

TAR CREEK FIELD INVESTIGATION

Task 1.2

**WATER QUALITY CHARACTERISTICS
OF SEEPAGE AND RUNOFF AT TWO
TAILINGS PILES IN THE PICHER FIELD
OTTAWA COUNTY, OKLAHOMA**

EPA Grant No. CX810192-01-0

**Prepared by
OKLAHOMA WATER RESOURCES BOARD
Water Quality Division**

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INTRODUCTION

Over sixty years of lead and zinc mining in the Picher Field of north-eastern Oklahoma and southeastern Kansas generated significant amounts of milling wastes (tailings), a majority of which are piled around the former mining towns of Picher and Cardin. Production of tailings began in the early 1900's when primary ore bodies were discovered, and lasted until the mid-1960's when major mining activities ceased. Throughout the mining era, tailings (locally referred to as chat) were accumulated and stored in giant piles. Significant volumes of rainwater are retained within the interstitial spaces of tailings. In presence of water, oxidation of iron sulfides (pyrite and marcasite) present in tailings can produce acid and result in liberation of heavy metals. Runoff and/or seepage from tailings piles may contain high concentrations of heavy metals which upon discharge into receiving streams can degrade water quality of the streams. Several of the existing tailings piles in the Picher Field drain into Tar and Lytle Creeks, the area's principal streams.

As a part of the Tar Creek field investigation program, EPA Grant No. CX810192-01-0, Work Element I, Task I.2, waters flowing at two tailing piles were sampled to determine their physical and chemical constituents. It is the intent of this report to address the characteristics of these constituents. Additional discussions relative to the mining and tailings history has been made and a brief description of the surface water hydrology of the area is provided in this report.

MINING AND TAILINGS HISTORY

The Tri-State lead and zinc mining region of Oklahoma, Kansas, and Missouri, has been one of the world's leading producers of lead and zinc concentrates (PbS and ZnS). The main part of the region, called the Picher Field, located in Ottawa County, Oklahoma, and Cherokee County, Kansas, was the last of the subregions to be discovered. Discovery of lead and zinc ores is dated as early as 1901 in the vicinity of Lincolville, Oklahoma, and in 1907 when richer ore bodies were found around Commerce, Oklahoma. Exploration continued in a northeasterly direction, along the Miami Trough, to the Cardin and Picher area where the richest of the ore deposits was discovered in 1912 (McKnight and Fischer, 1970). By 1917 boundaries of the Picher Field were well defined by numerous exploration holes and mine shafts. By then, the field was extended into Cherokee County, Kansas (Figure 1).

In 1904 the first output of lead and zinc concentrates was made from ores milled in the Lincolville area. With the expansion of the field in the following years, the number of operating mills increased significantly. In 1918 there were an estimated 230 mills built or under construction in the Oklahoma portion of the field.

Throughout the mining period, extraction and output of the metals fluctuated due to a variety of factors. Stimulated by a high market price and demand for lead and zinc during World War I, production increased and reached its maximum in 1925 when a maximum annual output for lead and zinc concentrates of 130,410 and 749,254 tons, respectively,

