

# CHANGES IN DISCHARGE WATER QUALITY IN A HISTORIC HARD ROCK MINING WATERSHED<sup>1</sup>

Jennifer A. Coffey and Robert W. Nairn<sup>2</sup>

**Abstract.** The chemical composition of nine abandoned mine water discharges at the Tar Creek Superfund Site were examined in 2001-2002 and compared to data collected in the mid-1980s. The site is a portion of the abandoned Tri-State Lead and Zinc Mining District of Oklahoma, Kansas and Missouri. In the initial water quality study conducted in 1983-1986, mine waters were characterized as having low to circumneutral pH and elevated metal concentrations. Fe, Zn and alkalinity concentrations ranged from 140-1836 mg/L, 47-200 mg/L, and 0-560 mg/L as CaCO<sub>3</sub> eq., respectively, and pH values ranged from 3.0-6.1. During the summers of 2001 and 2002, sampling of nine previously studied discharges was conducted. Data were compared with 1980s data to help characterize suspected changes in mine water chemistry. In situ parameters included pH, temperature, conductivity, dissolved oxygen, alkalinity, and turbidity. Samples were collected and analyzed for Fe, Zn, Cd, Pb, Ni, Mn, Cu, Ca, Mg, SO<sub>4</sub><sup>-2</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>-3</sup>, Cl<sup>-</sup>, F<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>, and Li<sup>+</sup> concentrations. In 2001-2002, mine waters were found to have circumneutral pH and exhibit substantial alkalinity with elevated Fe, Zn, Pb and Cd concentrations. Water quality ranges for data collected 2001-2002 were 51-197 mg/L for Fe, 4-11 mg/L for Zn and 124-414 mg/L CaCO<sub>3</sub> eq. for alkalinity. The range in pH values was 5.8-6.2. In general, most water quality data showed very little change when compared with data from the 1980s study. However, metal contaminant concentrations changed substantially with average decreases in Fe, Zn, and Mn of 78%, 96%, and 79%, respectively. Changes in mine water chemistry are presumed to have occurred due to filling of mine voids with water, which altered the amount of oxygen available at exposed sulfide surfaces, thus decreasing rates of contaminant production. Prior surface water diversions characteristically deemed as having little impact on mine drainage discharge or receiving streams quality, may have substantially modified mine pool hydrology, thus resulting in a general improvement in water quality. The current mine drainage chemical composition lends itself to implementation of passive treatment systems for effective metal removal.

Additional Key Words: lead, zinc, mine drainage, Tar Creek Superfund Site

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<sup>2</sup>Jennifer A. Coffey is an Undergraduate Research Assistant and National Science Foundation Research Experience for Undergraduates Fellow, and Robert W. Nairn is an Associate Professor, School of Civil Engineering and Environmental Science, The University of Oklahoma, Norman, OK, 73019, USA.

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## Introduction

The Tar Creek Superfund Site (Figure 1) was the scene of massive lead and zinc mining operations from the late 1890s until the 1960's (WDAMC and AIMME, 1931; Adams 1980; OWRB 1983; Parkhurst 1987; Smith and Fay 1997). These mines were dewatered during operations by extensive pumping. When the mining stopped, the mine voids began to fill with water. In 1979, water was first documented as discharging to the surface (Adams 1980). Water discharged to the surface through natural springs, boreholes, air vents, and open mine shafts. In the early 1980s substantial resources were focused on this area to determine sources of mine water pollution. The United States Geological Survey (USGS) conducted an extensive water quality assay of the mining area in order to determine the major sources of mine water input into the streams in this area of northeastern Oklahoma.

USGS and Oklahoma Water Resource Board (OWRB) both attempted to characterize the water quality in this area in the early 1980s. Many of the mine openings are still discharging

