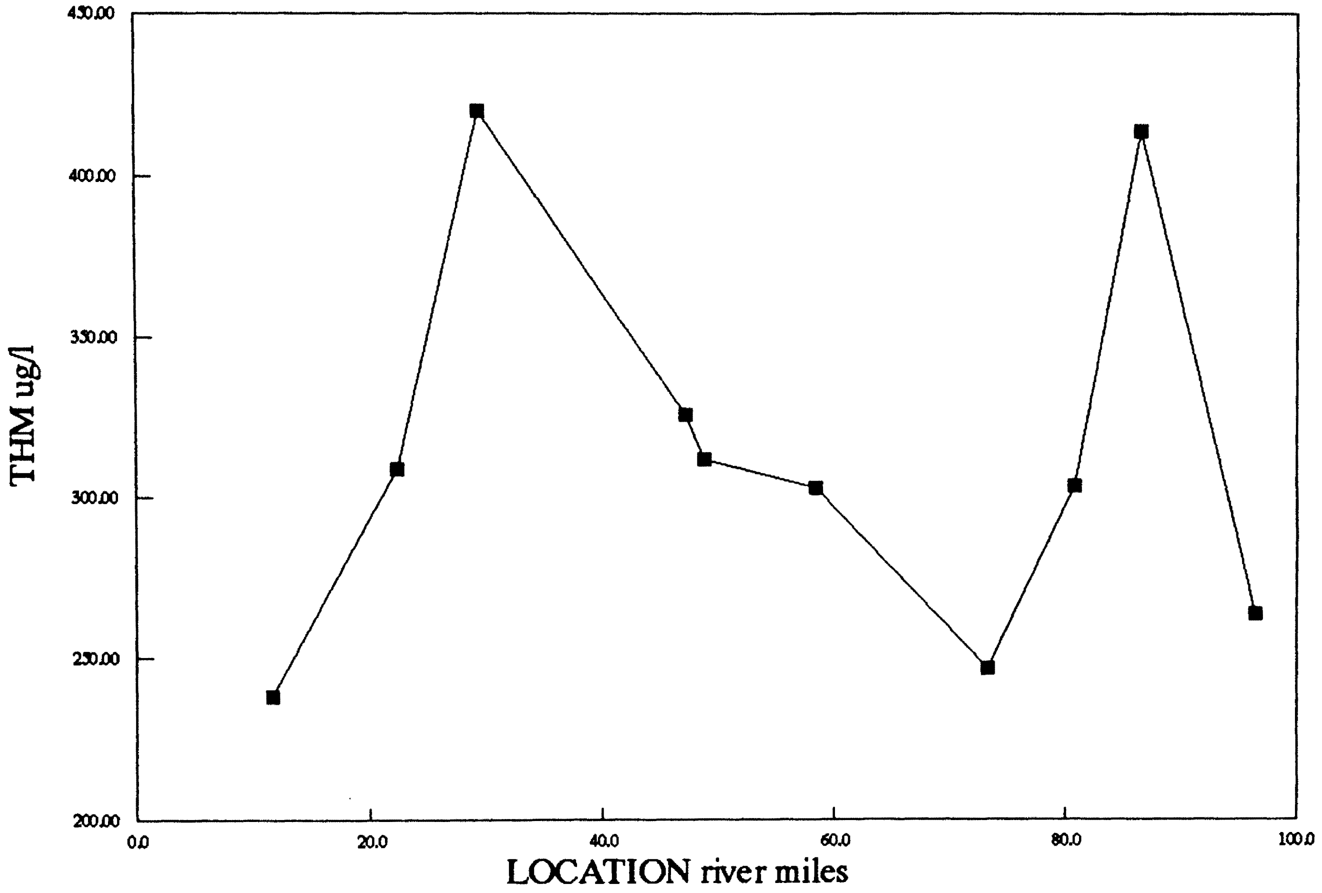

Figure 22 THM vs Location May 1988

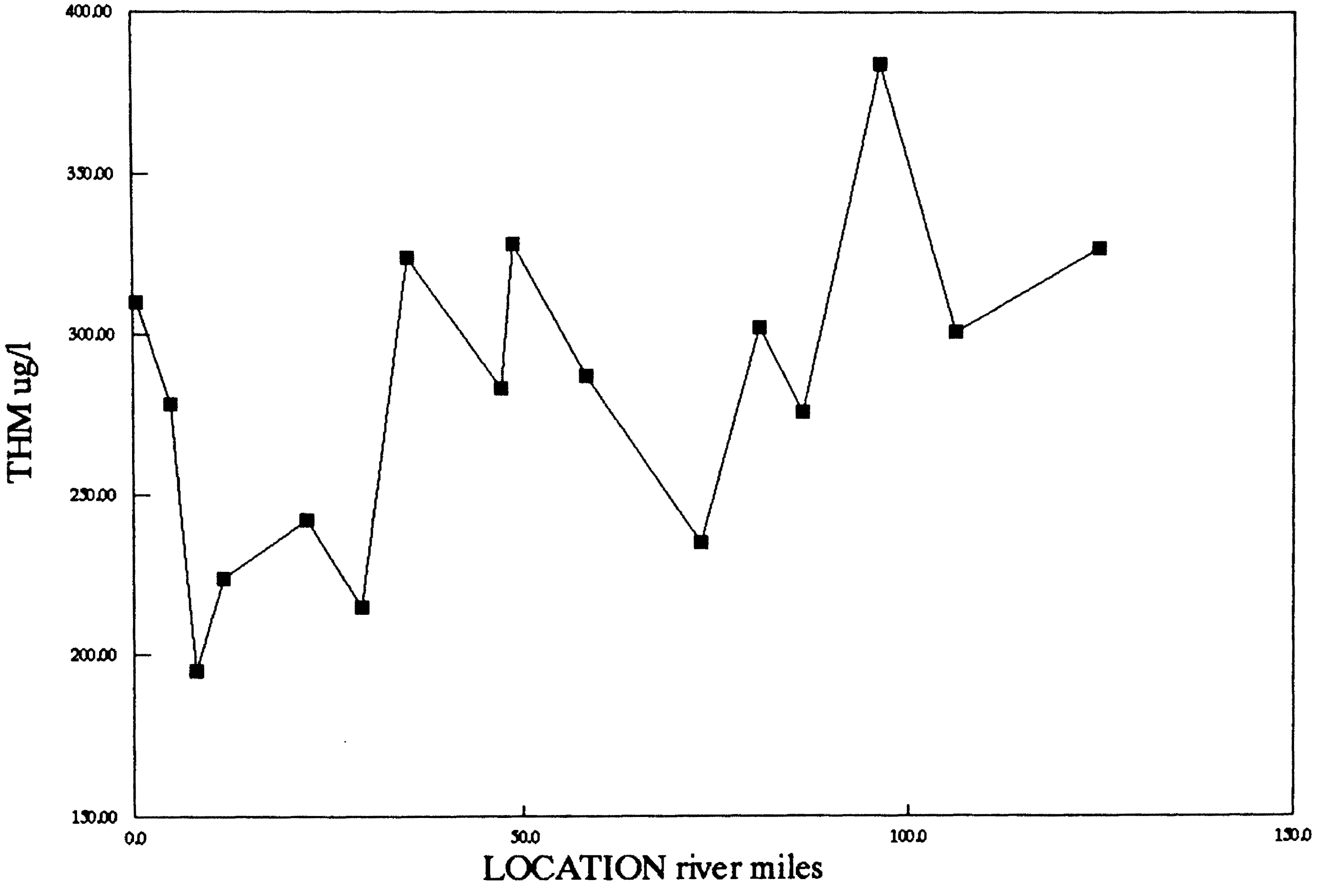

Figure 23 THM vs Location July 1988

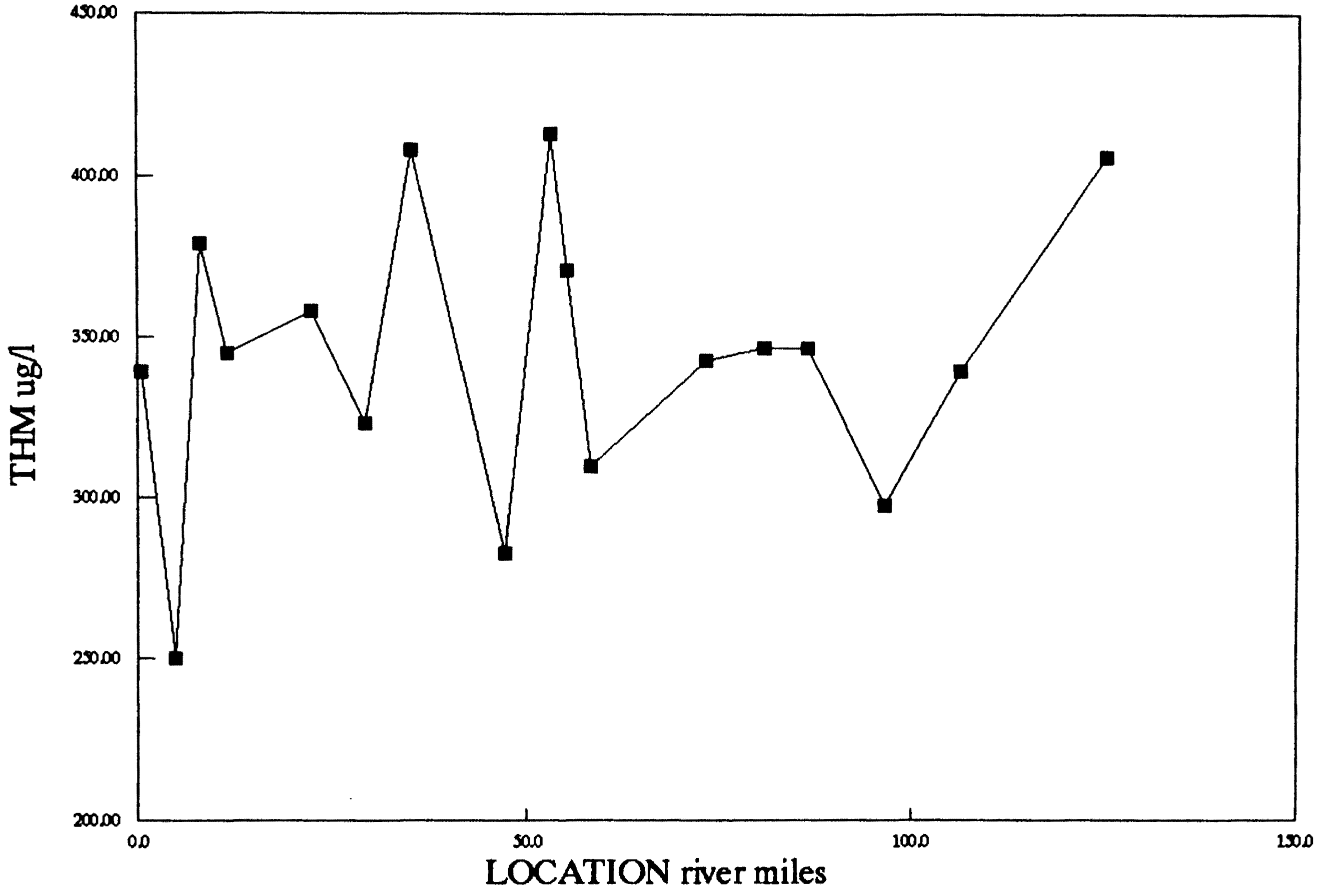

Figure 24 THM vs Location August 1988

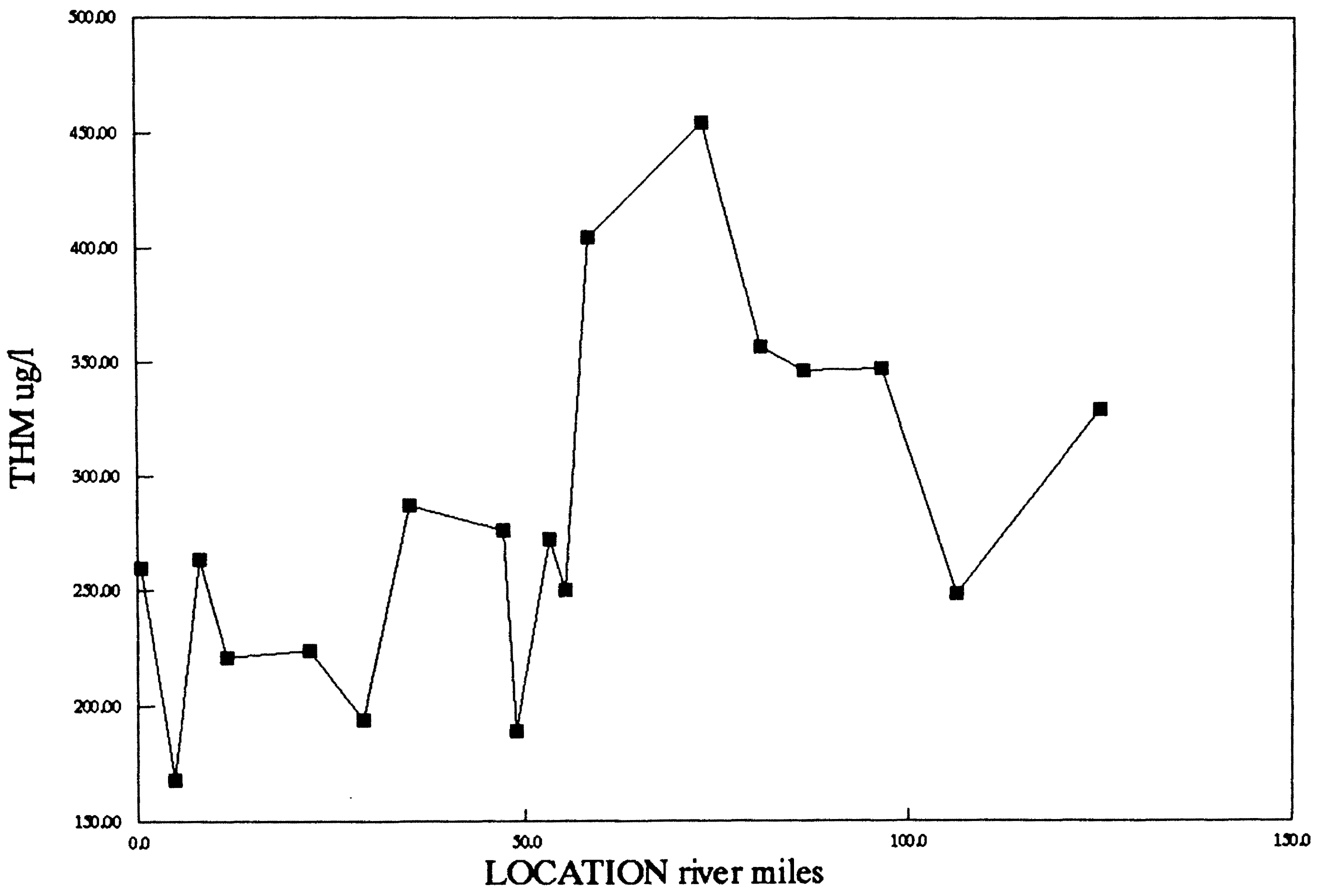

Figure 25 THM vs Location October 1988

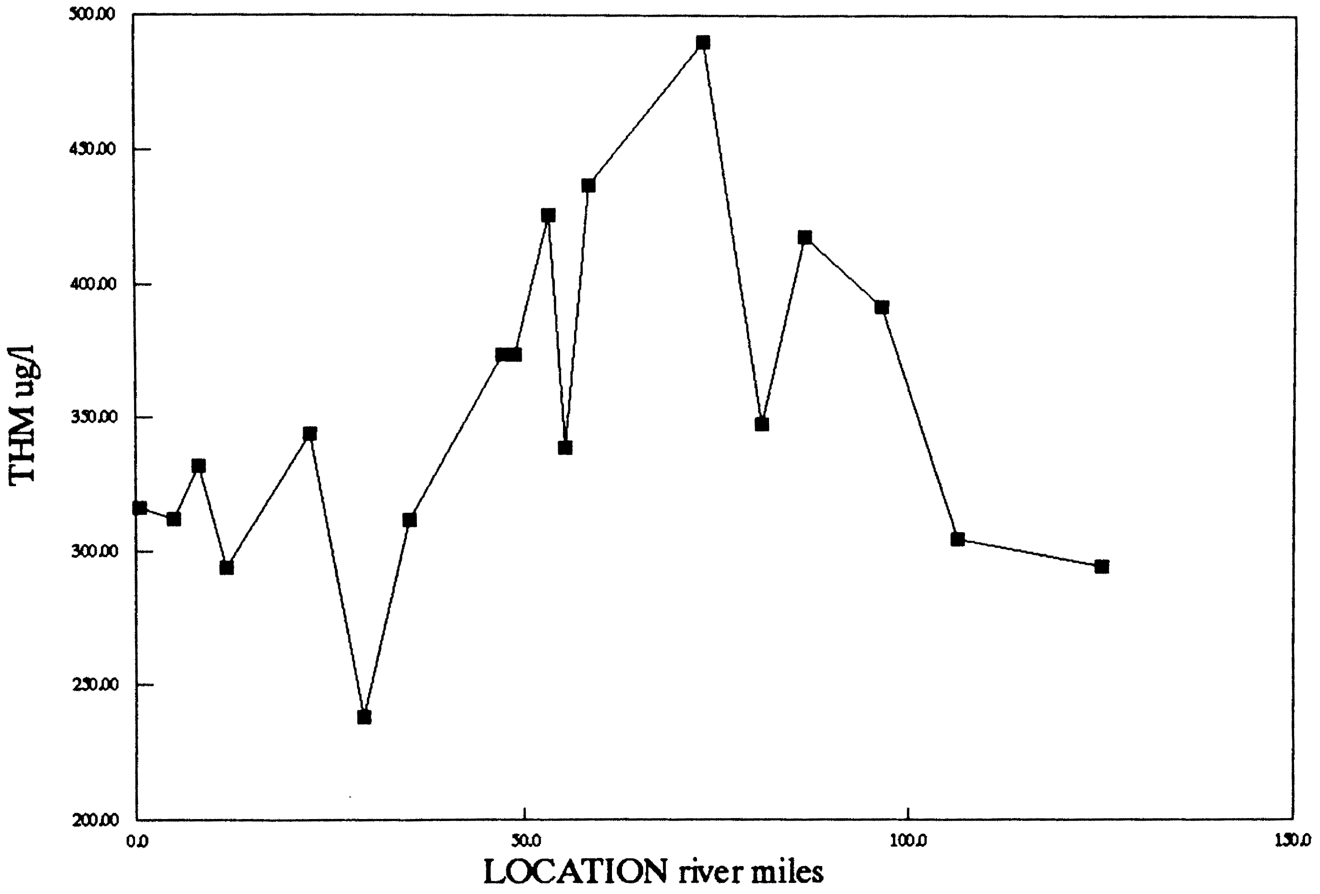

Figure 26 THM vs Location January 1989

