

**CLINCH RIVER PROJECT:
SEDIMENT CONTAMINANTS IN
THE LOWER CLINCH RIVER**



**U.S. Fish and Wildlife Service
Ecological Services
446 Neal Street
Cookeville, Tennessee 38501**

May 1996

U.S. FISH and WILDLIFE SERVICE / SOUTHEAST REGION / ATLANTA, GEORGIA

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W. Allen Robison, Steven R. Alexander, Tracey Hibner, and Mark Wilson

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EXECUTIVE SUMMARY

Sediment samples from three mainstem and seven tributary sites in the Clinch River Basin were analyzed for 21 organochlorine compounds, 19 metals, total volatile sulfides, total organic carbon, and particle size distribution. None of the organochlorine compounds were detected in any samples, and molybdenum was detected at only two sites.

Aluminum, boron, barium, beryllium, chromium, vanadium, total volatile sulfides, and total organic carbon were highest at one tributary site (Copper Creek, Site 12). The highest mercury concentration was found at another location (Site 10) on Copper Creek. The highest concentrations for copper and manganese (Site 4), and selenium and strontium (Site 8) were found at two mainstem sites.

Geometric means for 11 metals in the tributary site samples were within about 20% of those for mainstem sites. Barium, beryllium, copper, lead, manganese, nickel, selenium and strontium averages were higher for the mainstem sites. No statistical differences between mainstem and tributary site means were noted using log-transformed, dry-weight results normalized to 1% total organic carbon.

Total volatile sulfides were considered elevated at Sites 3 and 11, and highly elevated at Site 12. Each of these sites was also considered heavily polluted based on total volatile sulfides.

Manganese concentrations (geometric means) in tributary and mainstem sites were substantially greater than that found in surficial soils of the eastern United States. Tributary and mainstem manganese concentrations were also slightly higher than that reported for East Fork Poplar Creek, an impacted stream near Oak Ridge, Tennessee.

Chromium was considered extremely elevated at Site 12 (Copper Creek), and was in the same range as that reported for East Fork Poplar Creek. Chromium at Site 12 also exceeded the sediment limit of tolerance developed by the Ontario Ministry of the Environment (OME). Cadmium and zinc were typically below OME's no effect levels. Copper, iron and mercury were generally below OME's lowest effect levels.

Mercury, cadmium, and zinc concentrations were below sediment concentrations associated with reduced survival of rainbow trout early life stages. Cadmium and mercury were also below sediment concentrations associated with reduced amphipod and chironomid survival. Copper, lead, nickel and zinc concentrations were in ranges associated with reduced amphipod and chironomid survival in 10-day sediment toxicity tests.

Chromium, manganese, mercury and other metals in Copper Creek sediments may be impacting species known to occur in the creek that have been listed pursuant to the Endangered Species Act. Two listed fish species, three listed mussel species, and one mussel species proposed for listing as endangered have been found in Copper Creek.

The following items are recommended for consideration in any future investigations of the Clinch River: 1) analyze sediment samples for polycyclic aromatic hydrocarbons; 2) analyze sediment samples for acid volatile sulfide and simultaneously extracted metals; 3) use a suite of appropriate sediment toxicity tests, including larval and juvenile mussels; 4) measure contaminants in water and sediment in conjunction with toxicity tests; 5) conduct cholinesterase inhibition assays with non-listed mussel species; and 6) determine contaminant residues in non-listed mussel species which are co-located with listed species.

ACKNOWLEDGMENTS

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INTRODUCTION

In 1991, the Cookeville Field Office participated in a joint project to identify the causes of significant declines observed in fish and mussel species inhabiting the Upper Tennessee River Basin. The project also involved Fish and Wildlife Service Field Offices and Cooperative Research Units in North Carolina and Virginia. This report provides the results of sampling conducted by the Cookeville Field Office in the lower Clinch River.

STUDY AREA

The Clinch, Powell and Holston River drainages comprise the majority of the Upper Tennessee River Basin. The portion of the Clinch River watershed in Tennessee encompasses about 2612 square miles (Denton *et al.* 1994) and includes four major hydrologic units (Table 1). This area lies within the Valley and Ridge Physiographic Region, which is characterized by parallel ridges and intervening valleys. Ridge elevations range from 1495 feet to 3097 feet (Bays Mountain), while valley elevations average about 750 feet in the southern portion and 1000 feet in the northern portion (Miller 1974). This area has also been described by Omernik (1987) as part of the Central Appalachian Ridge and Valley Ecoregion.

This area is currently considered by the Fish and Wildlife Service to be part of the Southern Appalachian Ecosystem (FWS 1995). From the backwaters of Norris Lake to the Tennessee-Virginia border, both the Clinch River and the Powell River are designated as critical habitat for the slender chub (*Erimystax (=Hybopsis) cahni*). In addition, the Emory River, the Obed River, Clear Creek and Daddy's Creek in Morgan County; Clear Creek in Fentress County; and the Obed River (upstream to Interstate 40), Clear Creek (upstream to Interstate 40) and Daddy's Creek (upstream to Highway 127) in Cumberland County are designated as critical habitat for the spotfin chub (*Cyprinella (=Hybopsis) monacha*) (FWS 1992).

The Tennessee Department of Environment and Conservation (TDEC 1990) identified 11 major effluent discharges in the Clinch River Basin (Table 2). The 1990 fish consumption advisories covering Melton Hill Reservoir, the Clinch River below Melton Hill Reservoir, Watts Bar Reservoir, and East Fork Poplar Creek (including the Poplar Creek embayment) have not been lifted. The primary contaminants of concern in these advisories are polychlorinated biphenyls and mercury.

Other water quality concerns identified by TDEC (1990) at ambient monitoring stations in the Clinch River included ammonia, nitrate, and phosphorus (Table 3, Figure 1). Mining activities and wastewater treatment plants were targeted as sources of concern. Denton *et al.* (1994), identified a wider range of impacts (Table 4), however, six streams had improved designated use support and two had been downgraded (Table 5). The status of designated uses in lakes within the watershed is summarized in Table 6.

Table 1. Major hydrologic units for Tennessee portion of Clinch River watershed.

<u>Unit</u>	<u>Description</u>	Tennessee drainage area (square miles)
06010205	Clinch River from the state line to Norris Dam excluding the Powell River	724
06010206	Powell River from the Virginia state line to the river's mouth	387
06010207	Clinch River from Norris Dam to the mouth	636
06010208	Emory River including the Obed River	865

Table 2. Major Dischargers - Clinch River Basin.

<u>Permit #</u>	<u>Name</u>	<u>County</u>	<u>Receiving Stream</u>
TN0026506	Clinton STP #1	Anderson	Clinch River
TN0024155	Oak Ridge-West STP	Anderson	East Fork Poplar
TN0005410	TVA-Bull Run Steam	Anderson	Clinch River
TN0002950	USDOE-Gaseous Plant	Anderson	Poplar Creek
TN0002968	USDOE-Oak Ridge Y-12	Anderson	East Fork Poplar
TN0020532	LaFollette STP	Campbell	Big Creek
TN0024996	Crossville STP	Cumberland	Obed River
TN0002941	USDOE-Oak Ridge Nat Lab	Roane	Clinch River
TN0025437	Harriman STP	Roane	Caney Creek
TN0020885	Oliver Springs STP	Roane	Indian Creek
TN0005452	TVA-Kingston Steam	Roane	Emory River

Table 3. Other water quality concerns (see text) identified at ambient monitoring stations in the Clinch River Basin.*

<u>Map No.</u>	<u>Stream River Mile Station Number</u>	<u>County</u>	<u>Parameters of Concern¹</u>	<u>Comments</u>
24	Powell River 115.7 TN002180	Hancock	Nitrate, fecal	Mining activities
33	Crooked Fork 4.2 TN000709	Morgan	Nitrate	
30	Obed River 36.9 TN002005	Cumberland	Phosphorus, DO, ammonia, BOD, nitrate	STP discharge
23	Clinch River 189.9 TN000665	Hancock	Nitrate, fecal	Mining impacts
36	Clinch River 10.0 TN00000680	Roane	Nitrate	
31	Coal Creek 5.4 TN000705	Anderson	Nitrate	

¹Parameters of concern are those that exceeded fish and aquatic life or recreation criteria in more than 25% of the observations.

*TDEC 1990.

Figure 1. Tennessee Division of Water Pollution Control Ambient Monitoring Sites.

