November 30, 1974

To the Graduate Council:

I am submitting herewith a thesis written by Richard James Smith entitled "The Effect of Damming on Trace Metal Distribution in the Tennessee River-Fort Loudon Lake System of 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
Graduate Studies and Research

THE EFFECT OF DAMMING ON TRACE METAL DISTRIBUTION IN THE TENNESSEE RIVER-FORT LOUDON LAKE SYSTEM OF EAST TENNESSEE

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee

Richard James Smith

March 1975

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ABSTRACT

The purpose of this investigation was to determine the effect of Fort Loudon Dam on the distribution of trace metals in the Tennessee River-Fort Loudon Lake system of East Tennessee. The research entailed sampling and analyzing both water and bottom sediments from below Fort Loudon Dam and comparing the results with those of similar analyses from the lake above the dam.

The water samples were analyzed for pH, total, dissolved, and suspended solid content, and trace metal content. The bottom sediments were also analyzed for trace metal content, as well as mineralogy and grain size distribution. The chemical analyses for trace metal content were made by atomic absorption spectrophotometry.

It was found that the trace metal content of the water in Fort Loudon Lake generally decreased downstream toward the dam and that this trend closely followed the carbonate content (high in trace metals) of the bottom sediments. The trace metal content of the bottom sediments remained the same or even increased toward the dam. The high trace metal content of the fine grained sediments near the dam was not typical of sediment of that type (silt and clay). Therefore, it was concluded that metals were being incorporated into the bottom sediment from the water, thus making the area behind the dam an area for the accumulation of trace metals.

The results of the water and bottom sediment analyses of the samples from below Fort Loudon Dam confirmed this hypothesis. Below the dam the trace metal content of the bottom sediment was much lower

than above the dam, representing sorption and retention of metals by the sediments above the dam.

The trace metal content of the water samples from below the dam was much higher than expected, and much higher than the metal content of the water samples from above the dam. The reason for the increase in the metal content of the water was not understood, but was probably related to one or more possible explanations. Further research in this area could be used to prove or disprove the possible explanations.

The trace metal distributions in the Tennessee River-Fort Loudon Lake system were also related to industrialization, such as the zinc milling at Mascot, Tennessee.

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CHAPTER I

INTRODUCTION

Purpose

The primary purpose of this research was to determine the effect of Fort Loudon Dam on the distribution of trace metals in the Tennessee River-Fort Loudon Lake system of Eastern Tennessee. The research entailed sampling and analyzing both water and bottom sediments from below Fort Loudon Dam and comparing the results with those of similar analyses performed by other investigators above the dam. This research was conducted in conjunction with the United States Department of the Interior, Division of Water Resources Research Project Tennessee A-032, which is a study of the transportation and distribution of trace metals in East Tennessee drainage systems.

Location and Geology

The Tennessee River starts at the confluence of the Holston and French Broad Rivers near the city of Knoxville, Tennessee. From its confluence above Knoxville, the river flows southwestward, passing through the residential and industrial areas of Knoxville and through the Concord Park recreational area. This 90 kilometer section of the river is impounded by the Tennessee Valley Authority Fort Loudon Dam at Lenoir City, forming the Tennessee River-Fort Loudon Lake system (Figure 1).

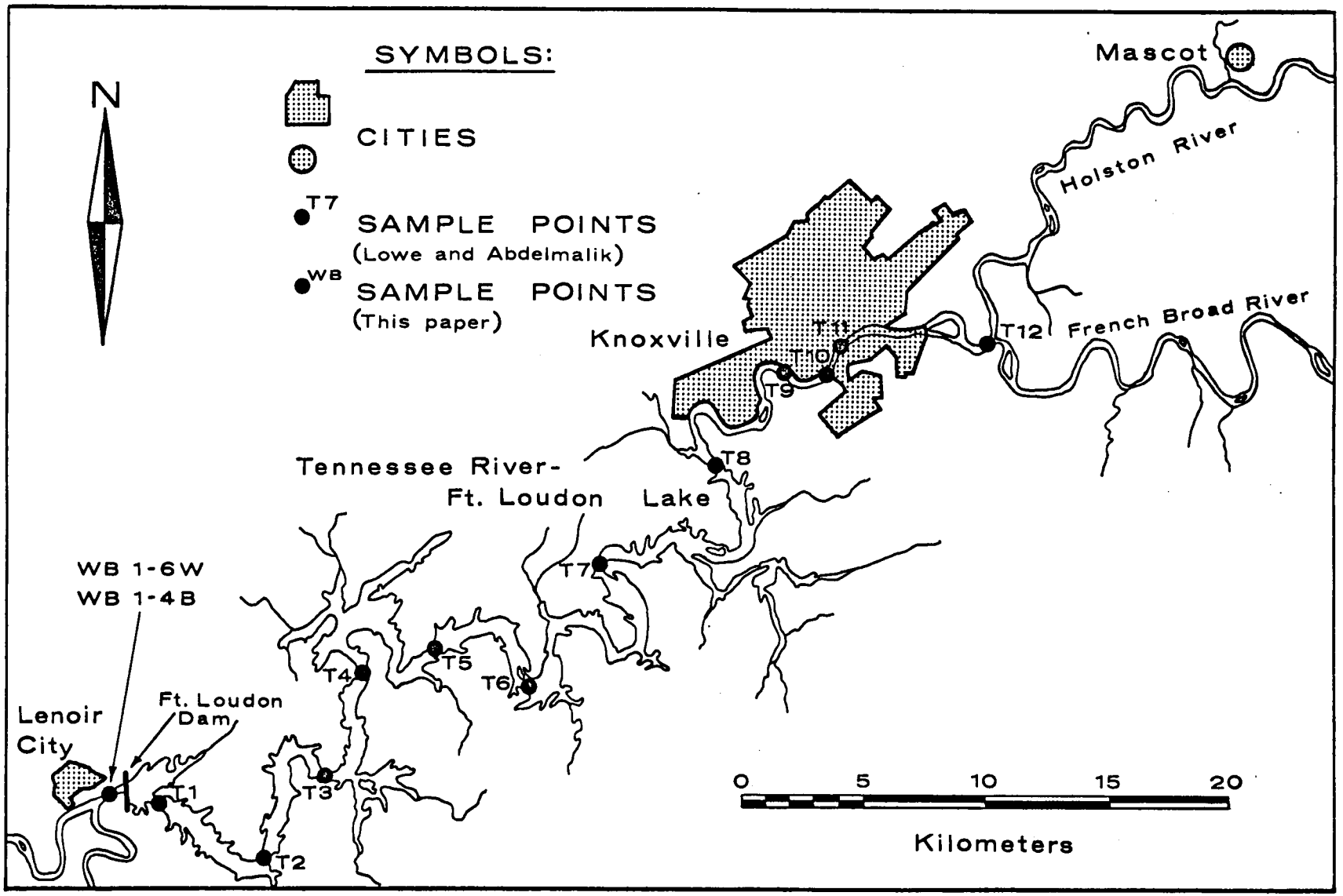


FIGURE 1. Tennessee River-Fort Loudon Lake system.

The Tennessee River-Fort Loudon Lake system lies in the Ridge and Valley physiographic province of the Appalachian Highlands (Fenneman, 1928). This part of the Ridge and Valley province is underlain by strongly folded and faulted strata which range in age from Cambrian to Ordovician. The predominent bedrock lithologies underlying Fort Loudon Lake are limestone and dolostone, with some sandstone and shale underlying the lower (downstream) part of the lake. The bedrock in the sample area below Fort Loudon Dam is made up of limestone, for the most part, with some shale found near the dam (Hardeman et al., 1966).

Sampling and Analyses

The six water samples and four bottom sediment samples used in this study were collected from the Tennessee River below Fort Loudon Dam (Figure 2). All ten samples were collected during the first week of April, 1974, at the end of the low water lake stage.

