

HEAVY METALS IN FLUVIAL SEDIMENTS  
OF THE PICHER MINING FIELD,  
NORTHEAST OKLAHOMA

By

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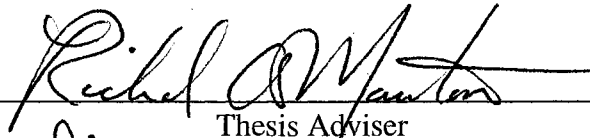
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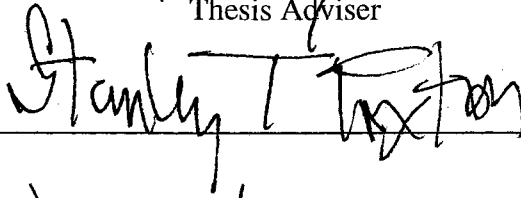
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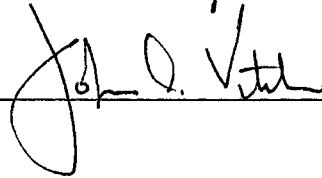
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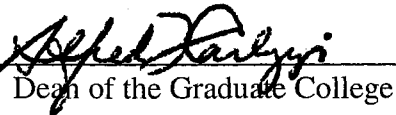
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## CHAPTER I

### INTRODUCTION

#### Problem Statement

Heavy metals are present in fluvial sediments of the Picher Mining Field as a result of lead and zinc ore mining. The first recorded ore production was in 1904 and the last record of significant production occurred in 1970 (Luza, 1986). The underground mine workings began to fill with water when mining and dewatering activities ceased, and acid mine water began discharging into Tar Creek from boreholes and air shafts in 1979 (OWRB, 1983). Water pumped from mine workings while the mines were operational was discharged into the Spring River (personal communication with Vitek, 2001). Over 360 hectares in the mining field remain covered with tailings piles (locally known as “chat”). The USGS collected stream sediment samples from Tar Creek in the 1980’s and analyzed the sediment samples for 16 different metals (Parkhurst et al., 1988).

I have chosen to concentrate on Pb, Zn, Cd, Ni, Cu, and Fe because of the adverse impact on the health of the ecosystem. Lead is particularly harmful to children and lead contamination has been linked to learning disabilities (Centers for Disease Control, 1991). Contamination by heavy metals in fluvial sediments is of interest to ranchers because young colts and calves were most likely to develop symptoms of trace metal toxicity through ingestion of contaminated forages. The animals recovered within a few



weeks when moved to meadows that had not been irrigated with surface water that had been impacted by a metal sulfide mining area (Levy et al., 1992).

### Purpose and Objectives

The purpose of the study is to determine if the concentrations of heavy metals have changed over time. The first objective is to assess fluvial sediments for Pb, Zn, Cd, Cu, Ni, and Fe and compare the results to those obtained by the USGS in 1983 and 1984. I will test the null hypothesis that no statistically significant differences exist in Pb, Zn, Cd, Cu, Ni, and Fe concentrations from the USGS data compared to the year 2000 data. It is important to determine if the concentrations of heavy metals in fluvial sediments of the mining area have changed over time so that the long term effects of ore mining can be evaluated after mining has ceased.

The second objective is to assess whether statistically significant correlations exist among heavy metals in fluvial sediments of the Picher Mining Field. I will test the null hypothesis that positive relationships do not exist among heavy metals, nor do relationships exist between particle size and heavy metal concentration when considering year 2000 data. Establishing that a correlation of heavy metals exists in the Picher Mining Field would be useful for possible remediation in the future.

## Study Area

The Picher Mining Field is located in Ottawa County in northeast Oklahoma and is part of the Tri-State lead and zinc mining district that includes portions of Oklahoma, Kansas, and Missouri (Fig. 1). Ore minerals were first discovered in the Picher Field in the early 1900s. The field reached its maturity in the 1920s and the process of reworking tailings piles to recover ores was begun; tailings piles were reprocessed for a second and third time during World War II. Most of the mining operations had been cut back or shut down by the late 1950s. Sporadic mining occurred in the 1960s, and the last recorded production occurred in 1970 (Luza, 1986). The Picher Mining Field is an ideal study area because of its extensive mining history and no remedial actions that affect fluvial sediments have been undertaken. A diversion dike was constructed in 1986 to divert Lytle Creek away from a mine collapse. In the Kansas portion of the Picher Mining Field, additional diversion dikes have been constructed and the Tar Creek channel has been moved.

The ore deposits of the Picher Field are primarily located in the Boone Formation, which is composed of Mississippian-age limestone that contains chert nodules (Fig. 2). The ore deposits and gangue minerals, such as calcite, replace limestone in zones throughout the Boone Formation, with sphalerite and galena as the commercial ore minerals (Table 1). Trace elements that can be found in the Boone Formation are iron, titanium, cadmium, gallium, manganese, cobalt, silver, germanium, antimony, and nickel (McKnight et al., 1970).

The eastern portion of Ottawa County that includes the Picher Mining Field has little natural relief. Landforms in the mining field with the most relief are the human-

made tailings piles situated at the angle of repose. Large trees and tall grasses dominated eastern Ottawa County before the area was settled. Most of the large trees and grasses are gone and brush has encroached (Newland et al., 1964). Tailings piles remain unvegetated, but vegetation is recovering in areas where tailings piles have been removed. The potential for moderate chemical erosion and strong pluvial erosion occur in Ottawa County because of its mean annual rainfall of 1070 mm (42 in.) per year and mean annual temperature of 13.9° C (57° F) (Dury, 1969).

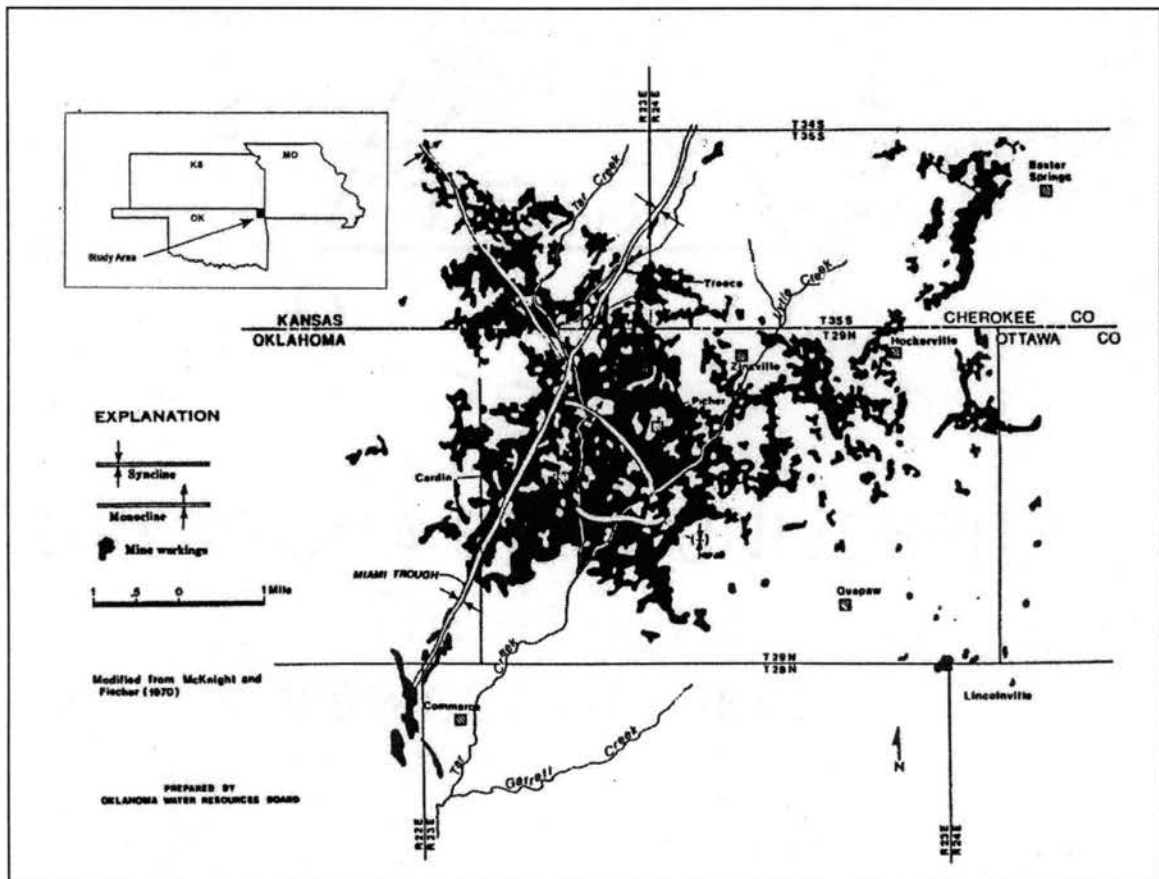


Fig. 1. The Picher Mining Field (OWRB, 1983)

Tar Creek and Lytle Creek are the main streams draining the mining field. The USGS gauging station on Tar Creek at 22<sup>nd</sup> Street in Miami, Oklahoma has been discontinued, but data are available from 1984 through 1993. The average discharge is approximately 400 cubic feet per second. Maximum discharge was 3600 cubic feet per second and minimum discharge was 100 cubic feet per second in the period between 1984 through 1993. Acid mine water discharges into Lytle Creek upstream of the Tar Creek-Lytle Creek confluence, so both streams are impacted. Groundwater in the Roubidoux aquifer has been affected by acid mine drainage. Public water wells tested by the USGS in 1992 revealed that seven out of ten wells tested had been contaminated by mine water. Mine water entered the Picher 1 well when its casing failed in 1985, so a new well was drilled into the Roubidoux aquifer (Christenson, 1995).