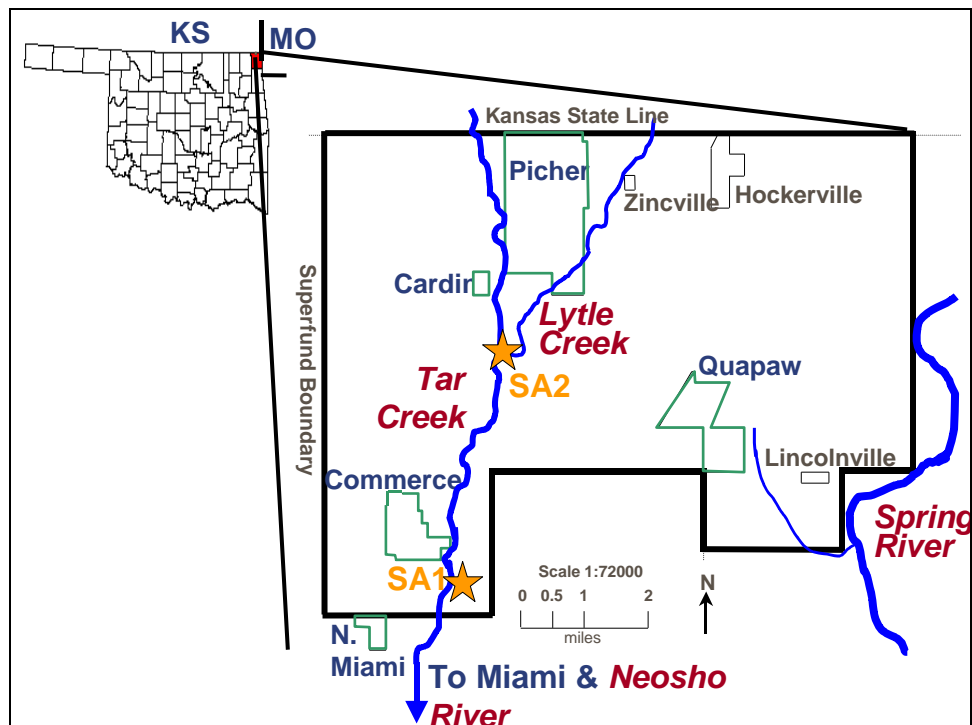


Figure 1. Location of the Tar Creek Superfund Site and the two water quality study areas in northeastern Oklahoma.

water today. In order to document changes in water quality composition over time, we revisited two of the areas studied by USGS. The first study area (SA1) receives continuous flow from two abandoned boreholes. Water from this area is eventually diluted by runoff from residential and industrial areas during storm events. Most of the discharges investigated in the second study area (SA2) flow intermittently, are highly variable and discharge directly to the receiving waters.

The purpose of this study was to attempt to document changes in mine water composition. Over the last twenty years, important biogeochemical reactions in the mining voids have likely resulted in substantial changes in discharge chemistry. No comprehensive water quality studies have been conducted in the watershed since the 1980s. Documentation of the current quality of individual discharges is essential when considering treatment options.

### **Materials and Methods**

SA1 and SA2 were sampled three times during the summers of 2001 and 2002. Samples were taken only when water was flowing from the discharges. Site A and B are borehole discharges located within SA1 (Figure 2). The quality of these discharges and the associated volunteer wetland has been documented in detail elsewhere (Brumley et al. 2002, Coffey et al. 2002, Nairn et al. 2002).

All other sample sites are located within SA2 (Figure 3). Site C is an open vertical mine shaft that discharges water intermittently. Site D is a sloped shaft that has been enclosed with a berm, thus forming a pond. The outflow of this ponded area was sampled. This site had intermittent flow as well. Site E is a pipe that appears to discharge water only after large storm events. Site F and G are vertical mine shafts that appear to flow continuously. Site H is a vertical mine shaft that flows intermittently. Site I is a previously undocumented discharge that flows continuously.

During each sampling event in 2001-2002, *in situ* measurements of dissolved oxygen, pH, alkalinity, turbidity, conductivity, and temperature were taken (OCC 2002). Two grab samples were collected for metals analysis (fixed with HCl and kept at 4°C) and non-metal cation and anion analysis (4°C). Metals analyzed included Fe, Zn, Cd, Pb, Mn, Ni, Ca, Mg, Cu via atomic absorption spectrophotometry after hot acid digestion. In addition,  $\text{SO}_4^{-2}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{PO}_4^{-3}$ ,  $\text{Cl}^-$ ,