The six water samples were collected by boat from the main part of the river channel. The first sample (WB-1W) was collected approximately 200 meters downstream from the dam. The remainder of the samples were collected at 200 meter intervals downstream from the first sample. Each sample was collected about half a meter below the surface of the water to avoid floating debris. No samples were collected below the confluence of the Tennessee and Little Tennessee Rivers in order to avoid contamination from other drainage systems. Shortly after collection the pH of each sample was measured, and the samples were refrigerated to retard the decomposition of organic material.

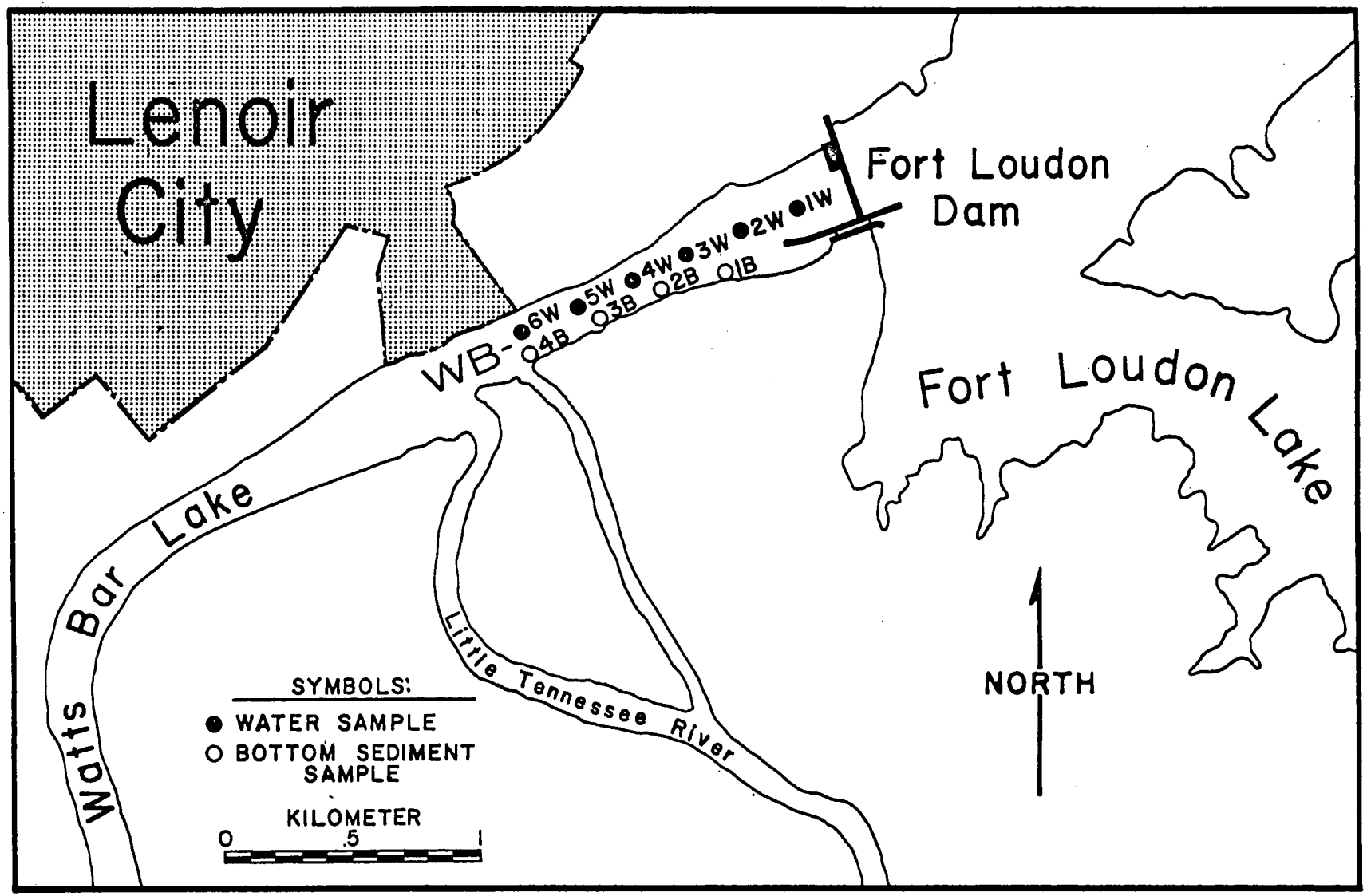


FIGURE 2. Sample area below Fort Loudon Dam.

The bottom sediment samples were collected along the southeast shore of the river (Figure 2). An attempt was made to sample the bottom sediments from the boat by use of a bottom "grab" sampler, but due to the compactness of the sediments in the main channel, this was impossible. The four which were collected were taken in approximately half a meter of water and were from the upper ten centimeters of bottom sediments. The bottom sediment samples were also refrigerated after collection.

Each of the six water samples collected was analyzed to measure the amount of solids present: total, suspended, and dissolved. The pH of each sample was also measured. The suspended material was then removed from each sample and the remaining supernatant concentrated for chemical analysis. Each sample was analyzed chemically for the following elements: calcium, cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead, and zinc.

The bottom sediment samples were analyzed for the same suite of elements as the water samples. In addition, each bottom sediment sample was separated into six size fractions, $>100\ \mu$, 50-100 μ, 5-50 μ, 2-5 μ, 0.2-2 μ, and $<0.2\ \mu$, and the weight percent of each size fraction measured. Each size fraction and bulk sample was analyzed mineralogically by x-ray diffraction.

Previous Work

Water and bottom sediment samples were collected from Fort Loudon Lake as a part of the Office of Water Resources Research Project A-032 (United States Department of the Interior). The locations of

the sample points are shown on Figure 1, page 2. These samples were analyzed by the same methods described above. The water sample analyses were made by N. T. Lowe and the bottom sediment samples analyzed by W. E. Y. Abdelmalik. The results of their research are presented in Chapter IV of this paper.

CHAPTER II

EXPERIMENTAL PROCEDURES

Water Samples

pH Analysis

The pH of each sample was measured soon after collection with a Beckman Electromate pH Meter. Before and after each measurement the instrument was standardized to compensate for meter drift. A buffer solution (pH = 7.0 at 25°C) was used for standardization. After the pH measurements, the samples were refrigerated to retard any chemical reactions due to organic decay.

Solids Analysis

Each water sample was analyzed for the weight of the total, suspended, and dissolved solids. The weight of the total solids in each sample was measured by evaporating a known volume of sample and weighing the remaining solids (Appendix A). The weight of the total solids in each sample was measured on three separate aliquots and the average used in all calculations.

The weight of the dissolved solids in each sample was measured by repeating the total solids procedure, but with particulate free sample instead of the total sample. The particulate material ($>0.01\ \mu$) was removed from the bulk samples by centrifugation at 20,000 rpm for four hours, using a Sorvall RCB-2 centrifuge with a SS-34 rotor. The supernatant was then decanted and used to measure the weight of the

dissolved solids. As with the total solids, the weight of the dissolved solids was determined three times and the average used for all calculations.

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

Chemical Analysis

Each water sample was analyzed for total metal content by atomic absorption spectrophotometry. Before analysis, the samples were centrifuged at 20,000 rpm for four hours to remove the suspended material. After centrifugation the supernatant was decanted and concentrated 50 times in order to make the trace metal concentrations high enough for detection.

The samples were concentrated by heating 500 ml of the supernatant until it was reduced to a volume of less than 10 ml. The concentrate was then transferred to a 10 ml volumetric flask and brought up to volume with deionized water. Three milliliters of hydrochloric acid were added to the original supernatant to keep calcium salts from precipitating during the concentration procedure.

Bottom Sediment Samples

Size Distribution Analysis

Each bottom sediment sample was separated into six size fractions: $>100\ \mu$, 50–100 μ, 5–50 μ, 2–5 μ, 0.2–2 μ, and $<0.2\ \mu$. The separations at 0.2 μ and 2 μ were made by centrifugation; the 5 μ

separation was by gravity settling, and the 50 μ and 100 μ separations were by sieving.