System	Series	Group, formation or member	Columnar section	Thickness (feet)	Description		
PENNSYLVANIAN	Des Moines	Bluejacket Sandstone Member (of Boggy Formation)		15-60	Brown to buff sandstone.		
		Savannah Shale		120 ±	Black and gray fissile shale, a little sandstone, thin black fossiliferous limestone (Doneley Member), thin coal and underclay seams (Branson, 1955).		
		Doneley Limestone Member of Branson, 1954					
		McAlester Shale					
		Warner Sandstone Member		30 ±	Black fissile shale with clay ironstone concretions, sparse siltstone, thin coal and underclay; brown coarse-grained sandstone (Warner) at base (Branson, 1955).		
	Hartshorne Formation		0-20	Dark-gray to black fissile shale, subordinate siltstone, sparse calcareous clay ironstone, and thin coal seams with underclay (Branson, 1955).			
		UNCONFORMITY					
	Marion	Hale Formation		0-83+	Alternating brown to black carbonaceous and locally ferruginous sandstone, dark shale, and fossiliferous bituminous limestone, partly oolitic.		
MISSISSIPPIAN	Chester	Fayetteville Shale		0-70	Black, bluish-gray, and greenish fissile or limy shale with local ironstone concretions, subordinate gray and brown to purplish crinoidal limestone, part bituminous, part oolitic.		
		Balesville Sandstone		0-70	Gray crinoidal to dense limestone, commonly oolitic, buff sandstone and green shale, interbedded.		
		Hindsville Limestone		0-85 ±	Gray crinoidal to dense limestone, commonly oolitic, locally cherty, a little sandstone and green shale.		
			UNCONFORMITY				
	Meramec	Quapaw Limestone		0-31+	Gray medium- to coarse-grained crinoidal limestone.		
		Moccasin Bend Member		0-140	Alternating chert and fine- to medium-grained brown limestone, some cotton rock; chert conspicuously brown and blue in lower part, paler above.		
		Baxter Springs Member		0-5	At base, bedded to massive pale chert or cotton rock, glauconitic at base (L bed); overlain and overlapped regionally by crinoidal glauconitic limestone and variegated chert, the limestone locally shaly or containing glauconitic oolite and phosphate nodules (K bed); topped by thin phosphatic and highly glauconitic crinoidal limestone containing variegated and, in part, very dark chert (J bed).		
		Shert Creek Oolite Member		0-51			
				DISCONFORMITY			
				Joplin Member		0-60	Brown oolitic limestone, only slightly glauconitic.
	Osage	Joplin Member		0-100	Gray crinoidal limestone and nodular or bedded chert; chert-free ledge near base.		
		Grand Falls Chert Member		25-95	Pale chert, cotton rock, and subordinate brown fine-grained limestone.		
		Reeds Spring Member		70-105	Blue, gray, and brown chert alternating with gray and brown fine-grained limestone; crinoidal bioherms locally at base.		
St. Joe Limestone Member			10-32	Gray to pink crinoidal limestone with massive ledge at top and greenish shaly zone below middle; sparse blue to gray chert.			
MISSISSIPPIAN AND DEVONIAN	Kinderhook and Upper Devonian	Chattanooga Shale		0-50	Black fissile shale, bleached greenish or yellow at top; locally a few inches of coarse-grained white sandstone at base.		
UNCONFORMITY							
ORDOVICIAN	Lower Ordovician	Cotter Dolomite		26+	Gray to brown dolomite, fine- to medium-grained, locally sandy; a little chert, in part oolitic.		

Fig. 2. Stratigraphic section of the Oklahoma portion of the Picher Mining Field (McKnight and Fischer, 1970)

Table 1  
Minerals of the Picher Mining Field

<b>Mineral Name</b>	<b>Chemical Formula</b>
Sphalerite	ZnS
Galena	PbS
Chalcopyrite	CuFeS <sub>2</sub>
Enargite	CuAsS <sub>2</sub>
Luzonite	CuAsS <sub>2</sub>
Pyrite	FeS <sub>2</sub>
Marcasite	FeS <sub>2</sub>

## CHAPTER II

### LITERATURE REVIEW

#### Transport of Metal-Contaminated Sediment by Fluvial Processes

The concentration of metals in fluvial sediment will generally decrease downstream from a single source because of the dilution effect of non-contaminated sediments. Minerals with higher densities will be the least readily dispersed metals in clastic form. Galena (PbS) has a density of  $7.4 - 7.6 \text{ g/cm}^3$  compared to sphalerite (ZnS), which has a density of  $3.9 - 4.1 \text{ g/cm}^3$ . Metals within ore or gangue minerals are sorted in a downstream direction with the denser materials traveling at a slower rate and remaining closer to the mine site for greater lengths of time (Miller, 1997).

Graf (1996) offers five primary attributes of fluvial systems that complicate the generalization of decreasing metal concentrations with distance downstream. The first attribute of fluvial systems involves the hydraulic processes that sort sediments and tend to transport the finer-grained particles greater distances. This is significant because metals often adsorb to finer particles in greater concentrations (Horowitz, 1985). Second, sediment does not move continuously through the fluvial system. Sediment moves in waves that are deposited unevenly. A portion of sediment that enters the fluvial system from the point source will become stored part way through the system. The third attribute of fluvial systems is the masking effect of a single point source when the stored

contaminated sediment is released and scattered downstream by high flow. The fourth attribute of fluvial systems is a function of stream power. Deposition of contaminated sediment occurs in places where stream power declines. The final attribute of fluvial systems is the introduction of sediment via tributaries that mixes with contaminated sediment and leads to abrupt declines in metal concentrations throughout the system.

### Erosion of Tailings Piles

Tailings piles generally consist of fine-grained particles of rock that are susceptible to wind erosion because they are basically unvegetated and can be dissected and disseminated easily (Toy et al., 1987). Precipitation that falls onto tailings piles can erode the piles by rainsplash erosion and by overland flow. Overland flow is an important mechanism for erosion on the steep slopes and highly erodible material of tailings piles (Knighton, 1998). Tailings also have relatively low permeability, so much of the precipitation that falls on them during an intense rainfall becomes runoff (Nimick et al., 1991). Tailings piles of the Picher Mining Field consist of angular, gravel-size limestone and chert fragments. Tailings piles of the mining field are unvegetated and have been disturbed by off-road vehicles.

### Metals in Floodplain Soils

Sediments on the floodplain act as sinks for metal contaminants, as well as sources of metal contaminants during future flooding events or from channel bank erosion. A study of mining-related zinc in the floodplain sediment by Lecce et al. (1997) revealed that overbank deposits are the largest contaminant sink in the Blue River watershed of



southwestern Wisconsin. Mining ceased 50 years ago and most of the tailings have been removed, but active channel sediment still contains high concentrations of heavy metals. Lateral migration of the stream is responsible for reintroducing much of the metal-contaminated sediment in the active channel.

### Association Among Heavy Metals Within the Fluvial System

Analysis of stream sediment in Wales by Wolfenden et al. (1978) suggests that the dispersal of metals with distance downstream is ranked as follows: copper > zinc > cadmium > lead. A study by Deacon et al. (1999) in the Upper Colorado River Basin of Colorado demonstrated a positive correlation among Cd and Zn, Cd and Pb, and Pb and Zn. Prusty et al. (1994) computed simple correlation coefficients of metals of the Tiri River sediments and found that Zn, Pb, Cd, Fe, and Mn are strongly correlated among each other (Table 2). Houba et al. (1983) computed correlation coefficients of heavy metals in the sediment of the Vesdre River of Belgium and found that the highest correlation was determined for Zn and Cd (Table 3).

Sphalerite is associated with galena, marcasite, chalcopyrite, calcite, and dolomite. Cadmium is associated with zinc minerals because of the similarity of the atomic structures. Pyrite may contain small amounts of Ni and Co. Sphalerite, galena, marcasite, and pyrite have isometric crystal structure. Chalcopyrite has a tetragonal crystal structure because it is derived from a sphalerite structure in which half of the Zn is replaced by Cu and the other half by Fe, which leads to a doubling of the unit cell (Klein et al., 1993). Heavy metal elements of the Picher Mining Field may be associated with each other because of the similarity of the atomic structures.

Table 2  
Correlation matrix of Tiri River sediments (modified from Prusty et al., 1993)

Metal	Zn	Pb	Cd	Cu	Fe
Zn	1.00	0.91	0.91	0.75	0.71
Pb		1.00	0.91	0.78	0.63
Cd			1.00	0.70	0.59
Cu				1.00	0.41*
Fe					1.00

Significant at  $p < 0.05$ ; \* Not significant

Table 3  
Correlation matrix of Vesdre River sediments (modified from Houba et al., 1983)

Metal	Cd	Zn	Cu	Pb	Fe
Cd	1.00				
Zn	0.87 <sup>1</sup>	1.00			
Cu	0.17	0.36 <sup>3</sup>	1.00		
Pb	0.67 <sup>1</sup>	0.70 <sup>1</sup>	0.66 <sup>1</sup>	1.00	
Fe	0.41 <sup>3</sup>	0.49 <sup>2</sup>	0.34	0.52 <sup>2</sup>	1.00

<sup>1</sup> Significant at  $p < 0.001$

<sup>2</sup> Significant at  $p < 0.01$

<sup>3</sup> Significant at  $p < 0.5$

## CHAPTER III

### METHODOLOGY

#### Sample Collection

Samples of fluvial sediments were collected at the same locations sampled by the USGS in 1983–1984 (Fig. 3). Some of the sites visited by the USGS in the 1980s were no longer accessible in the year 2000 because of construction near Commerce High School. Some sampling sites were inaccessible because of dense vegetation. Sediment samples were also collected in locations in which the USGS did not study. One of the non-USGS sampling locations was the Neosho River downstream from Tar Creek and upstream from Grand Lake to assess if heavy metals are moving toward the reservoir. The Neosho River sediment was collected with a Ponar grab sampler that was lowered from a bridge that spanned the river. The sediment from the grab sampler was placed in a stainless steel bowl that had been rinsed with river water. The sediment was then mixed with a stainless steel spoon and placed in 4-ounce glass sample jars with plastic, Teflon-coated lids.

Samples of sediments from Tar Creek were collected from areas of low turbulence or from pools in an attempt to collect finer-grained sediment. I attempted to collect the smallest-grained sediment possible to match the sediment described by the USGS. The sediment samples were collected with a stainless steel spoon and placed into a stainless steel bowl that had been rinsed with water from the stream. The sediment was

mixed with the spoon and placed in 4-ounce glass sample jars with plastic, Teflon-coated lids. The glass jars and lids were rinsed with water from the stream just prior to filling them. The glass jars and lids were labeled with a sample code at each sampling location and recorded in the field notes along with the GPS location. Bowls and spoons that were reused were rinsed with de-ionized water prior to use. The sampling techniques that I used are consistent with the Oklahoma Department of Environmental Quality method of sample collection.