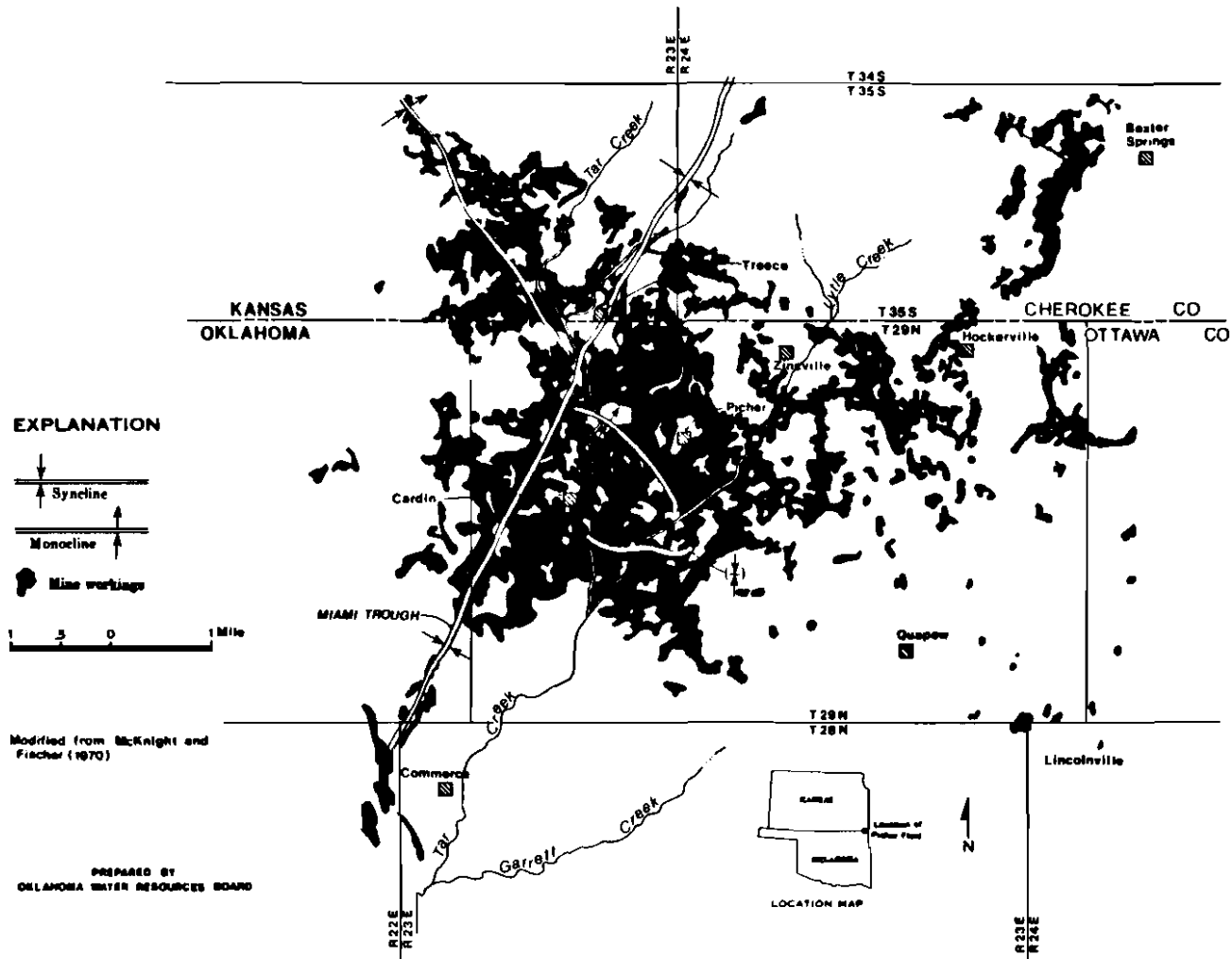


Figure 1. Generalized location of underground mine workings in the Picher Field, Oklahoma and Kansas.

were recorded (McKnight and Fischer, 1970). In the five years from 1921 through 1925, the Picher Field yielded 55% of the total zinc produced in the United States. However, depletion of resources along with such factors as depressed market values for metals and the economic depression in the 1930's resulted in an overall decline in the production rate. The last recorded output was in 1964 (Figure 2).

An outstanding feature of the Picher Field has been the recovery of lead and zinc concentrates from mill-waste materials. The giant tailings piles left after milling of the metals by jigging and tabling techniques contained recoverable quantities of mineral concentrates. The recovery from tailings which had begun as early as 1909 in the part of the field near Commerce increased during the second half of the 1920's. This was basically due to the introduction of flotation, an advanced extraction technique. Although in most operations only zinc was recovered, some tailings were also remilled for their lead contents. The recovery of lead and zinc from tailings depended primarily upon the efficiency of the initial milling process.

In the 1930's, encouraged by the higher profits drawn from a relatively easier operation, many of the large mining companies that worked previously on crude ore concentrated their operations on reworking the tailings. The peak of production from tailings came in 1936 when 26.5 percent of the annual zinc produced in the entire field came from reprocessing the tailings. As a result of the repeated remilling during World War II, tailings were soon depleted of lead and zinc concentrates. The lowest average annual grade of ores were reprocessed from the tailings in 1946 (McKnight and Fischer, 1970).

Since the cessation of mining operations in the latter half of the 1960's, available tailings (chat) have been a major source of income for the local area. A comparison of the historical aerial photographs indicates that over 50 percent of the chat has been completely recovered and most existing major chat piles are currently being processed for their commercial use as construction aggregate, mainly for railroad ballast, highway construction, concrete production, and sandblasting. The Annual Reports published by the Oklahoma Department of Mines show that, from 1970 through 1980, close to 8.2 million tons of chat from Ottawa County were sold (Table 1).

Research was conducted by the Oklahoma Geological Survey regarding the subsidence problems associated with the abandoned mine workings and aerial photographs from 1927 and 1980 were used to locate former tailings piles in the Oklahoma portion of the Picher Field. Based on the comparison of the photographs, 138 former chat piles have been completely removed and the land used for 51 of the removed chat piles has been reclaimed and is now being used in agriculture, housing, etc. In spite of remilling of the tailings and removal of the mill-waste materials for commercial use, many tailings piles still exist in the area. The most updated inventory of the tailings piles indicates that 87 minor and 33 major tailing piles remain in the area (Luza, 1983).

