To the Graduate Council:

I am submitting herewith a thesis written by Nathan Ted Lowe entitled "Distribution of Heavy Metals in the Tennessee River-Fort Loudoun Lake System, East Tennessee." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Geology.

Ralph M. Perhac, Major Professor

We have read this thesis and recommend its acceptance:

Accepted for the Council:

Vice Chancellor for
Graduate Studies and Research

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DISTRIBUTION OF HEAVY METALS IN THE TENNESSEE RIVER-FORT LOUDOUN LAKE SYSTEM, EAST TENNESSEE

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Nathan Ted Lowe

June 1978

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ACKNOWLEDGMENTS

The author wishes to express his appreciation to The Office of Water Resources Research, Department of Interior, for the financial aid which made this study possible. Special acknowledgment and gratitude is due Dr. Ralph M. Perhac for his guidance and encouragement during and after this study. Dr. Klepser and Dr. Byerly merit the author's appreciation for their helpful suggestions and manuscript reviews.

ABSTRACT

The purpose of this research was to define the heavy metal distribution in the Tennessee River-Fort Loudoun Lake system, and to study the relationships between the heavy metal content of the water and local geology, urbanization and industrialization, bottom sediment, and damming. Twelve water samples were collected from this reservoir which is located in the vicinity of Knoxville, Tennessee. The dissolved and total solid content of all samples were measured by ultracentrifugation and evaporation. The dissolved materials from each water sample were analyzed for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, and Ca by atomic absoption spectroscopy. The pH at each sample site was monitored over a 9-month period.

Evidence suggests that man's activities have had the greatest influence on the distribution of heavy metals in the river-lake system. The area behind the dam acts as a site of accumulation for water-borne sediments. Also, at least during one part of the year, the dam and the conditions it creates acts as a barrier for the mobility for certain dissolved heavy metals, particularly Zn and Cd.

The industrial area of Knoxville apparently introduced insignificant amounts of heavy metal to the river-lake system. However, mill tailings originally dumped into the Holston River at Mascot, Tennessee were observed to be a large contributor of dissolved Zn and Cd. Other than providing a source of Ca and serving to increase alkalinity of the water, the local geology appeared to play a rather insignificant role in influencing heavy metal distribution of the water.

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CHAPTER I

INTRODUCTION

Purpose

The primary purpose of this research was to define the heavy metal distribution along a major river flowing through an urban and industrial area to its impoundment. This was done by measuring changes in the heavy metal content of the water along the Tennessee River-Fort Loudoun Lake system at 12 sample sites in August 1973. As the chemical analyses are based on a single sampling which represents the river at a single seasonal state, the data in this paper represents only an approximation of true values. Specifically the research provides data on the distribution of heavy metals in the water of the Fort Loudoun Lake system and in the lake's bottom sediments (Abdelmalik, 1974). Relationships investigated in this study were those between the heavy metal content of the water and local geology, urbanization and industrialization, bottom sediment, and damming. This study is part of a program sponsored by the Office of Water Resources Research of the United States Department of Interior (Project No. A-032) studying transportation and distribution of trace metals in East Tennessee drainage systems.

Location

The Tennessee River-Fort Loudoun Lake system lies entirely within Knox, Blount, and Loudoun counties of East Tennessee, an area of urban, industrial, and agricultural uses. It begins where the Holston and French Broad Rivers join and extends 83 km (51.5 mi) to impoundment

at the Tennessee Valley Authority's (TVA) Fort Loudoun Dam at Lenoir City, Tennessee (Figure 1).

From the dam, the backwater spans 89 km (55 mi) upstream, 8 km (5 mi) above the start of the Tennessee River. The City of Knoxville (population about 175,000) is on the upstream half of the lake, about 73 km (45 mi) northeast of the dam.

Geologic Setting

The area lies within the Valley and Ridge province of the Appalachian Highlands Division. Topographically, it is characterized by northeast-trending, low, narrow, ridges separated by broad valleys. Karst features are common. These topographic expressions reflect the local bedrock geology. The area is underlain by Upper Cambrian and Middle to Upper Ordovician dolomites, limestones, shales, and sandstones of the Chickamauga and Knox Groups. These strata have been folded and faulted forming northeastward-trending outcrop belts that have been differentially eroded. The plunge of the folded strata is generally southwest. Northeastward striking thrust faults are common with the Knoxville Fault being the most prominent of several transected by the Tennessee River-Fort Loudoun Lake system. The less soluble, more resistant cherty dolomites, sandstones, and silty shales form the ridges. The more soluble, less resistant limestones, dolomites, and shales form the valleys. Local relief is about 60 m (200 ft). Weathering in the valleys is deep and irregular, and many limestone and dolomite beds are covered with a mantle of residual soil 15 to 30 m thick (Cattermole, 1958). A continuous layer of sediment now overlies the river/lake bed.