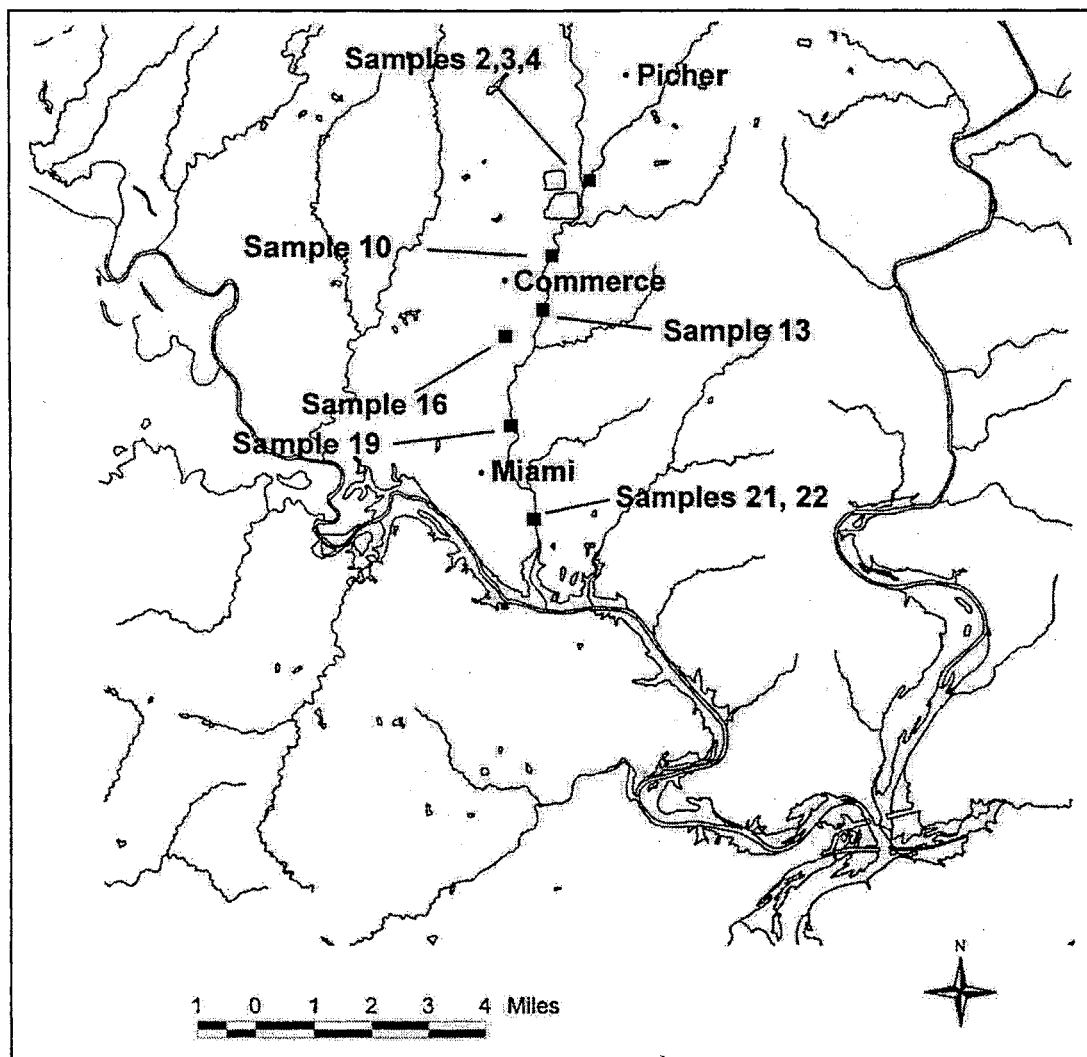


Fig. 3. Sample sites for fluvial sediments

## Laboratory Analysis

The sediment samples were sent to the laboratory at the Oklahoma Department of Environmental Quality in Oklahoma City, Oklahoma, within two days after the sediment collection. The samples were dried, digested with acid, and analyzed using Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) because this was a method used by the USGS. Each sediment sample was dried overnight at 10° C, pulverized, and sieved through a 2 mm (#10 U.S. Standard Series) sieve before digesting 0.5 grams of the sample in 10 mL of concentrated nitric acid for ten minutes using microwave heating. ICP-AES was then used to measure the characteristic emission spectra of the metal elements to determine the concentrations of the heavy metals. The laboratory techniques used are consistent with the Oklahoma Department of Environmental Quality methods of sample preparation and sample digestion by acid. The USGS placed the sediment sample onto 45 µm filter paper and scraped the sediment into a sample container (personal communication with Parkhurst, 2000).

## Statistical Analyses

The non-parametric Wilcoxon test for paired measurements was used to compare the year 2000 data to 1983–1984 data. Samples of sediments collected on 31 July 2000 were compared to the samples collected on 16 September 2000. No statistically significant differences exist at the  $p < 0.05$  confidence level between the two data sets. The 16 September 2000 data were compared to the USGS data because additional sample sites occurred that matched USGS locations that were not included in the 31 July

2000 data. Data from 16 September 2000 were compared to the quantitative chemical analyses from the USGS study because those sediments were dried, digested with acids, and analyzed by ICP-AES or Graphite Furnace Atomic Absorption (personal communication with Parkhurst, 2000).

### Sieving

Samples of sediment were spread out and air-dried for two days. I removed organic material with my fingers before the sieving process was begun. A total of 24 sieves were used for each duplicate sediment sample. Duplicate samples were collected 16 September 2000 at the same locations that samples were collected to be sent to the ODEQ lab. Duplicate samples were collected 16 September 2000 at most of the sample sites (see Appendices A through H for sample descriptions). Six sieves were stacked in a Ro-Tap machine with the largest mesh sieve at the top and the smallest mesh sieve at the bottom. The machine ran eight minutes for each group of sieves (the Ro-Tap holds a maximum of six sieves) so that the sediment would have an opportunity to move through all of the sieves. The sediment that remained in each sieve was weighed and reported in Appendix I (Appendix I includes particle size analysis curves).

## CHAPTER IV

### RESULTS AND DISCUSSION

Fluvial sediment samples were collected from 24 sites in the Picher Mining Field and the analyses for As, Cd, Cr, Cu, Fe, Ni, Pb, and Zn are listed in Appendices A through H. GPS coordinates for all sampling sites can be found in Table 4. The objective is to assess if the concentrations of heavy metals in the fluvial sediments have changed, so nine sample locations from 16 September 2000 were chosen to compare concentrations of Cd, Cu, Fe, Ni, Pb, and Zn to 1983-1984 concentrations because their particle size descriptions were similar to 1983-1984 USGS descriptions (Table 5) (see Appendices A through H for descriptions). As and Cr were not selected because they were not included in the quantitative chemical analyses by the USGS for the nine sample sites selected for comparison. No statistically significant differences at the  $p < 0.05$  level were detected between 1983-1984 data and year 2000 data when considering all nine sample sites. The area of the mining field that lies upstream of the confluence of Tar Creek and Lytle Creek is the most likely entry point of heavy metals into the fluvial sediments because acid mine drainage is discharging into Lytle Creek and tailings piles are near the banks of Tar Creek. Mine water that is discharging into Lytle Creek supplies metals to the sediments. Iron sulfide minerals (pyrite and marcasite) oxidize in the flooded underground mine workings and form sulfuric acid. Sulfuric acid formed from the dissolution of iron sulfide minerals will oxidize and dissolve other sulfide minerals

and will release trace elements associated with them (Emmons, 1940). Sulfide minerals such as sphalerite, galena, and chalcopyrite are being dissolved by the acid mine waters that have filled the underground mine workings and are being discharged into Lytle Creek upstream of the Tar Creek-Lytle Creek confluence.

Three sample sites are located upstream of the Tar Creek-Lytle Creek confluence and six sample sites are located downstream of the confluence. The statistically significant decrease in Fe that exists downstream of the confluence is probably related to the mixing effect described by Graf (1996). Lytle Creek sediments have high concentrations of iron because of the proximity to mine discharge. The concentration of Fe decreases downstream of the confluence as a result of the mixing of Tar Creek and Lytle Creek sediments. No statistically significant differences at the  $p < 0.05$  level exist when considering the three sample sites upstream of the confluence. Pb decreased by 96.7% and Zn decreased by 25.0%, but these changes are not statistically significant due to comparison of only three sample sites. The dramatic decrease in Pb concentrations since 1983-1984 is most likely because of drainage diversions that have been constructed since 1983-1984 (Fig. 4). The source of Pb may have been removed from the system when the Lytle Creek diversion was built in 1986. Pb concentration increases at sample site 16 because site 16 is a mine discharge point in which concentrations of all heavy metals considered increased.

Several high flows have occurred in the mining field since 1984. The USGS gauging station on the Neosho River, in which Tar Creek is a tributary, shows that flows have exceeded 50,000 cubic feet per second in 1985, 1986, 1993, 1994, 1995, and



Table 4  
Year 2000 sediment sampling sites

Sample #	Location	ODEQ code(s)	GPS Coordinates
1	Tailings settling pond near Douthat	OC24	N36 57' 39" W94 50' 25"
2	Mine discharge point into Lytle Creek	OC19	N36 57' 30" W94 50' 41"
3	4 m downstream from mine discharge point	OC20	N36 57' 30" W94 50' 41"
4	10 m downstream from mine discharge point	OC21	N36 57' 30" W94 50' 41"
5	Tar Creek upstream from confluence	TC12 OC17	N36 57' 29.28" W94 50' 41.89"
6	Lytle Creek upstream from confluence	TC13A/B OC18	N36 57' 29.28 W94 50' 41.89"
7	Tar Creek-Lytle Creek confluence	TC14 OC16	N36 57' 29.28 W94 50' 41.89"
8	Tar Creek downstream from confluence	TC11 OC15	N36 57' 29.28 W94 50' 41.89"
9	Tar Creek at Hwy 66/69 (red fine-grained sed.)	TC10 OC11	N36 56' 37.08" W94 51' 11.82"
10	Tar Creek at Hwy 66/69 (sand from bar)	TC9 OC12	N36 57' 29.28 W94 50' 41.89"
11	Tar Creek at Hwy 66/69 (clay)	TC8 OC14	N36 57' 29.28 W94 50' 41.89"
12	Tar Creek at Hwy 66/69 (overbank deposits)	TC7 OC13	N36 57' 29.28 W94 50' 41.89"
13	Tar Creek at New State Rd Mud and silt from pool	TC6A/B OC8	N36 55' 44.92" W94 51' 34.66"
14	Tar Creek at New State Rd Mud and sand from stream	OC9	N36 55' 44.92" W94 51' 34.66"
15	Tar Creek at New State Rd Des. cracks; efflorescence	OC10	N36 55' 44.92" W94 51' 34.66"
16	Mine discharge near Commerce High School	TC5A OC6	N36 55' 31.56" W94 52' 17.12"
17	Mine discharge near Commerce High School	TC4 OC7	N36 55' 31.56" W94 52' 17.12"
18	Tar Creek at 22 <sup>nd</sup> St.	TC3C OC5	N36 54' 00.243" W94 52' 03.883"
19	Tar Creek at 22 <sup>nd</sup> St. (duplicate sample)	TC3A/B OC4	N36 54' 00.243" W94 52' 03.883"
20	Tar Creek at 22 <sup>nd</sup> St. (duplicate sample)	TC3A/B OC3	N36 54' 00.243" W94 52' 03.883"
21	Tar Creek at Central Ave. (duplicate sample)	TC2B OC2	N36 52' 29.12" W94 51' 45.02"

Table 4 continued

22	Tar Creek at Central Ave. Iron "flakes" in sample	TC2A OC1	N36 52' 29.12" W94 51' 45.02"
23	Neosho River upstream from Grand Lake	TC1B OC23	N36 47' 55.87" W94 49' 09.25"
24	Neosho River upstream (duplicate sample)	TC1A OC22	N36 47' 55.87" W94 49' 09.25"

Table 5  
Comparable sample sites

Site & Year	Concentrations in ppm					
	Cd	Cu	Fe	Ni	Pb	Zn
2						
1983-84	14	24	246000	17	6800	2600
2000	11	<8	377840	28	121	3498
3						
1983-84	14	5.3	366000	73	6000	11000
2000	7	<8	415440	28	109	4082
4						
1983-84	26	4.8	392000	67	1500	11000
2000	10	<8	426960	45	109	5882
10						
1983-84	130	15	166000	46	200	14000
2000	9	7	39860	22	257	3636
13						
1983-84	7.9	19	177000	22	280	3900
2000	24	20	63720	67	234	4668
16						
1983-84	6.3	6.1	267000	1.4	350	980
2000	96	30	252000	230	862	17008
19						
1983-84	11	16	76000	41	270	2700
2000	13	19	83100	123	140	4456
21						
1983-84	32	64	133000	52	460	3400
2000	38	26	83020	131	206	11406
22						
1983-84	2.9	2.5	467000	28	<40	4900
2000	44	26	76340	154	235	15030

1998 (Fig. 5). These high flows probably account for the absence of an iron precipitate crust on the stream bed in the year 2000 that was reported by the USGS in the 1980s.