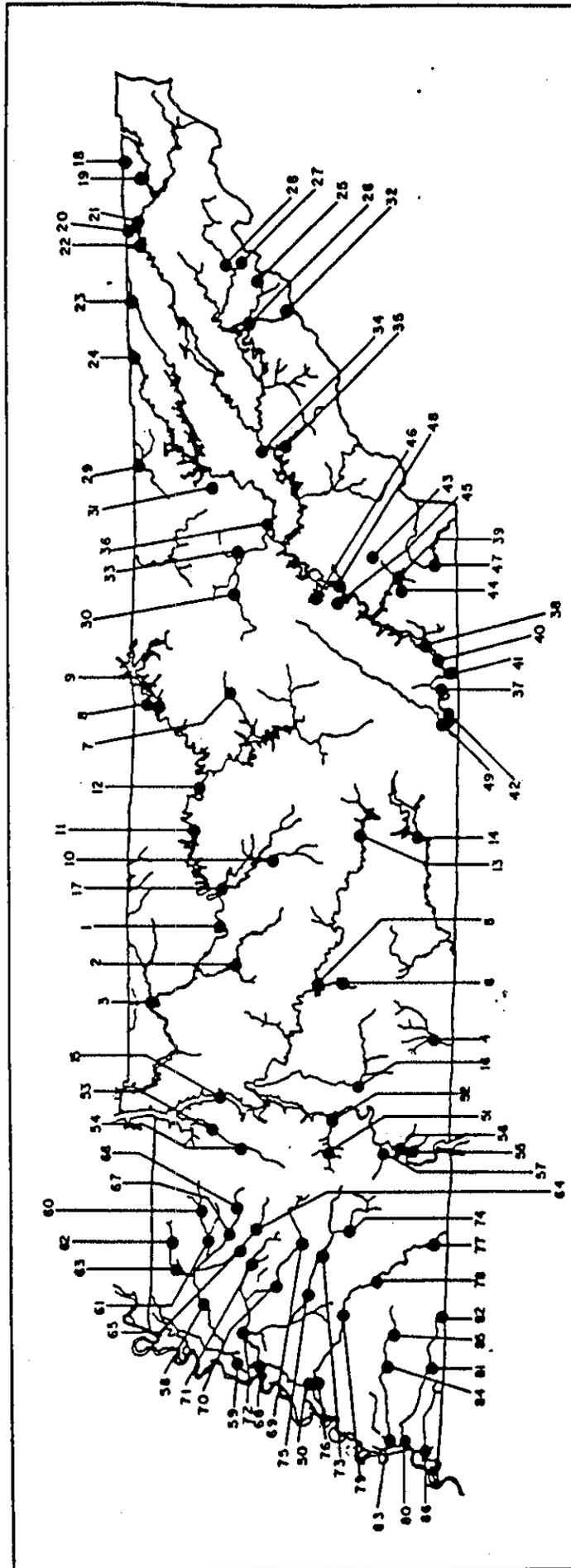


Table 4. Summary of impacted rivers in the Clinch River Basin in Tennessee.

<i>Waterbody Name</i>	<i>Waterbody Number</i>	<i>Size (miles)</i>	<i>Designated Use Support</i>	<i>Causes of Impact</i>	<i>Sources of Impact</i>	<i>Monitored or Evaluated</i>
Coal Creek	TN06010207COAL	10.3	partially supporting	nutrients, siltation, organic enrichment, low DO, pathogens	municipal point sources, surface mining, channelization	monitored
Russell Creek	TN06010206008	6.8	partially supporting	chlorine, nutrients, siltation, organic enrichment, low DO, pathogens, suspended solids	municipal point sources, storm water	evaluated
Hickory Creek	TN06010207004	8.1	partially supporting	unknown toxicity, siltation, habitat alterations, oil & grease	industrial & municipal point sources, other	monitored
Beaver Creek	TN06010207011	29.9	partially supporting	nutrients, siltation, organic enrichment, low DO, pathogens, filling & draining	municipal point sources, agriculture, wetland impacts, other	monitored
Clinch River	TN06010207019	12.5	partially supporting	organic enrichment, low DO, thermal, flow alteration	dam construction, upstream impoundment, flow regulation/modification	monitored
Poplar Creek including Brushy Creek	TN06010207020	33.8	partially supporting	priority organics, metals, nutrients, siltation, organic enrichment, low DO, pathogens	industrial & municipal point sources, surface mining, spills, waste storage leaks	monitored
Indian Creek	TN06010207INDI	3	partially supporting	nutrients, siltation, organic enrichment, low DO	storm water, resource extraction, channelization, no riparian vegetation	evaluated
Clinch River	TN06010207001	26	not supporting	priority organics, metals, siltation, thermal, flow alteration, radiation	industrial & municipal point sources, contaminated sediments, storm water, dam construction, upstream impoundment	monitored

Table 4. Continued.

East Fork Poplar Creek	TN06010207EAST	15	not supporting	priority organics, metals, nutrients, siltation, organic enrichment, low DO, pathogens, radiation	industrial & municipal point sources, storm water, other	monitored
Powell River	TN06010206006	30.7	threatened		future development	monitored
Powell River	TN06010206007	39.5	threatened		future development	monitored
Davis Creek	TN06010206026	19	not supporting	organic enrichment, low DO, siltation, pathogens	manure lagoons, pastures, septic tanks	monitored
Emory River	TN06010208001	22.6	threatened		future development	monitored
Emory River	TN06010208005	23.5	threatened		future development	monitored
Crooked Fork Emory River	TN06010208004	18	not supporting	pH, siltation, organic enrichment, low DO, pathogens	municipal point sources, pastures, agriculture, surface & subsurface mining, road, no riparian vegetation	monitored
Obed River including Otter Creek	TN06010208013	4.9	partially supporting	organic enrichment, low DO, nutrients, siltation, flow alteration	municipal point sources, land development, dam construction	monitored
Turkey Creek	TN06010201TURK	5	not supporting	nutrients, siltation, habitat alterations, pathogens, organic enrichment, low DO, oil & grease	municipal point sources, pastures, land development, stormwater, wetland impacts	monitored

Table 5. Changes in the use assessments in rivers in the Clinch River Basin in Tennessee.

<i>Waterbody Name</i>	<i>Waterbody Number</i>	<i>Size (miles)</i>	<i>1994 Designated Use Category</i>	<i>1990 Designated Use Category</i>
Coal Creek	TN06010207COAL	10.3	partially supporting	not supporting
Davis Creek	TN06010206026	19	not supporting	not listed
Emory River	TN06010208001	22.6	threatened	partially supporting
Crooked Fork Emory River	TN06010208004	18	not supporting	partially supporting
Big Creek	TN06010205BIG	5	fully supporting	partially supporting
Cove Creek	TN06010205COVE	5	fully supporting	partially supporting
Hinds Creek including Buffalo Creek	TN06010208016	26.4	not listed	partially supporting
Daddy's Creek including Byrd & Basses Creek	TN060102080015	58.4	fully supporting	threatened
Bull Run Creek	TN06010207014	35.1	fully supporting	threatened
Turkey Creek	TN06010101TURK	5	not supporting	partially supporting

Table 6. Summary of lake information in the Clinch River Basin in Tennessee.

<i>Lake Name</i>	<i>Size (miles)</i>	<i>Tropic Status</i>	<i>Designated Use Category</i>	<i>Causes of Impact</i>	<i>Monitored or Evaluated</i>
Big Ridge Lake	45	oligotrophic	fully supporting	fully supporting	monitored
Byrd Lake	47	eutrophic	partially supporting	pathogens, nutrients, organic enrichment, low DO	evaluated
Cove Lake	494	mesotrophic	threatened	mining in watershed	monitored
Melton Hill Reservoir	5,690	oligotrophic	not supporting	siltation, thermal alteration, PCBs, metals, unknown toxicity	monitored
Norris Reservoir	34,187	oligotrophic	fully supporting	fully supporting	monitored

MATERIALS AND METHODS

Analytical support, including laboratory quality assurance, for this project was provided through the Patuxent Analytical Control Facility located at the Patuxent Wildlife Research Center. Organic analyses were performed by the Mississippi State Chemical Laboratory in Mississippi State, Mississippi. Inorganic analyses were performed by the Environmental Trace Substances Research Center in Rolla, Missouri. Specific analytical methods are included in Appendix A.

Descriptive summary statistics, data transformations and statistical analyses were done following techniques in Snedecor and Cochran (1980) and Steel and Torrie (1960). QuattroPro 6.0 for Windows was used to calculate summary statistics, perform logarithmic transformations and run various statistical analyses.

QUALITY ASSURANCE AND QUALITY CONTROL

Quality assurance (QA) and quality control (QC) results were provided by the laboratories and are included in Appendix B. Blanks, duplicates, spikes and reference samples were analyzed. Recoveries for organochlorine analytes ranged from 67.5% (HCB) to 112.5% (DDE). Recoveries for metal analyses varied from about 63% (boron) to 108% (arsenic). Duplicate metals analyses were generally within 10% except for cadmium and selenium, which were close to detection limits where greater variability would be expected.

RESULTS

Sediment samples were collected at ten (3 mainstem and 7 tributary) sites in the Clinch River Basin (Table 7, Figure 2). Parameters measured in the field (water temperature, dissolved oxygen and conductivity) are shown in Appendix C. Samples were analyzed for 21 organic parameters and 19 metals (Table 8) and were also tested for total volatile sulfides (TVS), total organic carbon (TOC), and particle size distribution (Table 9). Total volatile sulfides ranged from 3.1% to 15.4% while total organic carbon varied from 0.6% to 9.7%. The highest value for each was measured at Site 12 (Copper Creek). The correlation coefficient calculated (0.870) for these two parameters was statistically significant ($\alpha=0.01, 8df$).

Sand particles comprised the majority of all samples except one (Site 1), and varied from 38.6% to 86.6%. Clay particles averaged 10% and did not exceed 16.7%. Silt particles comprised about 24% of the samples on average, and ranged from 10.1% to 44.7%.

Of the 21 organic parameters analyzed, none were detected in any of the sediment samples. With the exception of molybdenum (detected at two sites), selenium (seven sites), cadmium (nine sites) and arsenic (nine sites), all metals were detected at every site (Tables 10, 11). The maximum values for four metals were detected at two mainstem sites. Copper and manganese were highest at Site 4 while selenium and strontium were greatest at Site 8. Six metals (aluminum, boron, barium, beryllium, chromium, vanadium) were highest at one tributary site, Copper Creek (Site 12). Mercury concentrations were all less than 0.100 ppm, with the highest value (0.075 ppm) found at Site 10 in Copper Creek. Wet-weight results are shown in Table 10 and dry-weight results are included in Table 11.

The sites were divided into two groups, tributaries and mainstem, and summary statistics calculated using dry weight results (Table 12) and dry weight results normalized to 1% total organic carbon (Table 13). Geometric means for individual metals at the seven tributary sites were within about 20% of those for the three mainstem sites except for barium, beryllium, copper, manganese, nickel, lead, selenium and strontium (Tables 12 and 13), all of which were higher at the mainstem sites. Variability in the metals values was generally greater in the tributary samples. Statistical analysis of log-transformed ($\log(x+1)$), dry-weight results normalized to 1% TOC indicated no significant differences between the mainstem and the tributary sites.