The centrifugal separations were based on the mathematical relationship between the density and settling velocity of a spherical particle. This relationship is expressed as the Svedberg coefficient (Svedberg and Pederson, 1940). Bayer (1973) gives the mathematical calculations for the determination of centrifugal time and rotor speed.

The gravity separation at 5 μ was based on the relationship between the settling time for a particle and the height of the settling column used (Jackson, 1956). A more detailed description of the size separation procedure is in Appendix B.

Mineralogical Analysis

All bulk samples and size fractions, except the $< 0.2\ \mu$ fractions, were analyzed mineralogically by x-ray diffraction. The $< 0.2\ \mu$ fractions were not analyzed because of the lack of material obtained from the size separation procedure.

All bulk samples and size fraction greater than 5 μ were crushed before analysis. The bulk samples, 100 μ fractions, and 50-100 μ fractions were analyzed as pressed pellets. The remaining size fractions were analyzed from elutriated slides.

Chemical Analysis

The bottom sediment samples were analyzed for the same suite of elements as the water samples. The analyses were made by atomic absorption spectrophotometry. Before analysis, the organic material was removed from each sample by oxidation with nitric acid. The

samples were then dissolved using perchloric acid and hydrofluoric acid (Appendix C).

CHAPTER III

EXPERIMENTAL RESULTS

Water Samples

pH Analysis

The results of the pH measurements are listed in Table 1. As was expected, the pH values all fell within very narrow limits, the range being only 0.04 pH units. All six samples were also slightly alkaline, the average pH being 7.32.

Solids Analysis

The results of the solids analysis (Table 1) showed only a slight variation in the total solids content of the water samples. The samples ranged from 112 to 122 mg/liter, with an average value of 118 mg/liter and a standard deviation of only ± 3 mg/liter. The amount of total solids increased in a downstream direction, but the difference between samples WB-1W and WB-6W was so slight that such increase may not have been significant.

The amounts of dissolved and suspended solids showed a slightly greater range of values than the total solids. The dissolved solids ranged from 74 to 104 mg/liter and the suspended solids from 16 to 44 mg/liter (Table 1). No distinct trends were observed in either the dissolved or suspended solids, but the amount of dissolved solids was consistently higher than the amount of suspended solids, generally on the order of two or three times higher.

TABLE 1. Solid content (mg/l) and pH of water samples from below Fort Loudon Dam.

Sample	Dissolved Solids	Suspended Solids	Total Solids	pH
WB-1W	80	32	112	7.31
WB-2W	74	44	118	7.35
WB-3W	92	26	118	7.32
WB-4W	84	36	120	7.31
WB-5W	86	34	120	7.32
WB-6W	104	16	122	7.32
Average: (w/std dev)	87±11	31±10	118±3	7.32

Chemical Analysis

The water samples were analyzed using Perkin-Elmer model 290B and model 403 atomic absorption spectrophotometers. The model 290B was used to analyze for calcium, chromium, copper, iron, and manganese; the model 403 was used for cadmium, cobalt, nickel, lead, and zinc. The model 403 was used for those elements with low concentrations or which could not be analyzed with the lower sensitivity of the 290B.

The reproducibility on each instrument was consistently within a few percent of the amounts reported, but between instruments the amount of variation was greater. Franks (personal communication) reported from 6 to 30 percent difference for various elements between the model 290B and the model 403, but he found the amount of difference decreased as the concentration increased.

The metal content (in solution) of the water samples is shown in Table 2. Generally, there was little variation in the amount of a given element from sample to sample, with the possible exception of iron. The iron content of sample WB-2W was high relative to the other five samples. Even when the metal content in solution was converted to the metal content of the dissolved solids (Table 3) the relative difference between WB-2W and the other samples remained about the same.

Although the metal content of the water samples (Table 2) varied very little from sample to sample, there was considerable variation from one element to another. Except for calcium, the metal concentrations of the various elements analyzed were measured in parts per billion. The calcium content of the water samples was large enough to measure in percent. The remainder of the elements analyzed had low

TABLE 2. Metal content (ppm) of water samples from below Fort Loudon Dam.

Sample	Ca	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
WB-1W	1.35%	1.2	3.2	2	20	64	16	8	17	222
WB-2W	1.43%	1.0	3.2	2	18	104	10	7	17	226
WB-3W	1.40%	0.8	3.2	tr*	28	32	8	7	17	190
WB-4W	1.43%	0.8	3.2	tr*	17	36	6	7	14	214
WB-5W	1.50%	1.0	3.2	2	10	24	4	6	12	610
WB-6W	1.43%	1.0	3.2	2	11	36	6	6	12	214
Average (w/std dev)	1.42% ±.05%	1.0 ±.2	3.2 ±0	1.4 ±1	17 ±7	49 ±30	8 ±4	7 ±1	15 ±3	213 ±13

*Trace considered as zero for average calculations.

TABLE 3. Metal content (ppm) of dissolved solids in water samples from below Fort Loudon Dam.

Sample	Ca	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
WB-1W	16.88%	15	40	25	250	800	200	100	213	2780
WB-2W	19.26%	14	43	27	238	1400	135	95	230	3050
WB-3W	15.22%	9	35	tr*	304	348	87	76	185	2070
WB-4W	16.96%	10	38	tr*	202	428	71	83	167	2550
WB-5W	17.45%	12	37	23	116	279	47	70	140	2440
WB-6W	13.44%	9	30	19	104	340	57	57	113	2020
Average (w/std dev)	16.53% ±1.99%	12 ±3	37 ±5	16 ±12	202 ±79	600 ±430	100 ±58	80 ±16	174 ±44	2480 ±380

*Trace considered as zero for average calculations.

average concentrations (<17 ppb) with the noticeable exceptions of iron and zinc. The iron values for the various water samples were considerably higher than the other elements, but not nearly as high as the values for zinc. The zinc content of the water samples was at least an order of magnitude higher than the metal content of the other elements and in some cases two orders of magnitude higher.

The relative differences in the metal concentrations of the various elements (Table 2, page 14) remained about the same when converted to the metal content of the dissolved solids (Table 3), but the metal concentrations were increased by as much as 10^4.

Bottom Sediment Samples

Size Distribution Analysis

The four bottom sediment samples collected below Fort Loudon Dam were separated into six size fractions for grain size distribution analysis. After separation, the weight percent of each size fraction was measured (Table 4).

The first three samples (WB-1B, WB-2B, and WB-3B) had similar grain size distributions. Each of these samples was composed of predominantly sand-size material, with only minor amounts of silt and clay-size sediments. The fourth sample, WB-4B, was finer grained than the other three. WB-4B contained almost equal amounts of sand and silt-size material, but only slightly more clay than the other samples.

Mineralogical Analysis

Quartz, feldspar, dolomite, 7A, 10A, and 14A clays were identified in the bottom sediment samples by x-ray diffraction.

TABLE 4. Size distribution (weight percent) of bottom sediment samples from below Fort Loudon Dam.