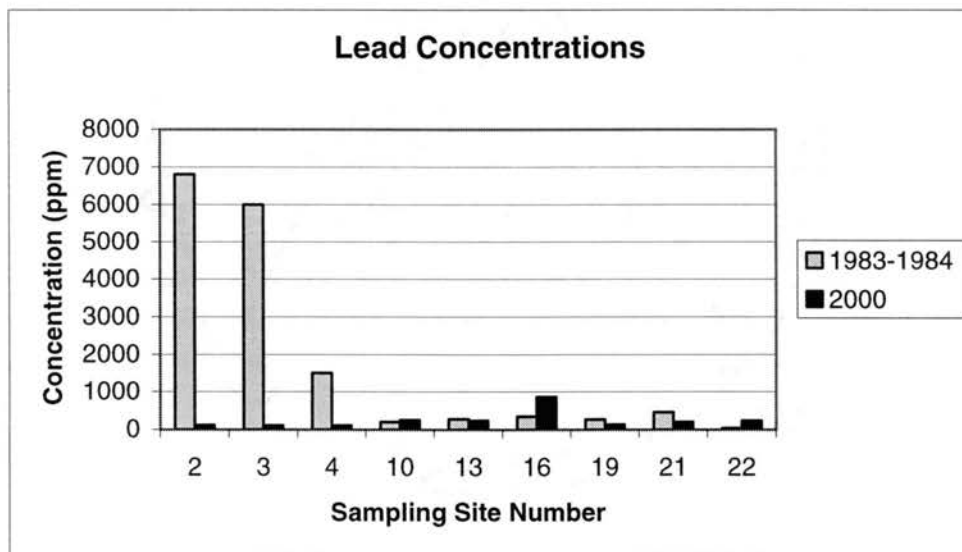


Fig. 4. Lead concentrations at comparable sample sites

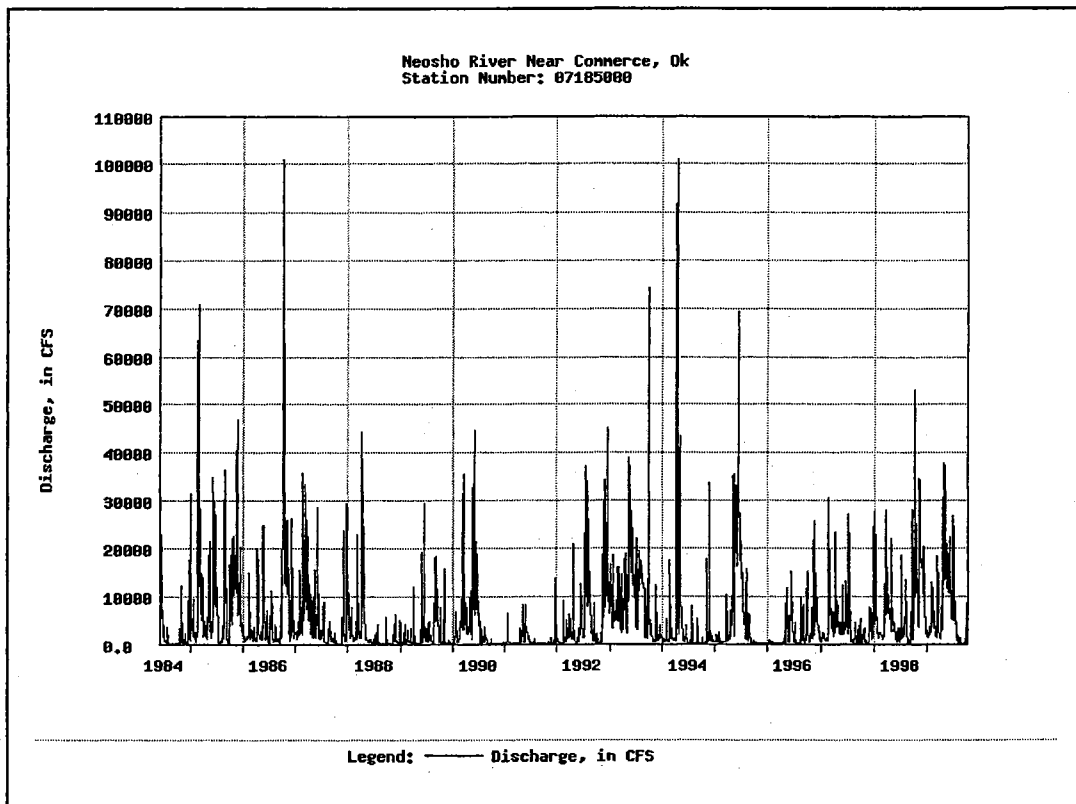


Fig 5. USGS hydrograph of the Neosho River station near Commerce, 1984-1999

Mill tailings were piled near streams in the mining field and large tailings piles remain on the western bank of Tar Creek near the community of Douthat. Work by Drake (1999) in the Kansas portion of the Picher Mining Field concluded that levels of lead and zinc in tailings leachate increase with decreasing grain diameter. Tailings were observed in sediments collected at many of the sampling sites. Rainsplash erosion and runoff from tailings piles that are adjacent to the stream bank can transport fine-grained material directly into Tar Creek. The erosion of tailings piles as a result of overland flow

suggested by Knighton (1998) occurs in the mining area because tailings were observed in sediments collected at many of the sampling sites.

Tailings settling ponds are present throughout the mining area and, in many cases, occur on the Tar Creek-Lytle Creek floodplain. A large tailings settling pond can be found south of the Tar Creek-Lytle Creek junction near the western bank of Tar Creek. Tailings settling ponds typically contain silt-sized and clay-sized particles that have high metal content. A sediment sample collected from a dried settling pond east of Lytle Creek contained the highest concentrations of Pb, Zn, Cd, and Cu of all the sediment samples collected in the year 2000. This was not unexpected because Horowitz (1985) found that metals often adsorb to finer particles in greater concentrations. Inverse correlations between particle size and heavy metal concentration exist in the Picher Mining Field (Table 6). Inverse correlations between particle size and heavy metal concentration are significant at the  $p < 0.05$  level for Cd, Cu, and Zn, but not significant for Fe, Ni, or Pb (Pb  $p = 0.0637$ ). Metals stored within the fine-grained sediments in settling ponds on the floodplain are vulnerable to reintroduction into the streams of the mining field during flooding.

Table 6  
Correlations between particle size and heavy metal concentration

	Cd	Cu	Fe	Ni	Pb	Zn
Cu	0.9013 0.0000					
Fe	0.6829 0.0101	0.3314 0.2687				
Ni	0.7011 0.0076	0.3852 0.1937	0.9439 0.0000			
Pb	0.8360 0.0004	0.9748 0.0000	0.1815 0.5530	0.2506 0.4088		
Zn	0.9667 0.0000	0.9695 0.0000	0.5054 0.0781	0.5603 0.0464	0.9320 0.0000	
phi	0.6032 0.0291	0.5593 0.0469	0.3875 0.1908	0.4086 0.1657	0.5278 0.0637	0.5892 0.0341

Statistically significant correlations of associated heavy metal elements exist at the  $p < .005$  level among Pb, Zn, Cd, Cu, and Ni. Deacon et al. (1999) found that strong correlations exist between concentrations of Cd and Zn, Cd and Pb, and Pb and Zn in the Upper Colorado River Basin of Colorado. The graph of Cd vs. Zn from the year 2000 data displays a positive relationship because Cd is associated with Zn minerals (Fig. 6). The graph of Cu vs. Ni from year 2000 data displays a positive relationship because of the association of Cu and Ni in chalcopyrite (Fig. 7). Graphs of Cd vs. Pb and Pb vs. Zn

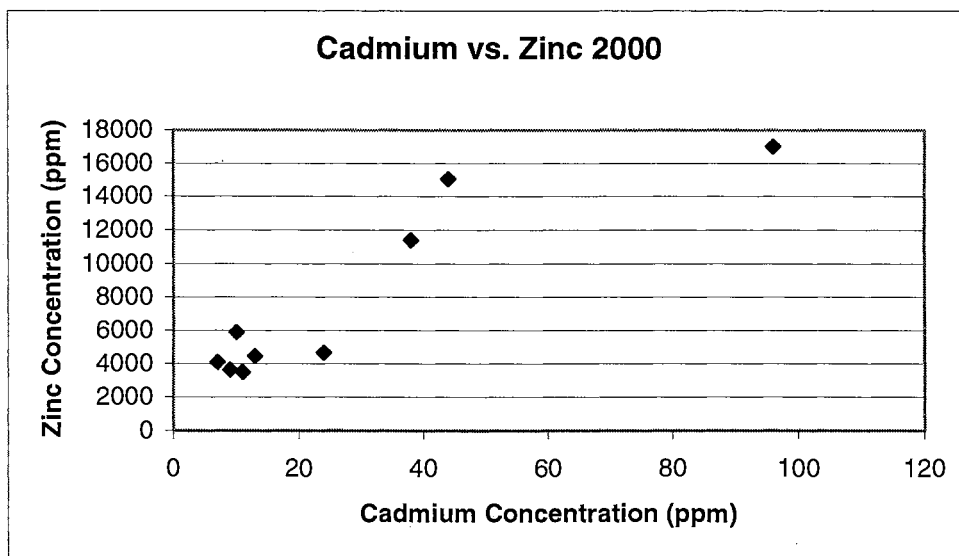


Fig. 6. Cadmium vs. zinc in year 2000 sediment samples

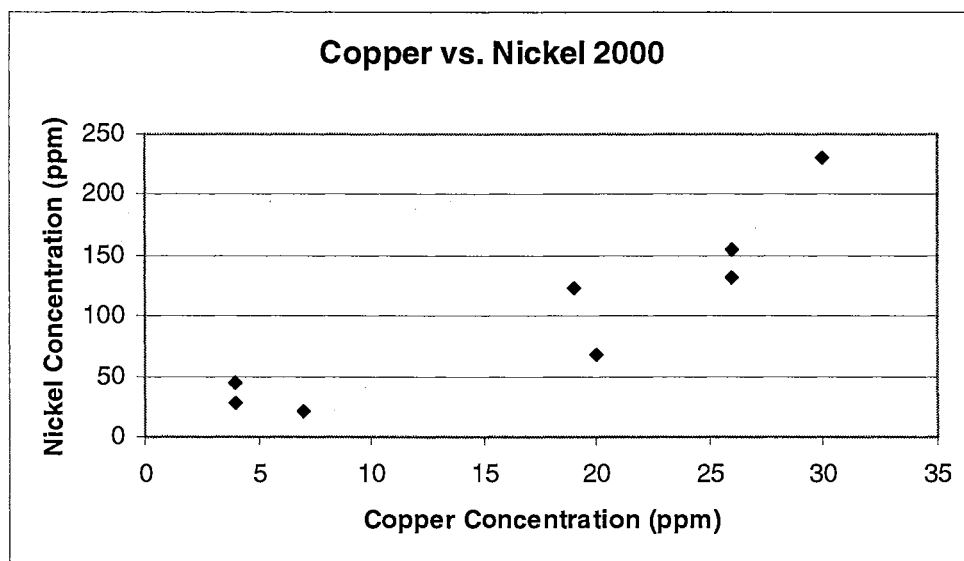


Fig. 7. Copper vs. nickel in year 2000 sediment samples

constructed from year 2000 data do not show correlations among the metals with distance downstream because concentrations of Pb did not vary much between sample sites.