At the tributary sites, all metals except chromium, molybdenum and strontium correlated significantly with aluminum. Likewise, all metals except boron, chromium, magnesium, molybdenum and selenium correlated significantly with iron. No correlation analysis was done on the mainstem site because of the limited number of sites which were sampled.

Table 7. Sampling sites for the Clinch River project.

Site Number	Latitude Longitude	County, State	Location
1	36°27'00" 83°26'36"	Claiborne, TN	Sycamore Creek at Raphsis Road
2	36°25'22" 83°19'46"	Hancock, TN	Big War Creek at Providence Church
3	36°33'55" 83°04'24"	Hancock, TN	Blackwater Creek - 0.5 mi northwest of Highway 33
4	36°33'32" 82°53'24"	Hancock, TN	Clinch River - 150 m downstream of Virginia State Line
5	36°36'15" 82°57'47"	Scott, VA	North Fork Clinch River - 80 m downstream of Highway 621
6	36°41'00" 82°45'00"	Scott, VA	Stock Creek - 0.5 km upstream of Highway 23 and Highway 871 junction
8	36°40'00" 82°44'00"	Scott, VA	Clinch River-Clinchport River Access Area
10	36°39'55" 82°41'55"	Scott, VA	Copper Creek - Highway 627 (Jennings Ford)
11	36°44'00" 82°27'00"	Scott, VA	Copper Creek - 150 m upstream of Highway 674
12	36°48'45" 82°15'00"	Russell, VA	Copper Creek - approx. 1.8 km upstream from confluence with Little Copper Creek

Figure 2. Clinch River and Tributaries Sampling Locations.

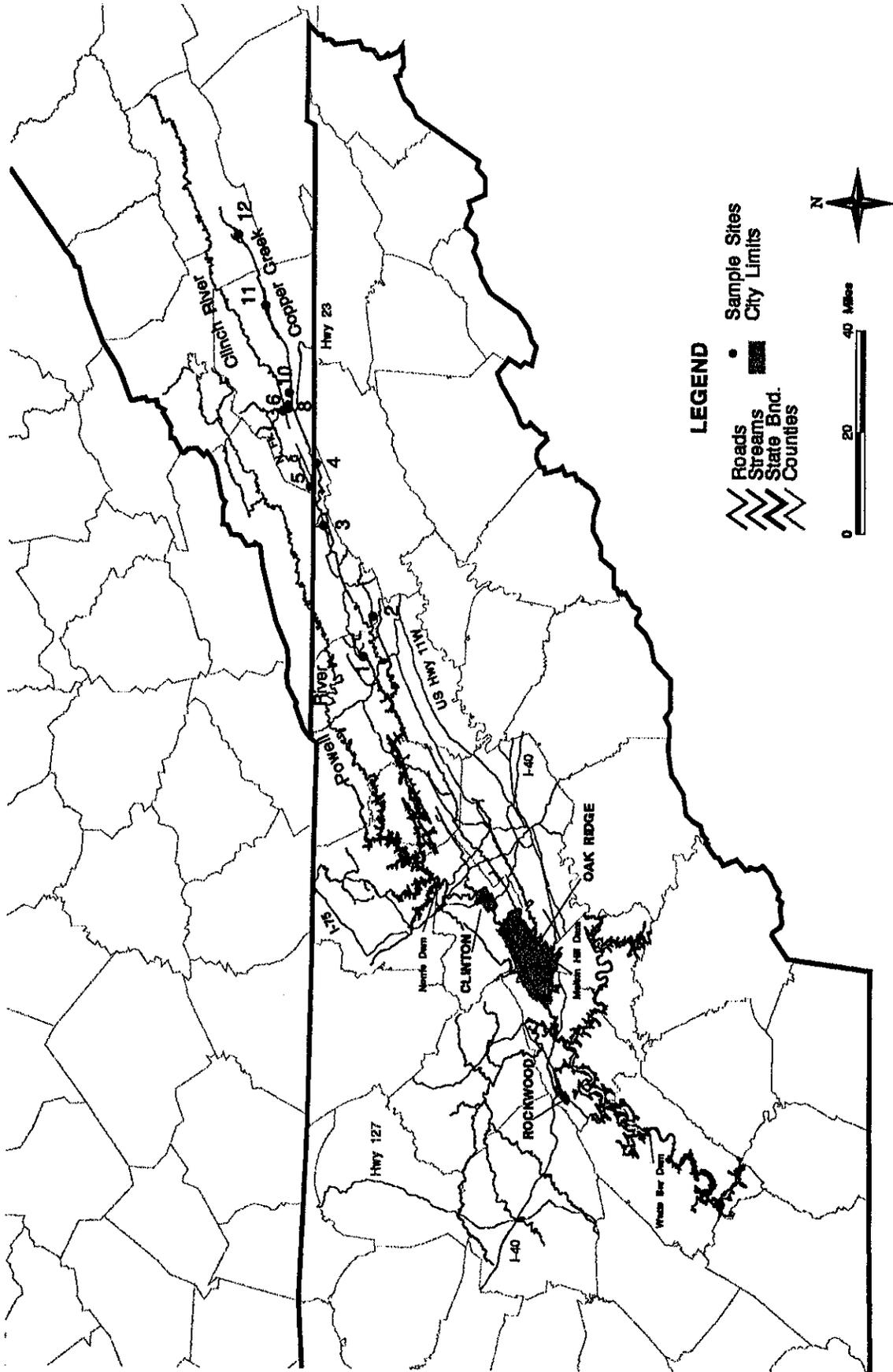


Table 8. Contaminants analyzed for the Clinch River project.

<u>Organic</u>	<u>Metals</u>
BHC (beta-; delta-; gamma-; isomers)	Aluminum (Al)
Chlordane (alpha-; gamma-; isomers)	Arsenic (As)
DDD (o,p'-; p,p'- isomers)	Boron (B)
DDE (o,p'-; p,p'- isomers)	Barium (Ba)
DDT (o,p'-; p,p'- isomers)	Beryllium (Be)
Dieldrin	Cadmium (Cd)
Endrin	Chromium (Cr)
HCB (Hexachlorobenzene)	Copper (Cu)
Heptachlor epoxide	Iron (Fe)
Nonachlor (cis-; trans-isomers)	Mercury (Hg)
Oxychlordane	Magnesium (Mg)
PCBs	Manganese (Mn)
Toxaphene	Molybdenum (Mo)
	Nickel (Ni)
	Lead (Pb)
	Selenium (Se)
	Strontium (Sr)
	Vanadium (V)
	Zinc (Zn)

Table 9. Clinch River sediment sample information.

<u>Sample Number</u>	<u>Sample Weight (g)</u>	<u>Percent Moisture</u>	<u>Percent TVS*</u>	<u>Percent TOC*</u>	<u>% Sand</u>	<u>Particle Size %Silt</u>	<u>% Clay</u>
1B	189.46	41.1	7.7	2.1	38.6	44.7	16.7
2B	100.77	47.5	6.3	1.1	74.9	14.0	11.1
3B	169.21	36.5	9.1	2.2	53.2	31.3	15.5
4B	120.15	36.5	3.1	0.9	81.5	15.3	3.3
5B	93.88	45.8	6.2	1.3	45.0	40.7	14.2
6B	184.19	33.7	4.1	0.6	76.1	17.9	6.0
8B	178.45	39.5	5.9	1.6	67.9	21.3	10.8
10B	159.52	40.4	3.4	0.5	86.6	10.1	3.3
11B	124.88	42.9	10.0	1.4	66.2	23.6	10.2
12B	134.35	57.0	15.4	9.7	66.3	20.5	13.2

*TVS - total volatile sulfides; TOC - total organic carbon.

Table 10. Metals detected in Clinch River sediment samples (ppm, wet weight).

<u>Metals</u>	Sites											
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>8</u>	<u>10</u>	<u>11</u>	<u>12</u>		
Al	3200	7310	8620	6350	7040	3980	3410	8010	5350	12,700		
As	6.30	2.30	2.90	---	4.40	5.50	1.70	3.10	4.80	2.70		
B	2.00	5.20	5.40	3.70	8.90	3.00	2.00	5.90	3.00	20.00		
Ba	34.7	45.20	61.90	51.00	51.80	42.40	46.00	61.80	38.20	75.50		
Be	0.36	0.51	0.66	0.52	0.52	0.32	0.37	0.58	0.50	0.70		
Cd	0.30	0.20	0.30	0.20	0.20	0.20	0.20	<0.10	0.20	0.20		
Cr	4.80	12.00	15.00	11.00	17.00	6.90	4.70	12.00	24.00	20.00		
Cu	5.40	6.00	8.60	9.10	7.80	7.40	7.30	7.70	3.80	8.30		
Fe	11,100	11,000	19,000	11,800	14,100	6740	7050	11,200	13,900	15,700		
Hg	0.006	0.020	0.007	0.024	0.020	0.031	0.023	0.044	0.027	0.030		
Mg	392	1210	1450	1990	1260	15,100	1170	2110	1160	2280		
Mn	191	350	462	527	426	482	269	407	391	503		
Mo	4.10	<0.50	1.00	<0.50	<0.60	<0.60	<0.40	<0.60	<0.50	<0.60		
Ni	10.00	8.70	19.00	9.70	13.00	7.70	6.00	8.80	5.80	12.00		
Pb	5.00	11.0	7.00	15.00	9.50	26.0	8.20	15.00	17.00	11.00		
Se	0.30	0.10	<0.10	0.10	<0.10	0.10	0.29	0.10	<0.10	0.30		
Sr	4.30	6.50	7.89	12.10	6.32	15.40	21.80	7.36	10.30	10.90		
V	13.00	12.00	15.00	11.00	14.00	12.00	6.40	15.00	17.20	20.30		
Zn	35.20	47.60	35.50	32.70	23.50	35.20	27.10	22.10	32.70	32.80		

Table 11. Metals detected in Clinch River sediment samples (ppm, dry weight).