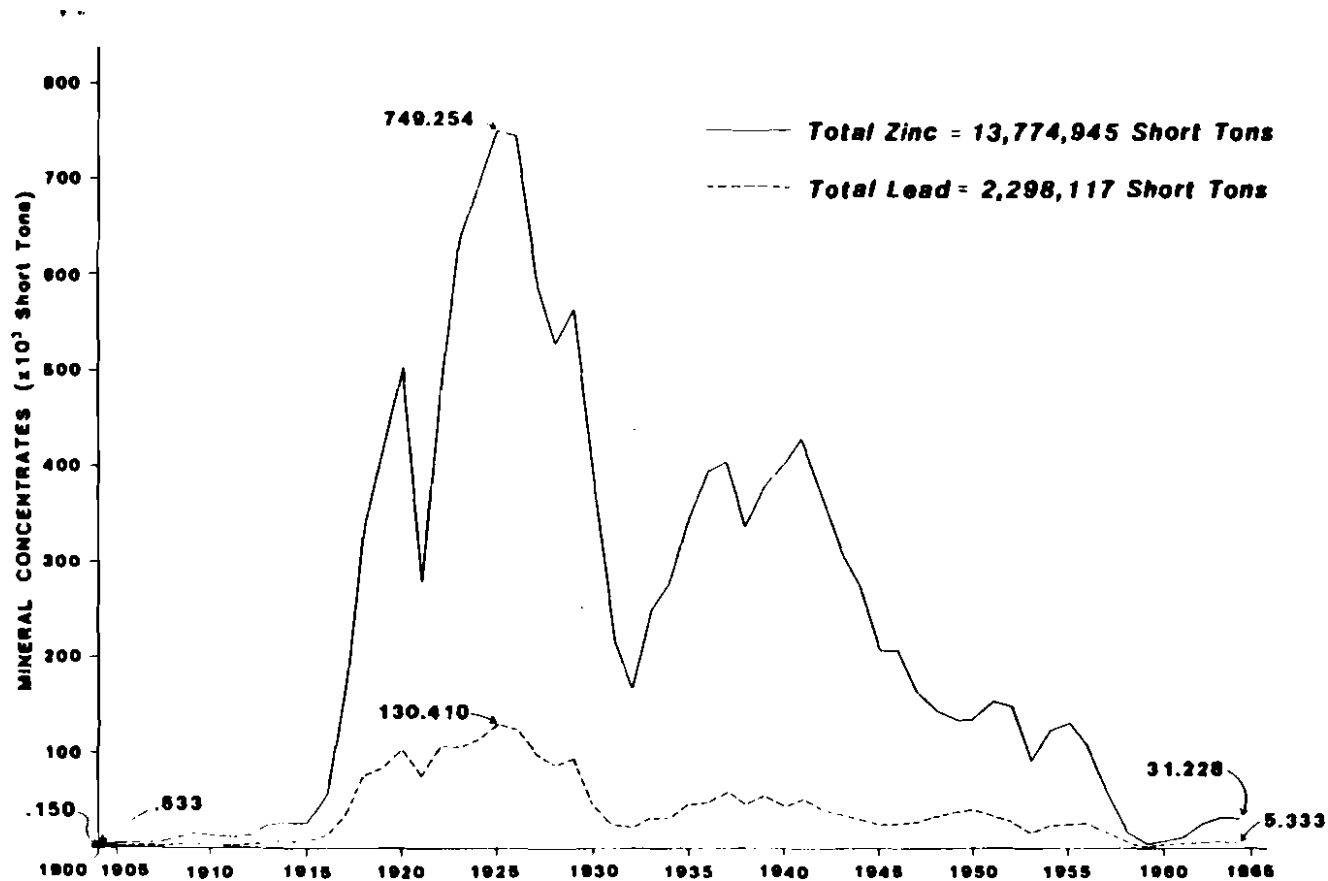


Figure 2. Lead and zinc production in the Picher Field, Oklahoma and Kansas.

Table 1. Chat sold from Ottawa County, Oklahoma, 1970 through 1980.

YEAR	CHAT SOLD (short tons)
1970	484,424
1971	371,059
1972	1,313,348
1973	868,440
1974	1,065,756
1975	565,508
1976	590,087
1977	759,087
1978	1,045,961
1979	926,582
1980	<u>202,038</u>
Total	8,192,290

DESCRIPTION OF TAR CREEK

Tar Creek is the principal drainage system in the Picher Field. With headwaters originating in Cherokee County, Kansas, Tar Creek flows southerly through the field between Picher and Cardin, and passing Commerce and Miami on the east it joins the Neosho River, one of two major rivers feeding Lake O' the Cherokees (Grand Lake). Tar Creek is a small ephemeral stream characterized with standing pools. With its major tributary, Lytle Creek, Tar Creek drains approximately 53 square miles of area (Figure 3). Tar Creek has no flow in its headwaters during dry periods. During wet periods, however, Tar Creek in addition to its natural drainage receives acid mine discharges from flooded mine workings and runoff from tailings piles. Except for the Pioneer Mine tailings pile which is located in Section 25, Township 29N, Range 22E1M, all major piles are concentrated within the Tar Creek drainage basin. The Pioneer tailings pile drains into Elm Creek, another tributary of the Neosho River.

EFFECTS OF TAILINGS PILES DRAINAGE

The adverse effects of runoff and seepage have evidently been a concern of mining companies since attempts were made in the past to protect the streams through construction of embankments at some of the major tailings piles. The extent of runoff from tailings piles varies with the size of the pile and the ability to which the pile can retain rain water. Some of the piles have produced runoff for periods longer than eight months. Runoff from tailings piles in the Tar Creek drainage basin reach Tar Creek and Lytle Creek either directly or through natural or man-made drainages.

To make an estimate of pollutant loading rates for the tailings pile, water quality and flow data collected during the five-day sampling period (between November 29 through December 3, 1982) as well as chat volume for the sampled tailings piles and the total chat volume present in the Oklahoma portion of the Picher Field were used for computation purposes. Total chat pile loading rates were calculated based on the average metal concentrations and flow data obtained from sampling of the two tailings piles (sites 4t and 5t). Although calculation of the exact loading of heavy metals contributed by tailings piles is imposible with the limited flow and water quality data, the estimates indicate that the heavy metal loadings from tailings piles are insignificant compared with loadings due to the underground mine discharges. The calculated loading rates are listed in Table 2.

The water quality data obtained at the Tar Creek field investigation stream site No. 7 at the Oklahoma-Kansas State Line can best identify the pollutant contribution from tailings piles into Tar Creek. The site is located at approximately 820 feet MSL where no mine discharges take place. However, the creek at this location crosses through a number of tailings piles and receives contaminated seepage and runoff directly from the piles. High concentrations of metals including cadmium, iron, lead, and zinc, and low pH levels have been measured at this location. A statistical summary of water quality data for site 7 is presented in Appendix B.