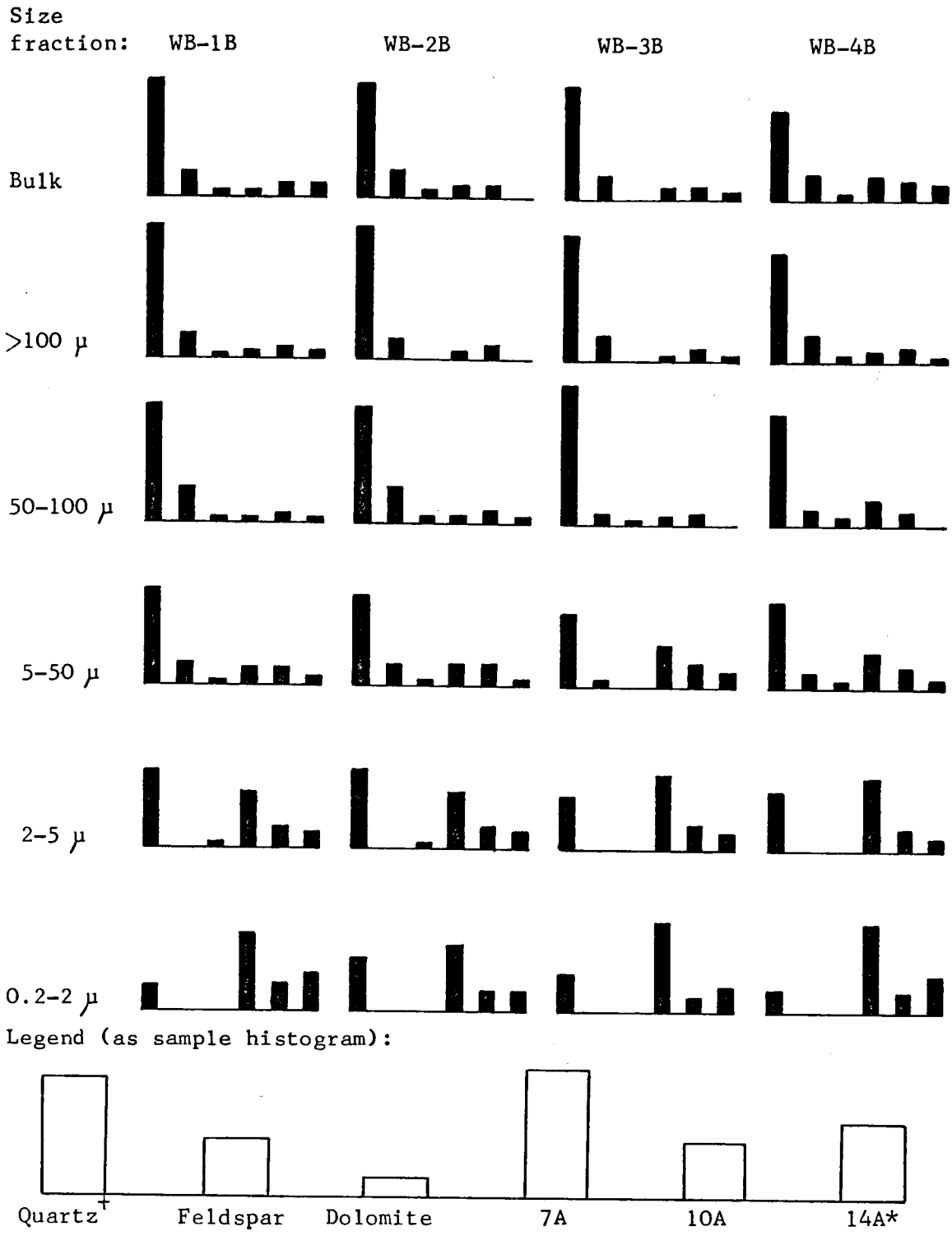
SIZE	WB-1B	WB-2B	WB-3B	WB-4B	Average(w/std dev)	
>100 μ	58.85	79.56	65.63	17.85	66.47 ± 26.62	sand
50-100 μ	26.41	12.09	17.18	30.48	21.54 ± 8.41	sand
5-50 μ	9.71	6.00	13.03	39.80	17.14 ± 15.38	silt
2-5 μ	2.54	1.39	2.74	8.41	3.77 ± 3.15	silt
0.2-2 μ	2.41	0.94	1.37	3.40	2.03 ± 1.10	clay
<0.2 μ	0.08	0.01	0.06	0.07	0.06 ± 0.03	clay
TOTAL	100.00	99.99	100.01	100.01	100.01	

The clay minerals were classified according to their basal spacings (Carrol, 1968). The 7A clay had a basal spacing of 7.2A and was probably kaolinite. The 10A clay had a basal spacing of 10.0A and was either mica or illite. The 14A clay did not display a consistent basal spacing and was probably a mixed layer clay. Vermiculite and montmorillonite were probably present in the 14A clay.

The mineralogies of the bottom sediment samples were determined semi-quantitatively, as well as qualitatively. The semi-quantitative analysis was made by using the x-ray peak areas of the minerals detected. The relative increase or decrease in the amount of a given mineral, either between samples or between size fractions of a single sample, was determined by comparing the x-ray peak areas. The most intense x-ray peak of each mineral was used to calculate the peak area, with the exception of quartz. The most intense (3.34A) quartz peak extended off the diffractogram, therefore the area of the 4.26A quartz peak was calculated and multiplied by three to approximate the area of the most intense peak.

Figure 3 shows the mineralogies of the bottom sediment samples. The relative amounts of the minerals in each size fraction are shown by the height of the bars in the histograms.

Quartz, 7A, and 10A clays were identified in all samples analyzed. The relative amount of quartz in each sample decreased with sample size, whereas the relative amount of 7A and 10A clays increased. The 14A clays also generally increased with decreasing grain size, but were not detected in four of the size fractions.



+4.26A quartz peak multiplied by three to approximate 3.34A quartz peak.

*Bar height represents peak areas from diffractograms

FIGURE 3. Mineralogy of bottom sediment samples from below Fort Loudon Dam.

Feldspars were identified in all size fractions greater than 5 μ. The relative amount of feldspars decreased with grain size, disappearing completely in the 2-5 μ and 0.2-2 μ fractions. Dolomite was detected in only minor amounts and showed no trend to its distribution.

Chemical Analysis

The analysis of the bottom sediment samples was by atomic absorption spectrophotometry. A Perkin-Elmer model 290B atomic absorption spectrophotometer was used to analyze for calcium, chromium, copper, iron, and manganese; a model 403 was used to analyze for cadmium, cobalt, nickel, lead, and zinc. The reproducibilities were within the amounts reported for the chemical analysis of the water samples.

The results of the chemical analysis are shown in Table 5. No noticeable trends were detected from the results of the chemical analysis, but significant differences in the relative concentrations of the various elements were observed.

The iron content of the bottom sediment samples was higher than the other metal concentrations. The average iron content for the four samples was 26,200 parts per million. The concentrations of calcium (1600 ppm), manganese (700 ppm), and zinc (150 ppm) were also relatively high, but not on the same order as iron. The remainder of the elements had concentrations of about 50 ppm or less. Cadmium had the lowest metal content, with an average value of 4 ppm.

TABLE 5. Metal content (ppm) of bottom sediment samples from below Fort Loudon Dam.

Sample	Ca	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
WB-1B	1660	5	38	46	4	21000	428	20	39	64
WB-2B	1250	3	55	32	12	24400	713	23	54	146
WB-3B	1860	3	48	19	12	26700	655	25	38	141
WB-4B	1600	4	65	55	27	32500	1020	29	55	252
Average (w/std dev)	1600 ±250	4 ±1	52 ±11	38 ±16	14 ±11	26200 ±4800	700 ±240	24 ±4	47 ±9	150 ±77

CHAPTER IV

RESULTS OF PREVIOUS RESEARCH

Introduction

The water and bottom sediment samples collected from Fort Loudon Lake were analyzed by N. T. Lowe and W. E. Y. Abdelmalik, respectively. The analyses were conducted by the same methods described above. The chemical analyses were, however, made using only the Perkin-Elmer model 290B atomic absorption spectrophotometer.

Water Samples

The pH of the water at the twelve sample sites in Fort Loudon Lake (Figure 1, page 2) was monitored monthly for the nine month period from October, 1973 through June, 1974; however, only the April, 1974 pH values were used in this study. These values were used because they were measured during the same approximate period as the water samples from below Fort Loudon Dam. The pH values of the water samples are as follows:

T-1W	T-2W	T-3W	T-4W	T-5W	T-6W	Average:
7.28	7.40	7.75	7.43	7.38	7.32	7.43
T-7W	T-8W	T-9W	T-10W	T-11W	T-12W	Average:
7.40	7.43	7.53	7.55	7.50	7.83	7.54

The grouping of the samples (T-1W through T-6W and T-7W through T-12W) was based on a natural split between samples T-6W and T-7W in the grain size distribution analysis of the bottom sediment samples.