<u>Metals</u>	<u>Sites</u>											
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>8</u>	<u>10</u>	<u>11</u>	<u>12</u>		
Al	5040	13,500	13,000	10,500	11,800	6960	7930	13,600	10,200	20,000		
As	9.85	4.20	---	4.80	7.30	9.69	3.90	5.20	9.20	4.20		
B	3.00	9.60	8.10	6.10	15.10	5.60	4.00	10.00	5.90	31.00		
Ba	54.70	83.40	93.30	84.30	86.90	74.30	107	105	72.80	119		
Be	0.56	0.94	1.00	0.86	0.87	0.56	0.87	0.98	0.95	1.10		
Cd	0.40	0.40	0.40	0.30	0.30	0.30	0.40	<0.20	0.30	0.30		
Cr	7.50	23.00	23.00	18.00	29.00	12.00	11.00	20.00	45.00	310		
Cu	8.50	11.00	13.00	15.00	13.00	13.00	17.00	13.00	7.20	13.00		
Fe	17,500	20,300	28,700	19,500	23,600	11,800	16,400	19,000	26,400	24,800		
Hg	0.01	0.04	0.01	0.04	0.03	0.054	0.054	0.075	0.051	0.054		
Mg	617	2240	2180	3280	2120	26,500	2720	3580	2210	3600		
Mn	301	646	696	870	714	843	627	691	745	792		
Mo	6.50	<1.00	2.00	<0.90	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00		
Ni	16.00	16.00	28.00	16.00	21.00	11.00	18.00	15.00	11.00	19.00		
Pb	8.00	21.00	10.00	24.00	16.00	45.00	19.00	25.00	32.00	17.00		
Se	0.50	0.20	<0.20	0.20	<0.20	0.20	0.68	0.20	<0.20	0.50		
Sr	6.70	12.00	11.90	20.00	10.60	26.90	50.80	12.50	19.70	17.10		
V	20.00	23.00	22.00	18.00	23.00	21.00	15.00	26.00	32.80	32.00		
Zn	55.40	87.90	53.50	54.00	39.40	61.70	63.00	37.60	62.40	51.70		

Table 12. Summary and comparison of metals results (ppm, dry weight) for tributary and mainstem Clinch River sites.

Metals	Tributary Sites			Mainstem Sites				
	Average	Standard Deviation	Geometric Mean	Average	Standard Deviation	Geometric Mean		
	Mean	Harmonic Mean	Harmonic Mean	Mean	Harmonic Mean	Harmonic Mean		
Al	11757.14	4940.991	9991.31	9794.91	10076.67	1969.425	9941.41	9801.127
As	7.06	2.796	5.96	6.11	5.33	1.762	5.15	4.986
B	10.46	9.385	8.51	6.72	8.40	5.897	7.17	6.248
Ba	86.07	21.606	72.23	81.29	92.73	12.423	92.20	91.699
Be	0.87	0.218	0.73	0.81	0.87	0.006	0.87	0.867
Cd	0.33	0.076	0.27	0.31	0.33	0.058	0.33	0.327
Cr	62.93	109.593	35.59	18.47	19.33	9.074	17.91	16.579
Cu	11.24	2.459	9.32	10.68	15.00	2.000	14.91	14.821
Fe	21214.29	5830.217	17862.23	19617.41	19833.33	3611.556	19615.38	19401.083
Hg	0.04	0.024	0.03	0.02	0.04	0.012	0.04	0.039
Mg	5846.71	9163.085	3673.54	1959.02	2706.67	580.115	2664.36	2621.866
Mn	673.43	177.111	561.50	606.30	737.00	123.122	730.29	723.784
Mo	1.93	2.050	1.55	1.24	0.97	0.058	0.97	0.964
Ni	16.57	5.798	14.22	15.16	18.33	2.517	18.22	18.108
Pb	22.57	12.921	18.85	16.47	19.67	4.041	19.40	19.133
Se	0.29	0.146	0.25	0.24	0.36	0.277	0.30	0.262
Sr	15.26	6.600	13.04	12.89	27.13	21.028	22.08	18.290
V	25.26	5.234	20.92	24.41	18.67	4.041	18.38	18.105
Zn	58.60	15.316	49.39	55.43	52.13	11.910	51.18	50.191

Table 13. Summary and comparison of metals results (ppm, dry weight) normalized to 1% total organic carbon for tributary and mainstem Clinch River sites.

Metals	Tributary Sites			Mainstem Sites				
	Average	Standard Deviation	Geometric Mean	Average	Standard Deviation	Geometric Mean		
	Mean	Harmonic Mean	Harmonic Mean	Mean	Mean	Mean		
Al	9818.48	8643.029	7001.71	4955.38	8566.61	3384.189	8066.40	7544.34
As	7.01	5.551	4.52	1.94	4.46	1.759	4.18	3.87
B	7.23	6.342	5.29	3.90	6.96	4.561	5.82	4.73
Ba	77.48	68.908	54.29	37.09	75.80	15.477	74.81	73.91
Be	0.75	0.611	0.55	0.37	0.72	0.211	0.70	0.68
Cd	0.27	0.160	0.21	0.13	0.27	0.055	0.27	0.26
Cr	22.72	12.913	18.12	12.48	16.39	8.324	14.53	12.49
Cu	10.59	9.491	7.12	4.54	12.43	3.682	12.10	11.81
Fe	16987.69	11202.925	13265.44	9065.42	16690.17	5847.378	15915.79	15090.58
Hg	0.05	0.055	0.02	0.01	0.03	0.011	0.03	0.03
Mg	8085.35	16084.125	1956.76	833.92	2325.07	1143.135	2161.84	2032.75
Mn	635.39	549.731	418.45	255.45	635.92	297.041	592.55	554.83
Mo	1.34	0.993	0.94	0.48	0.80	0.189	0.78	0.77
Ni	13.29	9.098	10.26	6.97	15.06	3.398	14.78	14.49
Pb	25.29	27.604	12.57	5.92	16.95	8.418	15.74	14.78
Se	0.21	0.127	0.17	0.13	0.27	0.141	0.24	0.22
Sr	15.03	15.353	9.12	5.42	20.71	11.871	17.92	15.06
V	22.02	16.939	16.10	10.83	15.69	5.589	14.91	14.07
Zn	51.22	35.480	36.96	21.56	43.23	15.216	41.52	39.97

DISCUSSION

Except for Site 12 (Copper Creek), total organic carbon values were considered to be within the normal range expected for this area. Based on a comparison with the guidelines for classifying sediments from harbors in the Great Lakes (USACOE 1977), total volatile sulfides were in the nonpolluted range (<5%) at Site 4 and Site 10; the moderately polluted range (5-8%) at sites 1, 2, 5 and 8; and the heavily polluted range (>8%) at sites 3, 11 and 12. Using the stream sediment classification developed for Illinois by Kelly and Hite (1984), total volatile sulfides were considered to be slightly elevated (>6.5%) at Site 1, elevated (>8.8%) at sites 3 and 11, and highly elevated (>13%) at Site 12.

The geometric mean concentrations of Mn measured at our Clinch River tributary and mainstem sites were substantially greater than the geometric mean for surficial soils in the eastern United States reported by Shacklette and Boerngen (1984). Geometric means for 17 other metals were below, or fell within about two standard deviations above, those reported by Shacklette and Boerngen (1984) for the eastern United States (Table 14). Because the values shown as below detection in Table 11 (denoted by a <) were set equal to the detection limit for calculation purposes, Mo appears higher in Table 14. It was only detected at two sites.

Application of the Illinois stream sediment classification developed by Kelly and Hite (1984) to the results for nine metals in the Clinch River (Table 15) indicated that Cd, Cu, and Mn at all sites, and all metals at Site 8, were in their respective non-elevated categories. Chromium was in the extremely elevated category at Site 12 and four metals (As, Cr, Fe, and Pb) were elevated at Site 11. Iron was also elevated at three other sites (3, 5, and 12).

Sediment guidelines for nine metals (As, Cd, Cr, Cu, Pb, Hg, Ni and Zn) were developed by Sullivan *et al.* (1985) for the State of Wisconsin. These guidelines range from 0.1 ppm (Hg) to 100 ppm (Cr, Cu, Ni and Zn). For these nine metals, none of our results exceeded the respective Wisconsin guidelines.

Stewart *et al.* (1992) reported concentrations (ppm, dry weight) of Cd (13), Cr (298), Cu (339), Hg (56), Ni (164), and Zn (954) in the sediment samples from East Fork Poplar Creek near Oak Ridge, Tennessee. Their results were much higher than most of ours except for Cr (310) at Site 12 (Copper Creek) and Mn. Manganese concentrations at nine of our sites were slightly higher than that (565) reported by Stewart *et al.* (1992).

The Ontario Ministry of the Environment (Persaud et al 1989; Jaagumagi 1992) has developed sediment criteria for ten metals. Of our 99 results available for comparison with these, only Cr at Site 12 exceeded the respective limit of tolerance level (33 ppm) or severe effects level (Table 16). Cadmium was below the no effect level (0.6 ppm) at all sites, while Zn was greater than the no effect level (65 ppm) only at Site 2. Copper, Fe, and Hg were below the respective 1989

Table 14. Comparison of geometric means for metals (ppm, dry weight) in Clinch River sediments with those reported by Shacklette and Boerngen (1984).