Cd, Ni, and Zn have higher concentrations of heavy metals in sediments downstream from the main mining area (Figs. 8a, 8b, 8c). Miller (1997) proposed that materials are sorted in a downstream direction with the denser materials traveling at a slower rate and remaining closer to the mine site for greater lengths of time. This may explain why lead concentrations have not varied much in the year 2000 sampling sites. Higher concentrations of Cd, Ni, and Zn downstream of the Tar Creek-Lytle Creek confluence could be because the particle sizes have changed. The crust that the USGS observed in 1983-1984 no longer covers the stream bed, so sediment is probably moving downstream. Cd and Zn display an inverse correlation between particle size and heavy metal concentration significant at the  $p < 0.05$  level in the Picher Mining Field, which may be related to a decrease in particle size in the downstream direction.

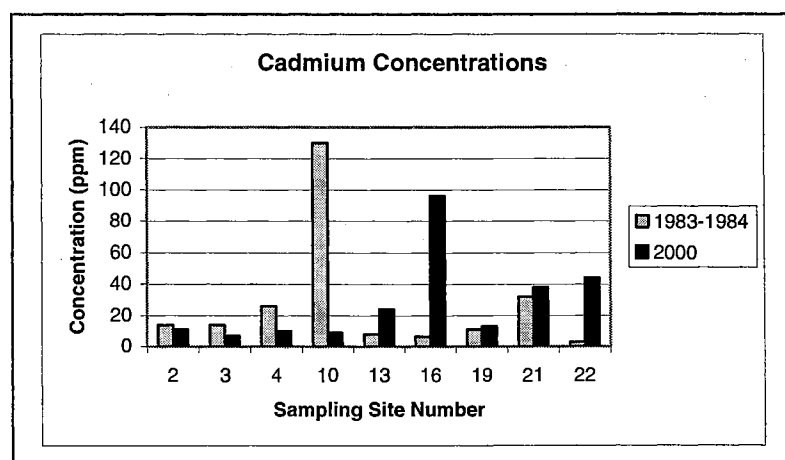


Fig. 8a. Cadmium concentration



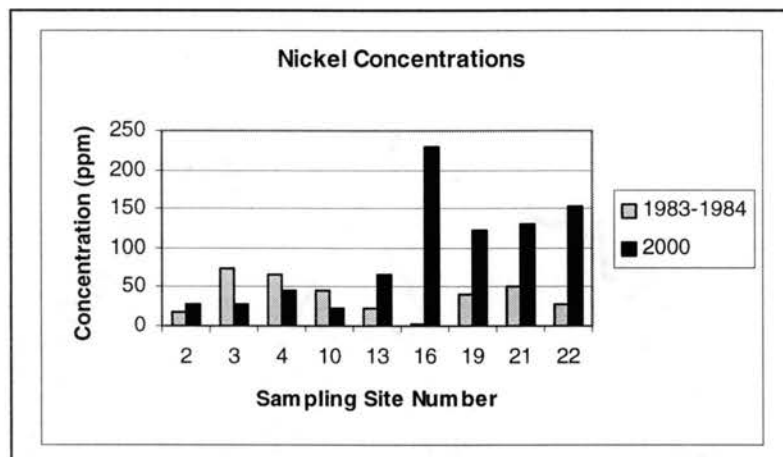


Fig. 8b. Nickel concentration

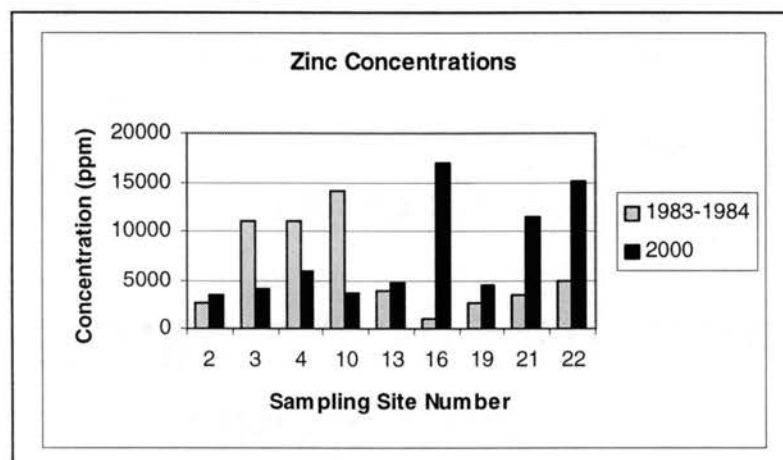


Fig. 8c. Zinc concentration

## CHAPTER V

### CONCLUSIONS AND RECOMMENDATIONS

No statistically significant differences exist in the concentrations of heavy metals in the fluvial sediments collected in the year 2000 compared to those collected in 1983-1984 when all nine sample locations are considered. Changes in the concentrations of heavy metals in the fluvial sediments in the year 2000 result from several factors. The decrease in concentrations of heavy metals in the upstream sampling sites (upstream of the Tar Creek-Lytle Creek confluence) is probably related to drainage diversion projects constructed after 1984. The increase in concentrations of heavy metals downstream of the confluence could be because particle sizes have decreased with distance downstream, keeping in mind that smaller sizes can adsorb higher concentrations. Alternatively, the downstream increase could be because of heavy metals derived from floodplain soils and tailings piles entering the stream. Additional studies are needed to ascertain the processes and importance of floodplain soils and tailings piles as active sources of heavy metals to streams.

This thesis has demonstrated the importance of particle size analysis in fluvial sediment studies. Particle size analyses were not reported in the 1983-1984 USGS study, which limits the inferences that can be made for comparisons to that study. A more effective approach to sample collection would be to collect samples at pre-determined

intervals along the stream reach. Sediment sample collection three to four times a year might reveal seasonal changes in heavy metal concentrations.

The residents of Picher, Cardin, and Douthat are left with the waste of lead and zinc ore mining. Heavy metals will continue to be added to the sediments of Tar Creek and Lytle Creek as long as the sources remain in the mining field. Crops should not be irrigated with water from Tar Creek or Lytle Creek until more research is done regarding the uptake of metals by plants. Tar Creek is a tributary of the Neosho River; which joins the Spring River to form Grand Lake of the Cherokees. Additional studies should be conducted to determine the effect of heavy metals on aquatic organisms because Tar Creek is supplying heavy metals to the sediments of Grand Lake of the Cherokees.

The Tar Creek Superfund Task Force organized by Oklahoma governor Frank Keating has proposed a wetland system as a passive treatment option for the mining field. High iron content will be eliminated by aeration and metals in surface waters will be eliminated by sulfate reduction. Remediation will not be successful until all the sources of heavy metals have been removed from the mining field. Sources exist in the forms of tailings piles, tailings settling pond sediments, mine water discharge, and floodplain soils. This type of clean-up would be extremely expensive and it would be difficult to find a location to store these wastes. The solution to best serve the residents of the mining field would be to move the towns of Picher, Cardin, and Douthat.

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**APPENDICES**

APPENDIX A  
HEAVY METAL CONCENTRATIONS  
Arsenic

**ARSENIC**

Sample #	Sample Code	September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
1	OC24 Tailings settling pond	<12	N/A	N/A	N/A	2000: Dry silty clay Desiccation cracks
2	OC19 Mine discharge into Lytle Creek	291	N/A	#47	N/A	2000: Red mud, silt, sand, & organic mat.
3	OC20 4m downstream from discharge	574	N/A	#46	N/A	2000: Red mud, silt, sand, & organic mat.
4	OC21 10m downstream from discharge	412	N/A	#43	N/A	2000: Red mud, silt, sand, & organic mat.
5	TC12      OC17 Tar Creek above confluence	<12	<12	N/A	N/A	2000: Mud, sand, tailings, & organic mat.
6	TC13A,B      OC18 Lytle Creek	80	86	N/A	N/A	2000: Iron precipitate from bank Upstream of confluence
7	TC14      OC16 Confluence Tar Creek and Lytle Ck.	115	25	N/A	N/A	2000: Red mud and tailings
8	TC11      OC15 Downstream from confluence	57	<12	N/A	N/A	2000: Mud, sand, tailings, & organic mat.
9	TC10      OC11 Hwy 66/69 Reddish fines	<12	25	#13	N/A	2000: Reddish-brown mud, silt, & tailings 1983-84: Layered iron precipitate
10	TC9      OC12 Hwy 66/69 Bar	16	16	#13	N/A	2000: Red mud, silt, & tailings from bar 1983-84: Layered iron precipitate



Sample #	Sample Code	September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
11	TC8 Hwy 66/69 Clay	16	63	#13	N/A	2000: Red clay and sand that has started to dry 1983-84: Layered iron precipitate
12	TC7 Hwy 66/69 Overbank	15	<12	#13	N/A	2000: Dry sandy overbank deposit 1983-84: Layered iron precipitate
13	TC6A,B New State Road Commerce	15	24	#12	N/A	2000: Iron precip from pool 1983-84: Layered iron precip, clay
14	OC9 New State Road Commerce	15	N/A	#12	N/A	2000: Mud, sand, & tailings from stream
15	OC10 New State Road Commerce	63	N/A	#12	N/A	2000: Overbank deposits, des cracks, efflorescence
16	TC5 Commerce High School	<48	<24	#10	N/A	2000: Iron precip, mud and tailings from water's edge 1983-84: Crusted iron precipitate
17	TC4 Commerce High School	<48	27	#10	N/A	2000: Iron precip, overbank deposits, desiccation cracks 1983-84: Crusted iron precipitate
18	TC3C 22nd St. (No rocks)	20	24	#6	N/A	2000: Grayish brown sed with mud to sand size particles 1983-84: Mud and sand
19	TC3A,B 22nd St. Miami (Sample w/rocks)	14	41	#6	N/A	2000: Grayish brown sed with mud to gravel size particles 1983-84: Mud and sand
20	OC3 22nd St. (duplicate, no rocks)	21	N/A	#6	N/A	2000: Grayish brown sed with mud to gravel size particles 1983-84: Mud and sand