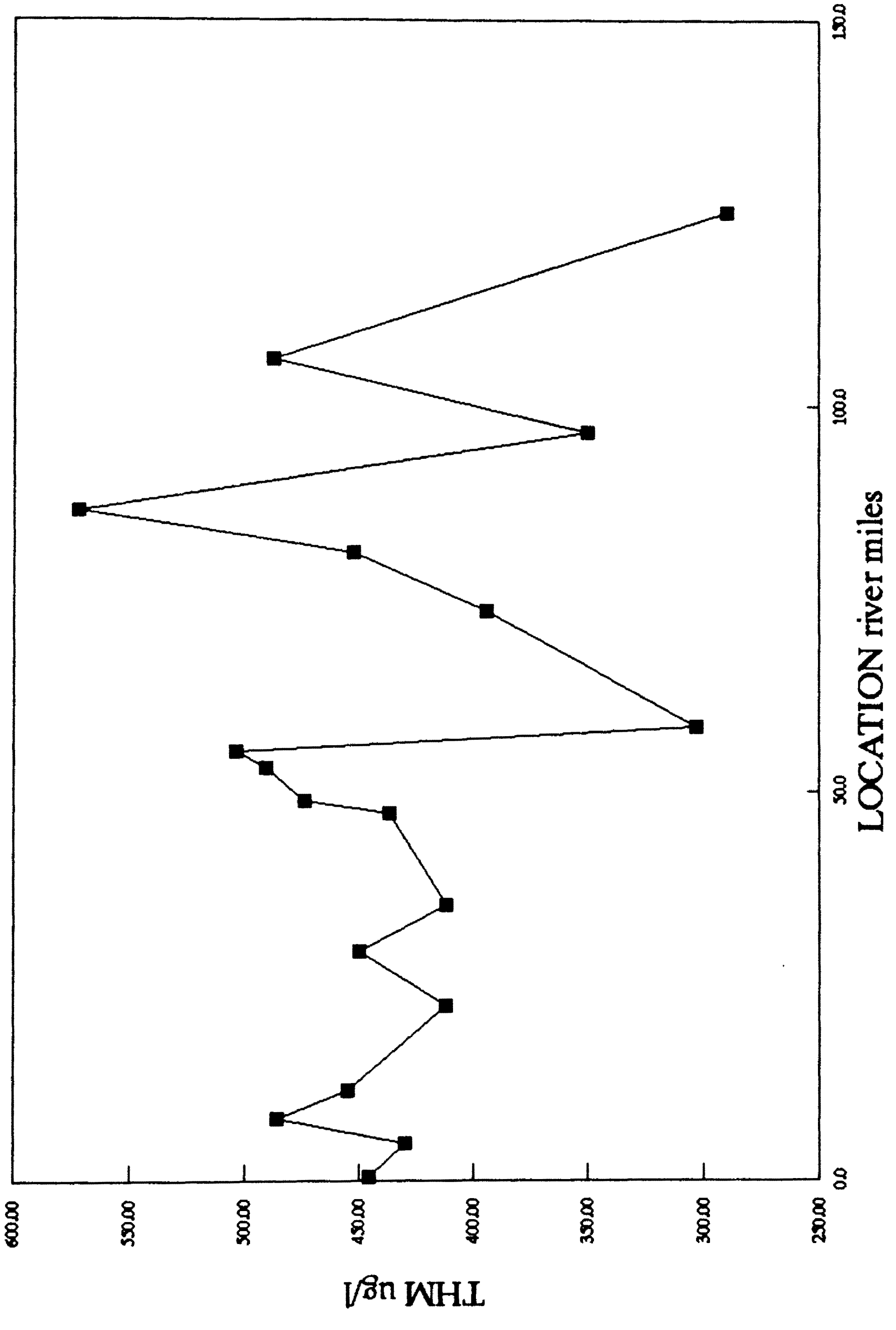

Figure 27 THM vs Location April 1989

APPENDIX E

TOC VS LOCATION GRAPHS

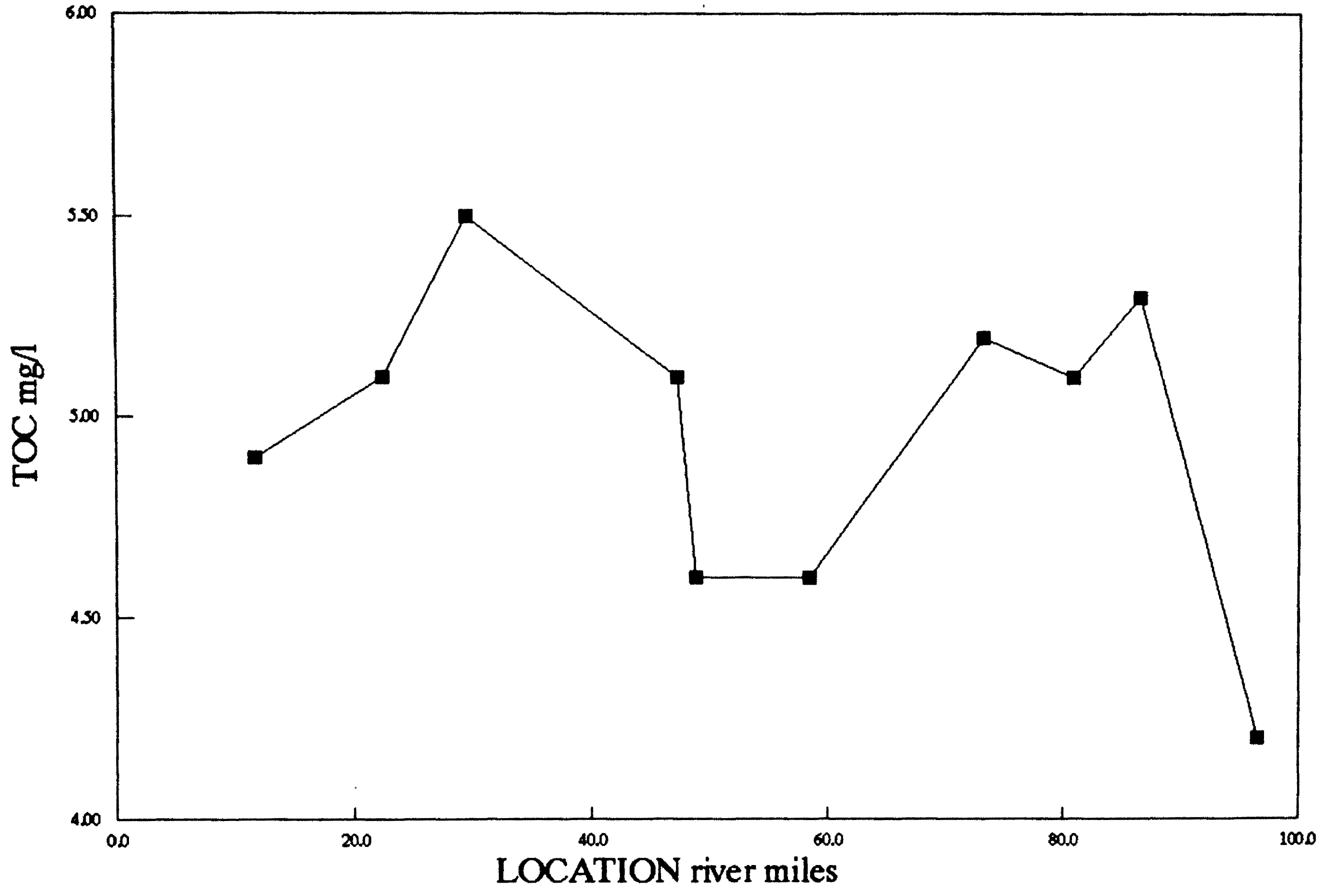

Figure 28 TOC vs Location May 1988

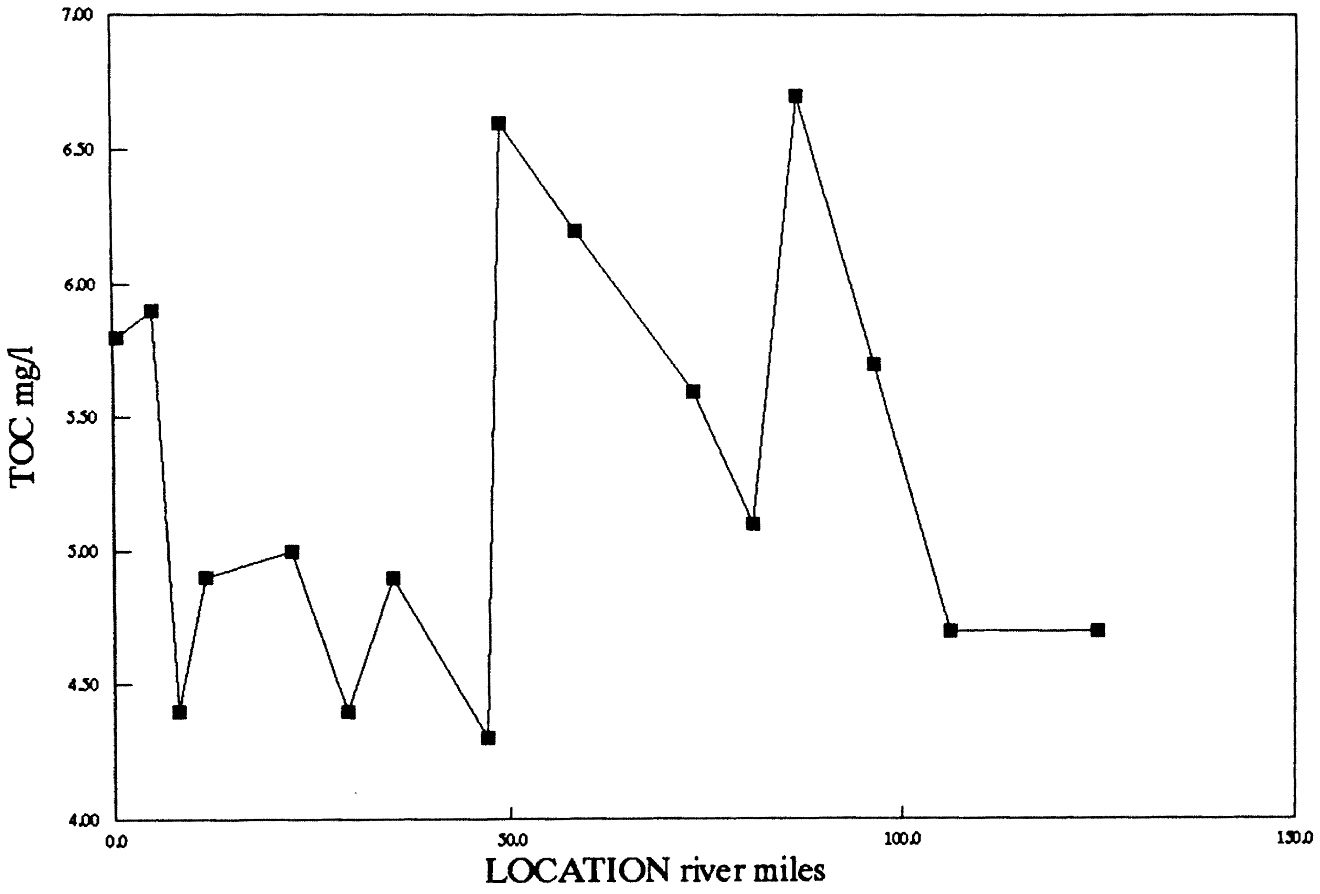

Figure 29 TOC vs Location July 1988

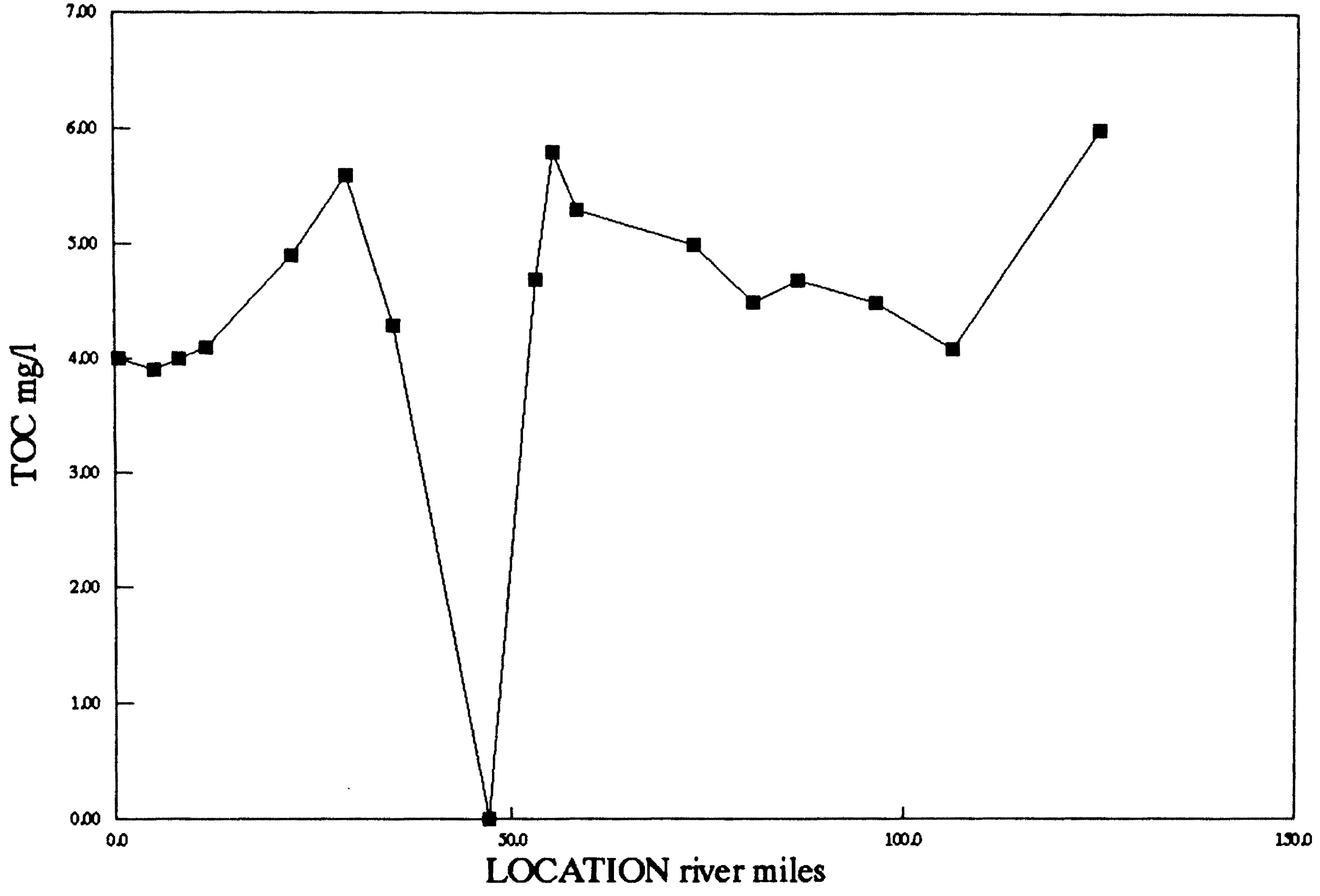

Figure 30 TOC vs Location August 1988

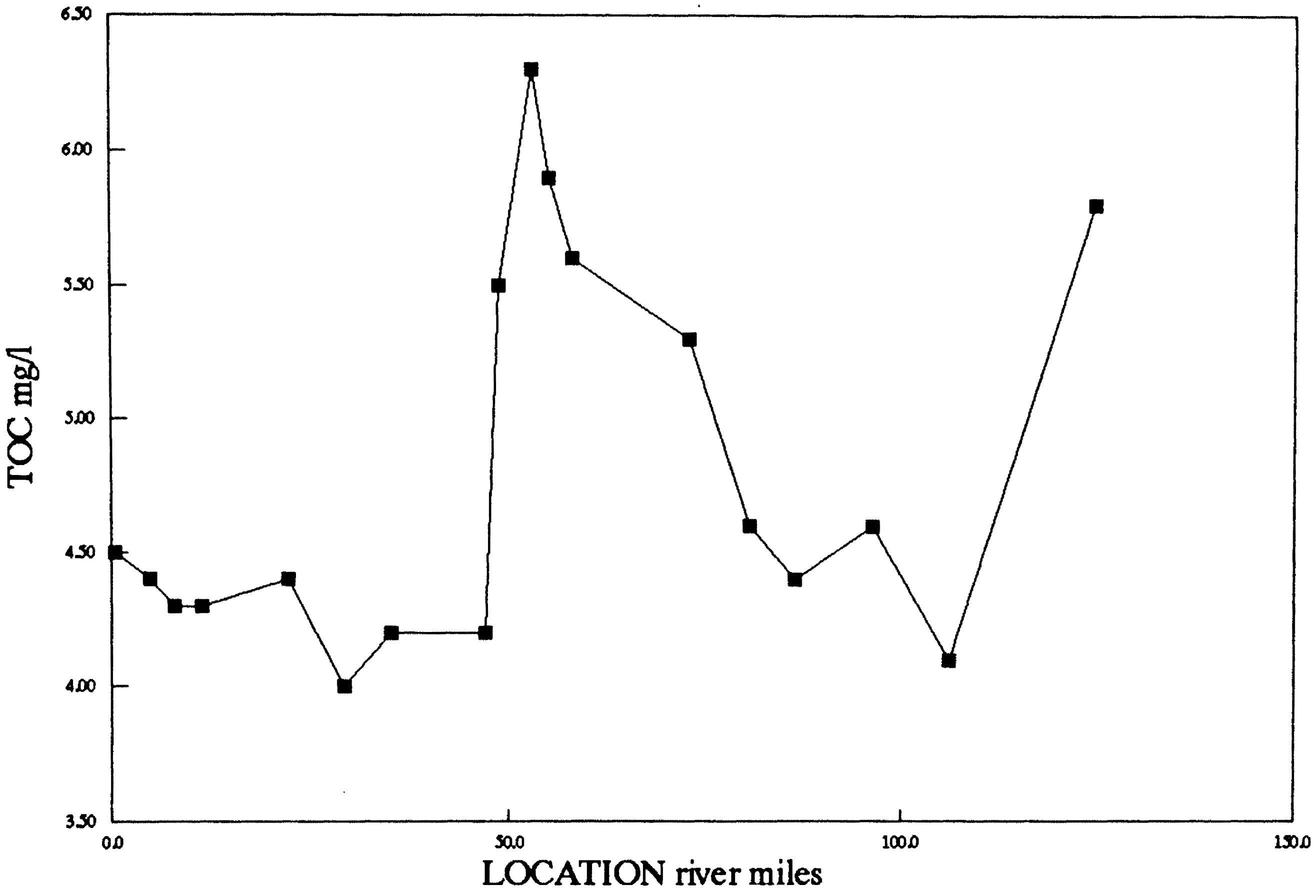