The results of the April pH measurements showed all samples to be slightly alkaline and also that the average pH of the upstream samples (T-7W through T-12W) was slightly higher than the average for the downstream samples.

The solids analysis (Table 6) showed that the water samples from Fort Loudon Lake contained a great deal more dissolved material than suspended material. It was also observed that the upstream samples contained more total solids than the downstream samples. The difference between the two groups of samples was in the amount of dissolved solids, which averaged 117 mg/l for the upstream samples and only 103 mg/l for those collected downstream. The amount of suspended solids was almost the same for the two groups of samples (10 mg/l for T-7W through T-12W compared to 11 mg/l for T-1W through T-6W.

The results of the chemical analysis of the water samples (Tables 7 and 8) showed very little difference between the metal content of the upstream and downstream samples, with the exceptions of cadmium and lead. These elements were present in very minor amounts in the upstream samples, but were virtually absent below sample T-7W.

Iron and zinc had the highest values of the heavy metals. The fact that the zinc values were on the same order as the iron values indicates a major source of zinc contamination. The source of the contamination was probably the zinc milling operation at Mascot, Tennessee (Figure 1, page 2).

TABLE 6. Solid content (mg/l) of water samples from Fort Loudon Lake.

Sample	Dissolved Solids	Suspended Solids	Total Solids
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
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

TABLE 7. Metal content (ppm) of water samples from Fort Loudon Lake.

Sample	Ca	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
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	12	72	2	nd	tr*	83
T-5W	1.06%	nd	nd	8	10	48	2	nd	tr*	140
T-6W	1.14%	1	2	8	10	32	tr*	nd	tr*	42
Average (w/std dev)	1.03% ±.07	.2 ±.4	.7 ±1	7 ±3	8 ±3	39 ±21	1 ±1	2 ±2	0	55 ±49
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	tr*	72
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)	1.14% ±.11	2 ±.5	3 ±3	4 ±4	9 ±5	41 ±22	1 ±1	3 ±2	3 ±5	56 ±32

*Trace considered zero for all calculations.

TABLE 8. Metal content (ppm) of dissolved solids in water samples from Fort Loudon Lake.

Sample	Ca	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
T-1W	10.89%	nd	22	tr*	89	489	22	44	nd	234
T-2W	12.80%	nd	nd	107	53	214	nd	53	nd	147
T-3W	9.22%	nd	nd	70	35	174	nd	35	nd	218
T-4W	10.00%	nd	nd	80	40	720	20	nd	tr*	860
T-5W	8.83%	nd	nd	67	67	400	17	nd	tr*	1780
T-6W	9.50%	8	17	67	100	266	tr*	nd	tr*	292
Average (w/std dev)	10.21% ±1.46	1 ±3	7 ±10	65 ±35	64 ±26	377 ±205	10 ±11	22 ±25	0	590 ±638
T-7W	9.50%	8	50	tr*	33	266	tr*	nd	tr*	292
T-8W	10.67%	11	nd	89	89	300	nd	tr*	tr*	289
T-9W	9.54%	15	nd	tr*	31	461	tr*	31	tr*	415
T-10W	10.50%	17	50	tr*	100	266	17	33	tr*	600
T-11W	9.33%	17	50	67	100	167	17	33	83	300
T-12W	9.17%	17	nd	67	133	634	17	33	83	942
Average (w/std dev)	9.78% ±.64	14 ±4	25 ±27	37 ±42	81 ±41	349 ±169	9 ±9	22 ±17	28 ±43	473 ±259

*Trace considered zero for all calculations.

Bottom Sediment Samples

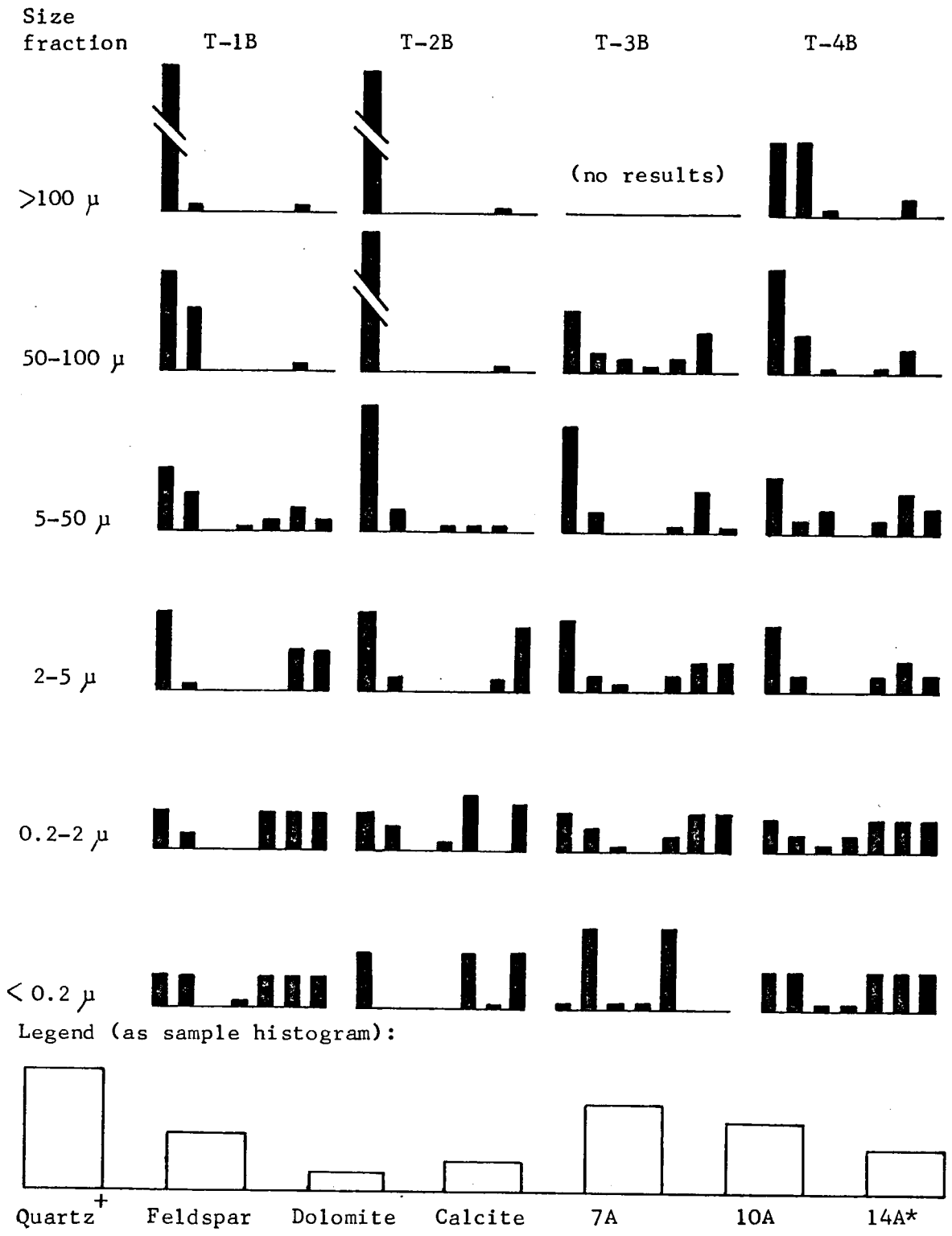
The twelve bottom sediment samples collected from Fort Loudon Lake (Figure 1, page 2) were separated into the same six size fractions as the samples from below the dam. The results of the size distribution analysis (Table 9) showed the downstream bottom sediment samples to be much finer grained than those collected upstream. The upstream samples (T-7W through T-12W) were composed almost entirely of sand-sized particles, whereas the downstream samples were predominantly silt-size. The clay content of the two groups also differed noticeably. The downstream samples contained about 20 times more clay than the upstream samples.