Sample #	Sample Code		September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
21	TC2B Central Ave. duplicate	OC2	19	51	#3	N/A	2000: Dk brown sed w/ leaves and roots 1983-84: Iron precip., organic mat.
22	TC2A Central Ave. Miami	OC1	20	58	#2	N/A	2000: Dk brown sed w/ leaves and roots 1983-84: Iron precip., organic mat.
23	TC1B Neosho River (duplicate)	OC23	<12	<12	N/A	N/A	2000: Dark gray mud
24	TC1A Neosho River	OC22	<12	<12	N/A	N/A	2000: Dark gray mud

APPENDIX B  
HEAVY METAL CONCENTRATIONS  
Cadmium

**CADMIUM**

Sample #	Sample Code	September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
1	OC24 Tailings settling pond	174	N/A	N/A	N/A	2000: Dry silty clay Desiccation cracks
2	OC19 Mine discharge into Lytle Creek	11	N/A	#47	14.00	2000: Red mud, silt, sand, & organic mat.
3	OC20 4m downstream from discharge	7	N/A	#46	14.00	2000: Red mud, silt, sand, & organic mat.
4	OC21 10m downstream from discharge	10	N/A	#43	26.00	2000: Red mud, silt, sand, & organic mat.
5	TC12      OC17 Tar Creek above confluence	26	50	N/A	N/A	2000: Mud, sand, tailings, & organic mat.
6	TC13A,B      OC18 Lytle Creek	39	20	N/A	N/A	2000: Iron precipitate from bank Upstream of confluence
7	TC14      OC16 Confluence Tar Creek and Lytle Ck.	37	8	N/A	N/A	2000: Red mud and tailings
8	TC11      OC15 Downstream from confluence	131	38	N/A	N/A	2000: Mud, sand, tailings, & organic mat.
9	TC10      OC11 Hwy 66/69 Reddish fines	16	12	#13	130.00	2000: Reddish-brown mud, silt, & tailings 1983-84: Layered iron precipitate
10	TC9      OC12 Hwy 66/69 Bar	9	15	#13	130.00	2000: Red mud, silt, & tailings from bar 1983-84: Layered iron precipitate

Sample #	Sample Code		September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
11	TC8 Hwy 66/69 Clay	OC14	17	65	#13	130.00	2000: Red clay and sand that has started to dry 1983-84: Layered iron precipitate
12	TC7 Hwy 66/69 Overbank	OC13	18	23	#13	130.00	2000: Dry sandy overbank deposit 1983-84: Layered iron precipitate
13	TC6A,B New State Road Commerce	OC8	24	18	#12	7.90	2000: Iron precip from pool 1983-84: Layered iron precip, clay
14	OC9 New State Road Commerce		9	N/A	#12	7.90	2000: Mud, sand, & tailings from stream
15	OC10 New State Road Commerce		83	N/A	#12	7.90	2000: Overbank deposits, des cracks, efflorescence
16	TC5 Commerce High School	OC6	96	84	#10	6.30	2000: Iron precip, mud and tailings from water's edge 1983-84: Crusted iron precipitate
17	TC4 Commerce High School	OC7	90	68	#10	6.30	2000: Iron precip, overbank deposits, desiccation cracks 1983-84: Crusted iron precipitate
18	TC3C 22nd St. (No rocks)	OC5	14	33	#6	11.00	2000: Grayish brown sed with mud to sand size particles 1983-84: Mud and sand
19	TC3A,B 22nd St. Miami (Sample w/rocks)	OC4	13	19	#6	11.00	2000: Grayish brown sed with mud to gravel size particles 1983-84: Mud and sand
20	OC3 22nd St. (duplicate, no rocks)		11	N/A	#6	11.00	2000: Grayish brown sed with mud to gravel size particles 1983-84: Mud and sand

Sample #	Sample Code		September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
21	TC2B Central Ave. duplicate	OC2	38	12	#3	32.00	2000: Dk brown sed w/ leaves and roots 1983-84: Iron precip., organic mat.
22	TC2A Central Ave. Miami	OC1	44	14	#2	2.90	2000: Dk brown sed w/ leaves and roots 1983-84: Iron precip., organic mat.
23	TC1B Neosho River (duplicate)	OC23	1	1	N/A	N/A	2000: Dark gray mud
24	TC1A Neosho River	OC22	1	1	N/A	N/A	2000: Dark gray mud

APPENDIX C

HEAVY METAL CONCENTRATIONS

Chromium

**CHROMIUM**

Sample #	Sample Code	September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
1	OC24 Tailings settling pond	23	N/A	N/A	N/A	2000: Dry silty clay Desiccation cracks
2	OC19 Mine discharge into Lytle Creek	<8	N/A	#47	N/A	2000: Red mud, silt, sand, & organic mat.
3	OC20 4m downstream from discharge	<8	N/A	#46	N/A	2000: Red mud, silt, sand, & organic mat.
4	OC21 10m downstream from discharge	<8	N/A	#43	N/A	2000: Red mud, silt, sand, & organic mat.
5	TC12      OC17 Tar Creek above confluence	14	9	N/A	N/A	2000: Mud, sand, tailings, & organic mat.
6	TC13A,B      OC18 Lytle Creek	<8	4	N/A	N/A	2000: Iron precipitate from bank Upstream of confluence
7	TC14      OC16 Confluence Tar Creek and Lytle Ck.	<8	4	N/A	N/A	2000: Red mud and tailings
8	TC11      OC15 Downstream from confluence	3	10	N/A	N/A	2000: Mud, sand, tailings, & organic mat.
9	TC10      OC11 Hwy 66/69 Reddish fines	22	3	#13	N/A	2000: Reddish-brown mud, silt, & tailings 1983-84: Layered iron precipitate
10	TC9      OC12 Hwy 66/69 Bar	5	<2	#13	N/A	2000: Red mud, silt, & tailings from bar 1983-84: Layered iron precipitate



Sample #	Sample Code	September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
11	TC8 Hwy 66/69 Clay & sand	6	10	#13	N/A	2000: Red clay and sand that has started to dry 1983-84: Layered iron precipitate
12	TC7 Hwy 66/69 Overbank	5	6	#13	N/A	2000: Dry sandy overbank deposit 1983-84: Layered iron precipitate
13	TC6A,B New State Road Commerce	34	46	#12	N/A	2000: Iron precip from pool 1983-84: Layered iron precip, clay
14	OC9 New State Road Commerce	35	N/A	#12	N/A	2000: Mud, sand, & tailings from stream
15	OC10 New State Road Commerce	16	N/A	#12	N/A	2000: Overbank deposits, des cracks, efflorescence
16	TC5 Commerce High School	16	13	#10	N/A	2000: Iron precip, mud and tailings from water's edge 1983-84: Crusted iron precipitate
17	TC4 Commerce High School	16	11	#10	N/A	2000: Iron precip, overbank deposits, desiccation cracks 1983-84: Crusted iron precipitate
18	TC3C 22nd St. (No rocks)	59	33	#6	N/A	2000: Grayish brown sed with mud to sand size particles 1983-84: Mud and sand
19	TC3A,B 22nd St. Miami (Sample w/rocks)	72	118	#6	N/A	2000: Grayish brown sed with mud to gravel size particles 1983-84: Mud and sand
20	OC3 22nd St. (duplicate, no rocks)	86	N/A	#6	N/A	2000: Grayish brown sed with mud to gravel size particles 1983-84: Mud and sand

Sample #	Sample Code		September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
21	TC2B Central Ave. duplicate	OC2	31	93	#3	N/A	2000: Dk brown sed w/ leaves and roots 1983-84: Iron precip., organic mat.
22	TC2A Central Ave. Miami	OC1	32	131	#2	N/A	2000: Dk brown sed w/ leaves and roots 1983-84: Iron precip., organic mat.
23	TC1B Neosho River (duplicate)	OC23	24	32	N/A	N/A	2000: Dark gray mud
24	TC1A Neosho River	OC22	27	25	N/A	N/A	2000: Dark gray mud

APPENDIX D  
HEAVY METAL CONCENTRATIONS  
Copper

**COPPER**

Sample #	Sample Code	September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
1	OC24 Tailings settling pond	224	N/A	N/A	N/A	2000: Dry silty clay Desiccation cracks
2	OC19 Mine discharge into Lytle Creek	<8	N/A	#47	24	2000: Red mud, silt, sand, & organic mat.
3	OC20 4m downstream from discharge	<8	N/A	#46	5.3	2000: Red mud, silt, sand, & organic mat.
4	OC21 10m downstream from discharge	<8	N/A	#43	4.8	2000: Red mud, silt, sand, & organic mat.
5	TC12      OC17 Tar Creek above confluence	22	30	N/A	N/A	2000: Mud, sand, tailings, & organic mat.
6	TC13A,B      OC18 Lytle Creek	26	12	N/A	N/A	2000: Iron precipitate from bank Upstream of confluence
7	TC14      OC16 Confluence Tar Creek and Lytle Ck.	8	5	N/A	N/A	2000: Red mud and tailings
8	TC11      OC15 Downstream from confluence	21	17	N/A	N/A	2000: Mud, sand, tailings, & organic mat.
9	TC10      OC11 Hwy 66/69 Reddish fines	35	6	#13	15.0	2000: Reddish-brown mud, silt, & tailings 1983-84: Layered iron precipitate
10	TC9      OC12 Hwy 66/69 Bar	7	5	#13	15.0	2000: Red mud, silt, & tailings from bar 1983-84: Layered iron precipitate

Sample #	Sample Code	September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
11	TC8 Hwy 66/69 Clay and sand	9	44	#13	15.0	2000: Red clay and sand that has started to dry 1983-84: Layered iron precipitate
12	TC7 Hwy 66/69 Overbank	11	18	#13	15.0	2000: Dry sandy overbank deposit 1983-84: Layered iron precipitate
13	TC6A,B New State Road Commerce	20	16	#12	19.0	2000: Iron precip from pool 1983-84: Layered iron precip, clay
14	OC9 New State Road Commerce	10	N/A	#12	19.0	2000: Mud, sand, & tailings from stream
15	OC10 New State Road Commerce	56	N/A	#12	19.0	2000: Overbank deposits, des cracks, efflorescence
16	TC5 Commerce High School	30	22	#10	6.1	2000: Iron precip, mud and tailings from water's edge 1983-84: Crusted iron precipitate
17	TC4 Commerce High School	34	20	#10	6.1	2000: Iron precip, overbank deposits, desiccation cracks 1983-84: Crusted iron precipitate
18	TC3C 22nd St. (No rocks)	16	21	#6	16.0	2000: Grayish brown sed with mud to sand size particles 1983-84: Mud and sand
19	TC3A,B 22nd St. Miami (Sample w/rocks)	19	17	#6	16.0	2000: Grayish brown sed with mud to gravel size particles 1983-84: Mud and sand
20	OC3 22nd St. (duplicate, no rocks)	21	N/A	#6	16.0	2000: Grayish brown sed with mud to gravel size particles 1983-84: Mud and sand