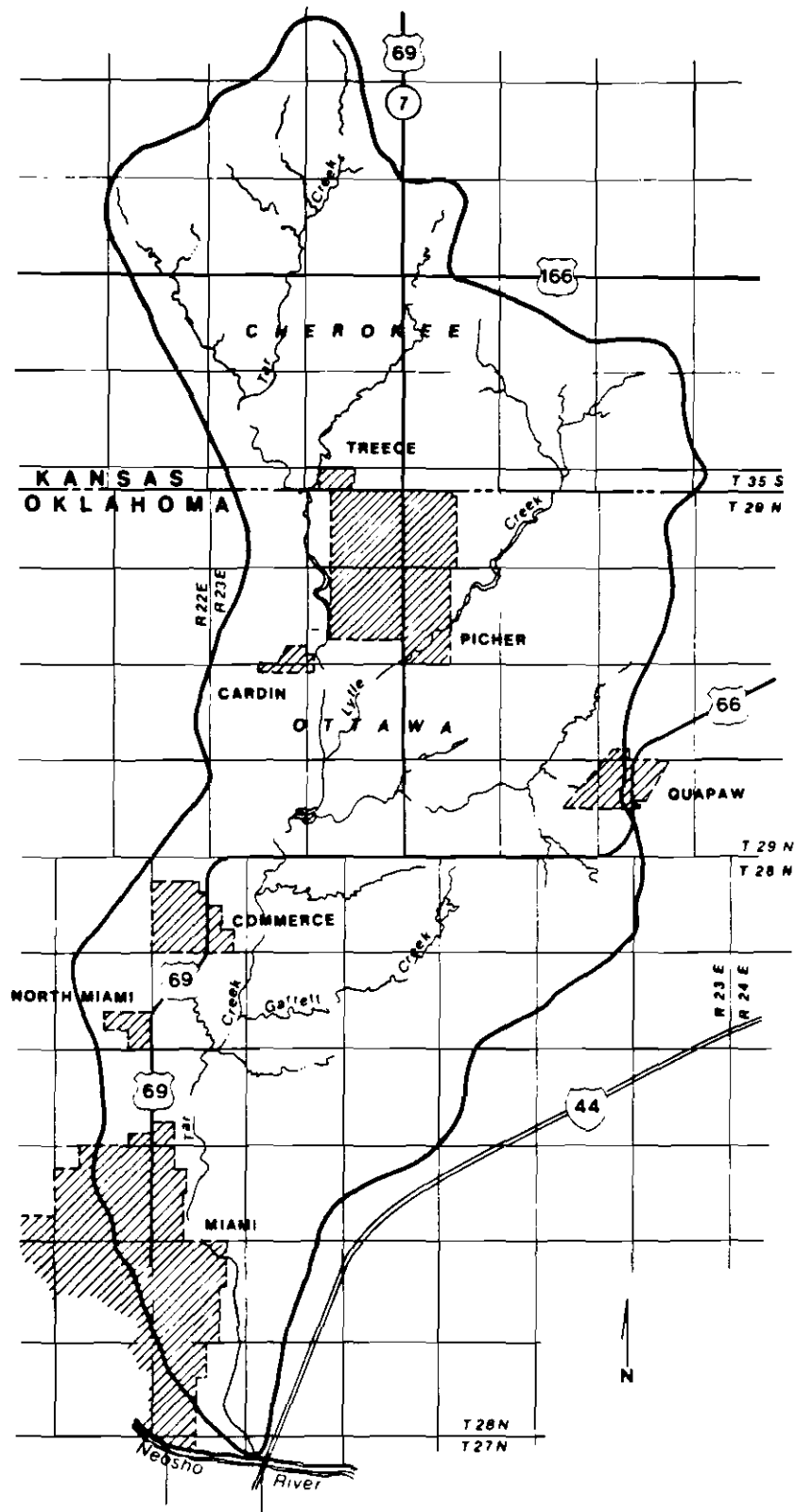


Figure 3. Tar Creek drainage basin.

Table 2. Metal loading rates for the tailings piles in the Oklahoma portion of the Picher Field.

Total chat volume	48.21 X 10 ⁶ Yd ³
Total flow	0.19 cfs (0.12 mgd)

LOADING RATES BASED ON AN AVERAGE OF METAL CONCENTRATIONS
AT SITES 4t AND St

	Average Concentration (µg/L)	Loading Rate (lbs/day)
Cadmium	153.0	0.153
Chromium	10.5	0.01
Iron	4,050.0	4.05
Lead	39.0	0.04
Zinc	27,450.0	27.50

DESCRIPTION OF THE SAMPLED TAILINGS PILES

Two tailings pile sites in the Oklahoma section of the Picher Field were selected for sampling of certain physical and chemical constituents. Sites 4t and St (Figure 4) are two of the largest existing tailings piles in the area. Figure 4, which has been modified from U.S. Geological Survey's topographic map printed in 1961, shows the approximate sizes of the tailings piles in that particular year. Since that time, many of the piles have either been partially or completely removed, therefore, tailings pile sizes for the entire field on the map are not valid for the present time. However, evidence suggests site St includes all tailings which ever existed at this site, but a small fraction of the site 4t tailings in the southwest corner has been removed.

Site 4t

This chat pile is located immediately northwest of the confluence of Tar and Lytle Creeks in Section 29, Township 29N, Range 23EIM. With a maximum height of 100 feet, it covers an area of 36 acres and is composed of approximately 2.55×10^6 cubic yards of chert fragments (Luza, 1983). No active recovery of chat from this site was observed during 1982. The land underlain by this chat pile conceals sections of three underground mines, Admiralty No. 4, Douthat, and See Sah.

The site 4t chat pile discharges runoff directly into Tar Creek at its western bank, a few hundred feet above the Douthat bridge. Runoff period for this site has varied from year to year, basically as a function of rainfall events. Usually it flows during the major portion of the year but stops during extended dry periods. During 1982 runoff from this site ceased completely for the period between early September through the first week in November. Historical maps indicate this site has been embanked at its eastern side along Tar Creek. The embankment, however, is partially absent at the southeastern section of the chat pile. Runoff from this site into Tar Creek occurs at this location.

Site St

Next to the Pioneer chat pile, Section 25, Township 29N, Range 22EIM, site St is the largest existing chat pile in the area. It is situated south of the Oklahoma-Kansas state line, Section 16, Township 29N, Range 23EIM, on the Swift and Commonwealth mine lands. It covers a surface area of 86 acres, has maximum height of 122 feet, and contains approximately 5.53×10^6 cubic yards of chert fragments (Luza, 1983). A comparison of aerial photographs and historical maps indicates the area covered by this tailings pile has remained unchanged over the years. Chat recovery from this site was not seen during 1982.