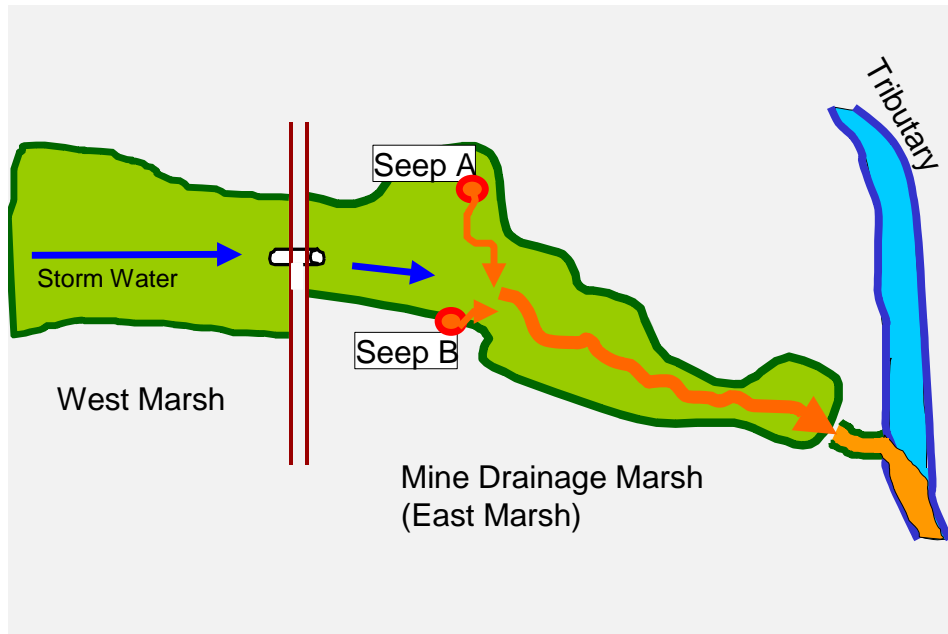


Figure 2. Water quality sampling sites within SA1, Tar Creek Superfund Site, northeastern Oklahoma

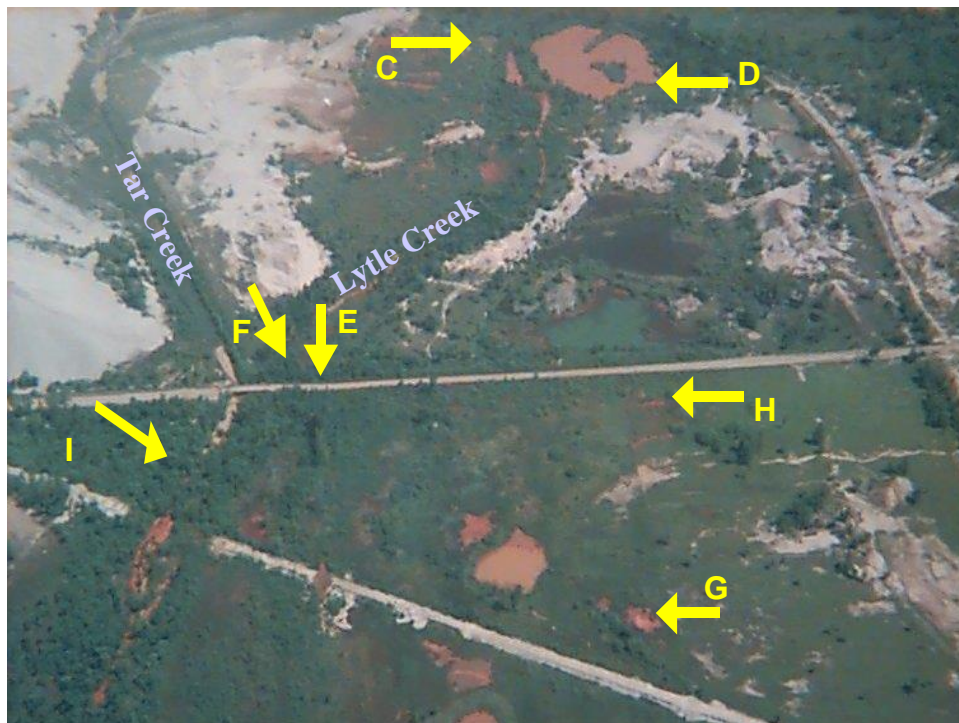


Figure 2. Water quality sampling sites within SA2, Tar Creek Superfund Site, northeastern Oklahoma

F<sup>-</sup>, Br<sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>, and NH<sub>4</sub><sup>+</sup> were analyzed via ion chromatography. All sample collection, handling and analysis were conducted according to standard methods (APHA 1995) at the University of Oklahoma Ecosystem Biogeochemistry and Ecology Laboratory. Samples for ion chromatographic analyses were filtered (0.25 µm) to remove particulates.

Data were then compared with water quality data generated by USGS (Parkhurst 1987). Parkhurst (1987) filtered samples that were collected for dissolved constituents with 0.2 µm filters in the field. Nitric acid was used to fix all samples except those collected for nitrate analysis. Hydrochloric acid was used on these. Methods of analysis for USGS samples followed Skougstad et. al. (1979) and Fishman and Bradford (1982). Fe, Zn, Pb, Cd, Cu, Ni, Mn, Mg, and Ca were all analyzed using atomic absorption spectrophotometry (Parkhurst, 1987). Table 1 summarizes the sampling regimes.