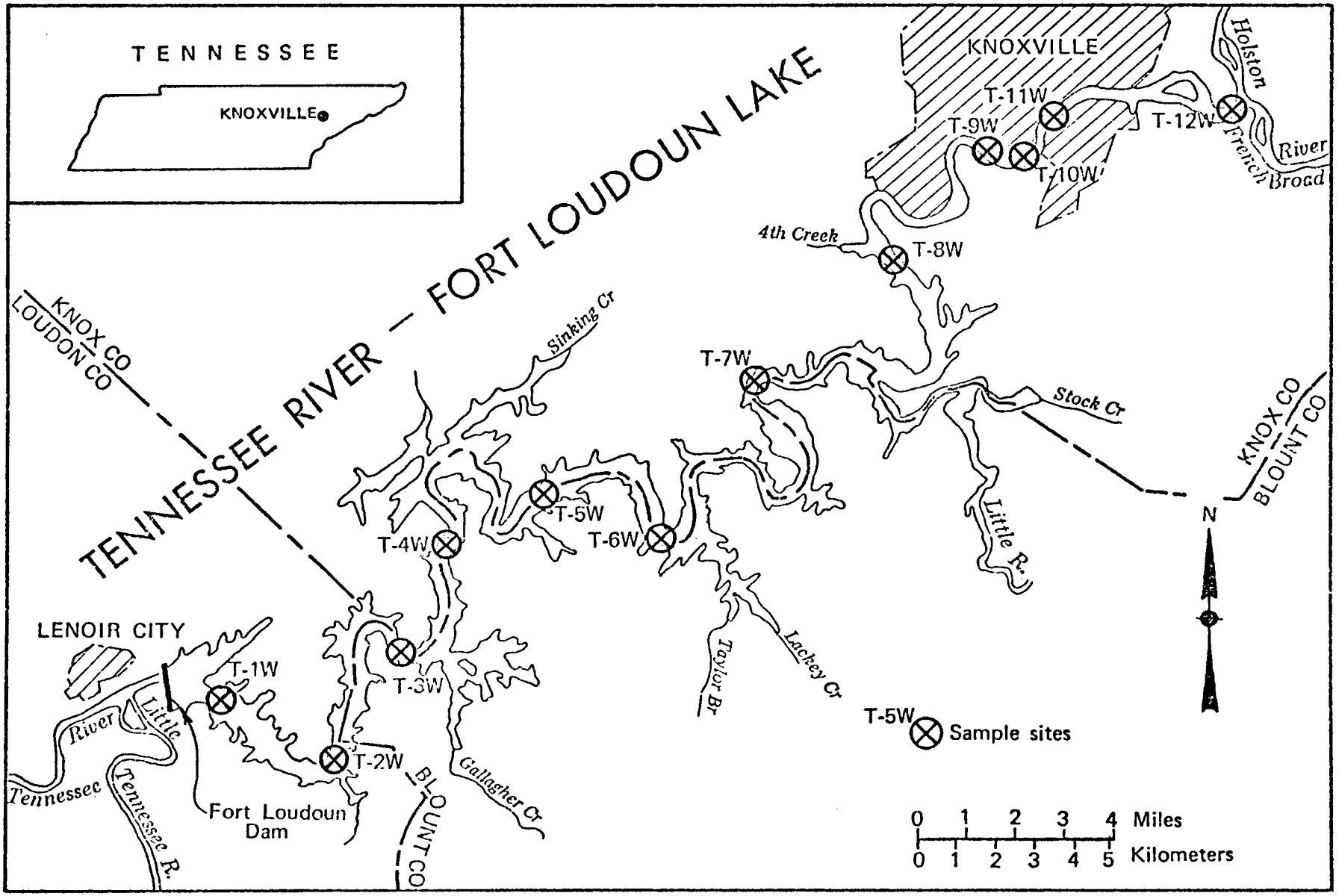

FIGURE 1. LOCATION OF SAMPLE SITES

Before the impounding of water behind Fort Loudoun Dam the depth of sediment on islands and flood plain ranged from 3 to 12 m (10 to 40 ft). This alluvial material ranges from black loam on the top, to clay and gravel on the bottom (TVA, 1949).

Hydrology

Before completion of the Fort Loudoun Dam in 1944, the Tennessee River bed covered about 1,800 hectares (4,500 acres). Measured at Lenoir City, average annual stream flow prior to damming was about 390 m^3/sec (13,800 ft^3/sec), with a minimum of 45 m^3/sec (1,600 ft^3/sec). The elevation of the river bed at Lenoir City was 222.5 m (730 ft) above sea level. Above their junction, the Holston and French Broad Rivers drain an area of 23,000 km^2 (8,900 mi^2) of rolling valley and ridge or mountainous terrain. Below their junction the two rivers, which become the Tennessee River, drain an additional area of 1700 km^2 (650 mi^2) to the dam. The total area drained above the dam encompasses 24,700 km^2 (9,550 mi^2) (TVA, 1949). In addition to the aforementioned two large headwater rivers, the Tennessee River has numerous small tributaries.