Metals	Eastern United States	Clinch River Tributaries	Clinch River Mainstem
Al (%)	3.30	0.999	0.994
As	4.80	5.96	5.15
B	31	8.51	7.17
Ba	290.00	72.23	92.20
Be	0.55	0.73	0.87
Cr	33.00	35.59	17.91
Cu	13.00	9.32	14.91
Fe (%)	1.40	1.79	1.96
Hg	0.081	0.03	0.04
Mg (%)	0.21	0.37	0.27
Mn	260	561	730
Mo	0.32	1.55	0.97
Ni	11.00	14.22	18.22
Pb	14.00	18.85	19.40
Se	0.30	0.25	0.30
Sr	53.00	13.04	22.08
V	43.00	20.92	18.38
Zn	40.00	49.39	51.18

*Values for Al, Fe and Mg are expressed as percent.

Table 15. Comparison of metals detected in Clinch River sediment samples (ppm, dry weight) with the Illinois stream sediment classification* developed by Kelly and Hite (1984).

Metals	Sites											
	1	2	3	4	5	6	8	10	11	12		
As	SE	NE	---	NE	NE	SE	NE	NE	SE	NE		
Cd	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE		
Cr	NE	E	E	SE	E	NE	NE	SE	HE	Ex		
Cu	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE		
Fe	NE	SE	E	SE	E	NE	NE	SE	E	E		
Hg	NE	NE	NE	NE	NE	NE	NE	SE	NE	NE		
Mn	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE		
Pb	NE	NE	NE	NE	NE	E	NE	NE	SE	NE		
Zn	NE	SE	NE	NE	NE	NE	NE	NE	NE	NE		

*NE-non-elevated; SE-slightly elevated; E-elevated; HE-highly elevated; Ex-extremely elevated

Table 16. Sediment quality criteria (ppm, dry weight) developed by the Ontario Ministry of the Environment.

<u>Metals</u>	<u>No Effect Level*</u>	<u>Lowest Effect Level</u>		<u>Limit of Tolerance*</u>	<u>Severe Effect Level**</u>
		<u>1989*</u>	<u>1992**</u>		
As	4.0	5.5	6.0	33.0	33.0
Cd	0.6	1.0	0.6	10.0	10.0
Cr	22.0	31.0	26.0	111.0	110.0
Cu	15.0	25.0	16.0	114.0	110.0
Fe (%)	2.0	3.0	2.0	4.0	4.0
Pb	23.0	31.0	31.0	250.0	250.0
Mn	400.0	457.0	460.0	1110.0	1100.0
Hg	0.1	0.12	0.20	2.0	2.0
Ni	15.0	31.0	16.0	90.0	75.0
Zn	65.0	110.0	120.0	800.0	820.0

* Persaud, et al. (1989).

** Jaagumaji (1992).

lowest effect levels (Table 16), and only one result (Cu at Site 8) exceeded the applicable 1992 lowest effect level (16 ppm). The majority of metal concentrations fell between the respective lowest effect levels and the limit of tolerance values or severe effects levels (Table 16).

Our Cd, Fe, Hg, and Zn results were typically near or below those reported by Birge *et al.* (1987) and Francis *et al.* (1984) for control sediment used to evaluate sediment toxicity. The average particle size distribution in our samples was also comparable to that reported by Birge *et al.* (1987) and Francis *et al.* (1984). These investigators noted that rainbow trout early life stage survival was reduced to 70%, 45%, and 23% when exposed to sediment containing 0.180 ppm, 1.050 ppm, and 12.10 ppm Hg, respectively. They also reported significant reductions in rainbow trout early life stage survival using sediment with 2.15 ppm Cd, and also with sediment containing Zn at 121.4 ppm.

In tests with Cd-enriched sediment using embryo-larval stages of the leopard frog (*Rana pipiens*), goldfish (*Carassius auratus*) and largemouth bass (*Micropterus salmoides*), Francis *et al.* (1984) reported significant mortality at hatching or posthatching when sediment Cd concentrations were about 1000 ppm. It is important to note, however, that these three organisms did not have direct contact with the sediment, and that they have a shorter developmental time than rainbow trout. Overall, our individual results for Hg, Cd, and Zn were below the sediment concentrations used by Birge *et al.* (1987) and Francis *et al.* (1984).

Becker *et al.* (1995) observed that amphipod survival was reduced at three sites and chironomid survival at four sites using 10-d sediment toxicity tests. They used sediments containing Cd (0.9-3 ppm), Cr (19-33 ppm), Cu (12-83 ppm), Pb (12-150), Hg (0.9-69 ppm), Ni (7-29 ppm), and Zn (50-220). In our samples, Cu, Pb, Ni, and Zn fell in these ranges at several sites, while Cd and Hg were below these ranges at all sites. Although we did not detect any organochlorine compounds in our samples, polycyclic aromatic hydrocarbons (PAHs) were not analyzed. In the samples tested by Becker *et al.* (1995), PCBs ranged from 0.10-0.36 ppm in three samples where survival was reduced, and PAHs varied from 23-330 ppm in four samples.

At all sites, six metals (Cd, Cu, Pb, Hg, Ni, and Zn) were below concentrations in control sediments used by Wiederholm and Dave (1989) in toxicity tests with *Daphnia magna* and *Tubifex tubifex*. Chromium at Site 12 was in the mid-range of the Cr concentrations reported by Wiederholm and Dave (1989). Acute tests (24-hr and 48-hr) were performed with *D. magna*. Survival, weight, and number of young were measured in the tests with *T. tubifex* which ran 270 days.

We found significant correlations of several metals with aluminum and iron, but our dataset is fairly small. Also, we are not aware of a suitable database for use in evaluating aluminum and iron as reference elements in this area, as some investigators have done in other parts of the country (Pardue *et al.* 1992; Schropp *et al.* 1990; White and Tittlebaum 1984, 1985).

Total volatile sulfides (TVSs) were analyzed, but acid volatile sulfides (AVSs) were not. The TVSs analytical procedure is completely different from the AVSs procedure, and we are not aware of a way to estimate AVS values from TVS results. Analysis of AVSs, and simultaneously extracted metals (SEM), should be considered in future investigations of metals in Clinch River sediments. While AVSs may help explain the toxicity of some metals (Allen *et al.* 1993; Ankley *et al.* 1994; Di Toro *et al.* 1992), it must be used cautiously (Chapman 1996).

Other studies on the Clinch River have investigated wastewater treatment plant (WWTP) effluents using the rainbow mussel (*Villosa iris*) and the Asian clam (*Corbicula fluminea*) (Goudreau *et al.* 1993), and assessed the impacts of Cu and Zn (in water) on benthic insect communities (Clements *et al.* 1992). The toxicity of Cu and Zn (in water), and sediment toxicity, to early life stages of mussels in the nearby Powell River have also been studied (McCann 1993).

Goudreau *et al.* (1993) reported that monochloramine and unionized ammonia likely inhibited mollusk recovery at least 0.1 km downstream from the seven WWTPs in their study. In studies with outdoor experimental streams, Clements *et al.* (1992) noted that several species of Ephemeroptera were completely eliminated when exposed to 25 ppb Cu for ten days, but that chironomids (Chironomidae: Orthocladini) abundance increased. In field studies on the Clinch River, these investigators reported that numbers of taxa and individuals were severely reduced downstream of the Clinch River Steam Plant (Russell County, Virginia), and did not recover to upstream numbers for about two miles downstream. Effluent Cu concentrations (ppb) measured by Clements *et al.* (1992) during 1986-1989 varied from 480 (1987) to 260 (1989). Corresponding instream concentrations measured about 50 m downstream from the effluent were 127 (1987) and 52 (1989). Although Cu and Zn concentrations were not reported for the recovery site, concentrations upstream of the effluent were below detection limits.

McCann (1993) found that glochidia of the Cumberland moccasin shell (*Medionidus conradicus*) were more sensitive to zinc (in water) than those of the pheasantshell (*Actinonaias pectorosa*) or the rainbow mussel in acute (24-hr and 48-hr) tests. For Cumberland moccasin shell glochidia, LC₅₀ values for Zn ranged from 423 to 75 ppb. Copper was found to be 5 to 15 times more toxic than Zn, and Zn appeared to reduce Cu toxicity in certain mixtures.

Although McCann (1993) conducted sediment toxicity tests using Powell River sediment and juvenile mussels, metal concentrations were not measured in the sediment samples. While her results did indicate that sediment in some areas of the Powell River may be toxic to juvenile mussels, toxicity could also have been linked to water quality. These studies illustrate that multiple contaminant impacts are occurring in the Upper Tennessee River Basin.

SUMMARY

Our study was limited to the collection and analysis of sediment samples. The current lack of national sediment quality criteria in the United States prompted us to use sediment quality guidelines developed in Canada. Based on these, our study did not indicate overall impacts from most individual metals at most sites. We do think that manganese may play an important role in impacts to mussel populations in the Clinch River. On average, it was elevated at mainstem and tributary sites, and exceeded the Canadian lowest effect levels at both groups of sites.

It should be noted that the Canadian sediment quality guidelines were not developed specifically for freshwater mussels. While these guidelines were developed for several individual metals, they do not address cumulative impacts from exposure to multiple metals. Although they are useful, we do not necessarily consider them to be strictly protective of mussel species, particularly species listed as threatened or endangered.