Figure 31 TOC vs Location October 1988

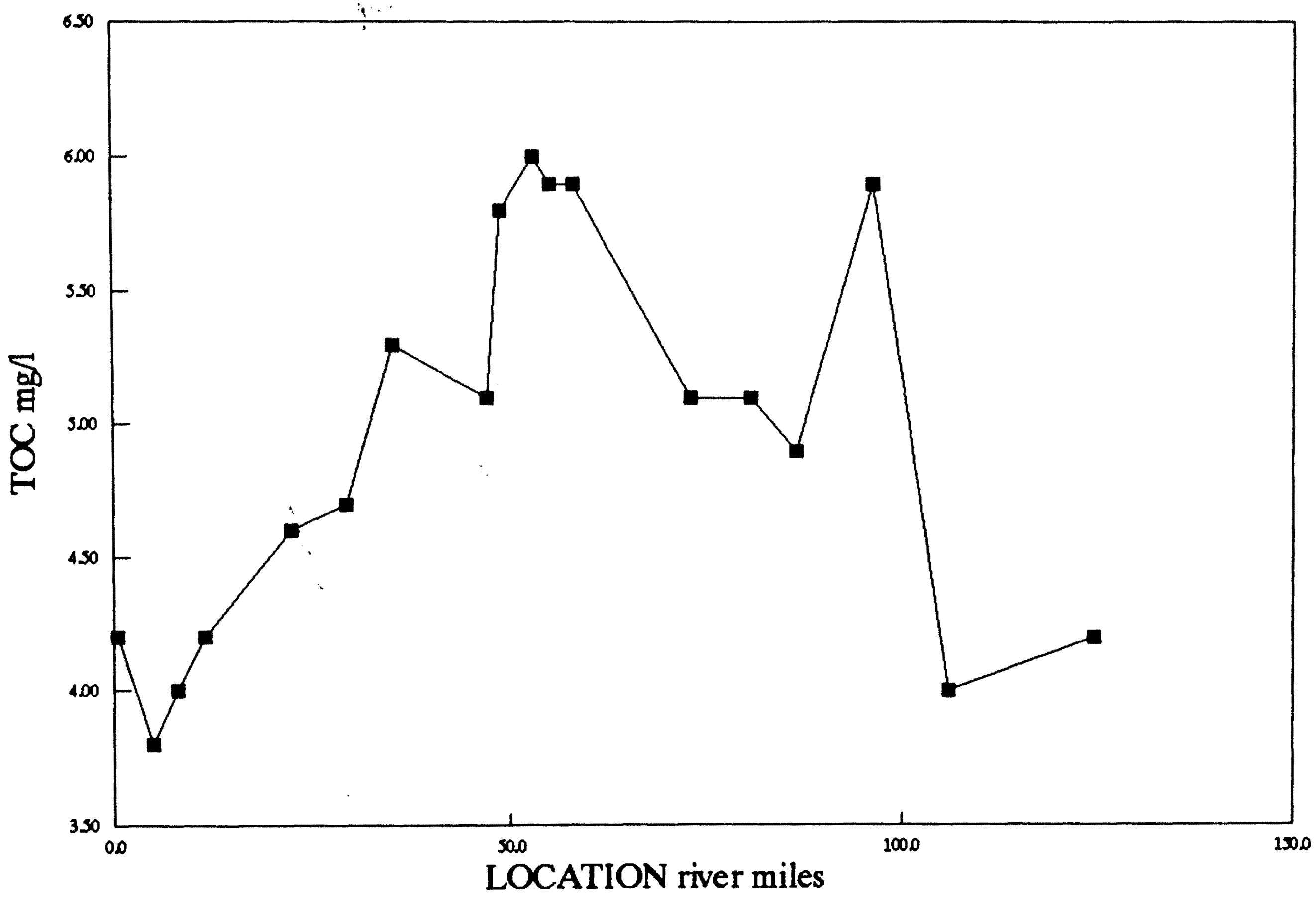

Figure 32 TOC vs Location January 1989

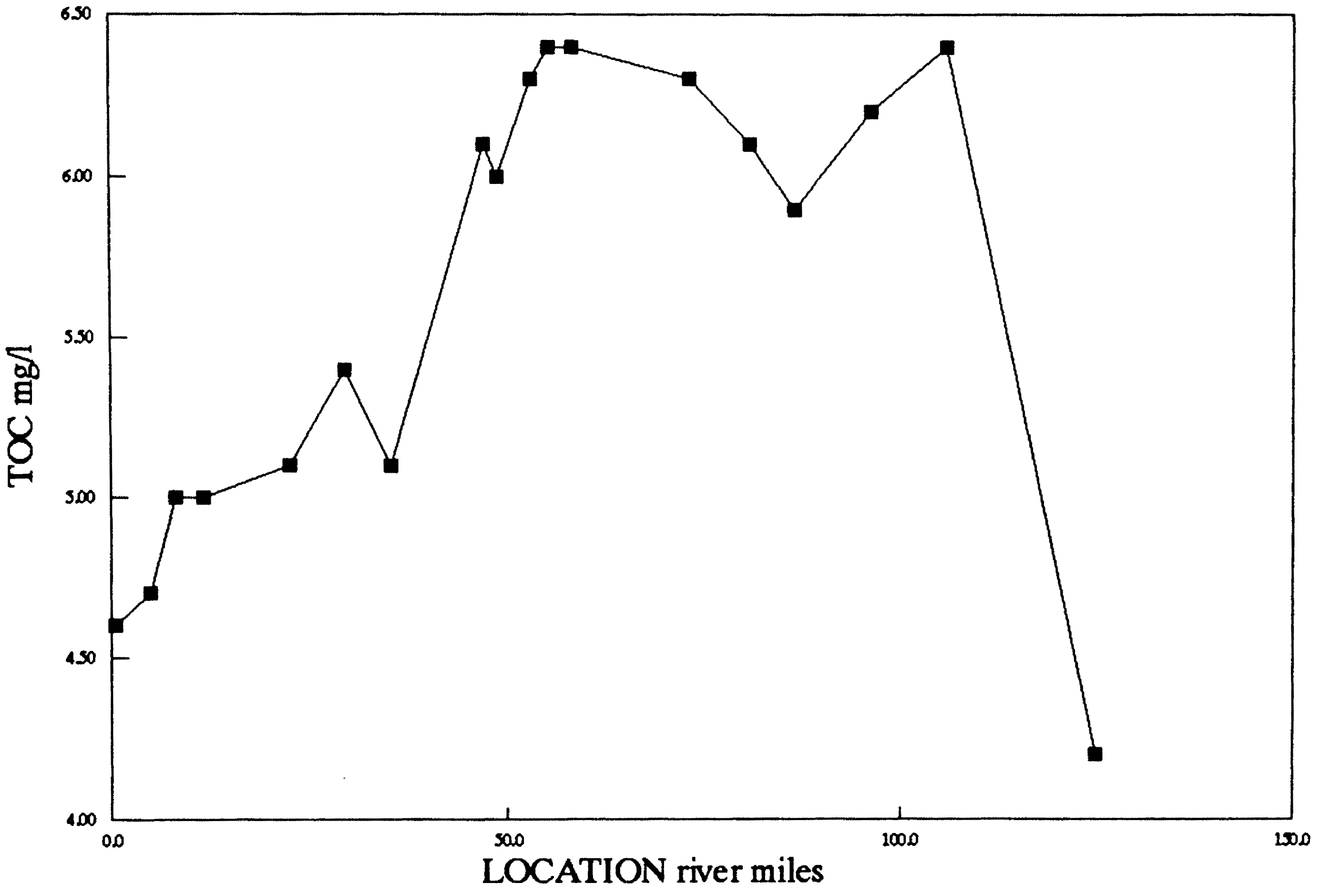

Figure 33 TOC vs Location April 1989

APPENDIX F

STATISTICAL DATA FOR CORRELATION BETWEEN TOC, THM, AND FLUORESCENCE

Statistical Data
For Correlation Between
TOC, THM, and Fluorescence

Date	Parameters	Sum of Squares	Good of Fit	Corr. Coef.