Reservoir Characteristics

Damming increased the narrow Tennessee River to an average width of 0.6 km (.4 mi) and its water area to 6,270 hectares (15,500 acres) at elevation 247.9 m (813 ft) which is full pool under normal operations. The reservoir is regulated by Fort Loudoun Dam for flood control and hydroelectric supply purposes. This regulation results in a seasonal high and a seasonal low reservoir volume. The reservoir is

low between November and April which corresponds to the time of greatest water discharge through the dam. Inversely, the reservoir volume increases during late spring and stays high until early fall (Figure 2), at which time discharge is cut back. Minor fluctuations in volume occur throughout the year as heavy rains and hydroelectric power demands dictate.

Meteorology

The average annual precipitation values for Knox County, and for the total drainage area above Fort Loudoun Dam, are about 116 and 119 cm (45.5 and 47 in), respectively. Mean annual surface runoff of the total drainage area is about 50 cm (20 in). In Knox County this runoff equals 48 cm (19 in). It is estimated that 18-23 cm (7-9 in) of this amount passes through the ground-water system before being discharged into streams (McMaster, 1973). Maximum precipitation comes with the large storms of winter and early spring. Midsummer showers and thunderstorms bring minor amounts of rainfall. September and October have the least precipitation. However, rainfall is fairly evenly distributed through the year. The greatest flood potential occurs in February and March, by which time the ground has become nearly saturated and rainstorms frequently drop 5-10 cm (2-4 in) of precipitation.

Research Procedures

Twelve water samples were collected. The dissolved and total solid content of each were measured using ultracentrifugation and evaporation. The dissolved material of each sample was analyzed chemically

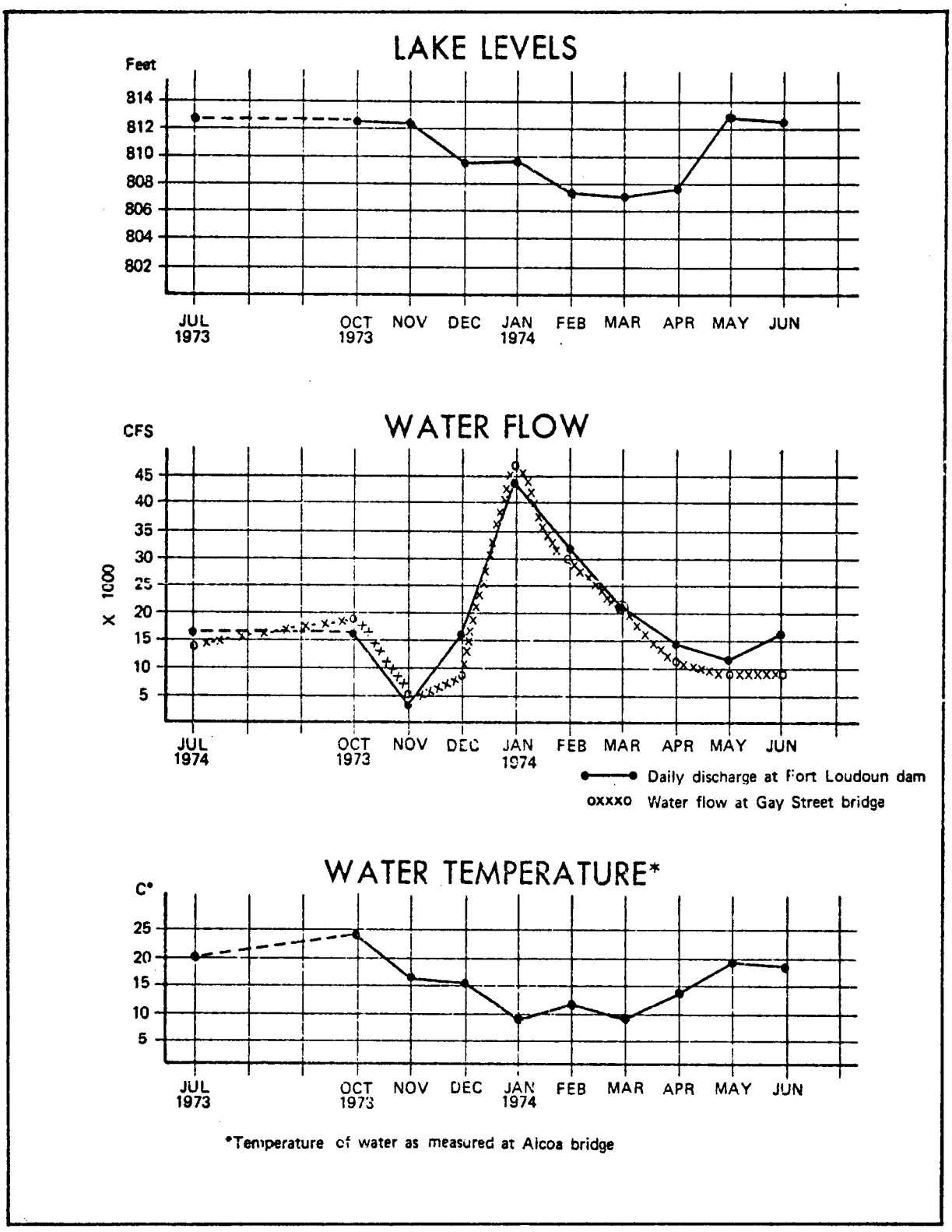

FIGURE 2. FORT LOUDOUN LAKE LEVELS, WATER FLOW, AND WATER TEMPERATURE FROM JULY 10, 1973 TO JUNE 1974

Source. Compiled from records, Tennessee Valley Authority River Control Branch, 1974.

for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn by atomic absorption spectroscopy. In addition to these metallic elements, the samples were analyzed for calcium. Each month, for 9 months, water pH in the vicinity of each sample site was monitored.