The most disturbing finding of our study is the situation observed at Copper Creek. A review of several recovery plans (FWS 1983a, 1983b, 1984, 1989) and discussions with Jim Widlak (FWS, personal communication) indicated that Copper Creek provides habitat for the threatened yellowfin madtom (*Noturus flavipinnis*), the endangered duskytail darter (*Etheostoma sp.*), three endangered mussels (shiny pigtoe, *Fusconaia cor*; fine-rayed pigtoe, *Fusconaia cuneolus*; and littlewing pearly mussel, *Pegias fabula*), and the purple bean (*Villosa perpurpurea*), which is proposed as endangered.

Sites located on Copper Creek had the highest concentrations of aluminum, barium, boron, beryllium, mercury and vanadium. Chromium exceeded the limit of tolerance established in the Canadian sediment quality guidelines. Manganese averaged 743 ppm (dry weight) at the three Copper Creek sites, which exceeded the Canadian lowest effect level. This may help to explain the declines in numbers observed for some species in this creek.

RECOMMENDATIONS

We recommend that the following activities be included in any additional investigations on the Clinch River:

- 1) determine contaminant residues in nonlisted mussel species which are co-located with listed mussel species;
- 2) conduct larval and juvenile mussel toxicity tests using sediment and water from the Clinch River and selected tributaries, including Copper Creek;
- 3) measure contaminants in water and sediment in conjunction with the toxicity tests;
- 4) conduct cholinesterase inhibition assays on non-listed mussel species;
- 5) analyze sediment samples for polycyclic aromatic hydrocarbons; and
- 6) analyze sediment samples for acid volatile sulfide and simultaneously extracted metals.

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APPENDIX A

ANALYTICAL METHODS

Organic Analytical Methods-Clinch River Project
Laboratory: Mississippi State Chemical Laboratory

Method

Code

Method Description

001

Analysis For Organochlorine Pesticides and PCBs In Animal and Plant Tissue

- I. Ten-gram tissue samples are thoroughly mixed with anhydrous sodium sulfate and Soxhlet extracted with hexane for seven hours. The extract is concentrated by rotary evaporation; transferred to a tared test tube, and further concentrated to dryness for lipid determination. The weighed lipid sample is dissolved in petroleum ether and extracted four times with acetonitrile saturated with petroleum ether. Residues are partitioned into petroleum ether which is washed, concentrated, and transferred to a glass chromatographic column containing 20 grams of Florisil. The column is eluted with 200 ml 6% diethyl ether/94% petroleum ether (Fraction I) followed by 200 ml 15% diethyl ether/85% petroleum ether (Fraction II). Fraction II is concentrated to appropriate volume for quantification of residues by packed or capillary column electron capture gas chromatography. Fraction I is concentrated and transferred to a Silicic acid chromatographic column for additional cleanup required for separation of PCBs from other organochlorines. Three fractions are eluted from the silicic acid column. Each is concentrated to appropriate volume for quantification of residues by megabore column, electron capture gas chromatography. PCBs are partitioned into Fraction II.

Inorganic Analytical Methods -- Clinch River Project
Laboratory: Environmental Trace Substances Research Center

Method

<u>Code</u>	<u>Method Description</u>
003	Nitric - Perchloric Digestion - (I.C.P.)

- III. Approximately 0.5 g. of sample are weighed into a freshly cleaned 100 ml. quartz Kjeldahl flask. (Samples containing a high percent of silica and sediment samples are digested in 100 ml. teflon beakers.) For water samples, 50 ml. of sample is measured into a teflon beaker. Slowly 15 ml. of concentrated sub-boiled HNO₃ and 2.5 ml. of concentrated sub-boiled HC104 added. Foaming may occur with some samples. If the foaming starts to become excessive, the container is cooled in a beaker of cold water. After the initial reaction has subsided, the sample is placed on low heat until the evolution of dark red fumes ceases. Gradually, the heat is increased until the HNO₃ begins refluxing and samples are then allowed to reflux overnight. This decreases the chance for charring during the reaction with HC104. After refluxing, the heat is gradually increased until the HNO₃ is driven off, and the reaction with HC104 occurs. When dense white fumes from the HC104 are evident, the samples are removed from the heat and allowed to cool. Two ml. of concentrated sub-boiled HCl are added. The flasks are replaced on the heat and warmed until the containers are hot to the touch or start to boil. They are then removed from the heat, and 5-10 ml. of deionized water added. Samples are then allowed to cool, diluted with deionized water in a 50 ml. volumetric flask, and transferred to a clean, labeled, 2 oz. polyethylene bottle.

Method

<u>Code</u>	<u>Method Description</u>
004	Inductively Coupled Plasma (ICP)

- IV. The instrument used for ICP analysis is a Jarrell-Ash Model 1100 Mark III with 40 analytical channels, controlled by a Digital Equipment Company (DEC) 11/23+ computer with two RLO2 disk drives, DEC VT100 terminal, and DEC LA120 Decwriter III. The instrument is standardized with a series of seven standards containing 36 elements. After the standardization, the detection limit is determined by taking ten integrations of the zero standard; three times the standard deviation of the mean is used as the detection limit. Instrumental quality control samples are then analyzed to check the ICP operation. If the values are acceptable, the samples are then analyzed. Standards are run every 10-15 samples to check for drift. If the drift is more than 5%, the instrument is restandardized. After the analysis is completed, the data are transferred to the Perkin-Elmer LIMS computer for calculation. The final detection limit for each element is further increased by 4% of the magnitude of the spectral interferences from the other elements. The data are checked before calculation to correct for possible errors

in sample number, weight, volumes and dilution. Results are calculated using the ICP calculation program written by ETSRC computer staff, which corrects for blanks, standard drift, spectral interferences, sample weight, sample volume and dilution. After quality control data are reviewed, a final report is generated using a Hewlett Packard laser jet printer.

Method

<u>Code</u>	<u>Method Description</u>
005	Percent (%) Moisture

- V. For animal tissue and sediments of sufficient size, percent moisture is determined by placing a weighed aliquot of the sample in a Fisher Isotemp oven and drying at 103 - 105 C. The dried sample is then weighed and the data entered into a computer program to generate the percent moisture and the final report.

Plants, and other samples too small for oven-dried moisture determination, are freeze-dried in a Labcono Freeze-Dryer 8. Initial and final weights are entered into a computer program to generate a percent moisture report.

Method

<u>Code</u>	<u>Method Description</u>
006	Homogenization

- I. Large tissue samples, such as whole fish, are first run through a meat grinder one or more times depending on the size of the sample. An aliquot of the ground sample is weighed and frozen. For smaller tissue samples and plant samples the entire sample is weighed and frozen. For sediments, the sample is mixed and an aliquot weighed and frozen. The frozen samples are placed in a Labcono Freeze Dryer 8 until the moisture had been removed. The dry samples are then weighed and further homogenized using a blender, or Spex Industries, Inc. Model 8000 mixer/mill with tungsten-carbide vial and balls.

Method

<u>Code</u>	<u>Method Description</u>
007N	Nitric - Perchloric Digestion - (Selenium)

- VII. Approximately 0.5 g. of sample are weighed into a freshly cleaned 100 ml. quartz Kjeldahl flask. Samples containing a high percent of silica and sediment samples are digested in 100 ml. teflon beakers. For water samples, 50 ml. of sample is measured into a teflon beaker. Slowly, 15 ml. of concentrated sub-boiled HNO₃ and 2.5 ml. of concentrated sub-boiled HC10₄ are added. Foaming may occur with some samples. If

the foaming starts to become excessive, the container is cooled in a beaker of cold water. After the initial reaction subsides, the sample is placed on low heat until the evolution of dark red fumes ceases. Gradually, the heat is increased until the HNO₃ begins refluxing, and samples are allowed to reflux overnight. This decreases the chance for charring during the reaction with HC104. After refluxing, the heat is gradually increased until the HNO₃ is driven off, and the reaction with HC104 has occurred. When dense white fumes from the HC104 are evident, the samples are removed from the heat and allowed to cool. Two ml of concentrated sub-boiled HCl are added. The flasks are replaced on the heat and warmed until the containers are hot to the touch or start to boil. They are removed from the heat, and 5-10 ml. of deionized water added. Samples are allowed to cool, diluted using deionized water in a 50 ml. volumetric flask, and transferred to a clean, labeled, 2 oz. polyethylene bottle.

Method

<u>Code</u>	<u>Method Description</u>
009	Arsenic and Selenium by Hydride

- IX. A Varian VGA-76 hydride generation accessory is mounted on either a Perkin-Elmer Model 603 AA or Model 3030 (B) AA and Electrodeless Discharge Lamps (EDL) are used. The instrument and EDL settings are taken from the instrument manuals. The burner mount for a Perkin-Elmer Model 10 Hydride generator has been modified slightly to hold the Varian quartz cell. The cell is aligned in the light path of the burner chamber and a very lean flame used to heat the cell. Two stock solutions are used (50% v/v sub-boiled HCl and 0.6% NaBH₄ in 0.5% NaOH) for selenium, and concentrated sub-boiled HCl and 1% NaBH₄ in 0.5% NaOH are used for arsenic. Samples are diluted in 10% v/v sub-boiled HCl. Standards are prepared by diluting Fisher 1000 ppm stock solutions in 10% v/v sub-boiled HCl in the range of 0 to 20 ppb. The instrument is standardized to read directly in ppb using S1 = 5.00 and S2 = 20.00. After standardization, the standardization is checked by reading other standards such as 2.00, 10.00 and 15.00 ppb, and an instrument quality control sample with a known value. If the standards and quality control sample results are acceptable, the detection limit is determined by reading the zero standard ten times and multiplying the standard deviation of the mean by two. Samples are then analyzed by taking an integrated reading for 3 seconds after the plateau is reached for the sample. This occurs approximately 45 seconds after the sample tube is placed in the sample. Standardization is checked every 8-15 samples and approximately 10% of the samples are checked by the method of additions to monitor matrix effects. Matrix effects are usually not significant with the VGA-76. The data are corrected for drift of the standard curve and entered into the AA calculation program. This program corrects for blank, dilution, sample weight and sample volume, and records the data in the LIMS database for report generation.