May	TOC THM	34283.44	0.327303	0.572104
May	TOC FLUOR	1984.1	0.099525	0.315475
May	FLUOR THM	34283.44	0.129177	0.359412
Jul	TOC THM	37081.11	0.129177	0.352722
Jul	TOC FLUOR	15879.75	0.006504	0.080645
Jul	FLUOR THM	37081.11	0.063341	-0.251677
Aug	TOC THM	26984.71	0.059023	0.242946
Aug	TOC FLUOR	5115.438	0.037544	0.193763
Aug	FLUOR THM	30983.53	0.003290	-0.057363
Oct	TOC THM	101087.2	0.076164	0.275978
Oct	TOC FLUOR	2686.944	0.004143	0.064370
Oct	FLUOR THM	101087.2	0.067498	-0.259804
Jan	TOC THM	65581.1	0.341055	0.583999
Jan	TOC FLUOR	651.1111	0.467468	0.683717
Jan	FLUOR THM	65581.1	0.141165	0.375719
Apr	TOC THM	82637.43	0.043840	0.209381
Apr	TOC FLUOR	2429.111	0.950828	0.975104
Apr	FLUOR THM	82637.43	0.048872	0.221071

Table 4

VITA

Robert Huddleston Walker Jr.

Candidate for the Degree of

Master of Science