The mineralogies of the bottom sediment samples were determined by x-ray diffraction. The semi-quantitative technique described on page 18 was also used for this analysis.

The results of the analysis (Figure 4) showed a noticeable difference in mineralogy between the upstream and downstream sediment samples. Those samples collected in the upstream part of the lake (T-7B through T-12B) had a much higher dolomite content than those collected farther downstream, whereas the downstream samples contained a relatively higher amount of quartz. The clay mineral content of both groups of samples was about the same, as was the amount of feldspars. The clay mineral content increased with decreasing grain size; however, the feldspars showed no consistent trend to their distribution. Calcite was found in only minor amounts.

TABLE 9. Size distribution (weight percent) of bottom sediment samples from Fort Loudon Lake.

Sample	sand		silt		clay	
	100 μ	50–100 μ	5–50 μ	2–5 μ	0.2–2 μ	0.2 μ
T-1B	3.12	5.89	41.38	19.89	25.10	4.12
T-2B	18.38	10.30	45.42	10.20	12.42	3.27
T-3B	1.12	1.60	48.68	20.69	24.06	4.20
T-4B	30.74	26.53	20.92	8.72	11.37	1.60
T-5B	0.30	0.77	61.88	12.44	20.10	4.19
T-6B	4.06	4.20	66.03	8.91	13.61	3.20
Average (w/std dev)	9.62 ±12.29	8.22 ±9.60	47.39 ±16.12	13.48 ±5.45	17.78 ±6.09	3.43 ±1.01
T-7B	84.95	3.10	8.36	1.62	1.61	0.32
T-8B	49.10	40.36	8.09	1.12	1.65	0.17
T-9B	95.37	1.71	1.84	0.52	1.16	0.08
T-10B	97.62	0.74	1.00	0.42	0.48	0.03
T-11B	93.04	2.92	2.50	0.82	0.25	0.04
T-12B	96.91	1.33	1.42	0.41	0.01	----
Average (w/std dev)	86.17 ±18.73	8.36 ±15.70	3.87 ±3.41	0.82 ±0.48	0.86 ±0.71	0.11 ±0.12



+4.26A quartz peak multiplied by three to approximate 3.34A quartz peak.

*Bar height represents peak areas from diffractograms.

FIGURE 4. Mineralogy of bottom sediment samples from Fort Loudon Lake.

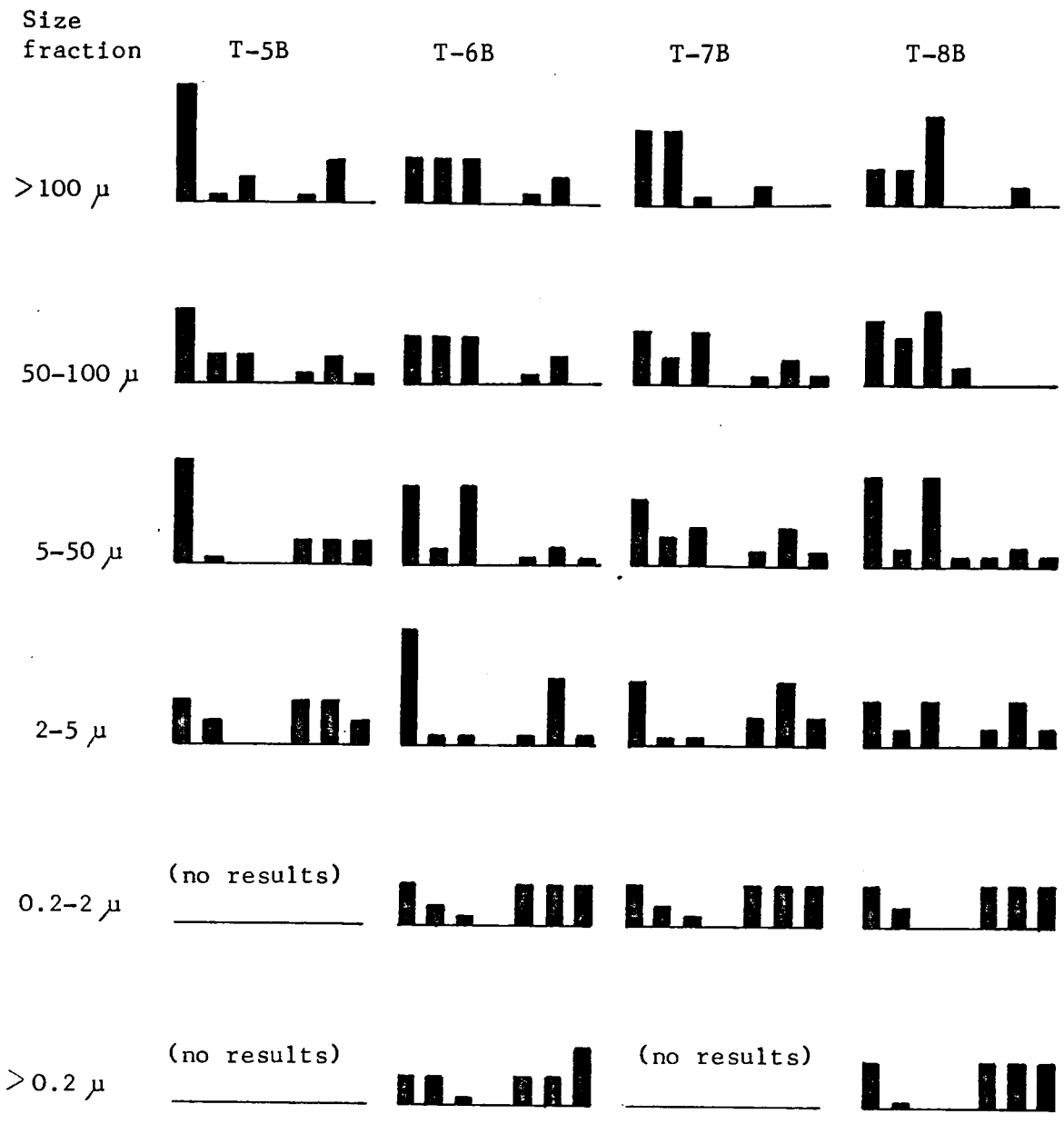


FIGURE 4. (continued)