Unlike site 4t, this site does not flow directly into Tar Creek. Because of this, a great deal of time was spent locating runoff at this site. The site was visited several times during August, September, and October 1982. No apparent runoff drainage was observed around the periphery of the pile. However, following intense precipitation during the first two weeks in November, seepage began to appear at the southern

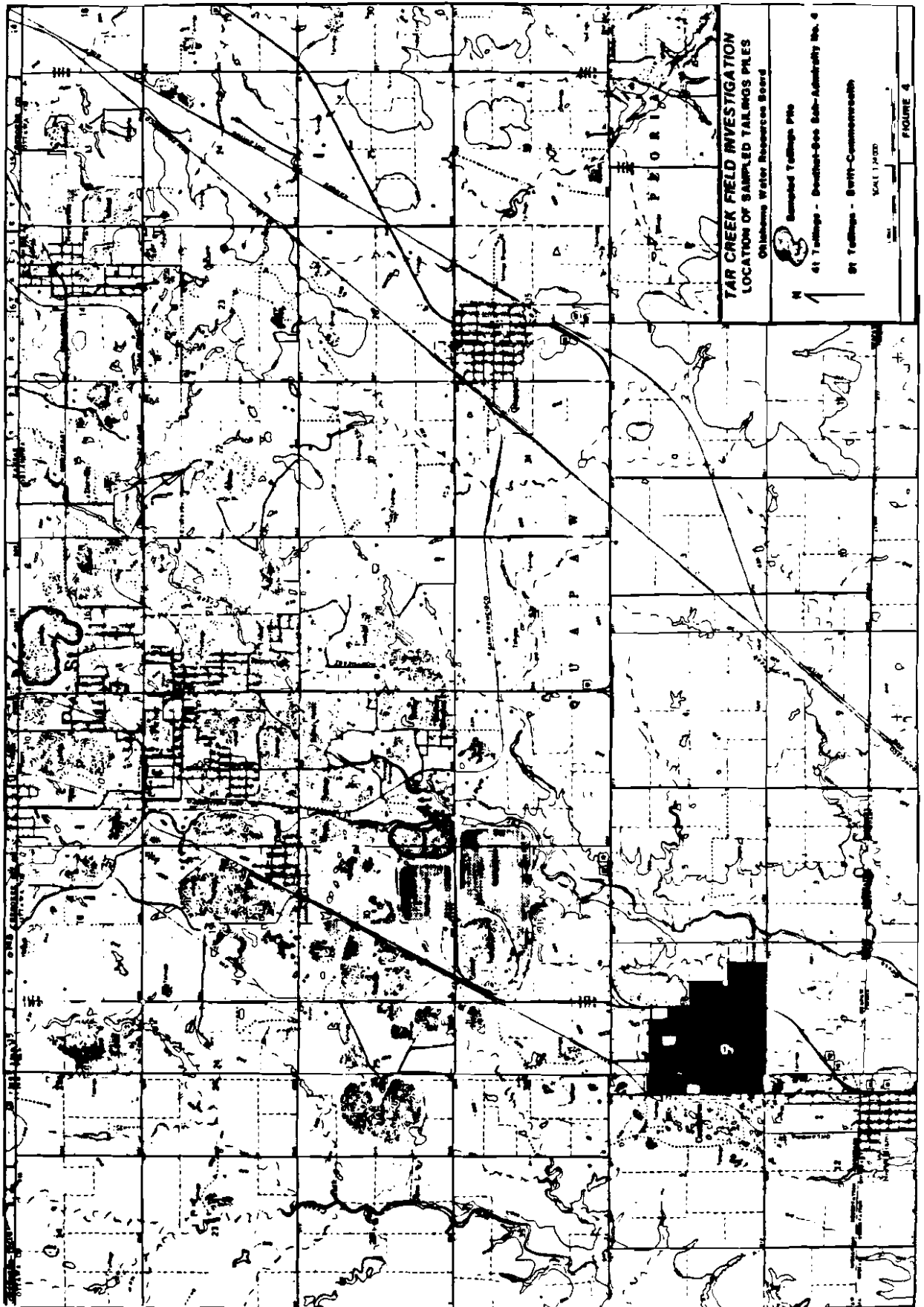


Figure 4. Location of sampled tailings piles.

base of the saturated chat pile. For sampling purposes, the seepage area was dredged to form a drainage channel, then runoff was allowed to drain for a few days in order to allow the subsurface waters to flow. Runoff from this site flows into a small tributary north of Picher. The tributary, in turn, joins Lytle Creek in the SW $\frac{1}{4}$, Section 21, Township 29N, Range 23EIM.

SAMPLING TECHNIQUES AND METHODOLOGY

Task I.2 of the Superfund Work Plan (Appendix A) was designed to provide an adequate assessment of the water quality characteristics of runoff at two tailings piles. In accordance with the work plan, grab samples were collected at each site beginning November 29, 1982, for five consecutive days. Filtered and unfiltered duplicate samples were collected in 250 ml plastic containers. Samples were filtered on site through 0.45 μ m-pore size filters using a hand-operated Nalgene PVC vacuum pump. Collected samples for metal ion analysis were preserved on site using nitric acid (pH<2). Field measurements of pH, dissolved oxygen (DO), and specific conductance were taken at each site using a Model 4041 digital Hydrolab. Calibration of the Hydrolab took place according to manufacturer's specifications, before and after each sampling period. Sample analyses were performed at the State Environmental Laboratory of the Oklahoma State Department of Health, in accordance with the Environmental Protection Agency's approved procedures.

During the course of the study, a large amount of data were collected. As can be expected with a large study of this type, validity of all the data is an ongoing question. Some questions about certain iron and zinc data were raised as a result of observations that dissolved metals were higher than total metals for some samples. An extensive investigation was undertaken to evaluate the possibility of both field collection and laboratory problems. It was concluded that the problems were due to some unaccountable error. It was further concluded, after consultation with all concerned state and federal officials, that the most prudent course of action would be to reject all of the data for samples where there were unaccountable discrepancies. Such discrepancies were shown for the samples collected at site St on December 1 and 3, 1982, therefore, these samples were not considered in the report.

Precipitation records were obtained at two different locations. A standard rain gage was used in Picher and an automated rain gage was maintained at the U.S. Geological Survey's site at the Blue Goose Mine well, SE $\frac{1}{4}$, SW $\frac{1}{4}$, Section 30, Township 29N, Range 23EIM. Additional rainfall data were obtained at the City of Miami.

Flow measurements were made every time prior to sample collection by a stopwatch-bucket procedure. A gallon container was used and the elapsed time to fill the container was recorded.