Other Related Investigations

The substrates in the lake, where water samples were taken, were also sampled, size fractionated, and analyzed both chemically and mineralogically (Abdelmalik, 1974). The relationships between metal distribution, particle size, and mineralogy were studied. R. J. Smith (1975) performed similar research on six water and six bottom sediment samples from just below Fort Loudoun Dam, to a point downstream just above the Little Tennessee-Tennessee River confluence. Smith did essentially the same analytical work on his water samples as the present author. Likewise, his analyses of the bottom sediments were done in manner similar to Abdelmalik's.

CHAPTER II

ANALYTICAL PROCEDURES

Sample Collection

Water samples were collected by boat from the main channel of the Tennessee River-Fort Loudoun Lake system in July 1973. Twelve sample sites (Figure 1, page 2, and Table 1) were chosen at fairly regular intervals from the junction of the French Broad and Holston Rivers to Fort Loudoun Dam. Specific sample site locations were selectively chosen to best reflect the industrial activity of Knoxville, the impounding action of Fort Loudoun Dam, and the local bedrock geology. Near Knoxville, spacing between sites was slightly reduced in order to assess the effects of industrialization. At each site, a 2-liter sample from a depth of a minimum of 15 cm (6 in) below the water surface was taken in a polyethylene container. When the samples were returned to the laboratory, they were immediately refrigerated at 4° C.

pH Analysis

Water pH at the north bank opposite each of the 12 sample sites was monitored on the first day of each month for nine consecutive months between October 1973, and June 1974. Measurements were made in the field with a Beckman Electromate pH Meter. Before each measurement, the instrument was standardized using a buffer solution of pH 7.0.

Material Analysis

The dissolved, suspended, and total material content was measured for each water sample. All suspended solids >100A were segregated by

TABLE 1. Sample site location data

Sample	Location (Lat/Long)	Underlying Bedrock (Formation/Rock Type)	Remarks
T-1W	35°46'50"N/84°13'17"W	Copper Ridge/dolomite	1.6 km (1 mi) upstream from Fort Loudoun Dam
T-2W	35°45'45"N/84°10'57"W	Knox Grp/dolomite, Mg limestone, limestone	Just upstream from mouth of Cloyd Cr.
T-3W	35°47'42"N/84°09'26"W	Knox Grp/dolomite, Mg limestone, limestone	Choto Bend
T-4W	35°49'37"N/84°08'26"W	Knox Grp/dolomite, Mg limestone, limestone	1.6 km (1 mi) downstream from Concord Rec Park
T-5W	35°50'35°N/84°06'10"W	Knox Grp/dolomite, Mg limestone, limestone	4.8 km (3 mi) upstream from Concord Rec Park
T-6W	35°49'40"N/84°03'32"W	Lenoir/limestone	Keller Bend
T-7W	35°52'38"N/84°01'38"W	Chapman Ridge/sandstone	Jones Bend
T-8W	35°55'10"N/83°58'58"W	Chapman Ridge/sandstone	1.2 km (3/4 mi) downstream from Fourth Cr. Treatment Plant
T-9W	35°56'44"N/83°56'38"W	Newala/dolomite & limestone	0.4 km (1/4 mi) upstream from Alcoa bridge. 1.2 km (3/4 mi) downstream from Third Cr. Treatment Plant
T-10W	35°56'39"N/83°55'36"W	Lenoir/limestone	≈100 m (330 ft) upstream from Third Cr. Treatment Plant
T-11W	35°57'29"N/83°54'54"W	Newala/dolomite & limestone	0.4 km (1/4 mi) downstream from First Creek
T-12W	35°57'33"N/83°51'02"W	Holston/limestone	Confluence of Tennessee and French Broad rivers

ultracentrifugation for 4 hours at 20,000 rpm. A Sorvall Superspeed RC2-B automatic refrigerated ultracentrifuge equipped with the SS-34 rotor was used. After centrifugation the supernatant, containing dissolved material, was decanted. A 10 ml aliquot of this supernatant was used to determine the dissolved material content of each sample. The effluent was placed in a weighing bottle and evaporated to dryness in an oven at 105° C. Following overnight drying the samples were allowed to cool in a desiccator prior to weighing. The weight of total dissolved materials in each sample was measured on two separate aliquots. The average weight was recorded.

The total solid value for each sample was measured by evaporating a known volume of sample to dryness and weighing the remaining solids as in the procedure above. As with dissolved material above, the weight of the total solids was measured twice and the average weight recorded.