Sample #	Sample Code		September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
21	TC2B Central Ave. duplicate	OC2	26	22	#3	64.0	2000: Dk brown sed w/ leaves and roots 1983-84: Iron precip., organic mat.
22	TC2A Central Ave. Miami	OC1	26	22	#2	2.5	2000: Dk brown sed w/ leaves and roots 1983-84: Iron precip., organic mat.
23	TC1B Neosho River (duplicate)	OC23	11	11	N/A	N/A	2000: Dark gray mud
24	TC1A Neosho River	OC22	11	9	N/A	N/A	2000: Dark gray mud

APPENDIX E  
HEAVY METAL CONCENTRATIONS  
Iron

Sample #	Sample Code	IRON			USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
		September 2000 (mg/kg)	July 2000 (mg/kg)				
1	OC24 Tailings settling pond	12072	N/A	N/A	N/A	2000: Dry silty clay Desiccation cracks	
2	OC19 Mine discharge into Lytle Creek	377840	N/A	#47	246000	2000: Red mud, silt, sand, & organic mat.	
3	OC20 4m downstream from discharge	415440	N/A	#46	366000	2000: Red mud, silt, sand, & organic mat.	
4	OC21 10m downstream from discharge	426960	N/A	#43	392000	2000: Red mud, silt, sand, & organic mat.	
5	TC12      OC17 Tar Creek above confluence	10950	6902	N/A	N/A	2000: Mud, sand, tailings, & organic mat.	
6	TC13A,B      OC18 Lytle Creek	120400	127440	N/A	N/A	2000: Iron precipitate from bank Upstream of confluence	
7	TC14      OC16 Confluence Tar Creek and Lytle Ck.	162160	26700	N/A	N/A	2000: Red mud and tailings	
8	TC11      OC15 Downstream from confluence	97900	9348	N/A	N/A	2000: Mud, sand, tailings, & organic mat.	
9	TC10      OC11 Hwy 66/69 Reddish fines	18798	47040	#13	166000	2000: Reddish-brown mud, silt, & tailings 1983-84: Layered iron precipitate	
10	TC9      OC12 Hwy 66/69 Bar	39860	24680	#13	166000	2000: Red mud, silt, & tailings from bar 1983-84: Layered iron precipitate	



Sample #	Sample Code	September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84	
11	TC8 Hwy 66/69 Clay and sand	OC14	47180	151600	#13	166000	2000: Red clay and sand that has started to dry 1983-84: Layered iron precipitate
12	TC7 Hwy 66/69 Overbank	OC13	39420	26360	#13	166000	2000: Dry sandy overbank deposit 1983-84: Layered iron precipitate
13	TC6A,B New State Road Commerce	OC8	66960	63720	#12	177000	2000: Iron precip from pool 1983-84: Layered iron precip, clay
14	OC9 New State Road Commerce		46820	N/A	#12	177000	2000: Mud, sand, & tailings from stream
15	OC10 New State Road Commerce		193600	N/A	#12	177000	2000: Overbank deposits, des cracks, efflorescence
16	TC5 Commerce High School	OC6	252000	141600	#10	267000	2000: Iron precip, mud and tailings from water's edge 1983-84: Crusted iron precipitate
17	TC4 Commerce High School	OC7	83100	134200	#10	267000	2000: Iron precip, overbank deposits, desiccation cracks 1983-84: Crusted iron precipitate
18	TC3C 22nd St. (No rocks)	OC5	75640	64520	#6	76000	2000: Grayish brown sed with mud to sand size particles 1983-84: Mud and sand
19	TC3A,B 22nd St. Miami (Sample w/rocks)	OC4	83100	134200	#6	76000	2000: Grayish brown sed with mud to gravel size particles 1983-84: Mud and sand
20	OC3 22nd St. (duplicate, no rocks)		86700	N/A	#6	76000	2000: Grayish brown sed with mud to gravel size particles 1983-84: Mud and sand

Sample #	Sample Code		September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
21	TC2B Central Ave. duplicate	OC2	83020	126920	#3	133000	2000: Dk brown sed w/ leaves and roots 1983-84: Iron precip., organic mat.
22	TC2A Central Ave. Miami	OC1	76340	169480	#2	467000	2000: Dk brown sed w/ leaves and roots 1983-84: Iron precip., organic mat.
23	TC1B Neosho River (duplicate)	OC23	18718	21100	N/A	N/A	2000: Dark gray mud
24	TC1A Neosho River	OC22	19582	18694	N/A	N/A	2000: Dark gray mud

APPENDIX F  
HEAVY METAL CONCENTRATIONS  
Lead

Sample #	Sample Code	LEAD		USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
		September 2000 (mg/kg)	July 2000 (mg/kg)			
1	OC24 Tailings settling pond	8410	N/A	N/A	N/A	2000: Dry silty clay Desiccation cracks
2	OC19 Mine discharge into Lytle Creek	121	N/A	#47	6800	2000: Red mud, silt, sand, & organic mat.
3	OC20 4m downstream from discharge	109	N/A	#46	6000	2000: Red mud, silt, sand, & organic mat.
4	OC21 10m downstream from discharge	109	N/A	#43	1500	2000: Red mud, silt, sand, & organic mat.
5	TC12      OC17 Tar Creek above confluence	476	572	N/A	N/A	2000: Mud, sand, tailings, & organic mat.
6	TC13A,B      OC18 Lytle Creek	908	342	N/A	N/A	2000: Iron precipitate from bank Upstream of confluence
7	TC14      OC16 Confluence Tar Creek and Lytle Ck.	183	166	N/A	N/A	2000: Red mud and tailings
8	TC11      OC15 Downstream from confluence	423	396	N/A	N/A	2000: Mud, sand, tailings, & organic mat.
9	TC10      OC11 Hwy 66/69 Reddish fines	392	230	#13	200	2000: Reddish-brown mud, silt, & tailings 1983-84: Layered iron precipitate
10	TC9      OC12 Hwy 66/69 Bar	257	168	#13	200	2000: Red mud, silt, & tailings from bar 1983-84: Layered iron precipitate

Sample #	Sample Code	September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
11	TC8 Hwy 66/69 Clay and sand	309	695	#13	200	2000: Red clay and sand that has started to dry 1983-84: Layered iron precipitate
12	TC7 Hwy 66/69 Overbank	289	341	#13	200	2000: Dry sandy overbank deposit 1983-84: Layered iron precipitate
13	TC6A,B New State Road Commerce	234	203	#12	280	2000: Iron precip from pool 1983-84: Layered iron precip, clay
14	OC9 New State Road Commerce	111	N/A	#12	280	2000: Mud, sand, & tailings from stream
15	OC10 New State Road Commerce	804	N/A	#12	280	2000: Overbank deposits, des cracks, efflorescence
16	TC5 Commerce High School	862	754	#10	350	2000: Iron precip, mud and tailings from water's edge 1983-84: Crusted iron precipitate
17	TC4 Commerce High School	793	694	#10	350	2000: Iron precip, overbank deposits, desiccation cracks 1983-84: Crusted iron precipitate
18	TC3C 22nd St. (No rocks)	126	256	#6	270	2000: Grayish brown sed with mud to sand size particles 1983-84: Mud and sand
19	TC3A,B 22nd St. Miami (Sample w/rocks)	206	167	#6	270	2000: Grayish brown sed with mud to gravel size particles 1983-84: Mud and sand
20	OC3 22nd St. (duplicate, no rocks)	147	N/A	#6	270	2000: Grayish brown sed with mud to gravel size particles 1983-84: Mud and sand

Sample #	Sample Code	September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
21	TC2B Central Ave. duplicate	206	190	#3	460	2000: Dk brown sed w/ leaves and roots 1983-84: Iron precip., organic mat.
22	TC2A Central Ave. Miami	235	257	#2	<40	2000: Dk brown sed w/ leaves and roots 1983-84: Iron precip., organic mat.
23	TC1B Neosho River (duplicate)	15	30	N/A	N/A	2000: Dark gray mud
24	TC1A Neosho River	19	22	N/A	N/A	2000: Dark gray mud

APPENDIX G  
HEAVY METAL CONCENTRATIONS  
Nickel

**NICKEL**

Sample #	Sample Code	September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
1	OC24 Tailings settling pond	30	N/A	N/A	N/A	2000: Dry silty clay Desiccation cracks
2	OC19 Mine discharge into Lytle Creek	28	N/A	#47	17.0	2000: Red mud, silt, sand, & organic mat.
3	OC20 4m downstream from discharge	28	N/A	#46	73.0	2000: Red mud, silt, sand, & organic mat.
4	OC21 10m downstream from discharge	45	N/A	#43	67.0	2000: Red mud, silt, sand, & organic mat.
5	TC12      OC17 Tar Creek above confluence	16	12	N/A	N/A	2000: Mud, sand, tailings, & organic mat.
6	TC13A,B      OC18 Lytle Creek	100	76	N/A	N/A	2000: Iron precipitate from bank Upstream of confluence
7	TC14      OC16 Confluence Tar Creek and Lytle Ck.	34	9	N/A	N/A	2000: Red mud and tailings
8	TC11      OC15 Downstream from confluence	31	12	N/A	N/A	2000: Mud, sand, tailings, & organic mat.
9	TC10      OC11 Hwy 66/69 Reddish fines	23	20	#13	46.0	2000: Reddish-brown mud, silt, & tailings 1983-84: Layered iron precipitate
10	TC9      OC12 Hwy 66/69 Bar	22	10	#13	46.0	2000: Red mud, silt, & tailings from bar 1983-84: Layered iron precipitate



Sample #	Sample Code	September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
11	TC8 Hwy 66/69 Clay and sand	26	54	#13	46.0	2000: Red clay and sand that has started to dry 1983-84: Layered iron precipitate
12	TC7 Hwy 66/69 Overbank	19	20	#13	46.0	2000: Dry sandy overbank deposit 1983-84: Layered iron precipitate
13	TC6A,B New State Road Commerce	67	46	#12	22.0	2000: Iron precip from pool 1983-84: Layered iron precip, clay
14	OC9 New State Road Commerce	37	N/A	#12	22.0	2000: Mud, sand, & tailings from stream
15	OC10 New State Road Commerce	85	N/A	#12	22.0	2000: Overbank deposits, des cracks, efflorescence
16	TC5 Commerce High School	230	104	#10	1.4	2000: Iron precip, mud and tailings from water's edge 1983-84: Crusted iron precipitate
17	TC4 Commerce High School	134	114	#10	1.4	2000: Iron precip, overbank deposits, desiccation cracks 1983-84: Crusted iron precipitate
18	TC3C 22nd St. (No rocks)	70	89	#6	41.0	2000: Grayish brown sed with mud to sand size particles 1983-84: Mud and sand
19	TC3A,B 22nd St. Miami (Sample w/rocks)	123	99	#6	41.0	2000: Grayish brown sed with mud to gravel size particles 1983-84: Mud and sand
20	OC3 22nd St. (duplicate, no rocks)	103	N/A	#6	41.0	2000: Grayish brown sed with mud to gravel size particles 1983-84: Mud and sand