Table 1: Summary information for mine drainage discharges sampled at the Tar Creek Superfund Site, northeastern Oklahoma. USGS refers to U.S. Geological Survey and OU refers to University of Oklahoma.

Site ID	Description	Years sampled	Data Source
A	Commerce Springs - Borehole	1984-85 2001-2002	USGS OU
B	Commerce Springs - Borehole	1984-85 2001-2002	USGS OU
C	Collapse W of Lytle - vertical shaft	1984-85 2001	USGS OU
D	Collapse E of Lytle - slope entry	1984 2001	USGS OU
E	Open air vent casing	1983-1985 2001	USGS OU
F	Borehole Discharge - vertical shaft	1983-1985 2002	USGS OU
G	RR Borehole - vertical shaft	1984 2002	USGS OU
H	Quebec Borehole - vertical shaft	1984-1985 2002	USGS OU
I	Undocumented	2002	OU

## Results and Discussion

For all sampled discharges, waters were found to be net alkaline and have pH 5.8-6.2 (Figure 4a). Iron concentrations decreased by an average of 78% when comparing 1980s data to 2002 data (Figure 4b). Similarly, zinc and manganese showed average decreases in concentration of 96 % and 79 %, respectively (Figure 4c-d). Magnesium concentrations decreased by 78% and calcium concentrations increased by 44% (Figure 4e-f). No noticeable increase or decrease was noted for anion concentrations. Temperature readings indicated that discharging underground mine water (i.e., not surface water) was being measured at each site. Overall, pH increased from marginally acidic to circumneutral today. Magnesium concentrations increased for SA1 and decreased for SA2. Calcium showed increases for both study areas. Table 2 shows the mean percent changes in historic water quality data versus present water quality data.

Changes in mine water chemistry are likely due to the mines completely filling with water. As the void spaces fill, interactions between oxygen in the atmosphere and/or infiltrating waters and the exposed ore are limited. Changes in the elevation of the mine water pools have resulted

Table 2. Summary of changes in metal concentrations for mine drainage discharges as percent change from 1980s to present day. Negative values indicate a decrease in average concentration, nd = not determined, na = not applicable due to lack of historic data.

Site ID	Fe	Zn	Mn	Ni	Mg	Ca
A	-70	-81	-66	-58	48	49
B	-70	-81	-66	-58	48	49
C	-68	-96	-77	-75	-83	54
D	-87	-95	-79	-85	-80	46
E	-74	-93	-75	-85	-73	47
F	-74	-93	-75	-85	-73	47
G	-74	-93	-75	-85	-73	47
H	-74	-93	-75	nd	-73	47
I	na	na	na	na	na	na