The suspended material content in each sample was calculated by subtracting the weight of dissolved material from the weight of total solids.

Chemical Analysis

Ultracentrifugation removed the suspended solids (>100A) leaving an effluent containing essentially only dissolved materials. Evaporation reduced a 500 ml portion of this supernatant to 5-10 ml. Occasionally during evaporation, 2-3 ml of HCl were added to keep calcium in solution. After evaporation, water was added, as necessary, to each sample to

bring each volume to 10 ml. This concentration factor of 50 times was necessary for instrument detection.

All samples were chemically analyzed using a Perkin-Elmer model 290B atomic absorption spectrophotometer. Since dissolved materials were never taken from solution they were analyzed directly, without further treatment, following the evaporation step. All samples were analyzed for Ca, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, all of which are either essential to biota, hazardous to biota, or indicators of industrial pollution. The heavy metals most indicative of industrial and urban pollution are Cd, Cr, Ni, Pb, and Zn.

Precision of the analyses was checked by duplicating analysis of selected samples. For example, all atomic absorption spectrophotometer readings were duplicated with the results being averaged. As a control, and a check on equipment, blanks were also prepared and analyzed. Precision averages 5%.

CHAPTER III

EXPERIMENTAL RESULTS

pH Analysis

pH measurements taken at the sample sites over a 9-month period showed that the water of the Tennessee River-Fort Loudoun Lake system is typically slightly alkaline (Table 2). The pH values ranged from a low of 7.0 to a high of 8.7, averaging 7.5. Results of the pH measurements are:

1. Between December and April when water levels were low, discharges great, and temperatures cooler, pH values are somewhat lower than during the months of May and June, when water levels were high, discharges reduced, and temperatures warmer (Table 2).
2. The average pH differs little for upstream and downstream samples between October and April. During May and June, however, the average pH was higher in the downstream half of the system than in the upstream half.
3. The highest average 9-month pH values were recorded upstream near T-11W and T-12W, and downstream between T-4W and T-1W.
4. The lowest average 9-month pH values were at sites T-8W and T-9W, just downstream from the center of Knoxville.

Solids Analysis

Most of the matter (91%) transported by the water occurred in the dissolved state (Table 3). The average dissolved material content

TABLE 2. pH Analysis of Water Samples

	SAMPLE	OCT/1973	NOV	DEC	JAN 1974	FEB	MAR	APRIL	MAY	JUNE	NINE MONTH AVERAGE
DOWNSTREAM	T-1W	7.1	7.3	7.3	7.2	7.3	7.3	7.3	8.6	8.5	7.5
	T-2W	7.2	7.1	7.4	7.3	7.3	7.3	7.4	8.5	8.2	7.5
	T-3W	7.0	7.5	7.2	7.1	7.7	7.4	7.8	8.5	8.5	7.6
	T-4W	7.0	7.1	7.3	7.1	7.4	7.4	7.4	8.4	8.2	7.5
	T-5W	7.0	7.3	7.2	7.3	7.5	7.4	7.4	8.5	7.8	7.4
	T-6W	7.2	7.6	7.1	7.2	7.4	7.4	7.3	8.7	7.2	7.4
	AVERAGE T-1W to T-6W	7.1	7.3	7.3	7.2	7.5	7.4	7.4	8.5	8.1	7.5
UPSTREAM	T-7W	7.2	7.6	7.0	7.2	7.2	7.2	7.4	8.0	7.3	7.4
	T-8W	7.2	7.6	7.0	7.0	7.2	7.3	7.4	7.3	7.4	7.3
	T-9W	7.3	7.7	7.1	7.4	7.7	7.3	7.5	7.6	7.4	7.3
	T-10W	7.2	7.8	7.2	6.9	7.4	7.4	7.6	7.9	7.3	7.4
	T-11W	7.1	7.8	7.3	7.2	7.5	7.5	7.5	7.9	7.5	7.5
	T-12W	7.2	7.8	7.3	7.7	7.8	7.6	7.8	7.2	7.8	7.6
	AVERAGE T-7W to T-12W	7.2	7.7	7.2	7.2	7.5	7.4	7.5	7.7	7.5	7.4
	TOTAL AVERAGE T-1W to T-12W	7.1	7.5	7.2	7.2	7.5	7.4	7.5	8.1	7.8	7.5

TABLE 3. Solid content (mg/l) of water samples from Fort Loudoun Lake.