WATER QUALITY CHARACTERISTICS OF THE SAMPLED TAILINGS PILES

The chemical analyses of the samples collected at sites 4t and St indicate water drained from these tailings piles contain high concentrations of cadmium, lead, zinc, and iron (Tables 3 and 4). The

Table 3. Water quality data for site 4t.

PARAMETERS	SAMPLING PERIOD				
	11/29/82	11/30/82	12/1/82	12/2/82	12/3/82
pH (su)	5.6	5.4	4.5	5.1	5.0
DO (mg/L)	1.1	0.5	0.0	0.3	0.3
Specific Conductance (μ mhos/cm)	2,620	2,630	2,650	2,330	2,520
Cadmium (Cd) total (μ g/L)	270	220	230	200	210
Chromium (Cr) total (μ g/L)	10	10	<10*	<10*	<10*
Iron (Fe) total (μ g/L)	180	<100*	<100*	120	<100*
Lead (Pb) total (μ g/L)	33	<20*	<20*	40	<20*
Zinc (Zn) total (μ g/L)	34,900	29,400	32,500	29,600	30,600
Cadmium (Cd) dissolved (μ g/L)	240	240	240	250	210
Chromium (Cr) dissolved (μ g/L)	<10*	<10*	<10*	<10*	<10*
Iron (Fe) dissolved (μ g/L)	210	<100*	<100*	<100*	<100*
Lead (Pb) dissolved (μ g/L)	25	<20*	<20*	<20*	<20*
Zinc (Zn) dissolved (μ g/L)	33,700	31,200	34,200	31,100	30,100

*Concentrations less than detection limit.

Table 4. Water quality data for site St.

PARAMETERS	SAMPLING PERIOD		
	11/29/82	11/30/82	12/2/82
pH (su)	5.3	5.1	5.0
DO (mg/L)	0.2	0.0	0.2
Specific Conductance (μ mhos/cm)	2,470	2,430	2,440
Cadmium (Cd) total (μ g/L)	46	20	26
Chromium (Cr) total (μ g/L)	12	10	<10*
Iron (Fe) total (μ g/L)	9,400	6,500	520,000*
Lead (Pb) total (μ g/L)	305	74	106
Zinc (Zn) total (μ g/L)	29,000	16,600	17,000
Cadmium (Cd) dissolved (μ g/L)	21	19	23
Chromium (Cr) dissolved (μ g/L)	10	<10*	<10*
Iron (Fe) dissolved (μ g/L)	6,500	6,400	12,300
Lead (Pb) dissolved (μ g/L)	<20*	<20*	53
Zinc (Zn) dissolved (μ g/L)	18,300	17,000	15,800

*Concentrations less than detection limit.

concentrations vary with the site and are dependent upon the type of residual metal-concentrates present in association with the tailings. The average dissolved zinc and cadmium concentration of site 4t samples are higher than those of site St, but the average lead concentrations are higher for site St. This gives the general indication that galena (lead concentrate) is the predominant metal concentrate present at site St while sphalerite (zinc concentrate) is predominant at site 4t. Presence of cadmium in high concentrations at site 4t is due to its association with sphalerite. Standard chemical analysis of sphalerite shows cadmium composes 0.3 percent of sphalerite.

Data derived from sample analyses indicate concentrations of metals, especially zinc and cadmium for site 4t samples and zinc and lead for site St samples, increase following rainfall events (Figures 5 and 6). This relationship which denotes the flushing effect of rainfall on metals is more clearly evident for site 4t samples. Table 5 shows the relationship between rainfall and flow at the sites.

In general, the highest concentrations of metals were found in samples collected during the first day of sampling, November 29, 1982, when zinc concentrations of 34,900 $\mu\text{g/L}$ and 29,000 $\mu\text{g/L}$ were measured for sites 4t and St, respectively. Cadmium content at site 4t was also highest for that day. The range of concentrations for lead at site St was between 74 and 305. The maximum lead concentration of 305 $\mu\text{g/L}$ was measured for the site on November 29, 1982. The peak concentration of lead at site 4t was only 40 $\mu\text{g/L}$.

The sample analyses indicate that concentrations of iron are significantly higher in site St samples. The maximum iron content of 520,000 $\mu\text{g/L}$ was measured at site St, whereas the highest concentration for site 4t was 210 $\mu\text{g/L}$. The presence of high iron concentrations at site St was detected during dredging of the channel for the site when heavy deposits of ferric hydroxide were formed along the channel shortly after its construction. Although iron was found in site 4t samples, no significant deposits of iron were seen at the site. A comparison of the data recorded at site 4t during this study period and those recorded during the initial study phase of the Tar Creek investigation in 1980 indicates that iron concentration has decreased significantly within the two year period. Concentrations as high as 600 $\mu\text{g/L}$ were reported for this site in 1980 (Oklahoma Water Resources Board, July 1981).

Among the five metal species investigated during this study, chromium was the only constituent found in very low concentrations. The highest concentrations of chromium (12 $\mu\text{g/L}$) were recorded at site St on the first sampling day. In most cases chromium was below the detection limit.

Field measurements of pH, dissolved oxygen, and specific conductance made during the sampling period show values of these parameters did not vary significantly during the sampling period. The range for pH at site 4t was between 4.5 and 5.6, and it was 5.0 to 5.3 for site St. The lowest and highest specific conductance readings were taken at site 4t (2,330 and 2,650 $\mu\text{mhos/cm}$), and a range of 2,430 to 2,470 $\mu\text{mhos/cm}$ was recorded at site St. Because samples were collected at locations near