Thesis: THE USE OF NATURAL WATER FLUORESCENCE TO DETERMINE TRIHALOMETHANE PRECURSOR VARIATIONS ALONG A WATER COURSE

Major Field: Geology

Biographical;

Personal Data: Born in Washington D. C., April 15, 1944 to Robert H. and Thelma Walker.

Education: Received Bachelor of Science degree in Geology from New Mexico Institute of Mining and Technology at Socorro, New Mexico in May 1974; completed requirements for the Master of Science degree at Oklahoma State University in July, 1993.

Professional Experience: Exploration Geologist, Gulf Oil, Midland, Texas, July, 1974 to February, 1978; Staff Geologist, Natomas North America, Tulsa, Oklahoma, February, 1978 to September, 1980; Division Geologist, Ozark-Mahoning, Tulsa, Oklahoma, September, 1980 to September, 1983; Manager Oil Division, Ozark-Mahoning, September, 1983 to April, 1986; Consultant Geologist, Tulsa, Oklahoma, April, 1986 to November, 1987; Pilot Plant Operator, Environmental Engineering and Technology, Tulsa, Oklahoma, November, 1987 to July 1989; Environmental Scientist, Tulsa Testing Incorporated, Tulsa, Oklahoma, July, 1989 to April, 1990; Environmental Engineering Aide, City of Tulsa, Tulsa, Oklahoma, April, 1990 to present.