Method

<u>Code</u>	<u>Method Description</u>
011	Nitric Reflux Digestion for Mercury

- XI. Approximately 0.5 g. of sample are weighed into a freshly cleaned 50 ml. round bottom flask with 24/40 ground glass neck. For waters, 10 ml of sample are measured into the flask. Five ml of concentrated sub-boiled HNO₃ are added and the flask placed under a 12-in. water-cooled condenser with water running through the condenser. The heat is increased to allow the HNO₃ to reflux no more than 1/3 the height of the columns. Samples are allowed to reflux for two hours, then the heat is turned off and the sample allowed to cool. The condensers are rinsed with 1% v/v HCl and the flasks removed. The samples are diluted with 1% v/v HCl in a 50 ml volumetric flask and then transferred to a clean, labeled, 2 oz. flint glass bottle.

Method

<u>Code</u>	<u>Method Description</u>
012	Mercury - Cold Vapor Atomic Absorption

- XII. Equipment used for Cold Vapor Atomic Absorption include: Perkin-Elmer Model 403 AA; Perkin- Elmer Model 056 Recorder; Technicon Sampler I; Technicon Pump II; a glass cell with quartz windows and capillary tube for entry and exit of the mercury vapor; and a liquid-gas separator. The samples are placed in 4 ml sample cups at least 3/4 full. The samples are mixed with hydroxylamine for preliminary reduction, then stannous chloride for reduction to the mercury vapor. The vapor is separated from the liquid and passed through the cell mounted in the light path of the burner compartment. The peaks are recorded and the peak heights measured. The standardization is done with at least 5 standards in the range of 0 to 10 ppb. The correlation coefficient is usually 0.9999 or better and must be at least 0.999 to be acceptable. A standard is run every 8-10 samples to check the standardization. This is usually less than 5%. Standards are preserved with 10% v/v HNO₃, 1% v/v HCl, and 0.05% w/v K₂Cr₂O₇. The solution concentrations are calculated and the data entered into the AA calculation program which corrects for blank, dilution, sample weight and sample volume, and enters the data into the LIMS system for report generation.

Method

<u>Code</u>	<u>Method Description</u>
015	Total Volatile Solids (TVS)

- XV. Aliquots of oven-dried samples are weighed into previously fired crucibles. The crucibles with samples are then placed in an oven and fired at 550°C for a minimum of 4 hours. The crucibles are allowed to partially cool and then placed in a desiccator until

they cool to room temperature, and are then weighed. The oven-dried weights and the weights of the samples after firing are entered into the computer and TVS is calculated using the following formula:

$$\frac{\text{Oven-dry Sample Weight} - \text{Fired Sample Weight}}{\text{Oven-dry Sample Weight}} = \text{TVS}$$

Method

<u>Code</u>	<u>Method Description</u>
018	Total Organic Carbon Analysis for Soil and Sediment - Dry Oxidation Method

XVIII. The analyst will need to make three (3) replicates of each blank and each sample. Label all the ampules with a high temperature grease pencil before weighing. Break all ampules open, trying to get as little glass inside the ampules as possible. When not using, cover the ampules with aluminum foil to keep additional contaminants out of the ampules.

Sample Preparation

Place ampule on pan of 5 place balance, tare to zero, add the desired mass of sample (usually 3-5mg), record the mass of the sample, put the ampule in the holding rack. Cover the ampule with aluminum foil. Start the same procedure with the next ampule. Add 100 ul of 10% HCl solution to all of the sample and blank ampules. The fizzing that may be observed is the reaction between the HCl and any inorganic carbon in the sample. Put the uncovered ampules into an oven and bake at 100 C for at least one (1) hour or however long it takes for sample to reach dryness. Prepare a set of KHP stds. ranging from 25 ug to 250 ug C following the KHP standard prep method. These will be used to determine a standard curve for TOC values.

KHP Standard Preparation

2.126 grams of Potassium Hydrogen Phthalate is weighed then transferred to a 100 ml volumetric flask. The dilution to 100 mls is done with boiled D.I. H₂O. (The D.I. H₂O is boiled to drive off as much carbon as possible). This reagent (which equals 10,000 ug/ml C) is further diluted to 500, 400, 300, 250, 200, 100 and 50 ug/ml C levels. One half ml (500 ul) pipet is then used to make the 250 thru 25 ug C standards. Spikes are also made from the same reagent.

At least 4 ampules are made of each standard, and more depending on the total amount of analyses. The standards are dried at 100 degrees C but usually take as long as 4 hrs. to dry because of their ½ ml liquid volume.

After all visible liquid has evaporated from samples and standards remove the ampules from the drying oven and allow to cool. When the ampules are cool, add one (1) dipper (200 mg) of the combusted cupric oxide to each ampule.

Purge each ampule with oxygen from the Purge & Seal Unit for 4 to 6 minutes and then seal. The ampules can then be carefully placed in the muffle furnace and baked at 550 C for 4-5 hours. Cool and then analyze using a non-dispersive infrared analyzer. (Oceanographic International Corp.)

Analysis

Set up standard curve using the KHP standards. Three or four ampules are broken of each standard to get a good representative curve. After the curve is established, begin analyzing the samples and determine their ugC according to this KHP curve. Detection limit for a 4 mg (0.004 gm) sample is 0.1% or 1000 ug/g dry weight

Method

<u>Code</u>	<u>Method Description</u>
019	Grain Size Determination

XIX. Sieve an air dried, crushed sample. Place approximately 10g of sample in a 500 ml Fleaker. Those samples with greater than 1.0% organic carbon (wet weight) need to be treated to remove organic matter. Add 10 mls deionized water, 10 mls 30% H₂O₂, and 1 drop acetic acid. Stir, cover and heat to approximately 60 C. Then add additional H₂O₂ in 5 ml increments at 15 minute intervals until organic matter is oxidized (no bubbling). If the reaction is too vigorous, slow with the addition of DI water. After organic matter is removed, oven dry the samples (still in Fleakers) at 105 C. Weigh samples. Add 10 mls sodium hexametaphosphate to each sample, and bring volume to approximately 150 mls with DI water. A blank consisting of 10 mls sodium hexametaphosphate and 150 mls DI water should also be made at this time. Put stoppers in the Fleakers and shake either for 4 hours or overnight (minimum 12 hours) on a horizontal reciprocating shaker (120 oscillations/minute).

Sieve samples through a 50 um sieve to remove sand fraction. Transfer the sand fraction that remains in the sieve to a weighing pan, oven-dry, cool in a desiccator and weigh. Arrange the fleakers for pipetting and bring volume to 400 mls with DI water. Determine average temperature of the suspensions, and cover each Fleaker with a watch glass.

Remove watch glass from the first Fleaker, cap with a rubber stopper, and shake vigorously for approximately 10 seconds. Then shake end-over-end for 15 seconds.

Remove rubber stopper and replace watch glass. Shake samples at approximately 2 minute intervals.

Pipet an aliquot at 5.0 cm below the surface within a 15-to 20-second interval, discharge into a weighing pan, rinse the pipet and add the rinse to the pan. Oven dry the aliquots, cool in a desiccator, then weigh. The correction factor for the weight of the sodium hexametaphosphate must be subtracted to obtain the weight of the clay.

Percentages of sand, silt and clay are then determined according to the following equations:

$$\% \text{ sand} = 100 (\text{total sand weight} / \text{total soil weight})$$

$$\% \text{ clay} = (\text{clay weight}) (400 / \text{pipette volume}) (100 / \text{total soil weight})$$

$$\% \text{ silt} = 100 \times (\% \text{ sand} + \% \text{ clay})$$

Table 1. Setting times at corresponding temperature for pipetting <2-um fraction at a 5-cm depth.

Temperature Settings <u>C</u>	Times <u>h:min</u>
17	4:22
18	4:15
19	4:09
20	4:03
21	3:57
22	3:51
23	3:46
24	3:41
25	3:36
26	3:31
27	3:26
28	3:22
29	3:17
30	3:13

APPENDIX B

QUALITY ASSURANCE/QUALITY CONTROL

Table B-1. Recoveries for Clinch River Samples.

<u>Analyte</u>	<u>Spike Level (ppm)</u>	<u>Amount Recovered (ppm)</u>	<u>Percent Recovery</u>
HCB	0.04	0.027	67.5
alpha-chlordane	0.04	0.039	97.5
beta-BHC	0.04	0.041	102.5
cis-nonachlor	0.04	0.038	95
dieldrin	0.04	0.039	97.5
endrin	0.04	0.036	90
gamma-BHC	0.04	0.04	100
heptachlor epoxide	0.04	0.043	107.5
mirex	0.04	0.039	97.5
o,p'-DDE	0.04	0.045	112.5
o,p'-DDT	0.04	0.043	107.5
oxychlordane	0.04	0.044	110
p,p'-DDD	0.04	0.045	112.5
p,p'-DDE	0.04	0.04	100
p,p'-DDT	0.04	0.041	102.5
trans-nonachlor	0.04	0.04	100

Table B-2. Duplicate Results for Clinch River Sediment Samples.