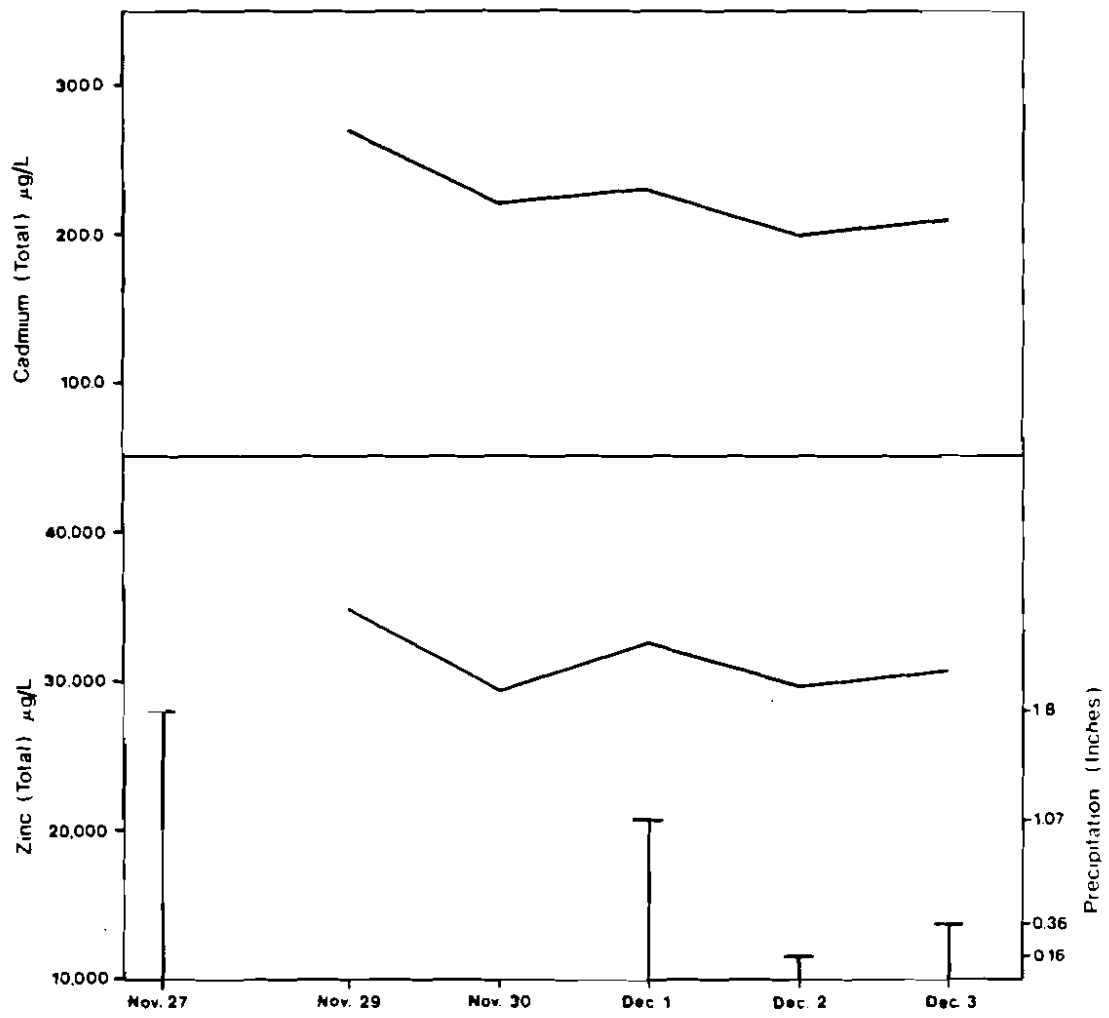


Figure 5. Effects of rainfall on concentrations of zinc and cadmium for site 4t (November 29 - December 3, 1982).