Sample #	Sample Code	September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
21	TC2B Central Ave. duplicate	131	132	#3	52.0	2000: Dk brown sed w/ leaves and roots 1983-84: Iron precip., organic mat.
22	TC2A Central Ave. Miami	154	157	#2	28.0	2000: Dk brown sed w/ leaves and roots 1983-84: Iron precip., organic mat.
23	TC1B Neosho River (duplicate)	18	21	N/A	N/A	2000: Dark gray mud
24	TC1A Neosho River	19	21	N/A	N/A	2000: Dark gray mud

APPENDIX H  
HEAVY METAL CONCENTRATIONS  
Zinc

Sample #	Sample Code	ZINC		USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
		September 2000 (mg/kg)	July 2000 (mg/kg)			
1	OC24 Tailings settling pond	50980	N/A	N/A	N/A	2000: Dry silty clay Desiccation cracks
2	OC19 Mine discharge into Lytle Creek	3498	N/A	#47	2600	2000: Red mud, silt, sand, & organic mat.
3	OC20 4m downstream from discharge	4082	N/A	#46	11000	2000: Red mud, silt, sand, & organic mat.
4	OC21 10m downstream from discharge	5882	N/A	#43	11000	2000: Red mud, silt, sand, & organic mat.
5	TC12      OC17 Tar Creek above confluence	6998	11070	N/A	N/A	2000: Mud, sand, tailings, & organic mat.
6	TC13A,B      OC18 Lytle Creek	11944	7172	N/A	N/A	2000: Iron precipitate from bank Upstream of confluence
7	TC14      OC16 Confluence Tar Creek and Lytle Ck.	9104	2392	N/A	N/A	2000: Red mud and tailings
8	TC11      OC15 Downstream from confluence	10962	5636	N/A	N/A	2000: Mud, sand, tailings, & organic mat.
9	TC10      OC11 Hwy 66/69 Reddish fines	3598	3902	#13	14000	2000: Reddish-brown mud, silt, & tailings 1983-84: Layered iron precipitate
10	TC9      OC12 Hwy 66/69 Bar	3636	3280	#13	14000	2000: Red mud, silt, & tailings from bar 1983-84: Layered iron precipitate

Sample #	Sample Code	September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84	
11	TC8 Hwy 66/69 Clay and sand	OC14	6466	12456	#13	14000	2000: Red clay and sand that has started to dry 1983-84: Layered iron precipitate
12	TC7 Hwy 66/69 Overbank	OC13	4938	5428	#13	14000	2000: Dry sandy overbank deposit 1983-84: Layered iron precipitate
13	TC6A,B New State Road Commerce	OC8	4668	3720	#12	3900	2000: Iron precip from pool 1983-84: Layered iron precip, clay
14	OC9 New State Road Commerce		3092	N/A	#12	3900	2000: Mud, sand, & tailings from stream
15	OC10 New State Road Commerce		15752	N/A	#12	3900	2000: Overbank deposits, des cracks, efflorescence
16	TC5 Commerce High School	OC6	17008	11496	#10	980	2000: Iron precip, mud and tailings from water's edge 1983-84: Crusted iron precipitate
17	TC4 Commerce High School	OC7	12712	10336	#10	980	2000: Iron precip, overbank deposits, desiccation cracks 1983-84: Crusted iron precipitate
18	TC3C 22nd St. (No rocks)	OC5	3158	7848	#6	2700	2000: Grayish brown sed with mud to sand size particles 1983-84: Mud and sand
19	TC3A,B 22nd St. Miami (Sample w/rocks)	OC4	4456	4664	#6	2700	2000: Grayish brown sed with mud to gravel size particles 1983-84: Mud and sand
20	OC3 22nd St. (duplicate, no rocks)		4566	N/A	#6	2700	2000: Grayish brown sed with mud to gravel size particles 1983-84: Mud and sand

Sample #	Sample Code		September 2000 (mg/kg)	July 2000 (mg/kg)	USGS site #	Concentration (ppm) USGS Quantitative 1983-1984	Field Observations Year 2000 & 1983-84
21	TC2B Central Ave. duplicate	OC2	11406	5772	#3	3400	2000: Dk brown sed w/ leaves and roots 1983-84: Iron precip., organic mat.
22	TC2A Central Ave. Miami	OC1	15030	6844	#2	4900	2000: Dk brown sed w/ leaves and roots 1983-84: Iron precip., organic mat.
23	TC1B Neosho River (duplicate)	OC23	204	241	N/A	N/A	2000: Dark gray mud
24	TC1A Neosho River	OC22	207	213	N/A	N/A	2000: Dark gray mud

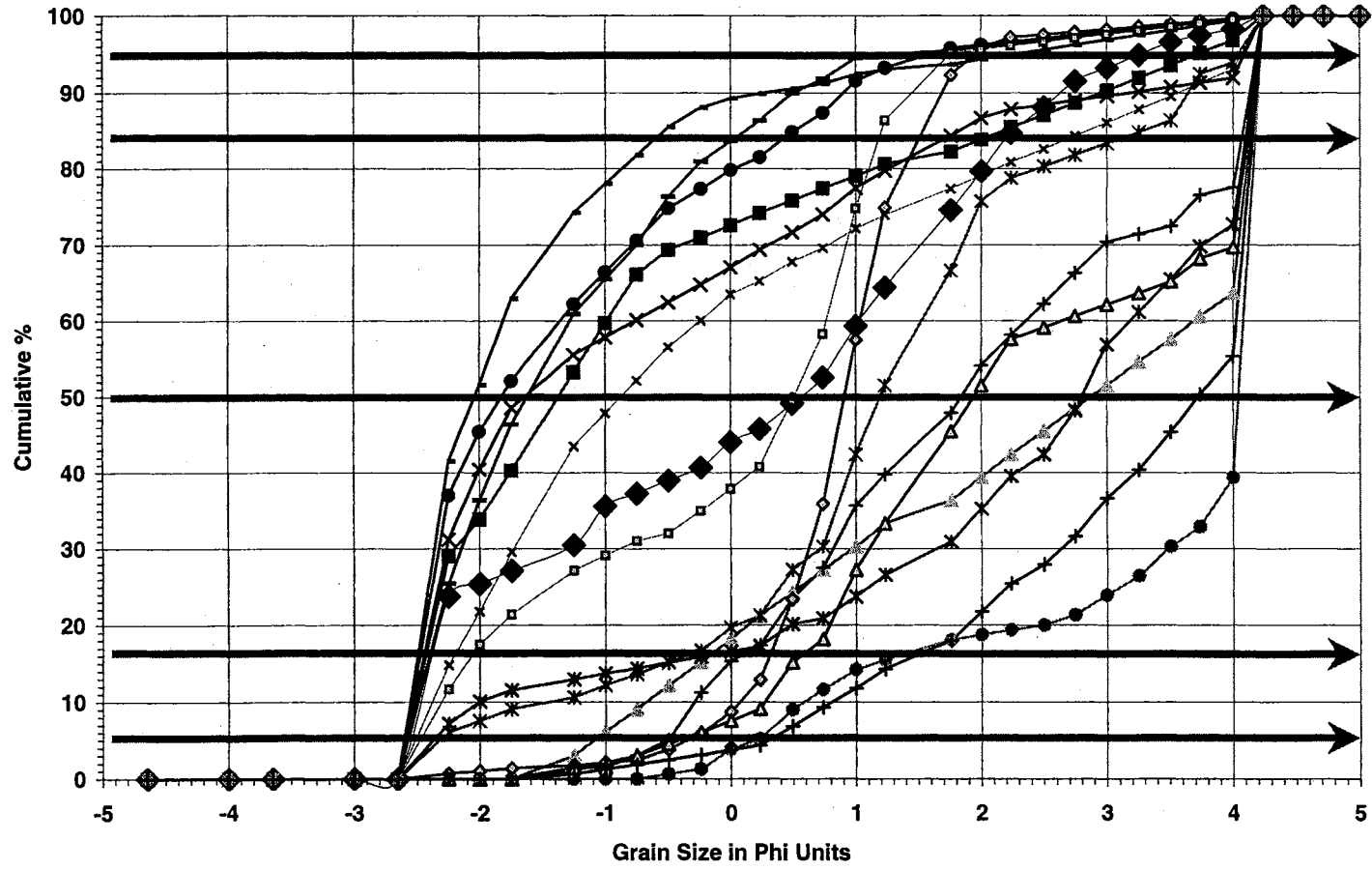
APPENDIX I  
Sieved Sediment Samples

Sieve Contents (grams)

Sample	#4	#5	#6	#8	#10	#12	#14	#16	#18	#20	#25	#30	#35	#40	#50	#60	#70	#80	#100	#120	#140	#170	#200	#230 < #230	
1	0	0	0	<1	<1	<1	<1	<1	<1	<1	2	2	2	2	3	3	3	2	3	4	3	4	4	4	36
2	0	0	0	<1	0	<1	<1	<1	<1	<1	2	1	3	2	4	2	2	<1	<1	<1	<1	<1	1	<1	10
3	27	8	7	6	2	2	2	2	2	2	2	2	3	2	4	2	1	<1	<1	<1	<1	<1	<1	<1	7
4	2	<1	<1	<1	<1	<1	<1	<1	1	<1	2	1	4	3	5	3	1	<1	<1	<1	<1	<1	2	<1	2
9	33	8	9	9	3	3	3	2	1	<1	<1	<1	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
10	28	12	11	16	5	5	7	5	3	3	4	2	3	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
11	12	6	4	6	2	2	1	3	3	3	9	9	17	12	9	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
12	1	<1	<1	<1	<1	<1	2	3	4	6	15	18	31	25	25	5	2	<1	<1	<1	<1	<1	<1	<1	<1
13	5	2	1	1	<1	<1	<1	<1	<1	<1	2	<1	2	2	3	3	3	2	4	6	3	3	3	2	19
14	44	10	8	12	5	5	5	3	3	2	4	3	5	2	3	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
15	0	0	0	<1	<1	<1	1	3	2	1	3	2	4	2	4	3	2	2	2	2	<1	<1	2	<1	11
16	0	0	0	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	6
17	17	8	9	16	5	5	5	4	4	2	3	2	3	2	4	2	2	2	2	2	2	2	2	2	8
18	18	3	4	8	4	4	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2
21	14	1	1	2	3	1	1	1	2	1	2	2	4	3	6	3	3	2	2	1	1	1	<1	<1	1
23	0	0	0	0	0	0	<1	<1	2	1	3	2	2	1	2	<1	<1	<1	1	2	2	3	2	5	47



### Picher Mining Field



VITA

Randa Noelle Hope

Candidate for the Degree of

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