<u>Analyte</u>	<u>Sample Number</u>	<u>Initial Result*</u>	<u>Duplicate Result*</u>	<u>Average</u>	<u>Relative % Difference</u>
% Moisture	8B	57%	61.6%	59.3	7.76
Al	10B	13600	15200	14400	11.11
As	10B	5.2	5.4	5.3	3.77
B	10B	10	11	10.5	9.52
Ba	10B	105	106	105.5	0.95
Be	10B	0.98	0.98	0.98	0
Cd	10B	<0.2	0.2	0.15	66.67
Cr	10B	20	21	0.5	4.88
Cu	10B	13	13	13	0
Fe	10B	19000	19100	19050	0.52
Grain Size-Clay	8B	13.2%	14.5%	13.85	9.39
Grain Size-Sand	8B	66.3%	63.7%	65	4
Grain Size-Salt	8B	20.5%	21.7%	21.1	5.69
Hg	10B	0.075	0.075	0.075	0
Mg	10B	3580	3690	3635	3.03
Mn	10B	691	685	688	0.87
Mo	10B	<1	<1	0.5	0
Ni	10B	15	15	15	0
Pb	10B	25	24	24.5	4.08
Se	10B	0.2	<0.2	0.15	66.67
Sr	10B	12.5	12.8	12.65	2.37
Total Organic Carbon	4B	1.6%	1.6%	1.6	0
Total Volatile Solids	10B	7.7%	7.7%	7.7	0
V	10B	26	27	26.5	3.77
Zn	10B	37.6	39.1	38.35	3.91

*Results are ppm, dry weight unless indicated otherwise.

Table B-3. Results for Reference Materials Analyzed with Clinch River Sediment Samples

<u>Analyte</u>	<u>S.R.M. ID</u>	<u>S.R.M. Name</u>	* Certified Reference Value (ppm / %)	Confidence Interval	Result (ppm / %)	Percent Recovery
Al	NIST 2704	Buffalo River Sediment	61100	1600	11700	19.15
As	NIST 2704	Buffalo River Sediment	23.4	0.8	18	76.92
Ba	NIST 2704	Buffalo River Sediment	414	12	80.5	19.44
Cd	NIST 2704	Buffalo River Sediment	3.45	0.22	3.3	95.65
Cr	NIST 2704	Buffalo River Sediment	135	5	72	53.33
Cu	NIST 2704	Buffalo River Sediment	98.6	5	84.1	85.29
Fe	NIST 2704	Buffalo River Sediment	41100	1000	27800	67.64
Grain Size-Clay	ETSR SCL-1	Clay	30.8%	1.6	31.3%	101.62
Grain Size-Sand	ETSR SCL-1	Sand	15.8%	1	16.7%	105.7
Grain Size-Silt	ETSR SCL-1	Silt	53.4%	1.8	52%	97.38
Hg	NIST 2704	Buffalo River Sediment	1.44	0.07	1.4	97.22
Mg	NIST 2704	Buffalo River Sediment	12000	200	7890	65.75
Mn	NIST 2704	Buffalo River Sediment	555	19	437	78.74
Ni	NIST 2704	Buffalo River Sediment	44.1	3	34	77.1
Pb	NIST 2704	Buffalo River Sediment	161	17	140	86.96
Se	NIST 2704	Buffalo River Sediment	1.1	--	0.7	63.64
Sr	NIST 2704	Buffalo River Sediment	130	--	32.3	24.85
V	NIST 2704	Buffalo River Sediment	95	4	21	22.11
Zn	NIST 2704	Buffalo River Sediment	438	121	375	85.62

* Only certified analytes list a confidence interval -- all others are considered reference values.

Table B-4. Metals (ppm, dry weight) and Total Organic Carbon (%) Recoveries for Clinch River Sediment Samples

<u>Analyte</u>	<u>Sample Number</u>	<u>Spike Level</u>	<u>Amount Recovered</u>	<u>* Spike / Background</u>	<u>Percent Recovery</u>
Al	11B	9900.988	10100	0.97	102.01
As	11B	9.901	10.7	1.08	108.07
B	11B	99.0099	62.1	16.78	62.72
Ba	11B	19.802	20	0.27	101
Be	11B	9.901	9.55	10.42	96.45
Cd	11B	9.901	9.4	33	94.94
Cr	11B	49.5049	47	1.1	94.94
Cu	11B	99.0099	92.8	3.75	93.73
Fe	11B	9900.988	10100	0.38	102.01
Hg	11B	0.996	1.049	19.53	105.32
Mg	11B	3960.396	3730	1.79	94.18
Mn	11B	1980.198	1825	2.66	92.16
Mo	11B	49.5049	43	49.5	86.86
Ni	11B	99.0099	89	9	89.89
Pb	11B	198.0198	178	6.19	89.89
Se	11B	9.901	8.8	49.5	88.88
Sr	11B	49.5049	46.9	2.51	94.74
Total Organic	3B	2.906977%	2.9%	4.84%	99.76
V	11B	49.5049	50.9	1.51	102.82
Zn	11B	396.0396	364.9	6.35	92.06

* For a spike to be a valid measure of method accuracy, this ratio must be higher than 1.0.

Table B-5. Metals and Total Organic Carbon Results for Procedural Blank Sample.

<u>Parameter</u>	<u>Result (total ug)</u>
Al	<2.00
As	<0.05
B	<1.00
Ba	<0.05
Be	<0.05
Cd	<0.10
Cr	<0.50
Cu	<0.20
Fe	<0.50
Hg	<0.008
Mg	0.34
Mn	<0.01
Mo	<0.50
Ni	<1.00
Pb	<2.00
Se	0.10
Sr	<0.50
Vn	<0.20
Zn	<0.10
Total Organic Carbon (TOC)	<5.00

APPENDIX C

FIELD SAMPLING INFORMATION

Table C-1. Clinch River Field Sampling Information

<u>Site</u>	<u>Date</u>	<u>Water Temperature (°C)</u>	<u>Dissolved Oxygen (ppm)</u>	<u>Conductivity (umhos)</u>
1	17 Sept. 1991	22.0	6.0	230
2	17 Sept. 1991	23.4	7.6	340
3	17 Sept. 1991	27.0	8.6	245
4	17 Sept. 1991	27.0	9.1	410
5	17 Sept. 1991	23.5	7.9	290
6	18 Sept. 1991	19.0	9.2	250
8	18 Sept. 1991	24.0	6.5	380
10	18 Sept. 1991	22.5	8.4	300
11	18 Sept. 1991	16.5	10.0	300
12	18 Sept. 1991	23.5	10.0	335

APPENDIX D

FIELD SAMPLING NOTES FOR CLINCH RIVER PROJECT

Site 1

Description/Conditions: Big Sycamore Creek at Raphsis Road, TN; foggy, no wind
Air temperature: 24.0 C
H₂O temperature: 22.0 C
Conductivity: 230 umhos
Dissolved Oxygen: 6.0 ppm (no correction factor for altitude was used)
Date Sampled: 17 September 1991

Site 2

Description/Conditions: Big War Creek at Providence Church 1/3 mile north of Indian Creek Road; still, hazy, sunshine
Air temperature:
H₂O temperature: 23.4 C
Conductivity: 340 umhos
Dissolved Oxygen: 7.6 ppm (no correction factor for altitude was used)
Date Sampled: 17 September 1991

Site 3

Description/Conditions: Blackwater Creek 1/2 mile northwest of Highway 33 on Livesay Road (across from Red Barn belonging to Livesays); partly cloudy, warm, hazy
Air temperature: 34.0 C
H₂O temperature: 27.0 C
Conductivity: 245 umhos
Dissolved Oxygen: 8.6 ppm (no correction factor for altitude was used)
Date Sampled: 17 September 1991

Site 4

Description/Conditions: Clinch River 150 m downstream from TN-VA state lines; partly cloudy, hazy, very warm, still
Air temperature: 33.0 C
H₂O temperature: 27.0 C
Conductivity: 410 umhos
Dissolved Oxygen: 9.1 ppm (no correction factor for altitude was used)
Date Sampled: 17 September 1991

Site 5

Description/Conditions: N. Fork of Clinch River approximately 80 m downstream of VA Highway 621 ford; warm, hazy

Air temperature: 26.5 C
H₂O temperature: 23.5 C
Conductivity: 290 umhos
Dissolved Oxygen: 7.9 ppm (no correction factor for altitude was used)
Date Sampled: 17 September 1991

Site 6

Description/Conditions: Stock Creek, under railroad trestle 0.5 km upstream from junction of VA Highways 23 and 871; foggy, still, cool

Air temperature: 20.0 C
H₂O temperature: 19.0 C
Conductivity: 250 umhos
Dissolved Oxygen: 9.2 ppm (no correction factor for altitude was used)
Date Sampled: 18 September 1991

Site 8

Description/Conditions: Clinch River at Clinchport River Access Area; cool, foggy

Air temperature: 21.5 C
H₂O temperature: 24.0 C
Conductivity: 380 umhos
Dissolved Oxygen: 6.5 ppm (no correction factor for altitude was used)
Date Sampled: 18 September 1991

Site 10

Description/Conditions: Copper Creek at Jennings ford of VA Highway 627; cloudy foggy, humid

Air temperature: 25.0 C
H₂O temperature: 22.5 C
Conductivity: 300 umhos
Dissolved Oxygen: 8.4 ppm (no correction factor for altitude was used)
Date Sampled: 18 September 1991

Site 11

Description/Conditions: Copper Creek approximately 150 m upstream of Va Highway 674; hazy sunshine, warm
Air temperature: 23.5 C
H₂O temperature: 16.5 C
Conductivity: 300 umhos
Dissolved Oxygen: 10.0 ppm (no correction factor for altitude was used)
Date Sampled: 18 September 1991

Site 12

Description/Conditions: Copper Creek approximately 1.1 miles upstream from confluence with Little Copper Creek; cattle in creek above and below site, partly cloudy, warm, hazy, wind picking up
Air temperature: 32.0 C
H₂O temperature: 23.5 C
Conductivity: 335 umhos
Dissolved Oxygen: 10.0 ppm (no correction factor for altitude was used)
Date Sampled: 18 September 1991