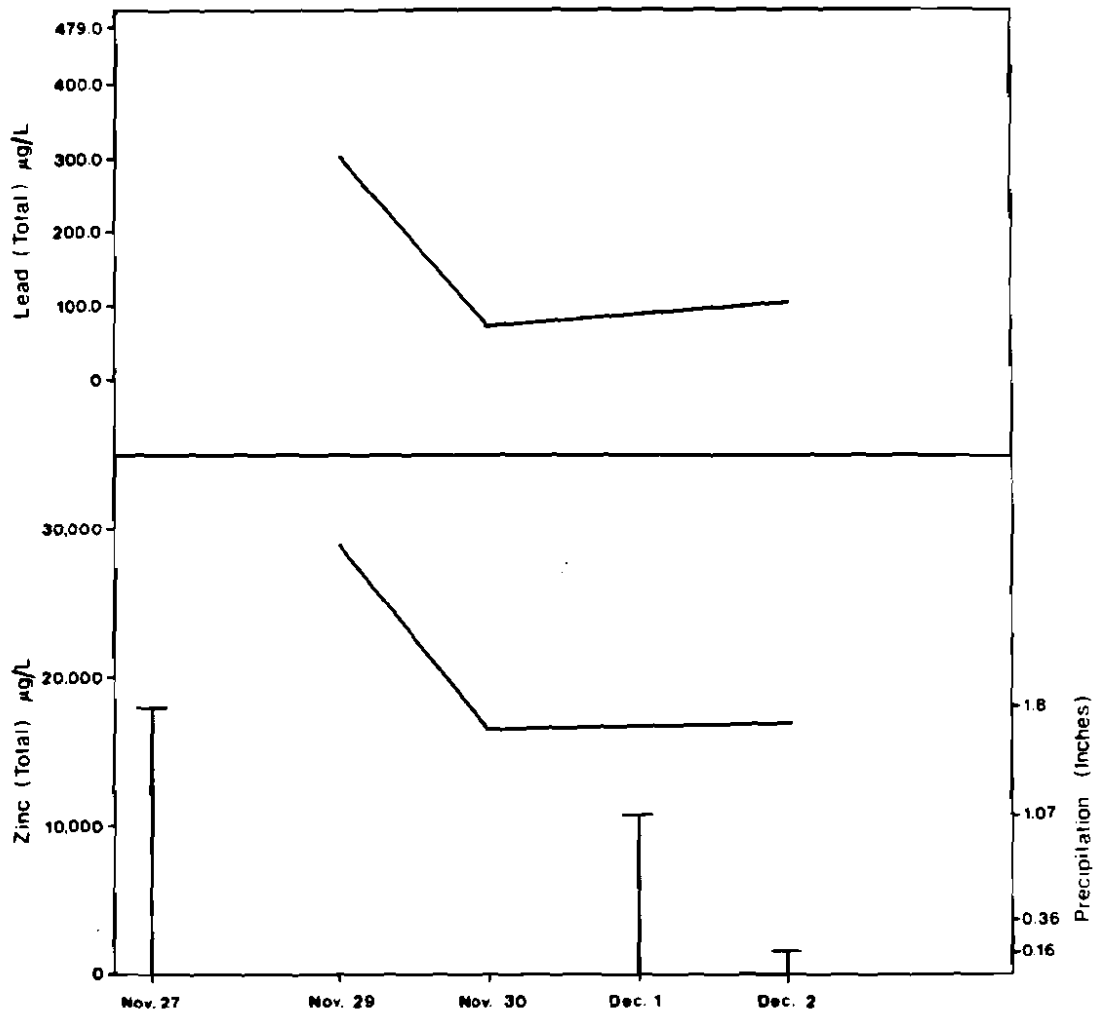


Figure 6. Effects of rainfall on concentrations of zinc and lead for site St (November 29 - December 2, 1982).

Table 5. Precipitation records and flow measurements.

DATE	PRECIPITATION (inches)	FLOW (cfs)	
		Site 4t	Site St
11/27/82	1.80		
11/28/82	0.15		
11/29/82	None	0.026	0.0067
11/30/82	None	0.022	0.0060
12/1/82	1.07	0.026	0.0062
12/2/82	0.16	0.026	0.0062
12/3/82	0.36	0.024	0.0062

the chat piles, very low dissolved oxygen concentrations were recorded. The values ranged from 0.0 to 1.1 mg/L.

Finally, because of the relatively stable discharges, no dramatic fluctuations in the metallic constituents of waters sampled at the chat piles were seen. In order to detect rapid changes in concentrations, hourly sampling and flow measurement during and after precipitation can be more helpful in determining any significant change during flooding period and the period after when metals are flushed out of the pile. Such a detailed study was conducted by Barks in the Joplin Mining District (Barks, 1977). The study shows metal concentrations increased dramatically a few hours after cessation of the rainfall.

CONCLUSIONS

The analytical results of the water samples collected at two tailings piles indicate waters flowing at these sites have a low pH and contain high concentrations of various heavy metals. These metals are leached out as a result of dissolution of sphalerite and galena by sulfuric acid which is formed by oxidation of pyrite and/or marcasite present in tailings piles. Of these metals, those which are less soluble will tend to precipitate after the pH is increased due to dilution, but highly soluble metals, including zinc and cadmium, will remain in solution and will reach the receiving streams.

The majority of tailings piles in the Picher Mining Field are situated within the Tar Creek drainage basin. At present, the adverse effects of tailings piles runoff on Tar Creek and its tributaries are masked by discharges of highly contaminated acid mine water from the flooded underground mines. However, upon abatement of mine discharges, mineralized tailings piles runoff to the surface waters of the area could have a significant impact on aquatic organisms.

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APPENDIX A

APPENDIX A

ELEMENT I - FIELD INVESTIGATION

<u>TASK No.</u>	<u>DESCRIPTION OF TASK</u>	<u>OUTPUT</u>	<u>START DATE</u>	<u>FINISH DATE</u>
I.2	This task evaluates the extent of water pollution contributed by nonpoint sources.	Samples, data, report	Month 1	Month 7
I.2.A	Identify two chat piles for sampling.	-	Month 1	Month 1
I.2.B	Collect samples of runoff from the two chat piles after one significant rainfall event. Collect one filtered and one unfiltered sample daily at each pile for five consecutive days.	Samples	Month 1	Month 6
I.2.C	analyze samples from I.2.B for pH, temperature, conductance, dissolved oxygen, iron, chromium, cadmium, zinc, and lead.	Final OSDH sample report for each sample	Month 1	Month 6
I.2.D	Prepare report containing analysis and interpretation of nonpoint source data.	Report	Month 7	Month 7

APPENDIX B

STATISTICAL SUMMARY OF WATER QUALITY DATA FOR SITE 7
(Oklahoma-Kansas State Line)

APPENDIX B

STATISTICAL SUMMARY OF WATER QUALITY DATA FOR SITE 7
(Oklahoma-Kansas State Line)

<u>PARAMETER</u>	<u>NUMBER OF SAMPLES</u>	<u>MEAN</u>	<u>STANDARD DEVIATION</u>	<u>MINIMUM</u>	<u>MAXIMUM</u>
Alkalinity, Total (mg/L)	3	112.0	53.5	73.0	173.0
Aluminum, Total (µg/L)	3	3*	0	3*	3*
Arsenic, Total (µg/L)	3	10*	0	10*	10*
Cadmium, Total (µg/L)	7	17.6	4.5	11.0	23.0
Chromium, Total (µg/L)	3	10*	0	10*	10*
Copper, Total (µg/L)	3	10.6	9.0	4.0*	20.0
Dissolved Oxygen (mg/L)	8	4.1	2.5	0.8	7.5
Fluoride, Total (mg/L)	8	0.3	0.1	0.2	0.4
Iron, Total (µg/L)	7	7,871	19,461	150	52,000
Lead, Total (µg/L)	5	72	100	20*	247
Maganese, Total (µg/L)	5	180	115	60	370
Mercury, Total (µg/L)	3	0.5*	0.0	0.5*	0.5*
Nickel, Total (µg/L)	3	56	25	28	78
pH (su)	9	6.5	0.5	5.8	7.4
Solids, Total (mg/L)	2	634	198	494	774
Dissolved Solids, Total (mg/L)	8	1,011	574	437	1,844
Specific Conductance (µmhos/cm)	9	1,249	485	590	1,676
Sulfate (mg/L)	8	627	406	189	1,296
Zinc, Total (µg/L)	7	5,870	4,219	2,100	13,800

* Concentrations below detection limit.