	Sample	Dissolved Solids	Suspended Solids	Total Solids
DOWNSTREAM	T-1W	90	16	106
	T-2W	75	31	106
	T-3W	115	2	117
	T-4W	100	8	108
	T-5W	120	6	126
	T-6W	120	2	122
	Average (w/std dev)	103±18	11±11	114±9
UPSTREAM	T-7W	120	12	132
	T-8W	90	4	94
	T-9W	130	4	134
	T-10W	120	12	132
	T-11W	120	18	138
	T-12W	120	12	132
	Average (w/std dev)	117±14	10±5	127±16

for downstream samples was about 14% less than that for upstream samples. Essentially, there was little or no difference in the average amount of suspended material between upstream and downstream samples. Thus, the differences in total matter content between sample sites were chiefly the result of the quantity of matter in the dissolved state. With the exception of one sample, the highest suspended material content were at the two extremities of the river-lake system (T-1W -T-2W and T-10W - T-12W). The sudden increase in the amount of suspended material in samples T-1W and T-2W was higher than expected and abruptly terminated a general decrease in the suspended material content downstream. The author has no explanation for this. Interestingly, this sudden increase in particulate content of samples T-1W and T-2W was marked with a reciprocal decrease in the dissolved material content resulting in a consistent net decrease in total material.

Chemical Analysis

Analytical precision, using the Perkin-Elmer 290B Atomic Absorption Spectrophometer, was typically within 5% of reported results. The sensitivity of the atomic absorption unit varied, depending upon the element being analyzed. Detection limits for the elements sought were: Ca = 200 ppb; Cd = 1 ppb; Co = 2 ppb; Cr = 8 ppb; Cu = 4 ppb; Fe = 4 ppb; Mn = 2 ppb; Ni = 1 ppb; Pb = 8 ppb; and Zn = 1 ppb.

The water upstream had a higher dissolved trace metal content than that downstream, nearer Fort Loudoun Dam (Table 4). Iron and zinc were found in the greatest concentrations of all trace metals sought.

TABLE 4. Dissolved metal content (ppb metal in water) of water samples from Fort Loudoun Lake.

	Sample	Ca %	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
DOWNSTREAM	T-1W	0.98	nd*	2	tr**	8	44	2	4	nd	21
	T-2W	0.96	nd	nd	8	4	16	nd	4	nd	11
	T-3W	1.06	nd	nd	8	4	20	nd	4	nd	25
	T-4W	1.00	nd	nd	8	4	72	2	nd	tr*	30
	T-5W	1.06	nd	nd	8	8	48	2	nd	tr*	50
	T-6W	1.14	1	2	8	12	32	tr*	nd	tr*	35
	Average (w/std dev)	1.03 .07	.2 ±.4	.7 ±.1	7 ±3	7 ±3	39 ±21	1 ±1	2 ±2	0	29 ±13
UPSTREAM	T-7W	1.14	1	6	tr*	4	32	tr*	nd	tr*	35
	T-8W	0.96	1	nd	8	8	27	nd	tr*	tr*	26
	T-9W	1.24	2	nd	tr*	4	60	tr*	4	tr*	54
	T-10W	1.26	2	6	tr*	12	32	2	4	10	36
	T-11W	1.12	2	6	8	12	20	2	4	10	36
	T-12W	1.10	2	nd	8	16	76	2	4	10	113
	Average (w/std dev)	1.13 0.11	2 ±.5	3 ±3	4 ±4	9 ±5	41 ±22	1 ±1	3 ±2	3 ±5	56 ±32

* Not detected, considered zero for all calculations.

** Trace, considered zero for all calculations.

Downstream a distinct trend was seen for certain metals. Zn, Pb, and Cd decrease noticeably. There was a general but subtle decrease in Cu. Co showed a general overall decrease whereas Cr increased slightly downstream.

When the amount of metal per weight of dissolved material (Table 5) was calculated from the metal concentrations of the elements in Table 4, little or no difference in metal distribution was observed. The most notable was the very large increase of metal concentration in the dissolved material.

TABLE 5. Metal content of dissolved solids in water samples from Fort Loudoun Lake. (ppm Metal in dissolved solids)

	Sample	Ca %	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
DOWNSTREAM	T-1W	10.9	nd	22	tr*	89	489	22	44	nd	234
	T-2W	12.8	nd	nd	107	53	214	nd	53	nd	147
	T-3W	9.22	nd	nd	70	35	174	nd	35	nd	218
	T-4W	10.0	nd	nd	80	40	720	20	nd	tr*	300
	T-5W	8.8	nd	nd	67	67	400	17	nd	tr*	416
	T-6W	9.5	8	17	67	100	266	tr*	nd	tr*	292
	Average (w/std dev)	10.2 ±1.5	1 ±3	7 ±10	65 ±35	64 ±26	377 ±205	10 ±11	22 ±25	0	268 ±91
UPSTREAM	T-7W	9.5	8	50	tr*	33	266	tr*	nd	tr*	292
	T-8W	10.7	11	nd	89	89	300	nd	tr*	tr*	289
	T-9W	9.5	15	nd	tr*	31	461	tr*	31	tr*	415
	T-10W	10.5	17	50	tr*	100	266	17	33	tr*	600
	T-11W	9.3	17	50	67	100	167	17	33	83	300
	T-12W	9.2	17	nd	67	133	634	17	33	83	942
	Average (w/std dev)	9.8 ±0.6	14 ±4	25 ±27	37 ±42	81 ±41	349 ±169	9 ±9	22 ±17	28 ±43	473 ±259

* Not detected, considered zero for all calculations.