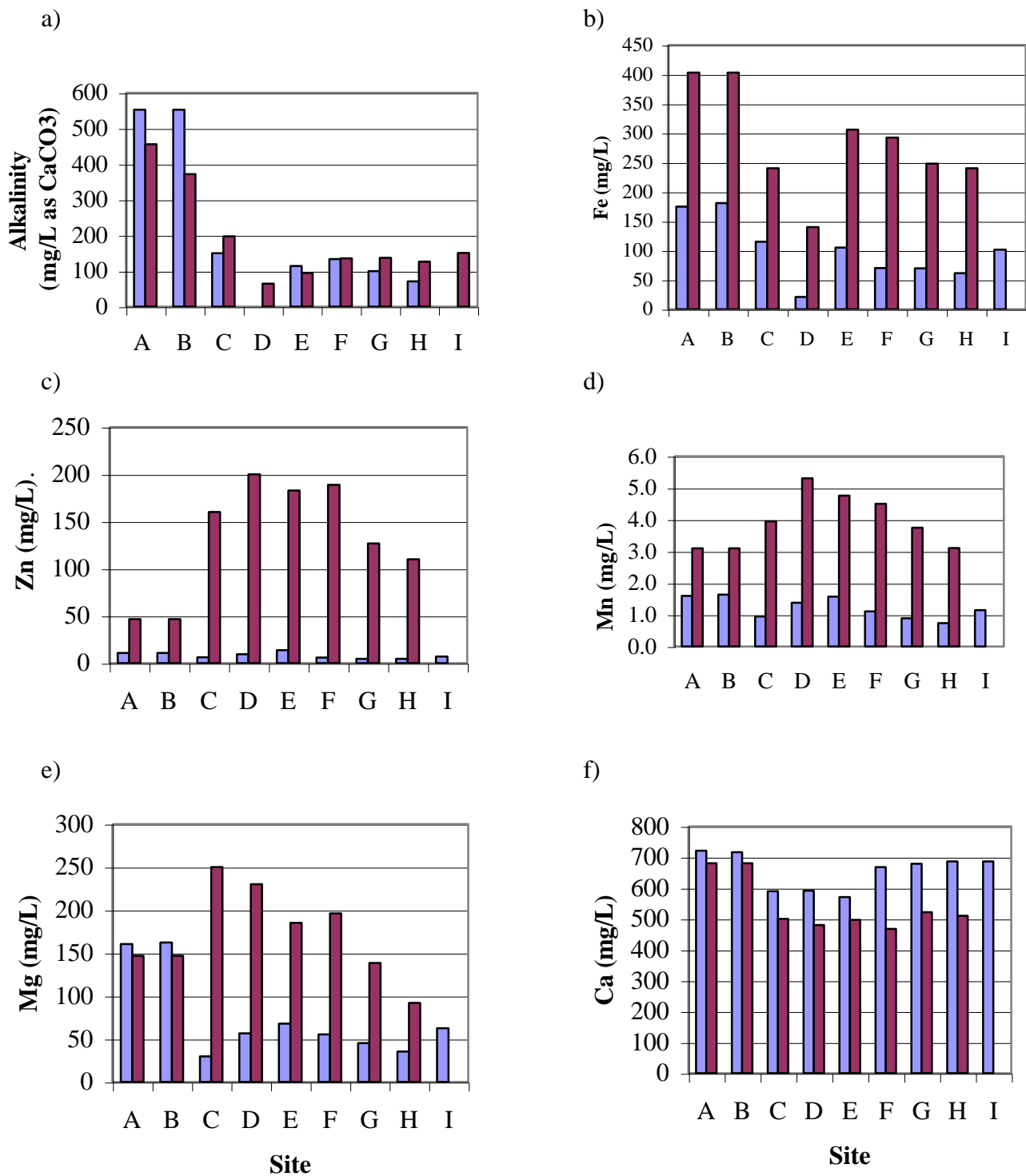


Figure 4. Water quality of nine discharges for a) alkalinity, b) Fe, c) Zn, d) Mn, e) Mg, and f) Ca for samples collected in 2001-2002 (OU, blue bars) and 1980s (USGS, red bars).

in at least some new discharges. However, many of the discharges flow intermittently. This indicates that the water level within the mines likely fluctuates due to regional precipitation patterns and that the mines are at least partially open to surface inflows. Changes in water levels cause the rock to be regularly exposed to oxygen or oxygenated waters, thus producing mine drainage. However, this mine water may be flushed from the mines during large storm events and the mine voids are temporarily filled with water. As the mines have filled, dissolved oxygen likely decreased thus affecting sulfide solubility. An overall decrease in metal concentrations in mine drainage discharges occurs. Filling of the mines with water also decreases the redox potential, which alters the solubility of metal species (Stumm and Morgan 1996).

No change was noted in sulfate concentrations, indicating that conditions within the mine voids are likely anoxic. In addition, fluctuations in water level in the mine voids account for seasonal changes in metal concentrations as well as noted changes in concentrations following storms or events when more mine drainage is flushed out of the mines. Samples taken at the beginning of high flow events showed marginally higher metal concentrations. This indicates that infiltrating waters during rain events, in at least some locations, may periodically flush the mines.

It is interesting to note that initial remediation efforts undertaken after the 1980s studies included the plugging of several openings, as well as large-scale attempts to halt surface water from entering the mine voids via diversion of surface inflows (U.S. EPA 2000). The elimination of mine drainage discharges due to these efforts has not been documented. Although these actions are typically deemed as having little impact on the quality of mine drainage discharges or the receiving streams, they may have substantially modified mine pool hydrology, thus resulting in a general increase in water quality. Comprehensive and long-term studies of the mine pool, discharge and stream quality are warranted.

### **Conclusions**

Mine water chemistry has changed from slightly acidic waters to net alkaline circumneutral waters. Metal concentrations for iron, zinc, manganese, nickel, and copper have decreased substantially. No change was recorded in measured anion concentrations. Values recorded for temperature, conductivity, and dissolved oxygen are very similar to those measured twenty years ago. These changes in mine water composition bode well for the viability of passive treatment as an option for removing metal contaminants from these waters.



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