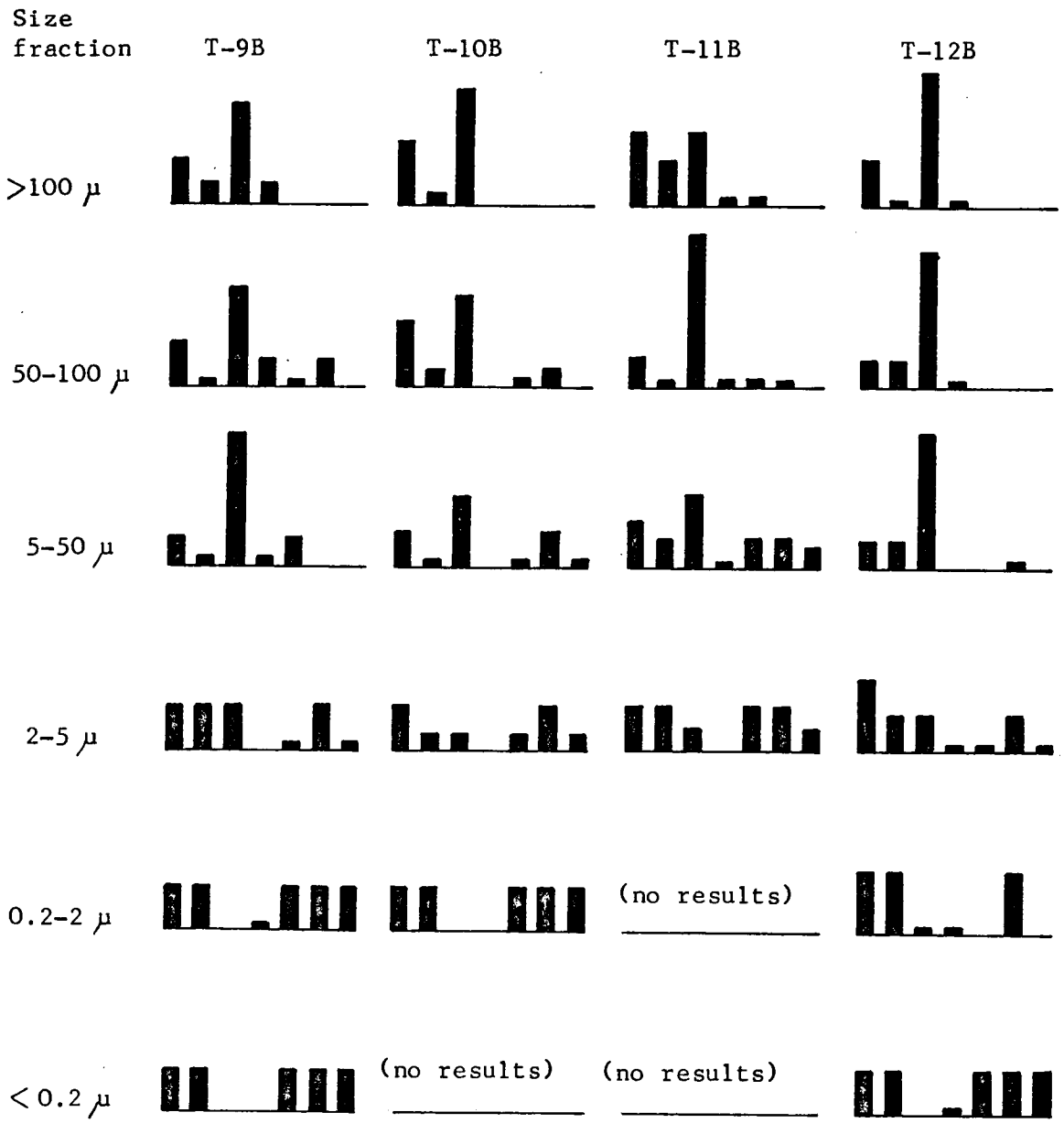


FIGURE 4. (continued)

The results of the chemical analysis of the bottom sediment samples (Table 10) showed three important differences between the upstream and downstream samples from Fort Loudon Lake. The calcium values for the upstream samples were much higher (about five times higher) than the values for the downstream samples. Iron and manganese, however, showed a downstream increase in metal content. The zinc values for the bottom sediments were relatively high throughout the entire lake.

TABLE 10. Metal content (ppm) of bottom sediments from Fort Loudon Lake.

Sample	Ca	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
T-1B	0.10%	9	47	253	38	3.42%	1420	122	141	748
T-2B	0.06%	5	47	117	40	2.80%	2800	103	148	189
T-3B	0.46%	5	53	233	46	4.24%	2130	128	74	954
T-4B	0.52%	8	20	100	33	2.66%	1250	139	73	572
T-5B	1.70%	8	51	132	41	3.60%	2070	74	142	1000
T-6B	2.24%	5	45	64	52	3.14%	1720	98	71	1060
Average (w/std dev)	0.85% ±.91%	7 ±2	46 ±13	150 ±76	42 ±7	3.30 ±.58	1900 ±560	111 ±24	108 ±39	755 ±331
T-7B	1.34%	5	30	119	27	2.12%	1120	115	131	400
T-8B	8.47%	11	37	109	22	1.61%	1060	96	69	1540
T-9B	8.46%	9	27	67	17	1.47%	912	91	75	1440
T-10B	3.14%	4	35	121	21	1.62%	729	120	154	486
T-11B	2.85%	5	30	76	36	2.50%	851	94	135	951
T-12B	6.25%	6	14	138	24	1.73%	1070	80	76	874
Average (w/std dev)	5.08% ±3.07%	7 ±3	29 ±8	105 ±28	25 ±7	1.84% ±.39%	957 ±152	99 ±15	107 ±37	949 ±472

CHAPTER V

DISCUSSION OF THE EXPERIMENTAL RESULTS AS THEY RELATE TO DAMMING

Introduction

The purpose of this study was to evaluate the effect of the damming of the Tennessee River on the distribution of trace metals. In this section the results of the water and bottom sediment analyses are compared and the inter-relationships studied to determine what effect, if any, damming had on the distribution of trace metals.

Water Samples

A comparison of the pH analyses (Table 1, page 12, and page 22) respectively), showed that the waters of the Tennessee River-Fort Loudon Lake system were slightly alkaline and that the pH of the water decreased in a downstream direction. The alkalinity of the water was, at least partially, the result of the zinc milling operation at Mascot, Tennessee (Figure 1, page 2). This operation had (until 1972) dumped large quantities of coarse-grained carbonate waste material into the Holston River, upstream from the sample area. This carbonate material tends to cause a slight alkalinity in the water.

The amount of carbonate material decreased downstream. This decrease was the result of settling of the coarse material, solution, and dilution away from the source area. The downstream decrease in

the carbonate material was reflected by the lower pH of the water downstream. The pH of the water did not, however, vary enough to effect the distribution of trace metals.

The effect of the dam was observed in a comparison of the solids analyses (Tables 1 and 6, pages 12 and 24, respectively). The suspended solids content of the samples from below Fort Loudon Dam was much higher (about three times higher) than that of the samples from Fort Loudon Lake. This difference represents the settling of the suspended material in the quiet water behind the dam and the suspension of material by the turbulent water below the dam.

The suspended solids content of the water samples from Fort Loudon Lake (Table 6, page 24) was not effected by the dam. There was no apparent difference in the average values of the upstream and downstream samples, but the downstream values did show more variation.

The amount of dissolved solids in the water samples decreased downstream. This trend paralleled the downstream decrease of the carbonate waste material from Mascot, and may have been related to the availability of the carbonates for solution.

The results of the chemical analyses (Table 2, page 14, and Table 7, page 25) showed a noticeable difference between the water samples collected above and below the dam. The metal concentrations in the water were higher for those samples collected below Fort Loudon Dam, with two exceptions, cadmium and chromium. The higher cadmium values in the upstream part of Fort Loudon Lake were undoubtedly the result of the Mascot milling operation, which extracts cadmium as a by-product. The high zinc values found in the water samples from

Fort Loudon Lake were also undoubtedly related to the zinc milling at Mascot, but unlike cadmium and chromium, the zinc values followed the general trend and increased below the dam. The increase was on the order of four times higher than the amounts reported in the lake.

The differences in the metal concentrations above and below the dam were exaggerated when converted to the metal content of the dissolved solids (Tables 3 and 8, pages 15 and 26, respectively) because of the lower dissolved solid content of the samples from below the dam.

The reason or reasons for the sudden increase in the dissolved metal content of the water below Fort Foudon Dam were not understood, but four possible explanations are:

1. The dam itself serves as a contaminant so that metal ions are added to the water as it passes through the dam.

2. The chemistry of the water above the dam may change vertically. The water which passes through the dam is drawn from approximately 40 feet below the surface. This water may have had a higher metal content than the surface water, which was analyzed as a part of the Fort Loudon Lake samples. The water which passed through the dam gave different values, when analyzed, than the surface water above the dam.

3. A source of contamination may exist somewhere between the sample sites above and below the dam, other than the dam itself. This contamination may add metal ions to the water before it reaches the samples sites below the dam.

4. Metal ions are dissolved from the suspended material in the water (and/or associated iron and manganese oxides and hydroxides) by

aggitation of the water and solids as they pass through the dam. The aggitation caused a reduction in the size of the particles, greatly increasing the total surface area, therefore allowing easier solution of the metal ions.

There was no physical evidence to support any of the first three explanations for the increase in the metal content of the water; however, the aggitation of the water as it passes through the dam was known to occur. Therefore, the fourth explanation was the most acceptable.