** Trace considered zero for all calculations.

CHAPTER IV

DISCUSSION OF RESULTS

Water Samples

Numerous factors influenced the pH of the river-lake system, with geology, climate, and man's activities being primary contributors. The exact role, mode, and magnitude each factor contributed are unknown. The high carbonate content of the local and regional geology was a major factor contributing to the alkalinity of the water. Seasonal changes in the weather correlated with fluctuations in the degree of alkalinity. pH correlated directly with water temperature as seen in Figure 2, page 6, and Table 2, page 13. Precipitation, and the resulting surface runoff into the reservoir, tended to increase pH slightly. Thus, climate apparently produced both short and long term variations in pH level during the 9-month period of study.

Evidence suggests that Fort Loudoun Dam introduced temporal and spatial variability of pH values. As with water temperature, pH values correlated with water level and water discharge (Figure 2, page 6, and Table 2, page 13). The degree of alkalinity increased with higher water levels and decreased with increasing discharge. Evidence was supportive for a dual role of the effects of the dam's impounding action on pH. During the months of lower water level, the increasing impoundment action of the dam had the effect of stabilizing pH from month to month. However, during higher water level the increasing impounding action acted substantially to increase and add variability to the pH of the

reservoir. The alkalinity between sample sites T-11W and T-7W (Table 2, page 13), which corresponded to the area of greatest urban and industrial development, decreased slightly. This indicated that man's urban and industrial activities may have served to lower the pH of the reservoir, but for the most part, these activities were insignificant in regard to changes in pH.

In general, the suspended particulate content of the water shows a decrease downstream (Table 3, page 14), indicating a settling effect in the quiet waters behind the dam. Likewise, the dissolved matter content also diminished downstream. This general downstream reduction in particulate and dissolved matter content correlated with the size distribution and mineralogy of bottom sediments (Abdelmalik, 1974, and Smith, 1975), especially if the possibly anomalous value at site 2 is deleted. Where the bottom sediment composition is enriched in carbonates the dissolved matter content is correspondingly high. Likewise, where the carbonate content is low, the dissolved metal content is also low. Abdelmalik's data showed a continual decrease in sediment size and in carbonate content of the bottom sediment downstream.

Bottom sediment analyses (Abdelmalik, 1974, and Smith, 1975, pp. 29-31) suggest a possible relationship between pH and the bottom sediments. Abdelmalik reported the sediment at Knoxville and above to comprise mostly coarse dolomite and quartz. Downstream, toward Fort Loudoun Dam, the sediment becomes finer, more clayey, and noticeably more quartzose. The pH value (Table 2, page 13) suggest that values tend to be slightly higher upstream than downstream. However, this

trend does not hold at those sites closest to the dam, especially during the spring and summer months which are characterized by a higher water level. During times of low water level and in areas less influenced by the impoundment action of damming during a higher level, data suggest that the pH of the water tends to reflect the mineralogy of the bottom sediments.

The amount of Cd, Co, Cu, Pb, and Zn in the water decreased downstream (Table 4, page 16). Interestingly, analyses by Abdelmalik (1974) indicate a corresponding downstream enrichment of these same metals in the bottom sediment. The concentration of the other heavy metals in the water changed little. The Cd and Zn content of the Tennessee River are unusually high as compared to waters in other parts of the state (Perhac, 1972; 1974; Perhac and Whelan, 1972). Livingstone (1963) reported that Cd has been detected in a major river only once, and that the mean content of Zn of ordinary lake and river water is about 10 ppb. Above Knoxville the highest Zn value was greater than Livingstone's "mean" by a factor of 11. The Zn and Cd content of the water did not reflect the underlying limestone bedrock, but apparently the nature of the bottom sediment. The dolomite-rich and calcite-poor bottom sediment (Abdelmalik, 1974) at Knoxville and above, reflects the transportation downstream of carbonate-rich tailings from the American Smelting and Refining Company's zinc beneficiation plant adjacent to the Holston River at Mascot, Tennessee (Perhac, et al. 1975 and Perhac and Tamura, 1977). The plant recovered cadmium as a byproduct from the dolomite host rock. Until 1972, they dumped considerable tonnages of

carbonate-rich tailings into the Holston River. Two facts that support this exogenous source for dolomite at the upstream sample sites are: (1) the sediment content contains an unusually high content of zinc and cadmium, and (2) the bottom sediment collected from the Holston and French Broad Rivers just above their confluence show a high dolomite content in the Holston sediment and very little in the French Broad sediment (Perhac, 1974). Apparently Cd and Zn are being dissolved from the bottom sediments (derived from the carbonate mill tailings). These metals are then transported in solution downstream and in quieter water are in some way incorporated into the bottom sediments behind the dam. The downstream bottom sediments reflect this transport of Cd and Zn. The concentration changes in zinc and cadmium in the downstream bottom sediments are quite low considering that the upstream sediment is composed of the zinc-bearing (Zn + Cd sulfide) dolomite, such dolomite being nearly absent in the bottom sediment of the downstream samples (Perhac, 1974).

As mentioned previously, only Cd, Co, Cu, Pb, and Zn were observed decreasing in water downstream and thus correlating with the increase in the same metals in the bottom sediment. Although continuous variations in water chemistry take place over a year (Table 2, page 13), it is unlikely that within the ranges of pH change occurring during the study that mobilization between water and bottom sediments of the metals Cr, Fe, Mn, and Ni, will occur. Mn and Fe are known to precipitate early during neutralization of an acid solution and are usually carried as discrete oxides or hydroxides. Except for conditions of high pH, the

mobility of Cr in the ionic form is considered low (Hawkes, 1962). However, Ni is mobile and at low concentrations under moderate alkalinity will remain in its ionic form.

The above correlation between heavy metal concentrations in water with types of bottom sediments below Knoxville is consistent with Krauskopf's findings (1956). He stated that Cu, Zn, and Pb are more strongly and consistently adsorbed by clay minerals than are other heavy metals in natural waters. This is particularly true under conditions of increasing surface area of adsorbent and increasing pH. He also stated that Co and Ni, although likewise divalent cations, are much less effectively adsorbed.

The concentrations of Mn and Fe in the bottom sediments below Knoxville were more than double the amounts above Knoxville (Abdelmalik, 1974). Lockwood and Chen (1973) stated that adsorption of various metals can be very efficiently localized by Mn and Fe oxides. This adsorption of unhydrolyzed cations on MnO_2 was attributed to ion exchange on the surface of the precipitated Mn material. Of various adsorbing oxides Mn was found to be the most effective, and one of the most common in natural environments. Jenne (1968), in earlier work, proposed that hydrous oxides of Mn and Fe furnished the principal control on the fixation of Co, Ni, Cu, and Zn in fresh water sediments. He states that the sorption and desorption of these heavy metals on these oxide coatings occur in response to:

1. aqueous concentration of the metal in question;
2. aqueous concentration of other heavy elements;
3. pH;
4. amount and strength of organic chelates and inorganic complex ion formers present in solution.

Jenne further suggests other controls on the concentration of heavy metals in fresh water may be:

1. organic matter;
2. clays;
3. carbonates;
4. precipitation as the discrete oxide or hydroxide.

It is apparent that the dam creates a site for the accumulation of heavy metals. One can easily imagine that dissolved metals in the water are adsorbed into clays and these clays settle and accumulate behind the dam. However, Perhac (1974) demonstrated through NH_4OAc extraction experiments that cadmium and probably the other heavy metals are not in sorption sites on clays in the bottom sediment. The manner in which heavy metals are incorporated is related to the settling of free iron oxides and organic matter both of which settle with clay minerals.

Conclusions

The significant results and conclusions of this research with regard to the distribution of heavy metals in the waters of the Tennessee River-Fort Loudoun Lake fluvial system are listed below:

1. The upstream half of the river-lake system typically contains a slightly higher concentration of dissolved heavy metal than downstream waters resulting in a net decrease in heavy metal concentration downstream.
2. The metal concentration for Cd and Zn are unusually high throughout the fluvial system.

3. Downstream a distinct trend exists for certain heavy metals. Cd, Pb, and Zn decrease noticeably. There is a general but subtle decrease in copper. Co shows a general overall decrease whereas Cr increases slightly downstream.
4. The dissolved solid content of the water reflects the nature of the bottom sediment rather than the underlying bedrock.
5. Heavy metals, particularly Zn and Cd, are being dissolved from dolomitic bottom sediments in the upper reaches of the Tennessee River. These cations are carried in solution downstream where in quieter waters the metals are incorporated into the bottom sediments behind the dam.
6. The industrial and urban areas of Knoxville, Tennessee are insignificant in increasing the concentration of heavy metals in the waters of the Tennessee River-Fort Loudoun Lake system. However, mill tailings dumped in the Holston River farther upstream are a large contributor of dissolved Cd and Zn in the waters of the study area.

Recommendations for Future Work

Seasonal changes in the heavy metal content of the water may be significant. Evidence of this comes from the variation in pH levels over a 9-month period, and the analysis of water samples that were taken ten months later on May 23, 1974, at sites T-4W, T-5W, and T-6W. These additional samples were analyzed chemically for Cu and Zn by the same analytical procedures as the original samples. The pH level, however,

was almost one unit lower. A comparison of the two sets of analyses for Cu and Zn content is given below (in ppb):

		T-4W	T-5W	T-6W
(1) Original Sample:				
	Zn	30	50	35
	Cu	8	12	30
(2) Sample of 5/23/74:				
	Zn	83	140	42
	Cu	12	10	10

Seasonal differences in the metal content of water are likely, but to what degree is unknown. Heavy metal content of the water in this study was determined for one period of time, a time of relatively high pH and high water level. A study of heavy metal concentration from samples taken under conditions of low water level, low pH, and high discharge would be desirable to gain an insight on the seasonal mobility of heavy metals in this unique river-lake system.

Additional research related to the study of the mechanism by which heavy metals are incorporated in the bottom sediment from the water would be merited.

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VITA

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