Bottom Sediment Samples

The results of the grain size distribution analyses (Tables 4 and 9, pages 17 and 28, respectively), showed that Fort Loudon Lake acts as a giant settling pond for sediments. A distinct division was observed between the upstream and downstream bottom sediment samples from Fort Loudon Lake. The coarse-grained upstream samples were the result of two factors: the zinc milling at Mascot, which dumped coarse-grained material into the river and the faster moving water in the upstream parts of the river, which keeps the fine material in suspension and carries it downstream. Below sample T-7B the bottom sediment was much finer. This was the result of settling in the quiet water behind the dam.

The bottom sediments collected below Fort Loudon Dam (Table 4, page 17) were slightly finer-grained than the upstream samples from the lake, but were still considerably coarser than samples T-1B through T-6B. An exception to this was shown by sample WB-4B. The reason

for the coarseness of the bottom sediments below the dam was the turbulence and velocity of the water at that point.

A comparison of the mineralogical analyses (Figures 3 and 4, pages 19 and 29, respectively), showed that the mineralogy of the bottom sediments did not reflect the bedrock geology. Instead, the effect of damming and the zinc milling at Mascot were reflected. The mineralogy of the bottom sediments from the upstream part of Fort Loudon Lake was mostly carbonate (dolomite), which represents the waste material from the mascot milling operation. Downstream the sediment was much finer grained, representing the settling of fine material behind the dam, and the predominant mineralogy was clay minerals, quartz, and feldspar. Below the dam the mineralogy was similar to that of the sediments in the lower (downstream) part of the lake.

The effect of damming on trace metal distribution was shown by the chemical analyses of the bottom sediments (Tables 5 and 10, pages 21 and 33, respectively). The metal content of the bottom sediments from the downstream section of the lake was the same as or higher than that of the upstream sediments, with two exceptions, calcium and zinc. The higher upstream values for these elements undoubtedly represents the effect of the zinc milling at Mascot. Downstream the concentrations of calcium and zinc decreased because of the settling, solution, and dilution of the coarse-grained carbonate waste material from Mascot.

The high metal concentrations in the downstream bottom sediments were the result of accumulation of metal ions by the fine-grained sediment (Perhac et al., 1974). Apparently, the metal ions were incorporated into the bottom sediment from the water.

The bottom sediments below Fort Loudon Dam had lower metal concentrations than those above the dam, with the exception of cobalt. Therefore, it was apparent that the bottom sediment was held up by the dam and enriched in trace metals, without passing through the dam to the sample area below, thus the dammed area serves as a site for the accumulation of trace metals (Perhac et al., 1974).

Conclusions

The damming of the Tennessee River had two important effects on the distribution of trace metals in the Tennessee River-Fort Loudon Lake system:

1. It created a site for the accumulation of trace metals, which were transported to the dammed area in solution and incorporated into the bottom sediment.

2. It caused an increase in the metal content of the water from the lake to the river below the dam. The reason or reasons for the increase in the metal content of the water were not understood, but the most acceptable explanation was that the aggitation of the water and suspended solids (as they passed through the dam) caused the solution of metal ions.

The distribution of trace metals in the Tennessee River-Fort Loudon Lake system was also effected by industrialization, such as the zinc milling at Mascot, Tennessee.

Recommendations for Future Work

The reason or reasons for the sudden increase in the metal content of the water below Fort Loudon Dam were not understood, but four possible explanations were given. Further research in the area of the dam, including vertical sampling of the water, sampling at the water intake and exhaust of the dam, extensive sampling near the dam to locate a possible source of contamination, and a study of the effects of physical aggitation of stream particles on the solubility of metals, could be used support or disprove these possible explanations and determine the cause of the increase in dissolved trace metals.

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APPENDICES

APPENDIX A

DETERMINATION OF TOTAL SOLIDS

The following procedure was used to determine the amount of total solids present in each water sample. The total solids include both suspended and dissolved material.

1. Determine the weight of a weighing bottle to the nearest 0.0001 gram.
2. Shake sample well and decant exactly 50 ml. of bulk sample into the weighing bottle.
3. Place the weighing bottle filled with sample in the oven to evaporate. Oven temperature should be set at approximately 90°C.
4. After the sample has evaporated remove the weighing bottle from the oven and place it in a dessicator to remove any excess moisture. Allow samples to remain in the dessicator overnight.
5. Remove the bottle from the dessicator and reweigh. The weight obtained in this step is that of both the bottle and the total solids. To determine the weight of just the solids subtract the weight of the bottle found in Step 1. (The weight of the solids found in this procedure will be in grams/50 ml and should be converted to mg/liter).

APPENDIX B

SIZE SEPARATION PROCEDURE

The following procedure was used in the separation of the bulk bottom sediment samples into six size fractions:

1. Place 10-15 grams of bulk sample into a 250 ml centrifuge bottle and fill with deionized water.
2. Suspend the sediment by shaking.
3. Centrifuge at 750 rpm for 5 minutes to settle all material greater than 2 μ.
4. Remove and save the supernatant (containing the less than 2 μ size fraction).
5. Resuspend the centrifugate with deionized water and repeat steps 3 and 4 twice, for a total of three times, saving the supernatant each time.
6. Remove and save the centrifugate (containing the greater than 2 μ material).
7. Take the supernatant from steps 3, 4, and 5 and centrifuge at 5000 rpm for 12 minutes to settle the greater than 0.2 μ size fraction.
8. Repeat step 7 twice, for a total of three times, removing and saving the supernatant each time.
9. Remove and save the centrifugate (containing the 0.2-2 μ material).

10. To recover the less than 0.2 μ size fraction, take the supernatant from steps 7 and 8 and centrifugeat 19,500 rpm for 4 hours.
11. Remove and discard the supernatant, saving the centrifugate (containing the less than 0.2 μ material).
12. To make the separation at 5 μ take the centrifugate from step 6 and suspend it in a settling column. The greater than 5 μ material will settle at a rate of 1 cm/400 seconds or less. Using a known height for the settling column, the time required for all the material greater than 5 μ to settle out can be determined mathematically.
13. Remove and save the supernatant (containing the 2-5 μ material).
14. Repeat steps 12 and 13 twice, for a total of three times, saving the supernatant each time.
15. To recover the 2-5 μ size fraction take the supernatant from steps 12, 13, and 14 and centrifuge at 5000 rpm for 30 minutes. Remove and discard the supernatant, saving the centrifugate (2-5 μ material).
16. Wet sieve the greater than 5 μ material through 53 μ and 105 μ stainless steel sieves to recover the greater than 105 μ, 53-105 μ, and 5-53 μ size fractions.

APPENDIX C

TOTAL SOLUTION PROCEDURE

The following procedure was used to put bottom sediment samples into solution for chemical analysis.

1. Place a known weight (between 0.1 and 0.2 grams) of sample in a 50 ml teflon beaker.
2. Add 5 ml of nitric acid (HNO_3) to the beaker and place on a sand bath at about 100°C.
3. Allow the acid to work almost to dryness, then remove the beaker and allow it to cool for 5 minutes.
4. After cooling add 3 ml of hydrofluoric acid (HF) and 1 ml of perchloic acid ($HClO_4$).
5. Return the beaker to the sand bath and heat at 120°-140°C. Place the lid on the beaker so that about 80 percent of the opening is covered.
6. Continue to heat until the mixture begins to fume vigorously (requires several hours). Once the mixture begins to fume, push the beaker down further into the sand bath to a temperature of about 200°C.
7. Continue heating at 200°C until a small, yellow, gelatinous globule remains. Remove the beaker and allow it to cool.
8. Transfer the globule to a 10 ml volumetric flask using deionized water and hydrochloric acid (HCl to rinse the teflon beaker. Bring the solution up to volume with deionized water.

9. To determine the amounts of trace metals in the reagents, repeat the entire procedure, using the same amounts of reagents, but without any sample. The amount of trace metals found in this "blank" must be subtracted from the amounts found in each sample.

VITA

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